

Pollutant Sorption by Desert Soils¹

Roger W. Ferenbaugh², William S. Gaud, and Jack S. States

*Department of Biological Sciences, Box 5640, Northern Arizona University,
Flagstaff, Ariz. 86011*

In recent years much attention has been given to the fate of air pollutants in the environment. Studies in which pollutant gases were removed by soils either from static air masses or from air streams which were passed through soil samples have demonstrated that some soils have extensive capacities for sorption of pollutants (ABELES et al. 1971, FUHR et al. 1948, GHIORSE and ALEXANDER 1976, PAYRISSAT and BEILKE 1975, PRATHER et al. 1973, SMITH et al. 1973, YEE et al. 1975). The techniques used in these studies, while demonstrating that sorption does occur, do not approximate natural conditions where pollutant-containing air passes over the soil surface. The sorption experiments reported upon in this paper were therefore undertaken to provide data for an ecosystem model to predict the potential impact of coal-fired power plants on the cool desert ecosystem found in the Kaiparowits Plateau and the Kaiparowits Basin of northern Arizona and southern Utah. Natural conditions were simulated by passing pollutant-containing air streams over the surface of soil samples. Similar techniques were used in two previous studies (SEIM 1970, TERRAGLIO and MANGANELLI 1966), but the soils used in those studies were quite different from the alkaline, calcareous soils investigated in the study reported upon in this paper. TERRAGLIO and MANGANELLI (1966) used an acid soil, which did not readily sorb sulfur dioxide, and SEIM (1970) used non-desert loams, silts, and clay loams from the state of Minnesota.

EXPERIMENTAL

Fumigations were conducted in a cylindrical plastic chamber

¹This study was funded by an environmental impact study grant from the Salt River Project and the Southern California Edison Company.

²Present address: Environmental Surveillance Group, MS 490, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, NM 87545.

about 45 cm in diameter and 15 cm high in which the pollutant-containing air entering the chamber was forced to pass over the soil surface because of the configuration of the inlet and outlet ports (Figure 2). The pollutant-containing air was introduced into the chamber through a circular teflon manifold which fit around the base of the interior of the chamber. The petri dish containing the soil sample was located in the center of the chamber, and the outlet port was inserted into the chamber and located just above the center of the petri dish. The airflow pattern was thus from the manifold across the periphery of the petri dish to the center of the petri dish. Each soil sample consisted of 400 g of soil, about 1.25 cm deep, in a 14.7 cm diameter glass petri dish, resulting in a surface area of slightly less than 170 cm². The petri dish was covered with a tight-fitting plastic cover and thus the soil was kept from contact with the surrounding air until the chamber walls were saturated and the pollutant concentration in the air passing through the chamber had stabilized at the desired level. The cover was then removed by means of a string which was attached to the plastic cover and which passed through a serum nipple covering a port at the top of the chamber. In this way the cover could be removed from the petri dish containing the soil sample without opening the chamber and disturbing the equilibrated pollutant concentration. After the cover was removed, the subsequent drop in pollutant concentration in the effluent air from the chamber was monitored. Fumigations with sulfur and nitrogen dioxides, provided from Matheson certified standards, were conducted at initial ambient concentrations of 0.25, 0.50, and 1.00 ppm. Desired concentrations were prepared by introducing the standards into the air streams entering the chambers through micrometering valves. Concentrations in the effluent stream were monitored continuously with Meloy sulfur and nitrogen oxide analyzers which were calibrated against National Bureau of Standards permeation tubes (SCARINELLI et al. 1970). The air flow rate through the chamber was 1675 cm³/min.

The entire Kaiparowits area and much of the surrounding land area, comprising hundreds of square miles, have similar soils. The major soil associations are the Ustic Torrifluvents-Lithic Torriorthents association of the Kaiparowits Plateau and the Typic Torripsamments-Typic Torriorthents association of the Kaiparowits Basin. Both of these soils are entisols. In general, the soils are moderately alkaline and calcareous sandy loams, supporting sparse vegetation, with a pH of 7.3-8.0 and an organic matter content of 0.30-0.45%. Soil characteristics were monitored biweekly for three years. The physico-chemical characteristics were found to be stable during that time, although precipitation modified the pH slightly. The soil samples used in these studies were representative composite surface samples which were sieved through a number 24 Tyler mesh screen prior to use. Portions of the sieved soil were either air-dried, oven-dried at 110-130°C, autoclaved, or moistened to field capacity. The samples were treated in these various ways to determine the effects of moisture and biological sterility on sorption characteristics. Untreated soil contained about 0.5% moisture, air-dried soil about the same

amount, and oven-dried soil essentially no moisture except for that which may have been chemically bound. The air passing over the soil samples was ambient air with a relative humidity of 20-40%, which is typical of that found in the Kaiparowits area. Sorption problems in the air lines and chamber, which can occur in moist air, are insignificant at these low humidities. The low humidity also precluded significant moisture uptake by the soils. Humidity was measured both with a sling psychrometer in the ambient air and a dewpoint hygrometer inserted in the air line. Fumigations were conducted for one hour, with occasional extended runs to determine how well the soils would continue to remove pollutant gases over a period of time.

RESULTS AND DISCUSSION

Two replicate samples were run for each pollutant gas under each set of soil conditions. The sorption curves resulting from the replicate runs were always nearly identical. Under some conditions where more than two replicates were run, the results from all replicates were nearly identical. Representative curves for sulfur dioxide sorption and nitrogen dioxide sorption by air-dried soil are shown in Figure 1. This figure also shows the result of carrying out the fumigation procedure using a covered petri dish which contained no soil. The uptake by the empty dish was negligible. Although the form of the sorption curve for both nitrogen dioxide and sulfur dioxide is similar, the soil removed a greater percentage of sulfur dioxide from the air. Using Student's *t* test, the difference in uptake between sulfur and nitrogen dioxides was found to be significant at the 0.001 level.

Table 1 shows the equilibrium sorption values established for each gas under each set of experimental conditions. These data were analyzed using an analysis of variance and Tukey's test for multiple comparisons (GUENTHER 1964). Tukey's test was used to compare the data for air-dried soil individually with the data for each of the other soil treatments. For sulfur dioxide, sorption by soil saturated to field capacity (63%) was significantly different from sorption by air-dried soil (44% average) at the 0.01 level. For nitrogen dioxide, sorption by oven-dried soil (47%) was significantly different from sorption by air-dried soil (34% average) at the 0.05 level. No significant difference from sorption by air-dried soil was found for any of the other soil treatments.

Sulfur dioxide is quite soluble in water, so the greater sorption of sulfur dioxide by moist than by air-dried soil is not surprising. Nitrogen dioxide, however, was sorbed less readily by moist soil, even though this gas is also highly soluble in water. The reduced sorptivity of nitrogen dioxide by moist soil has also been reported by SMITH and MAYFIELD (1978), who attributed the reduced uptake to interference with diffusion by the moisture in the interstitial spaces. A corresponding argument obviously does

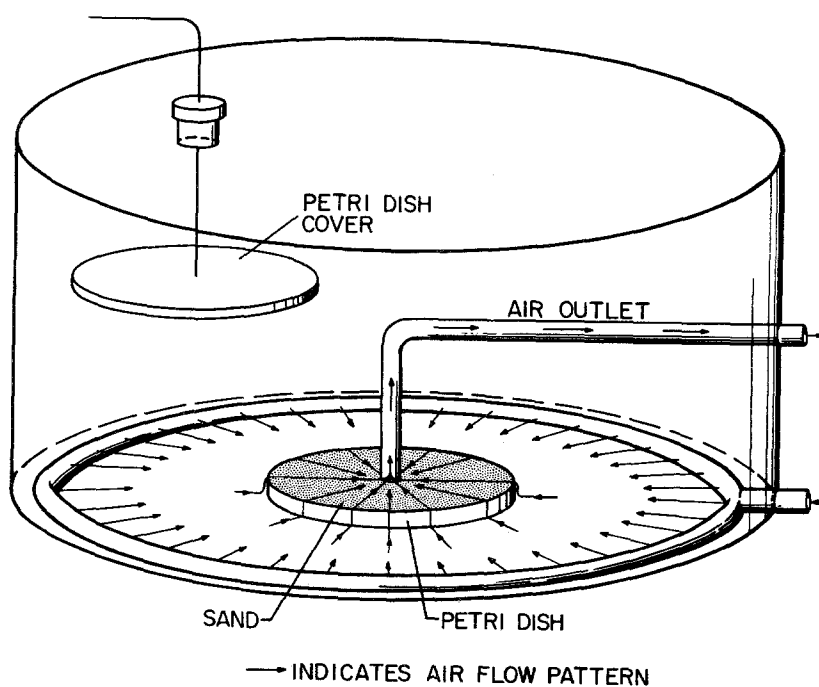
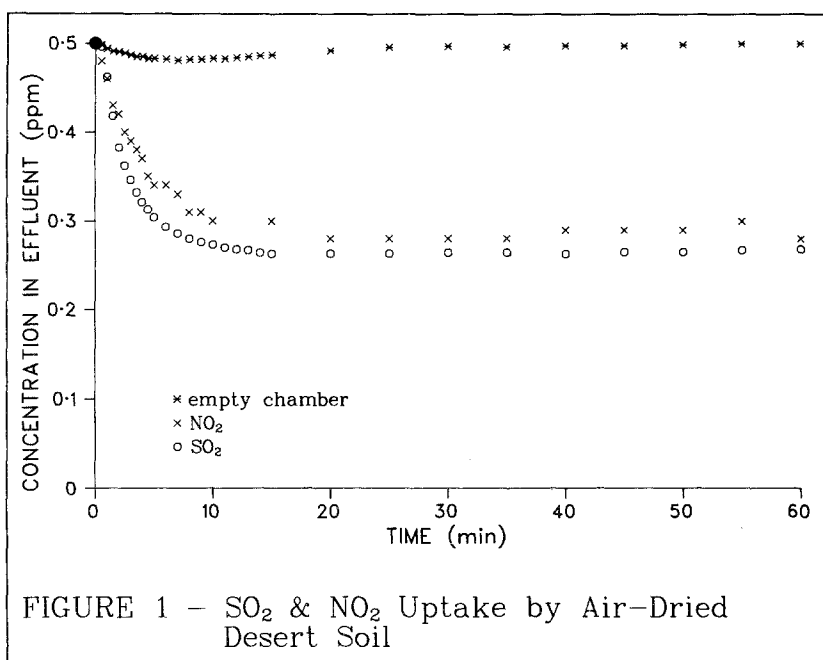


FIGURE 2 - Fumigation Chamber

TABLE 1
Sulfur and Nitrogen Dioxide Uptake by Desert Soil under Various Conditions of Moisture Content and Sterility

Soil Condition	Sulfur Dioxide				Nitrogen Dioxide			
	Effluent Concentration (ppm)		Uptake		Effluent Concentration (ppm)		Uptake	
	Initial	Final	Rate ³ ($\mu\text{g/hr/cm}^3$)	%	Initial	Final	Rate ³ ($\mu\text{g/hr/cm}^3$)	%
Air-Dried	1.00	0.57	0.54	43	1.00	0.65	0.40	31
Air-Dried	0.50	0.27	0.30	47	0.50	0.29	0.26	39
Air-Dried	0.25	0.15	0.13	42	0.25	0.17	0.12	33
Oven-Dried	0.50	0.32	0.24	37	0.50	0.26	0.32	47 ¹
Field Capacity	0.50	0.19	0.39	63 ^{2,3}	0.50	0.40	0.14	21
Autoclaved	0.50	0.28	0.27	44	0.50	0.26	0.31	46

¹ Significant at 0.05 level

² Significant at 0.01 level

³ Equilibrium uptake not established at one hour

not hold true for sulfur dioxide, however, which implies either that the uptake mechanisms are different for the two gases or that some factor other than blockage of the interstitial spaces with moisture is responsible for the reduced uptake of nitrogen dioxide in moist soils. PRATHER et al. (1973) have reported that nitrogen dioxide is sorbed more readily from moist air than dry air, but they also noted that nitrogen dioxide reacts with water vapor in air to form nitric acid. Sorption of nitric acid by soil may be a different phenomenon from sorption of nitrogen dioxide by moist soil, even though the nitrogen dioxide taken up probably undergoes disproportionation and oxidation to form nitric acid (BOHN 1972, GHIORSE and ALEXANDER 1976).

The fact that autoclaved soil did not take up sulfur dioxide differently from air-dried soil was expected as GHIORSE and ALEXANDER (1976) have demonstrated that microorganisms do not play a role in the uptake of sulfur dioxide. Microorganisms may be important, however, in subsequent chemical transformations. Both oven-dried and autoclaved soils removed a greater percentage of nitrogen dioxide from the air than air-dried soil. The reasons for this are not clear, as microorganisms are not directly involved in the sorption of nitrogen dioxide either (GHIORSE and ALEXANDER 1976, SMITH and MAYFIELD 1978). Perhaps treatments in which the soil is heated somehow alter the chemical and physical properties of the soil so that uptake of nitrogen dioxide is enhanced. If there were a significant amount of organic matter present in the soil, heat treatment could create sorption sites by cleavage of the organic matter, but the low organic matter content of these desert soils would seem to preclude this possibility.

Experiments in which sulfur dioxide and nitrogen dioxide were removed simultaneously from the air stream indicated that the sorption characteristics for each gas were unaffected by the presence of the other. This apparent lack of competition for sorption sites provides further evidence that the uptake mechanisms for the two gases are different.

The most significant aspect of these results is that desert soil does remove large percentages of the pollutant gases under simulated natural conditions. This indicates that in desert ecosystems where vegetation is sparse and much of the soil surface is bare, alkaline soil in either wet or dry condition may be a major sink for sulfur and nitrogen dioxides. This conclusion is reinforced by the data from experiments in which fumigation was continued for extended periods of time. Soil samples fumigated continuously for 24 hours removed sulfur dioxide and nitrogen dioxide at nearly the same rates during the entire fumigation period. Several days were required to saturate the soil samples. Furthermore, samples which had been saturated regained their sorptive capacity when allowed to sit for a day or more without fumigation. Thus, in a natural situation in which soil would be exposed only intermittently to sulfur dioxide and nitrogen dioxide because of varying meteorological conditions, there would be

periods during which the soil could recover its sorptive capacity. This recovery could be through a combination of chemical transformation and degassing. BOHN (1972) has noted that sulfur dioxide and nitrogen dioxide taken up by soil are oxidized to sulfate and nitrate, respectively, and the data of GHIORSE and ALEXANDER (1976) show that microorganisms are involved in the chemical transformations which occur after sorption of these gases. The sulfate and nitrate thus formed would probably have some beneficial use as nutrient sources by plants and other soil microorganisms or possibly could be decomposed to other nitrogenous or sulfurous gases by microbial action. Even though the soil could act as a significant pollution sink, however, does not mean that high ambient concentrations would not have deleterious effects on vegetation growing in the area (FERENBAUGH 1978).

REFERENCES

- ABELES, F.B., L.E. CRAKER, L.E. FORRENCE, and G.R. LEATHER: Science 173, 914 (1971).
- BOHN, H.L.: J. Environ. Qual. 1, 372 (1972).
- FERENBAUGH, R.W.: Water Air Soil Pollut. 10, 27 (1978).
- FUHR, I., A.V. BRANSFORD, and S.D. SILVER: Science 107, 274 (1948).
- GHIORSE, W.C., and M. ALEXANDER: J. Environ. Qual. 5, 227 (1976).
- GUENTHER, W.C.: Analysis of variance. Englewood Cliffs: Prentice Hall 1964.
- PAYRISSAT, M., and S. BEILKE: Atmos. Environ. 9, 211 (1975).
- PRATHER, R.J., S. MIYAMOTO, and H.L. BOHN: Soil Sci. Soc. Am. Proc. 37, 860 (1973).
- SCARINGELLI, F.P., A.E. O'KEEFFE, E. ROSENBERG, and J.P. BELL: Anal. Chem. 42, 871 (1970).
- SEIM, E.C.: Sulfur dioxide absorption by soil. Ph.D. Thesis. St. Paul: U. Minn. 1970.
- SMITH, E.A., and C.I. MAYFIELD: Water Air Soil Pollut. 9, 33 (1978).
- SMITH, K.A., J.M. BREMNER, and M.A. TABATABAI: Soil Sci. 116, 313 (1973).
- TERRAGLIO, F.P., and R.M. MANGANELLI: Int. J. Air Water Pollut. 10, 783 (1966).
- YEE, M.S., H.L. BOHN, and S. MIYAMOTO: Soil Sci. Soc. Am. Proc. 39, 268 (1975).