Technical note

An analytical system enabling consistent and long-term measurement of atmospheric dimethyl sulfide

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HIGHLIGHTS

- A fully integrated, automated system for the continuous measurement of airborne DMS.
- The proposed system was proved to be stable for 3 full growth cycles of phytoplankton.
- The system enabled the measurements of short-term and long-term airborne DMS trends.

ARTICLE INFO

ABSTRACT

We describe here an analytical system capable of continuous measurement of atmospheric dimethylsulfide (DMS) at pptv levels. The system uses customized devices for detector calibration and for DMS trapping and desorption that are controlled using a data acquisition system (based on Visual Basic 6.0/C 6.0) designed to maximize the efficiency of DMS analysis in a highly sensitive pulsed flame photometric detector housed in a gas chromatograph. The fully integrated system, which can sample approximately 6 L of air during a 1-hr sampling, was used to measure the atmospheric DMS mixing ratio over the Atlantic sector of the Arctic Ocean over 3 full annual growth cycles of phytoplankton in 2010, 2014, and 2015, with minimal routine maintenance and interruptions. During the field campaigns, the measured atmospheric DMS mixing ratio varied over a considerable range, from <1.5 pptv to maximum levels of 298 pptv in 2010, 82 pptv in 2014, and 429 pptv in 2015. The operational period covering the 3 full annual growth cycles of phytoplankton showed that the system is suitable for uninterrupted measurement of atmospheric DMS mixing ratios in extreme environments. Moreover, the findings obtained using the system showed it to be useful in identifying ocean DMS source regions and changes in source strength.

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1. Introduction

Dimethyl sulfide (DMS) is a volatile byproduct of the enzymatic breakdown of dimethyl sulfoniopropionate (DMSP), a compound produced by phytoplankton. DMS is a major natural source of tropospheric sulfur, which may have an impact on the radiative balance of the atmosphere (Bates et al., 1987; Simó, 2001). The potential role of marine DMS in regulating climate was highlighted by Charlson et al. (1987). In the proposed mechanism, atmospheric DMS is rapidly oxidized by hydroxyl radicals and is then transformed into sulfuric and methane sulfonic acids, both of which contribute to the formation of cloud condensation nuclei (CCN) (Shaw, 1983; Andreae and Crutzen, 1997). CCN may alter the radiation budget of the atmosphere via albedo change (Andreae and Rosenfeld, 2008), which could consequently influence the amount of incoming solar radiation, and thereby affect the temperature of the upper ocean. Change in the upper ocean temperature may change DMS production by shifting the major phytoplankton species (Simó, 2001; Stefels et al., 2007). Change in the production of DMS could lead to change in the production of CCN (Andreae and Crutzen, 1997). As a result, the production of DMS and regional/global climate may be closely linked. This linkage has yet to be experimentally demonstrated, but such a negative

feedback mechanism may in part offset the global warming resulting from anthropogenic CO_2 (Charlson et al., 1987).

It is not possible to test whether the production of DMS is positively linked to the production of CCN, because atmospheric DMS measurements lack adequate spatial and temporal coverage. This is largely because the measurement systems used to date have not been sufficiently sensitive, complex, and durable to enable consistent measurement of such short-lived DMS to be made over long periods (seasons to years). Various methods have been used to determine atmospheric DMS levels in field campaigns. Most published methods involve the time-consuming process of trapping atmospheric DMS either in a Pyrex glass tube filled with gold wire or in a canister, and then measuring eluted DMS in a laboratory (Leck and Persson, 1996; Persson and Leck, 1994; Preunkert et al., 2007). In situ measurements have also been performed by concentrating atmospheric DMS in a cryogenic trap from which the DMS was eluted and then analyzed (e.g., Bates et al., 1990; Cooper and Saltzman, 1991; De Bruyn et al., 2002; Kim et al., 2000, 2004; Swan et al., 2015).

The in-situ measurement systems include a component for DMS trapping and elution and a gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD) enabling DMS quantification. However, not all components were completely automated and integrated and, as a result, considerable manual input is required to operate the systems over extended periods (months to years). Moreover, to ensure measurement accuracy, some of the in situ analytical systems require regular calibration of the GC-PFPD against known moles of DMS released by a permeation tube containing pure liquid DMS. However, the use of this type of DMS standard over extended periods may result in significant uncertainty in DMS measurements because the amount of DMS released from the permeation tube may change over time (Kim et al., 2016). Therefore, another DMS standard should be used in parallel to evaluate the accuracy of the DMS permeation tube. This practice is particularly useful for long-term measurement of atmospheric DMS in remote locations.

A promising alternative analytical system is based on mass spectrometry (e.g., chemical ionization mass spectrometer) (Mungall et al., 2015). This newly introduced system is based on straightforward measurement principles and can provide highly time-resolved data. However, this system is expensive and its long-term durability has yet to be tested in the field.

We described here the key components of a fully integrated, automated analytical system for the continuous measurement of atmospheric DMS mixing ratios over extended periods (>a year). Measurements to assess its performance over 3 full growing seasons of phytoplankton demonstrated the consistency of the analytical system. Atmospheric DMS concentrations measured using the analysis system at the Zeppelin observatory (Svalbard, Norway) are also presented to highlight the utility of the proposed measurement protocol.

2. Materials and procedures

2.1. Components of the DMS analytical system

The analytical system for measuring atmospheric DMS mixing ratio comprised: (i) a thermostat-controlled inlet for maintaining the temperature of incoming ambient air approximately constant (i.e. to prevent the sudden influx of cold sample); (ii) an integrated unit for DMS trapping and desorption; (iii) a PFPD (Model 5830, OI Analytical, USA) housed in a GC (Agilent 6890N, Agilent Technologies, USA); and (iv) a calibration unit for the detector (Fig. 1). To detect low levels of atmospheric DMS (<1.5 pptv), a trap half-filled with Tenax TA 60—80 mesh (120 mg; Chrompack Inc., USA) and a

graphitized carbon trap (U-T14H2S, MARKES International, UK) were used for the 2010 and 2014—2015 field campaigns, respectively. The DMS trapping efficiency of the Tenax TA trap has been reported to be stable over a temperature range of −10 °C to 50 °C (Zemmelink et al., 2002). A DB-1 GC column (30 m long, 0.32 mm diameter, 5.0 μm pore size, J&W Scientific, USA) was used to separate the DMS peak from other chemical signals.

The PFPDs have been shown to be far superior to the flame photometric detectors (FPDs) in detection sensitivity (two orders of magnitude more sensitive) and consumes less H_2 and air (a factor of 20 less) (Cheskis et al., 1993). Therefore, PFPDs are commonly used for measuring reduced sulfur compounds, and have been shown to perform reliably (Steudler and Kijowski, 1984). The response of PFPDs is sensitive to the tuning conditions including the ratio of gases (H_2, air and He), the photomultiplier tube (PMT) voltage, and other factors. In particular, the PMT voltage needs to be adjusted to a specific level for optimal sensitivity for the target concentrations of the sulfur compounds, and the voltage chosen influences the linearity of the detection response (Kim, 2005). As a result, the tuning conditions are important in achieving optimal detector response for the target DMS concentrations. Detailed information about the components of the analytical system and its operating parameters are given in Table 1.

The proposed DMS system was remotely controlled throughout the study period. All required maintenances including the replacement of gases (H_2, air and He) and an oxidant and moisture scrubber were performed by local engineers at the Zeppelin observatory.

2.2. Sequence of DMS analysis

Analysis of atmospheric DMS mixing ratios using the analysis system described above was executed in a sequence involving pre-purging of the DMS trap, DMS trapping and subsequent elution, and DMS analysis. More detailed information on each measurement event (valve control, trap temperature, and the duration of each event) is given in Table S1. Prior to introducing the ambient air to the trap, the trap was flushed for 5 min using ultra-pure He gas (99.99%) to remove any DMS residue from the previous air sample analyzed. To achieve this, valve 2 (V2 in Fig. 1; Valco Instrument Co. Inc., USA) was set to the "on" position.

In operation, the stream of air flows through a thermostat-controlled inlet and a scrubber packed with KI and K_2CO_3 to ensure that oxidants and moisture are removed before the air sample reaches the DMS trap. The air sample was then drawn through a PTFE line at a rate of 100 mL min^{-1} for 10—90 min using a diaphragm vacuum pump (PM24463-86, KNF Neuberger, Germany). The duration of this process was determined by the atmospheric DMS mixing ratio and a mass flow controller (MODEL 3660, KOFLOC, Japan) that controlled the flow rate when V2 was set to the "off" position. The optimal volumes of air needed for an effective detection are shown in Table S2. When a sufficient amount of DMS for analysis has been trapped, the trap is heated to ~220 °C using a custom-made thermoelectric unit (Park and Lee, 2008), and the DMS is eluted from the trap. The thermoelectric unit increases the trap temperature from 20 °C to 220 °C within 1.5 min. In parallel, V2 is set to the "on" position, and He gas carries the eluted DMS into the GC column. The procedure for DMS elution and subsequent injection into the GC column takes ~1.5 min. For separation of the DMS, the gases in the trap are transferred to the capillary column in the GC oven at a constant temperature of ~50 °C, over a period of 3 min. The GC oven temperature is increased to ~240 °C to elute the DMS from the column, and ultra-pure He gas passes through the column carries the eluted DMS to the PFPD. A pressure controller built in the GC regulates the flow rate of the He stream containing