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An Intercomparison of Instrumentation for Tropospheric Measurements of Dimethyl Sulfide: Aircraft Results for Concentrations at the Parts-Per-Trillion Level

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This paper reports results from NASA's Chemical Instrumentation and Test Evaluation (CITE 3) during which airborne measurements of dimethyl sulfide (DMS) from six instruments were intercompared. Represented by the six instruments are three fundamentally different detection principles (flame photometric, mass spectrometric, and electron capture after fluorination); three collection/preconcentration methods (cryogenic, gold wool absorption, and polymer absorbent); and three types of oxidant scrubbers (solid phase alkaline, aqueous reactor, and cotton). The measurements were made over the Atlantic Ocean in August/September 1989 during flights from NASA's Wallops Flight Center, Virginia, and Natal, Brazil. The majority of the intercomparisons are at DMS mixing ratios <50 pptv. Results show that instrument agreement is of the order of a few pptv for mixing ratios <50 pptv and to within about 15% above 50 pptv. Statistically significant (95% confidence) measurement biases were noted among some of the techniques. However, in all cases, any bias is small and within the accuracy of the measurements and prepared DMS standards. Thus, we conclude that the techniques intercompared during CITE 3 provide equally valid measurements of DMS in the range of a few pptv to 100 pptv (upper range of the intercomparisons).

INTRODUCTION

Sulfur gases and their reaction products play important roles in the chemistry of the global troposphere and in the biogeochemical sulfur cycle [e.g., *Cullis and Hirschler*, 1980; *Rodhe and Isaksen*, 1980; *Frenay et al.*, 1983; *Ivanov and Frenay*, 1983; *Galloway et al.*, 1985; *Toon et al.*, 1987; *Saltzman and Cooper*, 1988; *Bates et al.*, 1987, 1990; *Andreae*, 1990; *Andreae and Jaeschke*, 1992]. Major sulfur gases include sulfur dioxide (SO₂), dimethyl sulfide (DMS), hydrogen sulfide (H₂S), carbon disulfide (CS₂), and carbonyl sulfide (COS). Atmospheric photochemistry results in the oxidation of reduced sulfur gases (DMS, H₂S, CS₂, and COS) to SO₂, methanesulfonic acid (MSA), and sulfuric acid. MSA and sulfuric acid are incorporated into the atmospheric aerosol and represent the dominant source of aerosol particles in the unpolluted marine atmosphere [*NASA*, 1984; *Andreae*, 1990]. Important scientific issues in atmospheric sulfur chemistry include (1) the relative role of the various

sources and sinks (natural and anthropogenic) of the major sulfur gases, (2) the rates and pathways of atmospheric oxidation of the sulfur species to SO₂ and the production of aerosols, (3) the vertical distribution of sulfur gases and aerosols and their transport between the mixed layer and free troposphere, (4) the role of sulfur in acid rain, and (5) the impact of sulfate aerosol production (stratosphere and troposphere) as it relates to the Earth's energy balance and climate [*Charlson et al.*, 1987].

The principal anthropogenic sulfur compound is sulfur dioxide, which is predominantly emitted during fossil fuel burning (about 70-100 Tg S/yr [*Cullis and Hirschler*, 1980]). Volcanoes are the major natural direct source of SO₂, with an emission rate on the order of 10 Tg S/yr [*Berresheim and Jaeschke*, 1983]. Terrestrial biogenic sulfur emissions are predominantly in the form of hydrogen sulfide and dimethyl sulfide; the total flux of reduced sulfur gases from terrestrial ecosystems is about 4 Tg S/yr [*Andreae and Jaeschke*, 1992]. The largest natural sulfur source to the atmosphere is the emission of DMS from the oceans, which amounts to some 15-40 Tg S/yr [*Bates et al.*, 1987; *Andreae*, 1990; *Erickson et al.*, 1990]. Seawater DMS is derived from enzymatic cleavage of biologically generated (via phytoplankton) dimethylsulfoniopropionate, and is subsequently transferred across the sea-air interface into the atmospheric boundary layer [*Bates et al.*, 1992; *Spiro et al.*, 1992]. The marine source of DMS represents at least 50% of the estimated natural sulfur emissions and has been studied in some detail. In particular, research has focused on the production rate of DMS as a function of biological and meteorological conditions, the conversion of DMS to other sulfur compounds, and the mechanisms by which reaction products are transported throughout the global troposphere. Several techniques have been used for the measurement of tropospheric levels of DMS. The question arises as to the validity of DMS measurements by these techniques, especially at the low tropospheric concentrations which are usually in the parts-per-trillion (pptv) range.

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As part of the NASA Tropospheric Chemistry Program, a series of field intercomparisons have been initiated to evaluate the state-of-the-art capability for measuring key tropospheric species [McNeal *et al.*, 1983; Hoell *et al.*, 1984; Gregory *et al.*, 1985; Beck *et al.*, 1987]. These intercomparisons, designated as Chemical Instrumentation Test and Evaluation (CITE), are conducted as part of NASA's Global Tropospheric Experiment (GTE). The primary objective of the first intercomparison, GTE/CITE 1, was the evaluation of the capability for measurements of background levels of carbon monoxide (CO), nitric oxide (NO), and the hydroxyl radical (OH) [Hoell *et al.*, 1984, 1985a, b]. CITE 2 extended the intercomparisons to the other major nitrogen gases, namely, nitrogen dioxide (NO₂), nitric acid (HNO₃), and peroxyacetyl nitrate (PAN) [Gregory *et al.*, 1990a, b, c, d]. The objectives of CITE 3 were to evaluate instrumentation for making reliable aircraft measurements of the major sulfur gases and to determine in a predominantly marine environment the abundance and distribution of the major sulfur gases over a wide range of atmospheric conditions.

This paper reports the results from CITE 3 during which airborne measurements from six DMS instruments were intercompared. Represented by the six instruments are three fundamentally different detection principles (flame photometric, mass spectrometric, and electron capture after fluorination); three collection/preconcentration methods (cryogenic, gold wool absorption, and polymer absorbent); and three types of oxidant scrubbers (solid phase alkaline, aqueous reactor, and cotton). The measurements were made from the Wallops Electra aircraft flown during August and September 1989 from Wallops Island, Virginia, and Natal, Brazil. Intercomparison results for SO₂, H₂S, CS₂, and COS are the subject of companion papers [Gregory *et al.*, this issue (a), (b)]. The abundance and distribution of sulfur species in

the marine atmosphere is the subject of numerous papers included in this issue of the *Journal of Geophysical Research*.

EXPERIMENTAL DESCRIPTION

DMS Instrumentation

Six DMS instruments participated in the intercomparisons. Table 1 summarizes the instruments. Four basic measurement approaches are represented: (1) gas chromatograph-mass spectrometer, (2) gas chromatograph/fluorination-electron capture, (3) gas chromatograph-flame photometric, and (4) gold wool absorption collection-flame photometric detection. All techniques use some form of gas chromatography (i.e., column separation) in the measurement principle, and all use a scrubber to remove oxidants from the air sample. The three gold wool techniques differ mainly in the type of oxidant scrubber used and minor operational procedures. As noted in the table, two of the techniques provided measurements of other sulfur gases and participated in the intercomparisons conducted for other sulfur gases. The notations in the last two columns of Table 1 are used in the paper to identify the instrumentation. A brief description of each instrument and its operation is given below. Detailed descriptions of the instruments are found in the references and companion papers. The experimental layout of the DMS instrumentation and the other CITE 3 instrumentation aboard the aircraft are discussed in the overview paper [Hoell *et al.*, this issue].

Gas chromatograph-mass spectrometer. Gas chromatography for separation of DMS from the sample stream followed by mass spectrometric quantitative analyses is the basic detection principle of the measurement. Sulfur gases in the incoming air stream are preconcentrated in a Teflon,

TABLE 1. Summary of

Technique	Organization and Investigator	Other Sulfur Measurements*	Sample Schedule†
Gas chromatograph-mass spectrometer	Drexel University, A. Bandy	SO ₂ CS ₂ COS	3-min sample every 12 min
Gas chromatograph/fluorination electron capture	NOAA PMEL, J. Johnson	CS ₂ COS	1-min sample every 10 min
Gas chromatograph-flame photometric	University of Miami, E. Saltzman		Consecutive 10-min samples
Gold wool-Na ₂ CO ₃ scrubber	Max-Planck-Institute, M. Andreae		10- to 20-min collections
Gold wool-cotton scrubber	Max-Planck-Institute, M. Andreae		10- to 20-min collections
Gold wool-KOH scrubber	University of Washington, R. Ferek		5- to 10-min collections

* All gases not necessarily measured simultaneously.

† As stated for operations during CITE 3.

‡ Typical sample schedules for CITE 3.

§ Precision at 50 pptv.

liquid-argon cooled trap. After preconcentration for several minutes (typically three during CITE 3), the trap contents are volatilized (via heating) into a carrier gas (helium). Separation of the sulfur gases in the carrier-gas stream occurs by a gas chromatography. The separated sulfur gases are then analyzed with a quadrupole mass spectrometer operating in a single ion mode. An isotopically labeled variant of DMS is constantly added (near the sample inlet) to the incoming atmospheric sample. Since the mass spectrometer can separately and simultaneously monitor the labeled (standard) and unlabeled (DMS sample) species, a standard addition calibration is included with each measurement. Thus, sample losses that may occur in the inlet of the instrument are accounted for, as is any variation in the sensitivity of the mass spectrometer.

A pretrap containing pellets of solid NaOH is used to remove ozone and other oxidants for the DMS measurement. Typically, about 3 to 4 min (start of trap heating to completion of analyses) are required for each sulfur gas measurement. Since the same instrument was used to monitor several sulfur gases, the data rate for DMS measurements during CITE 3 was about one sample every 10 to 12 min. The precision of the measurement for CITE 3 was 20%, 5%, 3%, and 1% for DMS mixing ratios of 20, 50, 100, and 500 pptv, respectively. Accuracy (primary standard) is of the order of 20%. The reader is referred to *Thornton et al.* [1990] for further details.

Gas chromatograph/fluorination-electron capture. Sulfur compounds in the incoming air sample are separated using gas chromatography and then are fluorinated with F₂ (200 ppmv) using a heated Ag catalyst. The fluorination product, presumably SF₆, is then measured using an electron capture detector. The F₂ stream is generated using a permeation source, and excess F₂ is removed by conversion to HF by reaction with H₂ on a heated Pd catalyst. The Pd catalyst

also destroys any response from halocarbons, making the system sulfur specific. Cryogenic preconcentration is required (typically 1 min during CITE 3) followed by a 4-min period for separation and analysis. DMS analysis requires an oxidant scrubber (glass fiber filter impregnated with NaOH). During CITE 3, the system was configured to measure COS and CS₂ as well as DMS. Since the oxidant scrubber (for DMS) interferes with the other sulfur gas measurements, separate samples were collected for the DMS measurement. Typically, the sample sequence was a DMS analysis followed by an COS/CS₂ analysis. As a result, separate DMS measurements occurred about every 10 min. Precision of the DMS measurement was estimated to be about 8% for mixing ratios in the range of 20 to 500 pptv. Accuracy (primary standard) was estimated to be 11%. In-flight calibrations (gas cylinder dynamically diluted) were performed at frequent intervals (e.g., one to two per hour). Additional discussion of the instrument is given by *Johnson and Lovelock* [1988] and *Johnson and Bates* [this issue].

Gas chromatograph-flame photometric. Samples are preconcentrated on a thermoelectrically cooled polymer (Tenax) and thermally desorbed to a packed column (Chromosil 330) with detection using a flame photometric detector. The sample is preconcentrated for a period of 10 min followed by desorption and analyses. The system is automated with two sample channels to provide contiguous 10-min measurements by alternating the sample collection and analysis procedures between the two channels. Oxidants are removed by passing the sample stream through a cooled aqueous KI solution (neutral) prior to preconcentration. Residual water is removed by trapping at -20°C. Precision of the measurements is estimated at 10 and 5% for mixing ratios in the range of 20 to 100 pptv and 100 to 500 pptv, respectively. Accuracy (primary standard) is of the order of 5%. In-flight calibrations (liquid standards) were performed

DMS Instrumentation

Accuracy, ‡ %	Precision, § %	Detection Limit ‡	Terminology	Symbol
20	5	1	Mass spectrometer	MS
11	8	5	Fluorination	FLUOR
5	10	1	Gas chromatograph	GC
20	10	1.5	Gold wool/NA ₂ CO ₃	GW-Na
20	10	1.5	Gold wool/cotton	GW-COT
20	8	1	Gold wool/KOH	GW-KOH

at the beginning and end of each mission. Instrument details are available from *Cooper and Saltzman* [this issue].

Gold wool absorption-flame photometric. The three gold wool absorption techniques used differed mainly in the oxidant scrubbers and minor procedural details employed by the two investigators. DMS is collected (preconcentrated) from ambient air by passing the sample stream through packed gold wool (wire) housed in a quartz tube. Upstream of the gold wool preconcentrator, ozone and other oxidants are removed by an appropriate scrubber. The oxidant scrubbers employed included (1) Anakrom impregnated with Na_2CO_3 (GW-Na), (2) Teflon housing packed with cotton (GW-COT), and (3) glass filter impregnated with KOH (GW-KOH). After preconcentration (typically 5 to 20 min) the gold wool tube is removed, capped, and stored for postflight analysis. Generally, DMS samples were analyzed within 24 hours of collection. Analyses consisted of thermal desorption of the sulfur from the gold wool and analyses by gas chromatography using a flame photometric detector. Sample collection times for CITE 3 were typically 5 to 10 min for boundary layer samples and 10 to 20 min for samples taken above the boundary layer. Replacement of gold wool tubes in the sample line requires only a few seconds; thus, for most CITE 3 flights, near-contiguous samples were taken for the duration of a scheduled "official" intercomparison period. (As discussed below, time periods of 30- to 60-min duration were scheduled during the flights to obtain the intercomparison data.) Precision estimates for the gold wool method are 10% for mixing ratios in the range of 20 to 500 pptv. Accuracy (primary standard) is about 20%. Inflight calibrations were not performed for the gold wool absorption measurements. The reader is referred to the references for detailed discussion of the techniques and minor differences in the procedures employed by the two investigators [*Andreae et al.*, 1992; *Andreae et al.*, this issue; *Ferek and Hegg*, this issue].

Data Protocol

The DMS intercomparisons included gas-standard tests (ground) and inflight intercomparisons. DMS gas standards were prepared (on site at Wallops Island, Virginia) and supplied (scheduled test) to each investigator team by personnel from the National Institute of Standards and Technology (NIST). The DMS data protocol for the intercomparison of the standards and flight data was similar to that used for the other CITE 3 intercomparison species. Measurements were conducted blind with no exchange of information between the investigator teams prior to submittal of their results. Final results (from the investigators and NIST) of the standards tests were submitted to the GTE project office during the field operations, typically within 48 hours after each test. Preliminary results from the airborne measurements were also submitted to the project office during the field operations. The results from the standards and flight measurements were analyzed by project personnel to monitor progress of the tests and to provide input into subsequent tests. After submittal of all DMS standards data, the final results from the standards tests were discussed with the DMS investigators during the field activities. Only a qualitative assessment of the progress of the flight intercomparison tests was provided to the investigators while in the field. Final flight data were submitted to the project office 3 months after completion of the field missions. These data were not adjusted (i.e., normalized to NIST) based on the results from the standards test.

As part of the data protocol for the ground standards test, the investigator or NIST had the option to declare a test invalid (when submitting the data) and request a retest. For the flight intercomparisons, data protocol required all measurements to be reported. Along with the submitted data, the investigator provided a comment code as to the quality of the data.

Detailed results of the flight intercomparisons (first release of results to the DMS investigators) were discussed during a data workshop convened approximately 6 months after the field mission. After the workshop, only minor changes to the DMS data base were made by the investigators. None of the changes were significant in affecting the intercomparison results. Data changes made after the workshop are given below.

Permission estimates of lower detection limits of many of the instruments were based upon laboratory results; accordingly, all investigators were given an opportunity to reevaluate (based on workshop discussions) the stated lower detection limits for their techniques. Most investigators revised (lowered slightly) the detection limits for their techniques. The data of Table 1 reflect the revised values.

After the workshop, the Max Planck investigator (GW-Na and GW-COT techniques) requested that all data from flight 6 be "commented" as questionable. During this flight the oxidant scrubbers were exposed beyond the rated capacity. In preworkshop submittal of the data from flight 6, some data had already been "commented" as such. These flight 6 data are not included in the analyses. Intercomparison analyses were performed including and excluding these data. While excluding the data does not improve the level of agreement among the techniques, exclusion does result in a slight improvement in the statistical quality of the results.

Standards Intercomparison

The standards intercomparison was performed by having each instrument sample from the output of a mobile DMS reference source provided by NIST. The values and uncertainties (about 10%) of the NIST gas mixtures were based on the values for the standard and subsequent dilution parameters. The output from the NIST system was sampled with the same sampling system (inlet, flow rates, etc.) used during the aircraft flights. Standards tests were conducted while at Wallops from August 7 to 24, 1989. A single mixing ratio, different for each investigator and in the range of 100 to 200 pptv, was provided to each instrument as installed aboard the aircraft. Each investigator was required to provide at least three separate measurements of the NIST standard. The average of the three values is compared to the NIST value to arrive at a level of agreement between NIST and the instrument, and the standard deviation on the average provides an estimate of precision. For the standards tests, no distinction was made between the Na_2CO_3 and cotton scrubber data reported by Max Planck. The gas standards test was repeated for the Max Planck investigator. Max Planck's permeation tubes were damaged during shipment to Wallops, and the investigator noted concern as to the condition of his primary calibration devices (DMS and H_2S). Results from the first test showed that agreement (35% difference) between the Max Planck measurement and NIST was not typical in comparison to the other investigators' results. Thus, the project requested a retest to verify the initial results. Prior to the retest, the investigator resubmitted (not knowing the magnitude or direction of the discrepancy with NIST) his earlier

data. Conclusions from the standards tests are discussed below.

Aircraft Flights

Twenty-one flights were conducted as part of the CITE 3 program. The first three were test flights based at the Wallops Flight Center (WFC), Virginia. DMS data obtained during these flights were designated "a priori" by the project as test data and not intercomparison data. Due to a security threat associated with worldwide NASA aircraft operations, the last two flights (ferry from Brazil to Wallops Island) were also designated as nonintercomparison flights. The remaining 16 flights including the ferry flights between WFC and Natal, were intercomparison data flights. DMS measurements were made by all techniques on each of the 16 flights with the exception of the gas chromatograph/fluorination-electron capture technique (flights 9 and 10).

Flights were predominantly over water off the coast of either the eastern United States or Natal. Flights from WFC sampled the marine mixed layer and free troposphere at various distances from the continent (marine and continental flow). Natal flights were generally northeast from Natal over the tropical Atlantic Ocean. Three night flights were flown from Natal. Flight altitudes ranged from 150 to 5000 m above sea level. Table 2 summarizes the 16 intercomparison flights. Details of the flights, type of air masses, and meteorological scenarios are discussed by *Shipham et al.* [this issue].

DESCRIPTION OF ANALYSES APPROACH: FLIGHT DATA

Intercomparison Data

As noted in Table 1, the DMS instrument sampling times and data reporting schedules are quite varied. As a result of this and the fact that each investigator routinely includes calibration/maintenance periods in the sampling procedures, the CITE 3 intercomparisons were performed using structured sampling periods. A priori official intercomparison (IC) periods were designated for each flight in order to improve the temporal overlap of the various measurements. (IC periods were not used for the ferry flights 11 and 12.) IC periods were designed considering the sampling schedules of all the sulfur instrumentation. Because of the interrelationship of measurements for some of the sulfur gases, a separate IC period for each sulfur gas was not practical. Each IC period corresponded to a region of constant-altitude flight and was 30 to 60 min in duration. The 30- to 60-min duration requirement was not dictated by the DMS techniques. Thus, within a single IC period, multiple periods of overlapping data (referred to in the text as overlap periods) generally occurred among the DMS measurements. During the IC periods, each instrument followed a prescribed sampling schedule. Candidate sampling schedules were established several months prior to the field mission (modified as required by field experience) and were designed to maximize temporal overlap of the sulfur data and to meet the

TABLE 2. CITE 3 Flight Summary

Date	Flight Number	Type of Flight	Takeoff, UT	Landing, UT	Altitudes, km
Aug. 22	4	Maritime, 800 km SE of Norfolk, Va.	1500	2110	0.2, 1.5, 5.0
Aug. 23	5	Maritime, 500 km SE of Norfolk, Va.	1515	2050	0.2, 1.5, 1.8, 2.5
Aug. 25	6	Maritime, 500 km east of Wallops, Va.	1530	2000	0.2, 1.5, 2.5
Aug. 28	7	Coastal, NW of Wallops, Va.	1450	2050	0.2, 1.5
Aug. 30	8	Coastal, Carolinas	1515	2130	0.2, 1.5
Aug. 31	9	Maritime, 500 km east of Wallops, Va.	1530	2130	0.2, 2.5, 3.5
Sept. 1	10	Coastal-shore, Virginia and New Jersey	1500	2015	0.2, 1.5
Sept. 9	11a	Ferry, Wallops to Puerto Rico	1240	1800	0.2, 3.0, 4.0, 5.0
	11b	Ferry, Puerto Rico to Barbados	1910	2130	0.2, 4.5
Sept. 10	12a	Ferry, Barbados to Cayenne, French Guyana	1200	1455	0.2, 4.0
	12b	Ferry, Cayenne to Natal, Brazil	1555	2115	4.0, 4.5
Sept. 12	13	Maritime, 400 km SE of Natal, Brazil	1155	1755	0.2, 2.0, 3.3, 5.0
Sept. 15	14	Maritime, 300 km NE of Natal, Brazil	1400	1935	0.2, 1.5, 3.5
Sept. 16	15	Maritime, night, same area as flight 14	0300	0900	0.2, 1.5, 3.5
Sept. 19	16	Maritime, 300 km east of Natal, Brazil	1400	1500	0.2, 1.5, 3.5
Sept. 20	17	Maritime, night, same area as flight 16	0300	0830	0.2, 1.5, 3.5
Sept. 22	18	Maritime, night, east of Natal, Brazil	0700	1230	0.2, 1.5, 3.0, 5.0
Sept. 22	19	Maritime, same area as flight 18	1630	2120	0.2, 0.5, 1.5, 3.0, 5.0

investigators' special needs in terms of instrument operations. Associated with each IC period was a preperiod or postperiod (5 to 15 min) designated as instrument calibration, maintenance, or free time.

The intercomparison data used in the analyses are the data measured during the IC periods and constructed by defining a "simultaneous" or "overlapped" measurement as one having some overlap between any portion of the sample period reported by the investigators. The instrument or measurement having the longest integration time set the overlap period, and as such, only a single measurement from that instrument is used for the overlap period. Where more than one value of DMS is reported by any one of the remaining instruments during the defined overlap period, the arithmetic average of those measurements is used as the intercomparison value. Using this procedure, several data bases were constructed by considering different combinations of measurement overlap (i.e., overlapping periods including data from all six techniques, combinations of five techniques, combinations of four). The term "data base" implies the ensemble of overlapped data periods constructed for a given combination of instruments and includes time periods from all 16 intercomparison flights. While numerous overlapping data bases have been constructed and analyzed, most of the results presented are from the prime data base (overlap periods involving data from all six techniques). Results from all of the data bases constructed were found to be similar.

While the structured IC period approach tended to maximize the temporal overlap among the various measurements, overlap among the measurements was by no means near 100%. For example, overlap between the gold wool techniques and the other techniques was only about 20 to 30%. By the nature of the sampling frequency of the various gold wool instruments, overlap among these measurements was higher and often approached 80%. Figure 1 is illustrative of the level of overlap typically planned during an overlap period which included measurements from all six techniques. The illustration shown is from a single IC period of 50 min duration and shows one of two overlapping DMS data periods that occurred during the 50-min IC period. The prime data base consisted of 53 overlapped data periods similar to

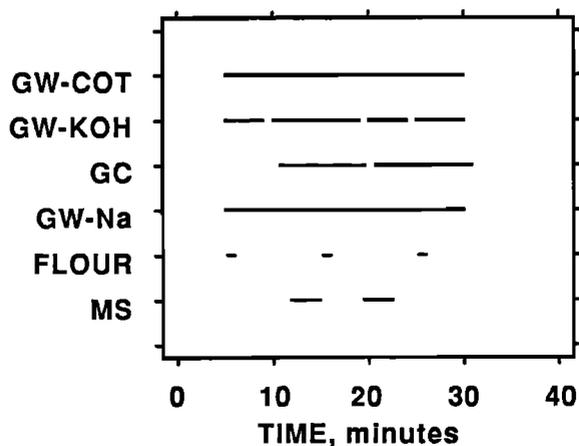


Fig. 1. Typical overlapping data period showing temporal overlap and sampling schedule of DMS measurements. DMS measurements during these periods were used in the intercomparison analyses.

that illustrated in Figure 1. Of these 53 periods, four are excluded from the analyses. Three are from flight 6 and include the data resubmitted by the Max Planck investigator and caveated as questionable. The fourth excluded overlap period is discussed in the next section. The remaining 49 overlap periods are the basis of the intercomparison analyses of the flight data presented in the paper.

Screening Analyses

The data base was examined to evaluate measurements that were not representative of the overall results, to identify data categories (i.e., subsets) under which intercomparison results should be stated independently, and to identify outlier events for which the DMS measurements should not be intercompared. In particular, the overlapped data base was evaluated to identify the influence of (1) the degree of temporal overlap (i.e., the ratio of common sample time of a measurement to the total duration of the overlap period), (2) data reported during periods in which significant ambient variations of DMS were occurring, (3) the altitude at which the measurements were made, (4) systematic day-by-day variability, (5) the nature and type of air mass (e.g., total sulfur, water vapor, or ozone content of the air), and (6) the distribution of DMS mixing ratios. In performing these analyses, numerous data correlations, regressions, confidence intervals, etc., were examined. Pertinent observations and conclusions from these analyses are given below.

Four of the overlap periods of the data base included some form of data reported by one or more of the techniques as below the detection limit of an instrument (1 to 5 pptv). Each of the periods were examined to check the consistency of all DMS data reported during these overlap periods. All data during these periods are consistent. In particular, all DMS concentrations reported during these time periods are only a few pptv. In order to include these data in the analyses, data reported as lower detection limit are assigned a value of the lower detection limit; i.e., data reported as below 2 pptv are assigned a value of 2 pptv.

The fourth overlap period (noted earlier) excluded from analysis was due to the gas chromatograph-mass spectrometer data (data point circled in Plate 2a). While there is no evidence to suggest that the measurement is in error, the levels of agreement between the gas chromatograph-mass spectrometer system and the other techniques are not typical of those observed during the other 49 overlapping data periods. Thus, for this reason alone, it has been excluded from the analyses as not representative. No other special cases, outliers, or abnormalities were identified in the prime data base.

DISCUSSION OF RESULTS

Standards Test Results

DMS standards intercomparisons showed that within the stated uncertainties (about 10% for NIST and 10 to 20% for each instrument), all the measurements agreed with the NIST standards. In the case of retest for the Max Planck investigator, both the retest data and resubmitted (prior to retest) data for the first test agreed with NIST values (+19% resubmitted, +6% retest). Agreement between the measurements from the various instruments and the NIST values ranges from about -3% to +19% with a tendency for most measurements to be high relative to NIST. At the 95% confidence level, no statistically significant biases exist between any investigator's measurement and NIST or between pairs of investigators' measurements.

If it is assumed that the NIST values are “correct” and with no error and that no biases exist among the techniques, then the standards test data may be used to estimate an ensemble level of uncertainty that might be expected for a single DMS measurement by any technique. The accuracy portion of the uncertainty is calculated from (1) as the average of the absolute bias. In this calculation, each investigator’s measurement (not the investigator’s average) of the NIST standard is treated as an equally valid and unbiased measurement of a known DMS concentration (NIST). This is equivalent to assuming that from the standards test there are 31 ($N = 31$) replicate measurements of an NIST standard.

$$\text{BIAS} = \left(\sum_{N=1}^1 \left| \frac{\text{NIST} - (\text{instrument value})}{\text{NIST}} \right| \right) / N \quad (1)$$

The precision part of the uncertainty may be estimated from the 1-sigma (1σ) value on the average bias of (1) and a 95% confidence level calculation as

$$\text{precision} = \frac{(t_{\alpha/2, N-1} \cdot 1\sigma)}{\sqrt{N}} \quad (2)$$

where i is the student’s t-statistic for $\alpha = 0.05$ and $N - 1$ degrees of freedom. The accuracy portion from (1) is 9.9% (31 samples) with a 1σ of 6.6%. The precision portion calculated from (2) is 2%. Thus the expected ensemble uncertainty for a DMS measurement (based solely on the standards test results) is of the order of about 12%.

Typical Flight Data

Plates 1 and 2 illustrate DMS data from two of the intercomparison flights. Plate 1 is for the flight of August 4 from Wallops Island, Virginia. Plate 2 is for flight 13 from Natal, Brazil. Both flights were over the ocean during daylight hours. Plates 2a and 3a show the DMS time series from the various instruments, and Plates 2b and 3b are the time series of flight altitude, ozone, and dew point temperature. The horizontal bars on the DMS data symbols indicate the sampling periods for each measurement. In many cases these bars are smaller than the plot symbol. The circled data point of Plate 2a is the previously noted and excluded data point of the gas chromatograph-mass spectrometer instrument. The results from the two figures indicate that qualitatively, all instruments tracked ambient variations in DMS associated with altitude changes and, in general, the magnitude of the reported values are in agreement. The data also illustrate the observation of lower values of DMS over the ocean at Natal than observed during the Wallops flights. Plate 3 is a portion of the data of Plate 1 which has been plotted to an expanded time scale and illustrates that, in some cases, temporal overlap among the techniques was not always as great as suggested by Figure 1.

Flight Intercomparisons

Figures 2 and 3 illustrate the general characteristics of the prime data set of overlapping data periods which include data from all six techniques. Figure 2 is a histogram of the DMS mixing ratios for the 49-sample data base. The abscissa of the histogram is the average DMS mixing ratio (avg) for an overlap period calculated as the arithmetic

average of the six values reported by the techniques during each overlap period. As indicated, almost all of the overlaps occurred at avg < 50 pptv, with approximately 60% occurring at avg < 25 pptv. Thus the intercomparison results are particularly meaningful for evaluating the validity for DMS measurements in the low pptv concentration range. Figure 3 shows the distribution of the time duration of the overlap periods. The abscissa is the total elapsed time of an overlap period. Overlap periods <20 min are generally from data taken in the mixed layer over the ocean, and overlaps of >20 min duration are the higher altitude, free tropospheric data. Overlap periods >40 min are associated with the ferry flights between Virginia and Brazil.

Figure 4 shows scatter plots of the DMS data where the abscissa is the average DMS (avg) as defined above for Figure 2. Figures 4a through 4f give results for the various instruments. The horizontal bars shown with the data represent the 1σ value of avg (six samples). The vertical bars represent 1σ associated with each measurement plotted as the larger of (1) the largest sigma reported for any single DMS value measured by the instrument during the overlap period, or (2) the sigma on the calculated average DMS for the instrument during the overlap period. Correlation and factor analyses suggest that avg is not significantly biased by data from any one technique and thus can be used as a “reference” for intercomparison purposes. (Correlation analyses of the data resulted in correlation coefficients of 0.93 to 0.98 for the individual measurements as compared to avg.) Linear regression results for the respective data are shown on each panel of Figure 4 and include the slope $+1\sigma$, intercept $+1\sigma$, and correlation coefficient r . These results are calculated using a linear model in which X is the independent variable and Y is the dependent variable. As such, it assumes that any uncertainty in X (DMS average calculated from six values) is small compared to the uncertainty in Y . The regressions were repeated where both X and Y were treated as dependent variables (i.e., equally likely to be in error), and results were not significantly different than those given in Figure 4. Table 3 summarizes the regression results.

Results from Figure 4 and Table 3 suggest good agreement between measurements from the individual techniques and the average reported DMS as well as among the techniques themselves. Regression coefficients are all above 0.9, and slope and intercept biases are within about 6% (one exception) and a few pptv, respectively. Considering the estimated accuracy and precision of the techniques (Table 1), one concludes that each instrument is measuring DMS to within their stated uncertainties.

While one concludes that each technique is measuring to within their stated uncertainties, the data base of Figure 4 can be examined for statistically significant biases. Results (F-statistic) from analysis of variance tests (ANOVA, techniques as labs and overlap periods as samples) and overlap periods (as samples) are positive; thus, at a 95% confidence level the data base can be used to test for biases. T-tests were performed to test the hypothesis as to whether any of the slope and intercept biases of Table 3 are equal to a slope of 1 and an intercept of zero. At a 95% confidence level, only one hypothesis was rejected. The slope bias between the gas chromatograph-fluorination technique and avg (Figure 4b) is statistically significant at a 95% level. The 95% confidence interval on the slope is 1.04 to 1.28, suggesting that the bias may only be a few percent.

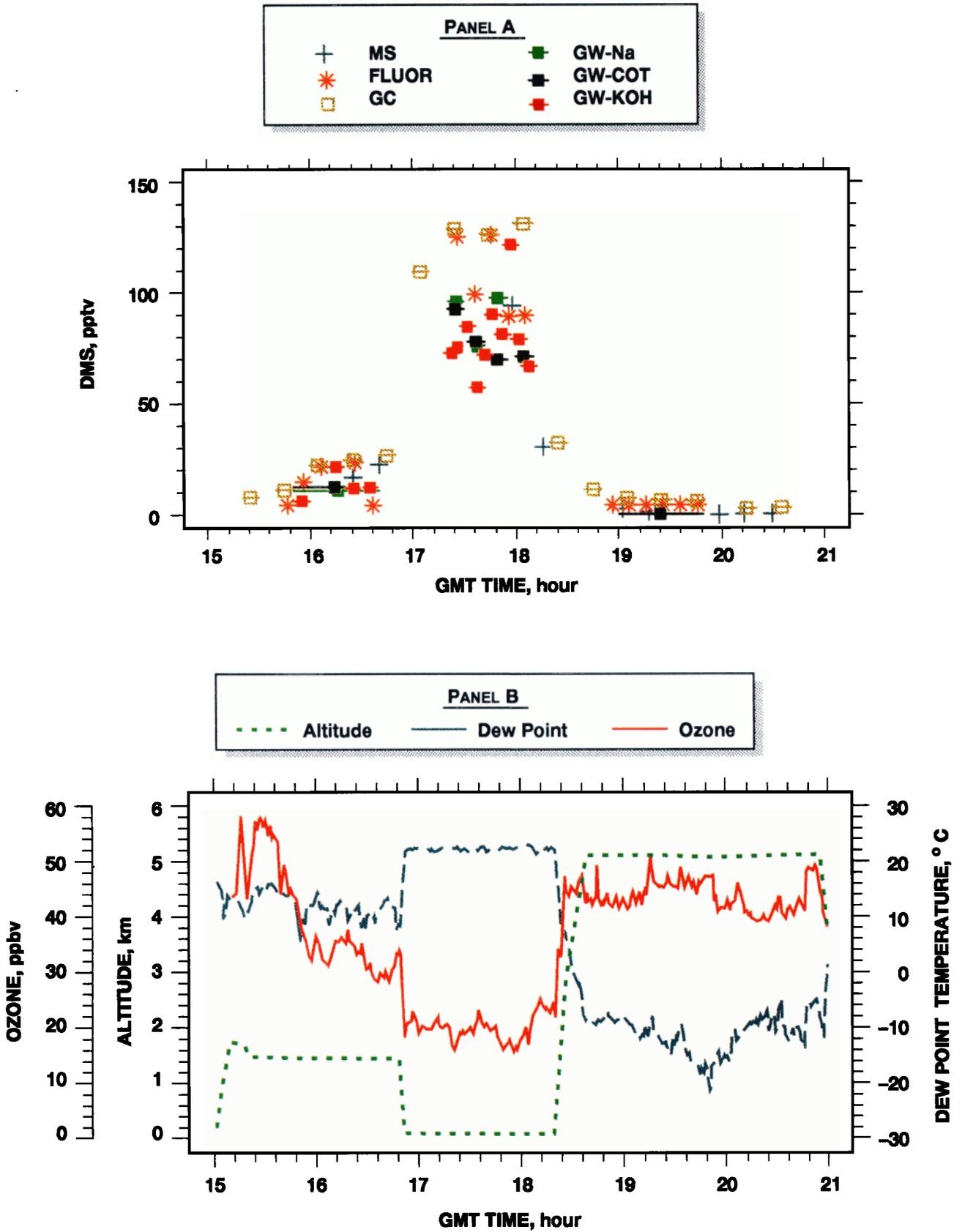


Plate 1. Time series of data for flight 4 of August 22, 1989. Data are over the ocean east of Virginia and illustrate typical ambient variations. (a) DMS data from six instruments. (b) Altitude, dew point temperature, and ozone data.

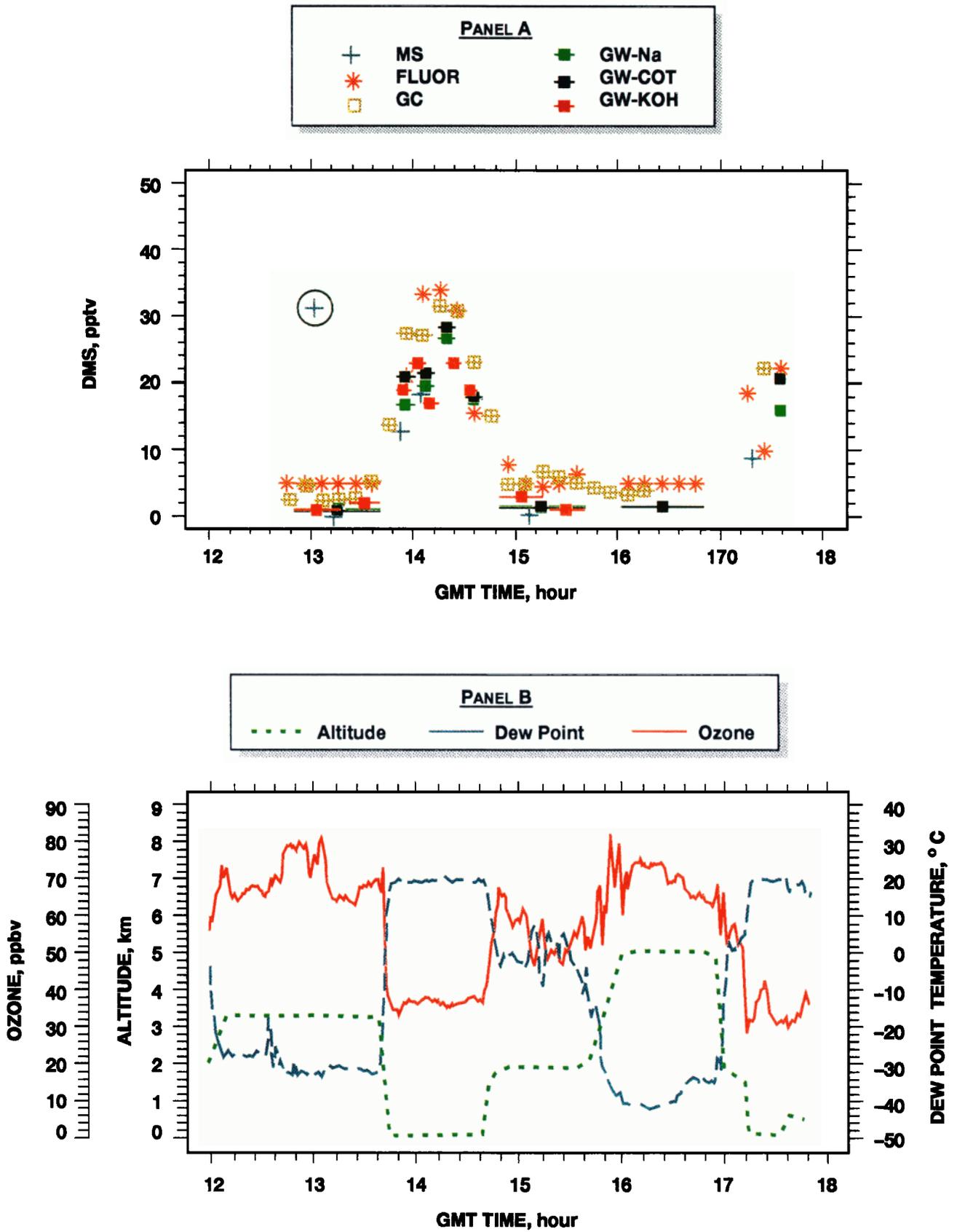


Plate 2. Time series of data for flight 13 of September 12, 1989. Data are over the ocean east of Natal, Brazil, and illustrate typical ambient variations. (a) DMS data from six instruments. (b) Altitude, dew point temperature, and ozone data.

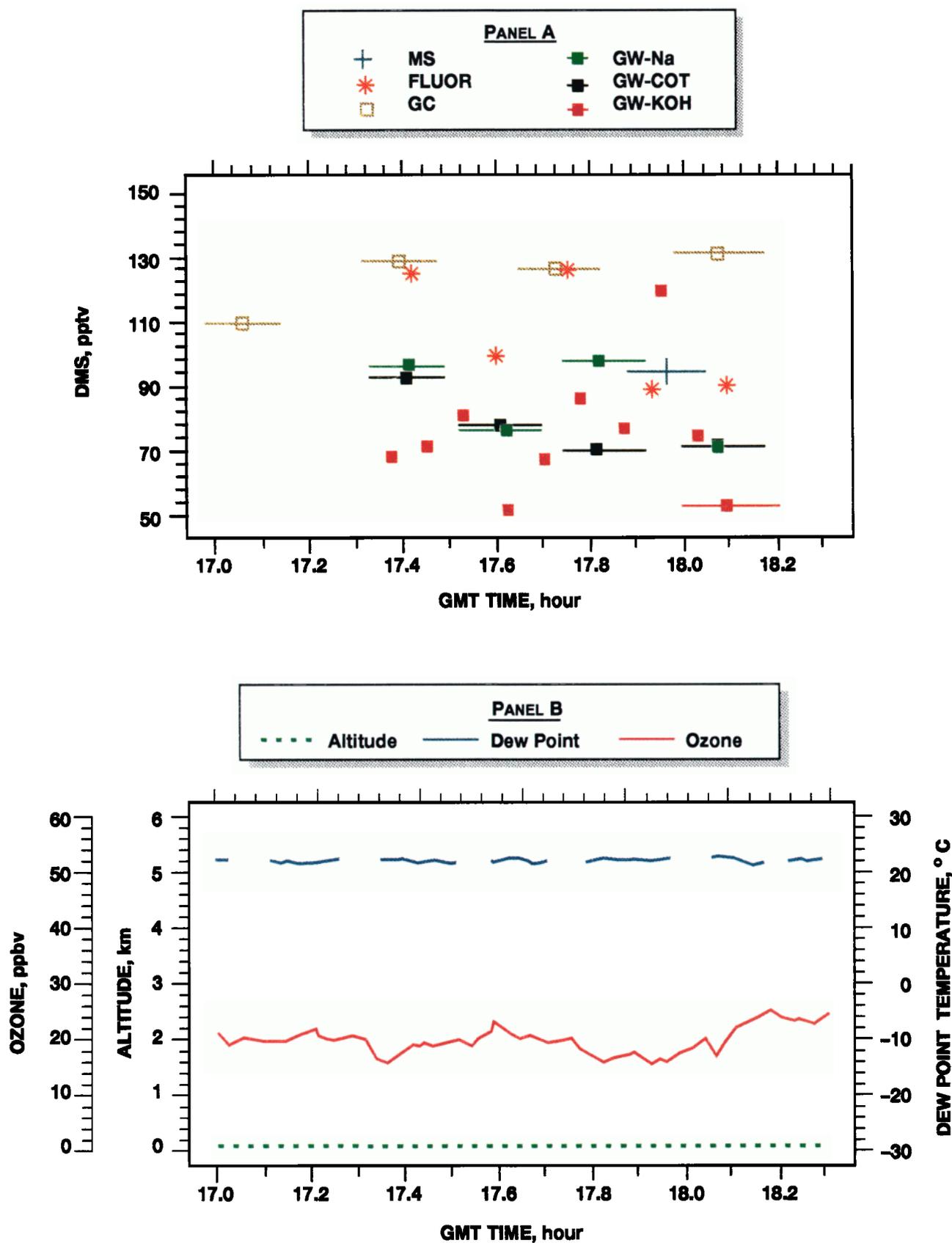


Plate 3. Expanded time series of a portion of the data of Plate 1. (a) DMS data from six instruments. (b) Altitude, dew point temperature, and ozone data.

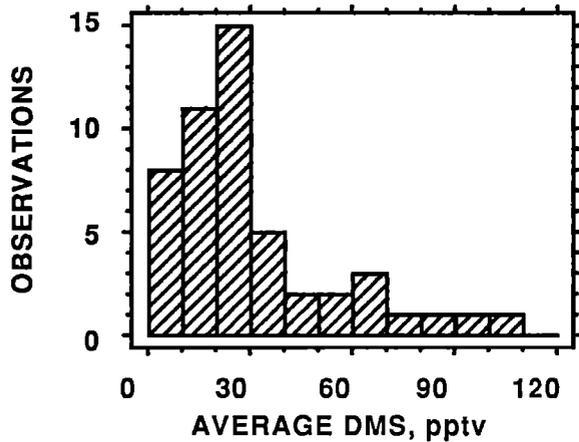


Fig 2. Histogram of average DMS concentration for overlap periods constructed by considering sampling overlap among all six techniques.

The tendency of the gas chromatograph-fluorination (FLUOR) to report slightly higher values of DMS was observed in all data bases. For example, the data of Figure 5 are from the data base constructed by considering time periods in which only overlapping data between the FLUOR and gas chromatograph-mass spectrometer techniques are considered. The average duration of these overlap periods is about 3 min, and each overlap includes a single sample from each technique. Common sample time between the two techniques during the overlap periods is generally 25 to 30% (one of the more highly temporal overlapped data bases that could be constructed which included data from the FLUOR technique). The regression parameters (both X and Y treated as dependent variables) are given in the figure. The indicated slope bias is the largest of any observed between the FLUOR technique and the other instruments (in fact, the largest for any pair of techniques). However, statistically the actual bias may only be a few percent, as the 95% confidence interval on the slope bias is 1.02 to 1.62. Additional analyses (other data bases, etc.) provide some evidence that the bias is probably only a few percent. For example, repeating the analyses of Figure 4 and excluding

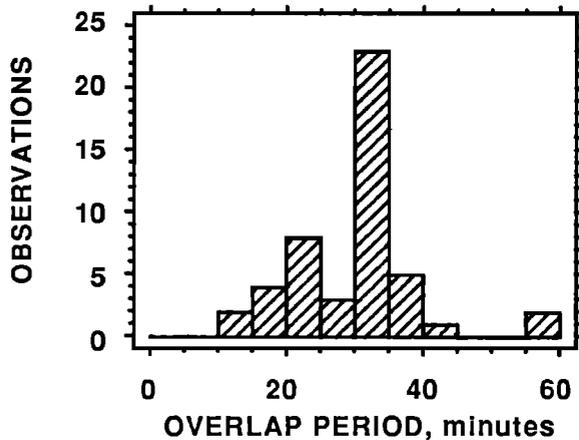


Fig. 3. - Histogram of the time duration of an overlap period for the data base constructed by considering sampling overlap among all six techniques.

the FLUOR data does not significantly change the level of instrument agreement observed among the other techniques.

Figure 6 plots the data of Figure 4 in a different format. The Y axis is now the delta difference between the instrument measurement and avg (i.e., instrument value minus avg) during an overlap period. The broken lines on each

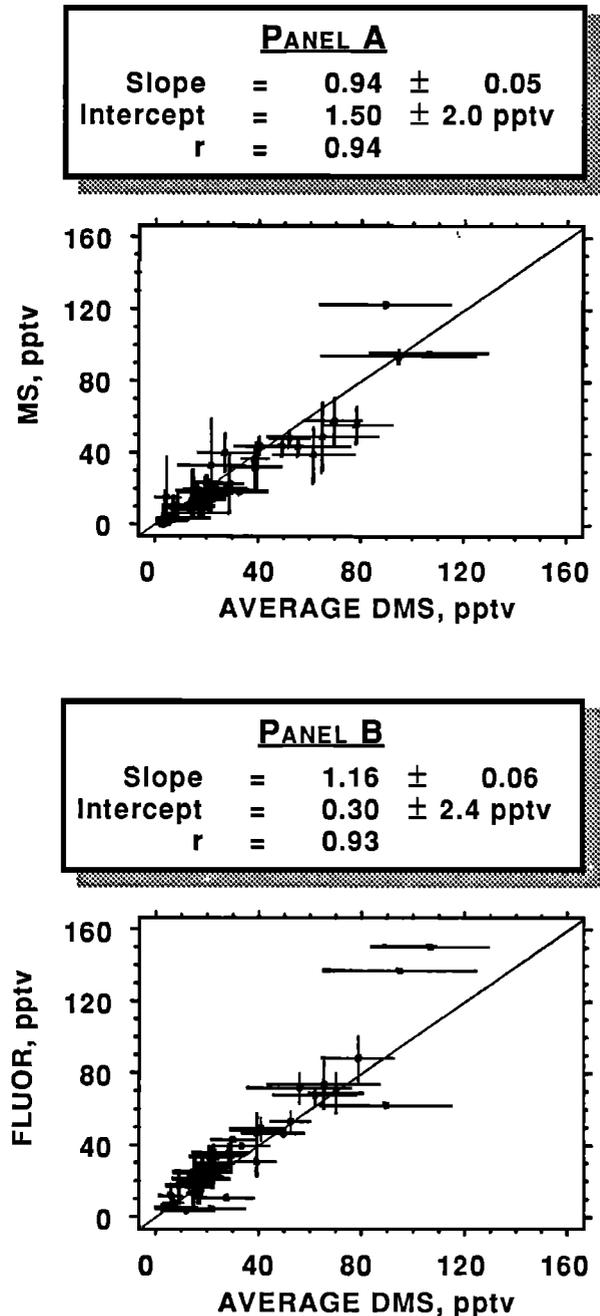


Fig. 4. - Scatter plots of DMS flight data: results from overlapping data (all six instruments) periods from the CITE 3 "official" intercomparison periods. Linear regression results of slope, intercept, $\pm 1\sigma$ values on the slope and intercept, and correlation coefficient are given in each panel. (a) Gas chromatograph-mass spectrometer instrument. (b) Gas chromatograph-fluorination instrument. (c) Gas chromatograph-flame photometric instrument. (d) Gold wool absorption collection with KOH oxidant scrubber instrument. (e) Gold wool absorption collection with Na_2CO_3 oxidant scrubber instrument. (f) Gold wool absorption collection with cotton oxidant scrubber instrument.

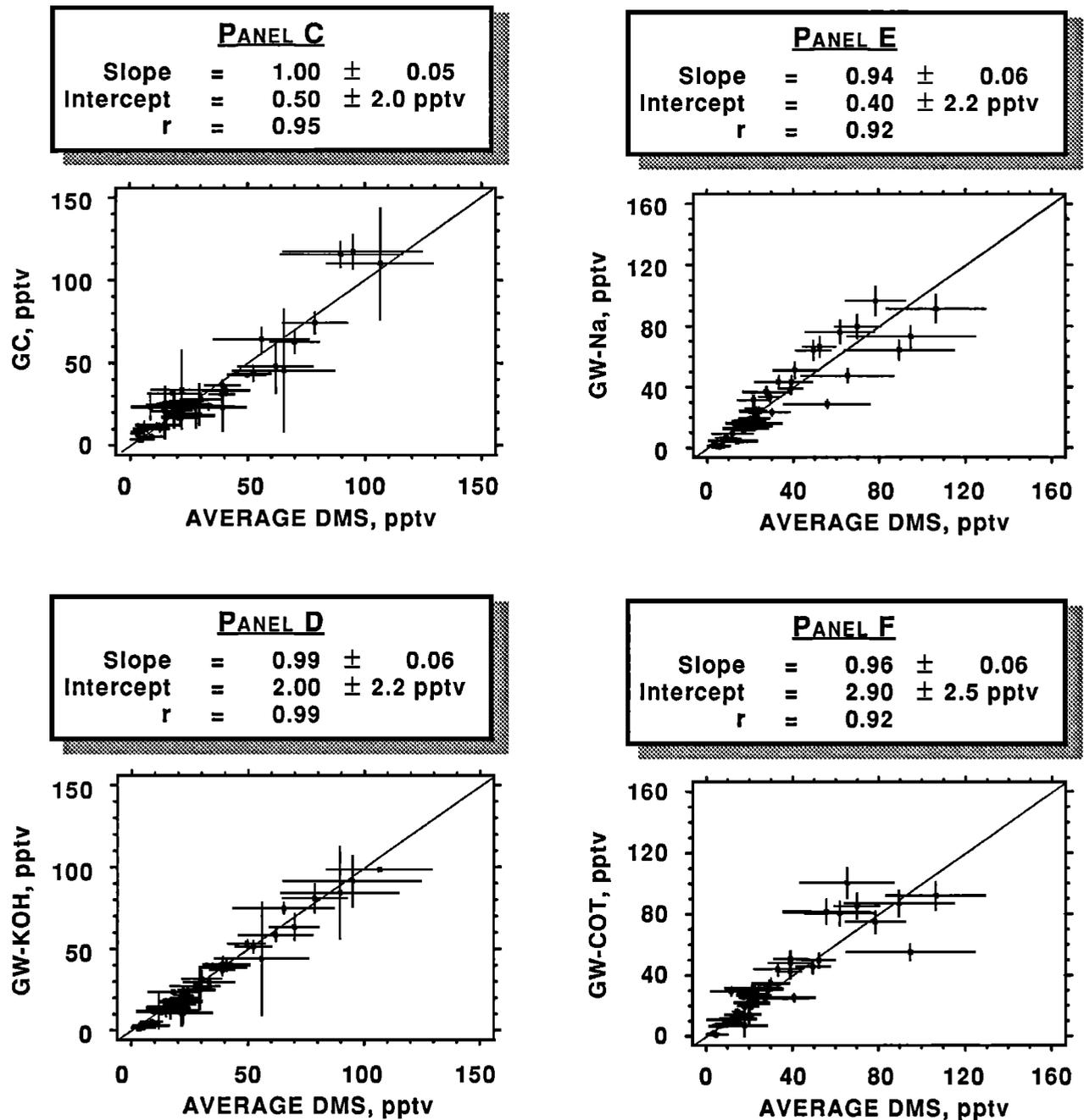


Fig. 4. - (continued)

panel represent the $\pm 10\%$ uncertainty region around the avg mixing ratio values. The data illustrate the tendency for the delta to increase, and perhaps be more variable, at the higher mixing ratios (e.g., above 50 pptv). What portion of this increase (and variation) is the result of ambient fluctuations (temporal variability) and the different sampling schedules of the instruments is not known. Table 4 summarizes the delta values of Figure 6, where the results are categorized into three mixing ratio ranges: avg <25 pptv, avg between 25 and 50 pptv, and avg >50 pptv. Each data entry is the average delta difference $+ 1\sigma$ calculated for the various mixing ratio categories. The number of samples (n) associated with each category is included in the column headers. The asterisks

indicate deltas which are statistically significant at 95% confidence (i.e., the 95% confidence interval on the average delta does not include zero). Table 5 highlights the results for avg <25 pptv and shows the average delta difference $\pm 1\sigma$ between pairs of techniques rather than between a technique and avg as shown in column 2 of Table 4. Again, the asterisked data indicate statistically significant deltas at the 95% confidence level. For each of the asterisked cases of Tables 4 and 5, the confidence interval range is only a few pptv from the zero delta value.

Equations (1) and (2) can also be used with the prime data base of 49 overlapping measurements to obtain an estimate of the "ensemble" uncertainty associated with an aircraft

TABLE 3. Summary of Linear Regression Results ($y = mX + b$)

Technique	Slope \pm Sigma	Intercept \pm Sigma	Correlation Coefficient
MS	0.94 ± 0.05	-1.5 ± 2.0	0.94
FLUOR	$-1.16 \pm 0.06^*$	-0.3 ± 2.4	0.93
GC	1.00 ± 0.05	0.5 ± 2.0	0.95
GW-Na	0.94 ± 0.06	0.4 ± 2.2	0.92
GW-COT	0.96 ± 0.06	2.9 ± 2.5	0.91
GW-KOH	0.99 ± 0.06	-2.0 ± 2.2	0.99

Technique symbols are defined in Table 1.

* The 95% confidence interval does not include the slope of 1.

measurement of DMS. Again, it is assumed that there are no biases among the techniques and that each instrument provides an equally valid measurement of DMS. This is equivalent to stating that there are six equally valid and independent DMS measurements during each of the 49 overlap periods, and that the avg for each overlap is the “true” ambient DMS concentration, i.e., 294 (6 times 49) independent measurements of a known (no error) DMS mixing ratio. In the case of the flight data, the results are calculated separately for those overlap periods in which $\text{avg} < 25$ pptv and $\text{avg} > 50$ pptv. The results are summarized below:

For $\text{avg} > 50$ pptv the accuracy portion of the uncertainty is 19.3% (1), and sigma from (1) is 13.8% for $n = 54$ samples (six measurements during each of nine overlap periods). The precision calculation (2) gives 3.9%. Combining the accuracy and precision estimates gives an estimated uncertainty

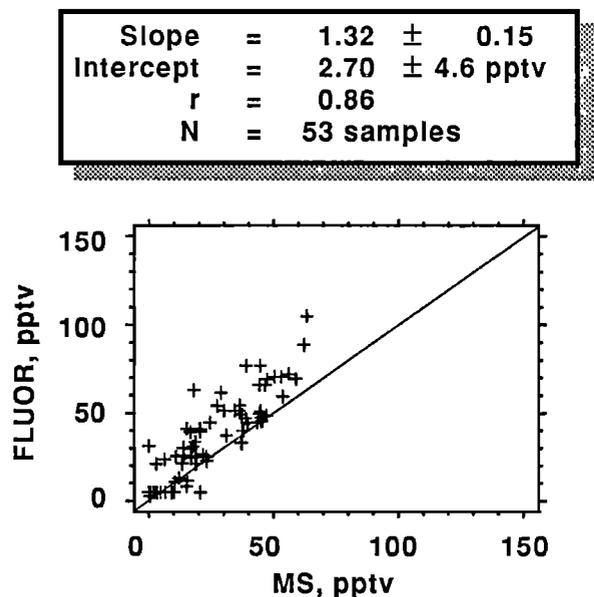


Fig. 5. - Scatter plot of DMS flight data: results from overlapping data periods from the CITE 3 “official” intercomparison periods. Data based constructed by considering only overlapping data between the gas chromatograph-mass spectrometer and gas chromatograph-fluorination techniques. Linear regression results of slope, intercept, $\pm 1\sigma$ values on the slope and intercept, and correlation coefficient are also shown.

of a DMS measurement from the aircraft of 23.2%. Similar calculations for $\text{avg} < 25$ pptv (180 samples or six measurements during each of 30 overlap periods) gives an uncertainty of 4.7 pptv (4.2 accuracy + 0.5 precision). The calculations were repeated excluding the FLUOR measurements during each of the 49 overlap periods. Results were almost identical, i.e., 23.0% ($\text{avg} > 50$ pptv) and 4.5 pptv ($\text{avg} < 25$ pptv).

The DMS data were also analyzed by averaging the instrument data over longer time periods. For these analyses, the earlier defined official intercomparison periods were designated as the overlap periods and the average DMS calculated for each instrument (arithmetic average of all data reported). Table 6, in the format of Table 4, summarizes the results for the three mixing ratio categories of interest. In some cases, data are not reported by all instruments for all the IC periods; thus the column headings show a range for the number of samples (n) in each category. Asterisked data indicate the statistically significant 95% confidence intervals. The results of Tables 4 and 6 are quite similar.

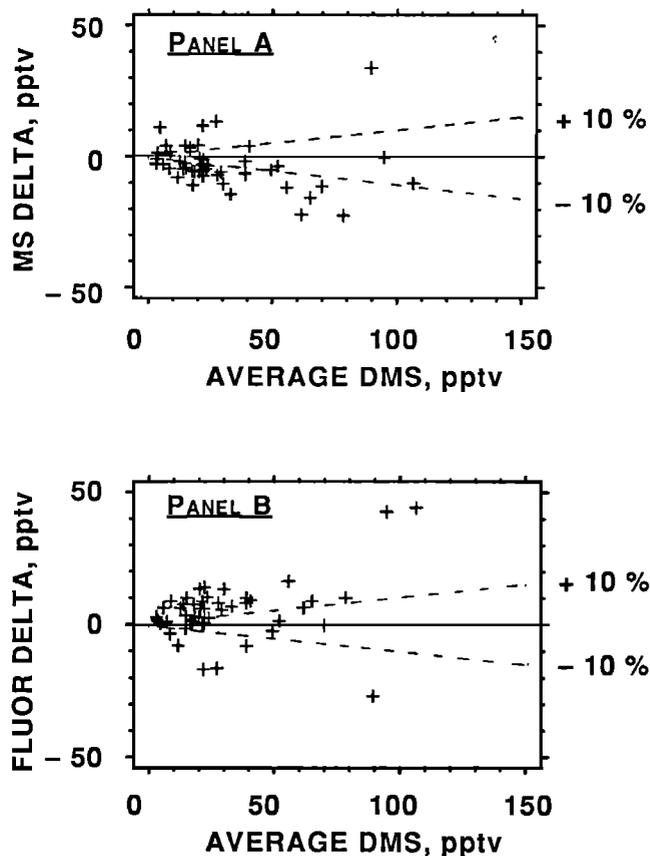


Fig. 6. - Delta difference plots of DMS flight data: results from overlapping data (all six instruments) periods from the CITE 3 “official” intercomparison periods. Broken lines represent a +10% uncertainty around avg. Data base is the same as that of Figure 3. (a) Gas chromatograph-mass spectrometer instrument. (b) Gas chromatograph-fluorination instrument. (c) Gas chromatograph-flame photometric instrument. (d) Gold wool absorption collection with KOH oxidant scrubber instrument. (e) Gold wool absorption collection with Na_2CO_3 oxidant scrubber instrument. (f) Gold wool absorption collection with cotton oxidant scrubber instrument

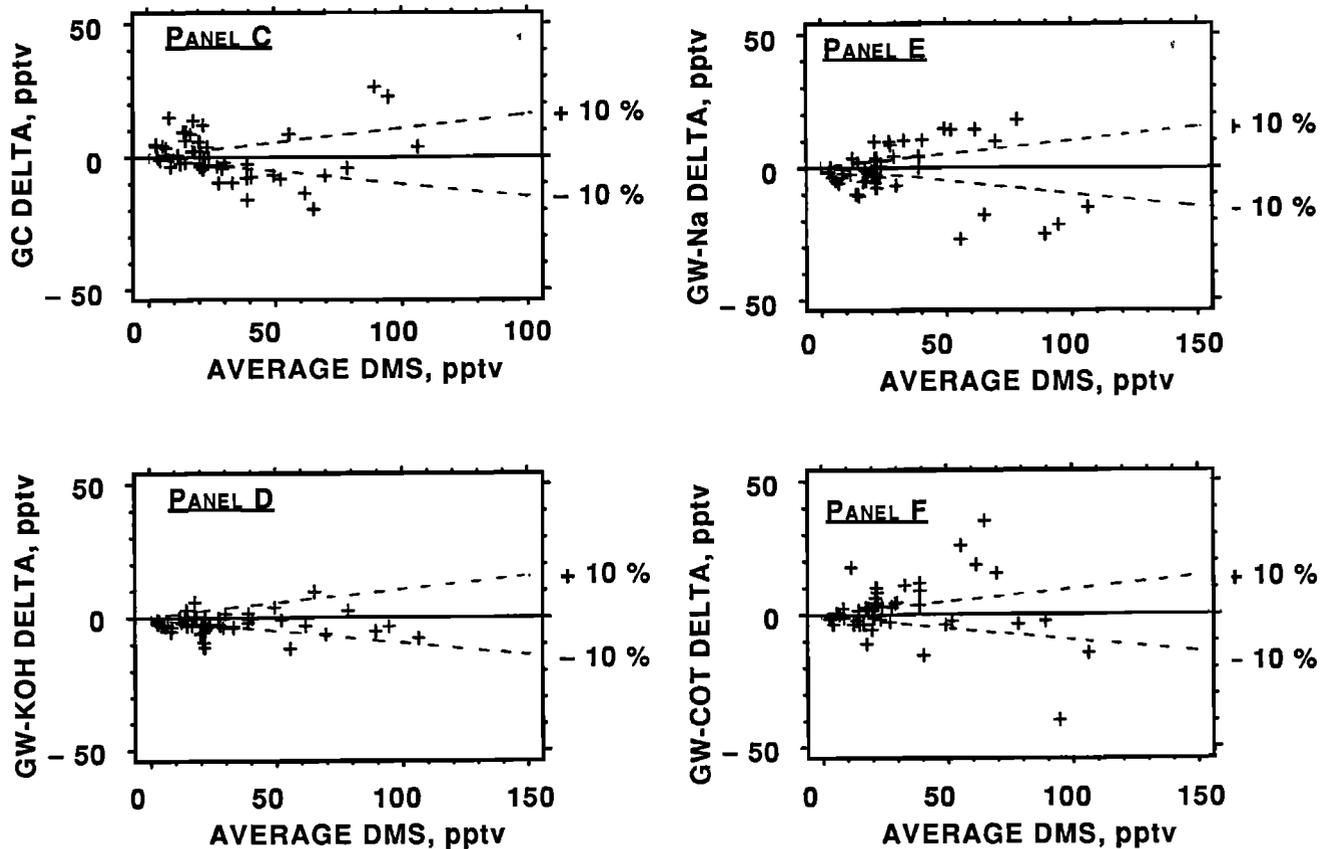


Fig. 6. (continued)

CONCLUSIONS

The CITE 3 intercomparisons provide a data base from which to evaluate DMS measurements from an aircraft platform. Data from six techniques representing three different detection principles as well as several collection/preconcentration and oxidant scrubbing methods are intercompared at various altitudes (0.15 to 5 km) predomi-

TABLE 4. Summary of Delta Analyses: Average DMS as Reference

Technique	Delta $\pm 1\sigma$, pptv		
	avg < 25 pptv ($n = 30$)	25 pptv < avg < 50 pptv ($n = 10$)	avg < 50 pptv ($n = 9$)
MS	1.8 ± 5.1	-4.1 ± 7.4	-7.1 ± 16.1
FLUOR	$3.2 \pm 6.1^*$	3.4 ± 8.9	11.4 ± 20.6
GC	$2.7 \pm 5.3^*$	$-7.0 \pm 4.0^*$	0.8 ± 14.9
GW-Na	$-2.4 \pm 4.3^*$	$6.0 \pm 5.8^*$	-5.7 ± 18.0
GW-COT	1.0 ± 5.3	2.5 ± 7.7	3.5 ± 21.7
GW-KOH	$-2.6 \pm 3.2^*$	-0.7 ± 2.3	-3.0 ± 5.9

Technique symbols are defined in Table 1. Delta = (Technique value - avg), pptv; n is number of samples.

* The 95% confidence interval on the average of Delta does not include zero.

nantly in a marine environment. Some results from Virginia-based flights were obtained in continental air. The majority of the intercomparisons are at DMS mixing ratios <50 pptv. To intercompare the measurements from the various techniques, numerous data bases were constructed from time periods of simultaneous (overlapping) measurements among the techniques. Results from the data bases are consistent and show that all the DMS techniques agree to within expected uncertainties, considering the 10 to 20% accuracy of the various measurements and calibration standards. While statistically (based on 95% confidence levels) significant differences (biases) exist among some of the techniques, they are small in magnitude and do not suggest that DMS measurements from any one technique are in error. When considering the average value for DMS (calculated from data supplied by all six techniques), any noted statistical significant bias is of the order of a few pptv for mixing ratios <50 pptv and within about 15% (most within 6%) for mixing ratios >50 pptv. One technique, gas chromatograph/fluorination-electron capture, consistently reported higher values of DMS than the other techniques.

In summary, one concludes that the DMS measurement techniques and associated collection/preconcentration methods and oxidant scrubbers intercompared during the CITE 3 can be relied upon to provide equally valid measurements of DMS in the range of a few pptv to 100 pptv (upper range of the intercomparisons). Selection of a specific technique is thus more dependent on the advantages and/or disadvantages associated with the field operations of the various techniques (e.g., desired sampling rate and

TABLE 5. Summary of Delta Analyses for Mixing Ratios < 25 pptv.

Technique X	Technique Y				
	FLUOR	GC	GW-Na	GW-COT	GW-KOH
MS	-4.9 ± 9.4*	-4.4 ± 7.1*	0.7 ± 7.2	-2.7 ± 7.7	0.8 ± 7.3
FLUOR		0.5 ± 9.2	5.6 ± 8.1*	2.2 ± 9.7	5.7 ± 6.0*
GC			5.1 ± 8.6*	1.7 ± 8.6	5.3 ± 6.0*
GW-Na				-3.4 ± 6.0*	0.1 ± 5.7
GW-COT					3.6 ± 7.1*

Delta values are obtained from technique X minus technique Y.

* The 95% Confidence interval on the average Delta does not include zero.

TABLE 6. Summary of Delta Analyses from IC Periods: Average DMS as Reference

Technique	Delta ± 1σ, pptv		
	avg	25 pptv < avg	avg
	< 25 pptv (n = 30)	< 50 pptv (n = 10)	< 50 pptv (n = 9)
MS	-0.2 ± 4.2	-2.7 ± 7.0	-10.7 ± 11.0
FLUOR	2.2 ± 4.6*	5.4 ± 6.8*	9.4 ± 7.4*
GC	2.3 ± 3.5*	-2.3 ± 11.2	1.0 ± 12.7
GW-Na	2.7 ± 3.9*	-2.5 ± 14.1	0.1 ± 14.8
GW-COT	-0.4 ± 3.9	2.2 ± 7.5	2.4 ± 15.3
GW-KOH	-2.4 ± 1.8	1.6 ± 5.2	-2.2 ± 1.4*

Technique symbols are defined in Table 1. Delta = (Technique value - avg), pptv; n is number of samples.

* The 95% confidence interval on the average of Delta does not include zero.

integration period; required support facilities of power, weight, space, personnel, etc.; and financial resources) than the uncertainty associated with the DMS measurement.

The CITE 3 data can also be used to provide a conservative estimate of the uncertainty associated with an airborne DMS measurement. Assuming that no bias exists among the six instruments, an ambient DMS measurement is estimated to be accurate to about 23% (mixing ratios >50 pptv) and 4 to 5 pptv (mixing ratios <25 pptv). A similar estimate using results from the ground-level standards tests of the instruments installed on the aircraft (more controlled sampling conditions) gave an uncertainty of the order of 12% for mixing ratios of 100 to 200 pptv.

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