

## Short communication

## An integrated sampler for shipboard underway measurement of dimethyl sulfide in surface seawater and air



Miming Zhang<sup>a,\*</sup>, Wei Gao<sup>b</sup>, Jinpei Yan<sup>a,\*\*</sup>, Yanfang Wu<sup>c</sup>, Christa A. Marandino<sup>d</sup>, Keyhong Park<sup>e</sup>, Liqi Chen<sup>a</sup>, Qi Lin<sup>a</sup>, Guobin Tan<sup>b,f,g</sup>, Meijiao Pan<sup>f</sup>

<sup>a</sup> Key Laboratory of Global Change and Marine - Atmospheric Chemistry (GCMAC) of Ministry of Natural Resources (MNR), Third Institute of Oceanography (TIO), MNR, Siming District, Xiamen, Fujian, 361005, PR China

<sup>b</sup> Institute of Mass Spectrometry and Atmospheric Environment, Jinan University, Tianhe District, Guangzhou, Guangdong, 510632, PR China

<sup>c</sup> School of Chemistry, Australian Centre for Nano-Medicine and ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, University of New South Wales, Sydney, NSW, 2052, Australia

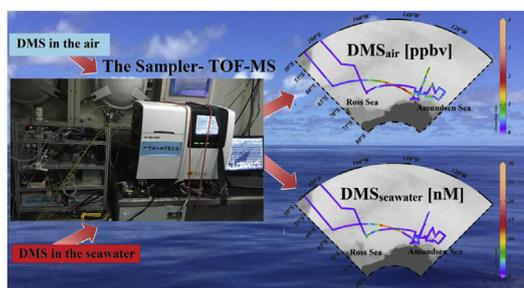
<sup>d</sup> Forschungsbereich Marine Biogeochemie, GEOMAR | Helmholtz-Zentrum für Ozeanforschung Kiel, Düsternbrooker Weg 20, 24105, Kiel, Germany

<sup>e</sup> Division of Polar Ocean Sciences, Korea Polar Research Institute, Incheon, 21990, South Korea

<sup>f</sup> Guangzhou Hexin Instrument Co., Ltd., Huangpu District, Guangzhou, Guangdong, 510663, PR China

<sup>g</sup> Guangdong Provincial Engineering Research Center for on-line Source Apportionment System of Air Pollution, Tianhe District, Guangzhou, Guangdong, 510632, PR China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Keywords:

Dimethyl sulfide  
Shipboard underway measurements  
Seawater  
Air  
Time-of-flight mass spectrometry

## ABSTRACT

Dimethyl sulfide (DMS), a marine-derived trace gas, can influence atmospheric compositions and has an impact on the global climate. To date, obtaining continuous and coupled shipboard underway measurements of DMS in seawater and air has been challenging. To address this issue, we report a custom-made sampling device based on the purge-and-trap technique. This sampler, in combination with a time-of-flight mass spectrometer (TOF-MS), was successfully utilized to perform coupled shipboard underway measurements of DMS in surface seawater and air around western Antarctica during the 34th Chinese Antarctic Research Expedition from February 2018 to April 2018. The seawater and air streams were continuously introduced into the sampler unit and subsampled every 10 min. The limits of detection (LODs) of DMS in seawater and air were found to be 0.07 nM and 32 pptv, respectively. The variability in the DMS levels in the surface seawater and air can be distinguished and evaluated based on the variations in the DMS peaks. These results demonstrated that the sampling device was effective for consistent, sensitive underway measurements of DMS.

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zhangmiming@tio.org.cn](mailto:zhangmiming@tio.org.cn) (M. Zhang), [Jpyan@tio.org.cn](mailto:Jpyan@tio.org.cn) (J. Yan).

## 1. Introduction

Trace gases, especially short-lived gases, play an essential role in atmospheric processes, as they can influence the oxidative capacity of the atmosphere, the formation of aerosols, and global climate change (Liss et al., 2014). The ocean is a main control of the atmospheric budget of many important trace gases. Among them, dimethyl sulfide (DMS) is an important biogenic trace gas that has received much attention. It has been hypothesized that DMS can regulate a part of cloud condensation nuclei (CCN), thereby influencing Earth's radiation budget (i.e., the CLAW hypothesis, named after the first letters of the authors' names) (Charlson et al., 1987; Vogt and Liss, 2009). The annual global oceanic emission of DMS is estimated to be approximately 28.1 Tg S (ranging from 17.6 to 34.4 Tg S) (Lana et al., 2011).

Despite the fact that DMS has been known to be an important oceanic trace gas for some time, it is still challenging to realize ship-board underway coupled measurements to determine the DMS in seawater (normal in the range 1–7 nM for the global oceans Lana et al., 2011) and air (pptv levels) continuously at high spatial and temporal resolutions. The measurement of DMS in seawater and air is important for understanding how oceanic DMS impact the atmosphere and DMS sea-to-air flux. Thus, to date, most DMS measurement techniques have been applied to either seawater or air samples. Techniques such as membrane inlet mass spectrometry (Kim et al., 2017; Tortell, 2005), equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) (Kameyama et al., 2009, 2010; Omori et al., 2013), the purge-and-trap technique coupled with gas chromatography-pulsed flame photometric detection (GC-PFPD) (Zhang and Chen, 2015; Zhang et al., 2017), and a membrane inlet-trap system coupled with a GC-PFPD (Park and Lee, 2008), have been developed to achieve continuous underway surface seawater trace gas measurements. Similar efforts have also been made to achieve consistent and long-term atmospheric DMS detection (Jang et al., 2016). One previous study even developed a measurement method for directly measuring the DMS air-sea exchange by PTR-MS coupled with the gradient flux technique, where the vertical profiles of DMS air concentrations above the ocean surface could be measured by this system (Tanimoto et al., 2013; Omori et al., 2017). Notably, Marandino et al. (2007, 2008; 2009) and Saltzman et al. (2009) performed pioneering work on developing a gas analysis system using a membrane equilibrator coupled with an atmospheric pressure chemical ionization mass spectrometer (APCI-MS). This system could either be used in a switching mode to measure both air and water or as two distinct systems to continuously measure air and water. The limits of detection (LODs) of these systems were 220 pptv and 0.1 nM for DMS in air (10 Hz) and water (1 Hz), respectively (Saltzman et al., 2009). These measurements were acquired rapidly because they did not require a pre-concentration step, as is needed with gas chromatography (GC) analyses. Nonetheless, to realize the coupled measurement of seawater and atmospheric DMS is not easy in the field experiment.

Our goal is to realize a consistent and integrated sampling and measuring system for surface seawater and atmospheric DMS. The two systems: 1) seawater and air sample trapping systems (the seawater sampling unit has been presented in our previous work (Zhang and Chen, 2015)) and 2) a sensitive time-of-flight mass spectrometer (TOF-MS) was integrated. The performance characteristics of this system, including its accuracy, stability and capability, were investigated during the 34th Chinese Antarctic Research Expedition (CHINARE ANT34th).

## 2. Method and experiments

### 2.1. The air-seawater gas concentration system

As shown in Fig. 1, the system consisted of three units: 1) a surface seawater sample purge unit, 2) an air sampler, and 3) an injection and detection unit (see Fig. S1 for a picture of the instrument). As previously

reported by Zhang and Chen (2015), the custom-made heating and cooling device, which consisted of thermoelectric coolers (C1208–2P4040, 12 V DC, 7.5 A, TELESKY, China) and a heater assembly (14-9828-220, 230 V AC, 5 A, Agilent Technologies, USA), was used to control temperature of the trap. Four automated six-port valves (V1 ~ V4, Vici Valco, USA) were employed: V1 and V2 were used to switch the gas stream of the seawater and air samples, V3 was used to switch the injection of seawater samples, and V4 was used to regulate the injection of the concentrated samples into the detector. The manual six-port valves (MV1 and MV2, Vici Valco, USA) were used for calibration work. A purge vessel (10 mL, Perspex<sup>®</sup>) was designed to purge the seawater samples. Two mass flow controllers (Aalborg, USA) were employed: one was used to regulate the purge flow (0–200 mL min<sup>-1</sup>), and another was used to regulate the air sampling flow (0–2000 mL min<sup>-1</sup>). A miniature air pump (0–6 L min<sup>-1</sup>, 24 V DC, 0.2 A, Qihaijidian, China) was used to transport the air samples. Two temperature sensors were inserted into trap 1 and trap 2 to monitor temperature variations. The drain valves (12 V DC, 0.2 A, Cole Palmer, USA, in which DV 1 is closed and DV 2 is open in the off status) and Nafion dryers (MD-050–24 P, Perma Pure, USA) were used to drain the waste water samples and dry the gas flow. The traps were 25-cm-long stainless steel tubes (Sulfinert<sup>®</sup>-coated stainless steel, 1.59 mm inner diameter (i.d.) × 1/8 in. Outer diameter (o.d.)) filled with 5 cm and 3 cm Tenax<sup>®</sup> TA (80 mesh, Supelco, USA) to trap the volatile compounds in the seawater samples and air samples, respectively. Under low trapping temperatures (i.e., as low as -25 °C), the collection efficiency of Tenax for highly volatile small molecules (i.e., DMS) can be improved.

The system parameters, such as purging time, heating time, and valve status, are automated using the Single Chip software installed on a controller (custom-made by the Xiamen Qianxinde intelligent device company, China; Fig. S2). These parameters are controlled with specially designed software (custom-made by the Xiamen Qianxinde intelligent device company, China; Fig. S3).

A single photon ionization (SPI) TOF-MS (SPI-MS 3000, Guangzhou Hexin Instrument Co., Ltd., China) was employed as the detector (Fig. 2). A polydimethylsiloxane (PDMS; thickness of 0.002 int; Technical Products Inc., USA) membrane was used in the injector of the TOF-MS. The membrane inlet technology is used to improve the detection limit of the MS for volatile organic compounds (VOCs) because VOC molecules can be concentrated in the membrane when they diffuse from the sample side to the detector side under high vacuum conditions. A vacuum ultraviolet (VUV) light generated by a commercial D2 lamp (Hamamatsu, Japan) was utilized for ionization. The SPI is capable of ionizing organic compounds under 10.8 eV. For ion detection, two microchannel plates (MCPs, Hamamatsu, Japan) assembled with a chevron-type configuration are employed. Each MCP features a finite diameter of 40 mm, a channel diameter of 5 μm and a bias angle of 8°. The voltage of the MCPs is closely related to the output signal. The peak width at the half maximum of a single ion is approximately 1.5 ns under a working voltage of 1500 v. A 350 MHz analog to digital converter (ADC, 8-bit, Guangzhou Hexin Analytical Instrument Co., Ltd., China) was used to measure and record the output current signal from the MCPs. This TOF-MS has an LOD of approximately 1 ppb for most trace gases without any pre-concentration procedure.

### 2.2. Analysis procedure

The analysis procedures for both the seawater and air samples were programmed to be automatic. First, the traps were refrigerated below -25 °C within 3 min. The seawater samples were collected in a 5 mL sample loop. When V1 and V3 were switched, the unfiltered seawater in the sample loop was introduced into the purge vessel within 1 min (Zhang and Chen, 2015). Then, V3 was switched back to obtain another seawater sample in the sample loop, and the seawater in the purge vessel was purged for 5.5 min with a 35 mL min<sup>-1</sup> gas flow. By

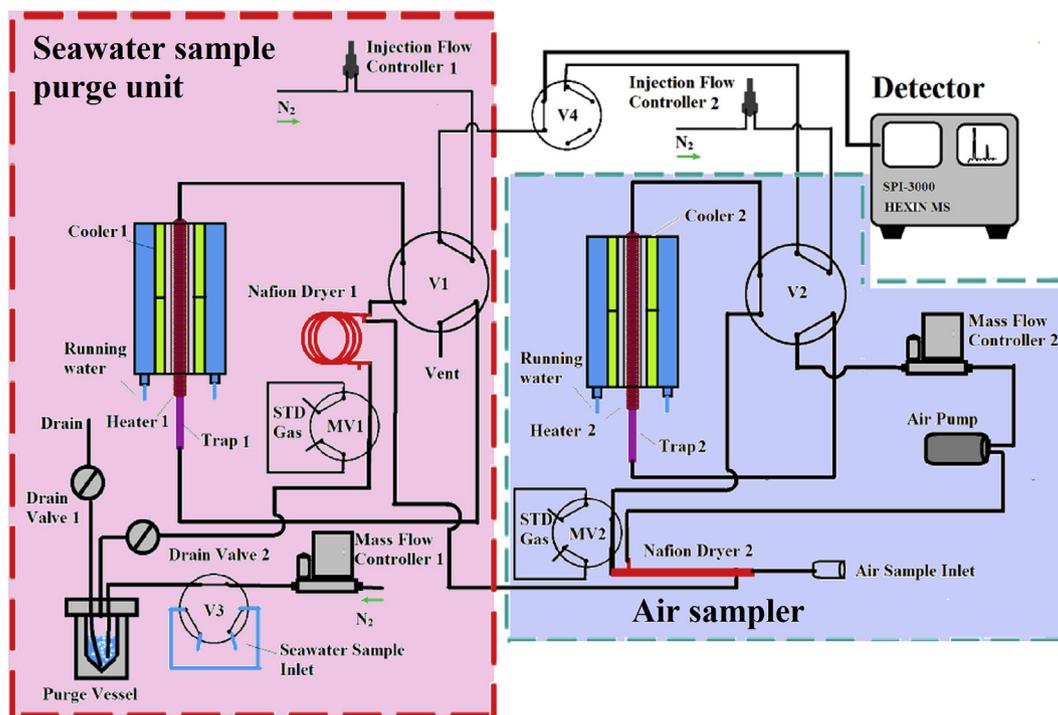


Fig. 1. The custom-made sampler (i.e., TOF-MS system). The system consisted of three units: 1) a seawater sample purge unit (highlighted in red), 2) an air sampler (highlighted in blue), and 3) an injection and detection unit. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

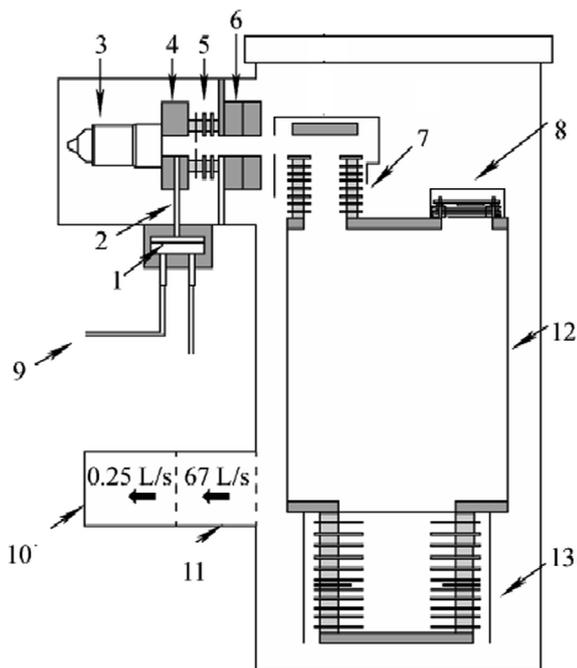


Fig. 2. Schematic of the SPI-TOF-MS system. 1. PDMS membrane injector, 2. Injector tube, 3. VUV lamp, 4. Ionization chamber, 5. Derivation electrode, 6. Einzel lens, 7. Ion acceleration region, 8. Ion detector, 9. Air sample inlet, 10. Micro-vacuum pump, 11. Mechanical pump, 12. Field-free drift tube, and 13. Reflector.

switching V2, the DMS in the air sample was trapped under the mean flow at  $65 \text{ mL min}^{-1}$  for 3.5 min. After the DMS in the sample was concentrated, V2 and V4 switched simultaneously, and trap 2 was heated to approximately  $150^\circ\text{C}$  in a few seconds and held for 1 min at that temperature so that the concentrated DMS could be totally injected into

the detector. Subsequently, after 2 min, V1 switched, and V4 switched back; similarly, the DMS concentrated from the seawater sample was rapidly desorbed into the detector under the same conditions as those for trap 2. The desorption gas flow rate was set to  $20 \text{ mL min}^{-1}$  for all analyses. Then, DV 2 and DV 1 worked, the gas flow was blocked, and the waste sample was pushed out through DV 1 in 1 min. Consequently, the entire system was returned to its standby status and prepared for the next sampling and measuring cycle. The entire analysis time for one seawater and air sample was 10 min (see Figs. S4–S6 for a better understanding of the changes in gas direction between analysis steps).

### 2.3. Field experiments

The system was installed in a temperature-controlled ( $\sim 25^\circ\text{C}$ ) chemical laboratory on the research vessel (R/V) Xue Long. To obtain seawater samples, the system was connected to the ship's seawater pump system, which had a sampling location of 4 m below the sea surface, and the seawater samples were continuously introduced into the system. The air sampling location, which was approximately 10 m above the sea surface, was selected as the front part of the ship to avoid contamination from ship track emissions. A black antistatic tube (1/4 in. o. d.) was used to transport the air sample continuously into the system.

According to our previous study (Zhang and Chen, 2015), a high DMS trapping efficiency was obtained under gas flow conditions ranging from  $60 \text{ mL min}^{-1}$  to  $80 \text{ mL min}^{-1}$ . A purge flow of  $35 \text{ mL min}^{-1}$  and a purge time of 5.5 min were sufficient to achieve a high analyte extraction efficiency (Scarratt et al., 2000). The injection flow was set to  $20 \text{ mL min}^{-1}$  to obtain a relatively good response with sharp peaks (the peak width was generally approximately 15 s). As a membrane inlet was employed, a higher injection flow would affect the resultant response signal, and a lower injection flow would influence the peak sharpness. Additionally, we use a gas standard for daily calibration. The preparation of a liquid DMS standard under harsh laboratory conditions is time consuming, and the manual process may also introduce some

errors. The certified DMS standard for gas was 5 ppm and was prepared in pure N<sub>2</sub> gas (> 99.999%) and stored in a high-pressure aluminum cylinder (8 L, 1-year shelf life) by the Chinese company Wuhanteqi. Different sample loops, such as 25  $\mu$ L, 50  $\mu$ L, 100  $\mu$ L, 250  $\mu$ L, 500  $\mu$ L, 25  $\mu$ L, and 1 mL, were employed for calibration. Standard gas samples were analyzed in triplicate to construct calibration curves. Moreover, the ion signal at  $m/z = 62$  was selected to represent the DMS during the experiments. In the maritime environment, the production of other compounds with the same molecular weight ( $m/z = 62$ ) is very limited; thus, we assume that almost no influence from other interferences occurred during the experiments. Standard calibrations were performed during the cruise under the parameters described in section 2.2. It should be noted that the calibration of air sample measurements was performed under a high-purity N<sub>2</sub> (> 99.999%, Linde Gas Company, China) gas flow to avoid contamination. MATLAB software was used to extract peak areas for the quantification analysis.

The cruise period was from 28 February 2018 to 17 April 2018, which is a long period of time to run the instrument, and it was hypothesized that the performance of the TOF-MS MCP and deuterium light could deteriorate with time, which would have a strong influence on the instrument response. Therefore, during the expedition, the detection system was calibrated every day. The calibration (one point) was performed twice a day, and the voltage of the MCP was increased slightly (generally 15–20 V depending on the standard gas signal) to ensure that there would be a sufficiently strong response for DMS.

Additionally, our PT-GC-PFPD was also onboard the ship (Zhang and Chen, 2015). This system was used to detect discrete seawater DMS and dimethylsulfoniopropionate (DMSP) samples. The seawater samples were collected directly from the ship's seawater pump system every 3 or 4 h along the entire cruise track and stored in 100 mL brown vials before they were analyzed. If the samples were not analyzed immediately, they were stored in a refrigerator at 4 °C. The gravity-filtered seawater samples were used for DMS analysis (0.7  $\mu$ m; glass fiber filter; Whatman, England). A total of 5 mL of each filtered seawater sample was directly transported into the sealed headspace bottles (20 mL, Thermo, USA) by a transfer liquid gun (5 mL, Thermo, USA). For each discrete seawater sample, two parallel filtered samples were prepared, which were then measured by the PT-GC-PFPD system (8 min for each sample). The seawater DMS data sets obtained by PT-GC-PFPD were compared with those obtained by TOF-MS.

### 3. Results and discussion

#### 3.1. Instrument performance

The shipboard calibrations exhibited excellent peak area reproducibility (i.e., 4.94% for seawater measurements and 4.92% for air measurements; Fig. 3). The calibration curves displayed excellent linearity for both the seawater ( $y = 27704.7 \times - 1508.1$ ;  $R^2 = 0.999$ ) and

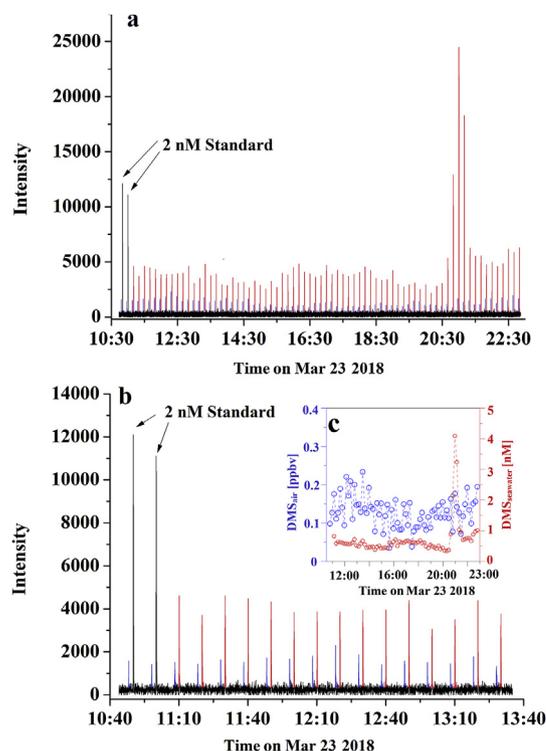


Fig. 4. Typical half-day observations during the CHINARE ANT34th. Note that b) shows the amplified region in a) between 10:40 and 13:40. The black, blue and red peaks represent the gas standard, air sample and seawater sample, respectively. The small plot, c), shows the calculated air (blue) and seawater (red) DMS levels. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

air ( $y = 50.83 \times - 1053.96$ ;  $R^2 = 0.997$ ) measurements (Fig. S7; five-point calibrations confirming the detector's linear responses are shown in the supporting material). System blanks were also tested under high-purity N<sub>2</sub> conditions for both seawater and air sample measurements. The values were the same as the baseline value at the peak times observed in the standard tests (Fig. S8). The DMS LODs, which were calculated by blank signal level plus 3 times the standard deviation of the blank signal (<https://goldbook.iupac.org/html/L/L03540.html>), were 0.07 nM for seawater and 32 pptv for air.

The ultimate goal of this study was to achieve the shipboard underway coupled measurements of trace DMS in seawater and the atmosphere. Fig. 4 shows typical half-day measurements obtained during the cruise, in which clear, sharp DMS peaks were obtained. The air and seawater samples could be easily distinguished from one another. A rough estimation of each seawater sample's DMS concentration could

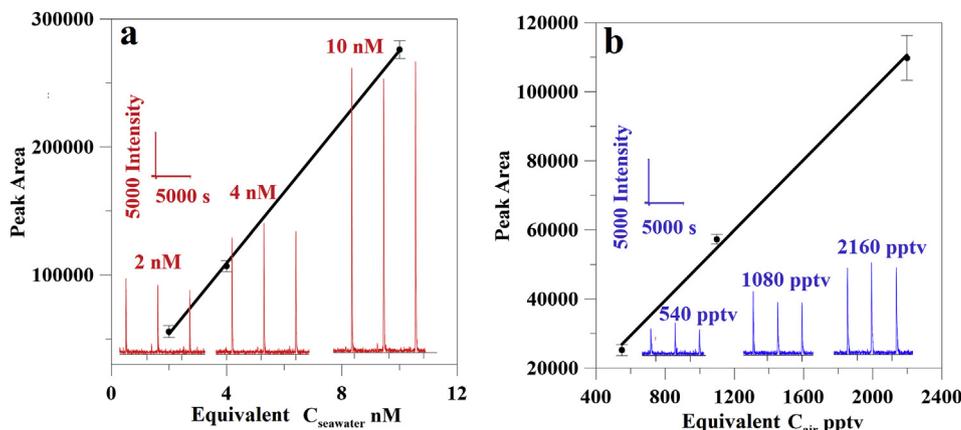


Fig. 3. Calibration curves for the a) seawater sample measurements ( $y = 27704.7 \times - 1508.1$ ,  $R^2 = 0.999$ ) and b) air sample measurements ( $y = 50.83 \times - 1053.96$ ,  $R^2 = 0.997$ ). Note that we used a 5 ppmv DMS standard gas (Wuhanteqi, China). Note that the equivalent seawater and air DMS concentrations were calculated from dividing amount of DMS standards by the volume of samples, i.e. 5 mL (seawater) and mean flow at 65 mL min<sup>-1</sup> for 3.5 min (air) respectively.

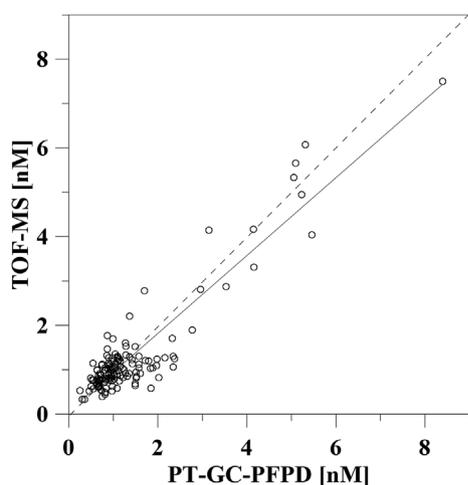


Fig. 5. Comparison between seawater DMS results detected by the purge-and-trap GC-PFPD and those detected by the custom-made TOF-MS device. The linear fit is  $y = 0.869x + 0.0897$  ( $n = 144$ ,  $R^2 = 0.82$ ).

be achieved by comparing its peak height with the standard peak of the DMS concentration (2 nM in seawater). The variability in the DMS levels in seawater and air can also be observed in the DMS peak height variations. Compared to the previous work reported by Saltzman et al. (2009), although our sampling resolution (10 min per sample) was lower than theirs (1 min per sample), our detection system exhibited much higher sensitivity basing on the LOD results.

### 3.2. Comparison between the custom-made TOF-MS system and the purge-and-trap GC-PFPD system

The results from the custom-made TOF-MS system and the purge-and-trap GC-PFPD system were compared for performance evaluation. As shown in Fig. 5, although both data sets were well correlated ( $y = 0.869x + 0.0897$ ,  $R^2 = 0.82$ ,  $n = 144$ ), obvious inconsistencies between the two systems can be seen, particularly when the DMS levels were low ( $< 3$  nM; slope = 0.42,  $R^2 = 0.25$ , and  $n = 133$ ; not shown). These uncertainties may arise from subtle changes in DMS levels during manual sampling and the analysis procedures for discrete GC-PFPD measurements of seawater. The detection uncertainties of the two different systems may also affect the results. However, we think that sample handing of the GC-PFPD samples poses the greatest problems. First, the filtering process may cause loss of DMS in seawater samples, as the seawater samples are directly exposed to ambient air. More importantly, however, filtering may break phytoplankton cells and release DMS into the sample, which is consistent with the GC-PFPD values being slightly higher than the TOF values over the entire measurement range (Fig. 5). Second, a much longer preparation time is required for the GC-PFPD samples, and many samples are stored in the refrigerator for more than 3 h before analysis, which may also cause changes in the DMS levels of the seawater samples (e.g., DMSP could be cleaved to DMS, which would also be consistent with the results shown in Fig. 5). Therefore, the measurements obtained using the custom-made TOF-MS system may be more suitable for obtaining accurate surface seawater DMS underway data than those obtained by the traditional manual PT-detector system.

### 3.3. Field measurement performance

The full DMS dataset obtained from the cruise expedition, with both air and water values, is shown in Fig. 6. The mean seawater and air DMS levels were  $1.7 \pm 2.5$  nM (ranging from undetected to 27.9 nM,  $n = 4366$ ) and  $0.26 \pm 0.41$  ppbv (ranging from undetected to 3.91 ppbv,  $n = 4255$ ), respectively. Compared with the dataset in the

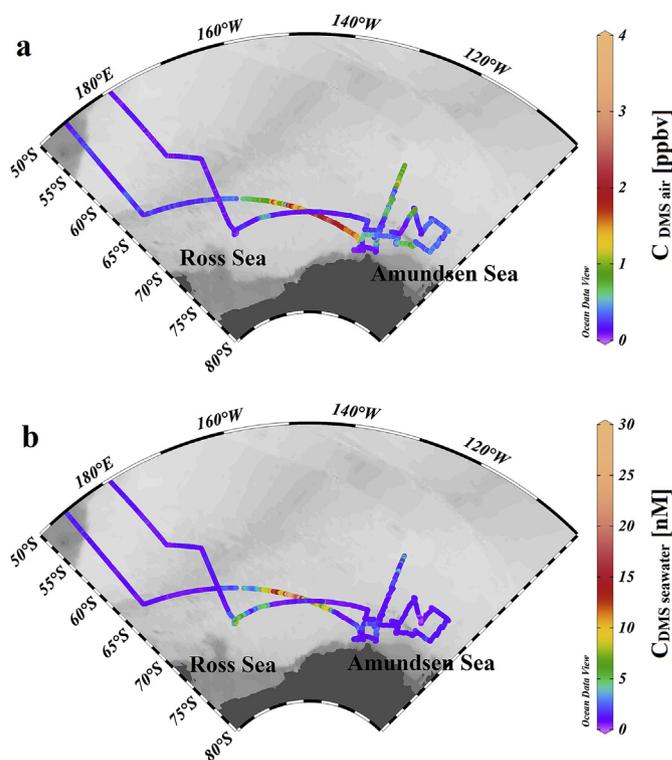


Fig. 6. Field data obtained during the CHINARE cruise for (a) atmospheric and (b) surface seawater DMS.

Global Surface Seawater DMS Database (<http://saga.pmel.noaa.gov/dms/>, Fig. S9), we obtained numerous surface seawater data points in areas previously uninvestigated for DMS in the Southern Ocean. The observed seawater DMS concentration hotspots in the Ross Sea sector were similar to the simulation results obtained by Lana et al. (2011). In the fall season in the Southern Ocean, the DMS levels were not as high as those in the summer season (Lana et al., 2011), which explained why we could only find a few seawater DMS hotspots during the expedition. However, it is difficult to find previously measured and available atmospheric DMS data in the Southern Ocean for comparison with ours because such investigations are rare. The atmospheric DMS variability was not always consistent with that in seawater. High wind speeds ( $> 10 \text{ m s}^{-1}$ ) and low air temperatures ( $< 0^\circ\text{C}$ , which extend the lifetime of DMS in the atmosphere) can strongly impact the air DMS, such that the DMS from other regions could be rapidly transported. The relatively high air DMS levels in the eastern part of the transect, where the seawater DMS levels were low, were possibly transported from the more western area of the cruise track with high DMS values (the large-scale hotspot in Fig. 6). We recorded a dominant wind direction from west to the east during the Southern Ocean portion of the cruise. Compared to the data obtained from coastal stations, such as Palmer Station ( $67.77^\circ\text{S}$ ,  $64.05^\circ\text{W}$ ; maximum DMS value of  $\sim 0.6$  ppbv) (Berresheim et al., 1998), Halley Station ( $75.58^\circ\text{S}$ ,  $26.31^\circ\text{W}$ ; maximum DMS value of  $\sim 0.3$  ppbv) (Read et al., 2008), and Dumont d'Urville Station ( $66.66^\circ\text{S}$ ,  $140.0^\circ\text{E}$ ; maximum DMS value of  $\sim 5.5$  ppbv) (Preunkert et al., 2007), the maximum atmospheric DMS levels (up to 3.91 ppbv) in more open waters were much higher than most of those observed over coastal regions. It is expected that high-resolution measurements of atmospheric DMS will yield a better understanding of the influence of oceanic DMS on atmospheric DMS levels and, thus, the oxidation products of DMS in air.

## 4. Summary

In this study, a custom-made system based on the purge-and-trap

technique and electric coolers was developed and evaluated during CHINARE ANT34th from February 2018 to April 2018. The system, coupled with a TOF-MS, was successfully deployed to measure DMS in seawater and air in a shipboard underway mode. The seawater and air streams were introduced into the system continuously and subsampled every 10 min. The LODs of DMS were determined to be 0.07 nM in seawater and 32 pptv in air. This system has been demonstrated to be able to sufficiently detect DMS in the field with excellent sensing performance. Furthermore, this system can be further developed for the measurement of other VOCs, such as isoprene and acetone. Using such instrumentation to measure a suite of trace gases in air-sea gradients can improve our current understanding of their global biogeochemical cycles and impacts on the atmosphere.

#### Author contributions

All authors contributed to writing this manuscript. All authors have given approval to the final version of the manuscript. The authors Miming Zhang and Wei Gao contributed equally. Dr. Miming Zhang developed the automated system, and Dr. Wei Gao provided the time-of-flight mass spectrometer (TOF-MS) for the observations.

#### Declaration of interests

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

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

#### Acknowledgments

We thank the Chinese Arctic and Antarctic Administration (CAA) of the Ministry of Natural Resources (MNR) and the crew of the R/V Xue Long for their support with the field operations. We sincerely thank the Guangzhou Hexin Instrument Co., Ltd., for their free support of SPI-TOF-MS 3000 and technical help with the Chinese Arctic and Antarctic Research Expedition since July 2017. We sincerely thank Mr. Meijiao Pang from the Hexin Company for his excellent skills in operating the TOF-MS system during the CHINARE ANT34th. We thank the engineer, Mr. Hongzhi Niu, from the Hexin Company for his kindness in preparing the TOF-MS and its periphery materials. Many thanks are extended to my teammate Prof. Zhaocai Wu from the Second Institute of Oceanography for his help with writing the MATLAB instructions. This work was supported by the National Natural Science Foundation of China (41706104, 41476172), with funding from the International Organizations and Conference and Bilateral Cooperation of Maritime Affairs, the Qingdao National Laboratory for Marine Science and Technology Foundation (No. QNLM2016ORP0109), the Scientific Research Foundation of the Third Institute of Oceanography, the SOA under contracts No. 2015031 and No. 2018014, the Ministry of Science and Technology and Key Research & Development Programs No. 2018YFC1406703, “Guangdong Special Branch Project” Science and Technology Young Pioneer Foundation (No. 2015TQ01X149), Provincial Science and Technology Plan Project of Guangdong (2016B030303004) and the Korea Polar Research Institute grant PE19060. Thank you for the anonymous reviewers and editors giving the useful comments to improve this manuscript.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2019.04.022>.

[doi.org/10.1016/j.atmosenv.2019.04.022](https://doi.org/10.1016/j.atmosenv.2019.04.022).

#### References

- Berresheim, H., Huey, J.W., Thorn, R.P., Eisele, F.L., Tanner, D.J., Jefferson, A., 1998. Measurements of dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, and aerosol ions at Palmer Station, Antarctica. *J. Geophys. Res.* 103 (D1), 1629–1637.
- Charlson, R.J., Lovelock, J.E., Andreae, M.O., Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud. *Nature* 326, 655–661.
- Jang, S., Park, K.T., Lee, K., Suh, Y.S., 2016. An analytical system enabling consistent and long-term measurement of atmospheric dimethyl sulfide. *Atmos. Environ.* 134, 217–223.
- Kameyama, S., Tanimoto, H., Inomata, S., Tsunogai, U., Ooki, A., Yokouchi, Y., Takeda, S., Obata, H., Uematsu, M., 2009. Equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) for sensitive, high-resolution measurement of dimethyl sulfide dissolved in seawater. *Anal. Chem.* 81 (21), 9021–9026.
- Kameyama, S., Tanimoto, H., Inomata, S., Tsunogai, U., Ooki, A., Takeda, S., Obata, H., Tsuda, A., Uematsu, M., 2010. High-resolution measurement of multiple volatile organic compounds dissolved in seawater using equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS). *Mar. Chem.* 122 (1–4), 59–73.
- Kim, I., Hahn, D., Park, K., Lee, Y., Choi, J.O., Zhang, M., Chen, L., Kim, H.C., Lee, S., 2017. Characteristics of the horizontal and vertical distributions of dimethyl sulfide throughout the Amundsen Sea Polynya. *Sci. Total Environ.* 584–585, 154.
- Lana, A., Bell, T., Simó, R., Vallina, S.M., Ballabrera-Poy, J., Kettle, A., Dachs, J., Bopp, L., Saltzman, E., Stefels, J., 2011. An updated climatology of surface dimethylsulfide concentrations and emission fluxes in the global ocean. *Glob. Biogeochem. Cycles* 25 (1), GB1004.
- Liss, P.S., Marandino, C.A., Dahl, E.E., Helmig, D., Hints, E.J., Hughes, C., Johnson, M.T., Moore, R.M., Plane, J.M., Quack, B., 2014. Short-lived trace gases in the surface ocean and the atmosphere. In: *Ocean-Atmosphere Interactions of Gases and Particles*. Springer, pp. 1–54.
- Marandino, C., De Bruyn, W., Miller, S., Saltzman, E., 2007. Eddy correlation measurements of the air/sea flux of dimethylsulfide over the North Pacific Ocean. *J. Geophys. Res.* 112, D03301.
- Marandino, C., De Bruyn, W., Miller, S., Saltzman, E., 2008. DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom. *Geophys. Res. Lett.* 35 (23), L23812.
- Marandino, C., De Bruyn, W., Miller, S., Saltzman, E., 2009. Open ocean DMS air/sea fluxes over the eastern South Pacific Ocean. *Atmos. Chem. Phys.* 9 (2), 345–356.
- Omori, Y., Tanimoto, H., Inomata, S., Kameyama, S., Takao, S., Suzuki, K., 2013. Evaluation of using unfiltered seawater for underway measurement of dimethyl sulfide in the ocean by online mass spectrometry. *Limnol. Oceanogr. Methods* 11, 549–560.
- Omori, Y., Tanimoto, H., Inomata, S., Ikeda, K., Iwata, T., Kameyama, S., Uematsu, M., Gamo, T., Ogawa, H., Furuya, K., 2017. Sea-to-air flux of dimethyl sulfide in the South and North Pacific Ocean as measured by proton transfer reaction-mass spectrometry coupled with the gradient flux technique. *J. Geophys. Res.: Atmosphere* 122 (13), 7216–7231.
- Park, K.T.P., Lee, K., 2008. High-frequency, accurate measurement of dimethylsulfide in surface marine environments using a microporous membrane contactor. *Limnol. Oceanogr. Methods* 6, 548–557.
- Preunkert, S., Legrand, M., Jourdain, B., Moulin, C., Belviso, S., Kasamatsu, N., Fukuchi, M., Hirawake, T., 2007. Interannual variability of dimethylsulfide in air and seawater and its atmospheric oxidation by-products (methanesulfonate and sulfate) at Dumont d'Urville, coastal Antarctica (1999–2003). *J. Geophys. Res.* 112 (D6), D06306.
- Read, K., Lewis, A., Bauguitte, S., Rankin, A.M., Salmon, R., Wolff, E.W., Saiz-Lopez, A., Bloss, W., Heard, D., Lee, J., 2008. DMS and MSA measurements in the Antarctic Boundary Layer: impact of BrO on MSA production. *Atmos. Chem. Phys.* 8 (11), 2985–2997.
- Saltzman, E., De Bruyn, W., Lawler, M., Marandino, C., McCormick, C., 2009. A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater. *Ocean Sci.* 5, 537–546.
- Scarratt, M., Cantin, G., Levasseur, M., Michaud, S., 2000. Particle size-fractionated kinetics of DMS production: where does DMSP cleavage occur at the microscale? *J. Sea Res.* 43 (3), 245–252.
- Tortell, P.D., 2005. Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr. Methods* 3, 24–37.
- Tanimoto, H., Kameyama, S., Iwata, T., Inomata, S., Omori, Y., 2013. Measurement of air-sea exchange of dimethyl sulfide and acetone by PTR-MS coupled with gradient flux technique. *Environ. Sci. Technol.* 48, 526–533.
- Vogt, M., Liss, P., 2009. Dimethylsulfide and climate. *Geophys. Monogr. Ser.* 187, 197–232.
- Zhang, M., Chen, L., 2015. Continuous underway measurements of dimethyl sulfide in seawater by purge and trap gas chromatography coupled with pulsed flame photometric detection. *Mar. Chem.* 174 (0), 67–72.
- Zhang, M., Marandino, C.A., Chen, L., Sun, H., Gao, Z., Park, K., Kim, I., Yang, B., Zhu, T., Yan, J., Wang, J., 2017. Characteristics of the surface water DMS and pCO<sub>2</sub> distributions and their relationships in the Southern Ocean, southeast Indian Ocean, and northwest Pacific Ocean. *Glob. Biogeochem. Cycles* 31 (8) 1318–2133.