Atmos. Meas. Tech. Discuss., 8, 13157–13197, 2015
www.atmos-meas-tech-discuss.net/8/13157/2015/
doi:10.5194/amtd-8-13157-2015

Atmospheric Measurement Techniques Discussions

Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-ToF-MS and off-line GC-FID

V. Perraud, S. Meinardi, D. R. Blake, and B. J. Finlayson-Pitts

Department of Chemistry, University of California, Irvine, CA 92697, USA

Received: 10 November 2015 – Accepted: 24 November 2015 – Published: 15 December 2015

Correspondence to: B. J. Finlayson-Pitts (bjfinlay@uci.edu) and D. R. Blake (drblake@uci.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Organosulfur compounds (OSC) are naturally emitted via various processes involving phytoplankton and algae in marine regions, from animal metabolism and from biomass decomposition inland. These compounds are malodorant and reactive. Their oxidation to methanesulfonic and sulfuric acids leads to the formation and growth of atmospheric particles, which are known to have negative effects on visibility, climate and human health. In order to predict particle formation events, accurate measurements of the OSC precursors are essential. Here, two different approaches, proton-transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) and canister sampling coupled with GC-FID are compared for both laboratory standards [dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS) and methanethiol (MTO)] and for a complex sample. Results show that both techniques produce accurate quantification of DMS. While PTR-ToF-MS provides real-time measurements of all four OSCs individually, significant fragmentation of DMDS and DMTS occurs, which can complicate their identification in complex mixtures. Canister sampling coupled with GC-FID provides excellent sensitivity for DMS, DMDS and DMTS. However, MTO was observed to react on metal surfaces to produce DMDS and, in the presence of hydrogen sulfide, even DMTS. Avoiding metal in sampling systems seems to be necessary for measuring all but dimethyl sulfide in air.

1 Introduction

Organosulfur compounds (OSC) such as methanethiol (CH_3SH, MTO), dimethyl sulfide (CH_3SCH_3, DMS), dimethyl disulfide (CH_3SSCH_3, DMDS), and dimethyl trisulfide (CH_3SSSCH_3, DMTS) have been measured in air (Nguyen et al., 1983; Andreae et al., 1985, 1993; Andreae, 1990; Aneja, 1990; Bates et al., 1992; Watts, 2000; de Bruyn et al., 2002; Xie et al., 2002; Jardine et al., 2015). In marine environments, DMS is the major organosulfur compound emitted from phytoplankton decomposition and al-

gae activities. Organosulfur compounds have also been reported from terrestrial biogenic sources including wetlands, soils, vegetation and biomass burning (Goldan et al., 1987; Bates et al., 1992; Kesselmeier et al., 1993; Crutzen et al., 2000; Watts, 2000; Meinardi et al., 2003; Geng and Mu, 2006; Yi et al., 2008; Jardine et al., 2015). In addition to these biogenic sources, several recent studies report organosulfur compound emissions from anthropogenic agricultural and composting activities, and from animal waste (Burnett, 1969; Williams et al., 1999; Filipy et al., 2006; Shaw et al., 2007; Trabue et al., 2008; Feilberg et al., 2010; Papurello et al., 2012; Meinardi et al., 2013; Zhang et al., 2013).

In the atmosphere, organosulfur compounds have short lifetimes with respect to OH radicals during the day and NO_3 radicals at night, leading to the formation of sulfur dioxide (SO_2) (and ultimately sulfuric acid, H_2SO_4) and methanesulfonic acid (CH_3SO_3H, MSA) (Hatakeyama and Akimoto, 1983; Grosjean, 1984; Barnes et al., 1988, 1994, 2006; Berresheim et al., 1990; Yin et al., 1990a, b; Tyndall and Ravishankara, 1991; Davison and Hewitt, 1994; Vandingenen et al., 1994; Capaldo and Pandis, 1997; Patroescu et al., 1999; Finlayson-Pitts and Pitts, 2000; Zhu et al., 2006; Berndt and Richters, 2012). For example, under a typical daytime OH concentration of 5×10^6 cm^{-3}, the lifetime of DMS in air is about 8 h, and for a typical nighttime NO_3 of 5×10^8 cm^{-3}, it is $\sim$ 30 min. In the presence of water, amines and/or ammonia, H_2SO_4 and MSA are known to form new particles in air (Kulmala et al., 2004; Bzdek and Johnston, 2010; Smith et al., 2010; Dawson et al., 2012; Zhang et al., 2012). These newly formed particles then grow to sizes able to scatter sun light and impact clouds, thus influencing the Earth's energy balance and climate (Finlayson-Pitts and Pitts, 2000; Kulmala and Kerminen, 2008; Hallquist et al., 2009; Zhang et al., 2012). In addition, particles negatively affect health and visibility (Dockery et al., 1993; Hinds, 1999; Pope III et al., 2002; Pope III and Dockery, 2006).

Because of their key role in the formation of new particles in air, it is critical to account for all sources of organosulfur compounds (OSC). Several sample collection strategies have been applied over the years to the measurement of OSC in air including the use of

Tedlar® chambers (Hansen et al., 2011), metal canister or glass vessel-based methods (Kesselmeier et al., 1993; Williams et al., 1999; Simpson et al., 2001; Meinardi et al., 2003, 2013; Blunden et al., 2005; Trabue et al., 2008; Beyersdorf et al., 2010; Guo et al., 2010; Khan et al., 2012; Zhang et al., 2013), solid sorbents (Filipy et al., 2006) or sorptive metal (Andreae et al., 1985), solid-phase microextraction (Xie et al., 2002; Lestremau et al., 2004) and cryotraps (Hofmann et al., 1992; de Bruyn et al., 2002). Subsequent analysis of the collected sample is typically performed by gas chromatography. However, quantifying these species is quite challenging due to their oxidation and loss on surfaces (Kuster and Goldan, 1987; Devai and Delaune, 1994; Katoh et al., 1995; Wardencki, 1998; Sulyok et al., 2002; Bashkova et al., 2003; Lestremau et al., 2004; Kim et al., 2006; Andersen et al., 2012). More recently, proton-transfer reaction mass spectrometry (PTR-MS) has been applied to the measurement of these species from various sources (Crutzen et al., 2000; Hayward et al., 2002; Aprea et al., 2007; Shaw et al., 2007; Feilberg et al., 2010; Kai et al., 2010; Hansen et al., 2012a, 2013; Papurello et al., 2012; Koga et al., 2014) including breath (Taucher et al., 1996; Herbig et al., 2009) and food (Aprea et al., 2007). This technique provides fast response, high sensitivity, and in general, relatively low fragmentation. It has been increasingly applied to the measurement of volatile organic compounds; however, it is sensitive only to molecules that have a proton affinity higher than that of water, and fragmentation does occur for larger compounds, which complicates attributions of peaks in complex mixtures (Buhr et al., 2002; Tani et al., 2003). In addition, despite that sample collection is not required, uptake or displacement on sampling lines can occur for some compounds (Christian et al., 2004; Mikoviny et al., 2010; Freshour et al., 2014).

In this paper, we report a comparison between two techniques for the measurements of trace OSC in air, including direct real-time measurements by proton-transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) and off-line stainless steel canister sampling coupled to GC-FID. Advantages and challenges associated with these two techniques are discussed with respect to sampling complex mixtures.

2 Materials and methods

2.1 PTR-ToF-MS

Measurements of OSC in air were performed using a high-resolution proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik). This instrument has been described previously (Jordan et al., 2009; Graus et al., 2010) and only the key features related to this particular study are presented here. The air sample was introduced via heated 1/16″ PEEK® tubing maintained at 70 °C (343 K) at a constant flow of 150 $cm^3 min^{-1}$. The instrument was operated under the standard ion drift tube conditions with a total voltage of 600 V (U_{drift}) and pressure between 2.10 and 2.15 mbar (p_{drift}). Under these conditions, the ratio of the electric field (E) to the number density (N) of the drift tube buffer gas molecules (E/N) was kept at values of 130–133 Townsends (Td) (1 Td = 10^{-17} cm^2 V $molecule^{-1}$) throughout all measurements, leading to the predominance of the cluster H_3O^+ in the ion drift over the higher mass water clusters (de Gouw and Carsten, 2007). Collisions of the H_3O^+ ions with a volatile organic compound generally results in a proton transfer reaction if the compound has a proton affinity (PA) higher than that of water (PA(water) = 691 kJ mol^{-1}). Because of the low energy ion source, the ionization process is generally considered "soft", and in most cases generates a single parent ion at $[M+H]^+$. However, many reactive compounds fragment, and all fragments must be taken into account to estimate the mixing ratios of the targeted species if they are derived from PTR-ToF-MS parameters rather than calibration with standards.

In this work, the mixing ratios of each OSC, C_{ppb}, were quantified based on Eq. (1):

$$C_{ppb} = \frac{1}{S} \times \frac{\sum(I_{mz} - I_{mz\_background})}{\left(\frac{I_{H_3O^+}}{10^6}\right)}, \quad (1)$$

where S is a calibration factor (or sensitivity) for the target OSC expressed in normalized counts per second per ppbv (ncps $ppbv^{-1}$) determined experimentally using pure

standards, I_{mz} and $I_{mz\_background}$ are the raw and background ion signal in counts per second (cps) respectively for one given OSC mass fragment, and ($I_{H_3O^+}$) is the ion signal in cps for the hydronium ion. The hydronium ion counts were in the range (0.7–2.90) × 10^6 cps over the entire period of the study. In practice, $I_{H_3O^+}$ is normalized to 10^6 cps to yield normalized counts per seconds (ncps). For each OSC, quantification was evaluated using the sum of the major fragments, although in principle, one peak would be sufficient when calibrations are carried out independently using authentic compounds (see Sect. 3.1). It is important to note that the calibration factor S depends strongly on the operating conditions, maintenance and tuning of the instrument and, as a result may differ between studies. Calibrations were performed regularly during the entire period of the study to ensure proper quantification. Multiple analyses of the same OSC standard concentration were used to evaluate the day-to-day instrument variation, from which an uncertainty of ∼ 30 % (two standard deviations) was derived for any given reported mixing ratio.

An alternative method for determining mixing ratios of VOCs directly from the PTR-ToF-MS source parameters ($U_{drift}, p_{drift}, T_{drift}$, length of the reaction chamber etc.), measured ion transmission efficiencies (T_r), published values of the kinetic rate constant (k) between the target H_3O^+ and the targeted OSC, and the reduced ion mobility of H_3O^+ ions μ_o (= 2.8 $cm^2 V^{-1} s^{-1}$) was described previously (de Gouw and Carsten, 2007) (see Supplement). However, this method requires determining the transmission efficiencies accurately as well as having evaluated and recommended rate constants for OSC with H_3O^+ ions, for which data are scarce (Passarella et al., 1987; Arnold et al., 1998; Lindinger et al., 1998; Španìl and Smith, 1998; Williams et al., 1998; Wang et al., 2004; Zhao and Zhang, 2004; Blake et al., 2009; Cappellin et al., 2010). As a result, this method typically yields larger uncertainties on the estimated mixing ratios.

In this work, mass spectra and temporal ion signal profiles were extracted using the PTR-MS TOF Viewer software (Ionicon Analytik version 1.4.0) and a modified Gaussian function fit for each peak (Graus et al., 2010). The PTR-ToF-MS is equipped with a time-of-flight mass filter with a resolution of ∼ 5000, which allows for accurate mass

determination. The lock masses used for the accurate mass determination were the isotopic peaks of the protonated water ion at m/z 21.0226 ($[H_3^{18}O]^+$) and the protonated acetone $[M+H]^+$ ion at m/z 59.0497, which was always present in room air sampled at the beginning of each run. For the source samples, the protonated ion for acetone at m/z 59 could not be used because it was also found in sufficiently high concentration to saturate the detector so the masses m/z 21.0226 ($[H_3^{18}O]^+$) and m/z 123.946 (a common contaminant peak corresponding to SiO_6^+ ion) were used instead.

2.2 Canister sampling coupled with GC-FID analysis

Samples were collected into evacuated 2 L electropolished stainless steel canisters. Prior to sampling, the canisters were cleaned and conditioned according to a procedure described previously (Blake et al., 1994). It has been shown that in order to increase the stability of certain compounds in the canister as well as provide reproducible split ratios at the injection, small amounts of water must be present in the canister prior to analysis (Colman et al., 2001). Ambient samples always contain some water; however laboratory generated standards do not. Thus, for an appropriate analysis of the standards, 18–20 Torr of water vapor was added prior to sampling (hereafter referred to as water-doped canisters), but no water was added to the ambient air canister samples.

At the beginning of an ambient air sample collection, the inlet valve of the canister was fully opened so that the canister reached its final pressure of ∼ 15 psig (1 atm) in less than a minute. The canisters were analyzed the same day as the collection. For analysis of each canister, 1350 cm^3 of air sample was concentrated by pumping it through a stainless steel loop (10 mL) filled with glass beads immersed in liquid nitrogen. This procedure assures trapping of most of the organic compounds of interest while more volatile species such as CH_4, N_2, O_2, Ar, etc. are pumped away. The concentrated sample was then vaporized by heating the loop with hot water (∼ 80 °C) and injected into a parallel three-GC system (Hewlett-Packard) using He as the carrier gas. Details of the complete analytical system can be found elsewhere (Colman et al., 2001).

The OSC of interest were identified by comparison with standards and quantified using a flame ionization detector (FID).

2.3 Gas phase OSC standards

A gas mixture containing 1.02 ± 0.05 ppm (uncertainty taken as 1σ) of dimethyl sulfide (DMS) and 0.948 ± 0.047 ppm (uncertainty taken as 1σ) of dimethyl disulfide (DMDS) in nitrogen was obtained from Scott-Marrin and used for calibration (uncertainty provided by the supplier). In addition, generation of gas phase OSC was achieved by injecting a solution of the pure standards in cyclohexane (Fluka, Spectranalyzed grade) using a syringe pump (Pump systems Inc., model NE-1000), into a stream of dry synthetic air (Ultra Zero Air, 99.999 %, Praxair) following a method similar to that described by Jardine and co-workers (Jardine et al., 2010) (see Supplement and Fig. S1 in the Supplement for details), hereafter referred to as the *dynamic injection system*. The standards included DMS (≥ 99 %, Sigma-Aldrich), DMDS (≥ 99 %, Sigma-Aldrich) and dimethyl trisulfide (DMTS, ≥ 98 %, SAFC). The mixing ratios after dilution were estimated using error propagation analysis (Harris, 1991), with an estimated accuracy of ±10 % (2σ) for the DMS/DMDS gas cylinder, and ±20 % (2σ) for the mixtures from the dynamic injection system.

A certified gas mixture containing 4.03 ppm of methanethiol (MTO) was obtained from Airgas. In addition, a pure gas phase MTO standard from Matheson (purity 99 %) was used to prepare our own gas mixture in the laboratory using a glass manifold. Ultra zero grade air was supplied from Praxair for dilution. The uncertainty in the mixing ratio of MTO in the primary mixture prepared this way was estimated to be ±1 % (2σ). Further dilution of the primary mixture prepared in a 6 L glass bulb was used for calibration as described in Sect. 3.2.

Lastly, for a separate series of experiments, generation of gas phase DMTS, MTO and hydrogen sulfide (H_2S) standards was performed using permeation tubes (VICI), which were each enclosed individually in a U-shaped glass tube and maintained at 50 °C using a thermostated water bath (LAUDA, model M20). A flow of 200 $cm^3\,min^{-1}$

dry, filtered air purified by passing through an FTIR purge gas generator (Parker Balston Model 75-62), carbon/alumina media (Perma Pure, LLC) and an inline 0.1 µm filter (DIF-N70; Headline Filters) served as the carrier gas and diluent through the permeation tube. Permeation rates for MTO and H_2S were determined gravimetrically giving values of 337 ± 106 and $133 \pm 14\,\mathrm{ng\,min^{-1}}$, respectively. The uncertainties represent those from repeated weight measurements and are higher for MTO than stated by the manufacturer (30 vs. 15 %) and lower for H_2S (10 vs. 25 %). The accuracy of the mixing ratios after dilution were estimated to be the same as that estimated for the primary gas phase mixing ratio, as this is the higher uncertainty in the system. It was not possible to determine accurately the absolute permeation rate for DMTS due to large variations in the weight of the tube and the presence of some DMDS in the outflow; however, even if the gas phase generation system could not be used for absolute calibration of DMTS, as described in Sect. 3.3, it was useful for the stability study where only relative mixing ratios were needed.

2.4 Sampling from a complex source

To compare the performance of both measurement methods on an urban source, the headspace above street waste bins from a residential area with many pets was sampled with both the PTR-ToF-MS and the canister/GC-FID method. Since it is known that livestock in agricultural areas is a significant source of OSC (Burnett, 1969; Williams et al., 1999; Filipy et al., 2006; Shaw et al., 2007; Trabue et al., 2008; Feilberg et al., 2010; Papurello et al., 2012; Meinardi et al., 2013; Zhang et al., 2013), the same might be expected for the bins. Two bins were sampled repeatedly: a 135 L bin and a 21 L bin, whose content had varied weights (1–8 lb). Before each sampling period, the bin was opened to ambient air to clear out the headspace above the sample. The PTR-ToF-MS inlet was then attached to the lid of the bin, and the sampling started when the lid was repositioned on the bin. This approach allowed for the measurement of emission rates of the sulfur compounds from the bin. After each 20 min sampling period with the PTR-ToF-MS, one canister was attached to the inlet of the container and a sample was

taken for comparison. Blank measurements from the bins themselves and plastic bin liners were also performed and show no detectable OSC compounds.

3 Results and discussion

3.1 Fragmentation pattern of the OSC in the PTR-ToF-MS

Signal response and fragmentation patterns in the PTR-ToF-MS were investigated from the analysis of the pure OSC standards (Fig. 1). Dimethyl sulfide, DMDS and MTO have known proton affinities (Lide, 1994) of 830.9, 815.3 and $773.4\,\mathrm{kJ\,mol^{-1}}$, respectively, well above the proton affinity of water ($691\,\mathrm{kJ\,mol^{-1}}$). As a result, these compounds are expected to be efficiently ionized in the PTR-ToF-MS and no relative humidity dependence of the signal is expected for these compounds. There are no reported values for the proton affinity for DMTS, but this compound is expected to behave similarly to DMS and DMDS.

As seen in Fig. 1a and b, MTO and DMS give one major peak corresponding to their respective protonated $[M+H]^+$ ions at nominal masses m/z 49 and 63 respectively. Accurate mass determination shows very good agreement with the expected elemental composition for the protonated ion within −0.6 mDa of the expected mass (Table 1 and Fig. S2 in the Supplement). In addition, the isotopic distribution for both parent ions agrees well with the presence of one single sulfur atom in the molecule with an $^{34}S/^{32}S$ isotopic ratio of ∼ 4 % (Berglund and Wieser, 2011).

The mass spectrum of the DMDS standard (Fig. 1c) shows a base peak at nominal mass m/z 95 corresponding to the $[M+H]^+$ ion and a fragment at m/z 79. Accurate mass determination (Table 1 and Fig. S2) confirmed the identity of the parent ion at m/z 94.9984 (−0.5 mDa away from $[CH_3SSCH_3 + H]^+$ exact mass), and the ion at m/z 78.9667 was attributed to the CH_3SS^+ ion fragment (−0.9 mDa mass difference). Under our experimental conditions, the peak intensity at m/z 79 was ∼ 38 % of the base peak (m/z 95). In the PTR-ToF-MS, the fragmentation of one species is gener-

ally governed by the electric field strength (E/N) applied to the drift tube (Tani et al., 2003). Our experiments were carried out at an E/N of 130–133 Td. Schuhfried and co-workers (Schuhfried et al., 2013) studied the fragmentation of DMDS at different E/N values using density functional calculations and reported a value for m/z 79 contribution between 20.7 % at E/N = 127 Td and 66.3 % at E/N = 140 Td. Our work is in good agreement with these calculations (Fig. S3). In addition, a very small fragment at m/z 49 from the DMDS standard was observed with an intensity of ∼ 4 % of the base peak (m/z 95), which is in good agreement with the value of 5 % predicted by Schuhfried and co-workers (Schuhfried et al., 2013).

Compared to the smaller OSCs, DMTS shows much more fragmentation in PTR-ToF-MS. Figure 1d shows the mass spectrum obtained when sampling DMTS standard from the dynamic injection system. Peaks corresponding to the protonated ion $[M+H]^+$ and CH_3SS^+ ions were observed at m/z 126.9711 (+0.1 mDa mass difference from $[CH_3SSSCH_3 + H]^+$ exact mass) and m/z 78.9680 (+0.4 mDa mass difference from CH_3SS^+ exact mass) respectively. Five additional peaks, previously reported as fragments in the DMTS mass spectrum (Mockel and Weiss, 1980), were observed at nominal masses m/z 93, 81, 61, 49 and 45 and were assigned to $CH_3SSCH_2^+$, $CH_3SSH_2^+$, $CH_3SCH_2^+$, $CH_3SH_2^+$, and CHS^+ respectively. These assignments are supported by the excellent agreement with the exact masses (see Fig. S2 and Table 1). It is important to note that the peak at m/z 80.9806 corresponds here to a fragment and is not due to the isotopic distribution of the major fragment at m/z 78.9680 (see Fig. S2). The intensity observed at m/z 80.9806 is 28 % of that of the peak at nominal mass m/z 79. This is much larger than the isotopic distribution expected for sulfur containing compounds, which would be 8.9 % for a $[CH_3\text{-}^{32}S\text{-}^{34}S]^+$ fragment (Berglund and Wieser, 2011). Finally, although a peak at nominal mass m/z 96 was also observed in the mass spectra of DMTS, accurate mass determination precluded the assignment to an S_3^+ fragment (Fig. S4) and the identity of this minor fragment remains unknown. This fragment was previously reported by Mockel and Weiss (Mockel and Weiss, 1980) from DMTS chemical ionization mass spectrometry analysis, however the study was done

using a quadrupole mass spectrometer which cannot provide exact mass information. In the present study, the relative intensities of the fragments observed, taking the base peak at m/z 79 to be 100, are 9 : 19 : 13 : 100 : 28 : 31 : 8 : 23 for m/z 45, 49, 61, 79, 81, 93, 96 and 127, respectively.

3.2 Quantification of OSC by PTR-ToF-MS

Calibration of the PTR-ToF-MS for DMS, DMDS and DMTS was performed using successive dilution of the 1 ppm certified gas cylinder for DMS/DMDS, and the outflow of the dynamic injection system for DMTS. The dynamic injection system was also used with DMS and DMDS standards to validate the technique. Very good agreement between the gas cylinder and dynamic injection system was observed for DMS/DMDS (Fig. S5), supporting its application to DMTS calibration. Measurements showed a linear dynamic range from 0 to ≥ 250 ppb for all three sulfides (Fig. S5). Analytical limits of detection were estimated as 3σ of the baseline noise, where peak-to-peak baseline variation was taken as 5σ (Skoog and Holler, 2007). Limits of detection (LOD) for DMS and DMDS were both 49 ± 15 ppt, while the LOD for DMTS was 81 ± 24 ppt.

Calibration for MTO was more difficult to achieve due to its loss and reactivity on surfaces. For example, losses on metal surfaces were observed when placing a ∼ 20 cm stainless steel or copper tubing in the sampling line between the certified 4.3 ppm MTO gas cylinder and the PTR-ToF-MS inlet. Figure S6 shows a drastic loss of MTO in both cases as soon as the metal tube is inserted. In addition, PTR-ToF-MS analysis from the certified gas cylinder revealed that DMDS was formed inside the regulator, which precluded the use of this standard for calibration (Fig. S6). As an alternative, we chose to perform the PTR-ToF-MS calibration using our own laboratory generated gas phase mixture of MTO in clean dry synthetic air from a gas cylinder of pure MTO. Once extracted from the cylinder, the gas was never in contact with any metal tubing or connectors. Known amounts of the pure standard were transferred into a previously evacuated 5 L glass bulb that was pumped on overnight. Successive dilutions in clean dry synthetic air were then made using a glass manifold to reach a final mixing ratio

of 4.08 ± 0.04 ppm MTO. This mixture was stored in a separate previously evacuated 6 L glass bulb overnight to make sure the mixture was well mixed in the bulb prior to its use. During preparation of the mixture, there was no evidence for MTO loss on the glass surfaces, consistent with the observation of Devai and DeLaune who reported a 90 % recovery after 24 h for MTO samples prepared in dry air in a 125 mL glass bulb (Devai and Delaune, 1994). Calibration mixtures were prepared by diluting a flow of 50 $cm^3 min^{-1}$ of the bulb contents with a flow of 1 to 7.5 $L min^{-1}$ of dry synthetic air. No evidence of any other OSC was observable in the PTR-ToF-MS spectra, apart from MTO. A linear dynamic range was observed from 0 to 200 ppb (Fig. S5) and an LOD of 65 ± 20 ppt was determined.

3.3 Analysis of OSC standards using the canisters and GC-FID

Quantification of DMS and DMDS (but not DMTS) using electropolished stainless steel canisters has been previously reported (Colman et al., 2001; Simpson et al., 2001; Meinardi et al., 2003, 2013; Beyersdorf et al., 2010; Guo et al., 2010). In this study, identification of the retention times for the three sulfides was performed by running standards (Fig. 2). The responses obtained from the FID were converted from area units into mixing ratios based on a per-carbon-response-factor (PCRF) as described previously (Simpson et al., 2001). Because the three sulfides contain two methyl carbons, and are thus likely to have the same FID response, we assigned a single PCRF to these compounds based on the PCRF for ethane. The LOD for the three sulfide compounds was 20 ppt for the analysis of 1350 cm^3 from the canister (Meinardi et al., 2013).

A direct intercomparison between the PTR-ToF-MS and GC-FID methods was performed for DMS/DMDS using a 1 : 100 dilution and a 1 : 7 dilution of the certified gas cylinder, as well as sampling a mixture of DMS (∼ 21 ppb) and DMDS (∼ 20 ppb) generated using the dynamic injection system. A separate experiment was performed for DMTS, using the dynamic injection system (∼ 22 ppb). Mixing ratios of DMS, DMDS and DMTS analyzed by GC-FID immediately after sampling were generally in good

agreement with the values reported by the PTR-ToF-MS within experimental errors as seen in Fig. 3.

The stability of the three sulfides in the water-doped canisters was also investigated. The study was performed by analyzing the canisters the same day of the standard sample collection and again after one week. First, the outflow of the dynamic injection system for all three sulfides was collected in two separate canisters with one canister analyzed on the same day, while the second was stored at room temperature for a week. Results are shown in Fig. 4, as the percentage of the mixing ratios measured after one week to that on the first day. Recoveries ranged from 53 to 68 % for OSC generated using the dynamic injection system. This could be due to two factors: the canisters might not have had the exact same initial concentration, and/or the presence of cyclohexane used in generating the calibration mixtures may induce artifacts and/or saturate the FID detector.

A second set of tests made using direct gas phase standards (certified gas cylinder for DMS and DMDS, and the permeation tube for DMTS) shows much better recoveries, ranging from 85 to 92 %. However, in all tests, the presence of DMDS was observed in the DMTS-doped canister analyzed after one week, suggesting that DMTS decomposes on surfaces to yield DMDS. Dimethyl disulfide was also seen as an impurity in the DMTS generated with the permeation tube by PR-ToF-MS, and is likely due to reaction in the permeation tube.

Methanethiol proved to be a challenging compound to analyze using the off-line canister/GC-FID approach. A 1.5 ± 0.02 ppm mixture of the pure gas phase standard in dry synthetic air was prepared in the laboratory and analyzed via the conventional method using the usual electropolished stainless-steel canister without water added prior to sampling. The resulting FID chromatogram (Fig. 5a) shows no MTO, but instead a significant peak for dimethyl sulfoxide ($(CH_3)_2SO$, DMSO) and DMDS. The presence of acetone was always observed as an impurity in those samples. Interestingly, when 18–20 Torr water was added to the canister prior addition of MTO mixture, the DMSO/DMDS ratio was reversed (Fig. 5b), with a higher contribution from DMDS

than DMSO. This water-doped canister was re-analyzed after 24 h, and the DMSO peak vanished, while the DMDS peak increased (Fig. 5c). To the author's knowledge, this is the first time that DMSO has been observed as an artifact from MTO sampling. Conversion of MTO into DMDS has been previously reported to occur on surfaces, such as old SilcoCan canisters (> 6 years old) due to possible cracks on the inert coating of the canister that exposed the metal surface (Khan et al., 2012), various solid sorbents (Katoh et al., 1995; Bashkova et al., 2003; Lestremau et al., 2004; Andersen et al., 2012; Hansen et al., 2012b) and on solid phase microextraction (SPME) fibers (Haberhauer-Troyer et al., 1999; Lestremau et al., 2004). The presence of metal ions and/or a thermal oxidation was suspected to be the source responsible for the reaction. The mechanism of formation of DMSO is not known, but may involve the reaction of MTO with the metal oxide surface whose catalytic sites become covered when water is present in the canister.

A new mixture of 1.8 ± 0.02 ppm MTO was made in a glass sampling vessel instead of a stainless steel canister and analyzed by GC-FID immediately. Results are shown in Fig. 6a for a dry mixture. A significant amount of DMDS is still present but MTO can now be observed in the chromatogram. The ratio of the MTO peak area to that of DMDS was 0.65. Because no conversion of MTO to DMDS in the glass bulb was observed using PTR-ToF-MS, it is likely that the short time (< 1 min) the sample stays in the stainless steel pre-concentration system was enough to allow chemistry to convert some of the MTO into DMDS. To test this hypothesis, a higher mixing ratio of MTO in dry synthetic air was prepared and analyzed without the pre-concentration step, reducing the contact time of the sample in the sampling unit to about 10 s before injection (in this case only 10 mL of the sample could be analyzed). The resulting chromatogram (Fig. 6b) shows that while DMDS is still present, the ratio of the MTO peak area to that for DMDS is now ∼ 7.5, about an order of magnitude larger. Devai and DeLaune (1994) previously observed that the stability of MTO in a glass sampling bulb is strongly influenced by the presence of water, with significant losses of MTO within the first hour in moist air. This observation strongly suggests that avoiding metal in sampling systems may not be

sufficient for accurate measurement of MTO. Given these issues with surface reactions of MTO, PTR-ToF-MS is the preferred analytical approach for this compound.

3.4 Application to a complex source mixture

Sources of OSC in urban and rural areas include those of non-marine origin such as human breath (Tonzetic, 1971; Taucher et al., 1996; Van den Velde et al., 2008, 2009), agricultural activities and pet waste (Burnett, 1969; Williams et al., 1999; Filipy et al., 2006; Shaw et al., 2007; Trabue et al., 2008; Feilberg et al., 2010; Papurello et al., 2012; Meinardi et al., 2013; Zhang et al., 2013). In this study, the two sampling and analysis methods, PTR-ToF-MS and GC-FID were applied to the investigation of organosulfur emissions from bins in a suburban location where most of the waste is from pets. This represents a complex mixture that provides a more realistic test of the applicability of these techniques to ambient air and sources than the relatively controlled laboratory samples described above. A typical mass spectrum of a bin sample is presented in Fig. S7a. There are clearly many compounds in the headspace of the bins, illustrating the difficulty of assigning all of the peaks based on the PTR-ToF-MS alone. However, peaks due to DMS and DMDS were clearly identified and confirmed by GC-FID measurements. A peak at m/z 49 was also present in the PTR-ToF-MS spectra, which corresponds to MTO. Positive identification and quantification were based on accurate mass determination along with the ratios of the different fragments defined for the standards. In addition, because DMTS shares common ions with DMDS (m/z 79) and MTO (m/z 49), a positive identification of DMTS was recorded only if nominal masses m/z 127 and m/z 81 (excluding the isotopic peak from m/z 79) were both present, and the ratio of m/z 79 to 95 was different than that observed for the DMDS standard, suggesting an additional contribution for m/z 79.

Dimethyl sulfide (DMS) and DMDS were clearly identified in all samples by PTR-ToF-MS and GC-FID, while DMTS was only detected in the canister samples. It is important to note that the peak at m/z 79 observed in all bin samples was exclusively from the DMDS CH_3SS^+ fragment, as shown in Fig. S7b. No evidence for DMSO or benzene

was observed in any bin samples with PTR-ToF-MS, as indicated by the absence of peaks at m/z 79.0218 and 79.0548 respectively. Due to sampling and analysis artifacts described above, MTO was only observed in the PTR-ToF-MS analysis. Mixing ratios of all four OSC measured using PTR-ToF-MS and off-line canisters/GC-FID are presented in Table 2.

As can be seen in Fig. 7a and Table 2, DMDS mixing ratios measured by GC-FID (ranging from 14 to 350 ppb) were systematically higher compared to the PTR-ToF-MS measurements (ranging from 1.5 to 165 ppb) with an average factor of two (Fig. 7a). Note that individual measurements may differ by more than this average value as indicated in Table 2. This is likely due to the presence of MTO and its conversion to DMDS as seen in the studies using individual compounds described earlier. Methanethiol was measured by PTR-ToF-MS and ranged from 33 to about 720 ppb. Thus, the excess DMDS measured in the canisters was attributed to the conversion of MTO to DMDS on surfaces.

For DMS, the GC-FID measurements were on average 27 ± 3 % larger than the PTR-ToF-MS derived mixing ratios. This could be due to differences in sampling: while the PTR-ToF-MS pulls a constant flow of 150 $cm^3\,min^{-1}$ from the top of the bin, the canister pulls a faster flow in a shorter period of time which could affect the flow dynamics in the bin, thus altering the mixing ratios somewhat.

Lastly, although DMTS was not observed in the PTR-ToF-MS spectra, this compound was observed by GC-FID. It has been previously reported that MTO can be converted to DMTS in the presence of H_2S and metals (Chin and Lindsay, 1994). Hydrogen sulfide was also observed in the source sample measured by PTR-ToF-MS at nominal mass m/z 35 (exact mass determination was performed to confirm the identity of the compound). Hydrogen sulfide is a relatively difficult compound to quantify by PTR-ToF-MS due to its low proton affinity (705 $kJ\,mol^{-1}$) (Lide, 1994) so that its signal depends on the relative humidity of the sample (Feilberg et al., 2010; Hansen et al., 2012a; Li et al., 2014). Calibration of H_2S was beyond the scope of this study, but the signal observed in the mass spectra was normalized to its highest value to see if it was correlated with the DMTS signal. As seen in Fig. 8a, DMTS was the highest for samples nos. 7 and 8, where MTO and H_2S were also high. Thus, it is possible that DMTS was formed in a reaction of MTO with H_2S on the surface of the canister and/or sampling lines rather than being emitted directly from the sample. Figure 8b and c shows the corresponding DMS and DMDS normalized mixing ratios, which exhibit a very different pattern. This suggests that DMS and DMDS are not involved in DMTS formation. However, it is noteworthy that DMDS by GC-FID is highest for samples nos. 7 and 8, supporting the reaction of MTO on surfaces as a source of DMDS.

To test whether MTO and H_2S react to form DMTS, a separate set of experiments were conducted where the outflow of a permeation tube containing gas phase MTO was mixed with the outflow of a second permeation tube containing gas phase H_2S, and analyzed by both PTR-ToF-MS and GC-FID. Figure 9 shows the results of the analysis for both techniques. While the PTR-ToF-MS only shows a peak at nominal masses m/z 35 and m/z 49 characteristics for H_2S and MTO protonated ions respectively, the canister GC-FID measurements show that DMTS is formed when both MTO and H_2S are present. In short, it is clear that MTO and H_2S react on metal surfaces to form DMTS and that MTO alone forms DMDS.

Lastly, because PTR-ToF-MS allows sampling in real-time, it was possible to determine emission rates for DMS, DMDS and MTO directly emitted from the bins. Between each sample, the bins were aired out, and a new waste sample was introduced. The lid on the bin was then closed and the increase in the OSC mixing ratios in the headspace was measured as a function of time. Results are presented in Table 3. Those values were integrated into a 3-D airshed model in a separate study to evaluate the importance of such continental sources on the formation of the OSC oxidation products methanesulfonic acid and sulfuric acids in a large coastal urban area (Perraud et al., 2015). In that study, there were a number of potential sources of atmospheric OSC that have not been yet quantified, and these techniques could be useful in the future.

In conclusion, OSC in air are challenging to measure, especially in complex mixtures characteristic of air. While PTR-ToF-MS provides real-time sampling capability,

fragmentation of parent ions in such mixtures dictates caution in assigning peaks to specific compounds without additional data such as GC-FID. In addition, species such as H_2S that have proton affinities close to that of water are not as easily measured due to the dependence on relative humidity. Canister sampling with GC-FID provides excellent sensitivity but can suffer from reactions on metal canister and analysis surfaces. The latter is also an issue if metal sampling lines are used in conjunction with PTR-ToF-MS.

The Supplement related to this article is available online at doi:10.5194/amtd-8-13157-2015-supplement.

Acknowledgements. We are grateful for funding from the National Science Foundation (Grant No 1443140) and the NSF Major Research Instrumentation (MRI) program (Grant No 0923323) for the PTR-ToF-MS. We would also like to thank A. Ezell Smith, M. L. Dawson, B. Love and G. Liu for their technical assistance during the bin measurements and C. Murray for the pure MTO gas standard.

References

Andersen, K. B., Hansen, M. J., and Feilberg, A.: Minimisation of artefact formation of dimethyl disulphide during sampling and analysis of methanethiol in air using solid sorbent materials, J. Chromatogr. A, 1245, 24–31, 2012.

Andreae, M. O.: Ocean–atmosphere interactions in the global biogeochemical sulfur cycle, Mar. Chem., 30, 1–29, 1990.

Andreae, M. O., Ferek, R. J., Bermond, F., Byrd, K. P., Engstrom, R. T., Hardin, S., Houmere, P. D., Lemarrec, F., Raemdonck, H., and Chatfield, R. B.: Dimethyl sulfide in the marine atmosphere, J. Geophys. Res., 90, 2891–2900, 1985.

Andreae, T. W., Andreae, M. O., Bingemer, H. G., and Leck, C.: Measurements of dimethyl sulfide and H_2S over the western north Atlantic and the tropical Atlantic, J. Geophys. Res., 98, 23389–23396, 1993.

Aneja, V. P.: Natural sulfur emissions into the atmosphere, J. Air Waste Manage., 40, 469–476, 1990.

Aprea, E., Biasioli, F., Carlin, S., Versini, G., Mark, T. D., and Gasperi, F.: Rapid white truffle headspace analysis by proton transfer reaction mass spectrometry and comparison with solid-phase microextraction coupled with gas chromatography/mass spectrometry, Rapid Commun. Mass Sp., 21, 2564–2572, 2007.

Arnold, S. T., Thomas, J. M., and Viggiano, A. A.: Reactions of H_3O^+ $(H_2O)_{(n)}$ and H^+ $(H_2O)_{(n)}$ $(CH_3COCH_3)_{(m)}$ with CH_3SCH_3, Int. J. Mass Spectrom., 180, 243–251, 1998.

Barnes, I., Bastian, V., and Becker, K. H.: Kinetics and mechanisms of the reaction of OH radicals with dimethyl sulfide, Int. J. Chem. Kinet., 20, 415–431, 1988.

Barnes, I., Becker, K. H., and Mihalopoulos, N.: An FTIR product study of the photooxidation of dimethyl disulfide, J. Atmos. Chem., 18, 267–289, 1994.

Barnes, I., Hjorth, J., and Mihalopoulos, N.: Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere, Chem. Rev., 106, 940–975, 2006.

Bashkova, S., Bagreev, A., and Bandosz, T. J.: Adsorption/oxidation of CH_3SH on activated carbons containing nitrogen, Langmuir, 19, 6115–6121, 2003.

Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the atmosphere from natural sources, J. Atmos. Chem., 14, 315–337, 1992.

Berglund, M. and Wieser, M. E.: Isotopic compositions of the elements 2009 (IUPAC Technical Report), Pure Appl. Chem., 83, 397–410, 2011.

Berndt, T. and Richters, S.: Products of the reaction of OH radicals with dimethyl sulphide in the absence of NO_x: experiment and simulation, Atmos. Environ., 47, 316–322, 2012.

Berresheim, H., Andreae, M. O., Ayers, G. P., Gillett, R. W., Merrill, J. T., Davis, V. J., and Chameides, W. L.: Airborne measurements of dimethylsulfide, sulfur dioxide and aerosol Ions over the southern ocean of Australia, J. Atmos. Chem., 10, 341–370, 1990.

Beyersdorf, A. J., Blake, D. R., Swanson, A., Meinardi, S., Rowland, F. S., and Davis, D.: Abundances and variability of tropospheric volatile organic compounds at the South Pole and other Antarctic locations, Atmos. Environ., 44, 4565–4574, 2010.

Blake, D. R., Smith, T. W., Chen, T. Y., Whipple, W. J., and Rowland, F. S.: Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands, J. Geophys. Res., 99, 1699–1719, 1994.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-transfer reaction mass spectrometry, Chem. Rev., 109, 861–896, 2009.

Blunden, J., Aneja, V. P., and Lonneman, W. A.: Characterization of non-methane volatile organic compounds at swine facilities in eastern North Carolina, Atmos. Environ., 39, 6707–6718, 2005.

Buhr, K., van Ruth, S., and Delahunty, C.: Analysis of volatile flavour compounds by proton-transfer reaction mass spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds, Int. J. Mass Spectrom., 221, 1–7, 2002.

Burnett, W. E.: Air pollution from animal wastes – determination of malodors by gas chromatographic and organoleptic techniques, Environ. Sci. Technol., 3, 744–749, 1969.

Bzdek, B. R. and Johnston, M. V.: New particle formation and growth in the troposphere, Anal. Chem., 82, 7871–7878, 2010.

Capaldo, K. P. and Pandis, S. N.: Dimethylsulfide chemistry in the remote marine atmosphere: Evaluation and sensitivity analysis of available mechanisms, J. Geophys. Res., 102, 23251–23267, 1997.

Cappellin, L., Probst, M., Limtrakul, J., Biasioli, F., Schuhfried, E., Soukoulis, C., Mark, T. D., and Gasperi, F.: Proton transfer reaction rate coefficients between H_3O^+ and some sulphur compounds, Int. J. Mass Spectrom., 295, 43–48, 2010.

Chin, H. W. and Lindsay, R. C.: Ascorbate and transition-metal mediation of methanethiol oxidation to dimethyl disulfide and dimethyl trisulfide, Food Chem., 49, 387–392, 1994.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2. first intercomparison of open-path FTIR, PTR-MS, and GC-MS/FID/ECD, J. Geophys. Res., 109, D02311, doi:10.1029/2003JD003874, 2004.

Colman, J. J., Swanson, A. L., Meinardi, S., Sive, B. C., Blake, D. R., and Rowland, F. S.: Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, Anal. Chem., 73, 3723–3731, 2001.

Crutzen, P. J., Williams, J., Poschl, U., Hoor, P., Fischer, H., Warneke, C., Holzinger, R., Hansel, A., Lindinger, W., Scheeren, B., and Lelieveld, J.: High spatial and temporal resolution measurements of primary organics and their oxidation products over the tropical forests of Surinam, Atmos. Environ., 34, 1161–1165, 2000.

Davison, B. and Hewitt, C. N.: Elucidation of the tropospheric reactions of biogenic sulfur species from a field measurement campaign in New Scotland, Chemosphere, 28, 543–557, 1994.

Dawson, M. L., Varner, M. E., Perraud, V., Ezell, M. J., Gerber, R. B., and Finlayson-Pitts, B. J.: Simplified mechanism for new particle formation from methanesulfonic acid, amines and water via experiments and ab initio calculations, P. Natl. Acad. Sci. USA, 109 18719–18724, 2012.

de Bruyn, W. J., Harvey, M., Cainey, J. M., and Saltzman, E. S.: DMS and SO_2 at Baring Head, New Zealand: implications for the yield of SO_2 from DMS, J. Atmos. Chem., 41, 189–209, 2002.

de Gouw, J. and Carsten, W.: Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257, 2007.

Devai, I. and Delaune, R. D.: Changes in reduced gaseous sulfur-compounds collected in glass gas sampling bulbs, Anal. Lett., 27, 2403–2411, 1994.

Dockery, D. W., Pope, C. A., Xu, X. P., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., and Speizer, F. E.: An Association between air-pollution and mortality in six United States cities, New Engl. J. Med., 329, 1753–1759, 1993.

Feilberg, A., Liu, D. Z., Adamsen, A. P. S., Hansen, M. J., and Jonassen, K. E. N.: Odorant emissions from intensive pig production measured by online proton-transfer-reaction mass spectrometry, Environ. Sci. Technol., 44, 5894–5900, 2010.

Filipy, J., Rumburg, B., Moount, G., Westberg, H., and Lamb, B.: Identification and quantification of volatile organic compounds from a dairy, Atmos. Environ., 40, 1480–1494, 2006.

Finlayson-Pitts, B. J. and Pitts Jr., J. N.: Chemistry of the Upper and Lower Atmosphere – Theory, Experiments, and Applications, Academic Press, San Diego, 969 pp., 2000.

Freshour, N. A., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., and Hanson, D. R.: Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer, Atmos. Meas. Tech., 7, 3611–3621, doi:10.5194/amt-7-3611-2014, 2014.

Geng, C. M. and Mu, Y. J.: Carbonyl sulfide and dimethyl sulfide exchange between trees and the atmosphere, Atmos. Environ., 40, 1373–1383, 2006.

Goldan, P. D., Kuster, W. C., Albritton, D. L., and Fehsenfeld, F. C.: The measurement of natural sulfur emissions from soils and vegetation – 3 sites in the Eastern United States revisited, J. Atmos. Chem., 5, 439–467, 1987.

Graus, M., Muller, M., and Hansel, A.: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, J. Am. Soc. Mass. Spectr., 21, 1037–1044, 2010.

Greaves, J. L. and Roboz, J.: Mass Spectrometry for Novices, Taylor and Francis, Boca Raton, FL, USA, 2013.
Grosjean, D.: Photooxidation of methyl sulfide, ethyl sulfide and methanethiol, Environ. Sci. Technol., 18, 460–468, 1984.
Guo, H., Simpson, I. J., Ding, A. J., Wang, T., Saunders, S. M., Wang, T. J., Cheng, H. R., Barletta, B., Meinardi, S., Blake, D. R., and Rowland, F. S.: Carbonyl sulfide, dimethyl sulfide and carbon disulfide in the Pearl River Delta of southern China: impact of anthropogenic and biogenic sources, Atmos. Environ., 44, 3805–3813, 2010.
Haberhauer-Troyer, C., Rosenberg, E., and Grasserbauer, M.: Evaluation of solid-phase microextraction for sampling of volatile organic sulfur compounds in air for subsequent gas chromatographic analysis with atomic emission detection, J. Chromatogr. A, 848, 305–315, 1999.
Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.
Hansen, M. J., Adamsen, A. P. S., Feilberg, A., and Jonassen, K. E. N.: Stability of odorants from pig production in sampling bags for olfactometry, J. Environ. Qual., 40, 1096–1102, 2011.
Hansen, M. J., Liu, D. Z., Guldberg, L. B., and Feilberg, A.: Application of proton-transfer reaction mass spectrometry to the assessment of odorant removal in a biological air cleaner for pig production, J. Agric. Food. Chem., 60, 2599–2606, 2012a.
Hansen, M. J., Toda, K., Obata, T., Adamsen, A. P. S., and Feilberg, A.: Evaluation of single column trapping/separation and chemiluminescence detection for measurement of methanethiol and dimethyl sulfide from pig production, J. Anal. Methods Chem., 2012, 489239, doi:10.1155/2012/489239, 2012b.
Hansen, M. J., Adamsen, A. P. S., and Feilberg, A.: Recovery of odorants from an olfactometer measured by proton-transfer reaction mass spectrometry, Sensors-Basel, 13, 7860–7871, 2013.

Harris, D. C.: Quantitative Chemical Analysis, 3rd edn., WH Freeman and Company, New York, USA, 1991.
Hatakeyama, S. and Akimoto, H.: Reactions of OH radicals with methanethiol, dimethylsulfide and dimethyl disulfide in air, J. Phys. Chem., 87, 2387–23295, 1983.
Hayward, S., Hewitt, C., Sartin, J., and Owen, S.: Performance characteristics and applications of a proton transfer reaction mass spectometer for measuring volatile organic compounds in ambient air, Environ. Sci. Technol., 36, 1554–1560, 2002.
Herbig, J., Muller, M., Schallhart, S., Titzmann, T., Graus, M., and Hansel, A.: On-line breath analysis with PTR-TOF, J. Breath Res., 3, 1–10, 2009.
Hinds, W. C.: Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles, John Wiley & Sons Inc., New York, 1999.
Hofmann, U., Hofmann, R., and Kesselmeier, J.: Cryogenic trapping of reduced sulfur-compounds using a Nafion drier and cotton wadding as an oxidant scavenger, Atmos. Environ. A-Gen., 26, 2445–2449, 1992.
Jardine, K. J., Henderson, W. M., Huxman, T. E., and Abrell, L.: Dynamic Solution Injection: a new method for preparing pptv–ppbv standard atmospheres of volatile organic compounds, Atmos. Meas. Tech., 3, 1569–1576, doi:10.5194/amt-3-1569-2010, 2010.
Jardine, K. J., Yañez-Serrano, A. M., Williams, J., Kunert, N., Jardine, A., Taylor, T., Abrell, L., Artaxo, P., Guenther, A., Hewitt, C. N., House, E., Florentino, A. P., Manzi, A., Higuchi, N., Kesselmeier, J., Behrendt, T., Veres, P. R., Derstroff, B., Fuentes, J. D., Martin, S. T., and Andreae, M. O.: Dimethylsulfide in the Amazon rainforest, Global Biogeochem. Cy., 29, 19–32, 2015.
Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Mark, L., Seehauser, H., Schottkowsky, R., Sulzer, P., and Mark, T. D.: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), Int. J. Mass Spectrom., 286, 122–128, 2009.
Kai, M., Crespo, E., Cristescu, S. M., Harren, F. J. M., Francke, W., and Piechulla, B.: *Serratia odorifera*: analysis of volatile emission and biological impact of volatile compounds on *Arabidopsis thaliana*, Appl. Microbiol. Biot., 88, 965–976, 2010.
Katoh, H., Kuniyoshi, I., Hirai, M., and Shoda, M.: Studies of the oxidation mechanism of sulfur-containing gases on wet activated carbon-fiber, Appl. Catal. B-Environ., 6, 255–262, 1995.
Kesselmeier, J., Meixner, F. X., Hofmann, U., Ajavon, A. L., Leimbach, S., and Andreae, M. O.: Reduced sulfur compound exchange between the atmosphere and tropical tree species in southern Cameroon, Biogeochemistry, 23, 23–45, 1993.

Khan, M. A. H., Whelan, M. E., and Rhew, R. C.: Analysis of low concentration reduced sulfur compounds (RSCs) in air: storage issues and measurement by gas chromatography with sulfur chemiluminescence detection, Talanta, 88, 581–586, 2012.

Kim, K. H., Choi, G. H., Choi, Y. J., Song, H. N., Yang, H. S., and Oh, J. M.: The effects of sampling materials selection in the collection of reduced sulfur compounds in air, Talanta, 68, 1713–1719, 2006.

Koga, S., Nomura, D., and Wada, M.: Variation of dimethylsulfide mixing ratio over the Southern Ocean from 36 to 70° S, Polar Sci., 8, 306–313, 2014.

Kulmala, M. and Kerminen, V. M.: On the formation and growth of atmospheric nanoparticles, Atmos. Res., 90, 132–150, 2008.

Kulmala, M., Vehkamäki, H., Petäjä, T., Maso, M. D., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Kuster, W. C. and Goldan, P. D.: Quantitation of the losses of gaseous sulfur-compounds to enclosure walls, Environ. Sci. Technol., 21, 810–815, 1987.

Lestremau, F., Andersson, F. A. T., and Desauziers, V.: Investigation of artefact formation during analysis of volatile sulphur compounds using solid phase microextraction (SPME), Chromatographia, 59, 607–613, 2004.

Li, R., Warneke, C., Graus, M., Field, R., Geiger, F., Veres, P. R., Soltis, J., Li, S.-M., Murphy, S. M., Sweeney, C., Pétron, G., Roberts, J. M., and de Gouw, J.: Measurements of hydrogen sulfide (H_2S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region, Atmos. Meas. Tech., 7, 3597–3610, doi:10.5194/amt-7-3597-2014, 2014.

Lide, D. R.: Handbook of Chemistry and Physics, 74th edn., CRC Press, Boca Raton, FL, 1994.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at ppt levels by means of proton-transfer reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass Spectrom., 173, 191–241, 1998.

Meinardi, S., Simpson, I. J., Blake, N. J., Blake, D. R., and Rowland, F. S.: Dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) emissions from biomass burning in Australia, Geophys. Res. Lett., 30, 1454, doi:10.1029/2003GL016967, 2003.

Meinardi, S., Jin, K.-Y., Barletta, B., Blake, D. R., and Vaziri, N. D.: Exhaled breath and fecal volatile organic biomarkers of chronic kidney disease, Biochim. Biophys. Acta, 1830, 2531–2537, 2013.

Mikoviny, T., Kaser, L., and Wisthaler, A.: Development and characterization of a High-Temperature Proton-Transfer-Reaction Mass Spectrometer (HT-PTR-MS), Atmos. Meas. Tech., 3, 537–544, doi:10.5194/amt-3-537-2010, 2010.

Mockel, H. J. and Weiss, J.: The electron-impact and chemical ionization mass spectra of dimethyltrisulfide, Fresen. Z. Anal. Chem., 301, 417–425, 1980.

Nguyen, B. C., Bonsang, B., and Gaudry, A.: The role of the ocean in the global atmospheric sulfur cycle, J. Geophys. Res.-Oc. Atm., 88, 903–914, 1983.

Papurello, D., Soukoulis, C., Schuhfried, E., Cappellin, L., Gasperi, F., Silvestri, S., Santarelli, M., and Biasioli, F.: Monitoring of volatile compound emissions during dry anaerobic digestion of the organic fraction of municipal solid waste by proton transfer reaction time-of-flight mass spectrometry, Bioresource Technol., 126, 254–265, 2012.

Passarella, R., Shul, R. J., Keesee, R. G., and Castleman, A. W.: Gas-phase reactions of sulfides, mercaptans, and dimethyl methylphosphonate with ionic species derived from argon and water, Int. J. Mass Spectrom., 81, 227–233, 1987.

Patroescu, I. V., Barnes, I., Becker, K. H., and Mihalopoulos, N.: FT-IR product study of the OH-initiated oxidation of DMS in the presence of NO_x, Atmos. Environ., 33, 25–35, 1999.

Perraud, V., Horne, J. R., Martinez, A., Kalinowski, J., Meinardi, S., Dawson, M. L., Wingen, L. M., Dabdub, D., Blake, D. R., Gerber, R. B., and Finlayson-Pitts, B. J.: The future of airborne sulfur-containing particles in the absence of fossil fuel sulfur dioxide emissions, P. Natl. Acad. Sci. USA, 112, 13514–13519, 2015.

Pope III, C. A. and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manage., 56, 709–742, 2006.

Pope III, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., and Thurston, G. D.: Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution, J. Amer. Med. Assoc., 287, 1132–1141, 2002.

Schuhfried, E., Probst, M., Limtrakul, J., Wannakao, S., Aprea, E., Cappellin, L., Mark, T. D., Gasperi, F., and Biasioli, F.: Sulfides: chemical ionization induced fragmentation studied with proton transfer reaction mass spectrometry and density functional calculations, J. Mass Spectrom., 48, 367–378, 2013.

Shaw, S. L., Mitloehner, F. M., Jackson, W., Depeters, E. J., Fadel, J. G., Robinson, P. H., Holzinger, R., and Goldstein, A. H.: Volatile organic compound emissions from dairy cows and their waste as measured by proton-transfer-reaction mass spectrometry, Environ. Sci. Technol., 41, 1310–1316, 2007.
Simpson, I. J., Colman, J. J., Swanson, A. L., Bandy, A. R., Thornton, D. C., Blake, D. R., and Rowland, F. S.: Aircraft measurements of dimethyl sulfide (DMS) using a whole air sampling technique, J. Atmos. Chem., 39, 191–213, 2001.
Skoog, D. A. and Holler, F. J.: Principles of Instrumental Analysis, Thomson Brooks/Cole, Belmont, CA, 2007.
Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of aminium salt formation in atmospheric nanoparticles: Implications for aerosol growth, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.
Španěl, P., and Smith, D.: Selected ion flow tube studies of the reactions of H_3O^+, NO^+, and O_2^+ with some organosulphur molecules, Int. J. Mass Spectrom., 176, 167–176, 1998.
Sulyok, M., Haberhauer-Troyer, C., and Rosenberg, E.: Observation of sorptive losses of volatile sulfur compounds during natural gas sampling, J. Chromatogr. A, 946, 301–305, 2002.
Tani, A., Hayward, S., and Hewitta, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223, 561–578, 2003.
Taucher, J., Hansel, A., Jordan, A., and Lindinger, W.: Analysis of compounds in human breath after ingestion of garlic using proton-transfer-reaction mass spectrometry, J. Agr. Food Chem., 44, 3778–3782, 1996.
Tonzetic, J.: Direct gas chromatographic analysis of sulphur compounds in mouth air in man, Arch. Oral Biol., 16, 587–597, 1971.
Trabue, S., Scoggin, K., Mitloehner, F., Li, J., Burns, R., and Xin, H.: Field sampling method for quantifying volatile sulfur compounds from animal feeding operations, Atmos. Environ., 42, 3332–3341, 2008.
Tyndall, G. S. and Ravishankara, A. R.: Atmospheric oxidation of reduced sulfur species, Int. J. Chem. Kinet., 23, 483–527, 1991.
Van den Velde, S., Nevens, F., Van Hee, P., Van Steenberghe, D., and Quirynen, M.: GC-MS analysis of breath odor compounds in liver patients, J. Chromatogr. B, 875, 344–348, 2008.

Van den Velde, S., van Steenberghe, D., Van Hee, P., and Quirynen, M.: Detection of odorous compounds in breath, J. Dent. Res., 88, 285–289, 2009.
Vandingenen, R., Jensen, N. R., Hjorth, J., and Raes, F.: Peroxynitrate formation during the nighttime oxidation of dimethylsulfide – its role as a reservoir species for aerosol formation, J. Atmos. Chem., 18, 211–237, 1994.
Wang, T. S., Smith, D., and Spanel, P.: Selected ion flow tube, SIFT, studies of the reactions of H_3O^+, NO^+ and O_2^+ with compounds released by Pseudomonas and related bacteria, Int. J. Mass Spectrom., 233, 245–251, 2004.
Wardencki, W.: Problems with the determination of environmental sulphur compounds by gas chromatography, J. Chromatogr. A, 793, 1–19, 1998.
Watts, S. F.: The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, Atmos. Environ., 34, 761–779, 2000.
Williams, J., Wang, N. Y., Cicerone, R. J., Yagi, K., Kurihara, M., and Terada, F.: Atmospheric methyl halides and dimethyl sulfide from cattle, Geophys. Res. Lett., 13, 485–491, 1999.
Williams, T. L., Adams, N. G., and Babcock, L. M.: Selected ion flow tube studies of H_3O^+ (H_2O) (0,1) reactions with sulfides and thiols, Int. J. Mass Spectrom., 172, 149–159, 1998.
Xie, Z. Q., Sun, L. G., Wang, J. J., and Liu, B. Z.: A potential source of atmospheric sulfur from penguin colony emissions, J. Geophys. Res., 107, 4617, doi:10.1029/2002JD002114, 2002.
Yi, Z. G., Wang, X. M., Sheng, G. Y., and Fu, H. M.: Exchange of carbonyl sulfide (OCS) and dimethyl sulfide (DMS) between rice paddy fields and the atmosphere in subtropical China, Agr. Ecosyst. Environ., 123, 116–124, 2008.
Yin, F. D., Grosjean, D., and Seinfeld, J. H.: Photoxidation of dimethyl sulfide and dimethyl disulfide. I: Mechanism development, J. Atmos. Chem., 11, 309–364, 1990a.
Yin, F. D., Grosjean, D., Flagan, R. C., and Seinfeld, J. H.: Photooxidation of dimethyl sulfide and dimethyl disulfide. 2: Mechanism evaluation, J. Atmos. Chem., 11, 365–399, 1990b.
Zhang, H. Y., Schuchardt, F., Li, G. X., Yang, J. B., and Yang, Q. Y.: Emission of volatile sulfur compounds during composting of municipal solid waste (MSW), Waste Manage., 33, 957–963, 2013.
Zhang, R. Y., Khalizov, A., Wang, L., Hu, M., and Xu, W.: Nucleation and growth of nanoparticles in the atmosphere, Chem. Rev., 112, 1957–2011, 2012.
Zhao, J. and Zhang, R. Y.: Proton transfer reaction rate constants between hydronium ion (H_3O^+) and volatile organic compounds, Atmos. Environ., 38, 2177–2185, 2004.

Zhu, L., Nenes, A., Wine, P. H., and Nicovich, J. M.: Effects of aqueous organosulfur chemistry on particulate methanesulfonate to non-sea salt sulfate ratios in the marine atmosphere, J. Geophys. Res., 111, 1–15, 2006.

Table 1. Accurate mass and elemental composition of the major fragments observed for the analysis of standard organosulfur compounds by PTR-ToF-MS.

	Accurate mass (Da)	Intensity (%)	Elemental composition	Exact mass (Da)	Absolute mass difference (mDa)[a]
Methanethiol (MTO)	49.0106	100	$[CH_3SH + H]^+$	49.0112	−0.6
Dimethyl sulfide (DMS)	63.0262	100	$[CH_3SCH_3 + H]^+$	63.0268	−0.6
Dimethyl disulfide	94.9984[b]	100	$[CH_3SSCH_3 + H]^+$	94.9989	−0.5
(DMDS)	78.9667[b]	38	CH_3SS^+	78.9676	−0.9
	49.0102	4	$CH_3SH_2^+$	49.0112	−1.0
Dimethyl trisulfide	126.9711[c]	23	$[CH_3SSSCH_3 + H]^+$	126.9710	+0.1
(DMTS)	92.9836[c]	31	$CH_3SSCH_2^+$	92.9833	+0.3
	80.9806[c]	28	$CH_3SSH_2^+$	80.9833	−2.7
	78.9680[c]	100	CH_3SS^+	78.9676	+0.4
	61.0122	13	$CH_3SCH_2^+$	61.0112	+1.0
	49.0108	19	$CH_3SH_2^+$	49.0112	−0.4
	44.9797	9	CHS^+	44.9799	−0.2

[a] All reported data are within the 3mDa acceptable mass difference defined by the Journal of Organic Chemistry (Greaves and Roboz, 2013).
[b] Fragments used for quantification of DMDS.
[c] Fragments used for quantification of DMTS.

Table 2. Results from source samples – Intercomparison between PTR-ToF-MS and GC-FID analysis. Errors were taken as ±20 % for the GC-FID values (Simpson et al., 2001) and ±30 % for the PTR-ToF-MS values (day-to-day instrument variation).

Bin	Waste	DMS (ppb)		DMDS (ppb)		DMTS (ppb)		MTO (ppb)	
nos.	weight and Vol^{a}_{bin}	GC-FID	PTR-ToF-MS	GC-FID	PTR-ToF-MS	GC-FID	PTR-ToF-MS	GC-FID	PTR-ToF-MS
1		61 ± 12	47 ± 14	350 ± 70	165 ± 50	33 ± 7	n.d.	n.d.	267 ± 80
2[b]	8lb,	–	7 ± 2	–	20 ± 6	–	n.d.	n.d.	33 ± 10
3[c]	135 L bin	15 ± 3 and 14 ± 3	10 ± 3	84 ± 17 and 64 ± 13	27 ± 8	2 ± 0.4 and 5 ± 1	n.d.	n.d.	59 ± 18
4		18 ± 4	13 ± 4	119 ± 23	44 ± 13	15 ± 3	n.d.	n.d.	111 ± 33
5	1 lb, 135 L bin	1.3 ± 0.3	1.2 ± 0.4	14 ± 3	1.5 ± 0.5	8 ± 2	n.d.	n.d.	33 ± 10
6[b]	1 lb,	–	23 ± 7	–	23 ± 7	–	n.d.	n.d.	[d]
7	21 L bin	19 ± 4	15 ± 5	120 ± 24	26 ± 8	188 ± 38	n.d.	n.d.	722 ± 217
8		15 ± 3	12 ± 4	97 ± 19	16 ± 5	145 ± 29	n.d.	n.d.	718 ± 215
9	3 lb,	11 ± 2	7 ± 2	27 ± 5	6 ± 2	33 ± 7	n.d.	n.d.	106 ± 32
10	135 L bin	11 ± 2	7 ± 2	26 ± 5	6 ± 2	27 ± 5	n.d.	n.d.	127 ± 38
11		7 ± 1	5 ± 2	23 ± 5	4 ± 1	34 ± 7	n.d.	n.d.	82 ± 25

[a] The volume of the bin (Vol_{bin}) was determined via two methods: measuring the weight of the container after filling it with water and by measuring the time to fill the bin with water at the flow rate of 41 L min^{-1}.
[b] No canister was sampled for bins nos. 2 and 6.
[c] Two successive canisters were sampled for bin no. 3.
[d] The signal for MTO saturated the detector.
n.d.: not detected.

Table 3. Emission rates from bins for DMS, DMDS and MTO determined by PTR-ToF-MS in molecules $cm^{-3}\,s^{-1}$. Errors on these values are typically ±4 % taken as the 95 % confidence interval.

Bin nos.	Waste weight and bin volume	DMS (molecules $cm^{-3}\,s^{-1}$)	DMDS (molecules $cm^{-3}\,s^{-1}$)	CH_3SH (molecules $cm^{-3}\,s^{-1}$)
1	8 lb,	1.32×10^{9}	4.37×10^{9}	7.12×10^{9}
2	135 L bin	1.35×10^{8}	3.74×10^{8}	6.51×10^{8}
3		2.37×10^{8}	5.74×10^{8}	1.36×10^{9}
4		2.92×10^{8}	9.64×10^{8}	2.51×10^{9}
5	1 lb, 135 L bin	2.45×10^{7}	2.78×10^{8}	7.12×10^{9}
6	1 lb,	6.36×10^{8}	7.16×10^{8}	$4.02 \times 10^{10*}$
7	21 L bin	6.18×10^{8}	1.09×10^{9}	3.01×10^{10}
8		4.85×10^{8}	5.66×10^{8}	2.95×10^{10}
9	3 lb,	3.17×10^{8}	2.65×10^{8}	4.83×10^{9}
10	21 L bin	2.94×10^{8}	2.70×10^{8}	5.18×10^{9}
11		1.88×10^{8}	1.75×10^{8}	3.22×10^{9}

* The emission rate for MTO was determined using the beginning of the sampling (from 0 to 10 min), where the signal was not saturating the PTR-ToF-MS detector.

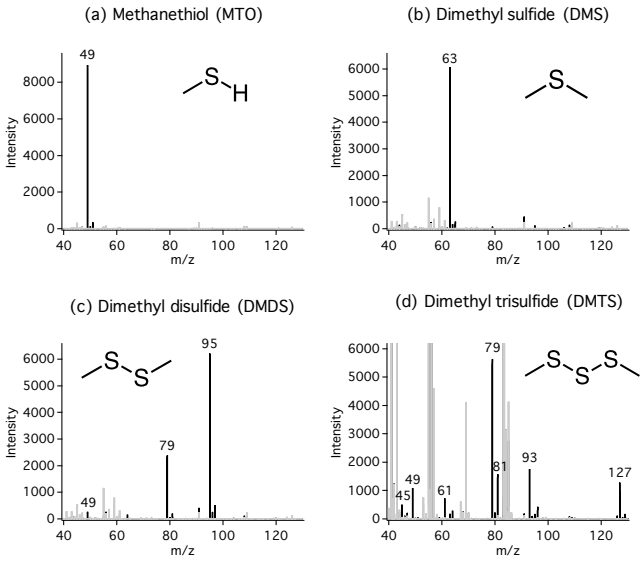

Figure 1. Individual PTR-ToF-MS mass spectra from each organosulfur compound: **(a)** methanethiol (MTO) from the laboratory generated gas phase standard, **(b)** dimethyl sulfide (DMS) and **(c)** dimethyl disulfide (DMDS) from injection of the individual pure liquid standards into air in a 100 L Teflon chamber, and **(d)** dimethyl trisulfide (DMTS) from the dynamic injection system. The peaks shown in grey correspond to background peaks.

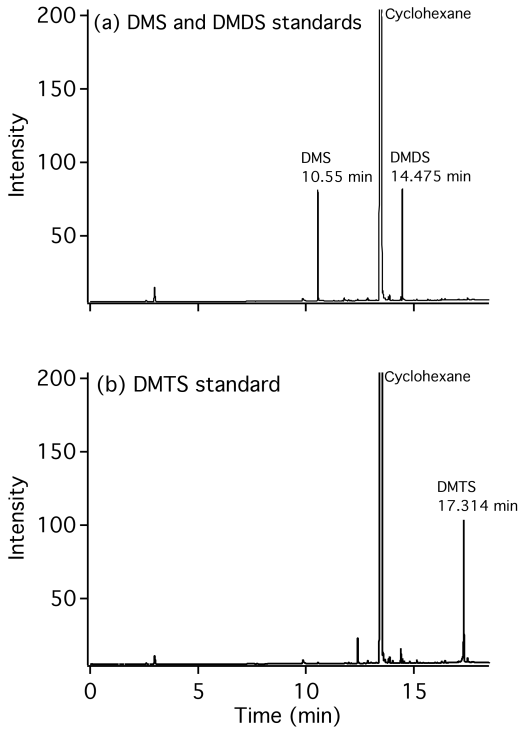

Figure 2. GC-FID chromatogram for **(a)** DMS (~ 21 ppb) and DMDS (~ 20 ppb), and **(b)** DMTS (~ 22 ppb) standards from the dynamic injection system. The cyclohexane peak is due to the solvent used in the injection system. Analysis followed immediately after canister samples were prepared.

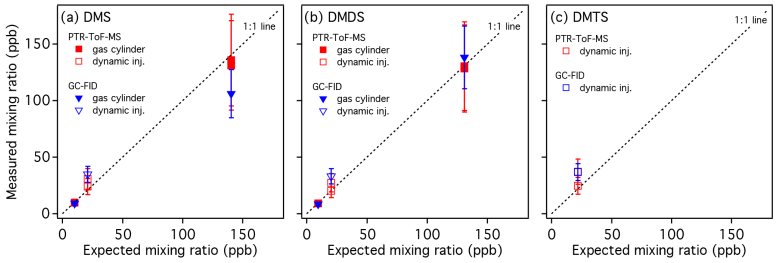

Figure 3. Comparison of quantification of DMS, DMDS and DMTS using GC-FID (blue markers) and PTR-ToF-MS (red markers). Standards were sampled from either dilutions of a certified gas cylinder (DMS and DMDS; filled symbols) and/or from the dynamic injection system (DMS, DMDS and DMTS; open symbols). Errors on the mixing ratios measured by the GC-FID method were taken as 95 % confidence interval (±20 %) as reported by Simpson et al. (Simpson et al., 2001) and errors on the mixing ratios measured by the PTR-ToF-MS were taken as 30 % corresponding to the day-to-day instrument variation. The 1 : 1 line corresponds to the line of perfect agreement between the mixing ratios measured by either the PTR-ToF-MS or the GC-FID and the expected value.

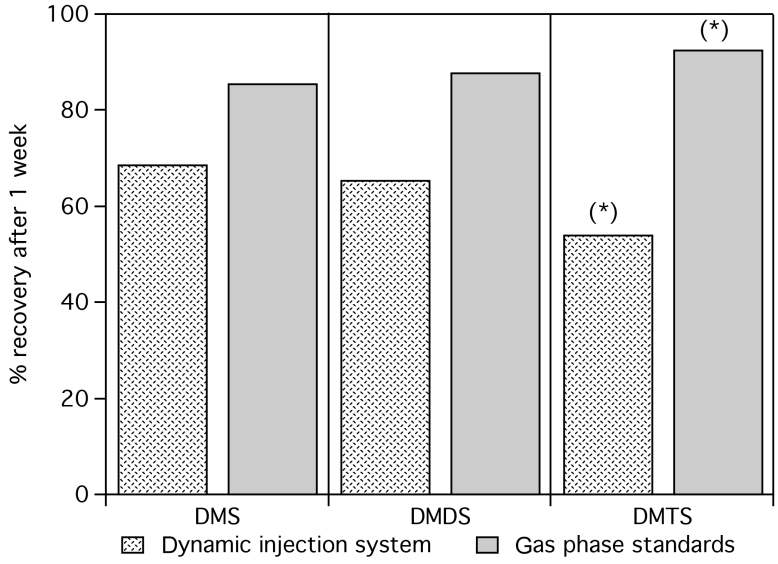

Figure 4. Recovery of DMS, DMDS and DMTS in electropolished stainless steel canisters after one week. Data include measurements made from the dynamic injection system (shaded bars; [DMS] ~ 21 ppb; [DMDS] ~ 20 ppb; [DMTS] ~ 33 ppb) and from a gas phase source (grey bars; [DMS] ~ 140 ppb; [DMDS] ~ 131 ppb; [DMTS] undetermined). The asterisks correspond to DMTS samples where DMDS was measured in the canister after 1 week, suggesting that DMTS decomposed on the surface of the canister.

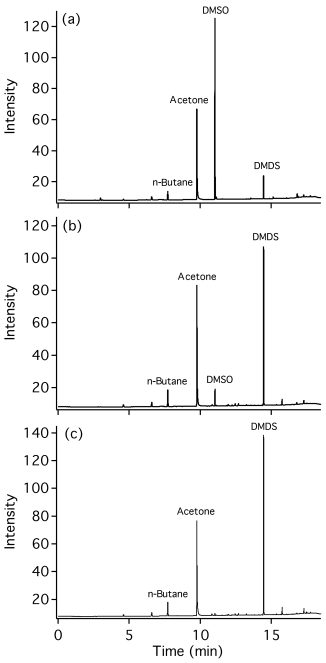

Figure 5. GC-FID chromatograms from the pure MTO standard mixture prepared in the laboratory in synthetic air sampled using stainless steel canisters under **(a)** dry conditions ([MTO] = 1.49 ppm); **(b)** with water present in the canister ([MTO] = 1.39 ppm); **(c)** same conditions as **(b)** but the canister was analyzed 24 h later.

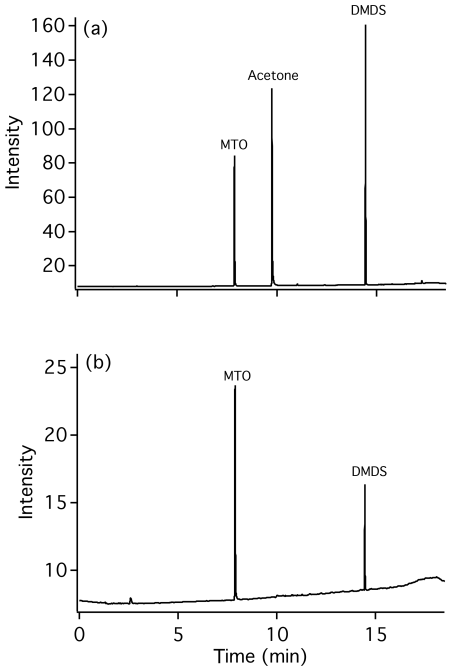

Figure 6. GC-FID chromatograms from the pure MTO standard mixture prepared in the laboratory in dry synthetic air sampled using a glass sampling vessel via **(a)** the conventional preconcentration method ([MTO] = 1.80 ppm) and **(b)** via a fast injection method ([MTO] = 12 ppm).

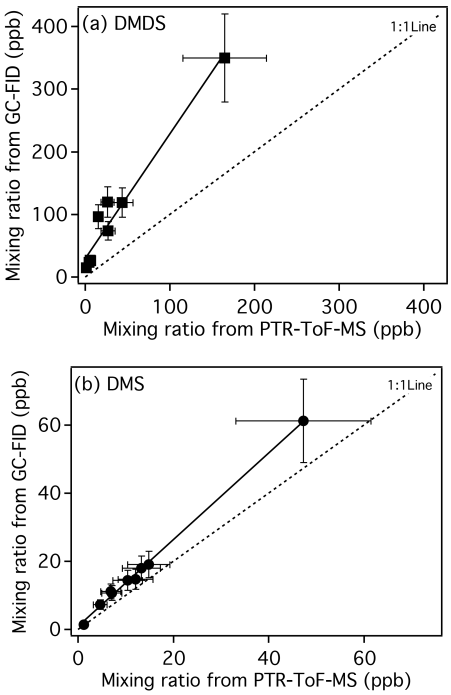

Figure 7. Intercomparison between GC-FID and PTR-ToF-MS measurements of **(a)** DMDS and **(b)** DMS from the bin source samples. The dotted lines correspond to the 1 : 1 line (line of perfect agreement) and the black lines correspond to linear regression fits with $y = 0.89 + 1.27x$ for DMS ($r^2 = 0.997$) and $y = 29 + 2.00x$ for DMDS ($r^2 = 0.956$).

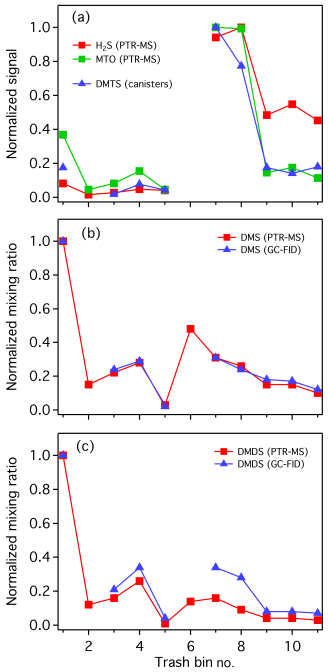

Figure 8. Normalized mixing ratios and signals obtained for all four organosulfur compounds from the source samples including **(a)** MTO, DMTS and H_2S; **(b)** DMS; **(c)** DMDS in different bins. No canister was sampled for bins nos. 2 and 6.

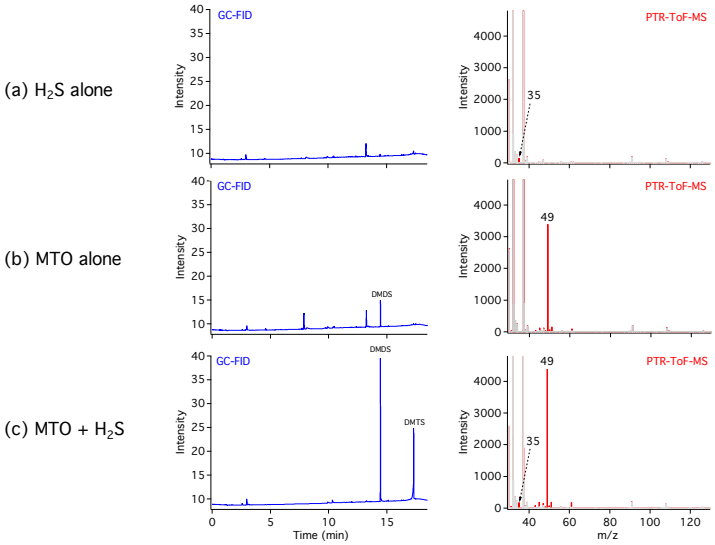

Figure 9. GC-FID chromatograms of **(a)** the H_2S standard in dry synthetic air (~ 460 ppb), **(b)** the MTO standard in dry synthetic air (~ 816 ppb) and **(c)** a mixture of the MTO and H_2S standard ([MTO] ~ 408 ppb; [H_2S] ~ 230 ppb) sampled using a water-doped stainless steel canister. Insets show the PTR-ToF-MS spectrum for each sample.