

*Presented 1986
@ GORC KONA*

**CONCENTRATIONS OF NON-CRITERIA AIR POLLUTANTS
IN THE VICINITY OF THE GEYSERS, CALIFORNIA**

Altshuler, Samuel L., Arcado, Theodore D., and Lin, Dr. Chin-I

**Pacific Gas & Electric Co.
3400 Crow Canyon Rd. San Ramon, CA, USA, 94583**

Abstract

Ambient air monitoring for non-criteria pollutants was conducted to assess the impact of geothermal steam utilization on the ambient air at The Geysers. The measurements revealed no exceeds of any ambient air quality standards, state, federal, or foreign. Except for mercury vapor, radon, and ammonia, all of the pollutants were measured at near detection limit concentrations using methods that are state-of-the-art. Mercury vapor seems to be more related to the known geologic cinnabar deposits and past mining operations in the area than to geothermal steam utilization at The Geysers.

Introduction

The Air Quality Unit of Pacific Gas and Electric's (PG&E) Department of Engineering Research conducted ambient air monitoring for non-criteria air pollutants in populated areas of Lake County, California. This area is predominately downwind of The Geysers, an area producing geothermal steam generating 1300 megawatts of electric power. The Geysers is located in the Mayacmas Mountains, approximately 90 miles north of San Francisco.

The non-criteria air monitoring began in August 1983 and was conducted to the end of July 1984. This program will again resume in August 1986 for one final year of operation. The program is a portion of the larger Geysers Air Monitoring Program (GAMP) which also includes continuous measurements for ambient hydrogen sulfide (H₂S) at six sites and meteorological parameters at eleven sites (nine wind direction/speed and temperature/dewpoint sites and two acoustic sounder sites).

GAMP was created to provide environmental measurements needed by industry and regulatory agencies for assessing the impact of growth of the geothermal industry at The Geysers. GAMP is supported by a consortium of 15 entities including power companies, steam suppliers, local

air pollution control districts, the California Air Resources Board (ARB), and the California Energy Commission. The Northern Sonoma County Air Pollution Control District (NSCAPCD) is the project manager for GAMP. PG&E performs all of the non-criteria monitoring, H₂S monitoring at two sites, and meteorological monitoring at three sites. The consulting firm, Environmental Systems & Services (ES&S), Kelseyville, California, performs the remainder of the monitoring for the GAMP consortium. The Lake County Air Pollution Control District (LCAPCD) performs quality assurance activities for GAMP. The ARB also performs quality assurance activities as well as specific chemical analyses at their Haagen-Smit Laboratory in El Monte, California.

The parameters selected for the non-criteria pollutant monitoring programs were chosen based on:

- (1) their presence in geothermal steam (mercury, arsenic, benzene, radon, ammonia, boron, and silicon);
- (2) their use in H₂S abatement systems at operating power plants (vanadium); and
- (3) their formation in the atmosphere as a result of geothermal emissions (sulfate).

This list is believed to cover all emissions from current geothermal steam utilization which are relevant in evaluating public health concerns in nearby populated areas of Lake County. The results of the monitoring program are described herein.

Method of Measurement and Analysis

Methods chosen for the measurement and analysis of the non-criteria pollutants have been selected based on their ability to provide:

- 1) measurements comparable to ambient air quality standards;
- 2) the lowest feasible level of detection;
- 3) the greatest precision; and
- 4) a cost effective program.

Altshuler

For these reasons, the respirable suspended particulates, sulfate, particulate boron, and ammonia (four 6-hour samples) measurements are performed on a 24 hour basis every sixth day in phase with the ARB's total suspended particulate sampling schedule. Mercury vapor is sampled using a continuous (hourly integrated) analyzer to further our understanding about its behavior at The Geysers. Conversely, radon (monthly) and benzene (one, one hour sample per month) are sampled less aggressively. Boron deposition is collected similarly to wet/dry deposition sampling performed elsewhere in acidic deposition monitoring programs.

Measurement Procedures & Accuracies

Table 1 presents the measurement procedures and estimated overall accuracy of each of the measurements. The overall accuracy is assumed to be the sum of the estimated component accuracies (flow, time, analyses, etc.) and, thus, represents a worst case assessment as it does not account for off-setting inaccuracies.

Quality Control/Quality Assurance Activities

Rigorous quality control and quality assurance activities were maintained throughout the program. These procedures were submitted to the GAMP consortium for approval prior to initiation of field measurements in 1983. These activities include routinely scheduled calibration audits and detailed record keeping of all activities. The results of these activities are reported with the original data.

Results

Table 2 lists the maximum concentrations of the measurement program. The following is a discussion of each of the parameters measured.

(A) Mercury Vapor

Mercury vapor measurements have revealed some of the most interesting data during the program both in magnitude and seasonal trends. Measurements in 1982 were generally an order of magnitude lower than similar measurements in the same calendar quarter of 1983(1). Mercury vapor data also exhibit a decline in magnitude as each program progressed from their summertime start date, Figure 1. We

speculate that this trend can be correlated to ambient temperatures with the belief that mercury vapor is being eluded from known soil deposits of cinnabar in the area. The 1983-84 data show a similar trend with lowest mercury measurements occurring in mid-winter. However, one of the highest mercury vapor measurements, 0.165 ug/m³, at Anderson Springs coincided with one of the first days of extensive rainfall, November 8, 1983. We have found no explanation for this phenomenon. Mercury vapor measurements do not correlate with particulate mercury measurements from the dichotomous sampler filters, coarse or fine.

(B) Ammonia

Ammonia concentrations were similar in magnitude to concurrent hydrogen sulfide concentrations at Whispering Pines in 1982(1). A significant relationship was determined for this four month data set. This is not unexpected as ammonia and hydrogen sulfide are usually emitted together in similar concentrations by volume from unabated geothermal activities. However, the ratio of hydrogen sulfide to ammonia emissions may differ from H₂S abated sources(1).

(C) Radon

Monthly radon measurements have been low to date. However, highest radon concentrations (3 to 4 pCi/l) have occurred in December 1983 during an extremely wet month. Conversely radon concentrations ranged from 0.2 to 0.7 pCi/l in January 1984, an extremely dry winter month.

(D) Respirable Suspended Particulates, (RSP)

The RSP measurements uniquely characterize the airborne particulates for the first time at The Geysers. It is significant that near detection limit quantities of particulate mercury, arsenic, and vanadium were measured during the program. Automotive emissions of lead and bromine were measured. Earth elements of iron, titanium, and silicon were commonly measured. Chlorine, believed to be ocean derived, was measured in greater concentrations on days with greater wind velocities coming from the coast. Size wise, coarse particulates (2.5 um to 10 um) dominated the size fraction in the summer of 1983 and more fine particulates (less than 2.5 um) dominate in the winter of 1983-84.

(E) Boron

Ambient particulate boron measurements are

low with little relevant interpretation currently discernable. The boron deposition measurements, more useful for vegetation impact assessment than public health, are difficult to interpret. Also, variations in rainfall have affected the reported data. The collection of dew in the dry bucket in the colder months (not uncommon in dry deposition sampling) contributes to the confounding of the results. Thus, these boron deposition data are more qualitative than quantitative.

(F) Benzene

Ambient benzene measurements have been very low and no relevant trends are evident. These data indicate that geothermal benzene emissions appear to have an insignificant effect on air quality in the area of study.

(G) Total Suspended Particulates, (TSP)

TSP concentrations measured to date have all been below the California 24 hour TSP AAQS, 100 ug/m³ and the EPA 24 hour AAQS, 260 ug/m³.

(H) Sulfates

The sulfate data measured using the hi-vol and the dichotomous sampler provide two unique data sets for comparison. The size fractionation of the sulfates in the dichotomous sampler shows that the majority of ambient sulfate is in the fine, less than 2.5 um, size. While the hi-vol and dichotomous data do not correlate statistically, they do show similar measurements both of which are in the range of their detection limits. We believe that the lack of correlation between the two sets of sulfate data is not due to artifact formation on the hi-vol filter paper since the hi-vol sulfate data is not consistently higher than the dichotomous data as it would have to be. Also, very little sulfur dioxide is present in the ambient in this area. Sulfate measurements at the two different sites in 1982 showed a significant relationship indicating area wide uniformity of sulfate concentrations(1).

Comparison of Results with Health Based Criteria

World-wide AAQS's for the non-criteria pollutants measured during the described programs are(2):

- 1) arsenic, 3 ug/m³ for 24 hours (Czechoslovakia and USSR),
- 2) mercury, 0.3 ug/m³ for 24 hours (USSR),

- 3) vanadium pentoxide, 2 ug/m³ for 24 hours (USSR),
- 4) ammonia, 100 ug/m³ for 24 hours (Czechoslovakia) and 200 ug/m³ for 24 hours (USSR), and
- 5) benzene, 800 ug/m³ for 24 hours (Czechoslovakia and USSR).

Presumed safe levels reported at the World Health Organization International Symposium, June 1974, in Paris, France are(3):

- 1) arsenic, 5.9 ug/m³ for 24 hours,
- 2) mercury, 0.8 ug/m³,
- 3) vanadium, 6.8 ug/m³, and
- 4) boron, 59 ug/m³ for 24 hours.

The Ontario Ministry of the Environment established the standards(4):

- 1) arsenic, 5 ug/m³ for 24 hours and 15 ug/m³ for 15 minutes,
- 2) mercury, 2 ug/m³ for 24 hours and 5 ug/m³ for 30 minutes,
- 3) vanadium, 2 ug/m³ for 24 hours and 5 ug/m³ for 30 minutes, and
- 4) ammonia, 3600 ug/m³ for 30 minutes, and
- 5) benzene, 10000 ug/m³ for 24 hours.

Clearly, the measured concentrations of these non-criteria pollutants in Lake County are much less than any of these standards.

Ambient concentrations of sulfate, RSP, and TSP were all less than their respective California AAQS, 25, 50, and 100 ug/m³ for 24 hours.

Conclusions

The non-criteria air monitoring program described herein is a progressive program designed to answer today's questions regarding ambient effects of geothermal power plant air emissions. Except for ambient hydrogen sulfide concentrations, all other criteria pollutants downwind of The Geysers are below existing ambient air quality standards in the state of California. Pollutants for which a standard does not currently exist for in California (mercury, arsenic, vanadium, benzene, ammonia, boron, silicon, and radon) are all below standards reported in the literature for other nations. Except for mercury vapor, radon, and ammonia, all of these pollutants were measured at near detection limit concentrations using methods that are state-of-the-art.

Mercury vapor does, however, warrant watching as an apparent increase in ambient concentrations has been measured from 1982 to 1983. These mercury

Altshuler

concentrations may be natural to the area and more related to the known geologic cinnabar deposits and past mining operations in the area than due to geothermal steam utilization. The higher December 1983 radon measurements compared to the January 1984 measurements suggest that rainfall patterns have a more measureable effect on ambient radon concentrations than geothermal emissions; more work is required to verify this observation. Ammonia concentrations, while measureable and statistically correlated to ambient H₂S measurements in 1982, are, nevertheless, very low when compared to health based criteria.

Data from the 1983-1984 program are providing a valuable baseline to assess future (1986-1987) GAMP data.

Acknowledgements

The authors wish to acknowledge California ARB Haagen-Smit personnel for their assistance in the program by providing chemical analyses.

References

1. Altshuler, S.L., Lin, C., and Arcado, T.D., "Concentrations of Non-criteria Pollutants in the Vicinity of Geothermal Power Plants at The Geysers, California", presented at the 77th Annual Meeting of the Air Pollution Control Association, San Francisco, Calif., June 1984.

2. Stern, A.C., Air Pollution, Vol. III, Sources of Air Pollution and Their Control, 1968.

3. Wilcox, S.L. et. al., "Establishing Safe Ambient Air Quality for Eighteen Hazardous Pollutants", Preprint, World Health Organization, 1974, presented at Organization International Symposium, Paris, France, 1974.

4. Ontario Ministry of the Environment, "Hazardous Substances List and Handbook", Report Number ARB-TDA-33-76, 1976.

TABLE 1
ESTIMATED MEASUREMENT ACCURACIES
AND DETECTION LIMITS

Parameter	Analytical Method	Relative Accuracy, %	Detection Limit
Mercury vapor -continuous -24 hour	Jerome analyzer gold film	± 10	10 ppt 0.004 ug/m ³
Radon	Type F, Trachetch	± 50	0.1 pCi/l
Boron (deposit)	ICP analyses	± 50	1 ug/m ² -d
TSP	Hi-vol, gravimetric	± 11	1 ug/m ³
Sulfate	Hi-vol & turbidimetric	± 15	0.3 ug/m ³
RSP, PM 10	Sierra dichotomous gravimetric	± 35	0.3 ug/m ³
RSP elements	XRF analyses (As,Hg,V,Si,S)	± 20	0.001 ug/m ³
Boron (part.)	Lo-vol & ICP anal.	± 20	0.01 ug/m ³
Ammonia	Lo-vol & specific ion	± 25 **	0.2 ug/m ³
Benzene	Gas chromatography	± 20	0.1 ppb

TABLE 2
MAXIMUM CONCENTRATIONS (UG/M3)
1983-84 PROGRAM
August 1, 1983 - July 31, 1984

	Anderson Springs	Glen Brook
Mercury vapor, hourly ppt	70	48
Radon, pCi/1	3.95	3.00
Boron wet/dry deposition, ug/m2-day *	<238/<78	<1071/<116
TSP	93	64
Sulfate	3.7	3.1
RSP PM 10	46.1	46.3
- arsenic (fine/coarse)	0.014/0.003	0.004/0.003
- mercury (fine/coarse)	0.005/0.005	0.004/0.008
- vanadium (fine/coarse)	0.002/0.004	0.003/0.002
- silicon (fine/coarse)	1.239/6.806	0.796/3.816
- sulfate (fine/coarse)	3.814/2.074	2.835/0.723
Boron particulate	0.56	0.88
Mercury vapor, 24 hour	0.165	0.273
Ammonia	14.15	17.8
Benzene, ppb	3.6	4.6

*Concentrations are biased high due to effects of rainfall and dew.

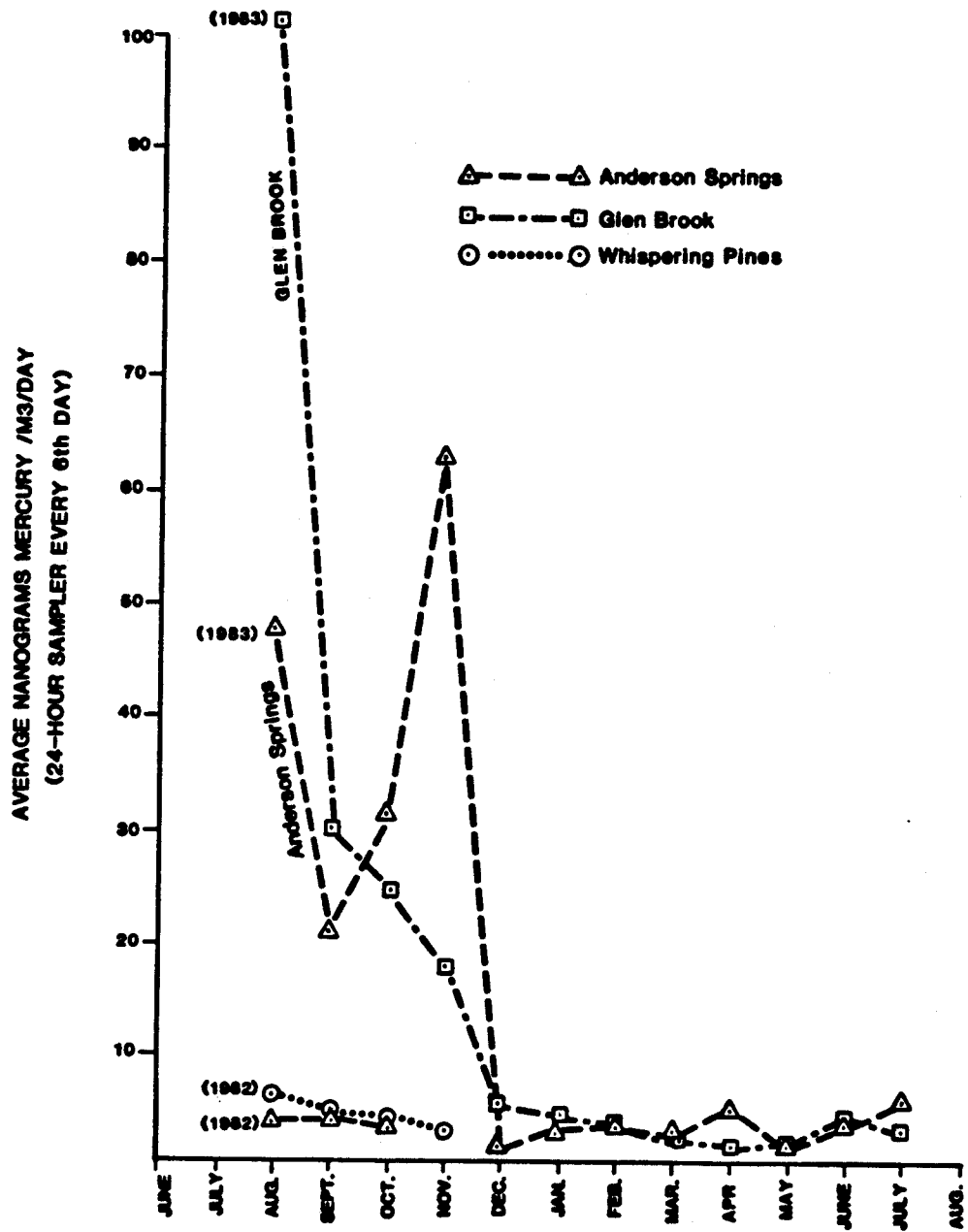


FIGURE 1. Monthly Average Mercury Measurements