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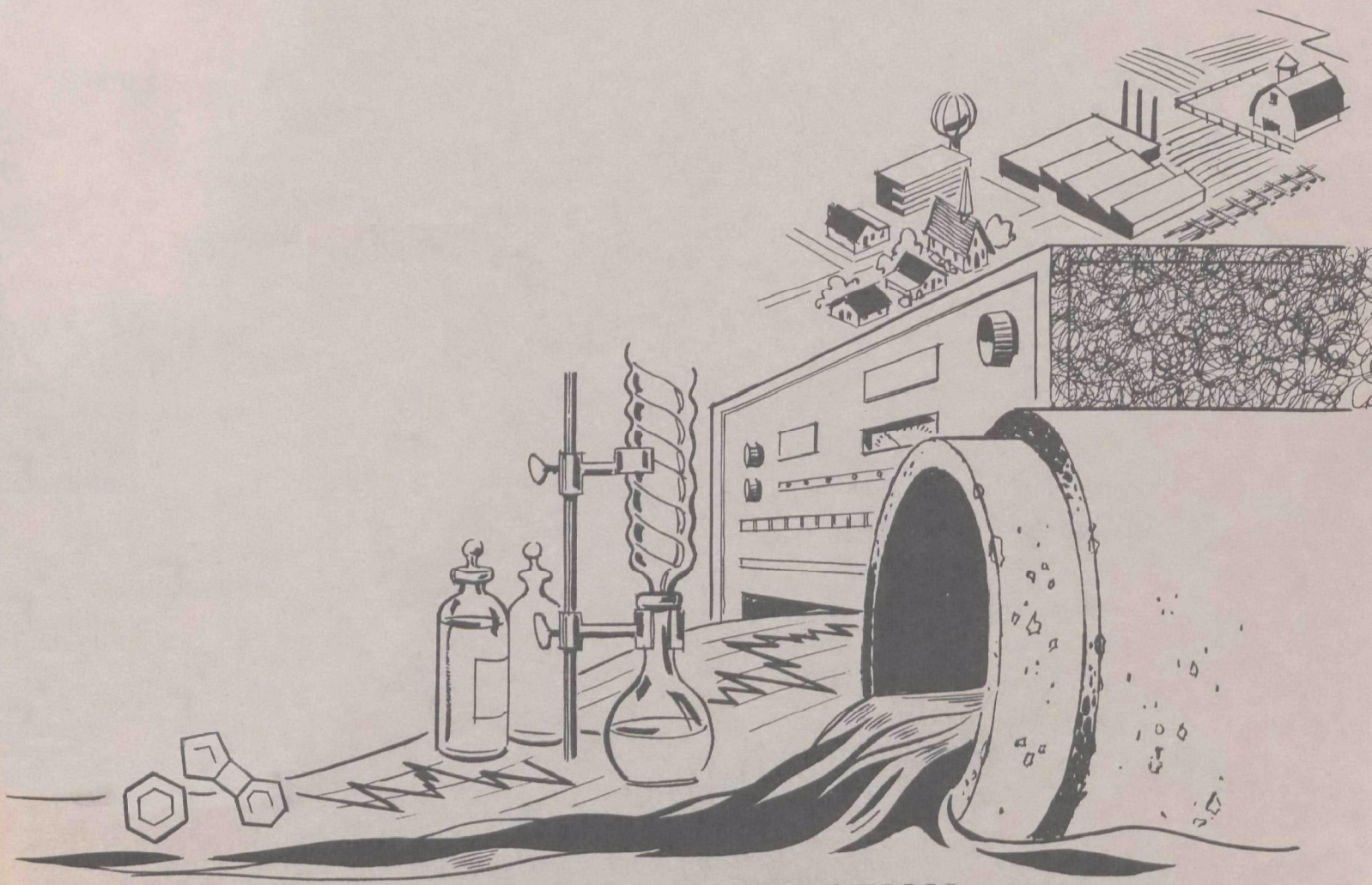
MONITORING MERCURY VAPOR NEAR POLLUTION SITES



U.S. ENVIRONMENTAL PROTECTION AGENCY

WATER POLLUTION CONTROL RESEARCH SERIES

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MONITORING MERCURY VAPOR NEAR POLLUTION SITES

by

Environmental Measurements, Inc.
215 Leidesdorff Street
San Francisco, California 94111

for the

Office of Research and Monitoring
ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

Field and laboratory measurements were made to demonstrate that mercury vapor in the air near mercury-polluted water or sediment can be detected using an extremely sensitive detector, the Barringer Airborne Mercury Spectrometer.

Areas were visited where the presence of mercury was known from fish, water, or sediment analyses; anomalous mercury levels ranging from 50 to more than 20,000 nanograms per cubic meter (ng/M^3) were detected. Ambient air contained from 0 to 50 ng/M^3.

Anomalous concentrations of atomic mercury vapor in air may be classified as natural or man-made. The largest anomaly detected was natural, emanating from a steam vent at The Geysers, California. The second largest was man-made, and was measured downwind from a large chemical plant.

Laboratory studies demonstrated that the mercury spectrometer is sensitive only to atomic mercury. By means of pyrolysis or combustion, organic compounds could be converted to metallic form and detected. To detect mercury pollution in water, pyrolysis appears necessary to convert combined mercury to the atomic state for measurement by rapid spectrophotometric techniques.

This report was submitted in fulfillment of Project Number 16020 GLY under the partial sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The presence of mercury vapor in the atmosphere was measured with the Barringer Airborne Mercury Spectrometer (BAMS). Repeatable threshold sensitivity of two to five nanograms per cubic meter (ng/M^3) was attained.

2. Mercury vapor was conveniently and rapidly measured in the atmosphere from a variety of mobile platforms. Installations of the BAMS were made in a compact automobile, a small van, a helicopter, and on a cabin cruiser.

3. Surveys were conducted in the vicinity of natural sources of mercury (mines, reported pollution sites, and geothermal vents) and over cultural sources (outfalls of sewage treatment plants, industrial sites, and waste disposal areas). Urban ambient monitoring was undertaken and demonstrated diurnal variations of mercury in the atmosphere.

4. Ambient air levels ranged from the zero level to peaks exceeding 80 ng/M^3 in urban areas (downtown San Francisco). The presence of anomalous peaks of mercury were narrowly confined near the sources of the vapor. A level exceeding 28,000 ng/M^3 was located at a geothermal steam vent; levels near the effluent of incineration smokestacks exceeded 50,000 ng/M^3. These high levels were uncommon; measured peaks were more frequently a few thousand ng/M^3.

5. The intent of the demonstration grant was to seek mercury vapor's presence to be used as a rapid means of surveying for mercury water pollution sites. The results in this regard were inconclusive for three reasons:

   Measurements were made near reported sites of mercury pollution; and no samples of water or bottom sediment were gathered simultaneously. Such corroborative evidence was not gathered because the reported sites were not located with sufficient accuracy to allow efficient sampling.

   Originally, the program was designed to monitor during hot and humid months in the vicinity of well-documented mercury pollution sites in the Great Lakes. Delayed funding precluded visitation of these sites (due to Winter) and most measurements were undertaken in California.

   The intensity of anomalies measured, which did not relate directly to water sites, was so much greater that

these were investigated, as a tracing method to detect sources, rather than to continue the search for minute atomic mercury levels directly over water.

6. Mercury vapor was shown to pass easily through a water overburden once equilibrium had been established.

7. Experiments were successful in showing that organic mercury compounds could be decomposed to release free elemental mercury. This was then directly measured with the spectrometer. Because mercury pollution has been reported to be present principally in organic form, and the vapor pressure of this organic form is reported some 40,000 times greater than the vapor pressure of elemental mercury, the ability to precondition the air sample so that "total" mercury could be measured was very encouraging.

In conclusion, the demonstration grant showed an ability to measure mercury in the air and demonstrated a technique for preconditioning this sample so that total mercury might be measured in the same fashion.

SECTION II

RECOMMENDATIONS

This program was limited to the demonstration of an ability to survey for atmospheric mercury pollution near water. During the course of the program, an evaluation of pyrolysis techniques were undertaken to determine if total mercury could be measured using the same rapid-response, high-sensitivity instrumentation. However, it was not within the scope of this program to do more than field demonstrate the techniques developed.

The success of surveying for atmospheric mercury and the ability to decompose its organic compounds leads to a recommendation that areas that have been tested in California are revisited using the pyrolyser to determine total mercury in the air.

All of the measurements made during the course of this demonstration grant were accomplished in winter months. The dependence of mercury vapor pressure on temperature suggests that much greater volume of material would be available in the summer months. It is recommended that measurements be made under hot conditions and that mercury samples to taken from the water and bottom sediments simultaneously while the presence of mercury vapor in the air is monitored. Visitation to sites in the Great Lakes' area are still recommended, as is a survey trip to investigate recent water sample measurements made by the Geological Survey from the Merced River, California.

Mercury plumes were measured emanating from industrial sites and natural sources. It is recommended that a detailed survey of these plumes be undertaken to determine their disposition and fallout character in rural and urban areas. Ancillary to this suggestion, a detailed survey in an area of high relief would delineate the effect of topography on the apparent channeling of mercury vapor to low-elevation reservoir collection areas.

The simple ability to measure mercury, much less total mercury, provides a fast and efficient method of survey. It is recommended that the technique be incorporated as a method to catalog mercury's storage or presence, at both natural and cultural sites. A building library of data would help assess the relative contribution of various sources of mercury pollution.

SECTION III

INTRODUCTION

Since the discovery of mercury in fish caught in Lake St. Clair, Ontario in 1970 (1), a great deal of interest in the United States has been centered on the presence of mercury in water and the relationship of this mercury to industrial and natural sources. A major problem in the study of mercury distribution in the environment has been the difficulty of location and chemical analysis of water and sediment samples.

Extremely sensitive instrumentation has been developed to detect mercury associated with ore deposits (2), and this equipment has been used in prospecting for ore deposits. Environmental Measurements, Inc. of San Francisco made application to the Federal Water Quality Administration for a grant to demonstrate the application of this prospecting instrument, the Barringer Airborne Mercury Spectrometer (BAMS), to locate places of water pollution. It was proposed to use this instrument to detect mercury vapor in air over sites of contamination.

Environmental Measurements, Inc. took delivery of the Barringer Airborne Mercury Spectrometer on December 8, 1970. A program of familiarization was first carried out. Subsequently, areas of known mercury pollution were visited; measurements were made of the mercury vapor in the air in the immediate vicinity of these sites. Natural and industrial sources were selected and visited, and the measurements were cataloged and displayed. In addition, a reconnaissance program involved traversing near industrial areas where mercury pollution had not previously been reported. This program revealed at least two new areas of mercury contamination.

The following sections describe the details of the surveying and environmental analysis carried out in this program.

SECTION IV

OBJECTIVES

The objective of this program was to demonstrate the applicability of a newly designed proprietary mercury monitor, the Barringer Airborne Mercury Spectrometer, to the rapid and efficient survey of mercury pollution in water. The primary purpose of this was to be able to locate polluted waters by detecting the vapors given off from such waters.

It became clear that the technique could also be used to detect the principal sources of the mercury which contributed to the pollution in the water. The secondary objective of the program, therefore, became the definition of specific sources of mercury pollution which could contribute mercury to the water or sediment.

SECTION V

MERCURY IN AIR

Mercury is the only metal to exist in a liquid state at standard conditions of temperature and pressure. Because of its toxicity and high vapor pressure, it presents special problems in storage, usage, and disposal.

The vapor pressure of mercury is markedly temperature dependent. Figure 1 illustrates the variation in vapor pressure

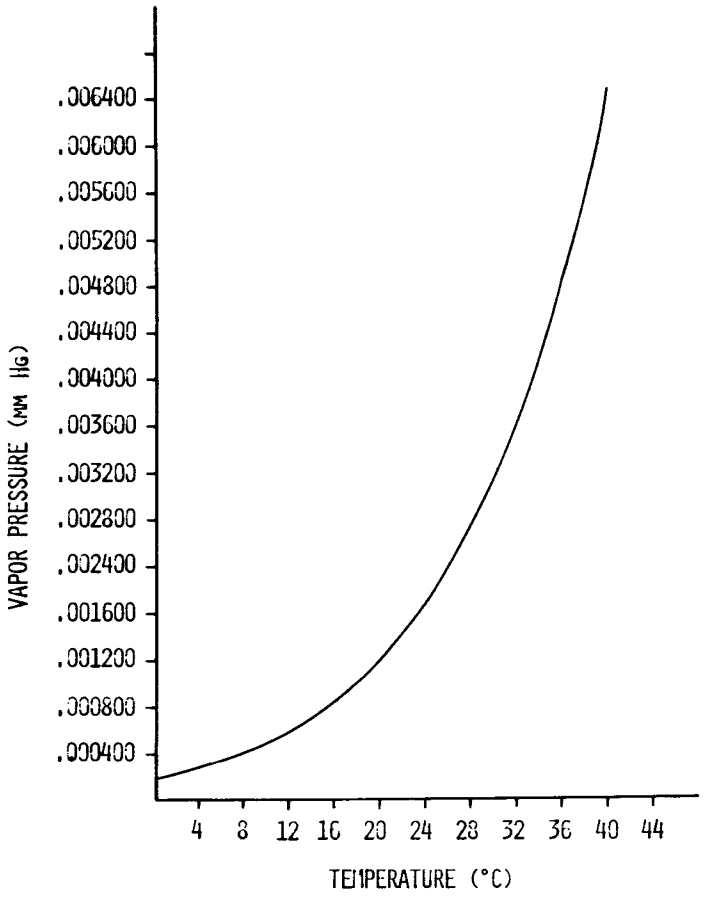


Figure 1
Temperature Dependence of Saturated Mercury

with temperature over the diurnal range commonly experienced in North America (3). The graph illustrates that over a cold night/warm day interval, the vapor pressure of mercury can vary ten-fold. This property is extremely important in the understanding of ambient levels of mercury detected in the air anywhere.

The vapor pressure of mercury is also reported to be dependent on barometric pressure. McCarthy, Meuschke, Ficklin and Learned (4) report work which indicates that as the barometric pressure drops, mercury vapor is released from the ground. This property would influence background levels in areas where mercury is widespread.

The customary unit of measure for concentration of mercury vapor in the air is the nanogram per cubic meter (ng/M^3). This is equivalent to parts per trillion by determining the weight of a cubic meter of air at normal conditions of temperature and air pressure. Since one cubic meter of air weighs 1205 grams, one ng/M^3 becomes $1.0 \times 10^{-9}/1.205 \times 10^3$ or approximately 1.0×10^{-12}, a part per trillion.

Certain industries producing and using mercury are hazards because of this high vapor pressure. The Socrates Mine in Northern California is so rich in mercury that the mercury vapors are above danger level, and the mine cannot be worked. The felt-hat industry is notorious for its cases of mercury poisoning.

In some chemical laboratories it is customary to cover mercury with a thick layer of water in the same container to seal off the poisonous mercury vapor. This technique has become a standard rule for safety (5). In Section VII the results of an experiment demonstrate that this rule is not totally effective.

The high vapor pressure of mercury has led to its use in prospecting not only for mercury but also for other metals with which it naturally associates. Geologists suggested that if an instrument could be developed to detect this mercury in air, it could be used as an airborne prospecting tool. The development of the BAMS was in response to this need; critical specifications were high sensitivity and rapid response.

Mercury vapor has been detected in ambient air near naturally occurring mercury deposits, in rural areas of agricultural activity, in urban areas and near certain specific industrial developments (4) (6) (7).

The Oak Ridge paper (7) reviews the standards for permissible mercury vapor in ambient air and under industrial conditions. The variation is extreme, ranging from 50,000 ng/M^3 in the United States to 1,000 ng/M^3 in Germany. This variation indicates the general uncertainty which exists concerning the importance of low levels of mercury vapor in the air.

The residence time of mercury vapor in air is not clearly known. The studies described in this report may contribute

to that knowledge. The high density of mercury (13.5955 g/ml at 0°C) suggests that it cannot be very long.

SECTION VI

THE BARRINGER AIRBORNE MERCURY SPECTROMETER (BAMS)

Theory of Design

The mercury measurements on this project were all made using the Barringer Airborne Mercury Spectrometer (Figure 2).

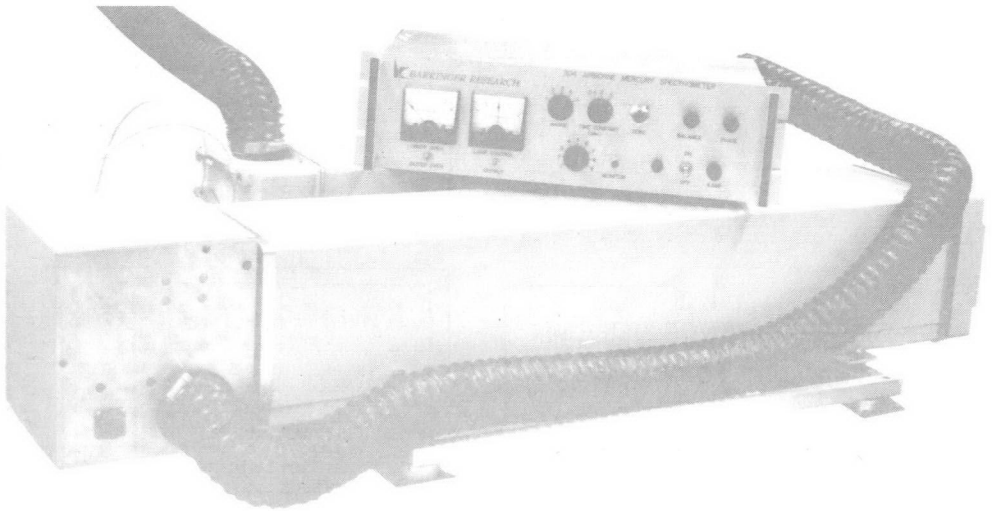


Figure 2
Barringer Airborne Mercury Spectrometer (BAMS)

This instrument is an atomic absorption spectrophotometer, specifically designed and built to isolate the 2536.5-angstrom emission and absorption spectra characteristic of atomic mercury vapor. The equipment was originally developed for exploration purposes and for laboratory soil sampling (2); subsequent design improvements (8) led to the rapid second-range response time and high nanogram-per-cubic-meter resolution needed for airborne use.

A system block diagram is shown in Figure 3. The air to be sampled is drawn through one side of a bivalve assembly into the sampling chamber. By operator choice, the air may pass freely or be moved through a palladium-chloride-saturated filter to absorb its mercury content. Repeated calibrations have demonstrated the efficiency of this filter's absorption to be in excess of 96 percent.

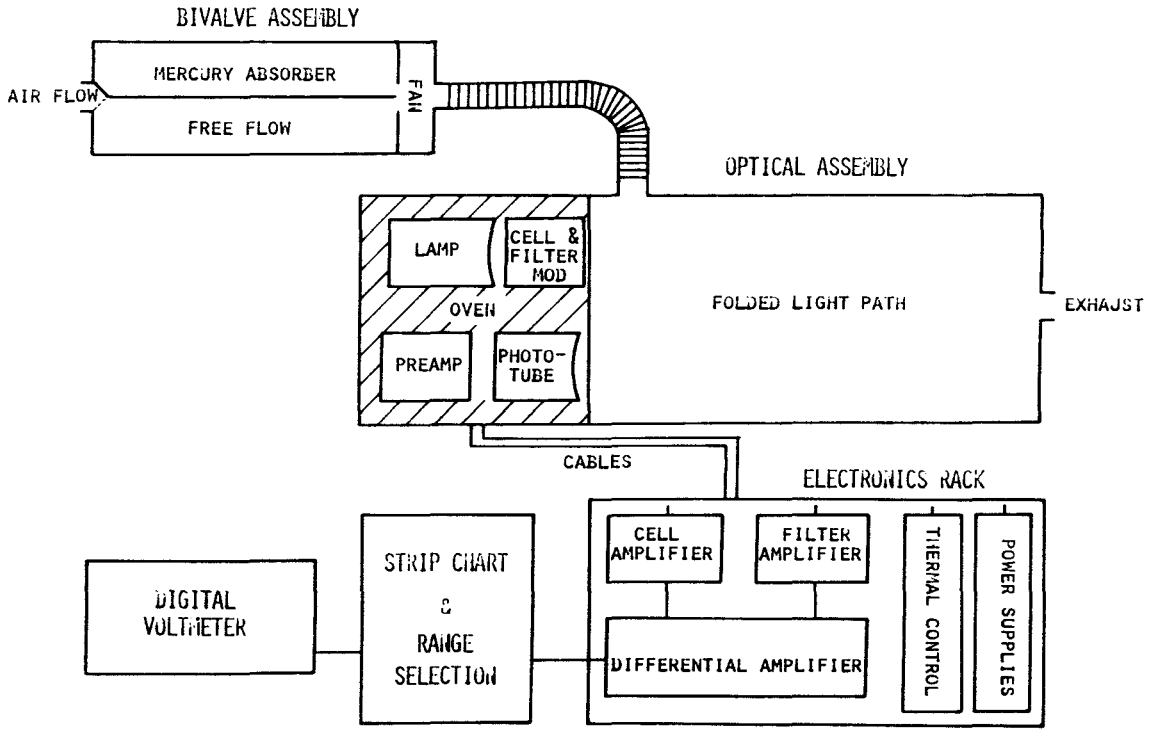


Figure 3
Simplified BAMS System Block Diagram

Under ambient pressure, the sample passes through the optical path of the spectrometer at about one-third cubic meter per minute. The entrapped sample volume is 0.016 cubic meter along a one-meter path. Mirrors allow light to pass along this chamber several times between energy source and photodetector. An effective six-meter pathlength produces the needed concentration-pathlength for high resolution dependent upon the Beer-Lambert Law of Absorption:

$$I = I_o e^{-acl}$$

WHERE I_o = incident light intensity
a = absorption coefficient (as a function of wave length)
c = concentration
l = path length

A commercial mercury-neon lamp is used as an energy source (9); it is operated at an elevated temperature to broaden the emission spectrum, and visible light is filtered out. Sequentially, a saturated cell of mercury (Case A) or a narrow

band interference filter, allowing the passage of the 2536.5-angstrom line (Case B), is placed in the optical path. In Case A, the mercury cell absorbs all of the transmitted light except the broadened line's edges; any sample in the chamber has no additional effect. In Case B, the chamber sample absorbs the emission line. The difference in the energy transmitted in each case, and monitored by a photodetector, is in direct proportion to the concentration of mercury present in the sampling chamber. This value is amplified and presented in the chart recorder (Figure 4).

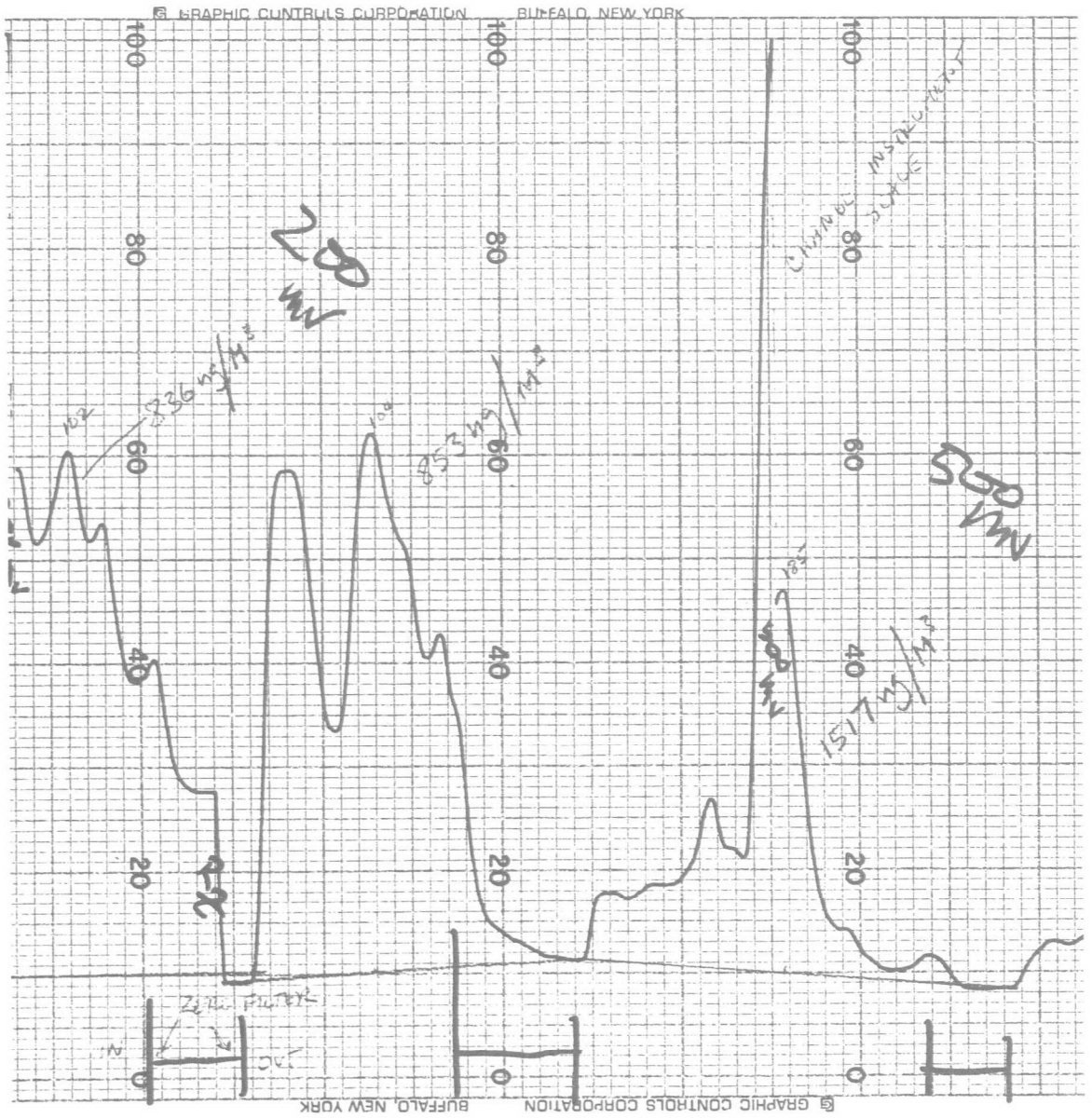


Figure 4
Example of Mercury Record at Industrial Site

The lamp and mercury cell must be carefully held in thermal control. This is accomplished by heaters controlling the environment of the electro-optical end of the spectrometer unit. Their control and all signal processing takes place at an electronic console, separated by cable from the spectrometer. Only system test and monitor features exist; all readings and scale changes are obtained on the separate chart recorder (or on a separate digital voltmeter). In the helicopter installation, the chart display was used for data reduction and analysis, and a DVM was used by the pilot to guide his positioning in the absence of visible plumes.

Calibration

Calibration is accomplished by injecting a known quantity of mercury into the air intake. The amount is obtained from a rubber-capped bottle, placed in a dewer for thermal stability, which contains liquid mercury at a known temperature. A cubic centimeter is drawn through the septum and injected by syringe into the intake hoses. As this mercury cloud passes through the chamber, the chart deflection is noted for calibration (Figure 5). (To give the feeling for the range provided by the vapor pressure of mercury, 1 cc is equivalent to 1380 ng/M^3 at 78° F, but only 180 ng/M^3 at 38° F).

The approximate value for calibrations during these tests was 10 nanograms per cubic meter for each millivolt. The sensitivity of the BAMS varied, over the course of the program, from 6 to 15 ng/M^3 per millivolt. This range, largely thermally dependent, shifted with aging characteristics of the lamp and with temperature of the air being drawn through. Calibrations were carried out at the beginning, during each hour or two, and at the end of each field day or measurement trip. Calibration shifts were never abrupt, and the most adjacent data were used for data reduction. The average value of calibration adjacent to each data set was used for analysis.

An alternate means of calibration was used in the laboratory. Because it agreed with the injection "shot" method described above, the faster procedure was used most frequently. This slower alternative technique also used a syringe of mercury vapor drawn through the septum. The vapor was then slowly "leaked" into the intake hose at a rate definitely slower than the system flow rate. An offset on the record, representing the calibration, would last during the input period. One-half cubic centimeter of vapor was injected in 20 seconds using a motorized syringe (to produce a constant stream of vapor); the system flow rate was measured at one cubic meter per 200 seconds. Therefore, the offset represents one-tenth of the quantity of mercury present in the syringe (which is

determined by the temperature of the mercury source vessel). The palladium-chloride filter was used to determine a zero presence of mercury. By switching the air through this chamber, then back through the non-absorbing chamber, any minor mercury present in the ambient air is measured.

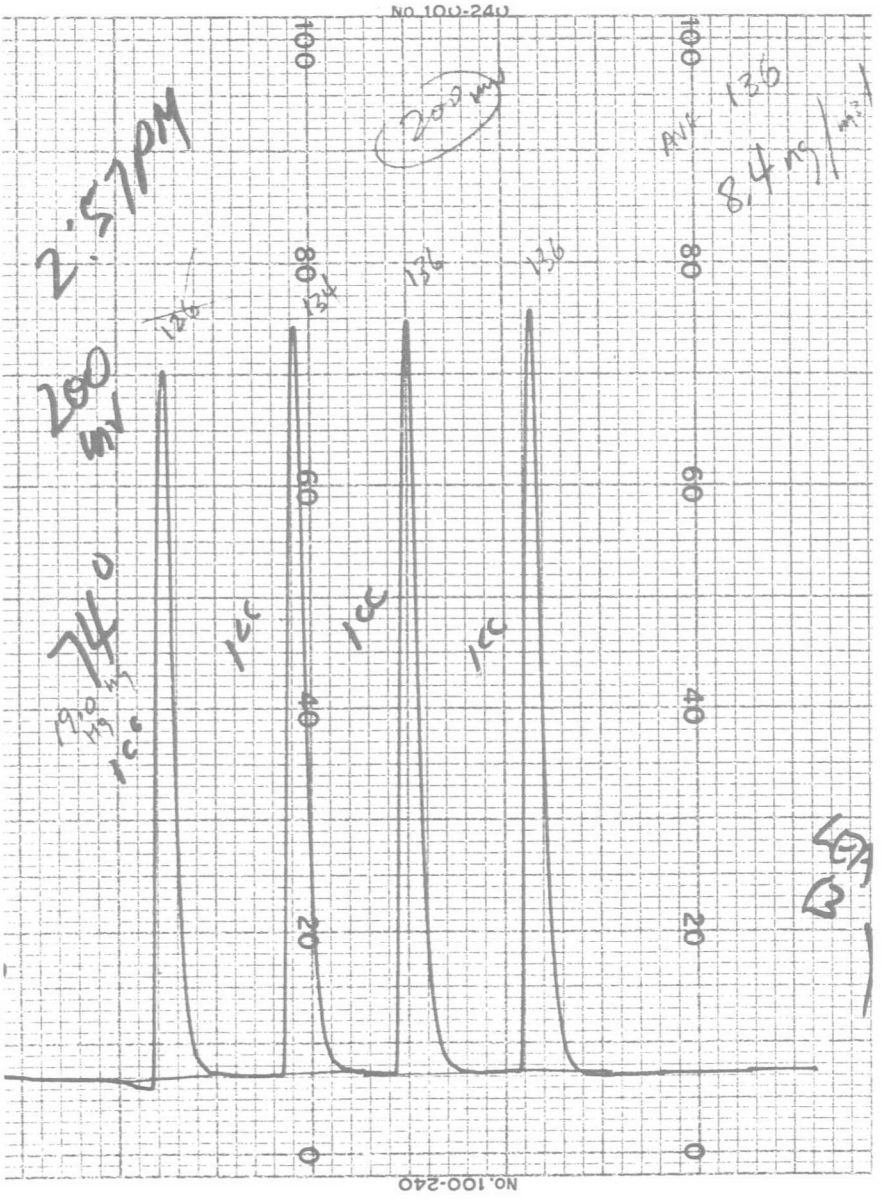


Figure 5
Typical Calibration Responses
(8.4 ng/M^3 = 1 millivolt)

System noise is reflected in the chart record as the amplitude of the trace under essentially clean air conditions. Under these conditions no deflection is noted in the record when the air is passed through the zero filter compared to when it goes directly into the spectrometer. Resolutions on the order of 2 to 5 ng/M^3 were possible under a wide range of environmental conditions.

Interferences

Some substances with absorption spectra in the ultraviolet region increase system noise due to the inefficiency of optical filters and the presence of additional emission lines in the lamp discharge. A judicious selection of thermal range allows the operator to adjust the system to minimize potential interferences. This is possible because the character and amplitude of the lamp's emission spectra is temperature dependent (9). For example, at optimum setting, sulfur dioxide absorption interference was measured to be less than 0.02 millivolt for each part per million of SO_2. This is the equivalent of about 0.2 ng/M^3 of mercury; it could still be distinguished from mercury signals by use of the zero filter (which absorbed the mercury).

During the course of the measurement program, sulfur dioxide was the principle source of concern for interference. In the vicinity of some sewage treatment plants, however, other gases also were detected as interference, as were the direct measurement of gasoline fumes or auto exhaust. Careful selection of appropriate thermal balance allowed a different setting of the oven temperature (from SO_2) to reduce this hydrocarbon interference to minor significance. The adjustment is somewhat time consuming; therefore, on some occasions the data were not used because of interferences. This happened, for instance, when the interference adjustment was optimized for auto fumes and a cloud of sulfur dioxide was encountered.

SECTION VII

LABORATORY EXPERIMENTS

Decomposition of Combined Mercury

Mercury is present in other than free atomic state, and mercury pollution is particularly present in organic combinations, such as methyl mercury (CH_3Hg^+) and dimethyl mercury [$(CH_3)_2Hg$]. These compounds do not report molecular absorption in the 2537-angstrom region. Tests to determine the practicality of decomposing these compounds by heat (pyrolysis) or light radiation were in progress at the Barringer Research laboratory in Toronto, Ontario. EMI participated in these experiments to assess the feasibility of preconditioning the atmospheric sample to allow measurement of total mercury. The BAMS would, thus, measure any atomic mercury present initially plus any amounts converted.

Organic mercury compounds reportedly have very much higher vapor pressures (10). This characteristic, if detection was convenient, could provide a large quantity of traceable material directly related to the most toxic forms of mercury pollution.

Laboratory tests were successful, but no field measurements were made within the limited scope of this grant.

Solar Radiation

A sample of dimethyl mercury was placed in a quartz cylinder (about 2 inches by 4 inches long) and exposed to direct sunlight for periods up to two hours. No detectable quantity of mercury was measured in portions drawn off this enclosure. (Daylight was a winter sun around noon in Toronto).

A 500-watt ultraviolet lamp was directed on a similar sample of dimethyl mercury. Mercury was detected within one minute. (The amounts were not calibrated with care because the mere existence of the atomic form was sought). In two minutes the quantity had tripled. In 2.5 minutes, twenty-five percent more atomic mercury was present, showing a linear response with time. The strong irradiation did decompose the compound, but the time required appeared to prohibit this approach for rapid mobile surveys.

Another approach was then considered, the use of direct heat.

Pyrolysis

Experiments to decompose organic mercury compounds by heat were in progress at the Barringer laboratory. The initial apparatus (Figure 6) was not acceptable because of its requirement for large power consumption. EMI cooperated in the building of a small apparatus, a prototype mobile pyrolyser, used successfully to convert several combined mercury compounds.

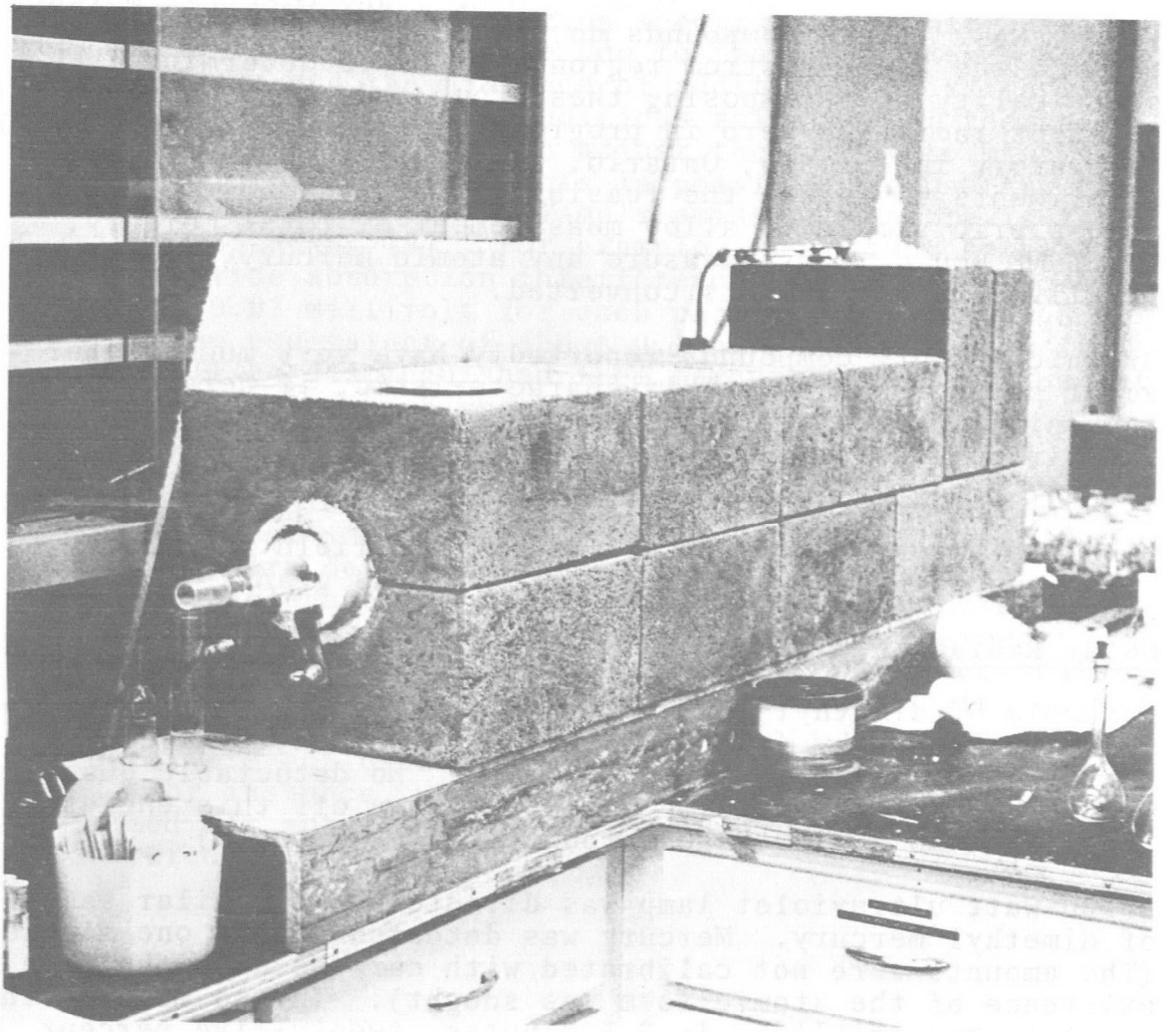


Figure 6
Initial Pyrolyser Apparatus

The apparatus (Figure 7) consists of a vitreous cylinder, about four feet long, wrapped in insulation. Nichrome wire was coiled and wound within, and ceramic beads filled the void. A thermalcouple placed at one end monitored the internal temperature. A variac controlled the current through

the wire. This assembledge was used to draw vapor through and directly into the spectrometer. A series of empirical tests were conducted using this array.

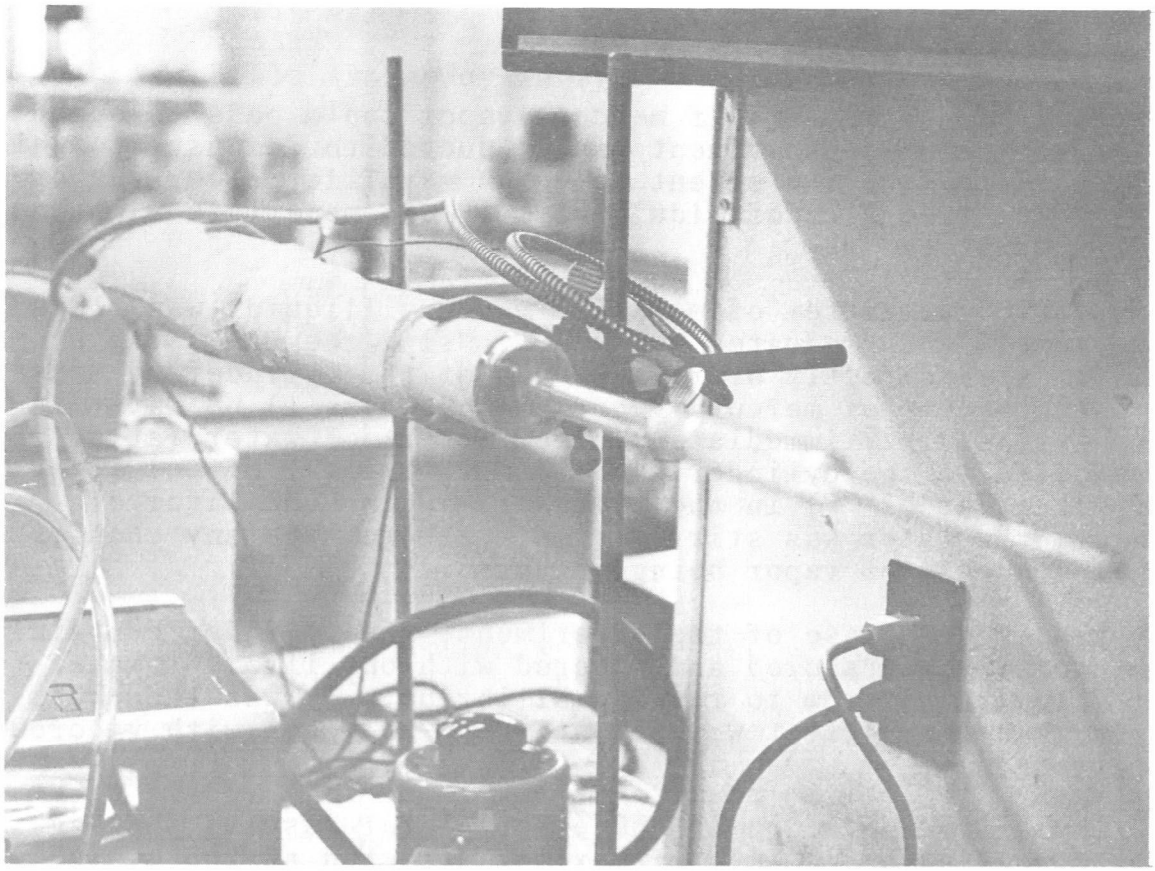


Figure 7
Experimental Moveable Laboratory Pyrolyser

The intent was to assess if decomposition occurred, not to set forth the boundary conditions of the phenomena. It was felt that much more care would be needed to do the latter. Temperatures ranging to 1000°C, various flow rates, and selected mercuric compounds were used.

Syringe quantities of 1 cc were injected into the pyrolyser at increasing temperature plateaus. Below a few hundred degrees, only modest amounts of elemental mercury were observed. At a point, the breakdown became obvious and noticeably greater amounts of mercury were observed. Increases in the quantity of mercury observed were on the order of 10 to 1 for methyl mercury and 15 to 1 for mercurous cloride.

Dimethyl mercury produced dramatic results. One twentieth of the sample (0.05 cc) of the other vapors produced off-scale results. Large amounts of atomic mercury were obviously present.

There is no question that these evaluation experiments deserve more thorough analysis. They appear to demonstrate a convincing means of monitoring "total" mercury.

Mercury Under Water

The question asked was if mercury vapor could pass through water. A simple experiment was conducted to demonstrate this and to determine the extent to which metallic mercury vapor emanating from 1 cc of liquid mercury can penetrate a column of water at 62° F.

One cubic centimeter of metallic mercury (liquid) was placed in a one liter graduated cylinder. Using the BAMS, the probe was located directly over the mouth of the cylinder to measure the amount of mercury vapor present with 1) no water in the cylinder, 2) immediately after 500 ml of water (at 62° F) was added to the cylinder, and 3) with a total of one liter of water (at 62° F) in the cylinder. Using one liter of water, the water was stirred vigorously to note any changes in the amount of vapor being measured.

In the second phase of the experiment, the cylinder containing the mercury was stored and covered with one liter of water to allow the system to reach equilibrium. It was then measured as before (first without stirring and then with vigorous stirring).

A tabular presentation of the experimental results showing the condition and amount of mercury detected at the cylinder mouth follows (see also Figure 8):

No Water in Cylinder

7,780 ng/M^3
6,500

500 ml Water over Mercury

1,430 ng/M^3
2,275
3,250
2,275
1,755
1,983

One liter Water over Mercury

65 ng/M^3
65
65

One liter Water over Mercury; Fully Equilibrated

759 ng/M^3
635
8,832 (shake cylinder)

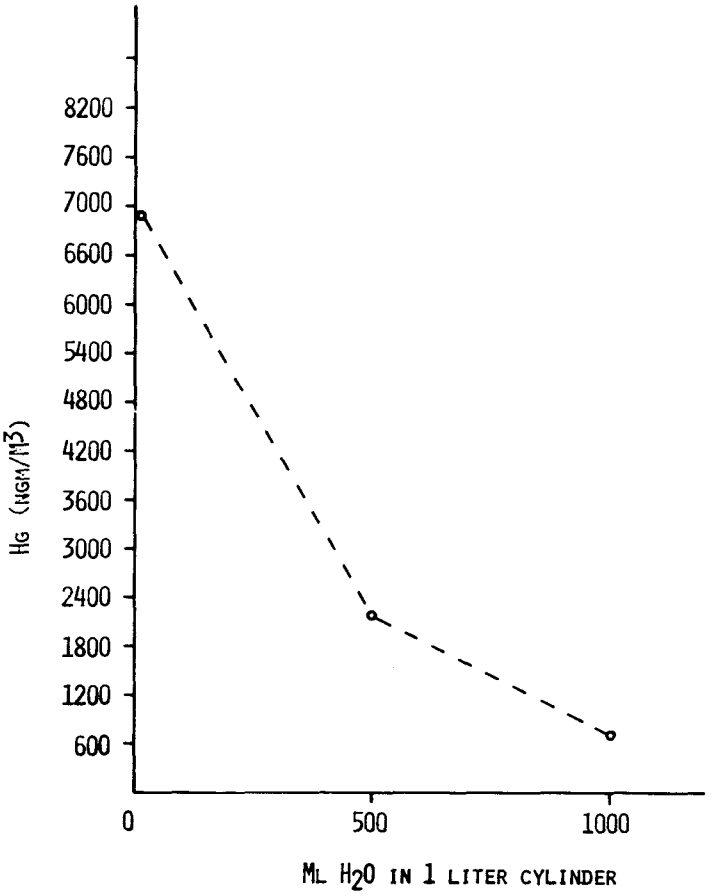


Figure 8
Mercury Vapor Dissemination Through Water

Metallic mercury vapor emanating from one cubic centimeter mercury passes through 500 ml of water rather readily at room temperature. Stirring increases the amount of vapor emanating from the water significantly.

Covered by one liter of water, a longer period of time is required before significant levels of mercury are given off. However, once equilibrium is reached, fairly high levels of mercury are released.

Meteorological conditions would greatly effect this phenomena in the nature state. Wind would blow the vapor, surely, but the churning water of a stream or wave action would also carry the vapor down stream or to shore.

SECTION VIII

THE FIELD PROGRAM

Specific measurement techniques were established to achieve the objectives of this program. The principal method of measurement was with the BAMS installed in a mobile laboratory, a Volkswagon microbus. Data were gathered both in "traversing" mode and in "stationary" mode. To track down suspected mercury polluted waters, the instrument was transferred to a boat. To study the mercury emanations from specific industrial sources, the instrument was installed in a helicopter. Each of these modes required special operating power and different methods of air in-take and measurement.

Measurements In Motion

For ground-level measurements, the instrument was installed either in a small car (Figure 9) or in the mobile laboratory.

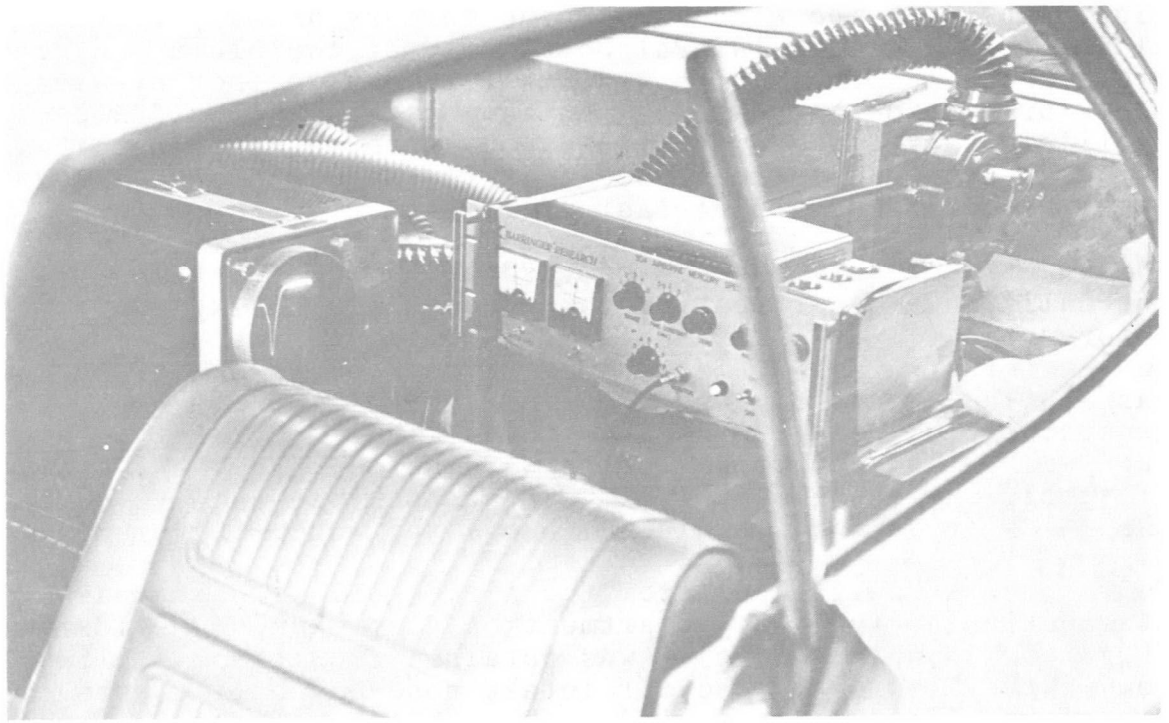


Figure 9
Vehicle Installation of BAMS

Power was supplied by a 60-cycle, 110-volt gasoline generator. The air intake was extended through a window and forward of the vehicle. The problem of a Venturi effect at the sampling

intake. This was effective at speeds below 50 miles per hour. Hence, while traversing, a speed of 30 miles per hour or less was generally used to provide a margin of reliability.

Because of the sensitivity of the instrumentation to temperature variations, the oven and the electronic console were both packed in insulating material. This effectively controlled sudden changes in temperature due to direct sunlight or erratic breezes blowing in through the windows. Both oven and filter were mounted on independent spring suspensions. This protected them from vibrations of the vehicle and reduced the associated noise in the data.

In reconnaissance, mercury was measured while the instrument was driven along selected streets and highways. Significant variations in mercury level were immediately apparent if they were encountered. By marking locations at frequent intervals on the chart records, it was possible to make maps showing the location of mercury vapor anomalies as they occurred.

Once a mercury anomaly was detected, the direction of wind was noted. The mercury was traced upwind to its source whenever possible. This was carried out by traversing at right angles to the wind across the mercury anomaly very slowly to define the lateral boundaries of the plume. As each profile was completed, the traverse line was offset by a block or two in the upwind direction, and another traverse profile was produced. Eventually, a traverse would detect no mercury; it could be concluded that the source of the mercury vapor was downwind of the last profile.

The waterborne surveys were carried out in cooperation with the California Department of Water Resources, using their 30' motor cruiser, the Blue Angel. The equipment was installed in the forward cabin (Figure 10). Since no appropriate power was available on the vessel, the 60-cycle, 110-volt gasoline generator was installed at the stern. The instrument intake tube was extended through the forward hatch. In the sampling of specific effluent out-falls a boat hook was used to extend the intake hose to a few inches above the water (Figure 11).

To measure mercury vapor from the air, the instrument was installed in the luggage compartment of a Jet Ranger Helicopter (Figures 12 and 13). Power was obtained from the 24-volt system in the aircraft. The air intake hose and baffle were extended outside through a window (Figure 14). The signal was recorded on the stripchart recorder and displayed on a digital voltmeter mounted adjacent to the pilot's instruments. This digital display permitted the helicopter pilot to monitor the mercury level in the air and, hence, to monitor the passage of the aircraft through an otherwise invisible plume. Traverses were run back and forth through the plume to detect and map the downwind anomalous mercury vapor.

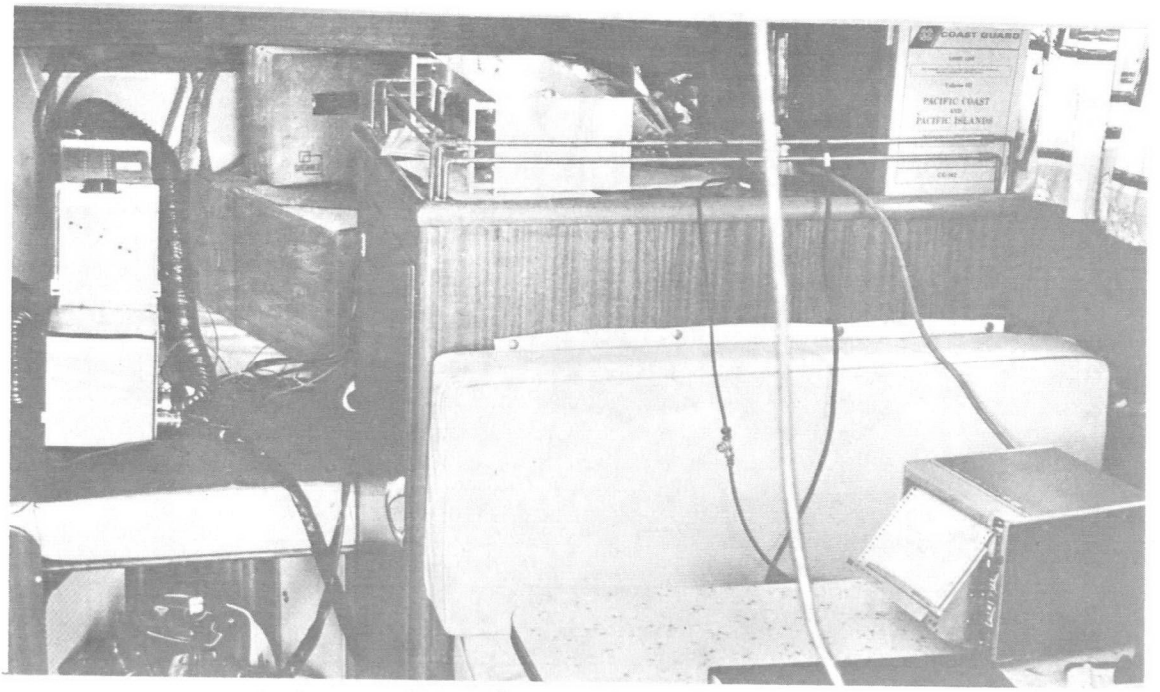


Fig. 10. BAMS on Boat

Fig. 11. Near Surface Sampling Over Water

Fig. 12. Helicopter Cockpit Installation of BAMS Readout

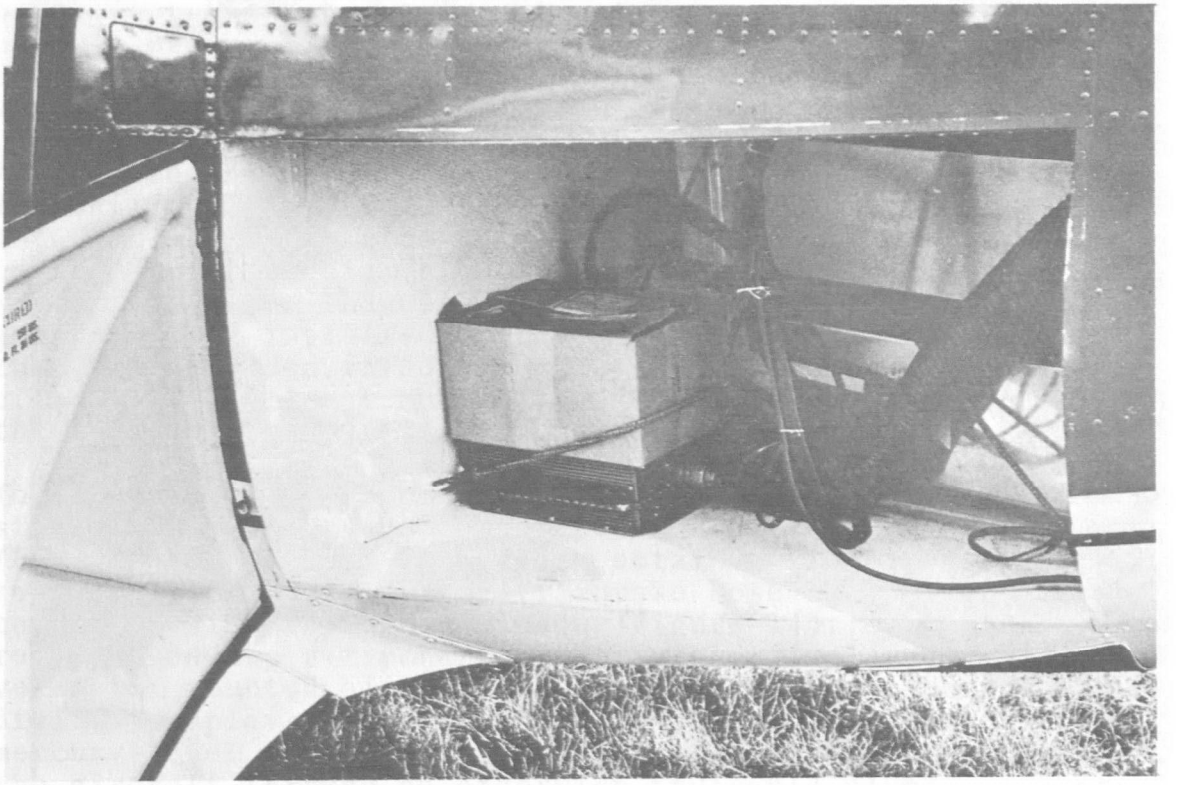


Fig. 13. Spectrometer, Bivalve Assembly and Power Converter Stowed in Helicopter Luggage Compartment

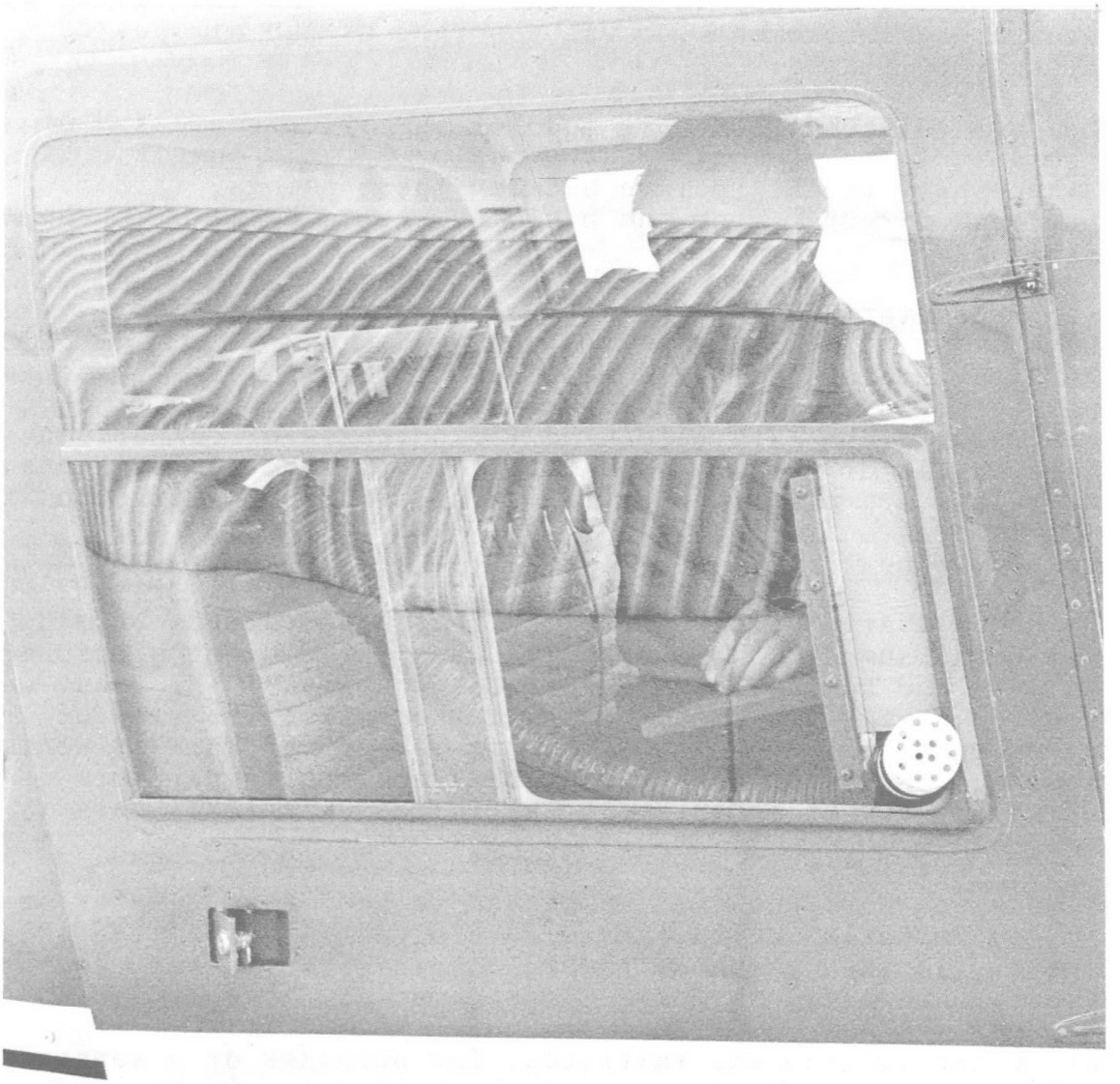


Figure 14
Sample Air Intake with Baffle

Stationary Measurements

To detect levels of mercury vapor between zero and 50 to 100 ng/M^3, the vehicle was stopped to measure for a period of a few minutes. This procedure was adopted for both highway and boat traverses, whenever such small levels were being sought. Hovering with the helicopter was used to monitor plumes emanating directly from stacks.

To obtain these small measurements, the air was sequentially passed through the palladium-chloride filter and filter by-pass. Thus, a series of offsets was detected which indicated the amount of mercury which either went around the filter and through the instrument or was absorbed as the air passed through the filter.

The data obtained from this mode of operation consisted of a series of measurements made at selected grid points. It is necessary to interpolate between these points, rather than read directly from the profile, as is the case in the moving traverses.

Data Presentation

The data obtained in these measurement programs are presented in tabular form listing the maximum signal detected at each site. Bar graphs are also used for purposes of comparison. Where levels of mercury were detected at selected locations, the values are plotted on a map to show their relative position.

Areas of Study

The demonstration grant requested that measurements be made during the summer months of 1970, when the ambient atmosphere was warm and humid, in The Great Lakes Region. The grant was received during the winter months; therefore, the site of measurement was moved to California to get the warmest weather possible. Nevertheless, the highest ambient temperature during any day of measurement was in the 70's (°F); this is still cool.

Areas which were known or suspected to be sites of water or air contamination by mercury were visited (4) (7) (11) (12). However, in the course of the reconnaissance program, previously unreported anomalies were detected.

Before the program was initiated, for purposes of a separate contract, measurements were made by helicopter in the Midwest, around industrial smokestacks and power plants (13). Because of the extreme mobility of the installation it was possible to visit a large number of sites in a short time. The measurements were made directly in the plumes and near stack exits. (The readings are probably higher than would have been detected on the ground due to the high concentration of the effluent close to the stack mouth.)

Areas of natural mercury occurrence in California were visited. At all of these sites traverses were made by driving around on the county roads and continuously recording the mercury levels and location.

In the San Francisco Bay Area, the industries which were known to be manufacturers or users of mercury were visited first and traverses were conducted on roads near the sites. These industries were located in Pittsburg, Millbrae, and San Francisco. Several community sewage treatment plants in the area were also visited. In the course of the reconnaissance program other anomalies were detected in Richmond, Berkeley, and Emeryville. These new areas were not thoroughly studied because this was not the intent of the demonstration.

Waterborne surveys were made during the course of regular investigations carried out by the California Department of Water Resources. In addition, industrial sites in Pittsburg, Selby, Martinez, and Richmond, and sewage outfalls from treatment plants and industries in the San Francisco Bay Area were visited.

SECTION IX

MEASUREMENT RESULTS

During the Course of the program, specific sites at which anomalous mercury vapor could be detected in the air were isolated (Figure 15). Many of these sites were visited more

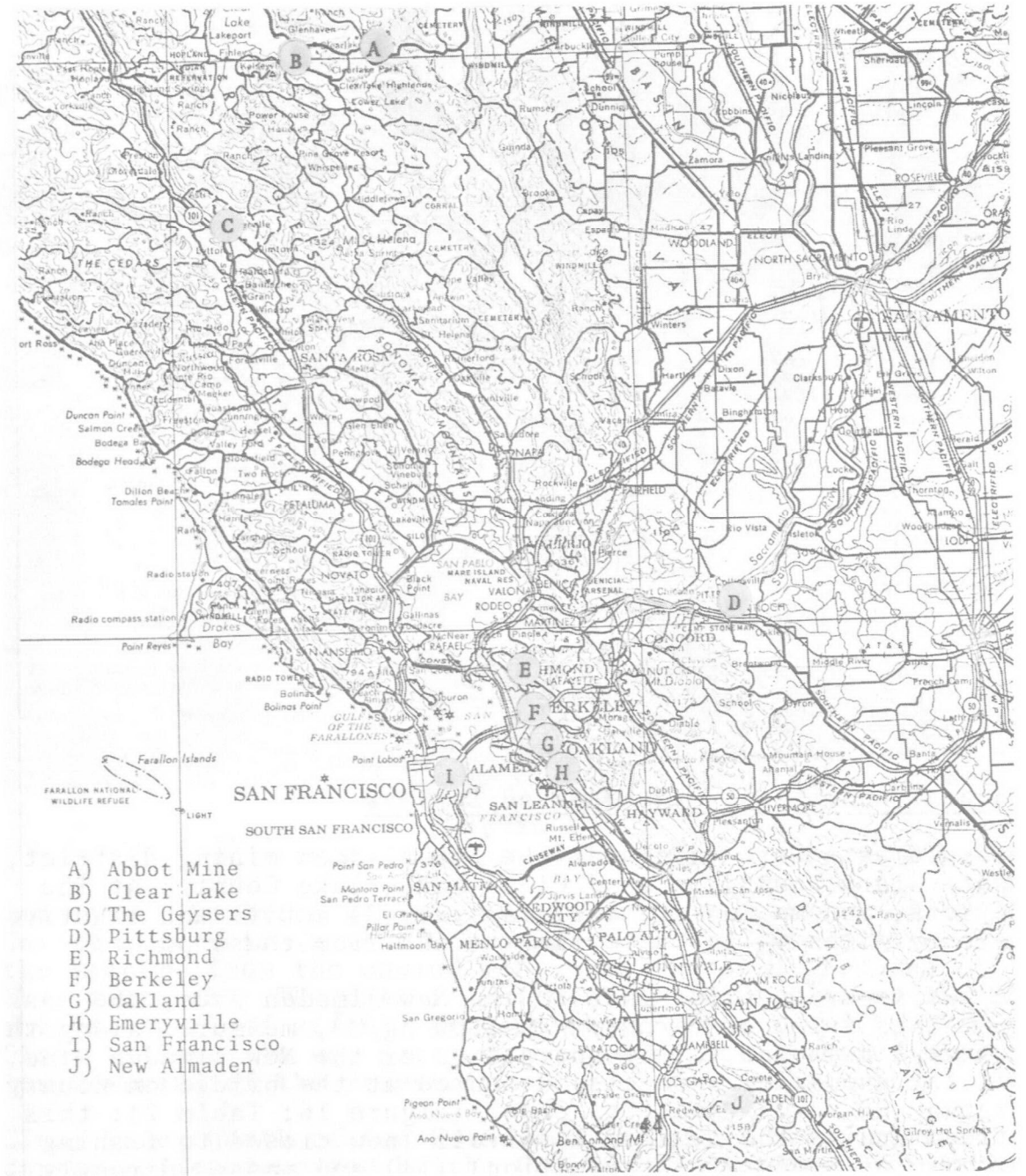


Figure 15
Location Map of California Investigation Sites

than once to confirm the measurements. The anomalies are classified as to origin: natural or man-made. Table 1 lists each site and presents the maximum measurement obtained.

TABLE 1

SUMMARY OF ATMOSPHERIC MERCURY MEASUREMENTS

Site*	Date*	Time	Wind	Mercury Background Level (ng/M^3)	Mercury Peak Value (ng/M^3)	Comments
Natural Sources						
Abbott Mine	12 February	PM	E	0	470	Low Population Density
Clear Lake	12 February	PM	E	0	150	Resort Area, Low Pop. Density
	2 April	PM	W	0	200	Resort Area, Low Pop. Density
The Geysers	15 February	PM	W	200-800	28100	Rural Resort Area
New Almaden	4 January	PM	Neglig.	0	1500	Rural
	24 March	PM	NW	5-15	449	Rural
Cultural Sources						
Berkeley	22 March	AM	W	10	800	Light Industrial-Residential
	24 March	AM	W	--	449	Light Industrial-Residential
	26 March	PM	W	10	154	Light Industrial-Residential
	30 March	PM	W	0	1050	Light Industrial-Residential
Oakland/ Emeryville	30 March	PM	NW	0	196	Light Industrial
	5 April	PM	W	0	688	Light Industrial
	6 April	PM	W	0	110	Light Industrial
Pittsburg	11 February	PM	E	50	770	Industrial Area
	12 February	AM	NW	0	1000	Industrial Area
	25 February	AM	N	0	0	On Boat
	22 March	PM	WNW	5	10	Residential
	1 April	AM-PM	N	0	4141	Industrial and Residential
San Francisco (Quicksilver Products)	18 March	PM	--	0	278	Commercial Area
	19 March	AM	--	0	152	Commercial Area
San Francisco	19 January - 26 Jan.	AM-PM	--	0	100	Ambient Measurements, Financial District
	7 & 8 April	AM-PM	--	0	35	Ambient Measurements, Financial District
Richmond	29 March	AM	NW	0	1400	Residential, Near Primary School
		PM	W	5	2000	Residential, Near Primary School
San Carlos (Boat Survey)	6 April	AM	--	0	21	Light Industrial

*All locations in California in 1971

Natural Anomalies, Ground-Based Surveys

Measurements were made near the New Almaden mining district, Santa Clara County; around Clear Lake, Lake County; at The Geysers, Sonoma County; and near various active and inactive mercury mines while traversing to and from these points.

In two separate trips made to the New Almaden area, the peak anomalous value of mercury was 1500 ng/M^3, measured along the roadways adjacent to the operations of the New Almaden Mine. Similar anomalies were also detected at the bridge on County Highway G8 across Alamitos Creek (Figure 16; Table 2); this stream drains the Almaden Reservoir (now closed to fishing because of mercury contamination) (14) and passes directly through the town of New Almaden. A third peak was detected northeast of the mine area away from all known or suspected

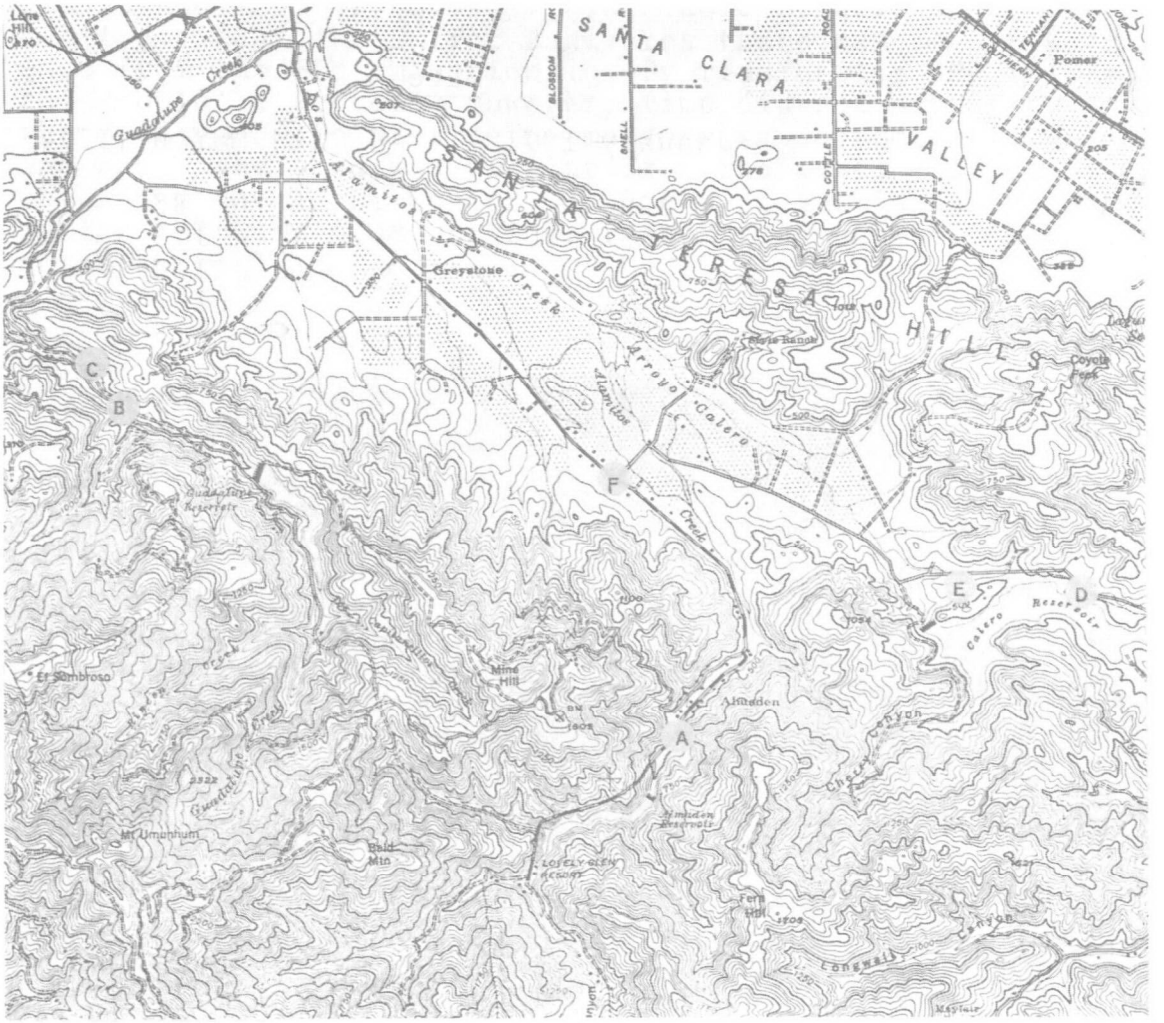


Figure 16
New Almaden, California

deposits. On March 24, a traverse was run downwind of the Calero Reservoir (also now closed to fishing) to determine if the mercury from the upwind mine area remained airborne at this distance. The data illustrate the general trend of the ambient level of mercury between the reservoir and the Santa Clara Valley. It was not possible to detect either a high or low downwind of the reservoir.

Clear Lake, north of San Francisco and the site of mercury contamination reported by the California Department of Water Resources (15), was visited twice. Under the different wind conditions quite different patterns of airborne mercury distribution were detected. On February 12 the wind was from

TABLE 2

NEW ALMADEN, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	Date	
	4 January 1971	24 March 1971
A	828	83
	765	145
		132
		132
		125
B	1500	165
C		257
		383
		317
		449
		139
		139
D		8
		9
		8
		11
		8
		12
		11
		9
		15
		15
		20
		16
		12
		20
E		7
		13
		16
		16
		15
		13
F		13
		13
		15
		11
		12

the northeast and an anomaly was detected at Buckingham Point (Figure 17; Table 3). The maximum signal at Buckingham Point was about 150 ng/M^3. On April 2, the Sulfur Bank and Buckingham Point sites (Figures 17, 18; Table 3) were specifically visited. Near the Sulfur Bank area there was some interference from the SO_2 emanations. (By readjusting the instrument this could be reduced; however, time did not permit). At the Buckingham Point site no mercury was detected on the second day. The wind was blowing from the west; this may indicate that the first mercury detected at Buckingham Point was in fact blowing from the Sulfur Bank area which lies to the northwest.

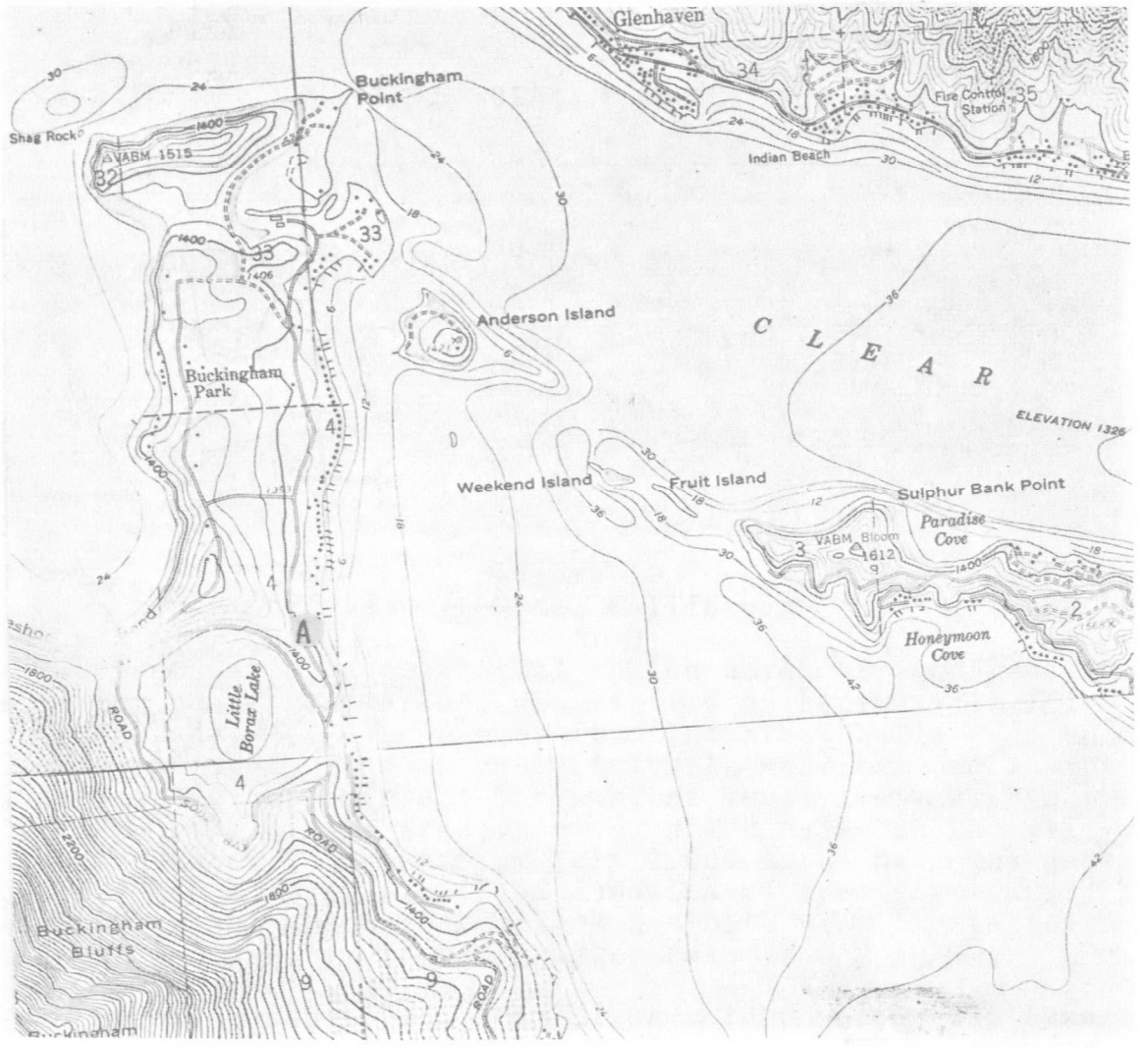


Figure 17
Clear Lake, California; Buckingham Point

TABLE 3

CLEAR LAKE & ABBOTT MINE, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	Date	
	12 February 1971	2 April 1971
A (Figure 17)	150	
B (Figure 18)		63
C (Figure 18)		162
		171
		140
D (Figure 18)		99
		153
E (Figure 18)		171
F (Figure 18)		221
		126
G (Figure 19)	470	

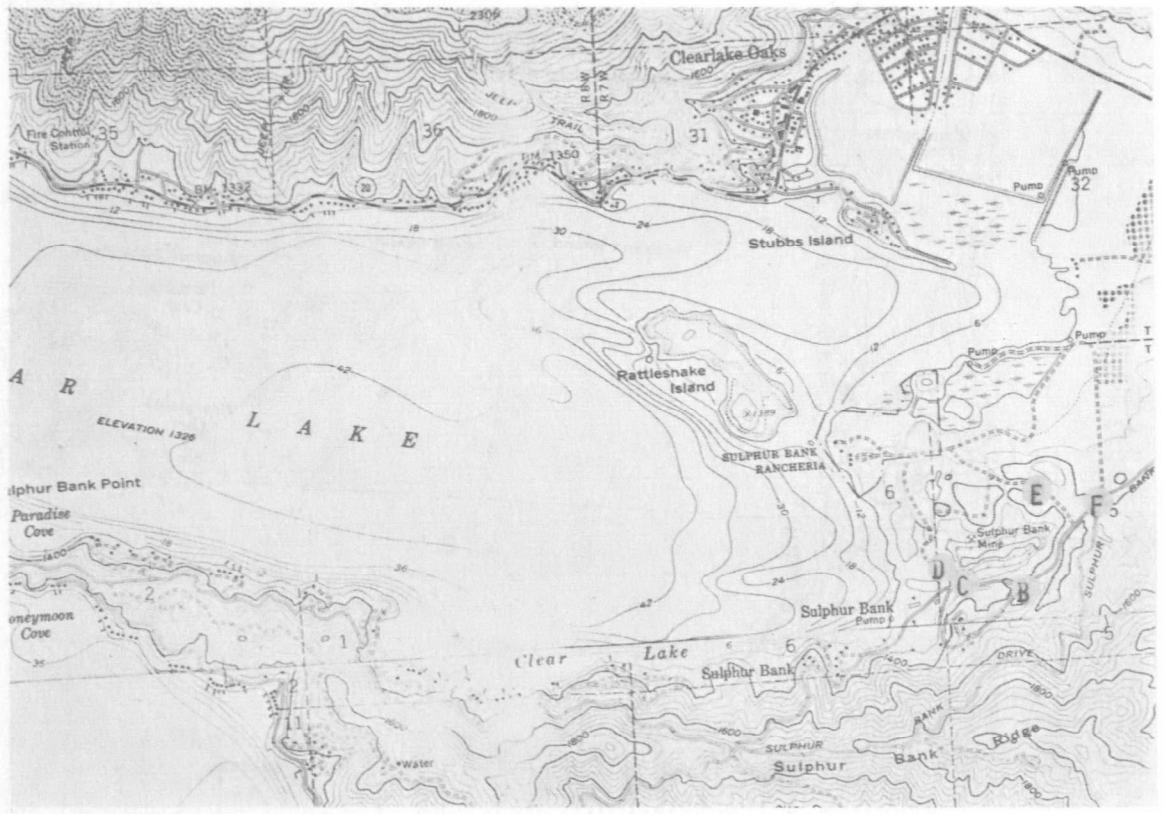


Figure 18
Clear Lake, California; Sulfur Bank Mine

In the course of traversing to Clear Lake, the Abbott Mine was passed on State Highway 20 (Figure 19; Table 3). An anomaly of approximately 470 ng/M^3 was detected even though the mine was across a valley from the road.

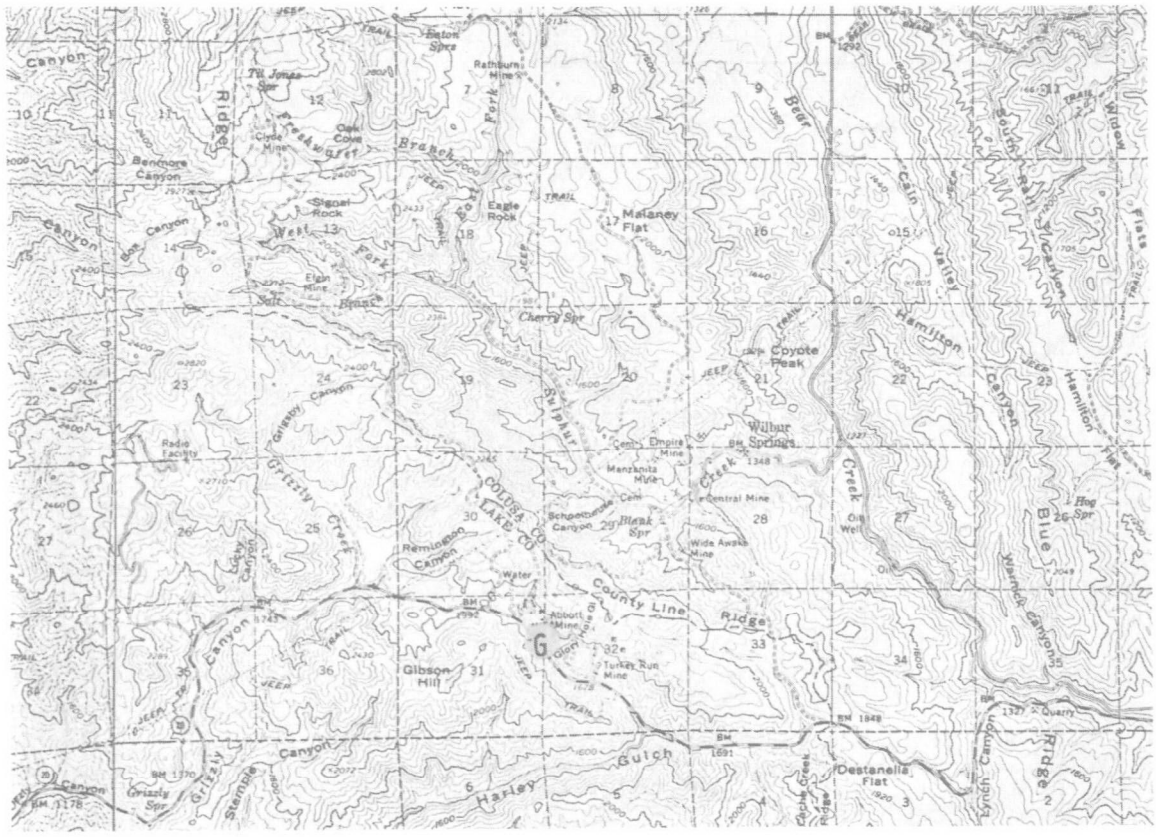


Figure 19
Abbott Mine, California

The Geysers area, a geothermal region north of San Francisco used for power generation, was visited on February 15 (Figure 20; Table 4). The plumes from the Steam Wells were specifically observed, as were ambient levels near the health resort and local mercury mines. The ambient levels ranged from 5 to 10 ng/M^3 west of the area, to around 400 ng/M^3 in the valley near the resort, to approximately 2,000 ng/M^3 near the geothermal steam power plant and downwind of specific vents. The maximum signal was detected from a single vent on the north side of the valley; it was greater than 28,000 ng/M^3.

Mercury was measured for several days in downtown San Francisco in January and February 1971. Daytime levels on the order of 35 ng/M^3 were common; peaks reaching 80 ng/M^3 were frequent. Nighttime levels ranged from zero to 10 to 15 ng/M^3. These

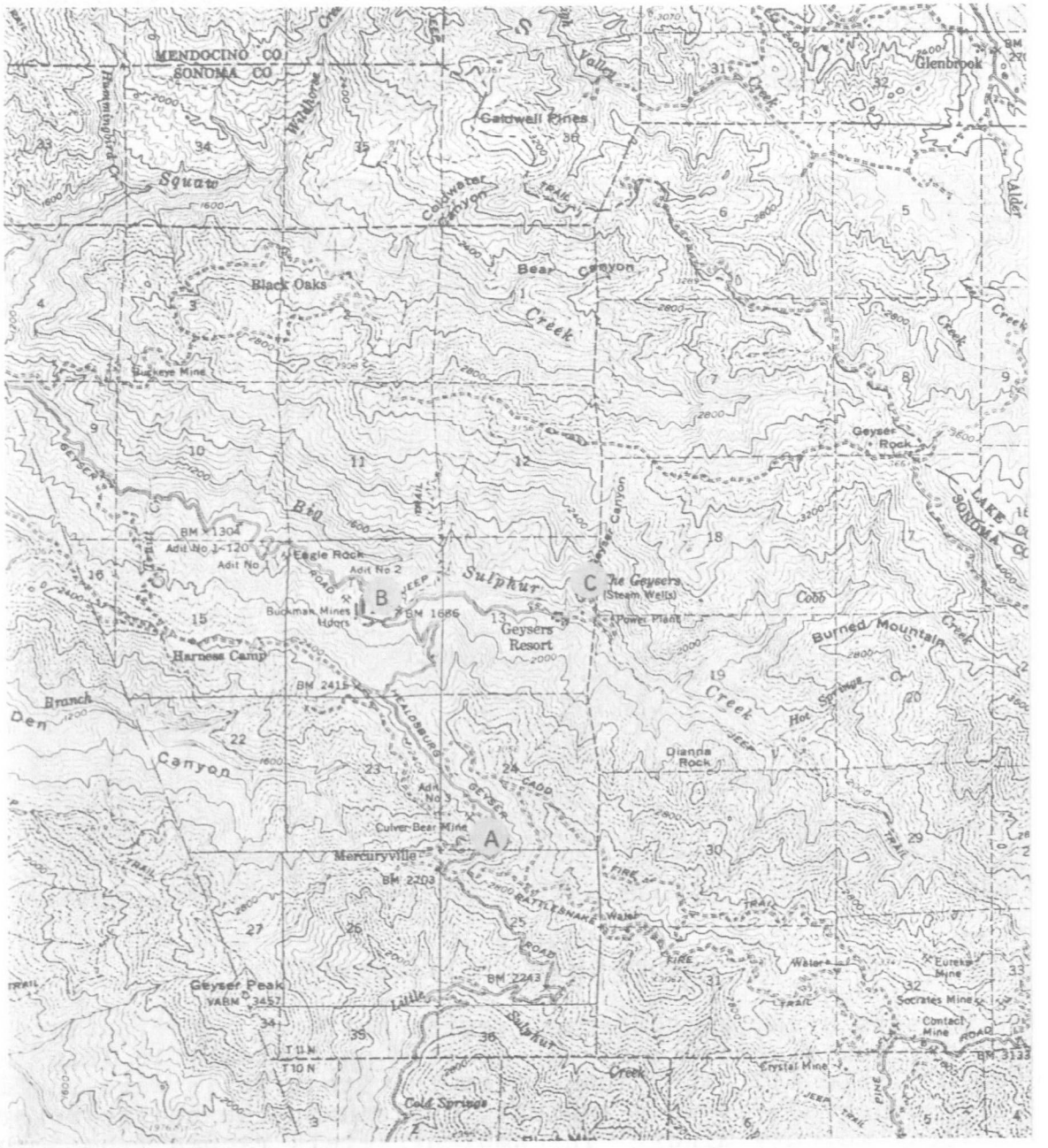


Figure 20
The Geysers, California

data exceed similar measurements, made by Williston (6) in the suburbs of San Francisco, by a factor of about three. The site of measurement was in the traffic congested financial district one block from the well known intersection of California and Montgomery Streets. (Certainly this mercury is the result of cultural development; it is mentioned here for comparison).

TABLE 4

THE GEYSERS, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	15 February 1971
A	51
B	108
	322
C	888
	874
	438
	430
	508
	572
	620
	918
	3510
	3600
	6200
	11080
	16800
	28100
	2350
	1106

While traversing over rural highways to or from target areas, mercury anomalies were detected. As an example, a single anomaly of 50 ng/M^3 was detected on State Highway 24 near Lafayette, Contra Costa County. A later traverse was run on the north side of the highway around the Briones and San Pablo Reservoirs (where the USGS reported mercury in the water) (11) but no anomalies were detected. Thus, the Highway 24 result was not explained. Other peaks detected enroute similarly went unresolved.

Man-Made (Cultural) Anomalies, Ground-Based Surveys

Three separate trips were made to Pittsburg, Contra Costa County (Figure 21; Table 5). A noticeable mercury signal was detected downwind of a large chemical plant. The signal varied in amplitude and in direction, dependent upon the wind, and a maximum value of 4,100 ng/M^3 was measured on April 1. The plume appeared to be directly downwind of the settling basin which this company uses for its effluent. A local representative of the company indicated that a chlor-alkali plant was in operation directly upwind of the site of measurement until April 1970. Unfortunately, due to the company's reluctance to permit a traverse northward to the river, it was not possible to delimit the boundaries of the plume.

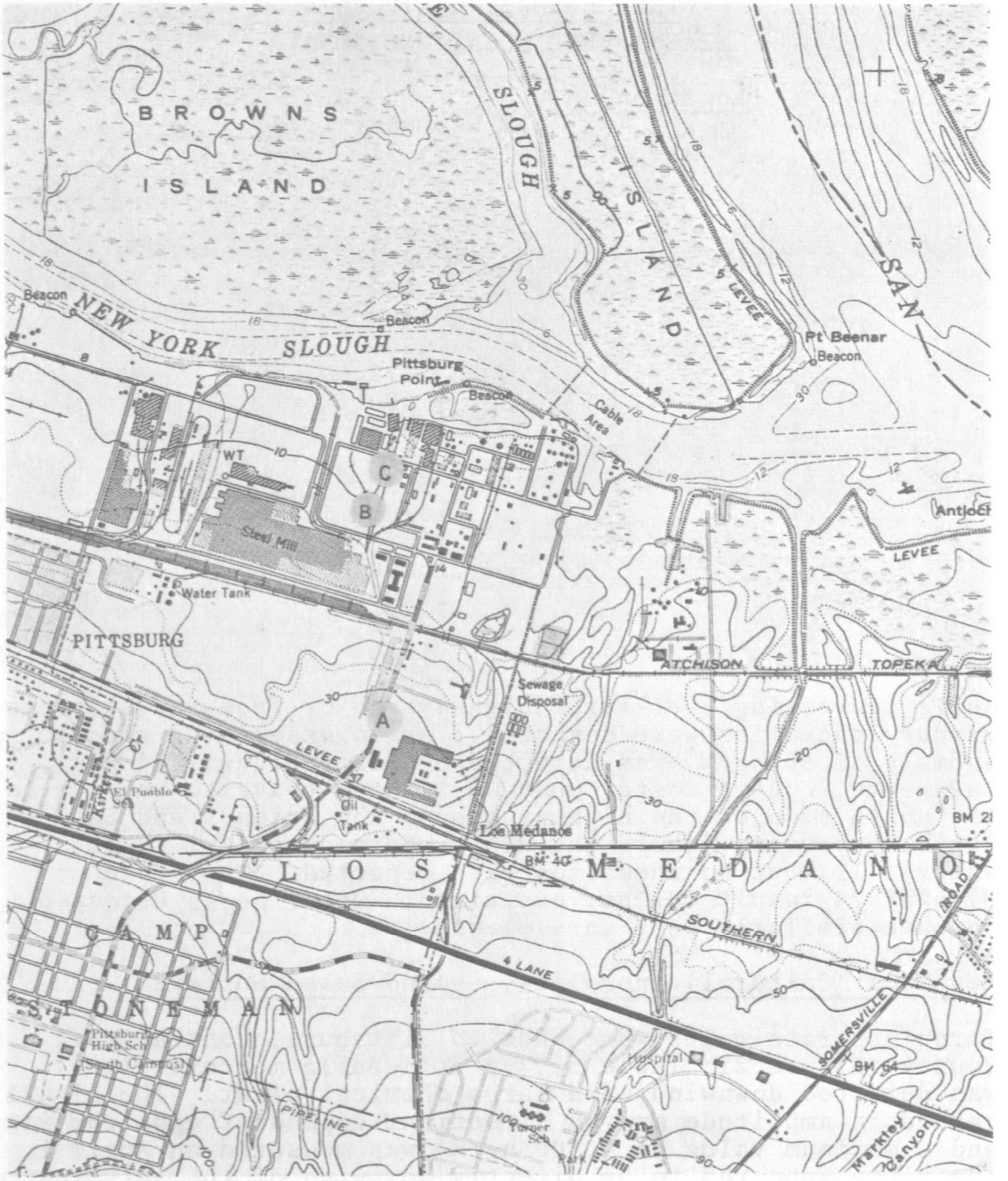


Figure 21
Pittsburg, California

A boat traverse was made to the river side of this plant along New York Slough on February 25. On this day the wind was from the northeast. No mercury anomalies were detected.

TABLE 5

PITTSBURG, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	Date		
	11 February 1971	12 February 1971	1 April 1971
A			361
			410
			754
			1968
			631
B	320	274	238
	308	223	287
	460		426
			492
			836
			853
			1517
C	340	850	2706
	606	394	1066
	390	637	2419
	418	109	1927
		830	1968
		464	1681
		1000	295
			1460
			1804
			2911
			4141
			2378

A reconnaissance through the City of Richmond, Contra Costa County, revealed a large plume emanating from the North Richmond area (Figure 22; Table 6). The maximum signal in this plume was detected in the playground of the Peres Public School, just downwind of a pesticide and defoliant plant. It was possible to trace this plume for a distance of about 1.5 miles across the central Richmond area. A change in the wind affected this distribution pattern so that by late afternoon it was blowing directly over the residential are of North Richmond.

Another noticeable mercury anomaly was detected downwind of a large bay-fill site near the Berkeley Yacht Harbor, Contra

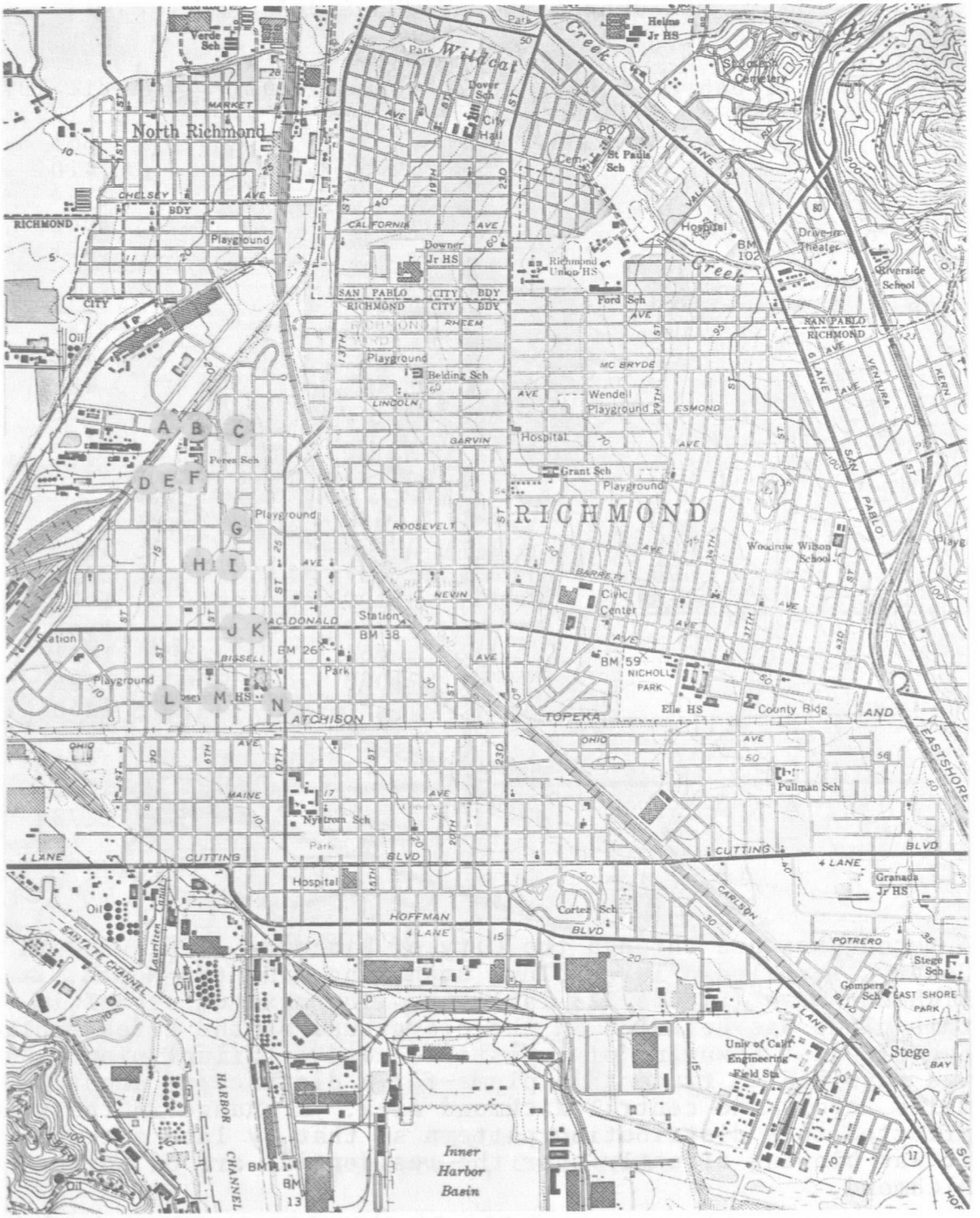


Figure 22
Richmond, California

TABLE 6

RICHMOND, CALIFORNIA

MEASUREMENT LOCATIONS & DATA

Location	Date 29 March 1971
A	1913
	1313
B	495
C	413
	360
D	1500
E	810
F	128
	150
	630
	1050
	1050
	775
G	48
	33
H	45
	30
I	90
	66
J	128
K	63
L	38
M	60
N	35

Costa County (Figure 23, Table 7). The maximum signal detected downwind, just west of Interstate 80, was 1,000 ng/M^3. The plume was also detected on I-80, although the high speed of traverse required for safety made it difficult to assess

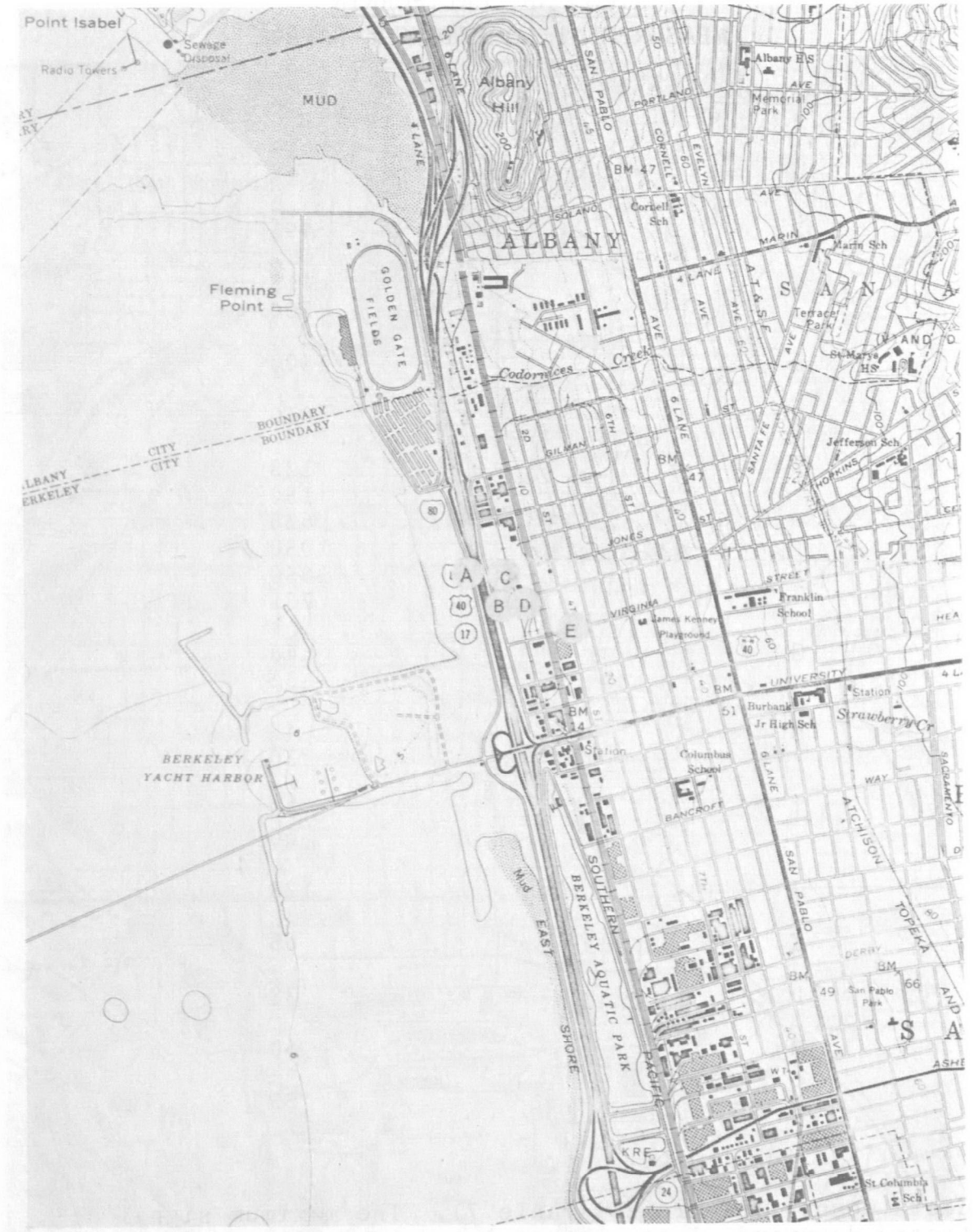


Figure 23
Berkeley, California

TABLE 7

BERKELEY, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	Date			
	22 March 1971	24 March 1971	26 March 1971	30 March 1971
A	800	449	154	917
	492			1050
				945
				875
				1050
				875
B				210
				196
				175
				175
				203
C				140
D				35
				28
				56
				98
				91
E				28
				28

the width of the plume. Immediately downwind of the freeway to the east, levels dropped off sharply. No more than 50 to 100 nanograms per cubic meter were detected on the local streets of the residential area.

A separate area of variable mercury concentration was detected in Emeryville, Alameda County (Figure 24; Table 8). Visits on three occasions over one week revealed anomalies. The maximum value was over 600 nanograms per cubic meter. Local industries include a paint plant, a chemical plant, and a scrap iron recovery facility. The specific source was not identified, however.

Visits were made to many of the local sewage treatment plants around the San Francisco Bay Area. Downwind of the East Bay Municipal District Sewage Treatment Plant flare (see Figure 24, sewage disposal), values as high as 110 ng/M^3 were detected; immediately upwind of the flare the ambient level was 0. No

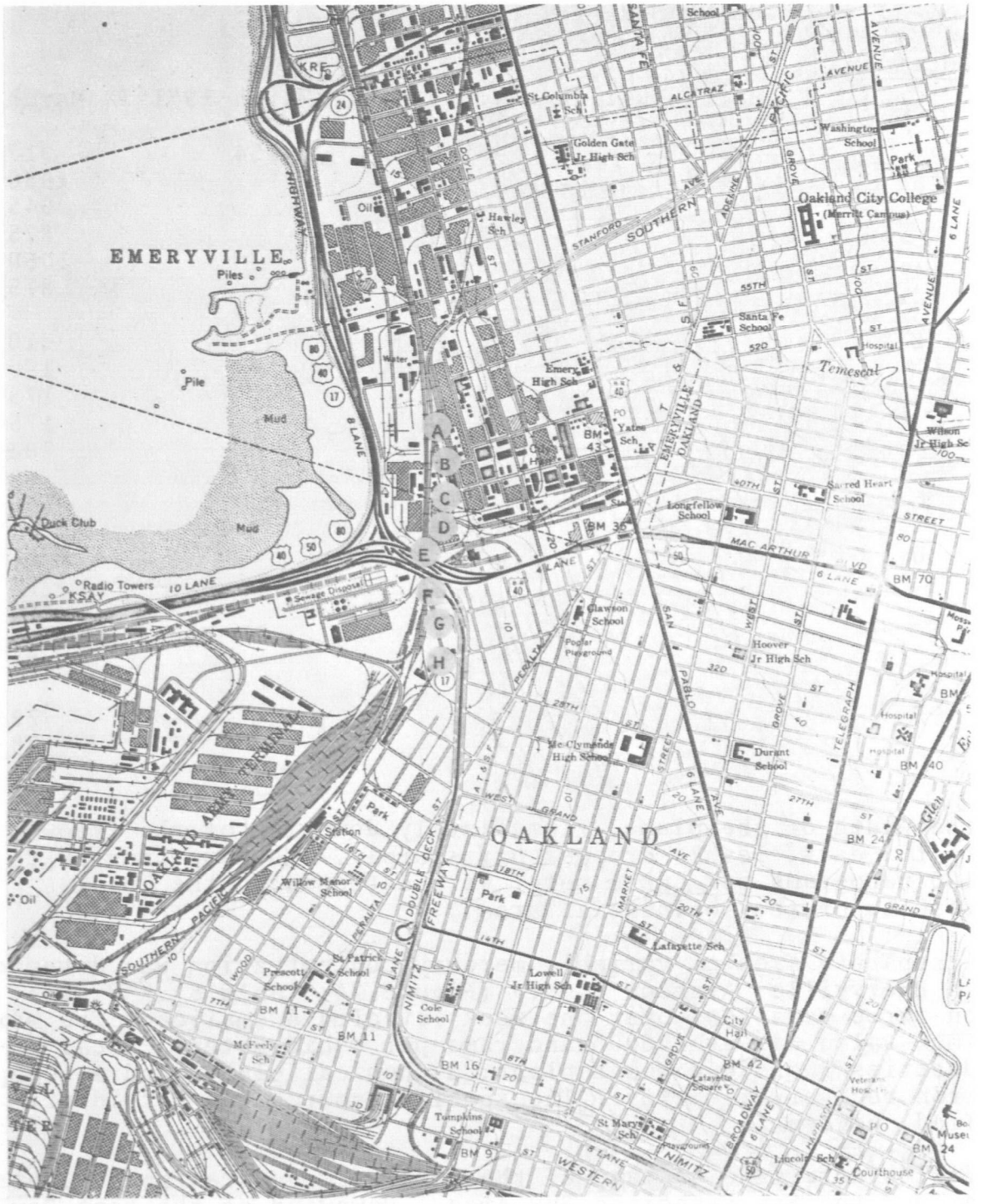


Figure 24
Oakland/Emeryville, California

TABLE 8

OAKLAND-EMERYVILLE, CALIFORNIA
MEASUREMENT LOCATIONS & DATA

Location	Date		
	30 March 1971	5 April 1971	6 April 1971
A			35
			42
			24
			24
			30
			26
B	63	688	45
	119		23
	112		70
	175		56
	38		18
	31		
	14		
C	196		12
	147		
D	28		
E	14		
	28		
	35		
	42		
	39		
	25		
F			12
			15
			9
			110
G			21
			11
			14
			12
H	10		

mercury vapor was detected in the air immediately over the effluent water leaving the filtration and treatment plant, even though measurements were made within two inches of the surface of the water. The plume from the plant incinerator did contain minor amounts of mercury.

No metallic vapor was detected downwind of other sewage treatment plants in the area. However, the outfall from a plant in San Carlos, San Mateo County, contained some mercury as reported under Boat Surveys, below.

The area immediately around the Quicksilver Products Company (7) of San Francisco was surveyed on a number of occasions because it was the only reported source of mercury in the City. The results were variable. Maximum anomalies on the order of 250 ng/M^3 were detected within one to two hundred feet of the site of the plant itself. Elsewhere, low ambient levels were measured. A single visit was made to the Garrett-Callahan Company (7) in Millbrae, San Mateo County; no metallic mercury was detected in the area.

Helicopter Surveys

As originally conceived, the demonstration grant was to incorporate aircraft usage if anomalies of sufficient size were observed. Fortuitously, a separate project (16) incorporated the use of a Bell Jet Ranger Helicopter to conduct measurements from a variety of combustion plumes. This experience was observed and is reviewed in lieu of carrying out separate flights to measure the ground-level findings reported herein. Operation characteristics were learned, and it was judged unnecessary to repeat flights to demonstrate the procedures.

Some results of the helicopter measurements have been reported (13). Data were gathered from plumes emanating from municipal incinerators, petroleum refineries, chemical production plants and power generation facilities. Figure 25 shows a view from the aircraft during plume measurements.

Peak concentrations of mercury from smokestacks in Missouri and Illinois (13) generally were less than 100 ng/M^3 from power plants, ranged to several hundred ng/M^3 near industrial sites, and reached several thousand ng/M^3 from incinerators. One peak value from an incinerator drove the instrument offscale to exceed 50,000 ng/M^3.

An example of the data obtained by helicopter from an incinerator is provided to illustrate the typical operation (Figure 26). The aircraft flew into the visible plume and hovered. If a signal was measured, it was recorded for a minute or so.

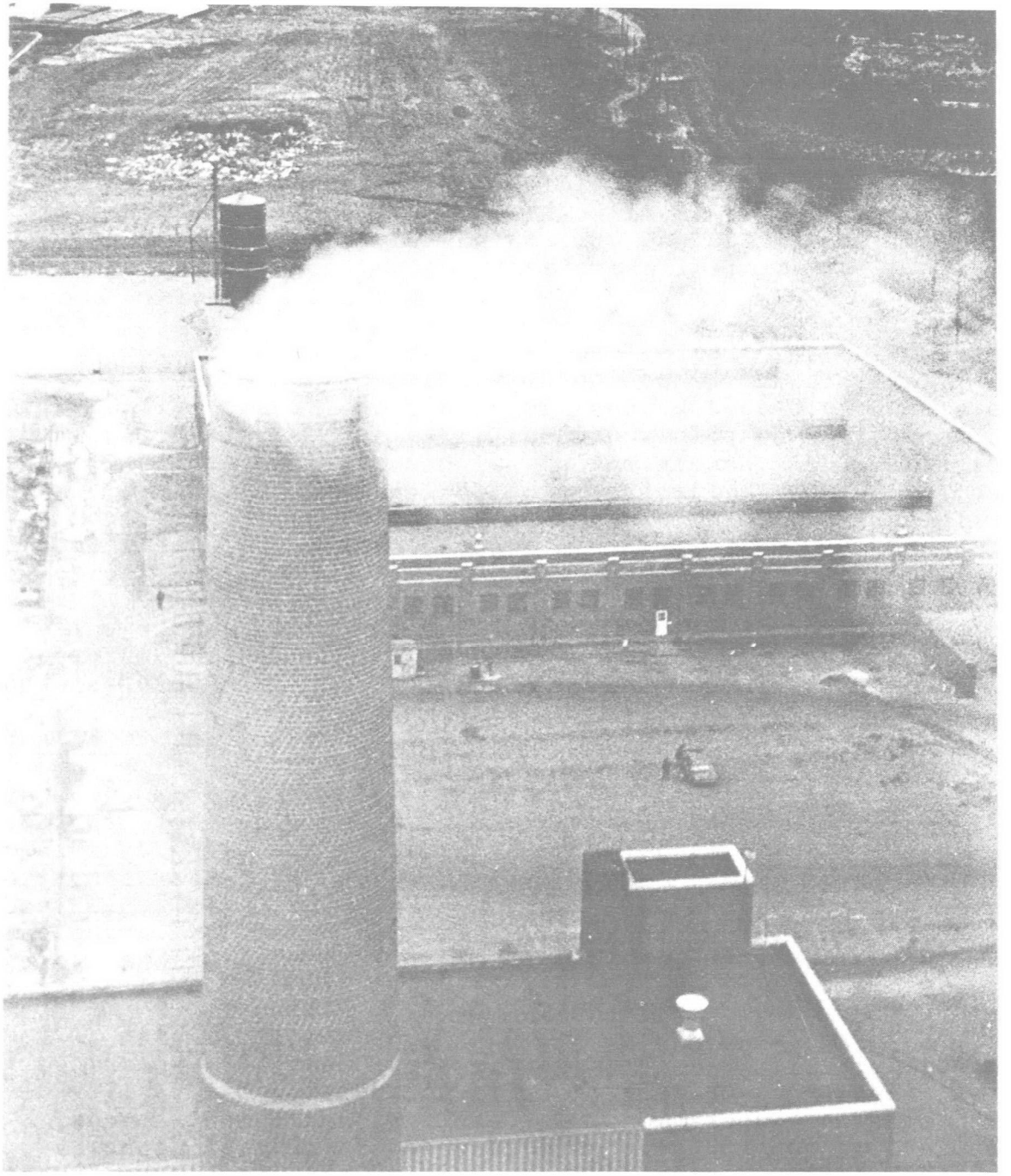


Figure 25
Location During Stack Sampling

(The measurement time was limited by the noxious character of the gas cloud and the ability of the crew to endure this). The helicopter then left the plume, giving the operators fresh

air to breathe, and returned in a moment with the mercury absorbing filter switched in. If no (or a very much reduced) signal was observed, the prior record was considered a valid measurement. Occasionally interference signals were observed, and the data were labelled unsuitable or questionable.

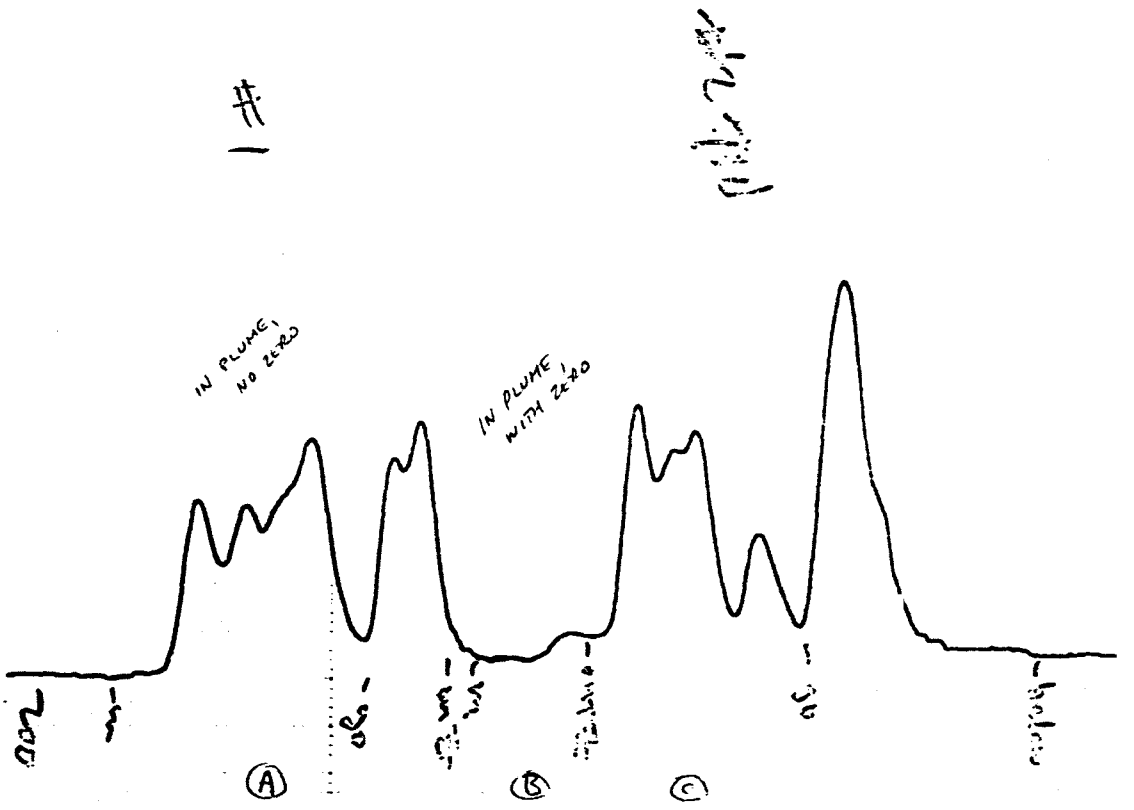


Figure 26
Helicopter Data, Chicago, Illinois

Sensitivity limits were investigated. Generally speaking, installation in the aircraft did not degrade the quality of the equipment operation. Certainly higher flight speeds, above 30 to 40 mph, prevented data collection principally because of the Venturi effect limiting the air intake. Most data were gathered while hovering or moving at low forward speeds.

The helicopter rotor does disturb the air in the vicinity; this effect is not significant at the door where the intake was fitted. For plume work, the air to be measured was drawn

past the craft so this "fan" effect was not a limitation. For near-ground, high resolution measurements the helicopter would have to be fitted with an intake which extended forward of the rotor. During a survey of this type a suitable forward motion would be required to avoid distrubing the air to be measured.

Our experience with the helicopter would indicate that an external appendage would be feasible, and survey would be possible near sites suitable for low level flight operations. Obviously buildings, strung lines and cables, stacks, trees, and high density population areas are all limits to this method of rapid measurement.

The use of fixed-wing aircraft seems limited for the measurement of atmospheric mercury associated with pollution, principally because the clouds of vapor detected to date are so localized. The density of the vapor also suggests that the plumes generally remain low to the ground. While the response of the BAMS is controlled principally by the air flow, the few second delay becomes critical during fixed-wing aircraft flights where five seconds at near-stall speeds of 80 miles per hour represent a ground-covered distance of 587 feet (179 meters). Such a delay in reporting the presence of the invisible vapor makes it very difficult to survey and locate at these speeds. The helicopter, on the other hand, enables slow traverses and rapid changes of direction.

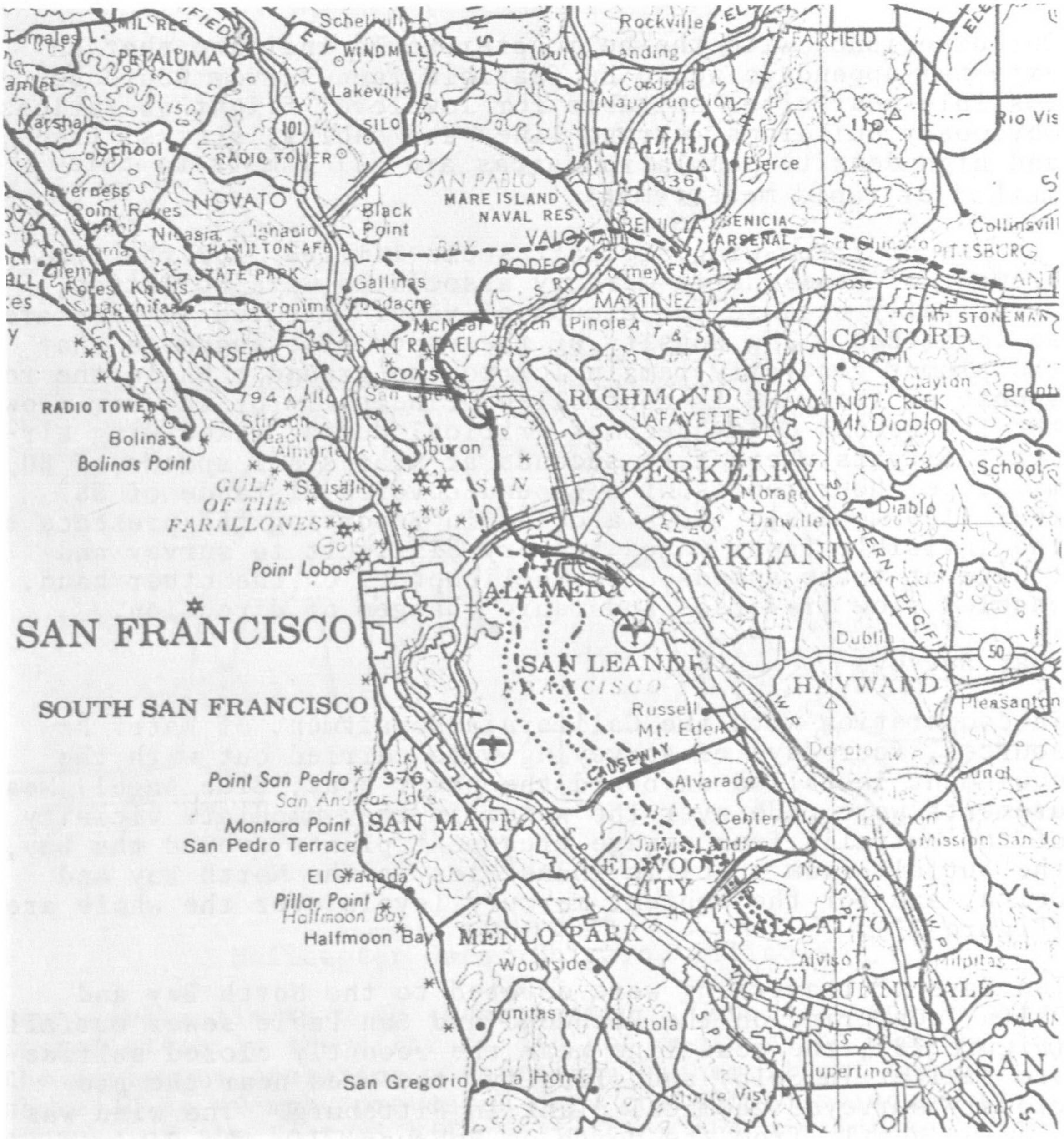
Boat Surveys

In cooperation with the California Department of Water Resources, four days of surveying were carried out with the equipment installed on board the power boat, Blue Angel. Measurements were made over the water in the immediate vicinity of the outfalls from sewage treatment plants around the Bay, the outfall from specific industries in the North Bay and Delta, and for the ambient mercury levels over the whole area (Figure 27).

Two days of traversing were devoted to the North Bay and Delta, centering on the Richmond and San Pablo sewer outfalls (Figure 28), the coastline near the recently closed sulfide ore smelter in Selby and, finally, the area near the previously surveyed chemical plant in Pittsburg. The wind was blowing gently from the north on February 24; the day's temperature was around 60°F. On February 25 the wind was strong from the north, and it was cold (about 40-50°F). No mercury vapor was detected anywhere in the North Bay area.

Two days of surveying in April concentrated on Southern San Francisco Bay. April 7 was devoted to the southern most

sloughs. Coyote Creek, Santa Clara County (San Jose), was penetrated to a railroad bridge with no significant mercury anomalies detected. The results were the same elsewhere -- negative.



KEY

——— February 24, 1971   -·-·- April 7, 1971

----- February 25, 1971   ········ April 8, 1971

Figure 27
Boat Survey Routes

Figure 28
Richmond, California, Sewage Outfall

On April 8 the ambient levels on the morning were very low, 0 to 5 ng/M^3; they increased later in the day to about 10 to 15 ng/M^3. Superimposed on this background was a single anomaly detected directly over the oil smear of the San Carlos Sewage Treatment Plant outfall. The maximum signal was approximately 50 ng/M^3.

On this day, a traverse was also made in the Islais Channel, San Francisco, in hopes of detecting mercury vapor near the site of a reported mercury anomaly in water (11). No clear anomaly above the 10 to 20 ng/M^3 ambient level was detected. (On April 9, measurements were made from adjacent roadways; no significant mercury was detected above the ambient level.)

SECTION X

DISCUSSION

The nature of the mercury vapor presence detected during the course of this program is quite varied. Near mercury-polluted waters, the vapor levels were low; they seemed to depend on the general background level as much as on emanations from the water. Sewage and waste treatment plants may emit vapor both from flares and incinerators. Near naturally-occurring mercury deposits, mercury vapor measurements can be distinctly high; the highest levels detected during the ground measurement program were from natural sources. In the vicinity of industrial users or producers of mercury, the vapor level can also be high.

New Almaden

The reservoirs near the New Almaden, California, mercury mining area have reported fish with mercury concentration greater than FDA limit of 0.5 ppm. On May 7, 1971, signs warning against consumption of fish taken from these reservoirs were posted (14). Because of the documented presence of mercury in these reservoirs, reported by the California Department of Water Resources, this area became a prime target for mercury vapor measurements.

The data that have been released indicate there is little mercury in the water itself (11) (15) (17). Further, sediment samples are reported to yield inconclusive results. The question of just how the mercury entered the reservoirs, and then the fish, is still being considered.

The anomalous peaks in mercury vapor detected at the bridge over Los Alamitos Creek in New Almaden suggest that vapor was being carried along by an evening air drainage pattern. The movement of air downhill along the gullies and valleys off New Almaden mining area (Figure 16) would carry mercury vapor emitted by the deposit over the Almaden reservoir through the town of New Almaden, and even across the Calero Reservoir.

The peak observed in the Alamitos Creek bed was not explained, or duplicated in measurement made on a later day. However, its presence was certain on the evening of January 4. Differences in the wind account for the change. Whether this peak represented mercury vapor from mercury already there was not discernable.

The similar peak near the Guadalupe Mine on Guadalupe Road and the small peak at the south end of Guadalupe Road are also

apparently at the base of air drainage channels. Their origin and extent were not apparent from these preliminary measurements.

The regional measurements made downwind of New Almaden on March 4 did not indicate a clear anomaly downwind or immediately upwind of the Calero Reservoir. The general broad ambient mercury level of 5 to 15 ng/M^3 appears to represent a pattern of dispersal from the ore deposit area. However, it might represent water or sediment laden with mercury which were emitting the vapor.

Since the mercury values detected in the water and sediment are reported to be mostly in dissolved form, it seems likely that greater levels of combined mercury vapor would be expected in the air. Pyrolysis would aid in detecting the presence of "total" mercury anomalies in water and sediment which this survey program did not detect.

Clear Lake

Fish taken from Clear Lake have also been found to be high in mercury (15). So far, however, no recommendations against consumption of Clear Lake fish have been issued.

The mercury vapor detected near Clear Lake varied on the two days of measurement because of the differing wind patterns. On February 12, the wind was from the east, and Buckingham Point experienced mercury vapor levels of 150 ng/M^3. On April 2, the wind was from the west and no mercury was detected on Buckingham Point. At Sulfur Bank, the vagueness of the data may have been due to the wind which was very strong, and may have produced a narrow, gusting, hard-to-locate plume.

The origin of the mercury vapor detected at Buckingham Point is in question. It may have been blown across the Lake from Sulfur Bank, or it might reflect a mercury concentration in the water near the Point or in the adjacent Little Borax Lake. The great distance from Sulfur Bank would suggest that any mercury vapor emitted then would fall out and be deposited in the water before it reached Buckingham. The lack of vapor when the wind was from the west suggests that the water just east of the Point could be the source.

San Francisco Bay

The surveys run on San Francisco Bay were aimed at detecting mercury vapor near the sites of water sampling programs which had previously yielded mercury values. Specific targets were Coyote Creek (Santa Clara County) and Islais Channel (San

Francisco County). In addition, the outfalls from various San Mateo County sewage plants were tested since industries were reported to use these sewer systems for their effluent. The lack of significant anomalies in elemental mercury vapor suggest that any mercury contamination is in combined form. However, the anomaly detected directly over the San Carlos sewer outfall was a positive indicator of metallic mercury.

The measurements downwind of the East Bay Municipal Utilities District flare, where waste gases are burned, showed mercury vapor with peaks of 100 ng/M^3. The flare might have reduced combined mercury to metallic form, which the BAMS could then detect. This contrasts with levels measured at incinerator stack exits with the helicopter. At the Stickney Dryer in Chicago several hundred ng/M^3 were measured (13); in garbage waste burners, much higher levels were found.

In the case of the flare and the incinerator, the plumes mostly blew inland, and any mercury they carried was deposited on an adjacent freeway and nearby industrial/residential areas. When the wind is from the east, however, these plumes extend over the Bay; the mercury would be deposited in the water.

Natural Mercury Deposits

The highest peak value of mercury vapor monitored on the ground during this program was identified at The Geysers, where greater than 25,000 ng/M^3 were measured emanating from a steam well (Figure 29). The steam from all the vents made a clear picture of dispersal downwind to the east on February 15.

Since the rate of fallout of mercury from a plume is not known, the possibility that mercury from The Geysers steam vent is blowing 20 miles north to Clear Lake exists. Similarly the extent to which the now-closed Sulfur Bank Mine has contributed to the mercury contamination of Clear Lake can only be speculated. Mining operations 50 years ago could have contributed to the mercury contamination which has been discovered just recently.

The natural mercury mineralization at New Almaden is apparently responsible for most of the mercury contamination in Santa Clara County. The vapor above natural concentrations of mercury has been known for a number of years (4). The mode of contamination of the water is not known, however. Certainly the air movement is a carrier of the gaseous mercury. The extent to which ground or surface water also is a carrier has not been determined.

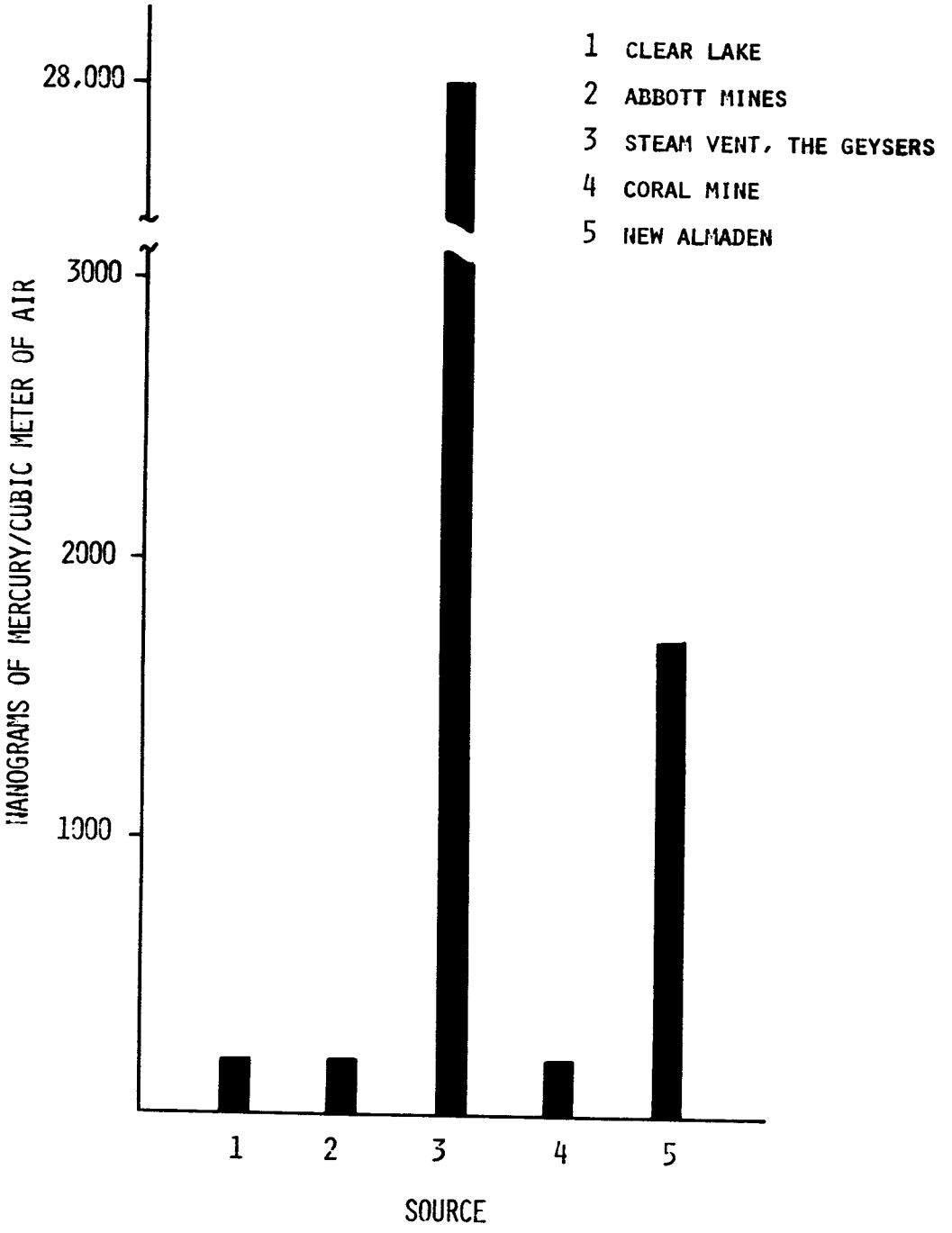


Figure 29
Peak Mercury Vapor Levels Near Natural Sources

Cultural Sources of Water Contamination

The effluent from known or suspected users of mercury has been monitored with some vigor; however, no concern has been felt for the vaporous emanations from these same industrial users. Due to the high vapor pressure of mercury, it is reasonable to expect some air contamination around these sites.

The magnitude of air contamination around these sites varies significantly (Figure 30) and depends on the topography and local meteorology. Large industrial installations using chlor-alkali processes would be expected to yield higher levels than the small manufacturer of electrical components.

The largest mercury vapor level near a cultural source was measured in Pittsburg near a large chemical plant which closed down its chlor-alki operation April 1970. This signal was detected downwind of an area which contains their settling pond and the approximate location of the now-closed cell. A company representative indicated that mercury had been detected in the ground near the cell site, and that this was probably due to spillage at the time of operation. It was not possible to discriminate the source area. However, if the settling basin now contains mercury deposits at its base, the water cover above it is not effectively sealing the vapor.

The second largest level was measured downwind of a large pesticide complex in Richmond. It was possible to map the distribution pattern of this plume for over a mile. During the days of measurement, the wind was from the north and northwest, and the plume was dispersed over the city. Of particular note, the plume passed directly through school facilities. On days when the wind was from the south and southeast, the plume would be spread over San Pablo Bay. The extent to which mercury fallout on land contributes to the mercury level in the water by subsequent drainage is not known.

Other industrial areas also showed mercury vapor. The identification of each source, and the extent to which this form of emission contributes to the mercury contamination of water requires more measurement and analysis.

Dispersion of Mercury Vapor

The parameters which control the dispersion of a mercury vapor plume still require definition. No plume from an industrial source was tracked for more than 1.5 miles. On the other hand, a major well-travelled highway seemed to be instrumental in dispersing the major plume in Berkeley.

Natural plumes may be of greater extent, perhaps because of less air turbulence in a rural environment coupled with their greater volume. More work is required in this area.

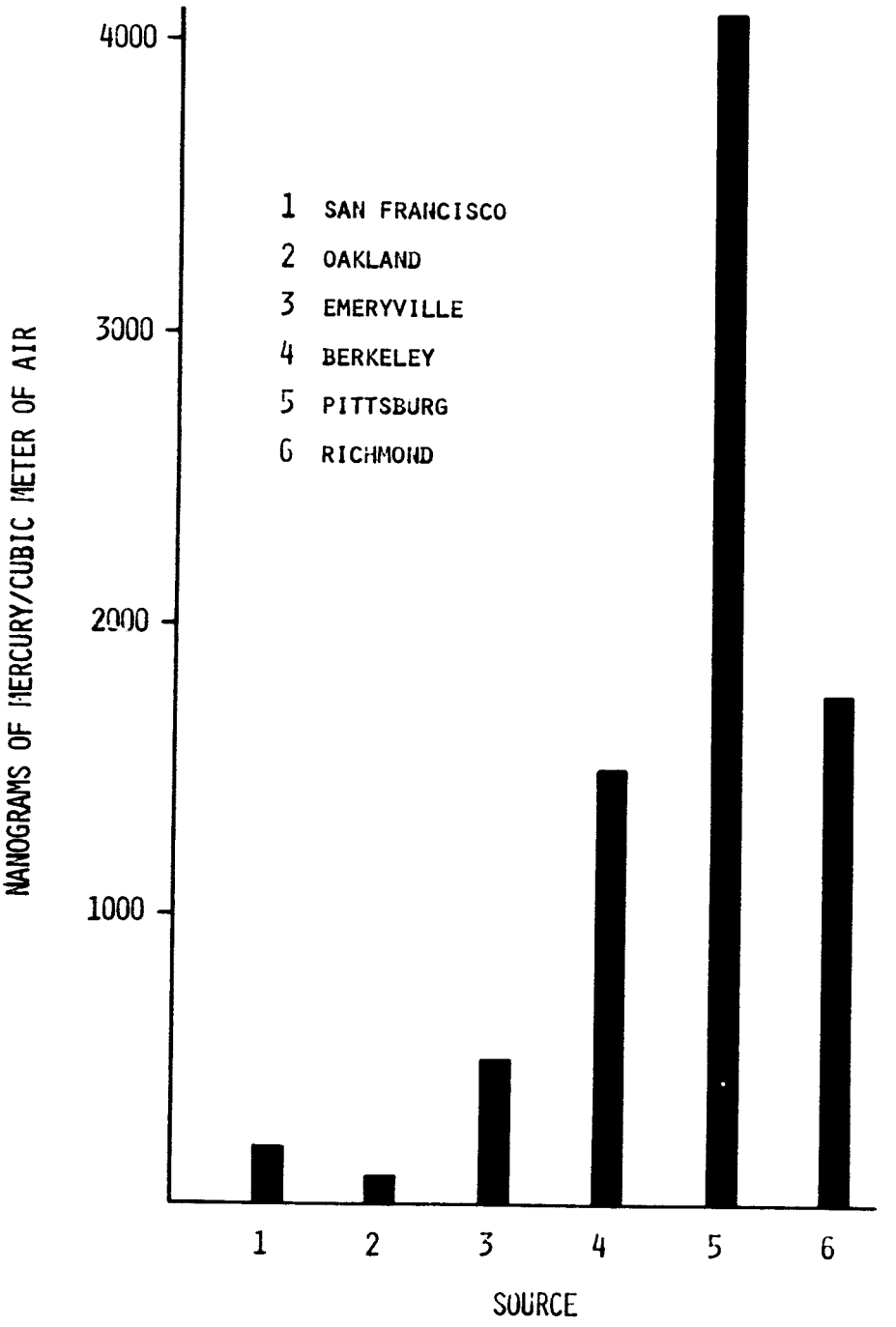


Figure 30
Peak Mercury Vapor Levels Near Cultural Sources

SECTION XI

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Dr. Teng-Chung Wu of the California Department of Water Resources was instrumental and very helpful in arranging our boat surveys. The high competence and skill of William R. Macke was appreciated particularly in his ability to locate our measurements with precision in the water.

Originally considered to be a two-month project, the enthusiasm and encouragement of all cooperating parties suggested that we carry out the work as described herein; no additional funds were requested.

SECTION XII

REFERENCES

1. Jervis, R.E., et al, Summary of Progress, Canadian National Health Grant No. 605-7-510 (Trace Mercury in Environmental Materials) for the period Sept. 1969-May 1970. Partial summarized in Chemical Engineering News, Oct 5 (1970).

2. Barringer A.R., "Interference-free Spectrometer for High-sensitivity Mercury Analyses of Soils, Rocks and Air," Applied Earth Science, Institute of Mining and Metallurgy, Volume 75, B120-B124 (1966).

3. Weast, Robert C. (Editor), Handbook of Chemistry and Physics, 51, p. D-145 (1970).

4. United States Department of the Interior, Geological Survey, "Mercury in the Environment," Geological Survey Professional Paper 713, (1970).

5. Anonymous, "Mercury and Mud," Scientific American, 223, No. 3, pp 82 and 86 (1970).

6. Williston, Samuel H., "Mercury in the Atmosphere," Journal of Geophysical Research, 73, No. 22, pp 7051-7055 (1968).

7. Wallace, Robin A., et al, "Mercury in the Environment: The Human Element," Oak Ridge National Laboratory, ORNL NSF-EP-1 (January 1971).

8. Barringer, A. R., "Method and Apparatus for Detecting Traces of Substances," Canadian Patent No. 789, 106 (July 2, 1968).

9. Kaye, Wilbur, "Emission Spectra of Argon, Helium, Krypton, Neon and Xenon Pen-ray Lamps," Pen-ray Rare Gas Lamp Spectra, Ultra-violet Products, Inc. (1964).

10. Thompson, H.W. and J.W. Linnett, "The Vapor Pressure and Association of Some Metallic and Non-metallic Alkyls," Transactions of the Faraday Society, 32, p. 681, (1936).

11. Durum, W. H., et al, "Reconnaissance of Selected Minor Elements in Surface Waters of the United States, October 1970," United States Department of the Interior, Geological Survey Circula 643 (1971).

12. Egenhoff, Elisabeth L., "De Argento Vivo," California Journal of Mines and Geology (Supplement) (1953).

13. Staff, "Mercury in the Air," Environment, 13 No. 4 (1971).

14. Anonymous, "Santa Clara Warns of Fish Mercury Hazards," San Jose Mercury, May 1, 1970.

15. Kahn, Ephram, Personal Communication, 1971.

16. Helicopter-borne mercury measurements were carried out in cooperation with the Committee for Environmental Information, St. Louis, Missouri.

17. Averitt, Robert, Personal Communication, 1971.

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27 Abstract

Field and laboratory measurements were made to demonstrate that mercury vapor in the air near mercury-polluted water or sediment can be detected using an extremely sensitive detector, the Barringer Airborne Mercury Spectrometer.

Areas were visited where the presence of mercury was known from fish, water, or sediment analyses; anomalous mercury levels ranging from 50 to more than 20,000 nanograms per cubic meter (ng/M^3) were detected. Ambient air contained from 0 to 50 ng/M^3.

Anomalous concentrations of atomic mercury vapor in air may be classified as natural or man-made. The largest anomaly detected was natural, emanating from a steam vent at The Geysers, California. The second largest was man-made, and was measured downwind from a large chemical plant.

Laboratory studies demonstrated that the mercury spectrometer is sensitive only to atomic mercury. By means of pyrolysis or combustion, organic compounds could be converted to metallic form and detected. To detect mercury pollution in water, pyrolysis appears necessary to convert combined mercury to the atomic state for measurement by rapid spectrophotometric techniques. (Langan-Environmental Measurements)

Abstractor Lee Langan | Institution Environmental Measurements, Inc.

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