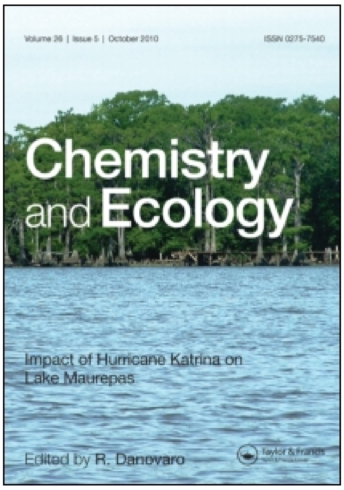

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Mercury Pollution in the Surface Environment of a Volcanic Area·

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The mercury content has been determined in samples of fumarolic gases, phreatic waters, soil and vegetation collected at Vulcano, Aeolian Islands, Italy. Volcanic activity is demonstrated as a source of natural mercury pollution whose extent has been evaluated here by studying the contribution of different components of the surface environment. The possible influences for living organisms are examined.

KEY WORDS—POLLUTION: MERCURY: FUMAROLIC GASES: PHREATIC WATERS: SOILS: PLANTS.

INTRODUCTION

Mercury is a trace element in the earth's crust and generally its normal terrestrial abundance in the world is about 80 μg Hg Kg^{-1} (Taylor, 1964). This element is easily mobilized as a result of thermal anomalies, and because of this hydrothermal solutions are normally responsible for the formation of mercury ores, mainly represented by cinnabar, HgS. According to Krauskopf (1951), mercury can be transported as HgS_2^{2-} ions in alkali sulfide solutions, as $HgCl_2$ in vapor phase and as vapor of metallic Hg.

Beside economic interest in mercury ores, in recent times the attention of researchers has been focussed on the influence of this element in atmosphere, farmland, natural waters and living organisms. Large-scale industrial activities can be responsible for the pollution of vast surrounding areas, because of the fallout of mercury particles contained in fumes. Similar poisoning of the environment may arise from geothermal plants. The extent of potential negative effects, however, can possibly be reduced by introducing some kind of clean-up procedure. Volcanic activity, on the contrary, represents a natural pollutant factor of wide variability which cannot be controlled, and exerts its initial influence in well defined geographical areas, but it can be detected all over the world.

In order to evaluate the cumulative effects produced by volcanic activity lasting some centuries with approximately uniform intensity, a study was undertaken on the island of Vulcano, Aeolian Islands, Italy. As can be seen in Figure 1a, the main activity is located at the crater (A), where a fumarolic field with temperatures between 200 and 600°C has been recorded during several centuries; paroxysmal events occurred mainly producing limited ejections of bombs and lapilli, with very small lava flows. The thermal area extends along a main fissure down to the beach, where lovely warm waters allow bathing even in winter time. The gases and phreatic waters have characteristic effects on the plants and livestock of the area.

Fumarolic emissions, natural waters, soil and crop samples have been considered here to determine the extent of the mercury input and of its permanent effects on the environment.

EXPERIMENTAL

Samples of condensates from fumaroles at different temperatures, of soil and of vegetation have been collected on the crater and at the beach of Vulcano; their locations are shown in Figure 1. The samples and analytical procedures are here described separately for different kind of samples. Total mercury analyses have been carried out by a Coleman MAS-50 Mercury Analyzing System using the

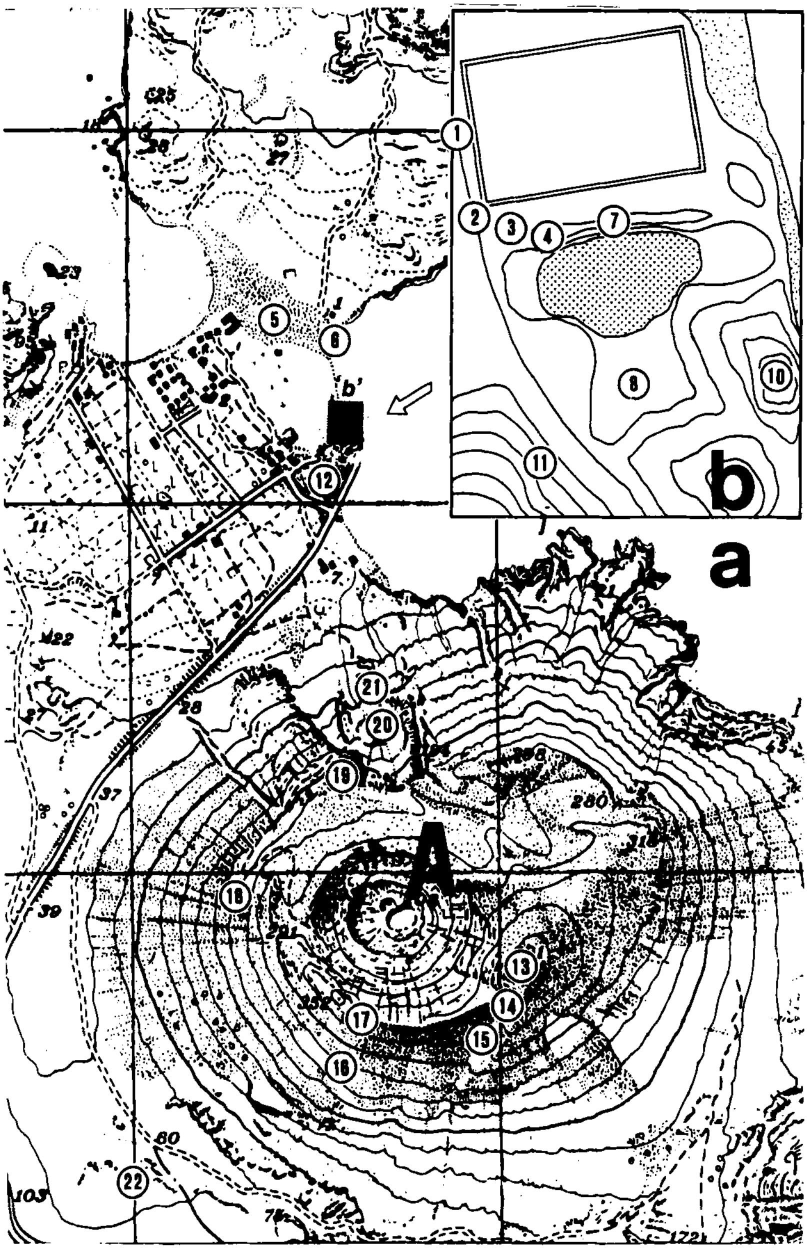

FIGURE 1 Locations of sampling sites, (a) main area, (b) beach fumaroles.

procedure proposed by Floyd and Sommer (1975). All reagents were analytical grade.

Condensates

Condensates have been collected in "Pyrex" bottles containing 4 ml of a saturated solution of potassium dichromate, acidified with nitric acid. The end of the apparatus, previously described (Piccardi 1982), impinged directly into the oxidizing solution and the receiver was shaken to ensure complete reaction and to retain all mercury in the collecting solution. Addition of potassium dichromate might be necessary to maintain strongly oxidizing conditions. Stannous chloride solution was added to portions of the sample, diluted to 100 ml with distilled water to reduce mercury to metallic form. The dilution of the sample was necessary because of high mercury contents and to maintain generation at constant volume; preliminary experiments showed that the same quantity of mercury in different volumes of water at the generation stage gave different results (Marigo *et al.*, 1981).

Soil

Soil samples have been collected from the A soil horizon, at a depth of about 5 cm below the surface. After air drying, samples have been sieved using a N°. 30 mesh US standards. Two aliquots of this fraction were then accurately weighed; the one was dried at 110°C for 24 hours to obtain the dry weight and the other was used for the analysis. All the results are referred to dry sample. The solubilization of mercury from 1 g of sample is carried out by digestion for 4 hours at 55°C in 30 ml of a solution of potassium dichromate 1.3 M in 10 M nitric acid, as proposed by Floyd and Sommers (1975). After cooling, the volume of the solution is adjusted to 100 ml with distilled water, and a second dilution to 100 ml of a known volume was carried out directly into the bottle used for the reducing procedure. In accordance with Bartha and Ikrenyi (1982) the complete dissolution of siliceous matrix, proposed by Omag and Paus (1971) was not considered necessary.

Vegetation

The determination of mercury in biological material by flameless atomic absorption technique should be preceded by complete destruction of organic compounds. Incomplete digestion results in complexation and absorption of mercury by degraded carbonaceous species so that complete reduction to metallic mercury cannot occur. Siegel *et al.* (1973), however, carried out a mercury determination in vegetation from volcanic areas, by simple predigestion overnight in concentrated nitric acid. Other reports suggest that organic substances are not completely destroyed by this procedure nor by subsequent treatment with hydrogen peroxide. To check this simple method proposed by Siegel, some grams of leaves of ivy, *Hedera helix* L. collected remote from possible mercury pollution were dried for 24 hours at 110°C then digested in concentrated HNO_3. To equal volumes of this nitric solution were added different quantities of mercury; a good correlation was obtained between the absorbances measured and the added mercury concentrations. The calibration passing through the origin, displays a lower slope than that obtained by using similar nitric reagents without digested vegetation; also different absorbances are observed for different concentrations of the digesting solution, and different slopes are also observed for different kinds of plant material. This digestion procedure is therefore not suitable for analytical determination using a standard linear calibration, but the linearity observed for the added quantities of mercury appears to guarantee a sufficient accuracy for adoption of the addition method. Consequently all the determinations of mercury in vegetation have been carried out by this latter procedure.

At Vulcano, leaves from *Genista ephedroides* DC and *Cistus incanus* L, representing common species of the area, have been collected. The leaves have been air dried, crumbled and homogenized; a portion was then dried at 110°C to obtain a dry weight, and another one was used fro the analytical procedure.

The leaves used for Hg determinations have not undergone any kind of washing, to retain the whole content of the metal actually present. The problems of mercury speciation and distribution in different parts of the crops studied are not taken into consideration here. The total amount of Hg is most relevant, since these same plants supply food for different kinds of local livestock. At Vulcano, cows and goats are normally found pasturing in these areas and by this way mercury can enter the human biological cycle.

ANALYTICAL RESULTS AND DISCUSSION

Table I gives the results obtained for condensates from the fumaroles of the crater. On the basis of published data for the main composition of the same condensates (Siegel *et al.*, 1973), no correlation was evident between mercury, H_2S or HCl concentrations; a weak negative correlation appears between mercury and temperature. Duchi (1979) previously measured the mercury content of Vulcano fumaroles, reporting values of 16 μg Hg m^{-3} for F 2 and 60 μg Hg m^{-3} for F 9. Our analyses, recalculated on the basis of the concentrations of the main constituents, give values between 4 μg Hg m^{-3} (F 2-3/81) and 240 μg Hg m^{-3} (F 11-8/82). These may be compared with values recorded elsewhere in the world, Table II.

It was also possible to estimate a total output of mercury to the atmosphere by relating the Hg contents in fumarolic fluids to SO_2 concentrations. The total mercury flux at Vulcano was estimated by Sabroux (1982) to be 13 tonne day^{-1}, and from the ratio of the median concentrations of Hg and SO_2 observed at Vulcano crater we can estimate a value of 17 g Hg day^{-1}. This is a low figure, if compared to that given by Dedeurwaerder *et al.* (1982) for Etna, 25 Kg Hg day^{-1}, by Olafsson (1975) for Heimaey (7×10^5 g Hg during five months of 1973 activity), Varekamp and Buseck (1981) for Mount St. Helens (1000–7000 tonne Hg $year^{-1}$).

TABLE I
Total mercury concentrations (μg Hg L^{-1}) in condensates

Data	F2	F5	F9	F11	F14
4/81	0.6	1.2	0.9	0.7	3.5
9/81	2.8	3.8	2.2	1.5	1.8
2/82	4.1	2.4	9.8	7.5	6.3
5.82	6.2	8.0	52.1	9.1	59.6
9/82	3.2	6.9	15.2	7.9	41.6

TABLE II
Geographical variations in the mercury content of fumarole condensate and in fumarole flow

Location	Condensate Concentration ($\mu g\,Hg\,l^{-1}$)	Author
Tolbachik, Kamchatka	20–88	Menyailov *et al.*, 1980
Surtsey, Iceland	350	Siegel *et al.*, 1973
Sulfur Banks, Hawaii	0.2–72	Siegel *et al.*, 1973
Kurili and Kamchatka	0.3–6	Aidin'yan and Ozerova, 1966
	Fumarole flow ($\mu g\,Hg\,m^{-3}$)	
Heimaey, Iceland	8–19	Olafsson, 1975
Tolbachik, Kamchatka	0.6–66	Menyailov *et al.*, 1980
Kurili and Kamchatka	0.3–4	Aidin'ya and Ozerova, 1966

The results obtained for mercury contents in soil samples are reported in Table III. As can be seen, the first set consisted of samples from the area (Ib-inset) surrounding the fumaroles of the beach; a strong alteration by fumarolic fluids had taken place, and high mercury concentrations have been observed. Something similar arises from the analysis of soils collected on the rim of the crater, where the fumaroles of highest temperature are located (zone A in Figure 1); the Hg content, ranging between 0.70 and 4.80 $\mu g\,Hg\,g^{-1}$, are associated with the continuous flow of the volcanic fluids. The other samples contained in Table III pertain to a wider area around the active cone and display lower values, but enhanced at the site "Forgia Vecchia" (19 and 20 in Figure 1), for which recent activity is reported. Two sets of samples have been collected, to evaluate the influence of seasonal changes on this kind of investigation. Some differences càn be observed, but if we take into account the mean values of the analytical results, a more coherent picture and a substantial constance of values can be verified.

Phelps and Buseck (1980) examining the detailed Hg distribution in soils of the Yellowstone geothermal area on a 50 m grid, found occasional anomalies with values up to 100 $\mu g\,Hg\,g^{-1}$. A strong correlation between Hg in soils and fumarolic activity has also been

TABLE III
Mercury concentrations ($\mu g\, Hg\, g^{-1}$) in surface soil samples

Sampling point	Sampling date		
	5/82	9/82	3/83
1	1.750		
2	0.100		
3	0.800		
4	0.950		
5	7.200		
6	0.080		
7	4.800		
8		3.970	
9	0.005		
10		0.042	0.061
11		0.082	0.063
12		0.040	
13		0.020	0.020
14		0.060	0.100
15		0.060	
16		0.023	0.020
17		0.040	0.040
18		0.014	0.083
19		0.142	0.130
20		0.122	0.062
21		0.081	
22			0.056

observed in vapor dominated geothermal systems in an area with a very low level of soil mercury (0.05 $\mu g\, Hg\, g^{-1}$). Very high Hg concentration were found by Cox (1983) in Hawaii over the Puhimau steaming area (25 $\mu g\, Hg\, g^{-1}$) and near a series of cracks and fissures between Hiiaka and Paushi craters (8.3 $\mu g\, Hg\, g^{-1}$). For Vulcano, the highest value of 7.2 $\mu g\, Hg\, g^{-1}$ has been found for a dark-gray clay ejected by a steam vent (sampling place no 5).

In the process of sampling at site no 7, several cores at different depths have been collected at various times by means of a hand operated device; on the basis of the results given in Figure 2 it is not possible to establish any specific trend in the depth distribution of mercury contents. However, the higher mercury contents in the samples collected in February 1982 can be correlated with the higher concentrations in carbon dioxide observed in the fumarolic

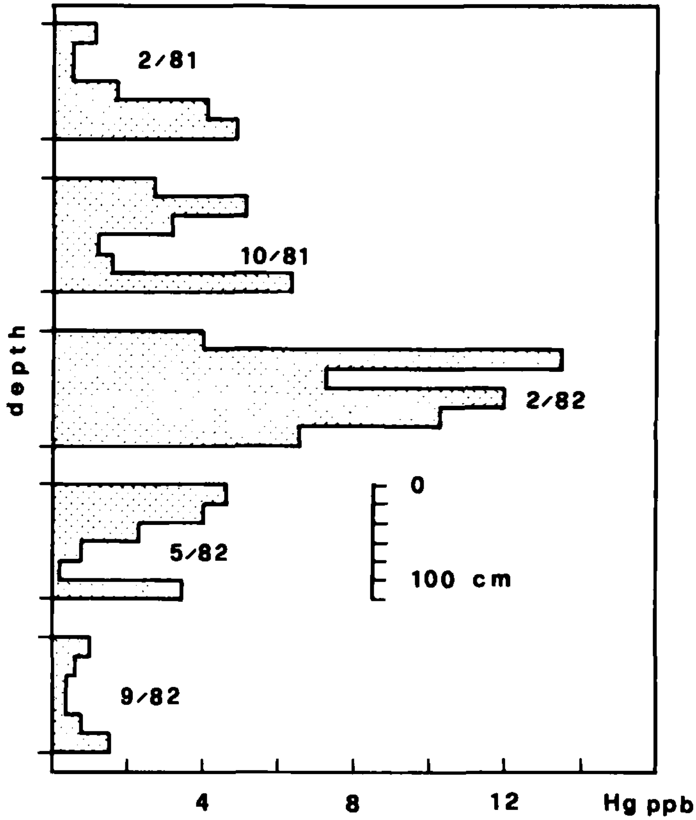

FIGURE 2 Depth profiles of total Hg at the same sampling sites at different times.

gases which in turn correspond to a greater degree of activity of the volcanic system. A series of cores collected at the site Piano, outside Figure 1, about 2 Km east of Monte Molineddo, display a gradual increase from the surface concentration of 0.005 μg Hg g^{-1} (sample no 9) to a value of 0.11 μg Hg g^{-1} at a depth of 90 cm. The samples consisted of fine brown earthy tuffs, without any distinct stratification. Complex soil morphology has already been observed by Gotoh *et al.* (1979) referring to mercury concentration in samples from the southern portion of Kagoshima prefecture (Japan) and by Cox and McMurtry (1981) in sediment cores of the East Pacific Rise.

Samples of phreatic waters, collected from the wells located in the populated area of Vulcano Porto and currently investigated to evaluate the extent of pollution by volcanic fluids (Martini, 1980) contain very low quantities of mercury (always below 0.5 and several times below 0.05 $\mu g\,Hg\,L^{-1}$).

Different content of metals in the leaves of some species of plants, collected at different sites enable us to distinguish specific conditions favourable to the accumulation in the natural environment. Table IV reports the analytical data obtained for leaf samples from living plants, collected on the island of Vulcano at the end of summer (September 1982) and soon after the rainy season (March 1983). As it can be seen in Table IV all the samples analyzed displayed significant mercury concentrations, especially samples collected in September 1982. Since soil samples were collected adjacent to the sites of the plant collections: it is possible to study the ratios between mercury contents of the soils and the plants. For *Genista*, whose data are reported in Figure 3, tentatively a linear trend might be indicated (excepting four samples collected in September); suggesting a ratio Hg(plants)/Hg(soils) of about 3. The *Cistus* results with a higher degree of scattering possibly suggest a lower ratio.

TABLE IV

Mercury contents ($\mu g\,Hg\,g^{-1}$) in the leaves of some plants from the sampling sites at different times

Plant	Sampling point	Sampling date	
		9/82	3/83
Genista ephedroides DC	15	0.333	
	16	0.519	0.110
	17	0.496	0.074
	19	0.404	0.139
	11	0.816	0.165
	12	0.569	
	20	0.352	0.186
	21	0.260	
Cistus incanus L	14	0.563	0.063
	16	1.046	0.044
	11	0.373	0.424
	22		0.345
Rumex brucephalophorus L	13	0.117	0.179

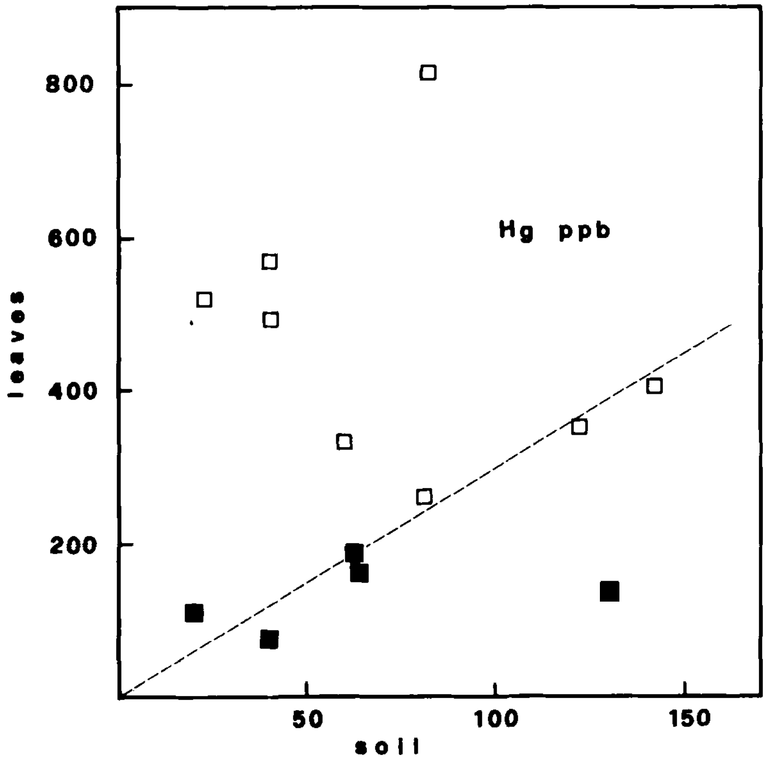

FIGURE 3 Hg content of *Genista ephedroides* leaves as a function of soil mercury level. Sampling period: 9/82, 3/83.

From other studies plants growing in environments with normal low mercury contents contain very small amount of mercury. However, the concentrations in plants increase at a very fast rate with the increasing mercury contents in soils. Shacklette (1970) reports that plants growing over cinnabar veins at Red Devil (Alaska) contain 0.3–3.5 μg Hg g^{-1} and Huckabee *et al.* (1983), by analyzing terrestrial plants in the area of the Almaden mine (Spain) found concentrations ranging from 0.20 to over 100 μg Hg g^{-1} at a distance of 20 Km and within 5 Km respectively.

Mercury can be easily absorbed by soils.

Nabrzynski and Gajewska (1982) found that plants took up more Cd and Hg than Pb. Different organs and different species of plants vary widely in their ability to concentrate mercury. Skripnichenko and Zolotareva (1980), studying the reactions of plants to heavy metals in culture media, found that Hg accumulation in parts of plants above the ground level was not dose dependent, while dose dependence could apply to the accumulation in roots. Siegel *et al.* (1973) have observed a bioconcentration of mercury by plants in Hawaii; the ratio between the concentrations in plants and in soils was claimed to change in exponential form. For *Vaccinium reticulatum* the value of R varied from 2 to 4.5 with the increasing concentration of Hg in the soil; while for *Lycopodium cernuum,* R attains values up to 66 for a mercury concentration in soil of 5.5 μg Hg g^{-1}.

CONCLUSIONS

Investigation of total mercury contents in gases, waters, soils and plants in the island of Vulcano appear consistent with the assumption that this metal is preferentially mobilized and introduced into the wider surface environment of this volcanic area. The contribution to the atmosphere and especially to phreatic waters do not appear hazardous for the human community; on the other hand the concentrations of mercury detected in affected soils and plants suggest some degree of enrichment in plant cycles and therefore potentially more harmful to both livestock and human beings of the area.

References

Aidin'yan, N. Kh. and Ozerova, N. A. (1966). Behavior of mercury in recent vulcanism, *Sovrem. Vulkanizm.*, **1,** 249–253.

Bartha, A. and Ikrenyi, K. (1982). Interfering effects on the determination of low concentrations of mercury in geological materials by cold vapour atomic absorption spectrometry, *Analytica Chimica Acta,* **139,** 329–332.

Cox, M. E. and McMurtry, G. M. (1982). Vertical distribution of mercury in sediments from the east Pacific rise, *Nature* (*London*), **289,** 789–792.

Cox, M. E. (1983). Summit outgassing as indicated by radon, mercury and pH mapping, Kilauea volcano, Hawaii, *Journal of Volcanology and Geothermal Research,* **16,** 131–151.

Dedeurwaerder, H., Decadt, G. and Baeyens, W. (1982). Estimations of mercury fluxes emitted by Mount Etna volcano, *Bulletin of Volcanology,* **45,** 191–196.

Duchi, V. (1979). Determination of Hg in natural gaseous phases: the fumaroles of Vulcano, *Atti. Soc. Tosc. Sci. Naturali,* **85,** 127–134.

Floyd, M. and Sommers, L. E. (1975). Determination of total mercury in soil and sediments, *Journal of Environmental Quality,* **4,** 323–325.

Gotoh, S., Otsuka, H. and Koga, H. (1979). Volcanic influence on mercury in soils of Kagoshima, southern Kyushu, Japan, *Soil Science and Plant Nutrition,* **25,** 523–537.

Huckabee, J. W., Sanz Diaz, F., Janzen, S. A. and Solomon, J. (1983). Distribution of mercury in vegetation at Almaden, Spain, *Environmental Pollution, ser. A,* **30,** 211–224.

Krauskopf, K. B. (1951). Physical Chemistry of quicksilver transportation in vein fluids, *Economic Geology,* **46,** 498–523.

Marigo, A., Pasquetto, A., Novo, A. and Zannetti, R. (1981). Trace metal analysis by atomic absorption, *Inquinamento,* **23,** 31–35.

Martini, M. (1980). Geochemical survey on the phreatic waters of Vulcano, *Bulletin Volcanologique,* **43,** 265–274.

Menyailov, I. A., Nikitina, L. P. and Schapar', V. N. (1980). Geokhimicheskie osobennosti eksalatsii bolschogo treschchinnogo Tol'bachinskogo izverwheniya, Nauka Moscow.

Nabrzynski, M. and Gajewska, R. (1982). Mercury, cadmium and lead levels in fruit, vegetables and soil, *Rocz. Panstw. Zakl. Hig.,* **33,** 121–130.

Olafsson, J. (1975). Volcanic influence on sea water at Heimaey, *Nature* (*London*), **255,** 138–141.

Omag, S. H. and Paus, P. E. (1971). Trace determination of mercury in geological materials by flameless atomic absorption spectroscopy, *Analytica Chimica Acta,* **56,** 393–398.

Phelps, D. W. and Buseck, P. R. (1980). Distribution of soil mercury and the development of soil mercury anomalies in the Yellowstone geothermal area, Wyoming, *Economic Geology,* **75,** 730–741.

Piccardi, G. (1982). Fumaroles gas collection and analysis, *Bulletin Volcanologique,* **45,** 257–260.

Sabroux, J. C. (1982). Measurements of the gas discharge at Vulcano (Italy), *Bulletin Volcanologique,* **45,** 277–278.

Shacklette, H. T. (1970). Mercury content in plants, *U.S. Geological Survey Professional Papers,* **713,** 35–36.

Siegel, B. Z., Siegel, S. M. and Thorarinsson, F. (1973). Icelandic geothermal activity and the mercury of Greenland icecap, *Nature* (*London*), **241,** 526.

Siegel, S. M., Siegel, B. Z., Eshleman, A. M. and Bachmann, K. (1973). Geothermal sources and distribution of mercury in Hawaii, *Environmental Biology and Medicine,* **2,** 81–89.

Skripnichenko, I. I. and Zolotareva, B. N. (1980). Reaction of plants to heavy metals in a culture medium, *Deposited Document Viniti* 409, through C.A. 94 78000.

Taylor, S. R. (1964). Abundance of chemical elements in the continental crust: a new table, *Geochimica et Cosmochimica Acta,* **28,** 1273–1285.

Varekamp, J. C. and Buseck, P. R. (1981). Mercury emission from Mount St. Helens during September 1980, *Nature* (*London*), **293,** 555–556.

C.N.R. Centro di Studio per la Mineralogio e la Geschimica dei Sedimenti.