Volatilization of Sulfur form Paddy Soils

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The major form of violatile sulfur compounds evolved from paddy soils was believed to be hydrogen sulfide produced through reduction of sulfate and degradation of organic compounds. It is known that hydrogen sulfide evolved causes damage to roots of rice plants in furrow slice under degraded paddy soil[13)].

Recent works, however, led to development of gas chromatographic techniques that permit detection and identification of trace (nanograms) amounts of volatile sulfur compounds[3,8,12,14)], and show that organic sulfur compounds such as mercaptans, alkyl sulfides, and other volatile sulfur compounds are also emitted from soils[2,4,5,7,8,9)].

The purpose of the present study is therefore to reinvestigate the forms of volatile sulfur compounds by employing these techniques, and to clarify the sources of these compounds released from paddy soils.

Measurement in paddy field

Field measurement was performed for 60 days at 7-day intervals in 1979 at an alluvial paddy field, where rice was growing under waterlogged condition. The glass cylinder to take gas sample is illustrated diagrammatically in Fig. 1. We detected evolution of 4 volatile sulfur compounds; carbonyl sulfide (COS), dimethyl sulfide (CH_3SCH_3), carbon disulfide (CS_2) and dimethyl disulfide (CH_3SSCH_3) as shown in Table 1.

The gas chromatograph used for determination of volatile sulfur compounds was a Shimadzu GC-5 instrument equipped with a Shimadzu 1A flame photometric detector fitted with a sulfur filter. Details of the gas chromatographic techniques employed have been reported previously[8,9)].

Volatilized S compounds from paddy soils incubated

To make sure the forms of volatile sulfur compounds released from other paddy soils under waterlogged conditions, we studied volatilization of sulfur compounds from 5 different paddy soils incubated under waterlogged conditions. The soils used (Table 2) were surface samples of paddy soils selected to represent a wide range in properties.

Table 3 shows that the following 6 volatile sulfur compounds were identified as products of microbial decomposition of sulfur-containing materials in the soils incubated under waterlogged conditions; hydrogen sulfide (H_2S), COS, methyl mercaptain (CH_3SH), CH_3SCH_3, CS_2, CH_3SSCH_3.

Of these volatile sulfur compounds, H_2S and CH_3SH were not detected under paddy field conditions, and from the soils incubated under waterlogged conditions when the incubated flasks were not shaken before taking the gas phase sample. It appears likely that the volatile sulfur compounds contained in bubbles within soil were released to the vessel atmosphere on shaking treatment, and that the H_2S and the CH_3SH evolved in the gas phase were oxidized and diminished rapidly when the sample were incubated without shaking since their lifetime is very short.

Effect of addition of organic materials

There are few reports in the literature of

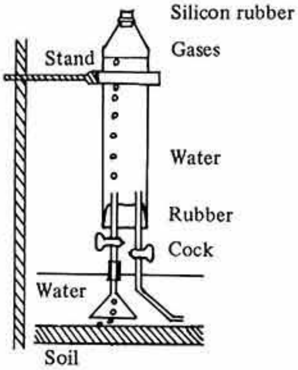

Fig. 1. The glass cylinder to take gas sample

Table 1. Volatile sulfur compounds evolved from a paddy field

Soil	H_2S	COS	CH_3SH	$(CH_3)_2S$	CS_2	$(CH_3)_2S_2$
Alluvial	0	180	0	250	100	850 ppb

The data indicate the maximum concentration of sulfur compounds in the glass cylinder atmosphere found in 7-day period during the experimental period of 60 days (June-August, 1979).

Table 2. Analyses of soils used

Soil	Soil group	Org-C	Total-N	Sand	Clay	pH	CEC (me/100g)
Fujimi	Gray lowland soil	0.77%	0.02%	95%	2%	4.7	5
Nyuzen	Gray lowland soil	0.95	0.07	78	7	6.8	6
Toyama	Gray lowland soil	1.44	0.13	70	13	5.3	8
Isehara	Andosol	5.22	0.53	61	12	5.9	26
Iwanuma	Peat soil	7.63	0.58	37	35	5.6	25

Table 3. Volatile sulfur compounds evolved from paddy soils incubated under waterlogged condition for 12 days (ng/10 g soil)

Soil	H_2S	COS	CH_3SH	$(CH_3)_2S$	CS_2	$(CH_3)_2S_2$
Fujimi	0	8(2)	54(8)	110(9)	0	163(10)
Nyuzen	0	4(2)	8(2)	80(4)	2(2)	50(2)
Toyama	0	4(2)	0	7(4)	3(2)	0
Isehara	0	3(2)	0	200(4)	0	50(4)
Iwanuma	680(4)	30(4)	900(8)	1050(4)	0	51(4)

Soil (10 g) was incubated (30°C) under waterlogged (10 ml water) condition.
Figures in parantheses indicate the day of the maximum amount of sulfur compounds evolved.
The data indicate the maximum amount of volatile sulfur compounds evolved on incubation.

Table 4. Evolution of sulfur compounds from Nyuzen soil under waterlogged condition treated with organic materials (ng/10 g soil)

Material	H_2S	COS	CH_3SH	$(CH_3)_2S$	CS_2	$(CH_3)_2S_2$
None	0	4(2)	8(2)	80(4)	2(2)	50(2)
City refuse compost	340(4)	15(4)	390(2)	287(2)	4(2)	120(2)
Bark compost	16(6)	6(4)	24(2)	62(4)	2(2)	43(2)
Sewage sludge	80(10)	18(4)	134(2)	823(2)	5(2)	120(2)
Rice straw	580(4)	47(4)	27(2)	300(2)	3(2)	51(2)
Rice straw compost	0	14(2)	0	80(3)	6(2)	0
Cattle manure	62(4)	17(4)	10(2)	100(2)	tr (2)	0

Soil (10 g) treated with material (100 mg) was incubated (30°C) under waterlogged (10 ml water) condition for 12 days.
Figures in parentheses indicate the day of the maximum amount of sulfur compounds evolved.
The data indicate the maximum amount of volatile sulfur compounds evolved on incubation.

research concerning volatilization of sulfur from paddy soils treated with composts, sludges, manures and plant materials. The volatile sulfur compounds evolved when Nyuzen soil treated with some organic materials was incubated under waterlogged conditions are shown in Table 4. The amounts of all sulfur compounds evolved from treated soils were consistently larger than the amount evolved from no treatment soil. There was a tendency that the amount of sulfur evolved from the soil treated with organic materials except rice straw were significantly correlated with total sulfur content of these materials[10].

More sulfur compounds were released, and more sulfur was volatilized, by decomposition of organic materials added in soils than by decomposition of organic matters in soils.

Sources of volatile S compounds

To identify sources of 6 volatile sulfur compounds released from the soils, we studied volatilization of sulfur from the soils incubated under waterlogged conditions after treatment with various organic or inorganic forms of sulfur, which were used in previous reports[9,10]

Numerous studies have shown that microorganisms can produce H_2S by reduction of sulfate. Many heterotrophic microorganisms can convert sulfur in organic substrates to H_2S under aerobic and anaerobic conditions[6]. We also detected evolution of H_2S from paddy soils under waterlogged conditions after treatment with sulfate, cystine and cysteine, provided that it took 30 days for sulfate to detect the evolution of H_2S.

Banwart and Bremner[4] have already reported that CH_3SH, CH_3SCH_3 and CH_3SSCH_3 are evolved from soils treated with methionine, methionine sulfoxide, methionine sulfone or S-methyl cysteine. We had the same outcome.

The remainder is in the form of COS and CS_2 of which sources are not known well. Although Banwart and Bremner[4] reported that COS is derived from soils treated with lanthionine or djenkolic acid, we detected evolution of COS from the soils treated with 5 of 17 S-containing compounds tested; cystine, cysteine, thiocyanate, lanthionine or djencolic acid[9,10].

We detected evolution of CS_2 from the soils treated with 5 of 17 S-containing compounds tested; cystine, cysteine, thiosulfate, lanthionine or djenkolic acid[11]. Although it has been reported that CS_2 is produced by decomposition of cystine, cysteine, lanthionine or djenkolic acid[4,9], our data indicate that sulfur involved in thiosulfate must be added to those compounds as candidate for the source of CS_2 released from paddy soils under waterlogged conditions since thiosulfates are found in soils[1,15].

Table 5. Volatile sulfur compounds evolved from paddy soils incubated under waterlogged condition after treatment with different forms of sulfur compounds

Form of S added	Volatile S compounds evolved					
	H_2S	COS	CH_3SH	$(CH_3)_2S$	CS_2	$(CH_3)_2S_2$
Sulfate	+*)	−	−	−	−	−
Thiosulfate	−	−	−	−	+	−
Methionine	−	−	+	+	−	+
Cystine	+	+	−	−	+	−
Cysteine	+	+	−	−	+	−
Thiocyanate	−	+	−	−	−	−

Soil (10 g) treated with S-containing compounds (500 ppm S) was incubated (30°C) under waterlogged (10 m*l* water) condition for 12 days.

*) It took 30 days for sulfate to detect the evolution of H_2S.

Typical results of the work described are presented in Table 5, which shows the form of volatile sulfur evolved when samples of paddy soils were incubated under waterlogged conditions after treatment with main S-containing organic and inorganic compounds. Lanthionine and djenkolic acid, therefore, are not given in Table 5 since little is known concerning the existence of these amino acids in soils.

The concepts of the role of soils in the atmospheric sulfur cycle are based on the assumption that volatilization of sulfur from soils mainly occurs through formation of H_2S by microbial reduction of sulfate or degradation of organic sulfur compounds. Recently it was pointed out, however, that CH_3SCH_3 and CS_2 may participate in the natural transfer of sulfur of biological origin, and that COS and CS_2 may play an important role in the atmospheric sulfur cycles because oxidation of COS and CS_2 initiated by reaction with OH can provide sources of atmospheric SO_2 and H_2S.

Application of composts, sludges, manures and plant materials has long been recognized as a method of supplying plant nutrients for crop production, and has been encouraged to reduce the environmental problems associated with disposing of these materials. There is a concern, however, that application of high rates of these materials to soils may lead to formation of sulfur gases that create odor and plant hazard problems.

There is a clear need for information concerning the formation of volatile sulfur compounds by decomposition of these materials in soils because there are evidences that sulfur gases can suppress or stimulate certain pathogenic organisms, and retard nitrification in soils.

The above results may provide a general information for some clarification of these problems.

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