Journal of Atmospheric Chemistry **9**: 411–417, 1989.

The Effect of Nitrogen Fertilization on the COS and CS_2 Emissions from Temperature Forest Soils

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(Received: 5 December 1988; revised: 7 April 1989)

Abstract. The net fluxes of carbonyl sulfide (COS) and carbon disulfide (CS_2) to the atmosphere from nitrogen amended and unamended deciduous and coniferous forest soils were measured during the spring of 1986. We found that emissions of these gases from acidic forest soils were substantially increased after nitrogen fertilization. The total ($COS + CS_2$) emissions were increased by nearly a factor of three in the hardwood stand and were more than doubled in the pine stand. Furthermore, vegetation type appeared to have an influence on which was the dominant sulfur gas released from the forest soils. The added nitrogen caused a dramatic increase in COS emissions from the hardwood stand (a factor of three increase), while CS_2 emissions from this site were not affected. We observed the opposite response in the pine stand; that is, the nitrogen fertilization had no affect on COS emissions, but did stimulate CS_2 emissions (a factor of more than nine increase).

Key words. Trace gases, carbonyl sulfide, carbon disulfide, acid rain, nitrogen fertilization, climate change.

1. Introduction

A variety of sulfur gases, including dimethyl sulfide (DMS), hydrogen sulfide (H_2S) and COS, have recently been recognized as playing important roles in the chemistry of the atmosphere and the heat budget of the Earth (Andreae, 1986). Annually approximately 40 Tg DMS–S and 14 Tg H_2S–S are emitted from oceanic and terrestrial ecosystems, respectively (Andreae, 1985; Ryaboshapko 1983). These gases have low concentrations in the remote atmosphere (DMS, 100 pptv and H_2S, 10 pptv) and short lifetimes (1 to 2 days) because they are rapidly oxidized in the lower troposphere. The annual emission of COS, predominantly from terrestral systems, is about 2.5 Tg COS–S. Its atmospheric concentration is relatively constant at 500 pptv throughout the troposphere because it is a relatively nonreactive species. The lifetime of COS is approximately 1 yr.

Carbonyl sulfide and one of its important tropospheric precursors, CS_2 (Sze and KO, 1979; Wine *et al.*, 1981; Jones *et al.*, 1983) are gases mainly produced by biological processes (Khalil and Rasmussen, 1984; Steudler and Peterson, 1984). Carbonyl sulfide is generally the dominant sulfur source for the stratospheric aerosol layer (Crutzen, 1976; Servant, 1986) which affects the Earth's heat budget by reducing the amount of solar energy entering the troposphere

(Cadle and Grams, 1975; Turco *et al.*, 1980; Servant, 1986). Increases in the aerosol layer would increase the temperature of the stratosphere and this could affect the reactivity and composition of other stratospheric gases (Servant, 1986). The sulfuric acid aerosol layer recently has been implicated in the depletion of stratospheric ozone by acting as a catalytic surface for the production of reactive chlorine species (Rossi *et al.*, 1987; Oppenheimer, 1987; Kerr, 1988; Tolbert *et al.*, 1988). Indirect evidence suggests that the flux of COS and CS_2 from the land and sea to the atmosphere may be increasing due to human activities (Hofmann and Rosen, 1980; Hofmann and Rosen, 1981; Kerr, 1988).

In the study described here, we tested the idea that nitrogen additions to forest soils might be the cause of these increases. Many biological processes in boreal and temperate forests are nitrogen limited (Aber *et al.*, 1983), and we wanted to know if the microbially-mediated production of COS and CS_2 is among them. Since many of these soils are receiving high inputs of nitrogen associated with acid rain (Likens *et al.*, 1980), the identification of a link between nitrogen inputs and gaseous sulfur outputs would be important to our understanding of the hypothesized increases in COS and CS_2 emissions to the atmosphere.

2. Experimental Procedures

In the spring of 1985, we established four fertilized and four control plots in each of two forest stands at the Harvard Forest in central Massachusetts: an 85-year-old mixed oak-red maple (*Quercus* sp. and *Acer rubrum*) stand, and a 60-year-old red pine (*Pinus resinosa*) plantation. The fertilized plots received four equal applications of nitrogen in the nitrate form between July and October of 1985. The total amount of nitrogen applied to the fertilized plots was 10 g N m^{-2} yr^{-1}, an amount 10 times higher than these forests normally receive in wet deposition (Barrie and Hales, 1984; Fay *et al.*, 1987), and an amount two times higher than that received by many similar forests in the polluted areas of western and central Europe (Georgii *et al.*, 1984; Nihlgärd, 1985; Hinrichsen, 1986).

Measurements of COS and CS_2 fluxes between the soils and the atmosphere were made in May 1986, using large (0.94 m^2) FEP teflon flow-through chambers to cover the soil surface (Steudler and Peterson, 1985). The chamber dimensions were 1.82 m long $\times$ 0.45 m wide $\times$ 0.254 m high with a volume of approximately 208 L. On each plot we set out a chamber and operated it continuously for 24 hr during which time we took eight three-hour integrated chamber air samples. During a 24 hr period, all four chambers were operated simultaneously, one chamber for each plot of a given stand-treatment combination (e.g., pine-control). Sampling of the four stand-treatment combinations took four full days. The sampling design allowed us to account for both spatial and diurnal variability associated with COS and CS_2 fluxes from forest soils.

Each chamber was operated so that ambient air was continuously drawn

through it at a constant velocity (0.07 m/s) and the difference in the gaseous sulfur concentrations between the input and output chamber air was used to calculate the net gaseous sulfur uptake or release. To make the sulfur concentration measurements, known volumes of the input and output air were drawn through traps containing the solid adsorbants Molecular Sieve 5A and Tenax GC. A Chromosil 330 column and a sulfur-specific FPD gas chromatograph were used to separate and analyze the sulfur compounds (Steudler and Kijowski, 1984). Flux data were compared with a one way Analysis of Variance (Ryan *et al.*, 1985).

3. Results and Discussion

Nitrogen fertilization increased the total of the combined COS plus CS_2 emissions from the soils in both stands (Table I). The total emissions were increased by nearly a factor of three in the hardwood stand and were more than doubled in the pine stand. Interestingly, nitrogen fertilization did not affect COS and CS_2 emissions in the same way in the two stands. The added nitrogen caused a dramatic increase in COS emissions from the hardwood stand (a factor of three increase), while CS_2 emissions from this site were not affected. We observed the opposite response in the pine stand; that is, the nitrogen fertilization had no affect on COS emissions, but did stimulate CS_2 emissions (a factor of more than nine increase).

The mechanisms responsible for the observed linkage between sulfur and nitrogen in forest ecosystems are not yet understood. We do know that many forests in New England, including the ones studied, are nitrogen limited (Aber *et al.*, 1983). We also know that sulfur-containing amino acids, methionine, cystine and cysteine, are precursors of COS and CS_2 (Bremner and Steele, 1978; Minami and Fukushi, 1981a; Minami and Fukushi, 1981b). Perhaps nitrogen additions to forest ecosystems increase the pool of sulfur-containing amino acids in soils through microbial synthesis of these compounds. Alternatively, the

Table I. Mean carbonyl sulfide and carbon disulfide emissions from nitrogen fertilized and non-fertilized forest soils. Flux units are micrograms sulfur per m^2 per day and the numbers in parentheses are the standard errors

Stand	Treatment	COS	CS_2	$COS + CS_2$
Hardwood	Control[a]	8.66 (6.92)	2.04 (0.53)	10.71* (6.64)
	Fertilized[b]	27.40 (7.34)	1.71 (0.23)	29.11* (2.06)
Pine	Control[c]	19.86 (8.98)	2.36* (0.17)	22.21 (10.18)
	Fertilized[d]	26.63 (10.33)	22.01* (3.55)	48.64 (13.88)

* Difference between control and fertilized treatments was significant at 0.05 level, $n = 4$ chambers.
[a] 12 May 1986, [b] 13 May 1986, [c] 16 May 1986, [d] 15 May 1986.

added nitrogen could be taken up by the trees, the sulfur-containing amino acids could be synthesized by the vegetation, and eventually the plant-produced amino acids could enter the soil system in plant litter or in leaf or needle leachate. There is support in the literature for both alternatives and we review it below.

Several laboratory studies have examined the relationship between the amount of sulfate-sulfur added and the amount of sulfur incorporated into the sulfur-containing amino acid pool. The experiments of Sagger and coworkers (1981) with bacterial and fungal cultures grown under three different sulfate concentrations and large nitrogen surpluses showed that in most cases, the amount of sulfur-containing amino acids in the microbes increased with increasing levels of sulfate. Ninety percent of the total sulfur in bacteria was found in the sulfur amino acid pool while fungi showed a wider range of between 58 and 94%.

The addition of sulfate to nitrogen-rich forest soils has been shown to result in the production of sulfur-containing amino acids and some volatile sulfur compounds. Fitzgerald and Strickland (1982) performed laboratory incubations of the upper soil horizon (0–5 cm) amended with sulfur-35 labeled sulfate. After just two days of incubation they found sulfur-35 labeled carbon-bonded sulfur and they isolated a number of sulfur-35 metbolites including cystine and cysteine.

Nitrogen additions to forest ecosystems have been shown to increase the amount of carbon-bonded sulfur compounds, including sulfur-containing amino acids, in plant foliage (Meiwes and Khanna, 1981; Margolis and Waring, 1986). Amino acid concentrations were very high in needles of spruce trees (*Picea abies*) growing in areas of Germany receiving high nitrogen inputs associated with acid rain (Zedler *et al.*, 1986). The researchers studying the German spruce forests estimated that the present levels of amino acids in the needles are several-fold higher than the levels in the same area 10 years ago. A particularly noteworthy result of the German study was the three-fold increase in the concentration of methionine, a sulfur-containing amino acid and a precursor of COS and CS_2 (Bremner and Steele, 1978).

The two mechanisms for the synthesis of sulfur-containing amino acids, microbial production and higher-plant production, may not be operating synchronously in the two stands. Increased microbial production of sulfur-containing amino acids may be a rapid response to nitrogen fertilization in nitrogen-limited forest stands. The increased production of sulfur-containing amino acids by higher plants may be slower, with the rates related to biological characteristics of the specific plants involved. For example, it is possible that within the one-year time frame of our study in the hardwood stand, the applied inorganic nitrogen was taken up by the trees, became incorporated in the foliage and roots as sulfur-containing amino acid nitrogen, was returned to the soil in amino acid form, and finally was released as inorganic nitrogen as the sulfur component of

the amino acids was transformed to either COS or CS_2 during the decomposition process. For this cycle to have been completed within our one-year study in the red pine stand the cycle could only include root turnover since new roots may turn over in less than a year while new needles stay on the trees for several years (McClaugherty *et al.*, 1982). Further research will be required to determine if the different organic sulfur gas flux patterns from the two forest stands were related to which of the mechanisms of sulfur-containing amino acid production was dominant in each stand.

While the mechanisms responsible for the nitrogen stimulation of gaseous sulfur losses are not yet clearly understood, the fact that there is a linkage between nitrogen inputs and sulfur gas outputs may have important implications for the global budget of COS and CS_2 and postulated changes in the budget. Large amounts of nitrogen are added to upland soils through acid rain deposition. The rates of these additions have been increasing over the past two decades (Husar, 1986; Stensland *et al.*, 1986). In addition, agricultural soils have also been receiving increasing levels of nitrogen fertilization (FAO, 1983). The increased rates of nitrate deposition in precipitation and nitrogen fertilization could be responsible for the hypothesized increases in COS and CS_2 emissions to the atmosphere discussed by Hofmann and Rosen (1980; 1981). By adding nitrogen to ecosystems, humankind may be stimulating the production of sulfur-containing amino acids that are then transformed by soil microorganisms to COS and CS_2. Increased emissions of COS and CS_2 may play an important role in determining the Earth's future climate and the chemistry of the stratosphere.

Acknowledgements

This research was supported by the Exxon Corporation and the Atmospheric Chemistry and Ecosystem Studies Programs of the National Science Foundation. We thank Elizabeth Ferry, Jane Tucker, Andrea Turner and Stephen Johnson for skillful field and laboratory assistance. We also thank the staff of the Harvard Forest for their cooperation.

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