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HYDROGEN SULFIDE, TRACE ELEMENT, AND SULFUR HEXAFLUORIDE TRACER TREATMENT FROM THE GEYSERS-CALISTOGA GEOTHERMAL RESOURCE AREA BASED ON AIRCRAFT AND SURFACE SAMPLING

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HYDROGEN SULFIDE, TRACE ELEMENT AND SULFUR HEXAFLUORIDE TRACER TRANSPORT FROM THE GEYSERS-CALISTOGA GEOTHERMAL RESOURCE AREA BASED ON AIRCRAFT AND SURFACE SAMPLING

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1. INTRODUCTION

The emission, transport and dispersion of pollutants from energy production areas in complex landforms is a subject of continuing concern with respect to assessments on whether emitted pollutants may cause a significant impact on the general public and environment through the mechanisms of chemical reactions, impaction, dry deposition and acid precipitation.

A limited surface and aircraft sampling study was conducted in the Geysers-Calistoga Geothermal Resource Area (GGRA) to collect initial data on the short-range (5 to 20 km) transport of pollutant materials and a sulfur hexafluoride (SF_6) tracer from this geothermal electrical generation area (The Geysers). The electrical generating capacity of the Geysers is undergoing extensive expansion. Power plant cooling towers and geothermal wells located on mountain ridges, slopes and valleys release a variety of emissions (Martin, etal. 1978). A potential environmental issue in this area is the release of hydrogen sulfide and its transport to surrounding communities and agricultural areas. Since these emissions can result in an odor nuisance if concentrations exceed 30 ppb (California Air Quality Standard) it is important to assess the transport and dispersion of the Geysers emissions to surrounding areas.

The ~~Battelle~~ (PNL) sampling study was accomplished during the DOE ASCOT Cooling Tower field program in August 1981 as part of the daytime limited mixing experiments (Gudiksen, 1982). On August 23 and 24, the ASCOT group conducted extensive meteorological and tracer experiments during the daytime hours. In addition to these two days, the PNL aircraft also sampled on August 20 and 21 for gaseous sulfur (H_2S) and airborne aerosols.

The goals of the PNL study were four fold: a) to define the types and quantities of airborne materials such as, H_2S, B, As, Cd, Pb, Cr and Hg that are emitted from the geothermal operations, b) collect data on the location, height and concentration of the airborne materials and SF_6 tracer, c) examine the role of vertical wind shear in the transport of the H_2S and SF_6 tracer plumes and d) if possible, estimate the flux of pollutant material being transported from the Geysers. The four-day study, although clearly insufficient to satisfy these four goals, nevertheless, was intended to provide initial data on the short-range (5 to 20 km) transport of pollutants from an area source (The Geysers) in complex terrain. The purpose of this paper is to discuss the initial data analysis and results in respect to the first three goals. A final analysis and conclusions will be reported in the future.

*P.W. Nickola passed away August 1982.

2. EXPERIMENTAL DESIGN

2.1 Site Description

The airborne and surface sampling was conducted over the GGRA located approximately 40 km north of Santa Rosa and about 65 km east of the Pacific Coast. Figure 1 shows the relative location of the GGRA and the major area of geothermal operations (The Geysers). The Geysers (shaded area in Fig. 1) are located in the Mayacmas mountains which are oriented in a northwest-southeast direction. The Russian River valley lies to the west and Clear Lake lies to the north of the Geysers. Prominent mountain peaks in the area are Cobb Mtn. (1439m), Boggs Mtn. (1122m), Mt. St. Helena (1324m), Mt. Hannah (1212m) and Mt. Konocti (1280m).

2.2 Instrumentation

2.2.1 Surface equipment

Surface samplers were used to collect airborne aerosols during the same period that the aircraft was sampling overhead. Standard high-volume samplers were placed at seven different locations within and in the vicinity of the Geysers (Fig. 1). Table 1 shows the range in elevations of the sampling sites. The location of the sampler sites were dictated by accessibility and availability of power.

The flow rate of each sampler was calibrated and set at approximately 0.50 m^3min^{-1}. Each sampler was monitored at the beginning and end of each experimental period. Table 1 shows the average flow rate and total air sampled per day for the different sampler locations. The Whatman No. 41 filters used in the high-volume samplers had an exposed area of 52.8 cm^2 (dia=8.2cm).

2.2.2 Aircraft Instrumentation

The aircraft sampling was conducted with the PNL Cessna 411 aircraft which was equipped with the following measurement and sampling systems: a PNL real-time SF_6 analyzer, real-time sulfur analyzer (Meloy SA285), an ozone monitor (Bendix 8002), a MRI integrating nephelometer, and a high-volume filter sampler. Atmospheric state parameters which were measured included air temperature, dewpoint and pressure altitude. Geographic coordinates (latitude, longitude) were obtained from a Global (GNS-500A) navigation

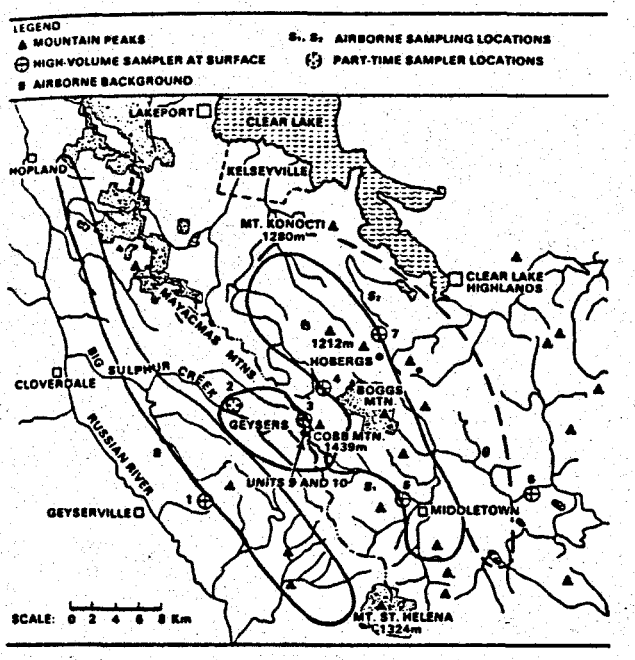

Figure 1. Geographic Setting of the Geysers-Calistoga Geothermal Resource Area (GGRA), The Geysers, and Location of Aircraft Sampling Flights and Surface High-Volume Filter Samplers.

TABLE 1

Surface high-volume sampler locations, elevations, average flow rates and average total air sampled.

Sampler Site	Elevation @ m.s.l.	Average Flow Rate (per day) meubemin-1	Average Total Air Sampled(perday)meube
1.BandM Brangus Ranch	591	0.54	198
2.Administration Center*	671	0.49(2)	163
3.Repeater(Geysers Rock)	1116	0.47	172
4.Sawmill Flat	722	0.47	176
5.Delfino(Middletown)	341	0.46	165
6.Loren	439	0.53	188
7.Lilla Ranch	731	0.50(2)	158

* Moved after two days to Lilla Ranch

system. These data and the real-time air quality and tracer data were recorded by a magnetic tape data acquisition system. The filters used in the airborne high-volume sampler were Zefluor membrane filters with an exposed surface area of 21.2 cm^2 (dia=5.2cm).

2.3 Experimental Procedures

The general flight procedure was to obtain background measurements in the morning hours just west of the Geysers at approximately 1050 m and 1550 m (m.s.l.). In the afternoon, the H_2S, aerosol, and SF_6 sampling was conducted east (and downwind) of the Geysers between 1000 m and 1900 m. Exceptions to this flight procedure occurred on August 20 when the procedure was reversed, and on August 21 when the background was taken in the early afternoon before sampling east of the Geysers. The principal sampling transects, shown in Fig. 1, were 5 to 12 km from the Units 9 and 10 power plant within the Geysers. These transects were flown in a race track manner at three different altitudes for an hour or more for each altitude. Each transect was flown from three to five times except for a transect at 18-20 km which was flown once. On August 21 and 23 the majority of sampling took place east of Boggs Mtn. on a northwest to southeast flight track.

The range of altitudes and distances for sampling H_2S and SF_6 in real-time was limited by the altitude sensitivity of the real-time samplers (baseline response varies with pressure) and the sampling of aerosols. The aerosol measurements required flying on a fixed path and altitude for a minimum of one hour in order to collect sufficient material for analysis.

The surface-based high-volume samplers were turned on at the beginning of the aircraft flight and operated continuously during the 7 to 8 hours of aircraft sampling.

2.4 Synoptic Weather Pattern

The synoptic and weather conditions during the four days of sampling were determined by the subtropical high pressure area off the California-Oregon coast and a deep, winter-like low pressure area in the northern part of the Gulf of Alaska. Between August 20 and 22, a ridge of high pressure on the Oregon-California coast induced a weak onshore pressure gradient and caused an influx of marine air into the GGRA, mainly in the afternoons. After August 22, the cold front from the Gulf of Alaska low pressure area had moved to the Washington coast and became quasi-stationary near Vancouver Island. On August 24, a new low pressure system and weak cold front moved inland into northern Washington. The surface front trailed southward through Oregon and northern California resulting in a slight cooling trend and a stronger influx of the marine layer inland.

All afternoons of the sampling days were essentially cloudless. Extensive morning marine stratus was present over the GGRA on August 23 but this cloud layer was dissipated by noon. The weak frontal passage during August 24 caused a few scattered and poorly developed fair weather cumulus over the northern mountain peaks in the afternoon. Figure 2 shows a time series of the available rawinsonde winds up to 2000 m for the four sampling days. Most all aircraft sampling flights were conducted during southwesterly to northwesterly upper-level winds. Temperature soundings taken in the experimental area by the rawinsonde and ASCOT tethersondes indicated an elevated temperature inversion on August 23. The depth of the inversion increased from 1200 m to 1500 m (m.s.l.) between 1000PST and 1700PST. No significant inversions were present during the other three days.

3. RESULTS AND DISCUSSION

3.1 Composition and Enrichment of Geysers Aerosols

The four days of sampling resulted in 41 filters. An initial selection of eight filters, five surface and three airborne samples, was made for X-ray fluoresence (XRF) and neutron activation analysis (NAA). To date three filters have been examined by XRF and all eight were examined by NAA. Of the more than thirty elements potentially identifiable by XRF and NAA only fourteen had air concentrations of sufficient magnitude to warrant further consideration.

The crustal enrichment factor (EF_c) was

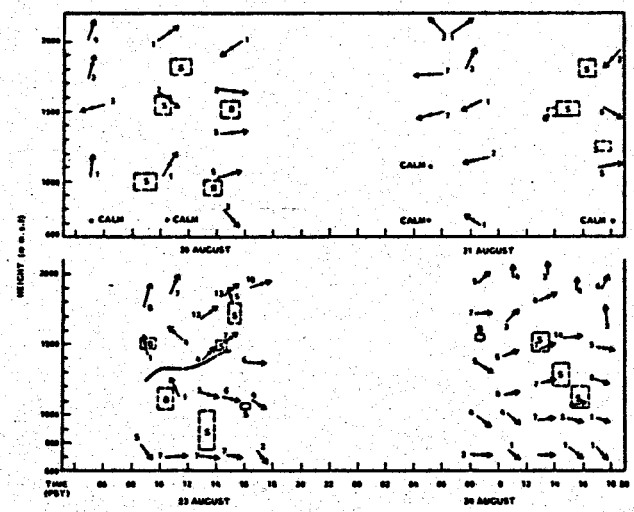

Figure 2. Horizontal Wind Direction and Speed as a Function of Height for August 20, 21, 23 and 24, 1982 at Sawmill Flats. Aircraft sampling heights and times represented by dashed boxes. B - Background, S - Sampling.

calculated for these fourteen elements in the eight filter samples. The crustal enrichment factor $EF_c=(C_x/C_{Fe})_{aerosol}/(C_x/C_{Fe})_{crust}$ expresses the relative enrichment of trace elements as compared to crustal abundance. A EF_c less than 1 indicates depletion of an element, whereas a value greater than 1 indicates enrichment of a given element relative to the referenced crustal material Fe. Generally, an enrichment factor of 10 or more is considered significant with respect to anthropogenic input to the atmosphere (Rahn, 1971). Table 2 shows the calculated enrichments for the selected surface and airborne filter samples.

Trace elements of particular interest in geothermal operations are As,Cd,Hg,S,Pb and Cr. The XRF analysis shows a wide range in enrichments for these elements. The NAA analysis shows an enrichment for As, Br and Cr and these results are consistent with the XRF analysis. Cadmimum and mercury results of the NAA analysis were subject to large analysis errors and are not shown. The enrichment of the near-surface aerosols in lead(Pb) and bromine(Br) could be the result of geothermal emissions (Lepel etal., 1978; Fruchter, 1980) although observed concentrations must also result, in part, from vehicle emissions associated with the Geysers operations and surrounding communities. Bromine may also be at least partially of marine origin although sodium enrichment factors suggest insignificant input of marine aerosol. The XRF and NAA analysis of the aircraft filters is incomplete. There may be some minor transport of As,Cr,Br and Zn from the Geysers based on the three filters analyzed to date.

3.2 H_2S (Gaseous Sulfur) Transport from the Geysers

One of the primary pollutants from the Geysers is gaseous sulfur in the form of H_2S. Surface and aircraft filter samples indicated sulfur enrichment in the collected aerosol. A

TABLE 2

Crustal Enrichment Factors for Trace Elements Detected in Selected Surface and Aircraft Filter Samples in the GGRA.

	Surface					Aircraft		
	(3) Repeater 8-23	(3) Repeater 8-24	(4) Sawmill 8-23	(1) Brangus 8-24	(5) Delfino 8-24	ZF-45	ZF-41	ZF-49
Element (XRF)								
As	<201	<35						
Br	145	32						
Cd	8790	1867	Analysis not complete (ABC)					
Cr	3	3				32	ABC	
Hg	<2670	284						
Mn	2	2				3		
Ni	3	3						
Pb	19	13						
S	214	26				85		
V	2	2						
Zn	8	3						
(NAA)								
As	28	4	24	18	6	<2	BD	<5
Br	81	14	139	104	78	<5	BD	<7
Co	1.3	1.4	1.2	1.3	1.4	2	BD	<2
Cr	3	2	3	4	4	<4	BD	<8
Sm	0.2	0.1	0.3	0.3	0.2	0.2	BD	0.1
Zn	8	3	8	4	13	<11	BD	<20

low concentration but measureable gaseous sulfur plume was detected on all four days in the eastern quadrants from the Geysers since the winds were generally from westerly directions. The range in maximum concentrations varied from 6 to 36 ppb. Concentrations between background levels and 25 ppb were detected at elevations between 1700 and 1900 m(m.s.l.), (Table 3). A brief synopsis of the results from two of the four days follows:

TABLE 3

Range of Average Maximum 20-sec H_2S Concentrations as a Function of Elevation for the Four Sampling Days(ppb).

	Elevation(m m.s.l.)				
Date	950-1200	1200-1395	1400-1600	1700-1900	Background
August 20	---	25-36	15-31	20-25	4
August 21	---	14	6-13	4-9	2-3
August 23	9-19	---	3-10	2-5	2-3
August 24	6-9	5-8	8-10	---	3-4

On August 20, the plume was detected between 1200 and 1900m and was found to be moving toward the north and northeast (Fig.3). Maximum concentrations varied between 15 and 36 ppb at distances 5 to 12 km from the GGRA. A definite H_2S odor was detected in the aircraft at 1500 m about 4 km from the Geysers.

On August 24, plume concentrations were lower than observed on August 20 and the plume was moving to the northeast. The plume between 950 and 1200 m originated from Anderson Creek south of Cobb Mountain and traveled eastward between Boggs Mountain and Middletown. The plume axis between 1400 and 1600 m was located near Cobb Mountain and moved northeastward. The shift in the plume axis was apparently the result of the wind direction backing with height. The sampling at higher elevations was done with southwest winds and the sampling in lower elevations was accomplished during a later period when wind directions were changing to the northwest.

3.3 SF_6 Tracer Transport from the Geysers

On August 23 and 24, a SF_6 tracer was released from Units 9 and 10 power plant cooling tower at a rate of 3 $gmsec^{-1}$ from 1300 PST to

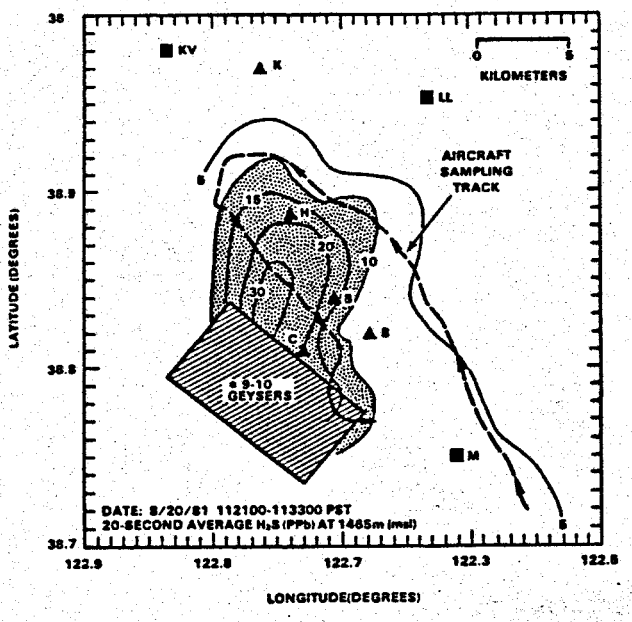

Figure 3. Transport of Gaseous Sulfur (H_2S) Plume from The Geysers as Depicted from Aircraft Sampling. Locations: M-Middletown, C-Cobb Mtn., H-Mt. Hannah, LL-Lower Lake, K-Mt. Kocnocti, KV-Kelseyville.

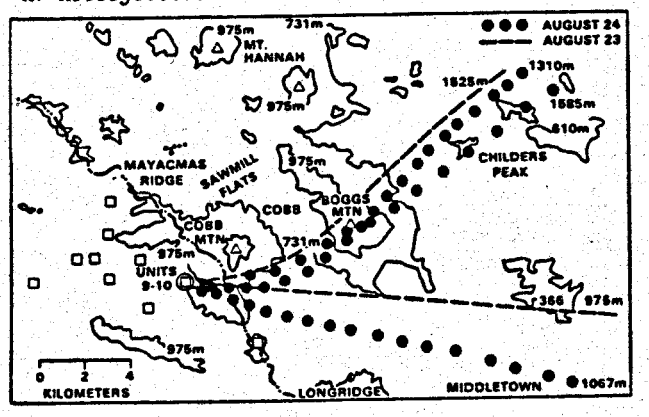

Figure 4. Change in direction of the average SF_6 plume centerline axis with height due to vertical directional wind shear as depicted by the aircraft sampling on August 23 and 24, 1981.

1900 PST. The altitude of Units 9 and 10 is 968 m (m.s.l.). The average maximum plume rise from the cooling tower as estimated by aircraft lidar was about 450 m (1418 m m.s.l.) on August 23 and 1100 m (2068 m m.s.l.) on August 24 (Uthe, 1982).

A SF_6 plume was detected over Anderson Creek and again east of Boggs Mountain between 1000 m and 1800 m (m.s.l.). Near source concentrations were as high as 550 ppt and decreased to 140-280 ppt at 12 to 14 km northeast of Boggs Mountain. Between 18 and 20 km, the plume became indistinct and difficult to detect.

The vertical directional wind shear observed on both sampling days changed the direction of the plume axis with height as discussed previously in regard to the gaseous sulfur plume. Figure 4 shows the average SF_6 plume axis as observed at two altitudes on August 23 and three altitudes on August 24. On August 23, SF_6 was not detected at the third altitude of 1800 m (m.s.l.). On these days the wind direction change with height was around 50 deg and 30 deg, respectively. The change in direction of the plume axis on August 23 was 40 deg and on the 24th was around 45 deg. The effect of the vertical wind shear was to spread the plume over a wider area than would happen if the wind shear was not present.

4. CONCLUSIONS

This four-day study, although clearly insufficient to define all the aspects of the transport problem for The Geysers nevertheless has provided initial data regarding the short-range transport of pollutants from The Geysers geothermal operations.

The initial analysis of the data has shown that a measurable plume of gaseous sulfur (H_2S) is emitted from the Geysers and transported by surface and upper-level winds to distances beyond 20 km. Only one day had concentrations above 30 ppb and on this day H_2S was detected as a distinct odor at 1500 m (m.s.l.) at 4 km or more from the Geysers. The initial data analysis of the H_2S and SF_6 plume data have revealed the important role that vertical wind shear plays in changing plume trajectories with height and enhancing diffusion of pollutants. Surface and aircraft sampling of aerosols indicate that small quantities of trace elements such as, As,Cd,Hg,Pb,Cr and Br may be transported from the area.

Acknowledgements

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5. REFERENCES

Fruchter etal. 1980: Mount St. Helens Ash from the 18 May 1980 Eruption: Chemical, Physical, Mineralogical, and Biological Properties. *Science*, 209, pp. 1116-1125.

Gudiksen, P. H. 1982: ASCOT Data from the 1981 Cooling Tower Plume Experiments in the Geysers Geothermal Area. UCID-19332, ASCOT-82-4, Vols. 1 and 2, Lawrence Livermore National Laboratory, Livermore, CA.

Lepel, E. A.,K. M. Stefansson and W. H. Zoller 1978: The Enrichment of Volatile Elements in the Atmosphere by Volcanic Activity: Augustine Volcano 1976. *J. Geophys. Res.*, 83, No. C12, pp. 6213-6220.

Martin, J. B. etal. 1978. Environmental, Safety and Health Standards Identification for Geothermal Energy. Report 1: Airborne Emissions. PNL-2583-1, Battelle Pacific Northwest Laboratories, Richland, WA.

Rahn, K. A. 1971: Ph.D. Thesis and Ann Arbor Report COO-1705-9, Univ. of Michigan, Ann Arbor, MI.

Uthe, E. E. 1982: Airborne Lidar Study of Plume Behavior in the Geysers Geothermal Area. UCID-19332, ASCOT-82-4, Vols. 1 and 2, Lawrence Livermore National Laboratory, Livermore, CA., 8-41 to 140.