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Photochemical production of carbonyl sulfide, carbon disulfide and dimethyl sulfide in a lake water

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ABSTRACT

Photochemical production of carbonyl sulfide (COS), carbon disulfide (CS₂) and dimethyl sulfide (DMS) was intensively studied in the water from the Aohai Lake of Beijing city. The lake water was found to be highly supersaturated with COS, CS₂ and DMS, with their initial concentrations of 0.91 ± 0.073 nmol/L, 0.55 ± 0.071 nmol/L and 0.37 ± 0.062 nmol/L, respectively. The evident photochemical production of COS and CS₂ in the lake water under irradiation of 365 nm and 302 nm indicated that photochemical production of them might be the reason for their supersaturation. The similar dependence of wavelength and oxygen for photochemical production of COS, CS₂ and DMS implied that they might be from the same precursors. The water cage effect was found to favor COS production but inhibit CS₂ and DMS formation, indicating that COS photochemical production was mainly from direct degradation of the precursors and the formation of CS₂ and DMS needed intermediates via combination of carbon-centered radicals and sulfur-centered radicals. The above assumptions were further confirmed by simulation experiments with addition of carbonyls and amino acids (cysteine and methionine), and the photochemical formation mechanisms for COS, CS₂ and DMS in water were derived from the investigations.

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Introduction

Carbonyl sulfide (COS), carbon disulfide (CS₂) and dimethyl sulfide (DMS) play important roles in the global sulfur cycle and have significant implications for the global climate change. COS is the most abundant reduced sulfur trace gas in the atmosphere with a mixing ratio of 500 ± 100 pptv and an average tropospheric life time of 2–6 years (Brühl et al., 2012; Chin and Davis, 1995; Griffith et al., 1998; Khalil and Rasmussen, 1984; Ulshöfer and Andreae, 1997). Due to its chemical inertness, it can be transported into the stratosphere, where it is ultimately converted to sulfate aerosols (Brühl et al., 2012;

Chin and Davis, 1995; Crutzen, 1976; Fried et al., 1993; Leung et al., 2002) that have great impacts on the earth's radiation budget as well as the stratospheric ozone concentration (Andreae and Crutzen, 1997; Brühl et al., 2012; Charlson et al., 1987; Fahey et al., 1993; Roche et al., 1994; Rodriguez et al., 1991; Solomon et al., 1993, 1996; Turco et al., 1980). The known COS sources include oceans (Ferek and Andreae, 1984; Khalil and Rasmussen, 1984; Zepp and Andreae, 1994), anaerobic soils (Castro and Galloway, 1991), marshes (Adams et al., 1981), precipitation (Belviso et al., 1987; Mu et al., 2004; Mu and Xu, 2009), oxidations of DMS and CS₂ (Barnes et al., 1994; Chin and Davis, 1993), anthropogenic sources and volcanoes (Chin and

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Davis, 1993), and the major sinks are vegetation (Geng and Mu, 2004; Sandoval-Soto et al., 2005), oxic soils (Castro and Galloway, 1991), oxidation and photolysis (Chin and Davis, 1993; Elliott et al., 1989). CS_2 is a minor sulfur-containing constituent in the sulfur cycle (Andreae, 1990) with an average tropospheric lifetime of 12 days (Khalil and Rasmussen, 1984). The major sources of CS_2 are oceans (Lovelock, 1974; Xie, 1999; Xie and Moore, 1999), soils (Kanda et al., 1995), wetlands (Watts, 2000), and anthropogenic sources (Chin and Davis, 1993; Khalil and Rasmussen, 1984), and the major sink is the $\text{OH} + \text{CS}_2$ reaction which is an important source for atmospheric COS (Chin and Davis, 1993). DMS is the largest natural source of sulfur in the global sulfur cycle, accounting for 90% of the total biogenic sulfur emissions from the ocean and 50% of the total biogenic sulfur emissions (Andreae and Raemdonck, 1983; Dacey et al., 1987). Once released in the atmosphere, DMS rapidly reacts with radicals (OH and NO_3) leading to sulfate aerosols which can scatter solar radiation and act as cloud condensation nuclei that are potentially important in regulating climate (Charlson et al., 1987; Faloona et al., 2005; Gondwe et al., 2003; Pandis et al., 1994). The known sources of DMS are from oceans (Bates et al., 1987; Kettle and Andreae, 2000), lakes (Reese and Anderson, 2009), salt marshes and estuaries (Steudler and Peterson, 1984), vegetation (Fall et al., 1988), soils (Geng and Mu, 2004; Yang et al., 1996) and freshwater wetlands (Hines et al., 1993), and the major sinks are reactions with OH radicals in daytime and with NO_3 radicals in the nighttime (Atkinson et al., 1984; Wilson and Hirst, 1996).

Supersaturated COS has been found in ocean and precipitation, which were mainly ascribed to the photochemical formation from the degradation of dissolved organic S compounds (Ferek and Andreae, 1984; Mu et al., 2004; Mu and Xu, 2009; Uher and Andreae, 1997; Ulshöfer et al., 1996; Weiss et al., 1995; Xie et al., 1998; Xie and Moore, 1999; Zepp and Andreae, 1994). Field studies indicated that photoproduction of COS in ocean depended on the location, with faster rates in coastal waters and slower rates in open ocean (Andreae, 1990; Kim and Andreae, 1987; Lovelock, 1974; Watts, 1991). Zepp and Andreae (1994) found that photochemical formation rate of COS in sea water was remarkably faster under the irradiation of shorter wavelength than under longer wavelength. Pos et al. (1998) postulated that both the sulfur-centered radicals and carbonyl radicals were required for COS formation. Laboratory experiments have found evident COS production in water after adding sulfur-containing amino acids under the UV irradiation (Ferek and Andreae, 1984; Flöck et al., 1997; Pos et al., 1998; Xie and Moore, 1999; Xie et al., 1998; Zepp and Andreae, 1994). Xie et al. (1998) further confirmed that amino acids (cysteine and cystine) in sea water were important precursors for photochemical formation of both COS and CS_2 , and proposed that photochemical production of COS and CS_2 might have the similar mechanism which was mainly initiated by OH radicals. DMS has long been recognized to be naturally formed through biological process of the enzymatic cleavage of dimethylsulphoniopropionate (de Souza et al., 1996), the reduction of dimethyl sulfoxide (Ginzburg et al., 1998), the methylation of hydrogen sulfide or methylmercaptan under anoxic conditions (Drotar et al., 1987) and the degradation of sulfur-containing organic compounds in aerobic environments (Richards et al., 1994).

Lake is an important part of the natural water bodies and usually affected by anthropogenic activities with input of various pollutants including dissolved organic S compounds. To our best knowledge, however, few studies only

investigated DMS emissions (Hu et al., 2007; Reese and Anderson, 2009) but no reports about COS and CS_2 emissions from lakes.

Therefore, the photochemical production of COS, CS_2 and DMS in the water from Aohai lake was intensively investigated in this study, and the possible pathways for photochemical formation of COS, CS_2 and DMS were proposed.

1. Materials and methods

1.1. Sample collection

Water samples used for the experiments were collected from a lake called Aohai (an artificial digging lake in the Olympic Forest Park, Beijing city) by using PET sampling bottles. The PET sampling bottles were thoroughly rinsed five times with ultrapure water before the collection. The water samples were stored at room temperature for 1–40 days and shield them from light prior to the experiments.

1.2. Experimental method

The initial dissolved and photochemical formed COS, CS_2 and DMS in the water samples were firstly enriched in an absorption tube and then analyzed by a gas chromatograph equipped with a flame photometric detector (GC-FPD, Shimadzu, Japan). The detail description of the method was given by Mu et al. (2002) and therefore only the modification was outlined here. A quartz bubbler (ID, 1.8 cm; length, 25 cm) was used for purging the water samples before and after irradiation. High purity nitrogen was selected as the purging gas which was further purified by passing a glass tube packed with molecular sieve 5 A (80–100 mesh) and immersed into liquid nitrogen. The flow rate (~80 mL/min) of the purging gas was controlled by a mass flow-meter. The bubbler was firstly flushed with the purified nitrogen for 10 min to remove the atmospheric COS, CS_2 and DMS, and then 10-mL water samples through a syringe filter of 15–20 μm were injected into the bubbler through a branch tube of the bubbler under the flushing. The initial dissolved or photochemical formed COS, CS_2 and DMS were enriched onto an enrichment tube after removing water by passing the air stream through a glass tube packed with granular calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). To make sure effective enrichment of the objective compounds, the enrichment tube (I.D. 4.3 mm, length: 150 mm) was packed with Tenax GC (80–100 mesh) and immersed into liquid nitrogen during the enrichment process. The enrichment tube was warmed up at room temperature for 30 sec to vaporize the purge gas, and then put into a thermal oven (kept at 160°C) with duration of 40 sec for liberating the adsorbed COS, CS_2 and DMS. The COS, CS_2 and DMS released from the enrichment tube were immediately transferred into the GC-FPD for separation and detection by turning a six-way valve connected with the enrichment tube.

Three types of ultraviolet lamps were used for irradiating the water samples, namely the low pressure mercury lamp (8 W) with central irradiation of 253.7 nm, a fluorescence lamp (8 W) with central irradiation of 302 nm and a fluorescence lamp (8 W) with central irradiation of 365 nm. Ten lamps for each type were fixed on a column bracket in a small

cubic chamber of 75 L and the bubbler was inserted into center of the column bracket during the experiments. In order to prevent inner ultraviolet out and external natural light in, the internal surface of the chamber was covered by aluminum film. In addition, there were two fans at the back of the chamber to maintain the inner temperature almost constant at room temperature.

Both static and dynamic methods were used to study the photochemical formation of COS, CS₂ and DMS. The static method was basically identical to the method used by our previous studies (Mu et al., 2004; Mu and Xu, 2009), that is, the photochemical formed COS, CS₂ and DMS were detected after the bubbler contained the water samples being irradiated for a time period without passing the purging gas. The dynamic method was conducted with continually passing the purging gas through the bubbler during the irradiation.

1.3. Chemicals

Tenax GC (40–60 mesh; Alltech Associates, Inc. America); granular calcium chloride (CaCl₂·2H₂O, analytical reagent, Southern chemical plant, Lanxi City, Zhejiang Province, China); methionine and cysteine (Biological reagent, 98.5%, Sinopharm Chemical Reagent Co., Ltd., China); acetone (analytical reagent, Sinopharm Chemical Reagent Co., Ltd., China); formaldehyde (guaranteed reagent, Sigma-Aldrich); DMS (guaranteed reagent, Sigma-Aldrich-Fluka); COS standard gas (104 ppmv, Center of Standard Reference Materials, Beijing, China).

2. Results and discussion

2.1. Initial dissolved COS, CS₂ and DMS in the water samples

The initial dissolved COS, CS₂ and DMS in the water samples from Aohai Lake were 0.91 ± 0.073 nmol/L, 0.55 ± 0.071 nmol/L and 0.37 ± 0.062 nmol/L, respectively. According to Henry's law, COS, CS₂ and DMS in the water samples were supersaturated, with saturation ratios (SR = (A) equilibrium air/(A) ambient air, A represented COS, CS₂ or DMS) of 67.78 ± 5.43 for COS, of 200.65 ± 26.03 for CS₂ and of 7.01 ± 1.17 for DMS, assuming the ambient COS concentration of 608 pptv (Cheng et al., 2015), CS₂ concentration of 50 pptv (Bandy et al., 1993) and DMS

concentration of 95 pptv (Conley et al., 2009). The supersaturation of COS, CS₂ and DMS in the water samples indicated that there were their formation sources in the lake.

Photochemical production of COS was suspected to be responsible for the supersaturation of COS in the lake water, as those for sea water and precipitation (Ferek and Andreae, 1984; Mu et al., 2004; Mu and Xu, 2009; Uher and Andreae, 1997; Ulshöfer et al., 1996; Weiss et al., 1995; Zepp and Andreae, 1994). The supersaturation of CS₂ in the lake water might be from the photochemical transformations of chromophoric dissolved organic matter or the release of possible algal (Xie and Moore, 1999; Xie et al., 1998). The supersaturation of DMS in the lake water was probably ascribed to the metabolism of sulfur-containing amino acids such as methionine by bacteria as well as algae or decomposition of sulfur-containing organic compounds (Fritz and Bachofen, 2000; Hu et al., 2007). To disclose the possible reasons for supersaturation of COS, CS₂ and DMS in the lake water, a series of experiments were designed in the following sections.

2.2. The influence of UV wavelengths on production of COS, CS₂ and DMS

The variation trends of COS, CS₂ and DMS concentrations in the water samples after irradiation with three kinds of mercury lamps (with central wavelengths of 253.7 nm, 302 nm and 365 nm, respectively) for different period (0–90 min) are illustrated in Fig. 1. It should be mentioned that each water sample was first purged by the high purified N₂ for removing the initial dissolved COS, CS₂ and DMS before the irradiation experiments, and the first values with irradiation time of 0 represented the initial concentrations of COS, CS₂ and DMS.

As expected, evident COS formation was found in the water samples under irradiation with the three wavelengths (Fig. 1a). In line with the finding of Zepp and Andreae (1994) for sea water, COS production in the lake water strongly depended on irradiation wavelength, *e.g.*, with the same duration of irradiation, COS concentration in the lake water under 253.7 nm irradiation was about a factor of 4 greater than under 302 nm irradiation, and about two orders of magnitude greater than under 365 nm irradiation. COS concentration in the lake water under the irradiation of 253.7 nm steadily increased with increasing duration and

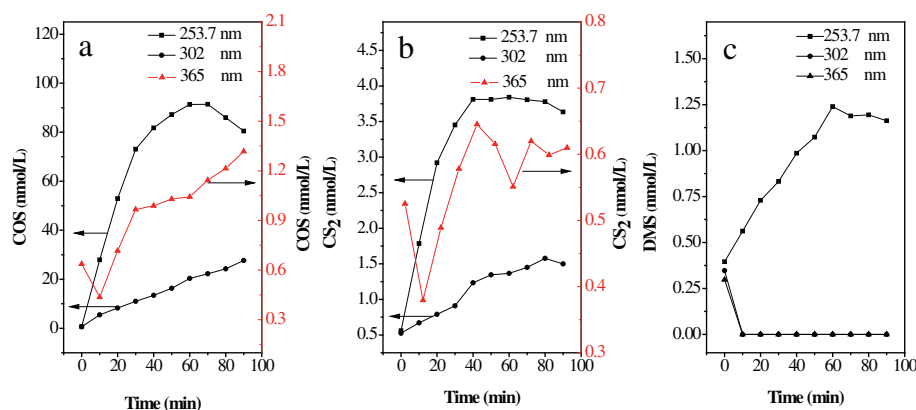


Fig. 1 – Photoproduction of COS (carbonyl sulfide), CS₂ (carbon disulfide) and DMS (dimethyl sulfide) in the lake water under three different UV wavelengths. (a) COS; (b) CS₂; (c) DMS.

reached a maximal value of 91.40 nmol/L at 70 min and then decreased with further increasing irradiation time, which was ascribed to the net effect of photochemical formation rate and hydrolysis rate of COS (Elliott et al., 1989; Mu et al., 2004; Mu and Xu, 2009). Although only the wavelengths greater than 295 nm of solar irradiation can reach in the troposphere, the production of COS in the water under 253.7 nm irradiation conducted by this study was useful to indicate COS production potential or the concentration of COS precursor(s), because consumption of COS precursor(s) in the water under the longer wavelengths was relatively slow (Mu et al., 2004; Mu and Xu, 2009). The extremely high COS concentration (91.40 nmol/L) induced by 253.7 nm irradiation in the lake water indicated that there are abundant COS precursor(s) which may play important role in water ecosystem (e.g., nutrients for microbe or small animals) besides on formation of COS.

Evident CS₂ photochemical formation was also found in the water with the three wavelengths irradiation (Fig. 1b), and in line with the finding of Xie et al. (1998). CS₂ production in water also strongly depended on irradiation wavelength, e.g., with the same duration of irradiation, CS₂ concentration in the lake water decreased with increasing wavelength.

Unexpectedly, evident DMS production was observed in the lake water under the irradiation of 253.7 nm, and the variation trend of DMS concentrations with increasing irradiation duration was similar with that of COS and CS₂ (Fig. 1c). The similar variation trends of COS, CS₂ and DMS in the lake water under irradiation of 253.7 nm indicated that COS, CS₂ and DMS might be from the same precursor(s), which will be verified by following sections. To our best knowledge, there are no reports about photochemical DMS formation in the literature.

2.3. Photochemical formation of COS, CS₂ and DMS by using static and dynamic methods

Hydrolysis of COS is an important loss channel in water (Elliott et al., 1989; Mu et al., 2004; Mu and Xu, 2009). To reduce COS loss via hydrolysis, dynamic method (with continue N₂ purging during the irradiation) was also used for investigating

COS production in the lake water under the irradiation of 253.7 nm. Unexpectedly, COS photochemical production in the lake water during the same duration of irradiation were much higher by using the static method (without purging during irradiation) than by using the dynamic method, whereas the variation of CS₂ and DMS concentrations was on the contrary (Fig. 2). In comparison with the dynamic method, the evident high production of COS in the lake water by using static method indicated that COS photochemical production might be directly from the degradation of its precursor(s) under the “cage effect” of water, whereas CS₂ and DMS production might need species other than its precursor(s) which contain S element. The above suspicions will be further certified in Section 2.5.1.

2.4. The influence of O₂ on COS, CS₂ and DMS production

Several studies indicated that the influence of O₂ on COS production in natural water was negligible under UV light irradiation with wavelengths above 295 nm (Mu et al., 2004; Uher and Andreae, 1997; Zepp and Andreae, 1994), whereas Ferek and Andreae (1984) reported that O₂ in the sea water evidently promoted COS production under 253.7 nm irradiation. The influence of O₂ on COS, CS₂ and DMS production was investigated in the lake water with pre-purging by N₂ and synthetic air under 253.7 nm and 302 nm irradiation, and the results are listed in Table 1. The evident reduction of COS production with the presence of O₂ under 253.7 nm irradiation was contrary to the finding of Ferek and Andreae (1984), and the negligible influence of O₂ on COS production under 302 nm irradiation was in line with the investigations by using UV light irradiation with wavelengths above 295 nm (Mu et al., 2004; Uher and Andreae, 1997; Zepp and Andreae, 1994). The different influences of O₂ on COS production under 253.7 nm and 302 nm irradiation were probably ascribed to the formation of different species of S fragments (such as carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals) via photochemical degradation of COS precursor(s). Both carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals were suspected to be converted into COS under extremely low O₂ concentration, whereas most of sulfur-centered radicals

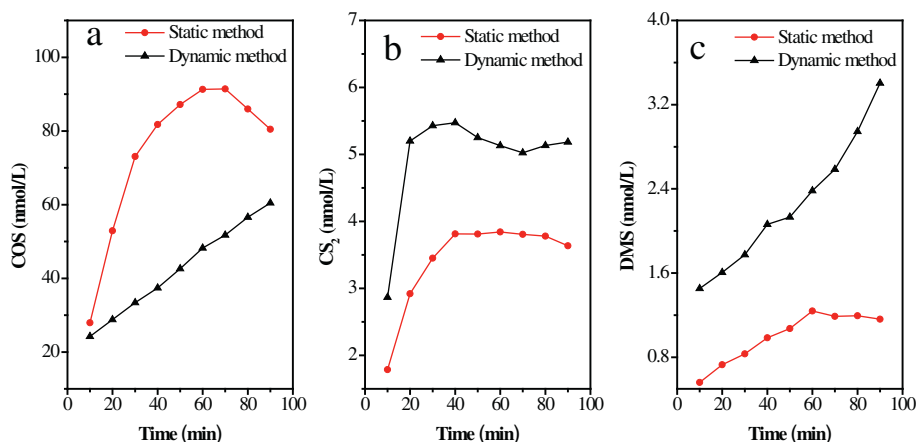


Fig. 2 – Photoproduction of COS, CS₂ and DMS in the lake water by using static and dynamic methods under the irradiation of 253.7 nm. (a) COS; (b) CS₂; (c) DMS.

Table 1 – COS, CS₂ and DMS concentrations (mean ± SD, N = 5) in the lake water under irradiation of 253.7 nm and 302 nm for 20 min after different purging treatments.

Data of sampling	Purging gas before irradiation	Purging gas after irradiation	Wavelength (nm)	Irradiation time (min)	COS (nmol/L)	DMS (nmol/L)	CS ₂ (nmol/L)
2014.7.25	N ₂	N ₂	254	10	27.61 ± 0.28	0.60 ± 0.01	1.95 ± 0.007
2014.7.25	N ₂	Synthetic air	254	10	27.03 ± 0.40	0.52 ± 0.01	1.96 ± 0.01
2014.7.25	Synthetic air	N ₂	254	10	17.83 ± 0.30	–	1.24 ± 0.03
2015.6.3	N ₂	N ₂	302	60	24.80 ± 0.49	–	0.90 ± 0.05
2015.6.3	Synthetic air	N ₂	302	60	24.41 ± 0.74	–	0.12 ± 0.03

COS: carbonyl sulfide; CS₂: carbon disulfide; DMS: dimethyl sulfide.

might easily react with O₂ to form high oxidation sulfur species and reduce COS formation. Evident reduction of CS₂ production was found in the water under 253.7 nm and 302 nm irradiation with the presence of O₂. The combination of carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals was suspected to contribute to CS₂ formation based on the structure of CS₂, and hence the possible fast reactions of sulfur-centered radicals and carbon-centered radicals in the neighbor of sulfur with O₂ greatly reduced CS₂ formation. The evident DMS production under 253.7 nm irradiation in the lake water after purging with N₂ indicated that both CH₃S_· and CH₃· were probably formed, and the disappear of DMS production after purging with synthetic air implied that CH₃S_· and CH₃· could easily react with O₂ to form other oxidized S compounds. No DMS production without the presence of O₂ under the irradiation of 302 nm indicated the energy of 302 nm was too weak to break the possible C–S bond of the potential precursor(s) for DMS production.

2.5. Possible precursors for photochemical formation of COS, CS₂ and DMS

2.5.1. Carbonyl compounds

Pos et al. (1998) postulated that acetyl or other carbon-centered radicals could react with the reduced sulfur compounds to produce sulfur-centered radicals which in turn react with the carbonyl group producing COS. In order to validate their postulation, COS production in the lake water with adding different amounts of formaldehyde and acetone was investigated under irradiation of 253.7 nm for 20 min, and the results are illustrated in Fig. 3a, b. The evidently steady decrease of COS production with increasing addition of formaldehyde (Fig. 3a) is contrary to the above postulation. It is interesting to be noted that the CS₂ production was steadily increased in the lake water with increasing addition of formaldehyde, but there was no discernable variation of DMS (data not shown). As for acetone addition, COS production obviously decreased when the addition of acetone was less than 0.068 mmol/L, and then increased with further addition of acetone to a maximal value, and sharply decreased again when acetone concentration was above 0.68 mmol/L. It should be mentioned that the maximal value of COS production in the lake water with the addition of acetone was almost at the same level of the original water (the first point of the data) under the same period irradiation, that is, acetone couldn't promote photochemical production of COS in the lake water. Amino acids have been recognized as potential precursors for photochemical production of COS and CS₂ in

water (Ferek and Andreae, 1984; Flöck et al., 1997; Pos et al., 1998; Xie et al., 1998; Zepp and Andreae, 1994), and Maillard-type browning reaction or aldol condensation reaction between amino acids and carbonyls has also been well documented (Nozière, 2005; Nozière et al., 2007, 2009; Nozière and Esteve, 2007; Nozière et al., 2009, 2010; Powelson et al., 2014; Sareen et al., 2010; Shapiro et al., 2009). The indirect evidence for

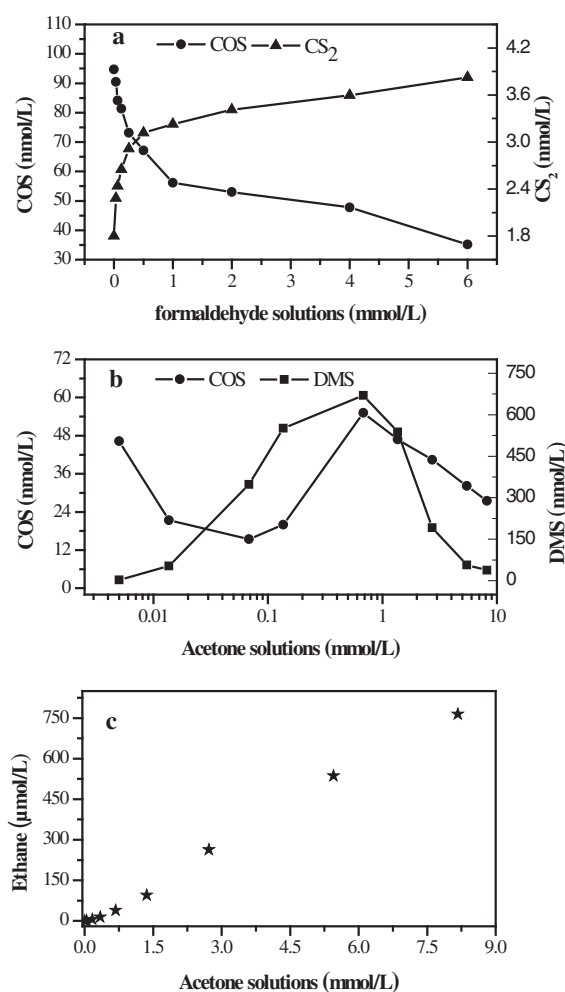


Fig. 3 – Photoproduction of COS and CS₂ (a), COS and DMS (b), and ethane (c) in the lake water samples added with different amounts of formaldehyde or acetone under 253.7 nm irradiation for 20 min.

consumption of acetone by possible the Maillard-type browning reaction or aldol condensation reaction could be seen in the production of ethane. Ethane production in the lake water with addition of acetone was mainly ascribed to the cage effect of water through the Reactions (1) and (2).



As shown in Fig. 3c, the production yield of ethane was evidently less with small amount acetone addition (below 0.068 mmol/L) than those with larger amount acetone addition. Because photochemical production of COS in the lake water with adding formaldehyde and acetone evidently decreased, the photochemical degradation of the light-absorbing compounds formed by the Maillard-type browning reaction or aldol condensation reaction was suspected to produce less COS than the direct photochemical degradation of amino acids. Whereas, the evidently increase of CS₂ in the lake after adding formaldehyde indicated that photochemical degradation of the products formed via the Maillard-type browning reaction or aldol condensation reaction might produce more CS₂ than the direct photochemical degradation of amino acids. Increment of CS₂ production was also suspected in water with addition of acetone, but the peak of CS₂ was overlapped by the strong peak of DMS. The complex relationship between photochemical production COS and the amount of acetone addition indicated that photochemical formation of COS in water was not due to simple reaction mechanisms, and hence more researches are still needed to disclose the reasons.

In contrast to COS production, DMS production in the lake water with addition of acetone slowly increased at small amount acetone addition, and then quickly increased to a maximal value, and sharply decreased when acetone concentration was above 0.68 mmol/L. In comparison with the original water under the same duration of irradiation, the remarkable DMS production in the lake water with addition of acetone indicated photochemical reaction of acetone participated DMS formation. The DMS precursor(s) in the lake water was/were suspected to be first converted to CH₃S· radicals which could combine with CH₃· radicals formed by photolysis of acetone (Reaction (1)) to produce DMS through Reaction (3).



Based on the above DMS formation mechanism, however, it is still difficult to explain the sharp decrease of DMS production in the lake water when acetone concentration was above 0.68 mmol/L. The strong absorption of the UV light around 280 nm by acetone was suspected to shield the DMS or COS precursor(s) from photochemical degradation when acetone concentration achieved to high values.

2.5.2. Amino acids

Cysteine (HO₂CCH(NH₂)CH₂SH) and methionine (HO₂CCH(NH₂)CH₂CH₂SCH₃), the two prevailing amino acids have been found to promote COS and CS₂ production in water under UV irradiation (Ferek and Andreae, 1984; Flöck et al., 1997; Pos et al., 1998; Xie et al., 1998; Zepp and Andreae, 1994). The contribution of cysteine and methionine to the production of

COS, CS₂ and DMS was investigated in the lake water under 253.7 nm irradiation for 20 min. Two pre-treatments of the lake water samples were adopted for comparison: 1) different amounts of cysteine or methionine were added into the lake water after removing the initial dissolved COS, CS₂ and DMS by using N₂ for 15 min (designated as Treatment I); 2) different amounts of cysteine or methionine were added into the lake water after depleting the precursor(s) of COS, CS₂ and DMS under 253.7 nm irradiation for 60 min followed by 15 min purging (designated as II).

In line with the finding of Xie et al. (1998), evident photochemical production of COS and CS₂ was found in the water after adding cysteine. As shown in Fig. 4a, COS production under both the two treatments was almost linearly correlated with the amount addition of cysteine. The slope of the linear correlation for Treatment II was about a factor of 2 greater than that of Treatment I, which was ascribed to different hydrolysis rates of COS under different COS concentrations (Elliott et al., 1989; Mu et al., 2004; Mu and Xu, 2009). The COS yield (for Treatment II) from the degradation of cysteine under 253.7 nm irradiation for 20 min was 2.4%, indicating that COS production measured only represented small fraction of its precursor(s) in the water. Compared with the initial COS production (the first data in Fig. 4a) without adding cysteine for Treatment I, if COS production was mainly from cysteine, the initial cysteine concentration would be as high as 1.65 μmol/L which may provide enough nutrients for sustaining aquatic microbes and small animals living. In contrast to COS, CS₂ production exhibited exponential increase with increasing cysteine addition (Fig. 4a). As mentioned in the Section 2.4, the O₂ in the water evidently suppressed photochemical production of CS₂ under 253.7 nm irradiation. Although the lake water was purged by N₂ before irradiation, small amount of O₂ in the treated water was probably enough to compete with the combination reactions for CS₂ formation under small amount addition of cysteine and resulted in the exponential growth of CS₂ production with increasing cysteine addition.

Similar to the addition of cysteine, evident photochemical production of COS and CS₂ was also found in the water after adding methionine (Fig. 4b), which was on the contrary to the finding of Xie et al. (1998). However, the yields (slopes of the linear correlations) of COS from the addition of methionine were about a factor of 2–4 less than those from the addition of cysteine and CS₂ production with the addition of methionine was about one order of magnitude lower than that with addition of cysteine. To achieve the initial COS production (the first data for Treatment I in Fig. 4b), the methionine concentration of about 3.36 μmol/L was needed in the lake water. It should be mentioned that the addition of both cysteine and methionine didn't cause DMS formation, indicating that photochemical degradation of cysteine and methionine could not produce CH₃· radicals for DMS formation.

In order to further investigate the photochemical formation mechanism of COS, CS₂ and DMS, the photochemical production of COS, CS₂ and DMS was further investigated in the lake water with the presence of amino acids (cysteine or methionine) and acetone. A constant concentration of cysteine (1.24 μmol/L) or methionine (1.01 μmol/L) and different concentrations of acetone were prepared in the lake water

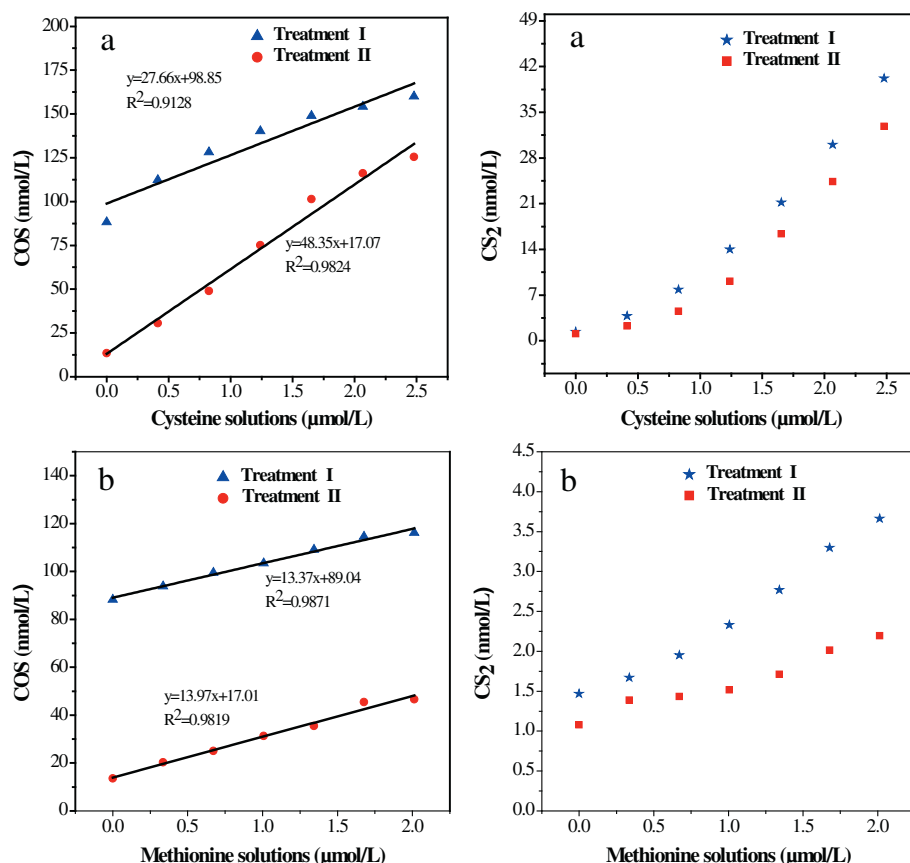


Fig. 4 – Photoproduction of COS and CS₂ in Treatment I and Treatment II samples added with different amounts of cysteine (a) or methionine (b) under 253.7 nm irradiation for 20 min.

samples after depleting the precursor(s) of COS, CS₂ and DMS under 253.7 nm irradiation for 60 min followed by 15 min purging, and photochemical productions of COS and DMS are illustrated in Fig. 5. Evident COS and DMS formations were found in the water samples with the addition of cysteine or methionine and acetone under 253.7 nm irradiation, and the

variation trends of COS and DMS were almost same as the original lake water with addition of acetone. Compared with the original water, the remarkable increase of both COS and DMS indicated that cysteine and methionine were the potential precursors of COS and DMS in the lake water. The peak of CS₂

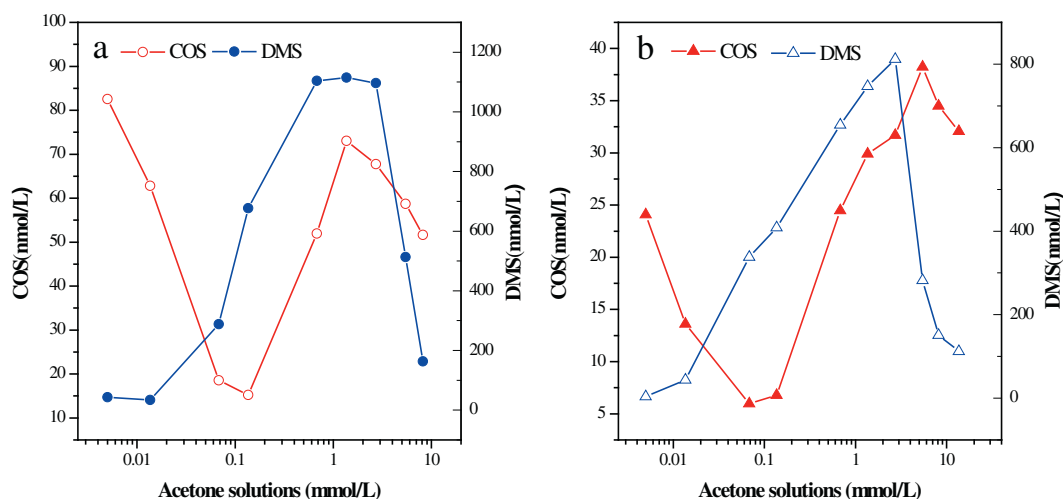
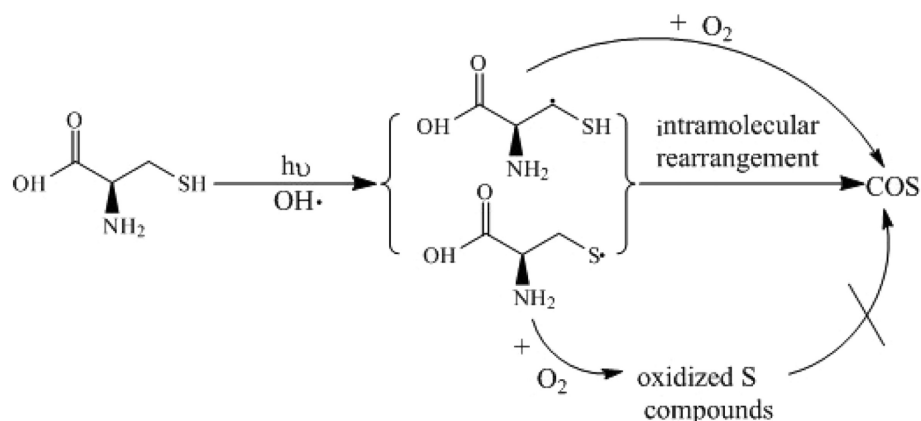


Fig. 5 – Photoproduction of COS and DMS in the lake water samples added with different amounts of acetone and constant cysteine (1.24 μmol/L) or methionine (1.01 μmol/L) under 253.7 nm irradiation for 20 min. (a) cysteine; (b) methionine.



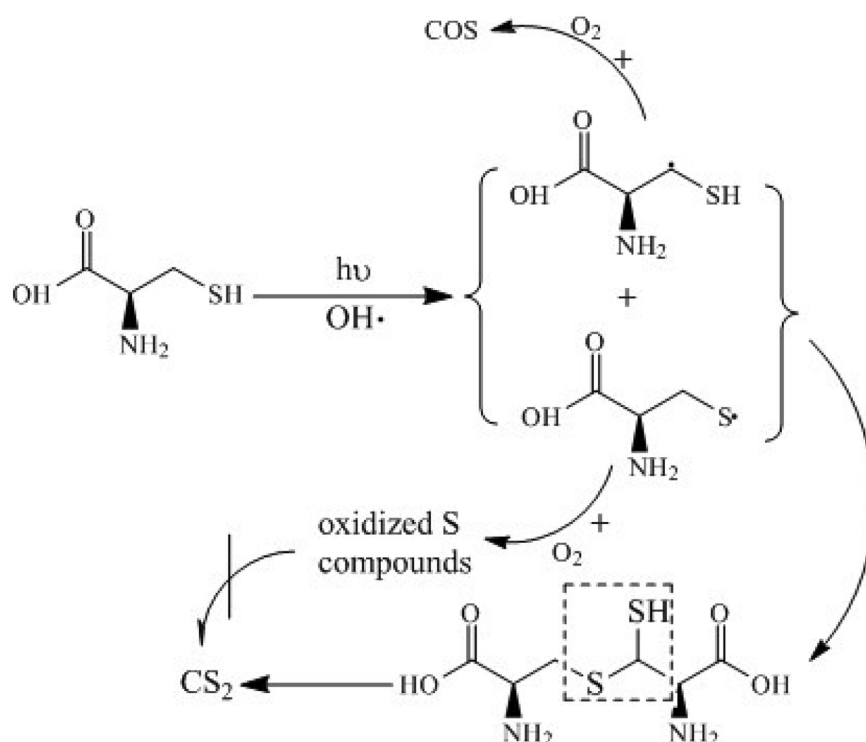
Scheme 1 – The photochemical formation mechanism of COS in water. COS: carbonyl sulfide.

was also overlapped by the strong peak of DMS under the condition of these simulation experiments.

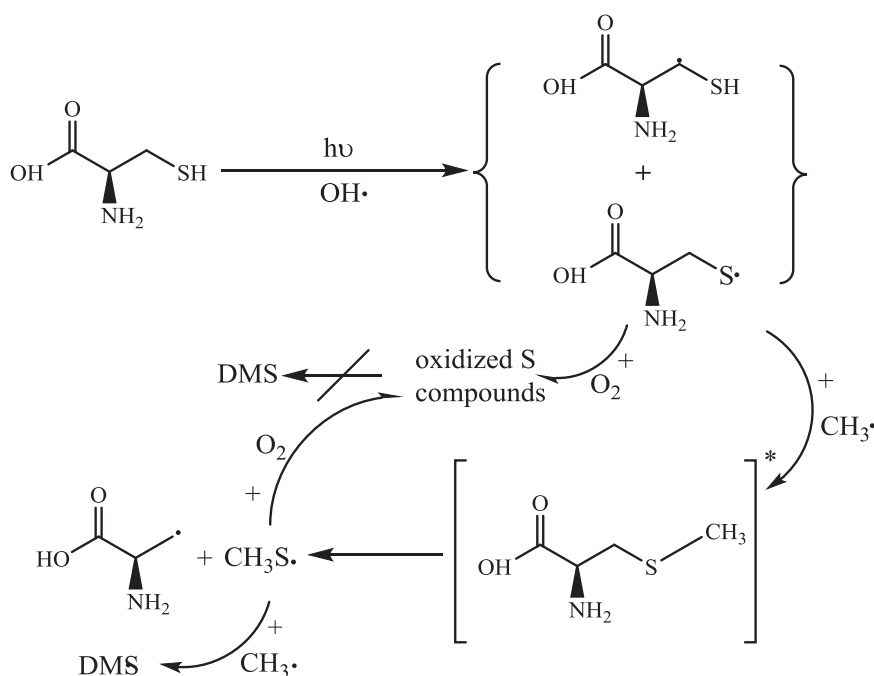
2.6. Photochemical formation mechanisms of COS, CS₂ and DMS

The photochemical formation mechanisms of COS, CS₂ and DMS were roughly derived from above results and illustrated in Schemes 1–3 with the photochemical degradation of cysteine as an example. As shown in Scheme 1, carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals were suspected to be firstly formed from photochemical degradation of their precursors, *e.g.*, COOHCH(NH₂)CH•SH and COOHCH(NH₂)CH₂S• from degradation of cysteine. Both carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals might undergo the

intramolecular rearrangement to produce COS. Because COS production was evidently suppressed with the presence of O₂ (Section 2.4) under 253.7 nm irradiation, the sulfur-centered radicals were suspected to react with O₂ to inhibit COS formation. Carbon-centered radicals in the neighbor of sulfur might be the dominant intermediates in the lake water under irradiation of 302 nm, which may produce COS via the intramolecular rearrangement or reaction with O₂ to account for the O₂ independence of COS production. Besides the competition of the intramolecular rearrangement and the reaction with O₂ of the sulfur-centered radicals, they may react with various radicals to form sulfur compounds other than COS, *e.g.*, the evident decrease of COS formation and increase of CS₂ and DMS with the dynamic method in comparison with the static method (Section 2.3). The structure



Scheme 2 – The photochemical formation mechanism of CS₂ in water. CS₂: carbon disulfide.



Scheme 3 – The photochemical formation mechanism of DMS in water. DMS: dimethyl sulfide.

of the intermediate species with S–C–S was necessary for CS₂ formation, and hence the combination of carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals was suspected to produce CS₂, *e.g.*, in Scheme 2, COOHCH(NH₂)CH₂·SH combined with COOHCH(NH₂)CH₂S· to form an excited intermediate which could further undergo degradation to produce CS₂. As mentioned above, the carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals easily reacted with O₂ to form COS and other oxidized S compounds to compete with the combination reactions, leading to evident reduction of CS₂ production (Scheme 2). The remarkable increase of DMS photochemical formation in the lake water with addition of acetone (Section 2.5.1) implied that CH₃· radicals played important role in the photochemical formation of DMS. No increase of DMS formation in the lake water with only addition of cysteine and methionine indicated that CH₃· radicals were difficult to be formed from the photochemical reactions of the two amino acids. Because there is no function group of CH₃· in cysteine, CH₃· was suspected to be from photolysis of organic compounds (such as acetone) in the lake water to account for DMS formation. The combination of CH₃· with sulfur-centered radicals (*e.g.*, COOHCH(NH₂)CH₂S·) might produce a transient species of (COOHCH(NH₂)CH₂SCH₃)^{*} which might easily decompose to CH₃S· (Scheme 3). The entire suppression of DMS formation with the presence of O₂ was probably due to the fast reactions of sulfur-centered radicals and CH₃· with O₂ (Scheme 3).

Previous studies have revealed that photochemical production of COS is a common phenomenon for both ocean (Ferek and Andreae, 1984) and precipitation (Mu et al., 2004; Mu and Xu, 2009), which was responsible for its supersaturation in the waters. Xie et al. (1998) found that photochemical reactions in ocean water could also make contribution to CS₂, and proposed

that the photochemical formation mechanisms for both COS and CS₂ were similar. The wavelength dependence of COS photochemical formation in the lake water investigated in this study was same as that in the sea water (Zepp and Andreae, 1994). Therefore, photochemical formations of COS, CS₂ as well as DMS were suspected to be the same characteristics for water samples from elsewhere.

3. Conclusions

The Aohai lake water was found to be supersaturated with COS, CS₂ and DMS, and evident production of COS and CS₂ in the lake water under irradiation of 302 nm and 365 nm implied that their supersaturation was probably ascribed to the photochemical formation. Besides COS and CS₂, photochemical production of DMS without the presence of O₂ was also observed when the lake water was exposed to 253.7 nm irradiation. The similar variation trends of COS, CS₂ and DMS with irradiation time indicated that they might be from the same sulfur precursors. The sulfur precursors were assumed to first produce carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals in the lake water under the UV irradiation. The evident “cage effect” and O₂ dependence of COS photochemical production revealed that both carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals could directly form COS through intramolecular rearrangement. CS₂ formation was assumed to be from the combination of carbon-centered radicals in the neighbor of sulfur and sulfur-centered radicals to form an intermediate species with the structure of S–C–S. DMS formation was found to depend on introducing external CH₃· radical which was assumed to react with the sulfur-centered radicals to form CH₃S· radicals, and the combination of CH₃· and CH₃S· was responsible for DMS formation. The remarkable

reduction of CS₂ and DMS with the presence of O₂ implied that the reaction of sulfur-centered radicals with O₂ greatly suppressed the combination reactions of the radicals. The extremely high photochemical production of the reduced sulfur compounds indicated that there were abundant precursors which may be important nutrients for sustaining microbe and small animal growing in the lake water.

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