Photochemical production of carbonyl sulfide in precipitation

Yujing Mu, Chunmei Geng, Meizhen Wang, Hai Wu, Xiaoshan Zhang, and Guibin Jiang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

Received 2 October 2003; revised 17 March 2004; accepted 15 April 2004; published 7 July 2004.

Precipitation samples (rain and snow) from 10 provinces in China were collected during the winter season. The concentration of initial dissolved carbonyl sulfide (COS) and its photochemical production rates by natural sunlight were measured. All investigated precipitation samples were found to be supersaturated with COS, and the initial dissolved COS concentrations were in the range from 17.7 to 48.2 ng L⁻¹. The COS saturation ratios (SR) for the investigated samples were in the range from 15.8 to 60.4. The COS photochemical production rates depended strongly on sunlight intensity and were independent of microbial activity as well as dissolved O₂. The amount of COS produced photochemically by sunlight irradiation for 14 to 50 days was ~1–2 orders of magnitude greater than that of initial dissolved COS.

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: carbonyl sulfide, photochemical production, precipitation


1. Introduction

Carbonyl sulfide (COS) is thought to be the major source of the stratospheric sulfate aerosol layer during volcanically quiescent periods [Crutzen, 1976] and thus has an impact on the Earth's radiation budget [Turco et al., 1980] as well as on heterogeneous chemistry leading to ozone destruction [Solomon et al., 1993]. Therefore considerable research has been conducted in order to identify the major atmospheric sources and sinks of COS.

Known sources of COS are from ocean, anoxic soils, wetlands, volcanism, precipitation, DMS and CS₂ oxidation, biomass burning, and anthropogenic sources. The COS global flux from above sources was estimated to be 1.31 ± 0.25 Tg a⁻¹ [Watts, 2000]. The major sinks of COS are oxic soils, vegetation, and reaction with OH. Reactions with O and photolysis also act as small sinks for COS. The global annual flux of above sinks was estimated to be 1.66 ± 0.79 Tg a⁻¹ [Watts, 2000]. Broadly, the COS budget is balanced within the uncertainties of the estimates.

Hofmann [1990] speculated that increased COS levels could be responsible for an observed increase in the background levels of stratospheric sulfate aerosol during the 1970s and the 1980s. However, the viewpoint that COS is the major source of stratospheric aerosol has been challenged [Kjellström, 1998]. Furthermore, no significant trend has been observed in the atmospheric mixing ratios of COS since the late 1970s to the mid-1990s [Bandy et al., 1992; Sturges and Penkett, 2001]. However, since the exact cause of the increase in stratospheric aerosol is still unresolved, it is still important to improve the estimates of the sources and sinks for COS.

The photochemical production of COS in the marine euphotic zone has been demonstrated by a number of laboratory and field experiments [Ferek and Andreae, 1984; Uhler and Andreae, 1997; Zepp and Andreae, 1994; Weiss et al., 1995; Ulshöfer et al., 1996]. These studies have shown that the photochemical formation of COS involves the photosensitized oxidation of dissolved organic sulfur compounds and is induced primarily by the UV part of solar radiation. Pos et al. [1998] studied the mechanisms for the photochemical production of COS and postulated that a sulfur-centered radical (thyl or sulphydryl radical) was likely to be the key species that reacts with acyl radicals to produce COS.

Belviso et al. [1987] first measured dissolved COS in rainwaters from a suburban site near Paris and found that rainwater was supersaturated with COS. They pointed out that the excess of dissolved COS increased with increasing water acidity. Watts [1991] determined a constant rate for COS production from marine precipitation as 4 ± 0.03 × 10⁻⁸ s⁻¹ (August at 52°N, noon sunshine). Both of the two studies indicated that COS production in rainwater due to photochemical processes cannot be neglected. However, data demonstrating photochemical production of COS in precipitation have not previously been published. In this paper we present the results from a series of experiments that were conducted in order to investigate precipitation as a source of COS to the atmosphere. COS photochemical production rates in freshly collected precipitation samples including rain and snow are given. The dependence of these

Copyright 2004 by the American Geophysical Union.
0148-0227/04/2003JD004206

D13301
1 of 7
rates on sunlight intensity, microbial activity, and dissolved oxygen concentration was investigated.

2. Experiment

[7] Precipitation samples were collected from 10 provinces in China during winter season (from December 2002 to March 2003). The sampling sites include both remote countrysides and urban areas. An enamel plate was used to collect all the precipitation samples. An exception was the sample from Waliguan, which was collected by the international standard method [Tang et al., 2000]. The enamel plate, which was rinsed with deionized water several times before sampling, is an iron pan covered with white enamel. The precipitation samples, except those collected in Beijing, were transferred rapidly into polyethylene bottles and stored at room temperature for 10–20 days without shielding them from light prior to the experiment. During all the experiments, COS concentrations were measured by a conventional purge and trap system.

[8] Investigating the dissolved COS in precipitation was our initial objective. Therefore the bubblers were only constructed by glass at the beginning. However, when we put one bubbler containing purged precipitation of Zhuanghai outside, unexpected high COS was produced under natural sunlight irradiation. In addition, photochemical production of COS in the investigated precipitation samples lasted a very long time. Previous studies [Zepp and Andreae, 1994; Weiss et al., 1995] indicated that the wavelength between 310 and 370 nm was largely responsible for COS photochemical production in seawater. Therefore, we thought that the glass might be less transparent for these wavelengths of sunlight, and a quartz bubbler was constructed for the Waliguan sample, which was received 20 days later than other samples. We also measured the transparency of the glass and the quartz used in this study as being between 290 and 380 nm by a UV visible spectrophotometer (752C, Shanghai analytical instrumental factory). It was obvious that the glass was less transparent for sunlight than the quartz was, especially for the wavelength between 310 and 370 nm (Figure 1).

[9] 50-mL precipitation samples were injected into clean and dry bubblers with a 100-mL syringe. All bubblers, except one, were constructed of glass and had the following dimensions: ID, 1.8 cm; length, ~28 cm; volume, ~70 ml. Every bubbler consisted of a glass filter (~0.5 μm) in the bottom and three branch tubes (OD of 5 mm). One of the branch tubes, located at the bottom of the bubbler, was connected to a mass flowmeter and used for introduction of the purge gas. The other two tubes were on the top of the bubbler and were used for injection of precipitation and for air sample collection. All joints were of short silica gel tubes, which were sealed by exterior iron stopcocks. The bubblers were always prepared by flushing them with high-grade helium (50 mL min⁻¹) in order to remove atmospheric COS originally inside the bubblers. The extraction was conducted for 30 min, during which time the air samples were collected into 5-L Teflon bags. To minimize the memory effects of the bags for COS, the bags were flushed three times with high-grade nitrogen prior to collecting the extractive air samples. The COS in the bags was immediately sampled by cryogenic trapping and analyzed by means of a gas chromatograph (GC) equipped with a flame photometric detector. Detailed description of the method may be given by Mu et al. [2002] and is therefore only briefly characterized here. The 800-mL air sample in the bag was preconcentrated onto a Teflon absorption tube filled with Tenax-GC and then stored in liquid nitrogen. Prior to analysis the absorption tube containing COS was allowed to cool off at room temperature for ~0.5 min in order to vaporize liquid nitrogen. The still cold tube was then immediately inserted into an injection port of the GC. The adsorbed COS was thermally liberated for ~0.5 min and transferred to the GC column through a six-way valve. The chromatographic separation was conducted using temperature gradient on a glass column (3 m × 4 mm) packed with 20% SE-30 on Chromosorb P (60–80 mesh). Optimum separation was obtained by starting the temperature program at 50°C, holding for 10 min, and then heating at 10°C min⁻¹ up to 120°C. The injection port temperature and the detector temperature were 160° and 240°C, respectively. Typical gas flow rates were as follows: nitrogen (carrier gas, 99.999% pure), 30; hydrogen, 40; and air, 40 mL min⁻¹.

[10] The analytical column employed in this study has been found to efficiently separate various volatile sulfur compounds (H₂S, COS, CS₂, thiols, sulfides, disulfides) [Tangerman, 1986; Mu et al., 2002]. The recovery efficiency of COS was ~94%, and the detection limit of COS for the 800-mL air sample was ~0.04 ng L⁻¹. The relative precision of the method was <6%, based on reproducibility of consecutive samples measured over a 30-day period (number of replicates n equals 30) using a compressed air sample. The standard material of COS (2%, COS/N₂), from Scott Specialty Gases Inc., had a certified accuracy of less than ±5%.

[11] A static chamber was used to directly measure the COS flux in the precipitation sample from Beijing. An enamel plate (29 × 19 × 1.8 cm) filled with fresh snow sample was put into a closed chamber with a volume of ~34.3 L. The inside of the chamber was covered with Teflon film to assure that the air in the chamber only had contact with the Teflon film and the precipitation. Makeup gas was introduced to the chamber through a silica gel tube (2 m × 4 mm). About 1 L of air in the chamber was collected every 20 min by a minipump (MP-30, Sibata) at a rate of ~2.5 L min⁻¹ after the chamber was deployed. The direct COS formation was measured both in the still frozen...
The adsorption of COS by the bottles is nevertheless the 10 fresh snow samples in Beijing were in the range of pH 7.08 to 7.10, the pH of the liquid was found to be very close to the air-water equilibrium value (the dissolved COS was 1.52 ng L\(^{-1}\)). This low concentration was 1000 pptv for the sample of Beijing and 500 pptv for others.

The bubbler was made of quartz tube.

The initial dissolved COS in precipitation samples included 10 snow samples in Beijing and nine snow or rain samples from other areas as listed in Table 1. Only the samples in Beijing (sampling date was from 15 December 2002 to 10 March 2003) were analyzed immediately after sample collection (the snow sample was melted at room temperature and then transferred directly into glass bubbler for purging). The Teflon bag on COS measurement could be neglected in this study.

### 3. Results and Discussion

#### 3.1. Initial Dissolved COS in Precipitation Samples

The initial dissolved COS and pH of 19 precipitation samples were measured. The precipitation samples included 10 snow samples in Beijing and nine snow or rain samples from other areas as listed in Table 1. Only the samples in Beijing (sampling date was from 15 December 2002 to 10 March 2003) were analyzed immediately after sample collection (the snow sample was melted at room temperature and then transferred directly into glass bubbler for purging). The initial COS concentrations of the 10 fresh snow samples in Beijing were in the range from 16.8 to 145.2 ng L\(^{-1}\). These values were much higher than that of the rain samples measured by Belviso et al. [1987] in France (the concentrations of the initial dissolved COS measured by them were in the range from 2.5 to 33.2 ng L\(^{-1}\), whereas the initial COS concentrations of the samples listed in Table 1 fell into the range given by Belviso et al. [1987]). It should be mentioned that all samples, except the one from Beijing, were stored for 10–20 days. During the stored period, COS might also be produced by photochemical reaction because of the light intensity in the room, where the samples were stored, was <2 \(\mu\)E s\(^{-1}\) m\(^{-2}\) (with E being einsteins). This low light intensity could not trigger remarkable COS formation (see section 3.2). The COS escape from these samples, its hydrolysis [Elliot et al., 1989], and wall adsorption, etc., could cause COS to be lost for the long storage time.

Previous study [Belviso et al., 1987] indicated that the rate of COS loss was >95% of the original COS content after a 6 hours of sunlight exposure. The COS concentrations in the two samples were in fair agreement.

### 3. Results and Discussion

#### 3.1. Initial Dissolved COS in Precipitation Samples

The initial dissolved COS and pH of 19 precipitation samples were measured. The precipitation samples included 10 snow samples in Beijing and nine snow or rain samples from other areas as listed in Table 1. Only the samples in Beijing (sampling date was from 15 December 2002 to 10 March 2003) were analyzed immediately after sample collection (the snow sample was melted at room temperature and then transferred directly into glass bubbler for purging). The initial COS concentrations of the 10 fresh snow samples in Beijing were in the range from 16.8 to 145.2 ng L\(^{-1}\). These values were much higher than that of the rain samples measured by Belviso et al. [1987] in France (the concentrations of the initial dissolved COS measured by them were in the range from 2.5 to 33.2 ng L\(^{-1}\), whereas the initial COS concentrations of the samples listed in Table 1 fell into the range given by Belviso et al. [1987]). It should be mentioned that all samples, except the one from Beijing, were stored for 10–20 days. During the stored period, COS might also be produced by photochemical reaction because of the light intensity in the room, where the samples were stored, was <2 \(\mu\)E s\(^{-1}\) m\(^{-2}\) (with E being einsteins). This low light intensity could not trigger remarkable COS formation (see section 3.2). The COS escape from these samples, its hydrolysis [Elliot et al., 1989], and wall adsorption, etc., would cause COS to be lost for the long storage time.

Previous study [Belviso et al., 1987] indicated that the rate of COS loss was >95% of the original COS content after a

---

**Table 1. The Initial Dissolved COS Concentrations and Total COS Productions in 10 Precipitation Samples**

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Level of pH</th>
<th>COS Concentrations, ng L(^{-1})</th>
<th>Average Production Rate, ng L(^{-1}) day(^{-1})</th>
<th>Irradiation Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhumadian, Henan</td>
<td>31 Jan. 2003</td>
<td>6.89</td>
<td>29.4(^e)</td>
<td>49</td>
</tr>
<tr>
<td>Changde, Hunan</td>
<td>08 Feb. 2003</td>
<td>6.24</td>
<td>29.9(^e)</td>
<td>54</td>
</tr>
<tr>
<td>Tianmen, Hubei</td>
<td>30 Jan. 2003</td>
<td>6.36</td>
<td>20.9(^e)</td>
<td>35</td>
</tr>
<tr>
<td>Shenyang, Liaoning</td>
<td>16 Feb. 2003</td>
<td>7.24</td>
<td>48.2(^b)</td>
<td>82</td>
</tr>
<tr>
<td>Jiayuguan, Gansu</td>
<td>25 Jan. 2003</td>
<td>10.6</td>
<td>21.1(^b)</td>
<td>32</td>
</tr>
<tr>
<td>Zhongxian, Chongqing</td>
<td>10 Feb. 2003</td>
<td>4.31</td>
<td>17.7(^b)</td>
<td>39</td>
</tr>
<tr>
<td>Haidian district, Beijing</td>
<td>19 Dec. 2002</td>
<td>7.08</td>
<td>25.3(^b)</td>
<td>47</td>
</tr>
<tr>
<td>Jiujiang, Jiangxi</td>
<td>06 Feb. 2003</td>
<td>3.96</td>
<td>26.5(^b)</td>
<td>45</td>
</tr>
<tr>
<td>Heze, Shandong</td>
<td>12 Feb. 2003</td>
<td>7.10</td>
<td>21.6(^b)</td>
<td>36</td>
</tr>
<tr>
<td>Waliguan, Qinghai</td>
<td>13 March 2003</td>
<td>7.29</td>
<td>32.9(^b)</td>
<td>27</td>
</tr>
</tbody>
</table>

\(^{a}\)SR is the COS saturation ratio of original precipitation samples at room temperature (291 K). The COS ambient concentration was 1000 pptv for the sample of Beijing and 500 pptv for others.

\(^{b}\)COS was stored in the airtight bottle for 6 hours in the dark at 290 K. We also collected two snow samples in Beijing on the roof of the main building of our research center by using Teflon film and the enamel plate simultaneously. The two samples were transferred rapidly into two identical bubblers. The difference of initial dissolved COS concentrations between the two samples was within the error of our GC analysis (<6%).

\(^{c}\)Regarding the Teflon bag, there was no evidence to indicate that the bag had any influence on the COS measurement within the short time storage (<1 hour). Therefore the impact of the enamel plate, the polyethylene bottles, the glass bubblers, and the Teflon bag on COS measurement could be neglected in this study.

\(^{d}\)The bubbler was made of quartz tube.
9-day storage period at 4°C in an open bottle. The initial dissolved COS for the investigated samples, except the one from Beijing, might be much higher than measured by this study.

[18] The COS saturation ratios (that is $[\text{COS}]_{\text{equil air}} / [\text{COS}]_{\text{amb air}} = \text{SR}$, with $[\text{COS}]_{\text{equil air}}$ being the air concentration of COS when the air was equilibrated with the dissolved gases in the water and $[\text{COS}]_{\text{amb air}}$ being the ambient COS concentration measured in the study) in the investigated samples could be obtained by Henry's law. Henry's law constant ($H$, mol/L/atm) was taken from De Bruyn et al. [1995], who found that for COS,

$$RT \ln (H/55.5) = A + BT$$

in water, $A = 4195$ cal K$^{-1}$ mol$^{-1}$, $B = -29.6$ cal K$^{-1}$ mol$^{-1}$, and $T$ is the temperature of water. The room temperature (RT) was ~291 K, and the mixing ratio of COS in Beijing was around 1000 pptv during our experiments. For other samples, because the ambient COS concentrations at these sites were not measured, the average global background value of 500 pptv was used. The dissolved COS in water under equilibrium with the air should therefore be only 1.60 ng L$^{-1}$ for the sample in Beijing and 0.798 ng L$^{-1}$ for others. These values are much lower than the initial COS concentrations of the investigated precipitation samples. This implies that the investigated precipitation samples were all supersaturated with COS. The COS saturation ratios (SR) for the investigated samples were in the range from 15.8 to 60.4 (Table 1).

[19] There are two hypotheses regarding COS supersaturation in precipitation: the first, that COS is formed by the reaction between strong acids and scavenged thiocyanate [Belviso et al., 1987]; the second, that organic matter (including sulfur containing amino acids) in precipitation was acting as COS precursor [Watts, 2000]. Further evidence for the photochemical production of COS from organic matter is provided on the basis of the following discussion on our investigated precipitation samples.

3.2. Photochemical Production of COS in the Precipitation Samples

[20] The 10 bubblers containing the above purged precipitation samples were sealed by stopcock and put outdoors under natural sunlight irradiation. According to the method described in section 2, the COS production was analyzed every evening after sunlight irradiation (from 0800 to 1500 LT). Figure 2 shows the COS formation during the irradiation days. The significant COS formation through successive days indicated that COS production appears to be independent of dissolved O$_2$, because the O$_2$ in the bubblers was stripped out initially. We also conducted an independent experiment to test the effect of O$_2$ on the COS production under natural sunlight irradiation. The result indicated that the precipitation sample stripped of O$_2$ showed a similar production rate of COS compared to the sample that was air-saturated. This finding agreed with the behavior of COS photoproduction in seawater observed by Uher and Andreae [1997] as well as Zepp and Andreae [1994], in contrast to the marked oxygen effect observed by Ferek and Andreae [1984] on irradiation of organic sulfur compounds in distilled water using short wavelength UV radiation.

[21] The average COS production rates (ng L$^{-1}$ day$^{-1}$) for the investigated samples, which were derived from the total amount of COS formation divided by the irradiation days, were listed in Table 1. The average COS production rates among the investigated samples varied from 27 to 82 ng L$^{-1}$ day$^{-1}$. This is probably due to different amounts of COS precursors present in the samples. The sample with maximum production rate was from Shenyang, Liaoning province, which is located in northeast China and is a heavy industry city. Heavy industry might be a source of COS precursors. The lowest COS production rate was obtained in the sample from the top of Mt. Waliguan, Qinghai province (China Global Atmosphere Watch Baseline Observatory, CGAWBO). This station is located on the northeastern part of the Tibetan Plateau ($36^\circ 17'N, 100^\circ 54'E, 3816$ m above sea level) [Jianzhong et al., 2002]. The lowest COS production rate of the sample might be ascribed to two
the production rates (from 28.2 to 337.2 ng L$^{-1}$) from the first period of clear days. This value was significantly lower than the dark formation of COS. The spikes of COS photochemical production experiments. This gave a maximum COS hydrolysis rate constant of 8.37 $\times$ 10$^{-3}$ s$^{-1}$ for all samples except the one from Jiaoyuguan and a lifetime of ~23 hours. As to the sample of Jiaoyuguan, COS hydrolysis rate constant was of 2.43 $\times$ 10$^{-3}$ s$^{-1}$. Since the air temperature was mostly below 10$^\circ$C, and the irradiation time was only 7 hours each day, the hydrolysis of dissolved COS is not believed to have significantly affected the photochemical production rates for all samples except the one from Jiaoyuguan.

[27] Further evidence of COS photochemical production in the sample in Beijing was provided by a static chamber method. The air concentrations of COS in the chamber with the still frozen snow sample did not change with time, even when exposed to noon sunshine irradiation. This indicated that frozen snow made no contribution to atmospheric COS. However, it increased sharply during sunlight irradiation when the snow sample was melted to water and air temperature was above 5$^\circ$C (Figure 4). When sunlight intensity dropped below 200 $\mu$E s$^{-1}$ m$^{-2}$, the COS concentration in the chamber decreased. This might be due to COS hydrolysis exceeding photochemical production in the sample. Comparing the air temperature in the chamber at the sample of Waliguan, which was irradiated in a quartz bubbler, was 127.2 ng L$^{-1}$ during the first day of irradiation, and then it dropped sharply through the later days (the COS production rates were only 42.3 and 8.28 ng L$^{-1}$ at the second day and fourteenth day of irradiation, respectively).

[24] Additional measurements of COS formation under different sunlight intensities were conducted on a clear day. Melted snow water was injected into 12 bubblers (50 mL each), which were kept in the dark by covering them with aluminum foil. Each bubbler was exposed to natural sunlight for 1 hour at different times of the day, and the light intensity was simultaneously recorded by a light meter (LI-COR 250) (Figure 3). Compared with photochemical production, the dark formation of COS was very slow; only a 52% increment (from 20 to 30.4 ng L$^{-1}$) was found during 60 hours of storage in the dark. These experiments confirm that COS formation in precipitation strongly depended on sunlight intensity. Previous studies [Weiss et al., 1995; Von Hobe et al., 2001] also found a significant COS formation in the dark for seawater. They concluded that COS production by a mechanism other than UV photolysis cannot be ruled out.

[25] COS hydrolysis may be a sink for dissolved COS [Elliot et al., 1989], although the concentration of H$_2$S was found to be below the detection limit of ~0.05 ng L$^{-1}$) during our irradiation experiments. COS hydrolysis rate in water depends on the value of pH [Elliot et al., 1989]. The pH values in the investigated samples varied from 3.96 to 10.56. Therefore the COS hydrolysis rate constant for our investigated samples was calculated by using the sum of the Arrhenius expression for pH < 6 and pH > 9 obtained by Elliot et al. [1989]:

$$k = \exp(24.3 - 10.450/T) + \exp(22.8 - 6040/T) \times 10^{(pH-pK_w)}.$$  

The unit of the rate constant $k$ is s$^{-1}$. To keep the equation simple, we assumed $pK_w$ equals 14.

[26] The highest temperature outdoor was ~16$^\circ$C during the COS photochemical production experiments. This gives a maximum COS hydrolysis rate constant of 8.37 $\times$ 10$^{-3}$ s$^{-1}$ for all samples except the one from Jiaoyuguan and a lifetime of ~23 hours. As to the sample of Jiaoyuguan, COS hydrolysis rate constant was of 2.43 $\times$ 10$^{-3}$ s$^{-1}$. Since the air temperature was mostly below 10$^\circ$C, and the irradiation time was only 7 hours each day, the hydrolysis of dissolved COS is not believed to have significantly affected the photochemical production rates for all samples except the one from Jiaoyuguan.

[27] Further evidence of COS photochemical production in the sample in Beijing was provided by a static chamber method. The air concentrations of COS in the chamber with the still frozen snow sample did not change with time, even when exposed to noon sunshine irradiation. This indicated that frozen snow made no contribution to atmospheric COS. However, it increased sharply during sunlight irradiation when the snow sample was melted to water and air temperature was above 5$^\circ$C (Figure 4). When sunlight intensity dropped below 200 $\mu$E s$^{-1}$ m$^{-2}$, the COS concentration in the chamber decreased. This might be due to COS hydrolysis exceeding photochemical production in the sample. Comparing the air temperature in the chamber at the
beginning of the experiment (9.6°C) with the temperature at the end (−4.8°C), it was clear that the increase of COS concentration was mainly caused by photochemical production. In addition, the steepest slope (8.18 pptv min⁻¹) of the linear least squares fit of the COS mixing ratios versus time was found when the air temperature was relative constant (at ~15°C) from 1050 to 1410 LT and the sunlight intensity was above 1000 μE s⁻¹ m⁻². This indicated again that the COS production depended on the sunlight intensity. The COS average production rate (R) could be calculated according to the following equation:

\[ R = \text{slope} \times \left( \frac{V_c}{V} \right) \times \left( \frac{M}{A} \right). \]

[28] The slope of the linear least squares fitting of the COS mixing ratios versus time (Figure 5, from 0910 to 1530 LT) was 6.7372 pptv min⁻¹. \( V_c \) is the volume of the static chamber (34.3 L), \( V \) is the molar volume at the average temperature of 12.4°C (23.42 L mol⁻¹), \( M \) is the molecular weight of COS (60 g mol⁻¹), and \( A \) is the area of the enamel plate (29 × 19 cm). The COS average production rate (R) was ~10.7 ng m⁻² min⁻¹ or 0.54 ng L⁻¹ min⁻¹ for ~6 hours of sunlight irradiation. The COS flux from precipitation measured by this study and oceanic COS flux estimates are summarized in Table 2. Our value of COS flux from the precipitation sample was much higher than the COS fluxes from open ocean and in the COS flux range from coastal water. It should be noted that the COS flux measurement by the static chamber method only represents a lower limit for the precipitation sample. First, the COS flux from the liquid to the gas phase depends strongly on the concentration gradient across the interface, and a high COS concentration was built up in the chamber during our experiment. Second, the ambient air continuously diluted the air in the chamber. Despite these uncertainties the direct flux measurement at least provided further evidence for COS photochemical production in the precipitation.

**3.3. Factors Affecting the Photochemical Production of COS**

[29] Another experiment was carried out to investigate the effect of biological activity on the production of COS. The precipitation samples were divided into four groups. Two of them were filtered by 0.45- and 0.30-μm filters, respectively; the third group was initially filtered by a 0.30-μm filter, then put into a quartz tube and irradiated by UV light from three low pressure mercury lamps (253.7-nm light) for 3 hours; the last group of samples did not receive any treatment. Each group contained three identical samples. One from each group was analyzed immediately after purging with He. The last two samples of the four sample groups were set outdoors under natural sunlight irradiation for 2–5 hours. Figure 6 shows the results of these measurements. There was essentially no difference for COS production between the 0.45- and 0.30-μm filtered samples, i.e., within the experimental uncertainty. However, they were both larger than that of untreated samples, which might be ascribed to light scattering or shielding of particles in the untreated samples. This also indicated that the COS precursors in the precipitation samples are unlikely to be bound to particles. The initial COS concentration in the UV irradiated bubbler was much higher than others, whereas the slope of the UV irradiated samples was less than the others, indicating that COS was formed by UV irradiation and COS precursors might be partly depleted during the UV irradiating period. If the 0.30-μm filter did not remove all the bacteria, these would nevertheless have been killed by the high UV intensities during the 3 hours of irradiation.
Figure 6. The COS production in precipitation samples incubated under natural sunlight irradiation.

[Ferek and Andreae, 1984], COS still formed in the UV irradiated bubblers indicated therefore that microbial production of COS could be excluded as the only COS-producing mechanism.

4. Conclusion

[30] Large temporal and spatial variation of COS concentration was found in precipitation, but all samples were highly supersaturated with COS. Previous studies have shown that this is probably caused by photochemical production, supposedly by a mechanism analogous to that producing COS in seawater. The high supersaturation ratios (15.8–60.4) of the investigated precipitation samples imply that precipitation could be an important source of COS.

[31] Natural sunlight could trigger COS production in the investigated precipitation samples. The COS production rates were found to be strongly dependent on sunlight intensity and independent of microbial activity and dissolved O₂. Because the COS precursor(s) in precipitation is/are soluble, when precipitation falls on the ground, part of it will be put into rivers and ocean where additional COS sources will be produced by natural sunlight. To quantify the COS source from precipitation, more measurements and calculations (residence times in clouds, falling drops, ground) are needed.

Acknowledgments. The authors are grateful to several undergraduate students, who are from University of Science and Technology Beijing, to Zhao Yucheng, who is working in China Global Atmosphere Watch Baseline Observatory for collecting precipitation samples, to the reviewers, and to Rolf D. Vogt, who is from University of Oslo, for improving our manuscript. This work was supported by grants from NSF (China) (20277044, 40275038, and 20170208), 973 Project (2002CB410800), and IPCAS (KZCX2-414).

References


Hofmann, D. J. (1990), Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years, Science, 248, 996–1000.


Tangeman, A. (1986), Determination of volatile sulphur compounds in air at the parts per trillion level by Tenax trapping and chromatography, J. Chromatogr., 366, 205–216.


