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# Automated, high frequency, on-line dimethyl sulfide measurements in natural waters using a novel "microslug" gas-liquid segmented flow method with chemiluminescence detection

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1   **Automated, high frequency, on-line dimethyl sulfide measurements in natural**  
2   **waters using a novel “microslug” gas-liquid segmented flow method with**  
3   **chemiluminescence detection**

4

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7

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15

16   **Abstract**

17   Dimethyl sulfide (DMS) is the major biogenic volatile sulfur compound in surface  
18   seawater. Good quality DMS data with high temporal and spatial resolution is desirable  
19   for understanding reduced sulfur biogeochemistry. Here we present a fully automated  
20   and novel “microslug” gas-liquid segmented flow-chemiluminescence (MSSF-CL)  
21   based method for the continuous *in-situ* measurement of DMS in natural waters.  
22   Samples were collected into a flow tank and DMS transferred from the aqueous phase  
23   to the gas phase using a vario-directional coiled flow, in which microvolume liquid and  
24   gas slugs were interspersed. The separated DMS was reacted with ozone in a reaction  
25   cell for CL detection. The analytical process was automated, with a sample throughput  
26   of 6.6 h<sup>-1</sup>. Using MSSF for DMS separation was more effective and easily integrated  
27   with CL detection compared with the commonly used bubbling approach. Key

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parameters of the proposed method were investigated. The linear range for the method was 0.05-500 nM ( $R^2 = 0.9984$ ) and the limit of detection (3 x S/N) was 0.015 nM, which is comparable to the commonly used gas chromatography (GC) method and sensitive enough for direct DMS measurement in typical aquatic environments. Reproducibility and recovery were assessed by spiking natural water samples (river, lake, reservoir and pond) with different concentrations of DMS (10, 20 and 50 nM), giving relative standard deviations (RSDs)  $\leq 1.75\%$  ( $n = 5$ ) and recoveries of 94.4 – 107.8%. This fully automated system is reagent free, easy to assemble, simple to use, portable (weight ~5.1 kg) and can be left in the field for several hours of unattended operation. The instrumentation can provide high quality DMS data for natural waters with an environmentally relevant temporal resolution of ~9 min.

39

#### 40 **Keywords**

41 Dimethyl sulfide; Chemiluminescence; Natural waters; Segmented flow; Automated;  
42 On site analysis

43

#### 44 **1. Introduction**

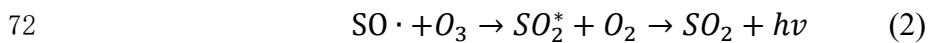
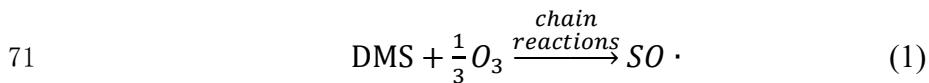
45 Dimethyl sulfide (DMS) is a climatically active biogenic gas with an estimated  
46 annual global emission of 28-31 Tg S a<sup>-1</sup>. Natural emissions account for approximately  
47 78% of the total natural reduced sulfur global flux to the atmosphere [1,2] by transfer  
48 from seawater, freshwater [3,4], soil [5,6] and plants [7]. After emission to the  
49 atmosphere, DMS can be oxidized to SO<sub>2</sub>, which is a precursor of sulfate aerosol  
50 particles that may act as cloud condensation nuclei (CCN) [8]. CCN are important for  
51 climate because they affect the radiative properties of the atmosphere and clouds by  
52 scattering solar radiation and influencing cloud microphysics and albedo [9,10].

53 DMS is volatile in natural waters and can be oxidized [11] and converted to other  
54 sulfur compounds by microorganisms [12]. The transient nature of DMS means that in-  
55 situ analysis is essential. Currently, the most commonly used method for DMS  
56 quantification is purge and trap gas chromatography (PT-GC) [13,14] coupled with  
57 flame photometric [15] or mass spectrometric detection [16]. These GC based

58 techniques involve bulky instrumentation, require controlled laboratory settings and  
59 have a relatively low sample throughput, which restricts the ability to make near-  
60 continuous measurements [17,18]. Techniques such as membrane inlet mass  
61 spectrometry (MIMS) [19], equilibrator inlet proton transfer reaction mass  
62 spectrometry (EI-PTRMS) [20-22] and atmospheric pressure chemical ionization-mass  
63 spectrometry (AP-CIMS) [23,24] have become attractive for real-time DMS analysis  
64 on research vessels. However, these devices are relatively heavy, fragile, expensive and  
65 labor intensive to deploy on a ship.

66 An alternative strategy for measuring DMS is using gas phase chemiluminescence  
67 (CL) based on the chain reaction of DMS with ozone to form the sulfur monoxide  
68 radical ( $\text{SO}\cdot$ ), which then reacts with ozone to produce light with a wavelength  
69 maximum ( $\lambda_{\text{max}}$ ) at 370 nm [25,26]. The reaction is summarized in eq. (1) and eq. (2).

70



73

74 Green *et al.* [27] adapted a laboratory-based gas phase CL instrument for real-time  
75 determination of DMS in marine samples. Air was bubbled through the sample to  
76 transfer DMS from the aqueous phase to the gas phase. DMS and ozone mixed in a  
77 reaction chamber and the CL signal was recorded using a photomultiplier tube. A short-  
78 pass optical filter was used to reduce CL interference from other gases but this also  
79 reduced the DMS signal by 89.7% and interference from methanethiol could not be  
80 eliminated. Toda's group have pioneered the development of simple methods for the in-  
81 situ measurement of DMS in seawater using gas phase CL in both sequential and  
82 batchwise approaches [28-31]. DMS was vaporized and introduced into the CL reaction  
83 cell by a physical shot or bubbling, while interferences from other gases were removed  
84 either by adding a heavy metal agent to the sample or by using a soda lime column.

85 Here we present a fully automated microslug segmented flow-chemiluminescence  
86 (MSSF-CL) system for the continuous measurement of DMS in natural waters. With

87 the proposed MSSF approach, nanomolar concentrations of DMS can be effectively  
88 transferred from the aqueous phase to the gas phase for CL detection. The whole  
89 analytical procedure, including *in-situ* sampling, separation, CL quantification and  
90 rinsing, was automated. This analytical system is easy to setup and operate, can be  
91 remotely operated and is light and portable (weight ~5.1 kg) and avoids the necessity  
92 of using any reagents other than oxygen. The performance of the automated system was  
93 demonstrated by several hours of unattended, high temporal resolution DMS  
94 measurement in the field.

95

## 96 **2. Experimental section**

### 97 **2.1. Reagents**

98 A 1.0 mM DMS stock solution was prepared by diluting a DMS certified standard  
99 (o2si, CA, USA) with methanol. The DMS stock solution was stored in a 20 mL glass  
100 vial with an aluminum screw top cap and airtight silicon septum at -10 °C in the dark  
101 to minimize evaporation. A 1.0 µM DMS working solution was prepared daily by  
102 dilution of the stock solution with Milli-Q water. A 10 ppmv DMS gas standard cylinder  
103 (in nitrogen (N<sub>2</sub>), Sichuan Zhongce Biaowu Technology, Chengdu, China) was used for  
104 calibration. The dilution of the DMS gas standard was achieved using a compressed N<sub>2</sub>  
105 cylinder ( $\geq$ 99.999% purity, Sichuan Qiao Yuan Gas, Chengdu, China). Compressed N<sub>2</sub>  
106 was also used as the gas source in the segmented flow line and the carrier gas to  
107 introduce DMS into the CL cell. An oxygen (O<sub>2</sub>) cylinder ( $\geq$ 99.99% purity, Sichuan  
108 Qiao Yuan Gas, Chengdu, China) was used as the source gas for ozone generation.

109

### 110 **2.2. Apparatus**

111 A peristaltic pump (YZ-15 pump head, BT50S driver, Lead Fluid Technology Co.,  
112 Ltd., Baoding, China) was used for water sampling. A set of three-way solenoid valves  
113 (VAS101, Riston, Jiashan, China) and a 9600-step syringe pump (PVS-100, Riston,  
114 Jiashan, China) equipped with a 10 mL syringe (Hamilton, CA, USA) were used for  
115 handling the aqueous samples and water. Ozone was generated by an ozone generator  
116 (M1000, Tonglin Technology, Beijing, China) with a maximum output of 1 g h<sup>-1</sup>. The

ozone output was adjustable by changing the generator working power. Mass flow controllers (S48 300/HMT, Horiba Metron Instruments, Beijing, China) were used to regulate gas flow rates in the analytical system. A glass made gas-liquid separator (Sichuan Shubo, Chengdu, China) was used for phase separation after the MSSF and the separated gas sample was injected into the CL detection system using an electrically actuated 6-port injection valve (Valco Instruments, Houston, USA) and a PTFE holding coil (2.5 m x 3.175 mm i.d.). The CL detection system comprised a CL reaction cell (40 mm x 25 mm i.d.) and a photomultiplier tube (PMT; R3550P, Hamamatsu Photonics, Japan). The reaction cell was made of stainless steel and the inside wall was chromium-plated to enhance light reflection. The PMT was located in an aluminum housing (95 mm x 55 mm i.d.) sealed from external light sources. An optical convex lens ( $d=25$  mm,  $f=25.4$  mm) was placed between the CL cell and the PMT to focus the light. The CL signal was recorded in photon counting mode using a multifunctional photon signal analyzer (Novaphoton Technology, Chengdu, China), with an integrated high voltage DC power supply for the PMT. The output from the detector was recorded in photon counting units (p.c.u.) and all CL intensity data are reported as the integral of p.c.u. over time. A schematic diagram of the CL system is shown in Fig. S-1.

134

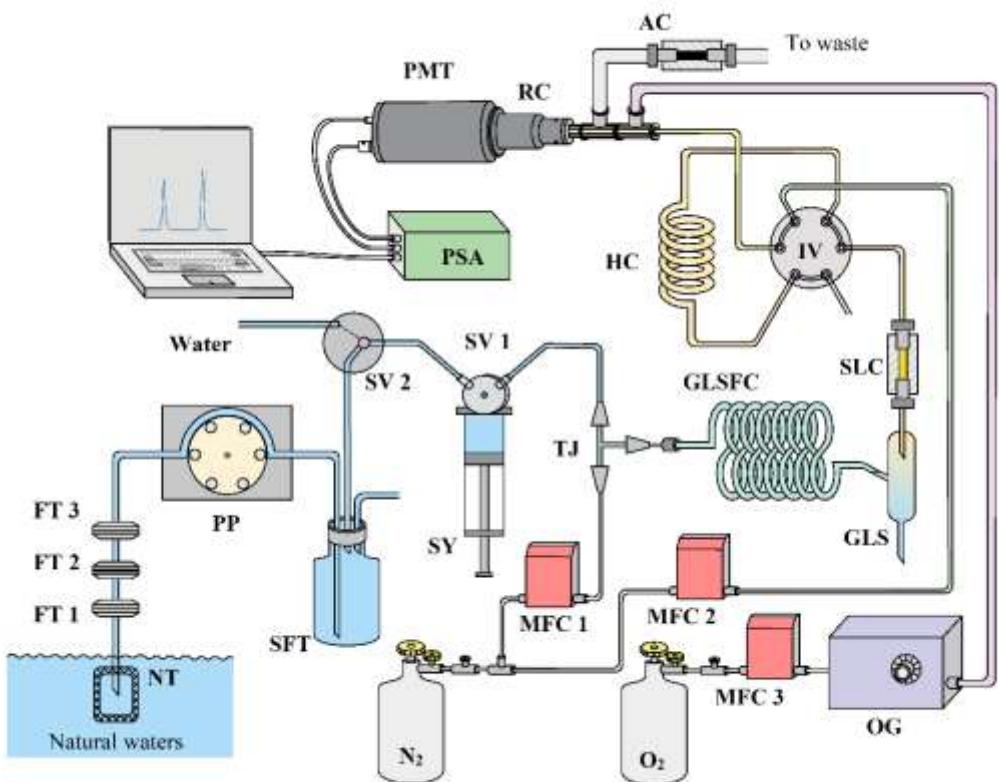
### 135 **2.3. Analytical procedures**

136 A schematic of the MSSF-CL instrument for the determination of DMS is shown  
137 in Fig. 1. Samples were collected by placing tubing with a 16 mesh (1.0 mm) nylon net  
138 over the opening below the water surface. With a peristaltic pump (PP) and a set of  
139 polyethersulfone (PES) filters (FT1, 50 mm x 100  $\mu\text{m}$ ; FT2, 50 mm x 10  $\mu\text{m}$ ; FT3, 50  
140 mm x 0.8  $\mu\text{m}$ ), samples were continuously collected into a 50 mL sample flow tank at  
141 200  $\text{mL min}^{-1}$ . The sample in the flow tank was either discharged to waste or held ready  
142 for analysis. 10 mL of sample was pulled into the syringe (SY) by the syringe pump  
143 (SP) at 150  $\text{mL min}^{-1}$  and subsequently expelled to the T-junction (PP, 0.3 mm i.d.) at  
144 2.0  $\text{mL min}^{-1}$ . Compressed  $\text{N}_2$  regulated by the mass flow controller (MFC) was  
145 delivered to the T-junction at a flow rate of 4.0  $\text{mL min}^{-1}$ . Segmented gas-liquid  
146 microslugs formed as the gas and water mixed at the T-junction and these microslugs

147 entered a vario-directional flow coil (PP, 20 m x 1 mm i.d., see Fig. 3 (c)). DMS  
148 transferred from the aqueous phase into the gas phase within the flow coil. The gas  
149 sample was separated in the gas-liquid separator and then passed through a soda lime-  
150 packed column that dried the gas stream and eliminated any potential signal  
151 interferences. Sample gas was collected in a holding coil (PTFE, 2.5 m x 3.175 mm i.d.)  
152 and a 6-port injection valve was switched periodically to pump the sample into the CL  
153 reaction cell at  $400 \text{ mL min}^{-1}$ . Ozone was delivered continuously into the CL reaction  
154 cell at  $200 \text{ mL min}^{-1}$ . DMS reacted with ozone in the cell to produce a CL signal, which  
155 was detected and amplified by the PMT and recorded by the photon signal analyzer in  
156 photon counting mode. Waste air was passed through an activated carbon column before  
157 discharge to the ambient environment. The system was rinsed three times with 10 mL  
158 of water, which was aspirated into the syringe and expelled towards the MSSF-CL system.  
159 The flow rate for both water and gas in the rinsing line was  $150 \text{ mL min}^{-1}$ , resulting in  
160 a 15 s period for a single washing cycle. The CL reaction cell and its connecting tubing  
161 for DMS introduction were shielded from light by wrapping them with aluminum foil.  
162 The photo of the proposed MSSF-CL analysis system was provided in Fig. S-2.  
163 Windows based, self-programmed software written in C++ was used to control the  
164 syringe pump, MFCs, solenoid valves and the injection valve. Details of the operation  
165 of these control units are shown in [Table S-3](#).

166

167



168

169 Figure 1. A schematic diagram of the proposed MSSF-CL instrument for the determination of DMS. NT, nylon net;  
 170 FT 1-3, filter; PP, peristaltic pump; SV 1 and 2, three-way solenoid valves; SFT, sample flow tank; SY, syringe; TJ,  
 171 T-junction; MFC 1-3, mass flow controllers; OG, ozone generator; GLSFC, gas-liquid segmented flow coil; GLS,  
 172 gas-liquid separator; IV, 6-port injection valve; HC, holding coil; SLC, soda lime column; RC, chemiluminescence  
 173 reaction cell; PMT, photomultiplier tube; PSA, photon signal analyzer; AC, active carbon column.

174

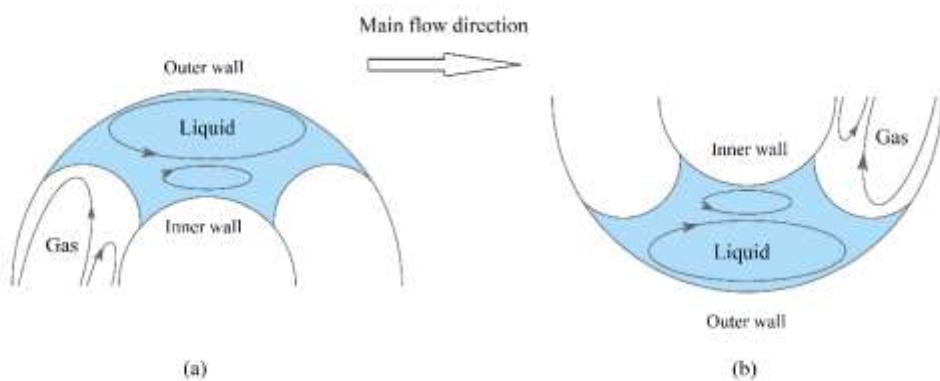
### 175 3. Results and discussion

#### 176 3.1. Flow and mixing regime

177 DMS must be effectively transferred from the aqueous phase into the gas phase  
 178 prior to its introduction into the CL cell. In a coiled, gas-liquid segmented flow,  
 179 centrifugal forces create a secondary flow and the liquid and gas slugs create two  
 180 counter rotating vortices that cause asymmetrical micro-recirculation towards the main  
 181 flow direction (see Fig. 2), resulting in increased mass transfer between the two phases  
 182 [32]. We used a 20 nM DMS solution to compare our gas-liquid segmented flow system  
 183 with the bubbling or ‘purging’ approach that is often used to transfer DMS from liquid

184 to gas phase (Fig. 3). DMS transfer from a 10 mL sample volume was 1.67-fold more  
185 effective using the gas-liquid segmented flow approach because the microslugs are a  
186 more stable and homogeneous gas-liquid dispersion system. DMS transfer is enhanced  
187 in the segmented flow compared to the bubbling approach because the surface area to  
188 volume ratio (gas-liquid contact area) is greater, the mass transfer diffusion distance is  
189 shorter and there is intense relative motion between the two phases [32-34]. Moreover,  
190 bubble films can form when air bubbles are introduced into the sample at higher speed,  
191 which could result in an inferior and unstable CL signal.

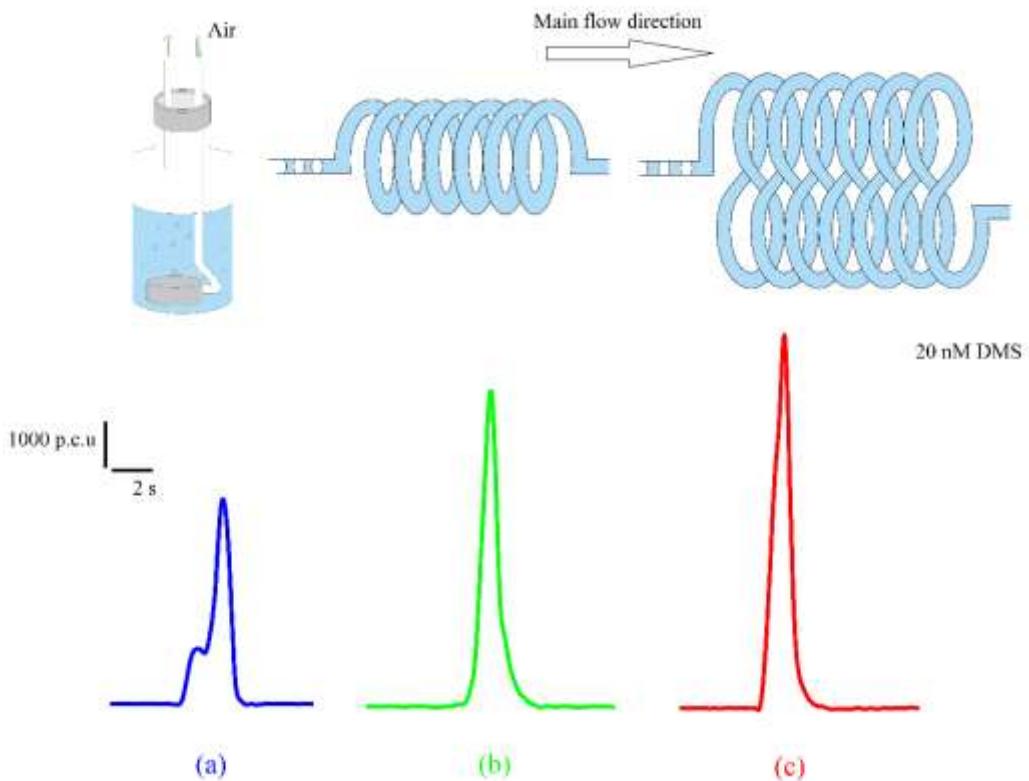
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193

194 Figure 2. Effect of gas and liquid slugs moving through a coiled tube in (a) clockwise and (b) counterclockwise  
195 directions.

196

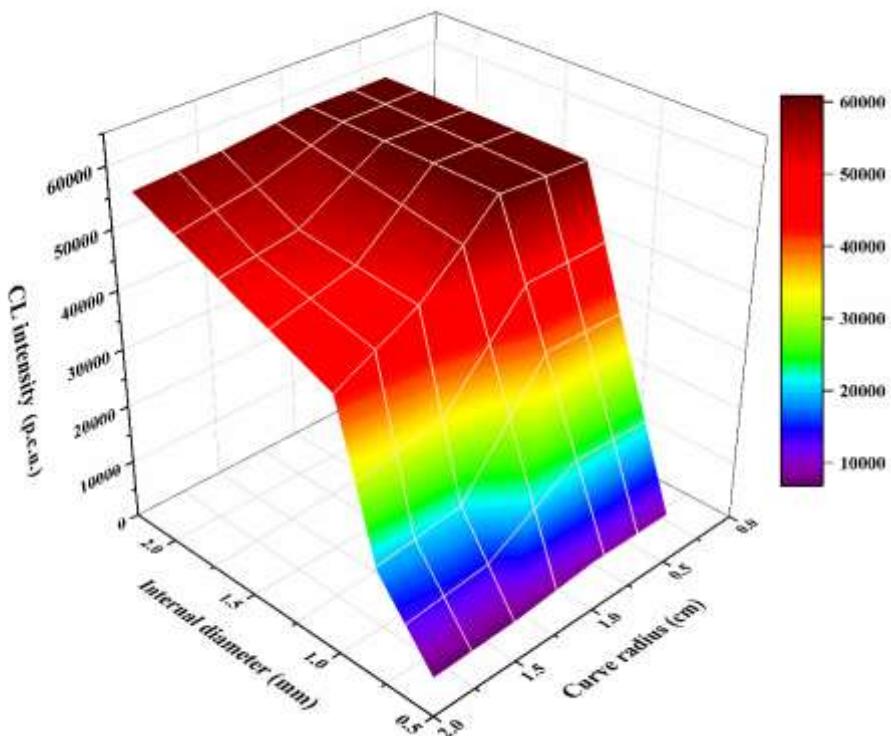


197  
198 Figure 3. A comparison of (a) bubbling, (b) unidirectional segmented flow  
199 for 20 nM DMS transfer. Bubbles were generated by introducing 20 mL of air through a quartz sand bubble stone.  
200 Both the unidirectional and vario-directional segmented flow setups used PP tubing (20 m x 0.79 mm i.d.) with 1 cm  
201 curve radius. Liquid and gas were delivered at 2.0 and 4.0 mL min<sup>-1</sup> respectively. Peak height recorded as photon  
202 counting units (p.c.u.).

203

204 We also compared vario-directional and unidirectional segmented flow. Vario-  
205 directional flow was achieved by entwining tubing on two glass rods in alternating  
206 clockwise and counterclockwise directions. The vario-directional flow gave a ~10%  
207 higher response than the unidirectional flow (Fig. 3). This may be because the rate of  
208 recirculation in liquid and gas slugs when the flow enters a coil is greater at the inner  
209 wall than at the outer wall. As the slugs move along the vario-directional segmented  
210 flow channel, the asymmetrical recirculation switches periodically (see Fig. 2), thereby  
211 increasing the relative motion between the two phases, resulting in enhanced DMS mass  
212 transfer. Note that the degree of this relative motion mainly depended on the size of the  
213 liquid and gas slugs and the curvature radius [33,35].

214 The geometry of the tubing (curve radius,  $R$ , and internal diameter,  $D$ ) in the gas-liquid  
 215 segmented flow coil significantly influences DMS mass transfer from the sample  
 216 microslugs (Fig. 3). A tighter coil radius enhances asymmetrical recirculation in the  
 217 microslugs, whilst increasing the internal diameter increases the contact area between  
 218 the gas and liquid phases and the retention time of the microslugs in the flow coil, all  
 219 of which enhance the CL intensity (see Fig. 4). However, we did not observe any  
 220 significant enhancement in CL intensity when  $D > 1$  mm and  $R < 1$  cm were applied,  
 221 suggesting that complete mass transfer was achieved at  $D = 1.0$  mm and  $R = 1.0$  cm and  
 222 hence these values were used for all subsequent experiments. Flow tubing with larger  
 223 internal diameter resulted in longer residence times (quantitative data for these  
 224 experiments are provided in Table S-4). The length of the segmented flow coil affected  
 225 the residence time of the microslugs in the tubing, which may have a positive  
 226 correlation on the efficiency of DMS mass transfer. We compared different length of  
 227 tubing (5, 10, 20 and 30 m). The efficiency of DMS mass transfer increased while the  
 228 tubing length increased from 5 to 20 m, and kept constant thereafter, indicating a  
 229 complete DMS mass transfer may occurred.



230

231 Figure 4. Effect of segmented flow tubing curve radius and internal diameter on 20 nM DMS mass transfer in MSSF-

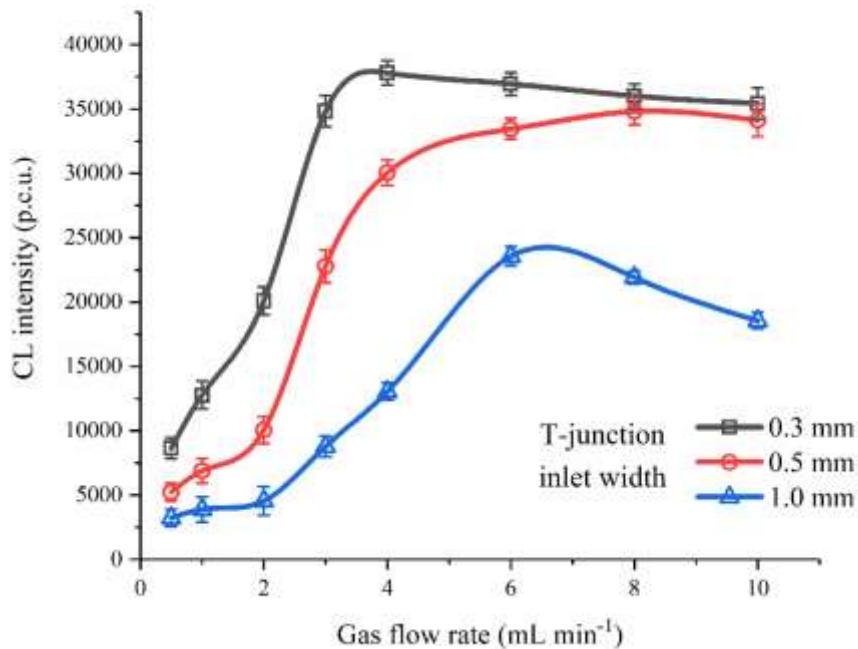
232 CL method (coil tubing length = 20 m; liquid flow rate = 2 mL min<sup>-1</sup>; gas flow rate = 4 mL min<sup>-1</sup>).

233

234 **3.2. T-junction geometry and gas / liquid flow rates**

235 Microslug formation in the proposed method was achieved using a T-junction and  
236 the size of the microslugs in the segmented flow were influenced by the dimensions of  
237 the T-junction [36], the flow rates of the fluid [37] and the relative viscosity of the two  
238 phases [38]. The effect of the T-junction inlet width and the gas flow rate were studied  
239 while keeping the sample flow rate constant at 2.0 mL min<sup>-1</sup> (Fig. 5). By increasing the  
240 gas flow rate, the gas and liquid drop volume ratio ( $V_{gd}/V_{ld}$ ) also increased, generating  
241 smaller liquid microslugs in the segmented flow. The total gas-liquid contact area was  
242 increased and DMS mass transferring consequently enhanced, resulting in a higher  
243 DMS signal. However, at higher gas flow rates (> 4.0 – 6.0 mL min<sup>-1</sup>), the DMS signal  
244 levelled off or decreased (Fig. 5). This may be because a higher flow rate leads to the  
245 use of a larger volume of gas, which is likely to dilute the DMS and ozone  
246 concentrations in the CL reaction cell. Moreover, the retention time of the microslugs  
247 in the segmented flow may be decreased at higher flows, resulting in reduction of DMS  
248 mass transfer efficiency. Different T-junction inlet widths (0.3 mm, 0.5 mm and 1.0 mm)  
249 were also compared. Smaller drops were generated when using a narrower inlet at the  
250 same flow rate, resulting in a higher DMS signal (Fig. 5). T-junction of inlet widths less  
251 than 0.3 mm was not investigated since it is unavailable. But the recovery for DMS  
252 measurements by using 0.3 mm inlet widths T-junction at gas flow rate of 4.0 mL min<sup>-1</sup>  
253 was 97.1% (n=3), indicating a complete DMS mass transfer. Consequently, the  
254 optimum conditions for generating the segmented microslugs were gas and sample flow  
255 rates of 4.0 and 2.0 mL min<sup>-1</sup> respectively through a 0.3 mm width T-junction.

256



257

258 Figure 5. Effects on CL intensity due to T-junction inlet width and gas flow rate through the coil. The segmented  
 259 flow setup used PP tubing (20 m x 1.0 mm i.d.) with a 1 cm curve radius and vario-directional flow. Error bars  
 260 represent  $\pm 1$  SD of triplicate measurements.

261

### 262 3.3. Effect of salinity on CL detection

263 It is important to be able to apply the MSSF-CL method to saline matrices in order  
 264 to study the biogeochemistry of DMS in natural waters. However, salt is often added to  
 265 aqueous samples to enhance the mass transfer of volatile compounds into the headspace  
 266 by lowering their partition coefficient [6,39]. A 20 nM DMS sample was spiked with  
 267 varying concentrations of NaCl (to give sample salinities, expressed as m/v NaCl, in  
 268 the range 0 - 5%, m/v), and subjected to analysis by MSSF-CL. As shown in Table 1,  
 269 no significant signal variation was observed, i.e. all results were within the mean  $\pm 2$   
 270 SD ( $58,800 \pm 650$ ; SD, standard deviation). Further evidence of the suitability of the  
 271 method for analyzing saline samples is shown in Fig. 6, which compares calibration  
 272 graphs for DMS (0 - 100 nM) in 0% and 3.5% NaCl. There is no significant difference  
 273 ( $t_{\text{calc}} = 4.956$ ;  $t_{\text{tab}} = 9.605$ ) between the slopes of the two calibrations.

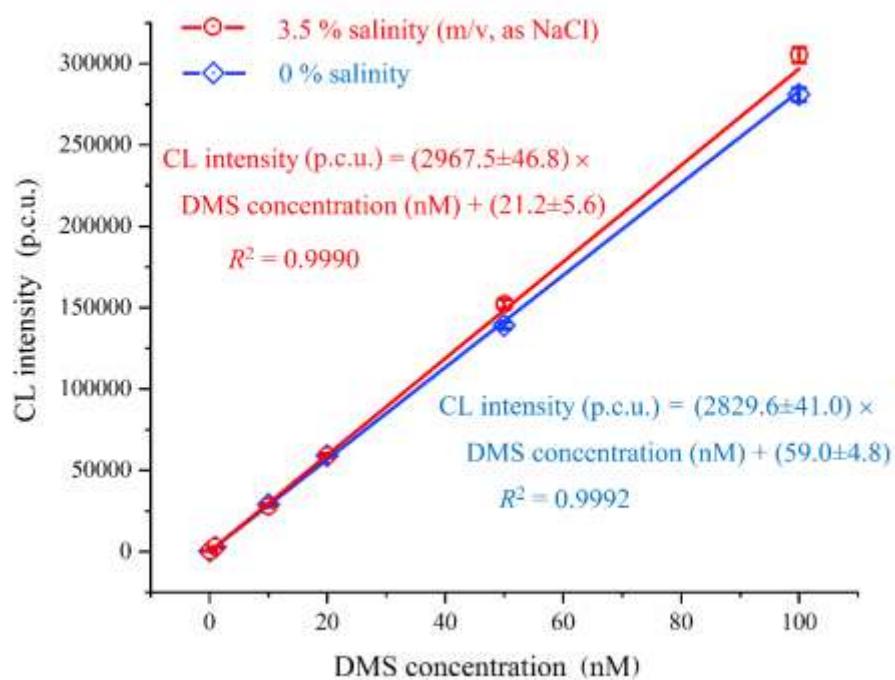
274

275 Table 1. Effect of sample salinity (as NaCl) for 20 nM DMS measurement by MSSF-CL.

Sample salinity (%, m/v)	CL intensity (p.c.u.)	RSD (n=3) (%)
0.0	59,200	1.3
0.5	58,500	1.7
1.0	58,700	1.6
1.5	58,800	1.6
2.0	59,000	1.5
2.5	58,200	1.6
3.0	58,500	1.7
3.5	59,200	1.5
4.0	58,800	1.4
4.5	59,000	1.3
5.0	58,600	1.7

276

277



278

279 Figure 6. Calibration graphs for DMS measurement by the proposed MSSF-CL method for samples with 0 and 3.5 %  
280 (m/v, as NaCl) salinity. Error bars represent  $\pm 1$  SD of triplicate measurements.

281

282 **3.4. Effect of ozone flow rate and concentration on CL detection**

283 DMS and ozone were introduced into the CL cell through concentric tubes and the  
284 CL reaction occurred in the center of the reaction cell. CL intensity depends on  
285 maximizing the emission within the cell window. We therefore investigated the effect  
286 of different ozone concentrations on CL intensity by adjusting the O<sub>2</sub> input flow rate  
287 and the power supplied to the ozone generator. Lowering the O<sub>2</sub> flow rate enhanced the  
288 CL signal due to a longer residence time in the cell and more efficient ozone production  
289 in the generator. If the O<sub>2</sub> flow rate dropped too low however, excess ozone was  
290 produced, resulting in a quenching of the CL signal. The effect of ozone flow rate and  
291 concentration on the DMS signal is shown in [Table S-5](#), with a maximum CL intensity  
292 achieved when ozone was delivered into the reaction cell at 200 mL min<sup>-1</sup> with a  
293 concentration of 6550 ppmv (with the ozone generator working at 40% of its maximum  
294 output). Air was not used as an ozone source in this study due to unstable ozone  
295 production (RSD  $\geq 10.2\%$ , n=5) at low flow rates ( $\leq 250$  mL min<sup>-1</sup>). It should be noted  
296 that the optimum flow rates of both ozone and the carrier gas, as well as the ozone  
297 concentration, vary over a relatively wide range when different shapes and sizes of  
298 reaction cell are used [27-31].

299

300 **3.5. Interference study**

301 Certain compounds positively interfere with the DMS measurement by reacting  
302 with ozone to produce a CL signal [27,29-31,40-42] and the effect of these compounds  
303 at three concentrations was therefore investigated using the relative CL intensity, which  
304 was defined as the ratio of the CL intensity of the potential interferent with DMS and  
305 the CL intensity of DMS alone. The results are shown in [Table 2](#). 100 nM of ethene or  
306 propene produces a CL signal equivalent to ~3.3-3.9 nM DMS. Ethene and propene are  
307 not found in most natural waters and therefore interferences would be negligible [43].  
308 100 nM Dimethyl disulfide (DMDS) produces a CL signal equivalent to 2 nM DMS.

309 The concentration of DMDS in freshwaters is typically no more than 17% of the DMS  
310 concentration [44,45], suggesting a maximum interference of ~1%. Methyl mercaptan  
311 ( $\text{CH}_3\text{SH}$ ) is a biologically generated sulfur compound found in natural waters [46] and  
312 is more volatile than DMS (Henry's law constant of  $0.39 \text{ M atm}^{-1}$  and  $0.56 \text{ M atm}^{-1}$  for  
313  $\text{CH}_3\text{SH}$  and DMS respectively). Previous CL work has reported a comparable (or higher)  
314 CL signal relative to DMS [13,29,30,31,47]. A column packed with soda lime was  
315 introduced between the gas-liquid separator and the holding cell. The column  
316 eliminated the  $\text{CH}_3\text{SH}$  interference, dried the sample gas and had no detectable impact  
317 on the DMS signal.

318

319 Table 2. Relative CL intensity (%CL =  $\text{CL}_{\text{spiked}}/\text{CL}_{\text{DMS only}}$ ) due to potential interference to the  
320 MSSF-CL signal from other compounds. Compounds were spiked into a 10 nM aqueous DMS  
321 aqueous sample.

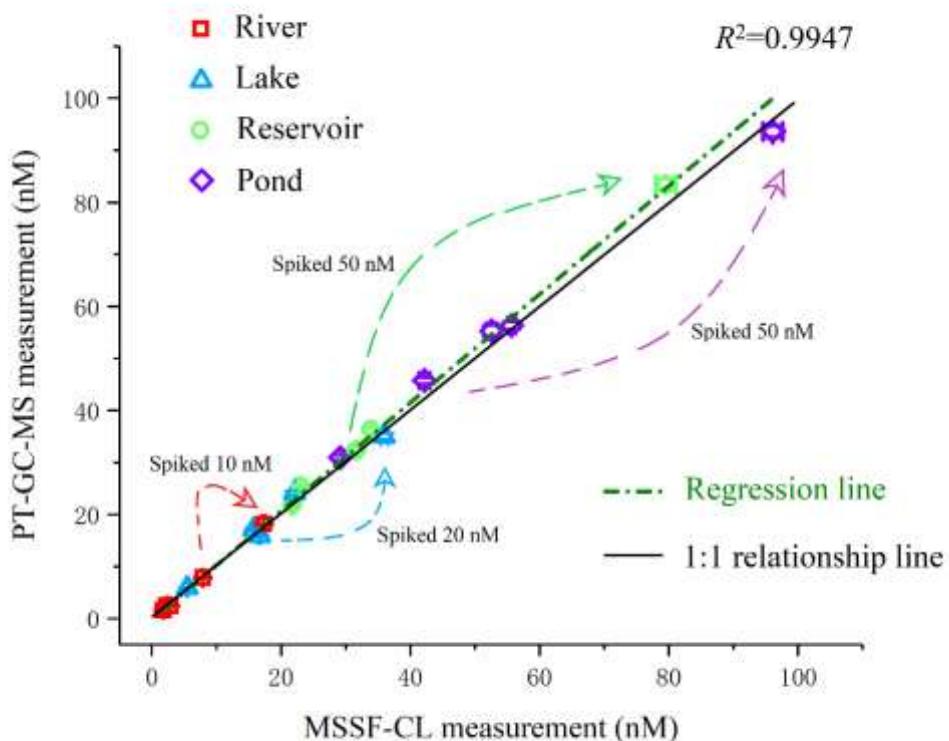
Compound	Relative CL intensity (%)		
	1 nM	10 nM	100 nM
DMS	100.0		
Isoprene	100.1	100.7	109.0
Ethene	100.3	104.1	132.7
Propene	100.3	103.4	139.1
Hydrogen sulfide	100.0	100.1	100.8
Methyl mercaptan	100.4	100.4	101.2
Carbon disulfide	100.1	101.2	110.0
Dimethyl disulfide	100.5	102.7	120.0
Carbonyl sulfide	100.1	100.2	100.4

322

### 323 3.6. Analytical figures of merit

324 Under optimum conditions, the linearity of the proposed MSSF-CL method for  
325 DMS determination was in the range 0.05-500 nM ( $R^2=0.9984$ ). The limit of detection  
326 (LOD) calculated from three times the signal-to-noise ratio was 0.015 nM. The

327 reproducibility and recovery of the MSSF-CL method was investigated by analyzing  
 328 four natural water matrices (river, lake, reservoir and pond; see Fig. 7 caption for further  
 329 matrix details) spiked with different concentrations of DMS (10, 20 and 50 nM). The  
 330 RSDs were  $\leq 1.8\%$  ( $n=5$  for each set of measurements) and recoveries were 94.4–  
 331 107.8%, indicating acceptable precision and accuracy for the analysis of natural water  
 332 samples. The complete analytical cycle (including rinsing) took 548 s, which provided  
 333 a sample throughput of  $\sim 6.6 \text{ h}^{-1}$ . A comparison of the MSSF-CL method with purge and  
 334 trap gas chromatography with mass spectrometric detection (PT-GC-MS) demonstrated  
 335 satisfactory agreement with minimal apparent bias (slope =  $1.042 \pm 0.018$ , intercept = -  
 336  $0.159 \pm 0.096$ ,  $R^2=0.9947$ ; see Fig. 7), which shows that the proposed method is robust  
 337 and can perform well for a broad variety of aqueous sample matrices. Analytical  
 338 conditions for the PT-GC-MS method are described in Method S-6 and the figures of  
 339 merit are given in Table S-7.



340  
 341 Figure 7. Comparison of DMS measurement in different freshwater samples by MSSF-CL and PT-GC-MS.  
 342 Regression equation (with 95% confidence intervals) follows  $\text{PT-GC-MS measurement (nM)} = 1.042 (\pm 0.018) \times$

343 MSSF-CL measurement (nM) – 0.159 ( $\pm 0.096$ ). Lake and pond samples were collected from East Lake (University  
344 of Electronic Science and Technology of China, Chengdu, China), river samples were collected from different sites  
345 along the Qingshui river (Chengdu, China) and reservoir samples were collected from Zipingpu and Tuanjie reservoir  
346 (Chengdu, China). A 50 mL plastic syringe equipped with a 0.22  $\mu\text{m}$  membrane filter was used for sampling. The  
347 syringe was filled while under water to prevent headspace formation. Collected samples were stored in the dark at  
348  $\sim 4$  °C in an expanded polypropylene ice cooler box until analyzed.

349

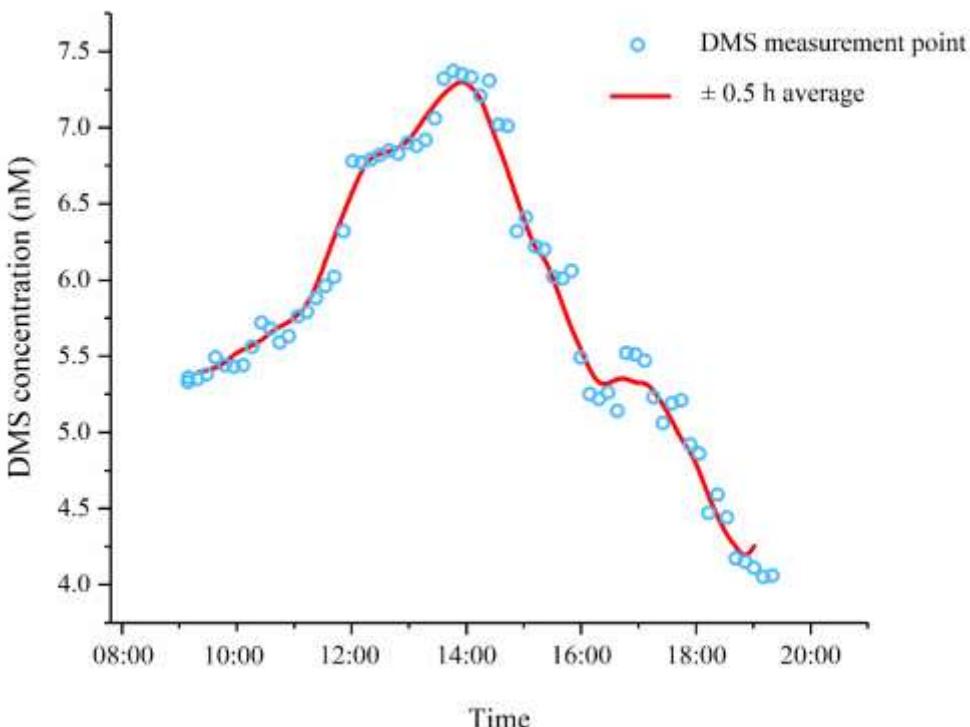
### 350 **3.7. Field analysis of freshwater samples**

351 The suitability of the proposed method for field deployment was evaluated by  
352 (pseudo)continuous monitoring to determine DMS in East Lake (University of  
353 Electronic Science and Technology of China campus, China) over a 10 h period (66  
354 samples) on the 17<sup>th</sup> May 2019. Samples were continuously collected at fixed position  
355 at a depth of 50 cm, as described in section 2.3, and introduced into the MSSF-CL  
356 system for DMS measurement (results shown in [Fig. 8](#)). The DMS concentration  
357 increased steadily from 09:00 hrs, reaching a maximum of 7.37 nM at 14:00. A  
358 significant drop was then observed, decreasing to 4.06 nM at 19:20.

359 The data in [Fig. 7](#) and [Fig. 8](#) are within the range of previous freshwater DMS  
360 observations [48]. The DMS observations follow a similar diurnal cycle that has been  
361 observed in other studies [27,49]. The proposed method is reagent free, portable (weight  
362  $\sim 5.1$  kg excluding the gas cylinders), simple to use and ideally suited for field analysis  
363 with good temporal resolution.

364 Compared with the recent reported CL based sequential and batchwise method for  
365 DMS field analysis [30, 31], the using of a novel microslug gas-liquid segmented flow  
366 for DMS phase transferring in this work was found to be highly effective and  
367 compatible with the whole automated measurement system that featured by its  
368 portability, ease of operation, and could be left in the field for several hours unattended  
369 operation.

370



371

372     Figure 8. Field analysis of DMS in freshwater by MSSF-CL. The MSSF-CL system was placed at fixed position on  
 373     a footbridge over the East Lake of University of Electronic Science and Technology of China campus, and samples  
 374     were continuously collected from 50 cm below the water surface and delivered into the MSSF-CL system for analysis.  
 375     DMS measurements were automatically carried out from 09:10 to 19:20 (local time) without interruption, providing  
 376     DMS data every ~9.1 mins. The red line is a ±30 min running average.

377

#### 378     **4. Conclusions**

379         DMS biogeochemistry has attracted significant attention in environmental studies  
 380     as a biologically-generated, climate-relevant sulfur compound. We have developed an  
 381     automated system based on gas-liquid segmented flow and gas phase CL detection for  
 382     the quantification of DMS in natural waters. DMS transfer from the aqueous phase to  
 383     the gas phase using a vario-directional, microslug gas-liquid segmented manifold was  
 384     highly advantageous compared with the commonly-used bubble purging approach.  
 385     Sample throughput, including *in-situ* sampling, separation, detection and washing, was  
 386     6.6 h<sup>-1</sup>. The system is portable, reagent free, uses off-the-shelf components and fittings  
 387     for ease of assembly/disassembly and can be deployed unattended in the field. The

388 geometry and flow rates in the gas-liquid segmentation system are critical for optimum  
389 performance, as are the flow rate and concentration of ozone in the reaction cell. Under  
390 optimum operating conditions the linear range for DMS detection was 0.05-500 nM  
391 ( $R^2=0.9984$ ), the LOD (3 x S/N ratio) was 0.015 nM, RSDs were typically  $\leq 1.8\%$  (n=5)  
392 and recoveries for spiked (10, 20 and 50 nM DMS) natural waters were 94.4–107.8%.  
393 The analytical performance of the proposed method means that it can be applied to the  
394 continuous measurement of low level DMS concentrations in natural waters. Sample  
395 throughput could be enhanced by the use of a multi parallel gas-liquid segmented flow  
396 manifold and/or tangential flow filtration. The multi parallel segmented flow manifold  
397 would introduce samples into different parallel gas-liquid segmented flows at  
398 prescribed time intervals and queue the sample gas prior to entering the CL cell. In-line  
399 tangential flow filtration could be incorporated to enable longer-term deployments.

400

#### 401 **CRediT authorship contribution statement**

402 **Geng Leng:** Conceptualization, Methodology, Formal analysis, Investigation,  
403 Writing - original draft, Writing - review & editing, Visualization, Investigation,  
404 Resources. **Chao Feng Jin:** Methodology, Writing - review & editing, Software,  
405 Visualization, Investigation. **Thomas G. Bell:** Writing - review & editing, Formal  
406 analysis, Resources, Conceptualization. **Simon J. Ussher:** Project administration,  
407 Writing - review & editing, Formal analysis, Resources, Conceptualization. **Paul J.**  
408 **Worsfold:** Supervision, Conceptualization, Writing – review & editing, Formal  
409 analysis, Resources. **Wei-Yi Li:** Validation, Writing - review & editing,  
410 Conceptualization.

411

#### 412 **Declaration of competing interest**

413 The authors declare that they have no known competing financial interests or  
414 personal relationships that could have appeared to influence the work reported in this  
415 paper.

416

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426

## 427 **References**

- 428 [1] C. L. Lee, P. Brimblecombe, Anthropogenic contributions to global carbonyl sulfide, carbon  
429 disulfide and organosulfides fluxes, *Earth-Sci. Rev.* 160 (2016) 1-18.
- 430 [2] A. Lana, T. G. Bell, R. Simó, S. M. Vallina, J. Ballabrera-Poy, A. J. Kettle, J. Dachs, L. Bopp, E.  
431 S. Saltzman, J. Stefels, E. S. Johnson, P. S. Liss, An updated climatology of surface  
432 dimethylsulfide concentrations and emission fluxes in the global ocean, *Global Biogeochem.*  
433 *Cy.* 25 (2011) GB1004.
- 434 [3] M. Sela-Adler, W. Said-Ahmad, O. Sivan, W. Eckert, R. P. Kiene, A. Amrani, Isotopic evidence  
435 for the origin of dimethylsulfide and dimethylsulfoniopropionate-like compounds in a warm,  
436 monomictic freshwater lake, *Environ. Chem.* 13 (2016) 340-351.
- 437 [4] J. O. Nriagu, D. A. Holdway, Production and release of dimethyl sulfide from the Great Lakes,  
438 *Tellus B* 41 (1989) 161-169.
- 439 [5] K. Huang, G. Zhuang, J. Li, Q. Wang, Y. Sun, Y. Lin, J. S. Fu, Relation between optical and  
440 chemical properties of dust aerosol over Beijing, China, *J. Geophys. Res.-Atmos.* 115 (2010)  
441 D00K13.
- 442 [6] H. B. Swan, E. S. M. Deschaseaux, B. D. Eyre, G. B. Jones, Surface flux and vertical profile of  
443 dimethyl sulfide in acid sulfate soils at Cudgen Lake, northern New South Wales, Australia,  
444 *Chemosphere.* 228 (2019) 309-307.
- 445 [7] C. M. Geng, Y. J. Mu, Carbonyl sulfide and dimethyl sulfide exchange between trees and the  
446 atmosphere, *Atmos. Environ.* 40 (2006) 1373-1383.
- 447 [8] K. J. Sanchez, C. L Chen, L. M. Russell, R. Betha, J. Liu, D. J. Price, P. Massoli, L. D. Ziembka,

- 448 E. C. Crosbie, R. H. Moore, M. Müller, S. A. Schiller, A. Wisthaler, A. K. Y. Lee, P. K. Quinn,  
449 T. S. Bates, J. Porter, T. G. Bell, E. S. Saltzman, R. D. Vaillancourt, M. J. Behrenfeld,  
450 Substantial seasonal contribution of observed biogenic sulfate particles to cloud condensation  
451 nuclei, *Sci. Rep.* 8 (2018) 3235.
- 452 [9] S. Twomey, The influence of pollution on the shortwave albedo of clouds, *J. Atmos. Sci.* 34  
453 (1977) 1149-1152.
- 454 [10] M. O. Andreae, D. Rosenfeld, Aerosol-cloud-precipitation interactions. Part 1. The nature and  
455 sources of cloud-active aerosols, *Earth-Sci. Rev.* 89 (2008) 13-41.
- 456 [11] S. H. Zhang, G. P. Yang, H. H. Zhang, J. Yang, Spatial variation of biogenic sulfur in the south  
457 Yellow Sea and the East China Sea during summer and its contribution to atmospheric sulfate  
458 aerosol, *Sci. Total Environ.* 488-489 (2014) 157-167.
- 459 [12] S. M. Turner, G. Malin, P. S. Liss, D. S. Harbour, P. M. Holligan, The seasonal variation of  
460 dimethyl sulfide and dimethylsulfoniopropionate concentrations in nearshore waters, *Limnol.  
461 Oceanogr.* 33 (1988) 364-375.
- 462 [13] B. Wang, E. C. Sivret, G. Parcsi, R. M. Stuetz, Determination of VOSCs in sewer headspace  
463 air using TD-GC-SCD, *Talanta* 137 (2015) 71-79.
- 464 [14] Y. Liu, C. Y. Liu, G. P. Yang, H. H. Zhang, S. H. Zhang, Bioindication assessment of activated  
465 sludge Adaptation in a Lab-Scale Experiment, *Environ. Chem.* 13 (2016) 127-139.
- 466 [15] M. M. Zhang, L. Q. Chen, Continuous underway measurements of dimethyl sulfide in seawater  
467 by purge and trap gas chromatography coupled with pulsed flame photometric detection, *Mar.  
468 Chem.* 174 (2015) 67-72.
- 469 [16] H. B. Swan, R. W. Crough, P. Vaattovaara, G. B. Jones, E. S. M. Deschaseaux, B. D. Eyre, B.  
470 Miljevic, Z. D. Ristovski, Dimethyl sulfide and other biogenic volatile organic compound  
471 emissions from branching coral and reef seawater: potential sources of secondary aerosol over  
472 the Great Barrier Reef, *J. Atmos. Chem.* 73 (2016) 303-328.
- 473 [17] T. G. Bell, G. Malin, G. A. Lee, J. Stefels, S. Archer, M. Steinke, P. Matrai, Special Issue of the  
474 5th International Symposium on Biological and Environmental Chemistry of DMS(P) and  
475 Related Compounds, Goa, India, 19-22 October 2010, Global oceanic DMS data inter-  
476 comparability, *Biogeochemistry* 110 (2012) 147-161.
- 477 [18] C. F. Walker, M. J. Harvey, M. J. Smith, T. G. Bell, E. S. Saltzman, A. S. Marriner, J. A.

- 478 McGregor, C. S. Law, Assessing the potential for dimethylsulfide enrichment at the sea surface  
479 and its influence on air-sea flux, *Ocean Sci.* 12 (2016) 1033-1048.
- 480 [19] P. D. Tortell, Dissolved gas measurements in oceanic waters made by membrane inlet mass  
481 spectrometry, *Limnol. Oceanogr. Methods.* 3 (2005) 24-37.
- 482 [20] S. Kameyama, H. Tanimoto, H. Inomata, U. Tsunogai, A. Ooki, Y. Yokouchi, S. Takeda, H.  
483 Obata, M. Uematsu, Equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-  
484 MS) for sensitive, high-resolution measurement of dimethyl sulfide dissolved in seawater, *Anal.  
485 Chem.* 81 (2009) 9021-9026.
- 486 [21] S. Kameyama, S. Yoshida, H. Tanimoto, S. Inomata, K. Suzuki, H. Yoshikawa-Inoue, High-  
487 resolution observations of dissolved isoprene in surface seawater in the Southern Ocean during  
488 austral summer 2010-2011, *J. Oceanogr.* 70 (2014) 225-239.
- 489 [22] H. Tanimoto, S. Kameyama, T. Iwata, S. Inomata, Y. Omori, Measurement of air-sea exchange  
490 of dimethyl sulfide and acetone by PTR-MS coupled with gradient flux technique, *Environ.  
491 Sci. Technol.* 48 (2014) 26-533.
- 492 [23] J. C. Jiang, Y. Wang, K. Y. Hou, L. Hua, P. Chen, W. Liu, Y. Y. Xie, H. Y. Liu, Photoionization-  
493 generated dibromomethane cation chemical ionization source for TOFMS and its application  
494 on sensitive detection of volatile sulfur compounds, *Anal. Chem.* 88 (2016) 5028-5032.
- 495 [24] E. S. Saltzman, W. J. De Bruyn, M. J. Lawler, C. A. Marandino, C. A. McCormick, A chemical  
496 ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide  
497 in near-surface seawater, *Ocean Sci.* 5 (2009) 537-546.
- 498 [25] T. J. Kelly, J. S. Gaffney, M. F. Phillips, R. L. Tanner, Chemiluminescent detection of reduced  
499 sulfur compounds with ozone, *Anal. Chem.* 55 (1983) 135-138.
- 500 [26] P. K. Arora, J. P. S. Chatha, Chemiluminescence from the reactions of ozone with sulphur  
501 compounds, *Can. J. Chem.* 62 (1984) 417-423.
- 502 [27] B. C. Green, D. J. Suggett, A. Hills, M. Steinke, Optimisation of a fast DMS sensor (FDS) for  
503 real time quantification of dimethyl sulfide production by algae, *Biogeochemistry* 110 (2012)  
504 163-172.
- 505 [28] K. Toda, P. K. Dasgupta, New applications of chemiluminescence for selective gas analysis,  
506 *Chem. Eng. Commun.* 195 (2008) 82-97.
- 507 [29] M. A. K. Azad, S. Ohira, K. Toda, Single column trapping/separation and chemiluminescence

- 508 detection for on-site measurement of methyl mercaptan and dimethyl sulfide, Anal. Chem. 78  
509 (2006) 6252-6259.
- 510 [30] D. Okane, E. P. Koveke, K. Tashima, K. Saeki, S. Maezono, T. Nagahata, N. Hayashi, K.  
511 Owen, D. P. Zitterbart, S. Ohira, K. Toda, High sensitivity monitoring device for onboard  
512 measurement of dimethyl sulfide and dimethylsulfoniopropionate in seawater and an oceanic  
513 atmosphere, Anal. Chem. 91 (2019) 10484-10491.
- 514 [31] N. Takanori, H. Kajiwara, S. I. Ohira, K. Toda, Simple field device for measurement of dimethyl  
515 sulfide and dimethylsulfoniopropionate in natural waters, based on vapor generation and  
516 chemiluminescence detection, Anal. Chem. 85 (2013) 4461-4467.
- 517 [32] M. Donata, S. W. Fries, R. V. R. Philipp, Gas-liquid two-phase flow in meandering  
518 microchannels, Chem. Eng. J. 135S (2008) S37-S45.
- 519 [33] D. Hakan, N. Selman, M. Metin, Mixing of miscible liquids in gas-segmented serpentine  
520 channels, Int. J. Multiphase Flow. 35 (2009) 1149-1158.
- 521 [34] J. Tan, Y. C. Lu, J. H. Xu, G. S. Luo, Mass transfer performance of gas-liquid segmented flow  
522 in microchannels, Chem. Eng. J. 181-182 (2012) 229-235.
- 523 [35] J. Stafford, Principle-based design of distributed multiphase segmented flow, Int. J. Heat Mass  
524 Tran. 100 (2016) 508-521.
- 525 [36] P. Garstecki, M. J. Fuerstman, H. A. Stone, G. M. Whitesides, Formation of droplets and  
526 bubbles in a microfluidic T-junction-scaling and mechanism of break-up, Lab. Chip. 6 (2006)  
527 693-693.
- 528 [37] T. Thorsen, R. W. Roberts, F. H. Arnold, S. R. Quake, Dynamic Pattern Formation in a Vesicle-  
529 Generating Microfluidic Device, Phys. Rev. Lett. 86 (2001) 4163-4166.
- 530 [38] J. D. Tice, A. D. Lyon, R. F. Ismagilov, Effects of viscosity on droplet formation and mixing in  
531 microfluidic channels, Anal. Chim. Acta 507 (2004) 73-77.
- 532 [39] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, (2 ed.),  
533 Proteomics(2006)
- 534 [40] W. A. Kummer, J. N. Pitts, R. P. Steer, Intraoperative ultrasonic localization of endocrine tumors  
535 of the pancreas, Environ. Sci. Technol. 5 (1971) 1045-1047.
- 536 [41] S. Ohira, J. Li, W. A. Lonneman, P. K. Dasgupta, K. Toda, Can breath isoprene be measured by  
537 ozone chemiluminescence, Anal. Chem. 79 (2007) 2641-2649.

- 538 [42] D. A. Exton, D. J. Smith, T. J. McGenity, M. Steinke, A. J. Hills, D. J. Suggett, Application of  
539 a fast isoprene sensor (FIS) for measuring isoprene production from marine samples, Limnol  
540 Oceanogr Methods. 8 (2010) 185-195.
- 541 [43] S. Schulze, D. Zahn, R. Montes, R. Rodil, J. B. Quintana, T. P. Knepper, T. Reemtsma, U.  
542 Berger, Occurrence of emerging persistent and mobile organic contaminants in European water  
543 samples, Water Res. 153 (2019) 80-90.
- 544 [44] D. Tanzer, K. G. Heumann, Gas Chromatographic Trace-level determination of volatile organic  
545 sulfides and selenides and of methyl iodide in atlantic surface water, Intern. J. Environ. Anal.  
546 Chem. 48(1) (1992) 17-31.
- 547 [45] P. R. Berube, P. D. Parkinson, E. R. Hall, Measurement of reduced sulphur compounds  
548 contained in aqueous matrices by direct injection into a gas chromatograph with a flame  
549 photometric detector, J. Chromatogr. A. 830 (1999) 485-489.
- 550 [46] M. E. Hines, R. E. Pelletier, P. M. Crill, Emissions of sulfur gases from marine and freshwater  
551 wetlands of the Florida Everglades: Rates and extrapolation using remote sensing, J. Geophys.  
552 Res. 98 (1993) 8991-8999.
- 553 [47] J. Sun, S. Hu, K. R. Sharma, B. Kellerlehmann, Z. Yuan, An efficient method for measuring  
554 dissolved VOSCs in wastewater using GC-SCD with static headspace technique, Water Res.  
555 52 (2014) 208-217.
- 556 [48] B. K. Reese, M. A. Anderson, Dimethyl sulfide production in a saline eutrophic lake, Salton  
557 Sea, California, Limnol. Oceanogr. 54(1) (2009) 250-261.
- 558 [49] S. J. Royer, M. Galí, A. S. Mahajan, O. N. Ross, G. L. Pérez, E. S. Saltzman, R. Simó, A high-  
559 resolution time-depth view of dimethylsulphide cycling in the surface sea, Sci. Rep. 6 (2016)  
560 32325.

561

562 **Figure and table captions**

563

564 Figure 1. A schematic diagram of the proposed MSSF-CL instrument for the  
565 determination of DMS. NT, nylon net; FT 1-3, filter; PP, peristaltic pump; SV 1 and 2,  
566 three-way solenoid valves; SFT, sample flow tank; SY, syringe; TJ, T-junction; MFC 1-  
567 3, mass flow controllers; OG, ozone generator; GLSFC, gas-liquid segmented flow coil;

568 GLS, gas-liquid separator; IV, 6-port injection valve; HC, holding coil; SLC, soda lime  
569 column; RC, chemiluminescence reaction cell; PMT, photomultiplier tube; PSA,  
570 photon signal analyzer; AC, active carbon column.

571

572 Figure 2. Effect of gas and liquid slugs moving through a coiled tube in (a) clockwise  
573 and (b) counterclockwise directions.

574

575 Figure 3. A comparison of (a) bubbling, (b) unidirectional segmented flow, and (c)  
576 vario-directional segmented flow for 20 nM DMS transfer. Bubbles were generated by  
577 introducing 20 mL of air through a quartz sand bubble stone. Both the unidirectional  
578 and vario-directional segmented flow setups used PP tubing (20 m x 0.79 mm i.d.) with  
579 1 cm curve radius. Liquid and gas were delivered at 2.0 and 4.0 mL min<sup>-1</sup> respectively.  
580 Peak height recorded as photon counting units (p.c.u.).

581

582 Figure 4. Effect of segmented flow tubing curve radius and internal diameter on 20 nM  
583 DMS mass transfer in MSSF-CL method (coil tubing length = 20 m; liquid flow rate =  
584 2 mL min<sup>-1</sup>; gas flow rate = 4 mL min<sup>-1</sup>).

585

586 Figure 5. Effects on CL intensity due to T-junction inlet width and gas flow rate through  
587 the coil. The segmented flow setup used PP tubing (20 m x 1.0 mm i.d.) with a 1 cm  
588 curve radius and vario-directional flow. Error bars represent  $\pm 1$  SD of triplicate  
589 measurements.

590

591 Figure 6. Calibration graphs for DMS measurement by the proposed MSSF-CL method  
592 for samples with 0 and 3.5 % (m/v, as NaCl) salinity. Error bars represent  $\pm 1$  SD of  
593 triplicate measurements.

594

595 Figure 7. Comparison of DMS measurement in different freshwater samples by MSSF-  
596 CL and PT-GC-MS. Regression equation (with 95% confidence intervals) follows PT-  
597 GC-MS measurement (nM) = 1.042 ( $\pm 0.018$ ) x MSSF-CL measurement (nM) – 0.159

598 ( $\pm 0.096$ ). Lake and pond samples were collected from East Lake (University of  
599 Electronic Science and Technology of China, Chengdu, China), river samples were  
600 collected from different sites along the Qingshui river (Chengdu, China) and reservoir  
601 samples were collected from Zipingpu and Tuanjie reservoir (Chengdu, China). A 50  
602 mL plastic syringe equipped with a  $0.22\text{ }\mu\text{m}$  membrane filter was used for sampling.  
603 The syringe was filled while under water to prevent headspace formation. Collected  
604 samples were stored in the dark at  $\sim 4\text{ }^{\circ}\text{C}$  in an expanded polypropylene ice cooler box  
605 until analyzed.

606

607 Figure 8. Field analysis of DMS in freshwater by MSSF-CL. The MSSF-CL system  
608 was placed at fixed position on a footbridge over the East Lake of University of  
609 Electronic Science and Technology of China campus, and samples were continuously  
610 collected from 50 cm below the water surface and delivered into the MSSF-CL system  
611 for analysis. DMS measurements were automatically carried out from 09:10 to 19:20  
612 (local time) without interruption, providing DMS data every  $\sim 9.1$  mins. The red line is  
613 a  $\pm 30$  min running average.

614

615 Table 1. Effect of sample salinity (as NaCl) for 20 nM DMS measurement by MSSF-  
616 CL.

617

618 Table 2. Relative CL intensity (%CL =  $\text{CL}_{\text{spiked}}/\text{CL}_{\text{DMSonly}}$ ) due to potential interference  
619 to the MSSF-CL signal from other compounds. Compounds were spiked into a 10 nM  
620 aqueous DMS aqueous sample.