JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 98, NO. D12, PAGES 23,291–23,304, DECEMBER 20, 1993

Operational Overview of the NASA GTE/CITE 3 Airborne Instrument Intercomparisons for Sulfur Dioxide, Hydrogen Sulfide, Carbonyl Sulfide, Dimethyl Sulfide, and Carbon Disulfide

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This paper reports the overall experimental design and gives a brief overview of results from the third airborne Chemical Instrumentation Test and Evaluation (CITE 3) mission conducted as part of the National Aeronautics and Space Administration's Global Tropospheric Experiment. The primary objective of CITE 3 was to evaluate the capability of instrumentation for airborne measurements of ambient concentrations of SO_2, H_2S, CS_2, dimethyl sulfide, and carbonyl sulfide. Ancillary measurements augmented the intercomparison data in order to address the secondary objective of CITE 3 which was to address specific issues related to the budget and photochemistry of tropospheric sulfur species. The CITE 3 mission was conducted on NASA's Wallops Flight Center Electra aircraft and included a ground-based intercomparison of sulfur standards and intercomparison/sulfur science flights conducted from the NASA Wallops Flight Facility, Wallops Island, Virginia, followed by flights from Natal, Brazil. Including the transit flights, CITE 3 included 16 flights encompassing approximately 96 flight hours.

INTRODUCTION

The goal of NASA's Tropospheric Chemistry Program is to develop an understanding of global tropospheric chemistry so that assessments can be made of the susceptibility of the atmosphere to long-term chemical changes. A major component of this program is the Global Tropospheric Experiment (GTE), which consists of a series of integrated field expeditions. Fundamental goals of the GTE are the development of advanced instrumentation to measure critical trace atmospheric gases; the application of these instruments to field measurements of trace gases in order to quantify their sources, sinks, and distributions; and the synthesis of new data sets to gain improved understanding of the fundamental chemical behavior of the atmosphere.

The field programs in the GTE have evolved into three major categories: (1) boundary layer studies, i.e., Atmospheric Boundary Layer Experiments (ABLE), (2) instrumentation evaluation missions, i.e., Chemical Instrumentation Test and Evaluation (CITE), and (3) exploratory/transport studies, i.e. Pacific Exploratory Measurements (PEM) and Transport and Atmospheric Chemistry Near the Equator (TRACE). The ABLE missions [*Ferek et al.*, 1986; *Talbot et al.*, 1986; *Gregory et al.*, 1986; *Harriss et al.*, 1988; *Harriss et al.*, 1992] are designed specifically to study the rate of exchange of material between the Earth's surface and its atmospheric boundary layer and the processes by which gases and aerosols are moved between the boundary layer and the free troposphere. These expeditions have been conducted in ecosystems of the world that are known to exert a major influence on global atmospheric chemistry and that, in some cases, are undergoing profound changes as a consequence of natural processes and/or human impact.

The exploratory/transport missions were initiated with the completion of the first major expedition, PEM-West A, in October, 1991. PEM-West A was conducted over the western Pacific Ocean with the overall objective of studying the long-range transport of primary and secondary ozone (O_3) precursors from the Asian continent. A second exploratory/transport mission, TRACE-A, took place in September 1992 with the objective of studying chemical and dynamical processes which contribute to the formation of the large-scale ozone maximum observed annually via satellite over the tropical south Atlantic Ocean. It is anticipated that additional PEM-West and TRACE missions will be conducted to study the seasonality of transport processes important to the Pacific and Atlantic regions.

GTE/CITE MISSION OBJECTIVES

The CITE missions have focused on the evaluation of the ability of airborne instrumentation to measure key tropospheric constituents. The CITE missions, in many instances, provide the instrumentation/techniques that are employed during the ABLE, PEM, and TRACE experiments. The first two CITE missions, CITE 1 and CITE 2, evaluated instruments for measurements of carbon monoxide (CO), nitric oxide (NO), the hydroxyl radical (OH), nitrogen dioxide (NO_2), nitric acid (HNO_3) and peroxyacetyl nitrate (PAN). The CITE 2 mission also included an emphasis on questions related to the abundance and partitioning among the major

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Paper number 93JD00453
0148-0227/93/93JD-00453$05.00

members of the odd nitrogen family. Results from CITE 1 and 2 can be found in the references cited by *Beck et al.* [1987] and *Hoell et al.* [1990].

The CITE 3 mission, described herein, is a continuation of the NASA intercomparisons with emphasis on the major sulfur species in the troposphere. In particular, the CITE 3 intercomparison focused on evaluation of instrumentation for airborne measurement of sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbon disulfide (CS_2), dimethyl sulfide (DMS), and carbonyl sulfide (COS). In addition to the instrument intercomparison objective, the CITE 3 mission incorporated an emphasis on questions related to the abundance and photochemistry of these sulfur species. This paper provides an operational overview of CITE 3 and a brief summary of the results. Companion papers in this issue provide the detailed description of the intercomparison tests and results, findings associated with the sulfur abundance/photochemistry issue, and a description of the meteorological scene for each flight.

CITE 3 Objectives

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; *Toon et al.*, 1987; *Bates et al.*, 1990; *Andreae and Jaeschke*, 1992]. Major sulfur gases include SO_2, DMS, H_2S, CS_2, and COS. Atmospheric photochemistry results in the oxidation of the reduced sulfur gases (DMS, H_2S, CS_2, and COS) to SO_2, methanesulfonic acid (MSA), and sulfuric acid. MSA and sulfuric acid are incorporated into atmospheric aerosols and represent the dominant source of aerosol particles in the unpolluted marine atmosphere [*NASA*, 1984; *Andreae*, 1990].

The principal anthropogenic sulfur compound is SO_2, which is predominantly emitted during fossil fuel burning [*Cullis and Hirschler*, 1980]. Volcanoes are the major natural direct source of SO_2 [*Berresheim and Jaeschke*, 1983]. The largest natural sulfur source to the atmosphere is the emission of DMS from the oceans [*Bates et al.*, 1987; *Andreae*, 1990; *Erickson et al.*, 1990]. The oceans are also a source of COS, H_2S, and CS_2, but with emission rates at least a factor of 10 lower than observed for DMS [*Toon et al.*, 1987]. Terrestrial biogenic sulfur emissions are predominantly in the form of H_2S, and DMS. The natural flux of CS_2 into the atmosphere is relatively small, and anthropogenic sources dominate CS_2 production near industrial regions.

Carbonyl sulfide is the longest-lived (lifetime of several years) and, thus, the most abundant sulfur trace gas in the free troposphere (500 pptv compared to less than 100 pptv for SO_2 and less than 10 pptv for CS_2, H_2S, or DMS) [*Torres et al.*, 1980; *Carroll*, 1985; *Bingemer et al.*, 1990]. The oceans are thought to be the largest single source of COS [*Rasmussen et al.*, 1982; *Ferek and Andreae*, 1984; *Turner and Liss*, 1985; *Brasseur et al.*, 1990] accounting for about one-third of the total tropospheric COS [*Khalil and Rasmussen*, 1984]. Carbonyl sulfide is also an important secondary product of atmospheric CS_2 oxidation [*Kurylo*, 1978; *Sze and Ko*, 1979] as well as being emitted during biomass burning and fossil fuel combustion. As a result of the long lifetime of COS, it is important to lower stratospheric sulfate aerosol production via oxidation mechanisms [*Crutzen*, 1976; *Toon et al.*, 1979; *Turco et al.*, 1980].

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 SO_2 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].

A major uncertainty in sulfur budget studies has been the validity of the various sulfur gas measurements. Moreover, although "modest" global data bases exist for some sulfur species, for others no data exist or are limited to a few measurements at isolated geographical locations. The CITE 3 sulfur data base and the results from both the intercomparison studies and the photochemical and budget studies reported in this issue are anticipated to significantly enhance our ability to evaluate the confidence level that can be placed in the existing data bases and to further the use of newer detection methods in this and future scientific investigations. Moreover, the CITE 3 field measurements, in themselves, have added substantially to the existing global data base on the abundance and distribution of major sulfur species.

Approach

The CITE 3 was initiated with the primary objective to test and evaluate via airborne field intercomparisons the capacity to make reliable measurements of the concentrations of the sulfur species SO_2, DMS, COS, CS_2, and H_2S. The secondary objective of CITE 3 was to determine, in a predominantly marine environment, the abundance and distribution of major sulfur species over a wide range of atmospheric conditions, including altitude, solar flux levels, atmospheric mixing ratios, and surface source strengths of sulfur. To address these two objectives, CITE 3 was conducted aboard the NASA Electra research aircraft with a suite of instruments for sulfur and ancillary measurements. The methodology adopted for the CITE missions has been intercomparison of airborne measurements obtained for the same species by instruments utilizing fundamentally different detection principles; thus, multiple measurements of SO_2 (five techniques), DMS (six techniques), H_2S (three techniques), CS_2 (three techniques), and COS (three techniques) were made aboard the aircraft. In some cases, techniques use the same detection principle, differing only in the method of sample collection and/or analyses procedures. However, each sulfur gas was measured by at least two techniques which employed fundamentally different detection principles.

The field activities of CITE 3 were conducted in three phases: (1) intercomparison of sulfur calibration standards, (2) measurements in ambient air over the North Atlantic Ocean with the aircraft based at the NASA Wallops Flight Facility, and (3) measurements in ambient air over the tropical Atlantic Ocean with the aircraft based in Natal, Brazil. Figure 1 shows the operational areas along with the transit flight tracks to and from Brazil.

The intercomparison of standards was implemented with the limited goal of elucidating systematic biases that might exist between the respective calibration standards employed to calibrate the sulfur instrumentation. This portion of CITE 3 was implemented on the ground after each instrument was completely integrated aboard the aircraft and prior to de-

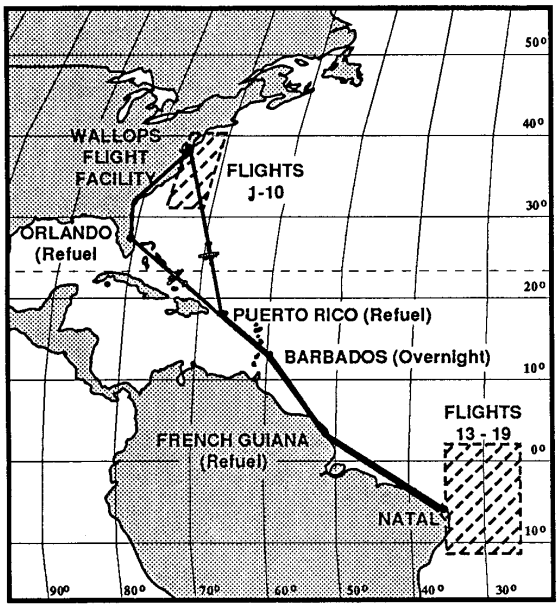

Fig. 1. CITE 3 test areas.

ploying to Natal, Brazil. A common calibration system, assembled, tested, and operated by the National Institute of Standards Technology (NIST), was used to provide to each instrument a "known" mixing ratio of the particular sulfur species in a dry nitrogen diluent. The intercomparison of standards was based upon comparison of known mixing ratio from the NIST calibration system with the measurements obtained by each instrument. A brief description of the NIST calibration system along with the results from each test is given by *Gregory et al.* [this issue (a),(b),(c)].

The two bases of operation for CITE 3 were selected to provide a wide range of ambient mixing ratios for the intercomparisons and to investigate sulfur chemistry (marine environment) in air masses of both natural and anthropogenic influence. The Wallops base provided ready access to relatively homogeneous air masses influenced by anthropogenic emissions from the east coast of the United States and exhibited sulfur mixing ratios ranging from the mid to upper high range of what could be anticipated in the global free troposphere. Further, Wallops provided a "logistically friendly" base of operations for the standards intercomparison and the initial phase of the ambient air intercomparisons. In contrast, the Natal phase of CITE 3 provided access to southern hemisphere marine boundary layer air with an extended oceanic fetch, and therefore with minimal impact from anthropogenic activities.

The CITE 3 intercomparison activities were guided by the protocol and experience gained during CITE 1 and CITE 2. The general protocol included (1) use of instruments utilizing different measurements concepts, (2) a focus on instruments with the potential for detection of tropospheric background concentrations of the respective sulfur species, (3) measurements from an aircraft platform, (4) ancillary measurements as required for evaluation of intercomparison results and for support of the sulfur chemistry science objectives, (5) blind tests for both the ambient air measurements and calibration standards, and (6) analysis and reporting of intercomparison results by an impartial third party (e.g., the GTE Project).

The data protocol adopted by the CITE 3 science team included (1) reporting of all data during test periods, (2) immediate notification of instrumentation problems and/or "suspect data," (3) no discussion of data during or after the test periods, (4) submittal of preliminary data to the GTE Project Office within 1-2 days after a flight or calibration standards ground test, and (5) submittal of final results within 60 days after completion of the CITE 3 flights. While all tests were conducted blind, the protocol adopted by the science team permitted disclosure of preliminary results reported in the field that indicated systematic or persistent discrepancies between instruments. All such disclosures were at the discretion of the project personnel and are reported in the respective intercomparison papers by *Gregory et al.* [this issue (a),(b),(c)].

As part of the protocol adopted by the science team, final results from the calibration standards tests were reported and discussed with members of the science team (including the sulfur investigators) during the field activities prior to departing to Natal, Brazil. As a result of data protocol, discussions of flight measurements and scientific findings (i.e., sulfur budget issues) while in the field were limited. Recognizing that such would be the case, the Mission Scientist was given the responsibility to interpret flight data and to provide direction as to scientific requirements in flight planning. The Instrument Scientist had similar responsibilities for the instrument intercomparisons. The Mission Scientist coordinated in-flight sampling and flight plan changes based upon flight data reported from the various sulfur and ancillary measurements. Data analyses and meteorological teams assisted the Mission and Instrument Scientists in the preparation and interpretation of data while in the field.

Preliminary results from some of the ancillary instruments (e.g., temperature, dew point, wind velocity, aircraft position, and O_3) were made available to each instrument team within 24 hours of completing each flight. The final results from all the ancillary measurements were made available to each team within 30 days of completing the CITE 3 flights. The final intercomparison data, reported to the GTE Project Office within 60 days of completing CITE 3 flight activities, were analyzed by GTE project personnel. Results of these analyses were presented to the CITE 3 science team during a data workshop convened 6 months after completion of the CITE 3 flight activities. At that workshop, all intercomparison data became available to each CITE 3 participant.

INSTRUMENTATION

Tables 1 and 2 list the intercomparison techniques and ancillary measurements, respectively, that were selected for CITE 3, and Table 3 defines the acronyms used in these tables. The layout of these instruments aboard the aircraft is shown in Figure 2. With the sulfur intercomparison instruments listed in Table 1, the CITE 3 payload had the potential of providing five measurements of SO_2, six of DMS, and three measurements each of H_2S, CS_2, and COS. However, because of operational problems or project/science team decisions to focus selected flights on particular sulfur species, the full potential of the sulfur measurements for a given specie were, at times, not utilized. Table 4 lists the sulfur intercomparison

TABLE 1. CITE 3 Sulfur Intercomparison Instruments

Species	Measurement Technique*		Principal Investigator and Affiliation
SO_2 H_2S, COS CS_2	CT/GC/FPD†	(Analysis 1) (Analysis 2) (Analysis 3)	D. C. Thorton, Drexel University
SO_2, DMS, CS_2 COS	CT/GC/MS/ILS†	(Analysis 1) (Analysis 2)	A. R. Bandy, Drexel University
DMS CS_2, COS	GC/IF/ECD (with scrubber) GC/IF/ECD (without scrubber)		J. E. Johnson, NOAA Pacific Marine Environmental Laboratory
DMS DMS H_2S	GWA/GC/FPD (Na_2CO_3)‡ GWA/GC/FPD (Cotton) NATUSCH		M. O. Andreae, Max-Planck-Institute for Chemistry
DMS H_2S	CT/GC/FPD NATUSCH		E. S. Saltzman, University of Miami
DMS SO_2	GWA/GC/FPD (KOH) FC/IC		R. J. Ferek, University of Washington
SO_2 SO_2	FC/CL CC/CL		H. -W. Georgii, Institut für Meteorologie und Geophysik

* See Table 3 for acronym definitions.
† Any two analyses can be performed for each sample.
‡ The type of scrubber used with the GWA techniques is noted

measurements on a flight-by-flight basis that were reported for each specie. Total sulfur (see ancillary measurements of Table 2) was measured (typically at 3-min resolution) on all flights except flight 5.

The five SO_2 instruments participating in the intercomparisons consisted of (1) flame photometric detection with cryogenic trapping and gas chromatography for speciation (CT/GC/FPD), (2) mass spectrometric detection with cryogenic trapping and gas chromatography for speciation (CT/GC/MS/ILS), (3) real-time chemiluminescent (RT/CL), (4) filter collection employing postflight chemiluminescent (FC/CL) analyses (same detection principle as technique 3 above), and (5) filter collection employing postflight ion chromatographic analyses (FC/CL). Three instrument techniques (e.g., CT/GC/FPD, CT/GC/MS/ILS, and CT/GC/IF/ECD) were configured to provide measurements of multiple species, although these measurements were typically not simultaneous, since different GC columns were typically required in order to optimize selectivity for a given set of sulfur species.

The six DMS measurements represented four basic measurement approaches: (1) CT/GC/MS/ILS, (2) electron capture detection with cryogenic trapping and gas chromatography for speciation (GC/IF/ECD), (3) CT/GC/FPD, and (4) gold wool absorption collection-flame photometric detection (GWA/FPD). The three gold wool techniques differ mainly in the type of oxidant scrubber used and minor operational procedures. Two of the DMS techniques also provided measurements of other sulfur gases.

Three fundamentally different detection principles were fielded for measurements of COS and CS_2: (1) CT/GC/FPD, (2) CT/GC/MS/ILS, and (3) CT/GC/IF/ECD. Each of these techniques employ cryogenic trapping and gas chromatography, and differ primarily in the final detection procedures.

TABLE 2. CITE 3 Ancillary Measurements

Variable	Measurement Technique*	Principal Investigator and Affiliation
O_3	Chemiluminescence	G. L. Gregory, NASA Langley
Aerosol number density/size	Knollenberg, FSSP, and ASASP	G. L. Gregory, NASA Langley
Total Sulfur	MFC/FD/FPD	S. O. Farwell, University of Idaho
CO	DACOM	G. W. Sachse, NASA Langley
$NO/NO_2/NO_y$	TP-LIF/PF/Au Conv.	J. W. Bradshaw, Georgia Institute of Technology
Aerosol collection	Filters/PIXIE	P. Artaxo, Universidade de Sao Paulo
Radon	Alpha Decay	E. Pereira, Instituto de Pesquisas Espaciais
In situ meteorological	Standard Aircraft Instrumentation	J. D. W. Barrick, NASA Langley

* See Table 3 for acronym definitions.

TABLE 3. Instrument Technique Acronyms

Acronym	Definition
ASASP	Active Scattering Aerosol Spectrometer Probe
CF	Continuous Flow
CT	Cryogenic Trapping
DACOM	Differential Absorption Carbon Monoxide Measurement
ECD	Electron Capture Detection
FC	Filter Collection
FD	Flash Desorption
FPD	Flame Photometric Detection
FSSP	Forward Scattering Spectrometer Probe
GC	Gas Chromatography
GWA	Gold Wool Absorption
IC	Ion Chromatography
IF	Internal Fluorination
ILS	Isotopically Labeled Sampling
LIF	Laser Induced Fluorescence
MFC	Metal Foil Collection
MS	Mass Spectrograph
PF	Photo Fragmentation
PIXE	Particle Induced X-ray Emissions
TP	Two Photon

The H_2S intercomparison measurements were made with three instruments representing two basic measurement techniques: CT/GC/FPD and two applications of the Natusch technique.

A brief description of each instrument is given in the intercomparison papers of *Gregory et al.* [this issue (a),(b)(c)]. Detailed instrument operation and CITE 3 performance are discussed in the various companion papers authored by the respective investigator teams.

Flight Operations

Integration of the instruments aboard the aircraft and shakedown test flights were conducted at Wallops. The shakedown flights included three test flights covering approximately 15 flight hours. Instrument integration and shakedown flights were conducted over approximately 3-1/2 weeks. The ground based sulfur calibration tests were conducted after an instrument was integrated on the aircraft and certified by the investigator as operational. As a result of schedules and instrument operational problems, some calibration tests were conducted during the 2-week intercomparison flight period (see below) at Wallops.

The initial phase of the airborne intercomparison and sulfur science tests was conducted at Wallops over a 2-week period. This included seven local flights encompassing approximately 40 flight hours. The transit flights to Natal, Brazil, providing a latitude survey, occurred over a 2-day period with refueling stops in Puerto Rico and French Guyana, and an overnight layover in Barbados (see Figure 1). The transit legs covered approximate 16 flight hours. The Natal portion of CITE 3 also included seven local flights encompassing approximately 39 flight hours. The return transit leg was declared a nonintercomparison flight due to logistical concerns that emerged just prior to the departure from Natal. Measurements during the return transit flight were, however, obtained by some investigators and are discussed in some of the accompanying papers in this issue. Table 5 summarizes for each intercomparison flight (4-19) flight dates, locations, times, and altitudes.

The flight profiles shown in Figure 3 illustrate the salient features of each flight. The flight numbers correspond to those used in the companion papers in this issue. All flights were predominantly over water off the coast of either the eastern United States or Natal, Brazil. While at Wallops and as required by the instrument intercomparisons, some flights (e.g., flight 10) entailed sampling over or near the continent for purposes of obtaining higher mixing ratios of the continental-source sulfur gases. Most flights from Wallops sampled the marine mixed layer and free troposphere at various distances from the continent. Natal flights were

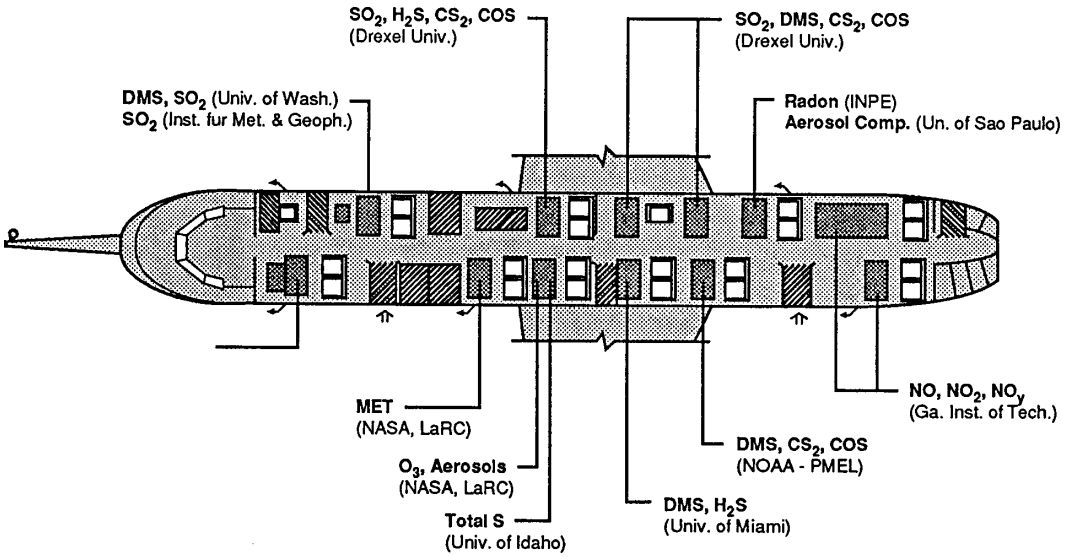

Fig. 2. CITE 3 instrumentation layout.

TABLE 4. Intercomparison Measurements Reported by Each Instrument for Each Flight

Flight Number	Drexel Univ. CT/GC/FPD				Drexel Univ. CT/GC/MS/ILS				NOAA-PML GC/IF/ECD			Univ. of Miami GWA/GC/FPD Natusch		Max. Planck CT/GC/FPD Natusch		Univ. of Wash. GWA/GC/FPD FC/IC		Inst. Mets. and Geophys. FC/CL	CC/CL
	SO_2	H_2S	CS_2	COS	SO_2	DMS	CS_2	COS	DMS	CS_2	COS	DMS	H_2S	DMS	H_2S	SO_2	DMS	SO_2	SO_2
4	y	y	–	y	y	y	–	–	y	y	y	y	y	y	y	y	y	y	y
5	–	y	y	y	y	y	–	–	y	y	y	y	y	y	y	y	y	y	y
6	–	y	y	–	y	y	–	–	y	y	y	y	y	y	y	y	y	y	y
7	–	y	y	–	y	y	y	–	y	y	y	y	y	y	y	y	y	y	y
8	y	y	–	–	y	y	y	–	y	y	y	y	y	y	y	y	y	y	y
9	y	y	–	y	y	y	y	–	–	–	–	y	y	y	y	y	y	y	y
10	–	y	y	–	y	y	y	–	–	–	–	y	y	y	y	y	y	y	y
11	y	–	–	y	y	y	y	y	y	y	y	y	y	y	y	y	y	y	–
12	y	–	–	y	y	y	y	y	y	y	y	y	y	y	y	y	y	y	–
13	y	y	–	y	y	y	y	–	y	y	y	y	y	y	y	y	y	y	–
14	y	y	–	y	y	y	y	–	y	y	y	y	y	y	y	y	y	y	y
15	y	y	–	y	y	y	y	–	y	y	y	y	y	y	y	y	y	y	y
16	y	y	–	y	–	y	y	–	y	–	–	y	y	y	y	y	y	y	y
17	y	y	–	y	–	y	y	–	y	–	–	y	y	y	y	y	y	y	–
18	y	y	–	y	–	y	y	–	y	–	–	y	y	y	y	y	y	y	–
19	y	y	–	y	–	y	y	–	y	–	–	y	y	y	y	y	y	–	y

Here y indicates measurements reported; dash indicates no measurements reported.

generally north to east from Brazil over the tropical Atlantic Ocean. Three series of flights (two each of flights 14/15, 16/17, and 18/19) were flown from Natal and focused on diurnal (day/night) events. Flight altitudes ranged from 150 to 5000 m above sea level. Details of the flights, type of air masses, and meteorological scenarios are discussed in detail by *Shipham et al.* [this issue].

Overview of Results

Overview of the Atmosphere: Ozonesonde Results

As part of the Natal deployment, ozonesondes were released from the Natal area. These sondes not only provide data on the "general state" of the atmosphere from the surface to about 11-km altitude (200-mbar pressure), but when compared to the seasonally averaged ozone data from this site during the previous 10-year period [*Kirchhoff et al.*, 1991] serve as a tracer to provide a frame-of-reference for the CITE 3 data base in terms of "typical" seasonal climatological results.

Four sondes were released during the CITE 3 Natal deployment. All releases were at 1200 UT or 0900 local time, which is the normal launch time for the Natal observation program. All sondes reached pressure heights of at least 10 mbar, except for the launch on September 22 which obtained a pressure height of only 20 mbar. The tropospheric ozone abundance, in Dobson Units (DU), given in Table 6 for each launch, is defined as the ozone concentrations integrated with height up to 200 mbar. These values range between 12.8 and 16% of the total ozone column integral. The 10-year mean for the total ozone column integral and the tropospheric abundance for September are 290.0 ± 10.3 and 36.2 ± 8.1 DU, respectively. Based on the 10-year data base, the September tropospheric abundance at the Natal site accounts for about 12.5% of the total ozone column integral. Note that tropospheric abundance for September 18 is unusually high at 50.5 DU (16% of the total column integral).

Figure 4 compares the individual sonde results to the 10-year spring averaged ozone profile. To aid in the identification of potential "layers" in the lower troposphere, temperature and relative humidity profiles are also shown for each sounding and inversion layers are indicated as hatched regions. It is quite apparent that tropospheric ozone concentrations during the period in which CITE 3 was operational in Natal, were larger than the 10-year climatological Spring mean. Also important to note is the frequent presence of ozone-enriched layers seen in each of the four CITE 3 soundings. In situ ozone soundings obtained aboard the aircraft also showed a high frequency of ozone-enriched layers [*Anderson et al.*, this issue].

Instrument Intercomparisons

The CITE 3 protocol included intercomparisons of calibration standards and ambient air measurements. A brief summary of the salient results from the instrument intercomparisons is given below. Detailed discussion of the instrument intercomparisons may be found in the papers by *Gregory et al.* [this issue (a),(b),(c)].

The intercomparison of standards was implemented with gas mixtures for SO_2, DMS, H_2S, and CS_2 with nominal mixing ratios in the 100 to 200 pptv range; COS standards

TABLE 5. CITE 3 Flights Summary

Date	Flight Number	Type of Flight	Takeoff, UT	Landing, UT	Altitudes, km
Aug. 22	4	Maritime, 800 km S.E. of Norfolk, VA	1500	2110	0.2, 1.5, 5.0
Aug. 23	5	Maritime, 500 km S.E. of Norfolk, VA	1515	2050	0.2, 1.5
Aug. 25	6	Maritime, 500 km east of Wallops, VA	1530	2000	0.2, 1.5
Aug. 28	7	Coastal, N.W. of Wallops, VA	1450	2050	0.2, 1.5
Aug. 30	8	Coastal, Carolinas	1515	2120	0.2, 1.5
Aug. 31	9	Maritime, 500 km east of Wallops, VA	1525	2115	0.2, 3.7
Sept. 1	10	Coastal-shore, Virginia & New Jersey	1500	2020	0.2, 1.5
Sept. 9	11a	Ferry, Wallops to Puerto Rico	1240	1800	0.2, 3.0, 4.0, 4.5, 5.5
	11b	Puerto Rico to Barbados	1910	2120	0.2, 4.5
Sept. 10	12a	Ferry, Barbados to Cayenne, French Guyana	1200	1455	0.2, 4.0
	12b	Cayenne to Natal, Brazil	1555	2115	4.0, 4.5
Sept. 12	13	Maritime, 400 km S.E. of Natal, Brazil	1155	1755	0.2, 2.0, 3.3, 5.0
Sept. 15	14	Maritime, 300 km N.E. of Natal, Brazil	1400	1935	0.2, 1.5, 3.5
Sept. 16	15	Maritime, night, same area as flight 14	0300	0830	0.2, 1.5, 3.5
Sept. 19	16	Maritime, 300 km east of Natal, Brazil	1400	2000	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	1240	0.2, 0.5, 1.5, 3.0, 5.0

were in the range of 400 to 600 pptv. Standards tests were successful for all but the continuous flow-chemiluminescent SO_2 instrument. Two scheduled tests of this instrument produced unusable results due to high instrumental "zero" blank measurements. Results from the standards phase of the CITE 3, suggested that any biases that might occur between flight measurements are (generally) not the result of the different calibration standards used by the investigators.

Ambient air measurements from the six DMS techniques representing three different detection principles, as well as, several collection/preconcentration and oxidant scrubbing methods agree to within expected uncertainties considering the 10 to 20% accuracy of the DMS calibration standards. The DMS flight results are from intercomparisons at DMS <100 pptv with the majority of the data at mixing ratios <50 pptv. While statistically (based on 95% confidence levels) significant differences (biases) exist among some of the techniques, they are small in magnitude (few pptv) and do not suggest that DMS measurements from any one technique are in error, although one technique, gas chromatograph/fluorination-electron capture, consistently reported values of DMS higher than the other techniques.

The ambient air H_2S results from the gas chromatograph-flame photometric technique and the Natusch techniques (two separate applications of Natusch) agreed on the average to about 15%. For mixing ratios <25 pptv, agreement averaged about 5 pptv. While the observed biases were statistically significant (95% confidence interval testing), one concludes, based on the stated accuracy and precision for the techniques and available standards, that measurements reported by the techniques may be considered equally valid ambient measurements of H_2S. Intercomparison flight results are from measurements at H_2S <100 pptv with most measurements at mixing ratios <25 pptv.

The COS results from the gas chromatograph-flame photometric, gas chromatograph-mass spectrometric, and gas chromatograph/fluorination-electron capture techniques generally agreed to within 10% and, on the average, to about 5%. There was a tendency (not statistically significant at 95% confidence) for the gas chromatograph-flame photometric measurement to be high compared to the other two techniques. However, based on the stated accuracy and precision for the techniques, available standards, and the analyses performed, measurements from the techniques may be considered equally valid in terms of measuring true ambient levels of COS. COS intercomparisons were at levels of 400 to 600 pptv.

The CS_2 results suggest that only the gas chromatograph-mass spectrometer has adequate sensitivity to measure the low CS_2 mixing ratios observed in clean, remote regions sampled over the Atlantic Ocean east of Brazil. Mixing ratios reported by the mass spectrometric system for these regions were generally in the 1 to 2 pptv range with an estimated detection limit of about 0.2 pptv. During these same time periods the gas chromatograph\fluorination-electron capture technique reported CS_2 values as below a detection limit of 2 pptv. The gas chromatograph-flame photometric technique did not measure CS_2 during the Brazilian deployment as a result of tradeoff between longer sampling periods to improve detection limits for the CS_2 measurement and participation in CITE 3 intercomparisons of the other sulfur gases. For CS_2 data reported above the detection limits (few pptv to about 50 pptv), the results indicate that the gas

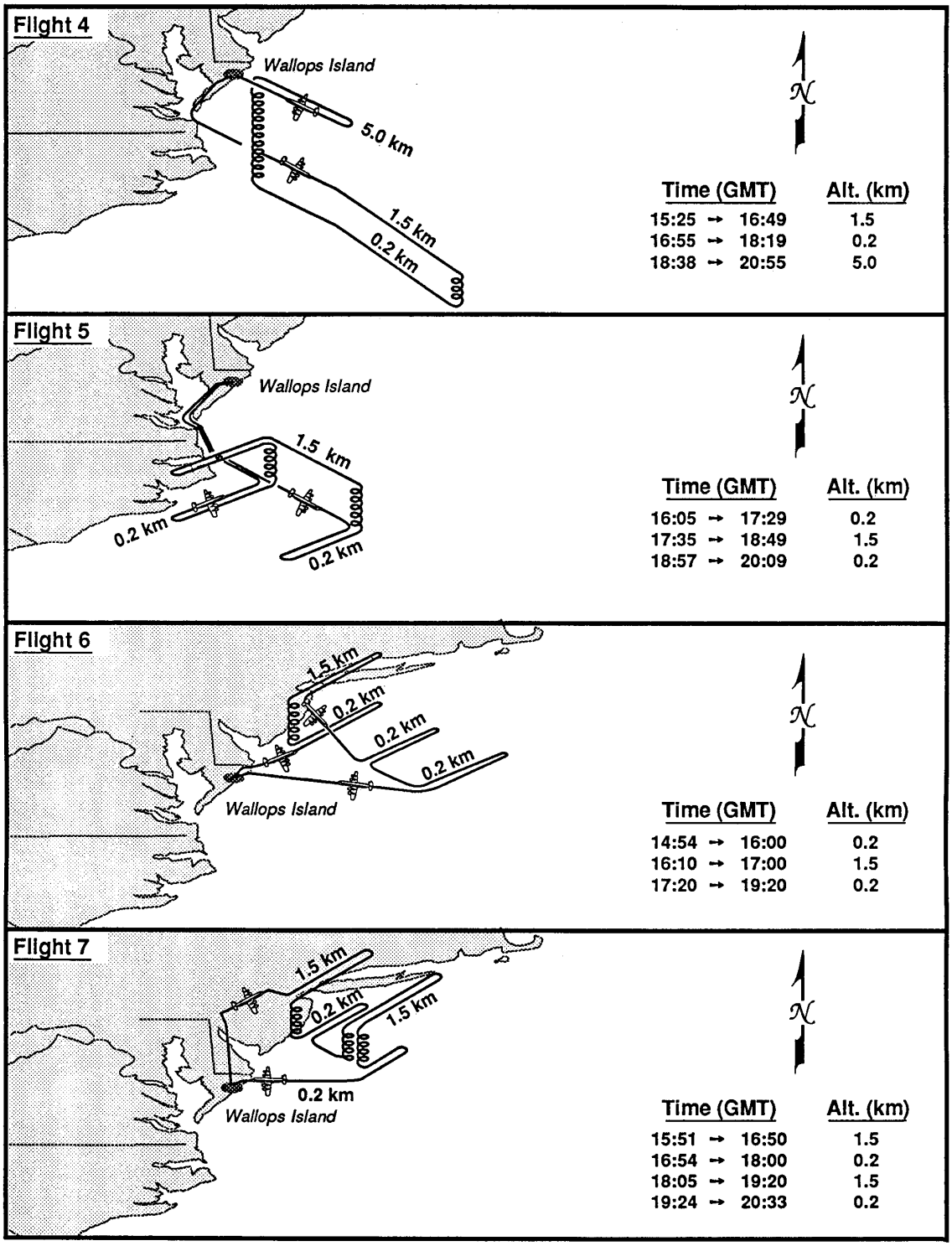

Fig. 3a. Profiles of flights 4-7 in the North Atlantic test area (August 22-28, 1989).

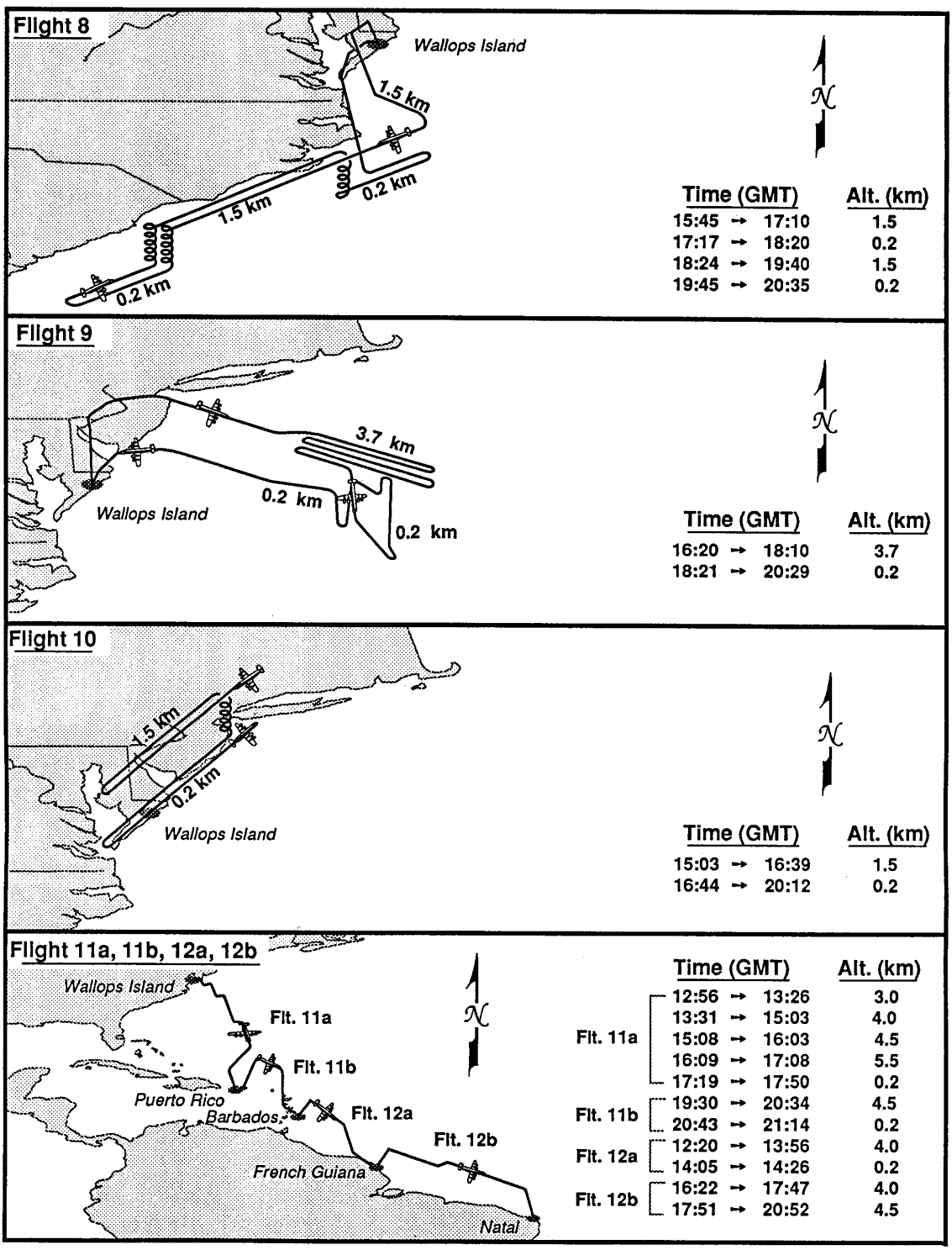

Fig. 3b. Profiles of flights 8-10 in the North Atlantic test area (August 30 - September 1, 1989) and profiles of transit flights 11 and 12 (September 9-10, 1989).

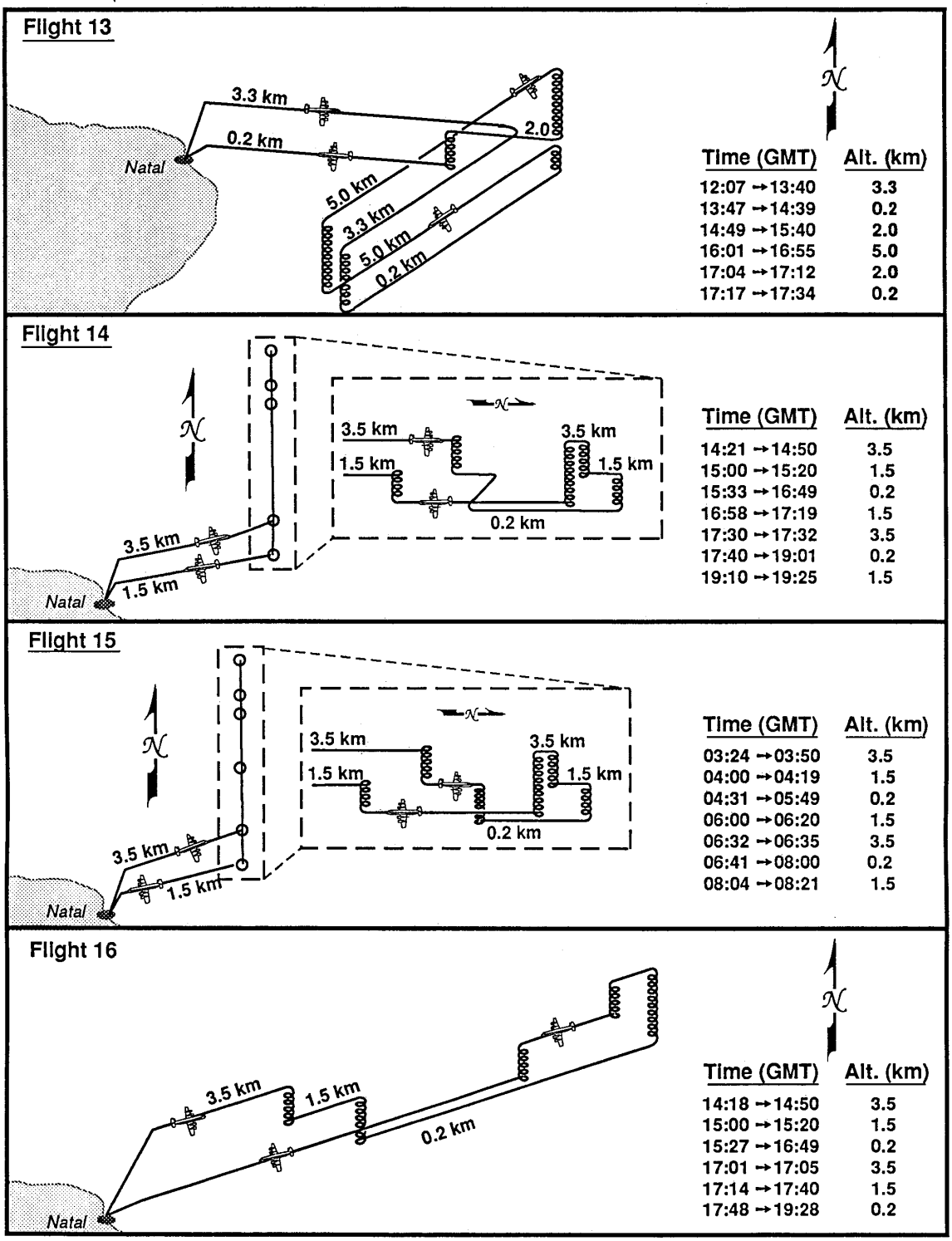

Fig. 3c. Profiles of flights 13-16 in the tropical Atlantic test area (September 12-19, 1989).

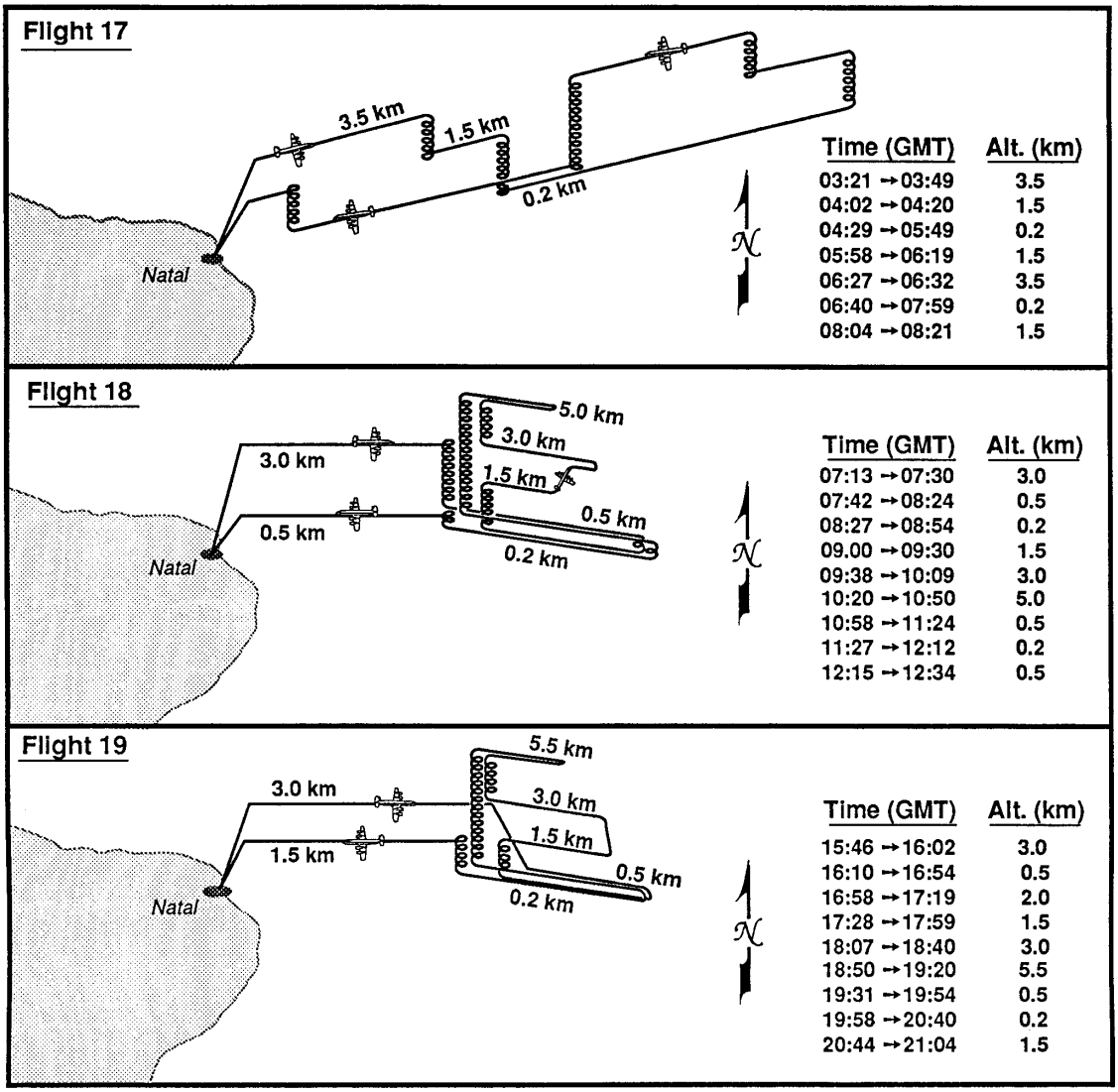

Fig. 3d. Profiles of flights 17-19 in the tropical Atlantic test area (September 20-22, 1989).

chromatograph-flame photometric, gas chromatograph-mass spectrometric, and gas chromatograph/fluorination-electron capture techniques agreed on average to within a few pptv to about 6 or 7 pptv. A constant offset bias of about 4 pptv was observed between the gas chromatograph-flame photometric and the gas chromatograph-mass spectrometric techniques (flame photometric high). The offset bias between the gas chromatograph/fluorination-electron capture technique and the other two techniques was observed to vary between flights and ranged from a few pptv to perhaps 6 or 7 pptv. While some of the observed biases were statistically significant and suggest that CS_2 values reported by the various instruments are different, one concludes, based on the accuracy of the CS_2 standards and the stated accuracy for each

TABLE 6. Summary of CITE 3 Ozonesonde Results at Natal, Brazil

Date in 1989	Launch Time, LT	Flight Duration, min	Burst Pressure, mbar	Tropospheric Abundance, DU
Sept. 15	0900	114	6.1	39.3
Sept. 18	0900	78	8.7	50.9
Sept. 20	0900	81	10.0	41.7
Sept. 22	0900	65	20.0	43.7

Tropospheric abundance is the integrated ozone column from the surface to 200 mbar pressure.

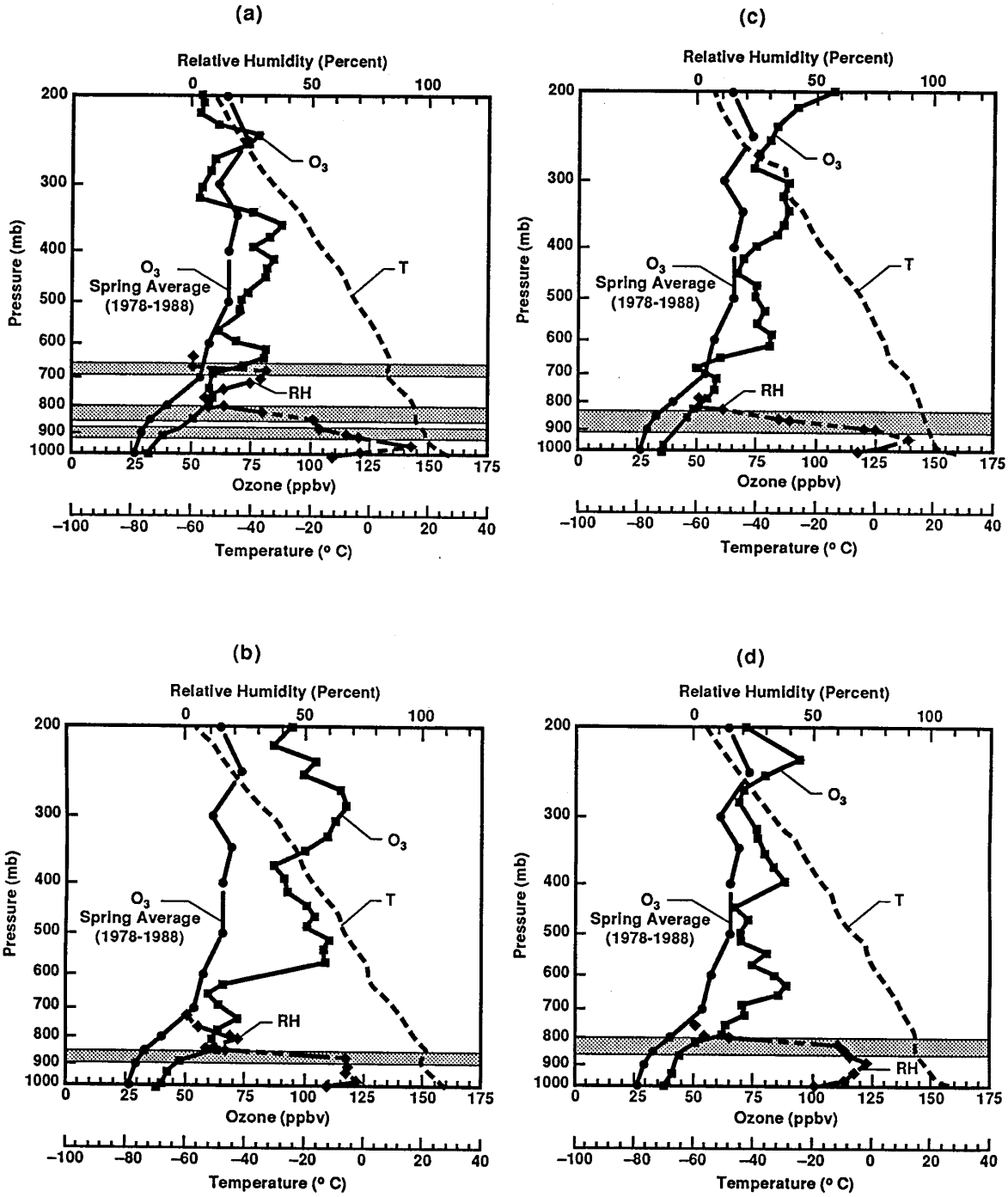

Fig. 4. Comparison of CITE 3 September 1989 ozone soundings to the 10-year spring average sounding at Natal, Brazil. O_3, ozone; T, temperature; RH, relative humidity; shaded areas identify regions of temperature inversions: (a) 1200 UT on September 15, 1989; (b) 1200 UT on September 18, 1989; (c) 1200 UT on September 20, 1989; and (d) 1200 UT on September 22, 1989.

technique, that in general measurements from any of the techniques in this range of mixing ratios can be considered to be equally valid.

The CITE 3 results relative to the SO_2 instruments were less than definitive. There was considerable disagreement among techniques and no single technique could, unambiguously, be identified as providing valid or, for that matter, invalid SO_2 measurements (some exceptions). Further, the data show that large differences in measured SO_2 can result depending upon the technique of choice and that these differences (based on comparison of pairs of measurements) are not always consistent in terms of magnitude and direction. As discussed by *Gregory et al.* [this issue (c)], ambient SO_2 variations combined with the different sampling schedules of the instruments may account for some of the observed disagreement between measurements. The CITE 3 data clearly indicate that a detection limit of 50 to 100 pptv is not sufficient for many tropospheric applications, and thus, the continuous flow-chemiluminescent technique, as applied during CITE 3, does not have sufficient sensitivity for most global sampling applications. Likewise, the filter collection-chemiluminescent technique may not be suitable for some applications. The reader is referred to *Gregory et al.* [this issue (c)] for additional findings from the SO_2 instrument intercomparisons.

Sulfur Budget Issues

In summarizing these results, we note that the CITE 3 data base provides a comprehensive data base from which one may begin to analyze various sulfur budget issues. The data base confirms existing sulfur observations and theories while, at other times, provides emphasis to reconsider other issues. For example, the data clearly confirm (1) the importance of the ocean as a source of DMS and the rapid oxidization of DMS after transport from the marine mixing layer; (2) the continental source of H_2S, CS_2, and SO_2 as compared to a marine source; (3) the existence of a COS latitinudal gradient (decreasing southward) estimated to be about 1.8 pptv/deg; (4) the higher concentration and variability of all sulfur gases in the northern hemisphere, thus verifying the importance of northern hemispherical anthropogenic emissions to global budgets; and (5) in the tropical Atlantic regions, devoid of major anthropogenic influences, photochemistry results in a net loss of ozone (3 to 5 pptv) during the day with a tendency for the marine mixed layer to be replenished at night via subsistence.

On the other hand, the data base raises important questions. For example, (1) In terms of global sulfur budgets, is the transport and influence of northern hemispheric air more important than originally viewed? (2) Is the COS budget complete, or are there missing source terms? (3) In view of the lower observed mixing ratios of H_2S and CS_2 in the tropical Atlantic (respectively, a factor of 3 and 10 lower than earlier data), what is the role and importance of the oceans as a source for these gases compared to continental sources? These and other issues are discussed in CITE 3 companion papers in this issue.

CITE 3 Data Archive

As with previous GTE field missions, all data obtained during CITE 3 have been archived in the GTE Data Archive at NASA's Langley Research Center. A copy of the archive can be obtained by contacting the GTE Data Manager, Mail Stop 483, Langley Research Center, Hampton, VA 23681.

Acknowledgments. The authors would like to acknowledge all CITE 3 participants and express thanks for the cooperation, support, and professionalism displayed throughout CITE 3. Special recognition is extended to the Wallops Electra flight and ground crews for the long hours spent in the field, preparing and flying the aircraft while based at Wallops Island, Virginia, and Natal, Brazil. To the hangar crew at Wallops, their support and helpful suggestions during installation of equipment and test flights at Wallops are appreciated. A special note of appreciation is extended to Jose' R. Alves and Francisco R. da Silva for their dedication in support of the CITE 3 program. Lastly, we acknowledge the support and hospitality of the Government and Citizens of Brazil during the Natal portion of the field program.

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(Received June 16, 1992;
revised February 12, 1993;
accepted February 16, 1993.)