COO-2530-11

SORPTION OF POLLUTANT GASES BY SOILS

Progress Report
for Period December 1, 1976-November 30, 1977

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August 1977

Prepared for

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-2530

MASTER

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Abstract

Studies of factors affecting sorption of nitrous oxide by soils showed that nitrate inhibits reduction of N_2O to N_2 by soil microorganisms and that the inhibitory effect of nitrate on N_2O reduction increases markedly with decrease in soil pH.

Emission of nitrous oxide was observed during incubation of soils under aerobic conditions. Research to account for this observation showed that N_2O is produced during nitrification of ammonium in well-aerated soils and indicated that N_2O production during nitrification of fertilizer nitrogen in soils may be significant in regard to the potential threat of fertilizer-derived N_2O to the ozone layer.

A gas chromatographic procedure was developed for determination of N_2O in air. It is rapid, sensitive, specific and precise, and it permits use of the xenon in air as an internal standard.

Techniques were developed for research on sorption of NO and NO_2 by soils, and studies of factors affecting NO_2 sorption by soils were initiated.

The capacity of diverse soils for sorption of SO_2 was found to be very significantly correlated with their surface area, $CaCO_3$ equivalent and acid-titratable basicity. Their capacity for sorption of H_2S was found to be very significantly correlated with their clay and extractable Mn contents.

Scope of work

Sorption of nitrous oxide by soils

Continuation of research on factors affecting sorption of N_2O by soils showed that soil microorganisms exhibit no capacity to reduce N_2O to N_2 under aerobic conditions and that their ability to reduce N_2O to N_2 under anaerobic conditions is markedly affected by nitrate. Low concentrations of nitrate retard reduction of N_2O to N_2 by soil microorganisms, and high concentrations of nitrate almost completely inhibit this process. The inhibitory effect of nitrate on N_2O reduction by soil microorganisms increases markedly with decrease in soil pH. These findings account for the observation in previous work that accumulation of N_2O during denitrification of nitrate in soils incubated in closed systems is promoted by high nitrate levels and low pH. They have important implications in regard to assessment of the effects of soils on the atmospheric concentration of nitrous oxide because they indicate that the percentage of nitrate N released to the atmosphere as N_2O through denitrification of nitrate in soils under anaerobic conditions is greatly affected by the nitrate level and that the ability of soils to act as a sink for N_2O is determined largely by their nitrate content.

Work summarized in our previous Progress Report (COO-2530-7) and recently published (Blackmer and Bremner, 1976) led us to conclude that the potential of soil as a sink for atmospheric N_2O deserves attention. Brice, Eggleton and Penkett (1977) have recently reported studies leading them to conclude that there is an important ground surface sink for atmospheric N_2O and that the magnitude of this sink is about twice the current estimated combined ocean source and soil source and more than an order of magnitude greater than the estimated stratospheric sink.

Emission of nitrous oxide from soils during nitrification of fertilizer nitrogen

It is generally assumed that N_2O is released from soils only through denitrification of nitrate by soil microorganisms under anaerobic conditions. However, control experiments performed during our studies of factors affecting sorption of nitrous oxide by soils showed that small amounts of N_2O were released from soils under aerobic conditions. Since it appeared unlikely that the N_2O released under these conditions was produced by denitrification of nitrate, we studied the possibility that N_2O may be produced during nitrification of ammonium in well-aerated soils. This study showed that nitrous oxide is released from soils during nitrification of ammonium and ammonium-producing fertilizers under aerobic conditions and indicated that this process may be significant in regard to the potential threat of fertilizer-derived nitrous oxide to the stratospheric ozone layer. Details of this work are reported in a paper recently submitted for publication in Science (copy attached).

Determination of nitrous oxide in air

Recent articles concerning the potential adverse effect of increased levels of atmospheric N_2O on the earth's protective ozone shield have emphasized the need for a reliable and precise method for determination of N_2O in air. We have developed a gas chromatographic method for this analysis that involves use of an ultrasonic detector and has the important advantage of permitting use of the xenon in air as an internal standard. This method is rapid (analysis time, ca. 9 minutes), specific, sensititve (1 ppbv of N_2O can be detected) and precise (standard deviation, 0.49%). It is not subject to interference by gases found in unpolluted or polluted air, and it permits accurate determination of very small changes in the atmospheric concentration of N_2O. Full details of this method will be reported in a paper now in preparation.

Sorption of nitrogen dioxide by soils

Soil properties affecting sorption of NO_2 by soils were investigated by determining the amounts of NO_2-N sorbed when air-dry and moist samples of 32 surface soils were exposed for 6.5 hours to an air stream containing 5% NO_2. The soils used were selected to obtain a wide range in properties, including pH, surface area, texture, organic-matter content, cation-exchange capacity, $CaCO_3$ equivalent and acid-titratable basicity. Statistical analysis of the relationships between soil properties and the capacity of soils for sorption of NO_2 will be completed before the end of the contract period. The data thus far obtained indicate that the capacity of soils for sorption of NO_2 is significantly correlated with their $CaCO_3$ and organic-matter contents.

Several problems have been encountered in attempts to prepare NO_2 gas mixtures and inject known amounts of NO_2 into sealed systems containing soils. They include sorption and liquefaction of NO_2 within gas syringes, corrosion and plugging of syringe needles, sorption of NO_2 by rubber septa, stopcock grease and several types of tubing, and instability of NO_2 gas mixtures and standards. These problems have been overcome by development of a method that permits quantitative injection of accurately measured amounts of NO_2 into sealed systems. This method involves use of a vacuum-manifold system, an 8-port sampling valve, and a temperature-controlled NO_2 cylinder.

Sorption of nitric oxide by soils

A Thermo Electron Model 12A Chemiluminescent NO_x Analyzer was purchased for research on sorption of NO by soils because recent literature indicated that this instrument should permit accurate determination of NO sorption by soils exposed to gas streams containing different concentrations of NO. We found, however, that this instrument has several defects not reported in the literature, the most serious being that some of its components sorb and subsequently release both NO and NO_2. Also, we found that commercially prepared NO and NO_2 standards used for calibration of chemiluminescent NO_2 analyzers are unstable and frequently contain no trace of NO or NO_2 when stored before use. However, preliminary work indicates that the problems encountered in use of the Model 12A Analyzer can be overcome by our modifications of this instrument, and the problems encountered with NO and NO_2 standards have been eliminated by development of a method of preparing these standards immediately before use.

Gas chromatographic studies showed that moist soils sorb NO quite rapidly under anaerobic conditions and that this process involves reduction of NO to N_2O and N_2 by soil microorganisms.

Sorption of sulfur dioxide and hydrogen sulfide by soils

Soil properties affecting the capacity of soils for sorption of sulfur dioxide and hydrogen sulfide were studied by determining the amounts of sulfur sorbed by air-dry and moist soils exposed for several hours to a stream of air containing 5% SO_2 or 2% H_2S. The soils used were surface (0-15 cm) samples of 41 soils selected to obtain a wide range in physical and chemical properties. They were characterized by the following analyses: pH, surface area, organic carbon, calcium carbonate equivalent, sand, silt, clay, cation-exchange capacity, exchangeable calcium, magnesium, potassium and sodium, total exchangeable cations, extractable iron, manganese and aluminum, total extractable metals, acid-titratable basicity, and percent base saturation. Table 1 shows the results of statistical analyses of the relationships between various soil properties and the capacities of air-dry and moist soils for sorption of SO_2, and Table 2 shows the corresponding results for sorption of H_2S. The data reported show that the capacity of soils for sorption of H_2S is very significantly correlated with their clay and extractable manganese contents and that the capacity of soils for sorption of SO_2 is very significantly correlated with calcium carbonate equivalent, surface area and acid-titratable basicity.

Studies to determine the mechanisms by which soils sorb SO_2 and H_2S are in progress. These studies have shown that most of the methods available for determination of different forms of sulfur are not specific and do not permit valid conclusions when applied to complex systems such as soils. However, the data obtained by these methods leave very little doubt that a substantial amount of the SO_2-S sorbed by soils is converted to sulfate S and sulfite S and that much of the H_2S-S sorbed by soils is converted to sulfide S and elemental S.

Role of microorganisms in the atmospheric sulfur cycle

A comprehensive review of current knowledge concerning the role of microorganisms in the atmospheric sulfur cycle was prepared for Volume 2 of Advances in Microbial Ecology. The attached copy of this review shows that work reported in Progress Report COO-2530-7 provided much of the information currently available concerning the role of soil microorganisms in the atmospheric sulfur cycle. It also shows that there is a good reason to question the current belief that the amount of sulfur emitted as H_2S to the atmosphere through microbial activity on land and in water exceeds the amount emitted as H_2S or SO_2 by industrial and other non-biological processes.

Table 1. Correlations between soil properties and capacities of air-dry and moist soils for sorption of sulfur dioxide

Soil property	Correlation coefficient (r)[a] A	M
pH	0.13	0.44**
Organic carbon	0.15	-0.07
Calcium carbonate equivalent	0.43**	0.90***
Sand	-0.37*	-0.25
Silt	0.06	0.10
Clay	0.69***	0.37*
Surface area	0.52***	0.47***
Cation-exchange capacity	0.32*	0.15
Exchangeable calcium	0.35*	0.76***
Exchangeable magnesium	0.02	-0.08
Exchangeable potassium	0.34*	0.15
Exchangeable sodium	0.13	0.29*
Total exchangeable cations	0.34*	0.71***
Percent base saturation	0.01	0.57***
Extractable iron	0.12	0.06
Extractable manganese	0.59***	0.10
Extractable aluminum	-0.20	-0.20
Total extractable metals	0.15	0.05
Acid-titratable basicity	0.45**	0.90***

[a] A, air-dry soils exposed to SO_2; M, moist soils exposed to SO_2.

*, **, ***, significant at 5%, 1%, and 0.1% level, respectively.

Table 2. Correlations between soil properties and capacities of air-dry and moist soils for sorption of hydrogen sulfide

Soil property	Correlation coefficient (r)[a]	
	A	M
pH	-0.20	0.20
Organic carbon	0.12	0.09
Calcium carbonate equivalent	-0.20	0.27
Sand	-0.48***	-0.47**
Silt	0.32*	0.24
Clay	0.50***	0.60***
Surface area	0.14	0.44**
Cation-exchange capacity	0.14	0.31*
Exchangeable calcium	-0.22	0.32
Exchangeable magnesium	0.01	0.11
Exchangeable potassium	0.29	0.12
Exchangeable sodium	0.46**	0.25
Total exchangeable cations	-0.20	0.33*
Percent base saturation	-0.22	0.01
Extractable iron	0.41**	0.08
Extractable manganese	0.56***	0.71***
Extractable aluminum	-0.30*	-0.18
Total extractable metals	0.43**	0.13

[a] A, air-dry soils exposed to H_2S; M, moist soils exposed to H_2S.

*, **, ***, significant at 5%, 1% and 0.1% level, respectively.

Remainder of current contract term

The remainder of the current contract term will be devoted to completion of research concerning the effects of various soil properties on the capacity of soils for sorption of nitrogen dioxide, sulfur dioxide and hydrogen sulfide, and to preparation of papers reporting the results of this research.

Literature cited

Blackmer, A. M., and Bremner, J. M. 1976. Potential of soil as a sink for atmospheric nitrous oxide. Geophys. Res. Lett. 3:739-742.

Brice, K. A., Eggleton, A. E. J., and Penkett, S. A. 1977. An important ground surface sink for atmospheric nitrous oxide. Nature 268:127-129.

Significant results

The significance of the work reported is reflected by the fact that requests for information about this work have taken up at least 10% of the principal investigator's time during the past 9 months. Most of these requests have related to the potential threat of nitrous oxide to the stratospheric ozone layer. User groups for information concerning the methods we have developed for research on denitrification in soils and for determination of N_2O in air have included scientists associated with the International Atomic Energy Agency (Vienna), the International Fertilizer Development Center (Florence), CSIRO (Australia), the USDA Agricultural Research Service, the Letcombe Laboratory of the British Agricultural Research Council, and several U.S. and foreign universities.

The most significant findings in the work reported are that nitrous oxide is emitted from soils during nitrification of fertilizer nitrogen and that nitrate has an inhibitory effect on reduction of N_2O to N_2 by soil microorganisms. These findings have important implications in regard to assessment of the contributions of soils to atmospheric N_2O and the potential threat of nitrogen fertilizers to the ozone layer. Also, work reported has met the need for a reliable and precise method of determining N_2O in air.

Compliance

The work reported has been carried out in compliance with the contract requirements.

The principal investigator has devoted approximately 40% of his time to the project since the beginning of the current term of the agreement and expects to devote at least 40% of his time to the project during the remainder of the current term.

Reprints & Preprints removed

Papers published or prepared during period of report

Published:

Banwart, W. L., and Bremner, J. M. 1976. Evolution of volatile sulfur compounds from soils treated with sulfur-containing organic materials. Soil Biol. Biochem. 8:439-443.

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Accepted for publication:

Blackmer, A. M., and Bremner, J. M. 1977. Gas chromatographic analysis of soil atmospheres. Soil Sci. Soc. Am. J. In press.

Bremner, J. M. 1977. Effects of soil processes on the atmospheric concentration of nitrous oxide. In Nitrogen in the Environment (D. R. Nielsen and J. G. McDonald, eds.), Academic Press. In press.

Bremner, J. M., and Steele, C. 1977. Role of microorganisms in the atmospheric sulfur cycle. In Advances in Microbial Ecology, Vol. 2, Plenum Press. In press.

Submitted for publication:

Bremner, J. M., and Blackmer, A. M. 1977. Nitrous oxide: Emission from soils during nitrification of fertilizer nitrogen. Submitted to Science.

In preparation:

Blackmer, A. M., and Bremner, J. M. Inhibitory effect of nitrate on reduction of nitrous oxide by soil microorganisms. To be submitted to Soil Biology and Biochemistry.

Blackmer, A. M., and Bremner, J. M. Determination of nitrous oxide in air. To be submitted to Journal of Environmental Quality.

Presented at meetings:

"Gas chromatographic analysis of soil atmospheres" (A. M. Blackmer and J. M. Bremner). At Annual Meeting of American Society of Agronomy, Houston, Texas, November 28-December 3, 1976.

"Effects of soil processes on the atmospheric concentration of nitrous oxide" (J. M. Bremner). At Kearney Foundation Workshop on "Nitrogen in the Environment", Lake Arrowhead, California, January 31-February 3, 1977.

"Microbial processes leading to emission and sorption of nitrous oxide by soils" (A. M. Blackmer and J. M. Bremner). At Denitrification Seminar organized by The Fertilizer Institute, San Francisco, October 26-27, 1977.

"Nitrification of fertilizer nitrogen as a source of atmospheric nitrous oxide" (A. M. Blackmer and J. M. Bremner). At Annual Meeting of American Society of Agronomy, Los Angeles, November 13-18, 1977.