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Environmental Protection
Agency

Proceedings and Summary Report

Workshop on Assessing and
Managing Mercury from
Historic and Current Mining
Activities

November 28 - 30, 2000
San Francisco, California

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Notice

The U.S. Environmental Protection Agency (EPA or the Agency), through its Office of Research and Development (ORD), sponsored a workshop in San Francisco, California on November 28-30, 2000 titled Assessing and Managing Mercury from Historic and Current Mining Activities. This document was compiled by Science Applications International Corporation (SAIC) under Contract 68-C7-001 from presentations and open discussion at the workshop. The views expressed in these Proceedings are those of the individual authors and do not necessarily reflect the views and policies of EPA. Scientists in EPA's Office of Research and Development have prepared the EPA sections, and those sections have been reviewed in accordance with EPA's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The references contained within the presentation abstracts have been provided by the speakers. For questions regarding abstract content or references, please contact the speakers directly.

Abstract

Mercury deposits in mines have been shown to pose a significant hazard to residents and wildlife where drainage from these deposits enters the environment through streams and rivers. For this reason, the extent of mercury contamination in the United States is of significant environmental concern. The U.S. Environmental Protection Agency (EPA) is investigating the many different sources of mercury contamination. As a result of these uncertainties, numerous EPA Program Offices–including the Office of Prevention, Pesticides and Toxic Substances (OPPTS), Office of Air and Radiation (OAR), Office of Water (OW), Office of Solid Waste and Emergency Response (OSWER), and Office of Research and Development (ORD)–have made commitments to enhance government, industry, and public awareness of potential hazards associated with the persistent, bioaccumulative, and toxic (PBT) effects of mercury in the environment. In fact, mercury is one of many PBT chemicals that continues to be an environmental concern, as generated hazardous waste or incidental release to the environment, long after its intended use. It is the Agency's intent to reduce the generation of PBTs, including mercury, in hazardous waste by 50 percent by the year 2005 through various pollution prevention and state-of-the-art disposal practices (EPA, 1998).

A workshop, Assessing and Managing Mercury from Historic and Current Mining Activities, was held on November 28-30, 2000 in San Francisco, California. The primary objectives of this workshop were to 1) identify state-of-the-science practices and techniques for reducing the use and release of mercury at its source, while understanding mercury fate and transport mechanisms and assessing mercury's impacts to human health and the ecology, and 2) determine what role ORD can play in the research activities required to fulfill the goal of the *Mercury Research Strategy (MRS)*. Presentations during the plenary session, technical sessions, and panel discussions addressed identifying and characterizing sources, mercury speciation and mobility, watershed impairment, watershed management tools and priorities, air emissions and impacts, and remediating and treating contaminated sites and materials. Presenters were from EPA, the U.S. Department of Energy (DOE), state agencies, industry, academia, technology developers, consulting firms, and international organizations. This report contains a summary of the material presented during the workshop, including technical session abstracts and summaries of the plenary session and the panel discussion. The final agenda and list of attendees are presented in Appendices A and B.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally C. Gutierrez, Acting Director
National Risk Management Research Laboratory

Contents

List of Acronyms

µg	micrograms
µg/g	micrograms per gram
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µg/m^3	micrograms per cubic meter
AER	Atmospheric & Environmental Research, Inc.
AFA-PRB	Alkali Fly Ash-Permeable Reactive Barrier
Ag	silver
AMD	acid-mine drainage
Au	gold
BAT	Best Available Technology
BDAT	Best Demonstrated Available Technologies
BLM	Bureau of Land Management
BVMI	Buena Vista Mines Inc.
CAA	Clean Air Act
CI	confidence interval
CLP	Contract Laboratory Program
cm	centimeter
cm^3	cubic centimeter
CM	cinnabar mine in southeastern Alaska
cm/sec	centimeters per second
COPC	constituents of potential concern
CRS	constant rate of supply
CS	contaminated sites
CVAFS	cold vapor atomic fluorescence spectrophotometry
D	demethylation rate coefficient
DEQ	Department of Environmental Quality
DOC	U.S. Department of Conservation
DOC/DMG	Department of Conservation, Division of Mines and Geology
DOE	U.S. Department of Energy
DOI	U.S. Department of the Interior
DTSC	Department of Toxic Substance Control
E	diffusion rate
E & E	Ecology and Environment, Inc.
EE/CA	Engineering Evaluation and Cost Analysis
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ERA	ecological risk assessment
EXAFS	extended x-ray adsorption fine structure spectroscopy
FASP lab	mobile field laboratory
FDA	U.S. Food and Drug Administration
FGD	flue gas desulfurization
ft/day	feet per day
ft^3/day	cubic feet per day
ft^3/s	cubic feet per second
g	grams
g/day	grams per day
g/L	grams per liter
g/t	grams per ton
GIS	geographic information system
GM	gold mine
GPR	ground penetrating/probing radar
GPRA	Government Performance and Results Act
HAP	hazardous air pollutants
Hg$_p$	particulate mercury
HgT	total mercury
HHRA	human health risk assessment
HP	Herman Pit
IC	Institutional Controls

kg	kilograms
kg/day	kilograms per day
kg/yr	kilograms per year
km	kilometer
km^2	square kilometers
L/min	liters per minute
lb	pound
lbs/hr	pounds per hour
lbs/yr	pounds per year
m	meter
m^2	square meter
m^2/s	square meters per second
m^3	cubic meter
m^3/hr	cubic meters per hour
m^3/min	cubic meters per minute
m^3/s	cubic meters per second
M	methylation rate coefficient
MACT	Maximum Achievable Control Technology
MeHg	methylmercury
mg/kg	milligrams per kilogram
mg/g	milligrams per gram
mg/m^3	milligrams per cubic meter
mg/L	milligrams per liter
Mg/yr	megagrams per year
MLF	mercury loss factor
MLM	Mother Lode Mine
MRDS	Mineral Resources Data System
MRPP	Mercury Recycling Pilot Project
MRS	Mercury Research Strategy
MTF	Mercury Task Force
MUF	mercury usage factor
NAAQS	National Ambient Air Quality Standards
NAFTA	North American Free Trade Agreement
NARAP	North American Regional Action Plan
NAS	National Academy of Sciences
NESHAPs	National Emission Standards for Hazardous Air Pollutants
NETL	National Energy Technology Laboratory
ng/g	nanograms per gram
ng/L	nanograms per liter
$ng/m^2/hr$	nanograms per square meter per hour
ng/m^3	nanograms per cubic meter
ng/ml	nanograms per milliliter
NGO	nongovernment organizations
NOAA	National Oceanic and Atmospheric Administration
NPL	National Priorities List
NRC	National Research Council
NRMRL	National Risk Management Research Laboratory (EPA)
NSF	National Science Foundation
NSPS	New Source Performance Standards
NV DEP	Nevada Division of Environmental Protection
NWR	National Wildlife Refuges
OAR	Office of Air and Radiation (EPA)
OIA	Office of International Affairs (EPA)
ONF	Ochoco National Forest
OPPTS	Office of Prevention, Pesticides and Toxic Substances (EPA)
OR-OSHA	Oregon Occupational Health and Safety
ORD	Office of Research and Development (EPA)
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response (EPA)

OW	Office of Water (EPA)
PA/SI	preliminary assessment/site inspection
PBL	planetary boundary layer
PBT	persistent, bioaccumulative, and toxic
pg/m^3	picograms per cubic meter
ppb	parts per billion
ppm	parts per million
PRE	preliminary risk estimate
PRG	preliminary remediation goal
RAGS	Risk Assessment Guidance for Superfund
RAO	Remedial Action Order
RCRA	Resource Conservation and Recovery Act
REDOX	oxidation/reduction
RfD	reference dose
RGM	reactive gaseous mercury
RIFS	remedial information feasibility study
RWQCB	Regional Water Quality Control Board
SBMM	Sulphur Bank Mercury Mine
SEDEX	sedimentary exhalitive
SME	silica micro encapsulation
SPIS	Superfund Public Information System
SSRL	Stanford University Synchrotron Radiation Laboratory
STAR	Science to Achieve Results (EPA)
SWRCB	State Water Resources Control Board
t/day	tons per day
t/yr	tons per year
TCLP	toxic characteristics leaching procedure
TGM	total gaseous mercury
THg	total mercury
TMDL	total maximum daily limit
TMeHg	total methylmercury
TRI	Toxic Release Inventory
UAO	Unilateral Administrative Order
UCL	upper confidence limit
UNR	University of Nevada, Reno
USBM	U.S. Bureau of Mines
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
XAS	x-ray absorption spectroscopy

Section 1
Executive Summary

1.1   Introduction

Anthropogenic releases of mercury to air, water, and land have adversely impacted human health and the environment for many years. EPA Program Offices–including the Office of Prevention, Pesticides and Toxic Substances (OPPTS), Office of Air and Radiation (OAR), Office of Water (OW), Office of Solid Waste and Emergency Response (OSWER), Office of International Affairs (OIA), and Office of Research and Development (ORD)–have made commitments to enhance government, industry, and public awareness of the potential hazards associated with the persistent, bioaccumulative, and toxic (PBT) effects of mercury in the environment. Key scientific questions have compelled ORD to support the Agency's mission to develop a *Mercury Research Strategy* (*MRS*, 1999) and to take a more proactive stance in identifying and implementing research programs designed to meet out-year goals in promoting the pollution prevention and risk management of mercury.

To answer these questions, ORD conducted a series of technology transfer workshops that focused on the following risk management areas of concern: combustion sources, noncombustion sources, mercury in mining, ecological impacts and assessment, and mercury retirement. This proceedings document presents and summarizes the findings of the workshop, "Assessing and Managing Mercury from Historic and Current Mining Activities," held from November 28 to November 30, 2000 in San Francisco, California.

1.2   Background

Mercury is the only metallic element that is fluid at ordinary temperatures. Its common name, quicksilver, means live or fluid silver. Metallic mercury is very dense, about 13.5 times as heavy as water. Its chemical symbol is Hg, for hydrargyrum (from the Greek words hydro, or water, and argyros, or silver). Most mercury comes from cinnabar, the only important ore of mercury, which consists of mercuric sulfide that occurs in brilliant red crystals or in red or brownish masses. To obtain pure mercury, refiners heat cinnabar in a flow of air. Oxygen in the air combines with sulfur in the ore, forming sulfur dioxide gas and leaving elemental mercury behind:

$$HgS \text{ (s)} + O_2 \text{ (g)} \rightarrow Hg + SO_2 \text{ (g)}.$$
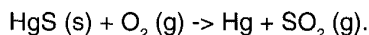
Mercury has many different uses. It is used in electrical switches, fluorescent lamps, mercuric oxide batteries, fungicides, pharmaceuticals, munitions, paper production, and the extraction of gold (1). Mercury was used extensively in gold mining in former centuries and even until the 1950s (2). Amalgamation, which relies on the contact of gold ore with mercury to form a gold-mercury amalgam, is one of the oldest processes available. The amalgam is then "roasted" (commonly by using a blowtorch), and mercury is driven off as a vapor. The unused liquid mercury is often lost to surface water. This process is strongly out of favor with the major mining companies due to the extremely toxic nature of mercury and the process's inferior performance when compared to the available alternatives, e.g., cyanide leaching. However, because of its simplicity, the amalgam process is still used extensively by artesian mines or deep bored wells in the third world countries and at small "mom and pop" mines (3).

According to the U.S. Geological Survey (USGS), mercury was produced as a byproduct at nine gold mining operations in Nevada, California, and Utah. Other gold mines in these states were believed to have recovered mercury, but data were not available to make estimates (4). Mercury may be a byproduct of gold mining due to the geology of mineral deposits containing the metal. In this case, the naturally occurring mercury is liberated from its mineralogical matrix. Recovering the mercury as a byproduct is environmentally favorable over dumping it into the tailings pond (2).

Mercury is a heavy metal that has no known metabolic purpose, is toxic to living organisms, and adversely affects the central nervous system of humans. Mercury can be converted from inorganic compounds such as cinnabar to organic forms such as methylmercury (MeHg), which is easily absorbed by living organisms. Mercury deposits and mines are a potential hazard to residents and wildlife because drainage from these

1

deposits enters streams and rivers that are part of the local ecosystem (1). For this reason, the extent of mercury contamination in the United States is of high environmental concern.

Presently, a number of gold mines and EPA Superfund sites are contaminated with mercury. The Carson River Mercury Site is a good example of the extent of mercury contamination. It consists of (1) sediments in an approximately 50-mile stretch of the Carson River in Lyon and Churchill Counties, beginning between Carson City and Dayton, Nevada, and extending downstream through the Lahontan Reservoir to Stillwater National Wildlife Refuge; and (2) tailing piles associated with the river. Mining began in the Carson River drainage basin in 1850 when placer gold deposits were discovered near Dayton at the mouth of Gold Canyon. Throughout the 1850s, placer deposits were worked for gold in Gold Canyon and Six Mile Canyon. These ore deposits became known as the Comstock Lode. The general milling process employed before 1900 involved pulverizing ore with stamp mills, creating a slurry, and adding mercury to the mixture. Mercury forms an amalgam with precious metals, which are then separated by distillation (retorting) of the mercury from the mixture, leaving the precious metal as the residue. After 1900, cyanide leaching and flotation processes replaced amalgamation. Elevated mercury levels in the Carson River drainage basin were discovered in the early 1970s when sampling conducted by the USGS revealed elevated levels in river sediment and unfiltered surface water in the Carson River downstream of pre-1900 ore milling sites. Subsequent studies by a number of investigators have further delineated the extent of mercury in river and lake sediment and water. Based largely on the information presented in these studies, the Carson River below New Empire was added to the National Priorities List (NPL) in August 1990 due to the widespread occurrence of mercury (5).

In December of 1997, EPA released an eight-volume report to Congress, mandated by the Clean Air Act, that evaluated the impact of mercury emissions to air on human health and the environment. The report estimated that about 159 tons of mercury were emitted into the air in 1995 from all U.S. industrial sources. One estimate of the total annual global input to the atmosphere from all sources–including natural, anthropogenic (human activities), and oceanic emissions–is 5,500 tons. Therefore, U.S. industrial sources contributed about 3% of the 5,500 tons released to the atmosphere in 1995. Based on the Mercury Study's emissions inventory, the highest emitters of mercury to the air include coal-burning electric utilities, municipal waste incinerators, commercial and industrial boilers, medical waste incinerators, chloralkali plants, hazardous waste incinerators, and cement manufacturers. The report did not mention mining operations as a mercury emissions source (6).

Mercury mines are all small by most mining standards. The largest is the New Almaden mine in California, where about 30 miles of horizontal underground workings were installed for exploration or development over a 100-year period. The only major deposit that has been mined by open-pit methods is the Sulphur Bank Mercury Mine in California, which was discovered 100 years ago. The 120-acre Sulphur Bank Mercury Mine site was initially mined for sulfur from 1865 to 1871. Mercury ore was mined intermittently by underground methods from 1873 to 1905. The mine, once one of the largest producers of mercury in California, has been inactive since 1957. The mine tailings extend into the Oaks Arm of Clear Lake along 1,200 feet of shoreline. Approximately 193,600 cubic yards of waste remain on site. Sediments from Clear Lake, soil, surface water, and fish are contaminated with mercury and arsenic. This was the only mercury mining site on the Superfund NPL list (7). Through the years, mercury has been produced by 300 mines in 11 states: Alaska, Arizona, Arkansas, California, Idaho, Nevada, New York, Oregon, Texas, Utah, and Washington. However, three-fourths of the domestic output has come from six mines, all of which are in California. The New Almaden mine near San Jose, California is the greatest mercury producer in North America, but most of its yield occurred prior to World War I. The New Idria mine in central California is the second most productive mercury mine in North America and was a major producer until the spring of 1972 (8). The western slopes of the New Idria formation in San Benito County drain to the Pacific Ocean. The eastern slopes of the New Idria formation flow to the San Joaquin river, where mercury affects the Panoche Creek. The Aurora mine, Alpine mine, and Larious Canyon mines are also major mercury contaminant sources (9). Mercury is currently only produced in the United States as a byproduct from gold mining; it is no longer produced from mercury ore. The last functional mercury ore mine, the McDermitt Mine in Nevada, closed in 1990 (10).

Since the closure of the McDermitt Mine, recovery of mercury as a byproduct from gold ores is the only remaining ore-based production process. In 1996, six U.S. gold mines (four in Nevada, one in California and one in Utah) produced metallic mercury as a byproduct. The names and locations of these mines are shown in Table 1 (10). No information was available on the amount of mercury recovered at each facility, although

the U.S. Bureau of Mines (USBM) reported that 70 tons of mercury were produced as a byproduct of gold ore mining in 1992. At this time, data are insufficient to estimate the amount of mercury emissions generated as a byproduct of gold ore mining. According to an industry representative, gold mines utilize mercury control emissions in order to recover as much mercury as possible (10).

Table 1. U.S. Byproduct Mercury-Producing Gold Mines (1996)

Mine	Location	Operator
Alligator Ridge	White Pines, Nevada	Placer Dome U.S.
Carlin Mines Complex	Eureka, Nevada	Newmont Gold Co.
Getchell	Humboldt, Nevada	FirstMiss Gold Inc.
McLaughlin	Napa, California	Homestake Mining Co.
Mercur	Toole, Utah	Barrick Mercury Gold
Pinson Mine	Humboldt, Nevada	Pinson Mining Co.

1.3   Purpose

The purpose of this workshop was three-fold:

1.   to convey public, nonprofit and private sector perspectives on the assessment and management of mercury associated with mining processes, residuals, and environmental impacts,

2.   to present past, present, and future efforts that address mercury production, contaminant reduction, and site remediation associated with mining and waste disposal practices, and

3.   to identify data gaps and information needs to improve mercury risk assessment and management practices associated with mining and environmental restoration activities.

Attendance at this workshop numbered over 300, including organizers and participants. Attendees represented: U.S. government agencies and departments–including the U.S. Environmental Protection Agency (EPA), U.S. Department of Energy (DOE), and USGS; state and local government agencies; tribal communities; nongovernment organizations (NGOs)–including the Meridian Institute and California Communities Against Toxics; industry–including Barrick Gold, Placer Dome and the Nevada Mining Association; academia; technology developers; consulting firms; and international participants.

1.4   Scope of the Proceedings Document

This proceedings document is organized in chronological order according to the workshop agenda. The agenda is included in Appendix A at the back of the document. The workshop started with a plenary session with presentations representing key stakeholder interests as depicted in Section 2. This was followed by concurrent technical sessions presented in the form of abstracts and technical briefs found in Section 3. Technical subject areas included modern mining, source identification and characterization, fate and transport, speciation, watershed impacts, air impact assessment, remediation and treatment, and a case study featuring the Sulphur Bank Superfund site. Many of the aforementioned mining sites and impacted areas were presented during the workshop. Section 4 captures the open panel discussion that concluded the workshop on the third day. Section 5 identifies some key points made during the workshop and future research needs. Appendix B in the back of this document lists the workshop attendees.

1.5   References

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(2)   Personal communications with Felix Hruschka (Mercury Expert). Mercury Network Homepage. http://www.hruschka.com/hg-net/mercurio.html(accessed Sept. 1998)

(3)   The Basic Processes of Gold Recovery. http://www.gold.com (accessed Sept. 1998).

(4)   USGS. Mercury. (http://minerals.er.usgs.gov/minerals/pubs/commodity/mercury/430396.txt (accessed August 1997).

(5)   EPA. Superfund. http://www.epa.gov/oerrpage/superfund (accessed September 1998).

(6)   EPA. Mercury Study Report to Congress: Overview. http://www.epa.gov/oar/mercover.html (accessed September 1998).

(7)   Superfund Public Information System (SPIS) CD-ROM and/or Superfund Web Site. http://www.epa.gov/superfund (accessed October 1998).

(8)   Bailey, E. H., Clark, A. L., Smith, R. M., *Mercury*, United States Mineral Resources, USGS Prof. Paper, pp. 401-414, 1973.

(9)   EPA. Draft Region 9 Mining Plan. *Mercury Contamination from Historic Gold Ore Processing in the Sierra Nevada Foothills and Abandoned Mercury Mines in California's Coastal Region*, June 14, 1999.

(10)   EPA. *Mercury Study Report to Congress*, Volume II: An Inventory of Anthropogenic Mercury Emissions in the United States, December 1997.

Section 2
Plenary Session

2.1 EPA: Developing a Strategy on Mercury Research — Jon Herrmann, EPA, NRMRL

Mr. Herrmann of the EPA, National Risk Management Research Laboratory (NRMRL), opened the meeting by thanking the attendees for their participation at this and two other workshops on mercury. This workshop is the third in a series of four workshops on mercury. The first two workshops addressed emission/deposition monitors and mercury retirement/disposal. A fourth workshop on aquatic and terrestrial transport is scheduled during May 2001 in Florida. These workshops were developed to provide direction for EPA's research efforts and to provide an opportunity for EPA to solicit input and suggestions from EPA Program Offices, vendors, academia, and other members of the environmental community.

Introduction

EPA's draft *Mercury Action Plan* (Federal Register, 1998) called for development of the *Mercury Research Strategy* (*MRS*), which guides the ORD Mercury Research Program and covers FY2001 to FY2005. The *MRS* summarizes the human health and ecological risks posed by mercury and MeHg and indicates that mercury needs to be considered on local, regional, and global scales. The *MRS* identifies the key scientific questions of greatest importance to the Agency and describes a research program to answer those questions. The goal of the *MRS* is to reduce the scientific uncertainties that limit EPA's ability to assess and manage mercury and MeHg risks. ORD will use the *MRS* to develop a multiyear implementation plan in FY 2001 for its Mercury Research Program.

In conducting the Mercury Research Program, in-house research efforts by ORD's laboratories and centers will be coupled with those of ORD's Science to Achieve Results (STAR) Grants Program. The STAR Grants Program sponsors extramural research with academic institutions and other not-for-profit entities. Some of the research described in the MRS will be undertaken in cooperation with organizations such as DOE and USGS. The MRS provides information on research needs and priorities that can be used by various stakeholders outside the Agency–including researchers in other Federal agencies, states, private industry, not-for-profit organizations, and academia–and may assist them in planning their own mercury research activities and programs. Finally, the *MRS* suggests that other scientific data and information not generally considered "research" are needed, such as inventories of sources and routine multimedia monitoring.

EPA Report: Mercury Study Report to Congress

The *Mercury Study Report to Congress* (EPA, 1997) described the magnitude of mercury emissions in the United States, identified mercury emission sources, assessed the health and environmental implications of those emissions, and evaluated the availability and cost of technologies for emission control. It is the most comprehensive human health and environmental investigation of mercury and MeHg available. The *Mercury Study Report to Congress* serves as the foundation for EPA's understanding of the risk assessment and risk management issues associated with mercury and MeHg. It contributes significantly to the strategic directions and the key scientific questions posed in the *MRS*.

In the *Mercury Study Report to Congress*, EPA concluded that a plausible link exists between human activities that release mercury from industrial and combustion sources in the United States and MeHg concentrations in humans and wildlife. In preparing the report,,uPA conducted a quantitative human health risk assessment of MeHg. The assessment estimated that between 1% and 3% of women of childbearing age (i.e., between the ages of 15 and 44) in the United States eat sufficient amounts of fish for their fetuses to be at risk from MeHg exposure. The *Mercury Study Report to Congress* also concluded that mercury poses risks to various wildlife, including some birds and fur-bearing mammals such as loons, mink, and otters. The *Mercury Study Report to Congress* comprehensively identified research needs to improve both mercury risk assessment and risk management.

National Academy of Sciences Report: Toxicological Effects of Methylmercury

The National Academy of Sciences (NAS) report, *Toxicological Effects of Methylmercury* (NRC, 2000), confirmed EPA's Reference Dose (RfD) of 0.1 micrograms per kilogram (µg/kg) of body weight per day. It viewed this RfD as a scientifically justifiable level for protecting human health from the adverse effects of MeHg. The NAS report estimated that more than 60,000 U.S. children are born each year with a risk of nervous system damage from MeHg exposures in the womb. It also noted the reduced performance of schoolchildren on neuropsychological tests in recent epidemiological studies, suggesting that prenatal MeHg exposures are likely to be associated with reduced school performance. The NAS report identified research needs related to better characterization of MeHg heath effects, enhanced estimation of MeHg dose-response relationships, and improved characterization of risk from current MeHg exposures. Finally, the NAS report recommended that every effort be made to establish a common scientific basis for exposure guidance among Federal agencies, recognizing that various agencies have responsibilities for this problem under differing legal and regulatory authorities.

Mercury in the Environment

As a liquid at room temperature, mercury is a unique metal that has proven itself useful for centuries in both industrial and consumer applications. Mercury is released in elemental and oxidized forms from a variety of human activities and natural sources. The exposure pathway addressed in the *MRS* is through fish consumption and consists of the following steps: 1) emission of mercury to the air; 2) mercury air transport, transformation, and deposition on land and water; 3) transformation of mercury to MeHg in water bodies; 4) MeHg uptake and bioaccumulation in fish; and 5) consumption of contaminated fish by mammals, including humans. Mercury and MeHg exposures can result in permanent damage to the brain and kidneys in both humans and wildlife.

The intentional use of mercury in products (e.g., batteries, paints) in the United States has decreased significantly in the past 20 years (Sznopoek and Goonan, 2000). However, since the 19th century, the total amount of mercury in the environment has grown by a factor of two to fives times that of preindustrial levels (Mason, et al.,1994). This situation raises concerns about increasing amounts of mercury in the global pool and the implications of mercury emissions for both human populations and ecosystems worldwide. In the United States, the most significant releases of mercury to the environment are emissions to the air. These air emissions come from combustion sources, such as power plants or incinerators. Mercury is also released from geologically bound sources through natural processes (e.g., volcanos, fires) and through mass transfer to the atmosphere by biologic and geologic processes from mercury that has been previously deposited (i.e., re-emission sources). In addition to air emissions, mercury is also released in other ways, including via waterborne discharges and direct disposal to the land. The releases of mercury to water and land are believed to be small compared to air emissions, but these releases can have significant local effects.

Depending on the chemical form in which it is released, the stack height of the source, air movement patterns, and other factors, mercury can deposit at local, regional, and global scales. Locally, within a 30-mile radius of some sources, a relatively high percentage of mercury may deposit on land and water. Regionally, different areas of the country experience different amounts of mercury deposition. The combined emissions of several mercury sources can travel hundreds of miles and deposit in distant regions of the United States. Modeling exercises by EPA have projected that the highest deposition rates from U.S. anthropogenic mercury sources occur in the southern Great Lakes and Ohio Valley, the Northeast, and scattered areas in the southeastern United States. Globally, mercury from other countries deposits in the United States, and U.S. emissions can travel around the world and deposit back into U.S. soil or water.

The particular form of mercury emitted is important in determining whether mercury is deposited near its emission source or travels great distances, perhaps circling the globe several times before eventually depositing. Mercury emissions from human activities take various inorganic forms, including elemental mercury vapor, gas-phase ionic mercury, and particulate-bound mercury. Once in the environment, these inorganic forms can be converted by naturally occurring processes into the highly toxic organic form—MeHg. The greatest concern regarding MeHg is the neurotoxic health effects associated with *in utero* exposures. Also, children exposed after birth are potentially more sensitive to the toxic effects of MeHg than adults because their nervous systems are still developing. Mercury also poses risks to wildlife, including some birds and mammals, such as loons, mink, and otters.

MRS Scope

While the NAS report confirmed EPA's RfD for MeHg, additional data and information are needed. A number of key scientific questions regarding assessment and management of mercury and MeHg risks remain to be addressed. ORD's *MRS* is part of the Agency's *Sound Science, Improved Understanding of Environmental Risk, and Greater Innovation to Address Environmental Problems Goal (Goal 8)*. Implementation of *Goal 8* is the responsibility of ORD under the Government Performance and Results Act (GPRA) (EPA, 2000). Although assigned to *Goal 8*, ORD's Mercury Research Program supports a number of other GPRA goals including those related to clean air, clean water, and safe waste management.

ORD's Mercury Research Program provides information, methods, models, and data to address the key scientific questions of greatest concern to EPA. The *MRS* goal seeks to reduce scientific uncertainties related to mercury and MeHg. The *MRS* presents the strategic direction for the Mercury Research Program over the next five years. It will assist ORD in the development of a multiyear implementation plan and will help in making decisions about future mercury research priorities. The results of the research program will inform the Agency's Program Offices and Regions and their activities to assess and manage mercury and MeHg risks. The *MRS* is oriented to domestic mercury and MeHg issues, although most of the research results will also be useful internationally. In preparing the *MRS*, six key scientific questions, associated research areas, and related research needs were identified. While it is a five-year research strategy, the *MRS* will undergo updates and adjustments based on ORD's annual research planning process.

Setting Research Priorities

The *MRS* was developed by a group of EPA scientists and engineers representing ORD and the Agency's Program Offices and Regions. To prepare the first draft of the strategy, the group was divided into eight writing teams focused on different aspects of mercury and MeHg risk assessment and risk management. The teams consulted a number of documents and individuals in preparing the *MRS*. The most influential document was the *Mercury Study Report to Congress*, which identified research needs across a number of areas. The writing teams developed six scientific questions formed around the research needs identified in the *Mercury Study Report to Congress* and other sources, including the Agency's Mercury Task Force (MTF).

The writing teams established the research needs for each of the six key scientific questions. The MTF assisted in this effort by identifying the regulatory and voluntary drivers for mercury and MeHg facing the Agency over the next five years. The writing teams integrated relevant international research issues into each research area. Research needs under each key scientific question were prioritized using three criteria: 1) provides timely scientific information and data needed to inform current and future Agency decisions on mercury, 2) fills data and information gaps on mercury not addressed by other organizations, and 3) supports the goals and objectives of ORD's Strategic Plan and research on risk assessment and risk management. In December 1999, an expert panel of ten external peer reviewers offered their individual and collective opinions of the draft *MRS* and its priorities. Many of the recommendations made by the peer panel have been incorporated into the final version of the *MRS*.

The writing teams made every attempt to balance priorities across the six key scientific questions. The priorities described in the *MRS* are only a snapshot in time and may well require adjustment in the coming five years. Priorities can change depending on a number of factors including progress in answering the key scientific questions, changes in regulatory deadlines, and research contributions by other organizations. These factors require that priorities and resource allocations be reexamined on an annual basis and that flexibility be a guiding principle in the annual budgeting process for the Mercury Research Program.

In the near term, ORD plans to focus on combustion risk management. In the longer term, ORD will emphasize research that enhances the fundamental understanding of noncombustion risk management, ecological effects and exposure, human health effects and exposure, and risk communication. Mercury fate and transport research will be a focus throughout the five-year time frame of the *MRS*. The *MRS* is aligned with current EPA Program Office and Region priorities and emphasizes mercury sources resulting from human activities in the United States. However, it does recognize the global nature of the mercury problem and the need for addressing impacts in the United States from emissions generated by other nations. The *MRS* is designed to be flexible and can accommodate redirection as a result of changing Agency priorities and perspectives.

Transport, Transformation, and Fate Research Area

Key Scientific Question

How much MeHg in fish consumed by the U.S. population is contributed by U.S. emissions relative to other sources of mercury (such as natural sources, emissions from sources in other countries, and re-emissions from the global pool); how much and over what time period, will levels of MeHg in fish in the United States decrease due to reductions in environmental releases from U.S. sources?

Prioritized Research Needs

- Improved understanding of the transport, transformation, and fate of mercury in the atmosphere
- Enhanced monitoring of atmospheric mercury deposition for model application
- Improved understanding of the transport, transformation, and fate of mercury in aquatic and terrestrial media
- Enhanced monitoring of mercury and MeHg in aquatic and terrestrial media for improved risk management

Research on mercury transport, transformation, and fate is highly supported throughout the life of the *MRS*. Research needs in this area will take some time to address fully because the transport, transformation, and fate of mercury, once it enters the environment, is very complex. This research will promote an improved understanding of mercury in the air and water, and on land. As fundamental understanding is improved, this research will inform the development of more cost-effective risk management approaches for mercury and MeHg.

Risk Management for Combustion Sources Research Area

Key Scientific Question

How much can mercury emissions from coal-fired utility boilers and other combustion systems be reduced with innovative mercury and multipollutant control technologies; what is the relative performance and cost of these new approaches compared to currently available technologies?

Prioritized Research Needs

- Improved understanding of managing mercury species in combustion processes
- Improved understanding of performance and cost of mercury emission controls
- Increased testing and evaluation of mercury continuous emission monitors
- Improved characterization of, and management approaches for, mercury control residuals

Research to manage risks from combustion sources addresses the most immediate mercury priority for the Agency and is well supported during the first years of the *MRS*. Combustion risk management research, including research on mercury in control residuals, will provide the Agency with the latest information on control technology performance and cost. This research will generate data and information that informs the preparation of a regulatory proposal for controlling mercury emissions from coal-fired utilities.

Risk Management for Noncombustion Sources Research Area

Key Scientific Question

What is the magnitude of contributions of mercury releases from noncombustion sources; how can the most significant releases be minimized?

Prioritized Research Needs

- Characterization of the mercury life cycle in human activities
- Improved understanding of mercury releases from sources and sinks
- Approaches for minimizing mercury releases from noncombustion sources

Research to manage risks from noncombustion sources is modestly supported in the early years of the *MRS*. Research in this area then increases as the need for risk management research on coal-fired utilities declines and other sources of mercury come to the fore. This research will provide information to support future assessment, rulemaking, and voluntary actions with an early emphasis on mercury source characterization. It will be followed by research on risk management approaches for those sources posing the greatest risks.

Ecological Effects and Exposure Research Area

Key Scientific Question

What are the risks associated with MeHg exposure to wildlife species and other significant ecological receptors?

Prioritized Research Needs

- Improved understanding of MeHg's toxic effects on avian and mammalian wildlife
- Refined ecological assessments for avian and mammalian wildlife risks
- Improved understanding of ecological impacts of MeHg on avian and mammalian wildlife
- Improved understanding of ecological impacts of MeHg on nonavian and nonmammalian species
- Identification of interactions among MeHg and other chemical and nonchemical stressors and effects on all ecological receptors

The effects of MeHg on ecological systems have been demonstrated, but there is a need to learn more about these effects, particularly in fish-eating wildlife. Support for this research area gradually increases over the life of the *MRS*. This research will assist the Agency in understanding the effects of exposures to mercury and MeHg on birds, mammals, and other forms of animal life. This research will also assist in the development of improved ecological assessments.

Human Health Effects and Exposure Research Area

Key Scientific Question

What critical changes in human health are associated with exposure to environmental sources of MeHg in the most susceptible human population; how much MeHg are humans exposed to, particularly women of child-bearing age and children among highly exposed population groups; what is the magnitude of uncertainty and variability of mercury and MeHg toxicokinetics in children?

Prioritized Research Needs

- Improved understanding of mechanisms of developmental neurotoxicity from MeHg
- Improved understanding of human compensation resulting from developmental exposures to MeHg
- Identification of impacts from aggregate exposures and synergistic effects of MeHg and other pollutants
- Improved understanding of the modulation of immune system response from MeHg exposure
- Biological monitoring for model development and improvement
- Development of toxicokinetic data on MeHg tissue distribution

The NAS report on the health effects of MeHg supported EPA's RfD of 0.1 µg/kg body weight per day as a scientifically justified level to protect human health. However, several research recommendations need to be addressed. Research in this area is supported at a relatively modest, but consistent level throughout the life of the *MRS*. There is a continuing need for ORD to provide scientific and technical assistance to the Agency in developing regulations and criteria based on the NAS-supported RfD.

9

Risk Communication Research Area

Key Scientific Question

What are the most effective means for informing susceptible populations of the health risks posed by mercury and MeHg contamination of fish and seafood?

Prioritized Research Needs

- Synchronization of fish consumption advisory messages for MeHg
- Improved understanding of exposure patterns in targeting of risk messages
- Understanding the use of risk information in making decisions about MeHg exposures

Research on improving communication to populations at risk from eating fish contaminated with MeHg is supported at a relatively modest, but consistent level over the life of the *MRS*. Research in this area will help the Agency to develop improved risk communication approaches targeted at populations that consume large quantities of fish. The most challenging populations are those individuals at greater risk due to possible nervous system damage such as the maternal-fetal pair, nursing mother-infant pair, and young children. This research area is one that is particularly amenable to collaboration with other organizations.

MRS Implementation

A number of groups, both internal and external to EPA, have a stake in the *MRS* and its implementation over the next five years. These groups are particularly interested in research program sequencing and timing in order to determine whether it is consistent with their needs, interests, and (for the Agency) target dates for regulatory and voluntary actions. The *MRS* is designed to provide broad strategic directions for ORD's Mercury Research Program, not schedules and time lines. More specific information will be forthcoming in ORD's multiyear implementation plan to be developed in FY 2001.

The *MRS* encourages engagement and partnering with various stakeholders. ORD believes that joint ventures enhance the Agency's own Mercury Research Program, as well as other mercury research efforts either planned or underway in the United States. ORD wants to strengthen research collaborations with the regulated community and other interested parties and gain their participation in mutually beneficial mercury research. ORD is seeking linkages to Federal agencies, states, communities, tribes, and other public and private organizations to gather insights from decision makers at various levels. Of particular interest are their mercury research needs and the actions they expect to take in both assessing and managing mercury risks. ORD welcomes input from any organization concerning the *MRS* and the Mercury Research Program described in this document.

2.2 Managing Mercury Issues on a Continental Scale — Luke Trip, Environment Canada

The North American Free Trade Agreement (NAFTA), developed to ensure trade equity between its members, includes a parallel environmental accord to ensure that the environment is not sacrificed for trade. The North American Agreement on Environmental Cooperation was established under NAFTA and is overseen by the Environment Ministers for the United States, Canada, and Mexico. This agreement resulted in the creation of the Commission for Environmental Cooperation, which provides for the development of the Mercury Action Plan under the Sound Management of Chemicals Program.

Of the 2,215 tons of anthropogenic mercury released to the atmosphere in 1995, 158 tons were from the United States, 70 to 90 tons were from Mexico, and 12 tons were from Canada. Approximately 2,000 tons of mercury were naturally released to the atmosphere. To understand the impact of these emissions, the following facts about mercury are useful to know:

- Mercury is a naturally occurring element, thus virtual elimination is not possible.
- Long-range atmospheric transport moves mercury great distances from the source.
- Environmental levels of mercury are increasing by 1% to 3% each year, based on recorded mercury intakes from bogs and swamps.

10

- Exposure to high levels of mercury can lead to kidney damage, liver damage, paresthesia, or death.
- Exposure to low levels of mercury can affect learning ability and muscle coordination in children.
- One cubic yard of mercury equals 10.00 tons or 9.08 million grams (g).
- Less than one third of a gram of mercury can contaminate a 25-acre lake.
- The majority of fish advisories in Canada and the United States are due to MeHg.
- The EPA-NAS RfD for mercury is 0.1 µg/kg of body weight per day.

Phase 1 of the North American Regional Action Plan (NARAP) on Mercury, which was approved in October 1997, calls for reductions in anthropogenic mercury pollution and for mercury levels and fluxes to be reduced to natural levels. Phase 2, which was accepted by the Council of Ministers on June 12, 2000, calls for "additional specific actions to further reduce anthropogenic releases together with specific targets and time frames." The action items contained in Phase 2 were based on recommendations from three workshops in 1998: Capacity Building in Zacatecas, Mexico; Public Consultation in Mexico City, Mexico; and Science Experts in Las Vegas, United States. The six major action items and 80 subaction items contained in Phase 2 were synthesized from over 300 recommendations. Phase 2 also includes a commitment to move from a voluntary to a regulated structure.

The six major action items identified in Phase 2 were:

- Management of atmospheric emissions
- Management in processes, operations, and products
- Waste management approaches
- Research, monitoring, modeling, assessment, inventories
- Communications activities
- Implementation and compliance

Each of these items is described in greater detail in the following sections.

Management of Atmospheric Emissions

The first action item called for reductions from major stationary sources using Best Available Technology (BAT). This includes coal-fired utilities and metal smelters.

Management in Processes, Operations, and Products

The second action item called for management of the following processes, operations, and products:

- Life cycle management
- Automotive vehicles and equipment
- Mercury cell chloralkali sector (reduced by 50% by 2006)
- Dry-cell battery manufacturing
- Electrical switches and relays
- Lamp manufacturing (mercury vapor lamps and fluorescent lamps)
- Health and dental care (blood pressure machines)
- Cultural and artisan uses

Waste Management Approaches

The following waste management approaches were identified under the third action item:

- Management of combustion and industrial processes, including pollution control
- Management of incinerator waste streams
- Wastewater treatment
- Mercury waste collection and handling
- Mercury retirement programs (very controversial)
- Continuation of reduction measures

Research, Monitoring, Modeling, Assessment, Inventories

The fourth action item supported the following research, monitoring, modeling, assessment, and inventory related issues:

- Developing consistent and comparable data
- Supporting the North American Mercury Monitoring Network
- Supporting the North American Mercury Research Program, specifically releases from contaminated sites (mines)
- Modeling atmospheric transport in North America
- Developing and maintaining inventories, reporting standards and criteria, particularly the development of an inventory of high level sites
- Developing new major construction initiatives

Communications Activities

The following communications activities were specified under the fifth action item:

- Inform North Americans (to reduce risk through a communication outreach program)
- Communicate best practices
- Develop a directory of recycling "databases"

Implementation and Compliance

The sixth action item on implementation and compliance addressed the following:

- Implementation of specific plans by each country within one year, the application of regulatory controls if voluntary actions are inadequate, and public reporting
- Verification of success (via audits), capacity building, and build improvements

Initiatives related to past and present mining activities include developing an inventory of high-level sites, assessing and controlling releases from contaminated sites, developing a mercury retirement program, and improving communication about best practices. Both Canada and the United States awarded contracts to develop inventories of high-level sites in November 2000, and Mexico recently put out a "call for proposals" for a two-part contract to develop an atmospheric emissions inventory and a high-level sites inventory.

The next steps to be taken in support of the NARAP on Mercury involve 1) assessing sector gaps in North America, particularly from dental amalgam waste management, historic and current mining, and petroleum refining and natural gas processing; 2) developing permanent mercury retirement options for excess from recycling and mining operations and from older, secure mercury mines; and 3) initiating a global mercury action plan.

2.3   Regional Office Perspective — David Jones, EPA Region 9

The environmental and human health impacts of historical and current mercury releases from mining operations are on the front burner for EPA Region 9. The environmental community's understanding of how different forms of mercury cycle in the environment is neither complete nor comprehensive. Appropriate responses to elevated levels of mercury in soil, sediments, or air require an understanding of science, economics, public policy, land use, risk assessment, and the personal lives and finances of many individuals. Although more than 26 million pounds of elemental mercury were used by the gold mining industry between 1850 and 1900, and much of that mercury remains in soils and sediments in California and Nevada, environmental officials need to determine whether to focus resources on cleaning up historical mercury contamination or addressing existing sources of mercury emissions. This issue needs to be put into perspective.

Understand the Risk Assessment Model for Mercury and Where There Is Discretion

The major concerns during a risk assessment are the pathways to an environmental or human receptor and the mercury concentrations that pose a risk to a receptor. Worst-case risk assessment default factors are

often used when site-specific information is unavailable. If species data are unavailable, the risk assessment personnel generally assume that all of the mercury is in a highly bioavailable form, such as mercury chloride or mercury oxide, rather than a less bioavailable form, such as mercury sulfide or elemental mercury. Final land use (e.g., residential, industrial, or recreational) is also considered during the risk assessment.

Project personnel at the Carson River Superfund Site were concerned about mercury in tailings in residential areas, particularly the potential for soil ingestion by children. Although a preliminary remediation goal of 23 milligrams per kilogram (mg/kg) in the soil has been used by EPA at sites where soil ingestion is a concern and species data are limited, this goal presumes that the mercury is present in a highly bioavailable form. Since 95% of the mercury at the Carson River Superfund Site is elemental mercury or mercury sulfide, a cleanup level of 80 mg/kg was established for this site. Because there was uncertainty about the relative absorption of different forms of mercury in the human intestine, a safety factor was used when this goal was selected.

Subsequent to EPA's Carson River decision, a DOE site near Oak Ridge, Tennessee was found to have mercury soil contamination similar to that of the Carson River Superfund Site. However, in this case, DOE performed laboratory studies to simulate the absorption rate of mercury in the human intestine. A final mercury cleanup level of 400 mg/kg was selected using this more precise data in the risk assessment. Thus, the cleanup level for mercury-contaminated soils in a residential area depends on how much data are collected and what the data show. The more information that is collected on the concentrations of the different mercury species, the mercury's bioavailability to humans, and the land use of an area, the more precise the risk assessment can be.

Understand How Cleanup Decisions Affect People's Lives

All parties want cleanup levels for mercury to be protective of human health. However, it is important to realize that cleanup levels can have a major impact on the economic and social life of residents. In the Carson River Valley, houses were built in areas with elevated levels of mercury. The soil cleanup level established for mercury (e.g., 20 or 80 mg/kg) may significantly impact whether residents are worried about their health. It can also have a significant impact on property values, which affects both their economic and social lives.

Although the public health protection is important, the public should not be needlessly alarmed in the process. It is important to understand how people's lives are affected by mercury investigations and cleanup actions, and to anticipate the types of questions they will have. Homeowners are typically concerned about their health and safety, as well as possible impacts on property values.

Be Aware of Background Mercury Levels in Historic Placer Mining Areas

At first glance, Greenhorn Creek, a tributary to the Bear River in California's Sierra Nevada foothills, appears to be located in a pristine setting. Investigation revealed that 1,000 cubic yards of placer mining debris with elevated levels of mercury and MeHg were located on a side tributary. Before a decision could be made whether to remove the material, information was collected on mercury levels in the surrounding soils and sediments. This investigation revealed that the stream bed was composed of mercury-contaminated hydraulic mining material deposited on the floor of the valley between 1850 and 1890. Although the stream bed was raised 200 feet during this period, about 100 feet of this debris had eroded away in the last 120 years. Project personnel had to decide whether removing 1,000 cubic yards of placer mine tailings would have any impact on mercury concentrations because this material currently sits on hundreds of thousands of cubic yards of placer mine tailings. Ultimately, decisions of this nature are site-specific and should not be made without a full understanding of the background mercury levels in the surrounding area.

Protecting Human Health Is a Primary Reason for the Cleanup of Mine Sluice Box Tunnels

Very high levels of mercury were identified in mine sluice box tunnels following a USGS-led multiagency study in the Bear River watershed. A tunnel in the Polar Star Mine had very high levels of mercury in sediments (up to 3% by weight) and high-level MeHg discharges from water that flowed through the tunnel. The EPA Region 9 Superfund program removed the mercury-laden sediments at the Polar Star Mine, in part because amateur or recreational "miners" had been collecting the mercury in the hope that it contained gold. The primary purpose of this removal action was to protect the health of these miners. Although the source of

MeHg to the environment was also eliminated, this was only a secondary benefit and not the motivating factor for the removal action. Mr. Jones anticipates that the protection of human health will be the primary focus for mine sluice tunnel cleanup actions in California in the near future. However, as mercury loadings and dynamics in different watersheds are better understood, cleanup actions may eventually be based solely on environmental factors.

Eliminating Perceived Regulatory Barriers to Mercury Cleanup Actions or Mercury Emissions Reduction Is Important

When amateur gold miners remove sediments, sands, and gravel from streams, they are also removing mercury. Since mercury in streams can bioaccumulate in fish and make them unfit for human consumption, this can be considered an environmentally beneficial activity. In 1996, State and Federal regulatory and land management agencies tried to design a program to collect mercury from amateur gold miners. Since the regulations appeared to require that recreational gold miners obtain hazardous waste permits, transport the mercury as a hazardous waste, and transport it to mercury-permitted hazardous waste facilities, efforts to collect this waste were stymied by perceived regulatory barriers.

Local, State, and Federal environmental and land management agencies met this year to develop mechanisms to collect mercury from amateur gold miners that are easy for the miners to follow and yet are consistent with environmental and health regulations. By focusing on areas of regulatory flexibility, the agencies were able to design a mercury collection program that does not require the mercury to be handled as a Federal or State hazardous waste. Since this program was developed, hundreds of pounds of mercury were collected over a three-month period. Project personnel estimate that costs were cut by 95% since the mercury did not have to be handled as a hazardous waste. Participants were encouraged to work with regulators to eliminate regulatory barriers that block common-sense, cost-effective opportunities to clean up mercury, rather than proceed with costly cleanups with no real environmental benefits.

Reducing Existing Air Emissions of Mercury Should Be a Top Priority

When EPA Region 9 staff received a draft copy of the 1998 Toxic Release Inventory (TRI) reports, they were surprised to find that more than 13,000 pounds of mercury are emitted to the atmosphere each year from Nevada gold mines. These emissions were much greater than anticipated.

Although gold mining companies in Nevada have made significant investments to capture the mercury released during gold processing, and current air emissions of mercury are consistent with facility air permits, national studies indicate that a lot of the mercury found in the Midwest and Southwest United States is from atmospheric deposition. Furthermore, elemental mercury released to the air in Nevada is more likely to deposit in Wisconsin or Florida than in Nevada.

In response, EPA has made the reduction of mercury air emissions a top priority. Although the cleanup of historic mercury contamination may not be physically or financially feasible, efforts to reduce existing mercury emissions need to be taken. In 1997, the United States and Canada signed a binational agreement to reduce aggregate releases of mercury to the air by 50% by 2006. EPA is currently working to meet this goal.

Since developing new national standards for mercury air emissions from Nevada gold mines will take time, the Nevada Division of Environmental Protection (NV DEP) and EPA Region 9 have initiated a dialog with representatives of the gold mining industry in Nevada to investigate creating a voluntary program to reduce mercury air emissions. The goal of the program is to achieve significant, permanent, and rapid reductions in mercury air emissions. If a voluntary program can be successfully launched, the mining companies may be able to reduce mercury air emissions much faster than required by State or Federal law.

Conclusion

After noting that his presentation reflects a perspective acquired through his involvement with specific mines over the last 10 years, Mr. Jones stated that our understanding of how mercury cycles in the environment is relatively new. After stressing the importance of good mercury risk assessments and recognizing the role of discretion in risk assessment calculations, Mr. Jones emphasized the need to understand how cleanup

decisions affect the lives of residents. He reiterated the importance of knowing the background mercury levels of soils and sediments in historic placer mining areas, as well as the importance of addressing existing air emissions of mercury and existing high levels of mercury in mine sluice box tunnels. Mr. Jones closed by voicing his hope that participant perspectives regarding the mercury puzzle will widen as a result of this workshop, and attendees will come to understand the mercury mystery together.

2.4 Mercury Emissions from Mining Operations in Nevada: a State Perspective — Jolaine Johnson, NV DEP

1998 TRI Reports

Mercury emissions from mining in Nevada were developed based on mercury emission data revealed in the 1998 TRI reports. According to these reports, seven mines in Nevada reported mercury emissions to the atmosphere, although approximately 25 smaller mines in the State will be required to report their emissions in the future. In 1998, 423 pounds of fugitive mercury emissions and 13,560 pounds of stack emissions were released to the atmosphere, for a net emission of approximately 7 tons.

Sources of Mining Emissions

After noting that most mining operations occur in remote areas like the Humboldt River Basin, Ms. Johnson listed the following sources of mercury emissions from mining:

- Historic amalgamation process (mercury was added to ore during mining operations in the late 1800s)
- Natural occurrences/emissions in regional ore
- Fugitive releases from ore handling (e.g., transportation, crushing, etc.)
- Stack releases from heated processes

Mercury Emissions in the United States

Ms. Johnson presented a table containing estimates from EPA's *Mercury Study Report to Congress* in 1999. Ms. Johnson had modified the table to include an estimate of mercury emissions from mining sites. According to this table, 3.4 tons of mercury were emitted by area sources, 137.7 tons by combustion sources, 15.6 tons from manufacturing, 1.4 tons from miscellaneous activities, and 7.0 tons from mining activities. Although natural sources were included in the table, no estimates of their contribution to the total were included.

Regulatory Requirements

Other than the direct mining of mercury, mercury releases from mining operations are not regulated under the National Ambient Air Quality Standards (NAAQS) or under the National Emission Standards for Hazardous Air Pollutants (NESHAPs) for gold or silver mining operations. Mercury releases from mining are also not regulated under the State of Nevada's Hazardous Air Pollutants (HAPs) requirements. Although there are regulatory requirements under Title V of the Clean Air Act (CAA), mercury is also not regulated under New Source Performance Standards (NSPS) regulations. Additional information on the regulatory requirements for mercury from mining activities is addressed in more detail in the following sections.

Unlike precious metal mining operations, mercury mining operations are regulated under NESHAPs and must meet a mercury emissions limit of 2,300 grams per 24 hours. However, because no mercury mines are in operation in the United States today, this is a moot point. It is important to note that there are no limits under NESHAPs for mercury emissions from gold or silver mining. Thus, facilities not subject to NESHAP requirements will need to comply with the CAA Title V requirement related to the use of Maximum Achievable Control Technology (MACT) at any new or modified major source with greater than 10 tons per year of HAPs. In the State of Nevada, the HAPs requirement (NAC 445B.349) states "an owner or operator shall not discharge HAPs that threaten the health and safety of the general public as determined by the director."

The health advisory level for fish consumption from the Food and Drug Administration (FDA) of 1.0 parts per million (ppm) mercury in fish tissue is enforced by the Nevada Division of Health. Ms. Johnson noted that this protocol is currently undergoing redevelopment.

Regional Monitoring Efforts

Between 1975 and 1999 the NV DEP collected 504 water chemistry samples from the Humboldt Basin. Although 25 instances of violations of the water quality standards were observed at dispersed locations, the causes of these violations are unknown (e.g., storm events, groundwater influx, sampling/analysis error, or regional or local activities). The USGS collected 312 water chemistry samples from the Humboldt Basin during the same period. Although 58 violations were observed at various locations, the causes for these violations are also unknown. In both cases, no recent violations or trends have been identified that explain or are related to the previously observed violations.

In addition to water chemistry analyses, the U.S. Fish and Wildlife Service (USFWS) analyzed fish tissue samples in 1998. Although no samples were at or above the 1.0 ppm advisory level, mercury concentrations ranged between 0.05 and 0.49 ppm. Since 1988, air quality at Jarbridge has been monitored under the Interagency Monitoring of Protected Visual Environments program. Mercury has not been detected at concentrations above the method detection limit of 0.1 nanograms per cubic meter (ng/m^3) since monitoring began.

Summary and Recommendations

After noting that there are currently no imminent and substantial threats in the region due to mercury emissions, and that the sources of mercury in the environment are unknown, Ms. Johnson listed the following recommendations:

- Continue environmental monitoring
- Support research efforts
- Develop a better emissions inventory
- Foster cooperative efforts to consider the feasibility and effectiveness of further control measures to reduce mercury emissions

2.5   USGS Mercury Research — Kate Johnson, USGS

Mining-related mercury research performed by the USGS can be separated into two broad categories: 1) the genesis of mercury ore deposits (e.g., from Almaden, Spain to the mercury mineral belts in Alaska, Canada, and Nevada) and 2) environmental impacts of mercury from mineral deposits. Specific areas of environmental impact research include the following:

- Characterization and speciation of mercury mine wastes
- Geochemistry of mercury in acid mine drainage
- Methylation and demethylation of mercury
- Fate and transport of mercury from mineralized sources

After noting the USGS efforts to develop a repository of large, long-term databases and its increasing focus on process research of downstream effects, Ms. Johnson provided information on a broad array of USGS efforts, including environmental impact research, the USGS database repository, and mercury research efforts and information from the National Uranium Resource Evaluation (NURE) resampling effort in South Carolina, Alaska, and Palawan in the Philippines.

Environmental Impacts

USGS research into the impacts of mercury on biota have focused on the following areas:

- Fish, birds, amphibians, and invertebrates
- Toxicology

- Minerals-related site-specific studies (e.g., the southwest Alaska mercury mineral belt, California Sierran gold belt, and the Palawan mercury deposit in the Philippines)

USGS Databases

The USGS has also been involved in developing mineral, water resource, and biologic national databases. The minerals databases include information on 1) the localities and character of mineral deposits, 2) commodity reports (production and reserves worldwide), and 3) national mineral resource assessment. Information on these databases can be obtained from http://mrdata.usgs.gov. The water resources databases contain real-time stream flow and water quality and quantity data. Information on the water resources databases and the biologic databases can be found at http://www.usgs.gov.

NURE Resampling

Ms. Johnson presented a map of the United States with sampling density information entitled "NURE Resampling Status - 25 Sept 2000." The map contained sampling density information relative to a 17-kilometer (km) grid. The results of the resampled NURE samples were used as the basis for a program for performing geochemical-based line samples. This map was followed by a U.S. map showing the analytical mercury results for the resampled NURE samples.

South Carolina

Two maps showing mercury concentrations in South Carolina coastal plain soils and stream sediments were presented. These maps are used to examine regional trends for mercury. Population information and boundaries of lithofacies were also included on the maps.

Alaska

A map of southwest Alaska, which contained information on the number of mercury localities, was presented. The information was collected under two studies developed to determine whether waste products from mercury mining efforts endanger local residents eating locally caught fish. Although a graph of mercury concentrations in muscle and liver samples from four types of area fish (e.g., pike, Arctic grayling, dolly varden, and salmon) indicated elevated mercury levels, all of the levels were below FDA action levels.

Palawan

A map of the Philippines, Indonesia, Taiwan, Papua-New Guinea, and Fiji, which identified locations where significant subduction-related mineral deposits can be found (including Palawan in the Philippines) was presented. The Palawan mercury mine was operated from 1955 to 1976. During its operation, mining wastes were dumped in the ocean, eventually forming a jetty composed of mine waste. Since 1995, at least 21 residents have been poisoned by mercury which is believed to have leached from the surface of the jetty and been passed through fish (via uptake) to humans in the area.

Ms. Johnson closed her presentation by encouraging participants to visit the USGS website at http://www.usgs.gov or to contact her at kjohnson@usgs.gov or 703-648-6110.

2.6   County Role in Mercury Assessment and Cleanup — Elizabeth Martin, Nevada County

Mercury contamination is a legacy of the historic gold mining that shaped Nevada County. Recent studies by the USGS and others have shown that MeHg has been found at significant levels in bottom-feeding fish such as bass. A health advisory limiting intake of certain fish (bass) is now under consideration by the Office of Environmental Health Hazard Assessment and the counties of Yuba, Nevada, and Placer.

Nevada County has become concerned about the possible recreational and economic impacts of mercury contamination as information about possible mercury contamination in the area has surfaced. County personnel are particularly concerned about possible impacts on development efforts in the area, since developers believe that the flat areas associated with old mine workings (e.g., tailings) are ideal for development.

17

Technical guidance and funding is needed to help the County decide whether it should require an environmental evaluation of former mining areas prior to development. County personnel also need to be trained in mercury contamination issues, particularly for gravel operations in rivers and streams.

In order to address the mercury contamination, the county first needs to determine the shape and location of the mercury contamination and to identify hot-spot remediation opportunities. Training and technical assistance is also needed at the county level to enable County staff to be able to identify and deal with mercury problems. Testing protocols and practices for assessing and responding to mercury contamination are also needed.

Although Nevada County is making progress, as demonstrated by a successful program for collecting mercury from residents, the County needs a protocol that can help County personnel interact with the various agencies interested in controlling the mercury contamination problem in Nevada County. Additional technical training is also needed to enable personnel to intelligently address the mercury issue and to improve interactions with other agencies on this issue.

A number of issues associated with pollution credit trading also need to be addressed in the near future, and remediation standards need to be developed that make sense to counties. After stressing the importance of local, State, and Federal agency cooperation when assessing and characterizing the mercury issue, Ms. Martin closed by noting that Nevada County and other Gold Country communities are ready to partner with government agencies and nonprofit organizations to address the mercury problem.

2.7 County Role in Mercury Assessment and Cleanup — Shawn Garvey, South Yuba River Citizens' League

The South Yuba River Citizens' League was established in 1983 and currently has over 4,000 members from within the watershed and around the country. Recently the League received a grant from EPA to represent the community and to hire technical assistance to help the community address contamination issues at the Wildcat Mine Superfund Site. The League's goal is to protect, restore, and preserve the entirety of the South Yuba River watershed.

Nevada County is an attractive area. Its pristine appearance camouflages some of the realities of its gold mining past, specifically arsenic and mercury contamination. As residents have become more aware of some of the realities of living in a former gold mining area, community activities and behavior have been affected. Mr. Garvey related four experiences that highlight how the community understands mercury contamination and how it affects the community's behavior.

Voluntary Water Quality Monitoring

The Yuba watershed has entered into the largest voluntary water quality monitoring program in the Sierra Nevada range. Over a three-year period, samples will be collected by 90 volunteers from 22 sites spread over a 1,300-square-mile watershed. The goal of the program is to address concerns about health impacts from the mercury and arsenic contamination that has moved from the Wildcat Mine to the river.

Potential Forestry Impacts in the Sierra Nevada Range

Logging is the predominant resource extraction activity in the area. The environmental community was supportive when the USGS and the State Water Resources Control Board became concerned about possible mercury impacts to the Bear River following a request for a timber harvest permit at Colfax below the Dutch Flat site. Their concerns resulted in a temporary delay of logging at this site.

Since the largest property owner in the county is a logging company that owns land at, below, and above the mining site, the community is concerned about soil impacts or disturbances that could result from logging near the mine and how mercury and arsenic concerns could impact the proposed logging.

Potential Impacts on Restoration Activities

Currently, 55 agencies, industry organizations, environmental groups, and a marina owner are cooperating on a river studies project to reintroduce wild salmon and steelhead above the Englebright Dam. A six-million-

dollar study is expected to be approved to investigate how to introduce salmon and steelhead above Englebright Dam. It involves possibly the largest timber restoration project ever attempted. Although a number of obstacles need to be addressed for this project to succeed, the biggest problem involves how to remove the Englebright Dam, since it contains approximately 50 years' worth of mercury-laden sediments behind it. Although the dam may be successfully trapping mercury and preventing it from entering the watershed system, Mr. Garvey questioned whether it made sense to maintain a dam with no flood control, no water supply capabilities, and limited recreational value simply as a long-term holding tank for mercury.

Land Conservation

The Yuba River Conservancy purchases land for conservation in key habitats and access areas near the Yuba River. After noting that historic mining operations had significantly changed the elevation and course of the Yuba River, Mr. Garvey stated that the pools and reservoirs in the gold fields near the Yuba River contain pools of mercury that miners still collect at night. Since the majority of properties that the Yuba Conservancy is considering purchasing are located in this area, the Conservancy is concerned about the possible presence and impact of mercury and arsenic contamination. These concerns have temporarily halted/stalled efforts to purchase some of this land.

After noting that the South Yuba Citizens' League does not have answers to these situations or many of the questions associated with the mercury contamination in the Yuba River watershed (e.g., whether it is safe to swim in or drink the water), Mr. Garvey supported the continuing collection of data in the Sierra and partnering efforts with local advocacy groups to establish priorities and to obtain and allocate funding in order to improve efforts to study and react to mercury contamination issues in the area. He recommended moving from studies to policy changes (e.g., development, health, restoration, and environmental policies) and from policy changes to actual improvements in human health conditions and the environment. He also recommended improving efforts to educate and communicate with communities on this issue.

2.8 The Management of Mercury in the Modern Mining Industry — Glenn Eurick, Barrick Gold Corporation and Dirk van Zyl, University of Nevada, Reno (UNR)

Dr. van Zyl opened with the following key points regarding mercury in mining:

- Mercury occurs naturally in trace concentrations associated with some precious metal ores and, as a result of processing these ores, mercury is produced as a secondary product.
- Precious metal mining operations in Nevada produce metallic mercury and handle mercury-bearing materials using sound management.
- The precious metal mining industry is the primary source of new metallic mercury produced in the United States.

His presentation covered the following topics: exploration, mining, beneficiation, air emissions, metal production, employee exposures, and conclusions and directions.

Exploration

Mercury is naturally occurring and is concentrated to varying degrees in precious metal mining regions in Nevada and the western United States. Since mercury naturally occurs with most precious metals, it is commonly used as a geochemical tracer in exploration. Exploration rock samples are typically analyzed for mercury and other metals. Mercury concentrations are also typically given consideration in ore body assessments for future development.

After showing a cross-section of an ore body, Dr. van Zyl noted that mercury is generally associated with sulfides (e.g., pyrite), and that cinnabar (i.e., mercury sulfide) is the simplest and predominant form of mercury in Nevada gold ores. Cinnabar is among the least soluble of the mercury sulfides in water.

A graph of mercury concentrations plotted against the depth of the borehole for four typical boreholes was displayed. The graph showed the variability associated with mercury concentrations in ore samples. This variation is due to a number of factors, including the type of ore body, the minerals present, etc.

19

Mining

During surface mining, material is blasted from the surface, the ore is sent to a plant for processing, and the waste rock is stored away from the work area. Composite surface rock is generally collected and analyzed for mercury and acid accounting. Meteoric water mobility analyses are also commonly performed on surface-mined rock; mercury is typically a component of these analyses. According to Dr. van Zyl, although less rock is produced during underground mining operations, the mined materials undergo basically the same sampling and analytical tests as materials from a surface mine.

Beneficiation

Beneficiation is the process by which precious metals and mercury are removed from ores. Beneficiation involves the following processes:

- Crushing/Grinding: Big rocks are reduced to little rocks, which are in turn reduced to powdered rocks.
- Pretreatment: Autoclaving or roasting of the ore prior to leaching.
- Leaching: Tank or heap leaching of the ore (using cyanide) to remove precious metals from the ore and deposit them on carbon. The residual ore, which has been stripped of the precious metals, is called tailing.
- Carbon Stripping: Precious metals are removed from the carbon and placed in solution.
- Carbon Regeneration: Heat regenerates the carbon for reuse.
- Electrowinning/Zinc Precipitation: Precious metals are removed from the stripping solution in solid form.
- Retorting: Precious metal solids are preheated to extract the mercury before gold is recovered.

During the beneficiation process, samples of ore, tailing, waste rock, and process and nonprocess waters are routinely monitored for mercury concentrations. Mercury concentrations in solid samples are typically analyzed with conventional metals analytical equipment but, due to sample heterogeneity, analytical precision is variable. Mercury concentrations in liquid samples can be performed for both total and dissolved values using conventional analytical techniques such as inductively coupled plasma (ICP) analysis.

Dr. van Zyl provided a more detailed discussion of mercury issues associated with ore pretreatment, ore sampling, and tailing. This information is summarized as follows.

Ore Pretreatment

Some ore pretreatment processes may require mercury air emission controls. State-of-the-art mercury capture and/or recovery systems such as scrubbers and polishing filters can be designed, constructed, operated, and monitored at mining sites to reduce mercury emissions at these sites. The mercury-bearing material collected via air pollution control devices can be used to produce metallic mercury either onsite or offsite. Mercury suppression by commercial reagents or sodium hydrosulfide may also be employed to precipitate mercury as an organic or mercuric sulfide.

Ore Leaching

Ore samples are typically collected after grinding, but before either pretreatment or leaching, and reanalyzed for metals including mercury. Typically mercury forms a relatively weak complex with cyanide during ore leaching and is removed with the precious metals. Since mercury has a great affinity for activated carbon, it is effectively captured for recovery with precious metals (e.g., gold and silver). Mercury also has a great affinity for sulfide.

Tailings

Mercury concentrations vary in tailing solids, which may include mercury cyanide, mercury sulfides, and other metallomercury complexes. Tailing solids are typically sampled and analyzed for metals using appropriate analytical methods. Tailing liquids are also sampled and analyzed for metals, including total and

dissolved mercury as required by environmental permits. Low concentrations of dissolved mercury are typically measured in the tailing. Tailing impoundments use effective containment liner systems.

The presentation was turned over to Mr. Eurick.

Air Emissions

According to Mr. Eurick, the following air pollution control devices are used in precious metal operations to remove mercury efficiently: mercury recovery/suppression processes, condensers/water chillers, wet electrostatic precipitators, wet scrubbers, baghouses, and carbon filters. In general, the emissions from selected or processing components are monitored for mercury on a site-specific basis, depending on the recovery process used, the mineralogy of the deposit, etc. Mercury emissions from precious metal mines can be measured using EPA stack testing methodology. EPA-approved test methods can also distinguish between particulate-bound mercury and total mercury (THg).

In the 1998 TRI reports, metal mining operations reported the release of 4,610 pounds of mercury compounds to the atmosphere. However, according to Mr. Eurick, approximately 9,409 pounds of mercury compounds, which were not included in the TRI estimate, were also released from new metal mining sources. A total of 29,656 pounds of mercury and compounds were released from "all sources (original and new)."

Metal Production

After noting that mercury is offered for sale in the market, Mr. Eurick noted that the State of Nevada produced approximately 30,000 pounds of mercury in 1999 and 40,000 pounds of mercury in 2000. Mercury production increased between 1999 and 2000 because new gold recovery technologies were installed during that period.

Employee Exposures

Employee exposures to mercury are minimized through material sampling and monitoring and comprehensive hazard recognition training. Employee exposure monitoring is routinely performed and tracked to ensure compliance with established occupational health standards. Containment and contingency plans are in place in the unlikely event of an accidental release.

Conclusions and Directions

Mr. Eurick presented the following conclusions:

- Mercury occurs naturally in association with some precious metal ores.
- Mercury can be recovered when processing precious metal ores and sold into commerce as a secondary product.
- Minimal releases of mercury to the environment occur.
- Mercury capture devices reduce emissions; additional technologies are being explored to further reduce emissions.
- Effective mercury management will continue to improve as the precious metal industry moves to meet future challenges.

Mr. Eurick closed by noting that increased attention needs to be paid to developing, applying, and understanding the following:

- In-process mercury balances
- Capture and recovery systems
- Air pollution control devices
- Offsite transport and deposition issues
- Technology transfer opportunities

Section 3
Technical Sessions

3.1   Modern Mining

3.1.1 Sources of Mercury from Mineral Deposits - James Rytuba, USGS

Introduction

Mercury deposits are distributed globally in 26 mercury mineral belts that are typically localized along major plate boundaries or intra-plate zones of extension. The mercury mineral belts consist of mercury deposits with significant production, which is greater than 1000 flasks (a flask contains 76 pounds of mercury), small mercury occurrences having small or no production, and areas of altered country rock containing elevated concentrations of mercury. In North America, the California Coast Range mercury mineral belt has been the largest producer of mercury and contains 51 mines that have produced over 1000 flasks of mercury (Figure 1).
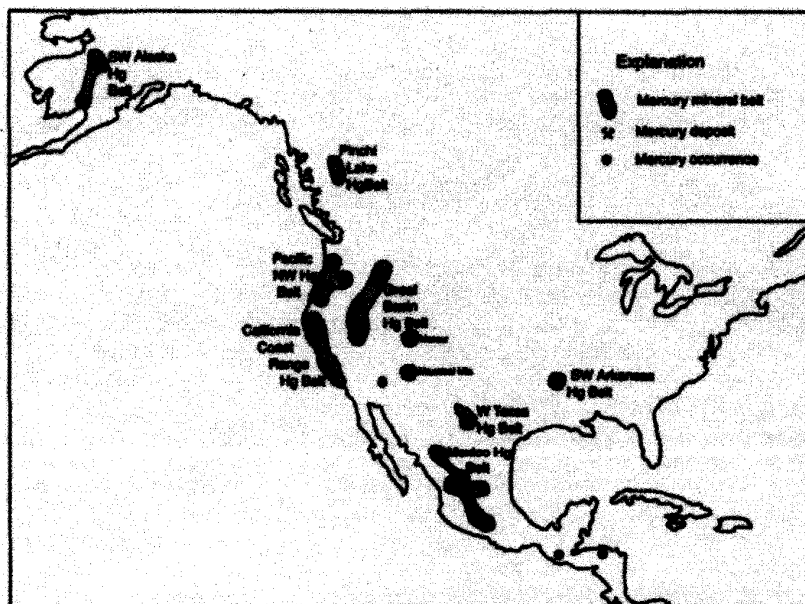
Figure 1: Mercury mineral belts in North America consist of mercury deposits with significant production and mercury occurrences with little or no production. Shaded areas indicate altered areas with elevated mercury concentration.

Mineral Deposits that Are Sources of Mercury

Three types of mercury deposits are present in mercury mineral belts: silica-carbonate type, hot-spring type, and Almaden-type. The Almaden-type deposits are the largest mercury deposits, accounting for over one third of the world's mercury production. Mercury is also produced as a byproduct of hot-spring type gold-silver deposits, sediment-hosted gold deposits, and zinc-rich massive sulfide deposits. Other mineral deposit types contain significant mercury concentrations and distinct mercury mineral phases, primarily cinnabar (mercury sulfide), but mercury has not usually been recovered as a byproduct from these deposits. These deposits include: polymetallic base metal replacement deposits, volcanogenic uranium deposits, antimony deposits, Franciscan-type and bedded manganese deposits, native copper deposits, and bedded

22

barite deposits. Much of the mercury produced has been used in the recovery of gold from placer deposits and in the processing of precious metal ores that utilized the mercury amalgamation process. The reprocessing of gold placer deposits and precious metal mine tailings, such as in the Zacatecas mineral district, Mexico, is a significant source of byproduct mercury.

Because of environmental concerns and the consequent low price of mercury, large-scale mercury mining has significantly diminished or ceased in most of the mercury mineral belts during the past two decades. In North America most mercury mines are closed except for several small mercury mines in Mexico. In the U.S. and Canada mercury is produced as a byproduct from the mining of hot-spring type gold-silver deposits, sediment-hosted gold deposits, and massive sulfide deposits. With increased concerns about the release of mercury to the atmosphere, limiting the release of mercury vapor from mining and processing will likely increase the amount of mercury produced as a byproduct from these mineral deposit types.

Most of the world's primary mercury production continues to come from the Almaden mercury district in Spain. The mercury deposits in this district are large and have very high grades, allowing for the production of mercury under most economic conditions. Other mercury deposits also contribute significantly to the total global production of mercury. These include deposits (listed in decreasing amount of production) in Kyrgystan, China, Algeria, Russia, Slovakia, Tajikistan, Ukraine, Mexico, and Slovenia. Significant mercury also continues to be produced in Finland as a byproduct of the mining of massive sulfide deposits. Similar deposits in the Urals, (former Soviet Union) and India also contain mercury, but it is released to the atmosphere rather than recovered during the smelting process.

Primary Mercury Mineral Deposits

Most mercury deposits that occur in the large mercury mineral belts can be classified as either silica-carbonate type or hot-spring type mercury deposits (Rytuba, 1996). The Almaden-type deposits are primarily restricted to the Almaden district in Spain. Silica-carbonate type and hot-spring type mercury deposits are usually spatially separated but in some mineral belts, earlier-formed silica-carbonate deposits can be overprinted by later-formed hot-spring type deposits (Rytuba, 1996).

Silica-carbonate type mercury deposits are associated spatially with serpentinite that has been altered to a mineral assemblage of silica and carbonate minerals. These deposits are generally small to moderate in size, and contain from 0.1 to 10.0 million metric tons of ore containing from 0.2 to 0.8 weight percent mercury. The deposits consist of vein and replacement ore bodies developed within and adjacent to silica-carbonate altered serpentinite. Silica-carbonate alteration is localized along regional faults that separate serpentinite from adjacent country rock, and the alteration commonly extends up to several kilometers along the fault zone beyond the margins of the ore bodies. The alteration assemblage is zoned from a central core of quartz-chalcedony-magnesite-pyrite-marcasite to a peripheral zone of magnesite-calcite-dolomite-magnetite. The initial alteration process consists of the addition of carbonate to the serpentinite followed by introduction of silica into the central core (Sherlock, et al., 1993). The peripheral zone of calcite-dolomite veining may extend for several kilometers outward from the mercury deposit. In addition to mercury, these deposits commonly have elevated concentrations of antimony (0.1 – 1000.0 ppm), arsenic (2-200 ppm), nickel (10-3000 ppm), cobalt (5 – 100 ppm), thallium (1-12 ppm), and zinc (2 –50 ppm). Copper is generally low, less than 50 ppm, and lead is essentially absent in these deposits. Pyrite and marcasite comprise from 2 to 10 volume percent in the ores except in deposits that formed adjacent to mafic volcanic vents, where iron sulfide can comprise up to 50 volume percent. Pyrite and marcasite are the primary acid-generating sulfides in these deposits. The primary ore mineral is cinnabar. Metacinnabar, the high temperature polymorph of mercury sulfide, is also commonly present and in some deposits it is the primary ore mineral. Elemental mercury is typically present but only in small amounts. More rarely, under extreme oxidizing and low pH conditions, mercury sulfates, chlorides, silicates and chromates are present as coatings in the upper part of the ore body. The impermeable serpentinite bodies are important in the localization of silica-carbonate type mercury deposits, because their fault-bounded margins impede and channel the flow of mercury-bearing hydrothermal fluids (Rytuba, 1996). Elevated levels of mercury and small mercury occurrences are present in the silica-carbonate-alteration zones. The large economic mercury deposits formed in structural traps, such as antiformal structures, where fluids were localized below impermeable strata. In the large deposits, the ore bodies are hosted both in silica-carbonate altered serpentinite and in adjacent permeable clastic sedimentary rocks.

Hot-spring type mercury deposits are associated closely with volcanic centers and form in the near-surface environment. The volcanic host rocks and associated clastic sedimentary rocks are altered to an assemblage of adularia, quartz, and sericite at depth, and near the surface, to an advanced argillic assemblage consisting of kaolinite, alunite, and cristobalite, which commonly contains elemental sulfur. Some of these deposits are hosted by hot spring sinter that was deposited at the surface, and consists of banded silica and beds of hydrothermal eruption breccia. Cinnabar is the main ore mineral and minor amounts of elemental mercury are present. Mercury sulfate, chloride, and oxide minerals are present in the upper parts of these ore bodies and formed during supergene alteration. Because these phases are very soluble, they commonly are only preserved in sealed vugs and fractures. The mineral corderoite, $Hg_3S_2Cl_2$, is the dominant ore mineral at only one hot-spring type mercury deposit, the McDermitt deposit, Nevada. These deposits have a trace element association consisting of lithium, boron, arsenic, antimony, gold, silver, thallium, and tungsten. Hot-spring type mercury deposits are often the near-surface expression of hot-spring type gold deposits that occur at deeper levels, below mercury-enriched sinter, such as at the McLaughlin gold deposit (Lehrman, 1986).

Almaden-type mercury deposits are the largest and highest-grade mercury deposits. These deposits commonly contain from 10 to 100 million metric tons of ore that ranges from 2.0 to 20.0 weight percent Hg. The Almaden deposit in central Spain is the single largest mercury deposit in the world. These deposits are associated spatially with mafic submarine vent complexes that consist of mafic dikes and sills, and oval craters typically with dimensions of 300 meters (m) by 150 m (Hernandez, 1985), and submarine calderas, such as at the Las Cuevas deposit (Rytuba et al., 1988). The deposits consist of massive cinnabar and elemental mercury replacement bodies hosted by quartzite, tuff breccia, submarine pyroclastic flows of mafic to intermediate composition, mafic dikes, and organic-rich black shale. Elemental mercury is the primary ore mineral in one deposit, Las Cuevas. Primary veins in these deposits are uncommon, and the cinnabar veins that are present fill gash fractures developed during later regional metamorphism of these deposits (Rytuba et al., 1988). The replacement deposits hosted by quartzite consist of stratiform zones of cinnabar, native mercury, pyrite, calcite, and quartz. The grade and thickness of ore bodies is highest near the margin of the volcanic craters and decreases systematically away from the craters. Mercury is the only ore metal in these deposits, and the only other trace metal present is zinc. No other mineral deposit type is associated with these mercury deposits.

Byproduct Mercury from Other Mineral Deposits

Massive sulfide deposits that contain elevated mercury concentrations are typically zinc rich. Mercury is present in sphalerite, the zinc sulfide. It occurs as a solid solution replacement of zinc (up to 41% mercury) rather than as a discrete mineral phase. The mercury concentration in massive sulfide deposits is a function of concentration of zinc and the environment of formation of the deposit. The concentration of mercury in volcanogenic massive sulfide deposits ranges from 1-998 ppm, and in sedimentary exhalative (SEDEX) type deposits from 6 to 2054 ppm (Schwartz, 1997). In North America the Balmat SEDEX deposit in New York has the highest mercury concentration, averaging 1200 ppm.

Hot-spring type gold deposits commonly have mercury concentrations that range from one to several hundred ppm. Cinnabar is the primary ore mineral in deposits where mercury concentrations are sufficient to recover byproduct mercury. However, corderoite is present in some of the deposits and is the primary mercury mineral in a few deposits. Mercury is concentrated in the upper parts of these ore bodies and locally may reach grades typical of hot-spring type mercury deposits. Sediment-hosted gold deposits have mercury concentrations from 10 to several 100 ppm. Mercury is present primarily as cinnabar and more rarely as mercury selenide phases. Mercury is also present in pyrite, and in solid solution in stibnite and orpiment.

Polymetallic base metal replacement deposits that contain high concentrations of zinc may have high concentrations of mercury. Like massive sulfide deposits, mercury is present in solid solution within sphalerite. The average mercury concentration in this deposit type is quite variable but generally low, ranging from 0.5 to 293.0 ppm (Schwartz,1997). These deposits only rarely contain cinnabar or tetrahedrite.

Antimony, manganese, native copper, bedded barite deposits, and volcanogenic uranium deposits contain relatively low concentrations of mercury, generally less than 100 ppm. Cinnabar has been reported in some of these deposits but the low mercury concentration usually precludes identification of the phases in which mercury resides. In native copper deposits mercury is present as an amalgam, and average concentrations of the ore bodies range from 0.9 to 19.0 ppm (Kerfoot et al., 2000). In antimony deposits mercury is present

in solid solution in stibnite, and concentrations can be as high as several weight per cent. In oxidized parts of antimony deposits, mercury is present as cinnabar or corderoite within antimony oxide phases.

Mining and Processing Methods

Mercury mine operations were typically small and utilized the comparatively inexpensive process of heating the mercury ore above the thermal stability limit of cinnabar to volatilize mercury and subsequently recovering liquid mercury in a condensing system. At a few of the largest mines flotation systems were used to upgrade the ore prior to roasting. Most mines have been underground operations with open stope mining of high-grade ore shoots. Ore bodies that were present near the surface were mined by open pit methods, but only a few mines have been exclusively open pit operations.

Mercury ores have been heated in a variety of retorts and several types of furnaces. Furnaces differ from retorts in that furnaces internally heat the ores, mix fuel combustion products and mercury vapor, and process a continuous feed of ore. Retorts consist of one or more pipes that contain a single charge of ore. In retorts the ore is externally heated and vapors from the fuel do not mix with the volatilized mercury. Because of their low cost, retorts have been utilized at small mines having small but high-grade ore bodies. In some of the larger mines with ore processing furnaces, retorts were utilized to purify sooty mercury recovered from the furnace condensing system. Furnaces that have been utilized include the Scott, Herreshoff, and several types of rotary furnaces. The rotary furnace was the most commonly utilized. It consists of a rotating, inclined iron cylinder into which ore is continuously fed and from which the roasted ore, termed calcine, is removed. Mercury vapors and other gases are drawn from the upper end of the cylinder into a dust collector (cyclone) and then processed in a condenser before being released through a stack. The Scott furnace was generally built of brick and consisted of a series of baffles upon which the ore migrated downward as it was heated. These furnaces were initially inefficient until considerable ore had been processed through them and the bricks had become saturated with elemental mercury. At the end of mining the bricks from the furnace were generally processed in a retort to recover the mercury.

Condensing systems, which cool the vapor from the furnaces in order to separate the liquid mercury from other stack gases, range from simple single pipe to complex multiple pipe systems. The condensing system usually consists of a pipe 8-15 inches in diameter and several hundred feet in length that is folded into a series of U and inverted U shapes. The base of each U in the condensing system is immersed in a water tank and each is equipped with a drain hole so that condensed elemental mercury can be collected in the tank. Both air and water-cooled condensing systems have been utilized. In the more simple retorts the condensing system consists of an iron pipe 2-4 inches in diameter and 5-10 feet long sloping downward from the top of the retort tube to a collection tank. About two thirds of the product recovered from furnace condensers is elemental mercury and the remainder consists of fine soot composed of rock dust, mercury sulfides and sulfates, fuel soot, water and finely dispersed elemental mercury. In the older mines this material was dried on steam tables. However, this process released mercury to the atmosphere and often was a serious source of mercury poisoning. Calcium carbonate was used to aid in the mechanical coagulation of finely condensed particles of mercury from soot and collected from the table through a small pipe leading to a collecting tank. In the larger and more modern mines mechanical mixers or a centrifuge was employed to remove mercury from the soot.

Mine Wastes and Tailings

Mine wastes generated in the mercury mining process, listed in increasing residual mercury content (concentration range noted in ppm) include; waste rock (10-100), low grade ore (100-1000), calcines (10-1000), condenser soot (1000-10000), and cyclone dust (>10000). Condenser soot and cyclone dust were generally reprocessed in a retort to recover mercury but often unprocessed condenser soot was discarded with calcines.

The speciation of mercury phases in mine wastes is important in determining the amount of mercury that is bioavailable when the exposure pathway is through direct ingestion of mine tailings. The speciation of mercury phases also determines the amount of mercury that is released from tailings and that becomes available for methylation and subsequent incorporation into biota as MeHg. Direct identification of mercury phases by X-ray absorption spectroscopy has been utilized to characterize mercury mine wastes (Kim et al., 1998). Extended X-ray adsorption fine structure spectroscopy (EXAFS) indicates that several mercury phases are formed during roasting of mercury ores: metacinnabar (high temperature polymorph of HgS), corderoite,

schuetteite ($HgSO_4$-H_2O) and mercury chlorides (Kim et al., 2000). All of these minerals are more soluble than cinnabar, and thus calcines can be a significant source of soluble mercury. Metacinnabar commonly is the dominant mercury phase in calcines derived from silica-carbonate type mercury deposits because during the roasting process cinnabar is converted to metacinnabar, and impurities introduced into the metacinnabar structure impede its conversion back to cinnabar upon cooling to ambient conditions (Kim et al., 2000). Calcines from hot-spring type deposits commonly contain mercury chloride and sulfate phases in addition to metacinnabar (Kim et al., 2000).

Mercury-enriched particles and vapor deposited down wind from furnace and retort sites cause local enrichment of mercury in soils. Mercury content is highest in surface, organic-rich soils, ranging from 5 to 25 ppm, and decreases to background levels at a maximum depth of 0.5 m (Figure 2). Mercury-contaminated soils and mine wastes constitute sources of mercury-enriched sediment that may be released from mine sites. Release and transport of mercury from mine wastes occurs primarily during storm events when large fluxes of mercury may be transported from mine sites primarily in and adsorbed on particulate phases.
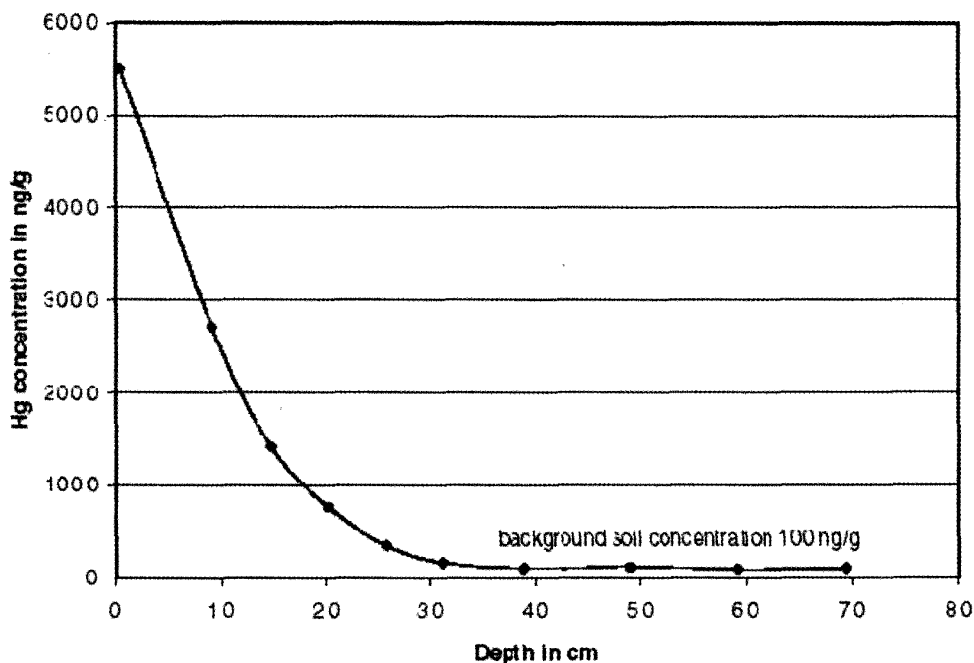
Figure 2: Profile of mercury concentration in soil impacted by release of particulate mercury and vapor from mercury mines in the New Idria mercury district, California.

Mine Drainage

Mercury mine drainage typically contains low levels of mercury and MeHg except where mine drainage flows through mine wastes and leaches mercury and methyl mercury (Rytuba, 2000). The total (unfiltered) mercury concentration for mine drainage that has not reacted with mine wastes ranges from .005 to 10.000 micrograms per liter (μg/L) for silica-carbonate and hot-spring type deposits (Figure 3). Total methyl mercury concentration of mine drainage ranges from <.003 to 1.26 nanograms per liter (ng/L) with highest concentrations associated with silica-carbonate type deposits (Figure 4). For both deposit types, filtered samples (0.45 μm) of mine drainage always have lower concentrations of mercury and MeHg indicating that a significant portion of both the THg and MeHg present is adsorbed onto particulate phases (Figures 3 and 4). Total mercury concentration in mine drainage that has reacted with mine wastes can be as high as 200 μg/L (parts per billion (ppb)). Elevated levels of mercury in mine drainage as well as high sulfate concentrations enhance methylation of mercury by sulfate reducing bacteria in environments impacted by mine drainage. In steams impacted by mercury mine drainage, mercury and MeHg are adsorbed onto iron oxyhydroxide and

clay particles and are transported primarily on these phases (Rytuba, 2000). In watersheds impacted by mercury-enriched mine wastes, mercury phases in the steam bed and in overbank sediments constitute major sources of mercury that can be persistently released to downstream environments.
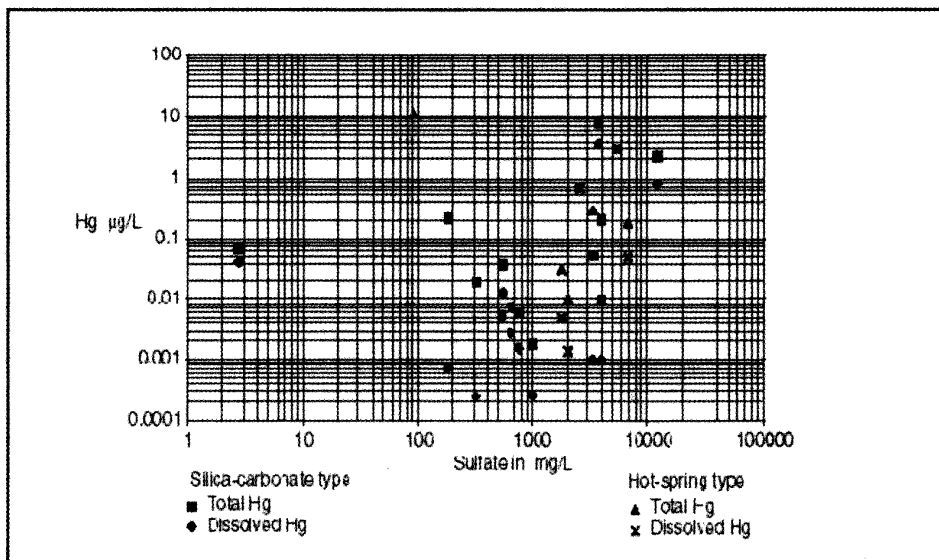
Figure 3: Mercury concentration in mercury mine drainage from silica-carbonate type and hot-spring type mercury deposits.
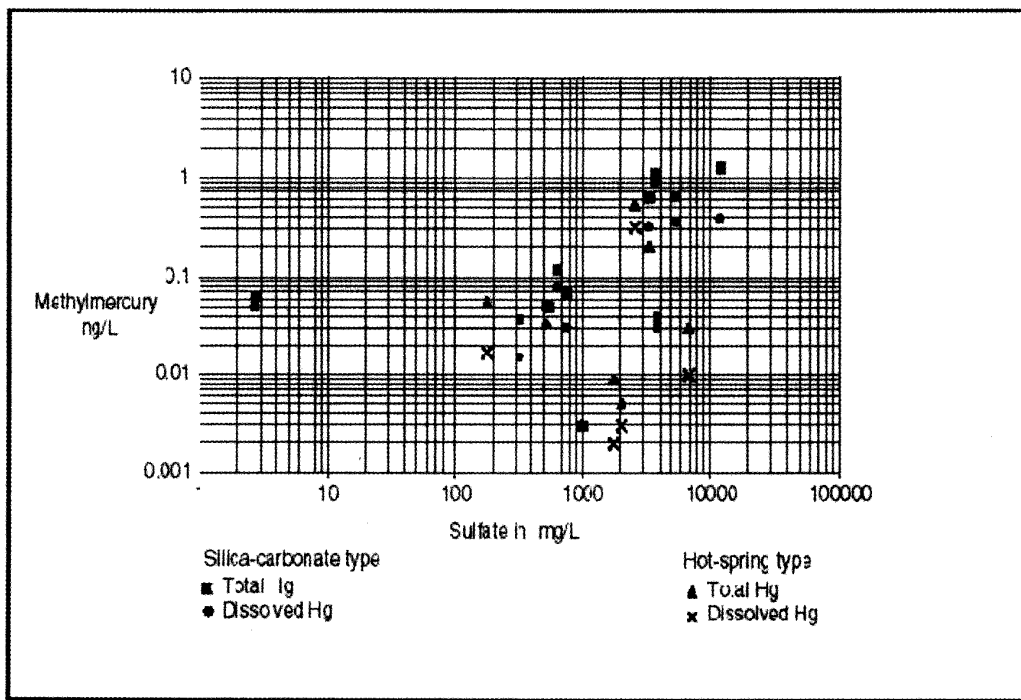
Figure 4: Methyl mercury concentration in mercury mine drainage from silica-carbonate type and hot-spring type mercury deposits.

27

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3.1.2 An Inventory of Mercury from Gold Mining Operations - Kumar Ganesan, Montana Tech of University of Montana

Introduction and Objective

The main objective of this research paper is to evaluate mercury contamination due to gold mining operations in Montana. This paper provides a review of the literature on the current estimates of mercury usage factor (MUF) and the methods available to estimate the amount of mercury in soil. It also discusses the fate of mercury in soils and tailings.

Background

Gold and silver mining in the United States of America released large amounts of mercury into the environment. It is assumed that 90% of mercury produced and imported by the U.S. between 1850 and 1900 was used for gold and silver extraction. At the turn of the 20th century the use of mercury for this process steadily decreased, and by the end of 1920 it was substituted with a cyanide process. About 60% of the mercury used in the gold and silver extraction process was released into the atmosphere mainly through the dry milling process, the mercury amalgamation with patio process, the squeezing of the amalgam, and the

burning of the mercury amalgam. The total amount of mercury emitted into the atmosphere between 1800-1920 was estimated to be 55,000 tonnes. However, the other 40% of the mercury, about 37,000 tonnes, was lost into soil and water through mine tailings and surface drainage. The methods used to estimate the amount of mercury are crude. There is no attempt being made to understand the extent of mercury contamination due to gold mining operations. There is very little information on the potential impact and fate and transport of mercury bound in the soil and sediments to the environment. Most of the recent studies focus on lakes and large water bodies that have received mercury mainly by atmospheric deposition processes. The fate of mercury in waste piles and tailings of old gold and silver mines, however, has not been assessed. It is assumed that mercury is present in the soil in the elemental mercury form, which has very limited dispersion characteristics and is mainly lost to the atmosphere by volatilization. However, mercury is known to undergo chemical transformation due to biochemical activities and may potentially pose a serious threat to water bodies. This paper attempts to evaluate the estimation techniques and the fate and transport of mercury in soil.

Mercury is also a naturally occurring element found in rocks, soils, water, and volcanic dust. Elemental mercury is the most common form found in nature. It can also exist in mono and divalent mercury forms, as well as in various organic and inorganic compounds.

Estimation Techniques

The amount of mercury in soils due to gold mining operations is currently estimated based on an average MUF, which is pound of mercury used per pound of gold produced. This value ranges from 1.5 to 4.0. It is assumed that most of the mercury used in the amalgamation process is lost into the environment. In many cases the mercury loss factor (MLF) is as high as the mercury usage factor. The MUF widely ranges from 1.5-4.0 and therefore the mercury loss estimate also varies widely. There has not been an attempt to verify or confirm these estimates through actual measurements or other means.

The second method by which mercury discharge to the environment was estimated was from the amount of mercury being imported and produced within the country during the Gold Rush era. It was assumed that 90% of the mercury was consumed in gold and silver production. This estimation technique is also very crude.

The direct and more accurate estimation technique is to actually measure the concentration of mercury in selected soil known to be contaminated with mercury and to use the results to estimate the amount of mercury in soils. By knowing the number and size of tailings that are contaminated with mercury, one can estimate the THg in the soil. It is not practical to sample all the tailings; however, representative sites may be tested to develop a mercury database to better understand the mercury problem. The difficulty here is that the mercury would have volatilized and the measurement will provide data on the current situation rather than the initial conditions. In addition, mercury could have undergone chemical changes and trans-located. Most of the mercury studies thus far are focused on lakes and water bodies where atmospheric deposition is the main source of mercury.

There have been attempts to measure mercury degassing from natural and manmade sources. The flux chamber method was used successfully to estimate the flux of mercury from such sources. The sample collection, recovery and analysis techniques must be improved to gather credible information. Again this data gives the amount of mercury that is being volatilized from the soil, and a mathematical model is necessary to obtain soil mercury content. In general Fick's law and Henry's law and a soil-water partitioning coefficient could be used to estimate the mercury flux from soil. It is also assumed that most of the mercury in the soil is in elemental form. The soil gas is expected to be in equilibrium with mercury in soil solution or with mercury in soil solid particle surface. One such equation based on the Fickian model is given below:

$Fs = 0.66(p-s) Do [C_{Hg-air} - C_{Hg-soil\ gas}] / D$; where Fs is the mercury flux, p and s are soil porosity and degree of soil moisture saturation, Do is the diffusion coefficient of mercury in air, D is the depth of soil, C_{Hg-air} and $C_{Hg-soil\ gas}$ are mercury concentration in air and soil.

Similarly, by using Henry's law, the mercury flux could be related to soil mercury content. It is important to understand the fate of mercury in soils in order to evaluate the potential health risks if any. Also it is essential for determining effective remedial technologies for mercury-contaminated soils.

During the Gold Rush several western states were explored for gold and silver. There is no accurate record of the gold and silver mines in Montana, especially during the 1800s when the gold amalgamation process was used. We have estimated that about 208 tons of gold were produced in Montana between 1800 and 1920. If we use the MUF of 1.5, then about 312 tons of mercury were used during this period. And if we make an assumption that 40% of this mercury ended up in soils and water (and 60% escaped into the atmosphere), then about 125 tons of mercury ended up in soil and water in Montana during 1800-1920. This could be as high as 500 tons if we use a MUF factor of 4.0 instead of 1.5.

Determining the Presence of Mercury in Soil

A gold mining site operated almost a century ago was the site selected to conduct this field study. The Great Divide Ski Area in the Marysville Mining District near Helena, Montana was reported to have some mercury in the soils in the ski slopes. Montana Tech's Geophysical Engineering Department and the Environmental Engineering Department used a Ground Penetrating/Probing Radar (GPR) along with metal resistivity measurements to identify the presence of mercury in the soil. The results from this study are not available for interpretation. However, initial data indicates that this technique is not very accurate for soils contaminated with very small concentrations of mercury.

Mercury in Soils and Its Chemistry

It is reported that in Carson River, Nevada, over 100,000 tons of mercury contaminated soil have been worked on, which has up to 4900 ug/g of mercury in soils. In Nova Scotia, tailings built in the 1840s still have mercury levels as high as 500,000 ug/g in soils. In the South Mountains Gold fields of North Carolina, sediments downstream of an old gold refinery built and operated in 1830 for thirty years contained up to 7.4 ug/g of soil. The moss samples collected in the vicinity showed up to 4.9 ug/g of mercury. These are some of the data that confirm the hypothesis that old gold mine tailings may have copious amounts of mercury still left in soil and its fate has not been evaluated.
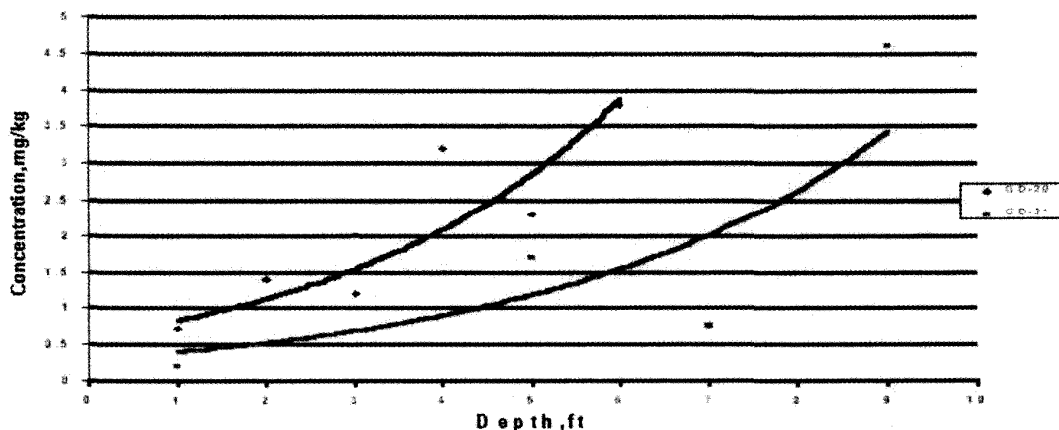
The preceding figure shows the mercury levels in gold mine tailings in Marysville, Montana. The mill was in operation in the mid 1800s. The Bureau of Land Management measured the mercury level in the soil in 1992.

The literature studies indicate the possibility of methylation of mercury in soil medium. It is assumed that the mechanism by which the conversion takes place is the same as in an aquatic environment. Mercury in soil may be methylated both chemically and biologically. The biological methylation involves three major coenzymes, S-adenosyl methionine, N^5-methyltetrahydrofolate derivatives and methylcorrinoid derivatives (vitamin B_{12}). These coenzymes are known to aid the methyl group transfer. Of the three coenzymes mentioned above, the methylcorrinoid derivatives are the only known agents capable of transferring the carbanion methyl group directly. Therefore, it is believed that the methylcorrinoid derivatives are the active agents in microbial methylation.

30

After an initial build-up of methyl mercury in soil, there appeared to be a mechanism that decreased the methyl mercury concentration with increasing time. However, methyl mercury could be persistent to all but specific biochemical processes. This process is not well understood. There are several parameters that affect the formation of methyl mercury in soil. These parameters are pH, Eh, soil mercury content, soil organic content, organic heavy metal content, salt content and composition of soil, presence of sulfur and chlorides, temperature, and microbial activity. The soil pH and redox potential dictate the availability of ionic mercury for the formation of methyl mercury. Also, the formation of mono or diMeHg depends on the pH of the soil. The temperature also plays an important role in the formation of methyl mercury, as methyl mercury is capable of volatilizing even at normal temperatures. The soil organic content and the presence of other heavy metal organics contribute to the methyl group required to form methyl mercury. The presence of sulfur as sulfide in the soil can readily form mercuric sulfide or Cinnabar, a very stable naturally-occurring compound. Hence, sulfide content in the soil can decrease the availability of ionic mercury. Microbial activity is also an important parameter in the formation of methyl mercury. Microorganisms seem to play a significant role in the formation and degradation of methyl mercury. The type of bacteria present dictates whether formation or degradation is supported.

Conclusions

It is postulated that thousands of tons of mercury from gold amalgamation processes may still be in tailings. The fate and transport of mercury in soil must be studied in order to effectively evaluate the potential health risk, if any, due to mercury in soils.

3.1.3 The Problem of Mercury Contamination in Gold-Mining Areas of Russia - Tatyana G. Laperdina, Chita Institute of Natural Resources, Siberian Branch of Russian Academy of Sciences

Mercury contamination in gold-mining areas of Russia is an extremely real problem, though at present solving this problem is not recognized by governmental bodies and so does not have financial support. It should be noted that the assessment of the intensity and scale of mercury contamination of different territories requires complex and expensive field and laboratory investigations.

Siberia and the Far East are the oldest and the richest gold-mining areas of Russia. Intensive gold-mining here started in the beginning of the 19th century. For the most part gold-bearing ores and sands were processed with the use of the amalgamation method for gold extraction, which has been used industrially since the second half of the 19th century. As a result of the long-term and intensive use of amalgamation, severe mercury contamination of technogenic and residential areas and cases of mercury intoxication of attendants were registered. This is the reason that since 1990, mercury has been officially prohibited for use at gold extraction plants, and since 1991, in the processing of gold-bearing ores and sands at dredges and hydraulic devices. Illegal and uncontrolled use of mercury still persists to the present. In connection with reorganization and decentralization of gold-mining in Russia, most of the archival data has become difficult to access. Therefore at present it is very difficult to assess the THg loading of different gold mining territories.

There is little published information on the results of investigations of mercury contamination of gold-mining regions of Russia. It is associated with the previous prolonged governmental restriction on publishing information on gold-mining and also with a previous lack of necessary methodical and instrumental equipment, especially for the analysis of mercury in contaminated and natural waters. The most comprehensive investigations on the estimation of mercury contamination were carried out in gold mines of the Chita Region (Table 1). The review of available literary data on mercury pollution of the environment is presented in Table 2.

Table 1. Mercury Concnetrations in the Environmental Compartments of Gold-Mining Areas and Background Zones of Chita Region

Sampling Sites	Rock Mineral, mg kg⁻¹	Atmos. Air, ng m⁻³	Soil, mg kg⁻¹	Water			Bottom Sediment mg kg⁻¹
				Dissolved, ng l⁻¹	Sediment mg kg⁻¹	mg kg⁻¹	
Mines "Tugir," "Uryum" (the Tungir-Olyokma raion)							
Background	0.049-0.134 (8)	≤5-8 (3)	0.013-0.14 (14)	≤5-15 (14)	≤5-50 (14)	1.0-45.5 (14)	0.024-0.072 (11)
Industrial		≤5-43 (4)	0.037-3.59 (6)	≤5-130 (16)	≤5-8830 (16)	0.02-21.7 (16)	0.016-0.131 (15)
Mine "Ksenyevsky" (the Mogocha raion)							
Background	0.001-0.012 (7)	≤1-6 (15)	0.024-0.094 (9)	≤10-60 (14)	≤5-380 (14)	1.3-112 (14)	0.008-0.091 (14)
Industrial	≤0.001-0.307 (13)	≤1-6 (28)	0.015-2.91 (25)	≤10-50 (42)	8-2240 (42)	0.7-1860 (42)	0.010-0.130 (33)
Mine "Beleyzoloto," including mine "Bukuka" (the Baley raion)							
Background	0.005-0.033 (12)	1-4 (10)	0.034-0.095 (9)	≤10-10 (13)	≤10-20 (13)	0.5-7.1 (13)	0.03-0.11 (9)
Industrial	0.006-0.780 (16)	1-40 (19)	0.099-1.24 (2)	≤10-5000 (41)	≤10-27800 (40)	0.6-321 (40)	0.10-3.24 (21)
Mine "Lyubov" (the Kyra raion)							
Background		5-11 (3)	0.03-0.11 (4)	≤5-10 (6)	≤5-60 (6)	0.4-1.1 (6)	0.01-0.04 (2)
Industrial		6-183 (23)	0.03-0.57 (12)	≤5-30 (24)	≤5-430 (24)	0.2-15.5 (24)	0.04-54.2 (17)

Table 2. Mercury Concentration in the Environmental Compartments of Gold-Mining Areas and Background Zones

Sampling Sites	Concentration Ranges of Mercury								
	Rock Mineral, mg kg⁻¹	Gravel, Tailings, mg kg⁻¹	Atmos. Air, ng m³	Industr. Air, ng m³	Soil, mg kg⁻¹	Water			Bottom Sediment, mg kg⁻¹
						Dissolved, ng l⁻¹	Particulate		
							ng l⁻¹	mg kg⁻¹	
Chita Region [Laperdina, 1995, 1996]									
Background	0.001-0.028		<1-11		0.013-0.14	<5-15	<5-380	0.4-112	0.008-0.11
Industrial	<0.001-0.307	0.43-54.2	<1-183	5-250000	0.015-3.59	<5-5000	<5-27800	0.2-1860	0.010-54.2
Republic of Buryatia (Irokendinskoe deposit) [Taisayev, 1991]									
Industrial									1.0-5.0
Krasnoyarsk Region [Roslyakov, 1995: Makarov, 1996]									
Background		0.01-759 g m⁻¹							0.034-0.18
Industrial									0.035-3.0
Novosibirsk Region (Affinage plant) [Roslykov, 1995]									
Background					0.03-0.08			0.04*	
Industrial					0.03-18.9			6.8*	
Republic of Yakytia [Bodienkov, 1984; Rukavishnikov, 1984; Omelchenkov, 1985]									
Background	0.01-0.04								
Industrial	0.15-4.0			100-230000					
Amur Region [Koval, 1997]									
Industrial		0.6-2000							
Khabarovsk Region [Koval, 1997]									
Industrial		1.0-1000							

*-Snow

As the results of investigations of several gold-mining territories have shown, the most severe mercury contamination is registered near gold extracting plants with the direct use of mercury in technological processes. Stable and, as a rule, local contamination of the territory fixed in these areas is characterized by high mercury concentrations in atmospheric air (40-183 ng/m³), in heaps and tailings dumps (0.43-2000 mg/

kg), in soils (0.57-3.59 mg/kg), in technogenic water reservoirs and streams (dissolved forms 60-5000 ng/L, suspended forms 380-27800 ng/L, and bottom sediments 0.130-3.24 mg/kg). Extremely high mercury concentrations were registered in the air of working places at dredges with sluice amalgamation (up to 10000 ng/m^3) and in the places of amalgams burning in gold extraction plants [up to 2 mg/m^3], as well as in enrichment tailings and contaminated ground nearby plants used for preparation and reprocessing of gold concentrates. High mercury concentrations registered in industrial zones have become the cause of an essential increase (>3 times) in mercury background levels in residential territories.

The investigations of the gold-mining areas (Table 2) were as a rule, of initiative, occasional character, and did not have financial support from the Federal and regional authorities. On the basis of these results it is impossible to correctly estimate the level of mercury contamination at all gold-mining areas of Russia. Hence, in connection with increasing environmental contamination, it is necessary to develop the governmental program determining the intensity and scale of mercury contamination of technogenic and residential territories, including measures to control and remediate contaminated territories. But taking into account the extremely difficult financial situation in Russia, one cannot hope to receive the financial support of the government at once and in sufficient amounts. Therefore it is necessary to carry out a number of primary measures which will contribute to the acceleration of development and government affirmation of the program to solve the problem of mercury contamination in gold-mining areas of Russia. In some regions of Russia (the Krasnoyarsk, Chita, Amur and Chabarovsk Regions), technologies for processing of mercury-bearing tailings of gold mines with separation of gold and mercury are being developed and used. In these regions specific regional programs determining stocks of and control over mercury contaminated areas are being developed at present.

The problem of negative impact of mercury contamination on the health of the population is complicated by a considerable decline of socio-economic living conditions in the severe climate of Siberia and the Far East, and also by contamination of traditional gold-mining areas with the other accompanying pollutants (arsenic, antimony, lead, etc.). The imbalance of macro- and micro component composition of drinking waters and food ration of the population, endemic deficit of vital microelements (selenium, iodine, etc.) intensify dangerous accumulation of mercury in living organisms.

3.1.4 Coal Cleaning as a Tool for Controlling Mercury Emissions from Coal Combustion - Michael A. Nowak (Presenter), U.S. DOE, National Energy Technology Laboratory; Carl Marond, U.S. DOE, National Energy Technology Laboratory; and Thomas J. Feeley, III, U.S. DOE, National Energy Technology Laboratory

Approximately 1.1 billion tons of coal are mined each year in the U.S. and the vast majority is used for electric power generation. The burning of coal for power production is estimated to contribute approximately one-third of the 150 tons per year of mercury emissions in the U.S. Approximately 50% of the steam coal is Eastern bituminous coal and 50% is Western subbituminous from the Powder River Basin. Approximately 75% of all Eastern coal is cleaned to some extent. Powder River basin coals are lower in sulfur and are not cleaned. Cleaning processes applied to Eastern bituminous coals are largely "conventional" techniques, normally processing coal having a size of +20 mesh or larger. Some preparation plants clean coal fines, but some operations employ little more than crushing to reduce coal to an appropriate size for ready transport to and handling at electric utilities. Crushing may liberate some large rock impurities from the coal. The extent that these coals are cleaned is driven by the characteristics of the as-mined coal and specifications for Btu, sulfur, and ash content that the utilities have negotiated into their contracts with coal suppliers. Because there is no economic benefit nor penalty, coal cleaning is not optimized for mercury or trace element removal.

The scope of an older (1978) DOE-sponsored study by BCR involved two coals. One was intended to be representative of the Appalachian Region of the U.S., and the other was intended to be representative of the Interior Region of the U.S. Coal preparation was limited to crushing, sizing, heavy-media cycloning, and hydraulic classifying. Correlation coefficients relating trace elements (but not mercury) to ash and sulfur reduction were determined.

BCR's observation that 70% and 55% mercury reductions at 80% recovery could be obtained using gravity techniques with 30-mesh topsize Upper Freeport and Illinois No. 6 coals needs to be received with caution.

Analytical techniques for analyzing trace elements in coal, particularly mercury, were still in their developmental stages. Some of the "clean" fractions had higher mercury concentrations than head samples, possibly owing to mercury volatilization from stored head samples. Also, the essential unit operation employed by BCR to reject ash and concomitant trace elements was hydroclassification. Hydroclassification is not considered a true gravimetric technique.

In 1993 DOE collaborated with Southern Company Services to determine the extent that selective agglomeration could remove trace elements from coal. Eighty hours of parametric testing were conducted at a scale of up to two tons per hour. The coals investigated in this study were Upper Freeport, Pittsburgh No. 8, and Illinois No. 5. Realizing that accurate analytical work was necessary to ensure acceptance of their findings, SCS employed a four-laboratory round-robin analysis of samples. Despite the analytical results being within the limits of available technology, the SCS project was plagued by poor data agreement among the four referee labs. For one coal (Upper Freeport), conventional cleaning plus selective agglomeration could reduce trace element concentrations significantly. However, one of the trace elements not significantly reduced was mercury.

CQ, Inc., realized the difficulty in trying to measure the mercury content of every raw coal and processed coal on a real-time basis and sought to avoid the problem by rigorous analysis of the few (25) data points publicly available in 1993. They determined that mercury reduction could be correlated to the mercury concentration in the raw coal, ash reduction, and sulfur reduction. The accuracy or confidence in the resulting predictive equations was lacking due to the need for more data points.

AMAX, with the support of DOE, set out in 1995 to produce a premium fuel, i.e., one that contained less than 2% ash and 0.6% S. Such deep reductions in ash and pyritic sulfur were expected to lead to significant trace element reductions. Five coals were collected for the study. These low-sulfur, high-volatile bituminous coals, were precleaned before being subjected to one of two advanced column flotation technologies, Kenflote & Microcel, or selective agglomeration. Tests with the column flotation techniques were performed at the 100 pounds per hour (lb/hr) scale and selective agglomeration was conducted with heptane at 25 lb/hr. Mercury reductions ranging from 36% to 51% were realized when three of the conventionally cleaned coals were subjected to advanced column flotation. Flotation had no impact on the other two coals. However, when examined on a ROM basis, it is clear that conventional coal cleaning was making a significant contribution to the overall mercury reduction. Selective agglomeration gave significant results for only one coal, but this coal was ground to a particle size of 20 microns. Again, conventional circuitry removed 57% to 82% of the mercury from the ROM coal. It should be noted that these coals started with relatively low mercury concentrations.

McDermott Corporation (1997) examined three Ohio Coals ranging in mercury concentration from 140 ppb to 300 ppb. The Ohio No. 6 coal was treated in a circuit using jigs, cyclones, centrifuges, and thickeners. The Meigs No. 9 circuit incorporated a heavy media bath, heavy media cyclone, and spirals. The Ohio 5/6 coal was simply crushed to 4 inches and processed in a jig at 1.55 specific gravity. The ash and sulfur contents of these ROM coals were reduced by 55% to 70% and 30% to 40%, respectively. Mercury content was reduced by 35% to 45%.

Three trace element control projects (CQ, Little Bear Laboratories, and Virginia Tech) were the result of a 1995 DOE solicitation called "Advanced Environmental Control Technologies for Coal-Based Power Systems." CQ examined four representative coals: Northern Appalachian (144 ppb Hg), Southern Appalachian (210 ppb Hg), Eastern Interior (151 ppb Hg), and Powder River Basin (98 ppb Hg). Their team examined modes of occurrence and physical, chemical, and biological coal cleaning. Examination of physical cleaning methods employed coals ground to four different mesh sizes and separated into five different gravity fractions. CQ also used the data to refine the predictive equations they developed in 1993. The data showed that individual coals respond differently to various techniques and conditions. Float sink data for the Southern Appalachian coal showed nearly 80% mercury reduction at 85% energy recovery but less than 20% mercury reduction at 60% energy recovery for the Powder River Basin coal. The highest mercury reduction with the Northern Appalachian was achieved with gravity separations and the lowest mercury reduction was achieved using agglomeration. Flotation gave intermediate results. Crushing Northern Appalachian coal to -100 mesh improved mercury reduction at 90% energy recovery from 25% to more than 50%. Treatment of coal with an ionic aqueous media at elevated temperature provided up to 50% mercury reduction in middlings fractions. CQ believed the mechanism was related to organic mercury bound in the organic fractions.

34

In collaboration with DOE and CQ, the USGS attempted to improve our understanding of the modes of occurrence of mercury in coal. This knowledge would help determine the best methods for removing mercury. Based on leaching and SEM microprobe analyses, the USGS concluded that for the four representative coals in the CQ study, the mercury occurs in three forms, with up to 65% of the mercury being associated with pyrite, 25% to 35% associated with organic fractions, and 5% to 30% associated with HCl soluble sulfides. Eastern Interior coal tended to have more mercury associated with pyrite, and Powder River Basin coal tended to have more mercury associated with organic fractions and HCl soluble sulfides.

Little Bear Laboratories undertook an investigation of bioleaching as a means to remove mercury from coal. Bioleaching had been successfully applied in ore processing and since mercury was associated with pyrite, it was hoped that bacterium such as T. Ferroxidans could liberate and/or solubilize mercury. During the course of the project, LBL also examined combined physical and biological cleaning methods to reduce the mercury concentration in coal. Neither T. Ferroxidans nor thermophilic bacteria were found to be effective in solubilizing or liberating mercury. However, treating 28 X 100 mesh coals with thermophiles made up to 30% of the mercury soluble in HCl.

Virginia Tech examined three coals, a Pittsburgh No. 8, Illinois No. 6, and a Coalburg seam coal. Characterization included mineralogy for natural fines (65 X 100) at nine density fractions. Virginia Tech found a strong correlation between mercury and pyrite, a weak correlation with ash and ankerite, and negative, weak correlation with the organic material. The following data for Pittsburgh No. 8 coal is representative of Virginia Tech's results. A dense-media circuit processing coarse coal could reject 37% of the mercury. Using an enhanced gravity separator, 85% mercury rejection at 85% combustible recovery could be achieved. Column flotation using 28 x 100 mesh feed coal could achieve 78% mercury reduction at 88% yield. Virginia Tech designed a conceptual three-component circuit that could achieve 75% mercury rejection.

In 1998, EXPORTech initiated a project on the removal of selected HAPs precursors by dry magnetic separation. Power plant pulverizers are designed to reject large (i.e., difficult to grind) particles and therefore tend to concentrate pyrite and other minerals in the pulverizer. Intended for processing of mill concentrate, EXPORTech tested their patented ParaMag separator with several coals, using a magnetic field to reject pyrite, and concomitantly, mercury. EXPORTech found that for two eastern coals, mercury reductions of 32% and 51%, respectively, could be obtained at more than 90% Btu recovery. Pyritic sulfur reductions were 47% and 38% respectively. Pyrite and mercury reductions of 75% were observed for one Western bituminous coal. The technique takes advantage of the fact that even coals that are not normally cleaned at the mine can be beneficiated. Thus, Powder River Basin coals were included in the tests. Pyritic sulfur reductions of 25% and 11% corresponded to reductions in mercury of 27% and 5%, respectively for the two PRB coals. Strong, positive correlations between mercury and pyrite concentrations were found for three Pittsburgh seam coals, an Upper Kittaning and a Lower Freeport coal.

In 1997, the U.S. DOE entered into an Interagency Agreement with USGS, which also partnered with Electric Power Research Institute (EPRI), various State Geological Surveys, coal companies, utilities, and EPA to generate characterization data on major coal beds that are currently mined and those expected to be mined within the next twenty to thirty years. The project is focusing on characterization of trace element concentrations in ROM and cleaned coals, but will also look at channel and reject samples.

The data presented here emphasizes percent reductions possible, not absolute values. As in all coal cleaning operations, liberation of the particles bearing undesirable components is critical. Mercury association with pyrite has been shown to be significant, and pyrite rejection is reasonably effective for removing mercury. Individual coal cleaning operations with specific coals can remove more mercury than when reported as "average values." More aggressive "conventional" cleaning and/or advanced technologies can make a significant impact on mercury reductions at preparation plants. The potential impact of coal cleaning must be assessed on a case-by-case basis and an assessment of current mercury reductions should be conducted. Powder River basin coals are not cleaned, but they represent a significant portion of our steam coal consumption and cleaning of these coals may represent a significant opportunity for mercury reductions.

Basic trace element characterizations of U.S. coal resources are lacking. Reliable standards and faster, cheaper, and more reliable analytical methods that can enable the characterization of those resources are needed. Coordination between programs such as ICR and NaCQI is logical, and support for these types of activities is also needed.

Ultimately, the viability of the precombustion mercury control option relies on the degree of control desired, the flexibility in obtaining the desired level of control, the acceptability by the end user of the product coal, the ancillary operations and transportation costs associated with delivering that product, and incentives for operators to optimize circuits for mercury rejection.

3.1.5 Mercury Emissions from Induration of Taconite Concentrate Pellets - Stack Testing Results from Facilities in Minnesota - Hongming Jiang, Ph.D., P.E. (Presenter), Minnesota Pollution Control Agency; Stuart Arkley, Q.E.P., Minnesota Pollution Control Agency; Trent Wickman, P.E., Minnesota Pollution Control Agency

Stack testing has been conducted since 1997 to determine mercury emissions to the atmosphere from taconite (low-grade iron ore) pellet indurating furnaces at all seven taconite pellet producing facilities on the Mesabi Range in northern Minnesota. Raw materials, products, and wastes associated with taconite pellet production have also been analyzed for their mercury content. These efforts were made to evaluate how much mercury is released to the environment, as a whole, during taconite pellet processing.

We have learned that mercury emissions to the atmosphere from the indurating furnace can be attributed to various factors. They include the high material throughput rate and the high processing temperature, which is a result of the intense heating from both fuel combustion and magnetite (Fe_3O_4) oxidation (an exothermic reaction). The mercury content of taconite ore is variable and therefore plays an important role in atmospheric emissions from plant to plant. At this time, it is not clear to what extent coal as a fuel contributes to mercury emissions, since the furnaces were fired with natural gas in all but one test. Mercury speciation has emerged as an important tool because the chemical form of mercury emitted (particulate-bound, oxidized, or elemental) plays a role in mercury removal from the stack gas stream, transport of mercury regionally and globally, and toxicological effects. One recent stack test found that more than 93% of the mercury emitted from the stacks was elemental mercury. Finally, our data analysis suggests that indurating furnace emissions are similar to emissions of coal-fired utility boilers in (total) mercury concentration.

The information reported in this paper is useful to regulatory authorities who may be contemplating control of mercury emissions from these and other similar sources. It is also useful to regulators, researchers, and concerned citizens who want to be informed of the current level of mercury emissions from these industrial sources.

3.2   Source Identification and Characterization

3.2.1 Contributions of Mercury to California's Environment from Mercury and Gold Mining Activities — Insights from the Historical Record - Ronald K. Churchill, Department of Conservation, Division of Mines and Geology (DOC/DMG)

California environmental mercury issues relate to historical mining operations in two ways. The first is to mercury mining activity. Between 1846 and 1981, about 103.6 million kg of mercury were produced within the state. The second is to historic gold mining activities that took place during the last half of the 19th century and the early 20th century, which depended upon gold recovery processes using mercury. Significant quantities of mercury were lost to the environment during both of these activities. This paper will show that historic records and reports from a variety of sources provide valuable information and insights into how and where these mercury losses occurred. They also allow estimation of the quantity and timing of these losses.

Most of the mercury deposits in California occur within a portion of the Coast Ranges geomorphic province extending from near Clear Lake in the north to Santa Barbara County in the south. Other mercury deposits are present in northwestern California, in the Basin and Range Province, and one small deposit was mined in the Sierra Nevada foothills. From historic records, the California DOC/DMG has identified 239 mines with production of at least one flask (34.0 to 34.7 kg) of mercury. An additional 54 sites may have had small unrecorded production. Based on published and unpublished data from the USBM and DOC/DMG, these

mines produced about 103.6 million kg of mercury. As is typical for metallic ore deposits, a few large mines account for most of the mercury production. The 25 largest mines account for about 100 million kg, or about 97%, of California's mercury production. The two largest mines, New Almaden and New Idria, account for about half of the total production. Cinnabar (HgS) is the dominant mercury ore mineral in most of these deposits. Some deposits also contain significant occurrences of metacinnabar (also HgS in composition) and, in a few instances, native mercury. Many mercury deposits were originally found by the recognition of the presence of silica-carbonate rock, a topographically prominent rock type commonly associated with many mercury deposits. Other deposits were found by panning stream sediments and hillside soils for the presence of cinnabar or native mercury.

Mercury ore processing routinely occurred at the mine sites. Mercury ore processing was relatively straight-forward and involved heating the ore in furnaces or retorts to break down the mercury sulfide ore minerals and liberate the mercury vapor. The mercury vapor was subsequently cooled and collected as liquid mercury in a condenser. Some mercury was lost to the environment wherever processing occurred. Mercury losses occurred by absorption into furnace bricks, trapping as fine droplets in solid residue, called soot, that formed in the condensers, as vapor that failed to be trapped in the condensers and exited to the atmosphere, during cleaning of the condensers and by spillage of recovered mercury during handling.

Mercury furnace losses gradually decreased over time as more efficient furnaces and better recovery practices were developed. By 1890, 15% to 20% losses could be achieved at well run plants, but losses at poorly run plants were still as much as 40%. By 1917, overall losses were believed to be about 25% and by 1950, losses of 5% to 10% were achieved at the best plants (Roush, 1952; Bradley, 1918). If it is assumed that an average furnace loss rate for all mercury ore processed in California is 25%, then roughly 34.5 million kg of mercury may have been lost to the environment from historic mercury mining activity. Some mercury lost at these sites was recovered later by processing old furnace bricks in new furnaces, mining and processing soil under old furnace sites, reprocessing soot and tailings piles, and processing gravel downstream of mercury mine sites.

From 1850 until the 1890s, the California mercury mines were the only domestic source of mercury in the U.S. During this period, mercury production greatly exceeded domestic need, and about 70% of the mercury produced in California was exported, primarily to other Pacific Rim countries. Small quantities of mercury were imported during this time but these were probably largely utilized for manufacturing of vermilion, other mercury products, and for felt manufacturing at factories in the eastern U.S. A large amount of California mercury was shipped to Virginia City, Nevada, for use in processing the Comstock Lode silver ores. With these exports, little or no foreign imports, and no other domestic mercury sources, it is very unlikely that the amount of mercury available for use in the gold mining industry in California could have exceeded 10.3 million kg during the period 1850 to 1890.

The discovery of gold in the Sierra Nevada Foothills in 1848 marks the beginning of significant gold mining activity in California. The DOC/DMG Minefile database contains approximately 13,500 historic gold mine and gold prospect listings for California. Most of these mines are located in the central and northern portions of the Sierra Nevada, the adjacent easternmost portions of the Great Valley, and the Klamath Mountains geomorphic provinces. Three types of gold deposits are dominant in these areas: 1) unconsolidated surficial placer deposits; 2) weakly to strongly consolidated ancient (buried) placer deposits, and 3) lode (quartz vein) deposits. *(Large low-grade disseminated gold deposits of several types have accounted for most gold production in the state for the last 20 years. Although some of these are located in the Sierra Nevada province, they will not be discussed further because mercury was not used in processing ore from these deposits.)*

Unconsolidated surficial placer deposits were the first gold deposits worked in California. These deposits were largely exhausted by 1858. Some mercury was undoubtedly used and lost in gold recovery from these surficial placers, but no records exist describing the quantities involved. About this time several technological innovations occurred that made the mining of ancient placer deposits and lode (hard rock) deposits practical. For the former, it was the development of a new method of mining called hydraulic mining. For the latter it was improvement in the design of the stamp mill for processing lode ore. Gold recovery in both of these operations depended upon the mercury amalgamation for gold recovery.

Hydraulic mining utilizes a high-pressure stream of water to expose and disaggregate ancient placer gravels. The gold bearing gravel is then transported by flowing water through a series of sluices (wooden

troughs). The bottoms of these sluices have perpendicular cleats extending the full width of the sluice. Mercury is placed behind these cleats to trap and hold gold by amalgamation. Sluices used at hydraulic mining operations ranged in size from hundreds to thousands of feet in length. Periodically the flow of water and gravel was stopped, the gold-mercury amalgam from the bottom of the sluice removed, and the gold and mercury recovered by retorting the amalgam. This method of mining reached its peak in the 1870s. Debris deposition and resulting flooding problems downstream of these operations led to a legal decision in 1884 that greatly curtailed the practice of hydraulic mining in the state. Other methods of placer mining that followed hydraulic mining, such as gold dredging, also utilized mercury amalgamation, but the mercury loss rates for these methods were much less. Estimates of mercury losses from placer mining are given in Table 1. These loss figures are based upon estimates of the amount of placer gold produced during different periods and published mercury loss rates per ounce of gold produced for different placer mining methods.

Lode gold mining is a mining technique where quartz veins are followed, usually by underground workings. The gold ore in and along the veins is removed and taken to a mill at the surface for processing to recover the gold. The predominant type of mill for processing lode gold ores from the late 1850s to about 1940 was the stamp mill. At the stamp mill, ore from the mine was roughly crushed and then slowly fed into a battery of stamps. A stamp battery consists of a series of adjacent steel rods held in a vertical, rectangular frame. Collars on the rods interact with a type of camshaft that raises the stamps and then lets them drop by gravity. The rods are fitted with very heavy cone-shaped metal shoes at the lower end which strike metal dies when dropped, pulverizing any ore caught in between. This process liberates grains of gold from its host quartz. This ore pulverization process takes place in a cast iron trough, called a mortar, which is filled with mercury.

Table 1. Calculated Mercury Loss from Placer Gold Mining Activity in California

Period	Oz Placer Gold* (Millions)	Hg Loss Rate* —oz Gold Recovered per Pound Hg Lost	Million Pounds Hg Lost	Million Kg Hg Lost	Percent
1848-1858	26.2	16	1.64	0.75	16.6
1859-1884	21.2	3	7.09	3.22	71.7
1885-1899	2.2	4	0.55	0.25	5.5
1900-1934	10.8	23	0.47	0.21	4.6
1935-1968	7.8	34.25	0.23	0.10	2.2
1969-1976	0.0	16	0.0	0.00	0
Total	68.2		9.98	4.53	100.0

*Production data compiled from Hill, 1929; Minerals Resources of the United States (USGS); and Minerals Yearbook (USBM-for example of loss rates see Review of 1940, p. 228) through 1976. Also see loss rates in Hanks (1882).

The mercury amalgamates with the freed gold and traps it in the mortar. Water moving through the stamp battery removes the finely pulverized quartz and other rock waste from the mortar. This slurry then flows over an inclined table lined with copper sheeting coated with mercury to catch additional fine gold that may not have been trapped in the mortar. Additional mechanical or non-mechanical devices were sometimes employed after the amalgamation tables for further gold recovery or recovery of sulfides containing gold. Periodically, the stamp mill was shut down and the gold-mercury amalgam scraped from the mortar and from the amalgamation tables for gold and mercury recovery by retorting.

Mercury was lost at both hydraulic mining and stamp milling operations. A principal way mercury was lost in both operations was through "flouring." Flouring is a situation where small particles of mercury, generated during the churning action of stamps in the mortar, or turbulent flow of gravel and water in the sluice, are able to float off with the water moving across these devices. Mercury was also lost by leakage through the bottom of sluices, through chemical reactions during ore milling and during retorting to separate gold from amalgam. For hydraulic mining, probably about one pound of mercury was lost for every three or four ounces of gold recovered (Hanks, 1882). Other methods of processing placer deposits recovered 5 to 10 times this amount of gold per pound of mercury lost. Mercury loss at stamp mills gradually decreased over time from about 0.06 pounds of mercury per ton of ore processed in the 1850s to about 0.03 pounds per ton in the 1890s and finally to about 0.004 pounds per ton in the 1930s and later (Preston, 1895; Richards, 1906; Ransom, 1918). Estimates of mercury lost during the processing of lode gold ores by stamp milling are given in Table 2. These losses are based upon estimates of lode gold produced, likely average ore grades during different periods, and published mercury loss rates per ton of lode ore processed.

Table 2. Calculated Mercury Loss from Milling Lode Gold Ore in California

Period	Oz Gold** (Millions)	Grade Oz per Ton	Tons Ore (Millions)	Hg Loss Rate Lb per Ton	Lbs Hg Lost (Millions)	Kg Hg Lost (Millions)	%
1848-1858	0.240	1	0.241	0.0600	0.0144	0.0065	0.5
1859-1884	6.379	0.5	12.758	0.0450	0.5741	0.2614	20.0
1885-1896	5.396	0.3	17.987	0.0313	0.5629	0.2553	19.6
1897-1934	18.335	0.25	73.343	0.0200	1.4668	0.6653	51.1
1935-1968*	6.898	0.11	62.710	0.0040	0.2508	0.1137	8.7
1969-1978*	0.023	0.11	0.209	0.0040	0.0008	0.0003	0.0
Total	37.271		167.248		2.8698	1.3017	99.9

*Stamp mills were widely used until World War II, then gradually replaced by ball mills and rod mills after the war. For these periods on the table, mercury loss has been calculated at stamp mill rate.

**Production data from Hill, 1929; Mineral Resources of the United States (annual USGS publication); and Minerals Yearbook (annual USBM publication). Gold produced from volcanogenic sulfide ores is not included in these totals.

It is important to note that the use of mercury amalgamation for gold recovery declined significantly between 1890 and 1920, not just in California but nationwide. This decline coincides with the development of the cyanide process for gold ores and a change in character of gold ores as the lode mines deepened. The cyanide process reduced or eliminated the need for gold recovery by mercury amalgamation at some mines. Traditional stamp mill methods did not work well on the deeper, unoxidized ores, and different ore processing methods were often utilized.

Rough estimates of mercury losses due to gold mining activity can be made from available historic information on gold production and mercury loss rates for different mining methods. Based upon the amounts of placer gold produced by different methods and the approximate mercury loss rates for those methods, the amount of mercury lost from all placer gold mining activity in California is probably about 4.5 million kg. About 3.3 million kg (71%) of this loss likely occurred between 1859 and 1884, the principal period of hydraulic mining activity in California. Based on the amount of lode gold ore processed during different periods and approximate mercury loss rates for those time periods, the amount of mercury lost in milling of lode gold ore is probably about 1.3 million kg. Roughly 0.5 million kg (40%) were lost during the period 1859-1896 and 0.6 million kg (51%) were lost between 1897-1934. The total amount of all mercury lost to the California environment from all gold mining activity, the sum of the placer mining and lode mining losses, is about 5.8 million kg. Probably 80 to 90% of this amount was lost in the Sierra Nevada geomorphic province. For comparison, the loss of mercury during processing of the Comstock Lode silver ores at Virginia City, Nevada, has been estimated at 6.75 million kg (Miller and others, 1994).

The estimates presented here put into perspective the magnitude of mercury losses from both ore processing at mercury mine sites and historic gold mining in California. While mercury losses from both activities were substantial, it is probable that six or seven times more mercury was released in the Coast Ranges from mercury mining than was released in the Sierra Nevada from former gold mining activities.

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3.2.2 Importance of Research of Historic Information on Mines in California that Used or Produced Mercury - Chris T. Higgins (Presenter), California DOC/DMG and Ronald K. Churchill, DOC/DMG

Introduction

Research of historic information is a necessary but sometimes neglected step in the study of any mine that produced or used mercury in California. Similar to the sleuthing techniques used by seismologists who study historic earthquakes and by exploration geologists who investigate old mining districts, this research often yields key information that can be applied to a range of investigations, from assessment and potential remediation of a single mine to estimates of statewide production and consumption of mercury (see Section 3.2.1). "Historic" information is defined here as that which documents the physical features and operational history of a mine. It includes less-traditional resources as well as the standard technical research literature. Perceptive interpretation and proper use of such information can substantially improve field investigation and evaluation of these mining areas as sources of on-site and regional chemical hazards.

Purpose

The purpose of this presentation is to summarize the importance, types, sources, and management of historic information about mercury-related mining, with use of examples from California. It is important that, although this paper focuses on historic information for California, the same types of information and sources are generally available to investigators who are studying mercury-related mining elsewhere. Furthermore, the same types and sources are applicable to the study of mines that produced or used mineral commodities other than mercury. We emphasize that to properly evaluate and remediate a mine or mining district, investigators need to know, as well as can be compiled, the history of that mine or district. Evidence we see today, either in the field or by reviewing only the most recent technical literature, often gives us a distorted or fragmentary view of historical conditions.

Importance of Historic Information

Research of historic information is important for several reasons. Commonly, documentation prepared during the 1800s and first half of the 1900s is the only remaining record of mining and ore-processing at individual mines or mining districts. Field investigations of non-operating mines today may encounter only ruins of workings and structures, which are commonly obscured by nature's attempt at reclamation. Many sites have undergone several phases of historical development, with the earlier phases of mining and ore-processing often partially destroyed or hidden by the later ones.

For design of a project to evaluate and possibly remediate a mine or mining area, there are specific technical reasons that historic information is important. First is safety in the field. Investigators should know as much as possible beforehand where physical and chemical hazards may be present. Unstable or obscured mine workings, hot water and fumarolic vapors, toxic processing chemicals, and high residual concentrations of mercury in tailings and furnaces have been encountered at given mines in California. Another reason is to grasp the geographic extent of potential sources of contamination. Finally, to locate, sample, and remediate specific sites of mercury contamination, historic information on mine production, techniques of ore-processing, and locations of mine workings and surface facilities can significantly help investigators focus limited field and laboratory funds. In summary, scrutiny of historic information is essential to improve the investigators' chances of safely and efficiently assessing and solving problems related to mercury contamination from mining.

Application of Research to California

Mining of mercury has been extensive in certain parts of California. Mining of gold, along with its use of mercury for amalgamation in ore-processing, has been even more widespread. This distribution of mining activity indicates that California has many sites that are candidates for evaluation of mercury contamination. Correspondingly, there is now and will be a significant need for historic information to evaluate these sites. Documentation of mining of mercury and its use in recovery of gold in California began in the middle 1800s. Since then, mining operations associated with mercury have been documented abundantly through numerous media.

General Types of Historic Information

Historic information can be grouped into six major types. These include written documentation, maps, photographs, artwork, oral documentation, and computer databases.

Written Documentation

When assembled together, historic written descriptions can give a fundamental picture of features, processes, and events at a mine. Documents prepared by technical investigators (e.g., geologists, mining engineers) are typically the first resource consulted. These include such traditional resources as published and unpublished technical reports by government agencies, mining companies, and consultants; papers in technical periodicals; theses and dissertations; and textbooks. Nonetheless, for some mines, investigators may find additional insights (or have to rely heavily on) written observations in less-traditional non-technical documents such as newspapers, personal journals, summaries of county histories, and promotional guides.

Maps

Maps provide a spatial portrayal of areas and sites that is often not as clearly documented in other media. For example, maps prepared during mining may show spatial details about mine workings and ore-processing facilities that may not be recorded otherwise. Topographic maps from the USGS are a common starting point for spatial orientation in a region or at a site, and it is important to note that there can be several editions and scales of topographic maps that cover a given area. Often, technical reports done by government agencies on mining areas have maps that accompany the written document. Other types of maps include those prepared for Federal Land Surveys and Mineral Surveys, and county assessors' offices. Unpublished mine maps (plan and cross-section) prepared by mining companies or their consultants can be excellent sources of large-scale detail of workings.

Photographs

Photography (ground and aerial) in many instances has no equal when documenting the history of a mine. It can quickly give the investigator a grasp of the physical environment at a point in time. Historic photographs can document locations of workings (shafts, adits, etc.), processing facilities (retorts, mills), disposal sites (waste dumps, mill tailings, etc.), and the general physical conditions at a mine. In some cases, photographs may be the only documentation that remains in the historical record to guide investigators in their assembly of the history of a mine.

Artwork

This category comprises diagrams, sketches, and paintings. A commonly useful portrayal of historic facilities at mines is the technical diagram. Typically, it documents the milling and processing of ore. Flow diagrams of ore-processing are common in the older literature. Perspective diagrams of furnaces at mercury mines are also common and can give some indication of the efficiency of recovery of mercury at a site. Finally, sketches and paintings by artists of the historic period occasionally reveal some detail of mining or milling that is not preserved in any other medium.

Oral Documentation

People who were part of mercury- or gold-mining operations are often one of the least explored resources of information about those operations. Although the general use of mercury in gold-mining in California declined significantly by 1920 and was very limited after World War II, mercury-mining in places continued into the 1970s. Many people who worked at mercury mines are still alive, and personal interviews with these people can provide details and direct observations of operations at specific mines. Formal interviews about mines and mining in California have been recorded through oral history programs.

Computer Databases

Many databases are available that contain information on mercury mines and gold mines in California. Although much of the data have been compiled from the categories of materials described above, some databases contain field observations and interpretations that are unpublished.

Sources of Historic Information

The standard sources of historic information include government agencies, libraries, museums, word-of-mouth ("people"), and indirectly, the Internet.

Government Agencies

Federal, state, and local government agencies are major sources of both published and unpublished information. The most common sources of information on mercury- and gold-mining in California include the Division of Mines and Geology of the California Department of Conservation (DOC), the USGS, and the now-defunct USBM. Since the 1800s or early 1900s, each of these agencies has published extensive serial collections of technical reports and maps. They have archived many unpublished materials, some of which are open to outside researchers. One example is an archive of reports and maps on mines, prepared by field staff of the USBM. All three agencies and the DOC's Office of Mine Reclamation have prepared computer databases on mines in California. Other Federal agencies with mining information include the U.S. Forest Service (USFS) and Bureau of Land Management. These agencies may have archaeological field reports on specific mine sites, which could provide clues to the history of a site. The Federal EROS Data Center maintains extensive aerial photography. Locally, offices of the county recorder and county assessor maintain documents on mines.

Libraries

Public, university, and government libraries can have a wealth of obscure information contained in such items as textbooks, summaries of local history, maps, photographs, newspapers, periodicals, mine reports, and oral histories. For example, the Library of the Division of Mines and Geology has operated continuously for over 100 years and contains many unpublished maps, consulting reports, and photographs. Several other research libraries have archives of documents on mercury- and gold-mining, such as the Randol collection at the Bancroft, which have been donated from various parties. In addition, the Bancroft administers an oral history program entitled "Western Mining in the Twentieth Century." Outside California, the Anaconda Collection at the University of Wyoming has unpublished technical documents on many mines in California and other states.

Museums

Most counties and regions in California have museums that focus on the cultural development of their local areas. Some have displays of artifacts, photographs, maps, artwork, and written documents that highlight a specific mine or mining district. Many are associated with well-established historical societies, which often publish periodicals and maintain small research libraries.

Word-of-Mouth

The potential benefits of interviewing people who live in or know about the history of a geographic area should not be underestimated. Local citizens, particularly those who work at libraries and museums, or who are members of historical societies, often know of people who are knowledgeable of a specific mine. A

casual conversation sometimes leads to an unexpected trove of information that can fill in gaps in the history of a mine. For example, descendants of local miners or mine owners may have maps, reports, personal journals, or photographs that were handed down in the family. In some cases, a person who worked at a mine may still be alive and can provide valuable first-hand observations and documentation of a mining operation.

Internet

Although considered here to be an indirect source of historic information that resides in the sources described above, the Internet can function as a tool to rapidly locate materials and references, either posted directly on-line or via indexes. The major research libraries in California are part of a consortium that contributes information on library holdings to a web page called the Online Archive of California. The Internet shows promise to save investigators significant amounts of time and funds in the future as more reports, maps, photographs, and other materials become available on-line.

Management of Research and Use of Historic Information

Successful research and use of historic information rely on three main tasks of management. They include: 1) preparation of a checklist of types and sources of information to be researched, 2) evaluation of the quality of the information collected, and 3) storage and integration of the information into the project.

Checklist of Information

At the beginning of a project, during its planning, a list of types and sources of historic information should be prepared. The organization of this list should help guide research of the information in a methodical way. The tasks of research should be assigned to appropriate members of the team of investigators, with the goal that any pertinent or significant information obtained during the research will be distributed to other appropriate members in a timely manner.

Quality of Information

All historic information must be evaluated critically for its reliability and accuracy of content. Errors in documentation and recollection as well as inaccuracies or inconsistencies in representation of information can be common. For example, features on maps may be incorrectly located, statements in newspapers may be false or exaggerated, and human memories may be confused about events that occurred long ago. Correspondingly, researchers must be alert to these discrepancies as they weigh the value of information collected. One way to verify quality and accuracy of information is to cross-check the information by determining if it is consistently portrayed by different sources and media.

Integration of Information

Two issues are important here. First is that, because most projects today involve teams of interdisciplinary investigators, colleagues must consciously share findings about the spatial and temporal features of a study area to derive the most value from each member's contribution to the project. Second is that the information must be physically stored and integrated in a way that allows its most efficient application and effect on the study. One approach is to incorporate this information as thematic layers into a geographic information system (GIS) for the project. Assembly of the layers can then give a spatial and temporal portrayal of a mine, which aids selection of features to be studied.

3.2.3 Mercury Associated with Lode Gold Mining in the Sierra Nevada Region, California - Roger P. Ashley, USGS

Introduction

The Sierra Nevada region of California is a world-class gold-mining province, having produced about 2800t of gold since 1848, including about 1000t from lode mines and the rest from placers (Clark, 1970). An individual district may include as many as several dozen mines, and there are more than 4000 lode gold mines with recorded production in the region. By modern mining standards, these mines, now mostly abandoned or inactive, are relatively small (few processed more than 1,000,000 metric tons of ore), and

high grade (average gold grade about 15 mg/kg). Amalgamation was used universally for gold recovery, with total loss of mercury to the environment from lode gold mills estimated at about 1000t (Churchill, 1999a).

The objectives of this study are to determine mercury concentrations in gold ores, mill tailings, waste rock, and mine and tailings drainage waters, and to evaluate whether historical lode gold mining may contribute significant amounts of mercury to aquatic systems in the region. The study attempts to characterize amounts of mercury that may be associated with lode gold deposits and mine wastes. However, it is not comprehensive because data are available only for a relatively small number of mines and districts.

The last major period of gold mining in the Sierra Nevada was in the 1930s, but some mining continues to the present. Although historical mines are the focus of this study, some recently active mines are included because they provide access to ores and altered host rocks. Mines active in the last 20 years have utilized modern methods for milling and management of mining wastes and waters, and amalgamation is no longer used for gold recovery.

This ongoing project is supported by the USGS Mineral Resources Program, and involves cooperation with the State of California EPA. The cooperation of numerous property owners is gratefully acknowledged.

Geologic Features of Sierran Gold Deposits

The most prominent features associated with Sierran gold deposits are alteration zones that are usually lighter in color than the surrounding rocks, and are laced with white quartz-carbonate veins. Hydrothermal solutions that deposited the gold reacted with the rocks to produce these alteration zones, replacing calcium, magnesium, and iron silicates with carbonate minerals, and adding potassium mica, quartz, and metal sulfide minerals. The alteration zones are usually tabular, because the thermal waters moved upward along planar fault zones. Host rocks include slate, greenstone (metamorphosed volcanic rock), serpentinite, and in a few districts, granite.

Most ore-grade zones are found in the veins, which typically contain a few percent sulfides. Less commonly the alteration zones contain disseminated ore with as much as 10% sulfides. Native gold with 15% to 20% silver is the valuable mineral. Gold tellurides occur in a few places. The most common sulfide mineral in the ores and altered rocks is pyrite (FeS_2). Arsenic-bearing minerals are also common, especially arsenopyrite (FeAsS). Sulfosalt minerals, mainly tetrahedrite, occur in some districts; relatively high mercury values may accompany sulfosalts. The most common minor sulfide minerals are sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS). No mercury minerals have been seen or reported.

Ore Processing

Most gold mines in the Sierra used stamp mills to finely crush the ore. Stamp mortars were enclosed in a battery box lined with amalgam plates; ore, water, and mercury were fed into the battery box. Mercury was supplied at a rate of 1-3 avoirdupois ounces [28-85 grams (g)] per troy ounce (31 g) of gold to be saved (Hammond, 1888; Churchill, 1999a). The resulting pulp was spread on outside amalgam plates for further gold recovery. Sulfides were separated from the pulp by various mechanical and gravity methods, and concentrates sent to a smelter. Many improvements were made in stamp mill design in California during the 1800s, but before 1890 mercury losses to tailings ranged from 6 gram per ton (g/t) to more than 20 g/t. Loss was due mainly to "flouring" of mercury (reduction to very small suspended droplets) produced by the battering action of the stamps (Churchill, 1999a). Use of stamp mills continued until the 1950s. Beginning in the 1890s, as cyanidation was introduced, rod or ball mills were increasingly used for the fine grinding needed, stamps were used only for coarser crushing, and amalgamation was done mainly on outside plates or in rotating barrels. By about 1910 mercury loss to tailings at improved mills had been reduced to 2-3 g/t (Finlay, 1918).

In the 1920s and 1930s tailings from earlier operations, particularly the larger ones, were reprocessed by cyanidation. If mercury is present in pulp subjected to cyanide leaching, some will dissolve, although not enough to consume significant cyanide (Dufourcq, 1918). However, whatever mercury is taken into cyanide solution will precipitate with gold when zinc is added.

Mercury in Ores, Altered Wall Rocks, and Mill Tailings

The average grade of historical Sierra Nevada gold mines was about 15 mg/kg. Amounts of mercury in ore-grade materials vary greatly, from less than 0.01 mg/kg to about 40 mg/kg, but ores from individual mining districts show distinctive ranges of values. Although amounts of mercury in ores are elevated above probable background levels (<0.05 mg/kg), they do not increase notably with increasing gold grade.

Altered wall rocks (<1 mg/kg gold) are an important component of waste-rock dumps. Altered rocks have less mercury than ores in all districts except the Alleghany district, where the ores have relatively little mercury. Mercury concentrations in many samples are similar to probable background levels (about 0.02–0.10 mg/kg; Rose and others, 1979).

High levels of mercury in sulfide concentrates at the Argonaut mine site (Jackson district) show that mercury is associated with sulfide minerals. Tailings subjected to amalgamation at both the Argonaut and Kennedy sites (labeled "Hg only") do not have significantly more mercury than tailings that were amalgamated and later reprocessed using cyanidation (labeled "Hg&Cy"). Mill tailings at the Lava Cap mine, treated only with cyanide, contain significantly less mercury.

Mercury in Drainage Waters

The Sierran gold ores generally have only a few percent sulfide minerals, and also contain carbonate minerals that neutralize acid. Consequently, mine drainage waters and waters that contact mill tailings have near-neutral pH. Metal-rich acid drainage is rare, occurring only where sulfide-rich ore or sulfide concentrates have been stockpiled.

The waters contain subequal molar amounts of carbonate, sulfate, and calcium plus magnesium, as would be expected where pyrite, the dominant sulfide mineral, is oxidized and the sulfuric acid produced is neutralized by the calcium-magnesium carbonate minerals present. Since mercury is likely associated with sulfide minerals, mercury concentrations should increase with increasing sulfate. Dissolved Hg (passing a 0.45 μm filter) generally does increase with increasing sulfate.

Dissolved mercury generally increases with increasing THg, but the percentage of dissolved mercury varies greatly. The proportion of THg present as methyl mercury is generally less than 1% but can be much higher. Conditions for methylation appear favorable where Fe(II)-saturated suboxic drainage water is oxidized, precipitating iron oxyhydroxides, especially in wetland areas.

THg exceeded 12 ng/L, the California standard for protection of aquatic life, in 13 of 21 samples from Argonaut tailings, where amalgamation was used, 3 of 14 samples from Lava Cap tailings, where only cyanidation was used, and 6 of 21 mine drainage samples.

Preliminary Observations on Impacts of Mercury Associated with Lode Gold Mining in the Sierra Nevada

Naturally-occurring mercury is only weakly to moderately enriched in lode gold ores or altered wall rocks. Therefore waste-rock piles and drainage from them should not be significant sources of mercury, and mercury levels in mill tailings should mainly reflect mercury added in processing.

Figure 1 shows cumulative lode gold production in California from the Gold Rush to World War II. The cumulative curve is based on state-wide production figures, but gold from the Sierra Nevada (about 85% of the total) dominates the picture. Although estimates of the proportion of total production that came from lodes in the early years are crude, it is reasonable to conclude that about half the lode gold was produced before 1910, coinciding with the period of relatively high mercury loss to tailings. Although gold grades were higher in early production (before about 1880), mines generally did not show consistently declining gold grades with time, so roughly half the gold ore produced was probably processed before 1910. California required mill tailings to be impounded beginning in 1912. Until then, mills were purposely built near streams to take advantage of water power, and so that seasonal floods would remove tailings. Consequently most tailings with relatively high mercury contents were washed away and are now entrained in stream sediments. Although these sediments should contain much of the roughly 1000 metric tons of mercury used in lode mining, mining of placers in the region, especially by hydraulic mining methods, may have contributed far more mercury to the Sierra river systems (Churchill, 1999b).

Lode gold mill tailings remaining in the Sierra (about 35-40 million metric tons), impounded mainly in the larger mining districts, should generally have relatively low average concentrations of mercury (<3 mg/kg).

Although drainage from mine openings and tailings piles may show elevated THg levels (>100 ng/L), discharges from individual sources of these types in the Sierra Nevada region tend to be small (<500 liters per minute (L/min)), producing loadings substantially less than 1 kilogram per year (kg/yr).

Hazardous conditions may exist at historic mine sites owing to use of mercury in past gold milling operations. Since amalgam was usually retorted to recover mercury for prompt reuse, areas around sites of retorts are likely to have mercury contamination in soils and structures. The cyanide process does not remove much natural or previously added mercury, but since mercury is efficiently removed when gold is precipitated with zinc, mercury contamination could also be found around sites of refining furnaces.

CUMULATIVE LODE GOLD PRODUCTION 1848-1956
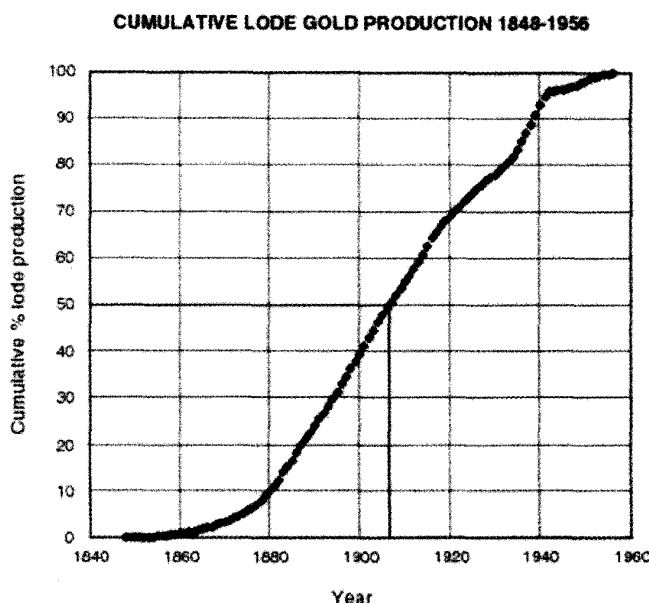
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3.2.4 Mercury Recycling Pilot Project (MRPP) - Richard Humphreys, State Water Resources Control Board

Introduction

Mercury has been widely used since the dawn of recorded history, first for precious metal extraction and later for industry and medicine despite its acute and chronic toxicity. Mercury also has the insidious ability to bioaccumulate and biomagnify up the foodchain. Thus, as adverse health affects from ingesting small amounts of mercury in food became a concern, concerted efforts are being made to find substitutes for mercury, lower mercury discharges from industry, and collect mercury stored by society. Prior mercury collection programs have been aimed at mercury-filled devices such as thermometers, mercury switches, and fluorescent tubes.

During California's Gold Rush, gold miners used large amounts of mercury (est. 20 million pounds) and lost most of it to the environment. Mercury is still found, sometimes in substantial amounts, in watersheds subjected to gold mining. In 1994, State Water Resources Control Board (SWRCB) and Regional Water Quality Control Board (RWQCB) staff conceived a pilot project to collect mercury from today's recreational gold miners (suction dredgers) who recover mercury along with gold from California's rivers and streams. The need for such a program resulted from an unconfirmed report that the Department of Toxic Substance Control (DTSC) had fined a suction dredger for turning in more mercury than regulations governing storage and transport of mercury by an individual allowed. The pilot project's objectives were to: provide an way for suction dredgers to discard unwanted mercury easily in an environmentally sound manner; and, to encourage suction dredgers to remove mercury from California's rivers and streams.

During August and September of this year, State and Federal agency staff finally initiated a pilot project to collect mercury from suction dredgers in Nevada, Sierra, and Placer Counties. As a follow up, Nevada County agreed to collect mercury at their September 23, 2000 household hazardous waste collection event. The following describes the pilot project's results and a followup, larger-scale mercury collection pilot project.

Mercury Recycling Pilot Project

Although there was interest in the pilot project in 1994, concerns about agency liability prevented its initiation in 1994 or in the intervening years. With the change in California's Administration in 1998 came a new interest in pursuing projects viewed as "proactive." Thus, the climate within State agencies became favorable for reconsidering the original mercury recycling pilot project. The USFS and Bureau of Land Management (BLM) were also interested in assisting with a mercury recycling project because it fit their abandoned mined lands initiative goals. Thus, earlier this year, the SWRCB, USFS, BLM, DTSC, DOC, Nevada County and the USEPA formed an informal partnership to enact a mercury recycling pilot project aimed at suction dredgers. Enacting such a program meant: resolving legal and regulatory concerns; developing a plan for handling, transporting, and shipping mercury to an end destination; and training staff.

SWRCB staff developed a health and safety plan for collecting mercury and that plan served as the technical basis for the variance DTSC granted to the participating agencies in August. The SWRCB health and safety unit provided training, and the SWRCB, USEPA, USFS and BLM provided staff and supplied equipment for the first collection phase, the "House Call" component, which began August 8, 2000.

47

Under the "House Call" component, two mercury pickup teams (comprised of SWRCB, USFS, BLM, and USEPA staff) made telephone-arranged visits to pick up mercury from private citizens. Additionally, the USFS/SWRCB team made spot visits to suction dredger camps along the Yuba River (Middle and North Forks) and Kanaka Creek. Pickups began August 8, 2000 and continued through September, during which the teams collected about 220 pounds of mercury.

As a followup to the "House Call" collection component, Nevada County collected mercury at its "household hazardous waste collection day" on September 23, 2000. State and Federal agencies agreed to assist Nevada County with additional cost that collecting mercury would entail. DOC and SWRCB staff interviewed several mercury donors at this event. Nevada County staff verbally reported that they collected about 30 pounds of mercury during the event.

Pilot Project Summary

Mercury Donors

Most of the mercury collected had been used for gold mining long ago (3 donors accounted for about 180 pounds). It had not been removed from streams by dredgers. Most donors were relatively old people (or their immediate heirs) who had acquired the mercury when it had a high value as a commodity (50 to 30 years ago) and did not pose the disposal problems that it does now. These donors usually donated 1 to 5 pounds of mercury. These donors had related stories about their unsuccessful efforts to discard mercury properly, and of "being interrogated" and "made to feel like a criminal" when they called County or State agency staff about discarding mercury in the past. Most donors knew that mercury was poisonous but had a poor understanding of its specific toxicity. These donors thought that a long-term, locally based disposal program for mercury would be successful.

Curiously, suction dredgers did not donate much mercury. During spot visits to dredger camps, some dredgers even asked if collection teams had mercury to sell. At this time it is unclear why suction dredgers did not participate although unannounced spot visits during the dredging season might be too intimidating. Better results might be had with telephone-arranged pickups at both the beginning and end of the season. Nevada County staff thought that suction dredgers might be better served by a "remote mercury collection pilot project" (patterned after an existing waste oil program). Participation by suction dredgers is important because:

- Their alleged predicament provided the impetus for developing and initiating the pilot project.
- They are the only group that would benefit from a long-term collection program, as they are the only group that accumulates mercury as a result of their activities.
- Their participation would result in an overall reduction of mercury in California's rivers and streams.

What Worked and What We Learned

- Publicity helps – The participating State and Federal agencies held a public meeting on June 26, 2000 to announce that a mercury pickup service would be offered later during the summer once the legal wrinkles were ironed out. The local media carried the announcement and potential mercury donors began calling State and Federal staff contacts within days. Additional press coverage and hence, public interest resulted from the USFS press release which reported that the USFS/SWRCB mercury collection team collected 140 pounds of mercury during the first day.
- Telephone-arranged "House Calls" are effective – Telephone-arranged visits worked well as opposed to spot visits to dredger camps which did not work at all. There are probably profound sociological reasons for this but they won't be discussed here.
- An initial "House Call" component would certainly be applicable in the "Mother Lode" counties where gold mining was once a major industry, and where many retirees now reside. Additionally, a "House Call" component has the potential to develop support for a sustained collection program by the local residents.
- Nevada County officials felt that the "Household Hazardous Waste Collection Event" was a success. The 30 pounds of mercury collected are roughly equivalent to the amount contained in 130 thousand thermometers.
- Collection efforts identified a new mercury donor group (older people) which may not be limited to a particular region.

- The total amount of mercury collected during the pilot project (250 pounds) is roughly equivalent to the amount contained in about 1 million thermometers.

Followup Efforts: Large-scale Pilot Project

Because the newly identified mercury donor group (older people) may not be limited regionally, the pilot project participants are planning a larger-scale mercury collection pilot project that would target the newly identified and potentially larger mercury donor group as well as suction dredgers. The larger-scale pilot project would include a mix of rural and urban counties centered in the Sacramento region, would run for at least three years, and would be patterned after the pilot efforts described above. A successful larger-scale pilot project would justify a statewide, county-based collection program because it would show that older people had a substantial stock of mercury regardless of where they reside. Additionally, the longer term of an expanded pilot project would give the original target group another chance to participate (and we really want them to participate).

Acknowledgments

This pilot project would never have been initiated if had not been for the perseverance of State and Federal agency personnel. I want to thank Bill Croyle of the Central Valley Regional Water Quality Control Board for his contribution in conceiving the project in 1994. Art Baggett (State Water Resources Control Board Member), Janine Clayton (USFS), Richard Grabowski (BLM), and David Jones (USEPA) all deserve credit for providing high level support. Lee Halverson (DTSC) deserves credit for writing an "air tight" variance. Rick Weaver (Tahoe National Forest), David Lawler (BLM), and David Jones all deserve credit for collecting over 200 pounds of mercury without spilling a drop.

3.2.5 Historic Gold Mining, Mercury Amalgamation, and Potential for Environmental Impacts in the Eastern U.S. - Robert R. Seal II, USGS

Introduction

The eastern U.S. has had a long and colorful history of gold mining, and mercury amalgamation has played an important role throughout much of this history. The first mention of gold in the U.S. is associated with Spanish and French explorers in North Carolina and Georgia in the mid-16th century (Craig and Rimstidt, 1998). Discovery of a 7.7 kg gold nugget in North Carolina in 1799 initiated the first gold rush in the U.S. Commercial production began in 1804 in North Carolina and has continued intermittently in the eastern U.S. until 2000. The discovery of gold in the Dahlonega region of northwestern Georgia in 1829 started the second gold rush in U.S. history; historians have given these miners the name "Twenty-niners" (Williams, 1993). The discovery of gold in the southeast led the U.S. Treasury to establish mints in Dahlonega, Georgia and Charlotte, North Carolina in 1838 (Pardee and Park, 1948). The Georgia gold rush provided a major impetus that led to the expulsion of the Cherokee Indians from the eastern U.S. to Oklahoma along the "Trail of Tears." The Haile mine in South Carolina was a strategic target for the Union forces during the Civil War because of its importance to the Confederate treasury (Speer and Maddry 1993).

Gold production in the eastern U.S. has come from quartz-gold vein and disseminated to massive sulfide deposits, their weathered equivalents, and from placer deposits. From 1804 to the present, eastern states have yielded approximately 3.4 million troy ounces of gold, with approximately half produced since 1988. Mercury amalgamation has had a central role in much of the gold mining in the east prior to 1940. The very nature of mercury amalgamation, its inexpensiveness, its portability, and its ease of use, makes its use difficult to track in a comprehensive fashion. The first documented use of amalgamation was in 1803 in North Carolina (Pardee and Park, 1948). The use of amalgamation has also been recorded extensively in Virginia, South Carolina, Georgia, and Alabama, but the time intervals and extent of use throughout the region are poorly documented.

The use of amalgamation also spans several generations of mining activity in the east. For example, early production in the Dahlonega belt (Georgia) used a variety of gravity methods, many of which employed mercury, to extract gold, initially from placer ores, and then later from milled ores for shallow lode deposits (Pardee and Park, 1948; Craig and Rimstidt, 1998). Miners left the Dahlonega gold belt as easily exploited placer and shallow lode ores dwindled at the beginning of the California Gold Rush (1849). They returned again after the Civil War to begin hydraulic mining of saprolitic ores using techniques learned in the Califor-

49

nia gold fields; the technique became known as the "Dahlonega method" (Pardee and Park, 1948; Williams, 1993). The hydraulic mining also used amalgamation as a prime gold extraction technique. Hydraulic mining of saprolitic ores was also used in North Carolina (Pardee and Park, 1948).

The purpose of this paper is to summarize the current state of understanding of the environmental impact of mercury associated with historic gold mining in the eastern U.S. This summary includes an overview of historic gold mining in the east and the known usage of mercury in gold extraction, a review of published studies pertaining to the impact of mining-related mercury on the environment, and a discussion of the potential extent of mining-related mercury contamination in the east and its comparison to contamination elsewhere.

Distribution of Gold Mines and the Use of Mercury Amalgamation and Other Techniques

Nearly 1,200 gold mines or prospects are known in the east, with the majority (96%) occurring in Virginia, North and South Carolina, Georgia, and Alabama (Figure 1; McFaul and others, 2000). Beyond the southern states, significant primary production of gold has only come from Michigan (202,600 oz) and Vermont (9,800 oz; Craig and Rimstidt, 1998). In the eastern U.S., the main historic gold districts or belts include, from north to south: (1) the Virginia gold-pyrite belt; (2) the Carolina slate belt (including the Eastern slate belt district), North and South Carolina; (3) the Dahlonega district (and extensions into northeastern Alabama), Georgia; and (4) the Hog Mountain district, Alabama (Feiss and Slack, 1989). The mines in these districts exploited low-sulfide gold-quartz vein (a.k.a. mesothermal, Mother Lode-type, shear zone-hosted) deposits, gold-bearing massive sulfide deposits, their weathered equivalents, and placer deposits derived from all of the above deposit types. Of these deposit types, both the unweathered and weathered low-sulfide gold-quartz vein deposits, including saprolitic ores, the weathered massive sulfide deposits, and the placer deposits were readily amenable to mercury amalgamation.
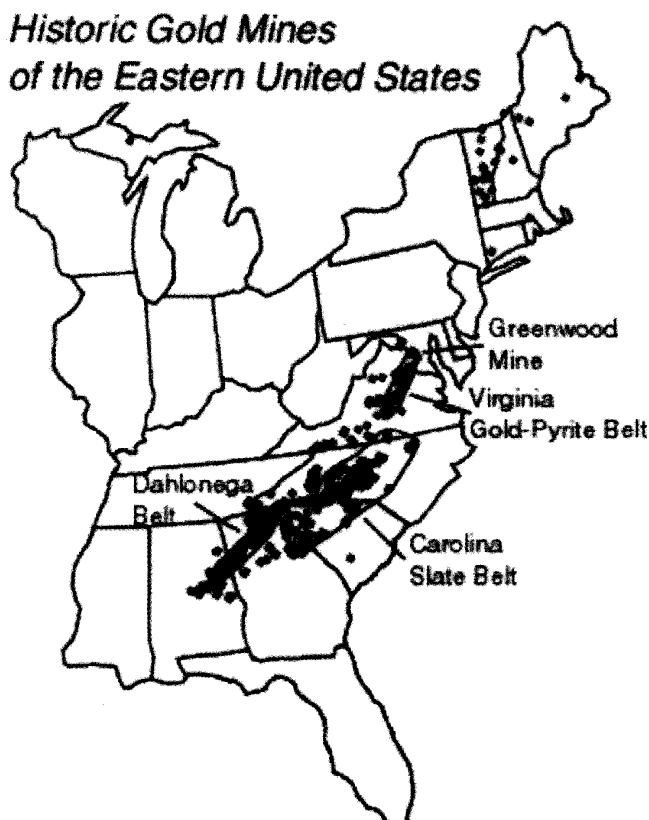
Figure 1. Location of historic gold mines and major gold-mining districts in the eastern U.S.

50

Mercury amalgamation has been used historically in all of the main districts and belts listed above. At present, documented use of amalgamation has been identified at nearly 50 sites, which is considered to represent a mere indication of the wide extent of its use, in light of the poor availability of historical records (Pardee and Park, 1948; Yeates and others, 1896; Sweet, 1980; Sweet and Trimble, 1983; Silliman, 1837; Smith, 1903; Watson, 1907; Seal and others, 1998a,b; 1999). For example, historical and recent accounts of mining practices in the Dahlonega belt suggest the common usage of amalgamation throughout the region, in spite of only 16 references of use identified in the literature (Yeates and others, 1896; Williams, 1993). A typical progression of mining in the Dahlonega belt started with placer mining, followed by hydraulic mining of saprolitic ores, the so called "Dahlonega method;" when hydraulic mining reached bedrock, underground mining began (Yeates and others, 1896; Pardee and Park, 1948; Williams, 1993). For all three phases of mining, amalgamation was commonly used, frequently in concert with other methods, such as chlorination (Yeates and others, 1896). At the Haile mine, South Carolina, the Designolle process, which employs a mercuric chloride solution, was tested on the ores in addition to traditional amalgamation (Pardee and Park, 1948). Throughout the eastern U.S., anecdotal evidence from recreational gold panners suggests near-ubiquitous usage of mercury amalgamation in many of these districts.

Geochemical Studies of Mercury in the Environment Related to Historic Gold Mining

Geochemical studies of the environmental impact of mercury related to historic mining in the eastern U.S. are limited in both number and scope and are summarized in Table 1. Studies have been conducted in Alabama, Georgia, North Carolina, Virginia, and Nova Scotia, Canada. Media investigated include water, stream and flood-plain sediments, panned concentrates, gold nuggets, mine tailings, moss, and fish tissue. Maximum concentrations for all media are summarized in Table 2.

Table 1. Published Studies on Environmental Mercury Geochemistry Related to Historic Gold Mining in the Eastern U.S. and Canada

Location	Scope	Source
Greenwood mine Virginia gold-pyrite belt	Water chemistry Mercury speciation (MeHg, THg)	Seal and others (1998a) Seal and others (1998b) Seal and others (1999)
Dahlonega belt, Georgia	Floodplain sediment geochemistry Water chemistry (THg)	Leigh (1994)
Dahlonega belt, Georgia Carolina slate belt, North Carolina Arbacoochee district, Alabama	Water chemistry (THg)	Mastrine and others (1999)
Talladega Creek, Alabama	Water chemistry (THg) Sediment geochemistry Panned concentrate geochemistry Gold nugget geochemistry	Miller and others (1997)
Carolina slate belt, North Carolina	Water chemistry (THg) Sediment geochemistry Panned concentrate geochemistry Gold Nugget geochemistry Vegetation Geochemistry Fish tissue geochemistry (THg)	Callahan and others (1994)
Goldenville, Nova Scotia, Canada	Tailings geochemistry Sediment geochemistry Vegetation geochemistry Water chemistry (THg)	Wong and others (1999)

Table 2. Maximum Concentration of Mercury in Various Media from the Eastern U.S.

Media	Location	Concentration	Reference
Water-Hg Total	Dahlonega belt, GA	1,420 ng/L	Leigh (1994)
Water-Me Hg	Greenwood mine, VA	34.6 ng/L	Seal and others (1998a) Seal and others (1998b) Seal and others (1999)
Stream sediments	High Point, NC	7,400 mg/kg	Callahan and others (1994)
Flood-plain sediments	Dahlonega belt, GA	3,900 mg/kg	Leigh (1994)
Panned Concentrates	Robbins, NC	784,000 mg/kg	Callahan and others (1994)
Gold nuggets	Robbins, NC	45.36 mass %	Callahan and others (1994)
Plant (moss) tissue	High Point, NC	4,900 mg/kg	Callahan and others (1994)
Fish tissue	High Point, NC	150 mg/kg	Callahan and others (1994)

Studies of mercury speciation in surface waters in and around the abandoned Greenwood mine, a low-sulfide gold-quartz vein deposit, in the Virginia gold-pyrite belt illustrate the potential for extreme geochemical environments in eastern settings (Figure 1; Seal and others, 1998a,b; 1999). The mine site is at the headwaters of Quantico Creek which empties into the Potomac River (Figure 2). Surface waters around the abandoned Greenwood mine were sampled and analyzed for their major and minor constituents including mercury speciation. The waters include samples within shaft depressions, and both upstream and downstream from the site. The waters from the shaft depressions display anomalously high dissolved concentrations of MeHg. Ratios of MeHg to THg in the dissolved fraction (up to 0.89) are also anomalous (Figure 3). The geological and geochemical environment in shaft depressions at the Greenwood mine favors the methylation, but not the demethylation of mercury. Water in the shaft depressions is characterized by stagnant, near-neutral pH (6.3 to 6.7), low total dissolved solids (< 160 milligrams per liter (mg/L)), low redox potential (D.O. < 1.3 mg/L), abundant organic matter, and moderate dissolved sulfate concentrations (2.5 to 16.0 mg/L). These conditions stimulate sulfate-reducing bacteria, which are the principal methylators of mercury under anoxic conditions (Compeau and Bartha, 1985). Demethylation is not favored because of anoxia and insufficient mercury and other heavy metals to induce gene transcription in microbes to detoxify MeHg (Robinson and Tuovinen, 1984). Dissolved mercury levels are depressed because the shaft waters are saturated with respect to cinnabar; low levels of other heavy metals are characteristic of low-sulfide gold-quartz vein deposits (Ashley, in press). Within the watershed, the percentage of MeHg rapidly decreases downstream of the shaft depressions. Dilution effectively decreases the total concentration of THg and MeHg at less than 10 km from the mine site.

Compared to mining districts in California (Ashley, in press), the waters in and around the Greenwood mine are characterized as having higher THg concentrations than waters of similar sulfate concentrations (Figure 4a). The percentage of dissolved mercury to THg is similar to ranges reported for waters from gold districts in California (Figure 4b). However, the percentage of MeHg relative to THg in unfiltered waters exceeds that observed in waters from mining districts in California by up to an order of magnitude (Figure 4c). The anomalous character of the mercury geochemistry of the Greenwood site can be attributed to the environmental setting, particularly features such deciduous vegetative cover, which provides abundant organic matter as leaf litter in the shaft depressions, and low topographic relief, which enhances stagnation of water. Ongoing studies are focusing on defining the full areal extent of mercury contamination at the Greenwood site, and investigating the bioaccumulation of mercury in the foodweb within the watershed.

Discussion

The eastern U.S. has had a long history of gold mining, much of which used mercury amalgamation as a primary ore processing technique. Published records indicate that amalgamation was used in every major gold district or belt in the east. However, the published record undoubtedly fails to reflect the full historic

extent of the use of this ore beneficiation technology. Nevertheless, mercury was used, and the limited number of investigations on mercury contamination related to mining indicates that it is making a negative impact on the environment. The single study of mercury speciation in mine waters in the eastern U.S. (Seal and others, 1998a,b; 1999) documents anomalous concentrations of MeHg, which can be attributed to specific features of the setting. These features, such as a dense, deciduous vegetative cover, a result of substantial rainfall, and low topographic relief, are characteristic of the southeastern U.S., but are in contrast to conditions in many parts of the historic gold mining regions of California. An unanswered question is whether the contrasts in environmental setting between the southeastern U.S. and the Mother Lode belt of California are sufficient to cause anomalous mercury speciation throughout the eastern U.S. This question can only be answered through regional scale studies of mercury contamination in historic, eastern gold mining districts. From a policy perspective, the magnitude and scope of such studies should be weighed against the potential scale of the problem. The southeastern U.S. (Alabama, Georgia, South Carolina, North Carolina, Virginia, Washington, DC, and Maryland) only produced approximately 3% of the gold mined in California. However, the area (237,000 square miles) and population (36,260,000) of this region are greater than the area (156,000 square miles) and population (33,145,000) of California.
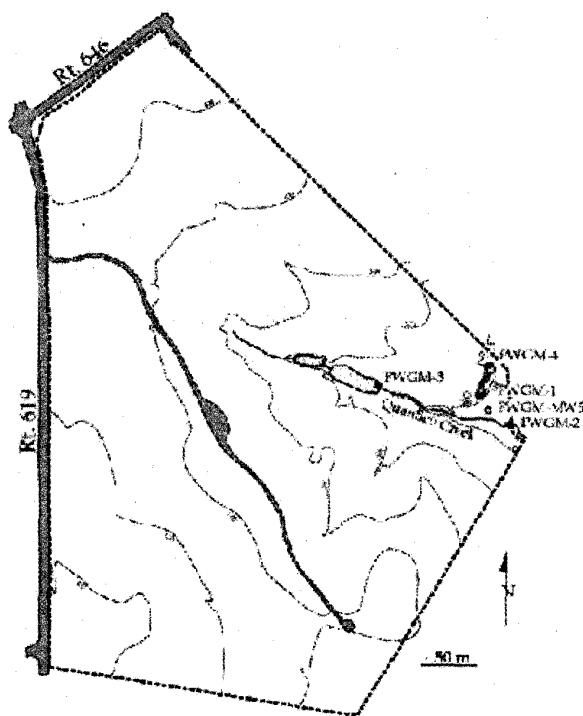
Figure 2. Map of the abandoned Greenwood mine area, Prince William Forest Park, Virginia.
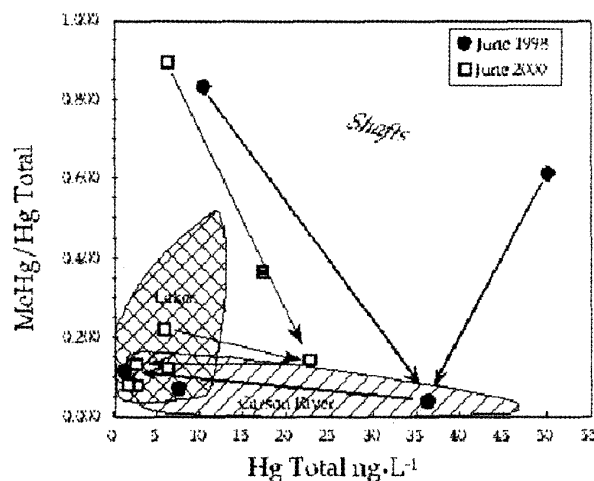
Figure 3. Relationship of dissolved MeHg/THg ratio for surface waters at the abandoned Greenwood gold mine and other surface waters reported in the literature. Lake data include lakes in Finland (Verta and others, 1994), Wisconsin (Watras and others, 1994), and New York (Bloom and Effler, 1990). Carson River, Nevada data are from Bonzongo and others (1996).
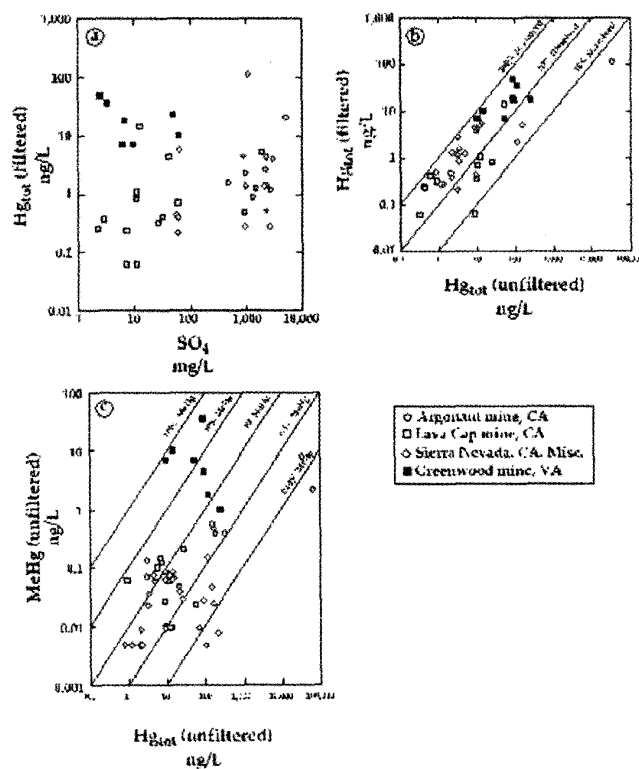
Figure 4. Comparison of mercury speciation and other hydrochemical data from the Greenwood mine with data from other abandoned gold mines (Ashley, 2000). a. THg (filtered) vs. SO_4; b. THg (filtered) vs. THg (unfiltered); c. MeHg (unfiltered) vs. THg (unfiltered).

54

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3.2.6 Characterizing Mercury in the Comstock Lode: Macro to Micro Techniques - Patrick Ritter, Ecology and Environment, Inc.

Overview

During the late 1800s, the silver rush brought a horde of miners to western Nevada. It also brought an enormous amount of mercury. From the discovery of the Comstock Lode in 1859, to approximately 1900, gold and silver was separated from the ore by a process that involved amalgamation with mercury. Large quantities of mercury were imported to the Virginia City area of Nevada (Figure 1) and a substantial amount was lost during ore processing. Over 100 former mill sites have been identified in the Virginia City area. Mercury-laden tailings were spread into surficial soils near most of these mill sites. Also, an estimated 14 million pounds of mercury was released into a 70-mile stretch of the Carson River, forming deposits in the river bottom and banks, floodplains, reservoirs, and wetlands.
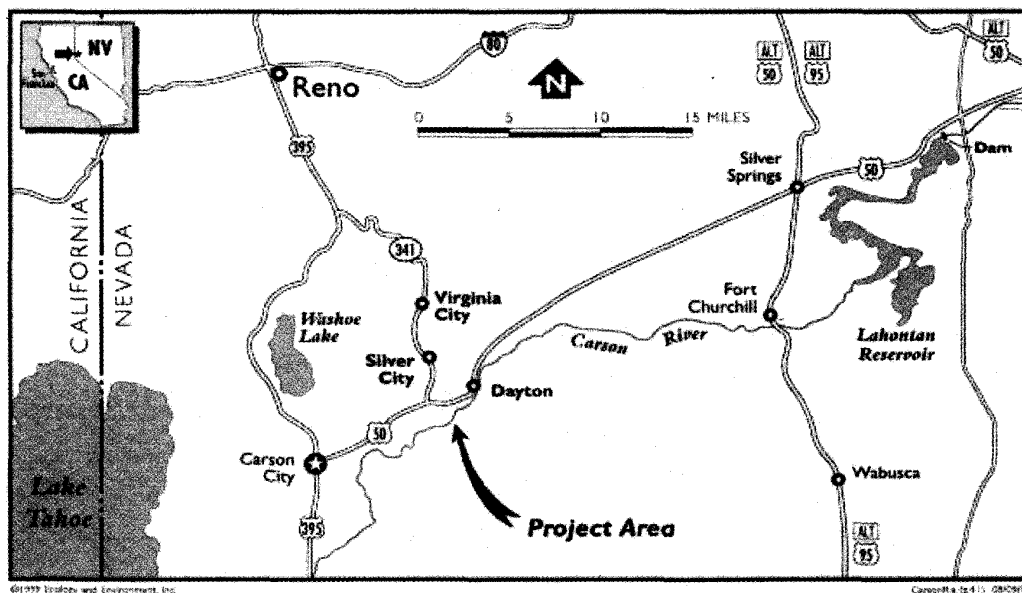
Figure 1. Location map.

Because of the widespread occurrence of mercury and elevated levels measured in sediments and biota, in August 1990, the USEPA designated the Carson River area the first Superfund site in Nevada. Ecology and Environment, Inc. (E & E), in consort with the EPA and other subcontractors, conducted a comprehensive characterization of mercury in soils; sediments; air; groundwater; surfacewater; vegetation; edible produce, fish and waterfowl; and terrestrial and aquatic biota as part of the Carson River Superfund project. To characterize mercury in such a vast area, that involved so many different media, a number of macro and micro characterization techniques were used, as summarized in Table 1.

Table 1. Characterization Methods - Carson River Mercury Site

Media	Analysis	Objective	Sampling Method
Soil: Primary Sources - Initial reconnaissance - Source areas - Residential soils	Hg(T), Trace Metals Hg(T), Pb, As Hg(T)	Identify COPCs, locate source areas Highest source contribution HHTA (mean & 95% UCL)	CRF & biased grab Biased grab Stratified random
Soil: Secondary Sources - Alluvial fans - Reservoirs/ lakes - Floodplains	Hg(T), Trace metals Hg(T), Trace metals Hg(T), Trace metals Hg(T), Trace metals Hg(T), Trace metals	HHRA exposure point concentration HHRA exposure point concentration HHRA exposure point concentration HHRA exposure point concentration HHRA exposure point concentration	Transects across streams Grab at beach use areas Transects perpendicular to flow Representative bank stratigraphy Stratified random at subareas
Soil: Subsurface	Hg(T)	Migration potential	Hand Digging'/ Power Augur/ Backhoe
Soil: Other characteristics - Mercury species - Physical characteristics - Precious metal content	Mercuric chlorid/sulfide Elementary mercury (analytical lab & centrifuge methods) Density, particle size, etc. Gold and silver assays	HHRA uptake potential HHRA uptake potential Remedial design Recovery potential	Representative grab Representative grab Representative tailings samples Representative tailings samples
Soils: Exacavated	Hg(T), TCLP (Hg, metals) Hg(O)	Disposal profiling Disposal profiling	Stratified random grid Visual observations, panning methods
Indoor Air - Dust - Vapor Outdoor Air - Dust - Vapor	Hg(T) Hg(O) Hg(T) Hg(O)	HHRA exposure point concentration HHRA exposure point concentration Worker/Community health & safety Worker/Community health & safety	NIOSH 8hr absorbent tube Jerome 411 NIOSH 6009 Low Flow; TSP/PM$_{10}$ Jerome 411
Groundwater - Domestic supply walls	Hg(T), As, Pb	HHRA exposure point concentration	Domestic wells & tapwater
Edible Produce - Gardens, orchards, - Bullrush roots	Hg(T) Hg(T)	HHRA exposure point concentration	Roots, leaves, fruits, & root soil, Roots & soil
Edible Fish Edible Waterfowl	Hg(T) Hg(T)	HHRA exposure point concentration HHRA exposure point concentration	Muscle tissue: walleye, white bass Muscle tissue: game ducks

Media	Analysis	Objective	Sampling Method
Surface -Carson River reaches - Lahontan Reservoir - Background reservoirs	Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species)	Mercury forms/ transformations, ERA Mercury forms/ transformations, ERA Mercury forms/ transformations, ERA	Near-surface grab Near-surface grab Near-surface grab
Surfacewater Characteristics	General chemistry, nutrients, Hg(species), trace metals	Identify other stressors, ERA	Near-surface grab
Sediment - Carson River pools - Lahontan Reservoir - Sediment porewater - Background reservoirs	Hg(T), Hg (species) Hg(T), Hg (species) Hg(T), Hg (species) Hg(T), Hg (species)	Mercury forms/transformations, ERA Mercury forms/transformations, ERA Mercury forms/transformations, ERA Mercury forms/transformations, ERA	Representative grab Sediment traps, grab, & Ekman dredge Near-shore grab & Ekman dredge Near-shore grab & Ekman dredge
Aquatic Biota -Zooplankton - Benthic macroinvertebrates - Aquatic Insects - Fish	Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species)	Mercury forms/transformations, ERA Mercury forms/transformations, ERA Mercury forms/transformations, ERA Mercury forms/transformations, ERA	Zooplankton nets (300 micron mesh) Kick nets Nets Gill nets, seining, electroshocking
Terrestrial Biota -Birds (blood, feathers, eggs, & livers) - Lizards	Ultra Clean Hg(T), Hg (species) Ultra Clean Hg(T), Hg (species)	Mercury forms/transformations, ERA Mercury forms/transformations, ERA	Mist nets (swallows, cormorants, juvenile herons, & egrets) Noose and line
Fish Stress Assessment	Condition factor analysis	Effects re: fish physiology and growth	Physiological examinations
Habitat Characterization	Water chemistry, substrate characteristics, taxa counts	Identify sensitive species habitats Observed vs. predicted effects to habitats	Rapid Bioassessment Protocol 2

Hg(T) Total mercury concentration
Hg(species) Methyl, dimethyl, ionic, & gaseous elemental mercury
HHRA Human Health Risk Assessment
ERA Ecological Risk Assessment
TCLP Toxic Characteristics Leaching Procedure
UCL Upper confidence limit
COPC Constituent of potential concern
Hg(O) Elemental mercury
Fish Walleye, Sacramento, Blackfish, Carp, Tahoe & Mountain, Suckers, and Green Sunfish

Source Identification

Former millsites, tailings piles, impoundments, millrace ditches, flumes, and other potential mercury source areas were identified based on existing historic and scientific records. This identification included the following macro-scale investigations:

- *Aerial Overflight/Ground Truthing*: Produce aerial photographs (1:12,000) and identify source features (e.g., tailing piles, impoundments)
- *Remote Sensing Survey:* Locate alluvial fan deposits
- *Historic Records*: Locate millsites from available records, including Historic American Engineering Record
- *Survey/Title Searches*: Identify millsites and descriptions
- *Millsite Features*: Locate and map millsite boundaries and features
- *Onsite Surveys/Ground Truthing*: Overlay historic features on current maps
- *Millsite Operations:* Estimate types and amounts of wastes from financial, operations, and other records

Primary sources included 113 individual millsites that were identified and mapped. Secondary sources included alluvial fans, floodplains, and reservoirs.

Source Characterization

After the source areas were delineated, biased sampling was performed to identify constituents of potential concern (COPCs), verify the type and size of sources, and determine whether additional sampling would be required:

- Perform XRF and laboratory analyses at locations of suspected highest mercury concentrations
- Collect 5-25 soil samples at identified tailings piles, millsites, impoundments
- Compare results to Preliminary Remediation Goals (PRGs) and background

At any location for which two or more of the biased samples exceeded the PRG, additional stratified random sampling was performed:

- Delineate subareas
- Determine number of samples needed (from one-sided t-test)
- Establish systematic grid at subarea
- Determine random coordinates and obtain sample
- Determine the mean and 95% UCL exposure point concentrations

Other Media

Little, if any, mercury was measured in groundwater, indoor air, and garden fruits and vegetables. These media were not, therefore, considered to be viable exposure pathways and were not characterized further. An extensive characterization was completed for surfacewater, sediment, terrestrial and aquatic biota (Table 1).

Analytical

A variety of analytical methods were used, depending on the data quality objective, detection limits required, and size of the area involved. Quality assurance procedures were applied for each method as appropriate:

- Field analytical (e.g., XRF)
- Contract Laboratory Program (CLP) analyses
- Mobile field laboratory (FASP lab)
- Specialized laboratory analyses (e.g., mercury speciation, gold/silver assays)
- Ultra-Clean sampling and analytical methods
- Waste profiling (e.g., TCLP for mercury and metals)
- Remedial bench testing (i.e., centrifuging with and without chemical additions)

Data Base

All samples were located using a GPS. Data was entered into a comprehensive data base that included sample identification number; location; depth(s); analytical method; land use description; media; subarea name and size; and relative source concentration. The data base also incorporated a statistical package so that key descriptors, such as variance, could be calculated and the number of additional samples needed could be quickly calculated while the sampling team was still mobilized at the subarea. After data validation was complete the characterization information was mapped using an ARC-Info system.

3.3   Methodology, Speciation, and Mobility

3.3.1   *Microbial Mercury Cycling in Sediments Associated with Historic Mining in California - Mark Marvin-DiPasquale (Presenter), USGS; Jennifer Agee, USGS; Charles N. Alpers, USGS; and Martha Thomas, University of California at Santa Cruz*

Background

The legacy of environmental Hg contamination in California stems largely from the close proximity of cinnabar (HgS) deposits in the central coastal mountains to the gold (Au) and silver (Ag) deposits to the north, south and east. During the gold rush of the mid-to-late 1800s elemental-Hg (Hg^0) was first produced from HgS, then transported throughout the state for use in Au/Ag mining via the amalgamation process. While the resulting Hg contamination is widespread and well documented in some areas, little is known about the microbial cycling of Hg in aquatic sediments associated with these mining areas. We have conducted preliminary research on potential rates of microbial MeHg production and degradation in sediments from one Hg-mining site (New Idria) in the Coast Ranges and from four Ag/Au mining areas in the Sierra Nevada.

New Idria, located in the central coast Diablo Mountain range, was the second largest Hg mine in North America, producing well over 16,000 tons of Hg^0 from HgS during its 118-year operation (1854-1972) (1, 2). Effluent from the mine, combined with leachate from the associated roasted-ore waste, currently drains into nearby San Carlos Creek. This leads not only to extreme Hg contamination but also to acid-mine drainage (AMD) conditions within the creek. This impaired water drains into the Mendota Water Fowl Management area, the headwaters of the San Joaquin River and ultimately the San Francisco Bay.

The Bear River and Yuba River watersheds lie approximately 350 km to the north-west of New Idria, across the Central Valley, on the western slopes of the Sierra Nevada. This was a region of extensive hydraulic mining of Au/Ag placer (alluvial) deposits from the 1850s to 1880s. It is estimated that 1,300 tons of Hg^0 was used in the Sierra Nevada, and of that 10-30% was lost during ore processing (3). Common throughout this area is an extensive network of remnant tunnel and ground sluices. These sluices were essentially inclined amalgamation troughs, charged with Hg^0, that carried a slurry of gold-bearing gravel and water. These remnant sluices often still contain visible amounts of liquid Hg^0 and Au-Hg amalgam. The Hg contaminated waters of the Bear/Yuba River watersheds eventually flow into the Feather and Sacramento rivers and ultimately to the San Francisco Bay.

MeHg is the most toxic form of Hg and is of concern because of its propensity to readily biomagnify within aquatic and terrestrial food chains. The production of MeHg from inorganic Hg(II) is primarily mediated by sulfate reducing bacteria in anoxic sediments (4). In addition to Hg-methylation, bacteria also degrade MeHg by a number of different pathways (5). Thus, the net production of MeHg is a balance between gross MeHg-production and gross degradation, and there is interest in determining what controls these processes and how they interact under various environmental conditions. This research examines these opposing pathways in the above suite of Hg-contaminated mining sites.

Methods

Sampling at New Idria was conducted in January 1999 at four locations, including one non-AMD impacted site (C-1) 3.2 km upstream of the mine and at three sites (AMD-1 through AMD-3) downstream of the mine. AMD-1 was located directly in front of a mine adit (1 m wide portal), where subsurface AMD emerges as

surface flow. AMD-2 was 0.1 km downstream of the mine adit, adjacent to a settling pond at the base of large roasted-ore waste pile. These two sites were upstream of the point where the mine effluent enters San Carlos Creek, with substrate largely composed of a bright orange precipitate, presumably poorly crystalline iron(III)-oxy-hydroxide sulfate (designated FeOOH), characteristic of AMD. Site AMD-3 was located 0.5 km downstream of the mine effluent and creek mixing-zone, and sediment was brownish-orange in appearance.

Sampling of hydraulic mining areas in the Sierra Nevada was conducted in November 1999, and included sediment from two drift-mine sluice-tunnels (S1, S2), and one exposed ground sluice (S3). Samples were taken from two separate locations (A&B) within S2 and S3. Two sites within Malakoff Diggings State Park were also sampled, the first being an organic-rich pond (MD_p) and the second a vent shaft (MD_{vs}) opening with effluent containing orange FeOOH precipitate similar to the New Idria AMD sites. Sediment from all three sluices was brown with little or no obvious FeOOH precipitate.

In all cases, surface sediment [0-4 centimeter (cm)] was sampled from locations with a shallow overlying water depth (5-15 cm) using appropriate trace-metal clean techniques. Subsamples for Hg-speciation analysis were taken and immediately stored frozen (Sierra Nevada samples only). The remaining sediment was stored in completely filled mason jars at 5°C for 2 to 36 days prior to further processing. All microbial sample processing was done on homogenized sediment in an anoxic (N_2 filled) glove bag. Individual samples consisted of 3.0 g of wet sediment in a crimp-sealed 13 cubic centimeter (cm^3) serum vial. Radiotracer amendments of ^{203}Hg(II) ($\approx$ 1 mCi, 570-1930 ng Hg*g wet sed^{-1}) and ^{14}C-MeHg ($\approx$ 10 nCi, 12 ng Hg*g wet sed^{-1}) were used to assess potential rates of Hg-methylation (6) and MeHg-degradation (7), respectively. Incubations were conducted at room temperature (20-22 °C) for 18-23 hours. Quality control consisted of autoclave-killed controls and replication (n=3) for each sample set. It is assumed that the ^{203}Hg-methylation and ^{14}C-MeHg degradation assays represent net and gross measurements, respectively. Sediment percent organic carbon (%C) was measured on a Carlo-Erba Elemental Analyzer (model: NA 1500 NCS), after acidification to remove carbonates. Sediment pH was measured with a Cole-Parmer (model: pH 20) meter by simply inserting the electrodes directly into whole sediment. Hg-speciation was conducted on unsieved wet sediment (n = 2 to 3). THg was quantified using acid digestion, Sn-reduction, gold trapping, and cold vapor atomic fluorescence spectrophotometry (CVAFS) detection (8, 9). MeHg was assayed by distillation (10), aqueous phase ethylation, G-C separation and CVAFS detection (11). Potential rates were calculated from radiotracer derived first-order rate constants and the amount of either ^{203}Hg(II) or ^{14}C-MeHg added.

Results and Discussion

Spatial trends in microbial Hg-transformations (potential rates) contrasted between sites upstream and downstream of the point of acid-mine discharge in New Idria. MeHg-production was at least 10-fold faster at site C-1 (upstream of the mixing zone) than at the three AMD sites (downstream of the mine) (Figure 1a). Conversely, MeHg-degradation was 10-fold faster at the AMD sites than at C-1 (Figure 1b). One interpretation of these trends is that net MeHg production was low in the AMD sites because gross MeHg degradation was high. Variations in sediment organic content could not account for the large spatial differences observed for these microbial processes, as organic-C was uniformly low (0.3 to 0.5%C) at all sites (Table 1). However, the shift from alkaline to acid drainage conditions and the associated formation of FeOOH presumably impacted bacterial communities. Rates of microbial MeHg-degradation were negatively correlated with pH, suggesting the importance of acidophilic bacteria in this process. Further, gaseous end-products of ^{14}C-MeHg degradation (e.g., ^{14}CH$_4$ and ^{14}CO$_2$) indicated that MeHg primarily degrades via an oxidative pathway at site C-1 and via a reductive detoxification pathway at the AMD sites (5). No clear relationships existed between Hg-transformation potential rates and in situ concentrations of THg and MeHg, although large errors were sometimes associated with these Hg-species measurements due to the heterogeneous nature of these unsieved samples. We speculate that spatial differences in Hg(II) bioavailability may also play a role in the development of different populations of Hg-cycling bacteria spatially in San Carlos Creek. Naturally abundant cinnabar (HgS) likely comprises the majority of Hg(II) in the upstream C-1 site. Since this form is very insoluble, we would expect the amount of bioavailable Hg(II) to be less at C-1 compared to the AMD sites, where the Hg(II) is derived largely from the acid-leaching of both subterranean HgS deposits and roasted ore waste. Thus, the higher concentrations of bioavailable Hg(II) at the AMD locations may select for microbial populations that are poised to degrade MeHg much more rapidly than at site C-1, where the bioavailable Hg(II) pool is presumably much smaller.
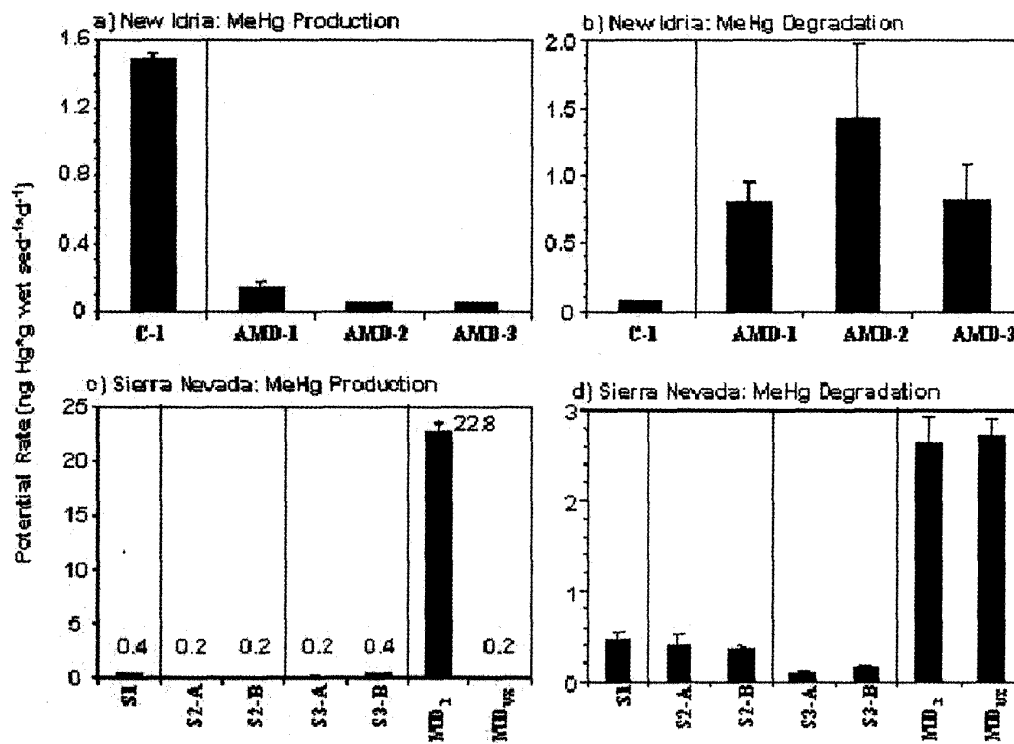
Figure 1. MeHg-production and degradation potential rates in sediments from San Carlos Creek (New Idria) and from a variety of sluices and associated hydraulic mining areas throughout the Bear River and Yuba River watershed of the western Sierra Nevada in California.

The highest potential rate of MeHg-production (23 ng*g wet sed^{-1}*d^{-1}) measured was in the organic-rich (12.2%C) pond sediment of MD_p in the Sierra Nevada (Figure 1c). This site also had the lowest sediment oxidation/reduction (redox) potential (+133 mV) compared to all other hydraulic mining sites (> +400 mV). Because decreased sediment redox is generally associated with increased activity of anaerobic bacteria (e.g., sulfate reducers), we conclude that the very high MeHg-production rate observed at MD_p was linked to the high organic content and increased microbial activity at this site compared to other locations. THg was also highest at MD_p (19.7 ppm), although this concentration was only two-fold higher than at Sluice S1, whereas the increase in MeHg-production was more than 50-fold. Thus, it is unlikely that the higher THg levels at MD_p significantly contributed to the high MeHg-production potential at this site. Similar to MeHg-production, the MeHg-degradation potential was also enhanced at MD_p compared to the three sluice sites (S1, S2, and S3) (Figure 1d). An argument can be made regarding the influence of organic matter fueling enhanced microbial degradation processes, as it was for MeHg-production. However, recent research also supports the concept that MeHg-degradation rates may increase with increasing Hg-contamination both within and across ecosystems (5). In addition, the FeOOH-rich MD_{VS} site exhibited equally high MeHg-degradation potentials as site MD_p, even though MD_{VS} had significantly less organic matter and lower in situ Hg-species concentrations. Because this result was similar to the low-organic FeOOH-rich AMD sites in New Idria, we speculate that bacteria associated with FeOOH particles (e.g., acidophiles, iron reducers/ oxidizers, sulfate reducers) may be particularly well adapted to degrade MeHg.

63

Table 1. Mercury Speciation and Sediment Characterization of Mining Sites

Site	THg (µg*g dry wt⁻¹)[a]	MeHg (ng*g dry wt⁻¹)[a]	Organic Carbon (%)	pH	Visible FeOOH?
New Idria					
C-1	7.9 ± 6.0	2.0 ± 0.4	0.5	8.1	No
AMD-1	3.5 ± 1.5	0.8 ± 0.0	0.3	2.9	Yes-dominant
AMD-2	16.8 ± 8.5	1.7 ± 0.4	0.5	2.6	Yes-dominant
AMD-3	5.6 ± 0.5	3.9 ± 3.7	0.3	7.1	Yes-dilute
Sierra Nevada					
S1 (Birdseye Tunnel)	9.6 ± 3.2	5.4 ± 1.7	1.0	6.9	No
S2-A (Polar Star Tunnel)	4.5 ± 1.0	0.3 ± 0.0	<0.07	4.4	No
S2-B (Polar Star Tunnel)	4.9 ± 2.1	0.4 ± 0.0	0.1	6.4	No
S3-A (Sailor Flat sluice)	<0.07	<0.07	0.1	4.8	No
S3-B (Sailor Flat sluice)	<0.07	<0.07	0.1	n.d.	No
MDp (pond)	19.7 ± 2.2	30.7 ± 7.7	12.2	5.5	No
MDvs (vent)	0.1 ± 0.0	0.1	1.8	6.5	Yes-dominant

[a] New Idria Hg-speciation data previously presented (12)
n.d. = not determined

Conclusion

Potential rates of MeHg-production and degradation by resident bacteria were more responsive to *in situ* geochemical conditions (e.g., organic content, redox, pH, FeOOH content) than to THg or MeHg concentrations. The highest potential rates for both processes were associated with an organic-rich pond, although high rates of MeHg-degradation were also associated with low-organic sites containing visibly high concentrations of FeOOH. This study demonstrates the importance of assessing both MeHg production and degradation to better understand the processes that control net MeHg production. Furthermore, this preliminary investigation of mining areas illustrates that microbial Hg- transformations are complex, spatially variable and only poorly understood. Continued work in such systems will likely lead to advances in the area of Hg-bioremediation. Bacteria from these and similar Hg-contaminated mining locations are presumably adapted to high concentrations and rapid cycling of Hg. The isolation of bacteria from these extreme environments may lead to the use of such organisms in future bioremediation projects.

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3.3.2 Uncertainty Analysis of the Carson River Mercury Transport Model - Rosemary W.H. Carroll (Presenter), Desert Research Institute and John J.Warwick, Department of Environmental Engineering Sciences, University of Florida

Introduction

The Carson River in west central Nevada is heavily contaminated with mercury derived from the Comstock Lode and other mining operations of the late-19th century. Past studies of the Carson River system have focused on modeling inorganic and MeHg transport (Carroll et al., 2000). Current understanding of inorganic mercury transport and fate is more than adequate, and model prediction occurs with reasonable accuracy. On the other hand, the biogeochemical processes that affect the methylation of inorganic mercury into MeHg are numerous and complicated. The resulting uncertainties in parameters that characterize methylation generate significant errors in predicting the water column MeHg concentrations.

During January 1997 a rain-on-snow event occurred in the Sierra Nevada to produce the largest recorded flood along the Carson River. This single extreme event caused tremendous geomorphic change through bank erosion and widespread overbank deposition (Miller et al., 1999). An unsteady flow, mercury transport model developed by Carroll et al. (2000) was calibrated with mercury water column data collected prior to the 1997 flood. This model proved a poor predictor of observed post-1997 flood MeHg water column concentrations. Carroll et al. (2000) showed that given a low flow regime, post-flood MeHg simulations have a larger model error, a change in error bias and a shift upstream of the peak MeHg concentrations when compared to pre-flood results. If it is assumed that the Carson River model adequately predicts pre-1997 flood MeHg water column concentrations, then these results suggest MeHg transport and fate may have been altered as a consequence of the flood. The objective of this study is to delineate model error in prediction associated with the mass transfer of MeHg from the bottom sediments along the Carson River. Given the model is a predictor of systematic behavior, it may be possible to use model results to test system response to the 1997 flood.

Site Description

A map of the Carson River basin is shown in Figure 1 with several reference locations marked. The Carson River flows eastward out of the Sierra Nevada Mountains just to the south of the Tahoe Basin. The section of the Carson River under investigation extends from the USGS gauging station near Carson City, Nevada (CCG) downstream to the river's confluence with Lahontan Reservoir. Flow in the Carson River is typical of most semi-arid fluvial systems in that it is highly variable. Flow is predominately from snowmelt in the Sierra Nevada with peak discharge generally occurring in the spring with a sustained moderately high hydrograph. Catastrophic floods, such as the January 1997 flood, however, are generated with rain-on-snow events that occur during the winter months.
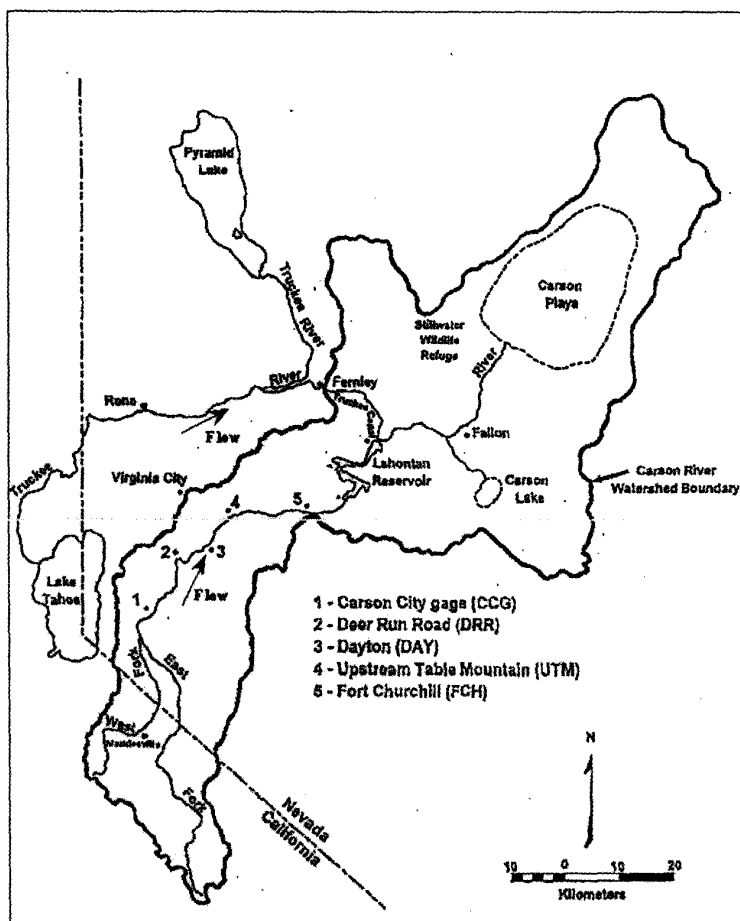
Figure 1. The Carson River Basin with reference locations marked.

Deterministic Model

Three computer models developed by the USEPA are used to simulate the transport and fate of mercury within the Carson River. These models were originally chosen and linked by Heim and Warwick (1997) with further modifications made by Carroll et al. (2000). RIVMOD is a one-dimensional hydrodynamic and sediment transport routine that simultaneously solves standard fluid equations of continuity and momentum (Hosseinipour and Martin, 1990). WASP5 is the USEPA Water Quality Analysis Simulation Program-5 that was developed to simulate the transport and transformation of various water body constituents via a mass balance approach (Ambrose et al., 1991). Finally, MERC4 is a subroutine contained within WASP5 (Martin, 1992). It was developed to specifically compute mercury speciation and kinetic transformation.

Water column MeHg concentrations were calibrated using two parameters. The first calibration parameter is directly associated with MeHg bank concentrations. Channel banks have much higher concentrations of mercury associated with sediment than those found within the channel bed (Miller and Lechler, 1998) and may actively control water column concentrations if bank erosion processes are significant. Carroll et al. (2000) adjusted $\lambda 2$ in equation (1) to a value of 22.0 µg/kg in order to best match water column data collected during a medium flow regime (17 cubic meter per second (m^3/s), 600 cubic feet per second (ft^3/s)). Here the boundary condition of MeHg bank concentration, $[MeHg]_{bank}$, is in units of µg/kg while S_0 is the designated longitudinal bottom slope of the model segment.

66

$$[MeHg]_{bank} = \frac{\lambda 2}{S_0^{0.5}}$$

The second calibration parameter defines the flow above which MeHg input via bank erosion no longer occurs. Carroll et al. (2000) found that MeHg input from bank erosion increases until 28.3 m^3/s (1,000 ft^3/s). Above 28.3 m^3/s, additional MeHg contribution from bank erosion becomes zero.

Uncertainty Analysis

Three parameters that affect the movement of MeHg from the bottom sediments are investigated: the diffusion rate (E), the methylation rate coefficient (M) and the demethylation rate coefficient (D). While the methylation and demethylation rates are allowed to vary independently, they are evaluated as a single ratio (M/D). After ranges are established for each parameter, a preliminary sensitivity analysis is conducted to determine the relative importance of each parameter. This is then followed by a more comprehensive Monte Carlo analysis.

Two separate flow regimes are simulated to evaluate the importance of bank erosion and diffusion on error propagation. The first scenario uses a steady state simulation of 28.3 m^3/s (1000 ft^3/s) at which MeHg input via bank erosion is at a maximum. No data exists for this discharge, but a range in possible model output given changing parameter values is established. The second scenario uses steady state flow of 1.42 m^3/s (50 ft^3/s) to represent a discharge in which diffusion processes dominate. Low flow model results are compared to data collected from July 23, 1997 until July 29, 1997 when discharge at FCH (segment 140) varied between 1.22 m^3/s – 1.81 m^3/s (43 ft^3/s – 64 ft^3/s).

Measured methylation and demethylation rates were taken from two separate studies (Heim, 1996; Oremland et al., 1995) in order to establish minimum and maximum potential rates. Unlike M/D, there is only one value for diffusion (4×10^{-12} square meter per second (m^2/s)) that exists from collected data (Heim, 1996), and it is not possible to constrain an acceptable range applicable to the Carson River. Instead, the variation of diffusion from its deterministic value of 4×10^{-12} m^2/s is done to closely mirror variations in the M/D ratio. Consequently, E is not included in the Monte Carlo analysis.

Results of the sensitivity analysis are provided in Table 1. These results show that output is equally sensitive to the M/D ratio and E. Results also show that both parameters have significantly more effect on model output during low flow regimes when velocities are slow and diffusion processes dominate. At higher flow regimes, bank erosion processes are more important. By increasing the mass transfer of MeHg out of the bottom sediments (increasing M/D or E), it becomes necessary to lower $\lambda 2$ through re-calibration (i.e., lower the impact of bank erosion on MeHg input). Subsequent dilution causes a decreasing trend in MeHg concentrations. One notable exception occurs at the highest M/D value (0.26). At this value, the calibration of MeHg water column concentrations proved too high despite forcing $\lambda 2$ to equal 0 $\mu g/kg$ (no MeHg input via bank erosion). Results show that for the M/D value of 0.26, the dilution of MeHg is not adequate to lower MeHg water column concentrations at 28.3 m^3/s (1000 ft^3/s). Since it is impossible to use negative bank concentrations to calibrate the model when M/D equals 0.26, it became necessary to constrain the upper limit of M/D. A value of 0.065 is found to be the maximum M/D ratio, and expected trends in equilibrium water column concentrations are maintained.

Table 1. Sensitivity Analysis Results Showing Parameter Ranges, Re-Calibration of λ2 End Equilibrium MeHg Concentrations

Value	λ_2(µg/kg)	Segment 140 (FCH) MeHg Equilibrium Concentration (ng/L)	
		1,000 ft³/s	50 ft³/s
M/D (dimensionless)			
0.00044	28	10.40	1.51
0.0091	22	9.03	6.31
0.016	18	8.23	9.87
0.044	9	7.32	25.70
0.065	0	5.97	37.80
0.26	<<0	21.50	146.00
E (m²/s)			
4.0*10-13	27	10.10	1.80
2.0*10-12	25	9.66	3.73
3.2*10-12	23	9.21	5.51
4.0*10-12	22	9.03	6.31
4.8*10-12	22	9.03	7.20
6.0*10-12	21	9.06	8.70
2.0*10-11	9	7.70	25.00
2.8*10-11	0	5.80	34.80

Monte Carlo simulations used methylation and demethylation rates described by independent, uniform distributions to reflect "decision uncertainty" (Warwick and Cale, 1986; Warwick and Edgmon, 1988). Given the continuum of possible M/D ratios calculated from randomly selected methylation and demethylation rate coefficients, a polynomial function, presented with equation (2), was developed for the auto-calibration of λ2 and was written directly into the WASP5 numeric code.

$$\lambda_2 = 1678[M/D]^2 - 521[M/D] + 27.3 \qquad (2)$$

Monte Carlo simulations using 100, 200, 400, 800 and 1,600 realizations were conducted for steady state flow conditions of 28.3 m³/s (1000 ft³/s) and 1.42 m³/s (50 ft³/s). Every Monte Carlo simulation was initiated with the same random seed. Model output is evaluated following each Monte Carlo simulation to estimate the 90% confidence interval (CI) along the entire length of the stream. Given a steady state flow of 28.3 m³/s (1000 ft³/s) the estimated 90% CI is shown in Figure 2a. Assuming 1,600 realizations describes the true output distribution, Figure 2a shows convergence upon the 90% CI occurs with 800 realizations with uncertainty in MeHg output at segment 140 equaling to 1.9 ng/L.

The same array of realizations (100, 200, 400, 800 and 1600) was used to define the 90% CI for steady state discharge of 1.42 m³/s (50 ft³/s). Output is shown in Figure 2b. Results show that, similar to the higher flow scenario, it appears that 800 realizations are necessary to accurately estimate the 90% CI. As expected the uncertainty in MeHg prediction increases with lower discharge, to produce a spread in the CI at segment 140 of 11.6 ng/L. Included within Figure 2b are data collected from July 23, 1997 until July 29, 1997. The criteria for assessing system response to the 1997 flood involves comparing the envelope of probable model outcomes with observed data. If a statistically significant change occurred to MeHg transport because of the 1997-flood (i.e., due to geomorphic change), then the established CIs would not incorporate the scatter seen in the data. Results show that probable model predictions account for all the MeHg data. Given that all observed points lie within the 90% CI, it is not possible to identify any significant change along the Carson River in terms of MeHg transport and fate.
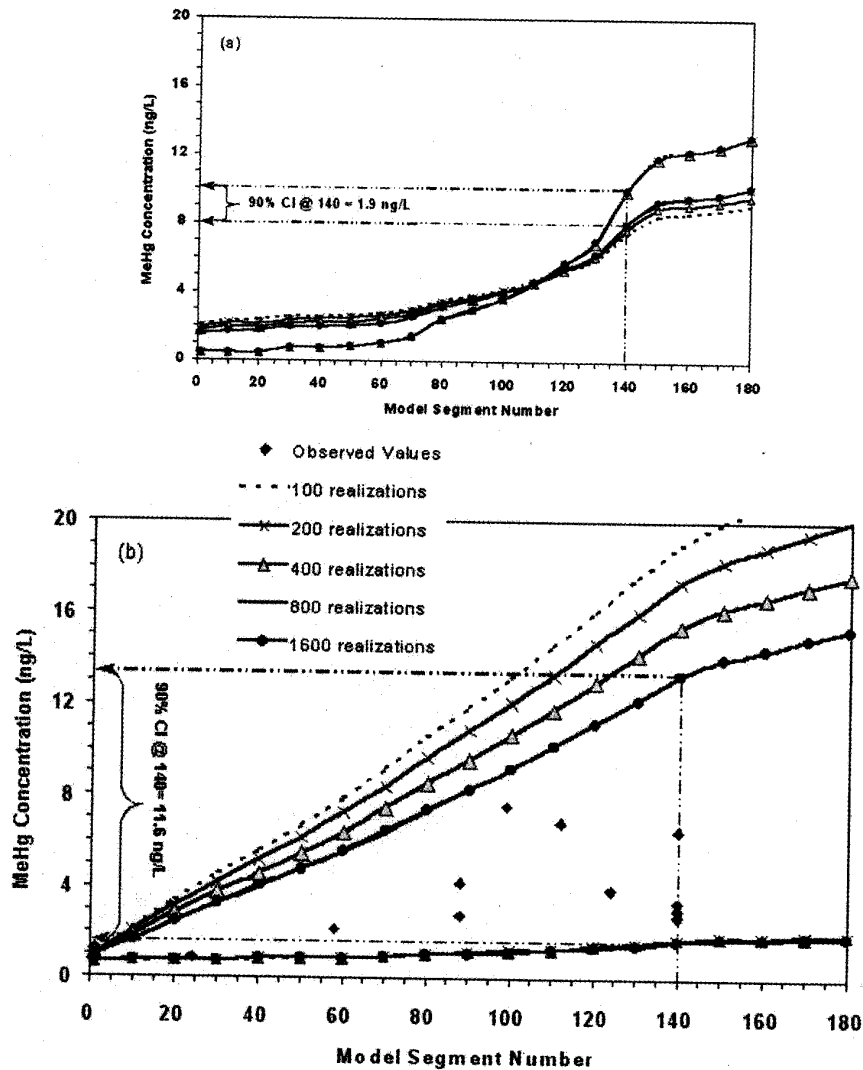
Figure 2. The 90% CI for several Monte Carlo simulations given steady state discharge of (a) 28.3 m³/s and (b) 1.42 m³/s.

Conclusions

This study addresses uncertainty in the mass transfer of MeHg from the bottom sediments into the overlying water column. Three parameters are investigated. These parameters include the diffusion rate, the methylation rate coefficient, and the demethylation rate coefficient. Results show that if the parameters are evaluated for equivalent magnitudes of change, then the M/D ratio is only slightly more influential on model output than the diffusion rate. Parameter sensitivity on MeHg water column concentrations is very high for both parameters during low discharge regimes. At low flow, slow velocities hinder MeHg dilution and the bank erosion process becomes negligent. Consequently, mass movement out of the bottom sediments, which is driven by the diffusion rate and the M/D ratio, dominates MeHg input. At higher discharge, parameter sensitivity is significantly reduced, and a negative correlation exists between the parameter and model output. In other words, by increasing the mass transfer of MeHg out of the bottom sediments (increasing M/D or E), it becomes necessary to lower the impact of bank erosion on MeHg input. Subsequent dilution causes a decreasing trend in MeHg concentrations.

A more comprehensive Monte Carlo analysis is conducted to test error propagation associated with uncertainty in methylation and demethylation rate coefficients. Unfortunately, it is necessary to exclude the diffusion rate from the Monte Carlo analysis because no data exists to constrain a range of values applicable to the Carson River. Methylation and demethylation are assumed to vary independently and are described by uniform distributions to reflect "decision uncertainty." It is discovered that the 90% CI can be defined with a minimum of 800 realizations per Monte Carlo simulation. As expected, error increases significantly with decreasing discharge. Given 28.3 m³/s (1,000 ft³/s) steady state conditions, uncertainty in the downstream reaches of the river is approximately 1.9 ng/L. Uncertainty increases to 11.6 ng/L for 1.42 m³/s (50 ft³/s). Results show that probable model output at low flow encompasses all of the scatter exhibited by the July 1997 MeHg data set. Therefore the Carson River mercury model is not capable of predicting a statistically significant response to the 1997 flood in terms of MeHg transport and fate. It is also notable that model results represent a conservative estimate of model error in prediction. Model results would undoubtedly produce a greater spread in possible MeHg output if either a larger CI was used or more model parameters were considered uncertain.

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3.3.3 Assessing the Mobility of Mercury in Mine Waste - Chris Sladek, Department of Geological Science, UNR and Mae Sexauer Gustin, Department of Environmental and Resource Sciences, UNR

Introduction

Assessing the speciation and mobility of mercury associated with mine waste is essential for determining if there are human and ecological health concerns associated with Hg contaminated sites, and if remediation actions should be taken. Sequential extraction methods are commonly used for this purpose. Nirel and Morel (1990) stressed that indiscriminate application of such methods can produce erroneous results. For example, speciation analysis for elemental mercury (Hg^0), soluble Hg, HgS and total Hg by separate labs of samples from the Carson River Superfund Site, Nevada, USA showed disagreement of up to 82% for total Hg, and even greater discrepancies for specific Hg species (Hogan and Smucker, 1994).

The initial phases of this project evaluated the efficiency of some procedures commonly used in sequential extraction methods for determining Hg speciation in sediments in an effort to develop a method for determining mobility of Hg species in mine waste. Pyrolitic methods were applied for the determination of volatile phases; leaching with chloride solutions was utilized for determination of soluble or mobile species; and acid digestions were used to extract strongly bound or relatively immobile species and for THg analyses. Pyrolitic extraction at greater than 80°C resulted in significant over estimation of Hg^0. A pyrolitic extraction conducted at 80°C for 8 hours removed 10.4 ± 0.5 % of Hg amended as $HgCl_2$, while extractions performed at 150 and 180°C for 8 hours removed 42.4 ± 1.4 % and 66.5 ± 1.5 % of Hg amended as $HgCl_2$ to natural sediments. Ammonium chloride was found to be more efficient than $MgCl_2$ in removing $HgCl_2$. The organic content of a sediment was found to interfere significantly with sequential extraction results. Inorganic amendments such as FeOOH and vermiculite also influenced extraction results but not as strongly as organic matter. Three acid digestions for total Hg were compared for their efficiency at removing Hg from silica encapsulated cinnabar (HgS): 1 HF : 1 HNO_3 : 3 HCL, aqua regia (1 HNO_3 : 3 HCl) and 3 H_2SO_4 : 7 HNO_3. Aqua regia was 89.9 ± 3.1 % as efficient as the HF digestion, while the 3 H_2SO_4 : 7 HNO_3 was only 40.8 ± 1.8 % as efficient as the HF digestion.

Methods for Evaluation of Mine Waste

After evaluation of various sequential extraction methods the following protocol was established for determining the mobility of Hg in mine waste. Because it was determined that the pyrolitic extraction removed soluble Hg, volatile and soluble Hg extractions were performed separately. An 80°C pyrolitic extraction for 8 hours was used to determine volatile Hg (Hg^0). This was followed by an aqua regia digestion for residual Hg. On a sample split, an NH_4Cl leach was used to determine soluble or exchangeable Hg (Hg^{2+}) followed by an aqua regia digestion for residual Hg. The results of the first extraction (pyrolitic or NH4Cl leach) were summed with the aqua regia digestion to determine total Hg and calculate the percent Hg extracted.

Since the mine wastes are typically low in organic material, binding of Hg to organic material was not expected to confound the extraction efficiencies. Extractions were performed on triplicate 1 g samples. Mercury analysis were performed using a Varian model 220 Spectra AA and VGA 77 hydride generator. Sodium borohydride was used as a reductant. A closed cell analyzer tube, which was heated to eliminate interference from water vapor, was used. The detection limit was 0.5 nanograms per milliliter (ng/mL) Hg in solution and the reporting limit was 1 ng/mL in solution.

The procedures above were applied to the following samples: Tailings from the Comstock mining district, Nevada, USA, where Hg^0 was used in amalgamation processing of gold ore; waste rock (altered serpentinite containing HgS), calcine (waste product from roasting serpentinite Hg ore) and condenser soot (waste from cleaning the mercury condenser tubes) from the New Idria mercury mining district, California, USA, waste rock from the Antelope district (altered limestone containing HgS) Nevada, and calcine (waste product from roasting limestone Hg ore) from the Table Mountain district, Nevada.

Results and Discussion

Results indicated that Hg in these waste products is largely immobile. Volatile Hg determined by deduction was within the error of total Hg determinations. Volatile Hg for the Comstock tailings was less than 4.2%, and soluble Hg determined using the NH4Cl leach was 0.16 % ± 0.01 of the extracted Hg in the Comstock

tailings. Volatile Hg from the New Idria waste materials ranged from less than 1.8% for condenser soot to 3.7% for waste rock containing visible cinnabar. Soluble Hg was 3.48 ± 0.08 % for calcine and 0.05 ± 0.003% for waste rock. The extractability of Hg from the Table Mountain calcine is much lower than the Idria calcine with Hg^{2+} below analytical detection limit.

Lechler et al. (1997) found Hg^0 to be approximately 90% of Hg in sediments from the Comstock district using a pyrolitic extraction temperature of 180°C. A silver and gold amalgam was identified in a sample of tailings from the Comstock district by backscatter imaging and energy dispersive X-ray analysis using a Jeol 840A scanning electron microscope. If elemental Hg in tailings is largely in the form of amalgams, it could explain the relatively low recovery at 80°C.

Additional leaches containing 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 0.1 M NaCl were used to simulate acid rock drainage. Sodium chloride was included because chloride is a common anion in most waters, and it is an effective ligand for Hg at low temperatures. Mercury leached from Comstock tailings increased from 0.09 ± 0.002 % to 2.61 ± 0.28 % with the addition of 0.1 M NaCl to 0.5 M H_2SO_4 leach. Mercury extracted from New Idria waste material using the 0.5 M H_2SO_4 + 0.1 M NaCl was 0.56 ± 0.06 for waste rock and 11.1 ± 0.53 % for calcine.

Extractions from the Antelope and Table Mountain waste material using this leach were 0.1 ± 0.01 % for waste rock and 0.01 ± 0.001 % for calcine. This lower extraction in comparison to the New Idria waste materials is likely due to a strong acid neutralizing potential because of the high carbonate content in the Antelope and Table Mountain waste material.

Rytuba et al. (2000) found Hg in streams impacted by mining in the New Idria district to be dominantly particulate and not dissolved. Dispersion of Hg downstream of Hg mines in Nevada is highly localized suggesting a low mobility of Hg (Gray et al., 2000). These findings are consistent with the extractability of Hg by the leaches used in this study. Decades of exposure may have leached much of the more soluble Hg from the waste materials analyzed. Since most of the samples analyzed were taken near the surface (approximately 10 cm depth), an analysis of Hg speciation through a vertical profile in a waste dumps should indicate if weathering related leaching has caused a depletion of soluble Hg near the surface. High rates of gaseous Hg flux have been measured from areas naturally enriched and contaminated by Hg, including some of the sites from which samples for this study were collected (Gustin et al. 2000). This suggests that volatilization may be a primary mechanism by which Hg is released to the environment from these waste products.

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3.3.4 Application of Selective Extractions to the Determination of Mercury Speciation in Mine Tailings and Adjacent Soils - Nicolas S. Bloom, Frontier Geosciences and Jodie Katon, Frontier Geosciences, Inc.

Introduction

Speciation is critical to understanding and modeling Hg contaminated soils because it is the particular distribution of compounds and their interaction with soil under aqueous conditions that determine their environmental mobility and bioavailability (Davis, et al., 1997). To address this need, we have refined and validated a robust solid phase analytical scheme based upon sequential selective extractions (Bloom, et al., 2000). Although no extraction scheme can provide true species-specific information, this method does provide precise and accurate data regarding the biogeochemically relevant fractionation of Hg in sediments and soils. This method differentiates Hg into behavioral classes including water soluble, "stomach acid" soluble, organo-chelated, elemental, and mercuric sulfide, while still providing sufficiently low MDLs for pristine studies. The speciation profiles generated have been inter-compared with other assessment techniques, such as EXAFS, TCLP, and a methylation bioassay that uses incubation with natural sediments. These experiments show that mine site media (soils and tailings) that contain higher percentages of inorganic Hg in the first three extraction fractions (water soluble, dilute acid soluble, and organo-chelated Hg) are more readily methylated than those containing most of their Hg in the last two extraction fractions (approximately Hg° and HgS). Long-term incubations suggest that all forms of Hg found at mine sites are methylated to some degree however, and they appear to convert slowly to the site-specific sediment Hg speciation profile, regardless of the initial speciation of the added material.

Experimental Methodology

Samples for this study were obtained from clients as parts of other unrelated investigations. Sediments were shipped to the laboratory via overnight courier, and then either processed immediately, or frozen until processing. Soils were sieved through a 2.0 or 1.4 mm sieve prior to homogenization and analysis, and were co-processed with extensive QC samples, including method blanks, certified reference materials, and pure Hg compounds suspended in kaolin.

Total mercury was determined by room temperature digestion in aqua regia (4:1 HCl + HNO_3). After overnight digestion, the samples were diluted to 40.0 mL with 0.02 N BrCl in 1N HCl, and aliquots analyzed by USEPA Method 1631 (dual amalgamation/CVAFS). Gas-phase Hg° concentrations were determined after equilibration for several days at room temperature (20–22°C) in half-full 500 mL glass jars with Teflon caps. For analysis, a small hole was drilled into the cap of each jar, and a gas-tight glass syringe was used to withdraw 5.00 mL of headspace gas. This was injected into an argon flow and carried onto a gold-coated sand trap, which absorbs the Hg by amalgamation. Traps were analyzed using EPA Method 1631.

Inorganic Hg speciation was determined by sequential selective extractions of separate 0.4 g aliquots of the homogenized solids (Bloom, et al., 2000) as indicated in Table 1. The extraction was performed using a 100:1 liquid-to-solids ratio in 40 mL vials. Each extraction step was conducted for 18±3 hr, with constant agitation, at 18-22°C. At the end of each step, the samples were centrifuged, and then the supernatant liquid was filtered through a 0.2 μ filter. The solid pellets were then re-suspended in the same extractant, re-centrifuged, and re-filtered. The two filtrates were combined in a 125 mL bottle, oxidized by the addition of BrCl, and diluted to 125 mL prior to analysis for total Hg by EPA Method 1631. After the rinse step, the sample pellet in the centrifuge tube was resuspended in the next extractant, and the entire process was repeated.

Table 1. Sequential Extraction Method Summary

Step	Extractant	Description	Typical Compounds
F1	DI water	water soluble	$HgCL_2, HgSO_4$
F2	pH 2 HCl / HOAc	"stomach acid"	HgO
F3	1N KOH	organo complexed	Hg-humics, Hg_2Cl_2
F4	12N HNO_3	strong complexed	mineral lattice, Hg_2Cl_2, $Hg°$
F5	aqua regia	cinnabar	HgS, M-HgS, HgSe, HgAu

Methyl Hg was quantified by extraction of separate 0.5 g aliquots from a $KBr/H_2SO_4/CuSO_4$ mixture into CH_2Cl_2 (Bloom, et al., 1997). After centrifugation to separate the aqueous and organic layers, an aliquot of the CH_2Cl_2 layer was then back-extracted by solvent volatilization into 60 mL of pure water prior to analysis for CH_3Hg. Aliquots of the final extract were analyzed by aqueous phase ethylation, purge and trap onto Carbotrap, isothermal GC separation, and CVAFS detection (EPA Draft Method 1630).

As a QA investigation, some samples were analyzed using EXAFS (Kim, et al., 1999) as dry powders in fluorescence mode with a 13 element high throughput Ge detector. Data were collected on beamlines 4-2 and 4-3 at the Stanford University Synchrotron Radiation Laboratory (SSRL). Natural sample EXAFS spectra were compared against a database of pure Hg compounds. Model compounds were powdered and diluted with boron nitride, and EXAFS spectra collected in the transmission mode. This technique requires samples with a total Hg concentration of greater than 100 μg/g, and can provide resolution of compounds that are in the model compound library, and make up more than 10% of the total Hg in the sample.

To assess their methylation potential, various substrates were mixed with a natural low Hg, high organic matter freshwater sediment and incubated in sealed vials. After processing and homogenization, the sediment had a pH of 6.4, contained 0.19 μg/g of total Hg, 0.0014 μg/g of methyl Hg, and 4.8% total organic carbon on a dry weight basis. When used in the incubation experiments, the sediment was first homogenized, together with some of the overlying water, to contain approximately 20% solids. In 125 mL glass vials with Teflon lined caps, 100 g of sediment were mixed with a small amount (0.01–3.00 g) of contaminated soils or pure compounds dispersed in kaolin to obtain a final total Hg concentration of about 5 μg/g (wet basis). The bottles were tightly sealed, and placed on a roller at approximately 5 RPM, where they were continuously homogenized for the first three weeks, and periodically after that time until aliquoting for selective extractions and CH_3Hg analysis. Incubations were conducted at room temperature, which varied from 18–22°C. Aliquots were taken for analysis at 1-week, 3-week, and 22-week intervals.

Speciation Results

Samples for Hg speciation were collected from two abandoned mine sites, including the Red Devil cinnabar mine in southeastern Alaska (CM) and a gold mine in central California (GM). Also included are the speciation profiles for several pure substances, and samples from particular sites that were contaminated by activities other than mining (CS). These samples are identified in Table 2, and the corresponding speciation information is presented in Table 3. As part of the method validation study, eight samples were submitted both for selective extractions and EXAFS analysis, three of which are shown in Table 4. Although the sequences of Hg compounds shown for EXAFS and for selective extractions are both listed in order of decreasing solubility, the reader must not make the mental correlation of each extraction fraction with the adjacent EXAFS species. Of the species reported by EXAFS, we expect $HgCl_2$, HgO and $HgSO_4$ to be leached quantitatively by the F1 + F2 fractions, while HgS, meta-HgS, and HgSe should all remain until the F5 extraction fraction.

Table 2. Sample IDs and Ancillary Parameters

Sample	Description	TCLP [Hg] µg/L (ppb)	Headspace Hg° (µg/m³)
HgCl²	Hg(II) chloride in kaolin	nd	nd
Hg°	elemental Hg in kaolin	1,334	16,478
HgS	red cinnabar in kaolin	0.04	nd
HgSO⁴	Hg(II) sulfate in kaolin	253,000	nd
GM-1	gold mine tailings (deep)	407	72.7
GM-2	gold mine tailings (surface)	28.3	5.6
CM-1	HgS mine soil, retort area (surface)	0.73	3.3
CM-2	HgS mine soil, retort area (10 cm)	0.14	0.1
CM-3	HgS mine soil, retort area (210 cm)	2,898	17.980
CM-4	HgS mine soil @ seep (surface)	0.14	19.7
CS-1	Hg° spill impacted arid soil (90) days	0.39	1,241
CS-2	Hg(NO$_3$)$_2$ floodplain soil (50 years)	nd	nd
CS-3	chlor-alkali plant soil (40 years)	18,900	16,800
CS-4	GM-1 incubated sediment (143 days)	nd	nd
CS-5	Hg(II) incubates sed (143 days)	nd	nd
CS-6	HgS incubated sed (143 days)	nd	nd

µg/L   micrograms per liter
µg/m3   micrograms per cubic meter

Table 3. Speciation Results for Selected Sediment and Soil Samples

| Sample | Mercury Concentrations, µg/g (ppm) Dry Basis | | | | | | |
	F1	F2	F3	F4	F5	Total	MHg
HgCl$_2$	2,302	77.0	4.04	2.10	0.79	2,386	*nd*
% of total	**96.5**	3.2	0.17	0.09	0.03		*nd*
Hg°	10.4	27.9	54.3	22,502	618	23,214	*nd*
% of total	0.04	0.12	0.23	**96.9**	2.7		*nd*
HgS	0.10	0.02	0.12	5.55	4,353	4,359	*nd*
% of total	0.002	0.001	0.002	0.13	**99.9**		*nd*
meta-HgS	0.02	0.17	0.43	18.6	10,407	10,426	*nd*
% of total	0.000	0.002	0.004	0.18	**99.8**		*nd*
HgSO$_4$	1,052	3,751	68.6	48.6	17.7	4,772	*nd*
% of total	**22.0**	**78.6**	1.4	1.0	0.37		*nd*
GM-1	2.19	15.28	6.41	13.78	4.07	41.7	*nd*
% of total	5.3	**36.6**	**15.4**	**33.0**	9.8		*nd*
GM-2	8.29	7.75	6.39	21.3	591	635	*nd*
% of total	1.3	1.2	1.0	3.4	**93.1**		*nd*
CM-1	0.44	0.04	1.33	9.59	500	511	0.006
% of total	0.09	0.01	0.26	1.9	**97.8**		0.001
CM-2	0.10	0.00	11.6	17.2	831	860	0.001
% of total	0.01	0.00	1.3	2.0	**96.6**		0.0001
CM-3	13.9	433	49.3	1,443	5,236	7,175	0.028
% of total	0.19	6.0	0.68	**20.1**	**73.0**		0.0004
CM-4	0.07	0.06	1.69	7.85	190	199	0.010
% of total	0.04	0.03	0.85	3.9	**95.5**		0.005
CS-1	1.27	0.06	0.32	15.7	19.9	37.2	*nd*
% of total	3.4	0.16	0.86	**42.2**	**53.5**		*nd*
CS-2	1.99	42.0	150	47.4	406	546	0.026
% of total	0.36	7.7	**27.5**	8.9	**74.4**		0.005
CS-3	133	211	112	72,689	188	73,333	0.009
% of total	0.18	0.29	0.15	**99.1**	0.26		0.000
CS-4	0.00	0.00	2.30	8.38	7.77	18.46	0.056
% of total	0.00	0.00	**12.5**	**45.4**	**42.1**		0.303
CS-5	0.01	0.01	2.53	10.61	4.51	17.66	0.106
% of total	0.06	0.06	**14.3**	**60.1**	**25.5**		0.600
CS-6	0.01	0.00	0.71	1.19	13.99	15.89	0.004
% of total	0.06	0.00	4.5	7.5	**88.0**		0.025

Table 4. Blind Intercomparison of Selective Extractions and EXAFS

Sample	Selective Extraction		EXAFS	
	Fraction	%	Species	%
Gold Mine Tailings Total Hg = 281 µg/g	F1 F2 F3 F4 F5	0.4 0.8 0.5 12.3 85.9	HgCl$_2$ HgO HgSO$_4$ m-HgS HgS	— — 12 — 88
Mixed Hg Standards in Kaolin (45.2% HgO + 18.2% HgCl$_2$ + 36.6% HgS) Total Hg = 3,522 µg/g	F1 F2 F3 F4 F5	46.2 17.9 0.5 4.9 29.1	HgCl$_2$ HgO HgSO$_4$ m-HgS HgS	49 24 — — 27
Gold Mine Tailings Total Hg = 635 µg/g	F1 F2 F3 F4 F5	1.3 1.2 1.0 3.4 93.1	HgCl$_2$ HgO HgSO$_4$ m-HgS HgS	— — — — 100

µg/g   micrograms per gram

Discussion

In the mine site and contaminated site samples thus far studied, most of the Hg present has been found in the F4 and F5 fractions. When combined with headspace Hg° analysis, we have usually been able to assign the most likely fractionation as mixtures largely of elemental mercury and cinnabar. Although the percentage of Hg found in water soluble and organo-complexed forms is usually quite small, because the total Hg values are very high at these sites, these samples can still contain high absolute concentrations of bioavailable and mobile forms. For example, a mine site soil, though containing 93% HgS + Hg°, still gave a failing TCLP value of 2,900 µg/L, well above the approximately 50 µg/L expected from Hg° alone.

The use of EXAFS analysis has generally supported the findings of the selective extraction method, although analytical limitations with each method make quantitative comparison beyond the HgS versus non-HgS concentrations difficult for most samples. We have also encountered some ambiguity regarding metacinnabar and the F4 fraction (Bloom, et al., 2000), which suggests that in some cases, mercury may be bound to reduced sulfur in such an amorphous or adsorbed state, that although registering as m-HgS by EXAFS, it nonetheless is found in the more bioavailable HNO$_3$ soluble fraction by selective leaching. The degree of this ambiguity appears to increase as total Hg concentrations go down, suggesting that high Hg levels (>100 mg/g) are necessary for the significant formation of crystalline, and thus less bioavailable, cinnabar phases.

These data also clearly provide evidence of the types of species transformations that may occur when Hg compounds are applied to natural soils and sediments. For example, in the case of floodplain soils contaminated 50 years ago by soluble Hg(NO$_3$)$_2$, most of the Hg is now present as non-bioavailable cinnabar (CS-2). On the other hand, when liquid Hg° was spilled on an arid mountain soil only several months ago, much of it appears to have transformed to other, non-volatile species, as is evidenced by an equilibrium headspace Hg° concentration well below saturation. This would be seen if liquid Hg° were present (CS-1). Similarly, the soil samples from an historic cinnabar mine and retorting facility (CM1-4) in Alaska, while still showing a predominance of the initial species (HgS and Hg°), show significant fractions of Hg in the more bioavailable fractions, resulting in the production of relatively high levels of methylated mercury, as well as failing (>200 µg/L) TCLP results.

Transformations of Hg from one species to another are evident in cases where pure Hg compounds were incubated with organic-rich sediments for 141 days. In all cases, there appears to be a tendency for the added Hg speciation to evolve to a profile more like the ambient sediment Hg speciation (mostly in the F3 and F4 fractions on the unspiked sediment). Thus, Hg(II) is rapidly distributed to the organo-complexed fraction (CS-5), with the resultant production of high levels of methyl Hg in the sample. Although the reaction is much slower for cinnabar, after 143 days, approximately 12% of the added HgS was found in more bioavailable fractions (CS-6), and a smaller, but significant level of methyl Hg was produced. When the

mine tailings (GM-1) were added to this sediment, much of the Hg was converted to the organo-complexed fraction, and this too resulted in high levels of methyl Hg production. The implication of these findings, if supported by future work, is that all Hg from mine sources has the potential to increase CH_3Hg production if transported to a wetland—with the major differences being in the kinetic rates of methylation, but perhaps not final equilibrium concentrations.

Acknowledgments

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3.3.5 Speciation of Natural Mercury-Bearing Materials Using X-Ray Absorption Spectroscopy - Christopher S. Kim, Department of Geological & Environmental Sciences, Stanford University; James J. Rytuba, USGS; Nicolas S. Bloom, Frontier Geosciences; and Gordon E. Brown, Jr., Department of Geological & Environmental Sciences, Stanford University

Introduction

The fate, transport, and potential bioavailability of mercury are inherently associated with its speciation in the environment. Determining this speciation, which we define as the specific phases of mercury and the relative proportions of these phases in a given sample, has implications for both the distribution of mercury from its source and its incorporation into the food chain. This is due to the varying solubility and reactivity levels of the multiple mercury phases that are known to exist in nature. The speciation of mercury is of particular interest at point sources such as mercury mining sites and gold mining operations where mercury was used in the gold extraction process. In addition to the different geologic modes of mercury ore deposition, the exposure, roasting, and weathering to which the large volumes of mine waste at these sites were exposed have resulted in a wide range of mercury speciation from one mine to the next. Furthermore, as mercury is transported from these sources, typically by rainwater, surface water, and mine drainage, it may undergo additional transformations such as dissolution, reprecipitation, sorption to sediment particle surfaces, and sedimentation of mercury-bearing particles out of the aqueous phase. Such processes, combined with the initial speciation of mercury, are critical factors in predicting the long-term mobility and consequences of mercury in natural systems.

This study expands upon previous research by the authors exploring the ability of XAS to determine the speciation of mercury in roasted ore (calcine) samples from mercury mines of the California Coast Range [1]. Wastes from additional mercury mines in this region, mercury mines in Nevada, and gold mines with associated mercury have been characterized. Mercury condenser soot and an iron oxyhydroxide precipitate from acid mine drainage have also been sampled and their mercury speciation determined, the latter through comparison with model mercury sorption systems studied in the laboratory. Additionally, a suite of mercury-bearing samples was analyzed for speciation using both XAS and selective chemical extractions, and the results compared. The continued investigation of a wide range of mercury-bearing materials and the comparison of the XAS technique with other methods further confirm the validity of this method for determining mercury speciation in natural samples.

Methods

Sampling and speciation analysis at the mercury mines were primarily confined to calcine piles, where THg concentrations are typically elevated to several hundred mg kg^{-1} (ppm). Calcines were sampled from piles at representative mercury mines of the California Coast Range mercury mineral belt (Gambonini, New Idria, Oat Hill, Sulfur Bank, Turkey Run) as well as mines in Nevada (Silver Cloud and Clear Creek). In addition to calcines, mixtures of condenser soot and calcine residue were collected from mercury condensers located at the New Almaden and Corona mines in California. An iron oxyhydroxide precipitate emerging from mine drainage at the Knoxville mine in California was sampled. Splits of each sample were sent to ChemEx laboratories to determine total mercury concentrations using aqua regia chemical extractions and CVAFS. Samples featuring THg concentrations of [Hg]T = 100 ppm were empirically determined to be sufficient for detailed speciation analysis using XAS.

A suite of six mercury-bearing samples provided by Frontier Geosciences served as the basis for an intercomparison study of the XAS and sequential chemical extraction techniques for mercury speciation. These samples, consisting of various gold mine tailings, fly ash from a copper smelter, and a composite of mercury minerals were analyzed using XAS in a blind fashion, without foreknowledge of the samples' identities. Following analysis, the speciation results using XAS were compared with speciation results as determined by the selective chemical extraction procedure developed by Frontier Geosciences [2].

All samples were prepared as dry powders in Teflon XAS sample holders; if necessary, samples were sieved to ≤ 0.5 mm particle size and ground in a mortar and pestle prior to loading in order to avoid sample heterogeneity. Samples were analyzed at the SSRL, where mercury L$_{III}$-edge EXAFS spectra were collected at room temperature in fluorescence-yield mode with a high-throughput germanium detector.

The EXAFS region of an X-ray absorption spectrum directly reflects the structure and bonding of mercury atoms in a given sample with their first- and second-shell neighbors. As such, the EXAFS spectrum of a homogeneous mercury phase should be distinct from those of other pure phases. This uniqueness of EXAFS spectra from one compound to the next permits them to be used as species "fingerprints" for the identification of unknowns. Therefore, an EXAFS spectrum of a natural sample may be deconvoluted into the sum of its separate components by comparison to a database of spectra compiled from individual mercury compounds. Determining the relative proportion of each model spectrum's contribution to the spectrum of the natural sample allows quantification of the various phases present within the sample, thus completing the speciation process. This model compound database, containing the mercury EXAFS spectra of several mercury minerals and sorption samples, was generated at Stanford University and used in all speciation analyses [1].

The linear least-squares fitting program DATFIT, which is part of the data analysis package EXAFSPAK [3], was utilized to fit the spectra from the natural samples with combinations of the spectra in the model compound database. Single-component fits to each individual spectrum in the database were first attempted to identify significant contributors (>10% of the overall spectrum) to the fit. Using the revised subset of model compounds, two-component fits were then attempted in a methodical manner. This iterative process was continued until no significant contributors remained. Quantitative results were then scaled as needed to 100% in order to determine the relative proportions of the various mercury phases identified in the sample. An example of this linear fitting procedure is shown in Figure 1, where the mercury EXAFS spectrum of a calcine from the Turkey Run Mine is found to consist of two primary components, cinnabar (HgS, hexagonal) and metacinnabar (HgS, cubic). These two components contribute to the overall fit in proportions of 58% and 42%, respectively.
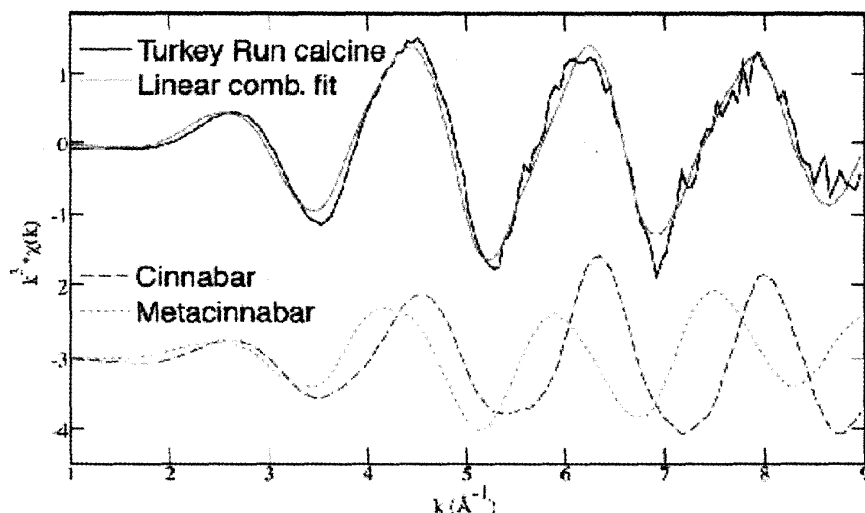
Figure 1. Linear fitting results for the Turkey Run Mine calcine, showing the natural EXAFS spectrum (black line), the linear combination fit (gray line), and the components which contribute to the linear fit (dashed/dotted lines). In this case, the calcine is found to consist of cinnabar and metacinnabar in proportions of 58% and 42%, respectively, when scaled to a total of 100%.

Results and Discussion

Table 1 compiles the results of speciation analyses conducted on the California and Nevada mine waste samples. Included are THg concentrations, type locales of the deposits, quantitative speciations of mercury in the samples, and residual values corresponding to each fit. The residual value may be a result of experimental noise inherent in the data (typically due to low THg concentrations) and/or the presence of a mercury phase that does not currently exist in the model compound database. Based on a comparison study of known mixtures of various mercury model compounds [1], it was found that fit components should be considered accurate to ±25% of their stated value, and fit components comprising less than 10% of a fit should be viewed with caution. This is in agreement with the results of Ostergren et al. determined from fitting the EXAFS spectra of mixtures of lead-containing phases [4].

80

Table 1. Speciation Analyses for Mine Calcines from the California Coast Range and Nevada. Linear fitting analysis was conducted in a k-range of 1-9 Å^{-1} except where indicated with a *, where a k-range of 1-9 Å^{-1} was utilized. Samples of condenser soot and calcine residue are indicated with a ^, and the Carson Creek sample was collected from a gold/silver mine where mercury was used in the amalgamation process.

Sample Location	Type Locale	Composition	Residual
Aurora Mine, CA $[Hg]_T = 700$ ppm	Silica-carbonate	56% Metacinnabar, HgS (cub) 26% Montroydite, HgO 18% Cinnabar, HgS (hex)	0.045
Corona Mine, CA $[Hg]_T = 550$ ppm^	Silica-carbonate	50% Cinnabar, HgS (cub) 39% Metacinnabar, HgS (cub) 11% Schuetteite, HgSO$_4$	0.052
Gambonini Mine, CA $[Hg]_T = 230$ ppm	Silica-carbonate	84% Metacinnabar, HgS (cub) 16% Cinnabar, HgS (hex)	0.326
New Almaden Mine, CA $[Hg]_T = 19500$ ppm*^	Silica-carbonate	75% Metacinnabar, HgS (cub) 25% Cinnabar, HgS (hex)	0.064
New Idria Mine, CA $[Hg]_T = 310$ ppm	Silica-carbonate	62% Cinnabar, HgS (hex) 38% Schuetteite, HgSO$_4$	0.101
Turkey Run Mine, CA $[Hg]_T = 1060$ ppm	Silica-carbonate	58% Cinnabar, HgS (hex) 42% Metacinnabar, HgS (cub)	0.036
Oat Hill Mine, CA $[Hg]_T = 940$ ppm	Hot-spring	58% Cinnabar, HgS (hex) 19% Mercuric Chloride, HgCl$_2$ 13% Corderoite, Hg$_3$S$_2$Cl$_2$ 10% Terlinguite, Hg$_2$OCl	0.281
Silver Cloud Mine, NV $[Hg]_T = 7240$ ppm*	Hot-spring	84% Cinnabar, HgS (hex) 16% Mercuric Chloride, HgCl$_2$	0.270
Sulfur Bank Mine, CA $[Hg]_T = 250$ ppm	Hot-spring	46% Metacinnabar, HgS (cub) 34% Corderoite, Hg$_3$S$_2$Cl$_2$ 20% Cinnabar, HgS (hex)	0.186
Carson Creek, NV $[Hg]_T > 100$ ppm*	Gold/silver	70% Cinnabar, HgS (hex) 30% Metacinnabar, HgS (cub)	0.188

The speciation results indicate that mercuric sulfide, either as cinnabar or metacinnabar, is the dominant mercury species in all samples; this is consistent with the fact that cinnabar is the primary ore mineral in mercury deposits. However, the high proportions of metacinnabar in many samples were unexpected. One possibility is that the elevated levels of metacinnabar were generated artificially during the ore roasting process, during which the ore was heated at temperatures in excess of the cinnabar-metacinnabar inversion temperature of 345°C [5]. This process may also have introduced impurities that impede the conversion back to cinnabar and are more prevalent in the metacinnabar structure [6].

In addition to mercuric sulfide, several minor mercury species have been identified in the samples, including montroydite (HgO), schuetteite (HgSO$_4$), and a variety of Hg-Cl phases. These species are likely to be disproportionately large contributors of mercury to the surrounding environment due to solubility levels that are orders of magnitude higher than those of the mercuric sulfides under typical surface oxidizing conditions. The accuracy of the XAS technique in identifying mercury phases can be observed when comparing the speciation of the samples with their type locales. Hg-Cl species were identified only in calcines generated from hot-spring mercury deposits, consistent with elevated levels of chloride in these local hydrothermal systems [7]. In contrast, samples collected from silica-carbonate mercury deposits, where high chloride levels are absent, are distinctly lacking in Hg-Cl phases as determined by XAS analysis. These results show both a dependence of mercury speciation on the geological origin of the initial mercury ore and the sensitivity of XAS in distinguishing between samples from the different ore types.

Results of the intercomparison study are shown in Table 2. Shading has been provided to indicate the correlations between the XAS speciation analyses and the sequential chemical extraction analyses, which are listed in order of increasing extraction strength. In general, the proportions of specific mercury phases as determined by XAS matches well with the percentage of THg that is removed by the individual sequential extractions. For example, the amount of mercury removed by aqua regia corresponds closely with the XAS-determined proportions of Hg-sulfides (cinnabar and metacinnabar) and, in one case, mercuric selenide, all of which can only be dissolved in this final step of the extraction series.

Differences between the two approaches are most pronounced in samples with the lowest initial Hg concentrations, i.e., GMT ([Hg]=145 ppm) and EU580 ([Hg]=127 ppm). In both cases, a phase identified by EXAFS analysis (mercuric oxide and metacinnabar, respectively) does not match with the extraction step that removed a comparable proportion of mercury from the sample. This mismatch may be due to poor crystallinity, particle size effects, or the presence of impurities, each of which may affect the solubility of a phase sufficiently to alter the extraction step at which the phase is removed from the sample. Also, analyses of samples with mercury concentrations close to the empirical threshold of 100 ppm are expected to have greater degrees of error in terms of species identification and their representation in a sample. Additional studies are required in order to correlate the presence of these particular phases more accurately with their reactivity under sequential chemical extractions.

Table 2. Results from Intercomparison Study Between EXAFS-Determined Speciation and Speciation Determined by Sequential Chemical Extractions. Extractions are listed in order of increasing extraction strength. Shading is provided to indicate correlations between analyses.

SAF, copper smelter fly ash, [Hg]T = 7,539 ppm			
		water	0.0%
		1N HCl	0.0%
		1N KOH	0.0%
Hg sulfides	54%	12N HNO$_3$	0.0%
Mercuric selenide	46%	aqua regia	100%

B31020, gold mine tailings, [Hg]T = 281 ppm			
		water	0.4%
		1N HCl	0.8%
		1N KOH	0.5%
Schuetteite	12%	12N HNO$_3$	12.3%
Hg-sulfides	88%	aqua regia	85.9%

MMS, mixed model standards [Hg]T = 3,490 ppm			
Mercuric Chloride	49%	water	46.2%
Mercuric Oxide	24%	1N HCl	17.9%
		1N KOH	0.5%
		12N HNO$_3$	4.9%
Hg-sulfides	27%	aqua regia	29.1%

GMT, gold mine tailings [Hg]T = 145 ppm			
		water	7.0%
		1N HCl	0.0%
		1N KOH	0.0%
Mercuric oxide	29%	12N HNO$_3$	23.1%
Hg-sulfides	71%	aqua regia	69.9%

B26025, gold mine tailings, [Hg]T = 635 ppm			
		water	1.3%
		1N HCl	1.2%
		1N KOH	1.0%
		12N HNO$_3$	3.4%
Hg-sulfides	100%	aqua regia	93.1%

EU580, marine sediments, [Hg]T = 127 ppm			
		water	0.0%
		1N HCl	0.0%
		1N KOH	1.0%
Metacinnabar	61%	12N HNO$_3$	68.6%
Cinnabar	39%	aqua regia	30.4%

The EXAFS spectrum of a mercury-bearing sample has been proven in the previous studies to aid characterization of the mercury species present in the sample. It may also be used to derive detailed molecular-scale information such as interatomic distances, coordination number, identity of nearest neighbors around a central mercury atom, and the degree of structural disorder. This is of particular utility in studying, at the molecular level, the uptake mechanisms of mercury onto various mineral surfaces, a topic of ongoing study by the authors. EXAFS investigation of a model system featuring Hg(II) sorption to goethite (alpha-FeOOH) has concluded that Hg(II) is present in this system as a bidentate inner-sphere sorption complex, forming a corner-sharing arrangement with the Fe(O,OH)$_6$ octahedra of the goethite surface [8]. Direct comparison with the mercury-bearing amorphous Fe-oxyhydroxide from Knoxville ([Hg]$_T$ = 220 ppm) indicates that a similar inner-sphere sorption complex forms between mercury and the substrate. This is the first known natural mercury sorption complex observed using XAS and has important implications for both the sequestration of mercury in sediments and its potential availability for methylation and subsequent ingestion by living organisms.

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3.4   Watershed Impairment: Defining Magnitude and Boundaries

3.4.1 *MeHg in Water and Bottom Sediment Along the Carson River System, Nevada and California, September 1998 - Karen A. Thomas, USGS*

Historically, from mid- to late-1800s, large quantities of mercury were imported from several mercury mines in northern California for use in the amalgamation of gold and silver ores of the Comstock mining area near Virginia City, Nevada (figure 1). Bailey and Phoenix (1944, p. 5) estimated that about 200,000 flasks of liquid mercury, each weighing 76 pounds, were imported. Although attempts were made by mill owners to recover the mercury from the amalgam during the milling process, most escaped to the environment in mill tailings. The tailings were deposited along several ravines tributary to the Carson River and along the river, in the reach between Carson City and Fort Churchill. About 7,500 tons of mercury are estimated to have been "lost" in the exposed tailings and became available to the Carson River through fluvial processes (Smith, 1943, p. 257). Abandoned mines and geothermal springs that discharge to the river upstream from the Dresslerville site (site 2; figure 1) also are potential sources of mercury contamination. Prior to the construction of Lahontan Dam in 1905, episodic floods in the Carson River Basin probably flushed much of the available mercury-laden tailings downstream to the Carson Desert (known locally as Lahontan Valley) (Glancy and Katzer, 1976, p. 42–47), specifically to Carson Lake, Carson Sink, and wetlands in Stillwater National Wildlife Refuge (Hoffman, 1994, p. 8). More recently, however, and partly as a result of the New Year's flood of 1997, Hoffman and Taylor (1998) showed that 20%, or about 1 ton, of the THg load entering

Lahontan Reservoir from January through September 1997, flowed past the dam. The spilled water subsequently was distributed throughout Lahontan Valley by the vast network of agricultural canals, laterals, and drains, including several shallow regulating reservoirs inside and outside of Stillwater National Wildlife Refuge.

Inorganic mercury, a known toxin and the most common form of mercury in Carson River sediments, is a source material for MeHg , an organic compound. MeHg is a neurotoxin known to bioaccumulate in aquatic organisms and to biomagnify up the food chain (Hoffman and Taylor, 1998). Although mercury can exist in several chemical forms in aqueous systems, MeHg, and possibly ionic mercury (Hg^{+2}), are considered the most important chemical species to biological receptors. Sulfate-reducing bacteria in reducing environments are implicated in the conversion of inorganic mercury to a methylated form making it readily available for uptake by aquatic organisms at successively higher trophic levels (Gilmour and Henry, 1991).

Mercury concentrations in water generally increased in a downstream direction from Markleeville (site 1; figure 1) to the point where the Carson River empties into Lahontan Reservoir (site 9). Downstream from the reservoir, the concentrations declined somewhat but were, for the most part, still elevated. The highest concentrations (7.83 ng/L and 9,040.00 ng/L for total methylmercury (TMeHg) and THg, respectively) were measured at site 9. This site represents a deltaic transition zone where river water mixes with reservoir water. The low-gradient, 5-mile reach of the river upstream from site 9 broadens laterally to form a deltaic plain containing many oxbows and rivulets with intervening marsh lands. The lowest mercury concentrations were found at the two most upstream sites (reference sites 1 and 2) on the East Fork Carson River, more than 50 river-miles upstream from the historic Comstock milling operations. At sites 1 and 2, TMeHg was 0.08 and 0.16 ng/L and THg was 4.94 and 3.42 ng/L respectively.

The 26-mile reach of the river from Dayton (site 5) to Lahontan Reservoir (site 9) tended to have the highest concentrations of both TMeHg and THg compared to other sampling sites in this study. THg at 6 of the 9 sites upstream from Lahontan Reservoir (sites 4–9) exceeded the State of Nevada chronic standard of 12 ng/L for the protection of aquatic life. The acute standard of 2,000 ng/L, dissolved, was exceeded only where the Carson River enters Lahontan Reservoir (site 9).
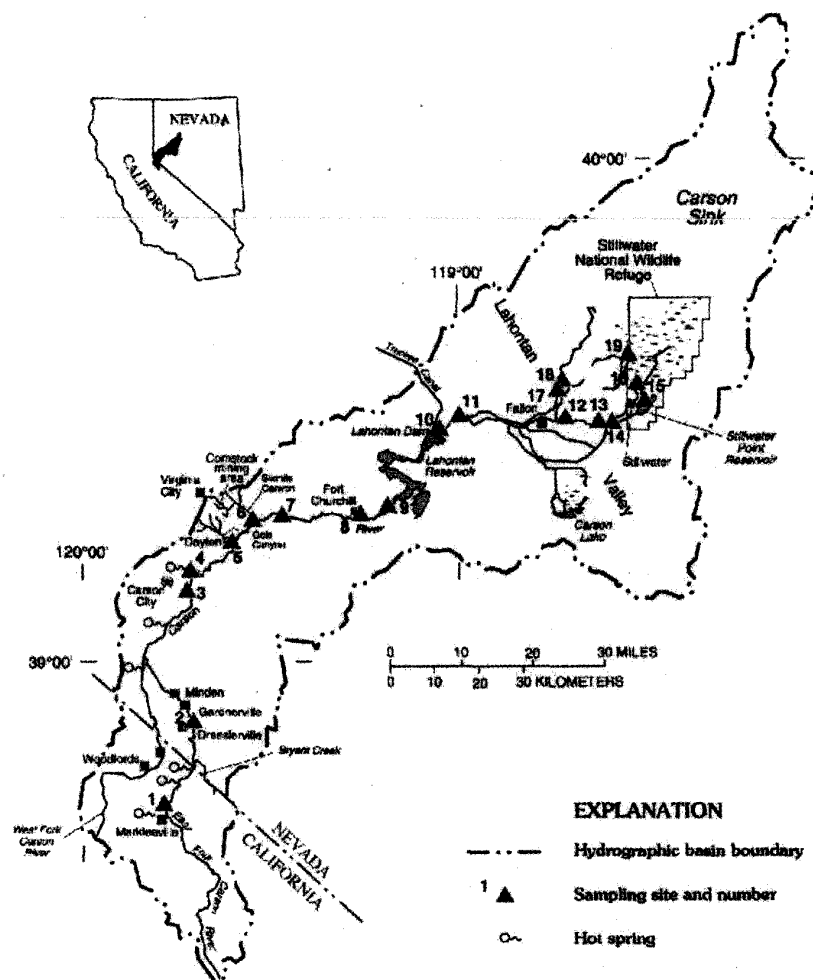
Figure 1. Location of sampling sites, Carson River System, Nevada and California.

Table 1. Mercury and Organic Matter Collected Along the Carson River System, September 14–16, 1998

Site no. (see Figure 1)	Water						Bottom Sediment, Dry Weight		
	Discharge, instantaneous (ft³/s)	Temperature (°Celsius)	pH (standard units)	Total MeHg (ng/L)	Total Hg (ng/L)	TOC (mg/L)	Total MeHg (ng/g)	Total Hg (ng/g)	LOI (Percent)
1	130	16.0	8.3	0.08	4.74	1.3	0.55	45.3	5.7
2	150	20.0	8.3	.16	3.42	1.5	2.73	66.2	5.5
3	135	17.5	8.1	ª.99	ª8.35	--	--	--	--
4	140	21.0	8.1	.68	31.1	6.9	1.21	78.4	1.7
				ª.68	ª20.8				
5	110	21.0	8.4	ªᵇ5.09	ª239	--	--	--	--
6	140	19.0	7.9	ªᵇ5.09	ª266	--	--	--	--
7	140	21.5	8.1	ªᵇ5.09	ª624	--	--	--	--
8	89	24.5	8.3	5.12	1,110	4.7	7.35	4,130	3.3
				ª4.86	ª1,110				
9	--	24.5	9.2	ª7.83	ª9,040	--	--	--	--
10	420	20.0	7.9	2.44	374	3.2	1.80	1,180	1.2
				ª2.73	ª333				
11	ᶜ338	19.0	7.8	3.01	370	3.1	1.38	4,110	1.3
12	E.50	23.0	--	.78	223	3.5	.56	204	2.9
13	25	26.0	8.3	.85	221	5.1	5.44	1,040	9.0
14	22	21.5	7.7	.73	782	7.7	1.88	1,640	2.0
15	55	22.5	7.8	3.14	103	12	5.34	2,540	14.0
16	22	20.5	7.7	1.52	693	7.5	13.4	13,100	6.1
17	ᶜ15	21.0	7.0	.93	202	5.3	.74	1,370	.93
18	14	26.0	8.4	1.34	205	5.5	1.34	778	.82
19	1.7	21.5	8.1	2.40	48.9	6.6	22.3	654	15.0

[Abbreviations and symbol: E, estimated; ng/g, nanograms per gram; LOI, loss on ignition; TOC, total organic carbon; --, no data. Analysis by USGS Research Laboratory, Middleton, Wisconsin, except as noted]
ªAnalyzed by Frontier Geosciences, Inc., Seattle, Washington.
ᵇIdentical concentration for three sites verified by laboratory.
ᶜFlow data provided by Truckee-Carson Irrigation District, Fallon, Nevada.

Of the 10 sites downstream from Lahontan Reservoir, TMeHg ranged from 0.73 ng/L in the inflow to Stillwater Point Reservoir (site 14) to 3.14 ng/L in the East-West Canal outflow from the same reservoir (site 15). In general, TMeHg concentrations downstream from Lahontan Reservoir were lower than those in the most contaminated reach of the river upstream from the reservoir, but were still about 5 to 20 times the highest background concentration of 0.16 ng/L. The highest TMeHg concentrations, about 3 ng/L, were found at the outflow of Carson Diversion Dam (site 11) and the outflow from Stillwater Point Reservoir (site 15), both of which represent wetland areas. THg at all ten sites downstream from Lahontan Reservoir greatly exceeded the 12 ng/L (chronic) standard for the protection of aquatic life. During this survey the acute standard of 2000 ng/L was not exceeded at any of the 10 sites.

Mercury concentrations in bottom sediments of the mainstem of the Carson River increased sequentially in the downstream direction, peaking near Fort Churchill (site 8), and declined downstream from that location (sites 10 and 18). The highest THg concentration found on the mainstem was 4,130 ng/g at site 8 (Table 1).

The lowest THg concentrations of 45.3 and 66.2 ng/g, were found at the two farthest upstream sites (sites 1 and 2).

The concentration of TMeHg in sediment was highly variable from one site to the next. The lowest concentration (0.55 ng/g) was found at site 1 near Markleeville, whereas the highest concentration (22.30 ng/g) was found near the terminus of the Carson River system in Paiute Diversion Drain below TJ Drain near Stillwater (site 19), hereafter referred to as Paiute Diversion Drain. The elevated concentration of 2.73 ng/g of TMeHg at site 2 near Dresslerville may reflect inputs of mercury from geothermal springs that discharge to the river and an abandoned mercury mine in a tributary basin, Bryant Creek (Lawrence, 1998).

Sampling sites downstream from Lahontan Dam, off the mainstem of the Carson River, had TMeHg and THg concentrations in sediment ranging from 0.56 ng/g and 204.00 ng/g, respectively, for site 12, to 22.3 ng/g of TMeHg at Paiute Diversion Drain (site 19) and 13,100 ng/g of THg at the Stillwater Slough (site 16). Stillwater Slough is considered a highly mercury-contaminated channel based on historical streamflow patterns in the area (Hoffman, 1994, p. 8 and Figure 5). Sites 9, 11, 13, 15, and 17 represent wetland environments which may tend to favor mercury methylation (Hurley and others, 1995). David P. Krabbenhoft and coworkers (USGS written commun., 1999) have found that surface area occupied by wetlands was the most important basin-scale factor controlling MeHg production. Of the wetland sites in Lahontan Valley, the highest concentrations of TMeHg in sediment were found in Harmon Reservoir (5.44 ng/g; site 13) and in Stillwater Point Reservoir (5.34 ng/g; site 15). In fact, these TMeHg concentrations are among the four highest that were found for the 10 Lahontan Valley sites.

For this survey, TMeHg overall represented about 0.2% of THg sediment concentration. With the exception of the anomalous high TMeHg:THg ratio for site 19 (3.4%), the highest ratios (1.2% to 4.1%) were in the mercury-poor, upstream reach of the river system, as represented by sites 1, 2, and 4. Excluding the data from site 19, the lowest ratios were found at the 10 sampling sites in the mercury-rich downstream part of the river system; for the most part, these ratios were substantially less than 1% (median=0.16%). Other researchers (Oremland and others, 1995; Chen and others, 1996) have suggested that TMeHg production appears to be directly proportional to the quantity of THg present at low THg concentrations. At high THg concentrations, little additional MeHg evidently is produced with increased concentrations of THg.

Organic carbon in sediments is important as a substrate and as an energy source for bacteria involved with methylation of mercury (Gilmour and Henry, 1991). Sites above Lahontan Reservoir contained low organic content (1.7% to 5.7%), which agrees with results by Chen and others (1996). Sites below Lahontan Reservoir have an organic content that varies from about 1% to 15%. The ratio of TMeHg:THg increases somewhat with increasing carbon content in bottom sediments, however, the relation is not strong ($r^2=0.22$) with the data widely dispersed about the trend line. Because only 22% of the variance of the TMeHg:THg ratio is explained by the effect of organic matter, other complex biotic and abiotic factors must be involved.

The most recent pre-1997-flood data on THg in unsieved, near-surface bottom sediments (G.C. Miller, UNR, oral commun., 1999) for the active channel appear to be those collected in January and June 1995 by Chen and others (1996). Of the sampling sites in the present survey, only Deer Run Road (site 4) and Fort Churchill (site 8) had sediment data to compare with the preflood concentrations in 1995. The data indicate that THg concentrations in sediment samples collected in 1998 at these two sites were substantially lower (50% or more) than in those collected in 1995. The 1998 data also were lower than the historic (1970–98) median concentrations for these two sites (site 4, median=710 ng/g, n=11; site 8, median=6,870 ng/g, n=7). The apparent reduction of concentration in the 1998 samples may have been caused naturally owing to the scouring action of the flood and the two subsequent spring runoffs of 1997 and 1998, and succeeding sediment deposition. Another possibility is an artifact owing to differences in sampling and analytical methodologies (for example, particle-size class on which chemical analysis was done), or both. However, the true cause of this reduction of concentration is difficult to discern with available data.

In summary, mercury in water increased in the downstream direction through the highly contaminated reach of the river from Dayton to Lahontan Reservoir. Downstream from the reservoir, mercury concentrations tended to decrease in the downstream direction, but still were greatly elevated compared to upstream background concentrations. In water upstream from Lahontan Reservoir, maximum concentrations of TMeHg were 7.83 ng/L and of THg were 9,040.00 ng/L. Downstream from the reservoir, maximum concentrations of TMeHg 3.14 ng/L and of THg were 782.00 ng/L. The upstream background concentrations in water were a maximum of 0.16 ng/L of TMeHg and 4.74 ng/L of THg. Bottom sediment upstream of Lahontan Reservoir

had maximum concentrations of TMeHg of 7.35 ng/g and THg of 4,130.00 ng/g. For sites downstream from the reservoir, the maximum concentration of TMeHg in sediment was 22.3 ng/g. The maximum concentration of THg was 13,100 ng/g. The upstream background concentrations in bottom sediment were a maximum concentration of only 2.73 ng/g and 66.2 ng/g of TMeHg and THg, respectively.

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3.4.2 The Impact of Mercury Mining on Tomales Bay Biota - Dyan C. Whyte, California Regional Water Quality Control Board, San Francisco Bay Region and Priya M. Ganguli, California Regional Water Quality Control Board, San Francisco Bay Region

Tomales Bay, located in the Gulf of the Farallons National Marine Sanctuary, provides winter habitat for thousands of migratory waterfowl and is renowned for its fishery and oyster beds. Preliminary studies in the Tomales Bay watershed suggest that discharges from the inoperative Gambonini mercury mine have resulted in elevated mercury concentrations in biota. The mine, located approximately 60 km north of San Francisco, was an open pit mercury mine that generated over 300,000 cubic meters (m^3) of waste. Drainage from the mine goes to Walker Creek, the second largest tributary to Tomales Bay. Water quality studies suggest that hundreds to thousands of kilograms of mercury have been discharged from the mine site to downstream waters since mining ceased in 1972 (Whyte, 1998) (Whyte and Kirchner, 2000).

In an effort to mitigate mercury transport from the Gambonini mine, the USEPA and the California Regional Water Quality Control Board (Regional Board) initiated an emergency Superfund cleanup action. The goal of the project, started in October 1998, was to eliminate, to the maximum extent feasible, the discharge of mercury-laden sediments from the 12-acre mining waste pile. The remediation effort entailed constructing a gravity buttress (to stabilize the failing waste pile), installing storm water runoff diversion structures, and

revegetating the area with native plants (Smelser and Whyte, 2000). In the winter of 1999, the Regional Board began a 5-year post-remediation monitoring program to evaluate the net environmental benefits of the project.

The fate of the mercury-laden mine sediments previously discharged remains a significant environmental concern. Over-bank and flood-plain deposits along Walker Creek, and the salt marshes and intertidal mudflats in the Walker Creek Delta, are potentially storing much of the mercury released from the Gambonini mine. Thus, the environmental impacts of mercury on downstream ecosystems are yet to be fully realized. In conjunction with monitoring water quality, we are evaluating the spatial distribution of mercury (total and MeHg) in estuarine sediments and biota, with the goal of preventing harmful effects to humans through the consumption of seafood and determining whether measures can be taken to mitigate adverse effects to wildlife.

Bay sediment mercury concentrations in the Walker Creek Delta (measured in the spring of 1999) were as high as 13 ppm and decreased with distance from Walker Creek. In a followup study (May 2000) we sampled intertidal sediments at 11 locations in the Walker Creek Delta by collecting 2 to 3 shallow cores, 5 m apart, and sectioning the cores into 1 cm, 2-5 cm, and 6-10 cm depths (a total of 98 samples). The mean mercury concentration (± one standard error) for the entire sample set was 1.5 ± 0.2 ppm. Individual samples ranged from 7.60 to 0.06 ppm. MeHg concentrations averaged 0.0015 ± 0.0002 ppm and ranged from 0.01140 to 0.00001 ppm. High MeHg concentrations were not correlated with high mercury concentrations: sediment samples with mercury concentrations greater than 3.2 ppm had relatively low MeHg concentrations. Sediments at 5 of the 11 locations (HP-S, HP-Preston, HP-N, OR-Mud, and OR-Island) exhibited statistically higher MeHg concentrations. MeHg concentrations were also higher in the top 1 cm of sediment and in sediments containing from 0.3 to 3.2 ppm THg. The elevated MeHg concentrations in the top 1 cm were most pronounced at stations where green algal mats occurred. The presence of these mats may enhance the oxygenated zone, thereby promoting optimal mercury methylation conditions (Gagnon et al., 1996).

Limited data on mercury concentrations in Tomales Bay biota (Whyte, 1998) suggest a strong spatial trend in mercury uptake consistent with sediment concentration trends. Resident bivalves (cockles) harvested from the Walker Creek Delta contained up to 0.34 ppm (wet weight) mercury while cockles harvested at the McDonald sediment sampling location (11 km south of Walker Creek) contained only 0.05 ppm mercury. Similarly, mercury concentrations in mussels transplanted in the Walker Creek Delta for three months during the 1996/97 rainy season ranged from 0.044 to 0.055 ppm (wet weight), while mussels transplanted in Tomales Bay north and south of the Delta ranged from 0.033 to 0.036 ppm. Mercury concentrations in commercial oysters grown in floating bags or on platforms in Tomales Bay for 1 to 2 years were all well below the FDA action level (1.0 ppm wet weight) and ranged from 0.029 to 0.049 ppm (wet weight). Mercury concentrations in cockles harvested from the Delta were almost an order of magnitude greater than those measured in the oysters and mussels. This is most likely because the cockles reside in the mercury-enriched sediments, while our transplanted mussels and the commercial oysters were suspended above the bay floor.

In an effort to better elucidate the potential for mercury bioaccumulation in biota proximal and distant to the Walker Creek Delta, we sampled intertidal invertebrates, at three of our sediment coring locations: HP-Dock and HP-S (in the Walker Creek Delta), and McDonald (11 km south of the Delta). Mercury concentration trends among the invertebrate species sampled likely reflect differences in their habitats and diets. The species exhibiting the highest mercury concentration was the introduced eastern mudsnail (Nassarius obseletus) (0.6 ppm, dry weight), which was abundant at HP-Dock. The mudsnail is an omnivore and eats the eggs and juveniles of the native snail, Cerithidea californica, and burrowing polycheate worms. It is also an herbivorous deposit feeder. Nassarius obseletus was not present at our other two invertebrate sampling locations. The burrowing ghost shrimp (Callianassa californiensis), abundant at the HP-S and HP-Dock locations, also contained relatively high mercury levels (0.39 - 0.45 ppm), as did the shorecrabs, pachygrapsus crassipes (0.45 ppm) and hemigrapsus oregonensis (0.27 - 0.31 ppm). The ghost shrimp are believed to predominately feed on organic detritus and microorganisms sifted from the mud. The shorecrabs are largely herbivores, as their main food source is algae. They will occasionally feed on dead animal matter, detritus, diatoms, and living prey such as limpets and snails. Shorecrabs (pachygrapsus crassipes) collected from the HP-S location contained 6 times more mercury than shorecrabs from McDonald, possibly reflecting the 14-fold increase in the top 1 cm MeHg concentration measured at HP-S relative to McDonald. The white bubble snail, Haminoea virescens, was sporadically abundant under clumps of the green algae, Ulva lactuca,

at both the HP-Dock and HP-S locations. The Haminoea are believed to be herbivorous, but little is known about their diet. Mercury concentrations in the Haminoea and Ulva samples were below the detection level. The mercury concentration in an Ulva sample from the McDonald area was also below the detection level. This data set suggests that estuarine invertebrate omnivores accumulate more mercury than herbivores and algae. Detailed studies are needed to better understand species feeding habits, and the link between sediment MeHg concentrations and invertebrate mercury uptake.

In addition to the invertebrate sampling, we sampled the ten most commonly caught and consumed fish species in Tomales Bay. Top-level predators and bottom dwelling fish contained higher mercury concentrations than other species. Mean mercury concentrations were highest in brown smooth hound sharks (1.31 ± 0.07 ppm wet weight) and leopard sharks (1.09 ± 0.08 ppm), followed by bat rays (0.56 ± 0.08), angel sharks (0.43 ± 0.06), halibut (0.26 ± 0.02), redtail surf perch (0.16 ± 0.04), shiner surf perch (0.10 ± 0.01), and jack smelt (0.06 ± 0.01). These concentrations are similar to mercury concentrations measured in fish from San Francisco Bay (SFEI, 1999), an estuary impaired by historic gold and mercury mining. The California Office of Environmental Health and Hazard Assessment has issued an interim health advisory for people consuming fish from San Francisco Bay and is currently considering a fish consumption advisory for Tomales Bay. Mercury fish data from both bays exhibit similar trends; for example, shark mercury concentrations increase with fish size (a surrogate for age). Additional information is needed on the feeding and migratory habits of these fish to determine aquatic food chain bioaccumulation factors.

Tomales Bay is an example of how a water body, once thought to be pristine, can be degraded by a small mine if mining wastes are not properly disposed. The outcome of our post-remediation monitoring efforts may be useful for assessing remediation strategies at other mines. In addition, results of our on-going watershed studies will contribute to understanding mercury cycling, bioavailability, and food web dynamics in complex estuarine ecosystems.

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3.4.3 Mercury in Native Metal Deposits: "Focusing Troughs" Reveal an Unexpected Source to Lake Superior Sediments - W. Charles Kerfoot and S.L. Harting, Lake Superior Ecosystem Research Center, and Department of Biological Sciences, Michigan Technological University; Ronald Rossmann, USEPA; and John A. Robbins, National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory

The perception that the Lake Superior watershed is influenced largely by long-distance transport of contaminants can be misleading. Along the shoreline, a high-energy coastal zone focuses terrestrial inputs into marginal troughs. Therefore, sampling only the central, deepest sediments misses these important anthropogenic contributions. Many of the sources are from mining operations which exploited the rich mineral resources of the basin for over 150 years, leaving tailing piles and abandoned smelters scattered throughout much of the watershed.

Mercury and copper inventories are low in central Lake Superior, increase toward shorelines and are highly correlated with copper and silver inventories, suggesting fine particle transport from terrigenous sources. Higher inventories are found in coastal troughs near mining regions, tripling previous estimates for mercury storage in Lake Superior sediments. In the Keweenaw Peninsula region, high mercury, copper, and silver inventories can be traced back to shoreline stamp sand piles, the parent native metal ores, and to smelters. Mercury is found in both copper and silver ores, but concentrations are consistently higher in Keweenaw native silver than in native copper, differing by an order of magnitude. Mercury concentrations are very low (< 5 ng g^{-1}) in the basaltic parent rock. Mercury was not imported into the region for amalgamation extraction of the Keweenaw Peninsula copper ore lodes, but was used for silver ores in the Silver City District and for gold ores in the Negaunee area in the central Upper Peninsula.

Mercury occurs as a natural amalgam in the native metals (copper, silver) mined in the Keweenaw Peninsula and was liberated as volatile Hg$_o$ during on-site smelting. The silver-enriched native copper deposits contain relatively high concentrations of mercury. Stamp mills operating in the Keweenaw Peninsula region alone discharged a minimum of 364 metric tons of tailings or "stamp sand" and regional smelters refined five million metric tons of native copper, the two sources together liberating an estimated 42 metric tons of mercury. Adding a conservative estimate of mercury contained in on-site poor rock piles raises the total to an estimated 116 metric tons of mercury.

The Keweenaw Peninsula deposits are by no means unique. We discovered that mercury commonly occurs in metal ore deposits as a trace constituent in the Lake Superior region (copper, silver, gold). "Arquerite" or mercurian silver, a natural mercury-silver amalgam, was noted previously at the Silver Islet Mine in Ontario. Cannon and Woodruff (1999), found that tailings piles from copper mining on Isle Royale contained up to 14 μg g^{-1} of mercury, similar to our reported range from the Keweenaw Peninsula. Again, the basalt bedrock had very low mercury concentrations (< 5 ng g^{-1}). Their research also found elevated copper and mercury anomalies in soil profiles adjacent to mine sites. Near the Minong Mine, BC-horizon soils ranged up to 1160 mg g^{-1} copper and 220 ng g^{-1} mercury. A-horizon soils averaged 290 mg g^{-1} copper and 70 ng g^{-1} mercury. The Isle Royale results are important in that the strata are connected to the Keweenaw Peninsula ore bodies through a syncline relationship, independently verifying mercury in the Portage Volcanic Series ore bodies. Assays of voucher specimens from Greenstone Formation ores in Ontario document the widespread incidence of mercury in regional silver and gold deposits (silver mines 6.8 + 4.2 μg g^{-1}, gold mines 7.5 + 9.3 μg g^{-1}). Mercury also is commonly present in silver, gold, copper, and lead deposits worldwide. Mercury was also imported for amalgam extraction in many Ontario precious metal mining districts such as the Lake Nipigon, Manitouwadge, and Marathon-Michipicoten regions.

Total surficial fluxes of mercury to Lake Superior, derived from sediment cores, range from 0.1-10.0 ng cm^{-2} yr^{-1} (mean + 95% CL, 3.2 + 0.5 ng cm^{-2} yr^{-1}), whereas surficial copper fluxes range from 1.1 to 19.9 mg cm^{-2} yr^{-1} (5.0 + 2.5 mg cm^{-2} yr^{-1}). Taking into account measurements of atmospheric loadings, only 29-49% of mercury and from 2-13% of copper loadings to Lake Superior sediments can be attributed to atmospheric loading although smelters were important point sources near the Keweenaw Peninsula. At present, shoreline sources dominate loading, accounting for an estimated 51-71% of mercury and from 87-98% of copper loadings to Lake Superior sediments. The greatest concern by the presence of mercury-containing mine waste deposited in and near watersheds is the conversion of the mineral-bound mercury to the more bioavailable methylated forms in wetland regions or in organic-rich sediments. A recent study by Jeong et al. (1999) of Keweenaw Waterway mine waste reveals that native copper within the mine waste slowly leaches from the tailings and is reprecipitated as soluble forms such as malachite and azurite on the surface of the tailings particles. As mercury is associated with the native copper, it can be assumed that mercury is being leached from these particles as well.

3.5   Air Emissions and Air Impact Assessment

3.5.1   *Uncertainties in Mass Balance of U.S. Atmospheric Mercury Emissions - Leonard Levin (Presenter), EPRI; Paul Chu, EPRI; and Christian Seigneur, AER*

Introduction

Mercury sources to air within the continental U.S. are thought to total about 140 megagrams per year (Mg/yr) (EPRI, 2000a), of a North American total of about 205 Mg/yr. Ionic state of mercury at emission is critical to deposition patterns: covalent mercury, Hg(II), is water soluble with an atmospheric lifetime of hours to days; elemental mercury, Hg(0), has a lifetime of 1-2 years before oxidizing and dissolving in precipitation.

The primary source of current mercury input to many U.S. water bodies is believed to be atmospheric deposition (Engstrom & Swain, 1998). Of this deposition, an unknown portion is made up of regional and local atmospheric emissions from U.S. point sources, and the balance from globally-circulating mercury from both U.S. and international atmospheric sources. These proportions may be about 60 and 40% respectively, at least for northern tier U.S. states. Speciation of industrially emitted mercury is similarly uncertain; a common default assumption is that 50% is in each ionic form when emitted from combustion sources (USEPA, 1998). That speciation is likely to impact the fraction that is transported beyond local scale. Calculations indicate that, for a combustion source stack height of 300m, less than 20% of the emitted mass of mercury will deposit within a radius of 50km even under the assumption that it is all ionic.

Additional data are also required on the distribution of background sources geographically, and the nature of the mercury emissions from them: how episodic, whether covalent or elemental, etc. Although rough calculations scaled by land area indicate background emissions might make up some 120 tons per year (t/yr) additional input to the atmosphere, local deposition may account for 50% or more of this, so that only 50-60 t/yr need be considered in the continental mass balance.

Recent measurements in Ontario, California, Nevada, and Tennessee have begun to quantify background emissions as an additional source of mercury into the North American balance. The background sources can be considered in two classes: natural background, and areas previously subject to anthropogenic activity, such as mining sites or mineral processing facilities. These latter "legacy" sites may be widely distributed. In addition, re-emission of deposited mercury may occur anywhere, including the subcategories making up background areas.

Current measurement data at background U.S. and Canadian sites for wet deposition are not yet sufficiently long or dense enough to act as a control on the emissions inventory. Modeling exercises combining regional and local scales spatially can be well-matched in general to these monitoring data (Seigneur et al., 1996), but still are too uncertain to act as a test of either model dynamics or inventories.

Anthropogenic Emissions and Contributions to Deposition

New measurements on mercury in coal burned by U.S. electric utilities, and on the concentrations and valence state of mercury emitted by a set of those utility plants, has shown that about 40% of the mercury coming into all U.S. plants as a whole is removed by control devices or flue gas constituents during combustion (EPRI, 2000b). Nationally, about 52% of the emitted mercury is in the elemental Hg(0) form, about 46% is ionic Hg(II), and the balance is particle bound.

These 1999 datum measurements were used to derive national, continental, and global inventories of mercury (Tables 1 and 2); for source categories other than coal utilities, earlier estimates of emissions were updated based on re-surveys of source operators (for U.S. sources) or on recent data on economic activity and particular source category changes (for non-U.S. sources).

Table 1. Global Anthropogenic Emissions of Mercury, All Sources, by Valence State, per Continent (Mg/yr)

Continent	Hg(0)	Hg(II)	Hg(p)	Total Hg
North America	110.9	80.0	14.1	205.0
South & Central America	151.7	14.7	9.8	176.2
Europe	268.6	149.2	90.5	508.3
Asia	559.7	334.1	22US	1117.2
Africa	123.1	73.8	49.2	246.1
Oceania	24.1	14.5	9.7	48.3
Total	1238.1	666.3	396.7	2301.1

Table 2. Anthropogenic Mercury Emissions, by Category, for Central North America (Mg/yr)

Source Category	U.S.	Southern Canada	Northern Mexico	Total
Electric Utilities	40.9	1.3	9.9	52.1
Iron Processing	15.3	0.3		15.6
Waste Incineration	28.8	US		32.2
Residential, Commercial, & Industrial Coal Burning	12.8			12.8
Mining	6.4	0.3		6.7
Chloralkali Facilities	6.1	0.05		6.2
Other Sources	30.1	9.4	23.6	63.2
Total	*140.6*	*14.7*	*33.5*	*188.8*
Hg(0)	75.6	8.7	17.3	101.6
Hg(II)	58.5	3.8	11.2	73.5
Hg(p)	6.5	2.2	5.0	13.7

These source inventories were used to simulate ground-level concentrations and total (wet + dry) deposition of total [Hg(0) + Hg(II) +Hg(part)] mercury, using a global chemical transport model and an Eulerian regional model called Trace Element Assessment Model, or TEAM. The results of these simulations are shown in figures 1 and 2.
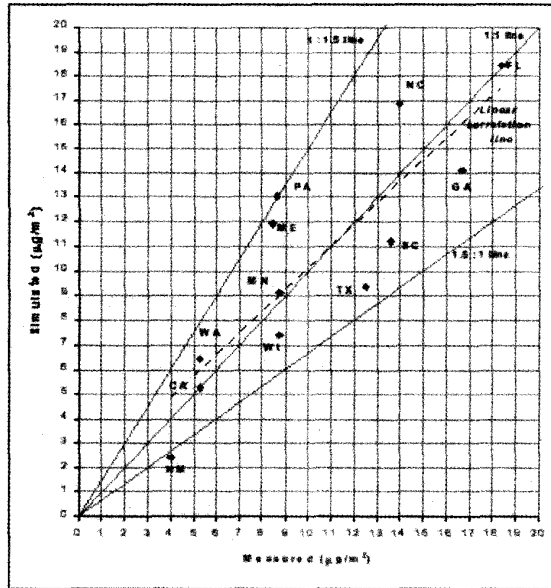
Figure 1. Observed vs. simulated wet deposition, all MDN stations by state. Simulated values based on grid cell averages for cells containing MDN stations (1998).

A sensitivity test of the modeling framework was performed to assess the potential impacts on total deposition within the continental U.S. of altered emissions from distant sources, and of the contributions of distant sources to U.S. deposition under current emissions.

The first scenario used the global model to assess changes in deposition at U.S. locations if Asian anthropogenic mercury emissions were to drop by 50%, then used resulting values of that model (which has a grid spacing of 100 km zonally by 80 km meridionally) as boundary conditions on the TEAM regional model (40 by 40 km spacing). The results of this simulation are shown in Figure 3.

95
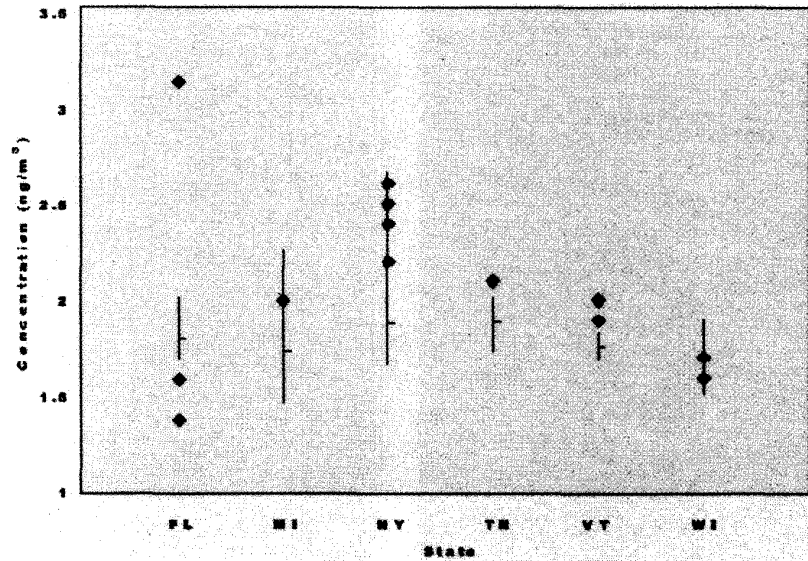
Figure 2. Observed (diamonds) vs. simulated (lines) ground-level concentrations of total mercury, by state, for various special measurement studies. Vertical lines represent ranges of values, horizontal line arithmetic mean, for grid cells spanning states.

■	5 to 10
■	10 to 20
■	20 to 25
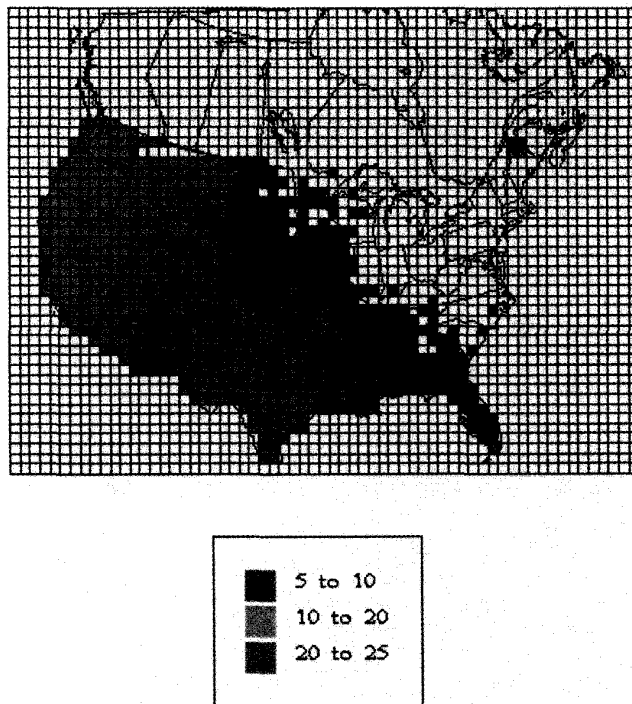
Figure 3. Percent changes in total deposition of total mercury for asian anthropogenic emissions reduction by 50%.

96

The second scenario was a sensitivity test of the global model, in which sequential model runs zeroed out continental emissions and assessed deposition at the model scale throughout the U.S. Difference fields were generated for each run between the base case with all sources "turned on", and the sensitivity case with each continent off, to develop continental contributions to local deposition. This is shown in Table 3.

Table 3. Estimated Contribution of Different Source Regions to Total Mercury Deposition Fluxes (μg/m2/yr) in Wisconsin, New York State, and Florida

Source Region	Wisconsin*	New York State	Florida
Anthropogenic:			
North American	4.64	4.39	US4
South American	0.33	0.36	0.42
Western Europe	0.54	0.62	0.46
Eastern Europe	0.86	0.97	0.71
Africa	0.22	0.25	0.24
Asia	2.22	2.40	2.38
Oceania	0.05	0.06	0.06
Total Anthropogenic:	8.86	9.05	7.71
Background:	9.26	10.14	8.85
Total:	18.12	19.19	16.56

* Grid cell includes eastern Wisconsin and Michigan

Contributions of Background Emissions to U.S. Deposition

In these anthropogenic mercury emission calculations, background emissions from natural and "legacy" U.S. sources were not explicitly evaluated, but instead included as a 1.6 ng/m³ background contribution.

Field measurements of emission rates from natural and anthropogenically-impacted background areas show a wide variability in rates of emission of total gaseous mercury with terrain characteristics, the occurrence of precipitation onto the surface, and other factors. Measurements in west-central Nevada in 1997 (Gustin et al., 1999) showed increased outgassing of THg following precipitation events (Poissant et al., 1999). It is still uncertain whether this is simple replacement of pore-space mercury gas by liquid water, or a more complex surficial action with hydrophilic Hg(II) remaining behind while hydrophobic Hg (0) is released.

Extension of these point measurements of background mercury in time and space is highly speculative at this time, since no general scheme for assigning outgassing rates to terrain characteristics is yet available. One extrapolation to the area of the continental U.S. yields background emission rates roughly equal to the total of current U.S. industrial emissions. Another extrapolation from Ontario measurements of mercury emissions from black shale yielded rates sufficient to explain a good portion of station-monitored atmospheric concentrations in northeastern states (Pai et al., 1999).

The control on a mass balance of U.S.-emitted mercury is the set of data on ground-level atmospheric concentrations and deposition nationally. Monitoring and sampling networks are only now beginning to reach spatial density and time extent that allow patterns and trends to begin to be discerned (NADP, 1999). These are still inadequate to provide good closure on goodness-of-fit for regional or local models of atmospheric mercury transport and deposition, and so these tools remain highly uncertain for purposes of assessing source-receptor relationships.

To simulate the contributions that might be made to these data by background sources, a simple box model was used. The model adopted a 6 km mixing height for mercury, and assumed no chemistry. Background emissions were taken as a uniform 2 nanograms per square meter per hour (ng/m²/hr) for the entire U.S. A speciation was assumed of 90% Hg(0)/10% Hg(II). Hg(II) emissions were deposited out at the rate of 3% per 10 km east of 90W, and 1% per 10 km west of 90W longitude, taken as the dividing meridian between high and low annual precipitation rates.

When these contributions are compared to 1998 data from the MDN stations, background contributions are found to range from 4-7% of total wet deposition in the east, but 10-12% in the west. These differences are due to the lower deposition values (and sparser coverage) in the western U.S.

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3.5.2 The History of Mercury Emissions from the New Almaden Mines, Santa Clara County, California - Michael F. Cox, New Almaden Quicksilver County Park Assn.

Visible waste products from mercury ore mining and processing that may be present at an abandoned mine site are: equipment, mine drainage, tailings from the ore processing (roasted ore is called calcines), and waste rock from ore mining. Investigations of pollution at mercury mines necessarily focus on these sources. Air emissions of mercury from mineralized rock and soil have long been of interest for prospecting and more recently for site mitigation. Overlooked in most site mitigation studies, however, are the effects of historic air emissions from ore reduction operations.

A cursory review of records and scientific studies concerning mining and pollution at New Almaden mine in Santa Clara County, California verifies that historical air emissions from ore roasting operations are potentially significant sources of pollution at larger mines. Recommended are additional investigations to substantiate the effect of historic air-borne emissions on district soils and waterways. This is an important issue to consider in the preparation of the Total Maximum Daily Load program for Guadalupe River watershed, discussed in separate conference[1] papers by others.

The New Almaden mine is located in Almaden Quicksilver County Park, a 4,200-acre park twelve miles southwest of San Jose, California. The New Almaden mine (actually a group of seven adjacent mines) operated from 1846 until late-1975, when the mines were closed and the property sold to the Santa Clara County Parks and Recreation Department.

The New Almaden mines rank among the world's richest, having remarkably produced 15.6 flasks of mercury (76 lbs. each) for each linear meter of the approximately 725 hectometers (45 miles) of workings in the mines. New Almaden is the largest mercury mine in North America and fifth largest in the world. Table 1 summarizes the production of the world's largest mercury mines through 1977. Table 2 summarizes the production data for the mine in five-year intervals. Figure 1 presents the Table 2 data in graphical form.

Table 1. Summary of the Total Production of the World's Largest Mercury Mines Through 1977 (1)

Mine or District	Product, Kg	Percent of Total	76-lb. Flasks
Almaden, Spain	271,000,000	32%	7,861,220
Monte Amiata, Italy	104,000,000	12%	3,016,852
Idria, Yugoslavia	102,000,000	12%	2,958,836
Huancavelica, Peru	52,000,000	6%	1,508,426
New Almaden, U.S.	38,000,000	5%	1,102,311
New Idria, U.S.	20,000,000	2%	580,164
Rest of U.S.	64,000,000	8%	1,856,524
Rest of World	188,000,000	22%	5,453,540
Total	839,000,000	100%	24,337,873

(2)

Year	Ore Treated, Kg X 10^6	Hg Product, Kg X 10^6	5-year Avg. Grade, %	Cummulative Ore, Kg X 10^6	Cummulative Hg, Kg X 10^6	Cummulative Grade, %
1850	6.56	2.14	32.62	6.56	2.14	32.62
1855	21.86	4.89	22.37	28.42	7.03	24.74
1860	18.25	3.59	19.67	46.67	10.62	22.76
1865	54.10	6.15	11.37	100.77	16.77	16.64
1870	54.21	3.24	5.98	154.98	20.01	12.91
1875	40.89	2.75	6.73	195.87	22.76	11.62
1880	117.48	3.93	3.35	313.35	26.69	8.52
1885	172.83	3.74	2.16	486.18	30.43	6.26
1890	123.81	1.96	1.58	609.99	32.39	5.31
1895	117.61	1.08	0.92	727.60	3US7	4.60
1900	159.83	0.87	0.54	887.43	34.34	3.87
1905	151.64	0.56	0.37	1,039.07	34.90	3.36
1910	185.73	0.90	0.49	1,224.80	35.80	2.92
1915	54.49	0.53	0.97	1,279.29	36.33	2.84
1920	57.41	0.41	0.71	1,336.70	36.74	2.75
1925	0.00	0.00	0	1,336.70	36.74	2.75
1930	30.13	0.20	0.66	1,366.83	36.94	2.70
1935	0.95	0.02	2.11	1,367.78	36.96	2.70
1940	70.49	0.18	0.26	1,438.27	37.14	2.58
1945	124.10	0.19	0.15	1,562.37	37.33	2.39
1950	0.72	0.01	1.39	1,563.09	37.34	2.39
1955	3.11	0.06	1.93	1,566.20	37.40	2.39
1960	24.33	0.11	0.45	1,590.53	37.51	2.36
1965	42.91	0.25	0.58	1,63US4	37.76	2.31
1970	77.60	0.27	0.35	1,711.04	38.03	2.22
1975	12.40	0.06	0.48	1,723.44	38.09	2.21
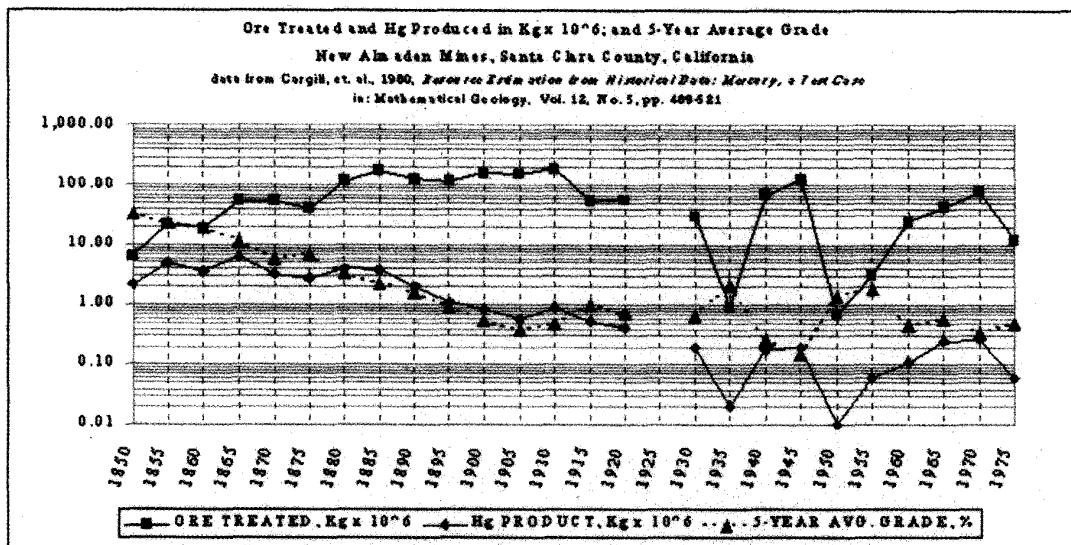
Figure 1a. Production from the New Almaden mines in five-year intervals (2).
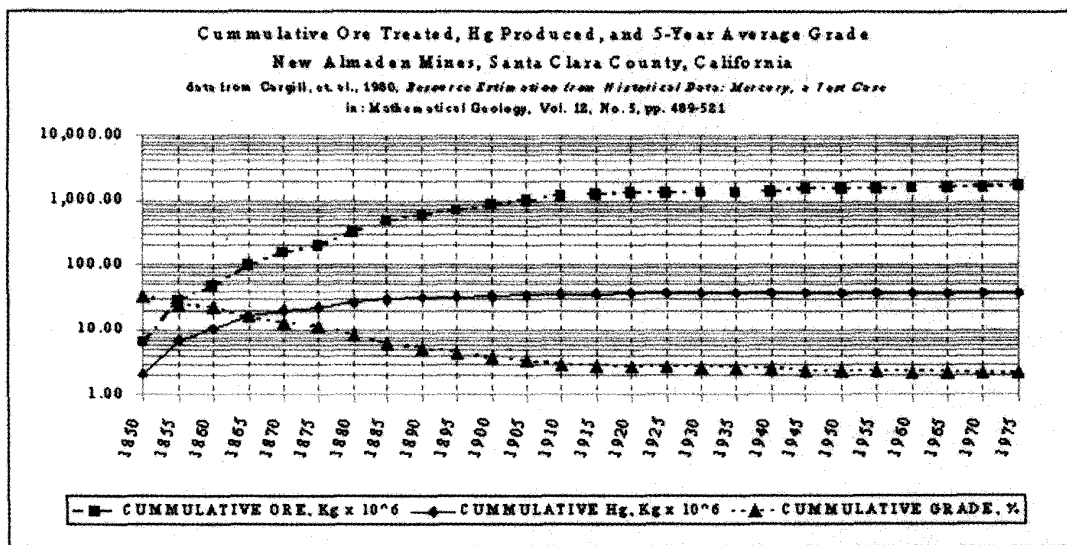
Figure 1b. Cumulative production from the New Almaden mines in five-year intervals (2).

The New Almaden mines are well documented, and have been the subject of numerous mining, geologic, and environmental investigations. The types of general mercury losses associated with mining activity at New Almaden are summarized in Table 3. The table is not meant to be exhaustive in detail. This paper focuses on fugitive air emissions from the primary furnace plants.

100

In 1987, concern about potential mining waste impacts resulted in the park being placed under a Remedial Action Order (RAO) from the California DTSC. Pursuant to the RAO, potential impacts to air, soil, water, vegetation, and park users were assessed by field studies between 1987 and 1994. The results are summarized in the Remedial Investigation (3), Risk Assessment (4), Feasibility Study (5), and Remedial Action Plan (6). As a result of the studies, in 1997 through 1998, a three-foot cap of clay soil was placed over calcines in five areas. Remedial action goals for the areas of mine waste range from 300 mg/kg to 500 mg/kg, depending on the area. The risk assessment determined the goals to be protective of park visitors and children under different exposure scenarios. Ecological remediation goals were not established, but the need to control soil erosion was noted in order to prevent the potential bioaccumulation of mercury from eroded mine waste and soil.

The California State Water Resources Control Board, San Francisco Bay Region is interested in the ecological aspects of all sources of environmental mercury in the Guadalupe watershed, and not just mining waste. The Board is currently hosting "stakeholder" meetings to arrive at a Total Maximum Daily Load (TMDL) for potential discharges to the watershed. The goal is to reduce sediment and water mercury concentrations to levels that protect human health and wildlife by preventing bioaccumulation above target thresholds in fish (to be determined) (7). The proposed stream sediment THg limit in the Draft TMDL Report is 0.4 mg/kg. The proposed thresholds to be achieved for fish are screening levels of 0.14 and 0.23 mg/kg THg, and an action level of 1.0 mg/kg (current FDA action level). The proposed threshold concentration for MeHg in water to prevent bioaccumulation and protect human and ecological health is 0.05 ng/L.

Table 3. Mercury Mining Losses at the New Almaden Mines and Potential Significance

Type of Mercury Loss	Mechanism of Loss	Potential Significance
Concentration mill tailings	Cinnabar values. Erosion, leaching and perhaps minor vapor emissions from tailings discharged to land.	Low
Furnace and retort dust and slag (burnt ore)	Cinnabar and mercury values, especially in "half-burned" rock. Erosion, leaching, and vapor emissions from discharge to land. Discharge of furnace dust with values, often by using water to slurry the dust. Slag often used for road base gravel and sometimes other gravel uses.	High
Furnace and retort condenser and soot clean-up water	Dissolved and particulate mercury and compounds. Runoff, infiltration, and perhaps vapor emissions from discharge to land.	Significant
Furnace and retort system leaks, spills, and fugitive emissions	Elemental mercury leaked to ground and air through defects (gaps and cracks), diffusion through brickwork, and poor operation of the furnace plant.	High (leaks & air emissions) Low (spills)
Mine drainage	Mercury dissolved in mine water discharge. Acid drainage is rare.	Low(?)
Mine ventilation and soil exhalation	Mercury vapor liberated by blasting and exposure of ore, and by natural exhalations of subsurface vapor.	Significant(?)
Mine waste rock	Cinnabar and mercury values remain in the rock, releasing mercury through erosion, leaching, and vapor emissions from waste rock dumped on surface and in mine. Minor use as construction material has also occurred.	Significant

Airborne emissions from ore reduction at the mines released significant quantities of vapor and particulate matter containing mercury, and the fate of the emissions may need to be assessed relative to the TMDL thresholds. Fugitive mercury vapor emitted during ore processing likely migrated into the atmosphere to become part of the global atmospheric mercury reservoir. Concern about the impact of atmospheric mercury on global waterways is a subject of much study. The potential impact of mist and fume loss has not been studied in any detail, but may be a significant source of mercury loading to surface soils in proximity to furnace plants. The magnitude of mist and fume loss at New Almaden is estimated from metallurgical studies of mercury ore reduction. The magnitude of the loss and unknown effect on local waterways suggest that historic air releases should be evaluated further. Similar investigation may be warranted at mercury mines with large production from furnaces.

At the New Almaden Mines, there are three primary furnace plants where large-scale ore processing occurred (8). From south to north, these are the Hacienda Furnace Yard, Mine-Hill Rotary Furnace, and Senator Mine. The plants operated over distinctly different time intervals and used different technology. This paper only considers the Hacienda Furnace yard. The Hacienda Furnace Yard operated from January 1846 until June 25, 1917, and used primarily wood-fired vertical shaft furnaces with brick and wood condensers. Some fume and mist loss data is available for the furnaces. The primary source of data used in the discussion herein is from Christy (9), (10), and Duschak and Schuette (11), (12). Christy studied the types of furnaces used throughout much of the production history of the Hacienda.

It should be noted that 95% of the total production of the New Almaden mines came from the Hacienda operations, and about 75% of all ore processed was processed at the Hacienda. Christy (10) estimated that in 1882 0.83% of the plant mercury yield was lost as vapor and 2.49% as mist. In 1882, the plant produced about 968,700 Kg of mercury, so the mist loss equals 24,120 Kg. Christy mentions evidence of significant losses from older style furnaces operated prior to 1875. Duschak and Schuette (11) point out that Christy uses theoretical calculations and did not measure mist loss directly. They also state that he uses the wrong vapor pressure of mercury in his calculations and therefore may have overstated the mist loss by an order of magnitude.

Duschak and Schuette use direct measurement at several mines to arrive at the data in the Table 4, modified by the author to correct some apparent mathematical errors. They point out that actual losses vary such over time within each plant and from plant to plant, that no generalizations can be reliably used in place of actual measurement. Figure 2 is data from their investigation that illustrates their point. None the less, it is useful to use their observed range of losses to evaluate the potential magnitude of mist loss from the Hacienda.

Table 4. Vapor and Mist Loss Determinations from Field Measurements

Mine à	New Idria No. 1 Rotary	New Idria No. 1 Scott (old)	New Idria No. 1 Scott (new)	Oceanic No. 1 & 2 Scott	Big Bend Scott (regular)	Oat Hill Entire System	Oat Hill First Chamber	Cloverdale Rotary
Daily Ore Processed (metric tons)	57	60	70	90	45	40	40	70
Daily Hg Produced (kg)	277	600	825	170	202	91	91	318
Gas Volume (m³/day) at stack conditions	40.040	69.800	97.430	62.800	30.000	24.048	26.400	40.000
Total Loss (grams per day)	7.747.74	2.024.20	8.281.55	2.951.60		721.44	1.671.12	
Vapor Loss (grams per day)	6.526.52	4.118.20	5.066.36	2.135.20		144.29	1.214.40	
Mist Loss by difference	1.221.22	-2.094.00	3.215.19	816.40		577.15	456.72	
Total Loss as % of Ore Content	2.72	0.34	0.99	1.71		0.79	1.80	
Total Loss as % of Production	2.72	0.34	0.99	1.71		0.79	1.80	
Vapor Loss as % of Production	2.36	0.69	0.61	1.26		0.16	1.33	
Mist Loss as % of Production	0.44	-0.35	0.39	0.48		0.63	0.50	

m³/day   cubic meters per day
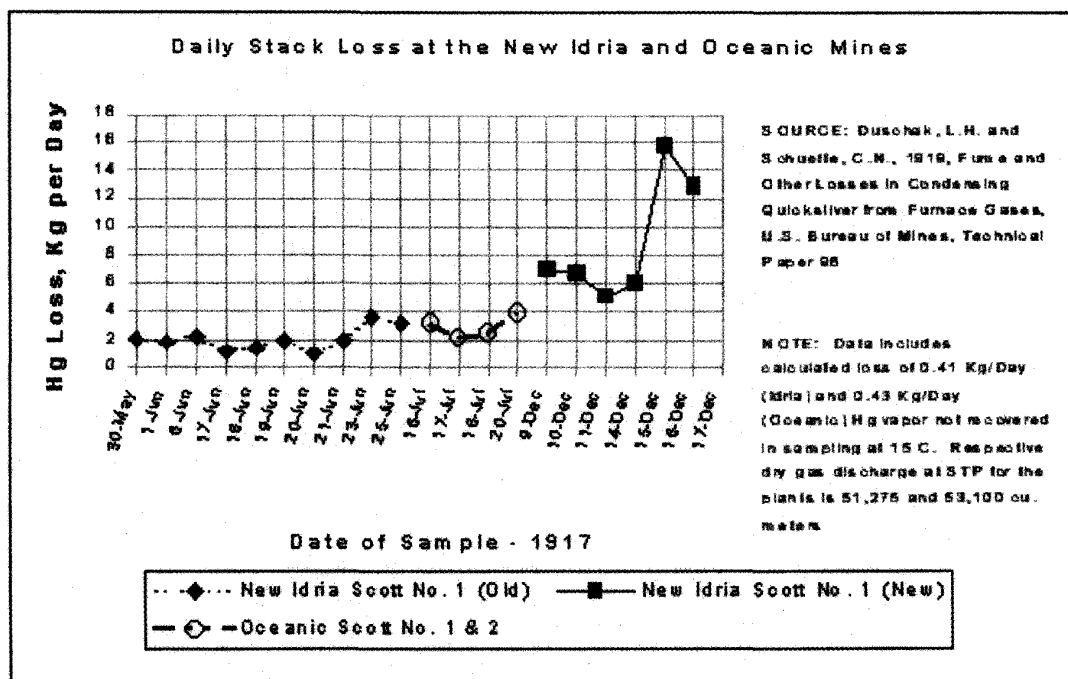
Figure 2. Stack loss estimates for three furnace plants.

Duschak and Schuette's data is characteristic of the furnace operations from about 1876 until 1917, when operations ceased at the Hacienda, a period of about 40 years. From Table 2, approximately 13,740 metric tons of mercury was produced during the period. The mist loss in Table 4 as a percentage of production ranges from 0.39% to 0.63%. This equates to a range of loss from the Hacienda of about 53,600 Kg to 86,600 Kg of mercury mist.

Based on Christy's account of the older type of furnaces common at New Almaden until about 1876, mist loss must have been as much as three times higher for the earlier interval. From Table 2, production for this interval is 22,760 metric tons of mercury. Duschak and Schuette's range of loss multiplied by a factor of three is 1.17% to 1.89%, and this equates to a range of loss of about 266,300 Kg to 430,200 Kg for the earlier production period. The total mist loss for the two periods ranges from 319,900 Kg to 516,800. This is a large number, especially considering it is one of three losses that may also be of equal or greater magnitude (vapor loss and loss in calcines).

Mist loss from Table 4 averages 38% of total loss (ignoring the negative value). If the Hacienda furnaces averaged 97.5% efficiency (a very generous assumption), estimated mist loss equates to 36,500 metric tons of mercury production divided by 0.975 and multiplied by (0.025 x 0.38), a mist loss of 355,641 Kg. The figure agrees well with the mid-point of the calculated range of loss. The table below uses a variety of loss assumptions for the entire product of the mines. The magnitudes of the losses clearly are significant in relation to the proposed TMDL sediment and water protection standards.

Table 5. Estimates of Total Mercury Loss for the New Almaden Mines as % of Yield

Sensitivity Analysis Using Different Values for Loss of Yield				
	Kg of Hg Prod	76-lb. Flasks of Hg Prod	Loss, % of Yield	Kg of Hg Lost	76-lb. Flasks of Hg Lost
Prior to 1875	26,690,000	774,229	15%	4,003,500	116,134
Post 1875	11,400,000	330,693	4%	417,240	12,103
TOTALS:	38,090,000	1,104,922		4,420,740	128,238
	Kg of Hg Prod	76-lb. Flasks of Hg Prod	Loss, % of Yield	Kg of Hg Lost	76-lb. Flasks of Hg Lost
Prior to 1875	26,690,000	774,229	10%	2,669,000	77,423
Post 1875	11,400,000	330,693	4%	417,240	12,103
TOTALS:	38,090,000	1,104,922		3,086,240	89,526
	Kg of Hg Prod	76-lb. Flasks of Hg Prod	Loss, % of Yield	Kg of Hg Lost	76-lb. Flasks of Hg Lost
Prior to 1875	26,690,000	774,229	5%	1,334,500	38,711
Post 1875	11,400,000	330,693	4%	417,240	12,103
TOTALS:	38,090,000	1,104,922		1,751,740	50,815

That the mist fallout may have impacted soils in the proximity of the furnace yard is suggested by one set of soil samples collected during the Dames & Moore Phase-III investigation. Figure 3 shows the results for colluvium soil samples collected during the investigation. Area CO-7 was selected to provide background results for soil overlying greenstone outside of the known area of mercury mineralization, similar to area CO-6. The samples from area CO-7 are clearly elevated relative to background. The outcrop does not show any indication of mercury mineralization.

There are two likely sources of the mercury. The first is dust coming from the dirt road adjacent to the area but 3 m below it in elevation. The road was used to haul ore and the road base averages about 100 mg/kg THg in the minus-two millimeter portion of the sample. The second possibility is that the elevated mercury represents accumulated mist fallout from the nearby Hacienda Furnace Yard (about 75 m lower in elevation and 300 m to the south). This can be investigated by collecting samples on hillsides east of the Hacienda, where there are no ore roads or known ore bodies.

The minimum mist loss of 319,900 Kg if distributed uniformly through the top 500 cm of soil over a 1 square kilometer (km²) area equates to a soil mercury concentration of about 400 mg/kg, assuming a mass of 1500 Kg per cubic meter for the soil.
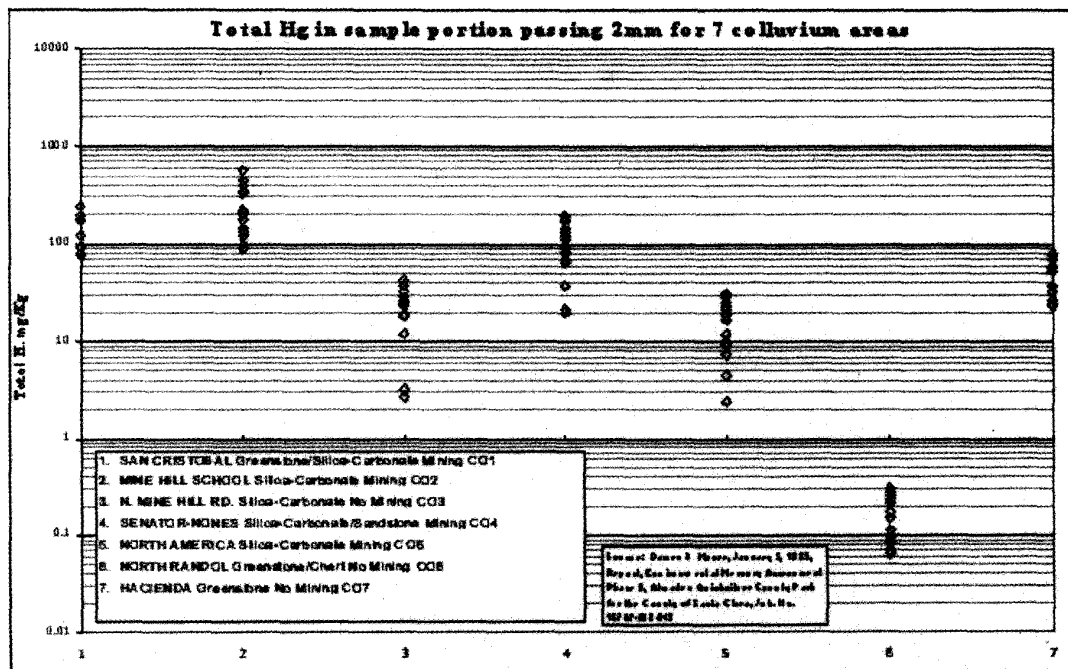
Figure 3. Total mercury results for phase-III colluvium soil sample areas.

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3.5.3 Atmospheric Mercury Emissions from Mine Waste - Mae Sexauer Gustin (Presenter), Department of Environmental and Resource Sciences, UN-R; Brian Fitzgerald, Department of Environmental and Resource Sciences, UN-R; David Nacht, Department of Environmental and Resource Sciences, UN-R; Rick Zehner, Department of Environmental and Resource Sciences, UN-R; Mark Coolbaugh, Department of Geologic Sciences, UN-R; Mark Engle, Department of Geologic Sciences, UN-R; Chris Sladek, Department of Geologic Sciences, UN-R; Robert Keislar, Desert Research Institute; James Rytuba, USGS; Steven Lindberg, ORNL; and Hong Zhang, ORNL

Mercury is naturally enriched in association with precious and base metal mineralization, and in fossil and active epithermal hydrothermal systems in high enough concentrations for mercury to be prospected for and mined. Areas surrounding mercury, precious and base metal deposits are naturally enriched in mercury. Because of this enrichment, mercury concentrations in substrate, soil gas and air have been used in exploration for mineral deposits. Mining associated with each of the above types of mineralization produces waste or disturbed rock material that is naturally enriched in mercury. Mercury in naturally enriched substrates occurs primarily as the mineral cinnabar (HgS) or as impurities in sulfide minerals. Mine waste may also be anthropogenically enriched in mercury when elemental mercury is used to extract gold from crushed rock and stream sediments. Elemental mercury that is added to ore may be transformed to other forms during ore processing and within the waste rock piles.

Volatilization is an important process by which mercury is removed from contaminated substrate (Engle et al., 2000 ; Sladek et al., this volume). Engle et al. (2000) demonstrated that mercury loss from naturally enriched substrate in the Ivanhoe Mining District, NV was primarily though volatilization (~99%). Sladek and Gustin (this volume) found that leaching of mercury is not a major mechanism by which mercury is removed from mine waste.

Currently, our understanding of the biogeochemical cycle of mercury is incomplete. One of the major uncertainties is the relative significance of nonpoint source emissions (mine waste, geologically enriched substrate, geothermal areas) with respect to emissions from point sources of atmospheric mercury (ore processing facilities, coal fired power plants, incinerators). Understanding the magnitude of emissions from these nonpoint sources is important for assessing their role in the global biogeochemical cycle of mercury and the effectiveness of regulatory controls on point sources.

In order to understand the environmental significance of mercury emissions from mines, mine waste and ore processing we must:

- Quantify the mercury emissions and the form of mercury being emitted (elemental mercury, reactive mercury, particulate bound mercury);
- Determine the emissions from associated undisturbed geologically enriched terrains;
- Assess the magnitude of the emissions as a function of time; and
- Determine the potential environmental impacts within the context of the biogeochemical cycle of mercury.

This paper discusses mercury emissions measured from mines and mine waste, the factors controlling the emissions, and the magnitude of the emissions relative to surrounding geologically/naturally mercury enriched terrains.

Methods

Mercury emissions reported in this study were measured using a cylindrical polycarbonate field flux chamber with a radius of 10.0 cm, a height of 3.5 cm, and a 1 L volume. Sixteen holes (1 cm diameter) were drilled around the circumference of the polycarbonate flux chamber allowing unrestricted airflow. The outlet and inlet air streams were sampled by a Tekran® Automated Dual Sampling unit and a Tekran® (Model 2537A) Cold Vapor Atomic Fluorescence Spectrometer. The Tekran® measures Hg concentration of the air in 5-minute intervals allowing for assessment of almost real time flux and of the influence of environmental parameters on Hg flux (Gustin et al., 1999a). Hg flux was calculated using the following equation:

$$F = Q^*(C_o - C_i)/A,$$

where F is the total flux of mercury in nanograms per square meter hour (ng/m^{2}hr); C_o and C_i are the Hg concentrations measured at the outlet and inlet in ng/m^3; A is the surface area exposed in the flux chamber in square meters (m^2); and Q is the flow of ambient air through the flux chamber in cubic meters per hour (m^3/hr). A chamber turnover rate of 5 to 10 L/min was used. Along with the measurement of mercury flux, air and substrate temperature, incident light, barometric pressure and substrate mercury concentration for the < 2 mm fraction of substrate 1 to 5 cm deep beneath the field chamber were also determined.

Study Sites

The Sulphur Bank Superfund Site, located on the eastern shore of the Oaks Arm of Clear Lake, CA, was originally mined for sulfur from 1865 to 1871, and then for mercury until 1957. An estimated 7000 tons of mercury were removed from the site, and over 1,250,000 tons of rock were mined, processed and disposed of at the site (Chamberlin et al. 1990). Because of elevated mercury concentrations in fish tissue from Clear Lake and clear identification of the Sulphur Bank Mine as the source of mercury to the lake, the mine site was listed as a Superfund Site in August 1990. For this study mercury emissions were measured from the mine waste at 22 locations.

The Knoxville Mining District, CA hosts three mercury mines, the Manhattan, Reed and Knoxville, as well as the McLaughlin Gold Mine, which has engulfed the Manhattan Mine. Mercury emissions were measured from eighty-six sites in the Knoxville Mining District and the adjacent Wilbur Springs area. Sampling locations included mercury and gold mine open pits and mine wastes, representatitive lithologic units (including altered and unaltered rocks) and CO$_2$ springs.

The Ivanhoe Mercury Mining District is located in north-central Nevada at the northern extent of the world-class gold-bearing Carlin Trend. This district includes at least four historic mercury mines with the Ivanhoe Mine being the largest. Approximately thirteen open pit gold mines are located along the Carlin Trend, where Hg is a common byproduct of the gold extraction process (Rytuba and Heropoulos, 1992). Mercury emissions were measured from mine waste, the open pits where mercury ore was extracted and from characteristic rock types in the District (n=29) (Engle et al., submitted).

The New Idria Mercury Mining District, located in south central California, includes the New Idria Mine, the second-largest historic producer of mercury in the U.S. (approximately 10,000 tons of production) and at least four other mines that produced minor amounts of mercury. Mercury emissions were measured from mine waste, and characteristic rock and rock alteration types in the district (Coolbaugh et al., submitted) (n= 40). Current research at the site is investigating the effect of remediation of mine waste on emissions.

At the Carson River Superfund Site, NV, ~75 mills used mercury to amalgamate gold and silver from the Comstock ore in the late 1800s. This site, which is anthropogenically contaminated in mercury, was listed as a Superfund Site in August 1990. It is estimated that 5.5 x 10^9 g of elemental mercury were lost during ore processing (Smith, 1943). Mercury emissions were measured from six areas of mill tailings, including one area where the ore had been reprocessed by cyanide heap leaching (n=25).

Results

Emissions from Mine Waste

Mercury emissions measured at Sulphur Bank ranged from 371 to 5580 ng/m²hr for mercuriferous rocks in the open pit and from 579 to 5442 ng/m²hr for the waste rock. Areas of recently disturbed material near the Herman Pit, with substrate mercury concentrations of 5 and 9 μg/g, exhibited fluxes of 8400 and 9500 ng/m²hr, respectively. Substrate mercury concentrations ranged from 0.6 to 5050.0 μg/g. Excluding one outlier, substrate mercury concentrations were less than 35 μg/g. The mean flux for the site (after removal of the flux measured from recently disturbed material) was 922 $\pm$ 556 ng/m²hr. A diel measurement of emissions from a representative site revealed an average nightime emission of 219 $\pm$ 24 ng/m²hr. Using these two average fluxes, an annual flux of 6.5 kg was obtained for the ~1200 x 1200 m² area.

For naturally mercury enriched substates, there is commonly a linear relationship between the logarithm of mercury concentration in substrate and the logarithm of mercury flux (Gustin et al., 2000). At Sulphur Bank, no such relationship existed. In addition, mercury fluxes were one to two orders of magnitude higher than would be expected given the substrate mercury concentrations. These two observations suggest that geologic processes at depth, such as the ongoing regional metamorphism, are important in controlling mercury emissions from the site or that surface disturbance has significantly exacerbated emissions from the area. The first seems more likely since mercury is actively being deposited at the site (Rytuba, 1993), and mercury is being emitted at CO_2 springs in the area. A diel pattern in Hg emissions (increasing emissions to mid-day and declining during the night) measured at the site indicated that surface processes are also important in controlling emissions.

In the Knoxville District, mercury emissions from the McLaughlin Gold Mine open pit ranged from 105 to 2866 ng/m²hr (n=7); from the Hg mine pits, 500 to 10000 ng/m²hr (n=3); from mine waste, 214 to 2100 ng/m²hr (n=5); and from processed Hg ore, 7330 ng/m²hr (n=1). Using an average flux of 674 ng/m²hr for the McLaughlin open pit and 1000 ng/m²hr for the mine waste, an estimated 15 kg Hg/yr is emitted from the ~ 3 km² disturbed area. Mercury emissions measured at night in the McLaughlin open pit declined to ~0 ng/m²hr. Mercury emissions from mines and mine waste in this district were positively correlated with substrate mercury concentration. Mercury emissions measured from representative lithologic units and CO_2 springs in the District ranged from 0 to 329 ng/m²hr and 389 to 1714 ng/m²hr, respectively. Since the McLaughlin Mine is located in a mercury mining district, emissions from this mine should not be used as indicative of emissions from other precious metal mines. For example, mercury emissions measured from the Relief Canyon pit, which is a sediment hosted gold deposit in central Nevada, were on the order of 60 ng/m²hr.

Mercury emissions measured from ore and mine waste in the Ivanhoe District ranged from 650 to 60000 ng/m²hr and 100 to 600 ng/m²hr, respectively. Engle et al. (submitted) estimated that 8.9 kg of mercury were emitted annually from the 0.1 km² area of mines and mine waste in the district, and 81 kg of mercury were emitted from a 582 km² area of undisturbed naturally enriched substrate surrounding the mercury mines.

Mercury emissions from mine waste and mining disturbed areas in the New Idria District ranged from 41 to 9600 ng/m²hr. Coolbaugh et al. (submitted) estimated that mercury emissions from a mining disturbed area of 0.6 km² were 2.7 kg/yr, while 15 kg/yr were emitted from a 220 km² area of undisturbed naturally enriched substrate within the district.

Mercury emissions from mine waste measured at the Carson River Superfund Site ranged from background levels (0-15 ng/m²hr), from mine waste that had been reprocessed using cyanide heap leaching, to 11500 ng/m²hr. Mercury emissions from the Carson River Superfund Site were crudely estimated to be 12.5 kg/yr.

Factors Controlling Mercury Emission from Mine Waste

The magnitude of the release of mercury from mine waste to the atmosphere is governed primarily by the mercury concentration in substrate and the general geologic setting. Excluding Sulphur Bank, a good correlation was found for the logarithm of mercury emissions versus the logarithm of flux ($r^2 = 0.65$, $p<0.05$) for mining disturbed substrate discussed in this study (n=41). Environmental parameters such as temperature, incident sunlight, precipitation, vegetation, coherence of the substrate and site disturbance all influenced the magnitude of emissions. Recently disturbed areas were found to exhibit significantly elevated emissions with respect to undisturbed areas. In fact, emissions from mercury mine waste several weeks after it had been moved and capped with ~2 feet of fill were as high as emissions measured from the waste

before it was moved and capped. Grasses were found to suppress emissions by 25 to 75 % from mine waste. Light and precipitation were both found to significantly enhance emissions. It should be noted that reported fluxes were measured under conditions of no precipitation. We recently measured a profound effect of fresh rainfall on mercury emissions from mercury-enriched soils (Lindberg et al., 1999). Under these conditions, mercury evasion can be enhanced by up to 5-fold over a several hour period.

Comparison with Emissions from the Surrounding Area

Mercury emissions from naturally enriched mine waste are 1 to 5 orders of magnitude greater than emissions measured from areas with no natural mercury enrichment (substrate < 0.08 μg/g of Hg; fluxes 0 to 15 ng/m²hr). Emissions from undisturbed naturally enriched substrate are 1 to almost 3 orders of magnitude higher. In most settings, the magnitude of emissions from naturally enriched substrate is directly correlated with the mercury concentration in the substrate. Since mines and mine waste represent only a small surface area with respect to the larger surrounding area that typically exhibits low levels of natural enrichment, emissions from both need to be quantified and scaled spatially and temporally in order for environmental ramifications to be assessed. Engle et al. (submitted) scaled up mercury emissions for an area of 586 km² within the Ivanhoe Mercury Mining District. They determined that the bulk of mercury emitted from the district (~90%) was from naturally enriched undisturbed terrain and the rest was emitted from the areas of actual mining and mine waste. Coolbaugh et al. (submitted) scaled up mercury emissions for a 230 km² area encompassing the New Idria Mercury Mining District and determined that 10% of the emissions were from mine waste and mining areas.

Conclusions

Ore processing, mining and land disturbance exacerbate mercury emissions that would be occurring from undisturbed naturally enriched substrate. Mercury emissions from mine waste and mining disturbed areas typically range from > 30 to 1000's of ng/m²hr and contribute kgs of mercury annually to the atmosphere. Fluxes from naturally enriched geologic substrate surrounding these areas range from 0 to 100's of ng/m²hr. The latter usually encompasses a larger surface area than mining disturbed sites and in general contributes more to the global atmospheric mercury budget.

Mercury emissions to the atmosphere in Nevada associated with mineral deposits occur from the ore roasting process, mine pits, mine waste and the surrounding naturally enriched terrains. Newmont estimated that through the process of gold ore roasting at the Twin Creeks Mine in 1999 ~550 kg of mercury were emitted; Barrick Goldstrike estimated an annual emission of 630 kg from ore autoclaving and refining at the Betz-Post Mine. Both of these facilities heat the ore to retrieve the gold. Most gold recovery at mines in Nevada is through the process of cyanide heap leaching which does not entail ore roasting, and thus mercury emissions associated with this process will be significantly lower. Zehner and Gustin (this volume), using LANDSAT imagery from 1994 and data from in situ field flux measurements, estimated that emissions from epithermal volcanic and sediment hosted recent/active mines was 78 kg/y and that roughly 13000 kg were emitted annually from undisturbed naturally enriched substrate. For comparison, an estimated 41500 kg were emitted in 1999 from 1663 coal utility boilers in the U.S. (Chu, 2000).

In order to accurately assess the environmental impacts of mercury emissions from ore processing and mine waste, consideration must be given to the magnitude of the emissions with respect to other sources, the longevity of the emissions and the mercury species being emitted. Ore processing by roasting constitutes a short term high concentration source. Cyanide heap leaching, a common process for removal of gold from ores, reduces the mercury concentration in mined rock and therefore could reduce overall emissions from mine waste. Mine waste and surrounding undisturbed naturally enriched substrate constitute long lived sources of mercury to the atmosphere. Planting vegetation on mine waste will reduce emissions, and we are currently investigating the effect of capping mine waste with substrate containing low mercury concentrations on emissions. One question that needs to be addressed is whether emissions from mine waste decline with time (as the effect of disturbance declines) to a flux that would be expected from undisturbed natural sources.

The form (Hg^{2+}, elemental Hg, Hg that is particulate bound) of the mercury emitted from each of these sources will influence the type of impact emissions will have on the environment. If the mercury emitted from ore roasting, mine pits, mine waste and naturally enriched areas is a reactive form (some form of Hg^{2+}) it may impact local ecosystems. If elemental mercury, it is thought that this form will enter the global atmospheric mercury pool and be broadly dispersed (although some studies have shown that it can be deposited

locally). If elemental mercury is the primary form then the magnitude of emissions relative to other sources and sinks on a global scale needs to be considered when determining the effectiveness of regulatory controls. The speciation of mercury being emitted from these sources as well as the potential for local deposition is unknown and needs to be investigated.

Acknowledgments

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3.5.4 The Importance of Emissions Speciation to the Atmospheric Transport and Deposition of Mercury - O. Russell Bullock, Jr, Atmospheric Sciences Modeling Division, Air Resources Laboratory, NOAA

Introduction

The atmospheric pathway of the global mercury cycle is believed to be the main source of mercury contamination to aquatic eco-systems throughout the U.S. and in most other nations where direct disposal of mercury to water has been largely eliminated. Although the spatial scope of transport and deposition is certainly global for atmospheric mercury as a whole, we now have compelling evidence that certain forms of mercury are very quickly scavenged from air by both wet and dry atmospheric processes and are not likely to travel very long distances through the atmosphere. Reactive gaseous mercury (RGM) and particulate mercury (Hg_p), while together making up only a small fraction of the total atmospheric burden of mercury, are thought to represent the majority of atmospheric mercury deposited to the surface. Mercury can be emitted to air in one of these forms, and travel only a short distance before deposition, or it can be emitted as elemental mercury gas (Hg^0) and move through the atmosphere for weeks or months, diffusing into the global atmosphere. Based on recent modeling and field studies, it now appears that most of the elemental mercury that is eventually deposited to the surface may do so through chemical conversion to RGM and/or particulate mercury. It also appears that emissions of RGM and Hg_p can be converted to Hg^0 by these same atmospheric processes under different conditions. While there remains considerable uncertainty about these chemical and physical conversion mechanisms, the expected deposition pattern for mercury from any source is certainly dependent on the chemical and physical form of that mercury when emitted. The term "speciation" is generally used to describe the determination of the fraction of a pollutant that occurs in various important forms. Mercury emission speciation is necessary for an assessment of mercury contamination from any source of atmospheric mercury.

Laboratory Evidence

All air pollutants tend to deposit rapidly to the surface if they are soluble in water. Less soluble pollutants tend to be deposited as particulate matter if they condense to the solid or liquid phase. Thus, low vapor pressure is another trait that leads to more rapid deposition. Table 1 shows the water solubility and vapor pressure of mercury and some of its compounds. The water solubility of Hg^0 is shown to be very low, indicating that significant scavenging and deposition by cloud and precipitation processes (wet deposition) should not occur. Also, the vapor pressure of Hg^0 is quite high for a metal. The indicated vapor pressure corresponds to a mass concentration of approximately 1.4×10^{-2} g m^{-3}. This saturation concentration for Hg^0 is seven orders of magnitude greater than concentrations typically found in ambient air and 140 times the Occupational Safety and Health Administration (OSHA) limit for mercury in the workplace. Thus, condensation of Hg^0 to form Hg_p in the atmosphere would not be expected, even in the most polluted locations. All of these physical properties indicate that Hg^0 emitted from mining activities, or any other source, should not readily deposit from the atmosphere.

Table 1. Physical Properties of Mercury and Some of Its Compounds
(From Schroeder and Munthe, 1998)

Property	Hg^0	$HgCl_2$	HgO	HgS	CH_3HgCl	$(CH_3)_2Hg$
Vapor Pressure (Pa)	0.180 @ 20°C	$8.99 \cdot 10^{-3}$ @ 20°C	$9.20 \cdot 10^{-12}$ @ 25°C	?	1.76 @ 25°C	$8.30 \cdot 10^{0}$ @ 25°C
Water Solubility (g/L)	$49.4 \cdot 10^{-9}$ @ 20°C	66 @ 20°C	$5.3 \cdot 10^{-2}$ @ 25°C	$\sim 2 \cdot 10^{-24}$ @ 25°C	$\sim 5-6$ @ 25°C	2.95 @ 25°C

On the other hand, $HgCl_2$ is quite soluble in water, and although its vapor pressure is high enough to pre-clude condensation to the particulate phase, this water-soluble gas should be readily scavenged from air by cloud water and precipitation. It can also be scavenged directly from the air by contact with water and vegetation at the surface. The organic compounds CH_3HgCl (methylmercuric chloride) and $(CH_3)_2Hg$ (dim-ethyl mercury) also have high vapor pressures combined with high water solubilities, and both of these highly toxic compounds should exist as a gas, but be readily scavenged from air by moisture aloft and at the surface. For all three of these highly soluble compounds, their existence as a gas allows more rapid diffu-sion through the air toward water and moist surfaces and increases their rate of dry deposition over that of a water-soluble aerosol. If any of these compounds are emitted from mining activities, they should exist in the atmosphere as RGM, deposit quite rapidly, and primarily affect the local-scale surroundings within the first day of transport from the point emission.

The vapor pressure of HgO is quite low as indicated in Table 1, and HgS certainly has a low vapor pressure by virtue of its existence as the common mineral cinnabar. HgO is only moderately soluble and HgS is extremely insoluble in water. Nonetheless, both of these compounds would exist in the atmosphere as Hg_P due to their low vapor pressure and should be scavenged from air, along with all other atmospheric aerosols, by cloud and precipitation processes and by dry deposition to the surface. Scavenging of Hg_P should occur at a significant rate, but not as quickly as for the water-soluble gases comprising RGM. If any of these Hg_P compounds are emitted from mining activities, their deposition from the atmosphere should occur within the first few days of transport from the point of emission.

Evidence from Field Observations

Until quite recently, the only separate species of mercury that could be routinely measured in air were total gaseous mercury (TGM) and Hg_P. Pioneering methods to measure gas-phase mercuric compounds were first demonstrated in the early-to-mid 1990s (Stratton and Lindberg, 1995). Reliable methods for routine measurement of RGM concentrations in ambient air have only been available for about two years (Stevens et al., 1998). The results from recently conducted field studies using this new RGM measurement capability in both manual and automated implementations have not yet been published. However, airborne measure-ments of speciated mercury air concentrations recently conducted in Florida by EPA's National Exposure Research Laboratory and NOAA's Air Resources Laboratory show that RGM concentrations are typically very low within the planetary boundary layer (PBL) away from sources of RGM, but that RGM concentra-tions are often significantly higher above the PBL. This suggests that dry deposition to the surface is efficiently scavenging RGM. No such phenomenon was observed for Hg^0 or Hg_P.

Some of the most revealing evidence for rapid RGM scavenging by dry deposition comes from experiences with various configurations of modern RGM sampling equipment. It is now known to the experts of RGM sampling that a short, large-diameter air inlet tube with an internal coating of highly cross-linked Teflon® is necessary to prevent a significant fraction of the RGM in sampled air from sticking to the inside wall of the inlet tube (Stevens, personal communication). This behavior suggests that RGM in air can be scavenged by dry deposition to many types of surfaces, not just water or vegetation.

It should be noted that before the existence and importance of RGM was understood by the scientific com-munity, it was generally believed that Hg^0 and Hg_P were the only significant species of mercury in air. Early studies of the behavior of what was thought to be only Hg^0 may have been confounded by the effects of the RGM component of TGM (Lindberg et al., 1991). Even after RGM was recognized as a component of gaseous mercury, some TGM measurements may have been influenced by RGM sticking to, or releasing from, air sampling trains. Now that the behavior of RGM in air sampling equipment is better understood, field studies employing new speciated mercury sampling methods should provide a better understanding of RGM's behavior in the atmosphere and the importance of mercury speciation to ecological damage assess-ment.

Evidence from Atmospheric Simulation Modeling

Many atmospheric mercury modeling efforts conducted since the mid-1990s have recognized the differing behaviors of Hg^0, RGM and Hg_P (Shannon and Voldner, 1995; Petersen et al., 1995; Bullock et al., 1997; Pai et al., 1997; Petersen et al., 1998; Xu et al., 2000). Lacking specific data on the composition and behavior of RGM, modelers have had to make a number of assumptions about its chemistry, and its subsequent dry

and wet deposition. Nonetheless, each of these modeling efforts cited above found very important differences between Hg^0, RGM and Hg_p in terms of their atmospheric behavior, transport distance, and deposition rate. An analysis of model sensitivity to mercury emissions uncertainty found a very strong dependence of simulated mercury deposition to the speciation of emissions (Bullock, 1998).

A comprehensive assessment of atmospheric mercury emission from, and deposition to, the U.S. was performed as part of the development of the USEPA's Mercury Study Report to Congress (USEPA, 1997). The simulation modeling performed for that assessment found a striking disparity between Hg^0, divalent mercury gas (i.e., RGM), and Hg_p, with respect to the fraction of U.S. emissions that eventually deposited to the surface within the model domain covering most of North America and surrounding coastal waters. Table 2 shows a mass balance analysis developed from a one-year simulation of mercury emission, transport, transformation and deposition. It shows that less than 2% of the Hg^0 emitted from anthropogenic sources in the U.S. deposited to the surface during the simulation, while more than 70% of the RGM and 38% of the Hg_p deposited during the same simulation period. It should be noted that Hg_p was assumed to be comprised of aerosol particles with a diameter of 0.3 microns for this modeling study. At this particle size, dry deposition of any aerosol matter is typically very slow. Hg_p in nature would exist in a variety of diameters, and dry depositional fluxes of Hg_p to the surface would likely be more significant than indicated in Table 2. Thus, the majority of both RGM and Hg_p emitted from the U.S. might be expected to deposit within the model domain, while the vast majority of Hg^0 emitted would diffuse into the global atmospheric background.

Table 2. Mass Balance Analysis from a One-year Simulation of Atmospheric Mercury Emitted from the U.S.. All Data Are Shown In Units of Metric Tons and Are Rounded to the Nearest Tenth. (Adapted from USEPA, 1997)

Source/Fate	Hg^0	Hg^{2+}	Hg_p	Total Hg
Total U.S. anthropogenic emissions	63.5	52.3	26.0	141.8
Dry deposited anthropogenic emissions	0.0	22.9	0.5	23.4
Wet deposited anthropogenic emissions	0.9	13.8	9.5	24.2
Mass advected from model domain	62.3	15.5	16.0	93.8
Remaining in air at end of simulation	0.3	<0.1	<0.1	0.4
Total deposited anthropogenic emissions	0.9	36.8	10.0	47.6

Conclusions

Laboratory investigation, field monitoring and simulation modeling all suggest that the behavior of mercury in the atmosphere is strongly dependent on the chemical and physical forms in which it occurs. These investigations do not suggest that the vast disparity among the behaviors of Hg^0, RGM and Hg_p in the atmosphere is dependent upon the source type or exhaust stack configuration. Due to the highly reactive nature of RGM, its emission into the lowest portion of the atmosphere from short exhaust stacks or from surface evasion should lead to shorter transport distances and higher local deposition rates than if emitted from tall stacks. This may also be true of Hg_p, if it is comprised of RGM weakly sorbed to more stable particulate matter. On the other hand, Hg^0 appears to be nearly inert and the height of release is unlikely to have much effect on its transport and deposition pattern, which is almost certainly global in scale under all conditions. Assessment of atmospheric mercury deposition from any industrial activity will require a confident speciation of the mercury emitted in addition to information about the THg mass.

Disclaimer

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3.5.5 *Atmospheric Mercury Fluxes as Recorded in Lake Sediments: The Lack of an Historic Global Signal from Au and Ag Mining - W.F. Fitzgerald, Department of Marine Sciences, University of Connecticut; C.H. Lamborg, Department of Marine Sciences, University of Connecticut; A.W.H. Damman, Division of Biology, Kansas State University; J.M. Benoit; Department of Geo. Sciences, Princeton University; P.H. Balcom, Department of Marine Sciences, University of Connecticut; and D.R. Engstrom, Science Museum of Minnesota*

Abstract

Using lake sediments from remote locations, we have reconstructed the atmospheric deposition of mercury (Hg) over the last ca. 800 years in both hemispheres. Significant findings include:

·   The current flux of Hg from the atmosphere in Nova Scotia was estimated using two independent methods: lake sediments dated with ^{210}Pb and rain collections (c/o Environment Canada and the Mercury Deposition Network). These two estimates are very similar (ca. 9 μg m^{-2} y^{-1}) and suggest that sediment cores are accurate records for Hg deposition from the atmosphere.

·   The ratio of current to pre-industrial Hg deposition rates observed in the 5 cores from Nova Scotia is a factor of 3-4x, indicating a significant anthropogenic impact since the advent of the Industrial Revolution. A similar trend is evident in the first cores from New Zealand, and this portion of the project is on-going. Furthermore, this increase is synchronous with increases in emissions of CO_2 from fossil fuel combustion on a global scale.

No evidence was found for an enhancement in atmospheric flux as a result of pre-industrial (< 1900) Au and Ag mining in either hemisphere. This finding implies that much of the Hg lost during mining operations and precious metal processing/refining ended up in tailings, soils and sediments and is now largely immobile with respect to large-scale atmospheric emission.

Introduction

Mercury is released to the atmosphere by natural and human-related processes (e.g., Nriagu and Pacyna, 1988; Mason *et al.*, 1994). In the atmosphere, Hg° vapor is the dominant chemical form and is slow to oxidize to more soluble species (e.g., Lamborg *et al.*, 2000). It is therefore available to be widely dispersed within the atmosphere, both intra- and interhemispherically (e.g., Fitzgerald, 1995). This implies that the atmospheric depositional flux of Hg at any location is integrative of sources on large and small spatial scales. Many studies have exploited this global/regional nature of Hg dispersion to estimate the change in the atmospheric burden of Hg on a global-scale by examining the depositional flux recorded over time in a natural archive from a remote location (e.g., Steinnes and Andersson, 1991; Swain *et al.*, 1992; Stewart and Fergusson, 1994; Landers *et al.*, 1995; Norton *et al.*, 1997; Benoit *et al.*, 1998; Lockhart *et al.*, 1998; Rognerud *et al.*, 1998; Lacerda *et al.*, 1999; Martínez-Cortizas *et al.*, 1999; Matsunaga *et al.*, 1999). Most of these studies have used lake sediments or ombrotrophic peat bogs as the archiving media and results from these studies are generally in agreement (Fitzgerald *et al.*, 1998). The picture that is emerging is one of a wide-spread increase in Hg deposition since the Industrial Revolution (ca. 1890 c.e.). Rarely, however, have these studies been conducted in conjunction with contemporaneous precipitation collections. Furthermore, information from the Southern Hemisphere is much more sparse than for the Northern Hemisphere. We report here findings on the Hg accumulation rates in lake sediments from two locations that are semi-remote and representative of their respective hemispheres.

Methods

Seepage/headwater lakes were sampled in Nova Scotia and New Zealand (Figure 1). To minimize con-founding factors, lakes were selected for simple morphology, small catchment size and minimal surface water exchange. Multiple cores were collected from each lake, and averaged results are reported where possible. The methods for lake sediment collection and analysis closely followed those of Swain *et al.* (1992). This summer (July-August, 2000), 15 additional cores (ca. 800 samples) were obtained from five carefully selected lakes in the tundra region of eastern Arctic, Alaska.

Figure 1. Sampling sites.

Lakes
- ◑ Big Dam East
- ◕ Beaverskin
- ● Upper Silver
- ◐ Hochstetter
- ◒ Kangaroo
- ◓ Sarah

Estimated Mercury Emissions Associated with Mining in the New World

South and Central America

North America

Global Industry

Adapted from Hudson *et al.* (1995)

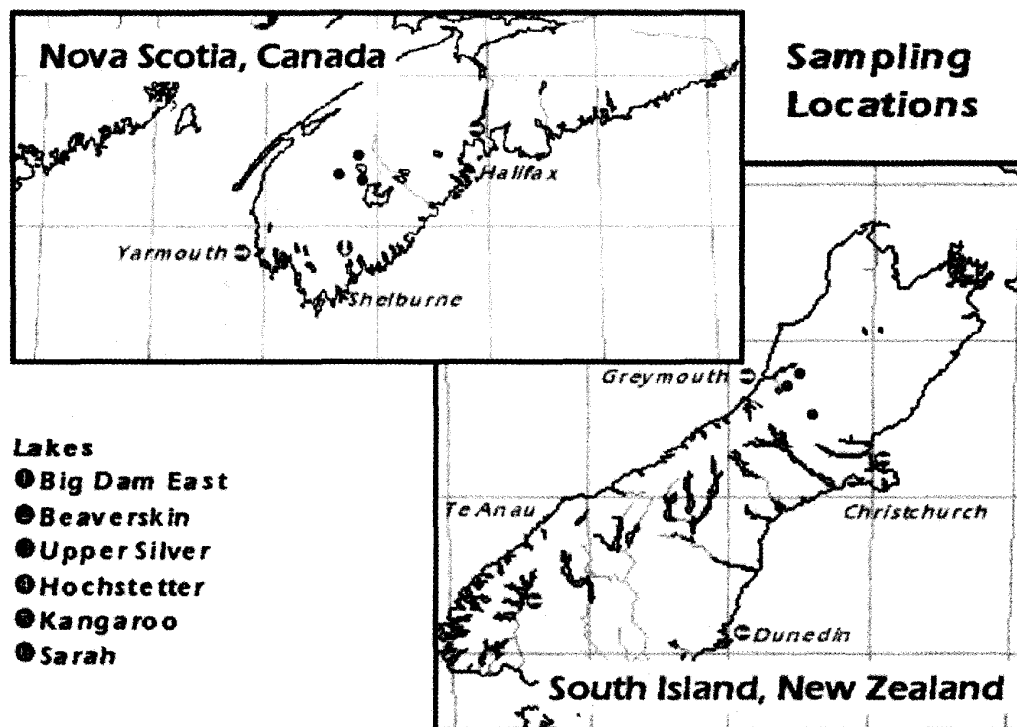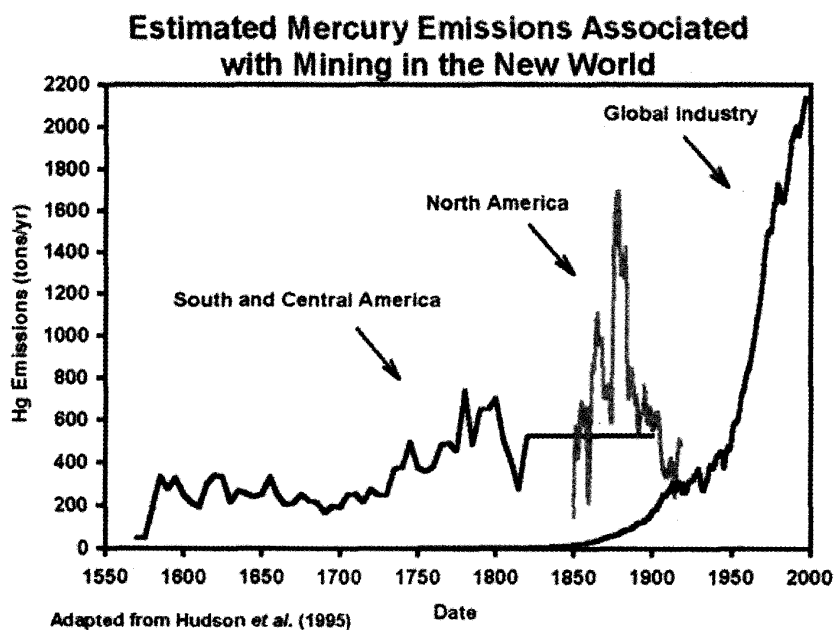**Figure 2.** Mercury emissions from mining and global industry (Hudson *et al.*, 1995).

Results

Most of the cores examined possessed 210Pb profiles that allowed application of the Constant Rate of Supply (CRS) dating model (Appleby and Oldfield, 1978). As part of the Mercury Deposition Network, the Atmospheric Environment Service of Environment Canada collects rainwater for Hg analysis at Kejimkujik National Park in Nova Scotia (where our lakes were situated). We therefore have two independent estimates of the current flux of Hg to Nova Scotia: precipitation and surficial lake sediments. These estimates agree closely (rain: 9 ± 3 per square micrograms year ($\mu g^{-2} y^{-1)}$; lake: 9 ± 2 $\mu g^{-2} y^{-1}$). At present, a similar comparison cannot be made in the region of New Zealand's South Island pertinent to our archive studies.

The temporal change in Hg deposition is well recorded in lake sediments from both locations. With some of the cores, reconstruction of almost 800 years of deposition was possible, and most cores recorded several hundred years. In both hemispheres, a clear increase in the flux of Hg to the sediments occurs around the mid-1800s and current flux ratio estimates appear to be about 3-4x that of the pre-industrial signals (i.e., an increase of 200-300%). The Hg emissions signals associated with pre-1900 mining activities in the Americas predicted by the analyses of Nriagu (1994) and Hudson et al. (1995) are not recorded in either location. However, the advent and time rate of change for fossil fuel combustion associated with the Industrial Revolution fits well with the character of the last hundred years of Hg deposition (Hg emissions scaled to CO_2 emissions. Keeling, 1994; Marland et al., 1994; Hudson et al., 1995). This is clearly not due to the relatively small size of mining losses of Hg compared with that of current industrial activity, as the data used in Hudson et al. (1994) indicate that the average losses of Hg from South and Central American mining, North American mining and current industry are about 600, 1200 and 600 tons y^{-1} (3, 6 and 3 Mmoles y^{-1}), respectively. The lack of a mining signal in lake sediments from the Southern Hemisphere has also recently been reported by Lacerda et al. (1999) working in Brazil and previously noted by several authors working in locations around the Northern Hemisphere (e.g., Swain et al., 1992; Landers et al., 1995; Lockhart et al., 1998; Rognerud et al., 1998; Martínez-Cortizas et al., 1999; Matsunaga et al., 1999). While the losses of Hg during Au and Ag mining are documented (Egleston, 1887; Nriagu, 1994), the lack of a global Hg signal associated with Hg mining and Au and Ag recovery suggests that either the Hg emitted to the atmosphere from these activities is removed rapidly and locally due to the chemical and physical form of the atmospheric Hg, or perhaps more reasonably, that most of this Hg was lost largely to tailings, soils and sediments. This sequestering significantly reduced the amounts introduced into the global atmosphere. Our newly initiated investigations of current and historic atmospheric Hg deposition in the tundra region of eastern Arctic, Alaska will allow potential regionalized/localized Hg deposition associated with Au and Ag mining to be scaled and assessed.

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3.5.6 Estimation of Mercury Vapor Flux from Natural Geologic Sources in Nevada - Richard E. Zehner, Department of Environmental and Resource Sciences, UN-R and Mae Sexauer Gustin, Department of Environmental and Resource Sciences, UN-R

Introduction

Areas geologically enriched in mercury are concentrated in three global belts that follow active plate tectonic boundaries and are associated with high crustal heat flow, volcanism, hydrothermal systems and alteration, and base and precious metal deposits. Naturally enriched substrates constitute long-lived sources of mercury to the atmosphere.

The relative contribution of mercury to the atmosphere from natural and anthropogenic sources is currently a topic of debate, with regulatory as well as scientific implications. While many anthropogenic sources

119

represent point discharges of Hg that are relatively easy to measure, most natural sources are diffuse and more difficult to characterize. Until recently, little work had been done to quantify mercury emissions from naturally enriched areas. Early estimates of Hg flux from the natural mercuriferous belts (~1.5 ng m²/hr) were derived by subtracting anthropogenic point source emission estimates and deposition estimates from the global atmospheric Hg pool (Lindqvist et al., 1991). Engle et al (submitted) and Coolbaugh et al. (submitted) demonstrated that mercury emissions from areas of natural enrichment were significantly higher than predicted from previous models.

This study focused on characterizing natural source mercury emissions from the State of Nevada, which is located in one of the global mercury belts. It employed a GIS approach to model and estimate the amount of mercury vapor flux emitted. A large geologic database of soil and rock mercury concentrations and in situ measurements of mercury emissions were the primary data used for scaling.

Natural Mercury in Nevada

Geologic sources of mercury in Nevada include the alteration zones around fossil and active hydrothermal systems, and the active geothermal systems themselves (Figure 1). The same systems that deposit mercury can also deposit other metals in economic quantities, such as gold, silver, and copper. Mercury occurring in the sulfide state or as elemental Hg has long been used as a pathfinder element in gold exploration. Many active gold mines in Nevada contain elevated mercury concentrations, and some produce mercury as a byproduct of cyanidation or smelting.

The geology of Nevada is characterized by at least four major periods of structural deformation that faulted and fractured crustal rocks, forming conduits for hydrothermal fluids. The last episode involved tensional forces that thinned the crust, leading to high crustal heat flow and copious hydrothermal activity. Geothermal systems resulting from the high heat flow hydrothermally altered large volumes of rock, and locally deposited or are currently depositing mercury and other metals within these altered zones. Nevada has hundreds of active hot springs and geothermal wells, and thousands of zones of alteration where past geothermal fluids flowed.

Figure 2 shows a cross section of a mineralized hydrothermal system. Hydrothermal fluids with temperatures up to 300°C can dissolve metals from deep crustal sources, transport them, and deposit them near the surface as the result of boiling, decreasing temperature, or mixing with cold groundwater. Mercury, being so volatile, deposits last, at or near the surface, at concentrations up to hundreds of thousands of times the average crustal value of 0.06 ug/g.
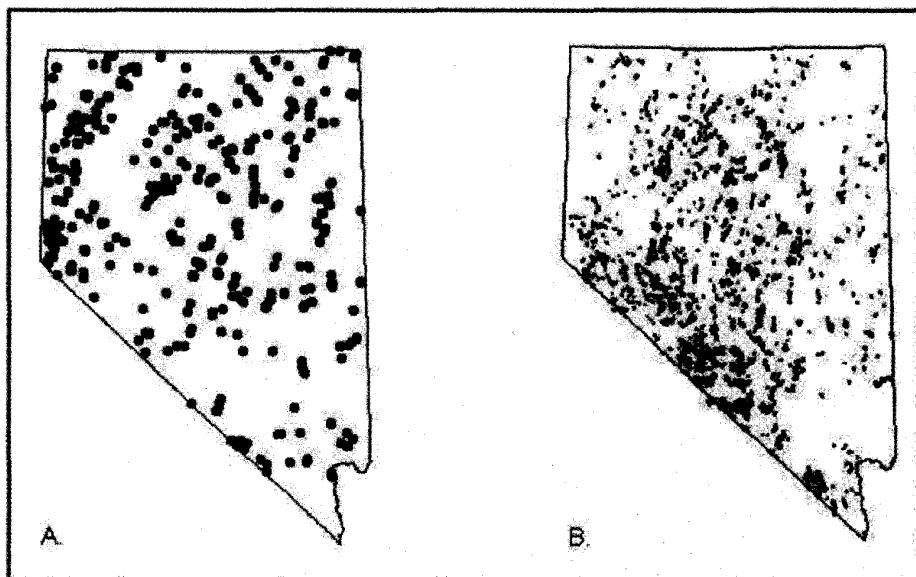
Figure 1. A. Location of active geothermal systems in Nevada, from Garside, 1994. B. Areas of Nevada with hydrothermal alteration as seen by LANDSAT 7 imagery (see text).

Modeling Mercury Flux

Mercury vapor is emitted from rock and soil as a function of substrate mercury concentration, light intensity, soil and air temperature, barometric pressure, and deep-seated sources. Mercury flux follows a diel pattern that peaks at midday, when sun intensity is greatest (Figure 3). Because of this cycle, flux measurements taken at different times from the same location and substrate will vary. Engle et al. (submitted) found this diel pattern closely follows a Gaussian distribution curve, and derived an equation that allows normalization of Hg flux measurements to a daily average flux.
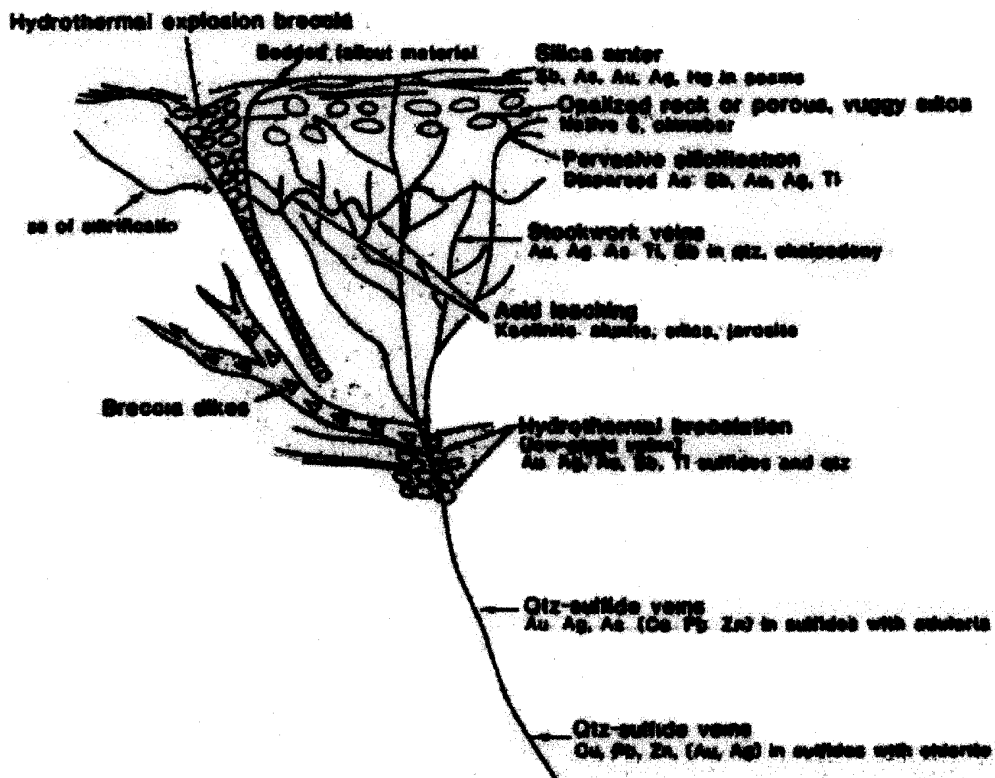
Figure 2. Cross section of a mineralized hydrothermal system, from Silberman and Berger (1985). Very hot mineral-laden water flows up faults and fractures and deposits metals on fracture walls (veins) and in the surrounding alteration envelope. These altered zones range up to hundreds of square kilometers in size with mercury concentrations in the 10^{-2} to 10^{1} ug/g range.
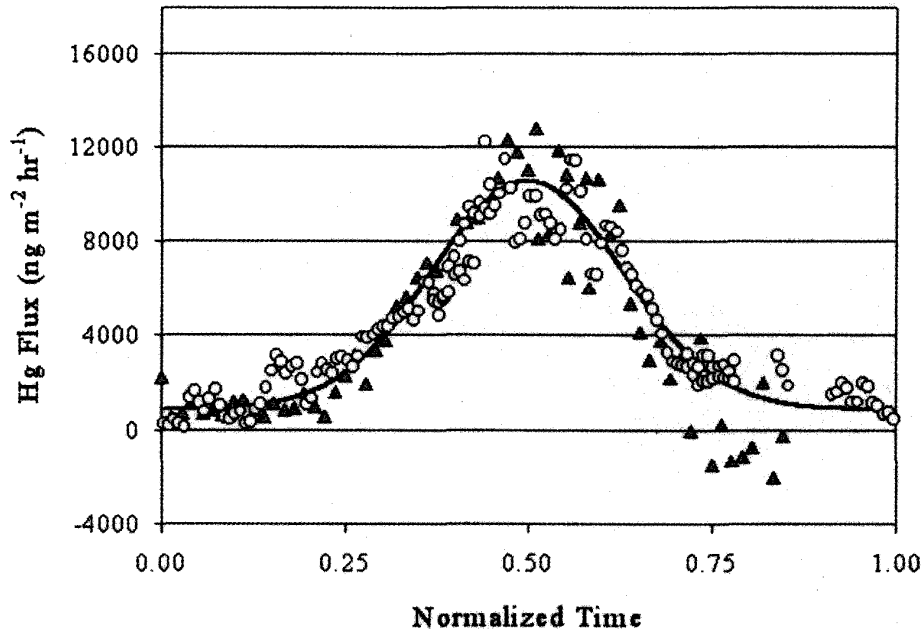
Figure 3. Diel curve from Engle et al. (submitted) showing mercury flux data from the Ivanhoe district, Nevada and the McLaughlin mine, California. Time is normalized to 24 hours = 1.00.

Figure 4 shows a distribution of ln[mercury concentration] in substrate (soil) versus ln[flux] that were normalized using the Gaussian equation. The sample points represent flux measurements taken in direct sunlight from a wide variety of geologic substrates and mercury concentrations. The equation for this curve, ln(normalizedflux) = 2.925 + 0.525 x ln(Hgsubstrate) + 0.027 x ln(Hgsubstrate)^2 was used in the model to convert soil concentration to an average daily flux for a 24-hour day having 12 hours of sunshine.

The GIS database used for the modeling consists of four primary layers: (1) a geologic map layer consisting of 1:250,000 scale geologic maps from Hess and Johnson (1997), (2) an alteration layer containing polygons derived from LANDSAT 7 images that emphasize clays and iron oxides indicative of hydrothermal alteration, (3) a sample layer composed of rock and soil mercury concentrations from samples taken throughout Nevada, (4) a meteorological layer which adjusts mercury flux to local conditions of sunlight and cloud cover, and (5) a layer containing data from active geothermal sources. The data was manipulated using ArcView 3.2, using grids and the Spatial Analyst 2.0 extension.

The geologic map layer utilized existing 1:250,000 scale county geologic maps of Nevada digitized into ArcInfo coverages (Hess and Johnson, 1997). These maps were compiled by various authors who mapped each county using different geologic units. The ArcInfo coverages were reclassified into 34 standard geologic surface units, mosaiced into one map, and converted to grid.
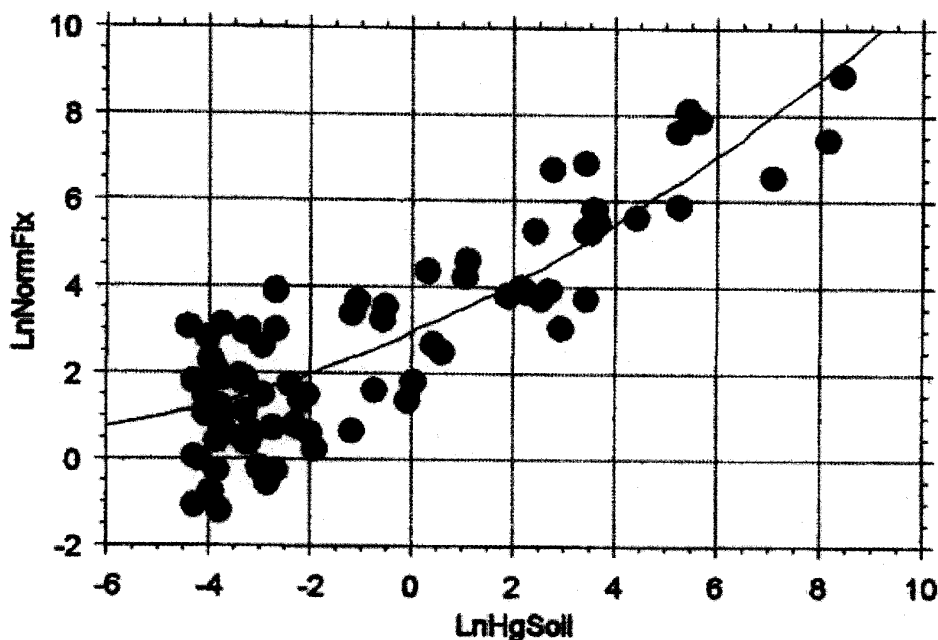
Figure 4. Graph showing relationship between ln soil concentration and ln vapor flux, from field flux data collected from a variety of unaltered and mercury-enriched rock types, during direct sunlight. R^2 value of curve is 0.726. The flux data is normalized to an average daily value using the Gaussian curve of Figure 3. The best-fit equation was used to estimate mercury vapor flux from rock and soil data throughout Nevada.

The alteration layer was produced by digitizing polygons around altered areas derived from 1994 LANDSAT 7 images of Nevada which emphasize aspects of hydrothermal alteration (Figure 1B). Specifically, a Band5/Band7 = red, Band3/Band1 = green, and Band3/Band5 = Blue ratioed image was created after masking out vegetation and cloud cover. In this image, clay alteration shows up in reds, iron oxides as greens, and unaltered rocks in blue. Care was taken not to include primary clay or iron oxides that are not the result of secondary hydrothermal alteration. LANDSAT 7 imagery uses pixels 30 m on a side; if the area of this pixel is composed primarily of materials other than this alteration (e.g., vegetation, fresh rock, etc.), it was not recorded as altered.

The mercury sample layer consists of 31,878 random and select rock chip, dump, and soil samples from a variety of sampling projects, including those focused on mercury and precious metal mineral exploration (Baedecker et al., 1998; Tingley, 1998; USGS and Kennecott Exploration Company, unpublished data). As such, it constitutes a non-random sample of the true mercury population of Nevada.

The database was first "cleaned" by removing samples with poor spatial locations or analytical methods. Next, the alteration layer was used to spatially separate samples into "inside" and "outside" groups. Samples "inside" alteration polygons were considered altered, while those "outside" the polygons could be either fresh or altered. A set of samples having associated trace element data and rock descriptions was used along with cumulative frequency plots to further separate "outside" samples into fresh and altered subpopulations.

Fresh samples were given a 1000 m radius of influence, altered samples were given a 100 m radius of influence, and areas with no samples were assigned the mean flux value of all fresh samples of that rock type.

Alteration polygons were classified into several groups using mine and prospect data from Mason and Arndt (1996), including: (1) Altered areas with or without historic metal mines, (2) altered areas associated with historic mines having mercury as a commodity, (3) active or recently active precious metal mines, (4) active or recently active mines reporting mercury as a byproduct, and (4) porphyry copper systems. Cumulative

124

frequency plots indicate these mercury samples fall into three populations. The first population, comprising 95% of the samples, ranges from 0.0 to 6.5 ug/g mercury. They were assigned a 1000 m radius of influence. The second altered population spanned 6.5 to 26.0 ug/g mercury; these samples were given a 100 m radius of influence. A third population, consisting of those samples above 26.0 ug/g mercury, was removed from the dataset as being non-representative. Areas not having samples were assigned either the average value of all altered samples (5.55 ng/m²hr; Group 1), or a value determined from actual flux measurements from these deposit types (Groups 2-4).

Because mercury flux is strongly affected by exposure to sunlight, a meteorological layer was added to the GIS to adjust flux values to cloudy conditions. To accomplish this, flux measurements were taken from the same location during intermittent sun and cloud conditions. An equation was derived that describes the difference in flux, which was combined with U.S. Weather Bureau data showing annual percent cloud cover for the region. The resulting layer was used to adjust the flux data, which is based on a completely sunny day, to one more accurately reflecting local cloudy conditions.

Finally, a layer was employed containing temperature data from active geothermal systems in Nevada, from Garside (1994). Scant data exists on flux emissions from active geothermal areas. For this study, a flux of 100 ng/m²hr was assigned to all geothermal springs with temperatures above 85°C, and a 90 m radius.

Conclusions

The average mercury flux calculated for the State of Nevada using this approach was 3.837 ng/m²hr, approximately twice the value estimated by Lindqvist et al. (1991). This amounts to a yearly natural emission of approximately 13,680 kg for Nevada.

Zones of alteration in Nevada, which comprise 3.3% of the area, emit approximately 12% of the mercury. The remaining 88% is from isolated altered zones outside the alteration polygons, and from unaltered rocks having very low concentrations exposed over very large areas.

Based on field measurements and substrate concentration, unaltered geologic rock units exhibit an average flux range of 3.18 to 4.29 ng/m²hr. The unaltered geologic unit with the highest flux was Recent playa and lake deposits, which averaged 5.30 ng/m²hr. However, this average is probably influenced by anthropogenic mercury migrating downstream from historic mining districts into lakes and playas.

Based on 1994 LANDSAT data, active and recently active precious metal mines constitute a small percentage of the THg emissions in Nevada. Our data indicate that substrate within recently active precious metal mines, constituting 0.1% of the area of Nevada, produce approximately 0.8% of the total natural mercury flux (77.5 kg/yr). Porphyry copper mines emit a negligible amount of mercury, compared with other sources.

This scaling exercise suggests that natural sources contribute significantly to the global mercury pool. Large areas of low natural mercury concentration generate more mercury flux than small regions of higher concentration.

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3.5.7 Mercury Emission and Re-emission from Diffuse Area Sources: The Dilemma of Small Emissions from Large Surfaces, the "Inert" Nature of Elemental Mercury Vapor, and Missing Sinks in the Global Mercury Cycle - S. E. Lindberg (Presenter), Environmental Sciences Division, ORNL; M. Gustin, UN-R; H. Zhang, Environmental Sciences Division, ORNL; and S. Brooks, NOAA-ATDD

Introduction

Atmospheric sources are significant in the cycling of Hg in the biosphere, but there have been few reliable measurements of air/surface exchange of Hg in terrestrial or aquatic systems until recently. The ability of mercury to form highly volatile compounds in soils and waters through chemical and biotic interactions gives it the unique ability to be re-emitted after deposition. In geological substrates, some mineral forms of Hg also release volatile elemental Hg vapor ($Hg°$). The role of re-emission and diffuse-source emissions such as from mining sites and geologically enriched soils can not be properly assessed until proven methods have been demonstrated. Similarly, the effectiveness of mandated point-source emission controls and remediation of contaminated areas such as historic and current mining sites cannot be determined without an understanding of the overall contribution of diffuse and point sources to regional and global cycles.

Surface Flux Measurement Methodology

In the last decade there have been significant developments in the areas of automated field analysis, flux chamber enclosure, and tower-based micrometeorological gradient methods for measuring gas-phase Hg fluxes over waters, soils, and vegetation (e.g. Meyers et al. 1996, Lindberg et al. 1995, Poissant and Casimir 1998, Gustin et al. 1999). Numerous groups have now applied these methods in flux campaigns around the world, and the data base on Hg fluxes has increased significantly. An important milestone was reached in 1997 when scientists from several countries collaborated in an EPRI-sponsored field intercomparison of Hg flux measurements using seven field flux chamber designs and four micrometeorological approaches at the Steamboat Springs Geothermal Area, Reno, Nevada (Gustin et al. 1999 a,b). This study discovered and quantified for the first time important controls on Hg fluxes from a diffuse Hg-enriched, desert landscape (Lindberg et al. 1999, Poissant et al. 1999, Wallschlager et al. 1999), developed new theories of Hg vapor emission from soils (Zhang & Lindberg 1999), and led to important improvements in flux measurement methods (Zhang et al. a & b, in prep.).

New Findings Regarding Hg Fluxes from Natural Landscapes

One particularly important observation of recent flux studies is that many conventional chamber measurement methods underestimate landscape-scale Hg emission rates, suggesting that much of the flux chamber data in the literature may be biased low (e.g. Carpi and Lindberg 1998). The bias results from the common use of relatively low flushing rates in soil flux chambers deployed at remote field sites. These low rates have the effect of suppressing soil fluxes, especially over enriched soils where diffusion gradients may be artificially reduced in poorly mixed chambers. A series of papers is now in review describing this phenonenon, its theory based on boundary layer development, and means by which to correct the problem (Zhang et al. a&b, in prep.). Another important finding from recent field and lab studies is that Hg fluxes from soils are strongly influenced by external factors in a manner suggesting that simple diffusion may not control fluxes from soils under all circumstances, as often proposed (e.g. Johnson and Lindberg 1995). Rather, the new data indicates that fluxes of Hg° from soils are controlled by surface exchange processes at the soil surface (Zhang and Lindberg 1999). Elemental mercury vapor seems to be loosely bound to mineral particles, and is readily released in exchange for other compounds or when energy is added to the system (e.g. in the form of solar radiation). We have demonstrated that both water and some atmospheric molecular trace gases both have the capacity to enhance Hg fluxes from soils which contain elemental Hg as a contaminant, or in a natural geological form (Lindberg et al. 1999, Zhang and Lindberg 1999). We and others have already demonstrated that soil Hg° can also be readily mobilized by solar radiation (Gustin et al. 1999, Carpi and Lindberg 1998). These processes have important implications for predicting Hg fluxes from former mining sites.

The Dilemma of Hg Re-emission and Scaling Small Fluxes from Large Areas

These observations are particularly interesting because nearly all recent data from direct measurements of Hg fluxes over diffuse surfaces indicate that the actual measured fluxes far exceed those derived from or used in global cycling models (e.g. see Gustin and Lindberg 2000a, Zhang and Lindberg 1999). Overall, the recent data base of measured fluxes often exceeds average values used for diffuse sources in global models by an order of magnitude or more. Hence, considerable effort is needed in developing methods for scaling field measurements from geologically enriched soils to the full landscape (see Gustin and Lindberg 2000 a & b, also Gustin this workshop). However, geologically enriched areas in the U.S. cover a relatively small area, and one might argue that the overall uncertainty of scaling these fluxes is most important in regional cycles, especially in the West. A more difficult problem concerns scaling Hg emissions and re-emissions from background landscapes. There is considerable evidence that Hg, once deposited, has the capability to be re-emitted from environmental surfaces (e.g. Mason et al. 1994, Kim et al. 1995), and that re-emission is significantly enhanced by green plants via a transpiration-like process (Lindberg et al. 1998). Such fluxes are readily measured, but separating the resulting atmospheric Hg into primary (emission) and secondary (re-emission) sources is no simple task. It has been estimated that man has introduced several hundred thousand tons of Hg into the atmosphere in the past few hundred years (Nriagu 1989), much of which has accumulated in recent surface soils.

It would require only a small percentage of this accumulation to be re-emitted to make a significant contribution to the atmospheric budget on regional and even global scales. Such flux estimates can vary widely and, of course, carry a large uncertainty because they represent very large areas. Herein lies the dilemma. For example, after scaling, a flux of 1 ng/m²hr (a very low flux for clean background soils, Zhang and Lindberg 1999) representing of an area of 100 km² (~6 average size golf courses) is equivalent to a flux of 1000 ng/m²hr (a very high average flux from Hg-enriched soils, Gustin) representing 0.1 km² (a typical area for a western mine spoil). Based on a scaling of background fluxes over forests, Lindberg et al. (1998) suggested that the global model of Mason et al. (1994) may have underestimated natural Hg fluxes by ~400-2000 t/yr (~40-300%). Their upper estimate (3200 t/yr) would exceed oceanic evasion and approach anthropogenic sources worldwide. In this analysis, Lindberg et al. used a relatively conservative scaling approach, but the large areas of background soils and forested areas involved suggest that even small fluxes from natural surfaces can dominate the global Hg cycle.

There has been considerable debate on the relative importance of so-called natural vs. re-emitted Hg sources in regional and global cycles (e.g. Rasmussen 1994, Fitzgerald et al. 1997). While this is an important debate, we should not lose site of the fact that neither source type is readily controlled or regulated, regardless of the ultimate source of the emitted Hg. If regulatory agencies do not include such surface sources in their development of emission control policies for industrial sources, an accurate cost-benefit analysis is not possible. In this regard, it is especially important to understand the role of "old Hg" in watershed bio-

geochemical cycles. Old Hg is that portion of the existing pool that is derived from past deposition of anthropogenic and natural atmospheric Hg. If the Hg which accumulates as MeHg in biota is largely derived from old pools within a lake or watershed, then reduction of industrial emissions may have less than the expected benefit on Hg levels in the aquatic food chain at sites distant from local sources (most lakes with elevated fish Hg fall into this category). This may mean that more severe reductions will be necessary to achieve the required reduction in Hg levels in fish, or that controls of industrial emissions will need to be in place for a long time before benefits are seen at remote sites.

This does not limit the need for a sound Hg regulation policy, but argues strongly for a more complete understanding of old and re-emitted Hg. While this has been an intractable problem for past field studies, recent developments and improvements in the stable isotopic analysis of Hg (e.g. Hintellman et al. 1997) provide hope for future success in separating and quantifying the roles of these processes in lake/watershed systems. The new international METAALICUS project is now being developed in Canada to address this issue (Mercury Experiment to Assess Atmospheric Loading in U.S. and Canada, http//www.biology.ualberta.ca/METAALICUS/METAALICUS.htm). This multi-collaborator and interdisciplinary study will involve a whole-ecosystem manipulation with different stable isotopes to distinguish between the accumulation of old vs newly deposited Hg in contributing to the current load of MeHg in aquatic biota. The project will also seek to develop the first ever field-scale relationship between Hg deposition rates and fish accumulation levels, while also separating out the relative contributions of Hg from uplands, wetlands, and in-lake sources. Preliminary data from exploratory isotope additions to upland soils, wetlands, and lake enclosures indicate that some of the newly deposited Hg (applied as Hg^{2+} salts in rain or throughfall) is rapidly reduced to $Hg°$ and re-emitted back into the atmosphere within a very short time of deposition (Lindberg, Hintelmann, St. Louis, Southworth, Krabbenhoft, and Amyot, unpublished data).

Atmospheric Speciation of Emitted Hg and Missing Sinks in the Global Cycle

Another major recent advance in Hg cycling was the development of methodologies for determining the speciation of atmospheric Hg. The discovery of measurable levels of water-soluble Hg compounds (reactive gaseous mercury, RGM) in both flue gas, and, more recently, ambient air has significant implications for modeling the fate of airborne Hg. Prior to about 1990, atmospheric Hg was considered to consist primarily of elemental Hg vapor ($Hg°$). This species is important because of its volatility and long residence time, making Hg a truly global pollutant since its lifetime in the atmosphere is on the order of 1y. Earlier studies by Brosset and Lord (1991) and Johnson and Braman (1974), while limited by then available approaches, suggested the potential for the existence of measurable levels of divalent Hg species in air. Although the earliest data has since proved to be quantitatively unreliable, we now realize that divalent species do exist in ambient air in low but important concentrations, and methods have been published which are now in routine use for these compounds (e.g. Stratton and Lindberg 1995, Landis and Stevens 2000). These studies have demonstrated that so called RGM can represent a few percent of total airborne Hg in ambient air distant from local sources (concentrations around 20-50 picograms per cubic meter (pg/m^3), but can reach levels several hundred times higher near point sources. More importantly, RGM, because of its higher water solubility and reactivity, exhibits a far higher dry deposition velocity and wet deposition washout coefficient than does $Hg°$, and may contribute to local ecosystem loading far in excess of its contribution to the atmospheric burden (Lindberg and Stratton 1998).

For these reasons, regulatory agencies and the scientific community as well have sought to emphasize the importance of RGM over that of its relatively inert and longer lived cousin, $Hg°$. Many have suggested that emission controls should first target RGM, then later address $Hg°$ which will be far more expensive to remove. For these and perhaps other reasons, some have also suggested that other sources of atmospheric emissions which are solely in the form of $Hg°$, such as geologic sources, historic and orphaned mine wastes, and active mining concerns, represent a lower regulatory priority. This is because the $Hg°$ emitted during these activities, being relatively insoluble and inert, simply joins the global pool where it is slowly oxidized to forms later removed by wet deposition in remote regions. However, the recent discovery of so-called mercury depletion events in the Arctic (Schroeder et al. 1998), and the first positive confirmation that the depleted Hg is converted to RGM and accumulated in local snowpack (Lindberg et al. in press), suggests that any and all sources of emitted $Hg°$ to the global atmosphere, including those diffuse emissions from mining activities, have the very real potential to rapidly accumulate in the biosphere.

Conclusions

All these advances and their recent applications have provided important clues to the behavior of Hg in the global biogeochemical cycle. There is no longer any doubt that Hg, once deposited, has the capability to be re-emitted from environmental surfaces, and that re-emission is significantly enhanced by green plants via a transpiration-like process. There is also no doubt that Hg associated with geological sources demonstrates a similar capacity. What is in doubt is the relative role of these so-called natural emissions in the global cycle, and to what extent "natural" emissions include re-emitted Hg. On the other end of the Hg "behavior scale," recently measured levels of RGM compounds support the hypothesis that the dry and wet deposition of Hg may be strongly influenced by the behavior of RGM and that elevated regional exposure may be possible near major point sources of RGM compounds. Source measurements have indicated that RGM is formed in combustion processes, and the recent discovery of so-called Hg-depletion events in the Arctic suggests that there may be atmospheric reaction pathways for the direct production of RGM from $Hg°$. All of these factors must be included in analyses of the risks and rewards of various control and regulation strategies.

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3.6   Watershed Impairment: Development Management Tools and Priorities

3.6.1   Mercury Contamination in Lahontan Valley Wetlands - Peter L. Tuttle (Presenter), Nevada Fish and Wildlife Office, U.S. Fish and Wildlife Service; Damian K. Higgins, Nevada Fish and Wildlife Office, U.S. Fish and Wildlife Service; and Jennifer L. Quashnick

Introduction

From about 1860 to 1900, mercury amalgamation was used in gold and silver ore milling operations in the Comstock Mining District (e.g., Virginia City) in the Carson River basin, Nevada. At least 7,500 tons of elemental mercury were imported to the region for ore processing, of which little was ultimately recovered (Bailey and Phoenix 1944). Much of the unrecovered mercury was discarded in mill tailings or discharged to the Carson River or its tributaries in mill effluent. Mercury has since become widely distributed in the lower Carson River basin. Investigations by the Department of the Interior (DOI) documented extensive mercury contamination in Lahontan Valley, including wetlands on Stillwater and Fallon National Wildlife Refuges (NWR; Hoffman et al. 1990, Hallock et al. 1993, Hoffman 1994, Tuttle et al. 1996, Tuttle et al. 2000). These shallow, alkaline wetlands provide ecologically important habitats for a diverse assemblage of migratory birds and resident wildlife. The DOI investigations documented that mercury concentrations in water, sediment, food chain organisms, fish, and migratory birds consistently exceeded levels associated with adverse effects to fish, wildlife, and their habitat. However, the severity of contamination varied widely with location.

130

In the 1990s, Federal and State agencies initiated efforts to restore wetlands in Lahontan Valley. These efforts include the purchase of sufficient water to restore and maintain 25,000 acres of wetlands, including 14,000 acres on Stillwater NWR. The acquisition of water is also expected to benefit water quality and reduce concerns with poor-quality agricultural drainage. However, water acquisition is not expected to alleviate concerns with existing mercury contamination in wetlands. In 1999, the Fish and Wildlife Service and the EPA initiated a joint investigation to: 1) evaluate the extent and severity of mercury contamination, 2) assess biological availability of mercury, 3) evaluate the interaction of total mercury (HgT) and MeHg in biotic and abiotic media, and 4) evaluate the ecological implications of contamination in important wetlands in Lahontan Valley. Information generated from this investigation will be used to identify and evaluate remedial options for mercury contamination in Lahontan Valley.

Methods

Water (filtered and unfiltered), surficial sediment (< 3 cm), and whole aquatic invertebrate (Corixidae, *Corisella* spp.) samples were collected from 19 major wetlands on Stillwater NWR from June to August, 1999. *Corisella* samples were collected from 20 other major wetlands in Lahontan Valley, including the Carson River corridor, Carson Lake wetlands, constructed wetlands on the Fallon Paiute Shoshone Indian Reservation, water management reservoirs, and hydrologically isolated wetlands (e.g., background sites). Temperature, dissolved oxygen, pH, and specific conductance were determined at the time of sample collection. HgT and MeHg analyses for water and sediment samples were performed by Frontier Geosciences, Inc. in Seattle, Washington. HgT and MeHg analyses for aquatic invertebrate samples were performed by Toxscan Inc., Watsonville, California.

Results and Discussion

Mercury in Sediment on Stillwater and Fallon NWR

The most severe HgT contamination in the Lahontan Valley agricultural area generally corresponded to water courses associated with historical (1850-1915) Carson River channels (Hallock et al. 1993). HgT concentrations in Stillwater and Fallon NWR sediments ranged from 55 to about 22,000 ng/g. The most severe HgT contamination on Stillwater and Fallon NWR occurred in areas closely associated with the historical water course (e.g., Carson River and Stillwater Slough) and declined along the flow path through the historical marsh complex. HgT concentrations were significantly lower in wetlands constructed in the 1940s. HgT concentrations in all wetlands exceeded the estimated background concentration for Lahontan Valley soils of 40 ng/g (Lico 1992).

MeHg concentrations in sediment ranged from 0.09 to 10.60 ng/g and concentration gradients were found on Stillwater NWR. Although sediment HgT concentrations were significantly higher in historical wetlands, the ratio of MeHg to HgT (percent MeHg) in samples from constructed wetlands was significantly higher. No difference in sediment MeHg concentrations was found between historical and constructed wetlands. When samples from Fallon NWR were excluded, a strong relationship (r^2=0.91) was found between HgT and MeHg concentrations in sediment. Depression of microbial activity and subsequent methylation rates at higher HgT concentrations (>15,000 ng/g) may, in part, account for the lower percent MeHg observed in Fallon NWR sediments (Chen et al. 1996). HgT concentrations in the Stillwater NWR wetland sediments were lower than concentrations associated with significant inhibition of methylation. MeHg concentrations in sediment were negatively correlated with pH of the overlying water column.

Mercury in Water on Stillwater and Fallon NWR

HgT concentrations in the water column ranged from 17 to 16,400 ng/g. MeHg concentrations ranged from 0.8 to 9.0 ng/g. Although HgT concentrations were significantly greater in historical wetlands, no difference in MeHg concentrations was found between historical and constructed wetlands. The majority of HgT occurring in the water column was in a particulate phase (e.g., non-dissolved). The proportion of HgT in a particulate phase in the water column increased with turbidity. Consistent with this, we found significant relationships between HgT in water and HgT in sediment (r^2=0.65), turbidity (r^2=0.67), and the combined effect of HgT in sediment and turbidity (r^2=0.87). Within the shallow wetlands of Stillwater and Fallon NWR, turbidity is largely controlled by wind and associated agitation of bottom sediment (Tuttle et al. 2000). Therefore, wind may be a dominant factor controlling HgT in the water column in wetlands.

Factors controlling MeHg in the water column on Stillwater NWR are less certain. Although we found a strong relationship between HgT in sediment and water, our data did not reveal a significant relationship between MeHg in the water and HgT or MeHg in sediment. HgT and MeHg concentrations in the water column did not appear to be controlled by pH, dissolved oxygen, or specific conductance.

Mercury in Aquatic Invertebrates on Stillwater and Fallon NWR

HgT concentrations in *Corisella* ranged from <500 to 1,400 ng/g, dry weight. Concentrations were less than the method detection limits in about a third of the samples. MeHg concentrations ranged from 130 to 1,450 ng/g. In those samples with detectable HgT and MeHg concentrations, the majority of HgT (~100%) occurred as MeHg. A concentration gradient of MeHg in *Corisella* was apparent along the flow path in both the historical and constructed wetland complexes on Stillwater NWR. MeHg concentrations in *Corisella* were significantly greater in constructed wetlands than in historical wetlands. We found a significant, but weak relationship (r^2=0.42) between MeHg concentrations in *Corisella* and MeHg in sediment. Stronger relationships were found when historical and constructed wetlands were examined independently (r^2=0.58 and 0.89, respectively). We also found a weak inverse relationship between MeHg in *Corisella* and water column pH (r^2=0.36). Statistical strength increased (r^2=0.63) when MeHg concentrations in *Corisella* were examined using multiple regression with MeHg in sediment and pH as independent variables. These results suggest that sediment contamination plays a role in the availability of mercury in Lahontan Valley wetlands. However, alkaline conditions in wetlands may moderate availability. The relationship between MeHg or HgT in water and MeHg or HgT in *Corisella* was not significant, suggesting that water was not the primary exposure pathway. *Corisella* are predaceous and may be expected to acquire mercury through diet. Bioaccumulation factors (BAFs) for MeHg in sediment to *Corisella* ranged from 60 to at least 1,700 times. BAFs were significantly higher in constructed wetlands (mean = 1,098) than in historical wetlands (mean = 414).

Mercury in Aquatic Invertebrates in Lahontan Valley

Patterns of HgT and MeHg in *Corisella* from other Lahontan Valley wetlands were similar to those on Stillwater NWR. The majority of HgT in *Corisella* occurred as MeHg. The highest mean concentrations per site group were found in artificial wetlands, including agricultural reservoirs, impounded areas on the Carson River, and constructed wetlands on Stillwater NWR and the Fallon Paiute-Shoshone Indian Reservation. MeHg concentrations in *Corisella* were lower in samples from known contaminated areas, including Carson Lake, Fallon NWR, Indian Lakes, and the historical Stillwater Marsh. Again, an inverse relationship was found between MeHg in *Corisella* and pH.

Mercury Redistribution in Lahontan Valley

HgT distribution patterns in Lahontan Valley indicate that anthropogenic mercury was transported to and deposited in Lahontan Valley by fluvial processes. Elevated HgT concentrations on Fallon NWR and historical wetlands on Stillwater Marsh indicate that substantial amounts of mercury were deposited in Lahontan Valley wetlands prior to the construction of Lahontan Dam in 1915 and the subsequent modification of flow paths to wetlands. However, elevated HgT concentrations in constructed wetlands indicate that HgT deposition on Stillwater NWR has continued since river regulation. Similarly, HgT concentration gradients in constructed wetlands indicate that mercury redistribution on Stillwater NWR has also continued. Significant HgT loads continue to enter Stillwater NWR in irrigation quality water and agricultural drainwater discharged to the wetlands. From 1994 to 1996, HgT concentrations in agricultural drains entering Stillwater Marsh ranged from <100 to 3,500 ng/L (Tuttle et al. 2000). During this period, Stillwater Slough delivered a median instantaneous load of 0.009 kilograms per day (kg/day) and Diagonal Drain delivered 0.027 kg/day to Stillwater NWR. Loads entering the NWR may increase substantially following high flow events in the Carson River (Hoffman and Taylor 1998).

Implications to Fish and Wildlife

Previous investigations identified concerns with HgT in water, sediment, aquatic invertebrates, fish, and bird diet, tissue residues, and eggs in Lahontan Valley (Hoffman et al. 1990, Hallock et al. 1993, Tuttle et al. 1996, Tuttle et al. 2000). These investigations did not evaluate MeHg in biotic and abiotic samples. Concerns with mercury persisted in 1999.

The EPA chronic (96-hour) criterion for HgT in water (12 ng/L) was exceeded in all wetlands on Stillwater NWR. Only one sample from Fallon NWR exceeded the acute (1-hour) criterion. All water samples were well in excess of a 0.05 ng/L MeHg criterion proposed for protection of piscivorous wildlife (Schwarzbach 1998), based on bioaccumulation and bioconcentration of mercury in aquatic food chains.

HgT in sediment from all wetlands in the historical Stillwater Marsh exceeded a sediment effect threshold for freshwater invertebrates (200 ng/g; Persaud et al. 1993). Sediment HgT concentrations in constructed wetlands were generally near this threshold concentration. A severe effect criterion for freshwater sediment (2,000 ng/g; Persaud et al. 1993) was exceeded in samples from Lead Lake and two sites on Fallon NWR. Effect criteria for MeHg in aquatic sediment are uncertain.

Because of the importance of Lahontan Valley wetlands to migratory birds, birds are perhaps the ecological endpoint of greatest concern. Diet is likely the most important pathway for avian exposure. Reproduction is considered one of the most sensitive toxic endpoints for mercury (Wolfe et al. 1998). MeHg concentrations in half of the *Corisella* samples from Lahontan Valley exceeded a 500 ng/g dietary concentration associated with reduced reproductive success in successive generations of mallards (Heinz 1979). The majority of *Corisella* samples exceeding this dietary effect concentration were from artificial wetlands. Conversely, concentrations in samples from wetlands with high HgT concentrations in sediment were generally lower than this effect level. All samples were well below a 3,000 ng/g dietary MeHg concentration associated with reduced reproduction in a single generation of black ducks and lesions in nerve tissue of hatchlings (Finley and Stendell 1978).

HgT concentrations in *Corisella* found in our investigation (<500 to 1,400 ng/g) were generally lower than concentrations found in previous Lahontan Valley investigations. Concentrations in these investigations ranged from 200 to 10,800 ng/g (Hoffman et al. 1990, Tuttle et al. 1996, Tuttle et al. 2000). The highest HgT concentrations in *Corisella* (and other biological samples) were generally found following the reflooding of wetlands that had been temporarily desiccated.

Summary and Management Implications

Based on the findings of this and other recent studies, several conclusions relevant to the management of Stillwater and Fallon NWR and other Lahontan Valley wetlands are available.

1. Substantial amounts of mercury were deposited in Lahontan Valley prior to regulation of the Carson River. However, the transport of mercury to Stillwater NWR via water supply is continuing. The redistribution of mercury on the refuge via water movement between wetlands has also continued. The movement of turbid waters between wetlands may promote HgT redistribution.

2. The availability of mercury to aquatic invertebrates appears to be controlled by MeHg in sediment. HgT concentrations in sediment and water do not appear to provide a suitable indicator of biological risk of mercury in Lahontan Valley wetlands. As such, selective wetland management based on HgT concentrations in sediment does not appear to be an effective remedial strategy for Stillwater NWR.

3. The proportions of MeHg of HgT in sediment and MeHg availability to aquatic invertebrates (e.g., BAF) were greater in constructed wetlands despite having lower sediment HgT concentrations. As a result, mercury risk to fish and wildlife appears to be greater in constructed wetlands.

4. Alkaline conditions in Lahontan Valley wetlands or related factors may provide some degree of protection against mercury availability or toxicity. More information is needed to assess the significance of pH and other related factors and the implications to wetlands management.

5. HgT concentrations in biological samples from Lahontan Valley wetlands have fluctuated over the past decade. Variability may be related to changes in hydrologic conditions within wetlands. The effects of changes in hydrologic conditions on rates of mercury methylation, demethylation, and MeHg retention in Lahontan Valley wetlands are uncertain. More information is needed to assess implications of changes in hydrologic conditions (e.g., moist soil management) to mercury availability and ecological risk in Lahontan Valley.

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3.6.2 Downstream Indicators of Mining-Related Mercury Exposure: Findings from the Sacramento-San Joaquin Delta and Its Tributaries - Darell G. Slotton (Presenter), Department of Environmental Science & Policy, University of California; Shaun M. Ayers, Department of Environmental Science & Policy, University of California; and Thomas H. Suchanek, Department of Wildlife, Fish, & Conservation Biology, University of California

In the course of numerous mercury source, distribution, and remediation studies throughout California, the UC Davis Mercury Research Group has utilized naturally occurring aquatic organisms as key indicators of relative Hg bioavailability. There is a tremendous amount of mercury moving through California waterways, largely as a result of historic mining practices. Only a portion of this total loading may be readily available to be converted into methyl mercury by sulfur reducing and other bacteria. Of the methyl mercury that is produced, only a portion may make its way through food webs into fish and top consumers. We have found that naturally occurring aquatic biota provide ideal indicators of relative biological mercury exposure, irrespective of THg loading. Different sets of indicator organisms have been found to be preferable in answering specific questions of relative temporal, spatial, and inter-habitat variation in mercury exposure. In this presentation, we will discuss new findings from our CALFED-funded mercury study in the Sacramento-San Joaquin Delta, now entering its third year. We will also compare and contrast biological signatures of mining-derived Hg in Coast Range historic mercury mining watersheds vs Sierra Nevada gold mining watersheds. The data indicate that meaningful, point source remediation options may exist, particularly in the Coast Ranges. Recent biological Hg findings throughout the Delta provide a new picture of the downstream dynamics of mining-derived Hg. We will also discuss supporting data from aqueous and sediment chemical assays, mass loading determinations, and laboratory methylation experiments.

Mercury contamination in both the Sierra Nevada and California Coast Ranges presents a biological signal that is clearly linked to historic mining. Low background levels of bioaccumulation have been established for both regions, with elevated concentrations present almost exclusively in association with known mining zones and, in certain cases, natural geothermal activity. Recent deep sediment core studies from pristine Lake Tahoe show that atmospheric deposition of mercury has increased dramatically over the past 100 years, but that this increase is consistent with global atmospheric mercury patterns rather than localized inputs (Heyvaert et al. 2000). In contrast, even the intense period of mercury mining, refining, and re-volatilisation associated with the California Gold Rush left only a trace signature of atmospheric deposition in the sediment record. However, at sites that now receive only atmospheric and geologic weathering sources of mercury, upstream of mining influences, biological signatures of mercury uptake are consistently very low in both Sierra Nevada and Coast Range watersheds. It appears that the typical California suite of water quality conditions is not conducive to the accumulation of problem levels of fish mercury from generalized sources including atmospheric deposition. This is in contrast to other regions where trace atmospheric deposition of mercury, alone, is sufficient to result in highly concentrated fish mercury. This includes the midwestern and northeastern portions of North America, Florida, and Scandinavia. In California, we have found that notably elevated Hg concentrations in biota are consistently associated with the additional bulk mercury contamination specifically associated with historic mining.

Sierra Nevada gold mining Hg demonstrates a dispersed signal today across many tens of river miles in each contaminated drainage (Slotton et al. 1995). A century or more after the major mining activity there, the biological record indicates that the historic mercury has not entirely left these systems. Instead, a pattern of notably elevated biotic mercury exists in certain drainages. In particular, the Yuba and Bear River watersheds remain notably contaminated at this time, relative to most other northwestern Sierra Nevada rivers. This is not surprising, in that these drainages are those closest to the Grass Valley/Nevada City historic hub of gold mining activity. Another elevated mercury region with the highest overall Sierra Nevada concentrations in stream biota was the Cosumnes River. Biota from the American and Feather River water-

sheds were considerably lower in mercury accumulation, and sites well upstream of historic mining in all Sierra Nevada watersheds investigated were uniformly lowest of all. While some strong point sources exist in the Sierra Nevada historic gold mining region, the primary distribution of residual contamination across the lengths of many rivers suggests that drainage-wide remediation may not be feasible here. Relative differences in invertebrate and fish mercury bioaccumulation across the region described a clear ranking of residual biological mercury contamination, though absolute fish mercury concentrations in the lotic environments were generally well below levels of concern. The major Sierra Nevada reservoirs which were built during the 20th century act as depositional sinks for residual mining related mercury moving downstream. These reservoirs can be expected to be important sites of mercury methylation. Recent work by USGS confirms several of these reservoirs to have dramatically elevated mercury in some fishes. Surprisingly, bioindicator mercury below Sierran reservoirs was uniformly low, suggesting that localized mercury methylation in those systems may primarily be incorporated within the reservoir food webs, with relatively little being exported. While potential fish concentrations of concern exist within certain reservoirs, fish mercury in Sierra Nevada streams and rivers was generally well below health guidelines or screening levels.

Coast Range Hg exhibits strong point sources in addition to drainage-wide distributions, with dramatic spike elevations in biotic mercury in association with abandoned mercury mines (Slotton et al. 1997, 1998). Certain of these sites appear to be important potential remediation targets. However, as the mercury mines necessarily occur in regions that are geologically enriched in mercury, a legitimate question is: "What is the point of remediating an abandoned mine (at considerable expense) if the entire watershed is a natural source of generalized mercury export?" We investigated this question in the Marsh Creek watershed of Contra Costa County, California. In mass loading studies during storm season runoff flows, we found that 95% of the entire downstream mass loading of mercury in the watershed was derived from the one mercury mine source, Mt. Diablo mercury mine, with 88% of the load attributable to a single mine tailings pile. This was despite the fact that 95% of the drainage's water volume and suspended sediment load derived from non-mine tributaries. Further, it was found that mercury was being transported from the tailings almost entirely in dissolved form. This dissolved mercury quickly partitioned onto co-precipitating iron oxyhydroxides upon mixing of mine flows with neutralizing stream flows, but surface-adsorbed mercury in this form may be significantly more available for methylation than other particulate mercury loads. These questions are being addressed in current CALFED-sponsored work in the Cache Creek drainage. In any case, the Mt. Diablo findings indicate that abandoned mercury mining sites in the California Coast Ranges may represent dominant ongoing sources of downstream mercury export relative to generalized, natural watershed sources, and that the form of this mine-derived mercury may be more bioavailable to methylating microbes.

In studies conducted in the Sacramento-San Joaquin Delta, downstream of both primary source regions, sediment Hg methylation potential was found to be 4-30 fold greater in organic-rich, depositional wetland areas, as compared to adjacent channels and flats, potentially confirming concerns over large-scale wetland restoration projects (Slotton et al. 2000). There is the concern that large wetlands restoration projects in the downstream depositional areas may result in significantly elevated mercury methylation to the overall system. However, flooded Delta tracts have thus far not been found to generate higher levels of localized Hg bioaccumulation, though their role in regional mercury methylation may be large. Flooded Central Delta tracts were among the lowest Hg bioaccumulation regions. Preliminary data suggest that net Hg bioaccumulation in the Delta may be relatively habitat-independent. The strongest apparent association was with general spatial proximity to Coast Range and Sierra Nevada mining sources, with an important additional elevated Hg bioaccumulation region in the West Delta, possibly linked to the fresh/saline transition and/or the entrapment zone.

Ongoing research seeks to define the most meaningful and cost effective potential remedial targets in the upper watersheds. Another major focus is the identification of primary mercury methylation regions and habitats throughout the system. Finally, the relative contribution of ongoing mercury inputs must be understood relative to that mercury already deposited in the Bay-Delta, and the potential for the system's meaningful recovery if those source terms could be significantly reduced.

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3.7 Remediation and Treatment

3.7.1 Reducing Mercury Production at Bald Mountain Mine - Jim Wickens, Bald Mountain Mine

Abstract

This paper discusses how Bald Mountain Mine dramatically reduced mercury production by treating process solutions with a liquid reagent called UNR 811A. The reagent is marketed by Cherokee Chemical Co., Inc. A summary of the bench tests comparing several different reagents is given. The ensuing plant trial is discussed and results are presented. The plant trial treatment costs are discussed. Finally, potential cost savings are discussed.

Introduction

Bald Mountain Mine produces gold. Mercury is a costly by-product of the gold production because no revenue is generated from the mercury. Minimizing or eliminating mercury production minimizes worker health and safety risks, reduces environmental liability, and reduces costs. In the long term, minimizing mercury production will make mine closure easier and less costly.

Bald Mountain Mine dramatically reduced mercury production by treating the process solutions with liquid reagents called UNR 811 and UNR 811A. Several reagents were bench tested before proceeding with a plant trial. Results from the bench tests and the plant trial are presented and discussed. Plant trial treatment costs are presented and discussed. Finally, potential cost savings are discussed.

The reagent complexes the mercury to form an organic sulfide precipitate. In independent tests, the precipitate passed acid mobilization tests and is considered stable.

Bench Tests

All of the results are presented as a percentage of mercury (or other metal) removed. Because the data were inconsistent and very difficult to analyze, it is impossible to give exact figures. However, values for mercury in the loaded eluate ranged from 4 ppm to 58 ppm. Mercury values in the heap pregnant solution ranged from 0.6 ppm to 0.8 ppm.

Test #1

Initially, the focus was on treating the carbon strip solution (loaded eluate) using Cherokee's UNR 1221. The UNR 1221 removes mercury from solution by complexing the metal as an organic sulfide precipitate. The concept was to eliminate mercury production by removing mercury from the loaded eluate prior to the electrowinning cells. The mercury selective component in UNR 1221 is sodium dimethyldithiocarbamate.

137

Although Cherokee Chemical Co., Inc. markets this product, application of the chemical was developed by the UNR. Subsequently, UNR was issued a patent for use of this chemical, and other dialkyldithiocarbamates, to remove mercury from gold bearing cyanide solutions. The results of Test #1 are summarized in Chart 1.

CHART 1
Hg Removed from Loaded Eluate - Test #1

ppm UNR 1221 Used
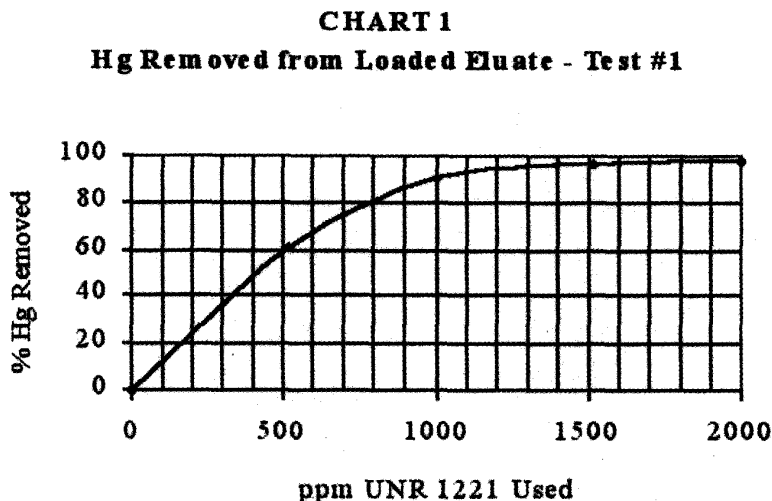
Test #2

The results from Test #1 justified a second test. Several other products were available for trial. Subsequently, Test #2 incorporated Cherokee's UNR 1221, UNR 1620, UNR 811, UNR 616, and Ashland Chemicals' MP-9. The MP-9 was a thiocarbonate product as opposed to the carbamate based UNR 1221. Table 1 below summarizes the products and their primary constituents.

Table 1.

Product	Primary Constituents
UNR 1221	Sodium dimethyldithiocarbamate
UNR 1620	Potassium dimethyldithiocarbamate
UNR 811	Carbono trithioic acid, disodium salt
UNR 616	Combination of UNR 811 and UNR 1221
MP-9	Carbono trithioic acid, disodium salt

In addition to the loaded eluate, the various products were tested on heap leach pregnant solution. The concept was to eliminate mercury production by removing mercury from the heap leach pregnant solution prior to carbon adsorption. This concept was very appealing because implementing the technology would require almost no capital expense. The reagent would be added to the pregnant solution from a tote. The precipitate is very fine and would be carried through the column sets to the barren solution spray pumps. Subsequently, the precipitate would be captured in the heaps.

The loaded eluate option would require the precipitate to be filtered from the loaded eluate prior to electrowinning. This would require capital expense for the filter equipment, facility modifications, and sludge handling equipment.

Furthermore, the loaded eluate option does not eliminate worker exposure to mercury, but the heap leach pregnant solution option would.

The reagents complex the mercury to form organic sulfide precipitates. In independent tests, the precipitates passed acid mobilization tests and were considered stable.

The results from Test #2 are summarized in Chart 2 and Chart 3 below.

138

CHART 2
Hg Removed from Loaded Eluate - Test #2

% Hg Removed
100
80
60
40
20
0

ppm Product Used
0   500   1000   1500   2000

UNR 1221   M P-9   UNR 811
UNR 616   UNR 1620

CHART 3
Hg Removed from Heap Preg. - Test #2

% Hg Removed
100
80
60
40
20
0

ppm Product Used
0   500   1000   1500   2000

UNR 1221   M P-9   UNR 811
UNR 616   UNR 1620
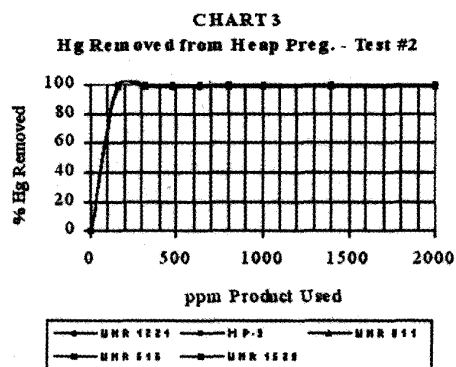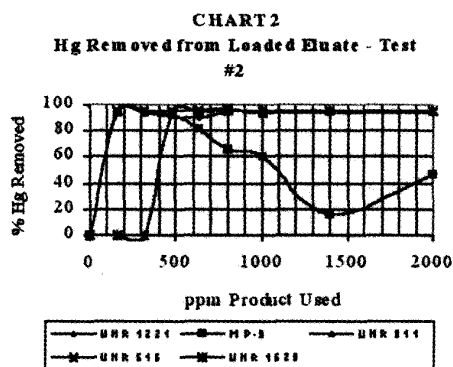
Except for UNR 1620 and MP-9, Chart 2 shows there was no significant difference between the different products treating loaded eluate. The mercury analyses for the 160 ppm and 320 ppm doses of UNR 1620 were extremely anomalous and it was assumed no mercury was removed. This assumption is likely invalid. The MP-9 demonstrated similar performance at lower dosages, but the amount of mercury removed significantly decreased as product dose increased.

Chart 3 shows there was no significant difference between any of the products treating heap leach pregnant solution. The dosage range was much too high for the mercury concentration. Simply stated, this was an oversight in test protocol.

In addition to mercury, the test solutions were analyzed for gold, silver, and a host of other elements. Gold concentrations were not affected by any of the products in either the loaded eluate or the heap pregnant solution. There was some indication that all reagents in both the loaded eluate and the heap pregnant solutions affected silver. Silver concentrations typically decreased with increased dosage. The effect on silver recovery would be further investigated. Also, there was some indication that the Cherokee products may reduce copper in the heap pregnant solution with increased dosage. Ashland's MP-9 did not seem to affect copper in the heap pregnant solution. In the loaded eluate, the UNR 616 and MP-9 may reduce copper concentration with increased dosage.

Test #3

The amount of tests and data analysis was becoming onerous. It was decided that this phase of tests would be restricted to one Cherokee product and Ashland's MP-9. Cherokee was asked to select their most competitive product. They selected UNR 811. The products were tested on loaded eluate only. For reasons undisclosed, management did not feel comfortable treating the heap leach pregnant solution.

A head sample was analyzed for mercury prior to treatment. From this analysis, a range of doses was selected to try and delineate the optimum dose.

The results from Test #3 are shown in Chart 4.

139

CHART 4

Hg Removed from Loaded Eluate - Test #3
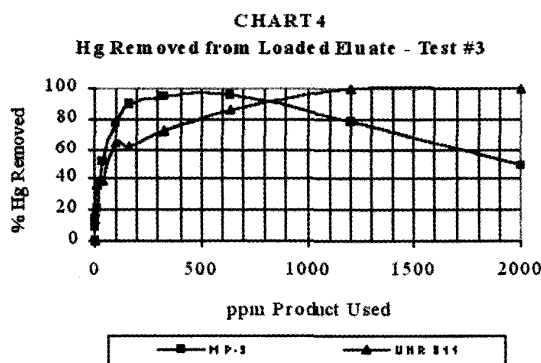
Chart 4 shows that MP-9 is more effective than UNR 811 at lower doses, but performs poorer at higher doses. As in the previous test, the MP-9 performance curve peaks just short of 100% mercury removal. At high doses, UNR 811 virtually eliminates all the mercury. Using MP-9 in an industrial application would require good control to avoid overdosing and wasting money. The UNR 811 would be more forgiving. Excess UNR 811 does not hurt performance, and the residual would be eventually consumed by soluble mercury somewhere in the process.

As in Test #2, other elements were monitored. Besides mercury, silver was the only other metal significantly affected. Chart 5 shows the effect of UNR 811 dosage on silver concentration. There is little or no effect up to 100 ppm. Plant doses are usually much less than 100 ppm. Therefore, silver recovery should not be significantly affected. However, it must be acknowledged that silver could be significantly affected by very high doses.

CHART 5

Ag Removed from Loaded Eluate - Test #3
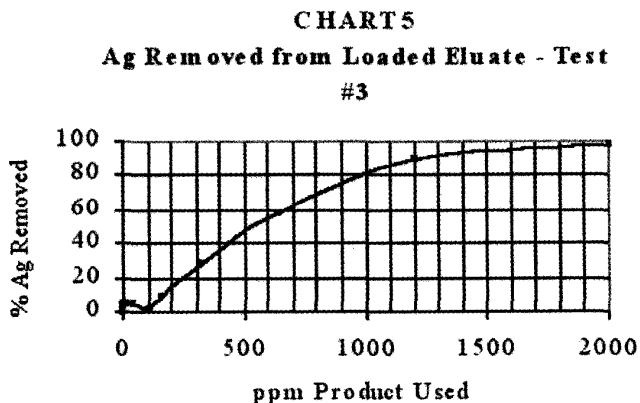
Test #4

Test #4 is another comparison between MP-9 and UNR 811. The purpose of this test was to try to replicate the results in Test #3. Also, Degussa's TMT 15 was added to the test. Degussa had heard of the tests and requested their product be included. Chart 6 on the next page summarizes the results.

140

CHART 6
Hg Removed from Loaded Eluate - Test #4
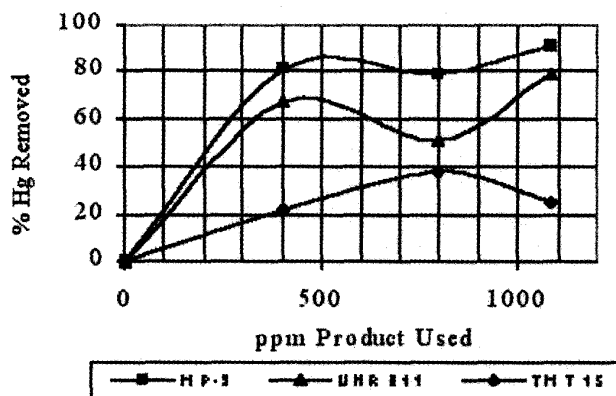
Chart 6 shows MP-9 was again more effective than UNR 811. The decrease in performance for both products at 800 ppm seems anomalous. TMT 15 was not competitive. Unlike the previous two tests, MP-9 did not show a peak in performance. Most likely, this is because the dosage range was not high enough to capture the peak. Also, the performance of MP-9 and UNR 811 did not replicate Test #3.

Plant Trial

Justification

Approximately 18 months had elapsed since the bench work began. A great deal of money had been spent on mercury analyses. It was taking four to six weeks to receive mercury analyses, and when they arrived, the analyses sometimes generated more questions than answers. Replicating results seemed impossible. A small amount of frustration was setting in, and it seemed like the bench tests could go on forever without producing anything quantitative. Besides, plant performance could be drastically different than the lab. However, the bench work proved the products remove mercury from process solutions. The only questions were, "How much and at what cost?" There were two courses of action. A plant trial could be performed to generate "real life" costs, or the project could be "back burnered" in favor of more pressing issues.

Cherokee and Ashland tabled proposals for a plant trial treating the loaded eluate. Using the results from Test #4, annual treatment costs were calculated. UNR 811 proved to be more cost effective. Although less MP-9 was required to remove an equivalent amount of mercury, the unit cost of MP-9 was significantly higher resulting in higher overall cost. In addition to the higher cost, overdosing MP-9 could result in decreased performance. Both proposals included all dosing equipment and an on-site method to measure mercury in the reagent cost. However, Cherokee proposed a cold vapor AA, which was more attractive than the Hach titration method proposed by Ashland.

Unfortunately, the annual cost to treat the loaded eluate with UNR 811 plus the required capital expense to use it far exceeded any potential savings. Treating the loaded eluate was not going to happen. However, another attempt was made to convince management to treat the heap leach pregnant solution. It seemed a total waste of effort to abandon the project without knowing what would happen in "real life." Even if the plant trial proved uneconomic, the information would be valuable. Intuitively, a plant trial was the right thing to do.

The costs were scaled from Test #4 to fit current mercury levels in the heap pregnant solution. Also, current operating costs from Beartrack Mine in Idaho were factored into the analysis. Beartrack was using UNR 811 with a great deal of success. Annual treatment costs for heap pregnant solution, based on the bench tests, were in the order of $120,000. In the end, management agreed to commit $20,000 for a plant trial. Expectations were that this would provide enough product to see a significant decrease in refinery mercury production and provide "real life" costs. In addition, it was felt that the $120,000 annual cost was very conservative. Actual costs were expected to be much lower. When the actual mercury levels were analyzed, it

141

became clear that mercury recovery to carbon was only about 20%. Therefore, the current levels were a function of a circulating load of mercury that had accumulated over a long period of time. Once the load was removed, mercury levels should drop significantly and stay low. Accordingly, the required amount of reagent should drop significantly. All analyses aside, the definitive proof would be reduced mercury production from the retort.

Implementation

At the time of the plant trial, Bald Mountain Mine was producing from two separate heap leach facilities, Process #2 and Yankee. The plant trial would take place at Yankee for several reasons. First, approximately 55% of the mercury produced came from Yankee. Secondly, Yankee was in the initial stages of closure, and the decreased gold concentration resulted in higher mercury recovery. Finally, any mercury removed by the reagent could dramatically improve closure time.

In addition, Cherokee introduced a new product, UNR 811A. UNR 811A was UNR 811 combined with an undisclosed amount of sodium diethyldithio-carbamate. The plant trial would incorporate head-to-head evaluation of these two products.

Some consideration was given to treating the barren solution, but treating the pregnant solution was more attractive. The intent was to complex the mercury before it had a chance to adsorb onto the carbon. Given the limited funds available for the plant trial, this appeared to be the best option for quick results. The risk was possible fouling of the carbon with the precipitate. However, the precipitates formed in the lab were very fine. Expectations were that the precipitate would carry through the column sets and get pumped to the heap. The barren solution option would likely work, but any effects would take much longer to materialize.

Results

There was no significant difference between UNR 811 and UNR 811A. The effect on refinery mercury production was almost immediate and dramatic. Chart 7 shows the reduction in refinery mercury production after treatment began on 17 May 1999 (denoted by the square). Prior to treatment, mercury production was typically 50 pounds per month or more. Immediately prior to treatment, production for April 1999 was 172 pounds. At the end of the first full month of treatment, production was down to 26 pounds. Refinery mercury production has ranged from 2 to 8 pounds per month since June 1999.

CHART 7
Monthly Refinery Hg Production
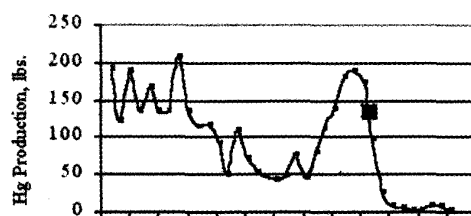
CHART 8
Hg Level - Yankee Process Preg
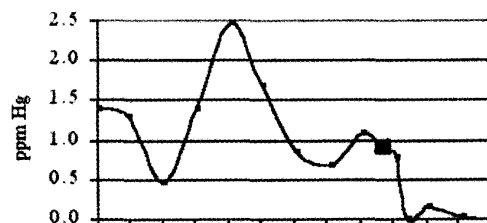
Chart 8 shows the reduced mercury content of Yankee pregnant solution after treatment began (denoted by square).

Based on the success experienced from treating Yankee pregnant solution, the plant trial was expanded to include Process #2. Again, the pregnant solution was treated prior to the carbon columns. At the time, Process #2 was expected to generate more mercury because of an ore change. Chart 9 shows the effects of treatment on mercury in the pregnant solution during treatment (between squares).

During the plant trial, overall recovery from the leach pads decreased. There were some skeptics questioning the effects of the reagents on gold recovery. To appease the critics, several cold AA leach tests comparing with reagent and without reagent were performed immediately. Out of 24 pairs, 22 showed higher AA values with reagent than without reagent. The other two were within AA machine sensitivity. Later, several

bottle roll tests were performed to support the cold AA findings. Again, the bottle roll results suggested the reagent improved recovery (if it had any effect at all). In retrospect, the poor leach pad recovery was (is) a function of preg robbing organic carbon in the LJ Ridge orebody.

Concerning silver recovery, Chart 10 summarizes gold and silver production.

The data do not indicate any problems with silver production. Although there is a dip in silver production during the trial period, the same dip occurs the previous year during the same time frame. This corresponds to mining in LJ Ridge Pit as opposed to Top Pit. Top Pit ore has more silver.

CHART 9

Hg Level - #2 Process Preg
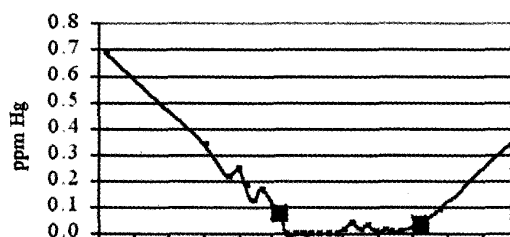
CHART 10

Monthly Gold and Silver Production
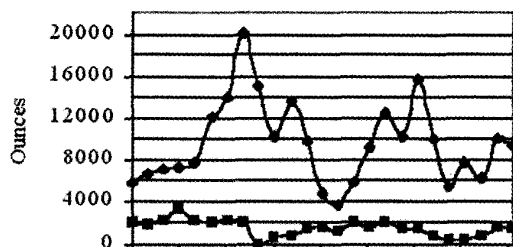
Another potential benefit associated with removing mercury from the process solution is higher recovery. Chart 11 summarizes Yankee gold recovery 38 days before and 38 days after treatment started (note: this chart was made at the time people were questioning the effects on recovery). Intuitively, less mercury competing for active sites on the carbon should improve gold recovery.

The chart shows gold recovery decreasing prior to commencing treatment, and this is because the heap is in closure. The trend continues after treatment started, but takes a sharp rise about a week later. It is unlikely the reagent was solely responsible for this improvement, but no other information is available. Perhaps carbon and/or irrigation was cycled.

Another phenomenon observed was the apparent mercury removal from carbon in the columns. Chart 12 below shows the difference in mercury levels before and after the carbon columns.

CHART 11

Yankee Process Gold Production
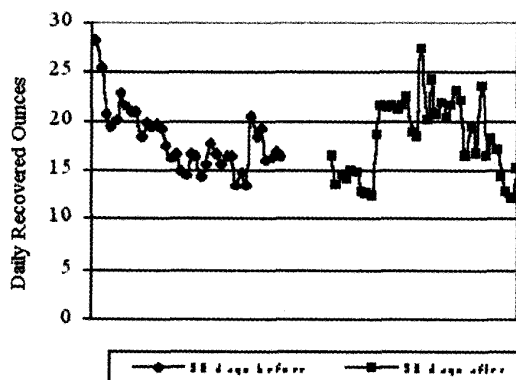
CHART 12

#2 Process Hg Levels
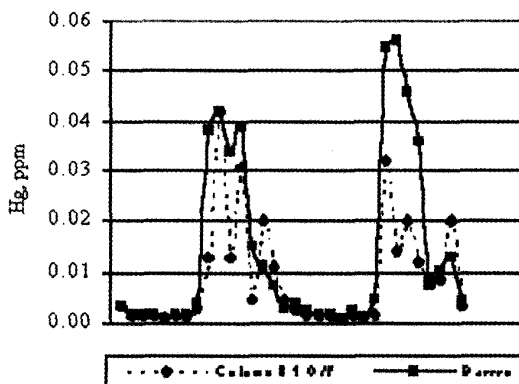
It is theorized that removing mercury from the solution upsets the solution chemistry equilibrium. Subsequently, mercury desorbs from the carbon to maintain that equilibrium.

143

Costs

Combining the Yankee and Process #2 plant trials, the total quantity of heap pregnant solution treated was approximately 590.5 million gallons. The weighted average mercury concentration was 0.40 ppm at the beginning of the trial and 0.01 ppm at the end. Approximately 1,900 pounds of mercury was removed at a reagent cost slightly under $10 per pound or 3¢ per 1,000 gallons treated. The total reagent cost was about $18,500.

In comparison, traditional closure uses fresh water rinsing and carbon adsorption to remove the mercury. The labor, power, and supplies are expensive. Even taking the gold produced during rinsing into account, a conservative equivalent cost to remove the same quantity of mercury would be approximately $4,000 per pound removed or $7.6M.

In addition, closing heaps as fast as possible is prudent. The ever-changing regulations and deteriorating public perception makes it harder and more expensive for mines to meet closure criteria.

Summary

Treating heap leach process solutions with mercury selective reagents to form stable organic sulfide precipitates is a very economic alternative to traditional closure practices. The potential cost savings are considerable.

The reagents tested appear to reduce other metals such as arsenic, nickel, and iron. This is more apparent in solutions with low cyanide concentrations. In the plant trial, there was no noticeable effect on gold, but intuitively, gold recovery to carbon should improve with less competition from other metals. The bench tests indicate silver recovery could be significantly affected by reagent doses exceeding 100 ppm.

Furthermore, the circulating load revelation has changed the approach to applying the technology to milling applications. For an operation like Cortez Gold Mines, it is not the small amount of mercury leaching from the ore in the mills at any particular point in time that presents the main problem. The main problem is the higher levels of mercury in the internal and external reclaim water systems that have built-up over time. So, by treating the reclaim water systems, Cortez was able to significantly reduce refinery mercury production.

Minimizing mercury production has several other benefits too. Without going into detail, some of these are:

- minimizing worker health and safety risks
- improving public perception and relations
- reducing environmental liability, short-term and long-term
- staying in business

Again, this technology is extremely promising for removing dissolved metals from process solutions. For example, products are available that selectively remove arsenic. These products require further investigation. Also, the precipitates formed from this method of treatment need to be subjected to other environmental tests such as meteoric water mobility and mobility under oxidizing conditions. The long-term stability of the precipitates must be defined before environmental stakeholders will "buy in." At the time of writing, a joint test program between Placer Dome U.S. Inc., Bald Mountain Mine, The UNR (Dr. Glenn Miller), and Cherokee Chemical Co., Inc. is underway investigating these concerns.

Acknowledgements

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3.7.2 Assessment and Remediation at the Mother Lode Mine, Crook County, Oregon - N. Toby Scott, Oregon Department of Environmental Quality (DEQ)

Background

Large deposits of mercury bearing rock types occur in the southwestern, central and southeastern parts of Oregon. The majority of the mercury is found in Tertiary aged host rocks including volcanic flows, breccias, plugs, tuffs, tuffaceous lakebed sediments, and marine and fluvial lakebed sediments. Cinnabar (HgS) is the most common mercury bearing mineral found and is usually deposited from mineralized hot waters which entered into fault zones, fractures, voids and in some places replaced the host rock as solutions cooled (Brooks, 1963).

Although little mining or processing has occurred in the last 20 years, the mining activities of the last century have left behind potential impacts to human health and the environment. The Oregon DEQ has recently begun the evaluation of approximately 40 former mines and 120 former prospects identified by the State's Department of Geology and Mineral Industries (Brooks, 1971). Although 90% of the production is from five mines, many of the smaller mines and prospects may pose an adverse effect on human health and the environment. The major criteria used to prioritize sites includes the reported production, amount of ore material excavated, proximity to vulnerable habitat, amount of disturbance to the land, and other site conditions that may present an unacceptable risk for current or future human health or the environment. DEQ Site Assessment program is conducting initial sampling at most of the former mine sites and at some of the larger prospect sites. Initial activities include site reconnaissance and preliminary sampling. The mine sites will be placed on the state's Environmental Cleanup Site Information database and based on the site discovery process will place a priority on each site for further assessment. DEQ has been working cooperatively with the USFS and BLM, to assist in the assessment process, since many of the sites are on Federal land administered by one of the agencies.

The Mother Lode Mine (MLM) is an example of how the USFS Ochoco National Forest (ONF) and DEQ have worked cooperatively to assess, evaluate risk pathways and concur on an effective remedy to meet both State and Federal standards. Although there are other contaminants at the site that were included in the recent remedial action, this paper will focus on the assessment and remediation of the contamination related to the mercury from mining operations.

History and Setting

The MLM, located in the Johnson Creek Area within the Ochoco mining district, was the location where mercury was first discovered in 1900. The MLM was one of four productive mines located along a north east trending zone of faulting and thermal alteration within the Eocene Clarno Formation. The occurrence of cinnabar deposits (mercury sulfide) is confined to broad, hydrothermally altered zones of faulting and fracturing defined by the structural trends (Brooks, 1963). The cinnabar is present in small, scattered ore bodies as fracture filling, thin veinlets, and coatings. The ore bodies typically occur in crushed, altered fault breccia and gouge, rich in clays, silica, and carbonates.

Since the discovery in 1900, at least 15 companies, individuals, or other entities have owned, operated, or leased the Mother Lode Mine Site, with several brief periods of inactivity (Brooks, 1963). Mining has consisted of both underground and surface mining. On-site milling processes over the years have included the use of a Gould rotary furnace, a double D-Tube Retort, a multiple Herreshoff furnace, a number of condensing systems, jigs, a disintegrator and a table concentrator (CES, 1997). At various times in the past, ore has been trucked off-site for further processing. Currently, the assorted entrances to the more than 3,000 feet of underground workings are caved in or destroyed. The actual mercury production between 1900 and 1972 for the mine likely differs from the published figure of 352 flasks and could be as high as 900 flasks (Brooks, 1971 and CES, 1998).

The Mother Lode Mine Site, at an elevation of approximately 5,900 feet above mean sea level, consists of approximately 6 acres on the north slope of Lookout Mountain. The area is part of the Canyon Creek drainage. Canyon Creek, which runs along the base of the site, flows northwest into Ochoco Creek about five miles northwest of the site. In addition to the mine history at the site, there are site specific conditions

145

that made the site vulnerable to environmental impact, including: 1) proximity to hiking trail and camping area, 2) partially exposed mine workings and buildings, and 3) slopes in excess of 20% prone to erode into Canyon Creek.

In general, land uses in the area of the site are limited to forest watershed management, cattle grazing, limited timber harvesting, recreation (hiking, fishing, camping, hunting, etc.) and limited minerals prospecting.

Site Assessment Investigation

The Mother Lode Mine was initially investigated by the USFS in 1991 due to the potential environmental impacts as well as physical hazards exposures at the site. A Preliminary Assessment/Site Inspection (PA/SI) was conducted in 1991 and found that the main contaminant of concern at the site appeared to be mercury and possibly arsenic in soil at the site (HC, 1992). The results of the investigation found THg in soil up to 23,500 ppm, with background levels at about 5 ppm Hg. In 1994, a Preliminary Risk Estimate (PRE) was prepared, focusing on the risk to hikers and campers using the area in and around the Mother Lode Mine. The PRE recommended site controls, such as signs and/or fencing to reduce or eliminate risks posed by the site to the hiker/camper (HC, 1994a). ONF conducted an additional site investigation in 1994 to allow the EPA to complete a hazard ranking evaluation of the site (HC, 1994b). The report concluded that, with the exception of mercury, concentrations of metals detected in soil, sediment, and surface water at the site were generally equal to values detected in the background samples.

Subsequent investigations by the ONF conducted under the oversight of the DEQ were completed to determine magnitude and extent of mercury contamination in soil, and evaluate adit seeps, surface water and sediment in Canyon Creek (CES, 1997, 1998). The investigation found elevated mercury in soils near the former mill buildings, the D-tube retort building, and the open pit mine. Sediments in Canyon Creek downgradient of the site were also found to be up to 20 times the background concentrations. Surface water in Canyon Creek and filtered adit seeps do not appear to be impacted from mercury or acid mine drainage effects. Adit seeps containing mercury-enriched sediment flowing into Canyon Creek, as well as physical erosion at the site may be mechanisms for the elevated sediment in the creek. Mercury concentrations in Canyon Creek sediment range up to about 10 ppm, about 20 times background levels. Testing for TCLP on a subset of samples indicated that soil exceeding 1000 ppm THg had the potential to exceed the regulatory TCLP limit for mercury (CES, 1998).

Risk Assessment

A site specific risk assessment was conducted at the site to evaluate potential human health exposures as well as ecological receptors. The Risk Assessment encompassed the EPA guidance for conducting Risk Assessments, entitled *Risk Assessment Guidance for Superfund* (RAGS), and the State of Oregon's established protocol for conducting human health and ecological risk assessments under Oregon Administrative Rules, Chapter 340, Section 122. A human health risk assessment was conducted for the case of a camper residing at the site for two weeks per year, a hiker walking through the site 1 day per year, and an angler consuming catchable fish (greater than 6 inches) located about five miles downstream of the site. The camper scenario resulted in the lowest concentration of mercury in soil to achieve acceptable risk levels (500 ppm) (CES, 1997).

The following ecological receptors were considered to pose a potential threat: fish in Canyon Creek, benthic invertebrates in sediment in Canyon Creek, and terrestrial wildlife in and around the processing areas of the mine. An acceptable ecological risk threshold for site soils was set at 2000 ppm (CES, 1997).

The DEQ revised Cleanup Law (OAR 340 122-115) defines the term "hot spot" according to the Oregon cleanup rules. In the case of mercury-contaminated soil at the site a "hot spot" is defined as "10 times the acceptable risk level for human exposure to each individual non-carcinogen." Since the acceptable risk level has been set at 500 mg/kg for mercury, the "hot spot" level would be soil with a concentration of 5000 mg/kg and above. Hot spots of contamination have a preference for treatment as defined in OAR 340-122-115.

Engineering Evaluation/Cost Analysis

The Oregon DEQ and the Ochoco National Forest have been working cooperatively under a Voluntary Cleanup Agreement to conduct an Engineering Evaluation and Cost Analysis (EE/CA) to evaluate remedies

146

that will meet both Federal and State cleanup requirements. The remedial action objectives for the site are to:

- Reduce human health and ecological risk by lowering maximum concentrations of mercury in disturbed surface soils to levels determined by the Risk Assessment
- Remove ACBM within the guidelines of DEQ per (OAR) 340-32-5620 through 5650 and Oregon Occupational Health and Safety (OR-OSHA) regulations per 29 CFR 1910.100 Asbestos
- Minimize or eliminate the risk to humans caused by the attractive nuisance of abandoned deteriorating mine buildings, previous mining activities, and mercury-containing rock and soil
- Retain significant historical evidence of mining activities to the extent possible while meeting health and safety concerns
- Mitigate vegetation-bare mining and milling waste piles.

In order to determine an appropriate remedial action for the site, a limited number of remedial action alternatives were evaluated as part of the EE/CA (CES, 1998). The remedial Action Alternatives for mercury impacted soil included:

- Alt-1—Institutional Controls (ICs)
- Alt-2—On-site containment w/ ICs
- Alt-3—Excavation, Chemical/Physical Treatment and on site disposal w/ICs
- Alt-4—Excavation, Thermal Treatment and on site disposal w/ICs
- Alt-5—Excavation and Off-site Disposal.

It was estimated that there was approximately 10-20 cubic yards of soils at or above a hot spot concentration. Approximately 250 CY of soil was estimated to be present above the acceptable risk level. The alternatives were evaluated based on the following criteria: effectiveness, implementability, reasonableness of cost, long-term reliability, and implementation risk (CES, 1998). Alternatives 3, 4, and 5 were considered the best to achieve protection at the site and Alternative 3 was selected for cost and logistical reasons. In addition to the contaminated soil, the remaining buildings on site had the potential to have mercury residues as well as asbestos. The Remedial Action Alternatives for mercury impacted building materials included:

- Alt-1—ICs
- Alt-2—Demolition and on-site disposal
- Alt-3—Demolition and off-site disposal.

Alternative 3 was selected as the preferred remedial alternative due to its long term effectiveness, ease of implementation and cost relative to the other alternatives.

The proposed removal action approved by DEQ and the USFS (ONF, 1999) pertaining to the mercury impacted soils include the following:

- Excavation, stabilization and on-site disposal of all soil exceeding 500 ppm THg
- Diversion of site surface water drainage around mine site
- Amend soil, with re-grading and re-vegetating bare low grade waste piles
- Preservation of 'new' processing mill and other buildings for historic purposes.

All mercury contaminated soil, along with limited amounts of mine wastes, were placed in the open pit repository. The soil was spread and mixed with the soil additive KB-SEA (KEECO, Lynwood, WA) in an attempt to reduce mercury solubility and leachability. The additive is silica micro encapsulation (SME). Its physical/chemical components include an initial exothermic reaction and pH adjustment, followed by an electrokinetic reaction and metal hydroxyl formation leading to silica encapsulation. Laboratory tests of impacted site soil indicate mixing the additive at a rate of 2% by weight would achieve the best reduction in mercury leachate (KEECO, 2000). Due to the inherent problems with field scale mixing of soil with the additive, the KB-SEA was mixed at a rate of 5%. Water was added to the mix at a rate of approximately 5% by weight and the mixture was compacted in 6-inch lifts. Confirmation samples were collected from the treated soil and analyzed at an on-site mobile lab for THg. All samples had concentrations below the acceptable risk level. In addition, total and TCLP mercury analyses were performed to verify the adequate treatment.

147

A total of 395 cubic yards of soil and mine wastes was excavated during the Removal Action and of that, 225 cubic yards were treated with the additive (CES, 2000). The remaining quantity is from mine waste dumps with acceptable mercury levels but with elevated sulfur content or low pH levels located at various locations around the Site. An additional 8000 cubic yards of low Hg mine waste soils was placed on top of the treated material and also compacted in lifts.

In addition to the soil treatment activities, the open pit and disturbed portions of the 6 acres were recontoured and revegetated to eliminate current erosional features. Drainage control devices were installed in the former open pit to prevent erosion of the repository, and to control surface water flows across the disturbed site area.

The remaining buildings on the site were prepared for demolition or for historical preservation. This included performing asbestos abatement and disassembly of mining equipment posing a safety risk. Most of the mine structures were demolished and transported to a solid waste disposal facility. The New Mill Building and the D-tube retort are part of the historical preservation efforts being pursued by a local historical group.

Future Work

Implementation of the removal action was completed during the summer of 2000. Additional investigation is planned for the sediments, and monitoring of the mine seeps and shallow groundwater related to the abandoned mine adits is ongoing.

Acknowledgments

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3.7.3 Mercury Pollution from the Hg Mining Area and Reclamation - Lin Yuhuan, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

China is a country rich in mercury deposits. In the past half century, the total amount of production was about 20,000 tons based on the statistics from big firms of mercury mining in Guizhou, Hunan, Kongdong, Sichuan and Shanxi. The mercury mining areas were located in mountainous regions that cover the bounds of Guizhou, Hunan, Sichuan, the north part of Kongdong, and the south part of Shanxi. The total area is several hundred square kilometers. The population is about 40,000-50,000 in these areas. The environmental situation is formidable due to the mining and pollution of mercury ore.

The waste ore, residues and wastes of refinement, which contain mercury and other toxic elements, such as, As, Pb, Cd, and sulfides, were deposited at the bank of streams, in the sloping lands and even in the valley. The pollution and environmental destruction often occurred in the rainy season, especially with the extended duration of the storms.

The investigation data illustrate that the concentration of mercury in the air of the mining area is higher than the background value by about 10 to 100 fold. The water and soil near the mining area were polluted seriously by the heavy metal. The concentration of the heavy metals, for example mercury, especially in the crops and plants of the area is very high. An epidemiologic investigation concluded that part of the population is polluted and injured.

The management and control of pollution in the area is handled by the local government and the mining firms. The efforts include: 1) the construction of tailing dams; 2) the improvement of treatment plant of waste water from the concentration dressing plant and from the leakage and leaching of the waste ore; 3) the covering of the tailing dam and residue, and then the planting of grass or ramie on the covering soil for removal of mercury; 4) the experiment of fixation of mercury in the polluted soil by lime powder and lignohumus during the planting.

The reclamation of the polluted areas has been a very difficult problem. The results of experiments showed that the success of the approach on the soil is limited by many parameters.

3.7.4 Historic Unreclaimed Mercury Mines in Asturias (Northwestern Spain): Environmental Approaches - Jorge Loredo, Universidad de Oviedo, Escuela de Minas

Mercury Deposits in Asturias

Mercury deposits are abundant in Asturias (northwestern Spain). They are located in Precambrian to Carboniferous formations, however deposits are mostly found in Carboniferous sediments, predominantly carbonates. The most important deposits are located in conglomeratic horizons or siliceous breccias in sandstones and are sometimes impregnating fractured lutitic carbonaceous sequences.

These mineralizations appear as irregular veins, granular aggregates or impregnations in rocks, generally in relation to fractured zones with high porosity, and usually coinciding with high contents of organic matter (Gutierrez Claverol and Luque, 1993). Generally, these mineralizations show a tectonic control; there is a clear spatial relationship between mercury deposits and late-hercynian fractures. The physical-chemical characteristics of the mineralizing fluids and the secondary permeability in the enclosing rocks suggest that these deposits are of epigenetic type and originated from hydrothermal solutions (Loredo et al., 1988).

Mercury generally appears in the form of cinnabar, but metacinnabar and native mercury occasionally appears too. Arsenic is usually present in the ore deposits as realgar and As-rich pyrite. Different mineralogical association types may be recognized in these deposits (Luque, 1985), but cinnabar-pyrite-melnikovite-marcasite-stibnite-galena and cinnabar-realgar-orpiment-fluorite-tetrahedrite-schawazite-native mercury, are the two main mineralogical associations, related to the exploited deposits. The gangue constituents are quartz, carbonates (ankerite, calcite and dolomite) and argilaceous minerals (kaolinite and dickite).

Historical Mining Activities

There is a long history of mercury mining in Asturias. Although mercury extraction in this region is known to date back to the Roman period (centuries I and II), it is in the 19th and 20th centuries, when mercury mining began to be an important and prosperous industry. The oldest mercury mining works known are located on the Miñera Valley, in the La Peña area, where in 1842 the first mining society of the modern age devoted to the extraction of mercury was created (Dory, 1894). From this time, different mining companies were created to exploit mercury in different parts of Asturias.

At the beginning of the 20th century an important crisis on mining mercury occurred at an international level. The repercussion was perceived by Asturian mercury mining companies, leading to the closure of several mines. It was in the 1940s when the activities were re-initiated in different ore deposits of the region. The decade between 1962 and 1972 represented the most active period of mercury mining in Asturias, and it is in this period when the most important mines (El Terronal, La Peña, La Soterraña, Brañalamosa, Maramuñiz, Piedracea, Olicio, Caunedo, etc.) were most productive. Asturias was at this time an important mercury producer on a world scale, with an average annual production of 15,000 flasks, representing approximately 5% of mercury world production.

The international mercury crisis in 1972 gave rise to not only the paralyzation of some important mining projects in the area, but the successive closure of all up till then active mines, between 1973 and 1974. Then, from 1974 there was not any extractive activity from mercury mines in Asturias. Some of the most important deposits were intermittently exploited from the 19th century until 1974, by underground mining works.

Although the mercury mining works in Asturias are very abundant, the most important of them, related to the volume of extracted minerals, are:

· "La Peña - El Terronal" in the area of Mieres (20 km southern Oviedo –capital city of Asturias-).
· "La Soterraña", in the area of Pola de Lena (30 km southern Oviedo).

In both places there were active mercury mining and metallurgical activities for years until 1974. Apart from these important mines, other small mines have been intermittently exploited in these areas (for instance: Los Rueldos and El Rucio in the area of Mieres, and Brañalamosa and La Maramuñiz, in the area of Pola de Lena). Mining works in other areas of Asturias had been less important, for example: Caunedo, Bufarrera, etc. Some of the mined deposits are located in sparsely populated areas, where land is predominantly used for cattle grazing. As a result of the historical mining activities, abundant spoil heaps of different age and dimensions, and with significant quantities of wastes with high contents in mercury, had been introduced in the area. Unfortunately, the legacy of the historical mining activities remains in the form of old industrial installations and significant quantities of wastes stocked in piles on the surface. No action was taken to minimize environmental impact after the mining closure in 1974. The potential of the abandoned wastes to pollute the environment is enhanced by the high content of arsenic in minerals of the paragenesis. Some minor spoil heaps have been colonized with vegetation, blending in with the surrounding landscape.

At the old mining works of "La Peña - El Terronal", the upper levels of the ore deposit have been mined by the Romans during their presence at the Iberian Peninsula in the first and second centuries. The modern extraction of mercury had been made by drift mining and by underground mining with exploitation in 12 levels. The late 1960s - early 1970s was a time of great production, corresponding to a moment when mercury prices were high. At that time, La Peña-El Terronal was the second largest mine in Spain (the first was Almadén mine), and the 8th largest in the world (Luque, 1992). There was a pyrometallurgic plant close to the mines where the ore was treated in furnaces at temperatures of approximately 580°C. At this temperature, the sulphide oxidizes to produce SO_2 and mercury vapour, which passes through a system of condensers to produce mercury metal. The ore was treated after leaving the condenser, and the gasses passed through large chimneys ascending the slopes of the mountain with the purpose of preventing contamination for workers. After closing down the mine in 1974, many flasks of impregnated mercury were collected from the chimney, representing a loss during the process and a considerable source of contamination for this area. Most of the tailings from the mining works were disposed forming piles in the Miñera river valley.

The second most important in magnitude from mercury exploitation existing in Asturias is La Soterraña mine, in Muñón-Cimero (Pola de Lena), about 30 km Southeast of Oviedo, capital city of Asturias. The

exploitation method was chambers and pillars. Tailing piles were placed in the neighborhood of the mine, on a hillside area. Concentration of mercury from extracted mineral took place at the site of the mine by means of retorts or tub furnace depending on the grade of mineral. The Soterraña mine produced a large part of the mercury for sale at that time in Asturias. Taking into account losses during mining and inefficient smelting, the total volume of mined mercury is important. Other less important mining works in this same area are Brañalamosa. The mining works are placed over the northern and southern slopes of the Brañalamosa stream, and in general, mining works and spoil heaps are covered by dense grove and thickets or by pasture for cattle. Spoil heaps are in the immediate areas of mining works, and material from here has been used for construction of rural paths on the area.

Environmental Approaches

The general high contents in arsenic of these ore deposits not only favored the environmental impacts of the mining works, but interfered with their metallurgical treatment, leading some companies to interrupt their mining activities before 1973-74. Research conducted to assess the environmental impact of contamination for historical Asturian mercury mining is being undertaken by the Department of Mining and Exploration of Oviedo University: Arias, 1997; Arias et al., 1998; Fernández Albarrán, 1997; Loredo et al., 1999; Pereira, 2000, Dávila; 2000; Baldo, 2.000.

The local geochemical level for mercury in the areas under study, in soils not directly influenced by old mining works, is 1.6 – 2.2 mg/kg. Comparatively, the range of mercury concentrations in surface soils in the world varies from 0.1 mg/kg to 0.5 mg/kg (Alloway, 1995). At the site of old mining and metallurgical works, systematic geochemical studies in superficial soils show very important mercury anomalies.

Anomalies in Soils

- *"La Peña – El Terronal" mining works (Mieres)*—In the area of old mining works of "La Peña – El Terronal", pH in soils range between 3.42 and 5.93, and mercury anomalies reach up to 472.1 mg/kg, which are clearly associated to waste piles and chimneys from pyrometallurgy treatment of ore. Arsenic concentrations in these soils vary from 6.0 mg/kg to 7287.0 mg/kg.

- *"Los Rueldos" mining works (Mieres)*—On the site of tailings disposal in Los Rueldos, 1 km from the before mentioned mining works, mercury concentrations in samples systematically distributed on the tailing pile, range from 14.0 to 2224.0 mg/kg; on the other hand, the arsenic content in the same samples ranges from 4746.0 to 62196.0 mg/kg.

- *"La Soterraña" mining works (Pola de Lena)*—At the site of La Soterraña mine, in Pola de Lena, soils have pH comprised between 4.74 and 7.59. Mercury and arsenic contents in soils vary widely from a background of 2.0 mg/kg to 501.8 mg/kg for THg, and from 32 mg/kg to 19940.0 mg/kg for arsenic.

- *"Brañalamosa" mining works (Pola de Lena)*—In the Brañalamosa area, 1 km from the before mentioned mining works, chemical analysis of the samples from the mined areas show mercury concentrations between 1.0 mg/kg and 895.0 mg/kg. Arsenic concentrations range from 19.0 mg/kg to 704.0 mg/kg.

Anomalies in Herbaceous Plants

- *"La Peña – El Terronal" mining works (La Peña)*—Herbaceous plants consisting of grass are very abundant at the site of the mining works. In soils of La Peña – El Terronal, in the area of Mieres, herbaceous plants present an average concentration of THg of 1.635 mg/kg, and the maximum value corresponds to 4.84 mg/kg (the average value of As content is 16.3 mg/kg, with a maximum value of 53 mg/kg).

- *"Brañalamosa" mining works (Pola de Lena)*—In Brañalamosa, in the area of Pola de Lena, herbaceous plants in soils of mined areas present mercury concentrations ranging from 1 to 155 mg/kg in roots, and from 1 to 69 mg/kg in stems (the average values are 32.9 and 14.3 mg/kg respectively in roots and stems); Arsenic content ranges between 4 and 27 mg/kg in roots and between 2 and 16 mg/kg in stems (average values are 12.5 and 7.9 mg/kg respectively).

151

Anomalies in Superficial Waters

- *"La Peña – El Terronal" mining works (Mieres)*—Mercury concentrations in superficial waters up stream and downstream of mining works in the Miñara stream which flows through the main spoil heap corresponding to "La Peña – El Terronal" mining works in Mieres are always lower than 0.001 mg/L (detection limit of the equipment used for analysis). Arsenic concentrations increase from values lower than 0.005 mg/L in samples collected upstream the mining works to values between 0.9 to 5.6 mg/L in samples collected downstream.

- *"Los Rueldos" mining works (Mieres)*—Water samples corresponding to leachates from the tailing pile in "Los Rueldos" mine, show very acidic pH between 2.43 and 2.50, average sulphates content of 2,900 mg/L, mercury concentrations lower than 0.001 mg/L, and arsenic concentrations between 5.3 and 8.3 mg/L.

- *"La Soterraña" mining works (Pola de Lena)*—Water samples downstream of the mining works, at the bottom of the spoil heaps, show mercury concentrations lower than the detection limit of the equipment used for analysis (0.001 mg/L) and arsenic concentrations range from 1.5 mg/L to 3.4 mg/L.

- *"Brañalamosa" mining works (Pola de Lena)*—In Brañalamosa stream in Pola de Lena mercury concentrations upstream and downstream of the mining works are always lower than 0.001 mg/L. Arsenic concentration increases from values lower than 0.005 mg/L (upstream of the mining works) to values between 1.0 and 1.9 mg/L (downstream of the mining works).

Soil survey geochemical data were used to plot contours of THg and arsenic concentrations in surface soils over the area surrounding the most important mining works in Asturias, and then delimitation of anthropogenic geochemical anomalies. Related to the high contents of mercury and arsenic in soils, it is necessary to keep in mind that soils in the area of mining works and spoil heaps are not natural soils but a mixture of soil components with waste materials.

Conclusions

As a result of the preliminary geochemical data obtained, mercury and arsenic are widespread and highly concentrated in soils affected by old mercury mining works in Asturias. Geochemical anomalies in soils around the old mining and metallurgical works of "La Peña - El Terronal," "Los Rueldos," "La Soterraña" and "Brañalamosa," are very significant in mercury and arsenic. They are clearly associated to tailings disposal and metallurgical operations in these areas, which are the most important sources of contamination. It is emphasized here that at sites close to the chimney of the metallurgical plants, THg and arsenic concentrations are specially high (472,140 and 7,287 mg/kg, respectively at "La Peña – El Terronal" site). Mercury and arsenic concentrations in soils decrease as a function of distance from the before mentioned sources. From the geochemical data it can be observed that mercury and arsenic anomalies in soils are very similar to each other in every studied area, which agrees with the high correlation factors between mercury and arsenic in soils (r = 0.885 in "La Peña - El Terronal" and r = 0.8767 in "La Soterraña"). Element distribution maps obtained from the soil survey surrounding the area of the mining and metallurgical works have revealed similar patterns of mercury and arsenic distribution.

The study and distribution of trace elements in soils of the urban area of Mieres downtown, located 4 km from the site of La Peña - El Terronal mining works, show evidence in some samples of their high content in mercury and arsenic. Therefore, the addition of mercury and arsenic to the urban soils in proximity to the mining area may be imputed to an anthropogenic source related to the mercury mining activity in the area, and to a transport by air of fine solid particles coming from the before mentioned sources.

High arsenic levels, related to leaching of arsenic-rich minerals stocked into the tailing piles, are observed in superficial waters downstream of the main mining works. These values are especially high at the bottom of the spoil heaps.

Herbaceous plants (grass) sampled and analyzed in the different areas with old mining works show high mercury and arsenic. In order to investigate the influence of mercury and arsenic levels in soils on uptake by herbaceous plants, their biological absorption coefficients (Brooks, 1983; Kabata-Pendias and Pendias,

1992) have been deduced: they range between 0.02 and 0.38 for mercury, and between 0.005 and 0.44 for arsenic.

According to the geochemical data from a systematical sampling of soils, herbaceous plants and superficial waters, at the sites of the historical mercury mining works and smelting operations in Asturias, it is evident that anthropogenic geochemical anomalies are present in the area. They present an important environmental impact, reflected mainly by elevated concentrations of mercury in soils and herbaceous plants (grass), and elevated concentrations of arsenic in soils, waters and herbaceous plants (grass). Geochemical and mineralogical data from materials stocked in the tailing piles suggest that minerals of arsenic (orpiment-realgar-arsenopyrite), and iron sulphides (pyrite-marcasite) contribute significantly to the high arsenic content found in waters downstream of the mining areas. In order to evaluate the extent of the contaminated areas, it is strongly advisable that political authorities carry out a detailed geochemical exploration into the area affected by these old mining works.

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3.7.5 Silica Micro Encapsulation - An Innovative Technology for the Control of Heavy Metals - Amy Anderson, Mining Services, KEECO

The Silica Micro Encapsulation Technology was developed by Klean Earth Environmental Company [KEECO] as a more effective and simpler approach to controlling heavy metals in aqueous and solid waste than traditional treatment technologies. The Silica Micro Encapsulation [SME] technology is comprised of readily available materials including calcium oxide, amorphous silica, crystalline silica and a variety of metal oxides. The proprietary manufacturing process of blending these components creates a reactive chemical product that, when introduced to metal-laden water or soil, ultimately results in the encapsulation of metals in a stable silica formation, or encapsulation. Over time, the silica encapsulation around the metals has demonstrated a tendency to strengthen, enhancing the stability of treated soil materials or of the sludge produced from water treatment. The base formula of the SME technology has been refined to create three separate products, KB-1, KB-SEA and META-LOCK, applicable to water, solid waste and radioactive wastewater respectively. KB-SEA is highlighted in the project examples to follow and has successfully demonstrated its ability to treat mercury-contaminated solid waste from mine sites and other industrial sources.

The principal function of typical solidification/stabilization (S/S) technologies involves changing the physical characteristics of the waste to improve handling and to reduce mobility of the contaminants by creating a physical barrier to leaching. This is generally accomplished through chemical interactions using pozzolanic mixtures or hydroxide, sulfate, phosphate or carbonate precipitates. Such techniques are capable of achieving reduced metal mobility under regulatory leach testing conditions. However, long-term stability is often in question as historic evidence clearly demonstrates that as pH conditions and/or as anaerobic conditions arise after disposal, metal immobility is compromised and migration often occurs, contaminating groundwater, aquifers or surrounding surface areas. The associated liability of such occurrences is significant.

While the SME reaction process and treated material characteristics may appear quite similar to typical S/S technologies, there are two inherently unique aspects of the technology that offer critical advantages related to cost and long-term stability. First, the chemical is formulated in such a manner that, when exposed to water it initiates a reaction process that involves not only precipitation and hydroxyl formation, but also an electrokinetic reaction. This reaction serves to enhance contact with the target metals by facilitating electrokinetic transport of the metal particles towards the SME reactive components. As a result, in a brine or salt solution, the SME reaction is quite vigorous. This electrokinetic factor improves chemical efficiency, thereby reducing overall chemical usage and project costs.

The second unique aspect of the technology is its silica component. Once initial metal bonding formations occur, the silica components form a tight matrix around the metals. This matrix, or encapsulation, is wrapped tightly and completely about the metal particle, greatly enhancing overall stability. Under independent review, the SME process has demonstrated that over time, unlike typical S/S technologies, the stability of the treated material and immobility of the metals is enhanced. This is evident irrespective of changes in pH and occurs in both aerobic and anaerobic environments. Thus, the long-term stability associated with the SME treated material is significantly greater than that produced by traditional S/S methods. For example, in a study conducted by Dr. William Chatham of Montana Tech of the University of Montana, he writes, "I have used sequential leaches to compare the stability of sludges produced by [the SME product] KB-1 and liming using Berkeley Pit water. A 4-stage high-density lime sludge was also evaluated. The KB-1 sludge was more stable than both of the lime-type sludges for all steps in the sequential leaches for all elements evaluated."

154

Equipment Considerations for Field Application of SME

After manufacture, all of the SME products are in the form of a dry, talc-like powder. For treatment of soil and other solid wastes, the SME product KB-SEA is incorporated into the waste material using readily available earth-moving equipment. Prior to introduction of the technology in a field setting, a brief treatability study is conducted in a laboratory to determine approximate chemical dosage ratios, range of control of the target metals (based upon pH and chemical dosage rates) and to support the selection of the appropriate mixing equipment. For projects in which a narrow range of chemical dosage is effective, the selected mixing equipment must be capable of effectively measuring chemical application rates based upon either weight or volume of the treated material, such as a ribbon blender or pug mill. For those projects that involve contaminated materials that successfully respond to treatment over a broad range of pH and chemical dosage increments, it is acceptable to incorporate a gross approximation of chemical per unit weight or volume of soil and a simple backhoe or front-end loader will suffice.

In addition to a chemical mixing device, other equipment required for treatment of solid substances with SME includes a forklift, chemical storage facility or other materials to keep the chemical dry and waste handling equipment if the post-treated material is to be moved to a final disposal location. In many cases, the treated material is simply left in-place due to the enhanced stability provided by the SME treatment.

Lagoon Sludge Project

KEECO was requested by a Canadian client to evaluate the ability of the SME Technology to treat mercury-contaminated lagoon sludge generated from a chlor-alkali facility. The THg content of the sludge contained an average of 65% mercuric sulfide and 15% elemental mercury. KEECO received a sample of the lagoon sludge and conducted a laboratory treatability study to determine chemical dosage rates required for successful treatment and the condition of the post-treated material.

The raw sample material was evaluated to establish baseline data. Sub-samples were then prepared and treated with incrementally increasing amounts of SME product KB-SEA at additional rates of 3%, 7% and 10% by dry sample weight and subjected to EPA Method 1311 TCLP for initial treatment data. Initial data suggested that lower dosage rates would achieve the treatment goals. Additional sub-samples were then treated with KB-SEA at dosage rates of 1%, 2% and a replicate 3% and subjected to TCLP testing. The original 3% treated sample was also re-tested to evaluate the effectiveness of longer curing time on the mercury stability. A period of 15 days had elapsed from the initial test to the time of the second TCLP test. All samples, raw and treated, were evaluated for paste pH and moisture content. The raw sample and sample treated at the 3% addition rate were also forwarded to an outside, independent laboratory for TCLP testing for data verification.

The raw sample was subjected to a total metals digest and exhibited mercury levels of 2.25 mg/kg. Under TCLP testing, the raw sample produced a mercury concentration of 0.295 mg/L in the collected leachate. The paste pH was 10.2 and contained 37.4% moisture.

After treatment with the SME product KB-SEA, the lagoon sludge demonstrated mercury concentrations in the TCLP leachate at levels below that of the regulatory action limit of 0.200 mg/L with a dosage rate of > 1% KB-SEA by dry weight of sludge. Increasing control was evident at higher dosage rates, with leachate mercury concentration decreasing in an almost linear fashion as chemical dosage rates were incrementally increased. In addition, as shown in Table 1, the 3% KB-SEA amended sample was tested again after 15 days of curing and demonstrated greater control of the mercury mobility than the initial test that immediately followed treatment. A 71% reduction in the mercury concentration of the leachate was achievable after 15 days of curing as compared to the 65% produced after only one day of curing.

155

Add Ratio (% KB-SEA by dry weight sludge)	TCLP Result Hg (mg/L)	Percent Reduction Hg Concentration
0 [Raw]	0.295	NA
1	0.197	33%
2	0.152	48%
3[1]	0.104	65%
3[2]	0.085	71%
3R	0.128	57%
5	0.083	72%
7	0.046	84%

[1]Original 3% amended sample.
[2]Same sample analyzed 15 days after original chemical amendment.

Overall, the treated sample results demonstrated reduced concentrations of leachable mercury throughout a broad spectrum of chemical dosage ratios, with increased control evident at higher chemical addition ratios. In a field setting, this broad range of control allows for flexibility in handling varying concentrations of mercury that are expected throughout the project treatment process.

An evaluation of overall cost of treatment for this project including labor, SME chemical and equipment totaled to a not-to-exceed unit cost of $35.00 U.S. per treated ton of sludge. This figure did not include transportation costs to a final disposal site or analytical testing.

Mother Lode Mine

The Mother Lode Mine, a former mercury mining and processing operation from 1906 to 1972, is located in Central Oregon on USFS property. During the past 4-5 years, on-going investigations have been conducted to identify sources of metal contaminated soils on the property with a specific focus on material containing high concentrations of mercury. These investigations identified approximately 450 cubic yards of soil that exhibited 500 mg/kg mercury or higher. Upper limits in some samples were as high as 26,000 mg/kg. This source material was collected and moved to an open pit for treatment in place with the SME product KB-SEA. If treatment achieved TCLP Hg levels of 0.200 mg/L or less, the material would remain in-place and final site restoration and capping activities would commence.

KEECO received a sample of the material and conducted a treatability study to identify chemical dosage rates and optimum range of control. Results of the study demonstrated that optimum treatment was achievable using a dosage rate of 2% KB-SEA by dry weight of the soil and 30% moisture. Modifications were made to the dosing rates to scale-up to field conditions and to accommodate the predicted changes in varying mercury concentrations. Treatment was accomplished using a backhoe for chemical incorporation into the soil and application of fresh water to ensure sufficient wetting to initiate a vigorous chemical reaction. Treatment was completed within a period of two days and involved the treatment of two "lifts" of soil. Samples of post-treatment soil were collected from each of the two separate lifts immediately after mixing with the SME product and wetting and shipped to an independent laboratory for total metals and TCLP testing.

TCLP testing showed that the treated samples exhibited mercury concentrations ranging from 0.0028 to 0.0008 in the leachate, well below the stated treatment goal for mercury of 0.200 mg/L. In addition, the concentration of THg evident under digest conditions in the treated samples were well below the raw material minimum concentration of >500 mg/kg. This suggests that the encapsulation of the mercury within the silica was not compromised under digest conditions.

156

These examples suggest that the SME Technology provides several distinct advantages over traditional treatment techniques for mercury contaminated waste materials including:

- Control of mercury to levels well-below regulatory action limits;
- Greater stability of mercury within the treated material as compared to traditional treatment methods;
- Enhanced stability over time due to the strengthening of the silica formation;
- Cost-competitiveness;
- Ability to leave treated material in-place versus off-site disposal.

3.7.6 Potential Economic Benefit from Innovative Mercury Separation Technology - Jeanette B. Berry, ONL; Juan J. Ferrada, Ph.D., ORNL; L. R. Dole, Ph.D., ORNL; James W. Van Dyke, ORNL; and John P. Hager, Ph.D., Colorado School of Mines

Abstract

The U.S. DOE teamed with the National Mining Association to select research projects that could significantly benefit the mining industry. This paper describes one such project—By-Product Recovery from Mining Process Residue. The Oak Ridge National Laboratory is researching and developing the SepraDyne® system—a high-vacuum, indirectly heated rotary kiln that operates at temperatures of up to 750°C.

The U.S. mining industry produces over 7,000,000 t/yr of process residue that may contain hazardous species as well as valuable by-products. Process residues are generated by (a) smelter off-gas cleaning—5,500,000 t/yr and (b) bag house dust and wastewater treatment—2,100,000 t/yr (USEPA, 1995). New approaches may be able to recover marketable by-products from this process residue to generate revenue and reduce disposal costs for the mining industry. For example, a rotary vacuum kiln was invented by a small U.S. business, SepraDyne®. This technology operates commercially at a copper mine separating mercury from sulfuric acid plant blowdown sludge, which also contains lead, copper, gold, and silver. Two materials result: (1) concentrated mercury and (2) process residue with extremely low concentrations of mercury. The concentrated mercury is either sold or treated and disposed. The "mercury-free" residue can be either recycled to recover additional copper or sold to recover lead, bismuth, and trace gold and silver (USEPA, 1991).

The paper summarizes this research and development project: (1) SepraDyne's® process is being developed and improved by modeling and evaluating process and thermodynamic variables, (2) key factors in the economics of by-product recovery are the value of acid plant sludge before separating mercury, after separating mercury, and the $500/ton treatment cost, and (3) kinetics and thermodynamic experimental results from investigations of two mixtures—mercury, sulfur and oxygen, and mercury and selenium—confirm that the presence of oxygen affects separation of mercury compounds and the recovery of elemental mercury.

Introduction

The DOE Office of Industrial Technologies, Mining Industry of the Future Program, is working with the mining industry to help promote the industry's advances toward environmental and economic goals. Two of these goals are (1) responsible emission and by-product management and (2) low-cost and efficient production (DOE, 1998). ORNL is working with the mining industry and the separation-process industry to develop a process that achieves these goals by separating mercury from process residue allowing valuable lead and metals to be economically recovered. The results of this project will contribute to sustainable production in the mining industry.

By-product recovery provides an opportunity for the mining industry to make environmentally-sound process improvements while generating revenue for the industry. SepraDyne®, a small U.S. business, has patented a technological breakthrough that uses an improved separation process to recover metals from mining process residue. The technology provides a processing environment for separating metals (primarily mercury) and destroying organic chemicals (e.g., dioxins, furans) that contaminate valuable products, such as copper and lead and traces of gold and silver.

To realize the potential of this technology, DOE and SepraDyne® co-funded work at ORNL, in collaboration with the Colorado School of Mines. This paper summarizes this research and development project including (1) process descriptions of mercury separation from acid plant sludge including baseline and vacuum rotary kiln mercury separation techniques, (2) process modeling of the SepraDyne® operations, (3) factors that influence the economics of by-product recovery, and (4) results of process chemistry kinetic and thermodynamic experiments on two mixtures—mercury, sulfur and oxygen, and mercury and selenium.

Process Descriptions of Mercury Separation from Acid Plant Sludge

Baseline Mercury Separation Technique

ORNL searched the literature, and interviewed mine and SepraDyne® personnel to determine the composition of the acid plant sludge and assess mercury separation techniques. This information indicates that acid plant sludge contains lead, copper, and bismuth, as well as trace quantities of gold, silver, and mercury sulfide (USEPA, 1991; Jeanette B. Berry and H. Patton, 2000). The mine used a traditional baking method to reduce the concentration of mercury to acceptable disposal levels for Resource Conservation and Recovery Act-regulated waste. The acid plant sludge was loaded into "baking trays" that were exposed to direct heat. Since the material was not mixed as it was heated, heating was not uniform. Consequently, the effectiveness of mercury removal varied. Since the process residue contained relatively high concentrations of mercury, the valuable lead and copper were not cost-effectively recovered (Berry and Talburt, 1999).

Rotary Vacuum Kiln Mercury Separation Technique

ORNL analyzed the SepraDyne® technology by visiting the operating site and evaluating the process. Initial evaluation indicates that this process has advanced by-product recovery by more effectively separating mercury on site with compact processing equipment. Mercury is removed to <10 ppm so that valuable metals, such as lead, can be economically recovered from acid plant sludge—the mine can market the lead bearing process residue to a lead smelter.

The heart of the SepraDyne® process is an indirectly heated rotary kiln that operates at a high vacuum and high temperature. These conditions produce an environment that volatilizes liquid and low- to moderate boiling-point metals such as mercury, arsenic, selenium, and cadmium. The process has also been shown to destroy organic compounds. Since air is eliminated from the kiln, combustion does not occur; and off-gas treatment equipment is minimized. The vacuum system has the following advantages over traditional thermal processes:

- Reduced oxidation of mercury and formation of mercury compounds because of the reduced oxygen in the processing environment.
- Reduced formation of organic products of incomplete combustion because of the reduced oxygen in the processing environment.
- Reduced capital and maintenance costs because complex off-gas treatment systems are not needed.
- Reduced particulate formation and dust.

The operating parameters and processing sequence of the rotary vacuum retort (illustrated in Figure 1) are as follows. Solid or semi-solid process residue is fed into the retort through a feeding system (a hopper/auger assembly). Once the unit is loaded, a vacuum is established and the retort is set into rotation. Heat is indirectly applied within an insulated firebox through burners fueled by natural gas, diesel oil, or propane. As an alternative, electric heating can be employed in sensitive environmental settings, or on sites with low-cost electric power. Residue is initially heated to remove the moisture. The water vapor and other low-boiling-point gaseous compounds are normally condensed in the off-gas treatment train, passing initially through an impinger system. If very-low-boiling-point organic chemicals are present, cryogenic cooling can be employed to condense these chemicals.

158

Figure 1. Vacuum Rotary Kiln Mercury Separation Process.
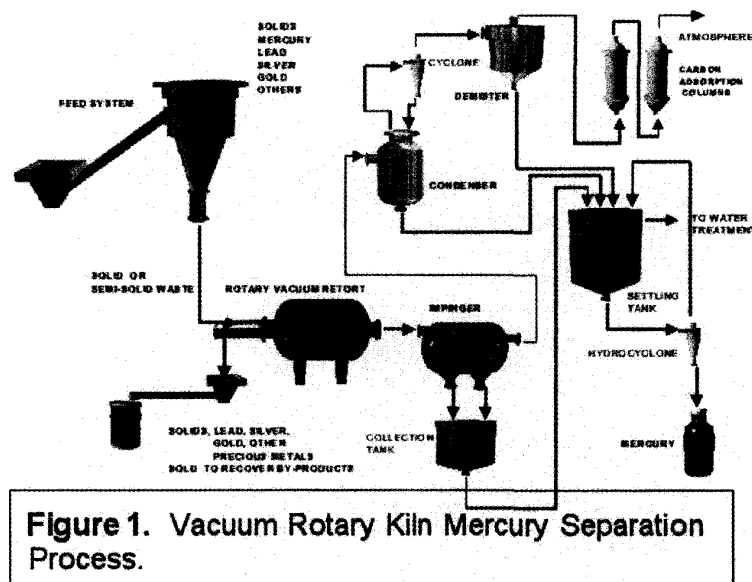
Once the material is dried, the retort temperature is raised to a target value, up to 600°C to 750°C, under a vacuum of greater than 0.7 atm (20 inches of Hg), and held at the target temperature for a set time. Organic compounds, including heavy tars and compounds of mercury volatilize under these conditions. Non-volatile chemicals and residual metals are separated from the condensed liquid, and the liquid is discharged to on-site wastewater treatment systems or the sanitary sewer. Waste heat from the process is exhausted to the atmosphere. Any trace hazardous vapors that have passed through the off-gas system are removed in the carbon absorption section. Mercury is recovered from the solids collected in the settling tank using a hydrocyclone. The material within the retort is maintained at the target temperature until system monitoring indicates that all of the contaminants of concern have been removed. After processing, the burners are turned off and the vacuum is released. The processed material is then conveyed via a screw feeder into a receiving vessel fitted with particulate air control equipment. Materials containing by-products are collected in separate containers for shipment. The mine sells the material to an off-site smelter for recovery of lead and trace quantities of gold and silver. Alternately, if the concentration of copper is high enough (e.g., >7 %), the mine returns the material to the onsite smelter for additional processing (Berry and Talburt, 1999).

Process Modeling

ORNL researchers modeled the SepraDyne® system using process modeling software, FLOW™, to analyze the effect of changing process equipment (e.g., improved materials of construction) and operating parameters (e.g., feed stream composition) (see Figure 1). FLOW™ is a modular computer simulation program that models and analyzes emerging chemical and physical processes. Process analysis starts with a simple material balance, using available data. Process developers use an icon-based, user-friendly interface to model material balances around each unit operation. These unit-operation material balances are then combined to calculate a material balance around the entire process. Analysis can be extended to evaluate process effectiveness, efficiency, and operability. ORNL modeled and evaluated the SepraDyne® system resulting in a basic understanding of process variables and their influence on the effectiveness of mercury separation. Continued process analysis is planned to better understand unit-operation alternatives, efficiency, operability, cost, risk and uncertainty.

ORNL and the Colorado School of Mines used thermodynamic models to predict compounds likely to result from critical processing steps. Feed stream data were provided by SepraDyne®. Version 4.1 HSC Chemistry for Windows Chemical Reaction and Equilibrium Software (by Outokumpu) was revised to reflect experimental results obtained by the participating researchers at the Colorado School of Mines (Fredrickson and Hager, 1996). Equilibrium species were estimated by minimizing the collective Gibbs free energies for

temperatures between 30° and 600°C (86° to 1112°F). ORNL developed a procedure to simulate a reaction path under vacuum by removing all of the gaseous species after each time-temperature-equilibrium step. This procedure recalculates the equilibrium composition of each subsequent reaction step using only the residual solids from the previous step. Along with an allowance for particulate carry-over, the collective gaseous species from all of the reaction steps were modeled to simulate the composition of the sludge that condenses from the off-gas.

Analysis of experimental data and model results led to a better understanding of the importance of oxygen in the oxidation rates of the metals present in the process feed and the importance of air in-leakage in the volatilization and separation of elemental mercury.

Process Chemistry Experimental Results

Since acid plant sludge contains high concentrations of sulfur and selenium, it is important to understand interactions between these elements and mercury in the presence of oxygen to better control the process and optimize the removal of mercury. The Colorado School of Mines conducted experiments on the chemistry of the Hg-S-O and Hg-Se systems specific to removal of mercury from acid plant sludge. Experiments to date have shown that operating conditions can dramatically influence process effectiveness (Hager, et al. 2000).

The results show that there are significant differences in the temperatures required to achieve rapid rates of volatilization. The most difficult compounds to volatilize are $HgSO_4$, Hg_2SO_4, and $HgSO_4*2HgO$. These three compounds all have volatilization temperatures in excess of 600°C for 100% volatilization in 60 minutes. The next most difficult compounds to volatilize are HgO and HgSe with minimum temperatures of 557° and 451°C, respectively. The least difficult compound to volatilize is HgS with a required temperature of 382°C. This highlights the importance of having accurate information on the speciation of the mercury in the acid plant sludge to correctly design operating temperatures for the retort. These results provide data necessary to calculate the required process temperatures over differing process periods. Also, the results obtained for HgS, for the two different reactor pressures, suggest that an increase in the reactor pressure from 0.07 to 0.13 atm (2.0 - 3.9 inches of Hg) could result in an increase in the required operating temperature of 40°C or more. In the case of mercury sulfates being the predominant species, it is possible that a required process temperature in excess of 700°C could be required for 100% volatilization with short residence time (e.g., 60 minutes).

Back-reactions of the mercury vapor, as it is transported from the experimental reactor to the condenser, were observed to be very rapid. This is a significant factor in considering the use of a vacuum retort/ condenser system to recover elemental mercury from smelter acid plant sludges. It is clear from the modeling studies that primarily mercury vapor is generated during the volatilization of the compounds investigated in this study. The extent to which mercury is transported as HgS(g), HgO(g), or HgSe(g) is insignificant. Mercury collected on the experimental condenser (i.e., a water-cooled cold finger) was generally in compound form, rather than as elemental mercury—confirmation under controlled, experimental conditions that recovery of a liquid mercury product is difficult from such a complex mixture. Excess oxygen in the system would increase the production of SO_2, increase the concentration of SO_2 in the off-gas stream to the condenser, and further increase the rate of the back-reaction of the gaseous mercury. Key factors for the successful separation of elemental mercury include (1) limited presence of oxygen and (2) the rate of condensation and quenching of the mercury vapor to prevent back-reaction to non-elemental forms (e.g., $HgSO_2$, HgSe).

Economics of By-product Recovery

Acid plant sludge contains lead and copper, as well as trace quantities of mercury sulfide. It is difficult to recover the economic value of this acid plant sludge because it is contaminated with mercury. When the concentration of lead and copper exceeds a certain value, brokers may purchase this contaminated process residue and aggressively treat it to recover the value of the remaining metals (e.g., lead). If the value of the acid plant sludge is more than the cost of mercury removal, by-product recovery generates net revenue for acid plant operations.

ORNL reviewed the economics of this process as background for collecting relevant data from the mining industry. To gain an understanding of the process economics, information is needed at various mercury

concentrations. Interviews with mining companies indicate that the concentration of mercury influences the value of the process residue, because the ability for down-stream processes to recover valuable by-products is significantly influenced by mercury concentration.

Economic values of each process residue are used to determine the cost-effectiveness of separating mercury—two processing stages and various final concentrations of mercury. The required information includes (1) value of a process residue before separating mercury (may be a negative value equal to the cost of disposal), (2) value of a process residue after separating mercury, and (3) value of a residue that cannot be sold (may be negative because of its disposal cost). The value of a process residue varies with mercury concentrations—for instance, data at <100 ppm, <50 ppm, and <10 ppm mercury would provide a basis for this economic analysis.

To evaluate the value of improved mercury separation techniques, the baseline processing cost of mercury separation should also be considered. For example, baking acid plant sludge in open trays may result in a relatively high final concentration of mercury, but may also be relatively inexpensive. While aggressive chemical extraction may result in low mercury concentrations, this process may be relatively expensive. Using this information, the economic analysis can ascertain the following variables: (1) processing cost saved, (2) the value of separating mercury, and (3) the final concentration of mercury that results in the highest net benefit for the mining industry.

This logic can be applied to other process residues to determine whether separating mercury would be cost effective. For example, smelter operations managers could use this analysis to determine whether their operation could generate revenue by receiving residue which is mercury-contaminated, and separating the mercury prior to smelting the metal-bearing process residue. A summary of the on-going economic analysis is shown in Table 1.

Table 1. Mercury Separation Economic Variables

A	Value of process residue before separating mercury	need data – may be negative		
	Concentration of mercury	<100 ppm	<50 ppm	<10 ppm
Value of process residue after separating mercury				
B	Acid plant sludge	need data	need data	need data
C	Other mercury contaminated residue	need data	need data	need data
Gross value after separating mercury				
D	Acid plant sludge (B - A)	calculate	calculate	calculate
E	Other mercury contaminated residue (C - A)	calculate	calculate	calculate
F	New technology mercury separation cost per ton	$500/ton	~$500/ton	~$500/ton
G	Processing cost per ton for next best technology	need data	need data	need data
H	Processing cost per ton saved by new technology (G - F)	calculate	calculate	calculate
Net value of separating mercury				
D	Acid plant sludge (D - F)	calculate	calculate	calculate
J	Other mercury contaminated residue (E - F)	calculate	calculate	calculate
Mercury removal level for highest net benefit based on highest value for each process residue				
	Acid plant sludge	Highest value in row I		
	Other mercury contaminated residue	Highest value in row J		

161

A preliminary assessment of available data indicates that if marketable by-products could be recovered from 30% of the U.S. mining industry's annual 7 million tons of process residue, because mercury was removed, the industry could generate $400 million in revenue from the recovered metals each year and could avoid disposal costs. This potential for economic gain motivates further study of more cost-effective separation of mercury to allow by-product recovery from mining process residues (Ferrada, et al., 1999).

Conclusions

The SepraDyne® process, which uses an indirectly heated rotary kiln that operates at a high vacuum and high temperature, shows promise as a mining by-product recovery system. The system is being operated commercially at a mining complex to separate mercury from acid plant sludge solids. DOE and the National Mining Association selected this process for a research and development project for the purpose of benefitting the mining industry.

ORNL and Colorado School of Mines are collaborating to develop this rotary vacuum kiln process by evaluating the process using engineering and economic assessments, by developing process and chemistry models, and conducting experiments on the fundamentals of the complex chemistry of acid plant sludge.

Both process modeling and experimental results indicate that oxidation of mercury controls separation of elemental mercury from this acid plant sludge, especially in the presence of selenium and sulfur. Separation of mercury under vacuum increases the amount of elemental mercury recovered. This developmental work also indicates that back-reaction of mercury with excess oxygen is very rapid—control of conditions under which mercury condenses influences the amount of elemental mercury recovered.

Data indicate that the SepraDyne® process is an effective process for separating mercury from acid plant sludge. The remaining sludge, which contains lead, and other valuable metals, is sold to a lead smelter for by-product recovery—the research team is verifying the economics of this by-product recovery operation.

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3.7.7 Removal of Mercury from Contaminated Water Using Alkali Ash Permeable Reactive Barrier (AFA-PRB) Material - Shahriar Jahanian, Temple University; Mozhgan Bahadory, Temple University; Hossein Rostami, Philadelphia University; and William Brendly, Philadelphia University

Over the past 15 years, about one half million sites with potential contamination have been reported to Federal or state authorities. Of these, about 217,000 sites still need remediation. The most common type of contaminants are metals, solvents and petroleum products. Heavy metals are present in two thirds of Department of Defense (DOD) and Superfund sites and about 50% of DOE and Resource Conservation and Recovery Act (RCRA) sites.

Alkali Fly Ash Permeable Reactive Barrier (AFA-PRB) is a newly developed material made with fly ash alkali activating solution and filler material (sand and coarse aggregates). AFA-PRB materials were used to remove mercury from contaminated water. AFA-PRB materials with high permeability of 10^{-2} centimeter per second (cm/sec) to 10^{-1} cm/sec were created. The reactive barrier material permeability must be in the range of 10^{-2} cm/sec to 10^{-1} cm/sec. AFA-PRB, from three ash sources with permeability of 10^{-1} cm/sec were produced and crushed into pelletized form. Effectiveness of the various barriers was determined by batch and column tests. Laboratory experiment indicates mercury ion reduces from 1000ppm to less than 3 ppm with 7 liters of solution and mercury ion from 10ppm to less than 2ppm. Analysis was performed by Atomic Absorption techniques.

Introduction

The EPA is interested in new technologies which can economically and effectively remove heavy metals from groundwater or wastewater. The primary heavy metals of concern are arsenic, cadmium, chromium, and mercury (1). These toxic materials may enter the environment from a variety of sources including abandoned dumping sites, wastes from metal plating and metal smelting, by-products from refining operations, and mercury from the improper disposal of fluorescent bulbs. These materials present a danger to both population and the environment. Groundwater pollution is perhaps the most dangerous because of the difficulty in treatment and the large percentage of the population which relies on groundwater for consumption. In this work, a novel method of removing mercury and stabilizing the heavy-metal-bearing residue is presented. The presence of heavy metals in the groundwater poses a health risk to humans.

There is a clear need for effective yet economical methods of remediation of groundwater to reduce adverse health impacts, and reduce the costs of remediation. The two common methods of dealing with underground water contamination are pump and treat and containment — both methods have shortcomings.

The pump and treat treatment method requires removal of contaminated groundwater to the surface, treatment, and return to aquifer. This method is effective but it is expensive, labor intensive, and requires the treatment of large amounts of water. Also, institutional barriers including surface water and groundwater discharge permits and groundwater rights must be considered. Recently, using permeable reactive barriers to treat contaminated water in situ has gained wide acceptance. A permeable reactive barrier may be defined as:

Subsurface emplacement of reactive material to intercept a contaminant plume, provide a preferential flow path through the reactive media, and transform the contaminants into environmentally acceptable forms.

Background on Coal Combustion Fly Ash

In 1996, the United States consumed 850 million tons of coal for electric generation. From this operation, about 90 million tons of coal ash was produced. Out of this 90 million tons, 55 million tons are fly ash, 20 million tons are flue gas desulfurization (FGD), 12 million tons are bottom ash and the rest are boiler slag (2).

Fly ash is by far the largest by-product produced. Only 27% of this huge quantity of fly ash (15 million tons) is reused or recycled; the remaining 73% is landfilled (2). The leading fly ash applications are:

Applications	% Used
Concrete	50
Structural Fill	14
Waste Stabilization	12
Mining Applications	5
Road Base	3
Other	16

ASTM C-618 classifies the fly ash into two groups, class F (low CaO), and class C (high CaO). The current work focuses on the utilization of class F fly ash. Ranges of composition of class F fly ash are shown below:

Oxides	% Content
Sio2	45-65
Al2o3	20-45
Fe2o3	3-12
CaO	3-10
MgO	1-3
Alkali	<1.5
SO3	1-5
LOI (%C)	0.1-6

The conventional approach of using fly ash has been as a filler in concrete. The addition of fly ash to concrete mixture has been practiced for decades. However, the level of utilization of fly ash without affecting its properties is limited. Recently, conversion of fly ash to zeolites has been reported by many researchers (3-6). Zeolites possess uniform molecular pore and large surface areas, making it an ideal material for molecular sieves.

Background on In-situ Permeable Reactive Barrier

Permeable Reactive Barrier or treatment walls are a relatively new method of groundwater remediation. The concept was first forwarded in 1989 at the University of Waterloo in Canada. The investigators conducted bench scale investigations using zero valent iron to break down chlorinated hydrocarbons. The first in situ demonstration was conducted in Borden, Ontario, Canada. In 1992, the permeable reactive barrier technology, "funnel and gate system" was first presented in scientific literature. In 1994, the first commercial application of permeable reactive barrier technology was installed in Sunnyvale, CA. This installation is still operating and has proven itself in terms of cost and effectiveness compared to pump and treat remediation. (Summary of RTDF, Sept. 18-19, 1997.) The prospects for Permeable Reactive Barrier as a cost effective alternative to pump and treat remediation are excellent. A considerable amount of effort is underway to investigate new cost effective materials which can be used to create new types of permeable reactive barriers with new functionalities. A promising new material called AAM barrier material has demonstrated the ability to remove heavy metals such as Cr from highly contaminated water.

AAM material can have permeability ranging from 10^{-2} cm/sec up to 10^{-1} cm/sec; AAM contaminated barrier materials utilize high permeability of 10^{-1} cm/sec. There exists a large body of literature on the various mechanisms of heavy metal removal and material used for permeable barrier technology (7-16). Materials range from clay minerals to synthetic zeolite from fly ash to zero valent iron and metal oxides.

Mechanisms for Heavy Metal Removal

The mechanisms of removal include physical and chemical reactions. They can be divided into two broad categories depending upon their reversibility for recovery applications (17):

1.   Removal only: separation/filtration, chemical precipitation, solidification/stabilization, and chemical redox reaction.

2.   Recovery and Reuse: adsorption, ion exchange, membranes, and electrolytic recovery.

Results on Heavy Metal Removal Ability of AAM

AAM barrier material was used to remove Cr from contaminated water. Fly ash from three different sources was used to produce reactive barriers of different permeability. AAM materials with permeability 10^{-2} to 10^{-1} were created. Only the highest permeability proved to be suitable for reactive barrier material. AAM barrier from three ash sources with a permeability of 10^{-1} was produced and crushed into pelletized form. To determine effectiveness of the various barriers, a batch test was performed. Based on that result, the column test was conducted. Three different types of class F fly ash were used in construction of AAM barrier material. Selected fly ashes for this experiment represent a wide range of ash generated by the coal burning operation. XRF was used to obtain the composition of fly ashes (provided by ash supplier). These fly ashes have the following compositions:

	Source I	Source II	Source III
SiO_2	61 1	63 2	53 8
Al_2O_3	2⁻5	19 4	23 4
Fe_2O_3	4 5	5 4	6 0
CaO	1 ⁻	4 3	8 9
MgO	0 9	1 3	1 9
Alkali	0 9	1 1	1 0
SO_3	0 3	1 4	0 9
LOI	2 ⁻	2 1	0 6

In this work, 10 g of barrier materials were added to 500 g of 1000 ppm solution of mercury. The removal ability of AAM from source 1 was less than source 2 and 3, while AAM from source 2 and source 3 had similar removal efficiency. AAM from source 2 had more work time during processing, thus AAM from source 2 was selected for column test. The table below shows the results of batch test of AAM for Hg removal ability:

AAM Barrier	1000 ppm Cr
Source 1	142
Source 2	0.7
Source 3	0.9

Column Test

The AAM reactive barrier constructed from fly ash obtained from source 2 was used in the column test. In this work, 7.5 liters of 1000 ppm Hg with increment of 0.5 liter were passed through 200 gm of barrier materials. Our results indicate that AAM is capable of removing mercury from 1000 ppm contaminated water.

From the result obtained in column test, AAM has the ability to remove Hg very effectively. AAM contaminant barriers are very economical. The cost of materials will be similar to the cost of a Portland cement system. The basic materials to create AAM are fly ash, sodium silicate, and sodium hydroxide. These materials are available all over the U.S. in bulk volume for commodity prices. The manufacturing cost will be similar to that of precast concrete products for manufactured material and ready mix concrete for ambient temperature applications. The cost of zeolites will be similar to the cost of currently available ion exchange materials. This represents the most significant cost. If AAM is viable as a contaminant barrier without the addition of ion exchange material, this will be the most economical option. Typical costs of materials for AAM compositions without stone are $40 to $50 per ton. The manufacturing operation for elevated temperature curing should increase this price to about $100 per ton.

Conclusion

Investigation of AAM in the past 3 years has demonstrated that fly ash can be transformed into an effective sorbent for heavy metals. AAM has the ability to remove heavy metals such as Hg from contaminated solution. 1000 ppm of mercury solution were reduced to about 0.7 ppm after passing through the optimized Controlled Permeability of AAM contamination barrier. Further work is needed on placing the material into a logistically sound product. The process has been successful with class F fly ash from many sources.

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3.7.8   Remediation and Legal Case Histories of the Buena Vista and Klau Mines, Two Mercury Mines in the Las Tablas Creek Watershed, San Luis Obispo County - Gerhardt Hubner, Central Coast Regional Water Quality Control Board and Daniel Suter, USEPA, Region 9

Buena Vista Mines Inc. (BVMI) owns two inactive mercury mines (Buena Vista and Klau Mines) in the Las Tablas Creek watershed of San Luis Obispo County, California. Both of these mines have been polluting surface waters (Las Tablas Creek, Klau Branch, and Lake Nacimiento) for decades. The Central Coast Regional Water Quality Board (Regional Board) has attempted through various enforcement mechanisms to get the mine owner and BVMI to abate and remediate on-going pollution emanating from these mines. Currently BVMI holds National Pollution Elimination Discharge System (NPDES) permits adopted by this Regional Board in 1993. Lawsuits have been filed in both State and Federal Courts in an attempt to get compliance with environmental laws. In 1997, the mine owner and BVMI pleaded guilty to Clean Water Act violations. In 1999, the USEPA issued an Unilateral Administrative Order to BVMI and its owners (Harold and Ed Biaggini) requesting that they conduct certain remedial work to abate the pollution and contamination from the mines. This year USEPA assumed control of both mines sites, and is in the process of completing the remaining remedial action items contained in the Order.

Background

Location

The Buena Vista and Klau Mines are located 12 miles west of Paso Robles in the Adelaida district of San Luis Obispo County. The mines are on adjacent patented properties on the eastern slope of the Santa Lucia range. The mines are also part of the Las Tablas Creek watershed, which drains to Lake Nacimiento.

167

Site Characteristics

The Buena Vista and Klau Mines consist of two abandoned mine sites which encompass approximately 175 acres and include five miles of underground workings, a two acre mine pit and eroded slopes comprised of approximately 300,000 tons of mines tailings, overburden and waste rock. At the Buena Vista Mine, approximately 100,000 cubic yards of mine tailings (commonly called the retort pile) was consolidated in a main drainage valley. This pile historically generated five to ten gallons per minute of acid mine drainage. Additional acid mine drainage is being generated in underground workings and expressed as surfacing acid mine drainage springs.

History

The Buena Vista Mine was first worked in 1876; the Klau Mine in 1874. The cinnabar that was produced at the mines occurred in high grade veins, pockets and disseminations. By 1903, the Klau Mine was the fourth largest producer of mercury in the State of California. During the operation of the Buena Vista, the mine reportedly produced 30 tons of rock/ore a day, at 5-30 lbs. of mercury per ton. By 1970, the total amount of mercury removed was estimated at 84,300 flasks, or 6.4 million lbs. of elemental mercury. In addition, the mine yielded $25 million in gross profits (by 1970) according to a local newspaper.

1993 Clean Lakes Report

A Federally funded study, conducted by a team of researchers at California Polytechnic State University at San Luis Obispo, concluded that Las Tablas Creek contributed 78% of the water borne mercury entering Lake Nacimiento. The Buena Vista Mine directly discharges contaminates to Las Tablas Creek; the Klau Mine discharges contaminates to a tributary of Las Tablas (Klau Branch). Background concentrations of mercury in sediment from Las Tablas Creek were reported at 2 mg/kg. Twenty feet or less from the Buena Vista Mine data indicated 72 mg/kg in sediment. The 1993 Clean Lakes Report estimated that 21 lbs. of mercury enter the lake each year.

Data from the Clean Lakes Report and fish tissue analyses conducted under the Toxic Substances Monitoring Program resulted in the California Department of Health Services issuing public health warnings for Lake Nacimiento for the consumption of fish. These postings continue to this day.

Environmental Impacts from the Mines

Water quality impacts from the mines are due to: 1) acid mine drainage caused by water and oxygen reacting with prevalent pyrite and marcasite prevalent in rock on-site; and 2) mercury rich waste rock mitigating off-site to surface waters.

During mining operations, mining waste including waste rock, tailings and mercury extraction wastes were dumped in drainage channels and various other places throughout the mine sites. Weathering and erosion from seasonal rains have caused erosion of these piles, resulting in waste rock being transported off-site to nearby surface waters.

Mercury is a toxic metal to both humans and aquatic life. Organic mercury species are more toxic and more soluble than the inorganic species. Much of the mercury at the site begins as inorganic mercury sulfide - cinnabar (although some free elemental mercury is still present at the sites). From there it is transported off-site to surface waters where it accumulates in bottom sediments. The sediment is further transported downstream or migrates up the food chain through bottom feeders. Through the process of methylation, mercury transforms to an organic species, becomes more toxic, and bioaccumulates in animals higher in the food chain.

Analytical data from Regional Board files reveal the following:

- Total mercury concentrations in sediment eroding from the Klau Mine to the Klau Branch ranged from 5.5 ppm to 16,500 ppm, with a mean of 2259 ppm.
- Samples taken from the retort pile at the Buena Vista were reported up to 940 ppm.
- Dissolved mercury concentrations in Las Tablas Creek directly below the Buena Vista Mine ranged as high as 0.046 mg/L.

- Water samples collected significantly exceed the EPA ambient water quality criteria for mercury of 0.000012 mg/L.
- For comparison purposes mercury concentrations in soil above 20 ppm are considered Hazardous Waste (per Title 22 California Code of Regulations).

Regional Board Involvement

The Central Coast Regional Water Quality Board has issued several waste discharge requirements and enforcement orders to the mine owner and BVMI going back to the 1960s. Currently, the mine owner holds a NPDES permit for both mine sites. The permit regulates the discharge(s) of pollutants from the mines. Specifically, the permit establishes effluent limitations for the discharge from the acid mine drainage treatment plant. The mine owner is not currently in compliance with those permits. Previous monitoring reports indicated that treated acid mine drainage from the treatment plant did not meet effluent limitations contained within the permit. No monitoring reports have been submitted since the summer of 1999.

Legal Proceedings

Several State and Federal criminal and civil cases have being filed over the last decade.

State Civil Case

On December 21, 1998, the San Luis Obispo Superior Court, upon the Board's request, dismissed the Board's State civil suit against BVMI, et al., without prejudice. This request was based on the Board's decision to transfer lead enforcement responsibility to the USEPA and the U.S. Department of Justice.

State Criminal Case

Dismissed Spring 2000. The judge in the case felt that the Federal criminal sentencing in December of 1999 provided sufficient justice, although this case involved separate violations of the Clean Water Act.

Federal Criminal Case

On December 7, 1999, in Federal District Court in downtown Los Angeles, Judge Keller convened a sentencing hearing for Harold Biaggini and his Buena Vista Mine Inc. Mr. Biaggini had previously pled guilty to one violation of the Clean Water Act. His Corporation, BVMI had also pled guilty to one felony violation of the Clean Water Act.

- To Mr. Biaggini:
  - Six months house arrest
  - Another year of supervised probation
  - $30,000 fine

- To the BVMI Corporation:
  - $300,000 restitution, to be placed in an escrow account to fund future remediation activities

- To both Mr. Biaggini and the BVMI Corporation:
  - Compliance with Federal and State Laws, including the Clean Water Act at both Buena Vista and Klau Mines
  - Obey all USEPA and California State Environmental Authorities

Federal Civil Case

On June 8, 2000, Federal Court Judge Keller issued an Order staying the federal civil action for six months. The U.S. Attorney's office requested the stay to allow the USEPA removal action to proceed, and determine what sort of action would be appropriate after the remedial work is completed. A reassessment would then be conducted. The next status conference on this matter is scheduled for December 6, 2000.

Recent Legal Posting

Mr. Harold Biaggini and his attorney recently posted disclaimers at the entrance to the mine sites. The disclaimer states that they are not a party to this year's USEPA removal action, and they are not responsible for impacts as a result of this work.

USEPA Role

A USEPA Action Memorandum was signed July 8, 1999, authorizing Federal funding for an Emergency Response Time Critical Removal Action at the Buena Vista and the Klau Mines. On July 12, 1999, a USEPA Unilateral Administrative Order (UAO) was issued to BVMI, Harold J. Biaggini and Edward C. Biaggini notifying that USEPA would proceed with actions outlined in the Action Memo and UAO if the respondents were unwilling to perform those actions. That UAO Order, under 106 CERCLA/Superfund authority, required certain remedial actions based upon a determination of an imminent and substantial endangerment to the public or welfare, or the environment. The mine owner did complete several of the action items required under the UAO. This included the installation of three sedimentation basins at the Buena Vista Mine and one at the Klau Mine, minor repair of retort cover, and installation of several erosion control measures at both mine sites.

In Spring of 2000, USEPA Emergency Response group did step in and take over the work to complete the remaining remedial actions after the mine owner refused to conduct or pay for any further remedial work as required. Under current status, below is a detailed accounting on the progress being made to complete the above listed actions.

The remaining work in the UAO includes the following:

- Preparation of a mine waste repository near the Open Pits area at the Buena Vista Mine. A leachate collection system, terrace and sloped banks, drainage system and cover system would also be constructed.

- Excavation and transportation of approximately 100,000 cubic yards of acid generating waste rock to the repository.

- Drain the existing lake at the Klau Mine. The existing dam would be breached and natural drainage would be created downslope.

- Regrade and fill in the area above the underground workings and old adits/mine entrances to prevent recharge of the underground working, and thus reduce future acid mine drainage generation.

- Preparation and construction of a mine waste repository at Klau Mine. Installation of a liner system, and collection system to receive mine tailings/waste from areas at the Klau Mine.

- Grade, recontour, and divert stormwater from existing slopes at both mine sites.

- Design and build a state of the art acid mine drainage treatment plant at the Buena Vista Mine.

The estimated cost to complete these actions at both the Buena Vista and Klau Mines is estimated to be approximately $2 million. USEPA has indicated that it will seek reimbursement from BVMI and Mr. Biaggini for past and present cost incurred as a result of this project.

A CERCLA or Superfund Section 104(e) Request for Information Letter was sent to Mr. Harold Biaggini and BVMI. Mr. Biaggini and the BVMI corporation are required to provide full financial disclosure of all its assets, property and institutions. USEPA staff is now making inquires into Mr. Biaggini's and BVMI's financial records to determine the validity of his claims as to his inability to pay for remedial and on-site works at both mine sites.

In a letter received by the Regional Board on July 20, 1999, USEPA stated its intent to place Buena Vista

and Klau Mines on the CERCLA National Priority List to ensure long-term remediation is completed, and also address long term site operation and maintenance issues. Presently, Regional Board staff does not believe that listing these sites is necessary.

Current Status

The mining waste retort pile at the Buena Vista Mine has been removed and placed in the repository constructed near the Open Pit area. The total volume of waste placed in the repository is approximately 118,700 cubic yards. Approximately 5000 cubic yards of mining waste has been placed in the Klau Mine repository. The Buena Vista repository has been covered, capped, and drainage channels installed. All water is being diverted to the southern or to the eastern drainage courses. The drainage course where the old retort pile formerly existed has been re-sloped and stabilized. Rock has been added to the bottom of the drainage valley. The California Conservation Corps is scheduled to arrive the week of October 30th to construct erosion barriers, place straw bales, and plant approximately 2500 native trees. Once this is completed, USEPA will hydro-seed the entire area.

Unfortunately, the new acid mine drainage treatment system will not be completed this year. Design and cost estimates have come in considerably higher than anticipated. The existing, temporary treatment plant utilizing baker tanks with sodium bicarbonate and aluminum sulfate addition will be used this winter. USEPA has hired a local person to watch over the treatment plant operation and erosion control measures for both sites. USEPA has indicated that it has sufficient funds available to pay for operation and maintenance of the sites through next spring. An irrigation system will be constructed to discharge the treated water to the hills located west of the old retort pile. The amount of water being generated on-site (and being collected for treatment) appears to be lower (as expected), but is anticipated to increase with the rains. USEPA is checking the integrity of the old storage tanks to ensure they will have adequate storage capacity for this winter. Sludge from the existing storage pond has been pumped to the upper pond, where the sludge will be dried and then removed.

Approximately 25,000 cubic yards of natural material has been placed on the Klau Mine repository as cover. The lower Klau Mine open pit has been filled in to promote drainage and minimize ponding. Due to the on-set of the winter season the re-sloping of the lower Klau site adjacent to the Klau Branch will have to wait until next spring.

In order to evaluate options for long-term operation and maintenance of the facilities, Regional Board staff prepared and sent a letter of interest to various environmental consultants on September 27, 2000. The letter requests that consultant(s) with institutional financial stability, and expertise in mine reclamation and long-term operation and maintenance of hazardous sites draft a response and submit a letter of qualifications to the Regional Board by November 1, 2000. However, this letter was not intended to mean that the Regional Board in any way was assuming long-term operation and liability for either of the mine sites.

Conclusion

A great deal of remedial and reclamation work has been accomplished at the Buena Vista and Klau Mines the past year and a half due to the presence of USEPA On-Site Removal team, their consultants and contractors. The remaining action items (acid mine drainage treatment plant, draining of the Klau lake and regrading of several slopes) will hopefully be completed next spring. The owner of the Buena Vista and Klau Mines continues to be noncompliant with Orders issued by the State and Federal government. Long-term operation of the acid mine drainage treatment plant, and maintenance of the cover system and the on-site erosion control measures still remain a concern. Regional Board staff is continuing to coordinate with USEPA in order to resolve these issues.

3.8   Sulphur Bank Mercury Mine

3.8.1 An Evaluation of Remote-Sensing Tools for Hydrologic Investigations - Richard Hammack, National Energy Technology Laboratory (NETL); G.A. Veloski, NETL; T.E. Ackman, NETL; J.I. Sams, USGS, Water Resources Division; R.M. Dilmore, Department of Civil and Environmental Engineering, University of Pittsburgh; Ellen Manges, USEPA, Region 9; and David Janney, Tetra Tech EM, Inc.

In collaboration with the EPA (Office of Research and Development in Cincinnati, OH and Region 9 in San Francisco), Tetra Tech EM, Inc., and the Elem Indian Colony, the National Energy Technology Laboratory orchestrated airborne geophysical surveys and conducted ground-based geophysical surveys at the Sulphur Bank Mercury Mine Superfund Site. The objective of these surveys was to determine if these rapid techniques can provide an accurate and useful "snapshot" of site hydrology. It is recognized that these techniques must be used in tandem with conventional hydrologic evaluation methods to achieve a comprehensive understanding of site hydrology. However, the hypothesis is that geophysical surveys can quickly delimit areas that require further study using conventional hydrologic testing, and thereby reduce the overall cost of the hydrologic assessment by focusing these more expensive and time-consuming activities on smaller areas. The Sulphur Bank Mercury Mine site was chosen because an extensive array of groundwater monitoring wells are being evaluated as part of the ongoing remedial information feasibility study (RIFS) for the site. When available, information from these wells will provide a comprehensive understanding of the geology and hydrology of the site, and provide verification for airborne and ground-based geophysical data from this study.

Goals for the current study were to:

·   determine the accuracy of the geophysical information, its spatial correctness, and its geologic or hydrologic interpretation,

·   determine the value of geophysical information to the understanding of site hydrology and geology, and

·   determine the cost effectiveness of geophysical techniques if used in conjunction with more conventional methods for collecting hydrologic information.

This investigation employed total magnetic field determinations (using fixed base stations to correct for diurnal variations) and horizontal- and vertical-dipole terrain conductivity measurements that were initially collected from an aircraft platform. Subsequently, selected anomalies identified by airborne geophysical surveys were made the subject of a more focused ground-based survey that employed identical geophysical techniques. The results were then interpreted based on published geologic maps and anecdotal information on mining history.

Total field magnetic results collected from aircraft showed that the Sulphur Bank Mercury Mine was located within a geologic zone with a distinct magnetic signature. This distinct signature was that of an andesite flow whose boundaries can easily be recognized even beneath Clear Lake (Figure 1). The airborne magnetic results also showed evidence for both known and previously unrecognized faults.
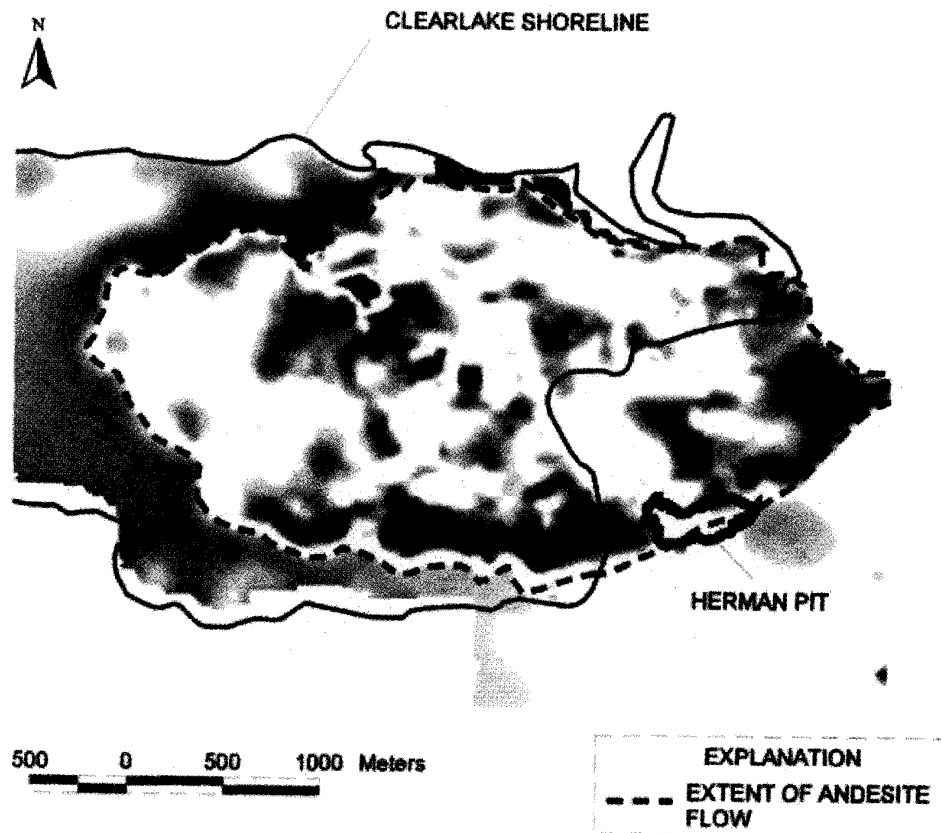
Figure 1. Total field magnetometry of Sulphur Bank Mercury Mine and vicinity. Darker areas are areas of higher magnetic field.

Airborne terrain conductivity results showed conductive zones that converge on Herman Pit (the now abandoned and flooded open-pit of the Sulphur Bank Mercury Mine) from the west, northwest, and north (Figure 2). These zones of anomalous electrical conductivity were primarily interpreted to be areas of water-saturated ground although other explanations were considered. Other possible explanations included:

- lake sediments because of their clay mineral content are more conductive than the andesite flow or the predominantly andesite-derived waste rock dumps on the site. In areas where the lake sediments are near to the surface, the increased conductivity of these sediments may be misinterpreted to be a hydrologic-based anomaly.
- the presence of conductive metal scrap which is pervasive at the site. Scrap metal is common near the surface but may also be present at depth in waste rock dumps.
- the possible existence of conductive mineralization. Deposits of conductive metal sulfide minerals may be present at the site, particularly along fault zones.
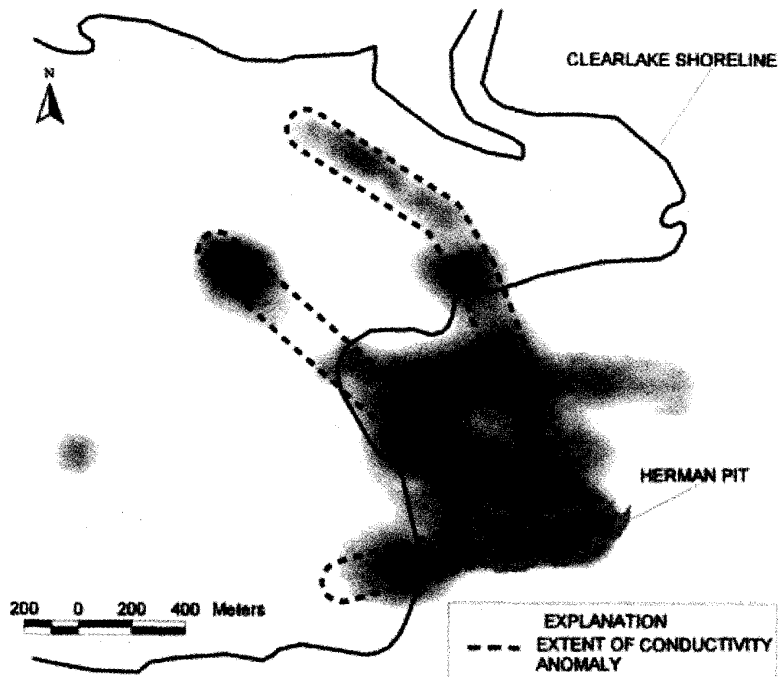
Figure 2. Airborne terrain conductivity of Sulphur Bank Mercury Mine collected at a frequency of 1500 hz using horizontal coplanar coil geometry. Darker areas are areas of higher conductivity.

Ground-based geophysical surveys were focused on the conductive zone (Figure 2) that extended westward from Herman Pit through piles of waste rock and into Clear Lake. A 200-m by 220-m grid (Figure 3) was established over these waste rock piles and included the area of anomalous conductivity identified by airborne surveys. A Geonics EM-34-3XL terrain conductivity instrument was used to measure conductivity using horizontal and vertical dipole coil configurations and transmitter/receiver separations of 20 m and 40 m. The ground conductivity survey results also contained an elongated conductivity anomaly that extended from Herman Pit to Clear Lake at the same location as the airborne anomaly. Possible interpretations could be a buried paleochannel where water is the electrically conductive medium, or a shear zone where water or mineralization could be responsible for the observed conductivity. Both interpretations are consistent with geophysical data and with known geologic and geomorphologic structures in the area. Although geologic and hydrologic information from the RIFS is not yet available to the public, conversations with the principal investigators working on the RIFS have indicated that geophysical results are consistent with the results of their detailed study.

The interim conclusions for this ongoing study are:

- airborne geophysical surveys were corroborated by ground-based geophysical surveys
- the results of airborne and ground-based geophysical surveys are consistent with the results of drilling and detailed geologic mapping
- airborne geophysical surveys are a very effective means for quickly acquiring data that is pertinent to the characterization of site geology and hydrology.

174
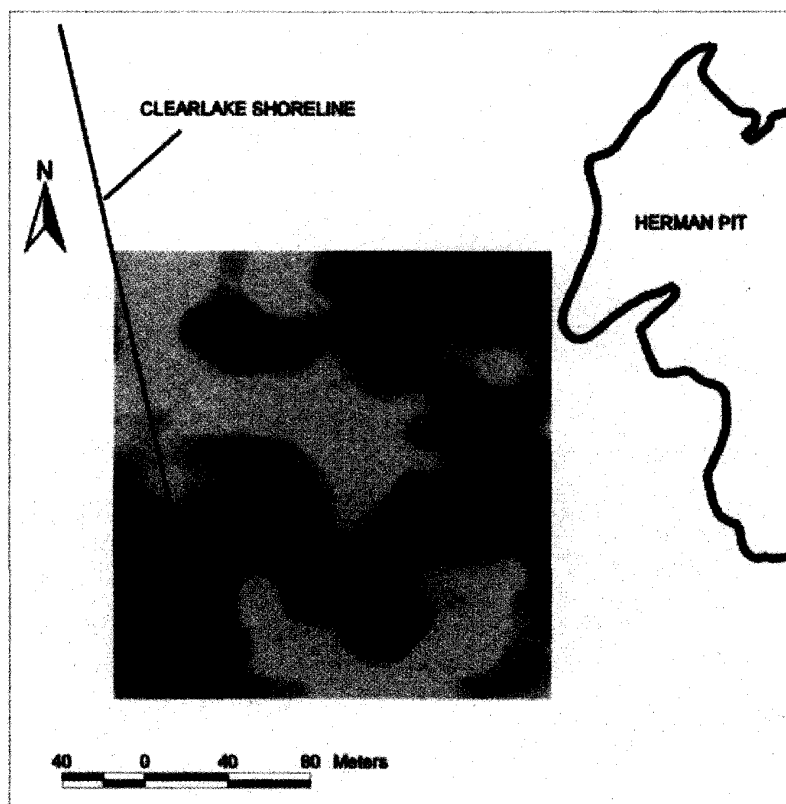
Figure 3. Ground-based conductivity survey collected using vertical dipole configuration and 40-m coil spacing. Darker areas are areas of higher conductivity.

3.8.2 The Active Hydrothermal System and Mercury Flux at Sulphur Bank Mine, California - Fraser Goff (Presenter), Los Alamos National Laboratory; Cathy J. Janik, USGS; Deborah Bergfeld, Los Alamos National Laboratory; and Dale Counce, Los Alamos National Laboratory

Sulphur Bank Mercury Mine (SBMM) hydrothermal system (Figure 1) formed between 44.5 and 34 kybp and is related to northward-migrating magmatism in the Plio-Pliestocene Clear Lake volcanic field (Hearn et al., 1981; Sims and White, 1981). About 2×10^6 t of S and 4.7×10^6 kg of Hg were mined intermittently from 1856 to 1957 (Becker, 1888; White and Roberson, 1962). Host rocks in the mine consist of faulted Franciscan Complex metasediments (Jurassic to Eocene) overlain by Quaternary sediments and basaltic andesite (Hearn et al., 1995). Thermal fluids rise from a small reservoir that is ~215°C at 500 m depth. Limited permeability, $CaCO_3$ scaling and environmental concerns prevented commercial geothermal development in the 1960s (Goff et al., 1977; Goff and Janik, 1993). Thermal modeling combined with geologic and geochemical data require that a young intrusive body underlies the SBMM area at a roof depth of ~4 km (Stimac et al., 1997).

SBMM fluids are geochemically distinct from other thermal fluids in the Clear Lake region (Figs 2, 3 and 4; White et al., 1973). Thermal waters are of $Na-HCO_3-Cl-B$ composition (≤9,000 ppm TDS) and ratios of I/Cl,

175

N_{tc}/Cl, Br/Cl and B/Cl indicate that the waters originate by thermal metamorphism of marine rocks (Goff et al., 1995). SBMM gases contain roughly 90% CO_2, 0.03–0.5% H_2S, 5–10% CH_4, $\leq$0.004% NH_3, and $\leq$6 x 10^{-7} % Hg (mol-% dry gas). Isotope values of $^3He/^4He$ (R/R$_A$) = 7.5 and $\delta^{34}S$-$H_2S \approx 0.0‰$ indicate mantle-magmatic origins whereas values of $\delta^{13}C$-$CO_2 \approx -10.5‰$ and $\delta^{15}N$-$N_2 \approx +2.5‰$ suggest contributions from organic remains in marine rocks.
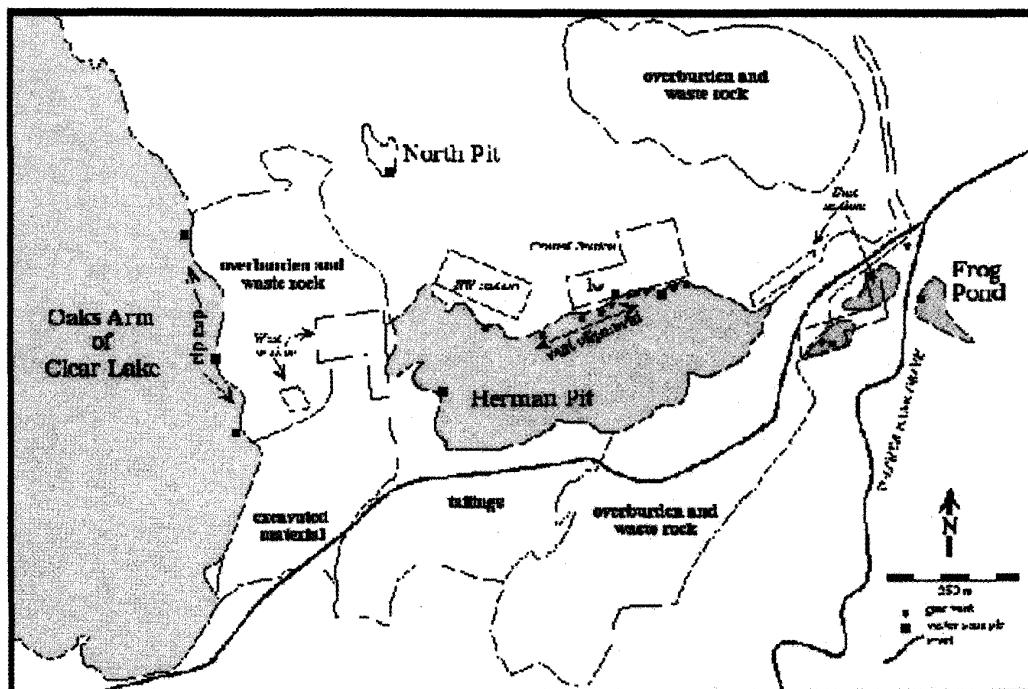
Figure 1. Location map of SBMM showing sample locations and CO_2 soil gas traverses; lw = leaking geothermal well (from Bergfeld, 2000).

Soil gas CO_2 flux at SBMM is variable depending on location (Figure 5) but a value of ~9 tons per day (t/day) is calculated from the log transformed data (Bergfeld, 2000). Measured CO_2 flux from gas vents in Herman Pit (HP) is ~1 t/day; thus, the total CO_2 flux at SBMM is about 10 ± 5 t/day. Combined with gas chemistry mentioned above, the maximum H_2S flux is <0.04 t/day and the maximum Hg vapor flux is <0.3 grams per day (g/day). These values are *maxima* because considerable H_2S and Hg are reacted and scrubbed into soil and shallow ground waters in the mine area.

Natural hot spring discharge at SBMM was measured in the late 1950s at roughly 0.2 to 0.4 cubic meters per minute (m³/min) (White and Roberson, 1962). Hot spring waters originate from the underlying geothermal system and now enter HP where they are diluted and mixed with roughly 50% young ground water and rain (Table 1). Although no reliable data on Hg contents in these waters exist from the past, thermal water in a presently leaking geothermal well geochemically resembles deep fluids and contains at least 0.0035 ppm Hg. The Hg content of HP water varies depending on depth, site, and season but may be as much as 0.0015 ppm. Thus, most Hg is precipitated from thermal fluids at the bottom and margins of HP. Present discharge of HP water into Clear Lake averages about 0.38 m³/min (Reller et al., 2000), so the amount of Hg transported into Clear Lake (excluding Hg leached from the intervening barrier) averages no more than about 1 g/day. Clear Lake water samples collected by the rip-rap adjacent to the barrier contain $\leq$0.0001 ppm Hg and overall there is $\leq$1% HP water mixed into lake water (Table 1; Bergfeld, 2000).
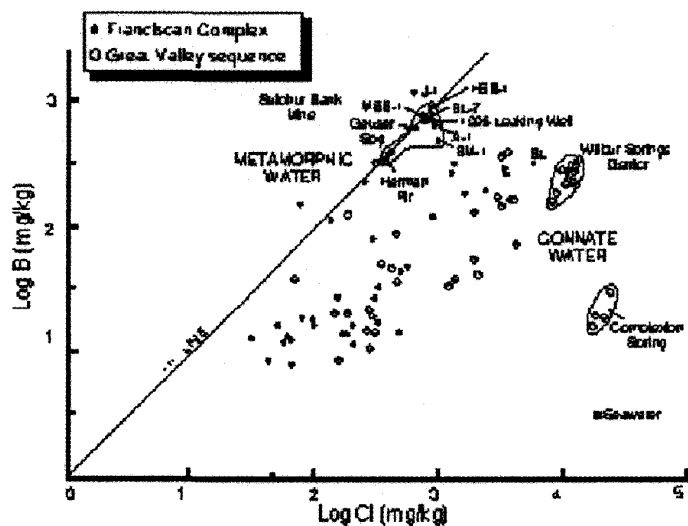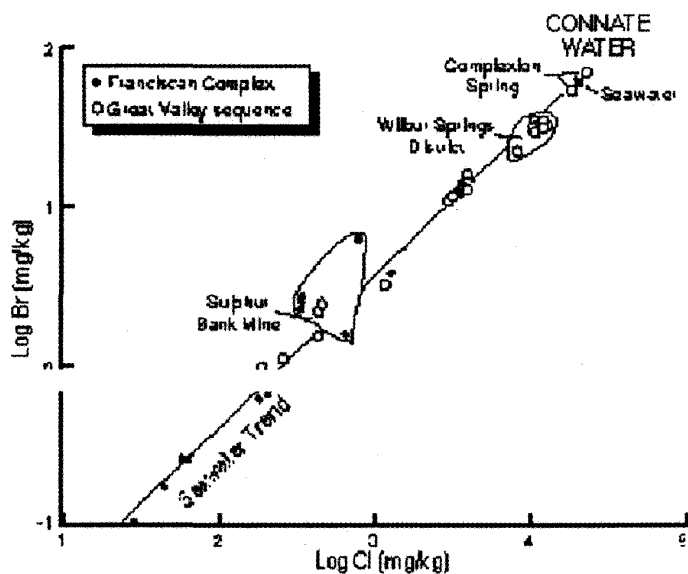
Figures 2 and 3. Plots of Br vs. Cl and B vs. Cl for thermal/mineral waters of the Clear Lake region. All waters including those from SBMM fall on the seawater trend (Figure 2) indicating interaction of hydrothermal fluids with marine rocks. In contrast, Figure 3 shows that SBMM waters have unusually high B/Cl caused by thermal metamorphism of marine rocks by subjacent magma (from Goff et al., 1995).

177
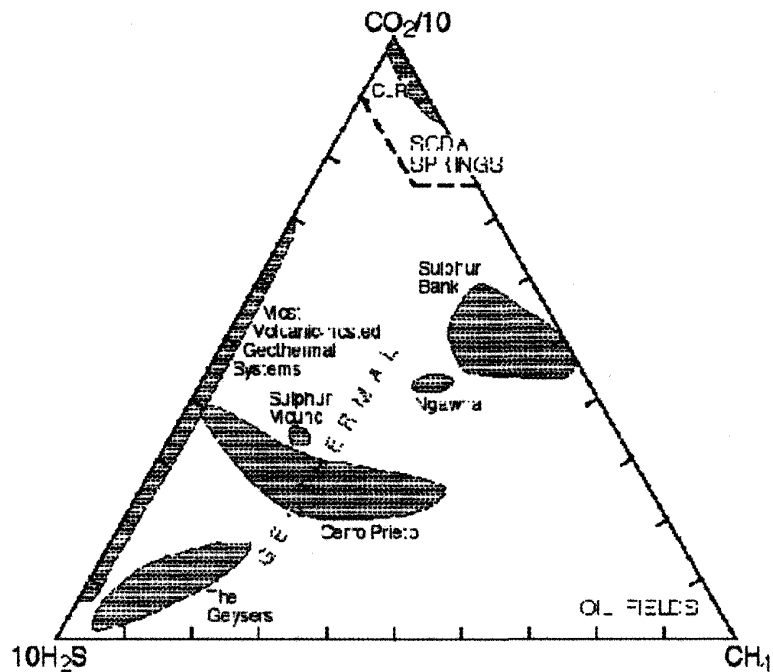
Figure 4. Triangular plot of CO_2 -H_2 S-CH_4 (mol-%) for gases from selected geothermal systems. Systems hosted in volcanic rocks have low relative CH_4 whereas those hosted in sedimentary rocks (e.g., The Geysers and SBMM) contain high relative CH_4. Most Clear Lake region sites produce extremely CO_2-rich gases, typical of Soda Springs. Ngawha, a system in New Zealand, closely resembles the SBMM system. Cerro Prieto is a large geothermal field in Mexico. Sulphur Mound is a small system 15 km south of SBMM (from Goff and Janik, 1993).
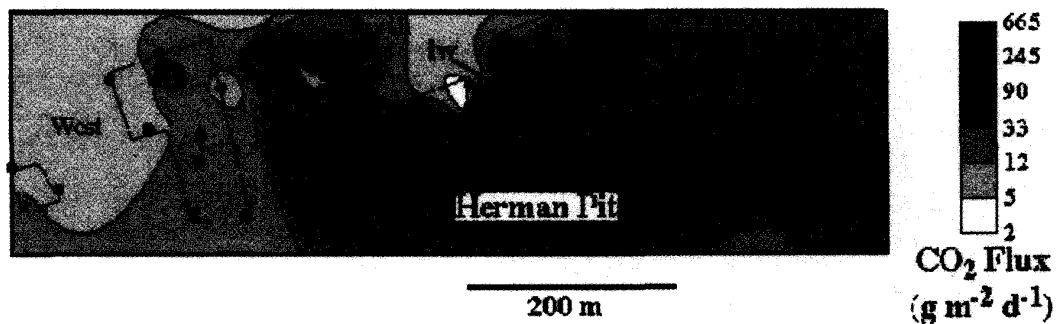
Figure 5. Generalized contour map of CO_2 soil gas flux measured at 62 sites at SBMM; values are in gram per meter squared per day (Bergfeld, 2000).

178

Table 1. Selected Chemistry in Some SBMM Waters, Clear Lake, and Other Thermal Waters (Bergfeld, 2000 and F. Goff and C.J. Janik, unpub.). Values are in ppm unless noted otherwise.

Site	Date	T(oC)	pH	B	Cl	NH4	SO4	Hg	Comments
SBMM Geothermal Water									
Geyser Spg	3/57	69.5	6.8	620	644	464	598	n.a.	White et al., 1973
Leaking Well	9/95	31.5	8.6	747	858	535	278	0.0035[a]	Magma-Sul. Bank #1
SBMM Pits and Ponds									
Herman Pit	9/93	23.5	3.1	336	335	288	3340	0.0003	North shore, gas vents
Herman Pit	12/93	14.0	3.1	333	350	355	3390	0.0006	North shore, gas vents
Herman Pit	12/93	14.0	3.1	329	355	365	3410	<0.0005	West end
Herman Pit	9/95	23.4	2.9	278	333	254	3460	0.0001	North shore, gas vents
Herman Pit	9/95	23.3	2.8	282	337	263	3580	0.0003	West end
Herman Pit	11/97	17.2	3.0	279	324	224	2730	<0.0001	North shore, gas vents
Herman Pit	11/97	17.6	2.9	286	318	220	2650	0.0012	West end
North Pit	9/95	21.0	2.4	6.6	6.7	20.4	4700	0.0004	Southeast edge
Frog Pond	9/95	24.5	5.8	0.09	4.8	<0.02	23.8	0.0001	Southwest edge
Clear Lake									
SBMM rip-rap	9/95	20.2	8.3	1.09	6.4	0.70	10.1	<0.00005	Center of rip-rap
SBMM rip-rap	11/97	15.9	8.5	1.03	5.7	2.06	8.1	<0.0001	North end rip-rap
SBMM rip-rap	11/97	15.6	7.5	3.70	8.4	2.74	35.4	0.0001	South end rip-rap
Clear Lake	12/93	12.0	7.9	1.44	18.3	0.06	7.2	<0.0005	End of pier in lake
Highlands	11/97	13.3	8.1	0.97	5.6	0.11	4.7	<0.0001	Edge of lake
Other Regional Thermal Springs									
Big Soda	9/95	31.0	8.6	13.0	62.5	5.7	0.21	<0.00005	Soda Bay, Clear Lake
Jones	10/95	55.0	8.8	302	11900	248	220	0.0017	Wilbur Springs area

[a] An unfiltered sample of this same water contained 0.066 ppm Hg.

Acknowledgments

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3.8.3 Recent Geochemical Sampling and Mercury Sources at Sulphur Bank Mercury Mine, Lake County California - David G. Jewett, USEPA, R.S. Kerr Environmental Research Center; Ellen Manges, USEPA, Region 9; and Gregory J. Reller (Presenter), Tetra Tech EM, Inc.

The Sulphur Bank Mercury Mine in Lake County, California has been identified as a significant source of mercury to Clear Lake. The mine was operated from the 1880s through the 1950s. Mining started with surface operations and then progressed to shaft and later open pit techniques. Pit mining created Herman Impoundment; a 20 acre, 90 feet deep pit located approximately 100 yards from the shore of Clear Lake to the west of Sulphur Bank Mercury Mine. The USEPA recently completed sampling of 65 wells, springs, and surface water bodies in the vicinity of the Sulphur Bank Mercury Mine to identify sources of mercury and groundwater pathways from the Sulphur Bank Mercury Mine to Clear Lake. The water samples were ana-lyzed for metals including mercury and major ions including B, Br, and Li. Ion ratios show that hydrothermal solutions are present in nearly all of the on-site sampling points. The hydrothermal solutions are diluted to varying degrees by surface water, and infiltrating precipitation. Dissolved mercury was detected at concen-trations up to 350 μg/L in groundwater. The sources of mercury in groundwater at the site are water-rock interaction, the hydrothermal system, and possibly suspended particulates.

Introduction

The SBMM is adjacent to Clear Lake in Lake County, California. Salient features of SBMM are the waste rock, tailings, and ore piles; Herman Impoundment, an active hydrothermal system, and naturally mineral-ized rock. A waste rock pile (waste rock dam) was placed between Herman Impoundment and Clear Lake. Water from Herman Impoundment seeps through the waste rock dam and discharges to Clear Lake. Con-sideration of these features resulted in identifying the following questions regarding sources of mercury and groundwater pathways from the Sulphur Bank Mercury Mine to Clear Lake:

1. Has the hydrologic system changed significantly since investigations by earlier workers such as White and Roberson? Since the late 1800s?

2 Do chemicals migrating in acid rock drainage from the waste rock, tailings, and ore piles transport mercury to groundwater?

3. What is the source for mercury discharging to Clear Lake in the vicinity of the waste rock dam?

Attempts to answer these questions are provided in the body of this paper.

Water Chemistry

Sixty-five sampling points (3 ponds, two springs, Clear Lake, a wetland, and 52 monitoring wells) were sampled for chemical analysis. The wells include two sampling points within the shallow (<200 feet deep) hydrothermal system as evidenced by water temperatures in excess of 80 °C. As part of this work wells screened within Franciscan Complex and Lake Bed sediments below the andesite of Sulphur Bank were sampled. The water samples were analyzed for metals and major ions. The chemistry data was then evaluated using graphical techniques to identify water from different sources at the site. Scatter plots, Stiff diagrams, and Piper plots were used to evaluate the chemical data. Scatter plots of ion concentrations (for example the B vs Cl, graph shown below) indicate that hydrothermal solutions are present in nearly all of the on-site sampling points. The hydrothermal solutions are diluted to varying degrees. Comparison of Stiff diagrams resulted in identification of several different types of water based on ratios of cations and anions. Comparison of selected scatter plots to Stiff diagrams and groundwater flow paths resulted in identification of an oxidation trend of hydrothermal solutions from reduced nearly neutral high temperature hydrothermal solutions (pH = 6.8, Eh = -300mV) to acid sulphate solutions (pH = 3, Eh = 500mV). This trend is also shown on the Piper plot by increasing sulphate along the groundwater flow path suggesting that sulphur species are oxidized as groundwater flows away from the hydrothermal system. Along this chemical trajectory lie the waters of greatest interest to understanding the sources of mercury at SBMM: water of Herman Impoundment, and groundwater within the waste rock dam water bearing zone.

May - June 2000 Hydrochemistry Data
Sulphur Bank Mercury Mine

181
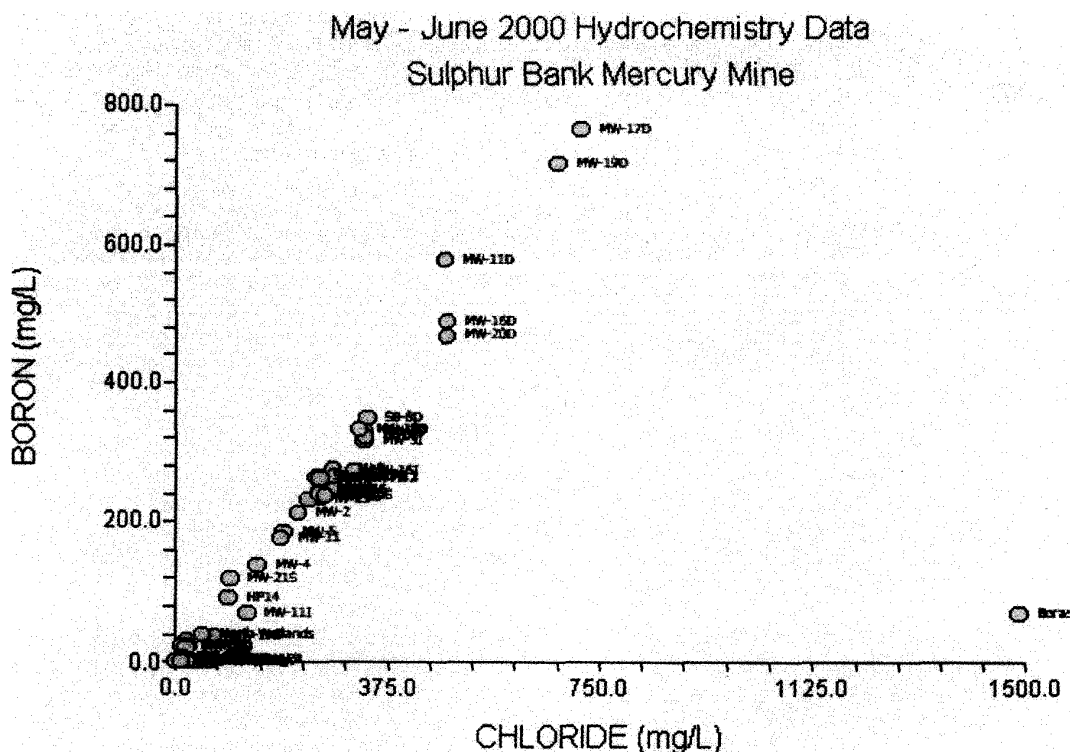
Water from Herman Impoundment is oxidized (Eh = 400V) and contains lower sulphate in comparison to the naturally occurring acid-sulphate water (Eh = 200mV). The sulphate concentration in Herman Impoundment is maintained by the flux of hydrothermal gas (predominantly carbon dioxide and methane with less hydrogen sulfide) constantly bubbling through Herman Impoundment. The gas is discharged naturally from the hydrothermal system. Water from Herman Impoundment seeps through the waste rock dam and discharges to Clear Lake. The Eh of groundwater within the waste rock dam water bearing zone varies from 327 mV to 507 mV, with no apparent spatial trends. The pH of groundwater across the waste rock dam ranges from 3.00 to 3.36. Water from Herman Impoundment is present in the waste rock dam water bearing unit, and may be present in the andesite water bearing zone. However, groundwater chemistry of Franciscan assemblage, lower lake sediment, and andesite water bearing zone wells chemically resembles cooled and/ or oxidized hydrothermal water instead of Herman Impoundment water.

Mercury Sources

Mercury content in the groundwater at SBMM ranges from below detection limits of 0.2 µg/L to 350 µg/L. Mercury concentrations detected in hydrothermal water range from 0.2 µg/L to 3.8 µg/L. Mercury was not detected in water from Herman Impoundment during this work. Mercury concentrations detected in groundwater from the waste rock dam water bearing zone range from 0.3 µg/L to 350 µg/L. In general, a trend of increasing mercury concentration along the flow path from Herman Impoundment toward Clear Lake is present in groundwater of the waste rock dam water bearing unit.

Previous workers have concluded that acid rock drainage is the main source of mercury in water at Sulphur Bank. However, surface water at Sulphur Bank, though acidic, does not contain appreciable dissolved mercury in comparison to the groundwater. For example, runoff samples collected in 1996 contained 0.1 µg/L to 1,600 µg/L THg, but only 0.1 to 2 µg/L dissolved mercury (Suchanek and others 1997, USEPA 1994). This indicates that acid rock drainage can not contribute significantly to the dissolved mercury observed in groundwater at the site. There is a significant quantity of sulphur within mining related rock at Sulphur Bank, and this sulphur creates acid when it contacts water. However, most of the acid drainage originating in this way flows into Herman Impoundment which contains low concentrations of mercury. Further, groundwater from monitoring wells screened within waste rock, tailings, or ore outside of the waste rock dam at the site does not contain elevated mercury contents. Of the 14 monitoring wells screened within or adjacent to waste rock, tailings, and ore outside of the waste rock dam, only 3 wells contain detectable mercury (maximum concentration 0.64 µg/L). Thus, acid rock drainage alone is not responsible for the observed mercury content of the groundwater. Instead, the water containing elevated mercury contents (with respect to the hydrothermal water) originates in Herman Impoundment and chemically evolves in contact with waste rock.

Potential sources for the elevated mercury concentrations present in groundwater at SBMM include the hydrothermal system, water-rock interactions involving in-situ rock not disturbed by mining, and water-rock interactions involving mining related rock such as waste rock, tailings or ore. Potential water-rock interaction paths include infiltration of precipitation through rock, seepage of Herman Impoundment water through rock, and hydrothermal solutions reacting with rock. Numerous workers have documented that the hydrothermal solutions at Sulphur Bank are actively depositing cinnabar. The current work supports the hypothesis that shallow (within approximately 200 feet of the ground surface) hydrothermal solutions contain mercury (up to 3.8 µg/L of mercury). This mercury is likely derived from near neutral, low Eh hydrothermal water which transports mercury upwards from deeper within the hydrothermal system. However, these natural processes do not explain the presence of up to 350 µg/L mercury in waste rock dam water bearing zone wells. Current observations such as the increase of mercury content along the flow path away from Herman Impoundment, and tendency of metal contents to increase with increasing Eh in groundwater at the site indicate that water-rock interactions may control mercury content of the groundwater through a change in chemical equilibria related to the mercury species present in solution. A firm conclusion as to whether the mercury present in waste rock dam wells is caused by interaction of Herman Impoundment water with waste rock, or infiltration of precipitation (or a combination of these factors) is not currently supported by available information.

However, the observation that the highest concentrations of mercury are associated with the highest measured Eh values in Sulphur Bank Groundwater indicates that aqueous chemistry may play a significant role in mobilizing mercury above the solubility of elemental mercury. The Eh of groundwater containing mercury above the solubility of elemental mercury (63 µg/L) is above 480 mV (486 to 502 mV). The measured pH and Eh of the groundwater within the waste rock dam water bearing zone is near the boundary between the

182

stability fields for elemental mercury and aqueous mercury chloride complexes. Thus, elevated Eh may lead to formation of aqueous mercury chloride complexes in turn resulting in dissolved mercury concentrations above solubility limit for elemental mercury.

Conclusions

Regarding the three questions given in the introduction.

The finding that warm nearly neutral hydrothermal water oxidizes to cooler acid-sulphate water that reacts with in-situ rock is consistent with earlier work at the site. The hydrologic system at Sulphur Bank has not changed significantly since investigations by earlier workers.

Mercury migrating in acid rock drainage does not appear to contribute a significant amount of mercury to groundwater at Sulphur Bank. Acid rock drainage alone does not provide a source for mercury observed at Sulphur Bank. Groundwater from wells screened in waste rock, tailings, and ore outside of the waste rock dam does not contain elevated (with respect to natural hydrothermal solutions) mercury.

As Herman Impoundment water seeps through the waste rock separating it from Clear Lake, mercury contents in groundwater increase away from Herman Impoundment. Current data do not support a firm conclusion as to the mechanism mobilizing this mercury. The mercury may be mobilized from the waste rock by seeping Herman Impoundment water as Eh and pH conditions vary along the flow path. Alternatively, infiltration of precipitation through the waste rock may mobilize mercury salts from oxidized waste rock above the water table or create an influx of particles containing adsorbed mercury. Perhaps a combination of these factors contributes to the observed mercury distribution.

3.8.4 Influence of Acid Mine Drainage from the Abandoned Sulphur Bank Mercury Mine on Methyl Mercury Production in Clear Lake (CA) - Thomas H. Suchanek (Presenter), Department of Wildlife, Fish & Conservation Biology; Amanda L. Bern, Department of Wildlife, Fish & Conservation Biology; Peggie King, Department of Wildlife, Fish & Conservation Biology; Kenneth McElroy, Department of Wildlife, Fish & Conservation Biology; Douglas C. Nelson, Division of Biological Sciences, University of California; Robert Zierenberg, Department of Geology, University of California; and William Shipp, Department of Geology, University of California

Introduction

The Sulphur Bank Mercury Mine (currently a USEPA Superfund site) was active intermittently along the shoreline of Clear Lake from 1872 to 1957 for processing cinnabar. Mining was accomplished initially by shaft mining, but after the turn of the century primarily by open pit mining, resulting in a 30 m deep excavation (the Herman Pit) now filled with ca. pH 3 fluids and separated from Clear Lake by a wasterock berm approximately 200 m wide. Beginning in 1992 we have investigated mercury contamination (both inorganic Hg and methyl Hg) in Clear Lake biotic and abiotic compartments and have made a preliminary estimate of the primary sources of mercury loading to Clear Lake. In 1995 we discovered a white alumino-silicate flocculent material (floc) in Clear Lake at the mine face that is positively associated with AMD from the Sulphur Bank Mine, and have followed the formation and distribution of this floc every year since (Figure 1). We have conducted preliminary studies on the extent of AMD flow into Clear Lake and further investigated the influence of the floc on the production of methyl Hg.
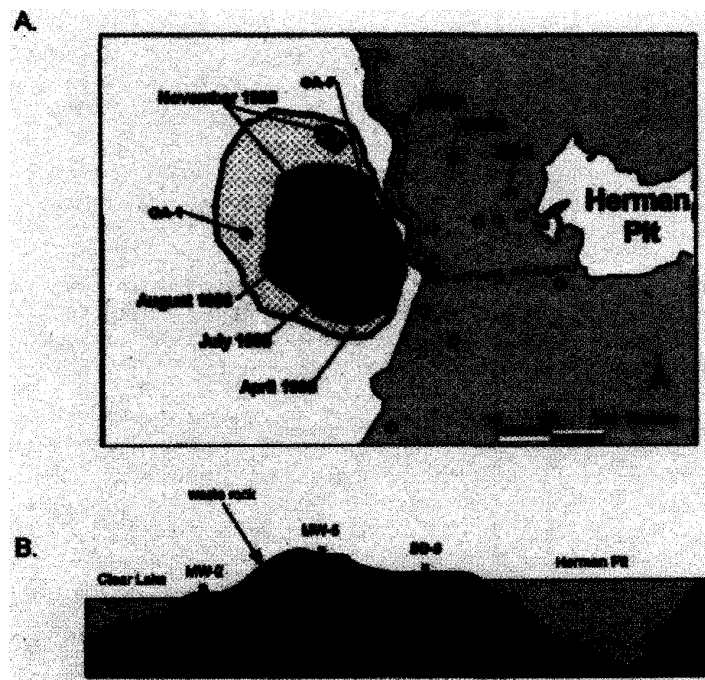
Figure 1.

1A. Distribution of floc in the nearshore region of the mine during 1998, showing a significant reduction in aerial coverage coincident with a reduction in precipitation from April through November.
1B. Cross-sectional view of mine site including the Herman Pit, three monitoring wells in the waste rock piles and Clear Lake. Dashed line indicates bottom of waste rock pile, which rests on an andesite sill. Note: Fig 1B not to scale.

Floc

The concentration of total (primarily inorganic) Hg in surficial sediments, in the vicinity of a long-term sampling site (OA-01) in the Oaks Arm of Clear Lake near the mine, ranges between 150-450 mg/kg (ppm) (Figure 2a). Thus, these sediments represent some of the most Hg contaminated sediments yet reported for any lake system in the world. However, surficial sediments from a site where floc is typically produced from AMD (site OA-OF) show considerably lower values of total Hg which range from ca. 25-100 mg/kg. For methyl Hg, however, the opposite trend has been observed. Sediments from OA-01 typically exhibit methyl Hg concentrations around 5-20 μg/kg (ppb), whereas sediments from the OA-OF site can, during peak methylation periods, reach upwards of ca. 100 μg/kg of methyl Hg, a value that is about 20-80 times higher than most all other regions in Clear Lake that have been sampled over the past 6 years (Figure 2b). Porewater sulfate at both the OA-OF floc site and OA-01 is also exceptionally high, with seasonal peaks reaching concentrations upwards of 4,000-5,000 mg/L (ppm), which also represents concentrations ca. 1,000-2,000 higher than most all other regions in Clear Lake that have been sampled over the past 6 years (Figure 2c). Based on these data alone, it appears that AMD from the mine reaches as far out into Clear Lake as OA-01 or beyond, $\geq$300 m from the mine face.
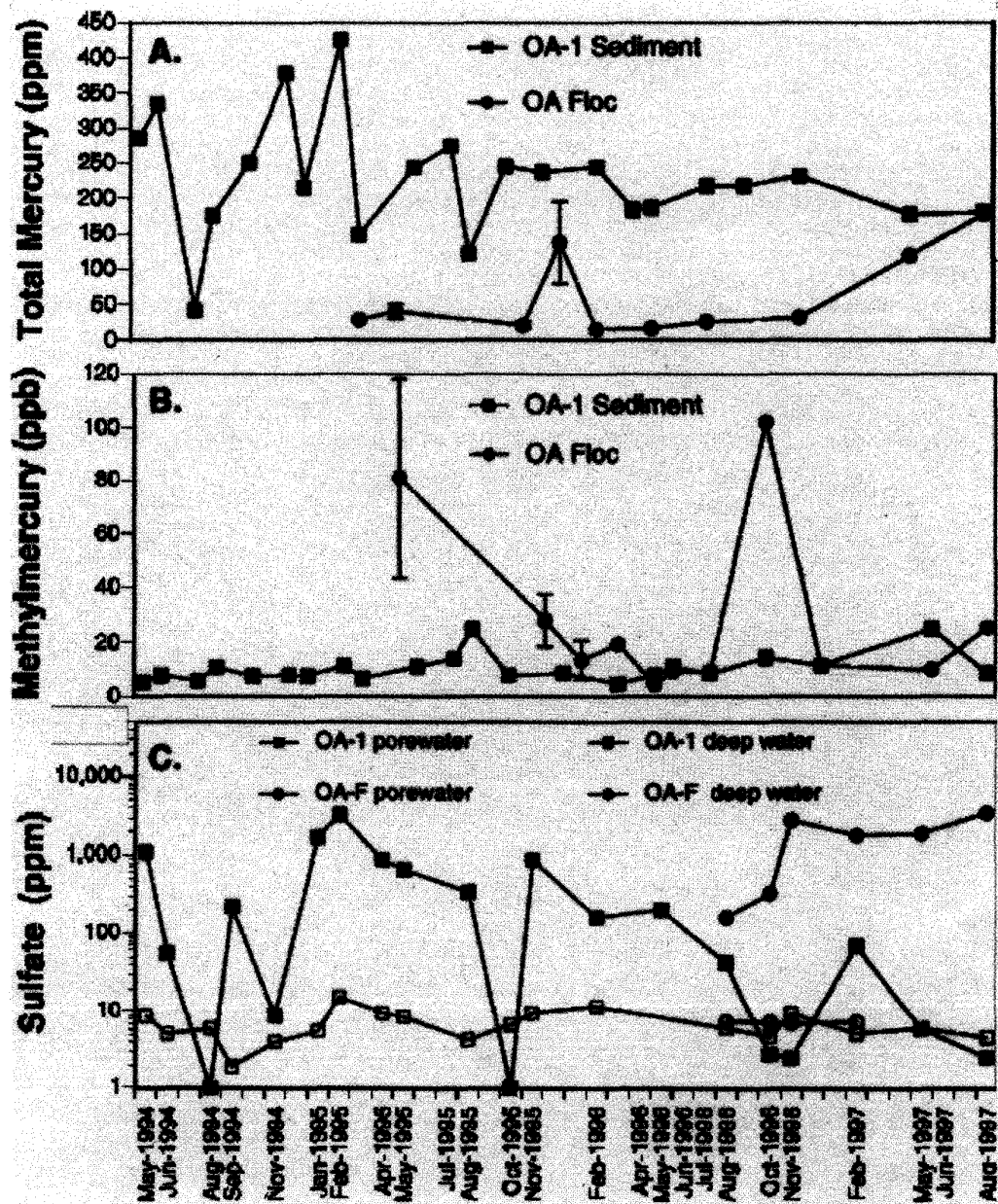
Figure 2. Long-term monitoring data for (A) THg [mg/kg (ppm) dry weight] and (B) methyl mercury [μg/kg (ppb) dry weight] in sediments, and (C) sulfate [mg/L (ppm) dry weight] in lake water and sediment porewater at sites OA-1 (ambient conditions near the mine) and OA-F (floc site) from 1994-1998.

Acid Mine Drainage

Rapid mixing of fluids emanating from sediments into the lake causes dilution that precludes characterization of the sulfate contaminated fluids from bottom water samples. A sediment porefluid study was initiated in order to establish the likely sources and flow paths of contaminant fluids entering the lake. Cores were collected along two east-west transects extending from the mine face out into Clear Lake about 70 m (Figure 3). A core collected at Site OA-04, 1.2 km from the mine face, served as a background control. Pore-fluids were extracted from 5 to 10 cm intervals down-core and were analyzed for major elements, selected minor elements, pH, $\delta^{18}O$, δD, and $\delta^{34}S$ of dissolved sulfate. Figure 4 shows down core profiles of pH, iron, sulfate and boron along one of the transects (B-B'). At the background site OA-04, pH is slightly alkaline, iron and boron concentrations are less than 0.05 mM and 0.1 mM respectively, and sulfate is ca. 0.03 mM near the surface, decreasing to levels below detection down core due to bacterial sulfate reduction. In contrast, all of the cores collected near the mine face show evidence of AMD including acidic pH and elevated iron and sulfate. Down-core profiles of geochemically conservative tracers, including Na, Cl, B, $\delta^{18}O$, and δD, converge toward compositions characteristic of waters in Herman Pit and indicate vertical flux of fluids derived from the mine site into Clear Lake. The shape of the porefluid profiles indicates predominantly diffusive transport of fluids in the core collected further from the mine face, but cores collected nearer to the waste rock dam indicate active vertical advection of AMD contaminated fluids. The concentrations of the deepest porefluids samples are consistent with derivation of all of the hydrothermally derived components by fluid mixing in Herman Pit and preclude a significant flux of hydrothermal fluid directly through the sediment.
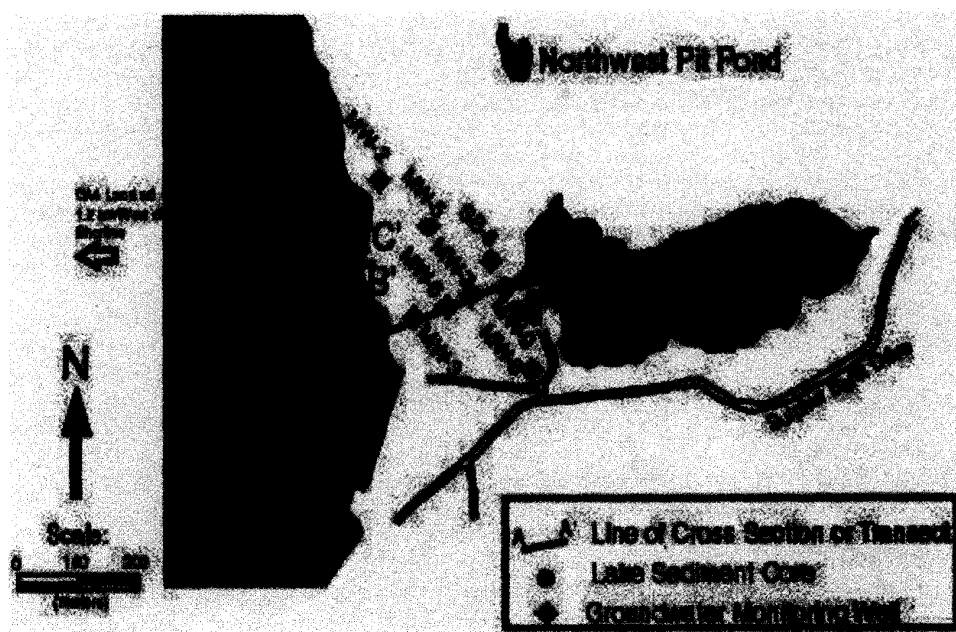
Figure 3. Region nearshore to Sulphur Bank Mine and Herman Pit showing transects used in this study.
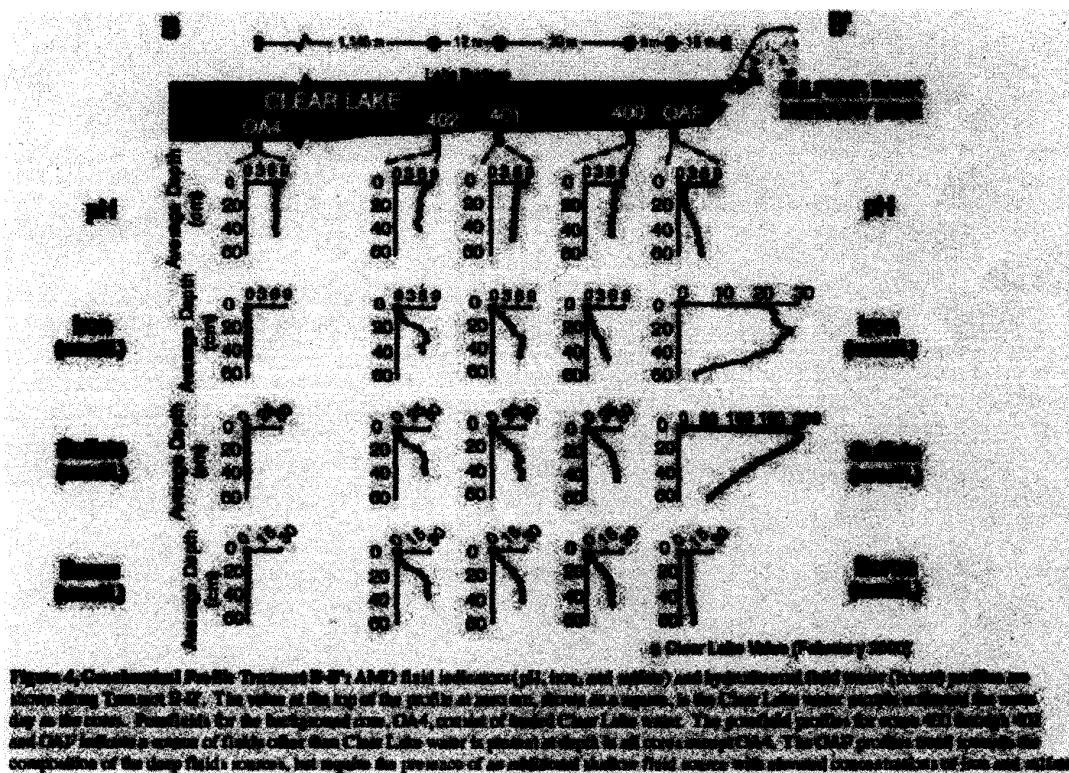
Cores collected in areas of active floc formation nearest the shore are also affected by a second fluid that is traveling through near-surface sediment by horizontal advection (Figure 5). These fluids are more dilute than Herman Pit waters with respect to conservative elements such as Na, Cl, and B, but have pH values as low as 3.8, sulfate concentrations (up to ca. 200 mM) more than 7 times those of Herman Pit waters and up to 45 mM Al. The geochemical characteristics and oxygen and hydrogen isotopic composition of these fluids demonstrate they are predominantly surface waters or shallow groundwaters that have been contaminated by acid and metals due to oxidation of pyrite and marcasite in mineralized waste rock. These highly acidic, oxidized fluids have the capacity to transport elevated levels of dissolved Hg to Clear Lake. Downcore depletion of sulfate, coupled with increases in $\delta^{34}S$ of dissolved sulfate, suggest that bacterial sulfate reduction is occurring, a process that would be expected to produce highly toxic and bioavailable methyl Hg.
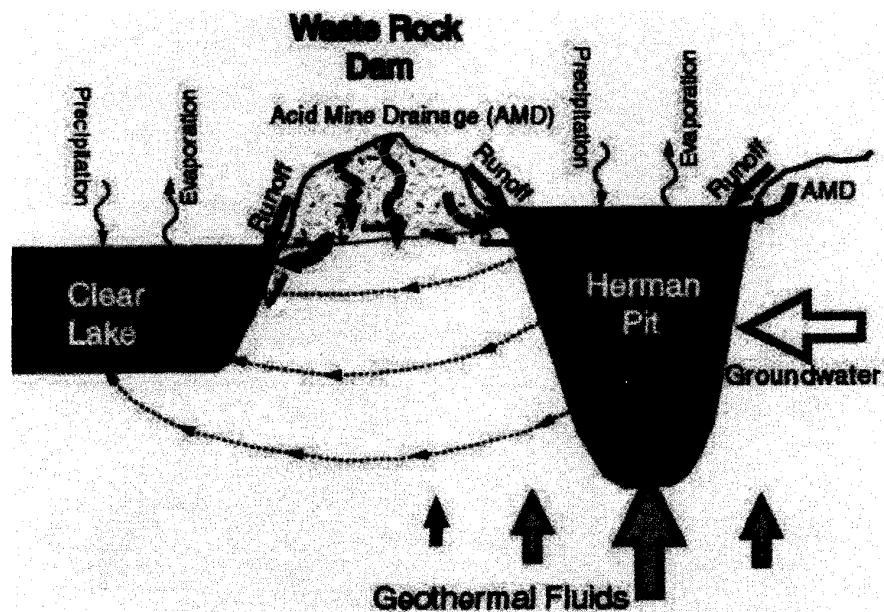
Figure 5. SBMM Hydrology Map: SBMM and the adjoining Clear Lake have typical water inputs and outputs, except SBMM receives a significant input from hydrothermal fluid.

Mercury Methylation

Production of methyl Hg from inorganic Hg is accomplished by groups of microbes that are principally or exclusively active in anoxic sediments. Studies by others have supported the view that sulfate-reducing bacteria are most active in this process in both freshwater and estuarine settings. Additionally, these studies have shown that methyl Hg production is sometimes enhanced by: 1) moderate acidity, 2) an intermediate concentration of sulfate, 3) mesophilic temperatures, 4) a readily available source of organic carbon and 5) a source of inorganic, bioavailable, Hg. The physical/chemical/biological conditions present in the vicinity of the Sulphur Bank Mercury Mine (e.g. at OA-OF) meet most or all of these criteria throughout the year. Increased acidity from AMD lowers sediment pH from typical Clear Lake water (ca. 8.0) to less than 4.0. The temperature of Clear Lake is highest during late summer and early fall (when the highest methyl Hg concentrations typically are detected). Wind-driven currents deposit many different types of organic matter (e.g. decomposing emergent macrophytes and bluegreen algae, dead fish) at the eastern end of the Oaks Arm of Clear Lake, producing a milieu resembling an organic soup near the mine. This decomposition also contributes to a considerably lowered oxygen tension in the region closest to the mine. There is ample inorganic mercury present in these sediments (see above), and sulfate-reducing bacteria (as well as a host of other potential methylating-microbes) are abundant in these sediments. Almost all of these conditions, some natural, some anthropogenically driven, may provide an optimal environment for the production of methyl Hg. However, the most acidic Clear Lake sediment porewaters measured (pH 3.7) nearest to the mine may be locally inhibitory to sulfate-reducing bacteria.

In order to test the effectiveness of sediments from different regions of Clear Lake to enhance methyl Hg production, we conducted a series of microcosm experiments. Sediment cores were collected from all arms of the lake, including some impacted heavily by AMD (OA-0F site). Cores were incubated for several days without Hg-amendment at in-situ temperature. The overlying water, which was rendered anoxic in some treatments and kept aerated in others, was sampled periodically and tested for increase in methyl Hg content over time. In some treatments chironomids were added to increase bioturbation and test the possibility that this would lead to greater methyl Hg efflux. Although all sediments from Clear Lake have a fairly uniform potential to methylate spiked-Hg^{++}, core tube microcosms that did not receive any Hg amendments gave a very different picture. Those core tubes that contained Clear Lake sediments with the highest concentration of AMD inputs from the mine (i.e. floc from site OA-0F) showed rates of methyl Hg efflux to overlying water that were roughly 20-fold higher than any of the other microcosms. All other "treatments" (i.e. overlying water oxic or anoxic, chironomids present or absent) had a marginal influence on efflux compared to whether the sediment was heavily impacted by AMD (efflux high) or collected several km from the mine (efflux low).

The use of molybdate ions (a specific inhibitor of sulfate-reducing bacteria) in slurry experiments showed that these bacteria are responsible for roughly only one third of the methylation potential at non-AMD impacted sites. Similar inhibitor studies have yet to be performed with the sediments that support the highest methyl Hg efflux because we have only recently understood the direct impact of AMD on such sites (e.g. OA-0F).

Summary/Conclusions

The unique environmental conditions adjacent to the Sulphur Bank Mercury Mine (as compared with all other regions in Clear Lake studied to date) appear highly favorable for the enhanced production of methyl Hg. These conditions appear to be created and influenced by natural and anthropogenic processes. Once methyl Hg is formed, it often adheres to particles which are then transported by wind-driven currents to other, far distant locations within Clear Lake (Figure 6). Understanding the role of AMD from the Sulphur Bank Mercury Mine on Hg methylation is critical for 1) establishing a remedial plan for the Superfund site, 2) establishing TMDL targets for Hg point source loadings/reduction and 3) ultimately lowering Hg concentrations in higher trophic level species such as channel catfish and largemouth bass in Clear Lake.
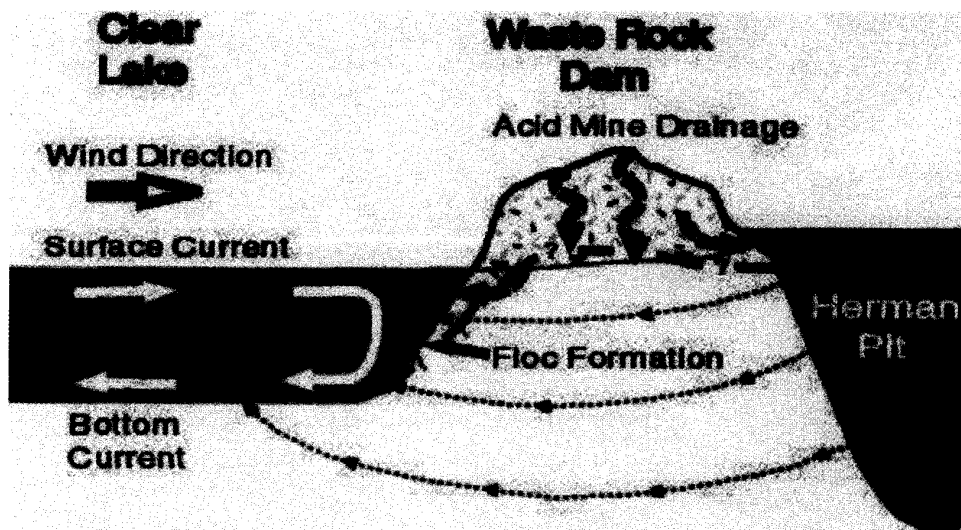
Figure 6. Diagrammatic representation of subsurface movement of mine fluids into Clear Lake, wind-driven currents and the region of floc formation.

3.8.5 Bounds on Subsurface Mercury Flux from the Sulphur Bank Mercury Mine, Lake County, California - David Jewett (Presenter), USEPA, NRMRL; Gregory J. Reller, TetraTech EM, Inc.; Ellen Manges, USEPA, Region 9; and Edward R. Bates, USEPA, NRMRL

Introduction

Clear Lake, located in Lake County, California, is one of the largest natural fresh water lakes in the state. Elevated mercury levels were first identified in fish from Clear Lake in the late 1970s and early 1980s. Although naturally occurring mercury deposits are common in this region, the SBMM, located on the eastern shore of the Oaks Arm of Clear Lake, is an obvious source of mercury entering the Clear Lake ecosystem. Over the past year, the USEPA has been conducting a comprehensive site investigation to characterize the hydrogeologic and geochemical setting at the SBMM. This presentation reports the preliminary results of the hydrogeologic investigation.

The Sulphur Bank ore deposit was discovered in 1857 and it has since been described as one of the most productive hydrothermal mineral deposits in the world. The SBMM is located at the intersection of several regional faults which serve as conduits for upwelling hydrothermal fluids and gases. Cinnabar was deposited along the faults just below the pre-mining water table and native sulphur was deposited at and near the ground surface. The SBMM was initially mined for the surface sulphur beginning in 1865. Subsurface mining of mercury began in 1872 and open pit mining operations began in 1927. The SBMM closed in 1957. The SBMM was once one of the largest mercury producers in California and it produced an estimated 1.03 x 10^7 lbs (4.7 x 10^6 kg) of mercury during its lifetime. Surface mining removed over 1.2 x 10^6 tons of material and produced a 23 acre, 90 ft deep open pit, known as the Herman Pit. The SBMM site encompasses approximately 120 acres of exposed mine wastes surrounding the Herman Pit, which subsequently filled with water when mining operations ceased. The Herman Pit collects surface and ground water from the site. The pit also receives gas and water input from local hydrothermal activity. Oxidation of H_2S gas and sulfide minerals has generated acidic water in the pit (pH ~3). The water level in the pit is approximately 12-15 ft higher than the level of Clear Lake creating a hydraulic gradient from the pit to the lake. Hydraulically important geologic units, from a ground water discharge/mercury loading point of view, include the waste rock/upper lake sediments unit, the andesite unit, and the lower lake sediments unit. Subsurface outflow from the pit passes through these units and leaches mercury before entering Clear Lake.

Previous studies have attempted to estimate subsurface flows from the Herman Pit to Clear Lake. Based on the rate at which the pit was pumped during mining operations, the California Regional Water Quality Control Board estimated discharge at 27,500 cubic feet per day (ft^3/day) (143 gpm). Researchers from the USGS calculated a discharge rate of 18,300 ft^3/day (95 gpm) using water level recovery data for the pit after mining ceased. Other investigations by Humboldt State University and Columbia Geosciences, Inc. have estimated ground water discharge from the pit at 19.2 ft^3/day (0.1 gpm) and 540 - 3,850 ft^3/day (2.8 - 20 gpm), respectively. Tracer studies conducted by UC-Davis, evaluating the rate of change in the concentration of a tracer in the pit over time, have yielded discharge rates ranging from 6.35 x 10^5 to 1.66 x 10^6 ft^3/day (3,300 to 8,600 gpm). For the most part, these studies were based on a limited amount of subsurface data from a variety of sources or surface measurements (pit filling and tracer studies) used as a proxy for subsurface discharge. Because the subsurface mercury flux is directly related to ground water discharge, determining a more accurate estimate of subsurface discharge rates is essential to evaluating mercury loading to the adjacent ecosystem. One goal of the ongoing USEPA study is to better understand and quantify subsurface discharge and mercury transport from the SBMM to Clear Lake.

Methods of Investigation

As part of the comprehensive hydrogeologic investigation at the SBMM, 33 borings, distributed throughout the site, were advanced using casing driven and reverse circulation drilling techniques. This drilling method allowed easier penetration of the mine waste and access to the lake sediments and andesite units underlying the mine waste. The monitoring wells were completed in four different geologic units (in stratigraphic order from upper to lower): mine waste/upper lake sediments, andesite, lower lake sediments, and Franciscan formation. These monitoring points, in addition to existing shallow monitoring wells, were used during the investigation. Water level data were collected from the wells during wet and dry periods. Hydraulic tests (an aquifer test and single-well tests) were conducted on a subset of the well network which included wells in all

of the different geologic horizons. Water quality samples also were collected from each of the wells. Samples were tested for mercury and a variety of other chemical parameters and constituents.

Results

The water table surface and ground water equipotential maps mimic topography at the site with less vertical exaggeration. Water level measurements indicate that Herman Pit is a ground water sink. A ground water divide is located in the northern area of the site between the pit and a wetland area. Ground water flows towards Herman Pit from the south, the east, and the north (south of the divide) in all geologic units (Franciscan, lower lake sediments, andesite, and waste rock/upper lake sediments) where the units are present. Water flows out of Herman Pit through the subsurface to the west towards Clear Lake. North of the divide, ground water flows in a northerly direction towards a wetland and Clear Lake. Ground water flow directions are generally the same during wet and dry periods. However, ground water gradients are greatest during dry periods when the water level of Clear Lake drops faster than the pit water level. Hydraulic gradient data for the dry and wet periods are presented in Tables 1 and 2. Hydraulic conductivity data for the waste rock/upper lake sediments, andesite, and lower lake sediments also are provided in Tables 1 and 2. Hydraulic conductivities (Table 1) are greatest in the waste rock/upper lake sediments (average K = 27.0 feet per day (ft/day)) and least in the lower lake sediments (average K = 0.86 ft/day). The average conductivity of the andesite unit is 3.57 ft/day.

Estimates of ground water discharge from Herman Pit to Clear Lake are provided for the dry period (Table 1) and the wet period (Table 2) monitoring events. Total discharge from Herman Pit, based on average hydraulic conductivity and gradient values, ranges from 4,264 ft^3/day (22.2 gpm) during the dry season to 3,133 ft^3/day (16.3 gpm) during the wet season. These calculations indicate that the hydraulic gradient is a greater influence on ground water discharge than the saturated thickness. The majority of ground water discharge from Herman Pit (approximately 65% during both wet and dry periods) moves towards Clear Lake through the waste rock/upper lake sediments unit. Average ground water discharge through the waste rock/upper lake sediments unit is 2,765 ft^3/day during the dry season and 2053 ft^3/day during the wet season. The andesite unit transmits approximately 29-30% of the discharge from Herman Pit (1,264 ft^3/day during the dry period and 920 ft^3/day during the dry period). The remaining discharge (approximately 5% of the total discharge) flows through the lower lake sediments. Upper and lower limits on subsurface discharge also will be calculated, based on maximum and minimum hydraulic conductivities, to provide constraints on ground water flow from the pit to the lake.

The average THg concentrations for water samples collected from wells located along the footpath from Herman Pit to Clear Lake are given in Table 3. The average THg in wells screened in the waste rock/upper lake sediments (n = 17 wells) was 51.5 ug/L. Total mercury concentrations were below detection limits for samples collected from wells screened in the andesite (n = 4 wells) and values of one-half of the detection limit were used to calculate an average THg concentration of 0.07 ug/L. Only one sample from a well screened in the lower lake sediments was above the detection limit and values of one-half of the detection limit were used for mercury concentrations in remaining wells. The average THg in wells screened in the lower lake sediments (n = 4 wells) was 1.03 ug/L. Only one round of water quality sampling has been conducted and analyzed to date. Estimated mercury fluxes from Herman Pit to Clear Lake for the dry period (Table 3) and the wet period (Table 4) are based on mercury concentrations from this single sampling event. Therefore, the difference in the average mercury loading is a function of the discharge associated with the dry and wet periods (Tables 1 and 2). The estimated THg loading from Herman Pit to Clear Lake via subsurface transport is 3.24 lbs/yr (1.47 kg/yr) during the dry period and 2.41 pounds per year (lbs/yr) (1.10 kg/yr) during the wet period. Over 99% of the mercury flux occurs through the waste rock/upper lake sediments during both monitoring periods. Minimum and maximum THg concentrations, coupled with minimum and maximum discharge estimates, will be used to evaluate limits on mercury loading for remedial and regulatory purposes.

Summary and Conclusions

The following summary and conclusions are based on work completed to date:

1.   Herman Pit is a hydrologic sink with water flowing towards the pit from the south, east, and north. Water exits the pit to the west via the subsurface and flows to Clear Lake.

2.   Ground water flow directions generally remain the same during wet and dry periods, however, hydraulic gradients are greater during dry periods when the difference between water levels in the pit and the lake are greatest.

3.   The waste rock/upper lake sediments unit is the most conductive geologic unit and the lower lake sediments unit is the least conductive.

4.   Ground water discharge from Herman Pit, based on average hydraulic conductivity values, is greatest during the dry period (4,264 ft³/day) when hydraulic gradients are steeper. Subsurface discharge during the wet period is estimated at 3,133 ft³/day. Approximately 65% of the subsurface discharge (during both wet and dry periods) is through the waste rock/upper lake sediments unit.

5.   Average THg concentration was greatest in water samples collected from wells screened in the waste rock/upper lake sediments (Avg. [Hg_{tot}] = 51.5 ug/L).

6.   The estimated THg loading from Herman Pit to Clear Lake via subsurface transport is 3.24 lbs/yr and 2.41 lbs/yr during the dry and wet periods, respectively. Over 99% of the mercury flux occurs through the waste rock/upper lake sediments.

7.   Maximum and minimum subsurface discharges and mercury fluxes also will be calculated in order to establish upper and lower limits for regulatory and remedial purposes.

Table 1 - Estimated subsurface discharge from Herman Pit to Clear Lake during dry period (data collected 9 February 2000; seepage width = 850 ft)

Geologic Unit	Avg. K (ft/day)	Sat. Thick (ft)	dh/dl	Q (ft³/day)	Q (gpm)	% Total Q
Waste Rock/Upper Lake Sediments	27.0	16.9	0.0071	2765	14.4	64.8
Andesite	3.57	55	0.0076	1264	6.6	29.6
Lower Lake Sediments	0.86	30	0.0108	235	1.2	5.5

ft/day   feet per day

Table 2 - Estimated subsurface discharge from Herman Pit to Clear Lake during wet period (data collected 25 April 2000; seepage width = 850 ft)

Geologic Unit	Avg. K (ft/day)	Sat. Thick (ft)	dh/dl	Q (ft³/day)	Q (gpm)	% Total Q
Waste Rock/Upper Lake Sediments	27.0	20.6	0.0044	2053	10.7	65.5
Andesite	3.57	55	0.0055	920	4.8	29.4
Lower Lake Sediments	0.86	30	0.0073	160	0.8	5.1

Table 3 - Estimated subsurface mercury flux from Herman Pit to Clear Lake during dry period

Geologic Unit	Q (ft³/day)	Avg. THg total (µg/L)	Hg Flux (lbs/yr)	Hg Flux (kg/yr)	% Total Hg Flux
Waste Rock/Upper Lake Sediments	2765	51.5	3.23	1.47	99.77
Andesite	1264	0.07	0.002	0.0009	0.06
Lower Lake Sediments	235	1.03	0.005	0.0025	0.17

Table 4 - Estimated subsurface mercury flux from Herman Pit to Clear Lake during wet period

Geologic Unit	Q (ft³/day)	Avg. THg (µg/L)	Hg Flux (lbs/yr)	Hg Flux (kg/yr)	% Total Hg Flux
Waste Rock/Upper Lake Sediments	2053	51.5	2.40	1.09	99.78
Andesite	920	0.07	0.0015	0.0007	0.06
Lower Lake Sediments	160	1.03	0.0037	0.0017	0.15

Section 4
Panel Discussion

4.1   Introduction

The panel was formed to reflect multiple stakeholder interests and the various viewpoints presented in the technical sessions. Each panelist was given ten minutes to summarize findings and main points of the technical session in the context of four key questions. An interactive question and answer session with the audience followed the summary presentations. The following comments reflect the opinions of panel members and the audience and are not statements of EPA policy.

Panelists:

- Luke Trip, Environment Canada
- Glenn Eurick, Barrick Gold Corporation
- Jim Rytuba, USGS
- Rick Wilkin, EPA, NRMRL
- Mae Gustin, UNR
- Jeanette Berry, Oak Ridge National Laboratory
- Ed Hanlon, EPA, ORD HQ

Key questions addressed in each summary:

- What are the two or three most important insights you want to convey to the audience regarding the management of mercury in mining?
- What are the two or three most critical/essential efforts that need to be taken to prevent, eliminate, treat, or dispose of mercury from mining-impacted sources?
- Cite two or three data gaps or information needs for the risk management of mercury resulting from mining activities and impacts.
- Prioritize the two or three most important research needs for managing risks associated with mercury in mining.

4.2   Session Summaries

4.2.1 Luke Trip, Environment Canada (Managing Mercury in Mining)

Considering the two or three most important insights to convey regarding the management of mercury in mining, Mr. Trip emphasized the importance of sharing information among all of the stakeholders with interests in managing mercury impacts resulting from mining activities, including governments, industry and other vested decision makers. He noted that mercury is a global pollutant presenting many environmental uncertainties and complexities and that we all need to do our part to address these issues. The environmental community needs to recognize that mercury is both a contaminant and a commodity and that developing countries use mercury to increase their national product (e.g., through precious metal mining and chloralkali production). Mr. Trip noted that storage and disposal options for recovered mercury need to be examined further. The environmental community needs to assess the retirement/management options for mercury.

Regarding the two or three most critical/essential efforts that need to be taken to prevent, eliminate, treat or dispose of mercury from mining-impacted sources, Mr. Trip stated that it is important to obtain the full details of any mercury stocks, whether they be small, large, national, or privately held. Some of this information will be collected as part of the new reporting criteria under the TRI of 10 pounds and 5 kilograms (kg) in Canada. He noted that the environmental community needs to focus on the management of the mercury stocks that will be generated, and that research is needed to develop technologies that can treat or store mercury. Although several interim solutions for treating low-level mercury contamination were presented during the workshop, he noted that no papers were presented on the ultimate solution needed for managing retired mercury.

194

In terms of identifying data gaps or information needs, Mr. Trip noted the need to determine how much mercury is being produced and stockpiled, and the impact that mercury produced during mining activities has on the environment and human health.

Regarding research priorities, important focal points are mercury retirement practices/techniques, and managing concentrated sources resulting from industrial activities (e.g., mining chloralkali). In Canada, facilitated sedimentation was the management technique for a large former mercury cell chloralkali facility. It was deemed not practical at this time to excavate and, hence, disturb the mercury. The amount of effort that should be spent to recover the residual mercury stock in the ground should be examined.

He closed by noting that North America is prepared to take a leadership role in the global management of mercury. He noted that the United Nations will be proposing a global mercury action plan.

4.2.2 Glenn Eurick, Barrick Gold Corporation (Modern Mining)

Mr. Eurick presented the mining industry representatives' response to EPA's questions. Mr. Eurick requested that his comments not be included in the written workshop summary.

4.2.3 Jim Rytuba, USGS (Source Identification and Characterization)

According to Mr. Rytuba, some of the principal problems in source identification and characterization involve quantifying mercury releases, identifying mercury sources, and determining where mercury resides after such a release. Both Chris Higgens and Ronald Churchill from the Division of Mines and Geology made presentations during this session, which summarized mercury releases and production in California, including the presentation of historic production records and maps detailing landscape changes at mines. These presentations highlighted the uncertainty in risk characterization regarding where the mercury from past releases currently resides.

This session also included a presentation by Richard Humphreys of the State Water Resources Control Board on pilot attempts to recover mercury from amateur mining activities in the Sierra Nevada range. Although the program recovered approximately 200 pounds of mercury, this material was primarily collected from elderly residents who had retired into the foothills rather than from the miners themselves. However, the Board still needs to determine what should be done with the recovered mercury. If the material is sold as a commodity, it is likely that it will be returned to the environment.

After noting that the United States spends a lot of money developing a strategic metal stockpile, including mercury, Mr. Rytuba noted that it may be possible to modify the program to purchase and stockpile mercury recovered as a result of environmental activities and store it with the strategic stockpile. Another possibility is to store the recovered mercury in former mercury mines (e.g., the McDermott mine in Nevada) since the formations where the mercury deposits were originally formed are geologically stable and in equilibrium with the mercury deposits still in the ground. Additionally, some of the mines have already been well characterized from an "ore genesis point of view," where information is gathered about the potential for mercury movement out of these sites.

With respect to some of the more concentrated pockets of mercury encountered at some mines, Mr. Rytuba noted that Robert Seal's (USGS) presentation on gold mining operations in the Northwest referred to a number of small ponds on National Park lands. These ponds have relatively high mercury concentrations in which MeHg comprises between 60% to 80% of the total mercury. Although the environmental community understands methylation and demethylation rates along with the variables that control these reactions in various aquatic environments, the methylation and demethylation rates in these hot spots are being controlled by factors that are not fully understood, with the resulting high concentrations posing a probable risk that is not quite realized.

4.2.4 Rick Wilkin, EPA, NRMRL (Methodology, Speciation, Mobility)

Seven different speakers made presentations during the Methodology, Speciation, and Mobility session, which addressed mercury fate and transport in aquatic environments. Mr. Wilkin noted that he planned to respond to the questions developed from EPA by addressing areas where research is needed to fill information gaps and by briefly discussing recently completed successful research efforts.

In the fate and transport session, MeHg was addressed relative to the geochemical factors that govern mercury methylation and degradation. Although the factors affecting these processes are fairly well known, Mr. Wilkin noted that a more thorough understanding of these processes may be needed. The effects of pH, oxidation state, and organocarbon concentrations in the presence of different types of mineral surfaces are qualitatively understood, but additional information is needed to develop quantitative models to evaluate methylation and demethylation. This information can also be used to develop remedies at specific sites.

For example, Mr. Wilkin noted that four of the presentations addressed bioavailability. Bulk mercury concentrations (measured via aqua regia or aggressive acid extraction) do not necessary equal or correlate to bioavailable mercury concentrations, since different forms of solid-phase mercury have different solubilities in water and stomach digestion acids (e.g., cinnabar is relatively insoluble in water and stomach acids; mercury chlorides and mercury oxides are very soluble in water and stomach acids). Since different forms of solid-phase mercury are more likely to appear in different types of deposits and in different steps during ore processing, it is very important to include speciation data in risk assessment studies. Mr. Wilkin noted that a number of sequential extraction techniques can be used to speciate mercury, and cited two studies from Geoscience and the University of Nevada on techniques to speciate solid-phase mercury. Stanford University has used x-ray adsorption spectroscopy to independently verify mercury speciation. In general, these methodologies for mercury speciation demonstrate fairly reasonable agreement, although some uncertainties remain to be resolved.

Mr. Wilkin closed his presentation by remarking on presentations made during the session on mechanisms for metal incorporation into tissue (i.e., bioaccumulation). During the session, Andy Davis presented a method for examining the geochemical processes that occur in the stomach and intestinal tract, including rates of reaction and residence times. This topic generated a lot of discussion and may warrant further investigation in the future.

4.2.5 Mae Gustin, UNR (Air Emissions and Air Impact Assessment)

Dr. Gustin noted that undisturbed areas that are naturally rich in mercury and have relatively low emissions contribute far more mercury to the atmosphere than relatively smaller mining areas with higher emissions. To understand the impacts of mercury emissions, it is important to put these emissions in the context of the global biogeochemical cycle by understanding all the various sources and sinks. Currently, there is significant uncertainty about global anthropogenic emissions, although a lot of research is in progress. As a result, the environmental community needs to be circumspect when making regulatory decisions.

She noted that the global impacts of elemental mercury emissions from mining may be more important than originally realized, given the deposition observed in the Arctic. The atmosphere appears to be a major pathway by which mercury leaves mining sites (e.g., emission estimates for the Sulfur Bank Superfund Site are six kilograms per year (kg/yr) and one kg/yr into the water). Environmental research and investigation are needed to determine whether there are many historic emissions where there is no evidence and, if so, where did the mercury go? She stated that all sites are different and actions for each site must be determined on a site-by-site basis.

Regarding efforts to prevent the dispersion of mercury, Dr. Gustin noted that fugitive dust controls need to be implemented because dust increases the surface area for natural mercury emissions into the atmosphere. Emissions can be reduced in mining areas by using vegetation or by capping waste piles. Cyanide heap leaching can also be used to pull the mercury through the ore to reduce the mercury concentrations in the waste. She noted that it is essential to consider that mining sites are in areas of natural enrichment when assessing impacts. Also, appropriate ways to deal with reclaimed mercury need to be determined.

Dr. Gustin identified a number of data gaps and information needs for the risk management of mercury resulting from mining activities or impacts. She stressed the importance of determining the species of mercury emitted from mining sites and naturally enriched areas because speciation influences the assessment of local, regional, and global impacts. For example, mercury(II) has more of a local or regional impact; elemental mercury has more of a global impact. To understand the global deposition of mercury, more data are needed on speciation reactions in the atmosphere. In addition to long- and short-term depletion data, remote sensing data are needed to scale up emissions from larger areas. She noted that if sources are truly greater than previously realized, the "missing" sinks (e.g., deposition to soil or deposition to vegetation) need to be identified.

Regarding research needs for managing risks associated with mercury in mining, Dr. Gustin noted that atmospheric speciation needs to be studied to better manage global and local impacts. Inventories on emissions from active sites (e.g., precious metal and other mines) also need to be developed.

4.2.6 Jeanette Berry, Oak Ridge National Laboratories (Remediation and Treatment)

Jeanette Berry's summary of the remediation and treatment session addressed the following topics: collaboration, incentives, standards, and data needs. Ms. Berry noted that the workshop was an excellent example of collaboration. During the session, mining companies, researchers, vendors, and international representatives all made presentations on treatment and remediation techniques, in addition to research needs. She noted that the United States has the incentives, regulatory framework, and economic drivers for collaboration that many other countries lack.

Ms. Berry noted that the incentives, both economic and regulatory, for controlling mercury emissions need to be better defined, particularly for non-U.S. countries. Cost-benefit analyses and life-cycle analyses need to be considered. Standards, including standards for technology treatment targets and for long-term stability tests (to avoid retreatment) are needed. Pathway analysis, to evaluate the effect of remediation, is also needed. An active interchange and relationship between the available treatment technologies and the current treatment standards similar to the Best Demonstrated Available Technologies (BDAT) should be established.

More data are needed on a wide range of techniques and technologies to remediate/control mercury contamination (e.g., pathway analysis) and to control emissions from current mining operations. Since the National Mining Association and DOE agree that the "future begins with mining," it is important to focus efforts on reducing/controlling the negative environmental impacts of mining rather than on closing mines. Ms. Berry noted a need for *in situ* remediation/mixing techniques, cost effectiveness information, effluent treatment and control technologies, and mercury speciation data (particularly in complex mixtures with gold, silver, lead, and zinc).

Currently generated material also needs to be examined. In addition to the composition and corrosiveness of process residues, additional information is needed on the material's economic value and safe handling procedures. Treatability studies need to be performed in collaboration with government (DOE, EPA, national laboratories, etc.), private industries, and universities.

4.2.7 Edward Hanlon, EPA, ORD HQ (Watershed Impairment)

Mr. Hanlon provided additional points made during the Watershed Impairment session, but not presented during the panel session. These comments are included in this summary of Mr. Hanlon's presentation. Mr. Hanlon's presentation was organized under the following topics:

- Main insights from the various presentations
- Key research needs
- Summary of research needs in the following categories: 1) measurement, 2) speciation/species, 3) fate/transport, 4) effects, 5) control of releases, and 6) remediation
- Key points made during the watershed session presentations, but not summarized in the wrapup session, including 1) significant insights regarding the management of mercury in mining and 2) data/research gaps or information needs for risk management of mercury in mining.

Main Insights from the Various Presentations

Most of the sites and areas discussed in the 11 watershed presentations are located in the western United States. In general, the vast majority of impacts seen from mercury releases are manifested as elevated mercury levels in fish. As noted during Charlie Alper's presentation, approximately 1,900 out of the 2,600 fish advisories posted throughout the nation are due to elevated mercury levels in fish. However, significant uncertainties still exist regarding whether the primary sources of mercury releases have been identified, and whether elevated mercury levels in fish will ultimately be reduced when remedies have been implemented.

Key Research Needs, in Order of Priority

According to Mr. Hanlon, procedures need to be developed to identify the best locations to employ remedies that will improve environmental/fish mercury levels. This research should also focus on answering the following questions: 1) What 'sources' should be remedied (e.g., above-water, point source release areas, contaminated sediment areas, contaminated marshland areas within the watershed)? 2) How significant are natural and man-made releases and how can these releases be assessed? and 3) How can uncertainties be reduced when determining TMDL allocations? Low cost indicator tests that can be used to predict elevated MeHg concentrations in edible fish, surface water, and food chain/upper trophic level species are also needed. It is also important to identify the factors affecting the release of mercury from sediments to water and the quantitative relationship between total mercury and MeHg in water, invertebrates, and bank/bottom sediments.

Summary of Research Needs by Category

Mr. Hanlon summarized the following research needs, listed in order of priority under the following categories: 1) measurement, 2) speciation, species, 3) fate/transport, 4) effects, 5) control of releases, and 6) remediation.

Measurement

1. Low cost indicator tests that should/can be used to predict elevated MeHg concentrations in edible fish, surface water, and food chain/upper trophic level species

2. How to use wet deposition traps to assess the influence of precipitation on elevated mercury concentrations in surface water, particularly in mountain/mining areas (Note: Dry deposition should also be assessed in this effort.)

3. Whether mercury availability to organisms varies depending on hydrologic conditions (e.g., wet versus dry periods, impact of tidal influences, aerobic versus anaerobic influences)

4. Compare filtered and unfiltered water samples because such samples have shown significant differences in mercury concentrations. Several presenters recommended taking unfiltered samples to help assess the effects of mercury in the environment.

Speciation, Species

1. Factors that affect the quantitative relationship between total mercury and MeHg in water, invertebrates, and bank/bottom sediments

2. The effect of reducing total mercury levels on MeHg formation (e.g., whether there are resulting reductions in MeHg formation)

3. Factors that control the methylation/demethylation of mercury (e.g., how does mercury move/change between forms in the environment?)

4. Mechanisms for the methylation of mercury also need to be better understood. (A few presenters noted that anaerobic bacteria are responsible for approximately 40% of the production of MeHg, but it is unclear how the remaining percentage of MeHg in the environment is produced.)

5. Mechanisms by which methylated forms of mercury in the environment get into organisms (plant and animal). This information is needed to help resolve the fact that high MeHg levels in the environment do not necessarily coincide with high MeHg in flora/fauna.

Fate/Transport

1. Factors that affect the release of mercury from sediments to surface water, including 1) data on the specific release, fate, transport factors, mechanisms, and trends that affect these releases, 2) information on releases from toxic/anoxic areas in lakes, bank and bottom sediments, silts/clays,

198

delta areas, and wetlands, and 3) data on what releases and sediment movement occurs during big storms and highly cyclic rainfall events (i.e., during long periods without rain and during rainstorms)

2. Data and tools to differentiate natural versus human-influenced releases

3. The significance of air deposition and releases to surface water mercury concentrations (Note: several mass balance efforts (e.g., for TMDL allocations) assumed significant air releases and impacts to surface water; however, other studies indicated while air deposition occurs, these releases are not the key or significant sources of contamination. Several speakers indicated that most air deposition assumptions and analyses were tenuous and potentially specious.)

4. More accurate surveys of world-wide mercury levels, including data on releases and deposition

5. Contaminated sediment deposition trends in streams, lakes, and reservoirs

Effects

1. Data on fish tissue mercury concentrations, including MeHg concentrations in edible fish, particularly during fish concentration peaks relative to source concentration releases

2. Low-cost indicator tests that could best assess or predict elevated fish tissue concentrations (e.g., to predict elevated MeHg concentrations in edible fish, surface water, and food chain/upper trophic level species)

3. Mean and upper percentile effects to fish, microbes, and invertebrates relative to varying water concentrations. (Note: this relationship varied significantly in several papers.)

4. Easy-to-apply models and methods to identify local effects of mercury contamination to species of concern

5. Factors that affect bioavailability in fish (e.g., hydrologic cycling, pH, and the presence of lower trophic level species)

6. Data that address whether published national effects levels apply at sites and regional/local areas because site-specific factors greatly influence the effects seen. According to Mr. Hanlon, this research need was developed in response to the following facts: 1) the 1 ppm FDA level for fish is significantly different from the 0.3 ppm level found in San Francisco Bay; 2) national sediment water quality criteria values are very conservative/stringent and may not apply at a local level; 3) the International Joint Commission's mercury numbers should be reworked, because–for at least one site–the numbers do not seem to apply; and 4) more thought is needed on whether a national MeHg number can or should be developed or relied upon (due to the inaccuracies indicated in the proposed methods and numbers).

7. How long does it take for a system to recover and for mercury levels to drop after a site is remediated?

Control of Releases

1. Methods that identify the best locations to employ remedies that will improve mercury levels in environment and fish. This research should focus on answering the following questions: 1) What sources should be remedied (i.e., above-water point source release areas, contaminated sediment areas, contaminated marshland areas within the watershed)? 2) How significant are natural and man-made releases and how can these releases be assessed? and 3) How can uncertainties be reduced when determining TMDL allocations?

2. Methods to ensure that, when remedies are conducted, environment/fish mercury levels will improve

3. Information on the cost-benefit of controlling releases from mining areas, including whether cleaning up mining source areas would help or is critical to protect the watershed (i.e., Is public health benefitting by controlling releases?). (This includes cost-benefit analysis of techniques for best controlling these releases.)

4.   Data on the amount of mercury stored in creeks, delta areas, reservoir/lake sediments, the amount of mercury moving into organisms and the water column, and the amount of mercury moving/re-leased into the oceans. The following questions also need to be answered: 1) Is brook sediment remediation necessary to effect a cleanup? 2) Once mercury from above-water source/release areas has been reduced, will stream sediments release significant concentrations? and 3) Will stream sediments decrease in concentration over time and, if so, what controls these releases?

Remediation

1.   Methods that identify the best locations to employ remedies that will improve mercury levels in environment and fish. This research should focus on answering the following questions: 1) What sources should be remedied (i.e., above-water point source release areas, contaminated sediment areas, contaminated marshland areas within the watershed)? 2) How significant are natural and man-made releases and how can these releases be assessed? and 3) How can uncertainties be reduced when determining TMDL allocations?

2.   Monitoring requirements for after remedies have been constructed (e.g., What should be monitored and for how long? What low-cost, low-operation/maintenance monitoring methods are available?)

3.   Data on whether wetlands are a remedy for mercury contamination. This includes wetlands management strategies for mercury management and triage pointers/consensus on which strategies will work for managing wetlands contaminated with mercury. (Note: Wetlands trap mercury, but methylation rates are significant.)

4.   Factors that promote demethylation in the environment

4.3   Panel and Audience Discussion

Glenn Miller (University of Nevada) commented that retiring mercury is a controversial issue. In addition to the need for substitutes to meet worldwide demands for mercury, a number of issues need to be resolved before stockpiling should proceed (e.g., Who will be responsible for stockpiling the mercury? How will the stockpiles be accumulated and managed on an international basis?). Luke Trip responded that, based on research performed in support of the NARAP, the current mercury stockpile in North America is sufficient to supply all foreseeable needs in the near future. Furthermore, if more mercury is needed, enough is pro-duced as a byproduct from gold and zinc mining that mercury mining should never be needed. Mr. Trip noted that there are no self-sufficient mercury mines in the world; all are subsidized by national governments to keep the price of mercury down. Mr. Trip believes that international mercury requirements can be met without having to mine new mercury.

Arnold Kuzmack (EPA, OW) agreed with Mr. Trip. He noted that some mercury uses are essential and even environmentally beneficial (e.g., use in flourescent lights). In some situations, mercury is cheaper than the alternatives (e.g., mercury in dental amalgams). After mentioning that these uses can probably be met with current stockpile/byproduct production, Mr. Kuzmack noted that large amounts of mercury are still being shipped to mining activities in South America and elsewhere; this mercury is ultimately released to the environment. He concluded that long-term storage and immobilization technologies followed by long-term isolation (as practiced in Sweden and by the U.S. nuclear waste storage program) can be considered for mercury retirement.

Jolaine Johnson (Nevada DEP) encouraged EPA panel members to address additional mercury research needs, including remedial technology development, along with EPA's current approach to prioritizing these research needs. Jon Herrmann (EPA, NRMRL) replied that EPA's *Mercury Research Strategy (MRS)* will be released by the end of calendar year 2000. This research strategy focuses on emissions from coal-fired utilities and noncombustion sources including mining. These two areas are the bulk of the risk management component of the strategy. A small component addresses research on risk communication. From a research perspective, the strategy targets those research areas that are most important to EPA program offices.

Steve Lindberg (Oak Ridge National Laboratory) commented that almost all industrial uses of mercury have alternatives; theoretically, mercury could be phased-out. He questioned whether containerizing and return-ing it to former mercury-containing formations is a viable approach to mercury storage/control from a

geological perspective. Jim Rytuba replied that mercury deposits have been in place for 15 to 30 million years, and that it may be beneficial to identify classes of mercury deposits that are particularly stable environments (e.g., open pit mines with partially removed ore and a perimeter of undisturbed host rocks that buffer transport).

Jeanette Berry commented that, from a chemical engineering perspective, she found it interesting that Mr. Kuzmack recommended developing a mercury storage program similar to the program used to store high-level and low-level nuclear waste. She surmised that, due to difficulties associated with radioactive waste, geologically stable procedures and methodologies will be needed to accomplish mercury storage (e.g., leach criterion identification, pathway analysis, and geologic formation analysis). Since mercury amalgamation can satisfactorily meet land disposal criteria, this may be a more logical alternative. Ms. Berry supported purchasing mercury to remove it from the market. She noted that it is important to consider the relationship between economic and regulatory incentives.

Luke Trip commented on regulatory challenges by citing the difficulties associated with the shutdown of a large mercury cell chloralkali facility in Maine. This facility had 26,000 pounds of mercury encased in steel cylinders, ready to be sold to India. Although there was an initiative in place to prevent the release of the mercury to the open market, the parties involved could not decide who would be responsible for receiving/storing the mercury, whether the mercury could be stored in any of the nearby states, and whether those states would allow the mercury to cross state borders. Mr. Trip finds this situation particularly interesting from a policy perspective since the New England Governors and the Eastern Canadian Premiers have developed a very robust mercury action plan with very stringent regulations on incinerator waste and utilities. Mr. Trip questioned why a group that is so committed to controlling mercury emissions to very low levels is not capable or willing to develop reasonable solutions for storing large volumes of mercury. After noting that this situation highlights some of the problems that will be faced when developing a mercury retirement program, long-term sequestering of mercury in abandoned mine sites is the best way to store large volumes of mercury. When asked whether storage and transport issues are a major discussion point during United Nations or regional discussions on mercury, Mr. Trip responded by saying that he expects the discussions to focus on who will be responsible for funding stockpile storage efforts and where the stockpiles will be located.

Bill Fitzgerald (University of Connecticut) commented that the environmental community does not really know whether mercury is increasing or decreasing in the global environment, despite remediation efforts that have occurred in a number of countries. Mr. Fitzgerald asked participants to consider setting up sites in areas free of background influences to look at atmospheric changes in mercury by evaluating gas-phase atmospheric effects or impacts over a three- to five-year interval (similar to studies being done for greenhouse gases). The results of this study could be used to evaluate the global effectiveness of remediation efforts and could also provide information on the residence time of mercury. This information could be used to restrain models and to directly assess the effects of global, regional, and local remediation efforts.

Dave Jones (EPA Region 9) commented that during the presentation on the Sulfur Bank mine, one speaker noted that only 40% of the bioavailable mercury was produced by sulfate-reducing bacteria. After commenting that a large number of the presentations also focused on this one mechanism, Mr. Jones asked ORD and others to provide additional information on other methods by which bioavailable mercury is produced. Mr. Kuzmack noted that the alternative pathways for producing bioavailable mercury involve the use of other bacteria and that the basic pathway is essentially the same. Some nonbacterial mechanisms also produce bioavailable mercury.

Mr. Kuzmack commented that EPA is considering placing a mercury monitoring site on a mountain in Hawaii, as per Mr. Fitzgerald's recommendation. When asked how long the monitoring effort would need to be in place to see a response, Mr. Fitzgerald responded that it would probably take three to five years to see potential confirmatory evidence and that the study would need to be done very carefully. When someone commented that the site location should be reconsidered since Kilauea is located next to the proposed monitoring site and submits a substantial ore deposit over time, Mr. Herrmann replied that the study organizers recognized the possible influences from Kilauea and were able to account for this situation.

Mae Gustin cautioned that long-term monitoring may not provide confirmatory verification because the environmental community still does not have enough information about atmospheric reactions and long-term cycling. Because mercury may be cycling constantly through the atmosphere, long-term monitoring efforts

may not provide the information needed to evaluate the impacts of remediation efforts. A number of uncertainties are associated with atmospheric reactions and a number of unknown reactions may be occurring that can pull the mercury out of the atmosphere (into sinks). Although it is a good idea to conduct monitoring, it is also important to recognize the uncertainties beforehand.

Mr. Fitzgerald responded that the oceans cover 70% of the earth and that measurements previously made over the ocean show very little standard deviation in terms of total gaseous mercury (e.g., less than 5% to 10%). This suggests that the residence time of mercury is relatively long and rapid cycling may not be occurring. Consequently, the proposed strategy for sampling over the ocean should proceed with caution biasing whether mercury is increasing or decreasing in the environment.

Referring to the discussion on the residence time of mercury in the atmosphere and the total mercury burden in the atmosphere over time, Russ Bullock (EPA, ORD) commented that the mercury burden can be reduced quickly by an oxidizing atmosphere, although these reductions could be occurring because of other pollution sources (e.g., photochemical smog).

Lynn Brickett (DOE, National Energy Technology Laboratory) commented on remediation efforts underway at a chloralkali plant exhibiting relatively stable mercury sulfide sediment contamination. Ms. Brickett asked EPA to comment upon whether it anticipates changes in its regulatory outlook for remediation as more information is obtained on how to measure mercury. After mentioning that ORD does not make policy, Mr. Herrmann noted that, as EPA obtains a better understanding of mercury speciation, solutions to these problems should reflect this improved understanding. Since cost-effective solutions are a necessity, digging up stable mercury contamination sites may be the least desirable option from a scientific perspective.

Clark Smith, a geochemistry consultant from Reno, suggested that the workshop could have benefitted from a marine geology/geochemistry perspective. The midoceanic regions are spewing sulfur- and mercury-laden gases into the ocean and further studies on these occurrences could be beneficial.

Amy Anderson (Klean Earth Environmental) noted that, although there is a plethora of information pertaining to long-term stability tests, there are no standard test procedures and protocols. Ms. Anderson asked if EPA is planning to develop a standard testing protocol for long-term stability, which could be provided to universities and vendors. Diana Bless (EPA, NRMRL) responded that this problem had been considered and that EPA was unable to identify an appropriate long-term stability test. She recommended that EPA consider developing such a testing protocol.

Section 5
Conclusions

5.1   Key Points

The following insights regarding the management of mercury in mining were developed by Ed Hanlon (EPA, ORD HQ) after the workshop.

1.   There are no simple ways to predict distribution, fate, and transport of mercury from a source area to a deposition area.

2.   The State of Nevada is the 5th largest producer of gold in the world.

3.   The most significant atmospheric mercury releases in 1998 were from mining ore processing facilities.

4.   'Hot spots' of elevated concentrations of mercury in the environment are significant sources of mercury contamination in fish.

5.   Of the approximately 26 million pounds of mercury 'unaccounted for' in mining areas of the Sierra Nevada range, approximately three to eight million pounds are associated with hydraulic mining activities.

6.   Many 'recreational miners' looking for gold wade in highly contaminated trenches and streams. This population of human receptors frequently stirs up sediments and releases mercury 'stored' in the streams, and may receive the highest exposure to mercury contamination of any human population.

7.   The presence of iron 'floc' frequently leads to demethylation of mercury.

8.   The USGS developed a special field method for collecting samples for elemental mercury analysis (to prevent labs from rejecting the samples). More information on this method can be obtained from Charlie Alpers.

9.   Approximately 80 percent of the rainfall in California flows into the San Francisco Bay, making it a well-flushed system. The major sources of mercury contamination in San Francisco Bay are mining releases and atmospheric deposition.

10.   The highest levels of methylmercury in sediments were found in the upper centimeter of a sediment core in delta and wetland areas (Dyan White's research).

11.   Thermal and hydraulic currents in lakes and reservoirs have been shown to cause mercury contaminated sediment particles to settle near the shoreline areas.

12.   Mercury levels mirrored copper water/sediment concentration levels on a 1:1 basis in water bodies.

13.   Mercury is frequently found as a natural amalgam in silver deposits.

14.   In the Sierra Nevada range, there has been a large increase in mercury concentrations in lakes and fish over the latter half of the last century, due to global air deposition (see Darrell Slotton's paper).

15.   In the Sierra Nevada range, certain invertebrates, insects, and amphibians should be used as indicators to identify areas with elevated fish mercury levels (see Darrell Slotton's paper).

16.   In the Sierra Nevada range, reservoirs are sinks for mercury and not much mercury is released from reservoirs (see Darrell Slotton's paper).

17.   In coastal areas, wetlands are a perfect habitat for 'mercury migrating microbes' (see Darrell Slotton's paper).

18. Remediating mining site releases will reduce elevated levels of mercury bioaccumulation in both the Sierra Nevada range and in coastal areas (see Darrell Slotton's paper).

5.2 Data Gaps and Research Needs

The following research needs were developed based on information presented during the closing panel discussion:

1. Mercury retirement practices and techniques need to be investigated. This includes developing a retirement and management plan for mercury recovered from industry, commodity market and remediation efforts.

2. Research is needed to better understand the geochemical and biochemical processes that control mercury methylation and degradation. Some of this data will be derived from pH effects, oxidation state, and organocarbon concentrations associated with various types of mineral surfaces.

3. Further investigation of the factors controlling methylation/demethylation rates in high mercury concentration locations.

4. More research is needed to determine how mercury bioaccumulates in tissues (e.g., biochemical processes that occur in the stomach and intestinal tract).

5. Atmospheric speciation research is needed to better understand global and local deposition and resulting adverse impacts (e.g., missing sinks).

6. Evaluate technologies for the purpose of remediating contaminated mining sites as well as controlling emissions from current mining operations (gold, silver, lead, and zinc mining).

7. Develop low cost indicator tests that can be used to predict elevated methylmercury concentrations in fish, surface waters and upper trophic level food chain.

8. Determination of the factors that affect the release of mercury from sediments to surface water.

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**Appendix A
Agenda**

Assessing and Managing Mercury From Historic and Current Mining Activities

Sponsored by the
U.S. Environmental Protection Agency
Office of Research and Development

November 28 - 30, 2000
Cathedral Hill Hotel
San Francisco, California

DAY 1 - Tuesday, November 28, 2000

7:30 AM – 5:00 PM - Registration & Name Badge Pickup

8:30 AM – 8:40 AM - Greetings & Opening Remarks – *Diana Bless, EPA ORD*

Plenary Session
Session Chair: Jon Herrmann, EPA

8:40 AM - 9:00 AM	EPA Developing a Strategy on Mercury Research - *Jon Herrmann, EPA*
9:00 AM - 9:20 AM	Mercury Management on a North American Scale - *Luke Trip, Environment Canada*
9:20 AM - 9:40 AM	Regional Office Perspective – *David Jones, EPA Region 9*
9:40 AM - 10:00 AM	Mercury Emissions from Nevada Mining Operations: The State Environmental Agency Perspective - *Jolaine Johnson, Nevada Division of Environmental Protection*
10:00 AM - 10:15 AM	USGS Perspective - *Kate Johnson, US Geological Survey*
10:15 AM - 10:30 AM	BREAK

10:30 AM - 10:50 AM	County Role in Mercury Assessment and Clean-up – *Elizabeth Martin and Shawn Garvey, South Yuba River Citizens League*
10:50 AM - 11:35 AM	The Management of Mercury in the Modern Mining Industry - *Glenn Eurick, Barrick Gold Corporation and Dirk van Zyl, UNR*
11:35 AM - 12:00 PM	Questions and Answers
12:00 PM - 1:30 PM	LUNCH

Session Moderators	**Modern Mining** *Glenn Eurick, Barrick Gold Corporation and Paul Scheidig, Nevada Mining Association*	**Source Identification / Characterization** *Jim Rytuba, US Geological Survey and Bill Stelz, EPA*
1:30 PM - 2:00 PM	Sources of Mercury from Mineral Deposits - *James Rytuba, US Geological Survey*	Contributions of Mercury to California's Environment from Mercury and Gold Mining Activities- Insights from the Historical Record - *Ronald Churchill, Division of Mines and Geology*
2:00 PM - 2:30 PM	An Inventory of Mercury from Gold Mining - *Kumar Ganesan, Montana Tech of the University of Montana*	Importance of Research of Historic Information on Mines in California that Used or Produced Mercury - *Chris Higgins, Division of Mines and Geology*

2:30 PM - 3:00 PM	The Problem of Mercury Contamination in Gold-Mining Areas of Russia - *Tatyana Laperdina, Chita Institute of Natural Resources*	Mercury Associated with Lode Gold Mining in the Sierra Nevada Region, CA - *Roger Ashley, US Geological Survey*
3:00 PM - 3:30 PM	BREAK	
3:30 PM - 4:00 PM	Coal Cleaning as a Tool for Controlling Mercury Emissions from Coal Combustion - *Michael Nowak, National Energy Technology Laboratory*	Mercury Recycling Pilot Project (MRPP) - *Richard Humphreys, State Water Resources Control Board*
4:00 PM - 4:30 PM	Mercury Emissions from Induration of Taconite Concentrate Pellets – Stack Testing Results from Facilities in Minnesota - *Hongming Jiang, Minnesota Pollution Control Agency*	Historic Gold Mining, Mercury Amalgamation, and Potential for Environmental Impacts in the Eastern United States - *Robert Seal, US Geological Survey*
4:30 PM - 5:00 PM	Mining Induced Emissions of Sediment and Mercury in Amazonia, 1970-2000, Determined from the Ground and from Space - *Kevin Telmer, University of Victoria*	Characterizing Mercury in the Comstock Lode: Macro to Micro Techniques - *Patrick Ritter; Ecology and Environment, Inc.*

5:00 PM - 6:30 PM - Poster Session / Reception [Cash Bar]

DAY 2 - Wednesday, November 29, 2000

Session Moderators	**Methodology / Speciation / Mobility** *Rick Wilkin, EPA*	**Watershed Impairment – Defining Magnitude and Boundaries** *Ed Hanlon, EPA*
8:00 AM - 8:30 AM	Microbial Mercury Cycling in Sediments Associated with Mining Activity in California - *Mark Marvin-DiPasquale, US Geological Survey*	The Carson River Mercury (Superfund) Site - *Wayne Praskins, EPA Region 9*
8:30 AM - 9:00 AM	Uncertainty Analysis of the Carson River Mercury Transport Model - *Rosemary Carroll, Desert Research Institute*	Mercury in the Carson River System, Nevada and California, 1998 - *Karen Thomas, US Geological Survey*
9:00 AM - 9:30 AM	Assessing the Mobility of Mercury in Mine Waste - *Chris Sladek, Department of Geological Science*	Distribution of Sediment Mercury Concentrations in the Humboldt River Watershed - *Robert Hall, EPA*
9:30 AM - 10:00 AM	Application of Selective Extractions to the Determination of Mercury Speciation in Mine Tailings and Adjacent Soils - *Nicolas Bloom, Frontier Geosciences Inc.*	Mercury Contamination in Waters Associated with Historic Gold Mining in the Bear River and South Yuba River Watersheds, CA - *Charles Alpers, US Geological Survey*
10:00 AM - 10:20 AM	BREAK	
10:20 AM - 10:50 AM	Speciation of Natural Mercury-bearing Materials Using X-ray Absorption Spectroscopy - *Christopher Kim, Stanford University*	Linking Sources to Violations: The Mercury Legacy of the New Almaden, California Mining District - *Khalil Abu-Saba, San Francisco Bay Regional Water Quality Control Board*

A - 3

10:50 AM - 11:20 AM	Environmental Reactions of Mercury Cyanide - *Glenn Miller, University of Nevada*	The Impact of Mercury Mining on Tomales Bay Biota - *Dyan Whyte, California Regional Water Quality Control Board, San Francisco Bay Region*
11:20 AM - 11:50 PM	The Effect of Arcane Geochemical Phenomena on Mercury Bioavailability - *Andy Davis, Geomega, Inc.*	Mercury in Native Metal Deposits: "Focusing Troughs" Reveal an Unexpected Source to Lake Superior Sediments – *Charles Kerfoot, Michigan Technological University*
11:50 PM - 1:10 PM	LUNCH	

Session Moderators	**Air Emissions / Air Impact Assessment** *Scott Hedges, EPA*	**Watershed Impairment – Developing Management Tools and Priorities** *Ed Hanlon, EPA*
1:10 PM - 1:40 PM	Uncertainties in Mass Balance of U.S. Atmospheric Mercury Emissions - *Leonard Levin, Electric Power Research Institute*	Mercury Contamination in Wetlands of Lahontan Valley, Nevada - *Peter Tuttle, U.S. Fish and Wildlife Service*
1:40 PM - 2:10 PM	The History of Mercury Emissions from the New Almaden Mines, Santa Clara County, California - *Michael Cox, New Almaden Quicksilver County Park Association*	Downstream Indicators of Mining -Related Mercury Exposure: Findings from the Sacramento-San Joaquin Delta and Its Tributaries - *Darell Slotton, University of California*
2:10 PM - 2:40 PM	Atmospheric Mercury Emissions from Mine Waste - *Mae Gustin, UNR*	Biological Indicators of Mercury Contamination from Historic Gold Mining in the Bear River and Yuba River Watersheds, California - *Roger Hothem, US Geological Survey*
2:40 PM - 3:10 PM	*The Importance of Emissions Speciation to the Atmospheric Transport and Deposition of Mercury* - O. Russell Bullock, NOAA Air Resources Laboratory	Controls on Mercury Availability and Uptake in Fish: Arizona Lake TMDLs – *John Hillenbrand, EPA*
3:10 PM - 3:40 PM	BREAK	

Session Moderators	**Air Emissions / Air Impact Assessment (Continued)** *Scott Hedges, EPA*	**Remediation and Treatment** *Paul Randall, EPA*
3:40 PM - 4:10 PM	Atmospheric Mercury Fluxes as Recorded in Lake Sediments: The Lack of a Historic Global Signal from Au and Ag Mining - *William Fitzgerald, University of Connecticut*	Reducing Mercury Production at Bald Mountain Mine - *Jim Wickens, Barrick Gold Corporation*
4:10 PM - 4:40 PM	Estimation of Mercury Vapor Flux from Natural Geologic Sources in Nevada - *Richard Zehner, University of Nevada*	Assessment and Remediation of the Mother Lode Mine, Crook County, Oregon - *N. Toby Scott, State of Oregon DEQ*

| 4:40 PM - 5:10 PM | Mercury Emission and Re-Emission from Diffuse Area Sources: The Dilemma of Small Emissions from Large Surfaces, the "Inert" Nature of Elemental Mercury Vapor, and Missing Sinks in the Global Mercury Cycle - *Steve Lindberg, Oak Ridge National Laboratory* | The Pollution of Mercury in the Mercury Mining Area and Reclamation - *Yuhuan Lin, Research Center for Eco-Environmental Sciences, ChineseAcademy* |

5:10 PM - 6:30 PM   Poster Session / Reception [Cash Bar]

DAY 3 - Thursday, November 30, 2000

Session Moderators	**Sulphur Bank Mercury Mine** *Ed Bates, EPA and David Jewett, EPA*	**Remediation and Treatment (Continued)** *Paul Randall, EPA*
9:00 AM - 9:30 AM	Unique Factors Effecting Site Characterization and Remedy Selection at the Sulphur Bank Mercury Mine Superfund Site, Lake County, CA - *Ellen Manges, EPA*	Historic Unreclaimed Mercury Mines in Asturias (Northwestern Spain): Environmental Approaches - *Jorge Loredo, Universidad de Oviedo: Escuela de Minas*
9:30 AM - 10:00 AM	An Evaluation of Remote Sensing Tools for Hydrological Investigations - *Richard Hammack, DOE*	The Use of Silica Micro Encapsulation for the Control of Mercury - *Amy Anderson, KEECO*
10:00 AM - 10:30 AM	The Active Hydrothermal System and Mercury Flux at Sulphur Bank Mine, California - *Fraser Goff, Los Alamos National Laboratory*	Potential Economic Benefits from Innovative Mercury Separation Technology - *Jeanette Berry, Oak Ridge National Laboratory*
10:30 AM - 10:45 AM	BREAK	
10:45 AM - 11:15 AM	Recent Geochemical Sampling and Mercury Sources at Sulphur Bank Mercury Mine, Lake County, CA - *Gregory Reller, Tetra Tech EM, Inc.*	Removal of Hg from Contaminated Water Using Alkali Fly Ash Permeable Reactive Barrier (AFA-PRB) Material -*Shahriar Jahanian, Temple University*
11:15 AM - 11:45 PM	Mercury Contamination in Clear Lake, California: Influence of Acid Mine Drainage on Methylmercury Production from the Abandoned Sulphur Bank Mercury Mine - *Thomas Suchanek, University of CA & U.C. Davis- Clear Lake Env. Research Center*	Remediation and Legal Case Histories of the Buena Vista and Klau Mines, Two Mercury Mines in the Las Tablas Creek Watershed, San Luis Obispo County - *Gerhardt Hubner, Central Coast Regional Water Quality Control Board*
11:45 AM - 12:15 PM	Bounds on Subsurface Mercury Flux from the Sulphur Bank Mercury Mine, Lake County, CA - *David Jewett, EPA*	Metallurgical Pretreatment for Mercury Removal by Alkaline Sulfide Leaching - *Suzann Nordwick, MSE Technology Applications, Inc.*

12:15 PM - 1:30 PM   Lunch

1:30 PM - 3:00 PM   Panel Discussion and Wrap-Up
                     Moderator: *Douglas Grosse, EPA*

4:00 PM   Depart for Sulphur Bank Mercury Mine Field Trip

Appendix B
List of Attendees

ASSESSING AND MANAGING MERCURY FROM HISTORIC AND
CURRENT MINING ACTIVITIES
November 28 - 30, 2000
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November 28 - 30, 2000
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November 28 - 30, 2000
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November 28 - 30, 2000
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ASSESSING AND MANAGING MERCURY FROM HISTORIC AND CURRENT MINING ACTIVITIES
November 28 - 30, 2000
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November 28 - 30, 2000
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November 28 - 30, 2000
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November 28 - 30, 2000
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