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AMBIENT AIR MERCURY CONCENTRATIONS AT THE GEYSERS

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ABSTRACT

From June 19 to December 16, 1986, PG&E conducted ambient air mercury measurements at six stations downwind of The Geysers in Lake County. The stations were located in populated areas on the eastern side, within the geothermal field at worst-case locations, and adjacent to geothermal plants and old mercury mining facilities. The mercury measurements were taken for 24 hours on a six-day cycle. The lower detection limit of this technique was approximately 1 ng/m^3 (nanogram per cubic meter) of air.

Overall, the ambient levels of gaseous mercury were low. The average was 5.8 ng/m^3 for the test period, with a maximum concentration of 23.6 ng/m^3. These data are similar to the estimated average atmospheric levels worldwide, 10 ng/m^3.

A statistically significant relationship was determined to exist between ambient mercury and air temperature. A correlation was also evident between rainfall and a decrease of mercury concentrations during the testing period.

INTRODUCTION

The Geysers-Calistoga Known Geothermal Resource Area (KGRA) is located on the eastern Mayacmas Mountain region of Lake and Sonoma counties. This region contains rich deposits of cinnabar ore, the principal ore processed in mercury mining. Mercury mining in this region began around 1861 and continued until about 1944 when the Socrates Mine stopped production. Surface deposits of cinnabar still exist, and the natural outgassing of metallic mercury vapor from these deposits and mercury entrained in the geothermal steam that is ultimately released into the atmosphere have become increasingly of concern. Several researchers have systematically investigated mercury vapor in geothermal steam (Robertson 1977, Crecelius 1976, Vostal 1972) and have followed the path of mercury through the geothermal power plant steam cycle and its ultimate release into the environment.

At The Geysers, three basic mechanisms could account for ambient gaseous mercury. Those processes are: 1) volatilization of mercury vapor from mercury-rich soils (i.e., cinnabar ore and mine tailings) (Robertson 1977), 2) entrainment in geothermal steam and release into the environment by natural venting and wellhead venting or from geothermal power plant cooling towers (Vostal 1972), and 3) volatilization from surface waters exposed to the air (DOI 1970).

In 1982, as part of the PG&E Geysers Unit 18 Public Health Compliance Monitoring required by the California Energy Commission (CEC), the PG&E Air Quality Unit conducted field monitoring of gaseous-metallic and particulate mercury in The Geysers area.

A larger study of the ambient air in the vicinity of The Geysers was undertaken in 1983 by a consortium of industry and local and state agencies including PG&E, the California Air Resources Board, and the CEC. This consortium initiated a study, the Geysers Air Monitoring Program (GAMP), which in 1983 and again in 1986 measured non-criteria pollutants of concern at The Geysers, including gaseous and particulate mercury (Altshuler et al. 1984).

After review of these studies, it was concluded that a more concentrated investigation of ambient metallic mercury vapor at The Geysers was warranted. In June 1986, the PG&E Air Quality Unit began that study.

This report contains the findings and analyses of The Geysers Ambient Air Mercury Program of 1986 and attempts to answer several key questions:

1. What are the ambient levels of mercury at The Geysers?
2. Is there a relationship between air temperature and ambient levels of mercury?
3. Is geothermal steam a major source of gaseous mercury?

4. Does rain have an effect on ambient levels of mercury either through a washing effect (lowering ambient mercury levels) or a process of erosion (exposing new soils to outgassing and thereby increasing ambient mercury levels)?

METHODOLOGY

Sampling Sites

Six sites were established for this study. Three of them were at existing GAMP monitoring stations and three more were established because of their proximity to the geothermal power plants, old mercury mining facilities, or natural meteorological drainage topography. Figure 1 is an area map with the mercury monitoring stations, power plants, and mercury mines indicated. The six stations were:

Anderson Springs. Located in a relatively densely populated area approximately 1 1/2 miles east and 1200 feet below Geysers Unit 13, this site was considered important because of the number of permanent residents living there and because historical data exist for ambient air concentrations of H_2S and mercury. This site was considered relatively clean, and little mercury was expected to be seen there. Abandoned mercury mines are located approximately 1 mile to the west and south of Anderson Springs.

Hobergs. This is a GAMP site located in a residential setting in Cobb, California. It is east of Bottle Rock Road, in a relatively high H_2S area near the crest of the ridge. This site was expected to monitor effects of westerly winds on mercury emissions from Geysers Units 11, 12, and 17.

Glenbrook. This is a GAMP site located at the northern end of The Geysers area. This site was positioned to monitor mercury emissions from the developed portion of the nearby KGRA during southwesterly winds.

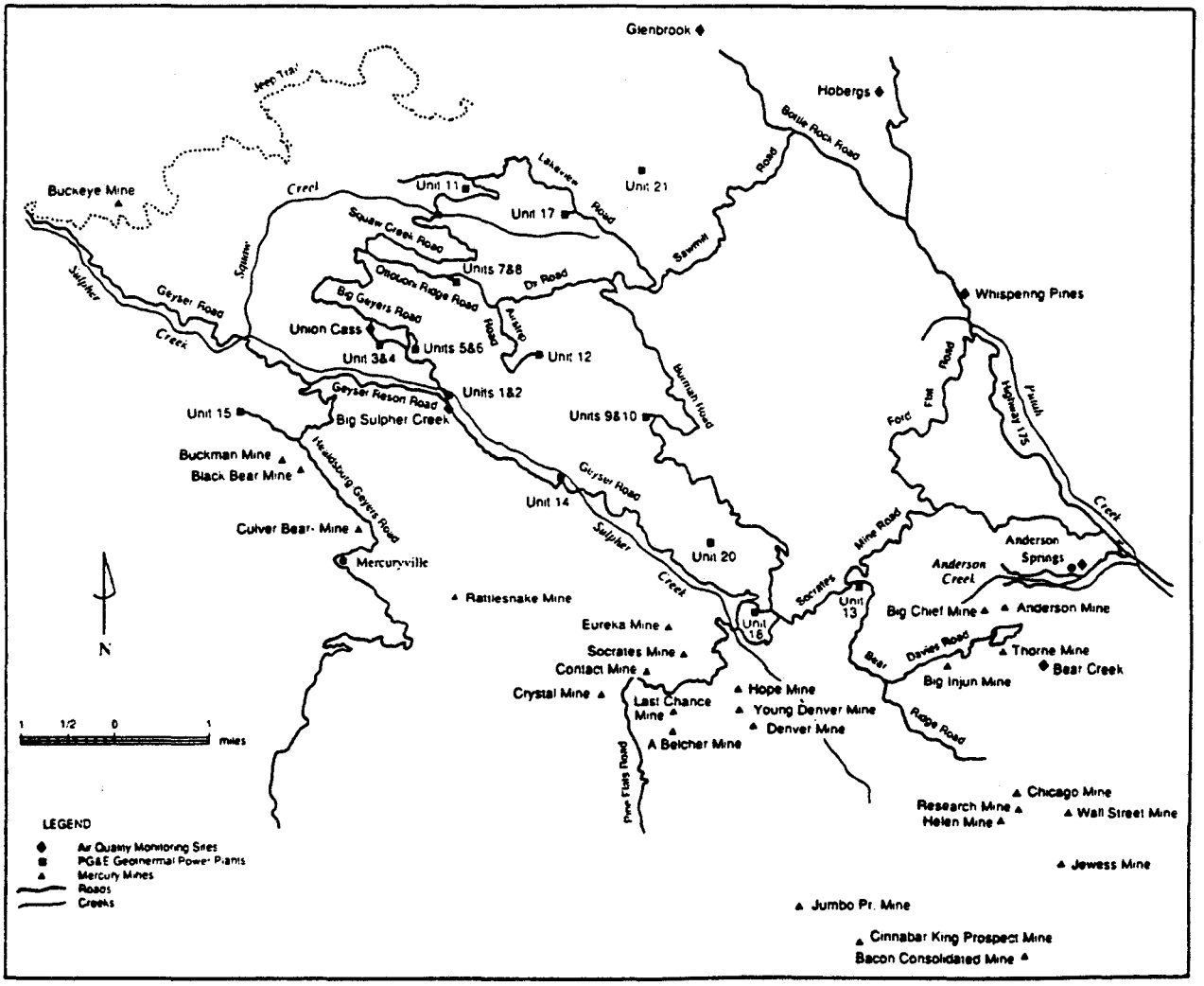

FIGURE 1. Mercury Mines in the Geysers Vicinty

Big Sulphur Creek and Union Chemical Abatement Storage Shed (CASS). These sites, located within the oldest developed area of The Geysers, were considered "worst case" locations. The Big Sulphur Creek site is located immediately south of Geysers Units 1 and 2, and the Union CASS site is between Units 3 and 4 and Units 5 and 6. These sites were located on the Big Sulphur Creek drainage and monitored air parcels that follow the diurnal patterns of wind along the Big Sulphur Creek. Mercury mines across the valley and adjacent to the Healdsburg-Geysers Road potentially influenced ambient mercury at these sites.

Bear Creek. This site is located 1 mile east of Geysers Unit 16 and is within 1/2 mile of Thorne and Big Injun mines.

SAMPLING PROTOCOL

The sampling equipment was housed in existing structures, when available. At the Bear Creek site, we used a "cotton region" meteorological shelter. The sample inlets were located approximately 3 meters above ground level and/or 1 meter above the sampler enclosures. Big Sulphur Creek was the exception; the inlet was located about 1 1/2 meters from the side of the building and 10 meters above Big Sulphur Creek at the UNOCAL pump station. In all cases, the sample lines were 3/16-inch (ID) FEP teflon tubing. Inlet line lengths were less than 5 meters and sample flow rates were approximately 0.7 liters per minute, so residence times within the probe were less than 8 seconds. All sites except Bear Creek were able to achieve satisfactory EPA siting guidelines. At Bear Creek, the sampler was located under the forest canopy in a narrow canyon with trees and bushes within 2 meters on two sides.

MERCURY ANALYSIS METHODOLOGY

Airborne mercury vapor was collected and measured using the Jerome gold film technology (McNerney 1983). The samplers drew ambient air across a mercury collection device (gold-coated coil) that absorbed mercury into the coating. The samples were subsequently analyzed on a Jerome Model 301 mercury analyzer.

The Jerome gold film method uses a two-step amalgam technique (sampling followed by analysis) for measuring mercury vapor. First, air passes across a gold-coated coil having a constant collection efficiency. After a pre-selected sampling period, the mercury is volatilized through heating for detection by the Jerome 301 analyzer. The volatilized mercury is collected on a gold film detector (a leg of a Wheatstone bridge) and the resulting change in resistance is proportional to the amount of mercury deposited. This procedure resulted in a detection limit of approximately 1 ng/m^3.

The mercury samplers consisted of sample lines, particulate filters, Mallcosorb filters, rotameters, pumps, dry test meters, and timers in conjunction with the gold coil collectors. Samplers located at sites using a sample distribution manifold (GAMP stations), also included a solenoid valve between the collector coil and the orifice to prevent backflow through the system during non-sampling times. Sites having AC power used a Dayton 7-day dial time switch and a Metal Bellows Model MB-41 air pump. Sites without AC power used an Irri-Trol battery-operated controller and a 12-18 volt DC Brailsford Model TD-4X2S pump. Those pumps were powered by 12-volt lead-acid marine batteries.

Mallcosorb filters removed H_2S (an interference) from the sample stream. The orifice and rotameters were used for setting the flow rates and checking for leaks in the system. The pumps were of a sealed positive displacement design, so the dry test meter recorded the total sample volume. The dry test meter records volume with a resolution of 0.001 ft^3 (2.83 x 10^{-5} m^3).

QUALITY CONTROL

The accuracy of the mercury measurements was maintained by injection of mercury standards into the Jerome 301 analyzer, which (as nearly as possible) duplicated the instrument's response to the 24-hour collection coil response. The 24-hour mercury measurements were based on a new calibration curve each time the collectors were analyzed. The mercury standards were precise volumes of mercury vapor taken from the head space of a vial containing liquid mercury at 0 degrees C (Arcado and Lin 1983b).

RESULTS OF ANALYSES

Data

Ambient gaseous metallic mercury data from the sampling sites were collected from June 19, 1986, to December 16, 1986. These data are presented in Table 1. Overall, the Union CASS site had the highest concentrations of mercury. An average mercury concentration of 8.6 ng/m^3 was monitored there during the sampling period. The high 24-hour value at Union CASS was measured at 17.3 ng/m^3 on August 24 and was the second highest value recorded for all sites. The Big Sulphur Creek site had the next highest mercury concentrations. An average of 7.2 ng/m^3 was measured there over the sampling period.

Hobergs recorded the lowest average ambient mercury concentrations, 4.5 ng/m^3. Interestingly, however, on September 11 the highest single measurement of mercury was recorded at this site, 23.6 ng/m^3. A review of the data and the QC documentation gives no indication that there was an instrument failure or other mishap that might have influenced the measurement. That datum was considered valid.

The average 24-hour mercury measurement for all stations during the sampling period was 5.8 ng/m^3. The

Table 1

GEYSERS MERCURY MONITORING PROGRAM
6-DAY SAMPLING CYCLE
ng/m^3 *
1986

SAMPLING DATE	HOBERGS	GLEN-BROOK	ANDER'N SPRINGS	BIG SUL. CREEK	UNION CASS	BEAR CREEK	HIGH VALUE	AVERAGE MERCURY
JUN 19	2.7	4.3	4.0	7.8	7.8	–	7.8	5.3
JUN 25	1.4	7.9	7.0	11.2	13.3	–	13.3	8.2
JUL 1	4.8	9.3	11.2	7.7	7.9	–	11.2	8.2
JUL 7	4.8	7.2	6.3	13.7	11.5	–	13.7	8.7
JUL 13	3.6	6.5	7.5	9.0	13.1	–	13.1	7.9
JUL 19	3.4	4.9	10.3	7.5	8.7	6.0	10.3	6.8
JUL 25	3.8	6.1	9.4	6.8	5.6	6.9	9.4	6.4
JUL 31	3.0	5.3	11.9	5.5	10.2	7.5	11.9	7.2
AUG 6	2.9	7.7	5.7	8.8	10.9	6.6	10.9	7.1
AUG 12	3.7	7.1	4.7	11.5	15.0	5.4	15.0	7.9
AUG 18	2.1	4.6	3.5	4.8	5.5	3.2	5.5	4.0
AUG 24	2.5	5.0	4.3	7.9	17.3	4.8	17.3	6.9
AUG 30	2.2	3.9	4.1	–	6.0	3.4	6.0	3.9
SEPT 5	1.9	4.8	6.8	–	10.0	4.8	10.0	5.6
SEPT 11	23.6	4.9	3.5	4.7	4.1	4.0	23.6	7.4
SEPT 17	2.4	4.3	3.4	-	5.2	3.2	5.1	3.7
SEPT 23	2.4	6.3	3.6	8.0	7.5	4.0	8.0	5.3
SEPT 29	2.0	5.2	3.8	6.7	4.7	3.8	6.7	4.4
OCT 5	1.7	4.3	2.7	4.5	–	3.6	4.5	3.4
OCT 7	–	–	–	–	7.9	–	7.9	7.9
OCT 11	4.0	4.1	3.9	6.9	7.5	4.2	7.5	5.1
OCT 17	1.5	3.8	3.4	4.0	12.3	4.0	12.3	4.8
OCT 23	2.1	4.2	2.6	3.8	8.6	1.8	8.6	3.9
OCT 29	3.8	4.1	3.4	–	9.5	3.8	9.5	4.9
NOV 4	1.1	5.5	5.0	9.7	5.6	13.8	9.7	6.8
NOV 10	4.1	16.0	7.6	7.4	6.8	2.7	16.0	7.4
NOV 16	1.9	6.2	4.1	5.4	6.5	–	6.2	4.8
NOV 22	3.0	4.0	3.6	4.4	4.4	3.1	4.4	3.7
NOV 28	3.1	4.7	3.5	6.7	8.8	3.7	8.8	5.1
DEC 4	1.7	4.2	3.6	4.9	6.6	5.4	6.6	4.4
DEC 10	2.0	4.9	–	4.8	6.6	4.6	6.6	4.6
DEC 16	3.7	5.1	3.5	3.8	3.9	2.9	3.9	3.8
AVERAGES	4.5	5.7	5.3	7.2	8.6	4.7	10.7	5.8

* 24-hour sample.
– missing data.

average of the high mercury measurements was 10.7 ng/m^3. Mercury concentrations were approximately two times greater at Big Sulphur Creek and Union CASS than at the lowest site, Hobergs. However, even at these worst-case locations, ambient air mercury concentrations are considered low when compared to other similar geologic deposition areas and worldwide estimates of mercury.

Mercury concentrations measured at The Geysers during this testing period were low. Ambient air mercury measurements taken by the Pacific Northwest Laboratory in 1975, away from the vicinity of The Geysers, were generally below the detection limit of 1 ng/m^3 but occasionally ranged from 1 to 18 ng/m^3 (Robertson 1977). The U.S. Geological Survey reported mercury concentrations over mercury mines ranging from 24 to 108 ng/m^3 (McCarthy et al. 1970). Other technical reviews on atmospheric mercury levels suggest that the average concentration throughout the world is 20 ng/m^3 (EPA 1980). It was concluded, however, that background levels in the northern hemisphere are about 2 ng/m^3. The EPA assumed that the atmospheric level of total mercury is 10 ng/m^3 in its most recent assessment of mercury health effects.

In a review of H_2S concentrations measured within Big Sulphur Creek Valley (the center of geothermal development at The Geysers), the H_2S concentrations have been observed to be an average of 5 to 10 times greater than those locations east of The Geysers in the populated areas of Lake County (Hobergs, Glenbrook, and Anderson Springs) (Altshuler 1987, SRI International 1980). It appears that there is a greater change of H_2S concentrations than of mercury concentrations with change of location.

ANALYSES

A series of trend analyses were performed to ascertain if relationships existed between gaseous metallic mercury data and other parameters such as ambient temperature, rain, H_2S, and particulate mercury. If significant relationships were found, certain deductions may be reached. For example, if gaseous mercury concentrations are statistically related to ambient temperatures, then soil is probably a source of mercury concentrations. It is known that volatilization of mercury from soils increases with temperature (Vostal 1972).

The statistically significant relationships that were established using the method of least squares and the linear relationship of two unknowns are contained in Table 2.

AIR TEMPERATURE AND GASEOUS MERCURY RELATIONSHIP

Figures 2 and 3 demonstrate the change of average mercury concentration with the change of average air temperature for the entire network and with the high temperature recorded during each individual sample day at any meteorology station. A positive relationship is evident in both cases. We can infer, therefore, that soil temperature and ambient mercury may have a cause-and-effect relationship, although no physical evidence has been established in this study to corroborate that supposition. The instability of cinnabar in a vapor-dominated system (Varekamp and Busick 1984) and the vapor pressure of mercury lend credence to this relationship, however.

We observed that air temperature in excess of 85 degrees F is inversely proportional to changes of ambient mercury (Figure 4). With an increase of air temperature at ground level (air temperature was measured at approximately 10 to 20 feet above the ground), vertical mixing of the atmosphere increases as the warm air rises. This results in the subsequent dilution of airborne pollutants, including mercury. On 5 of the 10 warmer days, no inversion layer was evident. An indication of an inversion layer is a warmer temperature recorded at the Unit 13 meteorology site than recorded at Anderson Springs. They are separated by 1200 feet in elevation and only approximately 1 1/2 miles of horizontal distance.

RAIN AND GASEOUS MERCURY RELATIONSHIP

On November 19, 1983, following a heavy autumn rain at Anderson Springs (one of the first major rain episodes of the season), an elevated mercury concentration was recorded. At that time, it was suggested that the heavy rains exposed fresh mercury rich soils for outgassing. This phenomenon was not witnessed later. In this study, we failed to correlate heavy rains with elevated mercury.

We did, however, correlate an increase of rainfall with a decrease in ambient mercury concentrations. An assumption made in this analysis was that the emissions of mercury are relatively constant and the reduction of mercury with increased rainfall is due to a washout of mercury by rain (Ferrara 1986). A decrease in temperature with weather fronts is another possible explanation, as is reduced escape routes of mercury vapor through rain-moistened soils. Figures 5 and 6 demonstrate the inverse relationship of rain to mercury in two data sets: (1) using all available data, and (2) plotting those sample days where rainfall was >0.01 inches of rain.

Table 2

Relationships of Mercury to Other Measured Parameters

Test of Relationship	Avg. Temp to Avg. Hg	High Temp to Avg. Hg	Temp >85 to Avg. Hg	Rain (in.) to High Hg	Rain >0.01" to Avg. Hg
n	32	32	10	32	16
slope	0.095	0.076	-0.29	-1.45	-1.08
y-intercept	0.05	0.30	32.8	6.2	5.7
Corr. Coeffic. (r)	0.58	0.58	-0.63	-0.44	-0.50
Critical r @ 95% confidence *	0.36	0.36	0.63	0.36	0.50

*Orkin and Drogin, 1975

CONCLUSIONS

In the six-month period from June 19 to December 16, 1986, ambient levels of metallic mercury measured in the vicinity of The Geysers ranged from 1.1 to 23.6 ng/m^3 of air. The overall average mercury concentration was 5.8 ng/m^3. The mercury monitoring site that recorded the highest average ambient mercury concentration was the Union CASS site located east of the Big Sulphur Creek drainage. This site is surrounded by Geysers Units 3, 4, 5, and 6. The Hobergs GAMP site recorded the lowest average levels of mercury during the test period. The higher levels of mercury in the test area, 10 ng/m^3 and greater, were generally associated with northwesterly winds at the Glenbrook and Anderson Springs sites.

A statistically significant relationship was determined to exist between ambient mercury and air temperature. This would indicate that one contributor of the ambient gaseous mercury is outgassing of mercury-laden soils. Above 85 degrees F, mercury concentrations decreased with an increase of temperature. This was probably due to the vertical mixing of the atmosphere and the subsequent dilution of pollutants.

Rain appeared to have an inverse relationship with mercury vapor concentration in ambient air. A weak but statistically significant correlation between an increase of rainfall measured since the last sampling period and a decrease of mercury concentration was established.

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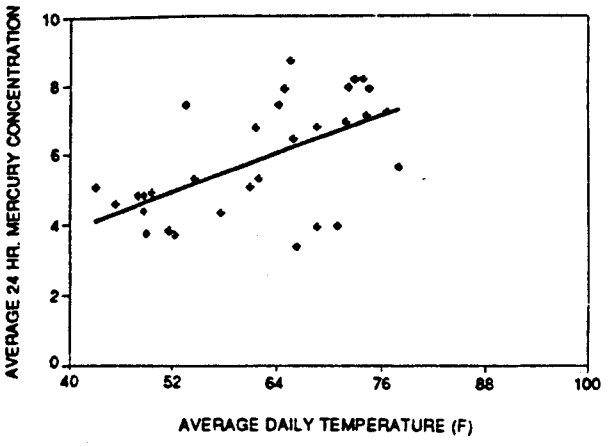

FIGURE 2. Average Daily Temperature and Average Mercury Concentrations

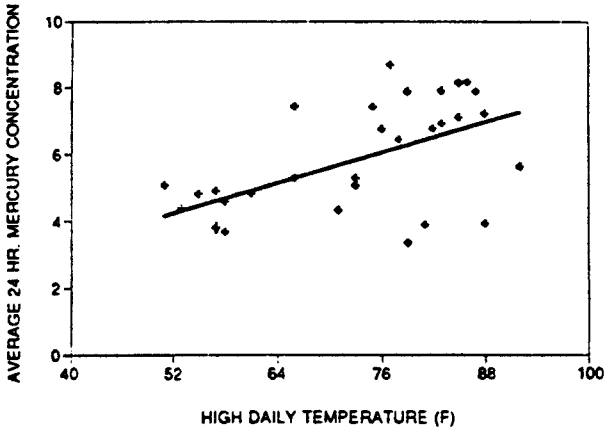

FIGURE 3. Average Ambient Mercury Concentrations and High Daily Temperatures

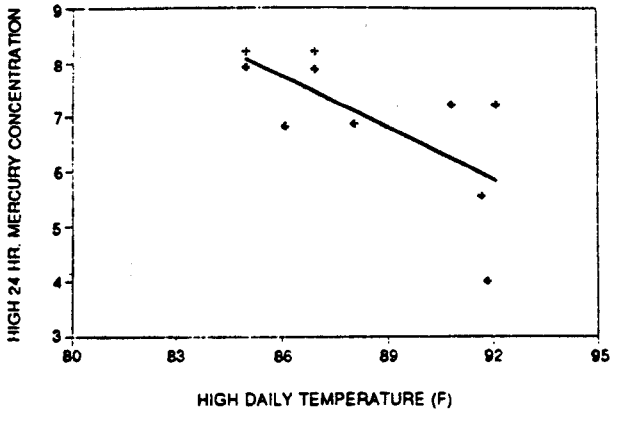

FIGURE 4. Maximum Ambient Mercury Concentrations and Average Air Temperature Above 85 Degrees F

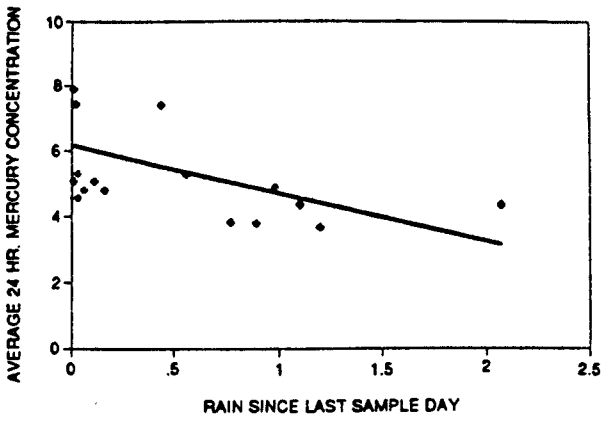

FIGURE 5. Ambient Mercury Concentrations and Rain Since Last Sample Day

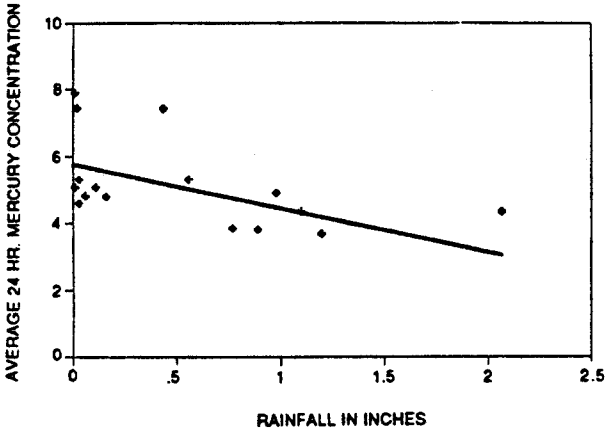

FIGURE 6. Ambient Mercury Concentrations and Rain Episodes Where Amounts are 0.01 Inches or Greater.