UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Helium, mercury, sulfur compounds, and carbon dioxide in soil gases of the Puhimau Thermal Area, Hawaii Volcanoes National Park, Hawaii

by

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Sampling

The objective of this work was to determine how concentrations of He, Hg, CO_2, and sulfur compounds in soil gases over and near the hot ground might be related to the thermal area. Soil and soil gas samples were collected along two perpendicular traverses across the thermal area laid out by the U.S. Geological Survey staff of the Hawaiian Volcano Observatory (fig. 1B). Two soil samples were collected at each site on the traverses. One sample was sealed in an air-tight can for helium analysis later, and the other sample was retained for Hg analysis. Soil temperature was measured at a depth of 15 cm at each site. Visible steam was noted where present.

A mixture of 3A, 5A, and 13X types of molecular sieve powder was placed at each site to collect and concentrate sulfur compounds and carbon dioxide rising through the soil. A cloth bag containing an envelope of molecular sieve mixture was suspended inside a piece of plastic pipe that was about 5 cm in diameter, about 30 cm long, and open at both ends. The pipe was buried in the ground to about one half its length (15 cm). To protect the molecular sieve from rain, the open pipe was covered with an empty soft drink can which had one end cut off. The molecular sieves were left in the ground for six weeks, then dug up and shipped to Denver for analysis.

A Matheson-Kitagawa toxic-gas detector was tested at the intersection of the two traverses, at a point near the intersection in the steaming ground part of the thermal area, and at site SW-3, which is not steaming ground. The detector was also tried at the Sulphur Bank Fumarole, about 5 km northwest of the thermal area (fig. 1). This detector uses a hand pump to pull air through detector tubes containing chemical reagents which produce characteristic color stains for different toxic gases. The gases tested for were sulfur dioxide and methyl mercaptan; the lower limit of detection was 0.5 ppm for SO_2 and 1 ppm for CH_3SH.

Analysis

Helium in the dead air space of the cans was measured by a modified helium leak detector, using the procedure of Hinkle and others (1978). Mercury in the soil was analyzed by the flameless atomic absorption method of Vaughn and McCarthy (1965). Sulfur compounds and carbon dioxide collected by the molecular sieves were analyzed by gas chromatography using the method of Hinkle and Kantor (1978). The molecular sieve samples were analyzed for sulfur compounds within two weeks of retrieval, and for CO_2 within four weeks of retrieval. The amount of moisture collected by the molecular sieves was determined by loss in weight after drying at 70°C.

Results

Helium concentrations ranged from 15 to 1,534 parts per billion in the total undried soil sample. The higher values occurred around the edges of the thermal area and near the fractures northwest of the area (fig. 2).

Mercury concentrations ranged from 0.04 parts per million (ppm) to much greater than 10 ppm, the upper limit of determination by the method used. Mercury is over 100 times more concentrated within the steaming ground than it is on the periphery of this area. Mercury is also higher near the fractures (fig. 3).

Carbon dioxide values ranged from less than 1 to 15 percent of gases absorbed on the molecular sieves, with the lowest concentrations centered over the steaming ground part of the thermal area. Highest concentrations of CO_2 are around the edges of the thermal area and also near the fractures (fig. 4).

The molecular sieve mixtures collected only one sulfur compound which did not have the retention time on the gas chromatograph of the COS, H_2S, CS_2, or SO_2 standards used. Because only one sulfur compound was detected, it was called simply "total sulfur". The "total sulfur" compound ranged in concentration from undetected to a chromatographic peak area of 6,000 units; a peak area of 6,000 units represents approximately 100 parts per billion of the sulfur compounds used for standardization of the instrument. Like CO_2, the lowest concentration of "total sulfur" was over the steaming ground part of the thermal area and highest around the edges of the thermal area and near the fractures northwest of the area (fig. 5).

Moisture collected by the molecular sieves was lowest (less than 10 percent) in the forest away from the thermal area and highest (greater than 25 percent) over the thermal area, following the same pattern as the soil temperature (fig. 6). Moisture was also high near the fractures northwest of the thermal area.

The Matheson-Kitagawa toxic-gas detector did not detect any SO_2 or CH_3SH in the soil gases at the sites tested in the thermal area. When the same detector tubes were tried with gases collected from the Sulphur Bank Fumarole, both tubes immediately filled with stain, the SO_2 tube showing greater than 300 ppm SO_2, and the CH_3SH tube showing a greater than 40 ppm H_2S interference.

Discussion

Volatile elements and compounds could be degassing from the magma and rising to the surface through fractures around the thermal area and to the northwest of it. All of the volatiles determined in this study have higher concentrations in those places. Mercury concentrations are highest over the hottest part of the area, where the heat of the magma appears to be pushing mercury up.

Although sulfur and CO_2 could be coming from the magmatic gas, their concentrations were lowest in the center of the thermal area. Because molecular sieves are extremely hydroscopic, those placed over the steaming ground, where both moisture and temperature are high, may have selectively collected moisture instead of gaseous sulfur and CO_2, while the molecular sieves in other areas of high moisture but lower temperatures (that is, between the fractures), may have collected moisture in which CO_2 and sulfur were already dissolved. When the graphs of CO_2 and sulfur concentrations are laid over the graphs of the soil temperature and moisture concentrations, no obvious relationship is apparent between soil-gas concentration and moisture content alone. However, over about 60°C very little gas was collected by molecular sieves which contained over 10 percent moisture (fig. 7). Because the Matheson-Kitagawa detector failed to measure SO_2 and CH_3SH in soil gases at and near the center of the thermal area, the concentration of sulfur compounds may be naturally low in that area.

The main source of sulfur and CO_2 around the periphery of the thermal area is probably vegetation which is decomposed and distilled by the heat. However, at least part of the sulfur and CO_2 collected over the fractures northwest of the area could have a magmatic origin.

Acknowledgements

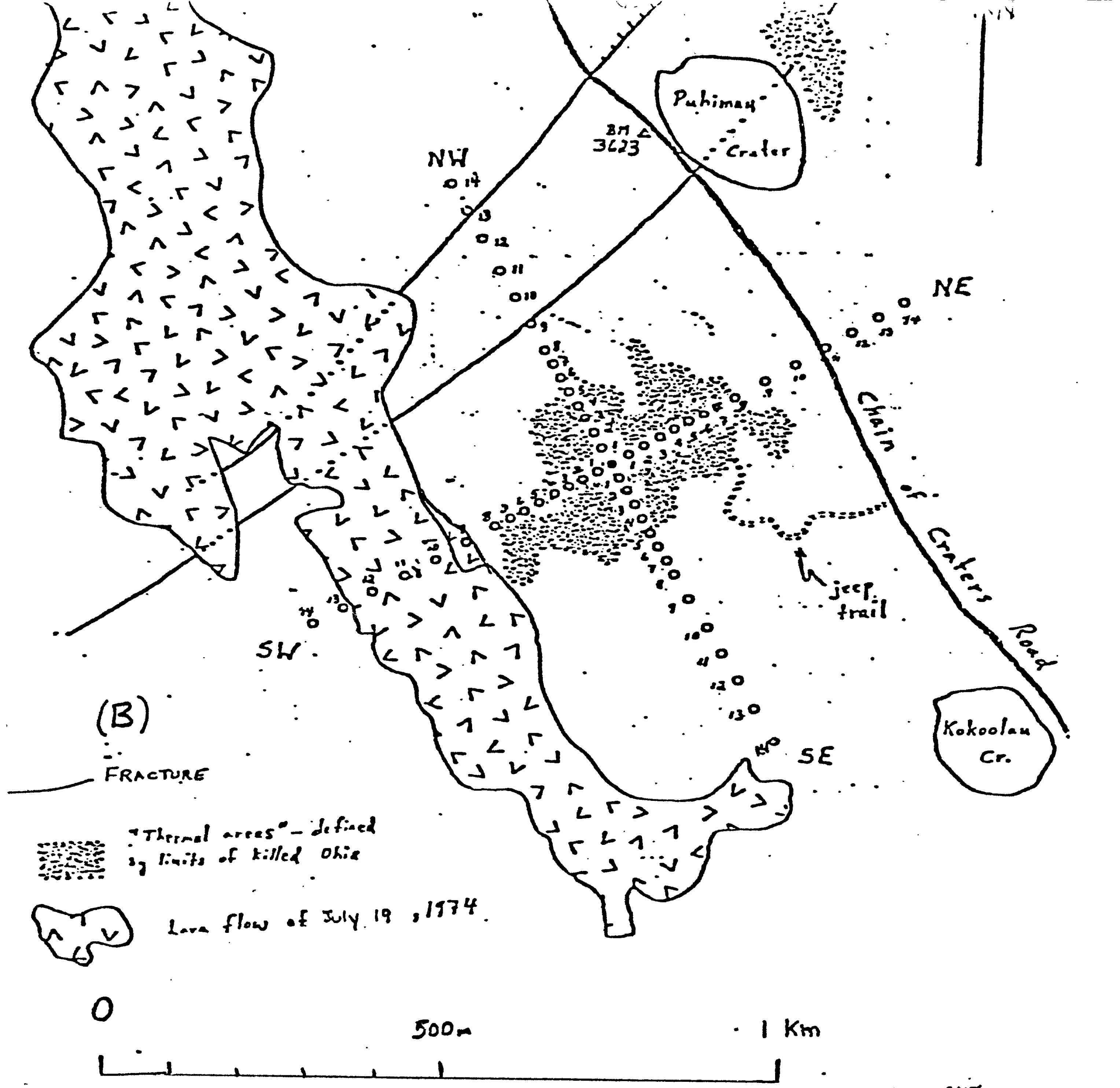
I want to thank Gordon Eaton and the staff of the Hawaii Volcano Observatory for collecting the molecular sieves after they had been in the ground for six weeks. Elizabeth Plasse analyzed the soil samples for mercury.

References Cited

Hinkle, M. E., Denton, E. H., Bigelow, R. C., and Turner, R. L., 1978, Helium in soil gases of the Roosevelt Hot Springs Known Geothermal Resource Area, Utah: U.S. Geol. Survey Jour. Research, (in press).

Hinkle, M. E., and Kantor, J. A., 1978, Collection and analysis of soil gases emanating from buried sulfide mineralization in southeastern Arizona: Jour. Geochem. Exploration (in press).

Vaughn, W. W., and McCarthy, J. H., Jr., 1965, An instrumental technique for the determination of submicrogram concentrations of mercury in soils, rocks, and gas, in Geological Survey Research 1964: U.S. Geol. Survey Prof. Paper 501-D, p. D123-D127.



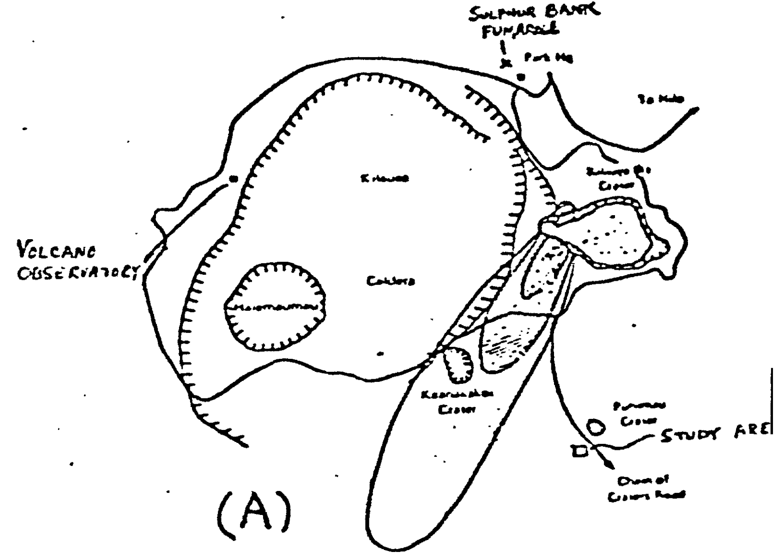
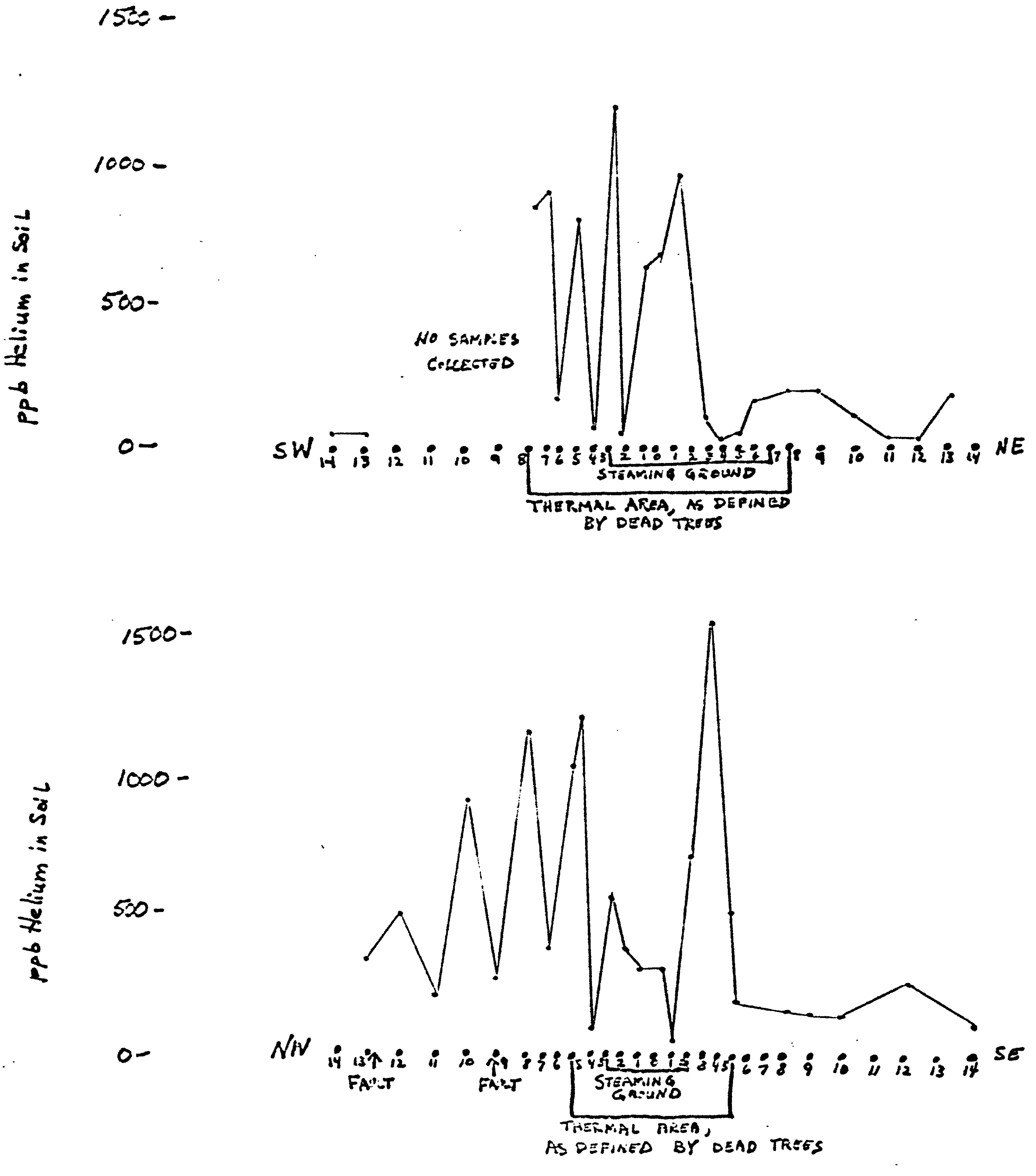


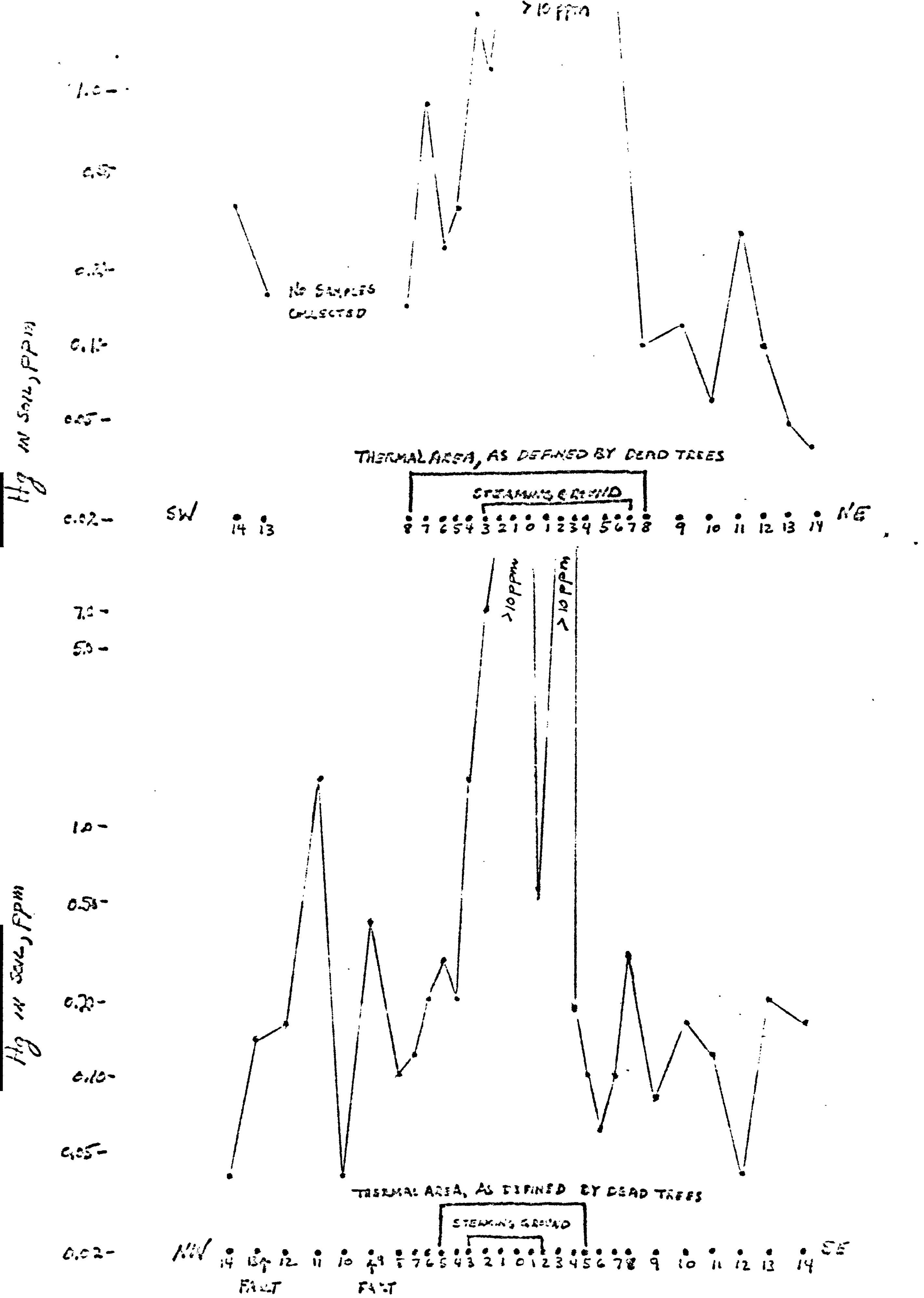
FIGURE 1.-- LOCATION MAP OF THE PUHIMAU THERMAL AREA (A), AND AN ENLARGED MAP SHOWING THE SAMPLE LOCALITIES (B), HAWAII VOLCANOES NATIONAL PARK ISLAND OF HAWAII



HELIUM IN UNDRIED SOIL SAMPLES

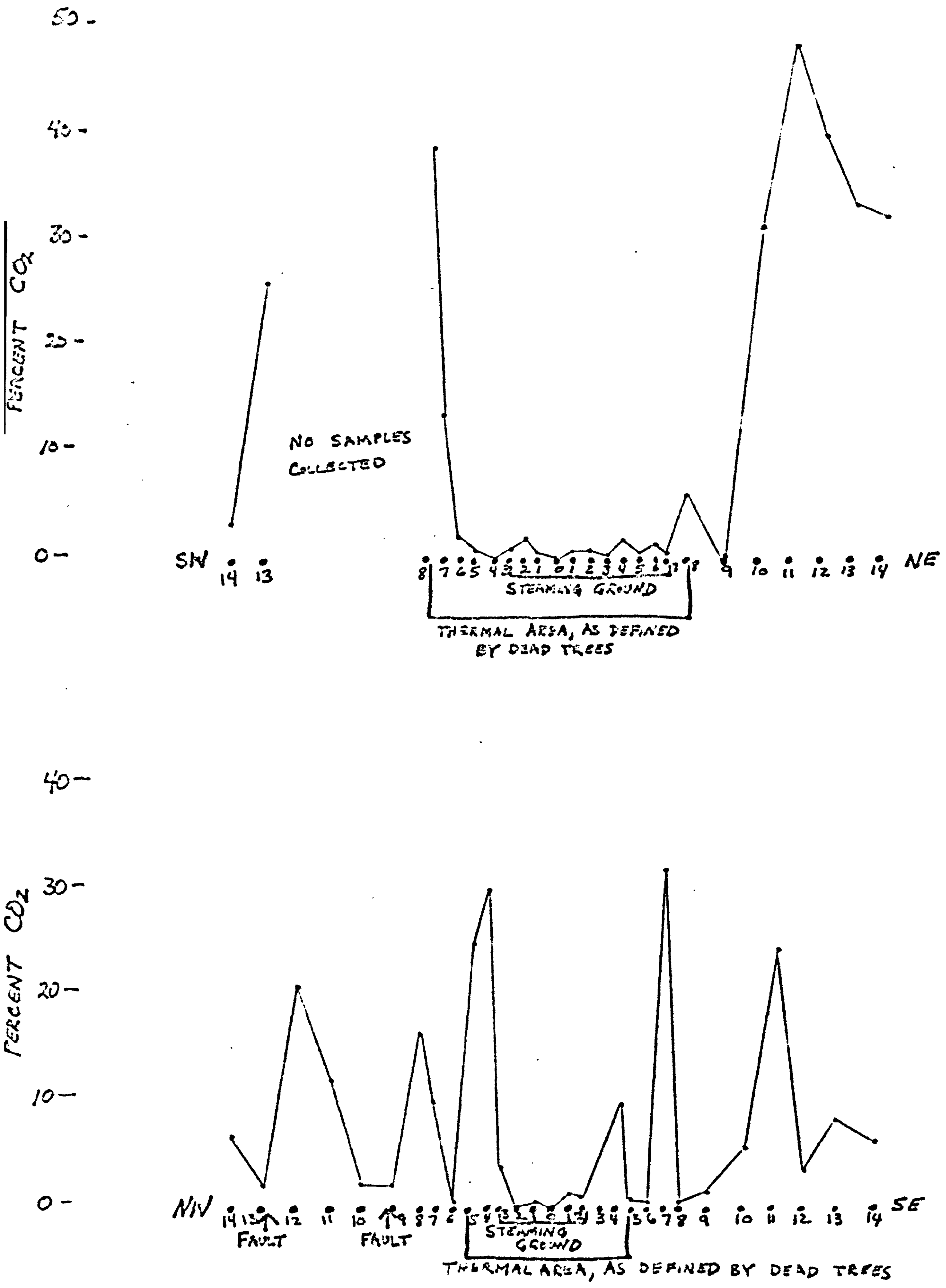
PUHIMAU THERMAL AREA

FIGURE- 2

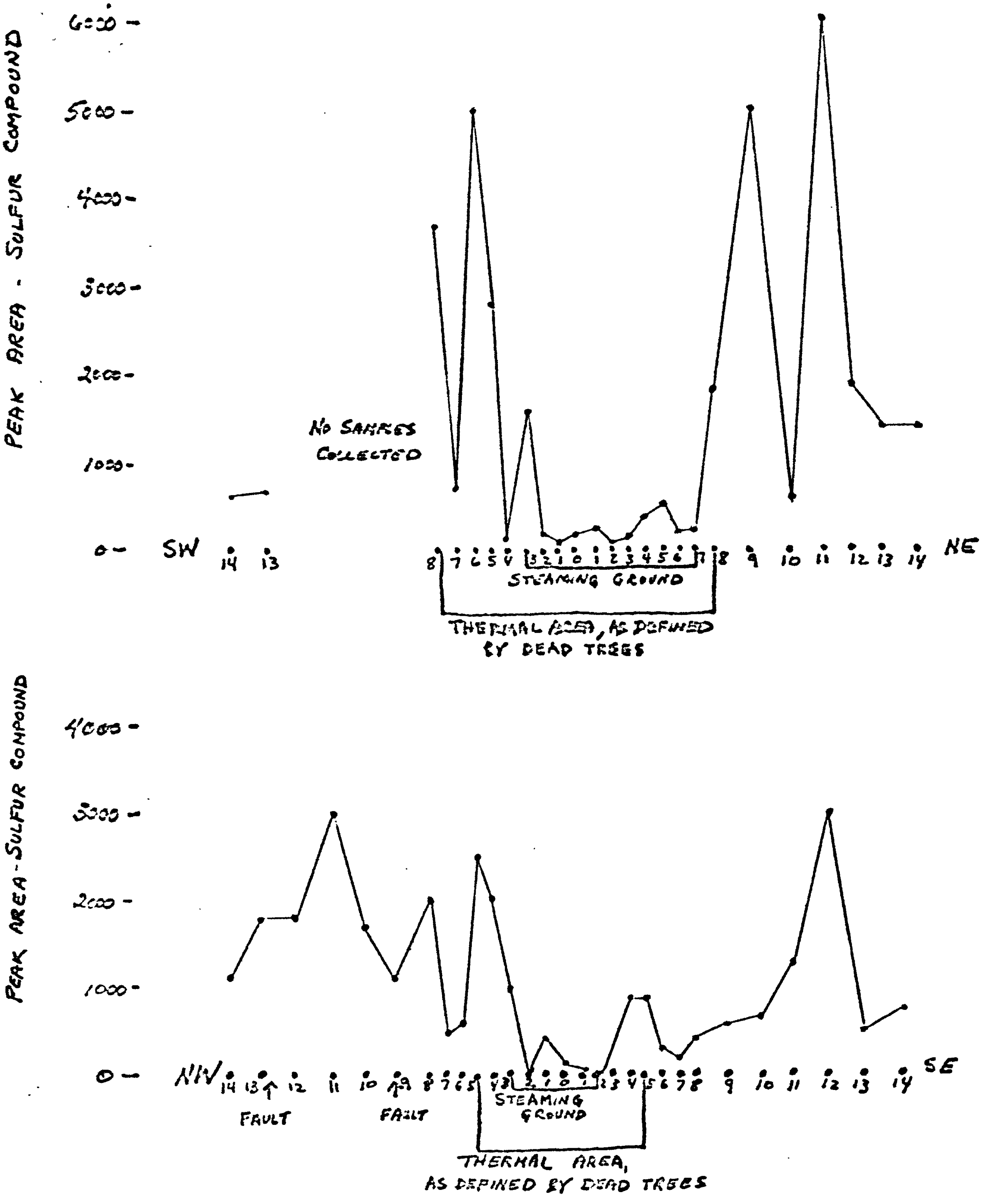


MERCURY IN SOILS
PUHIMAU THERMAL AREA

FIGURE 3



CARBON DIOXIDE COLLECTED ON MOLECULAR SIEVES
BURIED 6 WEEKS
PUHIMAU THERMAL AREA
FIGURE - 4



TOTAL SULFUR COMPOUND COLLECTED ON MOLECULAR SIEVES
BURIED 6 WEEKS

PUHIMAU THERMAL AREA
FIGURE- 5

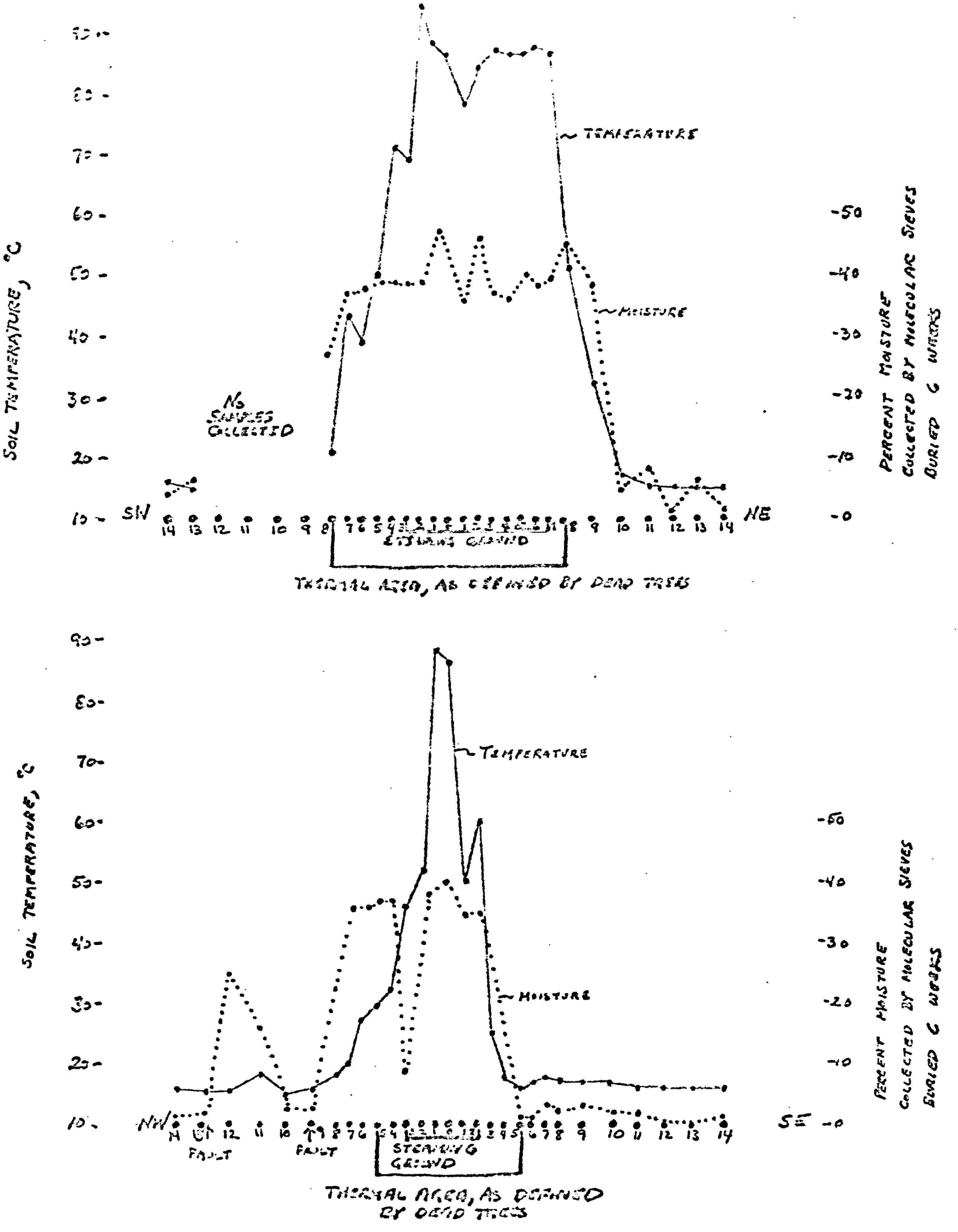


FIGURE — 6
SOIL TEMPERATURE AND MOISTURE

FIGURE 7

RELATIONSHIP OF SOIL TEMPERATURE TO CARBON DIOXIDE AND SULFUR COLLECTED BY MOL SIEVES