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Aircraft Measurements of Dimethyl Sulfide (DMS) Using a Whole Air Sampling Technique

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Abstract. We present a technique for the measurement of dimethyl sulfide (DMS) from airborne and ground-based platforms, using whole air sampling followed by gas chromatography with mass spectrometer and flame ionization detection. DMS measurements that were obtained during the 1999 NASA Pacific Exploratory Mission-Tropics B showed excellent agreement with independent in-flight DMS measurements, over a wide range of concentrations. The intercomparison supports two key results from this study, first that DMS can be accurately quantified based on ethane and propane per-carbon-response-factors (PCRFs), and second that DMS is stable in water-doped electropolished stainless steel canisters for at least several weeks. In addition, our sampling frequency and duration are flexible and allow detail in the vertical structure of DMS to be well captured. Sampling times as fast as 8 s were achieved and these data are suitable for DMS flux calculations using the mixed-layer gradient technique. Correlations between DMS and other marine tracers can also be readily investigated by this whole air sampling technique, because DMS is analyzed together with more than 50 simultaneously sampled hydrocarbons, halocarbons, and alkyl nitrates. The detection limit of the DMS measurements is 1 part per trillion by volume (pptv), and we conservatively estimate the accuracy to be ±20% or 3 pptv, whichever is larger. The measurement precision (1σ) is 2–4% at high mixing ratios (>25 pptv), and 1 pptv or 15%, whichever is larger, at low mixing ratios (<10 pptv).

Key words: aircraft, DMS, marine, whole air sampling.

1. Introduction

Dimethyl sulfide, or DMS (CH_3SCH_3) is the dominant sulfur species emitted from the oceans (Lovelock *et al.*, 1972; Andreae *et al.*, 1985; Bates *et al.*, 1992). Emissions from marine environments make up two-thirds of the natural sulfur source, and DMS is the major biogenic source of tropospheric sulfur (Andreae and Andreae, 1988; Schlesinger, 1991). In warm regions, the primary oxidation product of DMS is sulfur dioxide (SO_2) (Bandy *et al.*, 1996; Davis *et al.*, 1999). The sulfur dioxide can then be oxidized to form sulfate (SO_4^{2-}), which is believed to be the primary source of cloud condensation nuclei (CCN) in the remote marine atmosphere. The potential link between DMS and CCN represents a possible negative feedback for global warming (Charlson *et al.*, 1987). Because the underlying processes in this hypothesis remain poorly understood, there continues to be considerable interest in measuring DMS and better understanding its relationship to atmospheric sulfate levels (Andreae and Crutzen, 1997; Kettle *et al.*, 1999; Watts, 2000).

Here we present our ability to measure DMS as part of a whole air sampling protocol that we routinely operate from both ground-based and airborne platforms (Blake, D. R. *et al.*, 1992, 1996; Blake, N. J. *et al.*, 1997, 1999; Chen *et al.*, 1999; Wingenter *et al.*, 1999; Simpson *et al.*, 2000). The whole air sampling technique allows us to accurately identify and precisely quantify more than 50 halocarbons, hydrocarbons, and alkyl nitrates. Prior to the 1999 aircraft-based NASA Pacific Exploratory Mission-Tropics B (PEM-Tropics B), we expanded our analytical capabilities to include DMS measurements. Because DMS is sampled concurrently with a wide range of atmospheric compounds, the technique allows correlations between DMS and different marine tracers or other species to be unambiguously investigated. The technique also offers excellent vertical resolution and flexible sampling periods, such that the data are suitable for determining the flux of DMS using the mixed-layer gradient technique (see Lenschow *et al.*, 1999).

2. Experimental

The DMS measurements are made using a combination of *in situ* whole air sampling followed by analysis by gas chromatography (GC) with mass spectrometer (MS) and flame ionization detection (FID). Dimethyl sulfide analysis by gas chromatography is a well-established measurement technique (Ivey and Swan, 1995; Bandy *et al.*, 1996; Davison *et al.*, 1996; Lewis *et al.*, 1997; Berresheim *et al.*, 1998). Two highlights of our analytical technique are the accurate quantification of DMS based on ethane and propane per-carbon-response-factor (PCRF) calibrations, and the stability of DMS within water-doped electropolished stainless steel canisters for several weeks.

2.1. FIELD SAMPLING

The whole air samples were collected aboard the NASA DC-8 and P-3B research aircraft during 35 science flights of the PEM-Tropics B field campaign. The mission was conducted from March to April 1999, with major deployment sites at Hawaii, Kiritimati (Christmas Island), Tahiti, and Fiji. During each flight, air samples were collected in individual 2-L stainless steel canisters that were each equipped with a stainless steel bellows valve. Prior to being sent to the field, the canisters were conditioned and evacuated (in previous laboratory studies we have found that the cleaned, conditioned canisters do not outgas). Next, 10 Torr (1.3 kPa) of water was added into each canister to quench active surface sites. The water was introduced into each canister from a previously degassed reservoir of distilled, deionized water that was contained in a canister on one of the sampling manifolds in our laboratory. The 2-L sampling canisters were then grouped in arrays of twenty-four for shipment to the field. The canisters were linked together in rows of eight using Ultra-Torr union tees and stainless steel tubing, and the three rows of eight were linked using stainless steel flex tubing. The DC-8 was equipped to carry seven canister arrays aboard each flight, and the P-3B carried six.

To collect a sample, outside air was collected from beyond the laminar boundary layer of the aircraft via $\frac{1}{4}''$ stainless steel tubing aboard the DC-8, and $\frac{1}{2}''$ tubing aboard the P-3B. The wider diameter tubing aboard the P-3B was designed to accommodate faster sampling for application towards DMS flux calculations (see below). The inlets were at ambient temperature and were under flow at all times during the flight. We expect DMS to transmit well through the inlets because, like the other gases we report, its vapor pressure is low enough for it not to freeze out at the temperatures experienced by the inlet. The sample air was then pressurized by an oil-free two-stage metal bellows pump (Parker MB-602XP) and distributed via $\frac{1}{4}''$ stainless steel tubing to a flow-through gas-handling manifold. The manifold allowed the air to be selectively directed into any given canister. Each sample was collected in an individual canister that was filled to a final pressure of 40 psig ($\sim$375 kPa).

During PEM-Tropics B, approximately 140 samples were collected per flight aboard the DC-8, and 120 aboard the P-3B. The whole air samples were collected throughout each flight on both aircraft, roughly every 3–7 min during horizontal flight legs and 1–3 min during ascents and descents. The P-3B and DC-8 flight altitudes complemented each other, and the P-3B typically flew at low levels (500–18,000 ft) whereas the DC-8 operated at higher altitudes (17,000–39,000 ft) with occasional excursions into the boundary layer. During both horizontal and ascending/descending flight legs, the sampling duration could be lengthened or shortened by adjusting a bellows valve (Swagelok SS-8BG) that was located on the gas handling manifold upstream of the pump. The fastest possible sampling time was 8 s at low altitude (500 ft) and roughly 80 s at high altitude (39,000 ft). Typical horizontal sampling times were approximately 1 min and correspond to a sampling distance of about 12 km. The vertical resolution depends upon the sampling time and the ascent or descent rate, and was varied according to the circumstance. During standard altitudinal profiles the samples were usually collected every 1500–2000 ft. A typical vertical sampling distance was roughly 1000 ft aboard the DC-8, and 450 ft aboard the P-3B.

2.2. ANALYTICAL TECHNIQUES

After each flight the filled canister arrays were couriered back to our laboratory at the University of California-Irvine (UCI) for analysis. Within ten days of being collected the air samples were analyzed for DMS as well as 57 hydrocarbons, halocarbons and alkyl nitrates. During PEM-Tropics B, two identical systems (‘System 1’ and ‘System 2’) were operated simultaneously in order to halve the duration of the sample analysis. An individual sample was typically analyzed on one of the two systems, and occasionally on both systems to check that consistent results were obtained. Because it takes a few days for the analytical systems to equilibrate, they were operated continuously (24 hours a day) throughout the project in order to generate an internally consistent data set (Blake *et al.*, 1996; Simpson *et al.*, 2000).

To analyze a sample, a canister array was connected to either system and the air inside the tubing that links the canisters was evacuated. For each sample, 1520 ± 1 cm^3 (STP) of canister air was used for analysis. The sample air was passed through a preconcentration loop that is filled with glass beads and immersed in liquid nitrogen (Figure 1). The procedure is used to preconcentrate the less volatile sample components (e.g., DMS, hydrocarbons, halocarbons, and alkyl nitrates), while the more volatile components (e.g., nitrogen, oxygen, and argon) are pumped away. We avoid freeze-up problems in our preconcentration loop by using large $\frac{1}{4}''$ tubing and 10 cm^3 loops that are open through the first half, and full of glass beads in the second half. As a result, most of the water freezes along the edges of the stainless steel trap before the sample reaches the glass beads, where it could freeze and plug the flow. The flow was regulated by a mass flow controller (Brooks Instruments 5850E) and was kept below 500 cm^3 min^{-1} to ensure that the less volatile components were completely trapped. The preconcentration loop was then isolated before being warmed in a hot water bath (at 80 °C) to revolatilize the gases. The contents of the loop were next flushed into a helium carrier gas flowing with 48 psig (∼430 kPa) head pressure. The sample flow was reproducibly split into five streams, with each stream directed to a different column-detector combination. By using subambient temperatures for each column (Table I), the sample was cryogenically recollected in each chromatographic system after being split into the five streams.

Dimethyl sulfide was measured using three of the column-detector combinations that were available in both analytical systems. Each of the columns was housed within a separate gas chromatograph (HP-6890). The first column-detector combination (abbreviated as 'DB5ms/MS') was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 μm film thickness) output to a quadrapole mass spectrometer detector (HP-5973). The second combination ('DB1/FID') was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1 μm film thickness) output to a flame ionization detector (HP-6890). The third combination ('PLOT-DB1/FID') was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1 μm film thickness) and output to a flame ionization detector. The DB5ms/MS, DB1/FID and PLOT-DB1/FID combinations received 10.1%, 15.1%, and 60.8% of the sample flow, respectively. The remaining 14.0% was divided between two additional column/detector combinations that were not used to analyze DMS.

The split ratio is 'reproducible' when the different detectors yield quantifications that are within our measurement precision. We have found that the split

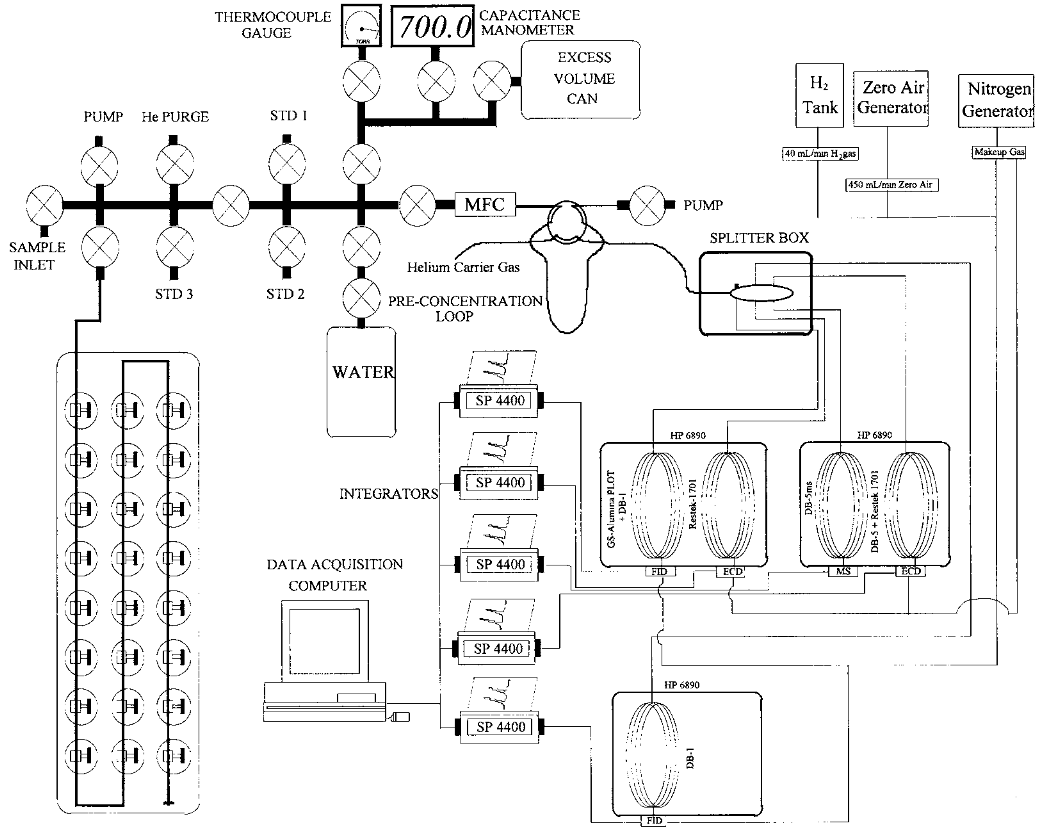

Figure 1. Analytical system used at UCI during the PEM-Tropics B mission, for the analysis of DMS as well as halocarbons, hydrocarbons, and alkyl nitrates. Two identical systems were operated continuously throughout the mission, in order to halve the duration of the sample analysis. MFC: mass flow controller; STD: standard.

Table I. Oven parameters for the 3 GCs that were used to analyze DMS. GC-1 housed the DB5ms column; GC-2 housed the DB1 column; and GC-3 housed the PLOT-DB1 columns

	GC-1	GC-2	GC-3
Initial temperature	–30 °C	–50 °C	–20 °C
Initial time	1.50 min	1.50 min	1.50 min
Rate 1	15 °C min^{-1}	18 °C min^{-1}	20 °C min^{-1}
Final temperature 1	50 °C	30 °C	200 °C
Final time 1	0 min	0 min	4.70 min
Rate 2	10 °C min^{-1}	13 °C min^{-1}	–
Final temperature 2	110 °C	145 °C	–
Final time 2	0 min	0 min	–
Rate 3	20 °C min^{-1}	25 °C min^{-1}	–
Final temperature 3	200 °C	200 °C	–
Final time	0 min	0 min	–
Cycle time	17.33 min	16.99 min	17.20 min

ratios are highly reproducible as long as the specific humidity of the injected air is greater than 2 g H_2O (kg air)$^{-1}$ (0.3 kPa at 298 K), which we ensure by the addition of 10 Torr (1.3 kPa) of water into each canister (see above). We also monitor the reproducibility of the split ratio by examining the calculated mixing ratios for a compound that gives a large signal, has good chromatographic characteristics, and is quantified on multiple detectors. For example, CFC-11 was detected on the MS and on two electron capture detectors (ECDs) that were also used during PEM-Tropics B, and it was used to monitor the split for the columns associated with the MS and ECDs. Propane was detected with high precision on both FIDs, and its output from the two FIDs was examined for every sample and standard. When the agreement between the two propane mixing ratios was within their experimental precision (1%), the split was deemed to be good. That is, a non-reproducible split occurs when the difference between the propane mixing ratios is greater than 1%. During PEM-Tropics B the split ratios were always reproducible and no adjustments were required.

The identification of DMS on both systems was the same for each FID, but differed between the FIDs and the MS. For each FID, all non-oxidized carbon compounds give a signal that is identified based on its retention time (RT). Both before and after the project, every RT was verified using individual compound standards. These are qualitative rather than quantitative standards, and they allow us to identify the exact retention time of each compound and any co-eluting peaks. For the DB-1 column, DMS elutes on the tail of acetone, just ahead of n-pentane. For the PLOT-DB1 column, DMS elutes between n-heptane and benzene. Identific-

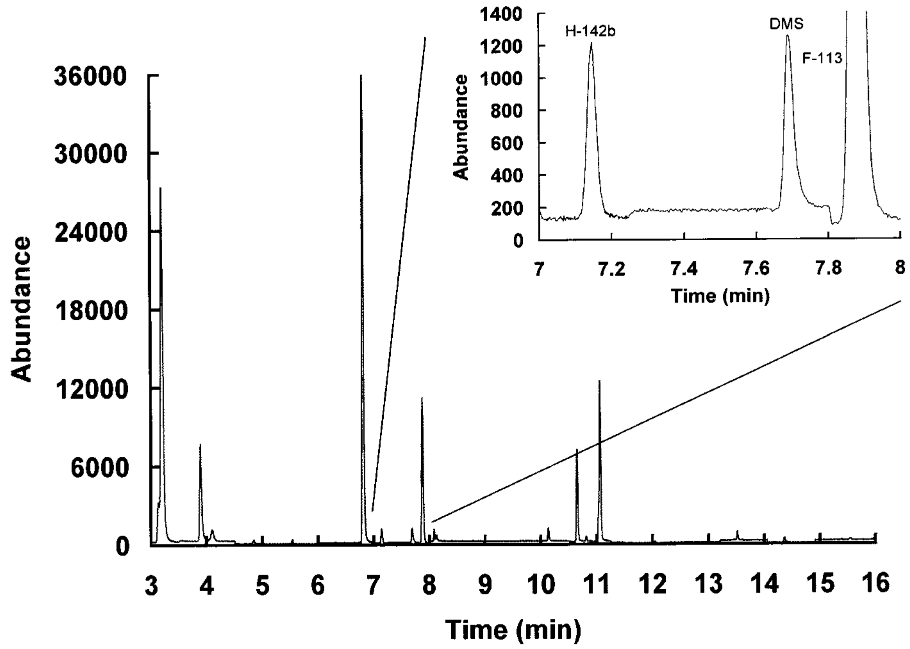

Figure 2. Mass spectrometer (MS) selected ion monitoring scan (SIMS) chromatogram for one of the PEM-Tropics B samples. The expanded window shows the DMS peak, which was quantified at 36.2 pptv. The SIMS method of identification for DMS uses ion 62.

ation standards were also run on the MS, and the RT was determined by analyzing for a specific ion (ion 62) that DMS generates in the MS. For the DB5-ms column, DMS elutes between H-142b and CFC-113 (Figure 2).

The signal from each detector was output to an integrator (Spectra Physics 4400), which produced hard copies of individual chromatograms, and to a personal computer where the data were digitally recorded using Labnet software (Spectra Physics, San Jose, CA). The baseline on each chromatogram was manually inspected for DMS, and the output from each column-detector combination was handled as follows. Dimethyl sulfide values from the DB1/FID and PLOT-DB1/FID combinations ('$\mathrm{DMS}_{\mathrm{DB1/FID}}$' and '$\mathrm{DMS}_{\mathrm{PLOT-DB1/FID}}$', respectively) were corrected for systematic temporal drift using two working standards of air that were analyzed every four samples, and a third standard that was analyzed twice daily. The two working standards were collected from rural areas of southern California, on the coast north of Cayucos and inland near Escondido. The third standard, collected at the White Mountain research station in California, was used as a check of the working standards. (The White Mountain standard was previously calibrated from static dilutions of standards prepared in our laboratory. Its absolute accuracy is tied to a manometer measurement and to how accurately the appropriate volume ratios are known for the dilution line that is used.) In the correction procedure, DMS values from the working standards are plotted against run time and a curve is fitted to the data. The curve is then normalized to its mean value. During PEM-Tropics B, the relative standard deviation in the working standards was larger than any perceived trend in the FID response with time. This was in part due to the very low levels of DMS in our working standard mixtures. That is, the DMS mixing ratios in the working standards were found to be too low to be useful.

Absolute DMS calibration standards were not used in our analysis, and the DMS detector response from the FIDs was converted from area units to mixing ratio based on a per-carbon-response-factor, in the same way as we routinely do for hydrocarbon measurements. The PCRF for each FID was calibrated using a combination of National Bureau of Standards, Scotty and UCI-made standards. We have been using this combination of standards for over 15 years to give an internally consistent data set. For short (C_2–C_4) alkanes, we have found that the PCRFs on the PLOT column are uniform with carbon number (Sive, 1998). Because ethane and DMS both contain two methyl carbons and therefore likely have the same FID response, we assigned a PCRF to DMS on the PLOT-DB1 column based on the PCRF for ethane. On the DB-1 column, the PCRF has been found to decrease by approximately 2–3% for each increasing carbon number after C_3 (Sive, 1998). We assigned the DMS PCRF on the DB-1 column based on 2/3 of the PCRF for propane.

For the DB5ms/MS combination, the signals from two adjacent peaks (CFC-11 and methylene chloride, CH_2Cl_2) were used to correct the detector response for systematic temporal drift and for steps (caused by filament changes and tuning). CFC-11 and CH_2Cl_2 were used rather than DMS itself because the DMS mixing ratios in the working standards were too low to be useful (see above). The two DMS values from the DB5ms/MS (based on the CFC-11 and CH_2Cl_2 normalizations) were then averaged to give a single DMS value for the DB5ms/MS. Because of the lack of an absolute standard, DMS mixing ratios for the DB5ms/MS (‘$DMS_{DB5ms/MS}$’) were assigned using the average of the slopes for [$DMS_{DB1/FID}$ vs. $DMS_{DB5ms/MS}$] and [$DMS_{PLOT-DB1/FID}$ vs. $DMS_{DB5ms/MS}$] (see Section 3.1). In this way, the DMS data from all three column-detector combinations are on the same absolute scale.

The limit of detection (LOD) for $DMS_{DB5ms/MS}$ was 1 part per trillion by volume (pptv), at a signal-to-noise ratio of about 6 : 1. By contrast, the signal-to-noise ratio at 1 pptv was about 2 : 1 for $DMS_{PLOT-DB1/FID}$. For $DMS_{DB1/FID}$, a signal-to-noise ratio of 2 : 1 corresponded to a mixing ratio of about 2 pptv. Because the DB5ms/MS detector response had a lower detection limit and a better peak than the DB1/FID and PLOT-DB1/FID, the DMS mixing ratios presented below (in Figures 6–11) are DB5ms/MS results. (A ‘better peak’ is more symmetric and has a smaller half-width at a given height.) We recall that the $DMS_{DB5ms/MS}$ mixing ratios were assigned using the $DMS_{DB1/FID}$ and $DMS_{PLOT-DB1/FID}$ values, which in turn were calibrated using a propane PCRF and an ethane PCRF, respectively. Even though our LOD for ethane and propane was 3 pptv, we were able to calibrate the $\text{DMS}_{\text{DB5ms/MS}}$ values to a lower LOD than $\text{DMS}_{\text{DB1/FID}}$ or $\text{DMS}_{\text{PLOT-DB1/FID}}$ based on the assumption that the MS response is linear in the 1–5 pptv range.

3. Results and Discussion

3.1. CALIBRATION

During PEM-Tropics B we recovered 2670 DMS measurements aboard the DC-8, of which 26% were above the detection limit, and 1826 aboard the P-3B, of which 62% were greater than 1 pptv. The percentage of detectable DMS mixing ratios was higher aboard the P-3B because it flew at lower altitudes than the DC-8 (closer to the oceanic DMS source), and because many P-3B flights were centered around a region of the Pacific Ocean known for high sulfur emissions.

When raw DMS area units are plotted against DMS mixing ratios that have been corrected with respect to CH_2Cl_2 and CFC-11, at least three distinct modes are evident for both analytical systems (Figures 3(a, b)). The three main modes were caused by a change in the sensitivity of the MS during the two times its filament was changed, on both analytical systems. There are also several smaller sensitivity changes that were caused by ‘tuning’ the MS detector. As the detector sensitivity dropped over time, the applied voltage was increased and the detector was re-tuned, thereby causing a small change in its sensitivity. Normalizing the DMS values with respect to CFC-11 and CH_2Cl_2 largely compensated for the sensitivity changes. On System 1 the DMS mixing ratios varied negligibly depending on whether the normalization was done with respect to CH_2Cl_2 or CFC-11. A plot of DMS mixing ratios that were normalized by CH_2Cl_2 vs. CFC-11 gives a slope of 0.99 with an r^2 of 0.996 (Figure 4(a)). Very good results were also obtained on System 2, and a plot of DMS normalized by CH_2Cl_2 vs. CFC-11 gives a slope of 1.04 with an r^2 of 0.996 (Figure 4(b)). Again, the two DMS values from the DB5ms/MS, based upon the CFC-11 and CH_2Cl_2 normalizations, were averaged to give a single DMS mixing ratio for the DB-5ms/MS. The plots in Figures 4(a, b) show that two small but distinct modes remained after the normalization procedure. While retuning could be responsible for these modes, we are unable to determine their cause with certainty.

The DMS mixing ratios from the DB1/FID and PLOT-DB1/FID combinations showed excellent correlation, with r^2 values of 0.996 and 0.991 on Systems 1 and 2, respectively (Figures 5(a, b)). However, on System 1 the mixing ratios from the PLOT-DB1/FID combination were on average 8.6% higher than those from the DB1/FID combination (Figure 5(a)). On System 2, the PLOT-DB1/FID values were 11.3% lower than the DB1/FID mixing ratios (Figure 5(b)). The observed differences most likely arise because the two systems are independent, contain different columns and give different response factors. Other compounds measured on both columns show similar differences, and this is why we routinely average the results from separate columns. Here, we recall that the DMS results from the DB-5ms/MS were assigned using the average of the slopes for [$\text{DMS}_{\text{DB1/FID}}$

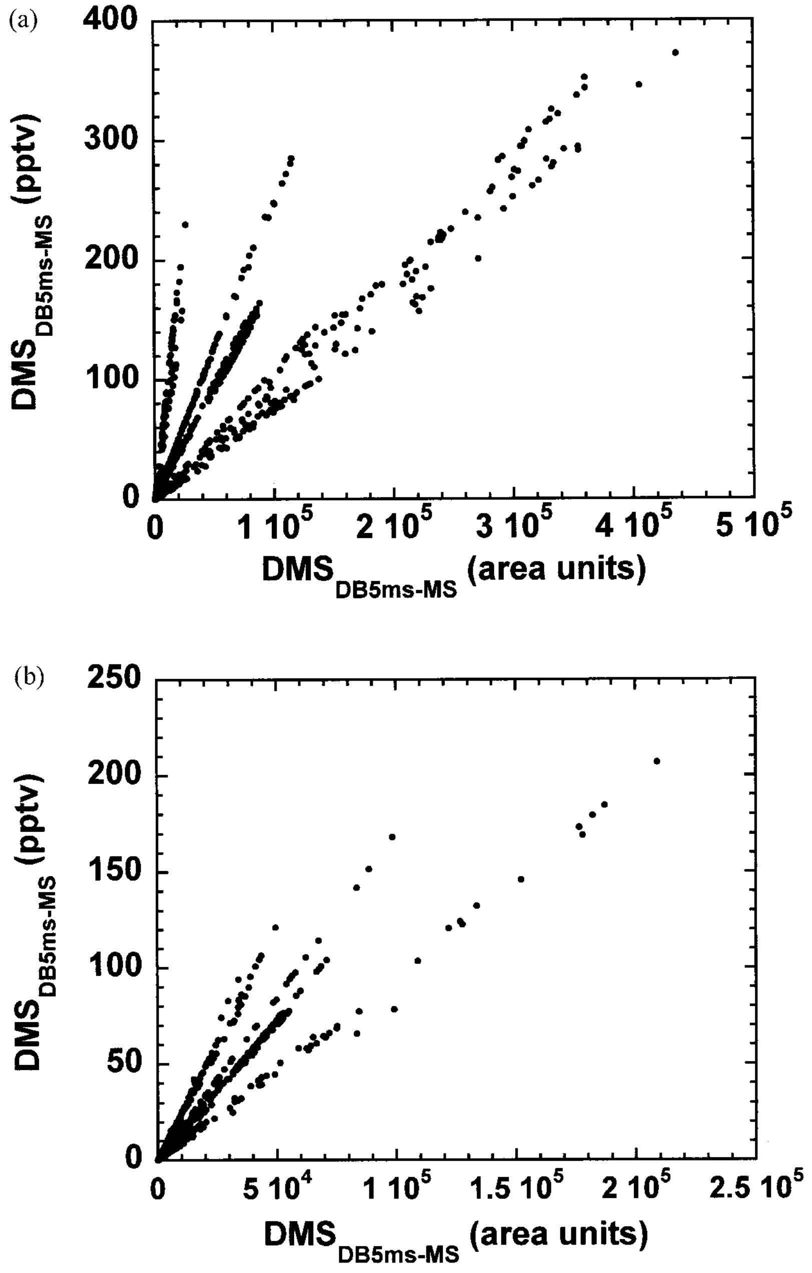

Figure 3. DMS mixing ratios corrected with respect to CH_2Cl_2 and CFC-11, vs. DMS area units obtained from the DB5ms/MS column-detector combination. (a) System 1; (b) System 2.

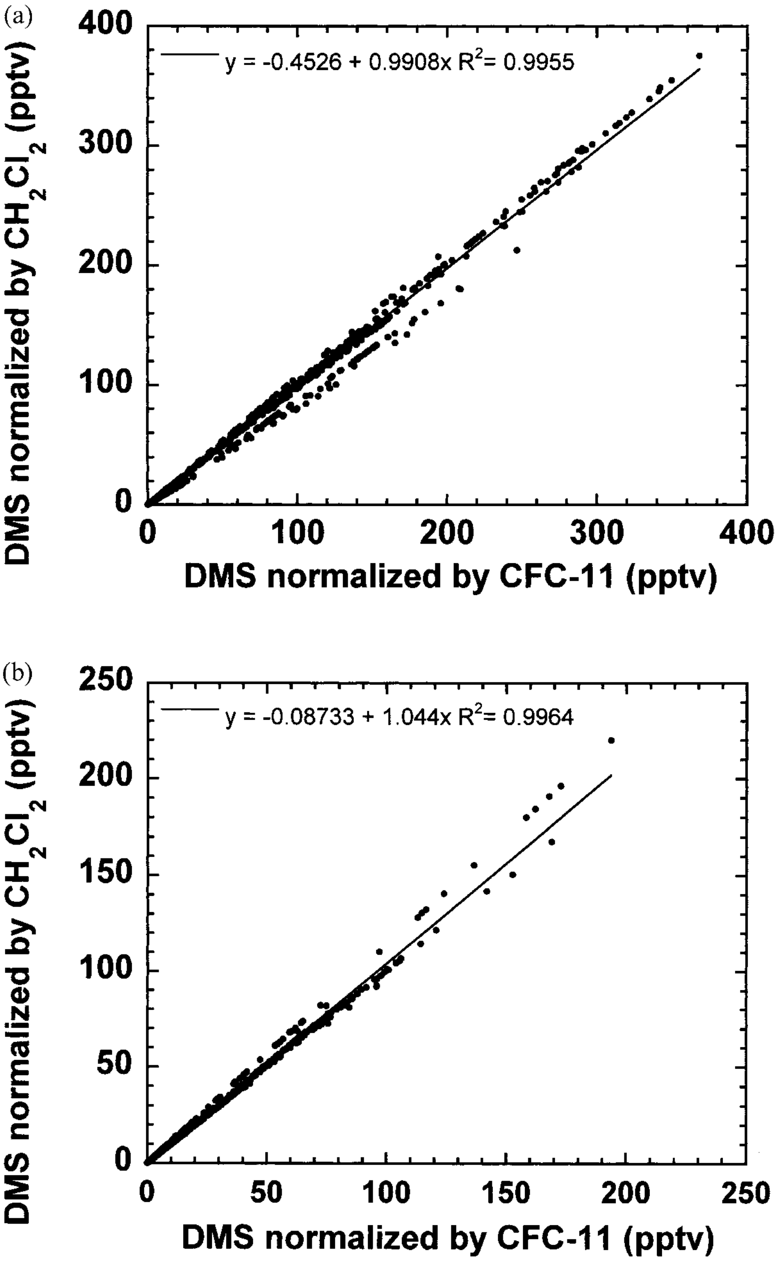

Figure 4. DMS mixing ratios for the DB5ms/MS column-detector combination, normalized by CH_2Cl_2 vs. CFC-11. (a) System 1; (b) System 2.

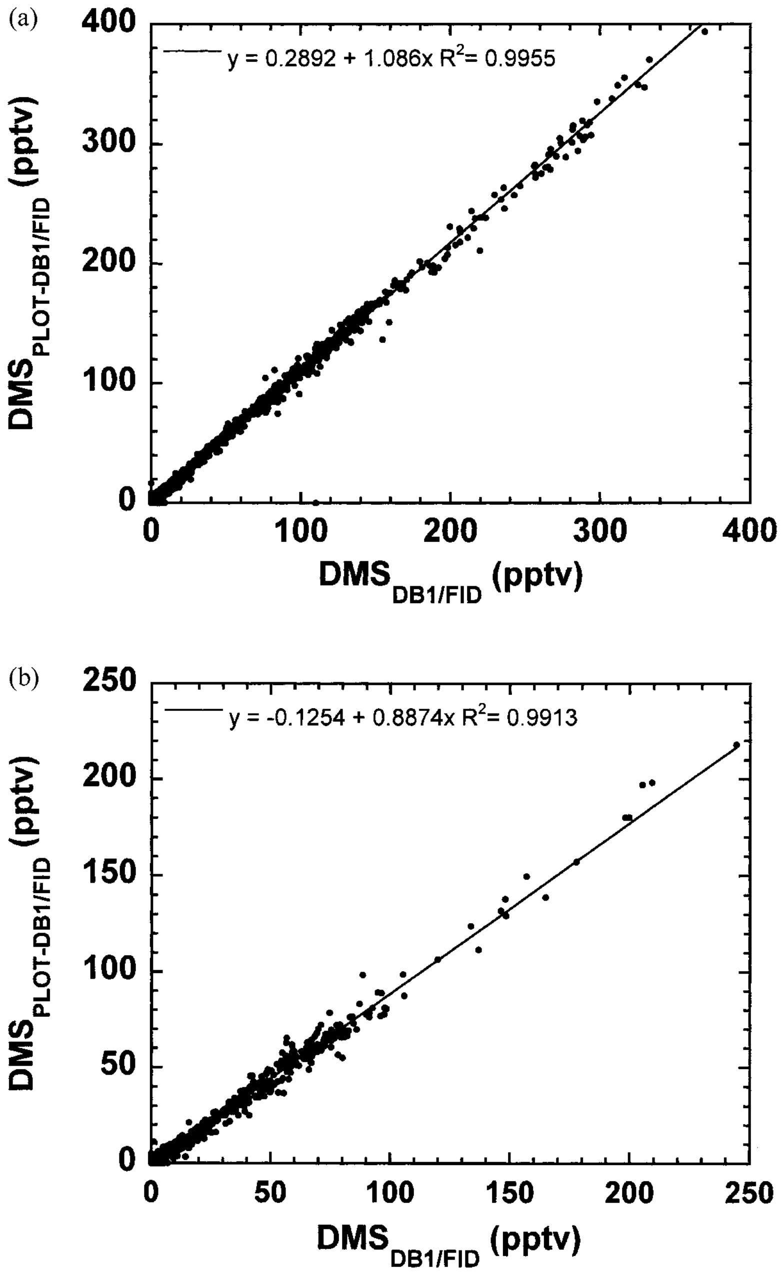

Figure 5. DMS mixing ratios for the PLOT-DB1/FID vs. DB1/FID column-detector combinations. (a) System 1; (b) System 2.

vs. $\mathrm{DMS_{DB5ms/MS}}$] and [$\mathrm{DMS_{PLOT-DB1/FID}}$ vs. $\mathrm{DMS_{DB5ms/MS}}$]. The differences between the DMS mixing ratios measured on the different systems and with different columns represents a limit for the accuracy of the DMS measurements. We conservatively estimate the accuracy of our DMS measurements at 95% confidence to be ±20% or 3 pptv, whichever is larger.

During PEM-Tropics B, our group detected DMS mixing ratios that ranged between 1 and 372 pptv. The precision of the DMS measurements was determined using constant altitude flight legs that contained at least 8 data points, and during which DMS showed little natural variability. (We did not determine the precision based on replicate analyses of sample air from the same canister. We collected 4500 samples during PEM-Tropics B, and we estimated that we would have needed to made replicate analyses of at least 10% of our samples to adequately determine our experimental precision by this technique; such an undertaking was beyond our means.) We made the assumption that DMS showed little natural variability using several criteria: (1) the P-3B was flying over an oceanic region known to give off DMS; (2) the data were collected at low altitude, close to the DMS source; (3) the DMS values were much (50–100×) greater than background values; and (4) the DMS mixing ratios were near-constant, in contrast to other periods during the mission. For example, during a transit flight from Hilo to Christmas Island on 13 March 1999, DMS varied between 106.2 and 116.3 pptv over a 1 hr period in the vicinity of Christmas Island, at an altitude of 500–700 ft. The precision (1σ) of these measurements was 1.1 pptv, or 1%. Based on the results from all suitable flight legs, the 1σ DMS precision was estimated to be 15% or 1 pptv (whichever is larger) at low mixing ratios (<10 pptv), and 2–4% at high mixing ratios (>25 pptv). The precision is expected to decrease accordingly (from 15% or 1 pptv to 2–4%) in the transitional range from 10 to 25 pptv. We note that these are conservative estimates of our measurement precision because a small, unquantified component of the DMS variability among these samples may be natural.

3.2. MEASUREMENTS DURING PEM-TROPICS B

Because the whole air sampling technique is capable of resolving 450 ft intervals during ascents and descents, the UCI measurements successfully capture detail in the vertical structure of DMS. For example, P-3B Flight 11, was a local sunset flight deploying from Christmas Island on 24 March 1999. The DMS measurements show enhancements during two boundary layer flight legs (800 ft altitude) and during the first horizontal flight leg at 4000 ft (Figure 6(a)). The data also show a clear inverse correlation between altitude and DMS mixing ratio throughout the series of altitudinal flight steps. An altitudinal profile of DMS during Flight 11 shows that there is excellent coverage during the ascents and descents, in addition to the horizontal plane (Figure 6(b)).

An additional advantage of the whole air sampling technique is that the DMS samples are collected simultaneously with more than 50 halocarbons, hydrocar-

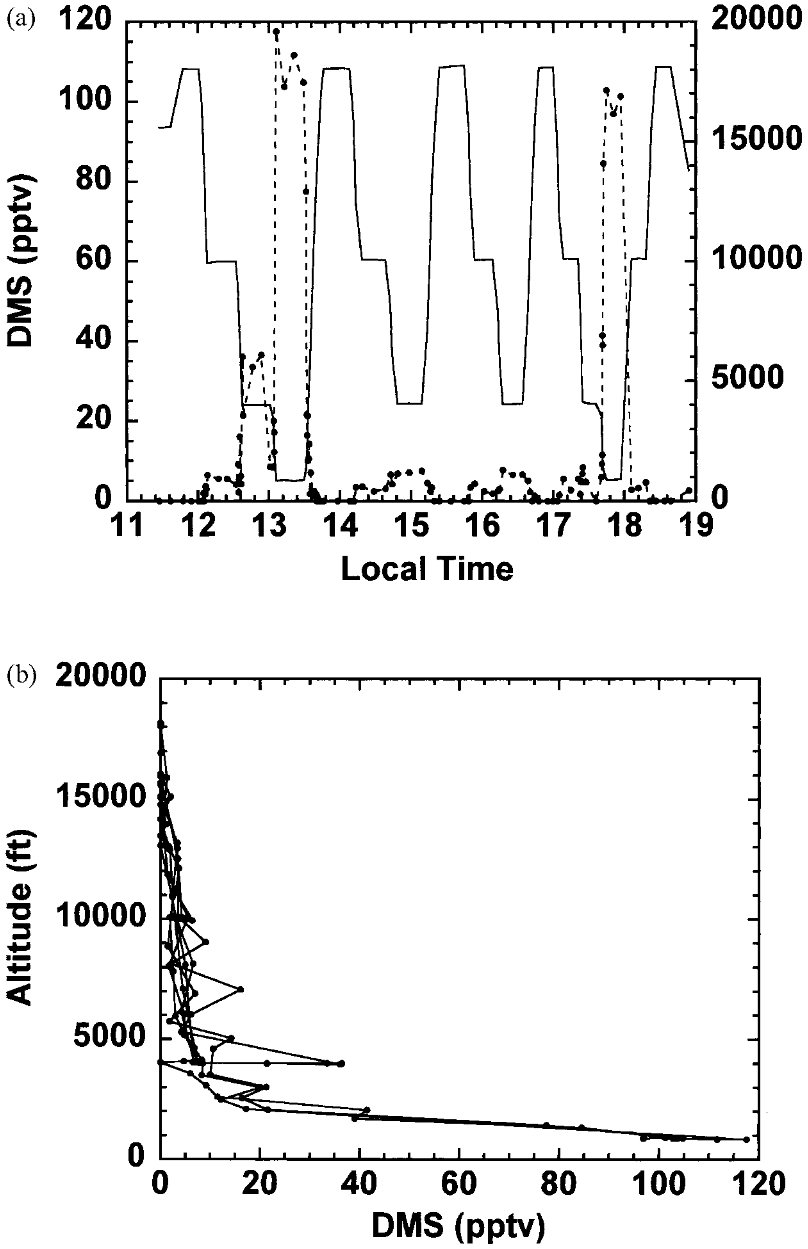

Figure 6. DMS mixing ratios measured during P-3B Flight 11 of PEM-Tropics B, a local sunset flight deploying from Christmas Island on 24 March 1999. (a) Time series; (b) Altitudinal profile. The solid line in (a) traces altitude.

bons, and alkyl nitrates. The coincidence of the measurements allows correlations between DMS and various marine tracers (e.g., methyl iodide, CH_3I; bromoform, $CHBr_3$; methyl nitrate, CH_3ONO_2) to be readily investigated, rather than searching for overlapping sampling times between data sets from two different groups. For example, during P-3B Flight 11, the DMS vs. CH_3I and $CHBr_3$ mixing ratios that were obtained at all altitudes (including the marine boundary layer) can be well described by a second-order polynomial fit (Figures 7(a, b)). By contrast, the mixing ratios of DMS and CH_3I were not correlated in the marine boundary layer during PEM-Tropics A (Cohan *et al.*, 1999). A more detailed comparison of the marine species measured during PEM-Tropics B will be given in an upcoming paper.

The wide ($\frac{1}{2}''$) inlet tubing aboard the P-3B was designed to enable fast air sampling for application towards flux measurements. During a local science flight deploying from Christmas Island on 22 March 1999, individual ‘flux circles’ of roughly 0.5° diameter were flown during a 30 min period in the boundary layer at 500 ft and 900 ft, and in the entrainment zone at 1300 ft. In each flux circle a sample was collected during an 8 s period every 90 s, for a total of 16 whole air samples collected during 30 min. The resulting altitudinal profile (Figure 8) will be used to determine the entrainment flux of DMS using a mixed-layer gradient technique (see Lenschow *et al.*, 1999).

PEM-Tropics B was a two-aircraft mission, and our group made the only DMS measurements aboard the DC-8. In addition to providing DMS data throughout each DC-8 flight, the measurements yield DMS profiles that extend from the boundary layer to the upper troposphere and lower stratosphere. For example, DC-8 Flight 8 was a sunset sulfur survey that flew over Christmas Island on 14 March 1999 and covered an altitudinal range of 1000 to 39,000 ft (Figure 9(a)). The DMS mixing ratios had a median value of 106 pptv in the boundary layer, at a mean altitude of 1100 ft. The mixing ratios were always less than 5 pptv above 10,000 ft, and the majority of measurements on this flight did not exceed the detection limit (Figure 9(b)). A notable exception is elevated DMS encountered at 8050 ft during a descent at 15:03 local time (LT), and again at 9400 ft during ascent at 16:05 LT (Figures 9(a, b)). The DMS mixing ratio reached a maximum value of 13 pptv during descent through the layer, and 11 pptv upon ascent.

The DMS measurements from both aircraft are consistent and are suitable for consideration as a complementary data set, because the same type of canisters were used on both aircraft; the same treatments were applied to all the canisters; and the samples collected aboard both aircraft were randomly analyzed on both systems. As a result, the DMS measurements from the DC-8 can be compared to P-3B values during coordinated DC-8/P-3B flights. For example, DC-8 Flight 8 supported P-3B Flight 6 during the sunset sulfur survey of 14 March. Other joint DC-8/P-3B flights deployed on 13 March, 4 April and 7 April 1999. During the joint flight of 14 March, the DC-8 ascended to 39,000 ft on several occasions and rarely flew below 18,000 ft (Figure 9(a)). By contrast, the P-3B mostly flew at altitudes below 4500 ft, with a mid-flight excursion to 15,000 ft (Figure 10(a)). That is, the main

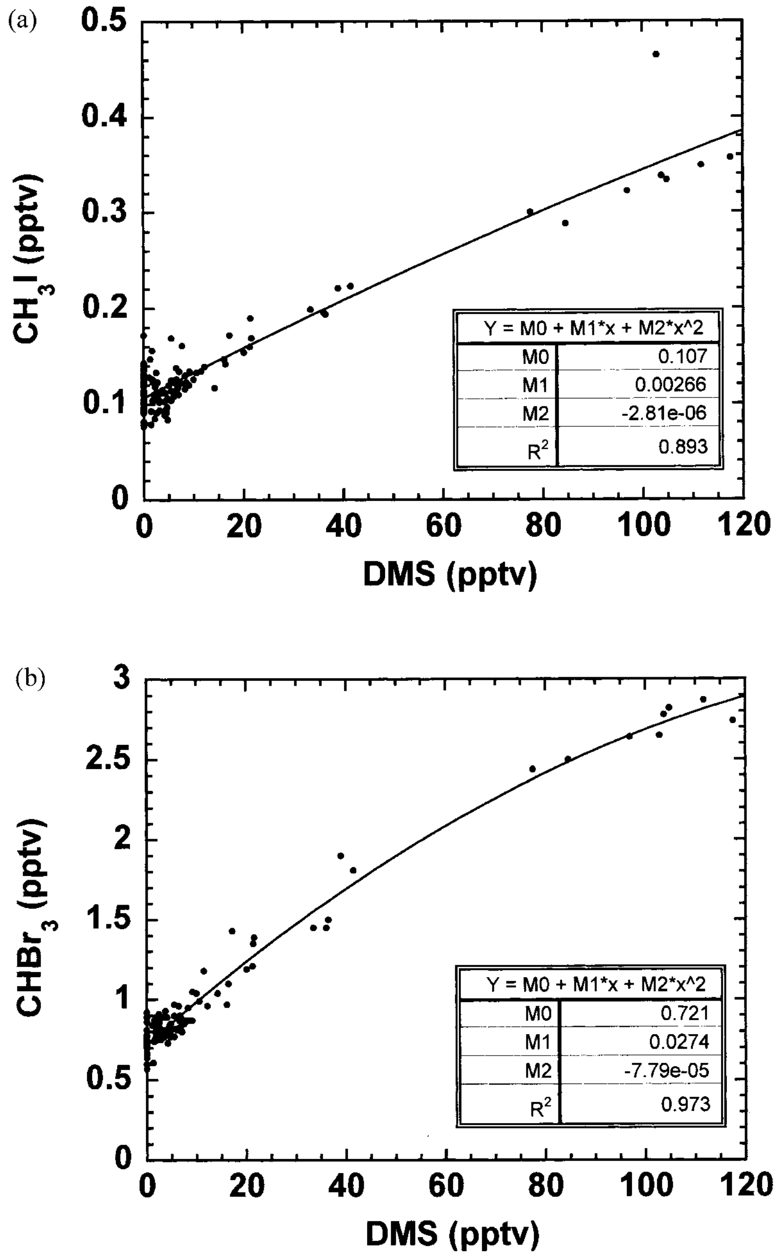

Figure 7. Correlation between DMS and two marine tracers during P-3B Flight 11 (all data). (a) Methyl iodide (CH_3I) vs. DMS; (b) Bromoform ($CHBr_3$) vs. DMS.

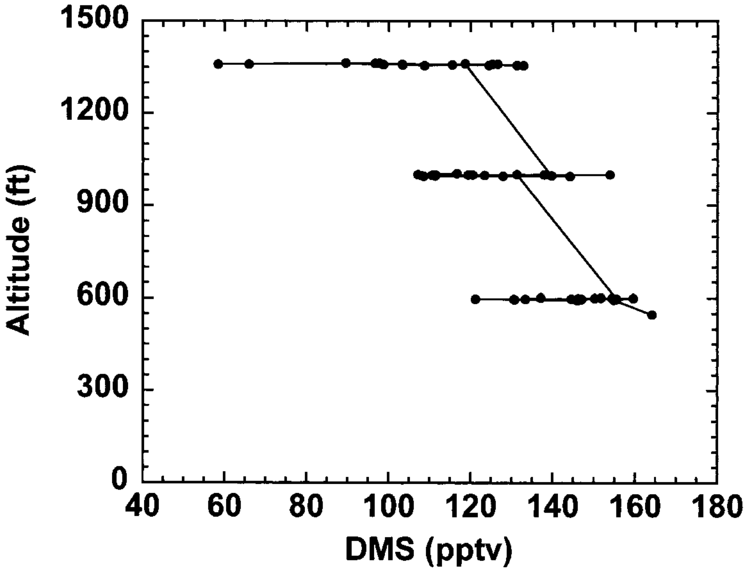

Figure 8. Altitudinal profile of DMS during the 'flux circle' portion of a local science flight deploying from Christmas Island on 22 March 1999.

flight altitudes of the two aircraft complement each other. Small DMS enhancements were detected aboard the P-3B at 8450 ft during the ascent to 15,000 ft at 14:33 LT, and at 8550 ft upon descent at 15:27 LT (Figure 10(b)). (A third DMS enhancement was encountered at 9200 ft during a descent from 15,000 ft at the start of the flight.) The altitudes of the two layers were similar to those of the layers encountered by the DC-8. However, the timing and positions of the two aircraft were not identical during the encounters with the DMS enhancements (the samples were collected over a 90 min period within a region of 1–1.5° latitude and 0.3–0.5° longitude), and the aircraft are most likely to have sampled different layers. During boundary layer flight legs, the DMS mixing ratios collected aboard the P-3B reached values greater than 100 pptv, comparable to the magnitudes measured aboard the DC-8 (Figures 9(a), 10(a)).

3.3. GROUP INTERCOMPARISON

During PEM-Tropics B, DMS was measured aboard the P-3B both by UCI, and by Drexel University via immediate in-flight analysis employing GC/MS with isotopically labeled internal standards and cryogenic enrichment (Bandy *et al.*, 1993, 1996; Thornton *et al.*, 1997). The technique has a 3–4 minute sampling time with a turnaround time of 5–6 minutes (Thornton *et al.*, 1997). The Drexel inlet was a $\frac{3}{8}''$ O.D. FEP Teflon tube which extended through an aft-facing aluminum pipe ($1\frac{1}{4}''$ O.D.; $\frac{3}{4}''$ I.D.). The teflon tube was heated to about 35–40 °C to prevent

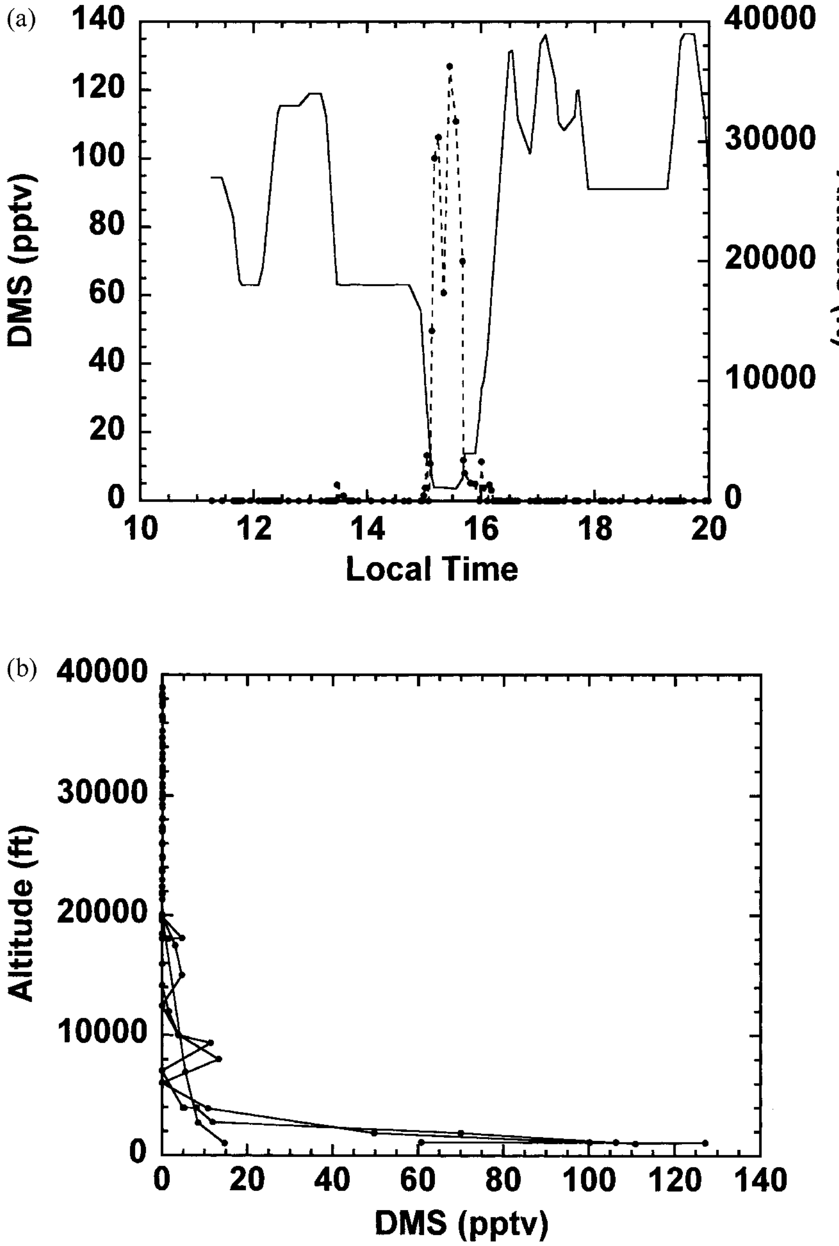

Figure 9. DMS mixing ratios measured during DC-8 Flight 8 of PEM-Tropics B, a sunset sulfur survey in the region of Christmas Island on 14 March 1999. (a) Time series; (b) Altitudinal profile. The solid line in (a) traces altitude.

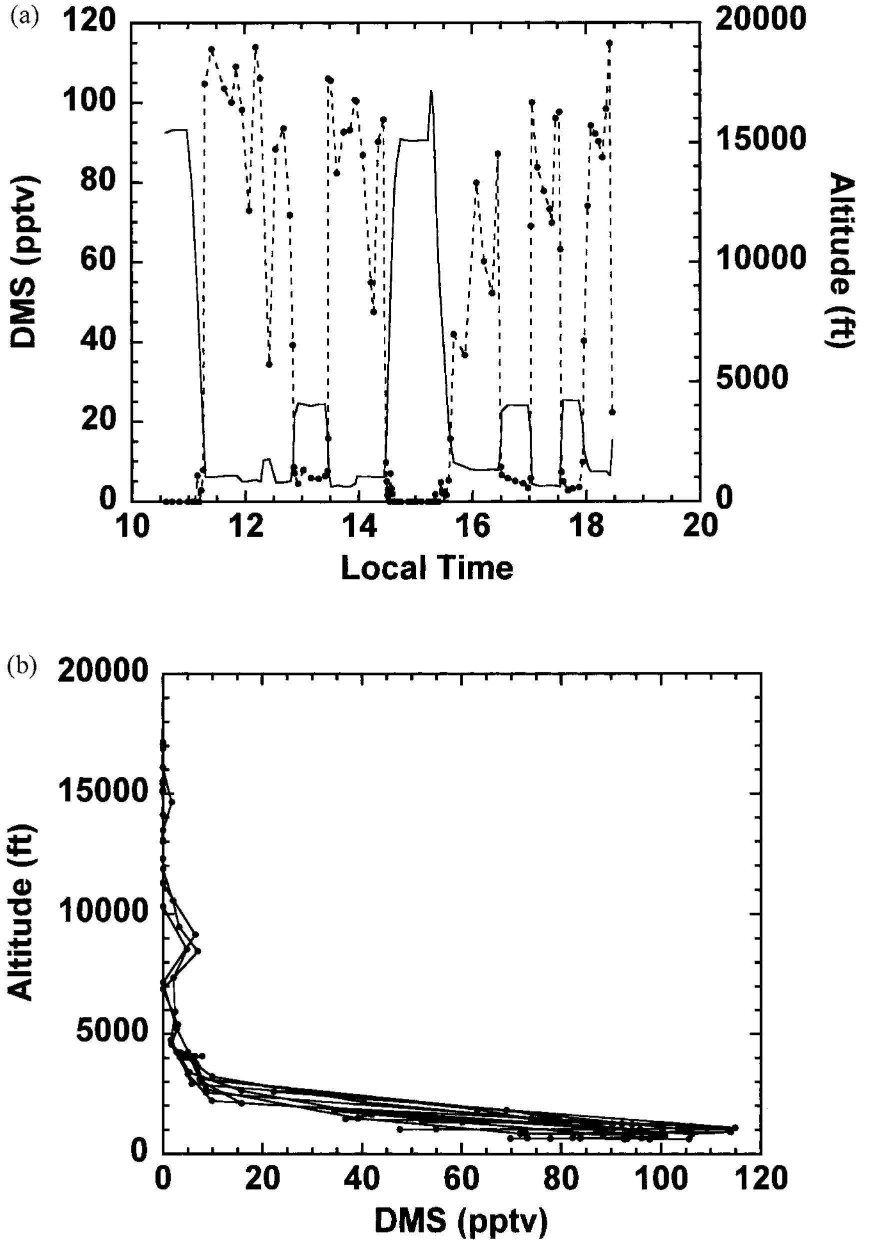

Figure 10. DMS mixing ratios measured during P-3B Flight 6 of PEM-Tropics B, during a coordinated flight with DC-8 Flight 8 in the region of Christmas Island on 14 March 1999. (a) Time series; (b) Altitudinal profile. The solid line in (a) traces altitude.

condensation. The Drexel and UCI measurements were made independently of one another and feature different modes of operation and temporal resolution.

The DMS mixing ratios measured by Drexel and UCI show remarkably good correlation over a wide range of concentrations (Figure 11(a)). During the 17 P-3B science flights, 499 data points were collected by each group during overlapping sampling periods. A plot of the Drexel vs. UCI DMS mixing ratios gives a slope of 0.986 with an r^2 of 0.975 (Figure 11(a)). At low mixing ratios ($<$50 pptv for both groups), the two data sets show a slope of 0.966, though with a much poorer correlation ($r^2 = 0.812$) (Figure 11(b)). Overall, the excellent agreement between the two data sets indicates that calibration based on ethane and propane per-carbon-response-factors yields accurate mixing ratios, and that DMS is not adversely affected by storage within the sampling canisters during the shipment to our laboratory for analysis.

4. Conclusions

We have added DMS to the suite of compounds that we routinely measure as part of a whole air sampling protocol during both ground-based and airborne missions. The DMS measurements are made using a combination of *in situ* whole air sampling followed by analysis using gas chromatography with mass spectrometer and flame ionization detection. Measurements during the recent PEM-Tropics B mission showed excellent agreement with independently observed DMS mixing ratios, indicating that DMS can be accurately quantified without any DMS standards based on ethane and propane per-carbon-response-factors, and that DMS is stable in water-doped electropolished stainless steel canisters for at least several weeks. The DMS results from the MS were corrected for step changes and systematic temporal drift in the detector response based on CFC-11 and CH_2Cl_2 values. We were able to report DMS mixing ratios as low as 1 pptv based on the assumption that the MS response is linear in the 1–5 pptv range.

During PEM-Tropics B our measurements yielded DMS profiles that extended from the boundary layer to the upper troposphere and lower stratosphere. The sampling technique allows flexible sampling periods and offers excellent vertical resolution, and the DMS mixing ratios can be applied towards flux calculations using the mixed-layer gradient technique. Because DMS is sampled concurrently with a wide range of atmospheric compounds, correlations between DMS and different marine tracers or other species can be readily investigated. The role of DMS in aerosol formation has become a major issue in global tropospheric chemistry, and our measurement capability will add to the database of DMS from which to improve our understanding of atmospheric sulfur chemistry.

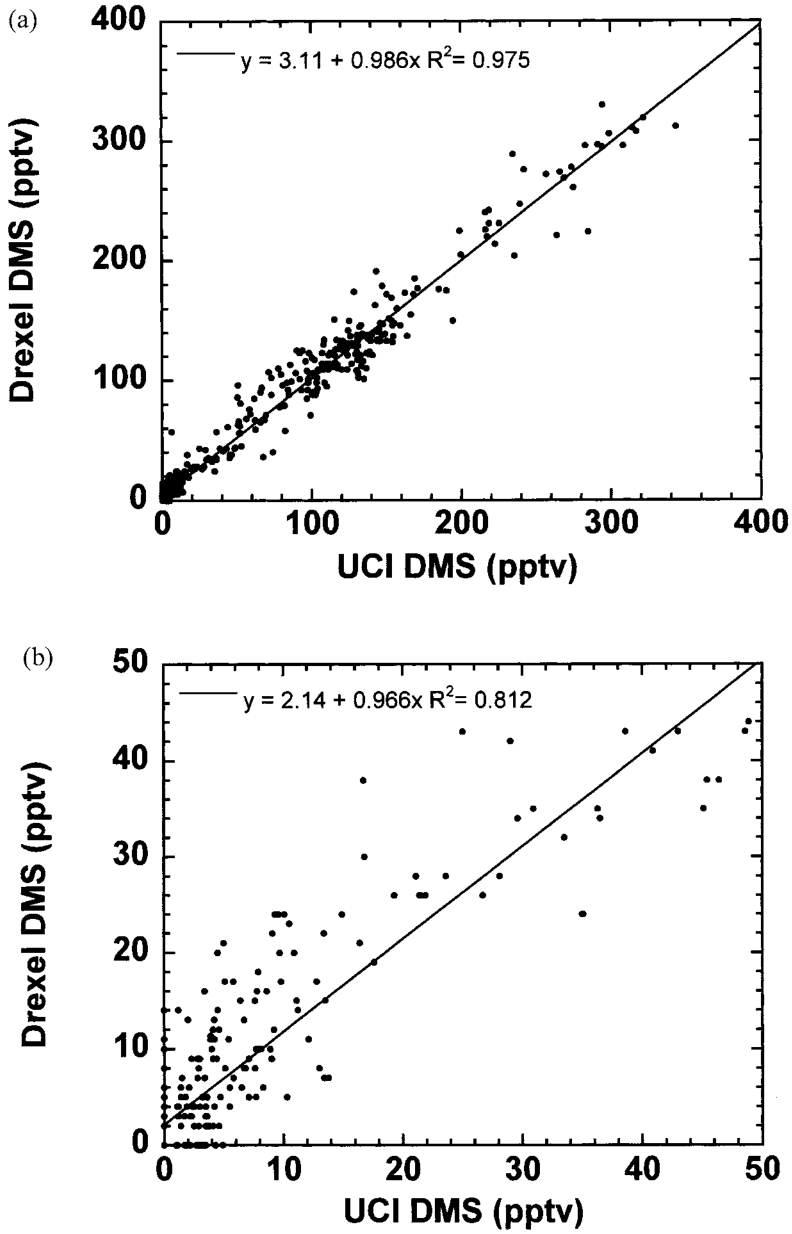

Figure 11. Correlation between DMS mixing ratios measured by Drexel University and the University of California-Irvine (UCI) during the 17 science flights of the P-3B during PEM-Tropics B. (a) All overlapping data (499 points); (b) both UCI and Drexel DMS mixing ratios less than 50 pptv.

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