



## HAWAIIAN VOLCANOES AND THE BIOGEOLOGY OF MERCURY

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### ABSTRACT

The global importance of volcanoes as a source of mercury appears to have been underestimated. The highly active Kilauea Volcano in Hawaii lies in the middle of one of the world's most productive forest ecosystems; hence it provides an ideal situation for the study of biological-geological-chemical interactions and interrelationships.

Mercury-rich emissions from Hawaiian volcanoes were discovered in 1971. Since then, the local sources of mercury in Hawaii, its chemical species, accompanying gases, release during lava weathering, dispersal, and vertical distribution have been studied. Parallel investigations have been made of bioaccumulation, biotransformation, and biovolatilization of mercury.

The most significant results during the period covered in this report, 1970–84, are:

1. Mercury emission data have been obtained from the Mauna Loa and Kilauea summit calderas, the Kilauea east rift and nearby fumaroles.

2. A provocative drop in mercury output was observed during the recent (1983–84) Puu Oo eruption compared to the 1977 Kalalua event.

3. The first measurements of mercury over a vertical range (rift level to 2,500-m elevation) were made during the 1977 Kalalua eruption.

4. The relation between  $Hg^0$  and  $HgX_2$  have been studied with respect to site, time, and distance, and a specific  $Hg-CO_2$  correlation has been derived.

5. The regulatory role of vegetation in mercury distribution as a sink and secondary source through facile conversion of the ion to  $Hg^0$  and its continuous release has been established.

6. It has been found that seedlings have a 300-fold greater sensitivity to  $Hg^0$  than mature plants, which respond by premature senescence.

### INTRODUCTION

Mercury is produced by Hawaii's active volcanoes, Kilauea and Mauna Loa, and by many other volcanoes the world over, including Hekla, Erebus, and St. Helens, irrespective of their chemical description (basaltic or andesitic) or location (midplate or plate margin). In spite of the element's global scarcity, mercury appears to be a ubiquitous constituent of volcanic gases, lavas, and pyroclastic deposits.

Recent flux measurements indicate that the amount of mercury attributable to volcanic activity has been underestimated in the past. Output figures from Mount St. Helens and several Central American volcanoes are remarkably similar to those reported from

Halemaumau, the main vent of Kilauea, which produces approximately 270 tons annually (Varekamp and Buseck, 1981; Siegel and Siegel, 1984a). If, in fact, 200–300 tons of mercury were released annually by each of the 50–60 terrestrial volcanoes considered active (1975–80 annual average from Simkin and others, 1981), then the volcanic contribution to the global total would equal or exceed the commonly cited value of  $10 \times 10^9$ – $20 \times 10^9$  g/yr for all mercury transfer to the atmosphere (U.S. National Academy of Sciences, 1977; Andren and Nriagu, 1979).

In 1970 we identified Kilauea as the major source of mercury in air over Oahu, 320 km away. Our work since that time has attempted to develop a comprehensive picture of the primary and secondary sources of the mercury, its sites of temporary storage, transfer modes, and sinks.

The cool upland forest in and around Hawaii Volcanoes National Park on the Island of Hawaii is one of the most productive ecosystems on this planet. Few volcanoes are situated in environments so heavily covered with vegetation as is Kilauea. Since the biosphere exerts a remarkable degree of control over the chemistry of the air, water, and soil, the location of Kilauea on Hawaii offers an exceptional opportunity to examine the transformation and distribution of volcanic mercury in a geobotanical and biogeochemical framework. On the other hand, few volcanoes are situated in locations so barren that their activity can be studied and their behavior interpreted without reference to geobiology; Mount Erebus in Antarctica may be one of those few (Siegel and others, 1980b) and therefore allow for interesting comparisons.

We have worked more than 15 years on this problem in Hawaii and elsewhere; much information has also been contributed by many others. Nevertheless, a great deal still remains unknown about the cycling of mercury on Earth, and this paper is only a progress report.

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### MINERALOGY, GEOCHEMISTRY, AND CHEMISTRY

For a more comprehensive review of mercury's physical parameters, the reader is referred to several excellent texts (King, 1951; Goldschmidt, 1954; Rankama and Sahama, 1950; Hem, 1970; Aylett, 1973).

The mineralogy of mercury is comparatively simple. Cinnabar is the only common mineral; it can be primary or found as an alteration product of more complicated base-metal sulfides containing mercury. Native mercury is frequently an oxidation product of cinnabar. The other known mercury minerals are curiosities; among them the oxysalts are indicators of arid climatic conditions. Traces of mercury may occur in some minerals, including tetrahedrite and tennantite (they are then called schwazite and hermesite), penroseite, argyrodite, clausenthalite, altaite, and sphalerite.

Mercury has a high ionization potential (I.P.) and tends strongly to remain in the elemental state. Its first I.P. is 10.39 eV (gold's is 9.20 eV and silver 7.53 eV), and its second I.P. is 18.65 eV.

Mercury has a uniquely low melting point ( $-39^{\circ}\text{C}$ ) and high vapor pressure ( $1.9 \times 10^{-3}$  mmHg at  $25^{\circ}\text{C}$ ), indicative of its very low interatomic forces. Its viscosity, similar to that of water, is also low.

Mercury vapor is almost all monatomic, even at room temperature; apart from the noble gases, mercury is the only element to show this behavior at such low temperatures. Viscosity measure-

ments suggest that the closest interatomic approach in the vapor phase is about 3.25 Å at 850 K, little greater than in the liquid state. Both absorption and emission spectra of mercury vapor yield data that indicate the presence of a very small proportion of weakly bonded  $\text{Hg}_2$  molecules.

The solubility ( $6 \times 10^{-6}$  g/100 g water at  $25^{\circ}\text{C}$ ) of  $\text{Hg}^0$  in air-free water is exceptional, being much higher than that of most other metals. Addition of air increases the solubility 700 times, up to a value almost identical with the solubility of  $\text{HgO}$  in water. Mercury is also appreciably soluble in n-hexane ( $2.7 \times 10^{-7}$  g/100 g at  $40^{\circ}\text{C}$ ), benzene ( $2.0 \times 10^{-7}$  g/100 g at  $20^{\circ}\text{C}$ ), methanol ( $3.6 \times 10^{-7}$  g/100 g at  $63^{\circ}\text{C}$ ) and dioxane ( $7.0 \times 10^{-7}$  g/100 g at  $25^{\circ}\text{C}$ ).

Oxygen and dry air do not react with mercury appreciably at room temperature, but the reaction may be greatly promoted by ultraviolet radiation. Ozone rapidly attacks mercury at room temperature to give  $\text{Hg}^{2+}$ .

All the halogens react directly with mercury at room temperature: mercurous halides seem to be formed first, followed by mercuric halides if halogen is in excess.

Air-free water below about  $200^{\circ}\text{C}$  does not react chemically with mercury. Other elements that react directly with mercury, especially on heating, include sulphur, selenium, and tellurium; on the other hand, nitrogen, phosphorus, arsenic, carbon, silicon, and germanium do not seem to combine with it. Dry halides such as  $\text{HX}$  ( $\text{X} = \text{F}, \text{Cl}$ ),  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ , and  $\text{AsH}_3$  do not react with mercury below about  $200^{\circ}\text{C}$ . Some reaction with  $\text{HBr}$ ,  $\text{HI}$ , and  $\text{H}_2\text{Se}$  occurs even at room temperature. Various nonmetallic halides react readily with mercury. Among oxides,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$  are without effect at room temperature, but  $\text{NO}_2$  reacts very rapidly to give mixtures of mercury (I) nitrite and nitrate as initial products.

Dilute hydrochloric and sulphuric acids do not react with mercury, but moderately concentrated solutions ( $>6N$ ) attack it superficially to give a little mercurous salt. Concentrated hot  $\text{H}_2\text{SO}_4$  dissolves mercury to yield  $\text{Hg}_2\text{SO}_4$ ,  $\text{HgSO}_4$ , and  $\text{SO}_2$ , and nitric acid gives a range of products depending on conditions that include  $\text{Hg}_2(\text{NO}_2)_2$ ,  $\text{Hg}(\text{NO}_2)$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{NO}$ , and  $\text{NO}_3$ . Phosphoric acid does not react appreciably.

Mercury is not attacked by alkali, but ammonia solutions in air rapidly lead to the production of Millon's base,  $\text{Hg}_2\text{NOH}$ .

Under natural conditions of temperature and pressure that occur in river and lake water and water-saturated sediment, mercury can be present in one or more of its three different oxidation states. The most reduced, in a chemical sense, of these forms is the metal, which has a distinct tendency to vaporize because it is a liquid at ordinary temperatures. The other two forms are ionic: where the average valence of mercury is +1, the more reduced of the two ions is the mercurous ion  $\text{Hg}_2^{2+}$ ; in oxidizing conditions, especially at low pH, the stable form is the mercuric ion,  $\text{Hg}^{2+}$  (Hem, 1970).

Although chemical oxidation reactions do not require the presence of oxygen, it is the most common oxidizing agent. Systems in contact with air tend to be oxidized, and in its absence reducing conditions readily become established. In moderately oxidizing conditions of pH above 5 the predominant mercury species in

solution is undissociated mercury. Its solubility, constant over the whole range of temperature where the liquid metal is stable, is fairly low (25 ppb), and the mercury exists as  $\text{Hg}^0$ . This solubility value represents the likely upper equilibrium limit of mercury in low-chloride surface streams and lakes.

Mildly reducing conditions, which are likely to occur in many lake and streambed sediments, can cause the mercury to be precipitated as cinnabar, which has an extremely low solubility. In the field at neutral pH,  $\text{Hg}(\text{HS})_2^0$  aq and  $\text{HgS}_2^{2-}$  have an equilibrium solubility lower than 0.002 ppb. Very strongly reducing conditions, however, may increase the solubility somewhat by converting the mercuric ion to free metal.

In solutions high in chloride the solubility of mercury in oxygenated water may be greatly increased by the formation of the uncharged  $\text{HgCl}_2$  complex, or anionic complexes such as  $\text{HgCl}_4^{2-}$  (Wagman, 1969).

The frequent departure of natural systems from equilibrium is well known and must be kept in mind when using equilibrium calculations. There are two aspects of mercury chemistry that are particularly important sources of departure from what is predicted theoretically. One of these is the formation of organic complexes and participation of mercury in biochemical processes, especially in the production of methyl mercury by sedimentary bacteria (Jensen and Jernelev, 1969). A secondary property of importance is the tendency for mercury to participate in dismutation reactions—that is, in reactions of the type  $\text{Hg}_2^{2+} \rightleftharpoons \text{Hg}^0 + \text{Hg}^{+2}$  that provide a means whereby mercury can be first converted to the liquid form and then escape as vapor.

Although there is some understanding of the aqueous chemistry of mercury, a considerable amount of basic research is still needed, especially on rates and mechanisms of reaction and on the behavior of organic mercury complexes.

## TOXICOLOGY

The onset of symptoms from mercury poisoning in humans is insidious, and the symptoms, with the exception of tremor, may often be ignored or attributed to other causes (Bidstrup, 1964). This is especially true of a peculiar emotional instability called erethism, which is defined by irritability, irrational outbursts of temper, excitability, shyness, and sometimes depression; such symptoms are often just attributed to an anxiety state.

The classic signs of poisoning by mercury in the inorganic form are gingivitis and stomatitis accompanied by excessive salivation or a metallic taste, burning, swelling and ashy discoloration of the mouth followed by intense thirst and abdominal pain; erethism; and tremor (Goldwater, 1951). Vomiting may occur, and in some cases circulatory collapse with a fatal outcome appears suddenly and at an early stage. Delayed effects on the kidneys or large intestine are generally the cause of death (Sollman, 1957). There is no clear difference between the acute, subacute, and chronic forms except that the symptoms develop more quickly and are of greater intensity, and generally the oral and gastrointestinal symptoms are more obvious in acute and subacute poisoning (Bidstrup, 1964). Mer-

curic chloride especially is irritating to the skin and mucous membranes, causing irritation, vesication, and corrosion. Absorption through the skin and mucous membranes may cause systemic poisoning.

Acrodynia (so-called pink disease) occurs in infants and young children; it is characterized by mental disturbances, insomnia, sweating, disordered sensation of the extremities, and peripheral vascular phenomena and is often fatal. Strong evidence exists that the absorption of mercury is the most important cause of this disease, although there is confusing etiology (Warkany and Hubbard, 1953).

When cinnabar,  $\text{HgS}$ , has been used for the red color in tattooing, mercury dermatitis has been reported, and occasionally an eczematous rash has spread to involve the entire body.

Acute poisoning from metallic mercury or its vapor rarely occurs now and is usually the result of an accidental exposure (Matthes and others, 1958), but historically it was a common occurrence among men exposed to mercury in certain occupations. Hunter (1955, p. 256) quotes from Ramazzini concerning miners and goldsmiths:

It is from mercury mines that there issues the most cruel bane of all that deals death and destruction to miners.

We all know what terrible maladies are contracted from mercury by goldsmiths, especially those employed in gilding silver and copper objects. Hence craftsmen of this sort very soon become subject to vertigo, asthma and paralysis. Very few of them reach old age, and even when they die young their health is so terribly undermined that they pray for death.

and also mirror makers:

you may see these workmen gazing with reluctance and scowling at the reflection of their own sufferings in their mirrors and cursing the trade they have adopted.

Acute and subacute poisoning among persons engaged in the mining and refining of mercury have been reported, but improvements in ventilation of mines, refinery processes, and the use of personal protective measures have reduced the numbers and severity of poisoning. Vouk and others (1950), reporting on environmental conditions in the Idria (Yugoslavia) mercury mines, stated that there were 93 cases in 1949 and 53 reported in the first half of 1950. In Idria mercury occurs both as cinnabar and in the free form, and the mining of  $\text{Hg}^0$  is particularly hazardous.

Concentrations of mercury in the air in pits where cinnabar, alone or with free mercury, is mined are 50–59  $\mu\text{g}/\text{m}^3$ . Dizon and others (1960) investigated a mercury mine in the Philippines, where it is a relatively new industry and the processes are highly mechanized. The highest atmospheric concentrations reported were 100–400  $\mu\text{g}/\text{m}^3$  in the vicinity of the ore crushers, and 6 of the 11 men employed at the crushers had symptoms of mercury poisoning. In Peru, Carlin and others (1960) reported that 16 out of 18 refinery workers were found to have high mercury excretion in the urine (average 224  $\mu\text{g}/\text{L}$ ), and 13 had definite evidence of mercury poisoning.

More general problems of animal toxicity have been discussed in detail in the compilations of Buhler (1973) and Nriagu (1979). Included are behavioral effects, cell and organ degeneration, and developmental abnormalities in birds, terrestrial vertebrates, and aquatic marine forms from mammals to fish.

In spite of the obvious role of plants in primary life support, the effect of mercury on vegetation has received little more than token attention until recently. From the first account of mercury intoxication of plants (Deiman and others, 1797), the only reports up to 1930 were those of Boussingault (1867a,b), Harrington (1917), and Le Van (1930). Zimmermann and Crocker (1933, 1934) and Ratsch (1933) revived the experimental study of mercury toxicity in conjunction with seed and greenhouse problems, but they did not recognize major developmental features of mercury toxicity and its dependency on the chemical species used.

Typically, plant-cell damage takes place with aqueous solutions containing as little as 10  $\mu\text{g/L}$  of  $\text{Hg}^0$  ion (Siegel, 1977).

In contrast, when 18 species and varieties of seeds were germinated in air containing 14  $\mu\text{g/L}$  of  $\text{Hg}^0$  vapor (Siegel and Siegel, 1979a; Siegel and others, 1984a), root growth was stimulated in 4 species, inhibited by 25 percent or less in 6, and did not exceed 50 percent inhibition in the 8 remaining species. Shoot growth was even less adversely affected; only 4 species were inhibited by more than 25 percent.

Of castor bean seedlings 20 days old in air containing 0.05  $\mu\text{g/L}$  of  $\text{Hg}^0$ , only 14 percent lost their leaves, and none showed zones of discoloration or morbidity after seven days. Coleus seedlings of the same age were even less affected. However, mature plants of both species after seven days in air containing 0.05  $\mu\text{g/L}$  of  $\text{Hg}^0$ , lose 50–90 percent of their leaves. In terms of toxic thresholds, mature plants are approximately 300 times more sensitive to mercury than seedlings.

At the concentration of 0.05  $\mu\text{g/L}$   $\text{HgCl}_2$  vapor has essentially no toxic effect on seedlings or mature plants.

The principal toxic effect of  $\text{Hg}^0$  seems to be an acceleration of the aging process mediated by induction of the plant stress hormone ethylene (Siegel and others, 1973b; Goren and Siegel, 1976).

## MERCURY IN HAWAII

### DISCOVERY

Mercury in Hawaii was first found in stream sediments on the Island of Oahu and later in the air (Siegel and others, 1973b). To determine the source of this mercury, widespread monitoring, sampling, and analyses were carried out. Air mercury levels on Oahu were found to be highest in the southeastern part of the island and lowest at sites facing the northeast tradewinds; this indicated that the primary source was the thermally active Island of Hawaii (Eshleman and others, 1971). The verification of volcanic-fumarolic mercury sources in 1970–71 led in turn to a program of study that has continued to the present. The main focus has been the active volcanic areas of Hawaii, but the studies have also included Iceland, Alaska, New Zealand, and Antarctica.

The sources of mercury on Oahu, with its long-dormant (or extinct) volcanoes Kaala and Waianae (Macdonald and Abbott, 1970), have provided us with opportunities for research involving residual mercury, mercury transport, and biological compartments. These subjects will be discussed later.

### PRIMARY SOURCES AND SPECIATION

There are two active centers of gas emission on the Island of Hawaii—the volcanoes Kilauea and Mauna Loa. Kilauea and the thermal features of the east rift zone have been studied extensively; the Mauna Loa summit caldera, Mokuaweoweo, has also been sampled, but emissions during flank eruption have only been measured for mercury during March 1984. The most commonly studied sites on Kilauea have been Halemaumau (the main vent) and the Sulphur Bank fumaroles, first sampled in 1970 (Siegel and Siegel, 1980, 1984a).

In our ongoing studies, air samples have been regularly collected in nitric acid/pyrex-fiberglass impingers at flow rates of 1–2 L/min for periods of 4–7 h, thus assuring a gas volume of at least 240 L (0.24  $\text{m}^3$ ). Samples have been analyzed by flameless atomic absorption (Eshleman and others, 1971; Siegel and Siegel, 1978, 1979; Siegel and others, 1985). Parallel sampling was also carried out by drawing air through gold-foil traps, which were subsequently stripped of mercury in nitric acid. Millipore filters were used to trap particles with diameters larger than 0.22  $\mu\text{m}$ . The nitric acid traps collect total mercury; the gold foil collects  $\text{Hg}^0$  only and millipore filters insoluble  $\text{HgS}$  (cinnabar). Cinnabar was verified by solubility in aqua regia and insolubility in cold nitric acid. Any difference observed between total mercury and particulate mercury plus  $\text{Hg}^0$  is considered to be  $\text{HgX}_2$ , presumably a mixed halide (Cadle, 1975), but mainly the chloride.

Another approach to air sampling is fallout measurement or deposition (Siegel and Siegel, 1977). Here copper foil, which reduces  $\text{Hg}^{2+}$ , and gold foil, which amalgamates  $\text{Hg}^0$ , are used to distinguish the mercury species.

We assume that copper foil collects both  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ , hence the amount of mercury trapped on gold foil subtracted from the amount of mercury on copper foil yields a value for  $\text{Hg}^{2+}$ . This calculation is valid only if the  $\text{HgS}$  particulate fraction is negligible.

The average total mercury concentration in the open air 2 m above the ground (at right angles to the slope) at Sulphur Bank ranged from 2,700 to 40,600  $\text{ng/m}^3$  through 1977, but in subsequent years exceeded 1,000  $\text{ng/m}^3$  only during January–February 1982, at the start of the current Puu Oo eruption series (fig. 35.1; table 35.1). The Halemaumau vent of Kilauea (fig. 35.1, table 35.2) has also been highly productive, behaving similarly to Sulphur Bank in eruptive and quiescent periods. Overall, it would appear that the normal value for mercury in air in the Kilauea summit area ranges from 400 to 1,000  $\text{ng/m}^3$ . Similar values are seen along the approach to Kilauea caldera from the northeast (as seen in the 500- to 1,000-m transects along the volcano highway; fig. 35.2). For the period 1971–78, the average mercury value in the immediate vicinity of the caldera lies between 400 and 1,400  $\text{ng/m}^3$ , but it falls off dramatically to the northeast into the tradewinds.

Air samples taken at Royal Gardens during the Kalalua rift eruption of 1977 show the mercury level rising suddenly from a putative baseline (June–July) of about 300  $\text{ng/m}^3$  to 200,000  $\text{ng/m}^3$  (200  $\mu\text{g/m}^3$ ) or more by September 15, then dropping precipitously after the fountaining and tremor ended in October (Siegel and Siegel, 1978).

TABLE 35.1.—Mercury concentration in air at the Sulphur Bank fumaroles Kilauea Volcano, 1971–1980

[s.d., standard deviation; part., particulates]

Year	Number of samples	Total mercury (ng/m <sup>3</sup> ) (± s.d.)	Mercury species (percent)		
			Hg <sup>0</sup>	Hg (part.)	HgX <sub>2</sub>
1971	26	28,400 ± 11,000	69	1	30
1972	27	3,700 ± 520	24	13	63
1973	10	4,900 ± 640	62	2	36
1974	9	4,500 ± 660	71	<1	29
1975	17	2,700 ± 390	44	<1	56
1976	24	8,600 ± 1,200	32	<1	68
1977	38	40,600 ± 4,680	28	<1	72
1978	26	500 ± 70	10	5	85
1979	29	880 ± 95	60	1	39
1980	29	500 ± 85	59	<1	41
241 (total)		9,528 ± 1,464 (avg)	45.9 (avg)	2.2 (avg)	51.9 (avg)

In all the measurements of mercury concentration in air, there appears a consistent downward trend by as much as 95 percent after about 1978. This trend downward may even apply to Mauna Loa mercury output, although the sample data are limited.

It is clear from the record, however, that Kilauea's mercury output since 1977 has not approached that of the Kalalua rift emissions, in spite of the far greater output of fluids and gases since January 1983. This leads to the provocative question of whether the mercury output of Hawaiian volcanoes is really declining. If so, is this phenomenon a long-term downtrend or merely the downward

limb of a cyclical process? Either alternative poses interesting challenges for interpretation.

With few exceptions, particulate mercury has not been found in samples of the air around Kilauea, even during periods of eruptive activity (table 35.1). The 10-year average of particulate mercury is 2.2 percent of the total, but commonly less than 1 percent of the total mercury was found on the filters.

The wide variation in Hg<sup>0</sup> and HgX<sub>2</sub> content of air samples was unexpected—Hg<sup>0</sup> ranged from 10–71 percent of the total at Sulphur Bank (Siegel and Siegel, 1979b). This was also seen in fallout data from the same location (Siegel and Siegel, 1977):

Date	Hg <sup>0</sup> (ng/m <sup>3</sup> )	HgX <sub>2</sub> (ng/m <sup>3</sup> )	Hg <sup>0</sup> /HgX <sub>2</sub>
1972 January	80 ± 9	377 ± 44	0.21
April	300 ± 31	1,220 ± 369	.25
1975 May	250 ± 31	540 ± 60	.46
December	438 ± 48	42 ± 7	10.43
1976 May	575 ± 66	250 ± 27	2.30
June	119 ± 22	612 ± 12	.20

On the other hand, concurrent fallout samples taken on Oahu, about 400 km northwest of Kilauea, always yielded far less total mercury (about 10 percent of that detected near Kilauea) and mostly as Hg<sup>0</sup>. At Halemaumau, Hg<sup>0</sup> accounted for 15–21 percent of the total mercury released, but on the floor of Kilauea, at the very active

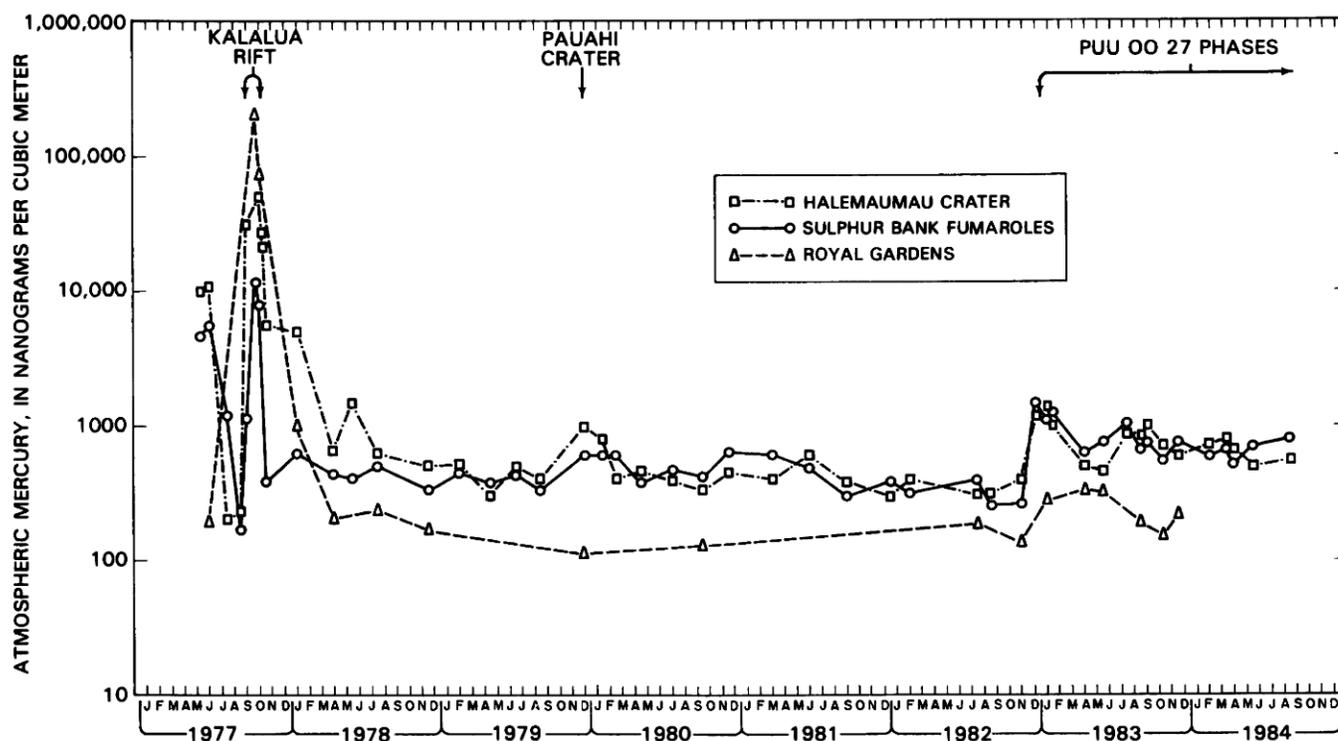


FIGURE 35.1.—Mercury emission record for Kilauea at Halemaumau main vent, the nearby Sulphur Bank fumaroles, and south of east rift at Royal Gardens, 1977–1984. Three events noted: major Kalalua rift eruption lasting nearly one month; one-day Pauahi Crater eruption of 1979; and exceptionally prolonged rift eruption at Puu Oo, beginning January 1983, through its 27th episode. Note that the ordinate scale is logarithmic.

TABLE 35.2.—Measurements of mercury in air at various locations on Kilauea and Mauna Loa Volcanoes  
[See also Connors, 1979]

Site	Sampling period	Total mercury (ng/m <sup>3</sup> )	Hg <sup>0</sup> (percent)	
Kilauea Volcano	Halemaumau	1971 August	40,500	16
		1977 August	48,100	21
		1978 August	1,400	15
	Caldera floor	1971 fissure	79,900	1
		1981 August	3,600	2
	1974 fissure	1978 August	29,800	2
		1981 August	1,900	5
	Kalalua rift	1977 August	1,200	22
		1977 September	>200,000	50
		1977 October	18,500	58
1977 November		500	80	
Puhimau thermal area	1978 January	5,800	72	
	1978 August	12,200	49	
	1981 January	930	56	
Mauna Loa Volcano	Mokuaweoweo caldera	1978 July	24,600	35
		Upper rift	1984 March	4,850

1971 and 1974 fissure the Hg<sup>0</sup> fraction fell to only 1–5 percent of the total emitted. During the 1977 eruption, the Hg<sup>0</sup> fraction rose from its minimum of 22 percent to a peak at 80 percent after the active phase ended.

Mercury is, of course, a minor constituent of volcanic and fumarolic gas emissions, wet or dry. It is accompanied by H<sub>2</sub>S, SO<sub>2</sub>, and CO<sub>2</sub> (Siegel and Siegel, 1979b, 1980). An exception is the Puhimau thermal dieback area, where sulfur in any form has only been detected in the parts per billion range (Phelps and others, 1979). This area formed in 1938–9 after an earthquake and magma shifting brought heat near the surface, causing several acres of forest to die; the ground temperature 5 cm below the surface here averages 97 °C.

At Halemaumau, measurements during 1971–78 gave mole ratios of 590 for H<sub>2</sub>S, 6,300 for SO<sub>2</sub>, and  $2.10 \times 10^6$  for CO<sub>2</sub> (table 35.3). Obviously, sulfur-mercury relations are highly varied, even within a single volcanic system, and are highly site dependent. It is, therefore, of special interest to note that the ratio CO<sub>2</sub>/Hg is nearly constant at Kilauea; individual measurements do differ somewhat, however, and data from other locations such as Mount St. Helens are distinctly different.

Lava flows constitute another source of mercury. Weathering brings about the slow release of soluble or solubilized constituents as the igneous materials degrade into soil minerals. Lava samples were analyzed by digestion of 100-mesh powder with 0.1N HCl to remove soluble and loosely bound mercury. This was followed by hot 2N HNO<sub>3</sub> digestion to remove any mercury complex with organic ligands, and then concentrated HF to destroy the silicate matrix

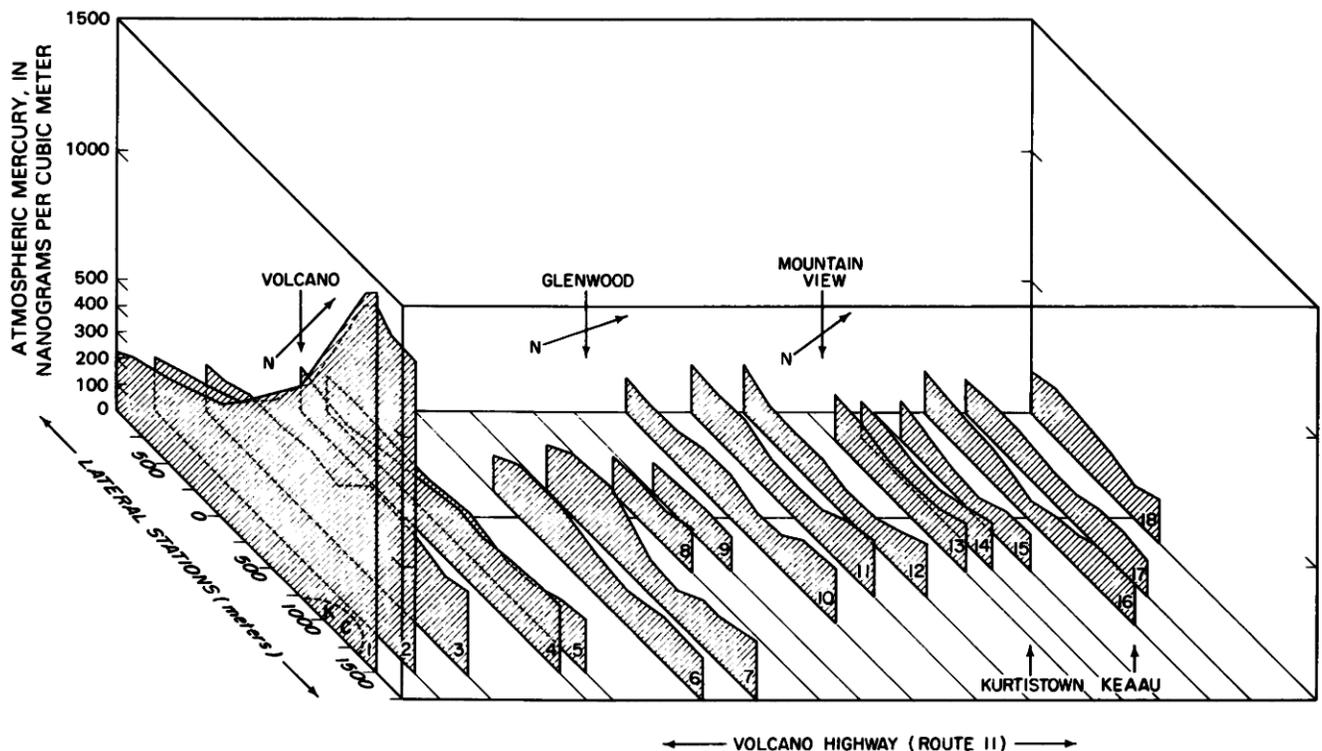


FIGURE 35.2.—Average atmospheric mercury concentration along volcano highway from Kilauea caldera (KC) northeast to the Village of Keaau. North is indicated at three villages. Highway is plotted as straight line perpendicular to transects 1–18.

TABLE 35.3.—*Relations between mercury and other gaseous emissions at thermal sites*  
[s.d., standard deviation; n.d., not determined]

Thermal site	Number of samples	Sampling date	Flux (tons/yr)	Plume ( $\mu\text{mol}/\text{m}^3$ )	Mole ratios		
					H <sub>2</sub> S/Hg	SO <sub>2</sub> /Hg	(CO <sub>2</sub> /Hg)10 <sup>-6</sup>
Kilauea Volcano							
Halemaumau	86	1971–80	260	0.054 ± 0.014	590	6,300	2.10
Sulphur Bank	18	1976–78	—	.012 ± 0.083	3,700	3,050	2.75
1971 Fissure	8	1977–78	—	.396 ± 0.055	0	239	2.75
1974 Fissure	8	1977–78	—	.146 ± 0.016	0	96	2.19
Puhimau Thermal	10	1976–78	—	.026 ± 0.005	0	0	3.66
Mount St. Helens	5	1980	365	.005 ± 0.002	—	2,750	.013
Costa Rica							
Fumarole Poas		1980–82	52	—	—	1,030,000	—
Volcan Arenas		1980–82	32	—	—	5,000	—

(Siegel and others, 1975). Samples from flows of 1840, 1923, and 1955 were obtained with the assistance of the late Gordon Macdonald; fresh Pauahi samples were collected in 1979. The results (below) suggest a 50 percent release in about 50 years and a gradual infiltration of oxidizable, presumably humic, complexing substrates.

Year of flow	HG concentration $\mu\text{g}/\text{kg}$ in lava		
	HCl soluble	HNO <sub>3</sub> soluble	HF digest
1840	5	81	45
1923	16	66	310
1955	10	59	970
1979	0	15	1,290

If Kilauea lava typically cools with about 1,000  $\mu\text{g}/\text{kg}$  of mercury and proceeds to release 90 percent, then this still constitutes only a minor source of the element. The 1840 eruption produced about  $400 \times 10^6 \text{ m}^3$  of lava weighing perhaps  $16 \times 10^9 \text{ kg}$ . Thus, this lava contained a total of  $16 \times 10^6 \text{ g}$  (16 tons) of mercury, of which about 14 tons was released in about a century. In contrast, Halemaumau yields 260 tons annually when it is not erupting (Siegel and Siegel, 1984a).

Of course, the impact of a small though continuous and localized release of mercury cannot be discounted as a possible selection factor for mercury tolerance in the endemic vegetation of Hawaii. It is clear, as we show below, that plants in volcanic areas can become well adapted to life in mercuric environments. Also, Hg<sup>0</sup> slowly released by lava at ground level will, like any heavy gas, tend to accumulate in enclosed pockets and depressions and form areas of local concentration.

At the end of the weathering process, some mercury remains in the clays and derivative soils. In areas of heavy precipitation, such as the Sulphur Bank, acid red clays are common and contain no readily soluble mercury, but when they are heated in closed vessels, their mercury output can be collected on gold foil and measured.

The following data on mercury release from Sulphur Bank soil were obtained in this way:

T(°C)	Rate (ng/kg·h)
25	0.254
70	5.67
120	68.1

Using this kind of data and the Arrhenius equation, we have calculated an apparent heat of activation of 13.81 kcal/mole (Siegel and Siegel, 1983). This value compares well with the molar heat of vaporization calculated similarly from CRC Handbook vapor-pressure data. Thus atmospheric mercury released from soils directly may have been held entirely as Hg<sup>0</sup>.

## DISPERSAL

The northeast tradewinds with velocity of 20–40 km/h constitute a major and well-known determinant of climate in Hawaii. However, the assumption that these winds continually cleanse the atmosphere of pollutants, conveniently displacing them to the southwest, is not borne out by experience. During the 1977 eruption, with tradewinds normal, measurements were made on samples of air from 30 m above ground level at a station on Oahu about 400 km northwest of Kilauea. The mercury content rose from 40 ng/m<sup>3</sup> to 160 ng/m<sup>3</sup> in only 30 hours after the first fountaining at Kalalua (Siegel and Siegel, 1978). The mercury released along the rift and at Halemaumau traveled no less than 13 km/h in a direction about 90° to the tradewind vector. Increases in atmospheric turbidity 1–3 days after the onset of fountaining in a volcanic eruption have often been observed, not only in Honolulu, but also on the west side of the Island of Kauai.

The tradewind air masses move southwestward across the North Pacific and then encounter the high relief and rough terrain of the Island of Hawaii, where they become turbulent. Furthermore, the major sources of emission extend from the tradewind zone upward into air masses moving in other directions. During the final stages of the 1977 eruption, mercury in the air showed a rapid dropoff above the Kalalua rift to an asymptotic value of about 1,000 ng/m<sup>3</sup> at elevations of 1,200–2,500 m (fig. 35.3). Mercury at these higher elevations was over 90 percent Hg<sup>0</sup>. This observation agrees with the fallout data discussed above that showed the proportion of Hg<sup>0</sup> in total mercury was higher on Oahu (sea level) than at the Sulphur Bank when samples collected at the same time were compared (Siegel and Siegel, 1977). The comparison of the Hg<sup>0</sup>/HgX<sub>2</sub> ratio at the two locations is as follows:

	January 1972	May 1975	June 1976
Hawaii	0.212	0.463	0.195
Oahu	2.86	3.16	3.31

It must also be recalled that the Mauna Loa caldera continually fumes at an elevation of about 4,500 m, and numerous fissures are always injecting hot mercuriferous gas into an often turbulent atmosphere. The gas column is subject in its dispersal to a variety of wind vectors, including some that carry the mercury northward and downward as it cools. These may account largely for the distribution of mercury on Oahu (fig. 35.4; see also, Siegel and Siegel, 1980), where higher values occur to the south and west. The

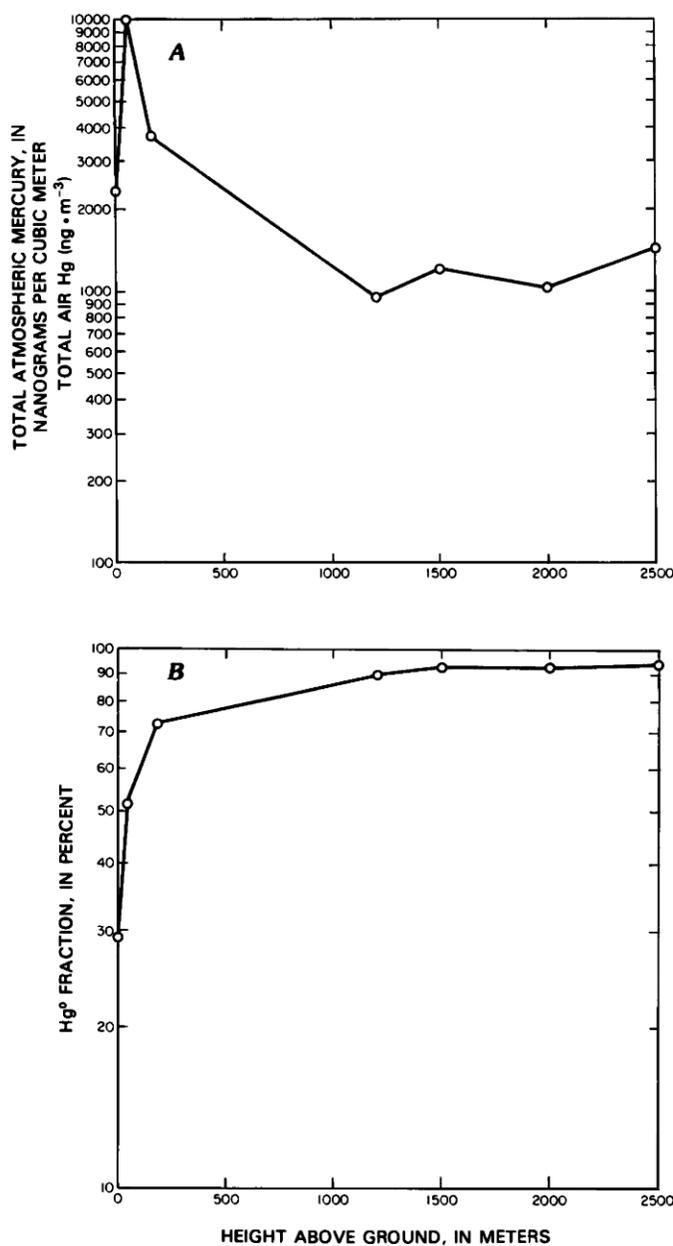


FIGURE 35.3.—Vertical distribution of atmospheric mercury over the Kalalau fissures during the 1977 eruption. Data obtained using dual-trap method: nitric-acid impinger and gold foil. **A**, Concentration from ground level to height of 2,500 m. **B**, Percentage of Hg<sup>0</sup> in total mercury.

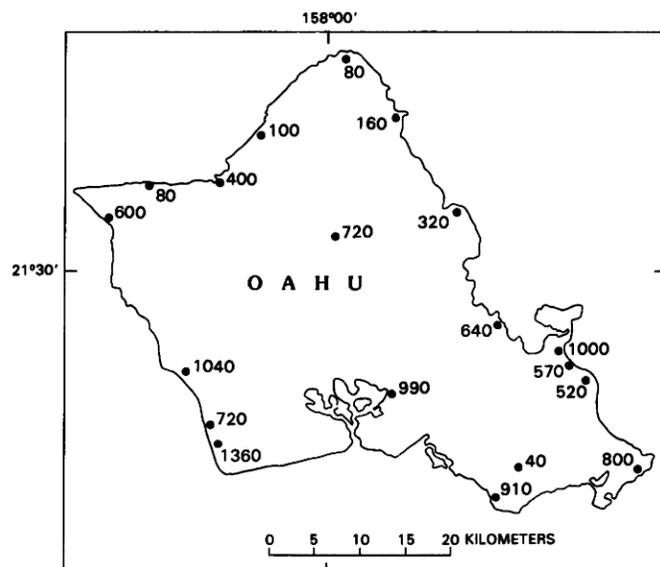


FIGURE 35.4.—Distribution of atmospheric mercury (in ng/m<sup>3</sup>) around Oahu at 2 m above ground. Figures are means of samples taken 1971–78.

same is true of the Island of Kauai. Residual thermal activity on Maui, however, tends to obscure the direct impact that the Island of Hawaii's volcanic activity may have on its mercury distribution, and anomalies are often related to anthropogenic pollution.

### GEOBOTANY AND BIOGEOCHEMISTRY

One factor relating to dispersal of mercury in Hawaii remains to be considered, however, and that is the role of vegetation in its cycling and dispersal. For example, toward the back of the Palolo Valley (Honolulu) the old, weathered soils contain little mercury, only  $15 \times 3 \mu\text{g/kg}$  (Siegel and others, 1975), yet the two grass species growing in that soil (*Digitaria* and *Andropogon*) contain much more ( $68 \pm 8$  and  $79 \pm 11 \mu\text{g/kg}$ , respectively). When these grasses die, their decaying residues retain most of the mercury ( $56 \pm 6 \mu\text{g/kg}$ ), which is then taken in by soil invertebrates, the earthworm *Lumbricus* ( $388 \pm 21 \mu\text{g/kg}$ ) and the millipedes *Trigonalis* ( $467 \pm 21$ ) and *Oxydus* ( $382 \pm 12$ ). In this simple example, the earthworm to soil mercury ratio is about 31.

All of the aquatic plants that we have encountered accumulate mercury (Siegel and others, 1973b, 1975, 1984b, 1985; Siegel and Siegel, 1982, 1984b), usually with sizeable enrichment (table 35.4). The same is true for marine animals including fish, but not limited to vertebrates. High ratios are in part a consequence of the low mercury concentrations found in natural (nonindustrial) waters. Near black sand (basaltic) beaches in Hawaii, the highest mercury levels yet found reach 2–3  $\mu\text{g/L}$ .

Many terrestrial plants also accumulate mercury, but nearly 300 samples from four widely separated areas (table 35.5) show a clear bimodality in the concentration ratio. Overall, 55–77 percent

TABLE 35.4.—Mercury accumulation in marine organisms

Sample	Content in organism (μg/kg)	Concentration ratio (organism/water)
Algae		
Hawaii		
<i>Ulva</i>	40–200	25–145
<i>Padina</i>	140–185	65–88
<i>Sargassum</i>	26–46	12–23
Iceland		
<i>Ulva</i>	106	1,060
<i>Mastigocladus</i>	380	3,800
Antarctica		
<i>Ulva</i>	1.5–3.1	8–16
Fish		
Hawaii		
Marlin	>500	>250
Tuna	220–1,370	110–685
Iceland		
Tuna	287	2,870
Antarctica		
Cod	36	200

TABLE 35.5.—Distribution of mercury concentration ratios in vascular plants at various localities

[Figures in percent of species; number of species sampled given beneath each locality name; after Siegel and others, 1975]

Mercury concentration ratio (plant/soil)	Iceland (79)	Hawaii (105)	New England (38)	Alaska (66)
<0.1	13	14	32	30
.1–0.67	10	22	10	0
.67–1.33	0	8	0	5
1.33–2.0	14	4	18	10
>2	63	54	40	55

of all the plants studied contained at least 1.33 times as much mercury as the soil around their roots, but 23–42 percent of the plants from the four locations contained less mercury than the soil in which they were growing.

Although it may seem reasonable to hypothesize a mechanism whereby plants exclude mercury, there are too many essential nutrient cations similar in charge and size to  $Hg^{2+}$ , among them,  $Ca^{2+}$  and  $Fe^{2+}$ , that could not be biologically distinguished. It is difficult to construct an energetically and structurally sound model that can include  $Hg^{2+}$  with virtually absolute selectivity. An alternate mechanism, however, was suggested when we found that mercury concentrations in air at Sulphur Bank were not determined by inorganic processes alone. Thus, an Arrhenius plot based on air samples taken at one meter over the vegetation on the flats, about 100 m from the fumaroles, shows that there are two slopes (fig. 35.5), implying two limiting processes or mechanisms. The higher temperature process ( $>20$  °C) has a slope parallel to the vapor-pressure line, but at lower temperatures mercury in air is limited by a process other than evaporation, possibly biological in nature.

This surmise has been verified experimentally in more than 40 species of plants (Kama and Siegel, 1980; Siegel and others, 1980a; Siegel and Siegel, 1983). Examples of terrestrial  $Hg^0$  producers include leaves of pineapple, sugar cane, ferns, mosses, lichens, and mushrooms (table 35.6).

This process that may be called biovolatilization is not unique to land species; the unicellular green alga *Chlorella* has been shown to possess a photosynthetic reduction system that generates  $Hg^0$  vapor (Ben-Bassat and Meyer, 1975, 1977).

TABLE 35.6.—Rates of elemental mercury release from various vascular plants [Uncertainty figures are one standard deviation; after Kama and Siegel, 1980; Siegel and others, 1980; Siegel and Siegel, 1983]

Vascular plant	Rate (ng/kg·m)	Plant	Rate (ng/kg·m)
Aloe	850 ± 50	Lichens	
Pineapple	820 ± 30	<i>Usnea</i>	660 ± 190
Coconut	240 ± 90	<i>Cladonia</i>	120 ± 30
Nutgrass	340 ± 45	<i>Stereocaulon</i>	840 ± 91
Staghorn fern	730 ± 45	Mosses	
Hibiscus	490 ± 45	<i>Leucobryum</i>	50 ± 215
<i>Leucanea</i>	3,050 ± 300	<i>Bryum</i>	400 ± 50
Pandanus	1,590 ± 390	<i>Polytrichum</i>	400 ± 160
Avocado	4,130 ± 220	Fungi	
Mangrove	100 ± 40	<i>Polyporus</i>	1,200 ± 105
Sugarcane	650 ± 40	<i>Fomes</i>	2,430 ± 1200
Papyrus	700 ± 49	<i>Trametes</i>	950 ± 480

Most of these studies on release of  $Hg^0$  from plants have emphasized Hawaiian species and the Hawaiian environment. However, the New Zealand manuka, *Leptospermum scoparium*, also appears to release mercury adaptively, keeping levels in tissue down and delaying or preventing toxic buildup (fig. 35.6). As soil

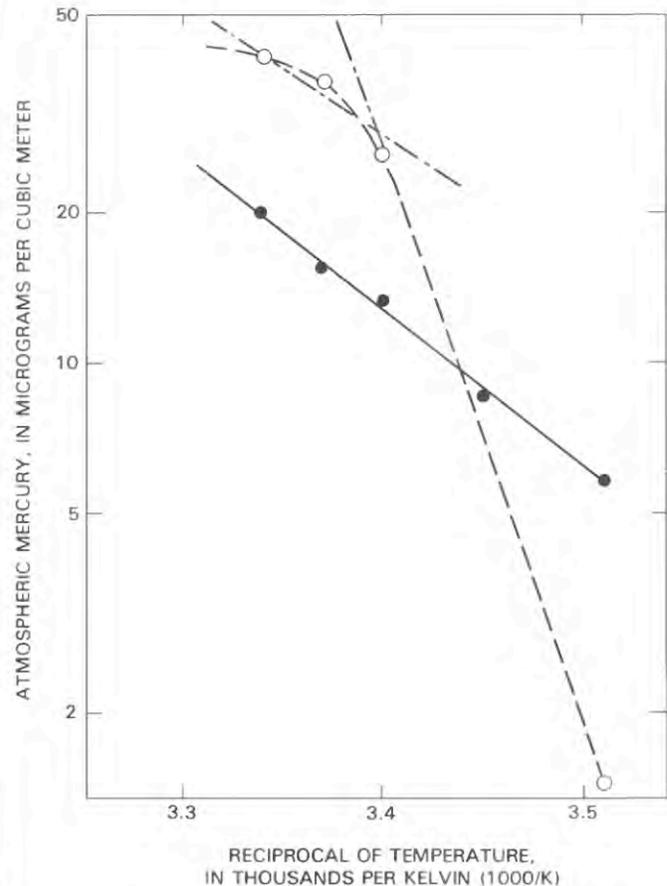


FIGURE 35.5.—Variation of atmospheric mercury concentration with air temperature over the vegetation near Sulphur Bank fumaroles. Data are presented as Arrhenius plot. Dashed curve, field data; dots and solid line, vapor pressure data. See text for discussion.

mercury rises approximately 30-fold from nonthermal Wellington to the Hell Gate thermal area, manuka shoots increase in mercury less than 5-fold. The detoxification mechanism, however, has increased the  $Hg^0$  release rate by a factor of 9.

Presumably,  $Hg^{2+}$  is taken up from soil and ground water and translocated rapidly into the leaves, where reduction is followed by evaporative release. In a number of leguminous species growing in Hawaiian soils, it has been shown that mercury in seeds is selectively eliminated during the ripening process, thereby reducing the concentration below that at which cytological damage to the embryo may take place (Ramel, 1969; Siegel and Siegel, 1985).

Re-emission of  $Hg^0$  may be followed by its direct uptake by nearby plants with or without toxic consequences according to species and concentration (Siegel and others, 1973a; Siegel and Siegel, 1979a). Accordingly, mercury as  $Hg^{2+}$  or its complexes may be taken up from soil or ground water and converted to  $Hg^0$  for subsequent release and, perhaps, re-uptake.

Such recycling processes in local areas may well lead to diffuse patterns of mercury distribution. This has been noted in the lower Puna district, the eastern portion of the Island of Hawaii, site of the Kilauea east rift zone. Mercury levels in the leaves of the native forest tree ohia, *Metrosideros collina* var. *polymorpha*, follow approximately the mercury levels along the east rift zone, as does the mercury content of the soil in which the trees grow (figs. 35.7, 35.8). In contrast, the distribution of mercury in air (fig. 35.9) shows far more sharply defined areas of concentration than the mercury content of either plant or soil. This seems to imply the direct degassing process along the rift zone proceeds substantially faster than the release from soils and plants.

Biological release of  $Hg^0$  is obviously a regulated process and it differs mechanistically from simple vaporization. Our data show that simple vaporization does occur in the soil; however, soil does not begin to release mercury until a concentration of about 25  $\mu\text{g}/\text{kg}$  (ppb) is attained (fig. 35.10). It is, in any case, clear that the impact of the ecosystem on mercury cycling is as great as the impact of natural mercury emission on vegetation and the ecosystem, though they are of a different character.

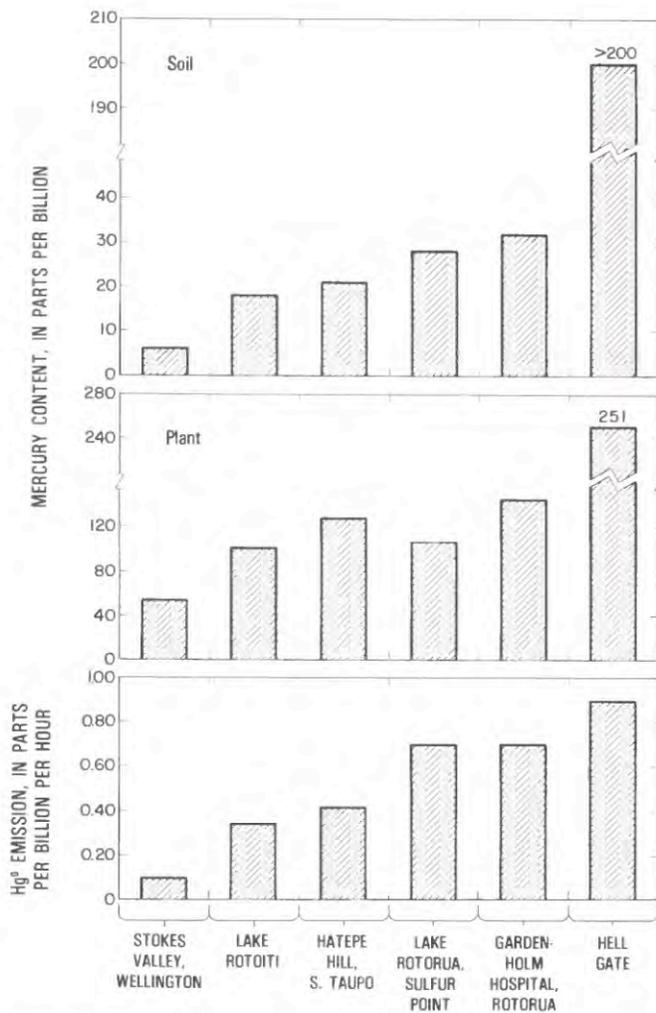


FIGURE 35.6.—Relation between mercury content of New Zealand soils and plants and rates of  $Hg^0$  emission by *Leptospermum scoparium*.

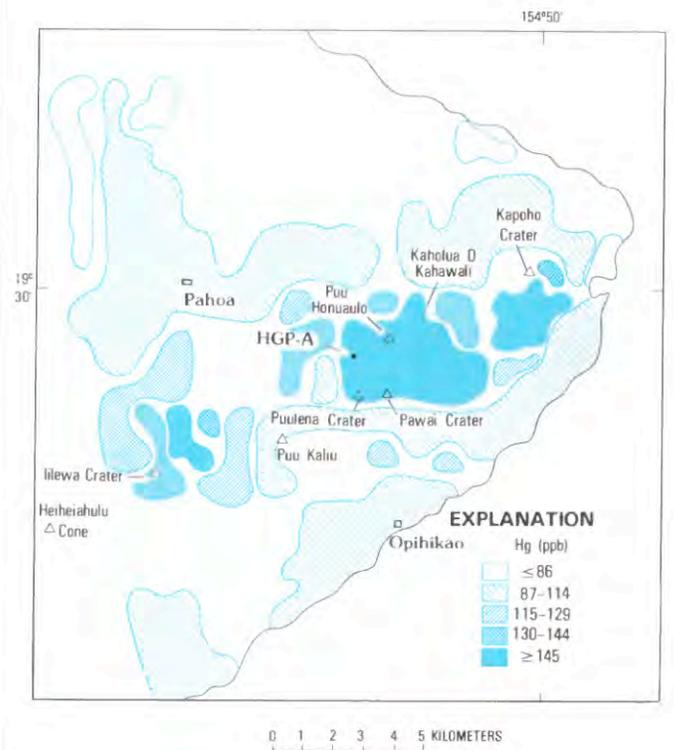


FIGURE 35.7.—Mercury content of ohia leaves (*Metrosideros*) East Puna District, Hawaii. Sampled areas delimited by closed lines; other areas not sampled because of poor access or other limitations. Samples collected between 1975 and 1982, excluding periods of heavy rains, strong winds, and volcanic eruptions. Midrange values of 87–114 ppb represent one standard error on either side of the mean for entire Puna collection.

## REFERENCES CITED

- Andren, W., and Nriagu, J., 1979, Global mercury, in *Biochemistry of mercury in the environment*: Amsterdam, Elsevier, p. 173–130.
- Aylett, B.J., 1973, *The chemistry of zinc, cadmium and mercury*: New York, Pergamon Press, volume 18.
- Ben-Bassat, D., and Mayer, A., 1975, Volatilization of mercury by algae: *Physiologia Plantarum*, v. 38, p. 128–132.
- , 1977, Reduction of mercury chloride by *Chlorella*: *Physiologia Plantarum*, v. 40, p. 157–162.
- Bidstrup, P.L., 1964, *Toxicity of mercury and its compounds*: Amsterdam, Elsevier.
- Boussingault, M., 1867a, Sur l'action deletere que la vapeur emanant du mercure exerce sur les plantes (premiere partie): Paris, Academie des Sciences Compte Rendu, v. 64, p. 924–928
- , 1867b, Sur l'action deletere que la vapeur emanant du mercure exerce sur les plantes (deuxieme partie): Paris, Academie des Sciences Compte Rendu, v. 64, p. 983–989.
- Buhler, D.R. ed., 1973, *Mercury in the western environment*: Continuing Education Publication, Corvallis Oregon, Proceedings of a Workshop, Portland Oregon, February 25–26, 1971.
- Cadle, R.D., 1975, Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere: *Journal of Geophysical Research*, v. 80, p. 1650–1652.

- Carlin, C.E., Corigliana, P.J., Gastanaga, C.A., and Ochoa, L.R., 1960, Occupational risk in a mercury plant: *Salud Ocupacional*, v. 5, p. 3 (Abstract Bulletin of Hygiene, 1961, v. 36, p. 440).
- Connor, J.J., 1979, *Geochemistry of Vegetation, Puhimau Thermal Area, Hawaii*: *Science of Total Environment*, v. 12, p. 241–250
- Deiman, Paats, Van-Troostwyck, and Lauwerenburgh, 1979, Experiences sur l'action du mercure sur la vie vegetale: *Annales de Chimie, Paris*, v. 21, p. 122–127.
- Dizon, G.D., Anselmo, J.E., and Villanueva, J., 1960, Examination of the risk in mercury mine in the Philippines: *Medicale Seguridad Trabado*, v. 8, p. 29. (Abstract Bulletin of Hygiene, 1961, v. 36, p. 745).
- Eshleman, A., Siegel, S.M., and Siegel, B.Z., 1971, Is mercury from Hawaiian volcanoes a natural source of pollution?: *Nature*, v. 233, p. 471–472.
- Goldschmidt, V., 1954, *Geochemistry*: Oxford, Clarendon Press, p. 287.
- Goldwater, L.J., 1951, *The toxicology of inorganic mercury*: New York Academy of Sciences Annals, v. 65, p. 498–503.
- Goren, R., and Siegel, S.M., 1976, Mercury-induced ethylene formation and abscission in citrus and coleus explants: *Plant Physiology*, v. 57, p. 628–631.
- Harrington, 1917, Further studies of the germination of Johnson grass seeds: *Proceedings of the Association of the Official Seed Analysts of North America 1916–1917*, p. 71–70
- Hem, J.D., 1970, Chemical behavior of mercury in aqueous media, in *Mercury in the Environment*: U.S. Geological Survey Professional Paper 713, p. 19–24.
- Hunter, D., 1955, *The Disease of Occupations*: London, English Universities Press, p. 256.

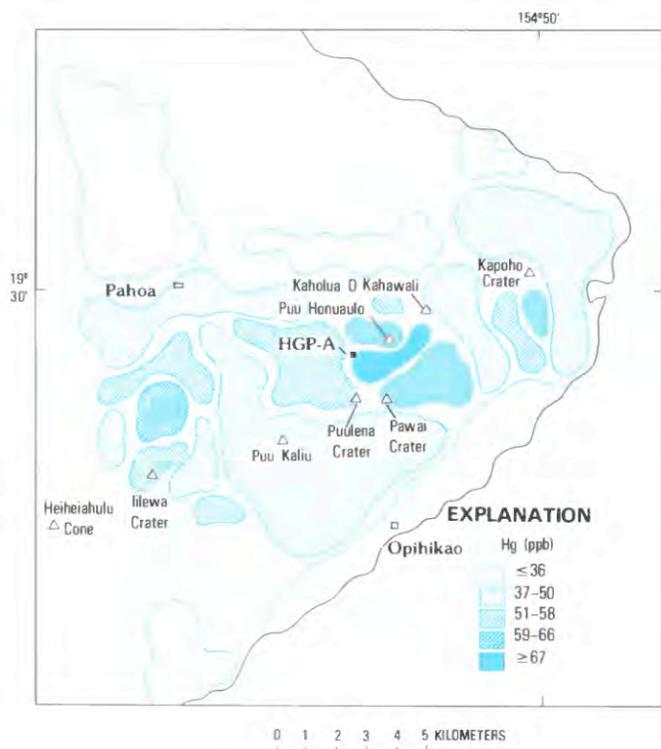


FIGURE 35.8.—Soil mercury content in East Puna District, Hawaii. Samples areas delimited by closed lines; other areas not sampled because of poor access or other limitations. Samples collected between 1975 and 1982, excluding periods of heavy rains, strong winds, and volcanic eruptions. Midrange values of 37–50 ppb represent one standard error on either side of the mean for entire Puna collection. Symbols same as in figure 35.7.



FIGURE 35.9.—Atmospheric mercury content in East Puna District, Hawaii. Sample areas delimited by closed lines; other areas not sampled because of poor access or other limitations. Midrange values of 96–191  $\text{ng}/\text{m}^3$  represent one standard error on either side of the mean for entire East Puna collection. Samples collected between 1975 and 1982, excluding periods of heavy rains, strong winds, and volcanic eruptions. Triangles, volcanic cones and vents; squares and rectangles, villages; dashed lines, roads; numbers in circles identify highways; HGP-A, Hawaii Geothermal Project—Abbott.

- Jensen, S., and Jernelov, A., 1969, Biological methylation of mercury in aquatic organisms: *Nature*, v. 223, p. 753-754.
- Kama, W., and Siegel, S.M., 1980, Volatile mercury release from vascular plants: *Organic Geochemistry*, v. 2, p. 99-101.
- King, C.V., 1951, Mercury: Its scientific history and its role in physical chemistry and electrochemistry: *New York Academy of Sciences Annals*, v. 65, p. 360-368.
- Le Van, W.C., 1930, The effects of metals on the respiration of *Lupine albus*: *American Journal of Botany*, v. 17, p. 381-395.
- Macdonald, G.A., and Abbott, A. T., 1970, *Volcanoes in the Sea, The Geology of Hawaii*: Honolulu, Hawaii, The University Press of Hawaii, 441 p.
- Matthes, R.T., Kirschner, R., Yow, M.D., and Brenna, J.C., 1958, Acute poisoning associated with inhalation of mercury vapor: *Pediatrics*, v. 22, p. 675.
- Nriagu, J., ed., 1979, *Biogeochemistry of Mercury in the Environment*: Amsterdam, Elsevier North-Holland Biomedical Press, 696 p.
- Phelps, D., Siegel, B., Siegel, S., Buseck, P.R., Copp, J., Hinkle, M., and Casadevall, T., 1979, The distribution of Hg in the Puhimau Area, Hawaii Volcanoes National Park: [abs.] American Geophysical Society Meeting, San Francisco, Dec. 3-7, 1979.
- Piotrowski, J.K., and Coleman, D.O., 1980, Environmental hazards of heavy metals: Summary evaluation of lead, cadmium and mercury: *Global Environmental Monitoring System Programme Activity*, London.
- Ramel, C., 1969, Genetic effects of organic mercury compounds. I. Cytological investigations on *Allium* roots: *Hereditas*, v. 61, p. 208-230.
- Rankama, K., and Sahama, T.G., 1950, *Geochemistry*: Chicago, University of Chicago Press, p. 334.

- Ratsek, J.C., 1933, Injury to roses from mercuric chloride used in soil for pests: *Floral Review*, v. 72, p. 11-12.
- Siegel, B.Z., Lascoma, M., Yaeger, E. and Siegel, S.M., 1984a, The phytotoxicity of mercury vapor: *Water, Air and Soil Pollution*, v. 23, p. 15-24.
- Siegel, B.Z., and Siegel, S.M., 1978, The Hawaii geothermal project: An aerometric study of the Kalalua eruption of 1977: *Environmental Science and Technology*, v. 12, p. 1036-1039.
- 1979a, Biological indicators of atmospheric mercury, in Nriagu, J., ed., *The biochemistry of mercury in the environment*: Amsterdam, Elsevier/North-Holland Biomedical Press, p. 131-159
- 1979b, Mercury and other toxic emissions from Kilauea: Site and time patterns: *Division of Environmental Chemistry, ACS/CSJ Chemical Congress*, Honolulu, Hawaii, April 1979, Abstracts, part 1, No. 30.
- 1982, Mercury content of *Equisetum* plants around Mount St. Helens one year after the major eruption: *Science*, v. 216, p. 292-293.
- Siegel, B.Z., Siegel, S.M., and Horsky, S., 1984, *Equisetum* plants and the cycling of mercury at Mount St. Helens: *Environmental Science and Technology*, v. 18, p. 174-181.
- Siegel, S.M., 1977, The cytotoxic response of *Nicotiana* protoplasts to metal ions: A survey of the chemical elements: *Water, Air, and Soil Pollution*, v. 8, p. 293-304.
- Siegel, S.M., Eshleman, A., Umeno, I., Puerner, N., and Smith, C.W., 1973a, *The general and comparative biology of toxic metals and their derivatives: Mercury and Lead*: Mercury in the western environment: Oregon, Continuing Education Publishing Company.

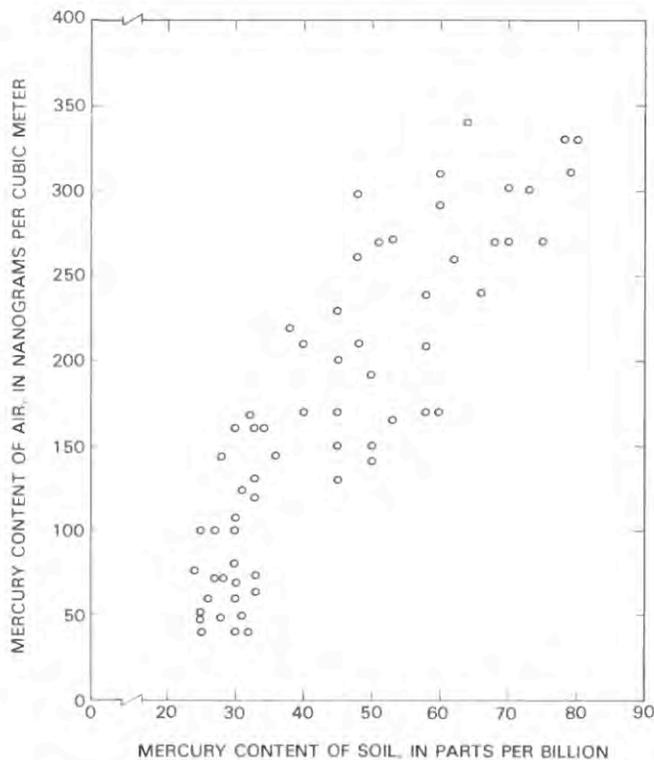


FIGURE 35.10.—Relation between atmospheric and soil mercury in East Puna District, Hawaii. Data represent replicated analyses of air and soil at same locations for 63 sample sites.

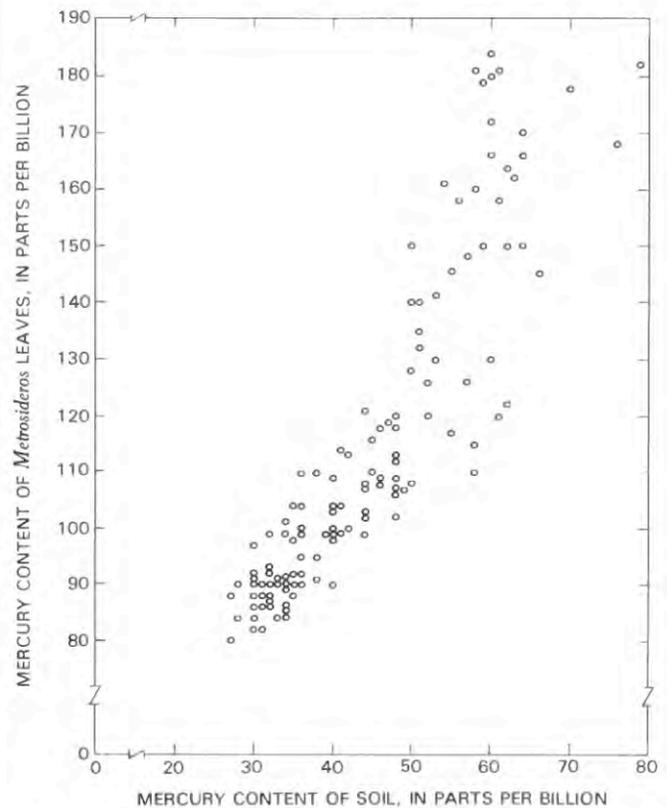


FIGURE 35.11.—Relation between mercury content of ohia leaves and soil in East Puna District, Hawaii. Data represent replicated analyses of leaves and soil at the same location for 121 sample sites.

- Siegel, S.M., Okasako, J., Kaalakea, P., and Siegel, B.Z., 1980a, Release of volatile mercury from soils and non-vascular plants: *Organic Geochemistry*, v. 2, p. 139-140.
- Siegel, S.M., and Siegel, B.Z., 1977, Mercury fallout in Hawaii: *Water, Air, and Soil Pollution*, v. 9, p. 113-118.
- 1980, Hawaii Energy Resource Overview: Geothermal, Siegel, B., ed., *The Environmental Impact*, UCRL-1552. Vol. 4. National Technical Information Service (NTIS), DE830-12947. p. 7-14, 99-127, 138-146.
- 1983, Vegetation and the atmospheric cycling of mercury: *Advanced Space Research*, v. 3, p. 135-139.
- 1984a, First estimate of annual mercury flux at the Kilauea main vent: *Nature*, v. 309, no. 5964, p. 146-147.
- 1984b, Regional differences in plant-soil mercury relations in *Equisetum*, *Plantago* and *Taraxacum*: *Organic Geochemistry*, v. 5, no. 4, p. 255-257.
- 1985, Differential elimination of mercury during maturation of leguminous seeds: *Phytochemistry*, v. 24, p. 235-236.
- Siegel, S.M., Siegel, B.Z., Eshleman, A.M., and Bachman, K., 1973b, Geothermal sources and distribution of mercury in Hawaii: *Environmental Biology and Medicine*, v. 2, p. 81-89.
- Siegel, S.M., Siegel, B.Z., Lipp, C., Kruckeberg, A., Towers, G.H.N., and Warren, H., 1985, Indicator plant-soil mercury patterns in a mercury-rich mining area of British Columbia: *Water, Air, and Soil Pollution*, v. 27, p. 73-85.
- Siegel, S.M., Siegel, B.Z., and McMurtry, G., 1980b, Atmosphere-soil mercury distribution: The biotic factor: *Water, Air, and Soil Pollution*, v. 13, p. 109-112.
- Siegel, S.M., Siegel, B.Z., Puerner, N., and Speitel, T., 1975, Water and soil biotic relations in mercury distribution: *Water, Air, and Soil Pollution*, v. 4, p. 9-18.
- Simkin, T., Siebert, L., McClelland, L., Bridge, D., Newhall, C., and Latter, J., Jr., 1981, *Volcanoes of the World*: Stroudsburg, Penn., Smithsonian Institution, Hutchinson Ross Publishing Co.
- Solhnan, T., 1957, *Manual of Pharmacology* 8th ed.: Philadelphia, Saunders, p. 1310.
- United States National Academy of Sciences, 1977, *An assessment of mercury in the environment*: Washington, D.C.
- Varekamp, J.C., and Buseck, P.R., 1981, Mercury emissions from Mount St. Helens during September 1980: *Nature*, v. 293, p. 555-556.
- Vouk, V.B., Fugas, M., and Topolnik, Z., 1950, Environmental conditions in the mercury mine of Idria: *British Journal of Industrial Medicine*, v. 7, p. 168.
- Wagman, D.C., Evans, W.H., Parker, V.B., Harlow, I., Bailey, S.M., and Schum, R.H., 1968, Selected values of chemical thermodynamic properties: National Bureau of Standards (US) Technical Note 270-3, p. 1-264.
- Warkany, J., and Hubbard, D.M., 1953, Acrodynia and mercury: *Journal of Pediatrics*, v. 42, p. 365.
- Zimmerman, P.W., and Crocker, W., 1933, The injurious effect of mercury vapor from biochloride of mercury in soil of rose houses: *Florists Exchange*, v. 81, p. 13.
- 1934, Plant injury caused by vapors of mercury and compounds of mercury: *Contributions of the Boyce Thompson Institute*, v. 6, p. 167-187.