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HAWAII ENERGY RESOURCE OVERVIEWS

volume
4

GEOTHERMAL

THE ENVIRONMENT

3. impact

S. M. SIEGEL & B. Z. SIEGEL

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OVERVIEWS OF GEOTHERMAL DEVELOPMENT IN HAWAII

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THE IMPACT OF GEOTHERMAL RESOURCE DEVELOPMENT IN HAWAII

(INCLUDING AIR AND WATER QUALITY)

by

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A. The Environmental Consequences of Natural Processes in a Volcanic-Fumerolic Region

Although geothermal development is projected for all the Hawaiian Islands, the active volcanic region in and around Kilauea, where the current Hawaii Geothermal Project well is located, is a unique situation. This area presents a series of engineering challenges, public concerns, and questions of investiment capital; however, for a purely environmental perspective questions of geothermal development may find ready answers in the moderately extensive studies conducted on volcanic activity and its impact on the environment. The following section deals with these issues.

1. Acute Ecological Effects

a. The Physical

Both seismic and eruptive activities in volcanic zones can, at their extremes, lead to local or regional catastrophe. In themselves such devastating effects of volcanism are of little concern with respect to the environmental impact of forthcoming and future KGRA development in Hawaii. However, the development of geothermal power in regions of active volcanism does have significant impact on investment risks and engineering design. To the extent that eruptive violence has shaped the extant flora and fauna of these islands by selection for stress resistance, its main features must be recognized.

A description of the 1959 Kilauea eruption (after Wentworth, 1966, Smathers and Mueller-Dombois, 1974) will suffice to characterize such major events in general. Kilauea Iki is a pit crater adjacent to the NE rim of the caldera of Kilauea volcano. The contained area rises nearly 1300 m above sea level and 6000 m above the ocean floor. Halemaumau, the main vent of Kilauea is a collapsed crater in the summit caldera. Kilauea Iki had two eruptions in recent historic time prior to the 1959 event, namely in 1832 and 1868. The December 1959 eruption originated at a rift in the crater wall and deposited a blanket of ash over an area of 500 hectares (5 km^2). The site soon came to be called "Devastation Area" and appropriately so.

> As lava poured from its rift, the Ohia (Metrosideros) forest on the crater floor and walls to a height of ca 115 m below the rim. Kilauea Iki crater was filled with a lava lake 140 m deep.
>
> Surrounding areas exposed to heat were rapidly desicated and the tender-dry vegetation ignited.
>
> The deposition of pyroclastics which accompanied fountaining reached rates of more than 10 cm/hr buried a large area of surrounding forest and stripped trees over an even greater one.
>
> Surrounding the area of complete burial, there lies a "tree mold" zone where whole trees not exploded and ignited left their imprints in the pyroclastic fallout. Further out the abrasive action of the pumice and scoria wrought extensive injury, but did not kill.
>
> Beyond the area of devastation, fume damage was evident and locally at least, these fumes were quite acidic. Vent condensates themselves exceeded an acidity equivalent to 1.9 N Hcl.
>
> Although the specific pattern of ash burial, stripping and excoriation and fume effects will vary from one eruption to another, the general pattern as set forth here is typical.
>
> In its aftermath, the eruption left massive pahoehoe (ropy) lava on the crater floor, a new cinder cone and areas covered with spatters or pumice to depths of as much as 46 m. Also created were 6 new habitats as distinguished by substrate type and remains of vegetation. Save for those sites on the cinder cone returning high near-surface substrate

> temperatures (e.g. 50^{o} at 6 cm depth) which were delayed 2-3 years, regeneration and colonization processes were rapid, starting almost immediately. For example, on the new crater floor, invasion and colonization from the edge one year post eruption included algal, moss and fern species penetrating 11 m inward. By 1962, 10 species had reached inward as far as 48 m; and by 1968, 30 species had advanced as far as 25 cm or 80% of the distance to the center. It should be remembered that this particular location was in effect the zone of total burial and incener- ation which began its cooling phases as a hard lava surface traversed by cracks venting their contained heat for some time.
>
> Undisturbed forest lay 6 cm from the edge of the new cone. In this more open environment above the lava lake, the grasses, herbaceous plants and shrubs had moved 10 m inward within the first year (although algae had colonized the entire distance to the cone slope). Overall, for higher plant forms, the half-way mark was reached or passed between years 3 and 4 post eruption and contact virtually completed for many vascular plants and all cryptogams by year 7. Within the devastation zone, regeneration of growth in surviving perennials (trees and shrubs) near the outer reaches attained 60-100% in some cases. Examples are species of *Metrosideros*, *Vaccinium* and *Styphelia*.

One of the consequences of a long history of volcanism and eruptive events of varying duration and destructive force has been the selection of individuals, and eventually populations, capable of withstanding and/or recovering from severe injury. A second lies in the presence of populations capable of invading and establishing vegetation on the new surfaces left in the aftermath of an eruption. That this capability should be a common feature of many Hawaiian species is implicit in the colonization history of the islands themselves.

b. The Chemical

Beyond the range of what may be appropriately considered "blast" and "attrition" zones, there remain the areas exposed during eruptions to gaseous emissions.

The toxicity of volcanic effluents is recognized, and will be considered below more specifically, but it is appropriate to note here that the release of H_2S, SO_2, SO_3 (H_2SO_4) hydrohalogens and mercury may be enhanced during eruptions over their normal output from fumeroles and vents (Siegel, B. and Siegel, S., Oct. 1977, Siegel, S. and Siegel, B., 1975 and Siegel, B. and Siegel, S., Sept., 1977).

For example, during the Kalalua eruption of September-October, 1977, the SO_2 and H_2S levels 1 km downwind from the nearest vent rose more than 25-fold over their August values. The H_2SO_4 concentration did not show a corresponding rise, but on other occasions, rainfall measuring pH 4.0 has been collected in Kona, some 75 km from the nearest vent.

Escalation of mercury during the 1977 eruption was better documented: Field measurements carried out prior to the event established firm baselines, permitting the conclusion that at various locations, the Hg level rose from less than 10 to over 400-fold.

c. A Note on Mercury Health Hazards During Eruption

Approximately 30 days prior to the onset of the 1977 Kalalua eruption on 13 September, air mercury levels were recorded at a number of locations in the Puna district, Island of Hawaii, as locations of the regular surveillance program associated with HGP-A. Subsequent measurements were taken approximately 1.5 and 17 days after its beginnings, and at 32 days, following the decline of fuming and cessation of tremors.

This sequence provides the first actual chronicle of volcanic rift zone air mercury levels over pre- through post-eruption phases (Table 1).

In spite of the importance in Hawaii of the NE tradewinds, air movements over seamount islands terrain may be highly irregular. Thus, the coordinated rise in air mercury at various stations does not necessarily point to coordinated increases in activity at those specific sites, but may rather, represent atmospheric dissemination after emission. This is clearly the case at Station 1, the experimental well HGP-A, which is off the rift zone itself and which had been shut down for many weeks at the time of the eruption. On the other hand, a long-inactive spatter cone at Heiheiahulu, 10 km E (downrift) from the active Kalalua fissure generated an ambient air mercury level of 7.9 $\mu g.m^{-3}$ on 31 July, 1977, some 45 days before the eruption when all other stations read 1.4 $\mu g.m^{-3}$ or less.

Whatever the relative contributions of enhanced local site emissions and dispersal from the eruption zone, an area of at least 250 km^2 and perhaps twice that ranged for some period of time from about 5 to more than 200 $\mu g.m^{-3}$. Put in perspective, McCarthy and others have concluded that the "normal" baseline air value lies between 0.003 and 0.03 $\mu g.m^{-3}$ with open air levels over the E. Pacific even lower (Siegel, S. and Siegel, B., 1975). Even on 9 October, with fountaining ended but continued fuming, aircraft surveys over the active zone revealed 5-18 $\mu g.m^{-3}$ at altitudes of 33-170 m. Near surface air values represent 4-24 hr. averages, not point or peak values, thus, the high ambient

Table 1: Time Course of Eruption-Related Mercury Release During the 1977 Kalalua Event

Station	Location	Air Mercury Level ($ug.m^{-3}$) on:			
		8/13	9/15	9/30-10/1	10/15
	(Relative to E. Rift Eruption Site)	-30d.	+1.5d.	+17-18d.	+32d.
1. Hawaii Geothermal Project-A	20 km ENE	0.5	0.2	4.9	1.1
2. Sulfur Bank	20 km WSW	0.2	1.1	11.3	-
3. Halemaumau (Kilauea Vent)	20 km WSW	0.2	2.0	50	2.5
4. Lava Field	ca 10 km SE 300m W of moving edge	0.5	-	69	1.2
5. Kalalua	1 km E	<0.5	>200	No Access	-

levels were sustained over significant time periods in terms of exposed organisms including man.

Lacking clinical data for exposed populations in and around the active rift zone, no firm conclusions about hazards can be drawn. It has been recently suggested that occupational thresholds for total Hg should be placed between 10 and 100 ug.m^{-3} (8 hr.) and general ambient values between 1 and 10 ug.m^{-3} (Gerstner, J. and Huff, J., 1977). There are no legislated ambient air quality standards for Hg, but the EPA recommended 30 day average concentration is 1 ug.m^{-3}. The latter figure will be reconsidered below, but it is obvious that the hazard potential of natural mercury levels generated during eruptions requires future assessment especially in relation to ambient levels, and developing geothermal sites.

2. Toxic Gas Emissions During Non-Eruptive Periods

a. Composition*

It has been demonstrated that the appearance of a new active fissure is associated with elevated emission of toxic gases and its dissemination into areas which ordinarily contain only low levels of these toxicants. It has been further shown that active fumeroles and vents may infect relatively small amounts of toxicants into the atmosphere at some time prior to the eruption

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*(Siegel, B. and Siegel, S., 23 Sept. 1977, Siegel, B. and Siegel, S., 10 Oct. 1977, Siegel, S. and Siegel, B., 1975, Siegel, S. and Siegel, B. 1978, Siegel, B. and Siegel, S., 30 April 1979, Siegel, B. and Siegel, S., 1978.)

itself. Low output prior to a specific eruption in no way implies that such sources are always negligible during longer periods of quiescence between eruptions, however. This is shown in the air mercury levels at the Sulfur Bank fumeroles over the period 1971-78 (Table 2). Obviously, periods of high mercury output occur frequently at this site, some far higher than those associated with the 1977 eruption. In spite of the approximately 250-fold variation in total Hg, the proportion of elemental vapor (Hg^{o}) varies over only a 3-fold range.

More recent measurements (1976-78) at various natural sites show abundant sulfur gases as well as mercury in some cases (Table 3). Most striking are the Hg levels at the 1971 and 1974 fissures only a few meters apart on the floor of Kilauea. In contrast one of these releases large quantities of SO_2 and CO_2 whereas the other produces little SO_2 and less CO_2.

Sulfuric acid measurements have not been as extensive as those for other gases. In July-August 1977, for example, the Sulfur Bank yielded air values of about 1 $mg.m^{-3}$ and the Halemaumau vent 6.6 $mg.m^{-3}$ under clear dry conditions, 1 $mg.m^{-3}$ during heavy rain. Outside of these specific sites, values were 0.25 $mg.m^{-3}$ and commonly less.

b. Toxicity-Mercury

It is, then, obvious that emissions along the segment of the Kilauea East Rift proximal to the main vent can maintain high air mercury levels in the absence of overt eruptive activity. The Sulfur Bank 7-year mean level of ca 16 $ug.m^{-3}$ (4 $ug.m^{-3}$ Hg^{o}) is probably representative of an area at least 300-400 km^2 in extent

Table 2: Fumerolic Mercury Emission at the Sulfur Bank, Kilauea*

Date	Total Hg (ug.m^{-3})	Hg^{o} (%)
April 1971	22.6	-
May 1971	20.5	-
August 1971	40.7	-
January 1972	2.3	21.7
April 1972	33.5	24.8
December 1973	0.9	22.6
July 1974	10.9	-
May 1975	2.6	31.5
May 1976	7.6	30.2
June 1976	47.5	27.4
August 1977	0.2	-
September 1977	11.3	40.6
August 1978	15.5	13.5

* (Siegel, B. and Siegel, S., 30 April 1979.)

Table 3: Representative Aerometric Values at Kilauea Emission Sites*

Site and Time	Hg ug·m^{-3}	H_2S ppm	SO_2 ppm	CO ppm	CO_2 ppm
Sulfur Bank (18)					
May 1976-Aug 1978	16.4	7.1	7.0	1.9	6272
Halemaumau (8)					
June 1976-Aug 1978	4.2	1.2	4.1	0.5	986
Kilauea (6)					
1971 fissure (Aug 1978)	79.2	0.02	21.2	1.2	18368
1974 fissure (Aug 1978)	29.2	<0.02	0.3	0.6	8288
Puhimau (8)					
December 1976-Aug 1978	5.2	<0.02	<0.02	1.3	2128

*(Siegel, B. and Siegel, S., 30 April 1979.)

on the Kilauea plateau, based on a 10-12 km radius around the main vent. Even at greater distances, e.g. the site of HGP-A, air mercury levels since 1975 during non-eruptive phases have ranged between 0.2 and 1.2 $\mu g \cdot m^{-3}$, fluctuating perhaps around 1 $\mu g \cdot m^{-3}$. Indeed, with the exception of extreme NNE Hawaii, in the quadrant most exposed to "clean" NE tradewinds, air mercury levels ca 1 $\mu g \cdot m^{-3}$ are common, with periods of heavy rain or strong winds as exceptions (fig. 1). Relative soil mercury levels reflect a similar distribution; even precipitation, although less differentiated regionally on the island suggests a similar pattern.

The long term health effects of these natural air mercury levels are not known, but it is clear that local resident populations are exposed to concentrations above recommended threshold. Little information exists pertaining to chronic mercury intoxication by inhalation in animals, although health standards might be applicable to some forms of mammalian life. Even less information is available about atmospheric exposures of plants. Recent experimental chamber tests with mercury have at least that provided preliminary indications of toxic dosages and some categories of plant response (Table 4).

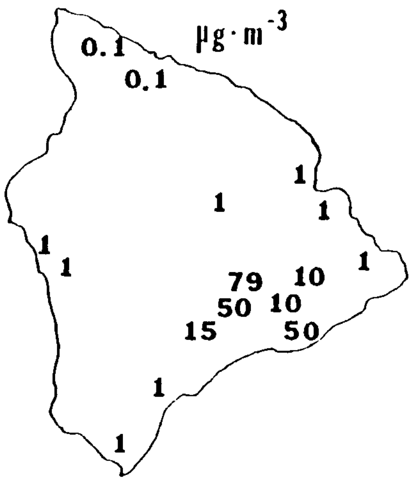
The two toxicants of much interest in geochemical terms are Hg^o and $HgCl_2$, which together appear to account for 90% of the aerometric data in the field. The biogeochemical importance of dimethyl mercury prompted its inclusion here. Although mercury allyls have not yet been analyzed in volcanic effluents

Table 4: Chamber Simulation Tests for the Phytotoxicity of Atmospheric Mercury

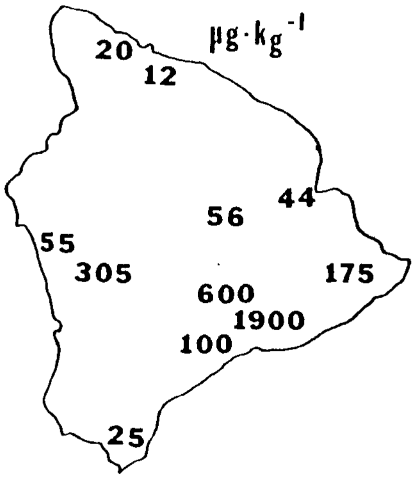
Form of Hg tested	Plant Response	Coleus		Oleander		Castor Bean	
		Hg Concentration (ug·m^{-3})					
		10	50	10	50	10	50
None (10 days)	Chlorosis (% leaf surface)	0		0		7	
	Necrosis (% leaf surface)	0		0		0	
	Abscission (% leaf drop)	3		3		10	
Hg^o (7 days)	Chlorosis	0	3	0	0	0	12
	Nicrosis	0	2	0	0	3	12
	Abscission	13	47	22	94	7	36
$HgCl_2$ (7 days)	Chlorosis	0	0	0	0	0	10
	Necrosis	0	6	2	10	9	23
	Abscission	0	4	4	8	0	0
$Hg\ (CH_3)_2$ (1.5 days)	Chlorosis	0	0	0	0	10	26
	Necrosis	0	8	3	12	5	15
	Abscission	11	32	8	24	14	32

Fig. 1: Distribution Patterns for Total Mercury in Air, Rainfall and Soils, Island of Hawaii. Figures for air and soil are 4-7 year averages; those for rainfall for 1972-73.

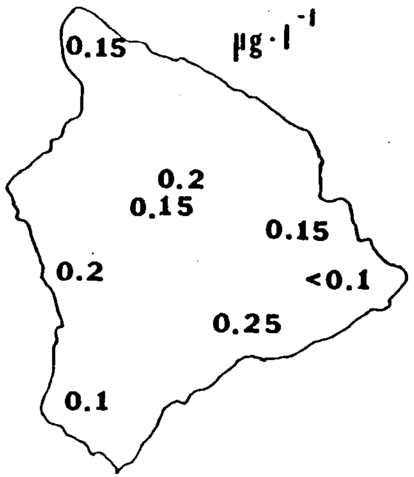
AIR



SOIL



RAIN



their presence in humic, well-watered mercuriferous soils is not unlikely. Methyl mercury is the most toxic derivative toward vertebrate and especially mammalian forms. It is not consistently so toward higher plants when compared with Hg^o vapor (Table 4), although it may act more rapidly by virtue of its hydrocarbon character, hence higher penetration rate.

Between the two inorganic forms of mercury, there is no question that Hg^o is far more effective as a toxicant, even at the lower concentration, and over a brief - 7 day - span of time. The effects of $HgCl_2$ are minimal except for higher concentrations on the seedlings. The chloride, as fallout requires a soil solution concentration of at least 100 $ug{\cdot}kg^{-1}$ to be effective against higher plants, but may be returned to the atmosphere as $(CH_3)_2Hg$ generated by soil micro lora or, more significantly as Hg^o generated by soil algae, fungi, lichens, mosses and higher plants.

c. Toxicity- Sulfur Compounds*

Depending upon location, the natural emission sources in Hawaii range H_2S ambients of 0.002 to high values of 1.2-7.1 (2 year average). These values offer no occupational hazard (Table 5). The higher levels are far in excess of the California

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* (Stopinski, O., 1978, Amer. Conf. of Gov., Indust. Hygienists, 1975, Martin, W. and Stern, A., 1974, U.S. Dept. of H.E.W., 1970, Amer. Lung Assoc., April, 1976, Amer. Lung Assoc., 1978, Siegel, B. and Siegel, S., 14 Feb. 1978, Hawaii Occupational Safety and Health Standards Act 57, 1972, Revised 1977.)

Table 5: A Summary of Environmental Standards for Sulfur Compounds

	STANDARD			
Compound	Occupational		Ambient Air Quality	
	Threshold Limit (8 hr. avg.)	Short Term (5 min.)	California ppm	National ppm
H_2S	10 ppm	20	0.03	-
SO_2	13 ppm	20	0.042 (24 hr) 0.5 (1 hr)	0.14 (24 hr, primary) 0.5 (3 hr, secondary
H_2SO_4	1 $\mu g.m^{-3}$	3	-	-

air quality standard and those of most other areas, both in and out of U.S. jurisdictions.

In the case of SO_2, with air values ranging from 0.02 ppm to high 2-year averages of 4-7 ppm and an extreme 3 m level of 21.2 ppm (1971 fissure), shows that even short term occupational health standards can be exceeded at natural sites, and Ambient Air Quality Standards readily and regularly.

Sulfuric acid levels rarely reached the occupational threshold limit value, but one case at the Kilauea vent in excess of the Short Term Limit was observed over a 1 hour interval.

Thus, as in the case of mercury, air contamination levels of sulfur gases in the hazardous range are not rare. The most severe excesses tend to be localized, fortunately.

There is little information concerning the direct effects of H_2S on individual plants, vegetation or eco-systems in general. It should be noted, however, that levels in excess of the general order detection level of 0.03 ppm are commonplace, not only in marine and fresh water sediments, but in swamp, marsh and bog environments in which many kinds of plants and soil microgiota flourish. Hydrogen sulfide has been suspected as a toxicant in forested areas close to pulp and paper mills but other reduced (organic) sulfur compounds may also be implicated.

Until recently, hydrogen sulfide has not been considered to be an important pollutant to vegetation. Its production by industrial sources such as paper mills has certainly created an odor problem, but subsequent agricultural effects have not been deemed important until now. Analysis of leaves near paper mills shows elevated amounts of sulfate. This is a characteristic result of hydrogen sulfide uptake and metabolism. Tree growth in these localities is probably affected by the hydrogen sulfide and, perhaps, other sulfides in the atmosphere. As far as aquatic species are concerned, the most important sources of sulfide are from paper mill effluents and from bacterial action in the bottoms of seas, lakes, and rivers. The introduction of sulfide from the atmosphere is probably negligible. Since natural sources of sulfide have been a feature of the environment during the evolutionary process, the aqueous environment may contain species that are tolerant to low concentrations of sulfide.

In 1936, McCallan et al (1936) noted that there was a scarcity of information on the toxicity of hydrogen sulfide to plants. They surveyed 29 plant species for susceptibility by exposing potted plants in a fumigation chamber. Damage to the leaves was greates in young, growing tissue. Leaves that were wilted immediately after the exposure become necrotic within 24 hr. The temperature during the tests varied from 23°C to 27°C. The relative humidity (RH) was from 82% to 100%. Hydrogen sulfide concentrations ranged from 28 to 560 µg/liter (20 to 400 ppm), and the duration of exposure was 5 hr. Benedict and Breen (1955) also measured effects of hydrogen sulfide (100 to 500 ppm) on several species. They noted considerable species differences and greater susceptibility in younger tissue.

The plant responses in these tests were variable. Resistant plants such as strawberry and peach showed no damage at 280 to 560 ug/liter (200 to 400 ppm). Susceptible plants such as cucumber, tomato and radish were injured at 28 to 80 ug/liter (20 to 60 ppm). The damage increased as the temperature was raised. There were some indications that wilted plants resisted injury, presumably because of stomatal closure.

Sequels to the above work were published in 1940 (Barton, 1955, McCallan and Setterstrom, 1940, McCalland and Weedon, 1940, Thornton and Setterstrom, 1940). McCallan and Setterstrom (1940) compared the length of times required to kill 50% of the organisms in sets of fungi; bacteria; seeds, leaves, and stems of higher plants; and animals, when exposed to 1,400 µg/liter (1,000 ppm) of hydrogen cyanide, hydrogen sulfide, ammonia, chlorine, and sulfur dioxide. Seeds of rye and radish, both wet and dry, were not affected by hydrogen sulfide. However, the plants tested--tomato, tobacco, and buckwheat-- were more resistant to hydrogen sulfide than any of the other gases tested. The animals tested (mice, rats, and houseflies) were more susceptible than the higher plants.

The results obtained by McCallan and Weedon (1940) demonstrated that fungi were not particularly susceptible to hydrogen sulfide. The fungi tested were certainly more resistant than the higher plants (McCallan and Setterstrom, 1940).

Thornton and Setterstrom (1940) endorsed the previous finding (McCallan and Setterstrom, 1940) that the foliage of higher plants is more resistant to hydrogen sulfide than to hydrogen cyanide, ammonia, chlorine, and sulfur dioxide: hydrogen sulfide had no effect on the pH of the exposed tissue.

Seed germination of rye and radish was not affected by hydrogen sulfide concentrations of 350 ug/liter (250 ppm) and 1,400 µg/liter (1,000 ppm) in tests made by Barton (1940). Although the results are not strictly comparable, Reynolds (1974) reported similar results indicating that aqueous solutions of sulfide at 25 and 50 mg/liter have no effect on the germination of lettuce seed.

Faller (1972) reported results of experiments in which young sunflowers were exposed to hydrogen sulfide fumigation, while these plants had no alternative nutrient source of sulfur. The experiment lasted 3 weeks. During this time the hydrogen sulfide gas concentration varied between a few micrograms per liter and 280 ug/liter (200 ppm). Both fresh and dry weights of the buds, the first five leaves, the stems, and the roots were taken. The plants exposed to hydrogen sulfide were heavier in all respects than the controls which were not supplied with sulfer in the nutrient solution. There was no evidence of lesions in the exposed plants which behaved as plants normally do when sulfate is present in the nutrient solution. Sulfur analysis of the plants showed the accumulation of sulfur, particularly in the roots. This contrasts with exposures to sulfur dioxide, during which sulfate accumulates in the leaves.

These results of Faller demonstrated that *hydrogen sulfide can act as the sole sulfur source for the nutrition of sunflower*.

McCallan *et al*. (1936) reported that normally grown flowers of sunflower were moderately damaged by exposure to hydrogen sulfide at 84 to 112 µg/liter (60 to 80 ppm) and 280 to 560 µg/liter (200 to 400 ppm). Thus, sunflower fell into the intermediate category as far as susceptibility to hydrogen sulfide was concerned. The results of Faller (1972) and McCallan *et al*. (1936) are, therefore, in marked contrast.

Continuous exposures of alfalfa showed that 4.2 µg/liter (3 ppm) of hydrogen sulfide caused visible lesions in 5 days. Yield was also reduced at that concentration and, in one variety, at 0.42 ug/liter (0.3 ppm). No effect was seen at 0.042 µg/liter (0.03 ppm). In normal agricultural practice, alfalfa is cut, then allowed to regrow. Thompson's exposure of alfalfa to hydrogen sulfide resulted in successive harvests that showed yield reduction clearly at 0.42 µg/liter (0.3 ppm). White or yellow lesions were the first visible damage to leaves. Ponderosa pine showed no effect of hydrogen sulfide concentrations at 0.042 µg/liter (0.03 ppm), but developed tip burn after 8 weeks of exposure to 0.42 µg/liter (0.3 ppm). The resistance of pine was consistent with the low accumulation of sulfur in the foliage.

Surprising results were obtained with alfalfa, lettuce, and sugar beets (Thompson and Kats, 1978). The yield of these vegetables increased after exposures to hydrogen sulfide at 0.03 - 0.100 ppm. These results are consistent with the results of Faller (1972) except that they were obtained at lower concentrations of hydrogen sulfide. The yield of lettuce was reduced at hydrogen sulfide concentrations of 0.3 ppm.

Sulfide toxicity in plants can occur in waterlogged soils. Ford (1973) reported this problem in citrus in the poorly drained flatwood areas in Florida. He determined by laboratory experiment that the threshold concentration of sulfide for root injury is 2.8 mg/liter (aqueous) after 5 days exposure. The formation of hydrogen sulfide in these waterlogged areas can be attributed to bacterial metabolism.

Rice also exhibits injury after exposure to sulfide. Hollis and his coworkers (Allam and Hollis, 1972, Joshi and Hollis, 1977, Joshi, Ibrahim and Hollis, 1975) studied this subject in the United States. There has also been extensive research in Japan (Baba, Inada and Tajima, 1965) and in India (Subramoney, 1965). Joshi *et al.* (1975) measured the effect of various sulfide concentrations on rice seedlings. Oxygen release, nutrient uptake, and phosphate uptake were all markedly inhibited by 1 mg/liter of sulfide; but the nutrient uptake by some varieties was stimulated by 0.05 mg/liter of sulfide. The relationship of oxygen release and nutrient uptake to resistance to physiologic responses (e.g., the conditions known as "Straighthead" and "Akagare") was studied in 28 varieties of rice. Resistant cultivars had higher oxygen release and lower nutrient uptake. The toxic effect of sulfide on rice roots is prevented if the bacterium *Beggiatoa* is present in the soil. Joshi and Hollis (1977) and Pitts *et al*. (1972) noted that the relationship between the rice seedlings and *Beggiatoa* is mutually beneficial. The bacteria oxidize the toxic sulfide, while the presence of the rice seedlings increases the survival of the *Beggiatoa*.

Aquatic Species

Marine. Theede *et al*. (1969) provided a summary of information concerning effects of hydrogen sulfide on marine organisms. They reported that sulfide concentrations of 7 mg/liter were found in the Black Sea at depths below 2,000 m, and that 6.13 mg/liter of sulfide was recorded in the North Sea mudflats. In their own experiments, they exposed lamellibranchs, gastropods, polychaetes, crustaceans, and echinoderms to sulfide concentrations of approximately 7.5 mg/liter. They observed pronounced differences among the species in ciliary activity and survival capacity of isolated gill tissue. The effects of sulfide were less pronounced at colder temperatures, and with mussels gill tissue survival was better at pH 7 than at pH 8. Thus sulfide from developed geothermal areas in Hawaii may have its most pronounced effect on the marine environment.

Fresh Water. There have been several reports of effects of sulfide on fresh water species. Colby and Smith (1967) made a comprehensive study of the effects of paper mill effluents. They measured sulfide concentrations in the water at several depths and at various distances downstream from paper mills. As far as 99 km from the paper mills, they observed oxygen deficiencies and elevated sulfide concentrations near the interface of water and sludge deposits. They thoroughly analyzed the pH and the dissolved oxygen and sulfide concentrations at different depths and temperatures. These parameters were compared with the survival of eggs from walleyed pike. Eggs placed on mats 30 cm above the bottom survived better than those placed on the bottom. In the laboratory, under conditions approximating those on the river, sulfide levels of 0.3 mg/liter (aqueous) were lethal to gammarids and to walleyed pike eggs and fry. Sensitivity to sulfides was greater at lower concentrations of dissolved oxygen. The concentrations of dissolved sulfides found in the river water ranted up to 8 mg/liter (aqueous).

Adelman and Smith (1970) made a systematic study of the interrelationship of sulfide toxicity and oxygen concentration. They determined the mean tolerance limits (TL_m) to sulfide for the eggs and fry of northern pike. They reported that the eggs are more resistant than the fry, the maximum safe sulfide concentration being 0.014 to 0.018 mg/liter (aqueous) for eggs and 0.005 to 0.006 mg/liter (aqueous) for fry. The ameliorative effect of higher oxygen concentration is more apparent in the fry than in the eggs.

The chronic toxicity of sulfide on gammarids was studied by Oseid and Smith (1974). A preliminary study showed that the LC50 was 0.022 mg/liter in an experiment lasting 96 hr. However, tests run for 65, 95, and 105 days showed that the maximum safe level of sulfide was 0.002 mg/liter--10 times less than the 96-hr LC50.

The poor yield of fish in stocked acid lakes is attributable to lethal amounts of sulfide. This problem can be solved by stocking the lakes with young adults which are relatively resistant to sulfide, or by raising the pH of the lakes. The beneficial effect of the higher pH results because the toxicity of sulfide is less than that of undissociated hydrogen sulfide. Bonn and Follis (1967) reported that the TL_m of un-ionized hydrogen sulfide was 0.8 mg/liter (aqueous) at pH 6.8 and 0.53 mg/liter (aqueous) at pH 7.8 At pH 6.8, undissociated hydrogen sulfide was about 50% of the total sulfide; at pH 7.8, it is about 10% of total sulfide. Bonn and Follis (1967) noted that in the shallow acid lakes of northeast Texas hydrogen sulfide reached its minimum concentration (0.15 mg/liter) in the winter months, and rose to its highest concentrations (0.8 mg/liter) of un-ionized hydrogen in the spring, presumably because the increased temperatures favored the bacterial production of sulfide.

The Environmental Studies Board of the National Academy of Engineering (1972) reported the maximum safe concentration of undissociated hydrogen sulfide to be 2 ug/liter. Furthermore, they suggested, to protect aquatic organisms, 1 ug/liter of total sulfides should not be exceeded.

More work has been conducted on the response of vegetation to sulfur dioxide than to any other air pollutant. Reviews of the literature have appeared frequently in the past, including those of Thomas (1951, 1961), Thomas and Hendricks (1956), Daines (1968), Negherbon (1960), Brandt and Heck (1968), and the Agriculture Research Council of London (1967).

Sulfur dioxide is emitted to the atmosphere during the combustion of many fuels, especially coal and petroleum, and in the roasting of sulfide ores during smelting operations. It is also emitted to the atmosphere in regions where active volcanism occurs not only from an active volcano but also from fumeroles and vents that are often found in such areas.

Although accurate figures are not available, it is known that significant economic loss in crop yields due to sulfur dioxide does occur annually. In certain agricultural areas, the losses to growers resulting from sulfur dioxide injury are sufficient to be of economic importance. In addition, there are substantial economic losses to ornamental vegetation used in landscaping, and to forest trees, particularly in coniferous and eastern hardwood type forests. Specific effects on tropical plants and ecosystems are unknown.

Markings on vegetation caused by sulfur dioxide are usually found in areas adjacent or close to the source. By contrast, markings due to photochemical air pollutants are often found many miles from industrial or urban sources because the compounds inducing the markings are produced as a result of reactions in the atmosphere.

During recent years the consumption of coal and petroleum for heating and power production has increased in urban areas with the result that sulfur dioxide markings on ornamental plantings and home gardens are occurring in urban areas and near large power plants serving numicipalities.

Different species of plants vary widely in their sensitivity to sulfur dioxide when exposed to this gas under conditions most favorable for its absorption by the plant. Studies have been made by several investigators and reviews of their work appear widely in the literature. Thomas and Hendricks (1956), and Negherbon (1960), present tables listing a large number of plants under the three categories of sensitive, intermediate, and resistant to sulfur dioxide. From these studies and from personal observations of the authors, the plants shown in Table 6 have been selected as useful indicators of the presence of atmospheric sulfur dioxide on the basis of their wide distribution and relatively high sensitivity and would be useful as indicators.

It should be noted that most trees, with the possible exception of larch, are rated as intermediate to resistant to sulfur dioxide. If the above trees are injured by sulfur dioxide the more sensitive weeds, garden and crop plants in the area should also show injury.

Nearly all varieties of pumpkin and squash that are commonly grown in gardens are very sensitive to sulfur dioxide and will frequently show markings when no other garden plants are marked.

Table 6: Selected Plants Which are Relatively Sensitive to Sulfur Dioxide

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CROPS

- Alfalfa
  - *Medicago sativa*, L.
- Clover
  - *Melilotus* & *Trifolium* sp.
- Cotton
  - *Gossypium* sp., L.
- Safflower
  - *Carthamus tinctorius*, L.
- Soybean
  - *Glycine max*., Merr.

GARDEN FLOWERS

- Bachelor's button
  - *Centarea cyanus*, L.
- Cosmos
  - *Cosmos bipinnatus*, Cau.
- Four o'clock
  - *Mirabilis jalapa*, L.
- Morning glory
  - *Ipomoea purpurea*, Roth
- Sweet pea
  - *Lathyrus odoratus*, L.
- Violet
  - *Viola* sp.
- Zinnia
  - *Zinnia elegans*, Lorenz

TREES

- Catalpa
  - *Catalpa speciosa*, Warder
- Mulberry
  - *Morus microphylla*, Buckl.

GARDEN PLANTS

- Beet, table
  - *Beta vulgaris*, L.
- Carrot
  - *Daucus carota var*. *sativa*, L.
- Endive
  - *Cichorium endivia*, L.
- Lettuce
  - *Lactuca sativa*, L.
- Okra
  - *Hibiscus esculentus*, L.
- Pepper (bell, chili)
  - *Capsicum frutescens*, L.
- Pumpkin
  - *Cucurbita pepo*, L.
- Rhubarb
  - *Rheum rhaponticum*, L.
- Spinach
  - *Spinacea oleracea*, L.
- Sweet potato
  - *Ipomoea batatas*, Lam.
- Swiss Chard
  - *Beta vulgaris var*. *cicla*, L.

WEEDS

- Careless weed
  - *Amaranthus palmeri*, S. Wats
- Fleabane
  - *Erigeron canadensis*, L.
- Lettuce, Prickly
  - *Lactuca scariola*, L.
- Mallow
  - *Malva parviflora*
- Plantain
  - *Plantago major*, L.
- Ragweed
  - *Ambrosia artemisiifolia*, L.
- Sunflower
  - *Helianthus* sp.

There are so many symptoms that develop on leaves of plants which resemble those due to sulfur dioxide that no one can truthfully state that he can observe a single leaf, without any additional knowledge, and the state that the injury was or is due to sulfur dioxide and to no other agent or factor. The positive identification of sulfur dioxide markings on vegetation can be made only after all foliar symptoms and related evidence have been considered. These include: (1) the presence of suspected sources of sulfur dioxide; (2) the species of plants that develop markings; (3) the type of markings that are observed; (4) the pattern shown by the severity of the markings and locations of occurrence, i.e., most severe near the suspected source on species known to be sensitive and decreasing in severity with distance from that source. This will depend upon the atmospheric conditions prevailing during the period of fumigation.

Mathematical equations expressing the relationship between the duration of exposure and the concentration of sulfur dioxide have been derived from data of limited time exposures that produce markings on plants (Thomas, 1961, Thomas and Hendricks, 1956 and Brandt and Heck, 1968). In recent years, workers in Germany (Guderian, Van Haut and Stratmann, 1960) have presented additional concentration - time equations which seem to give better agreement over a wider range of observations. Although these relations are of value in predicting what might occur under given conditions of a fumigation, they are not readily adaptable to assessing the economic loss sustained by a crop that has been injured by sulfur dioxide.

In general, yields of crops are not affected unless chronic or acute markings have developed on the leaves. Results seem to show that about 5% of the leaf area must be destroyed before the crop yield for such crops as small grains is significantly or measurably reduced. For alfalfa, experiments indicate that if the leaf destruction is of the order of a few percent (less than 5%) there is no residual effect on the yield even after several fumigations (Nat'l Research Council of Canada, 1939).

The estimation of economic loss to crop plants injured by sulfur dioxide is normally accomplished by taking leaf counts of injured leaves at sampling points throughout the field and from these counts estimating the percent leaf area destroyed for the entire crop. From the leaf-count data the loss in yield is calculated using the procedures described in the literature by several investigators (Thomas, 1961, Thomas, 1951, Brisley and Jones, 1950, and Brisley, David, and Booth, 1959).

Experiments have been conducted to study the effects of toxic amount of sulfur dioxide on the photosynthetic process.

Photosynthesis in alfalfa, which is highly sensitive to sulfur dioxide, was not affected by fumigations with levels up to 0.4 ppm unless the fumigation was continued long enough to produce acute or chronic markings. When visible markings did appear the photosynthetic rate was reduced in proportion to the reduction in the area of photosynthetically active (or injured) tissue. When alfalfa was exposed to sulfur dioxide concentrations of 0.5 ppm or above, the rate of photosynthesis was reduced during the exposure but quickly returned to normal when the fumigation ceased, provided that no acute or chronic injury had occurred. If such injury had occurred, the reduction in photosynthesis generally corresponded to the area of photosynthetic tissue that had been killed or otherwise affected (Daines, 1968, Nat'l Research Council of Canada, 1939 and Thomas, and Hill, 1937). In other words, no physiological effects unrelated to visivle injury have been found as a result of sulfur dioxide fumigations of plants. In recent years, injury without visible symptoms has been ascribed to sulfur dioxide (Bleasdale, 1959 and Guderian and Stratmann, 1962) but these occured under conditions where other air pollutants were present, hence, they cannot be positively attributed to sulfur dioxide alone.

Sulfur dioxide has been studied almost exclusively as a single air pollutant. Recently, however, studies have been conducted to determine the effectiveness of other gases or aerosols in the presence of sulfur dioxide in producing plant injury. Menser and Heggestad (1966) found that sub-lethal mixtures of ozone (0.037 ppm) and sulfur dioxide (0.24 ppm) produced ozone-like symptoms on leaves of Bel-W3 tobacco after an exposure of 2 hrs. This response was later substantiated and reported by

Heck (1968), who also states that a similar synergistic response between nitrogen dioxide and sulfur dioxide was found using the same variety of tobacco.

It is important to remember that annual plants vary over a wide range in sensitivity to sulfur dioxide as they grow from the seedling stage to maturity. This factor combined with differences in environmental conditions has led to much confusion over the relative order of sensitivity among various species of plants.

There is a range of plant markings produced by all air pollutants that visibly affect plants. Some markings are considered to be typical of a given pollutant and are used to identify the pollutant. This is true for sulfur dioxide. There are, however, several agents which produce markings on plants that very closely resemble sulfur dioxide markings (PAN, NO_2, CO_2, HCl). For this reason, it is necessary to examine several plant species within the area where sulfur dioxide injury is suspected in order to determine with any degree of certainty that sulfur dioxide is actually the causative agent.

Once sulfur dioxide enters the mesophyll tissue of the leaves it is exposed to many physical and chemical processes associated with living organisms. It reacts with water to produce the sulfite ion which is slowly oxidized to the sulfate nutritional sulfur and converted to an organic form (Thomas, Hendricks, Bryner, and Hill, 1944). The sulfite and sulfate ions are toxic to plant cells when present in excessive amounts. However, because of its reducing potential, the sulfite ion is estimated to be some 30 times more toxic than the sulfate ion (Thomas, Hendricks, Collier and Hill, 1943).

The accumulation of sulfite in the tissues of the leaves produces two general types of markings designated as chronic markings and acute markings, depending upon the rate of accumulation. If the accumulation rate is slow, the capacity of the cells to oxidize the sulfite ions may never be exceeded and no injury will result until sufficient sulfate accumulates to produce a salt effect. This type of chronic injury is characterized by a general chlorotic appearance of the leaf. A similar type of chronic marking usually occurs following a fumigation of relatively short duration due to the accumulation of sulfite at sub-lethal concentrations. Although the cells are not killed there is a bleaching of the chlorophyll which appears as a mild chlorosis or yellowing of the leaf or a silvering or bronzing of the undersurface silvering due to a collapse of cells immediately beneath the epidermis. While many plants show an ivory or white type of chronic marking, other plants which have strong red, brown, or black pigments normally concealed by the chlorophyll will exhibit these colors following injury.

Chronic type markings due to sub-lethal concentrations of sulfite appear similar to those due to an excessive accumulation of sulfate. In both cases, the leaf remains turgid and apparently continues to function at a reduced level of efficiency proportional to the amount of the uninjured tissue.

Acute injury resulting from the absorption of lethal quantities of sulfur dioxide appears as a margine of dead tissue which at first have a grayish-green water-soaked appearance; upon drying they take on a bleached ivory color. However, as with the chronic injury, brown, red or black colors may predominate in the injured area. After a period of time, the dead or necrotic areas may fall out leaving a very ragged appearance to the leaf. When the major portion of the leaf is so injured an abscission layer often forms at the base of the petiole and the leaf is shed. For most plants, the greater the exposure the closer to the margin the lesions extend until, with severe exposures, the entire leaf may be marked or killed.

The markings that develop on grasses and other monocotyledonous plants such as lilies and gladioli usually occur as necrotic streaks developing from near the tip and extending downward to the base of the leaf alongside the midrib. With grass leaves such as wheat, oats and barley, which usually bend at some point along the blade, the markings often begin at the bend.

Typical sulfur dioxide markings occur on needle-leaved plants such as pines, larch and Douglas fir (Pseudotsuga taxifolia, Brit.). The markings usually begin at the needle tip and extend toward the base. The degree of extension is related to the severity of the exposure. When successive exposures occur a distinct banding pattern often appears (Linzon, 1965). With moderate exposure to sulfur dioxide the older needles of conifer tend to become chlorotic and are shed prematurely. With exposure to larger dosages, needles develop a water-soaked a appearance which soon changes into reddish-brown necrosis of the tip. The necrotic pattern may first appear as bands around the needle with the terminal portion later turning a reddish-brown. Seldom is a completely green needle observed in an affected fascicle. The middle-aged needles exhibit the most necrosis, but the older needles are cast first. Expanding needles are rarely injured (Nat'l Research Council of Canada, 1939, Linzon, 1966, and Scheffer and Hedgcock, 1955). Needles tend to persist on young branches resulting in an absence of needles at the base of branches and at the bottom of the tree. This tendency for older needles to be shed prematurely results in an increasing needle shortage. Such trees have limited growth and may die prematurely (Scheffer and Hedgcock, 1955).

Oats, wheat and barley are fairly sensitive to sulfur dioxide and the tip dieback of leaf blades is a common symptom of injury. However, such tip killing can be produced by many natural causes such as drought, frost and hot weather. Tip dieback is also common on sulfur dioxide-resistant grasses such as corn, sorghum, Johnson grass and many native grasses.

It is characteristic to find both chronic and acute type markings on many plant species following an exposure to sulfur dioxide. This is an important factor used to identify sulfur dioxide injury in the field as opposed to markings caused by other agents. Often both types of markings may appear on the same leaf.

It is the consensus of opinion that sulfur dioxide enters the leaf tissue by way of the stomata. Thus, factors that affect stomatal opening will affect the response of plants to sulfur dioxide (Thomas, 1961, Thomas, 1951, Daines, 1968, Negherbon, 1960, and Ag. Research Council, 1967). Plants in which stomata close at night are much less sensitive to night fumigations than day fumigations. Conversely, plants whose stomata remain open at night are sensitive to both night-time fumigations. Since the stomata of most plants close at night, sulfur dioxide injury to plants results largely from day-time exposures (Katz, 1950 and Thomas, Hendricks & Hill, 1950). Resistance of plants to sulfur dioxide increases as the soil moisture approaches the wilting point (Zimmerman and Crocker, 1934). When the leaves are turgid they are more sensitive than when wilted, since wilted plants are likely to have closed stomate. Thus, moisture stress greatly reduces the sensitivity of plants to sulfur dioxide. Plants are generally more sensitive to sulfur dioxide as the humidity indreases, a response possibly due to the effects of humidity on stomatal opening. There is some indication, however, that at very high humidities of 70% or above some factor other than stomatal opening may be operating (Thomas, Hendricks, Collier and Hill, 1943). These are important considerations for many areas in Hawaii where geothermal development is expected to occur.

Plants have been found to be more susceptible to sulfur dioxide injury when the sugar content of the leaves is low, such as early in the morning as contrasted to afternoon following a photosynthetic period (Thomas, 1961).

Anhydrous ammonia escaping from storage tanks or tractor applicators on farms where is is being used as a fertilizer can produce markings which resemble sulfur dioxide injury. Normally such injury is not difficult to identify except where it occurs simultaneously with sulfur dioxide injury. Many factors can produce chlorosis such as iron deficinecy, lack of nitrogen, or presence of other pollutants such as flourides, insect injury and diseases, all of which may resemble and be confused with sulfur dioxide injury.

The general distinction in toxic dosages among species of varying sensitivity may be summarized as follows:

Exposure	Susceptible	Resistant
30 min.	1-4 ppm	_ca_ 10 ppm
8 hr.	0.05-0.5	_ca_ 2

Two-year ambient SO_2 averages of 4-7 ppm at the more active E. Rift locations place the environs of such emission sites well above the threshold toxicity values. Furthermore, this distinction in susceptibility applies only to cultivated forms of higher plants.

Epiphytic lower plants represent another order of sensitivity to SO_2:

Concentration Range (ppm)	Survival Status of Lichens
0.0035	Normal
0.0035-0.028	Mixed
0.028-0.105	Stress-most species
0.105	Most species absent

Epiphytic lichens and bryophytes are especially sensitive to pollution. The following epiphytes, Caloplaca cerina, Lobaria pulmonaria, Parmelia vittae, Caloplaca ferruginea, Physcia ciliata, Ramalina pollinaria, Ulota ludwigii, Pyrenula nitida, and eight species of Usnea, disappeared from the Netherlands during the last hundred years (Barkman, 1969). In the past, these epiphytes showed a marked decline in their abundance and vitality, a reduction in size (Usnea 50 cm in 1870, reduced to 10 cm in 1969), a loss of fertility (Evernia prunestri 6 cm long and fertile in 1869, only 1 mm in 1930).

Laundon (1967) offers a striking example of affected lichen colonies on limestone memorials erected in a London churchyard between 1751 and 1950. According to him Lecanora dispersa consistently occurs on over 80% of the stones, whereas the presence of Caloplaca heppiana, a more sensitive species, has dropped from a presence of about 90% on stones erected before 1751 to 0% on stones dated after 1901. Perhaps the rising air pollution has made the colonization of new surfaces by C. heppiana increasingly difficult, but it has not yet eliminated already established colonies.

There is an interesting field observation which has confirmed the regeneration of lichens after normal, unpolluted conditions were restored in an area formerly polluted with SO_2. Skye and Hallberg (1969) observed that the lichens near the Knarntorp shale-oil works disappeared as a result of increased levels of atmospheric SO_2 until production at the factory was terminated in 1966. By the summer of 1967 they already saw signs of recovery in certain lichen species which showed renewed growth in the lobes of their thalli.

Studies by Sernander (1926), Jones (1952), Skye (1958), Fenton (1960), LeBlanc (1961), Gilbert (1965), Rao and LeBlanc (1966), Coker (1967), Daly (1970), Taoda (1972), and others clearly demonstrate that the absence of lichens and bryophytes in cities and industrialized areas is mainly the result of the presence of polluting agents. Rydzak (1953, 1959), Klement (1956, 1958) and others have counter-suggested that the absence of lichens in cities is entirely due to a desiccation phenomenon ("drought hypothesis") is the most important environmental factor in determining whether these organisms will survive or perish in urban environments (LeBlanc and Rao, 1973b).

Since lichens are slow-growing and long-lived organisms with a special ability to accumulate substances from their environment (Smith, 1962), they are susceptible to many pollutants present in the atmosphere or brought down in the rain. This sensitivity is heightened by the fact that, unlike tropophytes, they never shed their toxin laden parts. Similarly bryophytes, especially the mosses, with their delicate and uncuticularized plant body, seem to have a great capacity for absorbing and accumulating polluting substances from the environment (Shacklette, 1965). Large volcanic areas (at least 25 sq. km) in Hawaii are heavily covered with a lichen (*Stereocaulon volcanii*) and any changes in its coverage could have significant impact on water retention, erosion, etc.

It must be emphasized, however, that although these effects of SO_2 reflect the impact of urban and industrial effluents on previously "clean" areas, there are no comparable data concerning SO_2-enriched natural (i.e. thermal) environments with long-standing lichen (and moss) flora. In such cases, selection for SO_2 resistance or tolerance may have taken place within a time frame of evolutionary magnitude.

The release of sulfur dioxide and nitrogen dioxide into the atmosphere from fossil fuel combustion is followed by a chemical transformation (hydrolysis) into sulfuric and nitric acids. Even without this man-made input, rainwater would be slightly acid (pH 5.8) if it were in equilibrium with atmospheric carbon dioxide. This relatively weak carbonic acid solution is one of the major factors in the chemical weathering of rocks.

The acidity of rain has increased significantly in recent years particularly in England, Scandinavia, and the eastern United States; for example, at the Hubbard Brook Experimental Forest in New Hampshire, the annual weighted average pH between 1965 and 1971 ranged between 4.03 and 4.19 (Likens *et al*., 1972). The lowest pH recorded at Hubbard Brook was 3.0. In a review of the literature, Likens *et al*. (1972) have suggested that large areas of the United States, which are meteorologically isolated from large industrial centers, notably the Pacific and eastern Gulf Coastal regions, still have relatively high rainfall pH values evidently controlled by carbonic acid.

Likens *et al*. (1972) have suggested several effects on forest ecosystems including changes in the rates of leaching of nutrients from plant foliage and soils. In Sweden, an annual reduction in forest growth during recent years has been possibly attributable to acid rainfall (Engstrom, 1971). An imbalance in the availability of calcium, magnesium, and potassium in shallow soils, already acid, because of the conifer forest cover, may best represent the conditions under which growth would be reduced.

The distribution of acid rainfall in the United States would not necessarily be similar to gaseous pollutants because it would not be a high frequency of stagnant days but rather the synoptic pattern typical of storm systems in relation to pollutant source areas that would control distribution. *The full significance of acid precipitation to forest ecosystems remains to be defined, especially in the tropics*.

Eriksson (1957) reported rainfall pH values and ionic composition data for the saddle road area between Mauna Loa and Mauna Kea at elevations up to *ca* 2000m - some two years after the Kilauea eruption of 1955. Below 1000m his samples averaged 5.0±0.3 and 5.4± 0.2 at higher levels, which were also more distant from the ocean. The composition differed significantly from seawater (relative to sodium) in being enriched in SO_4^{-2} and sometimes Cl^-. This indicates, then, contributions of volcanic H_2SO_4 and HCl to Hawaiian rainfall. Reference has already been made above to even more acidic rainfall (pH 4.0) in Kona, some 75 km from Kilauea, and its adverse effects on tomato crop yields (Kratky _et al_, 1974). This acid rain, also showed SO_4^{-2} and Cl^- enrichment.

Sulfuric acid is particularly efficient in aerosol nucleation when compared with other acids, presumably as a result of its large free energy of mixing in the liquid phase (Katz and Mirabel, 1974). In considering the effects of acid rain exposures it should be kept in mind that acid content of rainwater can vary greatly, even during a single precipitation (Seymour _et al._, 1978). It is also important to take note of differences in plant response to acidic aerosols. Some plants are sufficiently well buffered to allow for internal levels 1-2 pH units higher than those caused by acid deposition on their surfaces (Flücker-Keller _et al._, 1979).

A similar resistance phenomenon based upon neutralization has been reported in man, normal biogenic ammonia of the respiratory pathway being the protective agent (Larson _et al._, 1977).

It is again evident that locations exist, the Kilauea main vent (Halemaumau) for example, that introduce substantial quantities of H_2S and SO_2 emission.

South of the Halemaumau Caldera lies a vast desolation, perhaps 400 km^2 or more in area known as the Ka'u Desert. Its barrenness is striking because many similar areas are at least dotted with lichens, Boston fern and scrub of Ohia. The term "desert" in no way connotes xeric environment and the mean annual rainfall of about 1,200 mm, although highly seasonal, should support the sort of vegetation cover seen elsewhere in Hawaii on similar but younger substrata. It is reasonable, however, to suggest that the combined effects of H_2S, SO_2, H_2SO_4 aerosol, mercury and perhaps other emanations from Halemaumau, carried by the prevailing winds, offer all of the constraint necessary to colonization.

d. A Note on Transformations of Sulfur Compounds

Hydrogen sulfide sources are many and varied, but they are not commonly primary products. Biogenic H_2S originates commonly from microbial reduction of SO_4^{2} in stagnant or poorly aerated conditions. Higher organisms may also release it from breakdown of organic S compounds, but these in turn can be derived from sulfate as well. Anthropogenic sources may also involve reduction of oxygenated sulfur, either directly (e.g. pulping) or release of reduced sulfur of biogenic origin.

Natural volcanic sources were long considered to be primary, that is the direct consequence of magmatic degassing (Bullard, 1962), however this view is no longer supportable. Consideration of oxygen activity and of equilibrium composition limits suggest that SO_2 is the primary species contained in and released from magmas at temperatures of 800-1200°c. (Gerlach and Nordlie, 1975) and that excessively high levels of reduced sulfur may arise as an artifact of sampling procedures (Gerlach, In Press. 1979a, b). The high temperature reduction of SO_2 by ferrous minerals after degassing but at depth (with concomitant formation of hematite) is then a likely source of volcanic and fumerolic H_2S.

A consideration of bond dissociation energies (Cottrell, 1958) yields the stability series:

SO_2 (119) SO_3 (104) H_2S (ca 90)

Figures are $Kcal \cdot Mole^{-1}$.

Atmospheric SO_2 in volcanic regions has, then a dual origin from degassing and from oxidation of H_2S formed at depth. And SO_3 (hence H_2SO_4) is then a product of further oxidation.

In aqueous solution (e.g. ground water) the oxygenation of reduced sulfur results in the species (O'Brien and Birkner, 1977):

S^{-2}, S^o, SO_3^{-2}, $S_2C_3^{-2}$ and SO_4^{-2}.

The rates of oxygenation increase with pH and ionic strength but in acid media (pH 6) SO_4^{-2} is the favored product whereas pH 7 favors accumulation of SO_3^{-2} as well. Evidence supports a stoichiometric model:

$$4HS^- + 5.5\ O_2 \rightarrow S_2C_3^{-2} + SO_4^{-2} + 2H^+ + H_2O$$

The further reactions of atmospheric SO_2 are also photochemical in character (Sander and Seinfeld, 1976).

The primary photo processes involve both singlet and triplet intermediates:

$$SO_2 + hv \text{ -- } {}^1SO_2$$
$$SO_2 + hv \text{ -- } {}^3SO_2$$

and the reactions

$${}^1SO_2 + SO_2 \text{ -- } SO_3 + SO$$
$${}^3SO_2 + SO_2 \text{ -- } SO_3 + SO$$

Secondary chemical reactions then include reactions of ${}^3SO_2$ with O_2, giving SO_3 plus singlet or triplet atomic oxygen, and also yielding SO_4. The reaction of SO_2 with $o({}^3P)$ yields

SO_3 as does the reaction of O with SO_2 in the presence of $^3SO_2$.

Generation of SO_3 can also take place via reactions with O_3 or OH radical, and the presence of NO also facilitates SO_3 formation.

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B. Environmental Consequences of Geothermal Resource Development

From its inception, the Hawaii Geothermal Project's environmental program was predicted on the concept that the toxicology of fluids brought to the surface by human activity could be anticipated from a knowledge of natural fumerolic and volcanic effluents. Thus, it was pointed out (Siegel and Siegel, 1975) that "Pressures for intensified geothermal exploration may induce many enthusiasts to overlook a long-term potential hazard associated with the tapping of magmatic heat sources. We refer to the release into the atmosphere of substances far more toxic and persistent than the usual oxides and hydrides of carbon and sulfur".

This, in turn, was prompted by the first firm demonstration of high ambient air mercury levels around Hawaiian fumeroles (Eshleman, Siegel and Siegel, 1971). These concerns were not limited to mercury but also extended to other toxic elements found in geothermal fluids, including arsenic, antimony, thallium, etc. (Ellis, 1975).

If there are, in fact, no novel toxicants in geothermal effluents released by drilling, then qualitatively, at least, the local biota may well have been selected long since for resistance by exposure to steady fumerolic and periodic volcanic emissions. This possibility, although reasonable in a formal sense, has not yet been subject to field or laboratory verification. An examination of the composition of fumerolic and volcanic gases reveals quantities of some constituants (see Section A above) that probably exceed even the adaptive potential of rugged colonizers, at least in proximity to natural sources.

Furthermore, whatever situation may obtain on the Island of Hawaii where at least some selection pressure for toxicant resistance exists, the frequency of this capability must diminish along the axis of the island chain with increasing age and remoteness of active volcanism.

Whatever uncertainties exist with respect to site and time relations for "built-in" resistance to hydrogeothermal effluents, they cannot be applied casually to the entire ecosystem and certainly not to the late arrivals - man and his introductions.

1. HGP-A as a Site-Specific Model

a. Environmental Setting: The District of Puna Prior to Geothermal Development*

The Puna District, site of the exploratory gwothermal well, is the easternmost projection of the Island of Hawaii, comprising approximately one-eighth of its 4,038 square miles. Much of the District is formed by undissected volcanic uplands, that of Kilauea to the north and that of Kalapana to the south, but between, running from the Kilauea Caldera Complex eastward to the sea around Cape Kumukahi, is the

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*Based largely upon an environmental baseline study (Kamins, et al., 1976) and its updated EIS version (Kamins, 1978).

Puna cone and crater area, marked by pu'us and craters of recent eruptions, notably that of 1955.

With an estimated mid-1978 population of 8,300, Puna is the second most populous of the nine districts of the Big Island -- some distance behind South Hilo District, where approximately 41,000 people live. The basis of comparison is made clearer by noting that only two "towns" in Puna, Kea'au and Pahoa, contain as many as a thousand people. Most of the residents of Puna live near the chief enterprise of the area, the Puna Sugar Company, or in widely spaced clusters of houses along the coast. A slowly increasing number of people have homes in new and largely undeveloped subdivisions served by county-dedicated roads. There are only a dozen houses within a mile radius of the drill site itself.

Over half of the Puna District is thinly covered by histosols, sparse organic soils, which commonly occur on geologically young lava lands. In a band stretching across the west central part of the District -- to the west of the well site -- is an area of entisols, weakly developed soils found on old beach sand and volcanic ash. On this land has developed an area of marked environmental contrast: there is fertile soil and lush vegetation over the lower-lying fields, while the younger upper slopes are dotted with ohias, the most common and most widely distributed species of native tree in Hawaii. Despite abundant rainfall, much of the area around the geothermal site, where recent lava flows have blackened the land, is a suburban wilderness of empty subdivisions. In a few places, thin plumes of steam mark vents where the underground heat of the area escapes into the atmosphere. To the east, however, lies one of the major papaya areas of the State, and to the west, beyond a stretch of sparsely occupied subdivision, are productive sugar lands.

The fact that the project area was covered by lava flows as recently as 1955 necessarily enters into any consideration of long-term development. There is yet no means of estimating the probability of another lava flow, or of disabling earthquake, over the decades that a geothermal field may remain in operation. However, the vulnerability of a geothermal field to such destructive forces is not total. While any surface installations -- the gathering lines, separators, condensers, generators, etc. -- may be destroyed by quakes or by flows which are not diverted (as by protective dikes), the wells themselves are not necessarily so vulnerable. An earthquake of 7.2 Richter-scale magnitude was experienced as HGP-A was being drilled and scarcely affected the operation, so stable was the bore. Since lava flows seldom exceed 15 feet in depth, the wellhead could be protected by a reinforced concrete casement; even if a well site should be inundated with lava, as long as the wellhead was clearly marked, it could be opened.

The hydrology of the Puna District is not well established. It is believed that, as in other portions of the

Hawaiian Islands, the area is underlain by a lens of basal water floating on salt, with a relatively narrow band of dike-confined water (not floating on salt water) running across the southern part of the District, and with a coastal zone of brackish basal water west of Kalapana (Stearns, 1967). It may be that basaltic dikes block off the fresh water lens from the geothermal reservoir tapped by the experimental well.

Sampling of seven water wells within a radius of about two and one-half miles from the geothermal well site revealed high salinity (above 270 mg. per liter) in four of the seven and at depths no greater than a few hundred feet below sea level. While salination of basal water due to intermixing with underlying salt water is a common phenomenon in coastal areas, where unconfined fresh water lenses are thinnest and easily perturbed by tidal effects or heavy pumping, the relatively high salinity of inland wells (such as Malama-ki, Geothermal No. 3, and Airstrip Well) suggests that the Ghyben-Herzberg lens, in which fresh water floats on salt water, if it exists in the portion of Puna around the exploratory well site, is subject to greater intrusion by salt water at the high temperatures of this geothermal regime.

Groundwater in the area and, for control purposes, rainwater samples as well, were tested not only for the chemical characteristics (Table 7), but also for its microbiological qualities (Table 8). Moderately high values for coliform bacteria were recorded at Isaac Hale Park Spring,

PUNA, HAWAII, PRIOR TO DRILLING

EXPLORATORY GEOTHERMAL WELL

NAME	DATE	T^{o} C	pH	Na^{*}	K	Ca	Mg	Cl	HCO_3	SO_4	SiO_2	N^{**}	P
PAHOA STATION	1-6-75		7.30	36.0	2.72	1.58	2.7	13.5	48	21.1	50.0	0.252	0.078
KALAPANA STATION	1-6-75	28.5	7.68	89.6	5.20	5.30	6.6	132.2	38	37.2	44.5	0.070	0.056
KAPOHO SHAFT	1-6-75	25.5	7.80	85.8	6.60	42.4	37	16.9	372	20	53.6	0.378	0.233
AIRSTRIP WELL	1-6-75	33.0	7.42	238	13.6	23.0	28	303.5	48	204	71.3	0.014	0.040
ALLISON WELL	1-7-75	37.5	7.35	216	10.8	13.4	15	281	132	69.2	24.1	>14	<0.002
ISAAC HALE PARK SPRING	1-7-75	36.0	7.75	2020	86.0	32.4	200	3534	56	507	81.5	1.218	0.016
MALAMA KI WELL	1-7-75	52.3	7.02	2105	109	66.8	210	3811	144	471	100.7	0.280	0.006
GEOTHERMAL #3	1-7-75	93.0	6.85	2050	190	76.8	52	3274	30	314	96.6	0.003	0.006
RAIN AT KALAPANA STATION	1-6-75			4.5	0.25	0.25	0.75	7.2		~2.5	0	0.024	<0.002

*CHEMICAL DATA IN mg/ℓ

**NO_2^- + NO_3^- as N

TABLE 8. MICROBIOLOGICAL QUALITY OF GROUNDWATER
PUNA, HAWAII, PRIOR TO DRILLING
EXPLORATORY GEOTHERMAL WELL

WELL/SHAFT NO.	STATE NO.	NAME	DATE OF SAMPLE	COLIFORM MPN No. per 100 ml	FECAL COLIFORM MPN No. per 100 ml	REMARK
9-5	2986	PAHOA	1-6-75	<3	<3	Unchlorinated sample
9-7	2487-01	KALAPANA	1-6-75	<3	<3	Unchlorinated sample
9	3080-02	KAPOHO SHAFT	1-6-75	460	<3	
9-6	3081	AIRSTRIP	1-6-75	<3	<3	
9-9	2783	MALAMA KI	1-7-75	<3	<3	
---	----	ISAAC HALE BEACH PARK HOT SPRING WATER	1-7-75	1500	7	
---	2881	ALLISON	1-7-75	$\overset{=}{<}$24,000	93	Well bottom mud in sample

where the geothermally heated pool is used for casual bathing, and a much higher count was observed for the sample from Allison Well. Otherwise, no results of a cautionary nature were reported in the baseline study. As testing of the exploratory geothermal well proceeds, the existing water wells will be monitored for changes in chemistry or microbiology which may accompany the test flows.

Particular attention must be given to ascertaining if the chemicals commonly found in geothermal water or steam pose a threat to the environment. From May 1975 to date, the environs of HGP-A have been tested for mercury and toxic gases, particularly the sulfur compounds known to be emitted in geothermal areas. With respect to the fixed gases -- SO_2 and H_2S -- there has been no evidence of change from predrilling through recent flashing experiments (see section b, below). These values have been consistently at or below detection thresholds and well under hazardous levels in spite of the proximity (25 miles) of natural vents in the Volcanoes National Park which supply these sulfurous gases continuously. In these fumerole areas, the measurement during 1971-76 yielded peak values as high as 25 ppm for SO_2 and 5 ppm for H_2S. These toxic emissions apparently reach the HGP drill site area only infrequently and for brief periods. Their lack of persistence may be an important environmental consideration. Aside from convective and wind dispersal processes, these gases may be oxidized both photochemically and biochemically to sulfates, and the capacity both of soil microorganisms and vegetation for metabolizing these sulfur gases may contribute to ecological "detoxification."

The same consideration cannot be applied to mercury. It is a potential toxicant in any form, although more so in elemental and alkyl forms. Various figures have been cited for maximum allowable air mercury. Schroeder (1971) has suggested an 8 hour occupational limit of 10 $\mu g/m^3$ but recommends no more than 0.1 $\mu g/m^3$ as a reference figure, it is obvious from Table 9 that HGP drill site levels were at threshold at the time of the flashing experiment, but it will become clear below that up to the 22 July 1976 flashing, the mercury levels were area values not related to drill site operations. Hawaiian thermal areas are essentially like those elsewhere in the world with respect to mercury in air, water, soil and plants (Tables 10, 11), with norms tending to be appreciably higher than in nonthermal areas.

While there are trees on the Puna landscape -- ohia, mangoes, citrus, monkeypods and other ornamentals -- the District is by no means forest-covered. There are four state forest reserves in the District (Nanawele, Malama-ki, Keauhohana and Puna), but only the latter is extensive and none rate among the choice timber areas of the island. Norfolk pines have been planted east of Pahoa in an attempt to supply a local Christmas tree market, but they have not flourished.

It was beyond the resources of the Hawaii Geothermal Project to assess the lesser flora of the Puna District in

Table 9. Past Ambient Mercury Data at HGP-A and Other Sites,
Island of Hawaii

Date	Sulfur Banks	Halemaumau Kau	HGP-Puna	Hilo
		Concentrations ($\mu g \cdot m^{-3}$)		
Apr. 1971	22.6	-	-	-
May 1971	20.5	-	-	0.31
Aug. 1971	40.7	40.5	-	-
Jan. 1972	2.2	0.7	-	-
Apr. 1972	33.5	-	-	-
Dec. 1973	0.9	-	-	-
May 1975	2.6	-	1.1	0.44
May 1976	5.3-10.0	-	1.2	-
June 1976	47.5	5.0	0.9	-
July 1977	1.4	3.9	0.8	0.8
Feb. 1978	9.6	-	1.57	0.6
Aug. 1978	20.4	4.2	0.9	-
Nov. 1979	6.0	-	1.06	0.8

TABLE 10

MERCURY LEVELS OUTSIDE THE HGP-PUNA DRILL SITE AREA: COMPARATIVE AIR AND WATER DATA, 1971-1976

SAMPLE	Hg CONTENT
Air	$\mu g/m^3$
Thermal	
Hawaii	0.7-40.7
Iceland	1.3-37.0
U.S.S.R. Kamchatka-Kuriles	0.3-18
Non-thermal	
Hawaii	0.04-0.3
Iceland	0.62-1.0
New York	$\leq$ 0.014
Cincinnati	0.03-0.21
Eastern Pacific (open sea-west of California)	$\leq$ 0.0007
Water	$\mu g/l$
Poipu Beach (Kauai)	2.1
Kuhio Beach (Oahu)	2.3
Nuuanu Stream	0.6
Oahu aquifer	< 0.2
Rain, Hawaii, January 1972 Island of Hawaii, general	0.20-0.25
HVNP fumarole condensate, 1972	20-40
Western Atlantic, general	0.01-0.30
Hawaii aquifer (Puna)	$\leq$ 0.5

Table I1. Plant Bio-Concentration of Mercury in Relation to Exposure to Natural Geothermal Processes

Site	Exposure factors		Hg Bio Concentration Ratio Distribution		
			0–0.67	0.67-2.0	>2
	Proximity	Soil	(% of Samples)		
Iceland	<500 km,	Volcanic	10	10	80
Hawaii	<500 km,	Volcanic	16	14	70
Alaska	<1000 km,	Volcanic	30	12	58
New England	⩾3000 km,	Non-volcanic	42	18	40

any detail. However, the area within a one mile radius of the drill site was examined, and it seems sufficiently representative of those inland sections of the District which are not either in cultivation or well populated -- and these relatively empty places comprise the bulk of the District -- to warrant inclusion in this description of Puna at large.

The well site is on an exposed lava flow of 1955. The undisturbed part of the flow consists of barren aa, covered by a dense growth of lichens, with scattered ferns and ohia. Further off, around Lava Tree State Park approximately three-quarters mile to the west, there are areas of forest, the size of the trees being related to the age of the underlying lava flow, hence, mainly small to medium height. There are however occasional kipukas (islands of growth on land not subject to recent volcanism), in which some trees reach up to 100 feet. The groundcover around the trees consists largely of false staghorn ferns, grasses and several species of wild orchids. Around the larger trees are some treeferns and ieie vines (Freycinetia arborea). All these endemic species are common to areas of Hawaii covered by lava flows of no great age.

In locations disturbed by roads, footpaths, trails and bulldozer tracks, however, there is a heavy admixture of introduced trees, shrubs, vines and grasses. Such exotic flora are found, for example, in the vicinity of Lava Tree State Park and in many areas downslope from the well site.

This exotic plant population includes mango, papaya, guava, bamboo, kukui (*Aleurites moluccana*), sugar cane, bananas, Indian pluchea, Jamaica vervain, and sensitive plant (*Mimosa pudica*). A stand of Norfolk pines rises between the well site and the Park, and albizia grows along the road and at the Park.

It is impossible to make an absolute determination as to the absence of endangered and threatened species of plants within any area of appreciable size around the well site. However, in the process of making baseline studies of possible geotoxicants sometimes associated with geothermal activity, quadrat and transect analyses were carried out in May 1975 and re-examined in January 1976 at the well site. The genera of plants found at the site, identified in consultation with Dr. Darrel Herbst, then of the Department of Botany are: *Ageratum*, *Andropogon*, *Arundina*, *Asclepias*, *Brachiaria*, *Carex*, *Cassia*, *Castcilleja*, *Cuphea*, *Cyperus*, *Desmodium*, *Dicranopteris*, *Emilia*, *Erichtites*, *Erigeron*, *Lantana*, *Lycopodium*, *Melastoma*, *Melinis*, *Metrisideros*, *Nephrolepis*, *Pluchea*, *Pteridium*, *Rubus*, *Saccolepis*, *Spathoglottis*, *Sphenomaris*, *Stachytarpheta*, *Tritonia*, and *Veronia*.

Comparing these genera with the most relevant list of known endangered genera and species prepared by Charles Lamoureaux, Professor, Department of Botany for the adjacent Hawaii Volcanoes National Park -- and with the comprehensive list of endangered, threatened and extinct species presented by the Secretary of the Smithsonian Institution to the Congress of the United States as House Document N. 94-51, 15 December 1974, it is concluded that endangered and threatened species of plants, if present at all at the well site, are extremely infrequent. Thus, the probability that well site operations will create this type of biohazard is minimal.

With respect to the more general question of hazards to vegetation, it should be noted (1) that toxic emissions resulting from well operations are not likely to differ from those normal to natural vents and magmatic outgassing in Hawaii, and (2) that natural populations established by post-eruption colonization in areas of recent or current vulcanism may be more resistant to toxic geothermal emissions than would be the case in non-volcanic locations.

The region of Puna around the geothermal well site, limited as it is in natural food sources for mammals, is not rich in fauna. The sugar cane fields to the west and the papaya farms to the east of the site support the rats which are found on the main islands of Hawaii. The mongoose is also well established locally. On the slopes of the mountains feral goats are at once quarry for hunters and problems for those who would preserve the ecosystem, but they have not been seen in this section of Puna.

The only valued animals which might be disturbed or conceivably threatened by geothermal development in the District are birds. There are on the Island of Hawaii several species of indigenous of endangered species, and it was necessary to study the area around the well site to ensure that none of these species were adversely affected by geothermal operations. Consequently, the environmental assessment was limited to birdlife which might feed or breed in the area of Puna near the well site.

Field observations in February 1976 were concentrated on looking for the two species of endemic land birds which might be expected at the low elevation (approximately 600 feet above sea level) of the drill site. These are the Hawaiian hawk (*Buteo solitarius*), which is classified as "rare and endangered," and the Hawaiian short-eared owl, or pueo (*Asio flammeus sandwichensis*). No evidence of either was found -- perhaps because most of the native vegetation in the area has been replaced by exotic plants -- but of course it is possible that at times both species may occur in the general area. The hawk, in particular, is a wide-ranging species. This, however, is speculative, since no evidence for its presence was found.

Nor is the area heavily populated with introduced birds. During the survey, only seven species were observed: Spotted dove (*Streptopelia c. chinensis*), Melodious laughing thrush (*Garrulax canorus*), Japanese white-eye (*Zosterops j. japonica*), Common myna (*Acridotheres t. tristis*), House finch (*Carpodacus mexicanus frontalis*), Spotted munia (Ricebird) (*Lonchura punctulata*), and Cardinal (*Cardinalis cardinalis*).

It is the considered opinion of the ornithologist who studied the area that the activities at the geothermal well site have had no adverse effect on any bird species inhabiting the area. Even an adverse effect on some of the introduced birds would not necessarily be detrimental, since some of these species, as the house fince ahd spotted munia, have been highly pestiferous in destroying crops on Hawaii, but no impact on any species was discerned.

Puna has played a relatively insignificant role in the political history of Hawaii. During all of its known history, the District has produced no great family or chief whose support was crucial for control over land contested by warring factions. Why it was that Puna never developed a political power base -- for lack of population or lack of adequate food sources to support a sufficiently strong army -- is not clear, but it is evident that in Polynesian times control over Puna was wielded by the bordering districts of Hilo and Ka'u.

Consequently, there are relatively few archaeological sites in Puna, in comparison with the Kona coast or the northwest corner of the Island of Hawaii, and there is no major site of archaeological research interest in the District. The few sites that exist lie principally along the coast, some distance from likely areas of geothermal development, which are along the rift zones inland.

The most extensive archaeological site complex in Puna is Kahuwaii Village at Makaukiu, above Cape Kumukahi, the easternmost promontory of the Island. Around the cape to the south, near Isaac Hale Park, is Mahinaakaka heiau, in relatively good condition, except for the sea erosion of its eastern wall. Another ten miles down the coast are two additional heiaus and adjacent sites with petroglyphs, at Apua and Wahaula-Puuloa.

More petroglyphs are found near Kapoho, about three miles inland from Cape Kumukahi, and almost four miles from the exploratory geothermal well. These figures are unusual in that they are cut into the face of larger upright basaltic slabs, instead of the usual flat pahoehoe.

In the same general area, approximately two miles north of Kapoho, are the ruins of Kukii Heiau, repeatedly robbed of its stone -- for the building of the foundation walls of Iolani Palace in Honolulu in 1879, again for Queen Kapiolani's residence, and more recently for other construction.

With the exception of the petroglyphs at the Kapoho dome, none of the archaeological sites of Puna seem to be in the path of likely geothermal development in the District. If the Kapoho area is planned or authorized for development, protection of these petroglyphs should be assured before the development begins.

b. HGP-A Well Chemistry:
Water and Light Elements*
Analytical Results

In general the pH is low. Below the cased portion of the well (692 m (2270 ft.)), the pH rarely exceeds 5.0.

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*Based largely on Kroopnick et al. Hydrology and Geochemistry of a Hawaiian Geothermal System: HGP-A. Hawaii Institute of Geophysics. University of Hawaii. May 1978.

The February 14, 1977 depth profile collected shortly after the well was quenched represented the only set of samples with significantly higher pH values as a function of depth. At present, this sample is regarded as anomalous, but the reader should note that the anomaly persists for all water quality parameters analyzed from the sample collected that day. These samples also show high value of conductivity, salinity, chloride, and major cations. Inclusion of this sample will raise the values in statistical reporting, as illustrated in Table 8. Depth samples taken immediately after continuous flow discharge would be desirable in future tests to further evaluate the February 1977 depth profile results.

Because of the interdependence of conductivity, salinity and chloride and the similarity of depth profiles, they are presented together. In general, all three exhibited low values in comparison with those for open ocean water. The three parameters can be characterized as relatively free of variation with depth. Mean and median values for conductivity were 3,500 μmho/cm and 3,100 μmho/cm, respectively, with the standard deviation of 1,360 μmho/cm and coefficient of variation of 39%.

As with conductivity, salinity values are low. Typical open ocean salinity near Hawaii is 3.34%. The mean and median salinity of the depth samples were 2.6% and 2.3%, respectively. The standard deviation of all samples was 1.0%. This corresponds to a coefficient of variation of 39%. Chloride also exhibited low values and small fluctuations as a function of depth (fig. 2). Typical values for chloride in sea water approach 19,000 mg/ℓ. Depth sampling indicated a mean chloride concentration of 1,040 mg/ℓ and a median concentration of 925 mg/ℓ, equivalent to approximately 5% of ocean water. Statistically, the standard deviation of the samples was 465 mg/ℓ and the coefficient of variation was 45%.

All measurements indicated abnormally high silica levels at the HGP-A well when compared with normal Hawaii ground water and surface ocean water. Ground water silica levels rarely exceed 80 mg/ℓ. Silica concentrations at depth in the HGP-A well showed a mean of 440 mg/ℓ and a median of 420 mg/ℓ. The percentage make-up of volcanic rock forms in the Kilauea area is approximately 50%, followed distantly by aluminum oxide (Al_2O_3) at 12% (Stearns and Macdonald, 1946; Stone, 1977a). Individual silica profiles showed little variation with depth, but large variations were observed between sampling periods. The standard deviation was 230 mg/ℓ. The coefficient of variation was 52%.

Sulfide data contained in the HGP-A well depth profiles (Fig. 3) indicated high levels. Any trend with respect to depth is not apparent because of relatively few data points and possible inconsistencies in sample preservation and analytic methods. The data available to date exhibit mean and median sulfide concentrations of 135 mg/ℓ and 100 mg/ℓ,

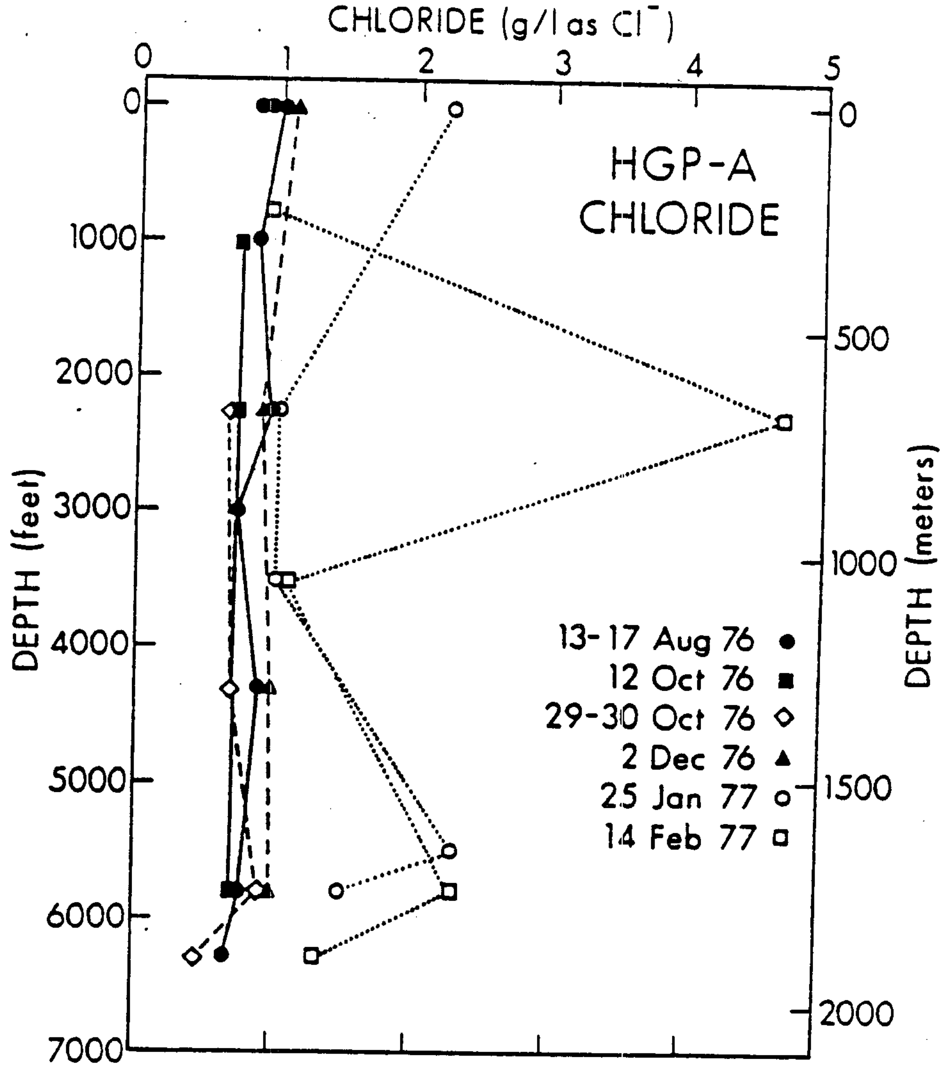

Figure 2. The downhole distribution of chloride for HGP-A.

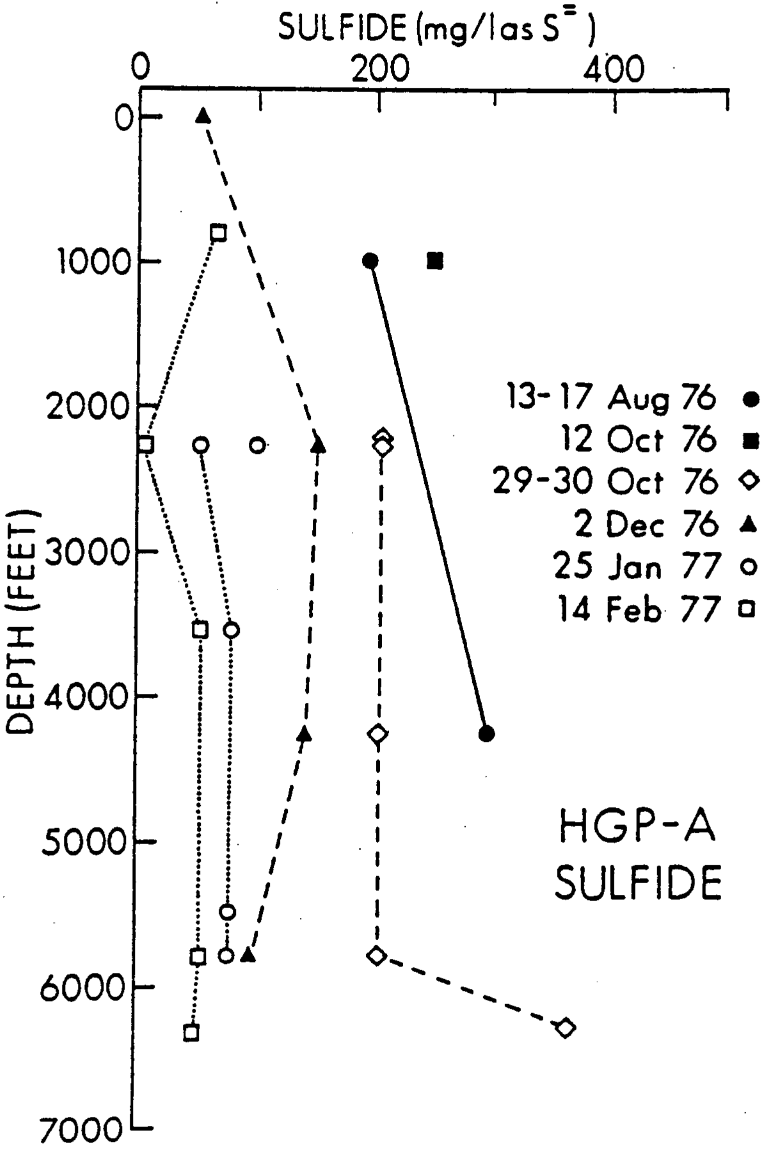

Figure 3. The downhole distribution of sulfide for HGP-A.

respectively.

Analysis of cation concentrations was not actively pursued in depth samples prior to December 1976. As with all other profiled water quality parameters, the cations appear relatively free of variation with depth. The February 14 samples are again regarded as a possible anomaly. The fact that the same anomaly is present in the seven parameters analyzed confirms the analytical validity of the anomaly; and the absence of possible sample contamination would imply that the water entering at 692-m (2270 ft.) depth had a higher proportion of sea water or saline water than water entering at other depths in the well on that occasion.

Low-flow depth profiles were obtained in order to test whether there is a significant flow into the well at 692 m (2270 ft.). The test procedure was to allow the well to discharge at a rate just slow enough to prevent flashing (50 gal/min), thus permitting aquifer water to enter the well and perhaps permitting the normal circulation of water with the country rock. Test results of water samples collected at 732 m (2400 ft.), 692 m (2270 ft.), and 638 m (2092 ft.) show relatively small changes in constituent concentrations as a function of depth (Fig. 4). Most water quality parameters exhibited a range of variation of less than 10% of either the mean or median values for each parameter. Magnesium and calcium demonstrate the largest variation, but these values are substantially below the median level for the no-flow depth sampling program. The

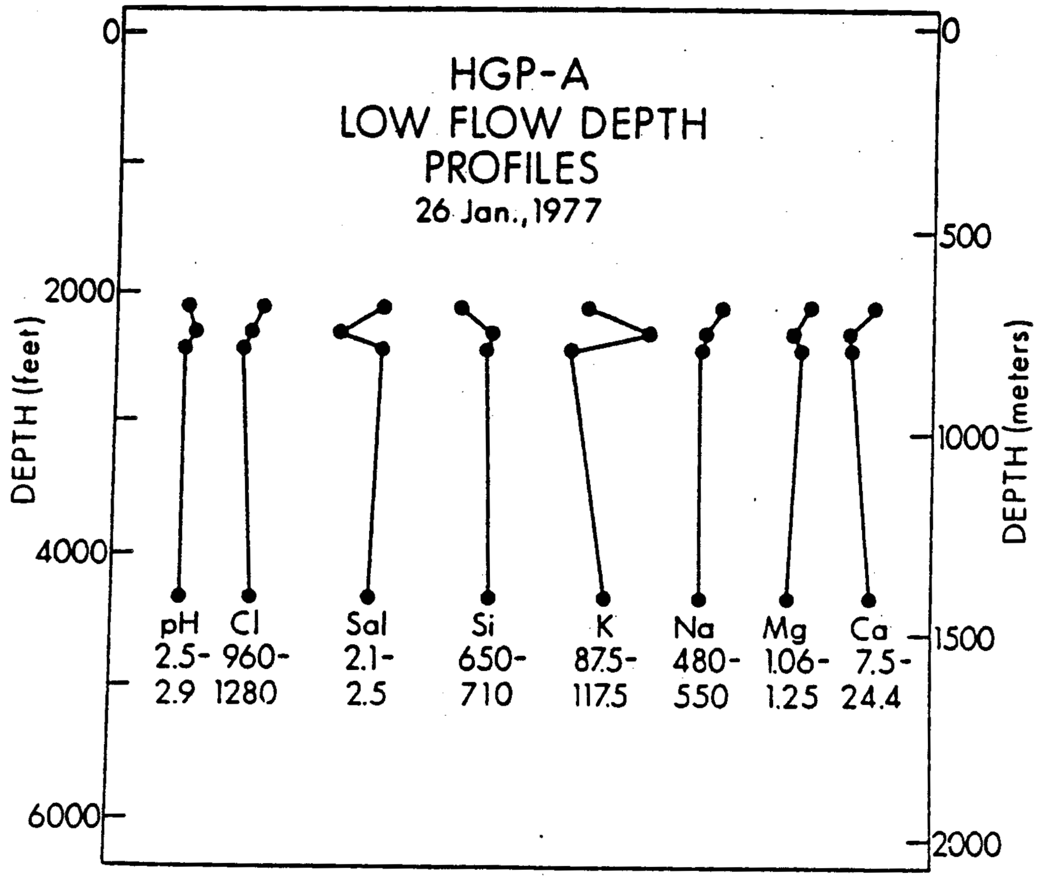

Figure 4. Summary of the data collected during the low-flow conditions. The samples collected from 692 m (2270 ft) appear anomalous for all the elements measured. The highest and lowest values for each parameter are listed below each profile.

results suggest, but do not conclusively show, that there was significant infiltration of water of different quality than that already present in the well. Insufficient flushing of the well could be responsible for the small shifts, because at the time of sampling only approximately 7000 gallons of water were withdrawn from a well whose volume is approximately 18,000 gallons.

The continuous flow condition was characterized by well discharge during flashing. Samples of the well fluid are collected and condensed at the condensate sampling station. Subsequent to steam separation, the liquid portion of the well fluid is sampled from the weir box. The results of the January-February 1977 continuous flow test are discussed here in detail.

A steady state condition for pH was established rapidly in both weir effluent and condensate samples. The steady state pH value was 8.5 at the weir and 4.8 in the condensate. The pH increase in the weir sample is expected since most of the acidic gases (CO_2, H_2S) were lost to the steam phase, exiting the cyclone separator. As with the depth profiling, the interdependence of electrical conductivity, salinity, and chlorides affords a convenient simultaneous evaluation. In general, all three parameters appear to be approaching or to have reached a steady-state concentration in the weir samples. The time required to reach or approach steady state is on the order of two to three days and is thus considerably longer than for pH. The steady-state value for conductivity is about 5900 μmho/cm for weir samples. Because of missing samples, the steady-state value for the condensate samples was not available over the entire sampling period. The conductivity of the condensate samples never exceeded 2400 μmho/cm. Salinity appeared to level off at approximately 4.6% for weir samples. As with conductivity, there is no definable steady-state value for the condensate water for salinity because of missing samples. The salinity of the condensate samples never exceeded 1.4%. Chloride appeared to level off near 2600 mg/ℓ for weir samples. The condensate level is approximately 850 mg/ℓ.

These and several other chemical parameters indicated a discontinuity or abrupt reversal in concentration four hours after the start of flashing. This was close to the time necessary to discharge one total well volume of liquid. Thus, the concentration discontinuity might reflect the flushing of the bore in order to obtain a truer aquifer water sample and hence be indicative of more than one source of the recharging water.

Reliable alkalinity data can only be obtained by measurement of the samples in the field. Unfortunately, lack of manpower prevented measurement of alkalinity on any samples other than those collected in January 1977. The alkalinity, reported as calcium carbonate ($CaCO_3$), was actually present as the carbonate ($CO_3^=$) species due to the high pH observed. The concentration variation with time is erratic and did not indicate any steady state. There appeared to be a steady-state concentration of silica of about 135 mg/ℓ in the weir discharge, whereas the concentration in the condensate was about 285 mg/ℓ (Fig.5). Between the condensate sampling port and their weir discharge, a large proportion of the silica was lost, probably as a result of precipitation. Based on an average value of 70% for steam quality and a total mass flow rate of 76,000 lb/hr, the resultant loss in silica amounts to approximately 450 lb/day. With the exception of magnesium, all cations exhibited a near steady-state condition after a relatively long (36-hr) equilibrium period. As with the majority of parameters, data were insufficient to define the steady-state concentrations for the condensate. Sodium reached a steady-state concentration of approximately 1300 mg/ℓ in the weir samples but never exceeded 400 mg/ℓ in the condensate samples. Potassium levelled off at the never exceeded 70 mg/ℓ. The steady-state concentration for calcium is 80 mg/ℓ. The condensate calcium concentration never exceeded 20 mg/ℓ.

The concentrations of the transition metals copper, chromium, and nickel were all less than 0.1 mg/ℓ (limit of detection). The zinc and manganese concentrations were about .20 mg/ℓ on unfiltered samples. Mercury is present and varies from less than 50 μg/ℓ at the end of the production test to several hundred at the beginning (S. and B. Siegel, personal communication). Cadmium and lead were barely measurable at the .01-mg/ℓ detection level.

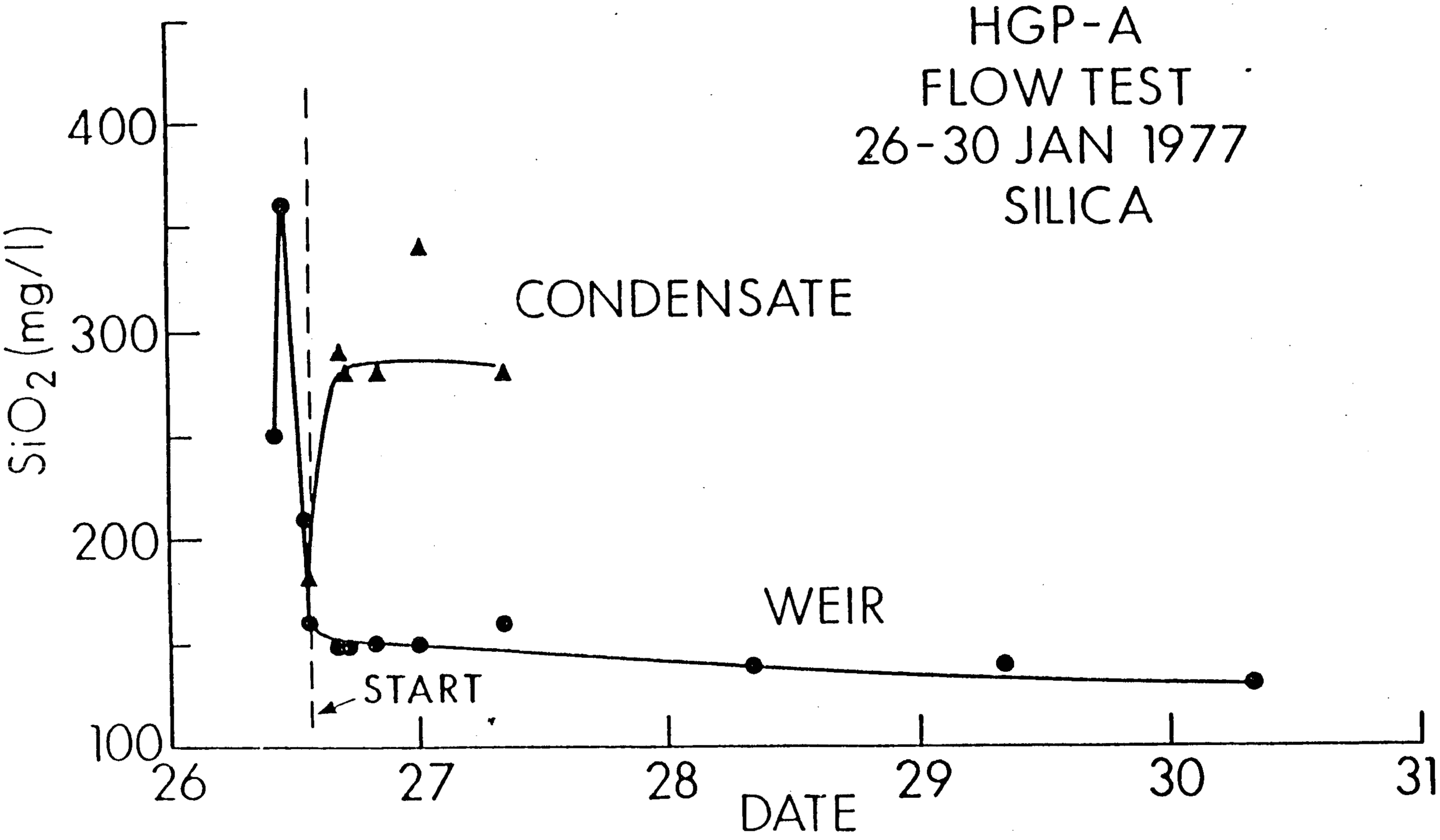

Figure 5. The approach of silica to steady state for water samples collected at the weir and from the condenser.

c. HGP-A Well Chemistry: Water and Heavy Elements

The expectation that HGP-A geothermal fluids would resemble those found in Iceland, New Zealand and elsewhere (and volcanic areas generally) in heavy elements content has been discussed above.

The earliest water samplings, carried out in May 1976 and again when the well was flashed in July yielded levels of ca. 0.005 $mg.\ell^{-1}$, above established safe limits for potable water (Table 12). With continuous flow however, the Hg level continued to fall. At shutdown in November of that year, a concentration of 0.001 $mg.\ell^{-1}$ was found which remained steady through August 1977. By July 1978, the Hg level had fallen below 0.0004 $mg.\ell^{-1}$.

The other heavy metals examined included cadmium, lead, thallium, arsenic, copper and zinc (Table 13). Of these Cd, Cu, Zn and Hg met potable water quality standards. Pb and As may have been too high for drinking standards but certainly met the requirements for irrigation usage on crops.

No water standards have been set for thallium, a highly toxic metal. It is infrequently encountered in nature, but has been found in some soil samples in the area around HGP-A.

Table 12. A Condensed Water and Air Mercury Chronology at HGP-A

Date	Well Status	Air $\mu g.m^{-3}$	Water $mg.\ell^{-1}$
May 75	Pre-drilling	1.1	-
May 76	Post-drilling	1.2	0.0046
July 76	Flashing	9.9	0.005
Nov. 76	Shut-down	10.0	0.001
Aug. 77	Flow test	0.8	0.001
July 78	Shut-down	1.2	0.0004

Table 13. Heavy Metal Content of HGP-A Surface Waters (During Flashing)

Heavy Metal	Drinking Water EPA-600/7-78-101	Well June '78 Sampling
	$mg \cdot \ell^{-1}$	
Cd	0.01	<0.01
Pb	0.05 (5)*	<1.0
Tl	-	<1.0
As	0.05 (1.0)*	<0.5
Cu	1.0	<0.01
Zn	5	<0.035
Hg	0.002	<0.0004

*Limit for Agricultural waters (U. S. Dept. Int. 1968, Fed. Water Pollut. Control Admin.). Lower levels, e.g. 0.1 $mg \cdot \ell^{-1}$ have been suggested, but 0.5 $mg \cdot \ell^{-1}$ seems to be the toxic threshold for crops.

Such a result could be interpreted as representing a very old age for the water (12,500 to 13,900 years). These ages are much greater than any that have ever been measured for a Hawaiian dike-confined ground water. Thus, we prefer to interpret the C^{14} data as further confirmation of the mixing model proposed above. According to this model, the live carbon contributed by ground water plus ocean water could be 20% ($\pm$10%) of the total, which easily accounts for the apparent depletion of C^{14} in the samples. Due to the extremely high porosity of the surrounding rock, several tons of organic matter (cottonseed hulls, bagasse, ...) were injected into the well during drilling. While we believe that this material has been cleared from the well, it is possible that some of the modern carbon (C^{14}) is coming from the oxidation of this organic material.

The tritium results showed values of less than 0.2 TU, indicating that no bomb-produced tritium has entered the aquifer and that an age of greater than 50 years is expected. Due to the errors discussed above, it is of course possible that the water has an age of up to several thousand years, but it is impossible to resolve such a time span with the present data.

CONCLUSIONS

(1) The water quality sampling program of the HGP-A well consisted of a series of five downhole water samplings at various depths under no-discharge condition, one similar sampling under very low discharge condition, and water

quality monitoring of the discharge of the longest discharge test, March-May 1977. The median values for the downhole water samples are: pH, 5; conductivity, 3100 μmho/cm; salinity, 2.3%; chloride, 925 mg/ℓ; silica as SiO_2, 420 mg/ℓ; magnesium, 1 mg/ℓ. Tritium vlaues of three samples all showed less than 0.2 TU, or at least 50 years old. The HGP-A well water is slightly saline and contains about 5-10 percent ocean water. The well water has lost a small amount of potassium and nearly all of its magnesium as compared with diluted ocean water, probably because of subsurface geothermal-geochemical effect. The maximum well fluid temperatures of 358° C (676° F) is higher than that of any Hawaiian ground water.

(2) The HGP-A well fluid, when discharged from the well, is principally a mixture of water and water vapor. Steam accounts for 66-70 percent of the mixture as computed from water chemistry data and confirmed by thermodynamic computations.

(3) The measured chemical parameters of the well under no-discharge conditions did not vary much with depth even at the well bottom (1983 m, 5851 ft., below sea level). This suggests the possible existence of deep dikes or intrusive bodies located on the ocean side of the well and acting as barriers against sea water encroachment.

(4) Mass balance calculations involving carbon, its isotopes C^{14} and C^{13}, and water and O^{18} indicate that 10 percent of the water comes from the ocean, 66 percent from ground water, and 24 percent from a hydrothermal source. The radiocarbon

activity of 20 percent of modern CO_2 is attributed to dilution of ground and shallow hydrothermal waters with dead magmatic carbon.

(5) During the flow tests, the concentrations of the water quality parameters in the discharge appeared to approach a steady state after one to three days. The prolonged period required to reach a steady-state concentration suggests incompleteness of well development or low permeability of the formation, or both. The transmissivity of 1 millidarcy-foot is about 5 orders of magnitude smaller than that for normal productive Hawaii water wells that are of much shallower depth than HGP-A. The water discharge rate of HGP-A is small and on the order of 30 gpm, although the total well discharge (water plus steam) was 76,000 lb/hr (equivalent to 150 gpm).

(6) During the January-February 15-day flow test, the 'steady-state' concentrations of the major water ions in the water portion of the discharge (weir) were: pH, 8.5; conductivity, 5900 μmho/cm; salinity, 4.6%; chloride, 3600 mg/ℓ; silica, 135 mg/ℓ; sodium, 1300 mg/ℓ; potassium, 225 mg/ℓ; calcium, 80 mg/ℓ. A large amount of silica was precipitated out, while the acidic gases CO_2 and H_2S were lost to the steam phase.

(7) The water level in the well rises from about 275 m (900 ft.) below ground level two days after well shut-in to about 30 m (100 ft.) below ground level 22 days after well shut-in. This behavior resembled semi-logarithmic

recovery in an artesian water well. The slowness of the rise is, however, not typical of artesian water well response but may reflect a condition analogous to a leaky aquifer or may be caused by a combination of the incomplete well development already noted and the recharge effects of the well fluids.

(8) The moderately high rainfall (mean annual, 318 cm (125 in.)) and the high surficial permeability of the Puna area permit substantial rain water infiltration. The circulation of subsurface water, whether it is infiltrated rain water or ground water transmitted to the Kapoho area, is still open to interpretation because of uncertainty about geologic formations for the area. It is fairly certain that the Kapoho reservoir is probably in poor hydraulic communication with ocean water. It is certain, however, that the ground water hydrologic regime tapped by HGP-A is distinctly different from that of adjacent ground water (as close as 1.5 km (1 mi.) from the well). The adjacent ground water is known to be basal water directly recharged by contemporary rain water and only mildly affected by geothermal sources as reflected by warm temperature and a shift in the relative proportion of the chemical constituents.

The March-May 1977 flow test data are generally consistent with prior flow test data in terms of patterns and trends. However, the magnitude of many water quality parameters including chloride, conductivity, salinity, silica, sodium, and potassium reached higher values for this, the longest flow test permitted so far. For example, the chloride concentration in the weir samples increased from generally 2500 mg/ℓ or less for the first three tests to about 3200 mg/ℓ in the last test (Fig.6). This increase may be interpreted as an indication of drawing of higher saline water into the geothermal reservoir as well discharge is maintained over a long period of time.

Discussion and Conclusions

The results of the continuous flow series indicate that after the initial flushing, most of the parameters exhibit a slow buildup toward a steady state. This is not typical for the normal Hawaiian ground water well. In general, Hawaiian water wells achieve quick equilibrium with respect to drawdown within a few minutes and water quality parameter concentrations within one-half hour of activation, reflecting the high permeability of the aquifer rock structure. HGP-A's retarded equilibrium period appeared attributable, at least in part, to low rock permeability and in part probably to incomplete clearing of drilling mud from the surrounding rock. The average formation transmissibility at the HGP-A well is approximately 1 millidarcy-foot, based on preliminary analysis of flow test data (Chen et al., 1976). This magnitude

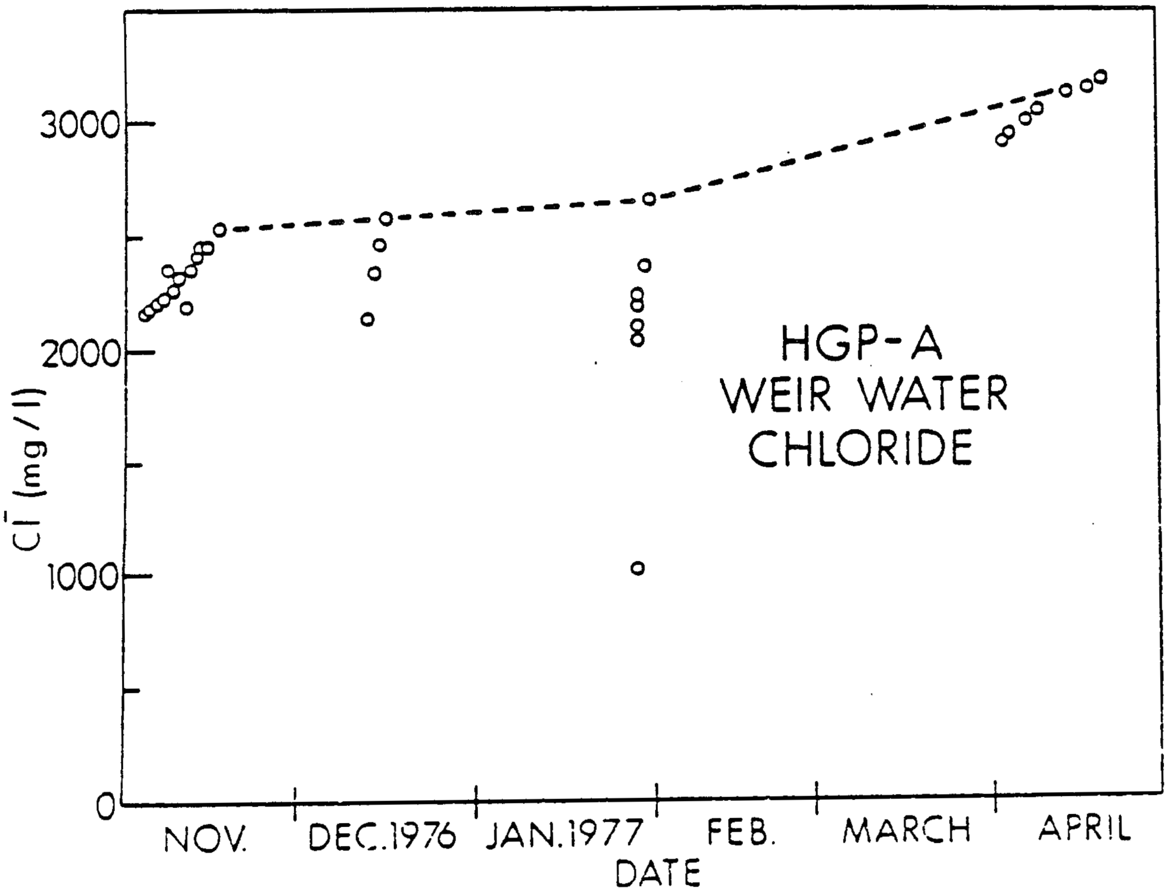

Figure 6. The chloride concentrations of samples collected from the weir plotted versus the date of sampling. The steady rise after each well has not reached equilibrium with the surrounding waters. To compare these results the reader must multiply them by (1-f) where f is the steam fraction of the discharge.

is miniscule compared with 10^5 millidarcy-foot for the very productive yet much shallower Hawaii water wells.

The water quality data obtained from the continuous flow tests can be used to compute the steam fraction of the total discharge. When we use conservative water quality parameters such as chloride and recognize that the condensate samples represent a combined steam and water sample and that the weir samples indicate the water portion only, we can calculate the steam quality (f) as follows:

$$f = \left[1 - \frac{C_c}{C_w} \right]$$

where

C_c = concentration in the condensate sample

C_w = concentration in the weir sample.

The steam quality calculations were performed using conductivity, chloride, and sodium data. These parameters should represent the conservative indicators. 'Conservative' in this case is used in the context of exhibiting less susceptibility to equilibrium changes through the sampling train. The steam quality results of this analysis noted in Table 9. show a range of 66 to 69% and are considered high when compared with those of other geothermal areas. This range is in close agreement with that computed using enthalpy and thermodynamic data (Chen et al., 1976) (Table 14).

A plot of the cation equivalents plotted as a function of chloride equivalents can be used to assess the proportion of sea water in a set of samples. The sea water dilution

Table 14. HGP-A steam quality (%)

Sampling Date/Time	Conductivity	Chloride	Sodium	Average	Computed from Thermodynamic Data
26 January 1977 4:30 p.m.	68	71	75	68	58
26 January 1977 8:00 p.m.	69	70	69	70	77
26 January 1977 12:01 a.m.	65	63	67	66	84
26 January 1977 8:00 a.m.	69	65	71	69	81
Average for Parameter	68	66	67	71	75

line acts as a reference for the linear regression line of the sample plots. Sodium, calcium, and potassium all exhibit parallelism with respect to the diluted sea water over a full magnitude of chloride concentrations. Sodium is within experimental error of overlapping the reference line. Potassium is depleted by about 56%. Calcium shows considerable scatter about the sea water dilution line. Magnesium is conspicuous by its extreme depletion (95 to 100%). The results of these analyses show clearly that the water samples were about 90% dilutions of sea water with a substantial loss of potassium and an almost complete loss of magnesium. These effects have been observed previously in geothermal systems (Ellis, 1970; Arnorsson, 1974; Kristmannsdottir and Tomasson, 1974) and in deep-sea sediment pore fluids (Gieskes, 1973). The reaction of freshwater and seawater mixtures with clay minerals can be described by equations such as those that follow:

$$\underset{\text{K-feldspar}}{2KAlSi_3O_8} + \underset{\substack{\text{meteoric}\\ \text{water}}}{4H_2O + 4CO_2} = 2K^{++} + 4HCO_3 + 4SiO_2 + \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4/} \qquad (1)$$

$$\underset{\text{Kaolinite}}{3Al_2Si_2O_5(OH)_4} + \underset{\text{saline water}}{2K^{+} + 2HCO_3^{-}} = \underset{\text{Illite}}{2K(AlSiO_4)Al_2(OH)_2 \cdot O_2(Si_2O_4)} + 5H_2O + 2CO \qquad (2)$$

$$\underset{\text{Kaolinite}}{2Al_2Si_2O_5(OH)_4} + \underset{\text{saline water}}{Mg^{++} + HCO_3^{-}} = \underset{\text{Chlorite}}{Mg_{10}Al_2(Si_6Al_2)_{20}(OH)_6} + H_2O + CO_2. \qquad (3)$$

Equation (1) represents the primary chemical weathering of an igneous rock to a clay. Sodium and calcium feldspars are commonly found in basalt. Equations (2) and (3) represent low temperature ion-exchange reactions that can occur in a weathered basalt. The reaction of kaolinite with sodium ion produces the clay mineral montmorillonite. In a petrographic description of the cuttings and core obtained during the drilling of HGP-A, Stone (1977) reports that montmorillonite is the dominant clay mineral between 594 m (1950 ft.) and 1189 m (3900 ft.). Below 1189 m (3900 ft.) chlorite is the dominant clay; minor amounts of actinolite ($Ca_2(Mg,Fe^{+2})_5(Si_4O_{11})_2(OH)_2$) and albite ($NaAlSi_3O_8$) also are present. Thus, these reactions can explain the observed depletions of potassium and magnesium.

Mahon (1966) and Fournier and Rowe (1966) observed independently that the silica content of high-temperature waters within hydrothermal areas is determined by the quartz-water equilibrium solubility. This has made possible a simple chemical method for determining the temperatures of the waters supplying drillholes. By assuming that waters reach the surface by an adiabatic isoenthalpic expansion of the original high-temperature water to a steam-water mixture, the silica concentrations on boiling surface waters that correspond to underground waters of certain temperatures can be calculated. Use of this method has enabled the measurement of temperatures in New Zealand geothermal areas to within about $\pm 2^{\circ}$ (Mahon, 1966). Using the Fournier and Rowe solubility data for quartz, $t = (1311/(5.196 - \log SiO_2)) - 273$, we calculate that the host rock surrounding HGP-A should have a temperature of 240° C (Table 15). This estimate represents the minimum temperature expected, since cooling in the bore or mixture with meteoric water would decrease the calculated

Table 15. HGP-A geochemical summary (concentrations in mg/ℓ of total discharge)

	Cl	Na	K	Ca	Mg	SiO_2	$S^=$	pH	TRIT.	t^* qtz	t^{**} Na/K	t^{***} Na/K/Ca
DOWNHOLE	1040	730	123	53.8	1.0	440	135	3	.1	240°C	250(WE)	231
Non-flowing (ave. of 5 profiles): mean	1040	730	123	53.8	1.0	440	135	3	.1	240°C	250(WE)	231
0	465	270	46	49.5	.7	230	96				252(FT)	
2270' (o2/14/77)	4720	2008	245	445	14.0	432	.66	3	-	240°C	211(WE) 210	210
Low flow (ave. of 4 samples)	1040	480	103	22.6	.25	710	-	2.5	-	286°C	287(WE) 294(FT)	248
WEIR BOX												
approximate steady-state (01/30/77)	780	390	68	24	.11	41	-	8.5	-	93	256(WE) 259(FT)	229

*Fournier and Rowe (1966): $t = 1311/(5.196 - \log(SiO_2)) - 273$; SiO in ppm.

**White (1968) and Ellis (1969): $t = 855.6/(.6269 + \log(Na/K)) - 273$; Na and K in moles.
Fournier and Truesdell (1973): $t = 777/(.4693 + \log(Na/K)) - 273$; Na and K in moles.

***Fournier and Truesdell (1973): $t = 1647/(\log(Na/K) + \frac{1}{3}\log(Ca/Na) + 2.241 - 273$; Na, K, and Ca in moles.

temperature. The maximum recorded temperature in the well was 358° C under static conditions. The highest temperature measured downhole during high volume discharge was 275° C.

The Na/K ratio in natural hot waters is controlled by a reversible temperature-dependent rock mineral equilibrium involving potash mica, potash feldspar, and albite (Ellis and Mahon, 1964, 1967), field results, and the results of Hemley and Jones (1964) have enabled an approximate relationship to be established between the Na/K ratio in natural hot waters and temperature. The sodium/potassium equilibrium adjusts relatively slowly after a temperature change, which enables useful information on conditions in the deep aquifer to be obtained. Applying the Na/K thermometer of White and Ellis, $t = (855.6/(0.6269+\log(Na/K)) - 273$ to the average values for HGP-A samples gives a temperature of 250° C. Fournier and Truesdell (1973) also derived a Na/K geothermometer from which we calculate a temperature of 252° C ($t = (777/(0.4693+\log(Na/K)) - 273$). Fournier and Truesdell then extended their model to include the calcium ion concentration:

$$t = \frac{1647}{\log \frac{Na}{K} - \frac{1}{3}\log \frac{Ca}{Na} - 2.24} - 273.$$

The temperature calculated for HGP-A using this equation is 231° C (Table 15).

The temperatures calculated from samples collected downhole during flow give the highest values; and the silica results and the Na/K results agree remarkably well (Table 16).

Table 16. Summary of downhole chemical parameters*

Parameter	Mean	Median	Standard Deviation	Coefficient of Variance
Conductivity	3670 μmho/cm 3500 μmho/cm	3100 μmho/cm	2270 μmho/cm 1360 μmho/cm	62% 39%
Salinity	2.8% 2.6%	2.3%	1.4% 1.0%	51% 39%
Chloride	1160 mg/ℓ 1040 mg/ℓ	925 mg/ℓ	810 mg/ℓ 465 mg/ℓ	69% 45%
Silica	440 mg/ℓ	420 mg/ℓ	230 mg/ℓ	52%
Sulfide	135 mg/ℓ	100 mg/ℓ	96.4 mg/ℓ	71%
Sodium	830 mg/ℓ 730 mg/ℓ	600 mg/ℓ	460 mg/ℓ 270 mg/ℓ	55% 37%
Potassium	135 mg/ℓ 123 mg/ℓ	123 mg/ℓ	56.0 mg/ℓ 46.4 mg/ℓ	42% 38%
Calcium	84.2 mg/ℓ 53.8 mg/ℓ	40 mg/ℓ	120 mg/ℓ 49.5 mg/ℓ	142% 92%
Magnesium	2.1 mg/ℓ 1.0 mg/ℓ	1.0 mg/ℓ	3.8 mg/ℓ 0.7 mg/ℓ	62% 69%

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*Where two values appear the upper value includes all samples, but the lower value excludes February 1977 depth samples at 692 m (2270 ft.).

When differences are found between the various formulas for calculating temperatures (e.g., weir box sample), the silica temperature corresponds very closely with that of the outflow water, whereas the Na/K ratio temperature relates to the downhole temperature. With cooling of water (e.g., through boiling on rising toward the surface), the Na/K exchange reaction is slower to readjust than the silica equilibrium (Ellis, 1970). The calculated temperatures during the low-flow conditions are thus in excellent agreement with the observed downhole temperatures during discharge (see Table 15 and Fig. 4).

The equations used to calculate the temperatures were derived for areas where the host rocks are of ryolitic, ignimbritic, and/or sedimentary composition. Application of the geothermometers discussed above implicitly assumes the presence of minerals such as albite, K-feldspar, and plagioclase. The Island of Hawaii is made up of layers of olivine basaltic flows and cinders. Mineralogic analysis of HGP-A cuttings and cores indicate the presence of olivine, plagioclase (An 75-80), clinopyroxene, augite, and magnetite in the upper section. At 762 m (2500 ft.), pyrite and quartz, along with vesicle fillings of quartz, calcite, montmorillonite, and zeolite have been found. Below 1372 m (4500 ft.), the rocks have been hydrothermally altered and are composed of the above minerals plus chlorite, actinolite, hematite, and albite. In view of this wide variety of minerals present in the altered basalt at depth in the well it should not be surprising that the geothermometry works so well. Kristmannsdottir and Tomasson (1974) have shown that in the Icelandic geothermal fields the change from montmorillonite to chlorite with depth in a well corresponds with a temperature of between 200 and 230° C. In HGP-A this mineralogic change occurred at 884 m (2900 ft.) where the temperature after prolonged shut-in is 250° C. This agreement may be fortuitous, however, since the pre-production temperature was only 100° C at this depth.

Two large CO_2 gas samples were collected during the March-May 1977 flow test (April 8 and May 15) for radiocarbon analysis. The interpretation of the carbon-14 and tritium data require that we first account for the source of the carbon dioxide. Analyses of the gases emanating from HGP-A give us a total CO_2 level of 714 ppm. Assuming that the carbon dioxide content of the sea water fraction of the recharge is unchanged during transit, 9 mg/ℓ of carbon comes from this source. Thomas (1977) presented models of Kilauea and HGP-A in which the C^{13} and O^{18} data were used to calculate that for HGP-A 66% of the recharge water is of meteroic origin, 24% has undergone hydrothermal alteration, and that 20% of the carbon can be derived from organic material leached from the highly porous surrounding rock. Additional carbon comes from the dissolution of deeper hydrothermal calcite and from the outgassing of deep-seated magmatic material. The C^{14} results indicate that the two samples have an activity of 21 and 18% of modern living carbon.

d. HGP-A Well Chemistry: Air

Aerometry at HGP-A dates back to May, 1975. At that time, a semi-cleared area existed around the prospective drill site but no heavy equipment had yet located there. The area adjoins Pohoiki Bay Road, a connection between Pahoa and the Black Sand beach but was then and is now little travelled. At no time have ambient levels of CO exceeded 1 ppm, even when heavy diesel-powered equipment was in use. Similarly, NO_x concentrations have not reached the 0.1 ppm level, nor would the low traffic density lead one to expect significant levels of N-oxides, or other oxidants.

Within the sensitivity limits of tube detectors, both SO_2 and H_2S were monitored from the 1975. Occasional H_2SO_4 aeresol measurements have been taken, but in general, acidity is a potential problem only where sustained fumerolic emissions are in evidence or periodically at more remote locations as a consequence of volcanic eruptions (see above).

In addition to sulfur gases, evidence for atmospheric introductions of mercury and arsenic has been sought. As (III) arsine has not been detected using sample volumes in excess of $0.5m^3$ collected over approximately 4 hr periods. Even in the plume at <u>ca</u> 3 m distance from the separaters, tube detectors sensitive to 0.5 ppm are also negative. The recommended As (III) air standard is 0.05 ppm (24 hr average).

The initially relatively less sensitive detector tube procedures for SO_2 and H_2S showed no change from the predrilling stage of May '75 through subsequent periods of flow and steam production tests up to the most recent measurements of January 1980 (Table 17). Even with more sensitive methods, the lowered detection limits of 30 ppb were not attained at 100 m downwind from the well head.

The assessment of the wells' contribution to air mercury levels was complicated by the relative proximity of active natural emission sites. Thus, in July 1976, when the well was flashed for the first time, the downwind mercury level apparently rose to 9.9 $\mu g \cdot m^{-3}$ from a previous month's value of 1.0 $\mu g \cdot m^{-3}$, and remained high into November of the same year (Table 17). In late June 1976, when the HGP-A ambient was low, the Kilauea fumeroles raised the air level at the Sulfur Bank to 47.5 $\mu g \cdot m^{-3}$ from a level of 7.6 $\mu g \cdot m^{-3}$ the previous month. And in November, at HGP-A shut down, the Sulfur Bank area still measured 17.4 $\mu g \cdot m^{-3}$. A delay of several weeks in high Hg levels between HGP-A and the Sulfur Bank area serve 40 km to the west may have been wind-related. In October, 1977, when the Sulfur Bank rose to 11.3 $\mu g \cdot m^{-3}$ from an all-time low of 0.2 $\mu g \cdot m^{-3}$, a 6-fold rise from its level of 2 months earlier.

The upsurge of air mercury levels during flashing was originally thought to have been a "burst" releasing accumulated mercury at depth. During the July 1976 testing, it was not known that in addition to Sulfur Bank activity a new East Rift Zone emission center — the Heiheiahulu spatter cone about 13 km to the west of the well — had been active for two months. Subsequently this cone was tested and found to be a highly intensive mercury emitter and one of the probable sources of the relatively high level recorded at the flashing of HGP-A. Subsequent measurements, made in July-September 1977, show the presence at the well site not only of air mercury but also of H_2SO_4 -- although the well itself had been shut down since May 1977. The presence of these toxic gases can only be ascribed to natural area contamination, not emanating form the well itself.

Tests conducted since drilling of HGP-A began have yielded no evidence of a sustained build-up of mercury or any other potentially toxic elements at or around the well site that can be attributed to geothermal energy development operations. The conclusion reached by the researchers is that "there is no reason to assume that HGP-A itself has negative emission features other than H_2S and noise, but is influenced by its proximity to natural geotoxicant sources (Siegel and Siegel, 1977).

The dependency was well illustrated in the chronology of the 1977 Kalalua eruption by comparing air mercury levels at various Kilauea sites with those at HGP-A before, during and after the main eruptive events (Fig. 7).

Mercury analyses of steam condensates reveals relatively high start up levels followed by rapid approach to an asymptotic emission rate of approximately 1 g per 24 hrs corresponding to approximately 100 K $lbs.hr^{-1}$ mass flow after an operating time >10 hr (Fig. 8).

Table 17. An Aerometric Chronology at HGP-A

Date	Well Status	Sulfur Bank Air Value ($\mu g \cdot m^{-3}$ Hg)	HGP-A Air Values (100 m) SO_2 ppb	H_2S ppb	Hg $\mu g \cdot m^{-3}$
May '75	Pre-drilling	2.6	<500*	<200+	1.1
May '76	Post-drilling	7.6	<500	<200	1.2
June '76	1st flow test	47.5	<500	<200	1.0
July '76	Flashing	-	<500	<200	9.9
Nov. '76	Shut down	17.4	-	-	10.0
Apr. '76	Shut down	-	<500	<200	-
July '77	Shut down	4.6	<300	<200	0.8
Aug. '77	Flow test	0.2	<300	<30‡	0.8
Oct. '77	Shut down	11.3	<300	<30	4.8
July '78	Shut down	3.8	<300	<30	1.2
Nov. '79	Shut down	6.0	<30**	<30	1.3
Jan. '80	Flow test	-	<30	<30	0.8

*ppb <500 and <300 denote detection limit values for tube SO_2 methods

**ppb <30 denotes detection limit value for instrumental SO_2 methods

+ppb <200 deonots detection limit value for tube H_2S methods

‡ppb <30 denotes detection limit value for ROTEC and Houston Atlas instruments.

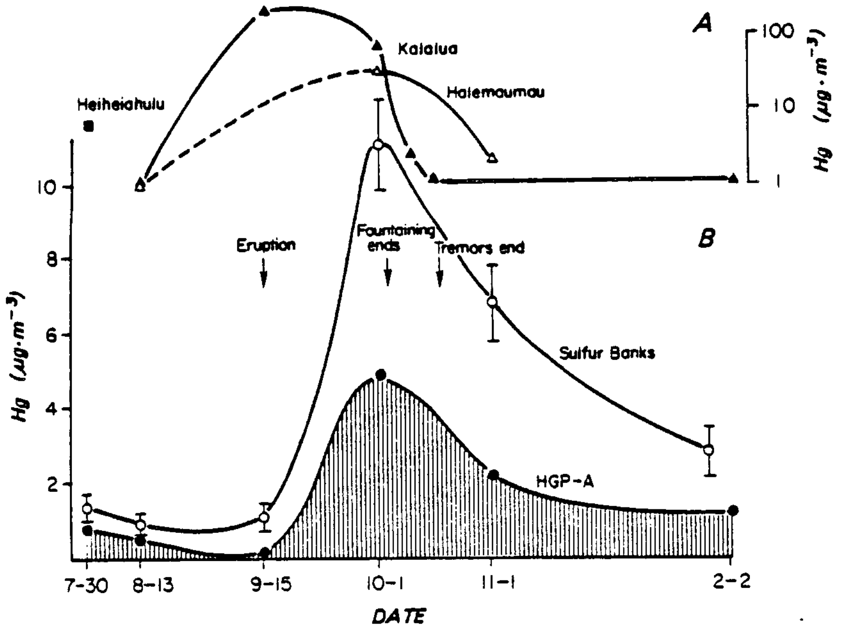

Figure 7. Time course of air mercury increase at Kilauea sites and HGP-A during the period of the 1977 Kalalua eruption.

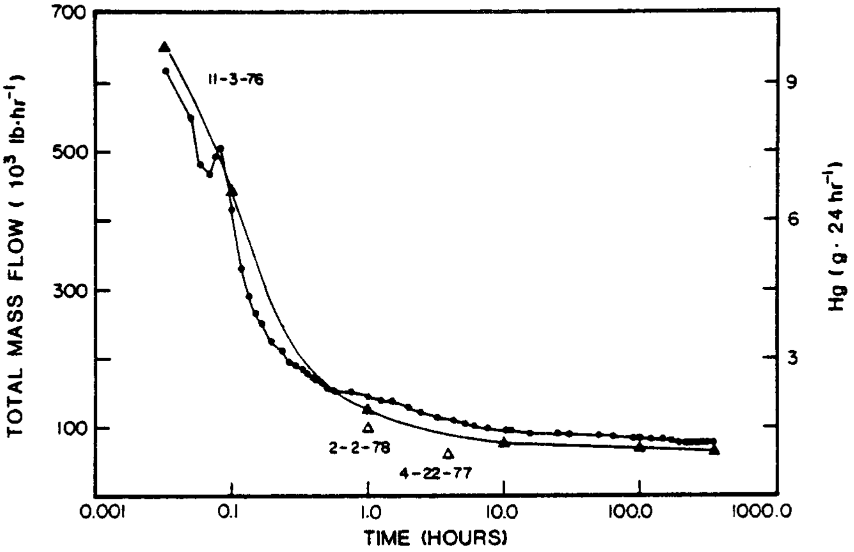

Figure 8. Relation between mass flow of geothermal fluid and release of atmospheric Hg at HGP-A.

Reference may be made here to EPA National Emission Standards 121:0461, 1976:

Incineration of wastewater, sludge

Hg allowed, 1600 g per day

Coal fired power plant

Hg allowed, 2300 g per day

Typically, Puna District residences make use of roof top water catchments. On April 7, 1977, following an extended 8 month period of flow tests, flashings and shut downs, local residents, near HGP-A voiced to the Hawaii County Council their objections to derous H_2S emissions and to the introduction, alledgedly, of toxicants into the rooftop water supplies. In response, the District Health Office for Hawaii County undertook an analysis of catchment water supplies. Five private residences were selected, three downwind relative to the normal tradewinds and 0.8-1.6 km from HGP-A; one somewhat more distant (3.5km) and WNW from the wellhead, and one "control" house over 8 km distant and slightly West of due North from HGP-A (Fig., 9, Table 18). The most serious complaints originated from the Nanawale Estates (Reich, r-) and to a lesser extent from the Leilani Estates residents South of the Kubera house (k). The results of analysis are all within safe water quality standards for human use.

e. HGP-A Well Chemistry: Radon

i. Report of Paul Kruger, Dept. of Civil Engineering, Stanford University 15 February, 1978

An experiment to test the feasibility of studying radon

Table 18. State of Hawaii Department of Health Rooftop Water Catchment Analyses near HGP-A (Downwind Sampling, 19 April 1977)

SITE Residence (map code)	Distance HGP-A (km)	SO_2	H_2S	Analysis ($mg \cdot \ell^{-1}$) F^-	$SO_4^=$	NO_3^-	AS	HG
Daniels (d)*	>8	1.0	ND	ND	ND	ND	ND	ND
Hughes (H)	0.8	1.0	ND	ND	ND	0.038	ND	ND
Kubera (K)	1.1	1.3	ND	ND	ND	ND	ND	ND
Rothblum (rb)	1.6	0.4	ND	ND	ND	ND	ND	ND
Reich (r)	3.5	0.2	ND	ND	ND	ND	ND	ND
40 CFR 142 or USPHS Recommended Limits for Potable waters for human use.		none	$2x10^{-4}$	2.4	250	10	0.05	$<2x10^{-3}$

*"Control" residence

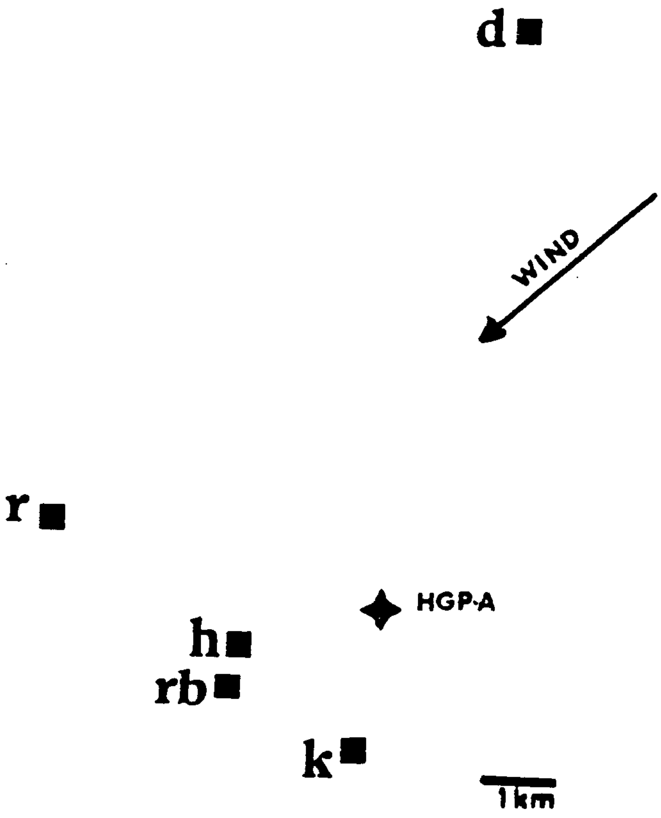

Figure 9. Site distribution for rooftop rain water catchings in relation to HGP-A downwind direction.

Table 19. Reservoir Radon Project HGP-A Puna, Hawaii
July 19, 1977
Sample Collection Data

Time (HST)	Sample No.	Bottle No.	P_{wh} (psig)	T_{wh} (°C)	Weir ht H(in)	P_{lip} (psig)	Orifice (in)
1133	Start		10	123	0	0	8
1205	1	1-3471	148	188	7.5	58.5	
1235	2	18-3290	122	180	6.75	46.0	
1305	3	13-3132	111	176	6.40	41.1	
1320	4	17-3125	105	175	6.31	39.0	
1335	5	11-3134	101	173	6.25	37.5	
1335	6	-3128	101	173	6.25	37.5	
1336	Stop						8
1422	Start		170	183	0	0	1.75
1455	7	5-3462	295	211	5.5	7.0	
1525	8	18-3432	365	225	5.5	7.5	
1555	9	19-3466	385	227	5.5	8.5	
1625	10	12-3131	395	229	5.5	8.5	
1636	Test aborted						1.75

Table 20. Reservoir Radon Project HGP-A Puna, Hawaii July 19, 1977
Russell James Flow Calculations

Sample No.	Weir Ht (in)	W (klb/hr)	P_g (psig)	$\frac{W}{P^{0.96}}$	h (Btu/lb)	Q_t (klb/hr)	Q_s (klb/hr)	X
1	7.5	162	58.5	2.626	700	363	201	0.55
2	6.75	124	46.0	2.415	720	295	171	0.58
3	6.4	109	41.0	2.292	736	265	156	0.59
4	6.31	105	39.0	2.296	730	258	153	0.59
5,6	6.25	103	37.5	2.303	733	250	147	0.59
7	5.5	74.6	7.0	3.886	602	134	59	0.44
8	5.5	74.6	7.5	3.802	600	137	62	0.46
9	5.5	74.6	8.5	3.645	617	139	64	0.46
10	5.5	74.6	8.5	3.645	617	139	64	0.46

concentration dependence on flow rate conditions in an undeveloped, steam-flashing reservoir was carried out at the HGP-A geothermal well in Puna, Hawaii on July 19, 1977. The well had been shut-in for an extended period under a local agreement to restrict flow testing of the well to a maximum of 4 hours per day. The test consisted of flowing the well for a total period of 4 hours, two hours with an 8-inch orifice plate providing maximum flow rate and two hours with a 1-3/4" orifice plate providing almost minimum flow rate. Orifice plate change consumed about 46 minutes, not sufficient to result in significant cooling of the wellbore system.

The test was accomplished by sampling the main steam line at the wellhead with evacuated bottles at half-hour intervals over the two 2-hour flow-rate periods, and recording the wellhead conditions and flow rate by the Russel James method (1962). The sample collection data and the calculation of flow rate by the James method are given below (Tables 19 and 20).

The radon analysis data (Table 21) and the radon, flow rate at the 8" orifice to a value of about 250 klb/hr consistent with a corresponding decrease in wellhead pressure and radon concentration, except for the last sample at 1335 HST. After the orifice plate change of 46 minutes, the well exhibited a reasonably steady flow rate, while the wellhead pressure rose to a maximum. The radon concentration showed a time profile similar to that at the larger flow rate.

Preliminary analysis of the data was made under the

Table 21. Reservoir Radon Project HGP-A Puna, Hawaii
July 19, 1977
Radon Analysis Data of Collected Samples

Time (HST)	P_{WH} (psig)	T_{WH} (^{o}C)	Q (klb/hr)	Rn (pCi)	V_c (ml)	(Rn) (nCi/l_c)
1205	148	188	363	129	111	1.16
1235	122	180	295	85	98	0.87
1305	111	176	265	75	99	0.76
1320	105	175	258	68	90	0.76
1335	101	173	250	154(?)	65	2.4
1335	101	173	250	44	48	0.92
1455	295	211	134	453	470	0.97
1525	365	225	137	428	531	0.81
1555	385	227	139	368	485	0.76
1625	395	229	139	428	495	0.86

general evaluation of radon as an internal tracer for geothermal fluid transport. Radon measurements are useful for study of geothermal reservoir behavior (Stoker and Kruger, 1975). A review of some of the data potentially derivable by radon concentration measurement was reported by Kruger, Warren, and Honeyman (1977). Among them are experiments focused on the relationship between radon concentration and flow regime in producing geothermal reservoirs. Steady-state production should result in steady-state contration of radon on the basis of a constant emanation of radon from the formation and a constant permeability field in the reservoir. Serveral models can be derived depending on radon emanaiton from three types of source: (1) hydrothermally-deposited radium close to the wellbore; (2) radium in a boiling liquid below some liquid-steam interface; and (3) radium present in the pathway from steam source to the well.

Data obtained for vapor-dominated reservoirs, such as The Geysers in California and Larderello, Italy suggest a relationship in which the radon concentration changes directly with change in flow rate; the transient time dependent on reservoir characteristics. The model of flow rate dependence of Stoker and Kruger (1975) for liquid-dominated reservoirs as confined horizontal flow is based on a derivation of the relationship between radon concentration and flow rate in which the radium concentration is uniformly deposited in a large reservoir. For these conditions, the radon concentration should show transients with flow rate proportional to $(1 - e^{-\lambda\tau})$ and for steady state flow show an equilibrium value independent of Q.

A comparison of the radon concentration and flow rates for the HGP-A well test is given in Table 4. In contrast to the tests at the vapor-dominated fields at The Geysers and Larderello where the ratio (Rn)/Q was approximately constant over large changes in Q, in this test the radon concentration was approximately the same over a change of about a factor of 2 in Q, in agreement with the liquid reservoir model. These short-period data suggest that the drainage from the HGP-A reservoir follows a radial flow pattern over a large reservoir in which the concentration of radon does not depend strongly on flow rate (Stoker and Kruger, 1975).

The transient form of the relation has a factor of $(1 - e^{-\lambda\tau})$ where t can be expressed by the volume swept by the flow rate, Q. If the volume swept, V_ϕ, does not depend strongly on Q, the change in concentration will vary according to $(1 - e^{-a/Q})$, where $a=\lambda V_\phi$. To verify such a radon concentration change with change in flow rate, a longer experimental period is proposed.

For a radon half life of 3.8 days, three fourths of saturation equilibrium is attained in one week. Therefore, a test of two-week duration is suggested, one week at 8" orifice plate flow conditions and a second at 1-3/4" orifice plate flow. During the two-week period, sufficient samples will be taken at each flow rate to ensure a mean standard deviation of less than ±3% (12 samples at each flow rate

The above results were arrived at as follows:

> The average radon concentration in samples of the well fluids collected under restricted production (137 K lb H_2O/hr) was 0.85 nano curies of radon per liter of water collected . The first assumption to be made is that radon is strongly partitioned into the vapor phase when the well fluids are flashed to steam (i.e., all the radon is in the gas phase ane none in the liquid). If one then assumes that all the water collected was condensed from steam, then the radon produced by the well is calculated as 0.85 n Ci/ℓ x 62 K lb/hr steam x 0.455 ℓ/lb = 23.9u Ci Rn/hr.

If one assumes that the water samples collected was a mixture of steam and unflashed well fluid a correction must be made to remove the water fraction; this correction is made by multiplying by the inverse of the steam quality (total discharge/steam discharge). For the present case, this factor is 2.21. Thus:

Radon discharge = 0.85 n CiRn/ℓ x 62 K lb/hr x 2.21 x
0.455 ℓ/lb = 52.8 uCi Rn/hr.

The calculation of radon concentrations in the air at the well site and down wind was made through the use of H_2S as a "tracer" for radon. The assumptions made for this calculation are (1) the H_2S and Rn partition ratios between the liquid and flashed steam phases are similar and (2) that atmospheric dilution of radon will be similar to that for H_2S.

based on a conservative individual relative standard deviation for a single sample of ±10%). The experiences gained during this first feasibility test indicates that the proposed next experiment can be run successfully. The standard deviations of the means at both flow rates should be sufficiently small to see if a dependence of effluent concentration with $1 - e^{-a/Q}$ exists.

ii. Report of Donald Thomas, Hawaii Institute of Geophysics (20 September 1978)

In regard to the radon radiation hazard presented by HGP-A, the radon concentrations in the well fluids have been determined by Dr. P. Kruger at Stanford University. These concentrations have been used to calculate the expected total radon output of the well per hour as well as the expected radon concentrations both a the well head and at a distance of 0.15 km. The results of these calculations are as follows:

Total radon = 23.9 uCi Rn/hr (during "normal" production)

= 192 u Ci Rn/hr (full discharge, worst case).

Radon concentration at well head = 6.68×10^{-3} p Ci Rn/ℓ air at well head (during normal discharge)

Radon concentration at distance of 0.15 km = 5.01×10^{-5} p Ci Rn/ℓ air (during normal discharge)

= 6.8×10^{-5} p Ci Rn/ℓ air (full discharge, worst case)

Note that EPA guidelines for upper levels of radon concentration in habitable structures is 0.5 p Ci Rn/ℓ air (O'Connell and Gilgan, 1978).

The H_2S concentrations in the well discharge is approximately 650 ppm while atmospheric concentrations of H_2S at the well head are approximately 4 ppm. Assuming the same dilution factor for radon, one may calculate:

0.85 n Ci Rn/ℓ_c = 0.85 p Ci Rn/gc 0.85 p Ci Rn/g x 4/650 =
0.0052 pci Rn/gm air

the average molecular weight of air is 28.8 g/mole and thus one liter of air weighs 1.284 g.

$5.2\text{x}10^{-3}$ p Ci Rn/gm air x 1.28g/ℓ = 6.68×10^{-3} p Ci Rn/ℓ.

The H_2S concentration at 0.15 km from the well head was found to be 30 ppB. If one assumes a dilution of radon by a similar factor (7.5×10^{-3}) the radon concentration at 0.15 km is:

6.68×10^{-3} p Ci Rn/ℓ x 7.5×10^{-3} = 5.01×10^{-5} p Ci Rn/ℓ air

The worst case calculation is done similarly using the higher radon concentration (1.16 p Ci Rn/ℓ).

As mentioned above, EPA guidelines for habitable dwellings is 0.5 p Ci Rn/ℓ air and is higher by nearly two orders of magnitude than the levels observed at the well site and by nearly four orders at a distance of 0.15 km.

iii. Report of Phillip Manly,
Gamma Corporation, Honolulu, Hawaii (2 February, 1979)

Radon-222, being a naturally-occurring isotope is regulated only by State Department of Health and Department of Occupational Safety and Health (DOSH) regulations. The regulations of the Nuclear Regulatory Commission do not apply because the isotope is not by-product or source material. Standards set by the Environmental Protection Agency for drinking water apply to radon only to the extent that radon daughters dissolved in water must meet the alpha activity limits.

The State Department of Health regulations (Chapter 33) set occupational limits on radon and its daughters in air of 30 pCi/l for a 40 hour week and 10 pCi/l for a 168 hour week. For areas where the general public may have access, the limits are set lower by a factor of 10.

The limits set by DOSH for occupational workers are the same as those set by the Department of Health. However, the DOSH regulations also introduce the concept of working level, where one working level is equivalent to 1.3E5 MeV/l of alpha activity from any combination of alpha emitting daughters of radon. The concept of working level was developed for use in uranium mines, where radon and its daughters were always present, but hardly ever in equilibrium. Measurement and calculation of air activity was made simpler when only total alpha activity had to be measured, without relating it to air concentration of radon.

Kruger measured an average radon activity in steam condensate of 890 pCi/l and 850 pCi/l for the two tests he made (Kurger, 1977). Donald Thomas used these data, along with data on the hydrogen sulfide concentration in the steam, at the well-head, and at the perimeter, to estimate worst case air concentrations of 9E-3 pCi/l at the well-head and 6.8E-5 pCi/l at the facility perimeter (Thomas, 1978).

An alternate method for calculating worst case concentrations involves calculating the radon activity in the steam itself. The steam condensate concentrations are divided by

1670 (the volume ratio of steam to water) and multiplied by 2.21 (the steam to total discharge ratio) to obtain an estimate of the air activity at the well-head:

$$A\ (\text{pCi/l}) = \frac{(890\ \text{pCi/l})\ (2.21)}{1670}$$

$$A\ (\text{pCi/l}) = 1.2\ \text{pCi/l} \quad \text{(well-head radon activity)}$$

Using the hydrogen sulfide ratio from well-head to facility perimeter (4 ppm/30 ppb = 133) the activity at the facility perimeter can be estimated at:

$$A\ (\text{pCi/l}) = \frac{1.2\ \text{pCi/l}}{133}$$

$$A\ (\text{pCi/l}) = 0.009\ \text{pCi/l} \quad \text{(facility perimeter radon activity)}$$

The worst-case estimates for radon activity at the well-head are a factor of 25 below the allowable limits for occupational workers, using a 40 hour work week. In addition, the estimates of radon activity at the facility perimeter are a factor of 1000 below the allowable limits for non-occupational workers, using a 168 hour residence time. According to the regulations, only when estimates of the exposure exceed 25% of the applicable limits should a monitoring program be instituted to monitor exposure. Such a program is clearly not necessary.

Situations could develop after additional construction of facilities that could allow concentration of radon daughter activities and lead to higher exposures. If the steam were routed into a closed building (e.g. turbine building) in which the radon could escape, then the particulate radon daughters might collect in the building in concentrations much higher than estimate above. In such cases, additional measurements of actual radon daughter activities should be performed to determine the actual radon and radon daughter activity levels.

Radon is continuously released from the ground. A worldwide flux average for the radon flux is 4.25E-5 pCi/cm^2-sec (Wilkening, et. al., 1972), or 0.095 $Ci-mi^2$-day. Some data on uranium activity in local soils indicates that the local flux may be 10 times less than the worldwide average (McMurtry, 1979).

At full power production the HGP-A well will be producing 3.5 MWe of power, with a steam consumption of 60,000 lbs/hr. The release of radon from the well is estimated to be:

$$\text{Rn (Cn/da)} = \text{60,000 lbs/hr)(.455 l/lb)(0.89E-9 Ci/l)} \times \text{(24 hr/da)}$$

$$\text{Rn (Ci/da)} = \text{5.8E-4 Ci/da (activity released)}$$

This release is equivalent to the release of radon from between one tenth and one square mile of land. Although on a worldwide scale the release is minimal, it may cause a local purturbation in the activity levels of radon and subsequent increase in radiation exposure.

A study has been performed comparing the radioactivity release of coal-fired power plants with the release from nuclear-powered plants and the new federal regulations (McBryde, et. al., 1979). In this study, the radon released from a 1000 MWe coal-fired plant were estimated at 0.4 Ci/yr. This release, along with releases of other uranium and thorium isotopes, resulted in higher population dose estimates than the emissions from a 1000 MWe nuclear-powered plant. By comparison, the HGP-A will release 0.2 Ci/yr. of radon.

After the steam is condensed, it will be allowed to percolate back into the groundwater. Depending on the time that the radon daughters have grown in from the radon in the steam before the radon was off-gassed, the activity levels in the condensate may exceed the 15 pCi/l limit for drinking water established by the EPA (the measured activity in steam condensate was 890 pCi/l). This addition of radon daughter activity to the ground water may cause in increase in alpha activity of drinking water at a well near the geothermal well.

From a preliminary assessment of the radon measurements made of steam condensate, it was concluded that the radon presented no hazard either to occupational workers or to the general public. The environmental impact was also estimated to be minimal on a worldwide scale. However, because of lack of data on the existing natural environment, the extent of the environmental impact on a local scale could not be determined. Additional sampling was recommended to determine the existing radon environment, and to measure any impact to it from the operation of the HGP- well.

f. HGP-A Well Chemistry: Soil and Vegetation Mercury in the Drillsite Area

On a global basis, the mean crustal abundance of mercury has been long established at <u>ca</u> 50 ppb, or 0.25 μg-atom$\cdot$Kg^{-1}, and the atomic abundance ratios for Tl, Cu and Fe respectively to Hg are accordingly 20, 636 and 3,360,000 (Table 22).

In the Puna District, Island of Hawaii, near the HGP-A well, the mean soil Hg level is about 12-fold higher than the world wide abundance figure. This is not reflected in commensurately higher concentrations of Tl, Cu and Fe, and the local atomic abundance ratios of 8, 48.5 and 270 show this. The Hg-enrichment of the local soil is 12.3-fold relative to Fe, and in satisfactory agreement, 13.1-fold relative to Cu. Both of these elements are geochemical non-volatiles, whereas Tl like Hg is volatile, albeit less so. Thus the Tl-Hg enrichment factor of only 2.5-fold. These data can best be explained by postulating an active, highly mobile source of Hg outside the HGP-A area, namely Kilauea and its East Rift. The Tl samples are too limited for any firm interpretation, but fumerolic and volcanic sources may contribute this element as they do Hg, but to a lesser degree.

These data are based on sampling carried out prior to the beginning of drilling operations at HGP-A in 1975. In view of the low Hg emission, about 1.4g per 24 hr and infrequent well operations, it is not likely that these ratios will have changed since the last sampling period, however a follow-up study is in order.

Like soils in the HGP-A area, local vegetation is also

higher in Hg content, than in the older weathered volcanic soils of Oahu (Table 23). The aggregate samples overlap in 5 species tested, and both collections represent ferns and angiosperms, and woody and herbaceous forms.

More site-specific sampling was carried out in the HGP-A at sites 100m downwind from the drillsite (Table 24). Beginning in May 1975, there appeared the same relation between the chronology of site operations and soil, plant, mercury levels seen above for air values. Again it is clear that if it were not for the comparative data dealing with natural processes taking place on Kilauea and its East Rift, the apparent impact of HGP-A on the Hg level of its environs could have served as a serious constraint upon site development. The mercury content of discharge waters was also analyzed and exhibits a down-trend over the 3 years recorded from the first flashing obviously unrelated to changes in air, soil and plant.

The distribution and cycling of primary natural geothermal mercury is complicated by the dual role of vegetation and soils as both primary sinks and secondary sources (Table 25).

Mercury injected into the atmosphere from vents, fissures and fumeroles of the Kilauea system normally contains a small percentage of particulates, the major forms of the element being Hg^o and $HgCl_2$. Ionic mercury entering the soil solution can be readily absorbed by plants via the roots, translocated to leaves, reduced and released as Hg^o. In addition, soils with sufficient organic and microbiological content can reduce Hg-ion to Hg^o or to $Hg(CH_3)_2$ followed by evaporation. Gaseous

Table 23. Collective Mean Mercury Content of Plants from Manoa Valley and HGP-A Sites

Location	Species Represented	Tissue Mercury
HGP-A, Puna Island of Hawaii	*Nephrolepis*, *Dicranopteris* *Lycopodium*, *Cyperus*, *Leucena* *Psidium*, *Metrosideros*, *Eucalyptus*	353 ± 63
Manoa Valley, Honolulu Island of Oahu	*Nephrolepis*, *Cyperus*, *Psidium*, *Leucena*, *Eucalyptus*, *Wedelia*, *Philodendron*	58 ± 26

Table 24. HGP-A Drillsite Soil and Plant Mercury Levels as Related Well Status

				Mercury Content			
				Cyperus		Metrosideros	
Date	Well Status	Air $\mu g \cdot m^{-3}$	Water $\mu g \cdot \ell^{-1}$	Soil	Plant $\mu g \cdot kg^{-1}$	Soil	Plant
May 75	Pre-drilling	1.1	-	43	130	d 59	263
May 76	Post-drilling	1.2	5.0	141	160	356	571
July 76	Flashing	9.9	4.6	140	171	381	584
Nov. 76	Shut down	10.0	1.0	207	189	474	608
Aug. 77	Flow test	0.8	1.0	130	117	250	522
July 78	Shut down	1.2	0.4	178	138	397	572

Table 25. Volatile Hg Emission Rates for Soils and Plants

Sample and Collection site	Total Hg $\mu g \cdot Kg^{-1}$	Hg^0 release (25^0) $\mu g.Kg^{-1} \cdot hr^{-1}$
Lichens		
Usnea (Kauai)	50	0.22
Cladonia (Hawaii)	178	0.04 ± 0.01
Stereocaulon (Greenland)	28	0.42
Mosses		
Leucobryum (Kauai)	26	0.41
Bryum (Hawaii)	200	0.08 ± 0.01
Basidiomycetes		
Fomes (Kauai)	88	0.56 ± 0.20
Trametes (Oahu)	86	0.31 ± 0.16
Soils		
Silty Clay Loam (Hawaii)	28	0.81 ± 0.08
Gypsum-Sulfur Clay (Hawaii)	450	0.25 ± 0.04
Red Clay (Hawaii)	270	0.28 ± 0.06
Sandy Loam (Hawaii)	54	0.84 ± 0.10
Clay Loam (Kauai)	213	0.07
Clay/Sublimate (Hawaii)	1100	0.07
Mean of 35 Vascular Plants (Oahu)	63	0.78 ± 0.36

Hg^o may be both absorbed and revolatilized by leaves. Plants dying from exposure to Hg^o or $Hg(CH_3)_2$ can induce toxic responses in healthy plants placed in their proximity through the combined effects of mercury re-emission and Hg-induced ethylene release. It is readily conceivable that this plant-mercury relationship is not unique, and that similar source-sink-source linkages may exist for arsenic, selenium and thallium.

2. The Geothermal Resource Potential of Hawaii*

a. General Geophysical-Geochemical Standards

The variability of the local geologic structures, and consequent complexity of the groundwater hydrology and geochemistry, have made it impossible to apply a single set of guidelines to the identification of potential geothermal reservoirs.

Ground water hydrology in Hawaii is primarily controlled by aquifer type, soil cover, and local rock permeability. It is therefore a function both of the age of the island and location on the island.

On the younger volcanic systems, the rock types above sea level are generally very permeable allowing rapid percolation of rainfall down to the freshwater lens which floats above the denser salt water in the basal aquifers. The hydrologic head of the basal water table increases by 0.5 meters per kilometer inland, which is typical of a Ghyben Herzberg lens system.

Impermeable ash is commonly found interbedded with the more open fractured basalt lava flows. These have the effect of impeding the downward flow of meteoric recharge and thus

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*With the exception of aerometric mercury survey data, this section is based largely on the final report of the Hawaii Geothermal Resource Assessment Program, Western States Cooperative Direct Heat Resource Assessment Program phase I. Hawaii Institute of Geophysic (DOE/ID/01713-4). 1979.

producing a localized perched water table. The near vertical dip angles of the dike systems within rift zones and calderas generally hinder the seaward flow of ground water through the basal aquifer. This results in an elevated water table up slope of the dike zone and depressed water levels down slope. High level dike impounded aquifers also occur in areas where cross cutting dike complexes perch local recharge.

The hydrogeology of the older islands is affected by alluviation and soil formation as well as by erosional exposure of high level aquifers. The formation of relatively impermeable sediment layers fringing the lower and submarine slopes of the island has the effect of restricting the outflow of fresh water from the basal aquifers. This results in a much thicker freshwater lens beneath the island than would otherwise be present. Impermeable soil cover at the surface hinders the downward percolation of meteoric water increasing surface discharge rates. Erosional exposure of ash-bed perched water tables and dike impounded aquifers has produced perennial, highlevel spring discharge which also increases surface discharge of freshwaters.

In general, ground water geochemistry has been found to be highly localized. It is strongly controlled by aquifer type, rock type, soil cover, surface land usage, and recharge-discharge rates. In younger islands having high recharge rates, basal outflow is very rapid; rock water interactions are minimal and thus groundwater silica concentrations are relatively low. Since sea water encroachment into the basal lens is significant only in near shore aquifers; most salts are present only in very low concentration in the inland areas. On those parts of the younger islands where recharge is low, the groundwater chemistry is quite different. Both tidal mixing and upward migration of sea water salts into the basal aquifers elevates the dissolved salts concentrations considerably; longer residence times of the groundwaters also increases silica concentrations. Thermal influences, such as those arising from a hot intrusive body, enhance both of these effects: mixing of saline and fresh waters is accelerated by thermal convection and dissolved silica concentrations normally increase with higher groundwater temperatures.

The presence of soil cover and longer groundwater residence times on the older islands both increase median silica concentrations by approximately a factor of two above those observed on the younger islands. Agricultural effects, particularly irrigation recharge, serve to elevate silica concentrations as well. The concentrations of other salts can be highly variable: high level dike impounded meteoric water contains quite low concentrations as weil some inland basal waters. In near shore basal aquifers, where heavy groundwater withdrawal has accelerated sea water migration into the freshwater lens, waters are brackish to saline.

The present assessment is based on information obtained from several types of regional surveys which have been carried out on Hawaii during the last 15-20 years. This appraisal of the potential for each area will be a qualitative assessment based on the following types of information:

<u>Surface geology</u>. Surface manifestations of rift zones, calderas, and recent eruptive activity are easily identifiable although, except in areas of obvious thermal activity (springs and fumaroles), they provide little information concerning subsurface conditions.

<u>Infrared studies</u>. Infrared imagery of land surface and near shore ocean waters can identify thermal spring discharges and above-ambient ground temperatures. At present, infrared surveys have been conducted only over the island of Hawaii.

<u>Seismic studies</u>. Passive earthquake monitoring can identify structural features (fractures, rift zones, etc.) normally associated with thermal systems. Relatively little passive seismic data is available for any island other than Hawaii for which there is excellent coverage. Seismic refraction surveys can be used to identify buried magma chambers and intrusives; studies applicable to the present survey have been conducted only on the Koolau volcanic pipe zone on Oahu.

<u>Magnetic field studies</u>. Aeromagnetic survey have been used to identify magnetic field anomalies associated with buried rift zones and caldera. Although aeromagnetic studies have been made for all the major Hawaiian islands, most of the surveys were flown at high altitude with a depth of penetration being on the order of 10 km.

<u>Gravity surveys</u>. Gravity data can provide information

on the locations of dense intrusive bodies and dike zones. Regional and reconnaissance gravity surveys of the type which have been done on Hawaii can provide little information on conditions of the identified systems at depth.

Groundwater temperature data. Near surface waters having temperatures significantly above ambient are strong evidence of a nearby geothermal reservoir. Groundwater temperatures in Hawaii can vary by several degrees depending on the altitude and temperature at which the water entered the subsurface aquifer. Further, the routinely available data (from the U.S. Geological Survey, State of Hawaii Board of Public Health and Department of Land and Natural Resources, and the counties Boards of Water Supply) were found to be of variable reliability and thus were of only marginal utility.

Groundwater geochemistry data. Near surface waters can have geochemical anomalies (i.e. unusual salts concentrations) which arise from high temperature rock-water interaction. The salts commonly used as indicators of thermally altered groundwater are: silica (SiO) - total concentration is a function of temperature; sodium, potassium, calcium (Na, K, Ca) - equilibrium concentrations in thermal waters are related to the empirically derived equation:

$$\log (Na/K) + \log (Ca/Na) = \frac{1647}{273 + T^{\circ}C} - 2.24$$

$B = 1/3$, $T \quad 100^{\circ}C$, $\quad B = 4/3$, $\quad T \quad 100^{\circ}C$,

chloride, magnesium (Cl, Mg) -- Chloride ion concentrations are commonly elevated in thermally altered groundwaters by contamination from magmatic volatiles where as magnesium ion concentrations are reduced by reaction with clay minerals. Cl/Mg ion ratios can be used to differentiate between cold, thermally altered water and fresh water mixed with sea water. Difficulties encountered in interpreting the groundwater geochemical data arose from: reliability of the available data, variations of silica concentration with local geologic setting (see above), and sea water contamination of near surface aquifers with brackish water (see above).

The data compiled during Phase I of the Direct Heat Resource assessment and presented in the Western State Cooperative Phase I Final Report consists of a brief outline of the regional geology and geophysics as well as a topographic-meteorologic-hydrologic profile of each island. The groundwater chemistry data that has been compiled is available in the form of edited, computer-generated, maps of all wells on each island having silica concentrations significantly above the median for the island. Included was the mapping of the most recently available chemical data for each of the identified water sources.

Those areas on each island having elevated Cl/Mg ratios were also denoted on map plots.

The data presentation for each island is followed by an interpretation and qualitative assessment of the geothermal potential for the island based on all the information presented. For present purposes, the summary assessment (below) will suffice. Identification and evaluation of the potential geothermal resources has been based on the geological, geophysical and geochemical data presently available for the State of Hawaii. The types of data used in the evaluation of the resource have been as follows:

Geological: Structural geology of the islands and volcanoes, age of the islands, and age and location of most recent volcanism on each island.

Geophysical: aeromagnetic data, gravity data, seismicity, infrared surveys, and groundwater temperature data.

Geochemical: elevated groundwater silica concentrations and anomalies in the Cl/Mg ion ratios in near surface waters.

The results of the survey have identified several areas in the State which may have significant geothermal potential and which should receive more intensive site specific surveys in the future. An appraisal of several of the potential thermal areas in the State has been made in terms of their probability for having a high or low temperature resource as well as their probability for near future development. The latter assessment is based on: the present state of the art in drilling and geothermal utilization technology, proximity to potential markets for heat/electric power produced, and local land use constraints (national park lands, urban residential zoning, etc). The tabulation below, presents a summary account of the potential resource areas; their ranking is on a scale of 1 to 10: 1 having the highest potential, 10 having the lowest. Although other areas in the State undoubtedly have thermal resources, their probability for development in the near future (1980-2000) is so small as to justify their exclusion from the present assessment.

Table 26. A summary of principle areas of geothermal resource potential in Hawaii.

Location*	High Temp. Resource	Low Temp. Resource	Probability for Development
Hawaii (H)			
1. Puna	1	1	3
2. Ka'u	2	1	7
3. South Point	3	2	3
4. Hualalai-North Kona	5	3	1
5. Kawaihae	5	3	1
6. Keaau	6	4	1
7. Kohala	7	5	8
Maui (M)			
1. Haleakala-Southwest Rift	3	2	5
2. Haleakala-East Rift	3	2	6
3. Pauwela	4	3	3
4. Lahaina	3	1	1
5. Olowalu-Ukumehame	3	1	2
6. Honokawai	5	4	2
Oahu (O)			
1. Waimanalo	7	5	1
2. Lualualei	8	6	1
3. Honolulu Volcanic Series	8	7	2
4. Haleiwa	9	7	3
5. Laie	9	7	3
6. Pearl Harbor	10	9	1
Kauai (K)			
1. Post erosional Volcanic Series	10	8	5

*See also Fig.10 below for approximate map distribution of these sites.

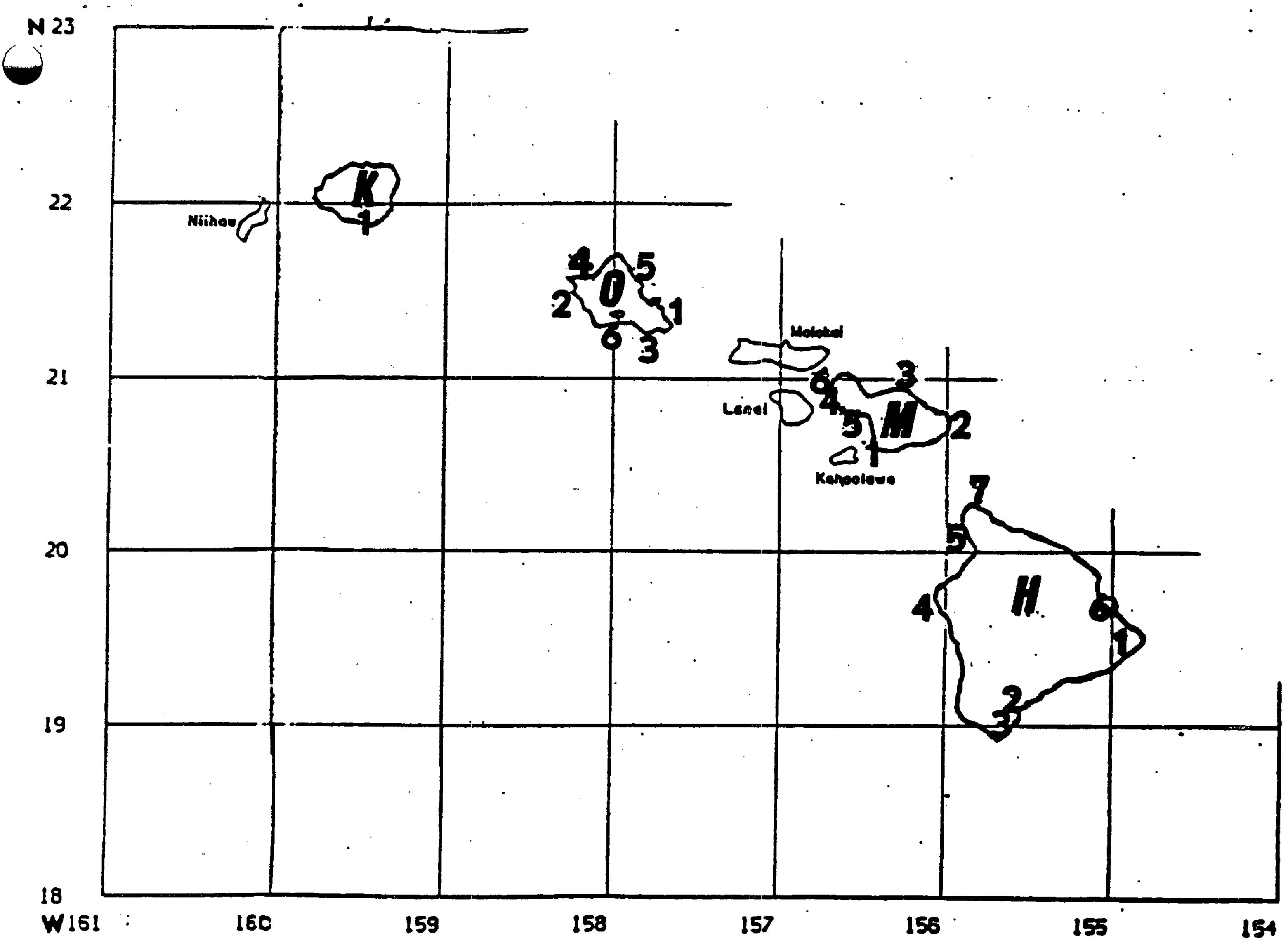

Figure 10. Areas of geothermal potential in the major Hawaiian Islands. (See table 26.)

b. Mercury

The addition of soil and water mercury analyses to the techniques for geothermal exploration was implicity in the early demonstration that the element is associated with volcanic and fumerolic activity. (Eshleman et al, 1971; Aidin' yan and Uzerva, 1966, Karasik and Morozov, 1966) and extensive later studies in widely separated volcanic systems (Siegel and Siegel 1979 a,b,c; Brill et al. 1979, McMurtry et al 1979, 1980, Siegel et al 1979, Siegel et al 1980 a,b, Phelps et al 1979).

Specific use of mercury in the condensed phase was suggested by Matlick and Burseck (1975). Soil and ground-water surveys were discussed in the Final Report in DOE/ID/01713-5, Hawaii Geothermal Resource Assessment Program (Investigation of Low Temperature Resource on the Island of Oahu, Hawaii). In a study of the Lualualei Valley, Waianae Coast, Oahu, the report states "The ability of soil mercury to assist in defining areas of subsurface thermal activity in areas which have no other obvious surface manifestations has led to the application of this technique. . .". It further concluded that in general soil Hg patterns arise from thermally driven outgassing; that mercury and radon outgassing are broadly associated, and that ground water and soil mercury levels are closely correlated.

Some 10 years of "roadside" sampling for atmospheric mercury onthe four major islands also suggest the indicater value of Hg aerometry. Understandably, air sampling at the one meter level is subject to the usual atmospheric perturbations. These include not only winds and convective processes, but also the masking effects of intense sources.

Thus, Hawaii itself, with intense emissions on Mauna Loa, at Kilauea and along Kilauea East Rift influences air levels over the entire ESE to WSW sector of the Island, with only NE-facing areas near baseline levels (Fig. 11).

In the case of Maui, of the six areas recognized by standard geophysical-geochemical methods, two can be closely confirmed by air sampling, especially the Haleakala SW rift, two additional areas in broad agreement and two negative (Fig.12; Table 27).

On Oahu, the two most promising areas, one on the Windward coast, one on the leeward Waianae coast are shown by both procedures (Fig. 13).

And on Kauai, there are possible air Hg anomalies in the post-erosional volcanic area, but also one unexplained high at the head of Waimea Canyon (Fig. 14).

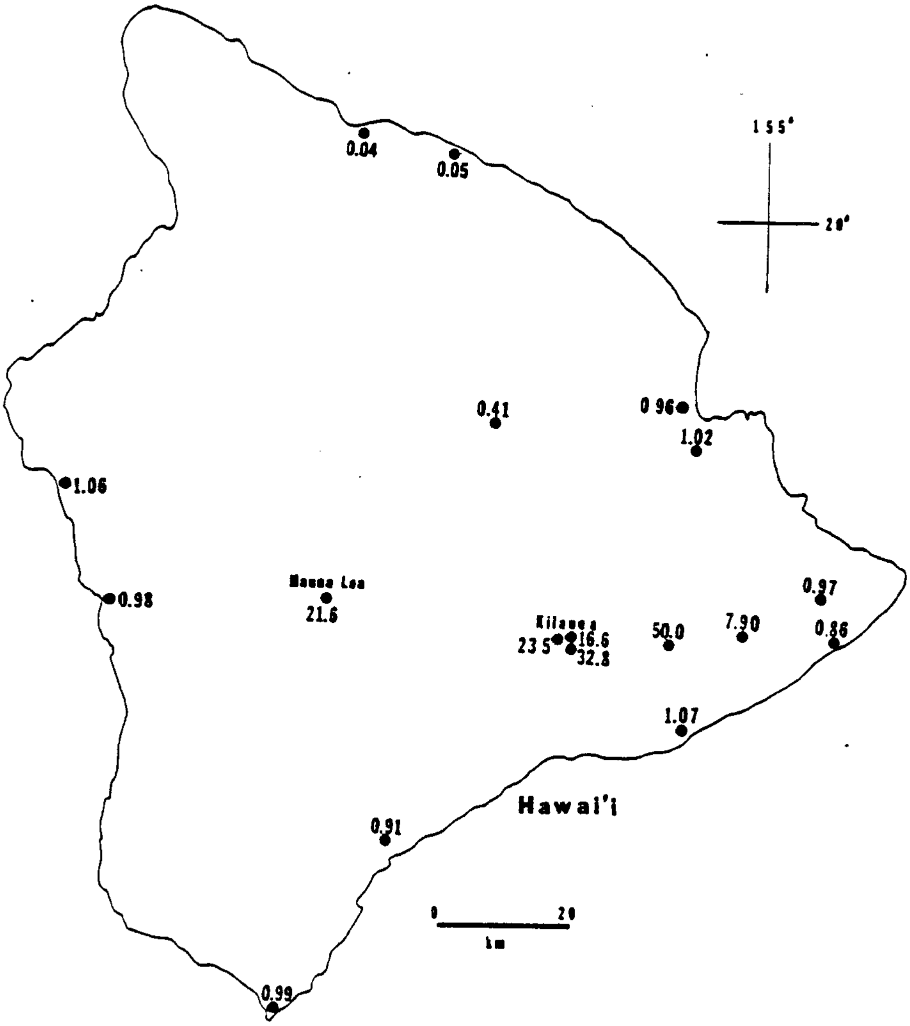

Figure 11. Atmospheric mercury distribution on the Island of Hawaii. All values in $\mu g.m^{-3}$ are means of 4-40 determinations over the period 1970-1979. Standard errors are ±20% of their means or less.

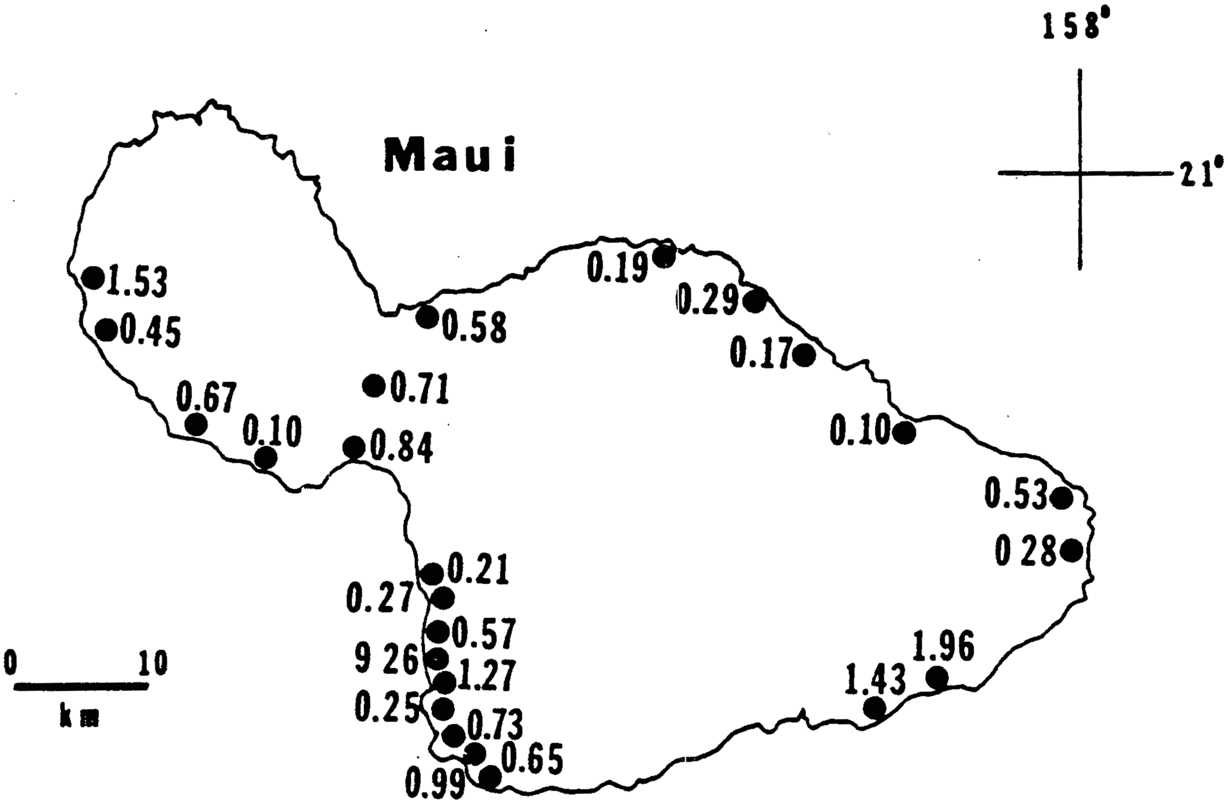

Figure 12. Atmospheric mercury distribution on the Island of Maui. All values in $\mu g.m^{-3}$ are means of 3-10 determinations over the period 1973-1979. Standard errors are $\pm$20% of their means or less.

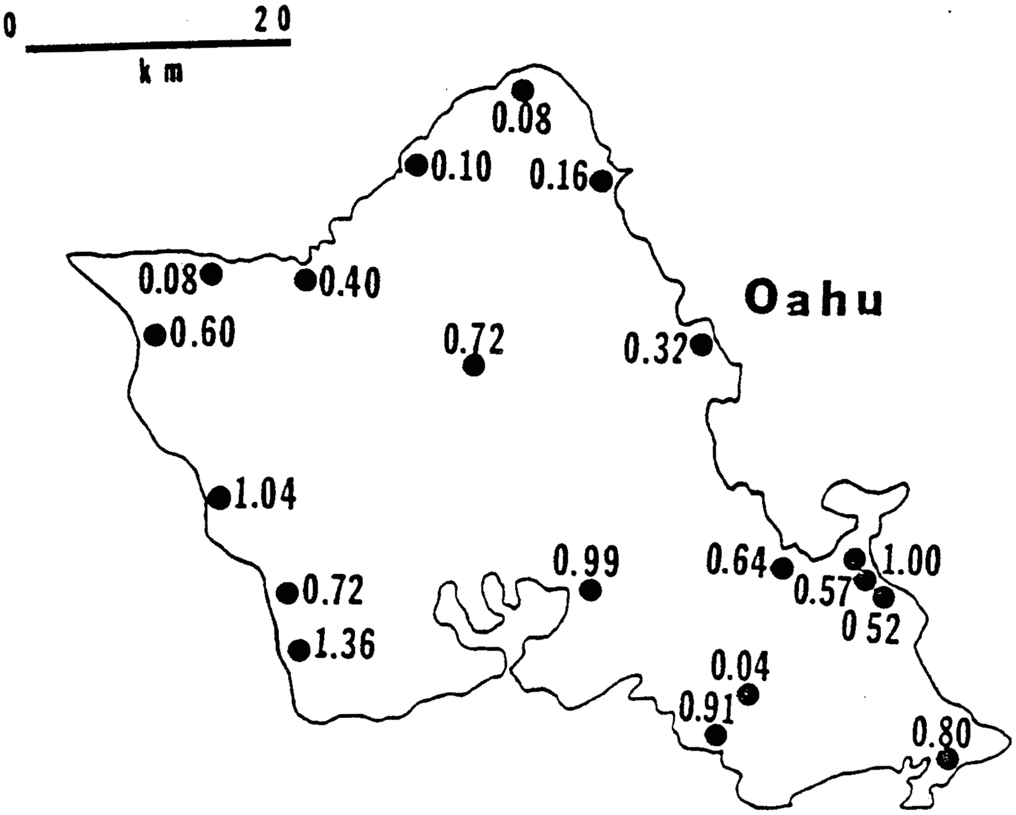

Figure 13. Atmospheric mercury distribution on the Island of Oahu. All values in $\mu g \cdot m^{-3}$ are means of 3-10 determinations over the period 1969-1979. Standard errors are ±20% of their means or less.

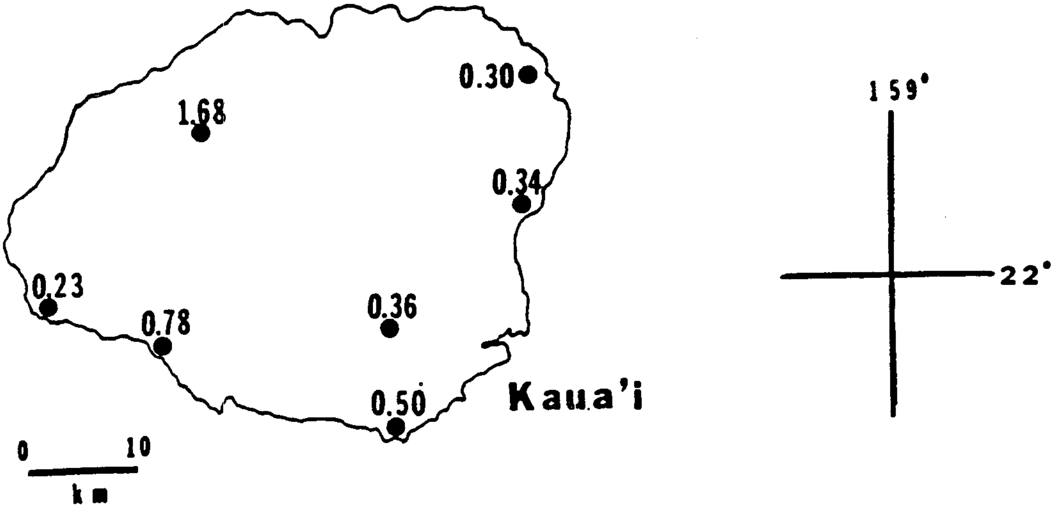

Figure 14. Atmospheric mercury distribution on the Island of Kauai. All values in $\mu g \cdot m^{-3}$ are means of 3-6 determinations over the period 1975-1979. Standard errors are ±25% of their means or less.

Table 27. Value of Mercury Aerometry in Geothermal Exploration: A Comparison for the Islands Lacking Current Volcanic-fumerolic Activity

Island	Sites By Standard Methods	Sites By Hg-Aerometry
Maui	Haleakala - SW Rift (1)	+
	Haleakala - E Rift (2)	±
	Pauwela (3)	−
	Lahaina (4)	±
	Olowalu-Ukumehame (5)	−
	Honokawaii (6)	+
Oahu	Waimanalo	+
	Lualualei	+
	Honolulu Volcanic	−
	Haleiwa	−
	Laie	−
	Pearl Harbor	−
Kauai	Post-Erosional Volcanic	±

Thus, in spite of its more fugitive character; Hg aerometry; a simple and inexpensive analytical procedure has genuine promise as an adjunct for exploration. As pointed out, the more detailed measurements taken at Lualualei support this conclusion.

Table 28. Environmental Toxicant Output in Relation to Scale-Up of Geothermal Energy Production

Energy Output megaWatts	Scale Factor		Possible Sources	Hg Emission* $g \cdot 24\ hr^{-1}$	H_2S Emission** metric $tons \cdot yr^{-1}$ Abatement %		
					0	97	99
3	1	(Kapoho)	1	1.09	277	8.3+	2.8‡
25	8.33	(Kapoho)	1	9.13	-	69.1	23.3
200	66.6	(Kapoho)	1	72.6	-	562.8	186.5
500	166.6	(Kapoho)	1	181.6	-	1383.	466.2
1000	333.3	(Hawaii)	4	363.	-	2766.	932.
3000	1000	(State)	10	1089.	-	8298.	2796.

*0.001 ppm wellhead maximum at 100 $kilo\text{-}lb \cdot hr^{-1}$, Steam Qual. 0.6

**700 ppm wellhead maximum at 100 $kilo\text{-}lb \cdot hr^{-1}$, Steam Qual. 0.6

+ current, using Caustic Soda and rockpile Sparger system

‡ Projected for completed generator facility.

c. Scale-up

Under current projections HGP-A will be a producing 3 megawatt (electric) generating station in 1981, operating at a mass flow of 100k-lb$\cdot$hr^{-1} with a steam quality of ca 0.6.

As of January, 1980, the well fluid contained about 0.001 ppm of Hg (very high estimate) and 700 ppm H_2S.

If it is assumed that the Kapoho reservoir is chemically homogeneous, and that HGP-A is a representative sample of that hydrogeothermal field, then the scale-factor for any future generating capacity, megawattage projected/3megawatts current can be used for projecting mercury and hydrogen sulfide emissions.

The most immediate future goal for geothermal development at Kapoho is 25 megawatts. This intermediate step would be followed, if performance and economic resources warrant, by development into 200-500 megawatt range. The latter is a projected ceiling for the Kapoho reservoir based on continuous operation into the late 21st century.

Beyond this single highly promising reservoir are the additional hydrogeothermal fields on the Island of Hawaii, with perhaps a potential of 1000 megawatts and a total ceiling value for the state lying between 2000 and 3000 mW.

Following present chemical emission standards, two potential limits to the overall development of geothermal energy resources are mercury and hydrogen sulfide. These limits are embodied in the EPA's National Emission Standards 121:0461 (1976) and the more recent 40CFR 51.24, Fed. Reg.

43 (118):26382 (1978), the 1977 Clean Air Act; Prevention of Significant Air Quality Deterioration (PSD).

The former sets upper limits on Hg output of 1600 or 2300 g per 24 hr. period, depending upon the nature of the facility. Using GHP-A as the operating model and assuming the Kapoho reservoir to be broadly representative of reservoirs, no amount of scale up seems capable of attaining emissions limits for Hg (Table 24),even on a state-wide level. And it is reasonable geochemically to expect the highest Hg levels to be associated with the Island of Hawaii.

The PSD limit for geothermal H_2S from any specific source is 250 tons per year. For present purposes, we define the Kapoho field as a source, hence, the 250 ton limit would apply not only to HGP-A as a generating facility, but to all subsequent wells and power stations on the Kapoho reservoir. Obviously, HGP-A itself, unabated is itself marginal assuming continuous operation at a mass flow of 100 Kilo-lb$\cdot$hr^{-1} and that the 700 ppm H_2S content is a steady state value under operating conditions.

Results of the well tests completed in January, 1980, show that of the 700 ppm wellhead H_2S, 22 ppm are released after caustic soda treatment and the use of the rockpile sparger system (L. Lopez, Geothermal-Generator Project Personal Communication, February, 1980). This gives an abatement value of 97%. At this efficiency, any power rating up to ca 90 megawatts would fall within PSD limits. It is expected, however, that the generating facility at HGP-A will provide readily for

99% abatement. Accordingly, the upper PSD limit Kapoho would become ca 268 megawatts ($\frac{250}{2.8}$ x 3 mW), at 99% abatement, the 932 tons of H_2S produced on the Island of Hawaii with 1000 mwatts output would be permissable if 4 or more of the 7 identified reservoirs were able to divide the emission burden more or less equally.

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