Distribution and Release of Volatile Organic Sulfur Compounds in Yangcheng Lake

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Abstract: Volatile organic sulfur compounds (VOSCs) function as a water–atmosphere link in the global sulfur cycle. It is generally believed that the vast majority of VOSCs are released from the ocean. However, due to the pervasive eutrophication and pollution of inland waters, the VOSC production and emission in rivers, lakes and reservoirs are attracting more attention. In this study, the temporal and spatial distributions of three VOSCs, including methanethiol, Dimethyl sulfide, and dimethyl disulfide in Yangcheng Lake, a eutrophic shallow lake, are investigated monthly and seasonally. Results show that VOSCs are higher in summer and autumn, with the western region as a hotspot. Our results show a positive correlation between VOSC and phytoplankton biomass (p < 0.05). Interestingly, from algal phylum composition, all the phylum, except those with low biomass, played a positive effect on VOSCs’ concentration. We did not find any specific phylum or species of cyanobacteria that contributed solely to the VOSCs. The water-air effluxes of Dimethyl sulfide (DMS) are estimated by a stagnant film model. The DMS effluxes from Yangcheng Lakes were higher than deep lakes and similar to the ocean, indicating that VOSCs, particularly DMS, in those eutrophic shallow lakes were non-negligible.

Keywords: volatile organic sulfur compounds; Dimethyl sulfide; eutrophic lake; efflux; phytoplankton

1. Introduction

Volatile organic sulfides compounds (VOSC) play an important role in the global sulfur cycle and contribute significantly to total atmospheric sulfide [1]. Dimethyl sulfide (DMS) was one of the important and ubiquitous volatile organic sulfides [2,3], with nearly 90% of the atmospheric biogenic sulfide released from the ocean [4,5]. DMS was oxidized in the atmosphere to sulfate aerosols and cloud condensation nodules, and the large number of aerosols and cloud condensation nodules in the atmosphere will reduce the solar radiation received by the Earth’s surface, and in this way affect the Earth’s climate change [6]. Under atmospheric circulation transport, the acidity of rainfall in uncontaminated areas was contributed by VOSC oxidation products [7]. Many VOSCs could produce irritating odor and damage the nervous system in excessive concentration. Among them, methanethiol (MT) and dimethyl disulfide (DMDS) are also important VOSCs in aquatic systems, as a precursor and degradation product of DMS.

Algal were considered to be important producers of VOSC, both in marine- and freshwaters [8–10]. DMS was mainly derived from dimethylsulfiniopropionate (DMSP) in algal cells in the marine environment, which was released into the environment either actively by algal cells or passively through cell rupture [11,12]. Enzymes were released by certain bacteria or phytoplankton cleaved DMSP into DMS and acrylic acid. The ocean was not only a source of VOSC but could also be a sink by bacteria consumption [13], in which DMS was converted to dimethylsulfoxide (DMSO) under sunlight exposure [14]. A large number of studies on VOSC had focused on the marine environment and the
effects of biological and chemical factors in the process of VOSC production or depletion in the surface ocean had been clearly described. This was dwarfed by the amount of literature on investigating the mechanisms of VOSC in freshwater environments. VOSC was commonly found in freshwater environments, especially in black smelly water bodies as a major contributor to odor. Some literature has found that the source and sink of DMS in the freshwater environment were distinct from the marine environment in the following ways: (1) active release of DMS from algal cells, (2) release of methionine from algal cell rupture generated by microbial lysis [15,16], (3) reduction of sulfate to reduced sulfur driven by sulfate-reducing bacteria and then generated under methylation [17]. From a biogeochemical perspective, the major precursor substances of DMS, similar to DMSP, have not been found in freshwater environments. Moreover, dimethyl disulfide and dimethyl trisulfide, which were less frequently recorded in the ocean, were contradictorily found in freshwater lakes.

As an important source of drinking water in the Suzhou area, Yangcheng Lake also functions as an aquaculture and tourist attraction, and was closely related to people’s lives. Since the rapid economic development in the last century, industrial, agricultural and domestic wastewater discharged into the lake has led to the deterioration of water quality and algal blooms. This has posed a threat to the security of drinking water sources in the lake. Wu et al. [18] previously found that phytoplankton in Yangcheng Lake was the main driver of the 2-methylisoborneol (2-MIB). VOSCs have not been systematically studied in Yangcheng Lake, and it’s not clear how phytoplankton relate to them.

In this study, we monitored the VOSCs content, lake water physicochemical properties and phytoplankton community structure in different areas of Yangcheng Lake and recorded the characteristics of the changes over a one-year period. The objectives were (1) to investigate the spatial and temporal distribution characteristics of VOSCs, (2) to reveal the influence of phytoplankton on VOSCs formation and production, and (3) To calculate the VOSCs effluxes.

2. Materials and Methods

2.1. Site Description

Yangcheng Lake (31°25′ N, 120°48′ E), a typical eutrophic shallow lake, is located in the south of Jiangsu Province as the third largest freshwater lake on the Taihu Plain, with a length of 17 km from north to south, a maximum width of 8 km from east to west, and an area of 117 square kilometers. The lake was divided into East zone (44.08%, 1.7–2.5 m deep), Middle zone (29.03%, 1.5–3.0 m deep) and West zone (26.89%, 1.7–2.5 m deep), those zones were divided by two longitudinal sand stalks (Figure 1). Among the three lake zones, the West zone receives upstream rivers, and the outflows are on the East zone. Since the 1950s, Yangcheng Lake outbreak with frequent algal blooms due to high nutrient input, especially in the West zone, where received the upstream rivers [19].

2.2. Sampling and Measurement

A total of 17 sampling sites were set up in Yangcheng Lake (Figure 1), of which sites 1–5 were located in the West zone, sites 6–10 were located in the Middle zone, and sites 11–17 were located in the East zone. All sites are sampled seasonally, with selected sites 3, 8, 13, 14, and 15 are sampled on a monthly basis. The dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature (T), and pH of the water were measured using a multi-parameter water quality meter (HORIBA U-50 Series). Samples for nutrients analysis were stored in plastic bottles in a 4 °C cooler box and refrigerated in the laboratory until analysis. Chemical indicators such as total phosphorus (TP), total nitrogen (TN), phosphate phosphorus (PO₄³⁻-P), nitrate nitrogen (NO₃⁻-N), ammonium nitrogen (NH₄⁺-N), and nitrite nitrogen (NO₂⁻-N) were determined using the standard methods for water and wastewater [20]. Dissolved organic carbon (DOC) was analyzed using a Multi N/C 3100(Analytik Jena, Germany). Samples of volatile organic sulfide were collected triplicated and sealed in 40 mL brown glass bottles without air bubbles and headspace. Phytoplankton
was sampled with a 1 L plastic bottle and preserved by 1% (10 mL) of Lugol’s reagent and left natural sinking for 48 h before transferring the algae (20 mL) from the bottom of the bottle to the reagent bottle. 20 mL of the concentrated sample was counted under an inverted microscope, referring to Utermöhl’s standard [21]. Identification was performed at the species or genus level using the most recent literature [22].

Figure 1. Locations of the sampling point in Yangcheng Lake.

2.3. VOSC Analytical Procedures

All samples of volatile organic sulfide were measured by the method of headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography (Agilent 7890A) with flame-ionization detection (GC-FID). Carboxen/polydimethylsiloxane (CAR/PDMS) fiber was selected for SPME fiber. Extraction conditions: 20 mL sample was added to a 40 mL headspace vial and magnetic stirring at 750 rpm at the temperature of 45 °C for 30 min. The fiber was desorbed in the injector at 250 °C for 7 min. The temperature of the detector was set to 250 °C. The auxiliary gas was composed of 50 mL/min of hydrogen, 65 mL/min of synthetic air, and 30 mL/min of helium. Separation was performed using a GS-GasPro capillary PLOT column (60 m × 0.32 mm I.D.). Helium was used as the carrier gas at a constant flow rate of 3 mL/min. The column temperature was controlled at 50 °C for 5 min, increasing from 25 °C/min to 250 °C for 7 min. The quantification was performed with the external standard method, and the method detection limits for MT, DMS, and DMDS were 18.6 ng/L, 28.5 ng/L, and 1.23 ng/L, respectively.

2.4. Estimation of Efflux of DMS

The methodology for estimating water-to-air DMS fluxes mainly includes a stagnant film model and eddy correlation [23,24]. For this study, the DMS effluxes were estimated based on a stagnant film model using the following equation [25]:

\[ F = k_w (c_w - c_g / H) \]  

where \( F \) is the water-to-air flux of DMS (\( \mu \text{mol} \cdot \text{m}^2 \cdot \text{d}^{-1} \)); \( k_w \) represents the gas exchange constant (\( \text{m} \cdot \text{d}^{-1} \)); \( c_w \) and \( c_g \) are the equilibrium concentrations of DMS in surface water and atmosphere respectively (\( \text{nmol} \cdot \text{L}^{-1} \)), and \( H \) represents Henry’s law constant. Frequently
used parameterizations Commonly used parameters for calculating gas transfer coefficients are LM86 [26], W92 [27], and N2000 [28]. The gas exchange constant in this study was calculated using N2000:

\[ k_w = \left( \frac{0.222U^2 + 0.333U}{Sc/660} \right)^{-1/2}, \tag{2} \]

where \( U \) is the wind speed (m·s\(^{-1}\)); \( Sc \) is the Schmidt number calculated following the method of Saltzman et al. [29]:

\[ Sc(t) = 2674.0 - 147.12t + 3.76t^2 - 0.038t^3, \tag{3} \]

where \( t \) is the temperature(°C).

The concentration of DMS in the atmosphere was too low to be almost negligible, so the formula for calculating the water-gas flux of DMS can be simplified as:

\[ F = k_wc_{w}, \tag{4} \]

3. Results

3.1. Water Physicochemical Properties

As shown in Figure 2, water temperature was 25.7 °C in summer and 12 °C in winter. pH values ranged from 6.97 to 8.99. The DO concentrations were lowest in summer (mg/L) and autumn (xx mg/L), but they were all greater than 4 mg/L at any seasons, which indicated Yangcheng Lake was well oxygenated, which also showed by ORP with mean of 162.69 ± 4.53 mV. There were significant seasonal differences of Nitrogen (TN, NO\(_3\)-N and NH\(_4\)-N), with concentrations decreasing greatly from spring to summer, and NO\(_3\)-N concentrations decreasing from 1.32 mg/L to 0.32 mg/L. The phosphorus (TP and DIP) did not show particularly pronounced seasonal fluctuations. The concentration of DOC were highest in summer and then gradually decrease in autumn and winter (Figure 3b–d).

Monthly variations of MT, DMS and DMDS are shown in Figure 3a. MT concentration increased from May to September, showing a hump-shaped tendency throughout the year. A progressive increase of DMS from May to July, followed by diminution. DMDS followed a similar pattern, with extremely low 1–2 order lower concentration than DMS. MT concentrations were 2–16 times higher than DMS and DMDS values.

Seasonal variation scales, MT, DMS, and DMDS concentrations in Yangcheng Lake water were highest in summer and then gradually decrease in autumn and winter (Figure 3b–d). MT ranged from 2.07–47.98 µg·L\(^{-1}\) in summer, with a mean concentration of 23.85 µg·L\(^{-1}\). Comparatively high concentrations of DMS were ranged from 0.10 µg·L\(^{-1}\) to 10.24 µg·L\(^{-1}\) in summer with an average of 1.59 µg·L\(^{-1}\). The average concentration and 87.5% of the site were above their odor threshold concentrations (OTC, 0.3–1.0 µg·L\(^{-1}\)). DMDS were low but detectable, with an annual mean concentration was 0.08 µg·L\(^{-1}\).

The spatial distribution of VOSCs in Yangcheng Lake showed significant variability in different seasons (Figure 4). Generally, MT, DMS, and DMDS were higher in the West zone, followed by the Middle zone, lowest in the East zone in all seasons. The concentrations of MT, DMS, and DMDS in all collected surface waters of Yangcheng Lake ranged from 0.04–47.98 µg·L\(^{-1}\), 0.01–10.232 µg·L\(^{-1}\), and 0.002–0.62 µg·L\(^{-1}\), respectively. The mean surface concentrations of MT, DMS, and DMDS in summer were 35.06 (22.76–47.98) µg·L\(^{-1}\), 1.38 (0.38–2.11) µg·L\(^{-1}\) and 0.33 (0.11–0.61) µg·L\(^{-1}\) in the West zone, 22.37 (7.01–39.83) µg·L\(^{-1}\), 0.92 (0.61–1.22) µg·L\(^{-1}\) and 0.35 (0.09–0.46) µg·L\(^{-1}\) in the Middle zone, and 26.79 (20.50–39.00) µg·L\(^{-1}\), 0.71 (0.25–1.93) µg·L\(^{-1}\) and 0.06 (0.05–0.08) µg·L\(^{-1}\), respectively. The surface distribution pattern of MT was very similar to that of DMDS, while DMS was slightly different from those, with hot spots observed more in the north of West zone. The surface distribution pattern of DMS and DMDS were similar in spring and winter with hot spots observed in the north
and south of the West zone, respectively. The MT concentration (site 8) in the Middle zone in autumn was as high as 30.53 µg·L⁻¹, which was significantly higher than the average concentration on the whole lake. This uniformed spatial pattern implied a possible mechanism that these VOSCs were related to the nutrients input and may to a eutrophic degree.

Figure 2. Seasonal variation of the physicochemical characteristics of the water in Yangcheng Lake.
3.3. Phytoplankton Community

A total of 79 species of phytoplankton were detected in the water bodies of Yangcheng Lake, with seven phyla: Cyanophyta, Chlorophyta, Cryptophyta, Bacillariophyta, Pyrrophyta, Chrysophyta, and Euglenophyta. Phytoplankton abundance varied considerably in different seasons (Figure 5a), with summer and autumn being the growing seasons for phytoplankton abundance reaching $2.98 \times 10^8$ ind/L and $5.39 \times 10^8$ ind/L, respectively. Cyanophyta, Chlorophyta and Bacillariophyta were the main phyla in the water column. Cyanophyta was the most abundant phytoplankton in summer and autumn. For cyanobacterial community structure (Figure 5b), seven species of cyanobacteria were
detected including *Microcystis sp.*, *Anabaena circinalis*, *Anabaena planctonica*, *Spirulina sp.*, *Planktothrix sp.*, *Phormidioideae sp.*, *Merismopedia sp.* The 7 abundant cyanobacteria were: *Microcystis sp.* > *Planktothrix sp.* > *Anabaena planctonica* > *Merismopedia sp.* > *Anabaena circinalis* > *Phormidioideae sp.* > *Oscillatoria sp.* In summer, cyanobacterial abundance percentages of *Anabaena planctonica*, *Planktothrix sp.*, *Microcystis sp.*, *Anabaena circinalis*, *Aphanizomenon sp.*, *Pseudanabaena sp.*, *Merismopedia sp.* were 31.82%, 19.45%, 8.96%, 4.48%, 2.94%, and 0.47%, respectively. In autumn, cyanobacterial abundance percentages of *Microcystis sp.*, *Merismopedia sp.*, *Planktothrix sp.*, *Anabaena planctonica*, *Anabaena circinalis*, *Oscillatoria sp.*, *Phormidioideae sp.* were 43.59%, 16.96%, 16.47%, 2.5%, 1.49%, and 1.49%, respectively. The abundance of other phytoplankton phyla was less in summer and autumn. For example, *Westella sp.* had nearly half of the abundance of all Chlorophyta in summer. The abundance of only one species of Cryptomonas, *Cryptomonas ovata*, was 5.9%. In autumn, more than 60% of the total abundance of *Aulacoseira granulata* was found in the diatom phylum.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (a) Seasonal variation in phytoplankton abundance; (b) analysis of seasonal differences in phytoplankton community structure.
3.4. Efflux of DMS

The effluxes of DMS observed in Yangcheng Lake ranged from 0.03 μmol·m⁻²·d⁻¹ to 24.87 μmol·m⁻²·d⁻¹, with an average of 3.92 ± 4.86 μmol·m⁻²·d⁻¹ (Figure 6). Mean DMS effluxes were 1.74 ± 0.29 μmol·m⁻²·d⁻¹ in spring, 6.93 ± 1.11 μmol·m⁻²·d⁻¹ in summer, 8.33 ± 2.99 μmol·m⁻²·d⁻¹ in autumn and 1.18 ± 0.25 μmol·m⁻²·d⁻¹ in winter. The maximum DMS efflux appeared at site 3 (autumn) because of the combined effect of the highest wind speed (4.4 m·s⁻¹) and relatively high DMS concentration (0.26 μg·L⁻¹). By contrast, the minimum DMS efflux was observed at site 11 (Winter) with the lowest wind speed (0.9 m·s⁻¹).

![Figure 6. Efflux of DMS from Yangcheng Lake in different seasons.](image)

4. Discussion

4.1. Compared with Other Freshwater Lakes

VOSCs were detected in most freshwater lakes, whether deep or shallow, eutrophic or oligotrophic. Following a thorough review of the literature, we found that the distribution and concentration of DMS correlated with the depth and eutrophication of the lake (Table 1). In deep lakes, the vertical distribution of VOSC concentrations showed a hump-shaped pattern, with peaks in the mixed layer during the stratification phase and little levels in the surface waters. The concentration of DMS and DMDS in the Yangcheng Lake exceeded those in the surface waters of Linsley Pond [30] and were similar to those in the mixed layer. Compared with other deep lakes, the concentrations were lower than those detected in the mixed areas of Fayetteville Green Lake [31] and Cadagno Lake [32]. Hence these findings suggested that shallow lakes, such as Yangcheng Lake, would have high DMS effluxes. Different concentrations and distributions of VOSCs in deep and shallow lakes were strongly related to their production mechanisms. After deep lake from stratification, sulfate reduction was the dominant process generating VOSCs. During upward diffusion, the VOSCs might be consumed by microorganisms or chemically oxidized. This formed the highest concentration in the mixed layer.

Higher concentrations of DMS were detected in eutrophic lakes. In contrast, the detected concentrations in Yangcheng Lake were higher than Dongting Lake [33] and Kinneret Lake [34], and all of these eutrophic lakes had a greater concentration of DMS than the oligotrophic Constance Lake [35]. This phenomenon is probably related to algae, as eutrophic lakes were more likely to produce higher amounts of algae. The DMS in the surface waters of deep Kinneret Lake [36] was derived from a freshwater dinoflagellate named Peridinium gatunense that grows in the lake in spring. As a shallow eutrophic lake, Yangcheng Lake should have high VOSCs concentrations in its surface waters, which it
Both MT and DMDS concentrations were higher in its surface waters than in those of other lakes.

Table 1. VOSCs concentrations in other types of freshwater lakes.

<table>
<thead>
<tr>
<th>Regions</th>
<th>Time</th>
<th>VOSCs Concentration</th>
<th>Types of Lake</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fayetteville Green Lake</td>
<td>Fall of 2008</td>
<td>MT: 37.99–136.6 µg/L; DMS: 2.28–3.55 µg/L; DMDS: 2.72–6.92 µg/L (Mixing layer)</td>
<td>Deep lake</td>
<td>[31]</td>
</tr>
<tr>
<td>Linsley Pond</td>
<td>April–July 2004</td>
<td>DMS: 0.01–0.85 µg/L; DMDS: 0–0.81 µg/L (Mixing layer) MT: 0.086–0.63 µg/L DMS: 0.009–2.54 ng/L (Mixing layer)</td>
<td>Eutrophication deep lake</td>
<td>[30]</td>
</tr>
<tr>
<td>Cadagno Lake</td>
<td>July 1996</td>
<td>MT: 0.086–0.63 µg/L; DMS: 0.18–2.24 µg/L; DMDS: 2.72–6.92 µg/L</td>
<td>Eutrophication deep lake</td>
<td>[32]</td>
</tr>
<tr>
<td>Kinneret Lake</td>
<td>December 2014</td>
<td>DMS: 0.028–0.14 µg/L (surface layer of water) DMS: 0.01–0.02 µg/L (surface layer of water)</td>
<td>Eutrophication deep lake</td>
<td>[34]</td>
</tr>
<tr>
<td>Constance Lake</td>
<td>9–23 July 2013</td>
<td>DMS: 0.074–0.168 µg/L; DMDS: 0.008–1.28 µg/L Mean: 0.17 µg/L Median: 0.11 µg/L</td>
<td>Eutrophication shallow lake</td>
<td>[35]</td>
</tr>
<tr>
<td>Dongting Lake 100 lakes in the middle and lower reaches of the Yangtze River</td>
<td>July 2008</td>
<td>MT: 0.04–47.98 µg/L DMS: Mean: 0.55 µg/L Median: 0.002–0.62 µg/L</td>
<td>Eutrophication shallow lake</td>
<td>[37]</td>
</tr>
<tr>
<td>This study</td>
<td>2018–2019</td>
<td>MT: 0.04–47.98 µg/L DMS: Mean: 0.55 µg/L Median: 0.002–0.62 µg/L</td>
<td>Eutrophication shallow lake</td>
<td>[36]</td>
</tr>
</tbody>
</table>

1 Deep lake is defined as a lake with a stratification period.

The vertical distribution of VOSCs in lakes differed significantly from that in the ocean, where the concentration of VOSCs decreased with depth [38]. Concentrations of DMS in the surface water of Yangcheng Lake were higher than those in the open sea (0.12 µg/L) and comparable to those in the offshore area (0.62 µg/L) [39–41].

4.2. Analysis of the Influencing Factors and Sources of VOSCs in Yangcheng Lake

The production of taste and odor compounds was related to environmental factors such as nutrients [42,43], temperature [44], and organic matter [45] in the water column and VOSCs were also closely related to environmental physicochemical factors. From the results of the correlation between VOSCs and environmental factors in Yangcheng Lake water (Figure 7a), there were significant correlations between the three VOSCs and temperature, especially the MT had the strongest correlation with temperature (r = 0.74, p < 0.05). VOSCs were more prone to be produced at higher temperatures, and MT was more directly influenced by temperature among the three VOSCs, and it was probably the first to be produced because of its simple structure. MT and DMDS were also significantly correlated with DO. The negative correlation with VOSCs and DO implied that low dissolved oxygen conditions were easier to produce VOSCs [46].
Figure 7. Spearman correlation was used to indicate interrelation between VOSCs concentrations and physicochemical parameters \((n = 108)\) (a), as well as phytoplankton abundance \((n = 108)\) (b). The asterisk indicates a significant difference, \(p < 0.05\).

Yang et al. [47] suggested that the taste and odor compounds were associated with ultra-high NH\(_4\)-N concentrations. In contrast, our results showed DMS and DMDS were significantly negative correlations with NH\(_4\)-N concentrations. Deng et al. [33] observed positive relationships between DMS and TN in Dongting Lake. Previous studies also found
that TN had a significant positive correlation with DMS and DMDS in Taihu Lake [48,49]. However, our study found no relationship between DMS and TN, whereas MT and DMDS showed a significant negative correlation. Significant correlations were also found between MT and TN:TP ratio.

The results of this study indicate that in Yangcheng Lake, the production of VOSCs was unclear with nitrogen. Concentrations of TN, NO$_3$-N, and NH$_4$-N were unable to be a signal for the presence of large amounts of VOSCs. MT and DMDS were correlated significantly with DOC. This is in agreement with the results of the laboratory water column [48] and Taihu Lake [49]. Additional taste and odor compounds discovered in the lake, such as 2-methylisoborneol, β-ionone, and β-cyclocitrinal, were related to organic debris [50]. High concentrations of DOC may trigger massive production of VOSCs.

Phytoplankton was a source of these taste and odor compounds. Higher quantities of VOSCs were frequently observed in regions of intense algal development [51], indicating a strong link between VOSCs production and phytoplankton. Deng et al. [37] found a feedback mechanism between phytoplankton and DMS concentrations in both marine and freshwater environments. The concentrations of DMS and chl-a were reported to have a significant positive correlation in Constance Lake [35]. Similar trends observed in phytoplankton abundance and VOSCs concentrations indicated that phytoplankton in Yangcheng Lake might be a key source of VOSCs. Six cyanobacteria with high abundance in this study, as well as other phytoplankton phyla, were subjected to bivariate correlation analysis to further investigate the association between VOSC and phytoplankton in Yangcheng Lake (Figure 7b).

Correlation analysis showed that VOSCs had significant correlation relationships with various phytoplankton in Yangcheng Lake. Cyanophyta had a significant correlation with MT, DMS, and DMDS, with $r$ up to 0.44, 0.27, and 0.38, respectively. This is in agreement with the results of Taihu Lake where VOSCs were considered to be produced from cyanobacterial bloom [52,53]. The top four cyanobacteria in terms of abundance were Microcystis sp. (26.42%), Planktothrix sp. (17.68%), Anabaena planctonica (12.17%), and Anabaena circinalis (2.37%), respectively (Figure 5b), all significantly associated with VOSCs. A significant negative correlation was observed between Phormidioideae sp. and VOSCs ($r = -0.27, p < 0.05$), which might be due to the fact that its growth cycles do not coincide with the emergence cycle of VOSCs. Many species of cyanobacteria were significantly correlated with VOSCs, but none of them had a high correlation coefficient. Cyanophyta, Chlorophyta, Euglenophyta, Pyrrophyta, and Cryptophyta were all found to be significantly correlated with VOSCs. Cyanobacteria had a higher correlation coefficient with VOSCs, which was likely due to the fact that Cyanobacteria was the most abundant phytoplankton phylum in Yangcheng Lake. The low concentration of methionine in diatoms [54,55] may explain the lack of a significant association between diatoms with 9.65% abundance and VOSCs. Currently, no exact precursor substances for DMS have been found in freshwater. Sulfur-containing amino acid cleavage was thought to be one of the main sources of DMS [56–58]. Similarly, the lack of a significant correlation might be due to the poor contribution of low-abundance Chrysophyta (0.67%) to VOSC. Given the strong link between most phytoplankton and VOSC, phytoplankton (particularly cyanobacteria [59,60]) was extremely likely to be a source of VOSC.

### 4.3. Effluxes of DMS

Accurate estimates of the water-to-air fluxes of DMS are essential to understanding the global cycle of biogenic sulfur and its effect on the Earth’s radiation. The water-to-air fluxes of DMS exhibited significant variability caused by clear differences in DMS concentrations and wind speeds among the sampling point. Although the concentrations of DMS in surface water were higher in spring than in autumn, the water-to-air fluxes of DMS in autumn were far higher than that in spring due to the increase in wind speed.

Historical data of DMS effluxes in other freshwaters and different areas of the sea in the literature are summarized in Table 2. Comparing the DMS efflux from this study with
other freshwater lake, we can see that the effluxes in summer and autumn were about 2 times higher than the previously reported 4 µmol·m²·d⁻¹ in the Trout Lake in May-October 1988, which was similar to the DMS efflux range of lakes in northern Canada.

Table 2. Historical data of DMS effluxes in other freshwaters and different areas of the sea from published.

<table>
<thead>
<tr>
<th>Regions</th>
<th>Date</th>
<th>DMS Efflux (µmol·m²·d⁻¹)</th>
<th>DMS Efflux Estimating Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constance Lake</td>
<td>July 2013</td>
<td>0.295</td>
<td>Stagnant film model</td>
<td>[35]</td>
</tr>
<tr>
<td>Trout Lake</td>
<td>May–October 1988</td>
<td>4</td>
<td>Stagnant film model</td>
<td>[61]</td>
</tr>
<tr>
<td>Lakes (southeast of Kenora in northwestern Ontario)</td>
<td>1995; 1996</td>
<td>0.058–15</td>
<td>Stagnant film model</td>
<td>[62]</td>
</tr>
<tr>
<td>Salton sea</td>
<td>May–September 2006; October–June 2007</td>
<td>300</td>
<td>Stagnant film model</td>
<td>[63]</td>
</tr>
<tr>
<td>Yellow sea and Bohai sea</td>
<td>June 2011</td>
<td>4.87</td>
<td>Stagnant film model</td>
<td>[64]</td>
</tr>
<tr>
<td>North Pacific</td>
<td>May–June 2004</td>
<td>5.1</td>
<td>Eddy covariance</td>
<td>[23]</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>July 2007</td>
<td>5.9</td>
<td>Eddy covariance</td>
<td>[65]</td>
</tr>
<tr>
<td>Northeast Atlantic</td>
<td>June–July 2007</td>
<td>5.2</td>
<td>Eddy covariance</td>
<td>[66]</td>
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<tr>
<td>Ryder Bay</td>
<td>2013–2017</td>
<td>0.01–968</td>
<td>Stagnant film model</td>
<td>[67]</td>
</tr>
<tr>
<td>Ross sea</td>
<td>December 2004; November 2005</td>
<td>0.2–24.3</td>
<td>Stagnant film model</td>
<td>[68]</td>
</tr>
<tr>
<td>This study</td>
<td>Spring</td>
<td>1.74 ± 0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>6.93 ± 1.11</td>
<td>Stagnant film model</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>8.33 ± 2.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>1.18 ± 0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Compared to other areas of the sea, the mean DMS efflux in Yangcheng Lake in summer and autumn was generally higher than the sea except in the Antarctic region. Wang et al. [39] used artificial networks to extrapolate global oceanic DMS efflux in the range of 0.5–20 µmol·m²·d⁻¹, and the highest DMS effluxes were concentrated in the high latitude summertime oceans. The range of DMS effluxes in Yangcheng Lake was similar to that in the ocean, so the atmospheric transport of sulfur from freshwater lakes was not negligible.

5. Conclusions

Clear seasonal patterns of VOSCs (MT, DMS, and DMDS) were found in Yangcheng Lake. VOSC concentration began to rise in the spring and then began to fall in the autumn and winter. The formation of VOSCs was favored by higher temperatures. The strong association between DOC and VOSCs suggested that DOC may be a source of VOSC or a key factor in the production process. Important links were observed between phytoplankton and VOSC, and cyanobacteria may be the main contributors to VOSC in Yangcheng Lake. A comparison of VOSC concentration levels in other freshwater lakes revealed that eutrophic shallow lakes were more prone to accumulate higher concentrations of VOSC in surface waters. The issue of VOSC in the freshwater environment should not be restricted to the problem of smell and odor, but its sulfur efflux appears to be a portion that cannot be overlooked in the trend of progressive eutrophication of freshwater lakes. Based on the cyclic variations in physicochemical properties and phytoplankton observed in Yangcheng Lake, it was postulated that a high quantity of phytoplankton not only contributed considerably to VOSC production but also may have generated ideal environmental circumstances for VOSC development. Nevertheless, the mechanism of phytoplankton acting on VOSC in freshwater was unknown, necessitating more research into the biochemical process of VOSC formation by freshwater phytoplankton.
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Data Availability Statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

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