WATER SAMPLING AND ANALYTICAL RESULTS FROM THE SULPHUR BANK MERCURY MINE SUPERFUND SITE, LAKE COUNTY, CALIFORNIA[1]

By

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Abstract. The Sulphur Bank Mercury Mine is an inactive open pit mine located in Lake County, California. The mine occupies 120 acres and is adjacent to Clear Lake. The mine's pit has been flooded by runoff and thermal spring activity creating a 23 acre acid mine water pond (Herman Pit). Mercury has been found at the mine site, in Clear Lake waters, and in fish in Clear Lake. Due to this mercury contamination and the mine's proximity to Clear Lake, the Sulphur Bank Mercury Mine was added to the National Priorities List in 1990 by USEPA (Superfund).

In 1991, the USEPA requested that the U.S. Bureau of Mines perform sampling and chemical analysis on waters taken from the mine pit, monitor wells, thermal spring waters, and surface waters of Herman Pit and Clear Lake. Field work began in August, 1992. An underwater hot spring sampler was designed and constructed by U.S. Bureau of Mines personnel. Along with sonar, it was first used to sample ambient water and thermal springs in both Herman Pit and Clear Lake.

In Herman Pit, at the mine site, the water has a pH of 3. An inflatable hypalon boat was used as the sampling platform on this chemically harsh environment.

Standard USEPA water sampling protocol was observed during all sampling events. All samples were split. One sample set was chemically analyzed within 24 hours of sampling. For these analyses, a portable laboratory was utilized. The other set of sample splits were sent to USEPA's analytical laboratory in Las Vegas, Nevada.

All analytical results suggest that mercury occurs in waters at the mine site. U.S. Bureau of Mines analytical results suggest that water at the mine site and springs within Clear Lake contribute to mercury concentrations within Clear Lake. USEPA analytical data suggests that mercury is confined to the mine site and not in Clear Lake.

Mercury is natural to the area as shown by the presence of the Sulphur Bank Mercury Mine. Background concentrations of mercury in the Clear Lake area would undoubtedly be much higher than background readings found elsewhere.

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Introduction

The Sulphur Bank Mercury Mine Superfund site is located in Lake County, California (Figure 1). The Superfund site is the result of over 100 years of uncontrolled deposition of mining/milling wastes. The site was placed on the United States Environmental Protection Agency's (USEPA) National Priorities List (NPL) in 1990. In 1991, Region IX of the U.S. EPA charged the U.S. Bureau of Mines with reconnaissance level sampling of surface water, ground water, and underwater thermal springs in order to determine if mercury at the site poses a threat to the environment. In order to do this it was necessary to design a sampling device that is capable of acquiring representative samples from underwater thermal springs.

Objectives

One of the objectives of this on-site work was to determine if mercury exists in surface and spring waters. If mercury exists, what form does it occur; how is it currently being deposited; and has the mining process exacerbated the mercury? To achieve these objectives, the U.S. Bureau of Mines sampled and analyzed surface waters and various underwater and surface hydrothermal springs.

Water Sampling

Underwater Hydrothermal Springs

Underwater Spring Sampler. The majority of the hydrothermal springs are underwater in Herman Pit and in Clear Lake. Herman Pit is acidic at pH 3. Therefore, a remote sampling device was needed. The U.S. Bureau of Mines designed, engineered, and assembled an underwater spring sampler (Figure 2).

The underwater sampler is composed of a standard one-liter teflon bailer with check valves at both ends. The lower end has a low flow variable speed submersible pump attached. Temperature probes are positioned at both ends with the lower probe used to find the spring while the upper probe indicates when the bailer is full of hydrothermal fluid after pumping. To assist in finding the spring, a video camera and light are housed in underwater cases and are attached by adjustable arms to the bailer. Also, a high definition sonar bottom profiler was used.

Herman Pit. Three hydrothermal spring samples and one surface water sample (ambient) were taken from Herman Pit using the remote underwater sampler (Figure 3). A duplicate of the ambient sample was taken for quality control. Two one-liter volumes were taken at each location. Splits of all samples were sent to EPA's Las Vegas contract laboratory (ICF Technology Incorporated). The splits consisted of a one-liter volume for metals and a 500-ml volume for anions.

Clear Lake. Two underwater spring and two surface water samples (ambient) were taken

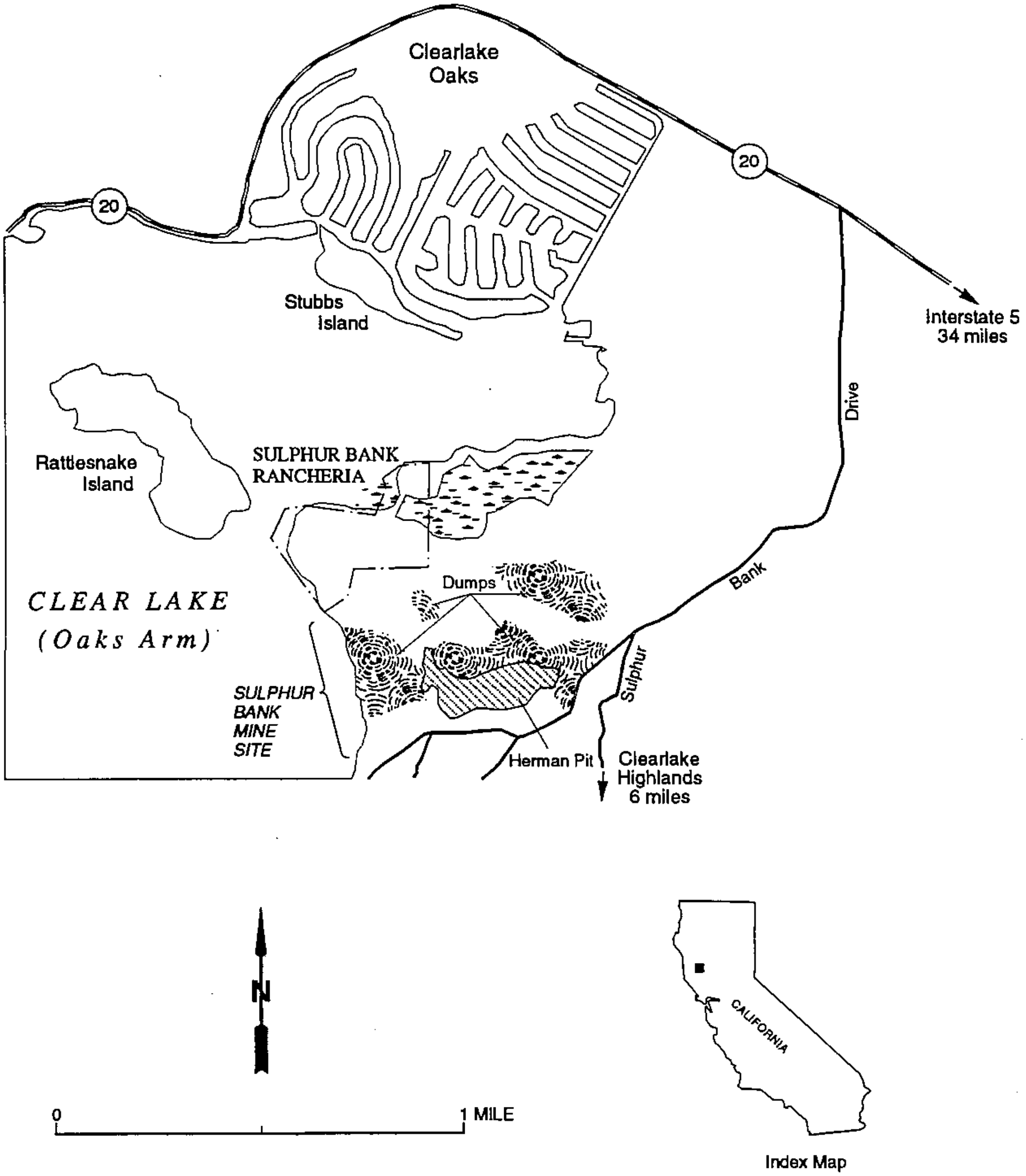

Figure 1. -- Location of the Sulphur Bank Mine Superfund site.

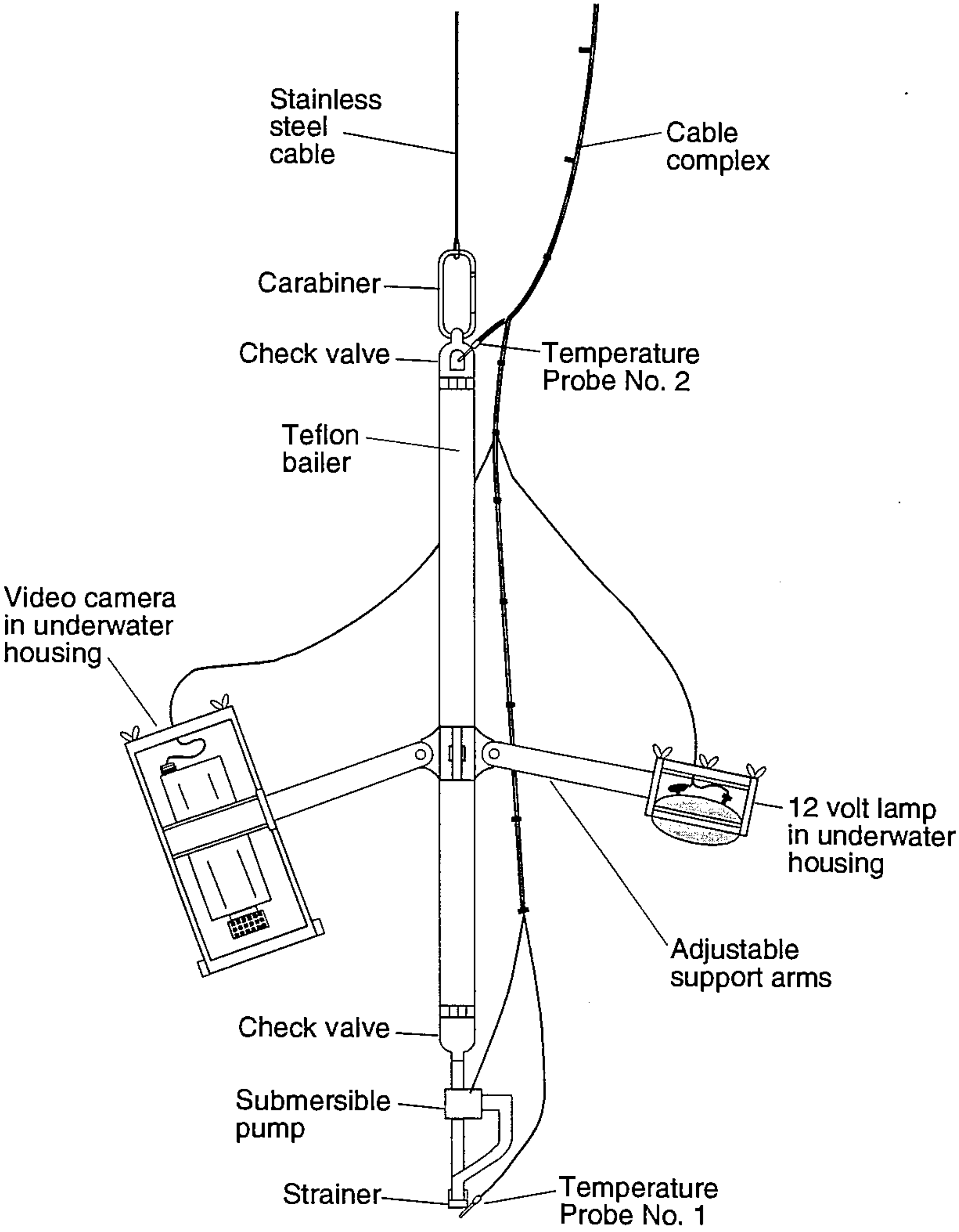

Figure 2. -- Sketch of the underwater hot spring sampler.

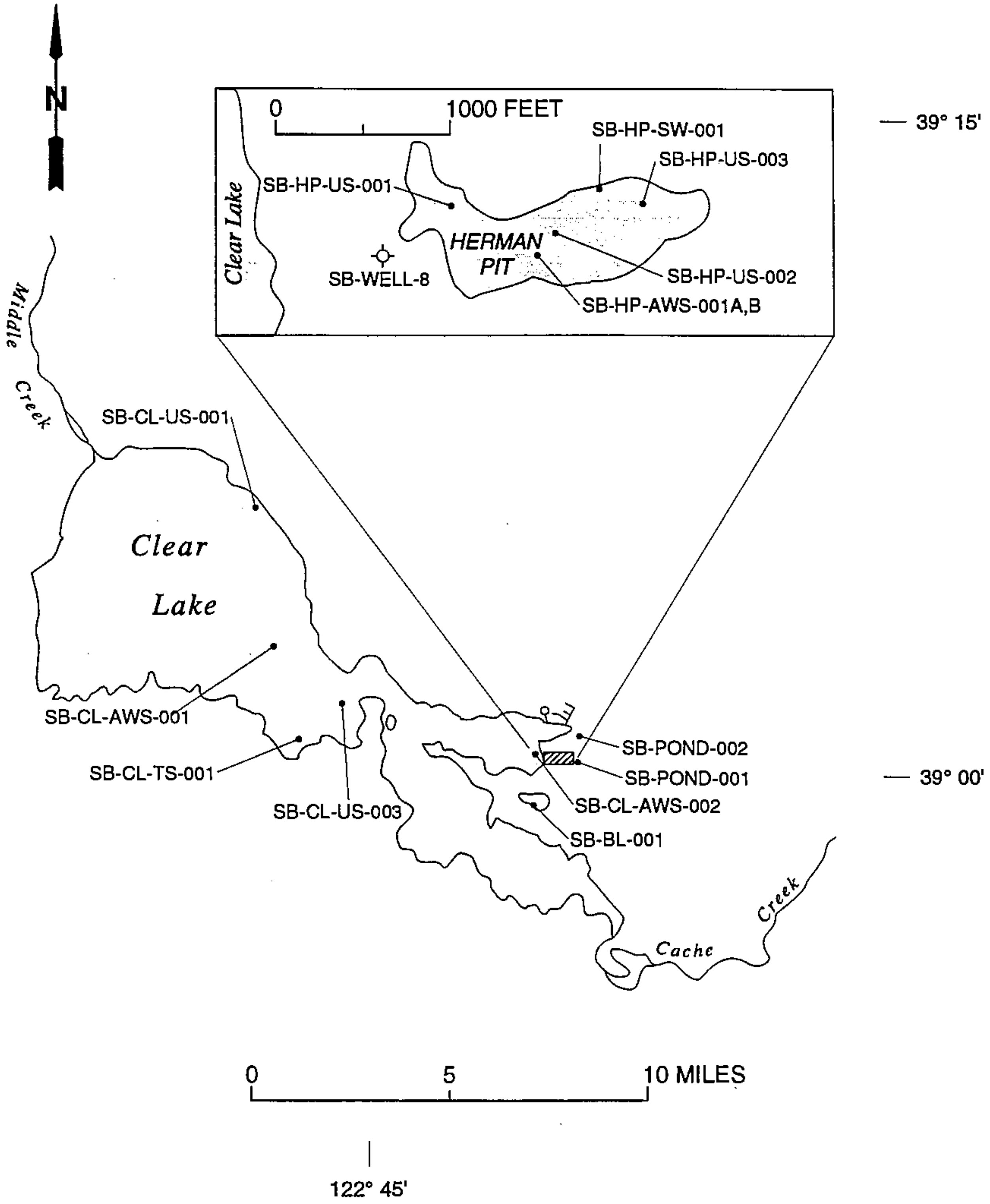

Figure 3. -- Sample location map.

from Clear Lake using the remote underwater sampler (Figure 3). Splits of one of the underwater springs and one of the ambient water samples were sent to EPA's Las Vegas laboratory.

Surface Hydrothermal Spring

Off-site Spring. One surface thermal spring found on a small island also was sampled (Figure 3). One split was given to EPA.

Ground Water

On-site Monitoring Well. One sample was taken from an on-site monitoring well (Figure 3). A one-liter teflon bailer was used to obtain the sample. Before sampling, three volumes of well casing water was purged using the bailer. One split was given to EPA.

Location Control

The underwater springs release both hydrothermal fluids and gas. The telltale bubbles on the surface from the generated gas are an indicator of the spring's general location on the bottom - especially since there are virtually no currents within the Herman Pit and Clear Lake. A 14-foot inflatable boat was used as an operating platform. Its composition is hypalon and neoprene which are resistant to acidic waters such as found in Herman Pit.

Sample Analyses

Physical and Chemical Parameters. A suite of physical and chemical parameters was obtained for each water sample. The physical parameters include pH, Eh, temperature, specific conductivity, total dissolved solids (TDS), and field dissolved oxygen (DO). All were performed in the field at each sample site and in the laboratory prior to analysis. This was done to ensure an additional level of quality assurance.

The chemical parameters include major cations and anions and heavy metals. These include SiO_2, Ca, Mg, Na, K, Mn, F^-, B, Br, Cl^-, Fe total, Fe^{2+}, Fe^{3+}, NO^{3+}, SO^{4+}, and S^{2-}. Heavy metals include Cd, Cr^{6+}, Co, Cu, Pb, Hg, Mo, Ni, Ag, and Zn.

Certain cations/anions such as Fe, S^{2-}, and SO^{4+} are very sensitive to changes of Eh (redox) with respect to time. Therefore, filtering using traditional aeration methods (vacuum or pressure) was not preferred or performed.

Ratios by weight were also calculated. These include Br/Cl, K/Na, and B/Cl. These ratios are useful in determining the water's commonality.

Near-site Laboratory

An analytical laboratory was setup by the U.S. Bureau of Mines in the town of Clear Lake, about one mile from the Sulphur Bank Mine site. Water samples were taken from the site and analyzed using wet chemistry methods. Analytical instruments included a laboratory spectrophotometer, pH/Eh meter (with Na and K probes), specific conductivity meter, and a dissolved oxygen meter.

Half (13 of 26) of the analytical methods performed at the near-site laboratory are USEPA approved for reporting purposes. These include Mn, F^-, Fe total, Fe^{2+}, Fe^{3+}, NO^{3+}, SO^{4+}, S^{2-}, Cr^{6+}, Cu, Pb, Ni, and Zn.

Cations and anions such as Fe total, Fe^{2+}, Fe^{3+}, Cl^-, SO^{4+}, S^{2-}, and metals were analyzed immediately. The remaining cations and anions were refrigerated and analyzed within 24 hours of sampling.

The mercury analytical procedure used is a newly developed prototype by HACH Company of Loveland, Colorado. The U.S. Bureau of Mines is working jointly with HACH on field testing the procedure. However, it is not approved by USEPA at this time. Recent Bureau field projects (in-house reports from the Gibraltar Mine, CA & U.S. Navy Indian Island, WA projects) which used this mercury procedure has shown promising results and that it is consistent with de-ionized blanks and standards with accuracy to ppb levels.

Off-site Laboratory

Fifteen splits from the 15 sample suite were sent to EPA's Las Vegas analytical laboratory. Samples tagged for metal analyses were preserved with nitric acid to a pH of less than 2. In following USEPA's sampling protocol, all bottles were refrigerated from sample time through shipment to the laboratory. The ice chest was documented, sealed, and shipped on August 28, 1992 from Clear Lake, California to Las Vegas, Nevada via Federal Express one-day service. USEPA's analyses were performed on September 17, 1992.

Quality Control

Sampling Technique

Standard USEPA water sampling protocol was observed during all sampling events. Splits were formed by filling an equal portion in each bottle then reversing the procedure until each bottle was full. Headspace was minimized for all samples. When transporting locally, agitation of the bottles was kept to an absolute minimum.

Blanks, Duplicates, and Standards

To insure quality control of the real-time analysis, a series of blanks, duplicates, and standards was analyzed concurrently with the other samples. The blank consists of an equal amount of de-ionized water. The duplicate indicates the analytical procedure's consistency.

For each heavy metal analytical procedure, a standard of known metal concentration in de-ionized water was prepared. The concentration was set within the range of expected results from the field samples.

Mercury Analyses

USEPA Laboratory Results

The highest USEPA concentration of mercury was 28.1 ppb in ground water from the monitoring well (Table 1; SB-WELL-8). An average concentration of 3.7 ppb mercury was found in underwater thermal springs within Herman Pit (SB-HP-US-001,002,003). A surface water sample from Herman Pit near a thermal spring had 6.3 ppb mercury (SB-HP-SW-001). The ambient water in Herman Pit measured 0.7 ppb mercury - only 0.4 ppb above detection limits).

Virtually no mercury was found in the Clear Lake samples - both in ambient water samples and underwater spring samples.

USBOM Laboratory Results

Results from the real-time analysis show that mercury is present in all waters in and around the Sulphur Bank Mine (table 1). The highest concentration of mercury, 10.1 ppb, was found in water issuing from a spring near the northwest shore of Clear Lake (sample SB-CL-US-001). The lowest concentration was in Borax Lake at 1.3 ppb (sample SB-BL-001) which is at the procedure's standard deviation. Mercury concentrations averaged 6.6 ppb from springs in Herman Pit while average spring concentration for Clear Lake is 8.0 ppb.

Mercury concentrations in ambient Clear Lake water at Oaks Arm (adjacent to the mine) has 7.3 ppb while the center of Clear Lake has only 3.7 ppb. The ground water monitoring well contains 8.5 ppb mercury.

Data Interpretation

The analytical results from USEPA's laboratory suggests that mercury is present at the mine site both in surface water (Herman Pit) and in ground water. One of the sources of mercury in Herman Pit are the underwater thermal springs as shown by the 3.7 ppb of mercury average spring concentration.

However, this mercury appears to be confined to the mine site since virtually no mercury was found at any of the sample sites in Clear Lake.

The U.S. Bureau of Mines analytical results illustrate a different scenario. Mercury is found in all waters at the mine site. Also, there is an increase of mercury in the eastern part of the lake as compared to the center.

The analyses suggest that the mine site may be a source of mercury augmented by ground water concentration and eventual flow into the eastern portion of Clear Lake. Also, prevailing westerlies form waves which erode mine waste and tails into the lake. These mechanisms could increase mercury concentrations in the eastern portion of Clear Lake. However, it is important to note that native and cinnabar forms of mercury, which would be found in the mine waste and tails, are virtually insoluble under standard pH water conditions such as found in Clear Lake.

Another source of mercury to Clear Lake are the underwater thermal springs within Clear Lake itself. The average

Sample Location and Numbers	Hg (ppb) USEPA Lab	Hg (ppb) USBOM Lab
Herman Pit:		
SB-HP-SW-001	6.3	5.1
SB-HP-AWS-001A	0.7	7.8
SB-HP-AWS-001B	0.7	8.8
SB-HP-US-001	1.7	6.8
SB-HP-US-002	4.3	6.3
SB-HP-US-003	5.0	6.7
Ave. U/W springs	3.7	6.6
Clear Lake:		
SB-CL-AWS-001	0.3*	3.7
SB-CL-AWS-002	0.3*	7.3
SB-CL-US-001	0.3*	10.1
SB-CL-US-003	0.9	5.8
SB-CL-TS-001	0.3*	3.9
Ave. U/W springs	0.6	8.0
Ponds:		
SB-POND-001	0.3*	2.4
SB-POND-002	0.3*	3.6
Borax Lake:		
SB-BL-001	0.3*	1.3
Groundwater:		
SB-WELL-8	28.1	8.5
Lab Stand. Deviation	-	+ 1.2
Detection Limits*	0.3	0.1

SB = Sulphur Bank
HP = Herman Pit
CL = Clear Lake
SW = Surface water
AWS = Ambient water sample
US = Underwater spring
TS = Thermal Spring
BL = Borax Lake
U/W = underwater

Table 1. Summary of Mercury analyses.

mercury concentration in Clear Lake springs are 21% greater than the average mercury concentrations from springs within Herman Pit.

Conclusions

Both sets of analytical data suggest that all waters at the Sulphur Bank Mine site contain Mercury. However, only the U.S. Bureau of Mines data show mercury in Clear Lake - especially from underwater thermal springs.

Mercury is present and natural to the Clear Lake area. It was deposited and concentrated here in the past as exemplified by the presence of cinnabar (HgS) ore found and mined at the Sulphur Bank Mine site.

It is important to note that natural background concentrations of mercury in the Clear Lake area would undoubtedly be much higher than background readings found elsewhere.

Recommendations

Only 15 water samples were taken at 14 sites. Therefore, the results and interpretation of these samples show only an insight to the actual nature of the aquatic chemistry at the mine site and area. To provide enough data to construct meaningful iso-concentration maps and to pin-point the exact sources of mercury, much more sampling is needed.