Uptake and conversion of carbonyl sulfide in a lawn soil

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Abstract

Carbonyl sulfide (COS) exchange fluxes between a lawn soil and the atmosphere as well as influencing factors (temperature and water content of soil) were investigated using a static cuvette. The optimal soil temperature and water content for COS consumption were about 298 K and 12.5%, respectively. The converting products of the consumed COS in the lawn soil were researched using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The peaks of gas-phase products of CO_2 and surface HCO_3^-, HS^-, SO_3^{2-}, HSO_3^-, and SO_4^{2-} species were observed. The possible mechanism of COS conversion in the lawn soil was discussed. The conversion rates of consumed COS into water-soluble sulfate in the lawn soil were studied by ion chromatography (IC). The experimental results show that about 50% sulfur from the soil consumed COS was eventually converted into water-soluble sulfate.
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1. Introduction

Carbonyl sulfide (COS) is the most abundant atmospheric sulfur gas in the remote troposphere (Möller, 1984; Andreae and Crutzen, 1997). COS is relatively inert in the troposphere and its tropospheric lifetime is greater than 1 year (Khalil and Rasmussen, 1984; Andreae and Crutzen, 1997). It can be transported into the stratosphere where its photo-oxidation is considered to be an important source for stratospheric sulfate aerosol layer during volcanically quiescent periods (Crutzen, 1976; Turco et al., 1980; Andreae and Crutzen, 1997).

Stratospheric aerosols influence the earth's radiation budget (Crutzen, 1976; Turco et al., 1980; Andreae and Crutzen, 1997), and are also believed to enhance ozone depletion (Crutzen, 1976). Understanding the global COS cycle is therefore of considerable importance.

Soils were previously considered to represent one of the dominant sources of COS (Adams et al., 1981; Khalil and Rasmussen, 1984; Möller, 1984). However, recent field studies present convincing evidence that soils act more as a sink than as a source for COS (Castro and Galloway, 1991; Kesselmeier et al., 1999; Kuhn et al., 1999; Watts, 2000). As the ambient concentration of a given trace gas controls the direction as well as the magnitude of its flux between biosphere and the atmosphere, earlier studies using COS free air for purging the

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enclosures masked the uptake capability of soils (Castro and Galloway, 1991). Although there is still only few data, and the estimation contains considerable uncertainty, it is now believed that oxic soils are acknowledged globally as a sink for atmospheric COS instead of as a source (Castro and Galloway, 1991; Kesselmeier et al., 1999; Kuhn et al., 1999; Watts, 2000).

Previous studies have indicated that carbonic anhydrase (CA) is the key enzyme for uptake of COS by different biological organisms (Bartell et al., 1993; Protoschill–Krebs et al., 1996; Kesselmeier et al., 1999; Kuhn and Kesselmeier, 2000; Kesselmeier and Hubert, 2002). Protoschill–Krebs et al. pointed out that CA *in vivo* splits COS into CO_2 and H_2S (Protoschill–Krebs et al., 1996). However, the emission of H_2S only accounted for 1–2% of the sulfur deposited as COS to the soil/plant system investigated by Bartell et al. (1993). Bartell et al. pointed out that further physiological study is required to resolve this problem (Bartell et al., 1993).

To our knowledge, very few studies focus on the conversion of COS in soils (Ren, 1999). In this study, high concentration (about 14 ppm) of COS was used to investigate its exchange rates and the possible conversion paths of COS in the lawn soil.

2. Materials and methods

2.1. Soil sampling

Lawn soil samples, consisting of sandy loam, were collected from a lawn in the north of Beijing city (115.26E, 39.58N). Samples were taken from the top 5 cm. Samples of 5 kg soil were collected at five different locations and mixed uniformly. The mixed sample was sieved with a stainless steel sieve (20 mesh size) for removal of twigs, pieces of roots, etc. The soil samples were stored in a polyethylene bag at ~276 K until being used. Soil water content was varied by air-drying or by moistening with deionized water. Dry weight of soil sample was obtained by drying it at 378 K for 12 h in an oven. The characteristics were determined according to standard protocols (Liu, 1996). Inorganic elementary analysis of the soil samples was carried out on an Elementary Vario El (Germany) system. X-ray fluorescence (XRF) data were obtained from a Bruker S4 Explorer spectrometer.

2.2. Enclosure system

COS uptake by the lawn soil was investigated using a static glass vessel with total volume of 2.72 L. The glass vessel consists of two glass tubes and a sampling port. The two glass tubes were connected with a pump (MB–21E, Metal Bellows Corp.) to insure the gases in the vessel well mixed. The sampling port was made of Teflon, which was sealed with a silicon septum. The vessel was put into a thermostatic bath to keep temperature constant. Prior to experiment, 2 mL of standard COS (2%, COS/N_2, Scott Specialty Gases Inc.) was injected into the vessel and incubated for 24 h. The change of COS concentrations was within the precision of our system ($<6\%$), indicating that the leakage and adsorption of COS in the system could be negligible. Soil samples of 50 g were placed into the vessel, and synthetic air passed for 5 min through the vessel, then sealed immediately. After the soil was pre-incubated for 30 min, a certain volume of standard COS was injected into the vessel, followed by 100 mL air to maintain the system in a positive pressure state.

2.3. Gas analyses

The headspace gas in the static glass vessel was analyzed on a gas chromatograph (GC–6A, Shimadzu) equipped with flame photometric detector. The detailed description of the analyzing method has been reported elsewhere (Mu et al., 2002). The relative precision of the measurements was 6%, on the basis of 10 replicates (Mu et al., 2002).

2.4. COS exchange rate measurement

The concentration of COS in the vessel containing the investigated soil showed a linear correlation ($R^2 > 0.95$) with time (less than 50 min) under our experimental conditions. The exchange rate (F_{COS}, $nmol\,g^{-1}\,h^{-1}$) of COS between soil and the atmosphere can be calculated on the basis of the slope κ ($nmol\,L^{-1}\,min^{-1}$) of the line, the volume of the glass vessel (V, L) and the dry weight of the soil samples (W, g):

$$F_{COS} = \kappa \times V \times 60/W$$

2.5. Determination of water-soluble sulfate

After being exposed to COS for a given time, the investigated soil was washed with 250 mL deionized water and transported into a 500 mL cone flask. Then

the cone flask was sealed immediately and shaken for 5 min on a swag bed (Liu, 1996). After stilling of the mixture for 2–3 min, the supernatant extracted liquid was swilled into a canister. The mixture was centrifuged for 30 min at 3000 r min^{-1}. The supernatant extracted liquid was filtered through a 0.45 μm filter. The concentration of sulfate in the solution was analyzed by ion chromatography (IC).

The IC was equipped with a guard column (IonPac AG14A–SC, 4 mm, Dionex, CA) to eliminate the organic matter, an analytical column (AS14A–SC, 4 mm, Dionex, CA), an anion suppressor ASRS–UL-TRA (4 mm, Dionex, CA) and a pulsed electrochemical detector (Dionex, CA). The eluant consisted of 3.5 mmol L^{-1} Na$_2$CO$_3$/1 mmol L^{-1} NaHCO$_3$ and was passed through the system at a flow rate of 1.2 mL min^{-1}. The injection volume of the liquid sample was 25 μL. The concentration of SO$_4^{2-}$ was calculated on the basis of its peak area. Calibration curve was derived for SO$_4^{2-}$ with concentrations ranged from 10.4 to 208.3 μmol L^{-1}.

2.6. In situ DRIFTS experiments

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Nexus 670 FT–IR spectrometer (Thermo Nicolet Instrument Corporation), equipped with an *in situ* diffuse reflection chamber and a high-sensitivity mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The lawn soil samples for the *in situ* DRIFTS studies (about 30 mg) were placed into a ceramic crucible in the *in situ* chamber. Mass flow controllers and a temperature controller were used to control the reaction conditions. Prior to recording the DRIFTS spectrum, the lawn soil samples were placed *in situ* in synthetic air at 298 K for 30 min, and a reference spectrum was measured. To prevent water loss from the soil, water vapor was supplied with the gas stream of O$_2$ and carried into *in situ* DRIFTS chamber. The infrared spectra were collected and analyzed using a data acquisition computer installed with the OMNIC 6.0 software (Nicolet Corp.). All spectra reported here were recorded at a resolution of 4 cm^{-1} for 100 scans.

3. Results and discussion

3.1. Soil characteristics

The lawn soil characteristics were determined according to standard protocols (Liu, 1996). Some properties of the lawn soil samples are as follows: pH 7.84, W_{water} 10.8%, $C_{organic}$ 9.63 g kg^{-1}, OM 16.6 g kg^{-1}, N_{total} 0.75 g kg^{-1}, P_{total} 0.93 g kg^{-1}, S_{total} 0.20 g kg^{-1}, SO$_4^{2-}$ 29.2 mg kg^{-1}. The inorganic elemental composition of the soil samples was determined by XRF measurement. The major inorganic element percentages in the lawn soil samples are as follows: Si 25.39%, Fe 10.73%, Ca 9.93%, K 4.98%, Al 4.94%.

3.2. Uptake of COS in the lawn soil under varying temperatures and water content

COS uptake by the lawn soil (water content was 10.5%) was investigated under varying temperature from 278 to 313 K. Fig. 1A shows the COS uptake rates in relation to the temperature regimes. The uptake rate of COS by the lawn soil increased with temperature up to an optimal at 298 K, followed by a decrease at higher temperature. A similar pattern of COS uptake was also observed by previous studies (Lehmann and Conrad, 1996; Kesselmeier et al., 1999). The optimal temperature for COS uptake in soil was in the range between 283 and 318 K reported by Lehmann and Conrad (1996), and in the range between 288 and 293 K reported by Kesselmeier et al. (1999).

The exchange rates of COS under 10 different water contents of the lawn soil (0–30% dry weight) were also investigated. Fig. 1B shows the correlation between the water contents and the COS uptake rates of the lawn soil. The ambient temperature was held constant near the temperature optimal (298 K, see Fig. 1A). The uptake rate of COS increases sharply as the water content increases, and reaches a maximum around 12.5%, then followed by decrease at higher water content. The optimal water content for COS uptake is in the range from 7.5% to 15%, which agreed very well with the optimal range reported by Kesselmeier et al. (1999). Their results indicated a zero exchange at water content below 6%. However, the COS uptake rate was evident when water content was below 5% in this study. The high COS concentration used in present work may magnify its uptake rate.

It should be mentioned that the uptake rates measured by this study must be overestimated due to extremely high concentration of COS being used (Conrad and Meuser, 2000). However, the non-linear relationship between COS uptake rate and temperature or water content was similar to previous study which used ambient air (COS
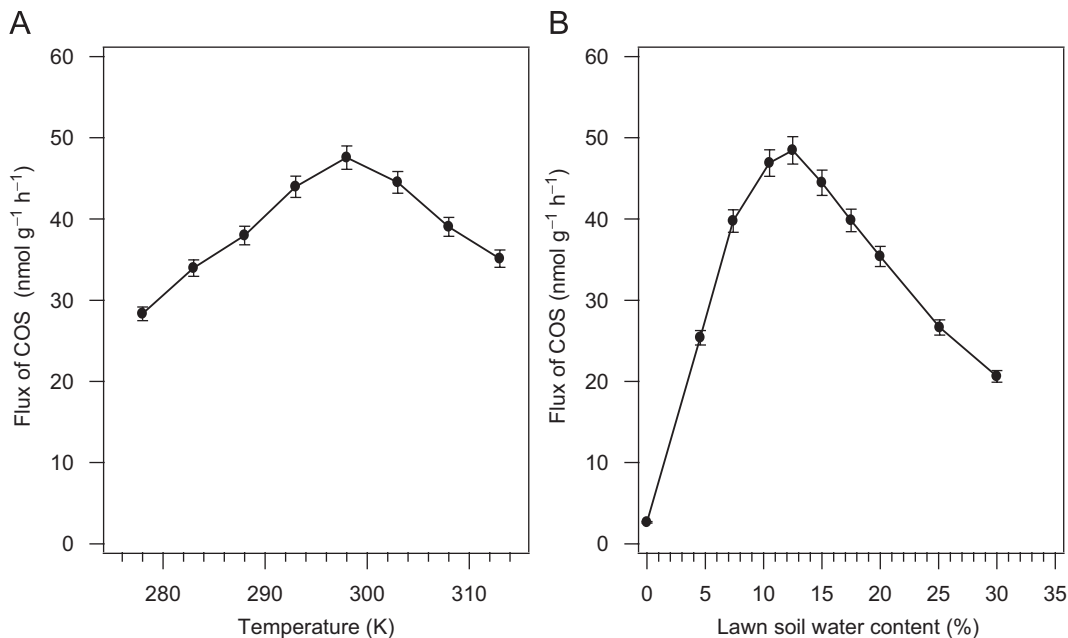
Fig. 1. COS uptake in the lawn soil (the water content of soil was 10.5%) varies with the temperature regimes (A). COS uptake in the lawn soil (the temperature of soil was 298 K) in relation to the soil water content (B). The initial COS concentration in all experiments was 14 ppm. All the data replicated two or three times and used the average value.

concentration of ~ 500 pptv) as sweep gas (Lehmann and Conrad, 1996; Kesselmeier et al., 1999), indicating that the biological process was probably the dominant path for COS uptake by the lawn soil under fumigation of high COS concentration. To further examine whether the COS uptake depended on physiology, the lawn soil was heated in an oven at 433 K for 2 h, then the sterilized lawn soil was moistened or not with deionized water to the optimal soil water content (12.5%). Fig. 2 shows COS exchange rates between the lawn soil and the atmosphere. The original lawn soil absorbed COS very rapidly, whereas the sterilized lawn soil absorbed COS very moderately. Therefore, biological processes might be mainly responsible for COS uptake by the lawn soil under high COS concentration.

Kesselmeier et al. (1999) pointed out that carbonic anhydrase (CA) can be regarded as the dominant factor for consumption of COS by their investigated soil. The observed optimal soil water content and temperature pointed to an enzymatically catalyzed process (Radmer and Kok, 1979; Kesselmeier et al., 1999; Kuhn and Kesselmeier, 2000). An enzyme increases the turnover with increasing temperature, but this trend is superimposed by a decrease of activity if the temperature
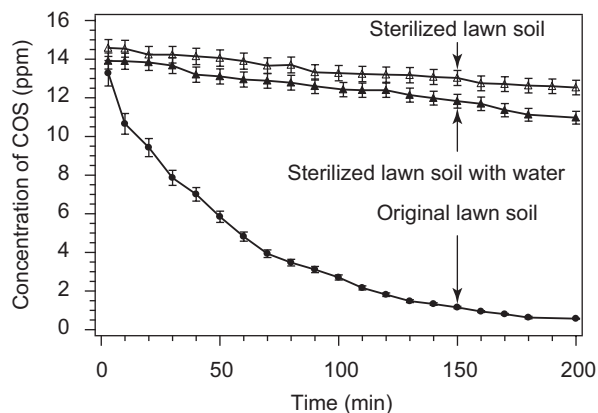

Fig. 2. Concentration of COS versus time in the original lawn soil, the sterilized lawn soil moistening with water, and the sterilized lawn soil at 298 K.

range exceeds a certain value owing to reorganization and/or denaturation of the enzyme structures (Kesselmeier et al., 1999). In addition, COS uptake is strongly dependent on oxygen. The uptake rate of COS by the lawn soil samples decreased 70% when the air in the vessel was changed into high purity nitrogen. This implied that the biological organisms for the uptake of COS are the aerobe.

3.3. The conversion of COS in the lawn soil

In order to research the possible products from COS conversion in the lawn soil in detail, the *in situ* DRIFTS experiments were performed. Fig. 3A shows the changes in the *in situ* DRIFTS spectra on the lawn soil surface. After the lawn soil was exposed to a flow of 500 ppm COS in synthetic air at 298 K for 10 min, the *in situ* DRIFTS spectrum was recorded and shown as line a in Fig. 3A. Following that, the inlet and outlet were closed for 60 min, and then the *in situ* DRIFTS spectrum was recorded and shown as line b. As line a in Fig. 3A shows, after the lawn soil was exposed to COS for 10 min at 298 K, many bands appeared. Strong peaks due to gas-phase COS appeared at 2071 and 2052 cm^{-1} (Lavalley et al., 1979). The peaks at 2361 and 2337 cm^{-1} are attributed to gaseous carbon dioxide (CO_2) (Amenomiya et al., 1977; Morterra et al., 1977; Rege and Yang, 2001). The peak located at 1560 cm^{-1} is assigned to surface hydrogen thiocarbonate ($HSCO_2^-$) species as an intermediate of the hydrolysis of COS (Lavalley et al., 1979; Hoggan et al., 1994). At the same time, the bands at 1653

and 1437 cm^{-1} due to surface HCO_3^- species are also appeared (Amenomiya et al., 1977; Morterra et al., 1977; Lavalley et al., 1979; Rege and Yang, 2001). The subtract spectrum from b to a (amplified 10 times) also shows that, after the lawn soil exposed to COS in the closed system for 60 min, the peaks for gas-phase CO_2, surface HCO_3^-, and $HSCO_2^-$ species increase in intensity with time, while the peaks for gaseous COS gradually decrease. These results indicated that the exposure of the lawn soil to COS could result in the formation of gas-phase CO_2, surface HCO_3^-, and $HSCO_2^-$ species, etc. at 298 K.

Because the quantity of COS added in the closed system was very small, the peaks of products were very faint. To further confirm the products from conversion of COS on the surface of the lawn soil, a similar experiment was also performed in a flow system for the original lawn soil (Fig. 3B). The surface HSO_3^- (1242 cm^{-1}, Laniecki et al., 1987; Mitchell et al., 1996) and SO_4^{2-} species (1363 cm^{-1}, Saur et al., 1986; Meunier and Ross, 2000; Goodman et al., 2001) were observed in addition to the surface HCO_3^- and $HSCO_2^-$ species. It is also found
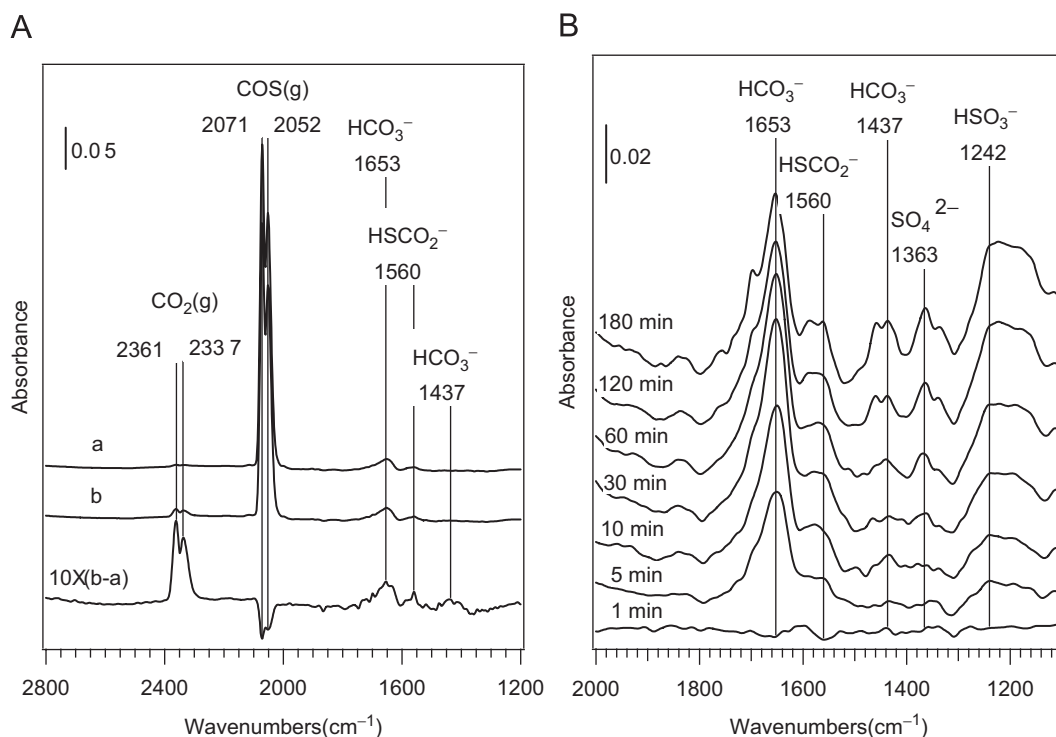

Fig. 3. (A) The *in situ* DRIFTS spectra of the lawn soil after exposure to 500 ppm COS in synthetic air for 10 min (a), then in the closed system for 60 min (b), and the subtracted spectrum from b to a (amplified 10 times). (B) Dynamic changes of *in situ* DRIFTS spectra of the lawn soil as a function of time at 298 K in a flow of 500 ppm COS in synthetic air. The water content of the lawn soil was 10.5% and the temperature was 298 K.

that the peaks for surface HCO_3^-, HSO_3^-, $HSCO2^-$, and SO_4^{2-} species increase in intensity with time in the soil.

As mentioned above, CA enzyme *in vivo* splits COS into CO_2 and H_2S (Protoschill–Krebs et al., 1996). However, Bartell et al. (1993) observed the emission of H_2S only account for 1–2% of the sulfur deposited as COS to the soil/plant system and no H_2S were detected in our above experiments, which were probably due to its high reactive activity on the surface of the soil. To further investigate the formation of H_2S from the conversion of COS in the lawn soil, *in situ* DRIFTS experiment with higher concentration COS was performed. The lawn soil were exposed to a flow of 5000 ppm COS in synthetic air at 298 K for 10 min (line a in Fig. 4), and then the inlet and outlet were closed for 6 h (line b in Fig. 4). It is evident that a new peak at $2517 \, cm^{-1}$ due to the surface HS^- species, which derived from the reaction of H_2S with surface hydroxyl (Lavalley et al., 1979; Davydov et al., 1998; Travert et al., 2002), was observed. In addition, the bands at 1057 and $1040 \, cm^{-1}$ are due to surface SO_3^{2-} species (Chang, 1978; Laperdrix et al., 2000; Goodman et al., 2001). The negative peak observed at $1653 \, cm^{-1}$ and a broad peak

ranging from 3000 to $3500 \, cm^{-1}$, were assigned to adsorbed water (Meunier and Ross, 2000; Goodman et al., 2001; Rege and Yang, 2001). As the subtract spectrum shown, after the lawn soil exposed to COS in the closed system for 6 h, the peaks for gas-phase CO_2, surface HCO_3^-, and SO_4^{2-} species increase in intensity with time, while the peaks for gaseous COS, adsorbed water and surface SO_3^{2-} species gradually decrease. The observed CO_2 increase and waterconsumption in the vessel containing the lawn soil may partly be due to COS hydrolysis, soil respiration and COS consumption through the CA enzyme. It should be noted that surface SO_3^{2-} could be gradually converted to SO_4^{2-} species on the surface of the lawn soil (Fig. 4C).

The above results indicated that the exposure of the lawn soil to COS could result in the formation of gas-phase CO_2, surface HCO_3^-, HS^-, SO_3^{2-}, and SO_4^{2-} species in air at 298 K. The surface SO_3^{2-} species was an intermediate, and surface SO_4^{2-} species was a final production for the COS conversion in the lawn soil.

The *in situ* DRIFTS experiments confirmed the formation of surface SO_4^{2-} species. However, the signal of surface SO_4^{2-} species is too weak to quantify it. In order to investigate the conversion
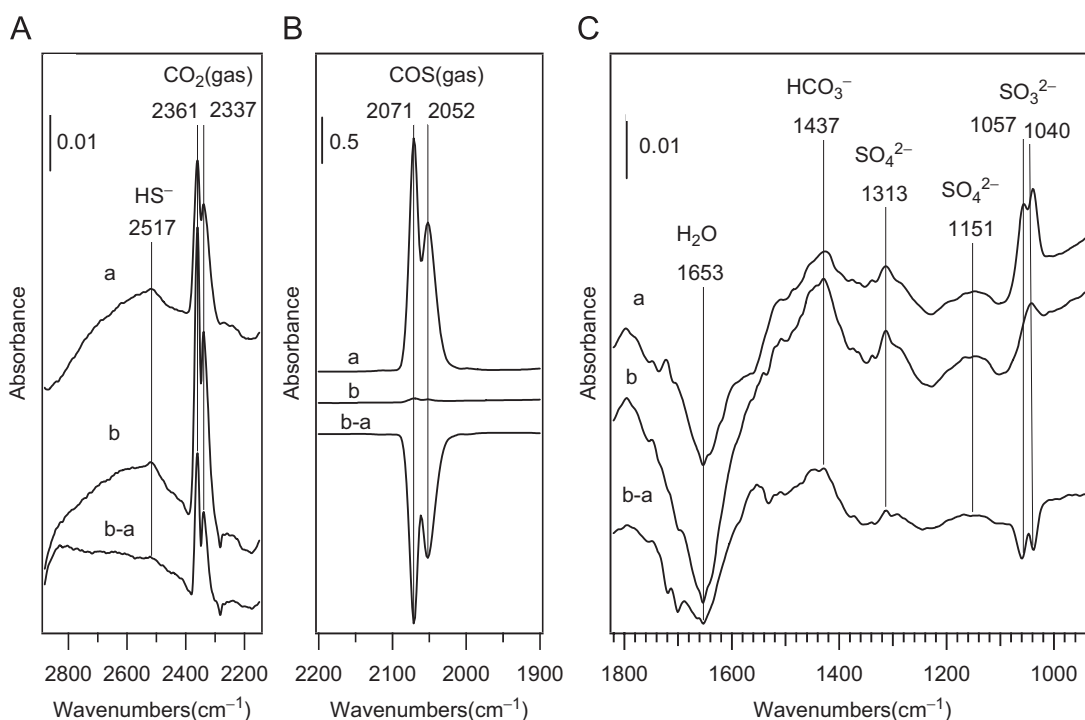

Fig. 4. Dynamic changes of *in situ* DRIFTS spectra of the lawn soil as a function of time after exposure to 5000 ppm COS in synthetic air for (a) 10 min, then in the closed system for (b) 6 h. The soil water content was 10.5% and the temperature was 298 K.

rate of soluble sulfate, the IC was used to quantify sulfate. COS (1.072 mg) was injected into the vessel containing the investigated original lawn soil (the water content of the lawn soil was 10.5%) incubated at 298 K. Fig. 5A shows the rates of COS conversion to water-soluble sulfate versus time. The rates of COS conversion into water-soluble sulfate increased rapidly with COS exposure time up to 24 h, and then remained constant. No COS could be detected after 6 h incubation, only 22% of COS was converted into the water-soluble sulfate, whereas about 50% COS was converted into water-soluble sulfate after 24 h incubation, indicating a time lag existing between COS uptake and its conversion. This phenomenon was supported by the evidence that the conversion of the sulfite to sulfate provided by the *in situ* DRIFTS experiments (Fig. 4C).

We also performed a series of experiments under different COS additions (0.1–8.04 mg) at 298 K for 48 h. As shown in Fig. 5B, for all experiments, the conversion rates of COS to water-soluble sulfate, seemed to be independent of the amount of COS addition, and were about 50%. Considering the soil has a strong adsorption effect on sulfate, the rates of COS conversion to sulfate must higher than that of the observed water-soluble sulfate.

3.4. The pathway of uptake and conversion of COS in the lawn soil

Kim and Katayama (2000) also observed sulfate formation in thiocyanate-containing waste water treatment using sulfur-oxidizing bacteria—*Thiobacillus thioparus* THI115. COS was found to be the intermediate during the degradation of thiocyanate, and sulfate was produced as the final products. Kelly et al. (1993) proposed that metabolism of COS by *T. thioparus* involves hydrolytic cleavage of COS to CO_2 and H_2S, and energy is generated from oxidation of H_2S to sulfate. Overmann and Gemerden (2000) also pointed out that the physiological metabolism of sulfide by *Thiobacillus* can produce sulfate. Chapman (1990) investigated autotrophic thiobacilli in 43 Scottish agricultural soils, neutrophilic thiobacilli, typically *T. thioparus*, were found in 84% of the soils with MPN (Most Probable Number) counts ranging from 1 to $10^5\,g^{-1}$. We also found the surface HS^- species in our *in situ* DRIFTS experiment (Fig. 4A).

In addition, H_2S oxidation by Fe (III) might be another loss path for H_2S. The iron oxides goethite, lepidocrocite, ferrihydrite and hematite are important Fe (III)-containing constituents in soils (Neal et al., 2001). Reductive dissolution of hematite by
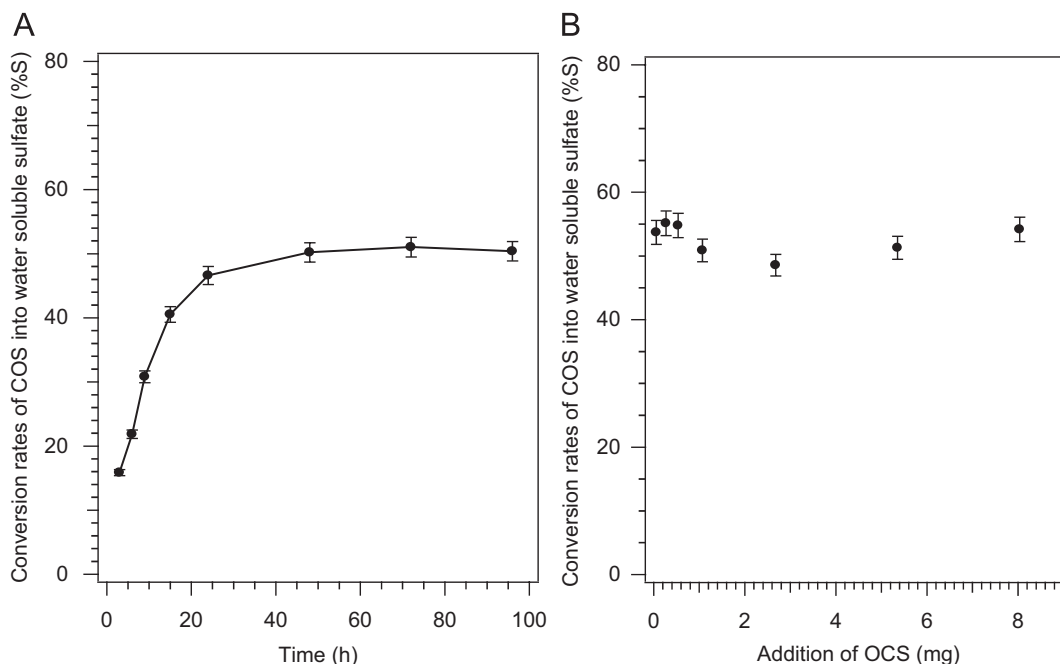

Fig. 5. (A) The conversion rates of water-soluble sulfate in relation to the exposure time in the original lawn soil at 298 K. The initial addition of COS was 1.072 mg. (B) The conversion rates of water-soluble sulfate vary with COS addition (mg). All the data replicated two or three times and used the average value.

H_2S is complex, and many intermediates (S_n^{2-}, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$) were observed (Pyzik and Sommer, 1981; dos Santos Afonso and Stumm, 1992; Davydov et al., 1998; Herszage and dos Santos Afonso, 2000; Neal et al., 2001). dos Santos Afonso and Stumm postulated the formation of FeS^- and $FeSH$ surface complexes by exchange O^{2-} for S^{2-} and HS^-, these new surface groups would then undergo electron transfer (dos Santos Afonso and Stumm, 1992). The existence of SH^- and SO_3^{2-} groups at the hematite surface has been confirmed using FTIR spectroscopy (Neal et al., 2001), and it was also observed on the soil surface after being exposed to COS by this study.

Therefore, we proposed that the lawn soil uptake COS may start with the enzymatic catalysis by CA

enzyme or hydrolysis to form CO_2 and H_2S, and then H_2S is quickly converted into sulfate by *Thiobacillus* and Fe (III).

To certify whether H_2S is the intermediate of the conversion of COS, similar experiments were also performed for the uptake and conversion of H_2S in the lawn soil. Compared with COS, the conversion rate of H_2S in the original lawn soil to sulfate was about same level as that of COS (Figs. 5A and 6B), although H_2S could be easier to be absorbed or reacted in the soils due to its high reactivity (Figs. 2 and 6A). Therefore, the conversion of COS to water-soluble sulfate might be through H_2S in the lawn soil.

The results of duplicated experiments ($n = 3$) of 8.04 mg COS uptake by 50 g lawn soil (water
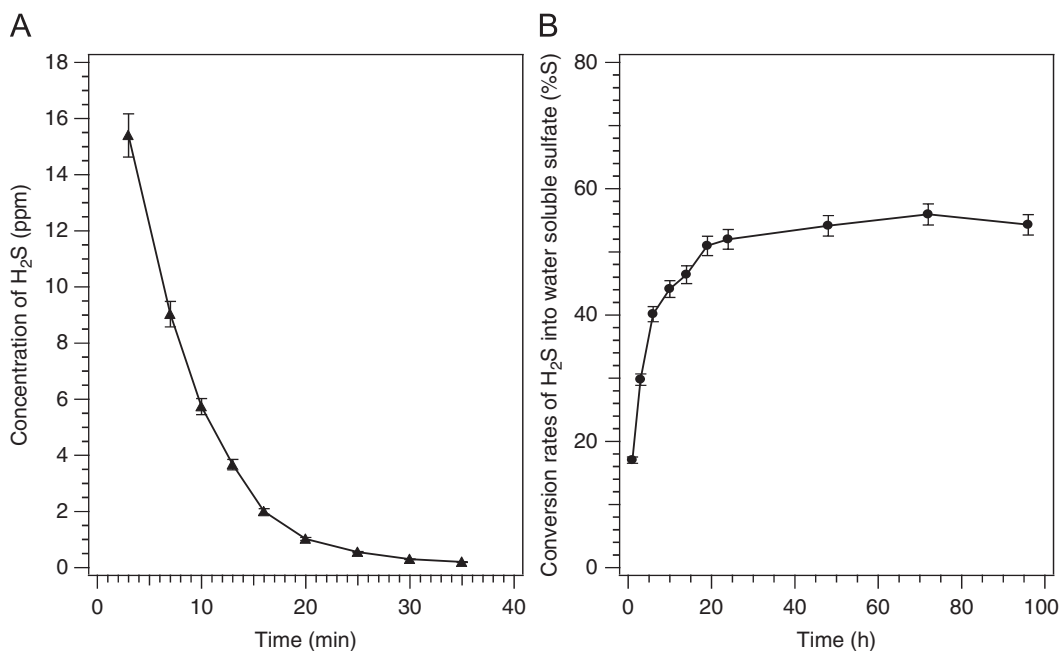

Fig. 6. (A) The concentration of H_2S versus time in the lawn original soil sample at 298 K. (B) Conversion rates of water-soluble sulfate in relation to the exposure time in the lawn original soil sample at 298 K. The initial addition of H_2S was 0.702 mg.
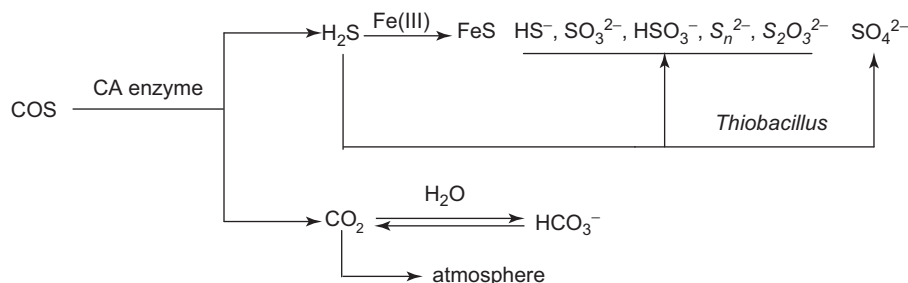

Fig. 7. Mechanism of conversion of COS in the lawn soil.

content was 10.5%) at 298 K showed that the total sulfur (Liu, 1996) in the lawn soil before and after the COS uptake was $195 \pm 2\,mg\,Kg^{-1}$ and $289 \pm 8\,mg\,Kg^{-1}$ (dry weight), respectively, indicating that the consumed COS by the lawn soil was completely converted to other sulfur compounds.

On the basis of above knowledge, we conclude that the uptake and conversion of COS in the lawn soil can be illustrated as the following possible schematic (Fig. 7). The COS consumed by the lawn soil mainly through the CA enzyme to produce CO_2 and H_2S, and then carbon dioxide reacts with water in the soil to forming hydrogen carbonate. H_2S is probably oxidized by Fe (III) or sulfur-oxidizing bacteria—*Thiobacillus thioparus* in the lawn soil, and produces water soluble sulfate and other sulfur compounds.

4. Conclusions

The uptake rates of COS by the lawn soil depended on ambient temperature, soil water content, soil type, and so on. The non-linear relationships between COS uptake rates and temperature as well as soil water contents indicated that COS consumption in the lawn soil was probably dominated by biological processes. About half of consumed COS by the lawn soil was converted into water-soluble sulfate through H_2S. Because the water-soluble sulfate is the major available sulfur for plants, the uptake of COS by soils might be a path of sulfur supplement for vegetables especially in remote areas.

Acknowledgments

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