

# Emissions of Biogenic Sulfur Gases ( $H_2S$ , COS) from *Phragmites australis* Coastal Marsh in the Yellow River Estuary of China

LI Xinhua<sup>1</sup>, ZHU Zhenlin<sup>1</sup>, YANG Liping<sup>1</sup>, SUN Zhigao<sup>2,3</sup>

(1. Shandong Institute of Agricultural Sustainable Development, Jinan 250100, China; 2. Institute of Geography, Fujian Normal University, Fuzhou 350007, China; 3. Key Laboratory of Humid Subtropical Eco-geographical Process, Fujian Normal University, Ministry of Education, Fuzhou 350007, China)

**Abstract:** Emissions of biogenic sulfur gases (hydrogen sulfide ( $H_2S$ ) and carbonyl sulfide (COS)) from *Phragmites australis* coastal marsh in the Yellow River estuary of China were determined during April to December in 2014 using static chamber-gas chromatography technique with monthly sampling. The results showed that the fluxes of  $H_2S$  and COS both had distinct seasonal and diurnal variations. The  $H_2S$  fluxes ranged from 0.09  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  to 7.65  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ , and the COS fluxes ranged from -1.10  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  to 3.32  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ . The mean fluxes of  $H_2S$  and COS from the *P. australis* coastal marsh were 2.28  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  and 1.05  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ , respectively. The *P. australis* coastal marsh was the emission source of both  $H_2S$  and COS over the whole year. Fluxes of  $H_2S$  and COS were both higher in plant growing season than in the non-growing season. Temperature had a dramatic effect on the  $H_2S$  emission flux, while the correlations between COS flux and the environmental factors were not found during sampling periods. More in-depth and comprehensive research on other related factors, such as vegetation, sediment substrates, and tidal action is needed to discover and further understand the key factors and the release mechanism of sulfur gases.

**Keywords:** biogenic sulfur gases; hydrogen sulfide; carbonyl sulfide; emission flux; *Phragmites australis* coastal marsh; the Yellow River estuary

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## 1 Introduction

Volatile sulfur gases are both foul smelling and noxious and have profound impacts on the environment (Cooper *et al.*, 1987; Robert *et al.*, 2014), such as acid deposition, greenhouse effect, and formation of aerosols (Aneja, 1990; Robert *et al.*, 2014). Sulfur gases emitted from natural sources are identical to that from human activities and are one of the major sources of sulfur gases in the atmosphere (Watts, 2000). However, emissions of sulfur gases have high spatio-temporal variability, leading to a large uncertainty in the global atmos-

pheric sulfur budget (Watts, 2000; Tassia *et al.*, 2013).

Wetlands are one of the most important natural sources of sulfur emissions. Sulfur gases emitted from wetlands are one or several orders of magnitude higher than those emitted from inland due to their unique natural and ecological conditions (Istvan and Delaune, 1995). Studies have shown that the sulfur gases emitted from the wetlands are mainly hydrogen sulfide ( $H_2S$ ), carbonyl sulfide (COS), dimethyl sulfide (DMS), carbon disulfide ( $CS_2$ ), methyl mercaptan (MeSH) and dimethyl disulfide (DMDS) (Cooper *et al.*, 1987; Morrison and Hines, 1990; Delaune *et al.*, 2002; Li *et al.*, 2006b; Yi *et*

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Corresponding author: SUN Zhigao. E-mail: zhigaosun@163.com

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al., 2008; Zhou et al., 2009; Whelan et al., 2013; Li et al., 2014). The emission rates are affected by many factors, including temperature, tides, oxidation-reduction potential (Eh), vegetation type, soil substrate (Morrison and Hines, 1990; Delaune et al., 2002; Li et al., 2006b; Whelan et al., 2013). Among them,  $H_2S$  is highlighted with a higher emission fluxes in the saline wetland along inshore areas and seashore (Howarth, 1984) and is also closely related to iron cycling, carbon mineralization and methane emissions (Nedwell and Watson, 1995; Bridgman et al., 1998; Long et al., 2013; Scott et al., 2014). The global sources and sinks of  $H_2S$  are estimated as  $7.72 \pm 1.25$  Tg/yr and  $8.50 \pm 2.80$  Tg/yr, respectively. However, the budgets for  $H_2S$  have much greater uncertainty due to the very limited data with greater variation (Yang et al., 1998; Watts, 2000). COS is the most abundant and probably the most long-lived sulfur gas in the atmosphere (Kuhn et al., 1999), and the sink and source of the budget for COS are well balanced within the limits of uncertainty although the understanding of source and sink of COS is controversial (Watts, 2000). Many studies abroad have reported sulfur gases emissions from wetlands including salt marshes (Cooper et al., 1987; Morrison and Hines, 1990; Delaune et al., 2002; Whelan et al., 2013), mangrove swamps (Cooper et al., 1987), tidal marshes (Azad et al., 2005), freshwater wetlands (Cooper et al., 1987; Delaune et al., 2002) and rice paddies (Kanda et al., 1992). In China, the studies on sulfur gases emissions from wetlands started quite late and the related research mainly focused on the freshwater wetlands in the Sanjiang Plain (Li et al., 2006b), coastal salt marsh in the eastern China (Wang et al., 2009; Zhou et al., 2009) and rice paddies (Yang et al., 1998; Yi et al., 2008), while information on the coastal marshes in estuaries (such as the Liaohe River estuary, the Yellow River estuary and the Minhe River estuary) was scarce.

The Yellow River is well known as a sediment-laden river. Every year, approximately  $1.05 \times 10^7$  t of sediment is carried to the estuary (Cui et al., 2009) and deposited in the slow flowing delta, resulting in a vast floodplain and natural marsh landscape (Xu et al., 2002). Coastal marsh is one of the important ecological forms in the Yellow River estuary, with a total area of  $964.8 \text{ km}^2$ , accounting for 63.1% of the total area of the Yellow River estuary (Cui et al., 2009). Limited by water and salinity stress, plants growing in the coastal

marsh of the Yellow River estuary are mainly halophytes including annual *Suaeda salsa*, *Tamarix chinensis*, and *Phragmites australis* (Zhao and Song, 1995), of which *P. australis* is one of the most dominant species and can tolerate the different degree of water and salinity stress. Therefore, the *P. australis* coastal marsh is widely distributed in the Yellow River estuary and its distribution area in the Nature Reserve of Yellow River Delta is about 32 772 ha (Zhao and Song, 1992). The *P. australis* coastal marsh plays an irreplaceable role in conserving water sources, protecting against the wind and strengthening dyke, regulating climate, and improving the coastal ecological environment.

Current research on the biogenic elements cycle in the coastal marsh of the Yellow River estuary of China is mainly focused on the accumulation and distribution features of essential elements for plants (C, N, P, S, and other trace elements) (Mou et al., 2012 ; Sun et al., 2013a), distribution of elements in soils (Yu et al., 2010; Sun et al., 2013a), and greenhouse gas emissions (Jiang et al., 2012; Chen et al., 2013; Sun et al., 2013b; Zhang et al., 2013; Sun et al., 2014b). To date, the studies on the emissions of sulfur gases from the coastal marsh of the Yellow River estuary of China have not been previously reported, except the research on the sulfur gases emissions from the *S. salsa* coastal marsh in the Yellow River Estuary of China (Li et al., 2014). Given the sulfur gas emissions from the *P. australis* coastal marsh in the Yellow River estuary of China have not been studied, we investigated the seasonal and diurnal variations of sulfur gases emissions from the *P. australis* coastal marsh in the Yellow River estuary of China by using static chamber-gas chromatography technique to provide essential data for evaluating the impacts of sulfur gases emission on the atmospheric environment and further exploring the sulfur cycle in the natural coastal marsh of the Yellow River estuary of China.

## 2 Methods

### 2.1 Study area

The study was carried out in the coastal marsh of the Yellow River estuary, which is located in the Nature Reserve of Yellow River Delta ( $37^{\circ}35'N$ - $38^{\circ}12'N$ ,  $118^{\circ}33'E$ - $119^{\circ}20'E$ ) in Dongying City, Shandong Province, China. The nature reserve has a typical continental monsoon climate with distinct seasons. The average

annual temperature is 12.1°C, and the average temperatures in spring, summer, autumn, and winter are 10.7°C, 27.3°C, 13.1°C, and -5.2°C, respectively. The temperature changes significantly during early spring and winter, and the freeze-thaw cycles frequently occur in top-soil in majority days, with the frozen depth ranging from 0 to 15 cm. The average annual evaporation is 1962 mm, and the average annual precipitation is 551.6 mm, of which about 70% occurs between June and August. The soils in the study area are dominated by intrazonal tide soil and salt soil (Tian *et al.*, 2005), and the main vegetation includes *P. australis*, *Imperata cylindrica*, *Triarrhena chinensis*, *S. salsa*, and *Limonium sinense* (Sun *et al.*, 2014a).

## 2.2 Collection and analysis of gas samples

Three repeated monitoring points were distributed in the typical *P. australis* coastal marsh in the intertidal zone of the Yellow River estuary. Plants were evenly distributed in the three repeated monitoring points. The gaseous sulfur fluxes were measured from April to December in 2014 and were collected every month. Each sampling period was at 8:00–10:00 a.m. Diurnal measurements (every 4 h for 24 h) were conducted once during 19–20 June, 2014.

Gas samples were collected by using a closed chamber method (Sun *et al.*, 2014b; Li *et al.*, 2006a). The chamber was made of polycarbonate with an internal height of 1.0 m, covered an area of 0.25 m<sup>2</sup> (0.5 m in length and 0.5 m in width) of the test field. Each chamber had a small fan for mixing the air in the internal top. To avoid disturbing the soil, the chambers were placed on a stake driven into the ground installed on 10 December 2011. Meanwhile, a boardwalk was installed for minimizing disturbance to the field site during the sampling. Four gas samples of the chamber air were collected into a 1000-ml Tedlar bags by a small sampling pump at a flow rate of 2 L/min at 0, 20, 40, and 60 min after the chamber was set up. The sulfur fluxes were determined by measuring the temporal change of the concentration in the air inside the chamber. Therefore, a positive flux refers to the emission from the wetland to the atmosphere, and negative flux refers to the absorption by the plants and soil from the atmosphere.

The concentrations of H<sub>2</sub>S and COS were determined as described in detail by Li *et al.* (2006a). The gas flux is calculated according to the equation:

$$F = \frac{dc}{dt} \times \frac{M}{V_0} \times \frac{P}{P_0} \times \frac{T_0}{T} \times H \quad (1)$$

where  $F$  refers to gas flux ( $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ );  $M$ , the molar mass of the gas, the value of  $M$  for H<sub>2</sub>S and COS are 34.08 g/mol and 60.07 g/mol, respectively;  $P_0$ ,  $T_0$ , and  $V_0$  refer to the air pressure, air temperature, and molar volume of the ideal gas at standard conditions (1013.25 hPa, 273.15 K, and 22.41 L/mol, respectively);  $H$ , the height of sampling chamber;  $P$ , sampling point pressure;  $T$ , the absolute temperature during sampling;  $dc/dt$  was regression curve slope showing changes in time-based gas concentration during sampling.

## 2.3 Environmental measurements

Air temperature and soil temperatures (0, 5 and 10 cm) were measured in each position during gas sampling. Soil volumetric moisture and electrical conductivity (EC) in 0–5 and 5–10 cm depths were determined in situ using high-precision moisture measuring instrument (AZS-2) and soil & solution EC meter (Field Scout), respectively.

## 2.4 Statistical analysis

Data graphics was generated with Origin 7.5, and statistical analysis was performed by using SPSS13.0. The results were presented as means of the replications, with a standard error (S.E.).

## 3 Results

### 3.1 Environmental variables in *Phragmites australis* coastal marsh

The changes of air temperature and ground temperature in the *P. australis* coastal marsh during the sampling period were consistent (Fig. 1), and the highest temperatures were all found in August, the lowest temperatures were all found in December. The ranges of air temperature and ground temperatures (0 cm, 5 cm, 10 cm) were -4.20–29.4°C, -2.95–34.2°C, -1.95–33.03°C, and -0.64–31.44°C, respectively. Dissimilar variations of soil moisture and EC were observed (Fig. 2 and Fig. 3). With increasing of soil depth, generally soil moisture increased while EC decreased. The ranges of EC (0–5 cm, 5–10 cm) were 12.62–19.3 mS/cm, 10.95–18.27 mS/cm, respectively, and the ranges of soil moisture (0–5 cm, 5–10 cm) were 0.272–0.307 cm<sup>3</sup>/cm<sup>3</sup> and 0.265–0.309 cm<sup>3</sup>/cm<sup>3</sup>, respectively.

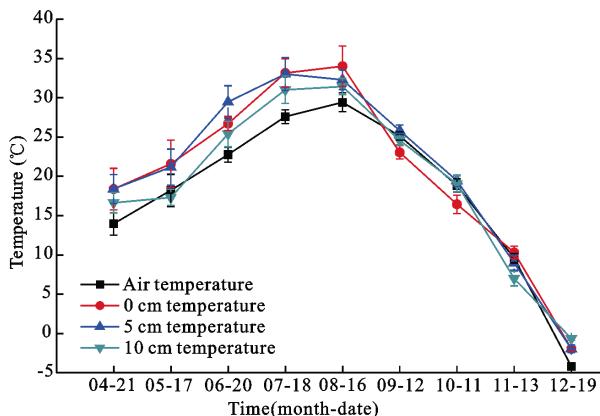


Fig. 1 Variations of environmental temperature in *Phragmites australis* coastal marsh

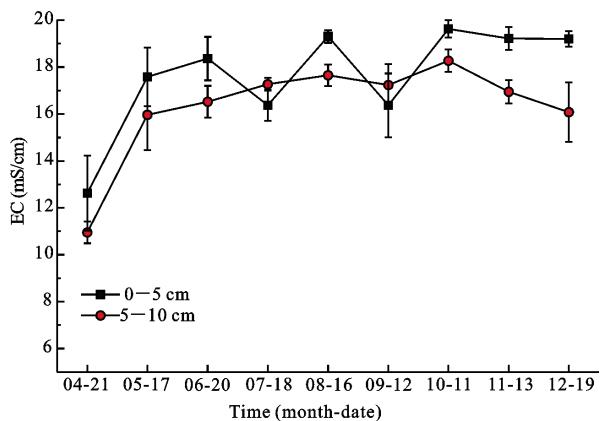


Fig. 2 Variations of soil electrical conductivity (EC) in *Phragmites australis* coastal marsh

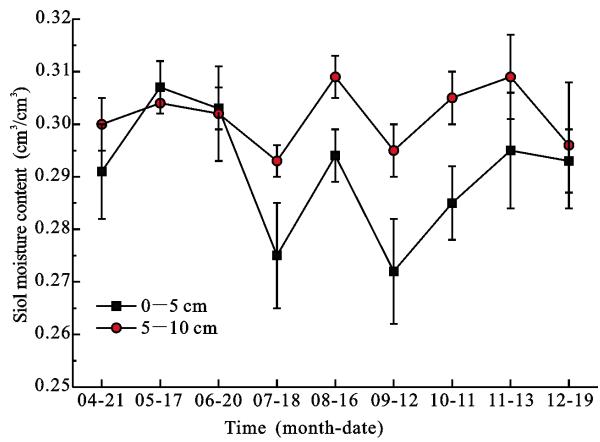


Fig. 3 Variations of soil moisture content in *Phragmites australis* coastal marsh

### 3.2 Seasonal variations of $H_2S$ and COS emission fluxes

The  $H_2S$  and COS emission fluxes from the *P. australis* coastal marsh varied with distinct seasonal variation (Fig. 4). The emission fluxes of  $H_2S$  ranged from  $0.09 \mu\text{g}/(\text{m}^2 \cdot \text{h})$

to  $7.65 \mu\text{g}/(\text{m}^2 \cdot \text{h})$  with an average emission intensity of  $2.28 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ , and the coefficient of variation was 98.9%. Based on this result, we can conclude that the *P. australis* coastal marsh was an emission source of  $H_2S$ . The emission of  $H_2S$  presented a characteristic of single-peak change. As the temperature gradually increased from April to August, the *P. australis* began to sprout at the end of April and then started to grow vigorously. During this period,  $H_2S$  fluxes increased with an emission peak ( $7.65 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ ) in August. As the temperature began to decrease and plants were ripe and dead from September to December, the emission flux of  $H_2S$  showed a gradual decline with a low peak ( $0.09 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ ) in December. The flux of COS ranged from  $-1.10 \mu\text{g}/(\text{m}^2 \cdot \text{h})$  to  $3.32 \mu\text{g}/(\text{m}^2 \cdot \text{h})$  with an average emission intensity of  $1.05 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ , indicating that the *P. australis* coastal marsh was also a source of COS. This conclusion is different from the result of study in the *Calamagrostis angustifolia* wetlands of Sanjiang Plain in which COS is absorbed by the *C. angustifolia* wetlands (Li et al., 2006b). In addition, it was found that the coefficient of variation was up to 113.3%, such a greater variation showed that the emission of COS was affected by many factors that can vary dramatically during different periods. From April to May, the COS fluxes increased and then decreased, presenting an absorption peak with an absorption value of  $-1.10 \mu\text{g}/(\text{m}^2 \cdot \text{h})$  in June, which may be correlated with the vigorous growth of plants during this period. Plants are considered as the biggest sink of COS, and their process of growth can boost the metabolism of COS and greatly influence their emission (Fall et al., 1988; Li et al., 2006b). In July, the COS emission fluxes reached the maximum value ( $3.32 \mu\text{g}/(\text{m}^2 \cdot \text{h})$ ), then from August to December, the COS emission fluxes decreased.

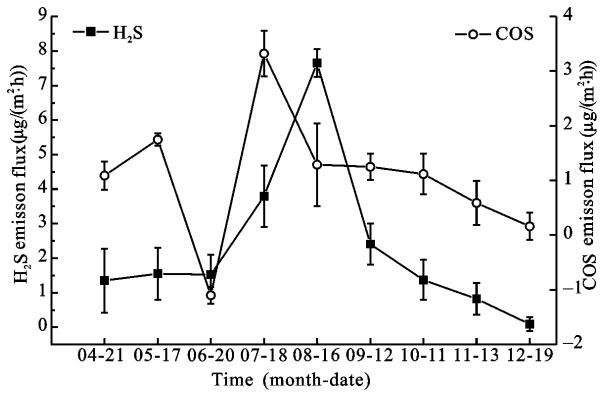


Fig. 4 Seasonal variations of  $H_2S$  and COS emission fluxes from *Phragmites australis* coastal marsh

### 3.3 Diurnal variations of H<sub>2</sub>S and COS emission fluxes

Measurements of diurnal variation of H<sub>2</sub>S and COS emission fluxes from the *P. australis* coastal marsh were performed on 19–20 June. The results are shown in Fig. 5. The diurnal variation of H<sub>2</sub>S emission flux changed inconsistently. Its 24-h emission fluxes ranged from 0.35 µg/(m<sup>2</sup>·h) to 2.90 µg/(m<sup>2</sup>·h) with an average value of 1.42 µg/(m<sup>2</sup>·h), and the coefficient of variation was 66.3%. The maximum and minimum fluxes of H<sub>2</sub>S were observed at 12:00 in the daytime and 0:00 in the evening, respectively. The diurnal variations of COS ranged from -1.65 µg/(m<sup>2</sup>·h) to 1.23 µg/(m<sup>2</sup>·h) with an average value of 0.45 µg/(m<sup>2</sup>·h), and the coefficient of variation was up to 264.6% that varied similarly to seasonal variation with a greater variability. The COS fluxes reduced gradually from 8:00 a.m. to 12:00 a.m., and the maximum absorption value was -1.65 µg/(m<sup>2</sup>·h) at 12:00 a.m. According to literature report, plants are the most important sink of COS, and plants can absorb COS through their stomata (Melillo and Steudler, 1989). Besides the absorption of COS through stomata, some other mechanism could also be responsible for the better absorption performance of *P. australis* during this period. However, further research is required to examine the way in which *P. australis* absorbs COS as well as metabolic activities relating to COS absorption. From 12:00 a.m. to the second day 4:00 a.m., the COS emission first increased and then decreased.

### 3.4 Relationships between environmental variables and H<sub>2</sub>S, COS fluxes

The correlations between sulfur gas fluxes and environmental variables are shown in Table 1. Among them, only the correlation between temperatures (include air

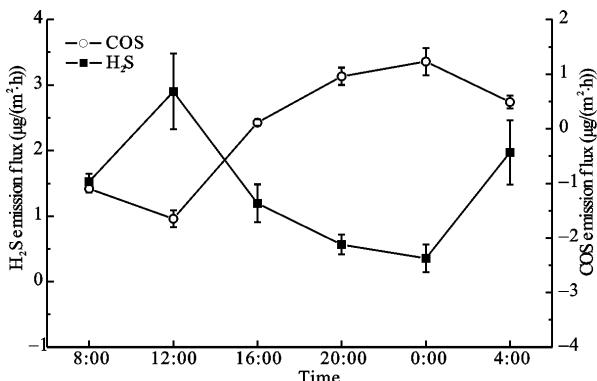


Fig. 5 Diurnal variations of H<sub>2</sub>S and COS emission fluxes from *Phragmites australis* coastal marsh

temperature, 0-cm, 5-cm, and 10-cm ground temperatures) and H<sub>2</sub>S emission fluxes were significant ( $p < 0.05$ ) (Table 1). The environmental variables determined in the *P. australis* coastal marsh were excluded in the stepwise linear regression. The 0-cm ground temperature ( $X$ ) was the dominant factor controlling the H<sub>2</sub>S emissions ( $Y$ ) in *P. australis* coastal marshes ( $Y = 0.133X - 0.538$ ,  $R^2 = 0.644$ ,  $P = 0.009$ ). However, for the COS fluxes in *P. australis* coastal marshes, the environmental variables determined during sampling periods were all excluded, indicating that COS fluxes were regulated by multiple site-specific factors.

## 4 Discussion

### 4.1 Effect of seasonal variables on sulfur gases emission

Previous studies indicated that the sulfur gas emissions are affected by seasons (Delaune *et al.*, 2002, Li *et al.*, 2014). In this study, it was found that the emission fluxes of H<sub>2</sub>S and COS were dramatically influenced by seasonal variation. From a whole-year perspective, the temperature is relatively higher and plants grow vigorously from May to October. While the temperature is relatively lower and plants are in dormant from November to April in the following year. Therefore, the average emission fluxes of H<sub>2</sub>S and COS during plant growing season and non-growing season were calculated separately (Table 2). As shown in Table 2, the average H<sub>2</sub>S emission in plant growing season was 3.05 µg/(m<sup>2</sup>·h), which was about 4.0 times the average value in the non-growing season (0.75 µg/(m<sup>2</sup>·h)). Similarly, during plant growing season, the average emission flux of COS was 1.27 µg/(m<sup>2</sup>·h), which was about 2.1 times the average value of non-growing season (0.61 µg/(m<sup>2</sup>·h)). According to literature report, the emission of H<sub>2</sub>S and COS mainly occurs during plant growing season, and the growth process of plants has significant roles on the emission of sulfur gases (Li *et al.*, 2006b; Whelan *et al.*, 2013). However, no studies have directly determined the roles that plants play during the emission of sulfur gases or the related functional mechanism concerned in this study. All these remain to be discussed in detail in the following research.

### 4.2 Effect of environmental factors on emission of sulfur gases

All the environmental factors during the measured periods

**Table 1** Pearson correlation analysis between  $H_2S$ , COS fluxes, and environmental factors

| Item   | Air temperature | Ground temperature |        |        | Electrical conductivity (EC) |         | Soil moisture |         |
|--------|-----------------|--------------------|--------|--------|------------------------------|---------|---------------|---------|
|        |                 | 0 cm               | 5 cm   | 10 cm  | 0–5 cm                       | 5–10 cm | 0–5 cm        | 5–10 cm |
| $H_2S$ | 0.760*          | 0.802**            | 0.739* | 0.790* | 0.046                        | 0.308   | -0.229        | 0.101   |
| COS    | 0.395           | 0.410              | 0.354  | 0.387  | -0.302                       | 0.090   | -0.525        | 0.026   |

Notes: \* $P < 0.05$ ; \*\*  $P < 0.01$ .

**Table 2**  $H_2S$  and COS fluxes in warm season (May–October) and cold season (November–April) from *Phragmites australis* coastal marsh ( $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ )

| Variety | Annual average | Growing season | Non-growing season |
|---------|----------------|----------------|--------------------|
| $H_2S$  | 2.28           | 3.05           | 0.75               |
| COS     | 1.05           | 1.27           | 0.61               |

varied due to the hydrology, seasons, plants, and so on, which would influence the magnitudes and variations of  $H_2S$  and COS emissions (Istvan and Delaune, 1995; Delaune *et al.*, 2002; Li *et al.*, 2006b). Previous studies have indicated that temperatures have dramatic influences on sulfur gas emissions (Staubes *et al.*, 1989). In this study, we found the correlations between  $H_2S$  flux and temperatures were significant ( $P < 0.05$ ), while the correlations between COS flux and temperatures were not significant ( $P > 0.05$ ). This conclusion is consistent with the report of Kanda *et al.*, (1992), which studied the emission of sulfur gases in rice, wheat, and corn fields. In addition, soil salinity content is considered as a key factor that affects the vegetation distribution along the Yellow River delta wetland (He *et al.*, 2009). In this study, we used electrical conductivity (EC) to represent the soil salinity. However, it turned out that the correlations between EC and  $H_2S$ , COS emission fluxes were not significant ( $P > 0.05$ ) (Table 2). Previous study on the correlations between the emission flux of sulfur gases and soil salinity showed that the impact of salinity is dependent on the type of sulfur gases (Xing *et al.*, 2007). Since sulfur-oxidizing microorganisms live in different soil layers for different desulphurization and oxidation processes and have different adaptability to salinity,  $H_2S$  is mainly produced during the dissimilatory reduction of sulfate, which is completed by sulfate-reducing bacteria (Xing *et al.*, 2007). Dissimilatory sulfate-reducing bacteria lay in deep soil layers and their growth is influenced by soil salinity content, and higher salinity in the soil may suppress the growth of sulfate-reducing bacteria (Hironta *et al.*, 2007). Our results indicated that the correlations between soil moisture and

$H_2S$ , COS emission fluxes were not significant ( $P > 0.05$ ) either. However, there was a negative correlation between soil moisture at the 0–5 cm depth and  $H_2S$ , COS fluxes, and a positive correlation between soil moisture at the 5–10 cm depth and  $H_2S$ , COS fluxes, indicating that the soil moisture in different soil depth had different effects on sulfur gas emissions. This could be attributed to the fact that soil water content of the observation point did not meet the water requirement for the vigorous growth of dissimilatory sulfate-reducing bacteria. In general, the optimal soil water content for sulfur gas emissions ranges between 50%–75% (Qiao *et al.*, 2000), which is also the favorable growth condition for other soil microorganisms (Chen *et al.*, 1989).

Besides the poor correlations between the sulfur gas fluxes and EC, soil moisture, our studies also demonstrated that other factors, such as soil substrate, Eh, and vegetation type might play important roles in the generation and emission of sulfur gases and reduce the impact of EC and soil moisture. Due to the limited objective conditions, we only measured several environmental factors during the sampling period. Therefore, more in-depth and comprehensive research is needed to discover and further understand the key factors and the release mechanism of sulfur gases.

#### 4.3 Comparisons with other measurements in wetlands

Previous studies that have examined the  $H_2S$  and COS emissions from different coastal marshes and fresh marshes reported that the  $H_2S$  and COS fluxes are in the range of 0.00 to 79.2  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  and -2.18 to 18.69  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ , respectively (Table 3). The magnitudes of  $H_2S$  fluxes determined in this study were in the range of 0.09–7.65  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ , which were higher than those from freshwater marshes in the Sanjiang Plain, Northeast China and Louisiana Gulf Coast (Delaune *et al.*, 2002; Li *et al.*, 2006b), but significantly lower than those from the brackish marsh in Louisiana Gulf Coast (5.29–79.2  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ ) (Delaune *et al.*, 2002). In addition,

**Table 3** Literature data of H<sub>2</sub>S and COS emissions from different marshes

| Location                                  | Marsh type         | Vegetation                        | H <sub>2</sub> S flux ( $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ ) | COS ( $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ ) | Reference                    |
|-------------------------------------------|--------------------|-----------------------------------|---------------------------------------------------------------------|---------------------------------------------------|------------------------------|
| Yellow River estuary of China             | Coastal marsh      | <i>Phragmites australis</i>       | (0.09–7.65) <sup>b</sup> 2.28 <sup>a</sup>                          | (0.16–1.75) <sup>b</sup> 1.05 <sup>a</sup>        | This study                   |
|                                           | Coastal marsh      | <i>Suaeda salsa</i>               | (2.00–7.31) <sup>b</sup> 4.97 <sup>a</sup>                          | (–1.16–2.52) <sup>b</sup> 0.92 <sup>a</sup>       | Li <i>et al.</i> , 2014      |
| Mustang Island of USA                     | Coastal salt marsh | <i>Batis maritima</i>             | –                                                                   | (11.03–15.36) <sup>b</sup> 13.19 <sup>a</sup>     | Whelan <i>et al.</i> , 2013  |
| Sanjiang Plain of Northeast China         | Fresh wetland      | <i>Calamagrostis angustifolia</i> | (0.00–1.08) <sup>b</sup> 0.34 <sup>a</sup>                          | (–2.18–0.92) <sup>b</sup> –0.29 <sup>a</sup>      | Li <i>et al.</i> , 2006b     |
| Ariake Sea of Japan                       | Tidal flat         | Muddy                             | (0.07–1.16) <sup>b</sup> 0.68 <sup>a</sup>                          | –                                                 | Azad <i>et al.</i> , 2005    |
|                                           |                    | Sandy                             | (0.29–0.81) <sup>b</sup> 0.56 <sup>a</sup>                          | –                                                 |                              |
| Mississippi River                         | Salt marsh         | <i>Sparina alterniflora</i>       | (0.52–5.88) <sup>b</sup> 2.46 <sup>a</sup>                          | (0.83–10.98) <sup>b</sup> 6.63 <sup>a</sup>       |                              |
| Deltaic Plain region of coastal Louisiana | Brackish marsh     | <i>Sparina patens</i>             | (5.29–79.2) <sup>b</sup> 21.22 <sup>a</sup>                         | (1.63–18.69) <sup>b</sup> 6.05 <sup>a</sup>       | Delaune <i>et al.</i> , 2002 |
|                                           | Fresh marsh        | <i>Sagittaria lancifolia</i>      | (0.00–1.13) <sup>b</sup> 0.30 <sup>a</sup>                          | (0.32–3.42) <sup>b</sup> 1.09 <sup>a</sup>        |                              |

Notes: a, means in different observation periods; b, values in brackets are the range of H<sub>2</sub>S and COS emission fluxes

the magnitudes of COS fluxes determined in this study were in the range of –1.10–3.32  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ , which were lower than those from coastal marshes on Mustang Island and Louisiana Gulf Coast, and were completely different from the fresh marsh in the Sanjiang Plain, Northeast China that absorbed COS from the atmosphere.

There are several reasons why substantial variation exists in the results from different studies. First, the soil physicochemical characteristics, such as soil texture, moisture content, organic carbon content, soil microorganisms, and soil salinity are substantially different in different study sites. Reduced gas emission is strongly associated with habitat and salinity gradient (Delaune *et al.*, 2002). Second, the chemical and biological properties of soil under different vegetation types lead to different emission mode of sulfur gases. Plants can emit COS and vegetation are the largest sources of COS (Whelan *et al.*, 2013). In contrast, Li *et al.* (2006b) indicated that plants can absorb COS. Third, different time of the year can be an important factor affecting sulfur emissions since microorganism is regulated by temperature. Delaune *et al.* (2002) and Li *et al.* (2014) both found that the sulfur gas emissions rates are higher during the warmer months compared to the colder months.

## 5 Conclusions

(1) The fluxes of H<sub>2</sub>S and COS from the *P. australis* coastal marsh in the Yellow River estuary exhibited distinct seasonal variations. The H<sub>2</sub>S fluxes ranged from 0.09  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  to 7.65  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  with an average emission flux of 2.28  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ . The COS fluxes ranged from –1.10 to 3.32  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$  with the average emission

of 1.05  $\mu\text{g}/(\text{m}^2 \cdot \text{h})$ . Therefore, the *P. australis* coastal marsh in the Yellow River estuary was the emission source of both H<sub>2</sub>S and COS.

(2) The diurnal variations of H<sub>2</sub>S and COS fluxes from the *P. australis* coastal marsh in the Yellow River estuary were also evident. The fluxes of H<sub>2</sub>S and COS were the highest at 12:00 a.m., however, H<sub>2</sub>S was emitted, and COS was absorbed. The lowest fluxes of H<sub>2</sub>S and COS were at 0:00 a.m. and 4:00 p.m., respectively.

(3) The H<sub>2</sub>S and COS fluxes were both higher in plant growing season than in the non-growing season. It was found that temperature had a dramatic influence on the H<sub>2</sub>S fluxes, and the 0-m temperature (*X*) was the dominant factor that regulated the H<sub>2</sub>S emissions (*Y*) in *P. australis* coastal marshes ( $Y = 0.133X - 0.538$ ,  $R^2 = 0.644$ ,  $P = 0.009$ ). However, the dominant factors impacting COS fluxes have not been found in this study. Therefore, in-depth and comprehensive studies on other related factors, such as vegetation, sediment substrates, and tidal action are needed to discover and further understand the key factors and the release mechanism of sulfur gases.

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