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In this Issue

A Note From the IGAC Chair

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Aerosols and Photooxidants

One of the key activities sponsored this year by IGAC and the Commission for Atmospheric Chemistry and Global Pollution of IAMAS is the Joint International Symposium on Global Atmospheric Chemistry that will take place at Seattle, Washington, USA on 19-25 August, 1998. Several hundred scientists will attend the meeting. The program—both posters and oral presentations—will focus on interesting issues related to aerosols and photooxidants. These atmospheric trace constituents are central to our understanding of potential impacts of human activities on Earth's climate and on the terrestrial biosphere. For details on the Symposium see http://saga.pmel.noaa.gov/cacgp98/.

In order to study the processes that affect the chemical composition of the atmosphere, the scientific community, very often under the IGAC umbrella, has planned and carried out large research programs with well defined scientific objectives. An important example is provided by the "Global Tropospheric Experiment" (GTE) organized under the leadership of NASA in the U.S. A paper presented in this issue of IGAC*tivities* summarizes the key findings that have resulted from an impressive series of GTE field campaigns in different regions of the world. It focuses on questions as important as the sources and sinks of tropospheric ozone and nitrogen oxides, the influence of biomass burning on global tropospheric chemistry, the role of hydroxyl radicals, the importance of sulfur chemistry, and the effect of continental outflow on the composition of the global troposphere. The GTE campaigns have made a significant contribution to our understanding of the physical and chemical processes affecting tropospheric photooxidants and aerosols. It is my hope that future issues of this newsletter will present summaries of other national and regional programs that address these and other aspects of global atmospheric-biospheric chemistry.

The chemical nature and physical properties of aerosols and their role in climate forcing have been widely discussed in recent years. In the January issue of IGAC*tivities* (No. 11), several articles addressed this question and summarized new scientific insights. In this issue, we publish a comment on one of these papers and a response regarding the chemical composition of tropospheric aerosols observed during an IGAC-sponsored field campaign. This discussion highlights the complexity of the problem and calls for further studies on these issues.

I hope to see you in Seattle this summer.

GLOBAL CHANGE
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Science Features

The NASA Global Tropospheric Experiment: Recent Accomplishments and Future Plans

Contributed by R.J. McNeal, NASA Headquarters, D.J. Jacob, Harvard University, and D.D. Davis and S.C. Liu, Georgia Institute of Technology, USA

1. Introduction

The NASA Global Tropospheric Experiment (GTE) is a program of aircraft–based experiments dedicated to improving our knowledge of global tropospheric chemistry and of its implications for the biosphere, climate, and stratosphere. The program arose in the late 1970's and early 1980's to address science priorities established in a National Academy of Sciences study (NAS, 1984). It has taken advantage of NASA's research aircraft fleet, technological innovation, and experience in managing large–scale projects.

Changes in the levels of tropospheric chemical species are key observables in greenhouse gas buildup and in degradation of air quality in clean air regions of the world. The troposphere is also the ultimate source and sink for trace gas species in the stratosphere, so a full understanding of stratospheric ozone depletion is not possible without an understanding of tropospheric chemistry. The scale of such phenomena makes tropospheric chemistry a natural, highly important target for space observations. NASA is developing systems that, early in the next decade, will provide global–scale tropospheric chemistry observations of some key species from space. With a few notable exceptions, such as distributions of H_2O, CO, CO_2 and O_3, most tropospheric chemistry studies by NASA have so far been conducted from aircraft.

The NASA aircraft provide excellent platforms for the investigation of chemical and transport processes in the troposphere. They can sample with high vertical resolution through the depth of the tropospheric column over an extended range, and they can carry a large payload of *in situ* measurements that is particularly effective when complemented with ground–based and sonde measurements. They also will play a particularly important role in calibration and validation of future tropospheric chemistry space measurements.

The measurement of tropospheric composition from aircraft has a relatively short history. Twenty years ago, reliable instrumentation was available only for O_3, CO, and a few long–lived gases and only with relatively poor time resolution. The measurement requirements of global tropospheric chemistry are very challenging. A long–standing commitment of GTE has been to meet this challenge by (1) broadening the ensemble of species measured from aircraft; (2) increasing the accuracy, time resolution, and compactness of instrumentation; and (3) developing new technology for chemical flux measurements. GTE has conducted the Chemical Instrumentation Test and Evaluation (CITE) series of missions to provide rigorous, double–blind instrument intercomparisons as a necessary step to gain confidence in the data base being generated. This activity has resulted in high–quality aircraft payloads that have provided *in situ* characterization of a large ensemble of species needed to address global tropospheric chemistry questions.

Guided by science priorities of the tropospheric chemistry community, GTE has conducted missions in diverse parts of the world that are particularly important in understanding atmospheric chemical change (Table 1, Figure 1). The ABLE experiments focused on the surface sources and sinks of atmospheric gases and aerosols and the meteorological processes that mix such gases into the boundary layer and the free troposphere. The TRACE–A and PEM projects measured the distributions of aerosols and gases over a greater altitude range (up to 12 km) and over very wide geographical areas They have provided a baseline against which to measure future pollution impacts on the remote troposphere and defined a test bed for tropospheric chemistry process models.

The GTE experiments have produced many important scientific results. Since ABLE 3–B in 1990, they have been conducted as IGAC experiments with international partners. The entire GTE data base is available to the public through the GTE home page at http://www–gte.larc.nasa.gov.

The more recent GTE experiments (PEM and TRACE–A), conducted over the Pacific and Atlantic oceans, have focused on the sources and sinks of O_3 and related gases (e.g., NO_x, CO, hydrocarbons) in the remote troposphere. They have examined the sources of sulfur gases and the implications for aerosol formation, and they have probed the long range transport and chemical evolution of continental plumes. We review here some of the major accomplishments from these recent missions and briefly describe challenges and plans for the future.

Table 1. Field Missions of the Global Tropospheric Experiment.

	—INSTRUMENT INTERCOMPARISON—	
CITE–1A	OH, CO, NO/Tropical Environment	November 1983
CITE–1B	OH, CO, NO/US West Coast	April 1984
CITE–2	NO_2, HNO_3, PAN/US West Coast	August 1986
CITE–3	SO_2, CS_2, COS, H_2S, DMS/N. & S. Atlantic	September 1989
	—FLUXES & BOUNDARY LAYER EXCHANGE—	
ABLE–1	Tropical Atlantic	June 1984
ABLE–2A	Amazon, Dry Season	August. 1985
ABLE–2B	Amazon, Wet Season	May 1987
ABLE–3A	Alaska	August 1988
ABLE–3B	Canada	July 1990
	—GLOBAL SCALE PHOTOCHEMISTRY & TRANSPORT—	
PEM–West A	North Western Pacific	September 1991
TRACE–A	Tropical Atlantic	September 1992
PEM–West B	North Western Pacific	March 1994
PEM–Tropics A	Tropical & Southern Pacific	September 1996
PEM–Tropics B	Tropical Pacific	March 1999
TRACE–P	North Western Pacific	(TBD) (2001?)
or		
TRACE–B	Brazil	(TBD) (2001?)

2. Current Status of the Aircraft Instrumentation

The primary platform for the more recent GTE missions was the NASA DC–8 aircraft, which has a ceiling of 12 km, a cruising speed of 800 km h^{-1}, and a 10 hour flight endurance. The latest PEM–Tropics A mission also deployed a P–3B aircraft with ceiling of 8 km, cruising speed of 500 km h^{-1}, and 10 hour endurance. Figures 2a and 2b show the DC–8 and P–3B instrument payloads in PEM–Tropics A. The DC–8 payload included *in situ* measurements of O_3, H_2O, peroxides, CH_2O, CO, hydrocarbons, halocarbons, a suite of nitrogen compounds (NO, NO_2, peroxyacetylnitrate (PAN), HNO_3), organic acids, dimethylsulfide (DMS), SO_2, bulk aerosol composition, and UV irradiance. A differential absorption lidar (DIAL) aboard the DC–8 measured ozone and aerosol vertical profiles remotely in real time above and below the aircraft (Browell *et al.*, 1996). These profiles are an important data product, and they also provided a guide for adjustment of flight tracks to exploit interesting measurement opportunities encountered during flight.

The DC–8 payload in PEM–Tropics A included a new–generation instrument for sub–pptv measurements of NO and NO_2 that uses the photofragmentation two–photon laser induced fluorescence (PF–TP–LIF) technique (Sandholm *et al.*, 1997; Bradshaw *et al.*, 1998). Accurate measurement of NO down to the pptv level is necessary for quantifying the chemical production of O_3 in the remote troposphere. Figure 3 shows a sample vertical profile of NO concentrations taken by this instrument over the South Pacific during PEM–Tropics A. Concentrations of NO in the marine boundary layer (MBL) were 1–2 pptv, well below the detection limit of earlier instrumentation.

The PF–TP–LIF instrument incorporated a highly modified sample inlet system designed by Bradshaw *et al.* (1998) to overcome potential decomposition of complex nitrogen oxides in the inlet system, a suggested source of interference in previous attempts to measure NO_2. The PEM–Tropics data show that the decomposition problem has been substantially eliminated by the new inlet design. Figure 4 compares the NO/NO_2 concentration ratios measured in PEM–Tropics A to the values computed with a photochemical steady state model (Schultz *et al.*, 1998; see also Bradshaw *et al.*, 1998). Remarkable agreement is found, in sharp contrast to results from PEM–West A where the deviation between predicted and observed NO_2 was nearly a factor of 4 (Crawford *et al.*, 1996). Even in the MBL with NO concentrations below 1 pptv, the agreement is within 30% and the variance is well captured. The P–3B payload in PEM–Tropics A included measurements of O_3, H_2O, OH, peroxides, CO, hydrocarbons

and halocarbons, NO, a suite of sulfur species (DMS, SO_2, methanesulfonic acid(g), H_2SO_4(g), non–seasalt sulfate, and methanesulfonate), and aerosol composition and size distributions, including ultrafine particles. The OH measurements were made with the Chemical Ionization Mass Spectrometry (CIMS) technique (Eisele and Tanner, 1991). The measurement of OH from aircraft with other techniques has a long and difficult history (Crosley, 1995). The ground–based version of the CIMS instrument had previously been intercompared successfully with a long–path absorption instrument (Mount *et al.*, 1997), and the aircraft version performed extremely well in PEM–Tropics A (Mauldin *et al.*, 1998a). Values measured in the MBL near Christmas Island are shown in Figure 5 and clearly demonstrate a detection sensitivity in the range of 10^5 cm^{-3} (Davis *et al.*, 1998).

3. Sources and Sinks of Tropospheric Ozone and NO_x

A major objective of the TRACE–A and PEM missions was to improve understanding of O_3 production and loss in the remote troposphere. A strikingly consistent picture of the factors that control remote tropospheric O_3 has been developed, which is markedly different from the prevailing view of 20 years ago. NO_x levels drive ozone photochemistry, and tropospheric NO_x levels are sufficiently high that photochemical production dominates the stratospheric flux in controlling column O_3 density. Stratospheric intrusions where they occur are dramatic events that strongly impact on the tropospheric ozone column density locally, but the relentless photochemical production of O_3 on a global scale, driven by NO_x from ever–growing global sources, ultimately dominates the tropospheric O_3 budget.

In the GTE missions, column O_3 production and loss rates are products derived from models that are run using the large base of reliable data gathered during the aircraft flights. During PEM–West B (February–March, 1994) the column O_3 photochemical production rate at subtropical latitudes (Crawford *et al.*, 1997a , Figure 6) is nearly 12 times larger than the nominal average northern hemispheric flux of O_3 from the stratosphere (Mahlman *et al.*, 1980). Such high production rates are a consequence of high levels of NO_x from

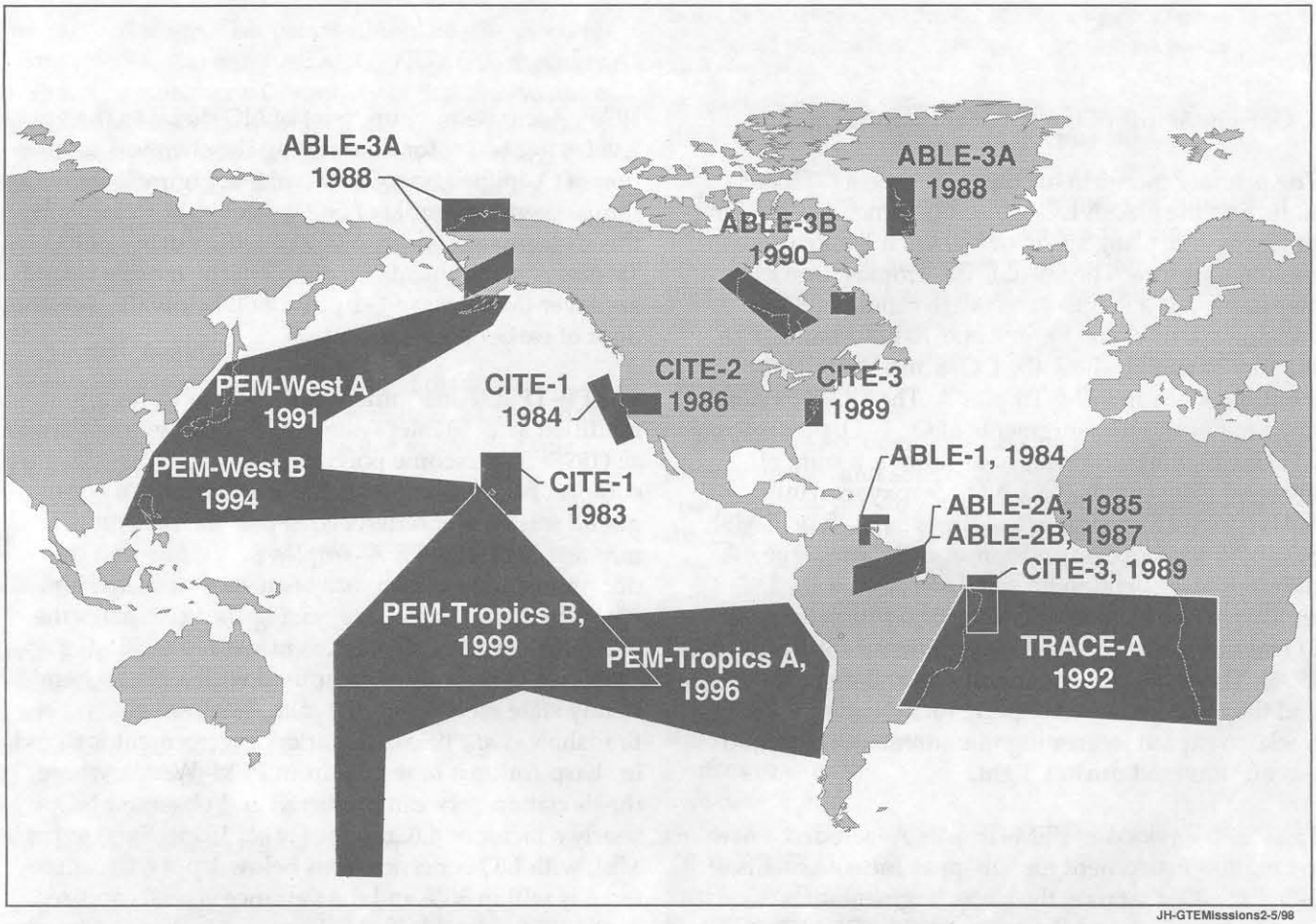

Figure 1. Study regions for missions conducted by the Global Tropospheric Experiment.

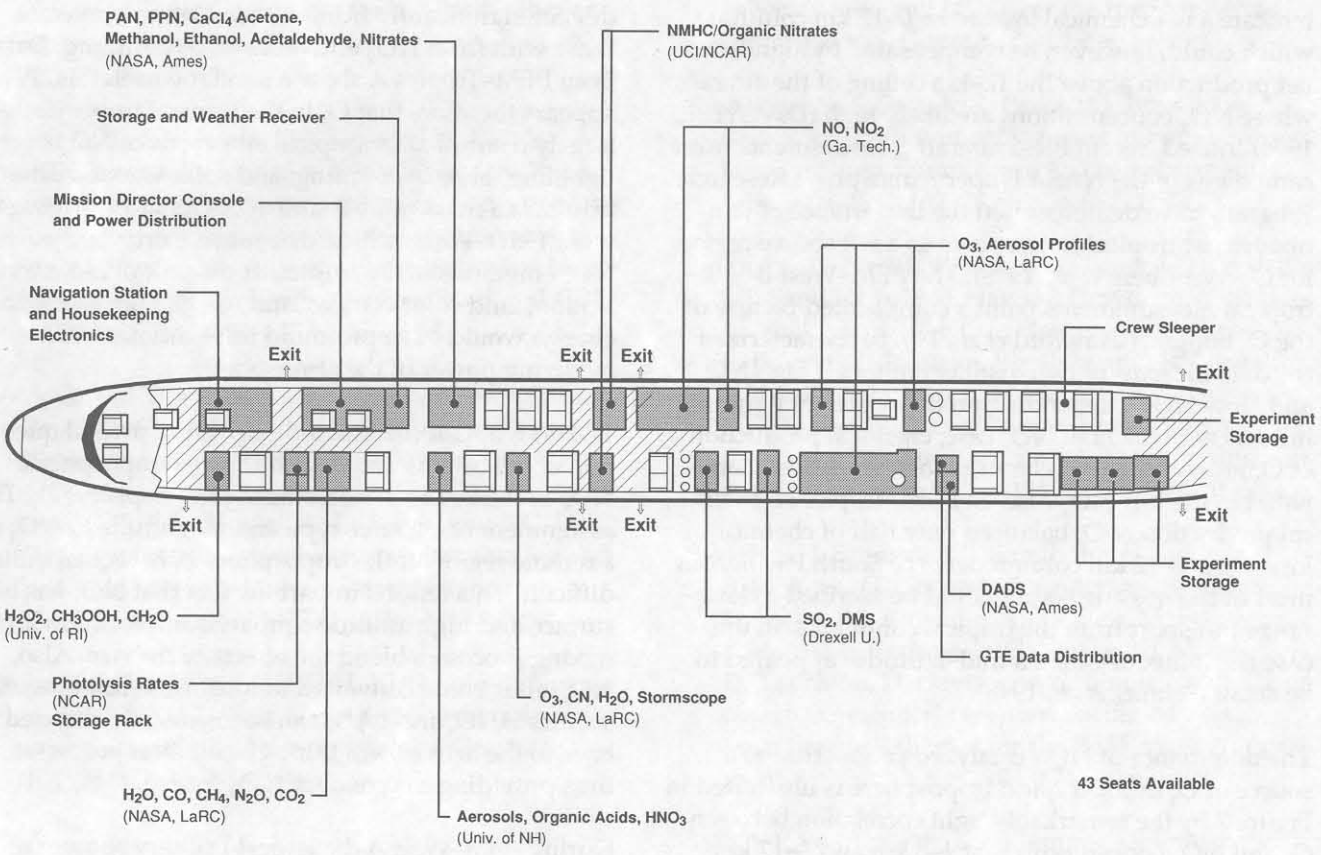

Figure 2a. Instrument layout on the NASA DC–8 Aircraft during PEM–Tropics A.

low altitude continental outflow of industrial emissions from Asia. During PEM–West A (September–October, 1991) the NO_X concentrations were generally lower, but the corresponding O_3 production rate at subtropical to mid–latitudes was still nearly 6 times the average stratospheric flux (Davis *et al.*, 1996). The difference in NO_X levels between the two missions was a result of the seasonal variation in Asian outflow of NO_X pollution to the western Pacific, which is strongest in early spring (Merrill *et al.*, 1997). Column production rates of O_3 in PEM–Tropics A were comparable to those in PEM–West A (Schultz *et al.*, 1998). Column production rates over the South Atlantic during TRACE–A were considerably higher, reflecting the strong influence of biomass burning (Jacob *et al.*, 1996; Thompson *et al.*, 1996).

The argument for the dominance of photochemistry is not based on column production rates alone. Photochemical loss rates are not driven by NO_X concentrations, which show large spatial and temporal variability, and the loss rate calculations convincingly demonstrate the importance of the photochemical source. The calculated O_3 loss rates from the PEM–West missions were substantially larger at mid–latitudes than the stratospheric O_3 flux, and these loss rates would have led to a much lower O_3 concentration than was observed, if the stratosphere were the only or even the dominant source of O_3. Interestingly, however, the loss rate was smaller than the calculated photochemical column production rate (Figure 5). Thus, the PEM–West data show that on average there is net photochemical production at mid–latitudes over the northwestern Pacific, particularly in the upper troposphere. The western Pacific is, therefore, an exporter of photochemically–produced O_3 to the eastern and the southern Pacific regions, where the effect of local photochemical production in determining O_3 densities is smaller because of lower NO_X concentrations.

In the tropics, the ensemble of data from the PEM and TRACE–A missions suggest that O_3 is largely determined by chemical production and loss with less impact from O_3 imported by long range transport processes. In some cases net production in the upper troposphere is balanced by net loss in the lower troposphere (Davis *et al.*, 1996; Jacob *et al.*, 1996). In TRACE–A, a close balance between chemical production and loss of O_3 was found for the 0–12 km column (Jacob *et al.*, 1996). The tropical data from PEM–West A

indicate a net chemical loss in the 0–12 km column, which could, however, be compensated by significant net production above the 12–km ceiling of the aircraft, where NO_x concentrations are likely high (Davis *et al.*, 1996) Indeed, recent ER–2 aircraft measurements from campaigns of the NASA Upper Atmosphere Research Program have demonstrated the importance of the uppermost tropical troposphere as a net source region for O_3 (Wennberg *et al.*, 1998). The PEM–West B tropical measurements paint a complicated picture of the O_3 budget. (Crawford *et al.*, 1997b) characterized the data in terms of two distinct regimes, "high NO_x" and "low NO_x", depending on the degree of lightning influence. In the high NO_x case, chemical production of O_3 nearly balanced chemical loss, while loss dominated in the low NO_x case. In PEM–Tropics A, chemical production of O_3 balanced only half of chemical loss in the 0–12 km column over the South Pacific, but most of the missing source could be ascribed to long–range transport from the tropical continents. In this case the influx of O_3 from mid–latitudes appeared to be small (Schultz *et al.*, 1998).

The dominance of NO_x–catalyzed production as a source of O_3 in the tropical troposphere is illustrated in Figure 7 by the remarkably tight correlation between O_3 and NO_x concentrations at 4–8 km and 8–12 km altitude for the PEM–West A and B, and TRACE–A missions (Crawford *et al.*, 1997b). The only points that deviate significantly from the correlation curve are those with fresh NO_x emissions from lightning. Data from PEM–Tropics A show a similar correlation. It appears therefore that O_3 in the tropical troposphere is largely controlled by tropical emissions of NO_x from lightning, biomass burning, and soils. Ozone in the tropics is a major global source of OH radicals (Logan *et al.*, 1981). We conclude that future perturbations to NO_x emissions in the tropics, as a result of industrialization, land colonization, land use change, or climate change would have profound implications for the oxidizing power of the atmosphere.

The GTE data focus attention upon the pivotal question of the origins and distribution of tropospheric NO_x as the key to understanding tropospheric O_3. The assignment of a source type and magnitude to NO_x to a remote region of the troposphere is, however, quite difficult. This reflects in part the fact that NO_x has both surface and high altitude primary sources, and vertical mixing processes blend the effects of the two. Also, NO_x, after being converted to longer lifetime species such as HNO_3 and PAN, can be chemically recycled back to the active form through chemical processes, thus providing a secondary NO_x source.

During PEM–West A the largest primary sources of NO_x in the upper troposphere were lightning and surface emissions carried aloft by deep convection

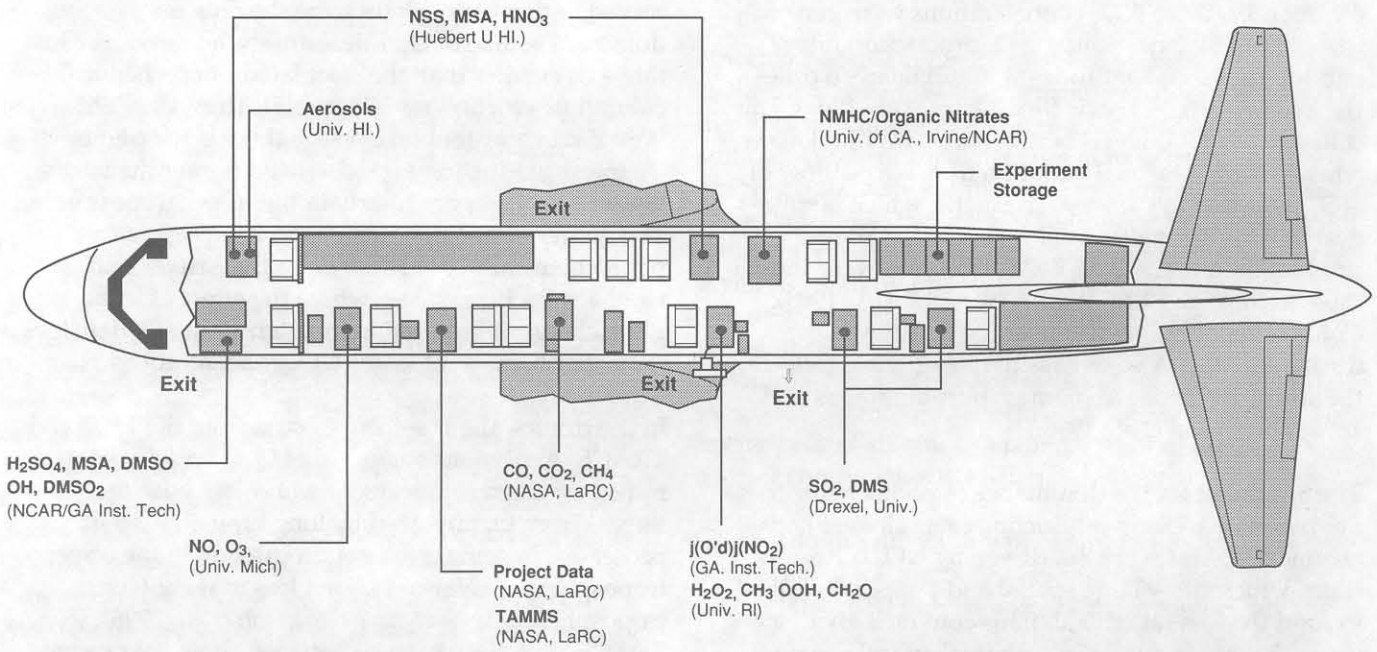

Figure 2b. Instrument layout on the NASA P–3B Aircraft during PEM–Tropics A.

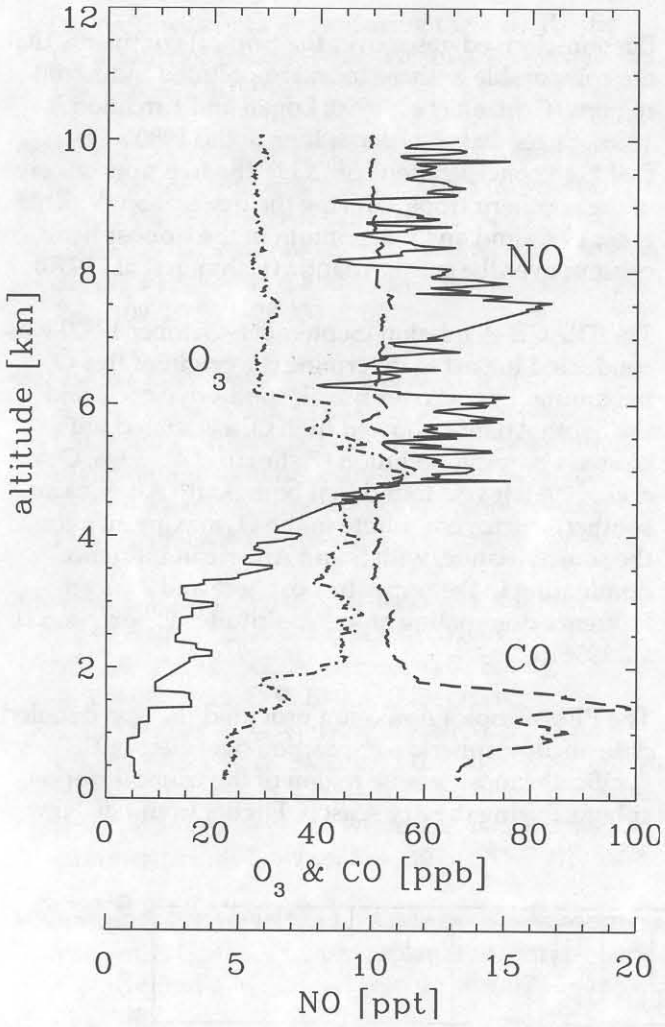

Figure 3. Vertical profiles of NO, O_3, and CO concentrations measured northeast of Tahiti (4°S, 135°W) on 16 September 1996 during PEM–Tropics A.

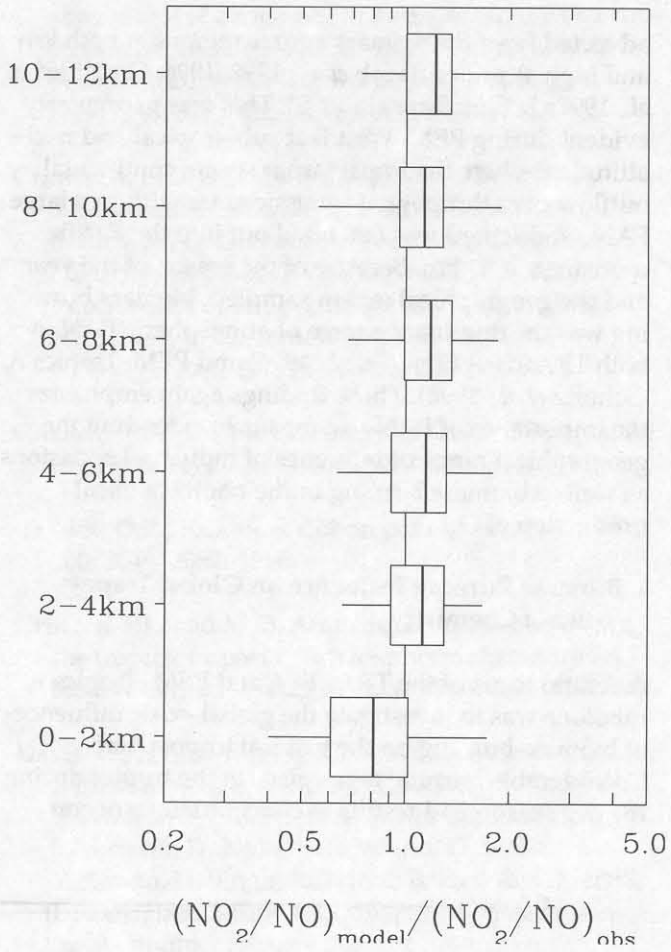

Figure 4. Comparison of observed NO_2/NO concentration ratios in PEM–Tropics A to values computed by a photochemical equilibrium model constrained with the ensemble of other aircraft observations. Statistics are shown in 2 km altitude bands for the ensemble of 1–minute observations made during the mission. Vertical lines are median values, boxes extend over the central 50% of the data (25th to 75th percentiles), and horizontal lines extend over the central 90% of the data (5th to 95th percentiles). From Schultz *et al.* (1998).

(Davis *et al.*, 1996; Singh *et al.*, 1996; Wang *et al.*, 1998). Crawford *et al.* (1997b) suggested that during PEM–West B for tropical marine regions the source of NO_x was variable, depending strongly upon the origin of the air parcel being sampled. In some cases (e.g., the earlier cited "low NO_x" regime) the parcels came from an oceanic region with considerable deep convection, but no lightning, and the NO_x appears to have been predominantly of the chemically recycled type. For "high NO_x" parcels, trajectory analysis combined with chemical tracer analysis strongly suggest that the NO_x in the air masses had its origin in lightning and deep convection over southeast Asia/Indonesia (Crawford *et al.*, 1997b; Kawakami *et al.*, 1997). This NO_x was transported to the detection point by high altitude winds. In the latter case, then, NO_x was influenced by both primary sources and some recycling of HNO_3. For TRACE–A and PEM–Tropics A there is evidence at high altitudes that some fast recycling mechanism for converting HNO_3 into NO_2, not currently in models, was operating to produce a substantial fraction of the observed NO_x (Jacob *et al.*, 1996; Singh *et al.*, 1997; Schultz *et al.*, 1998).

At lower altitudes the atmospheric lifetime of NO_x against oxidation becomes much shorter (i.e., 1 to 2 days), so that rapid decay of NO_x concentrations is expected away from its major primary continental sources. Concurrent measurements of NO, PAN, and HNO_3 in the PEM and TRACE missions have thus permitted a more complete analysis of the chemical sources and sinks of NO_x. The results show that NO_x in the marine atmosphere below 6 km altitude is largely maintained by thermal decomposition of PAN

advected from the primary source regions at both low and high altitudes (Jacob *et al.*, 1992, 1996; Crawford *et al.*, 1997a,b; Schultz *et al.*, 1998). This was particularly evident during PEM–West B at sub–tropical and mid–altitudes, where the impact from strong continental outflow of anthropogenic emissions (resulting in large PAN production) was extended out into the Pacific more than 2000 km. Because of the season of the year and the geographical region sampled, biomass burning was the dominant source of atmospheric PAN in both TRACE–A (Singh *et al.*, 1996) and PEM–Tropics A (Schultz *et al.*, 1998). These findings again emphasize the importance of PAN as a means of extending the geographical range of influence of industrial emissions as well as biomass burning in the photochemical production of O_3.

4. Biomass Burning Influence on Global Tropospheric Chemistry

A central focus of the TRACE–A and PEM–Tropics A missions was to investigate the global–scale influence of biomass burning on the tropical troposphere. Considerable burning takes place in the tropics during the dry season and results in concentrations of combustion–derived gases over the tropical continents that are comparable to those found in polluted industrial regions (Crutzen *et al.*, 1990; Logan and Kirchhoff, 1986). Space–based observations in the 1980's identified high concentrations of CO in the free troposphere of the southern tropics during the dry season (Reichle *et al.*, 1990) and an O_3 maximum in the tropospheric column over the south Atlantic (Fishman *et al.*, 1990).

The TRACE–A mission (September–October 1992) was conducted in part to determine the origin of this O_3 maximum. Flights over Brazil, southern Africa, and the South Atlantic showed high O_3 associated with biomass burning pollution (Fishman *et al.*, 1996; Olson *et al.*, 1996). It was found that both South America and southern Africa contribute to the O_3 maximum over the south Atlantic, with South American influence dominating in the upper troposphere and African influence dominating at lower altitudes (Thompson *et al.*, 1996).

The PEM–Tropics A mission provided the first detailed data on atmospheric composition over the South Pacific, the most remote region of the tropical troposphere, during the dry season. Flights from Fiji, New

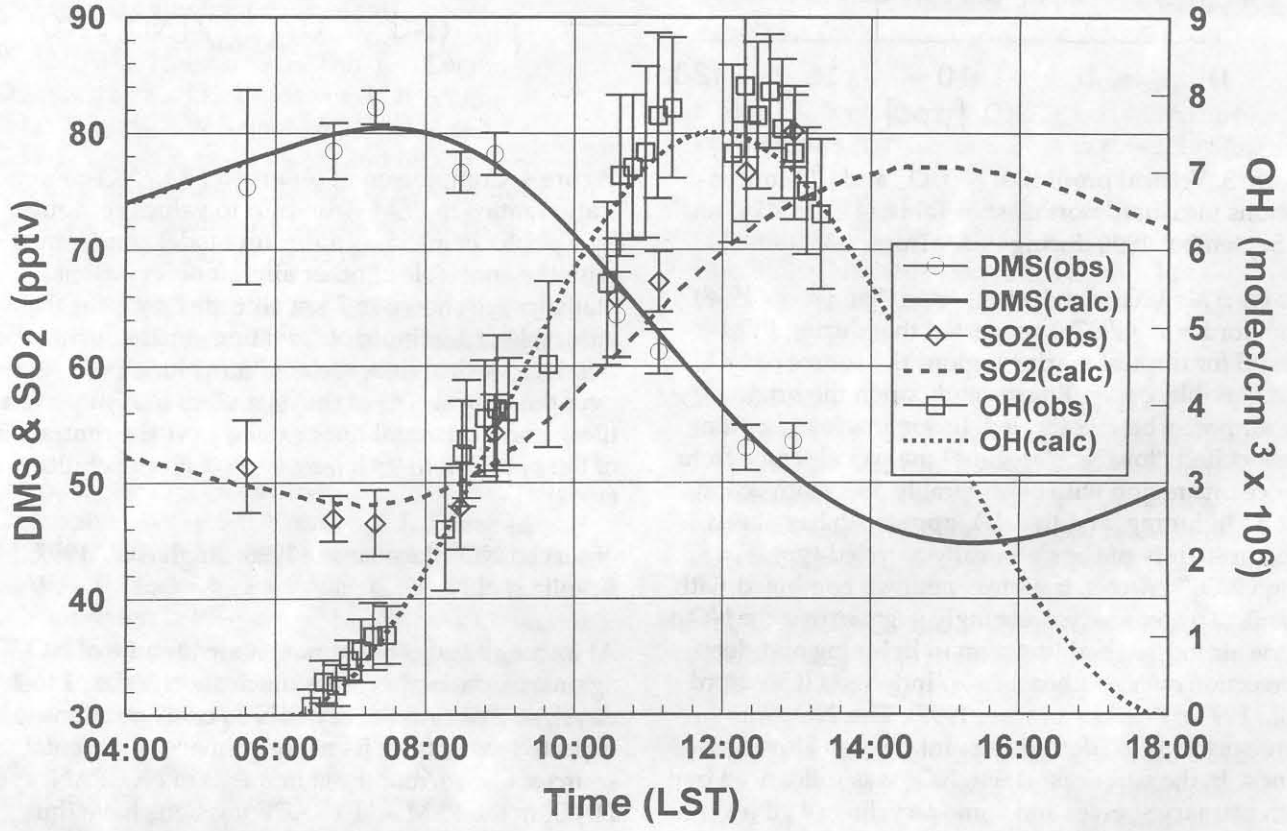

Figure 5. DMS, SO_2, and OH comparison: Model simulation vs. observation made during NASA GTE PEM–Tropics A, P–3B Flight 7 near Christmas Island, August 24, 1996.

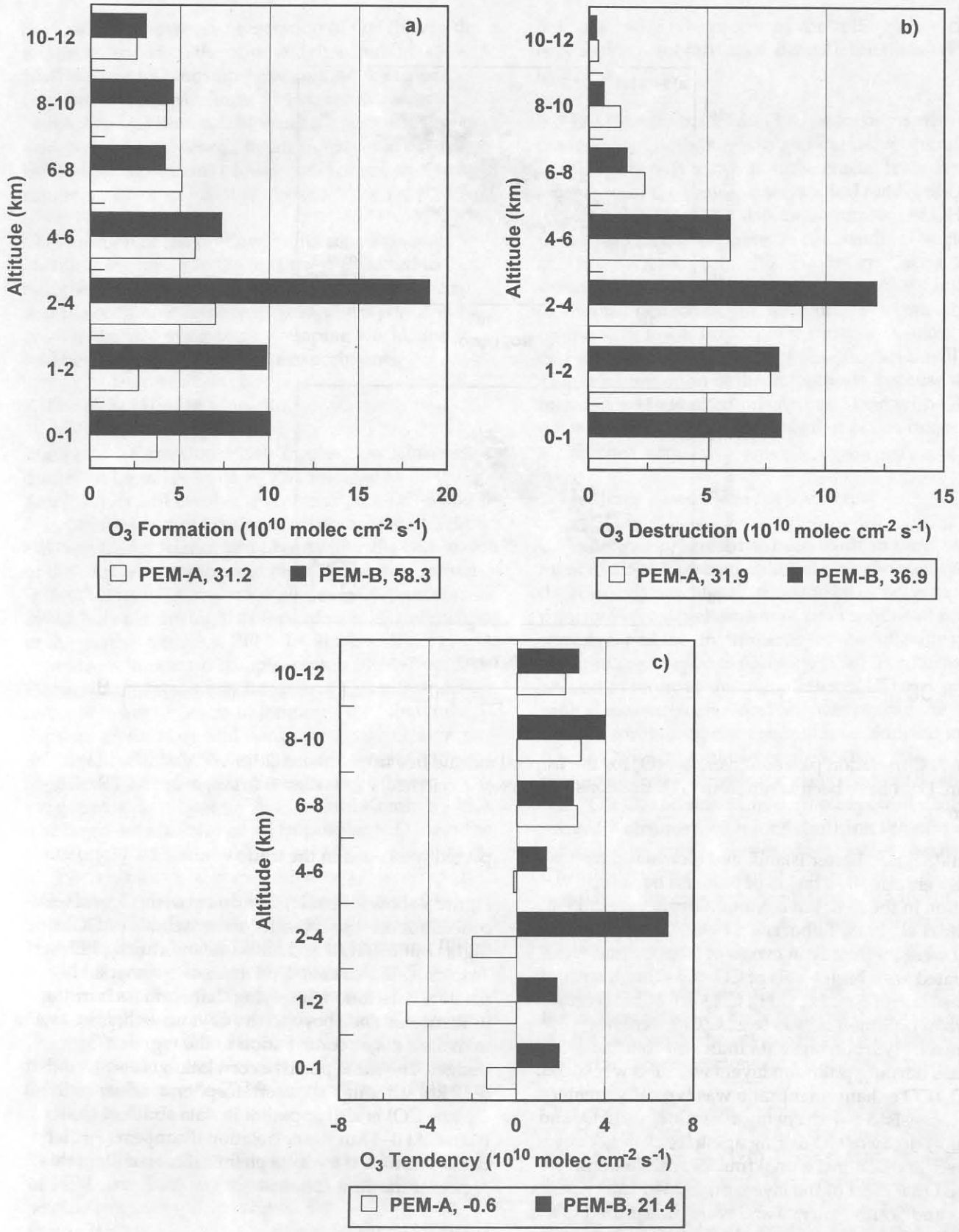

Figure 6. Diurnal–averaged column–integrated values of (a) production of O_3, $F(O_3)$; (b) destruction of O_3, $D(O_3)$; and (c) net production of O_3, $P(O_3)$. Values are calculated from time dependent box model using median observed conditions for PEM–West A (18–42°N) and PEM–West B (20–30°N). Total tropospheric column amounts are annotated at the bottom of the figure.

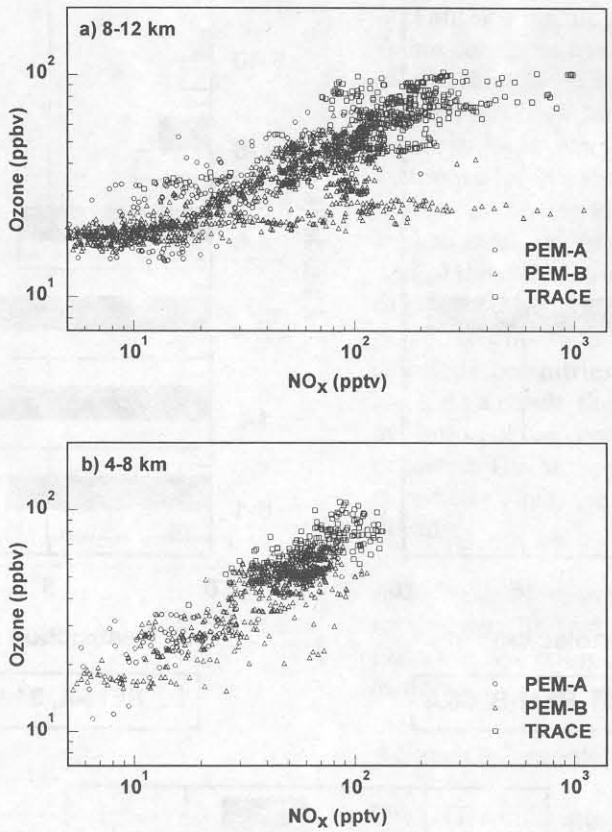

Figure 7. Correlation plot of O_3 versus NO_X for the tropical marine free troposphere (20°S–20°N): (a) 8–12 km, (b) 4–8 km. Data have been taken from GTE missions PEM–West A (circles), PEM–West B (triangles), and TRACE–A (squares).

Zealand, Tahiti, Easter Island, and Guayaquil frequently encountered layers of biomass burning pollution in the 2–12 km column (Gregory *et al.*, 1998; Schultz *et al.*, 1998; Talbot *et al.*, 1998). O_3 levels in these layers were frequently in excess of 80 ppbv and were associated with high levels of CO and other tracers of biomass burning (C_2H_2, C_2H_6, CH_3Cl, CH_3Br) (Figure 8). Urban pollution tracers (e.g., C_2Cl_4) were not enhanced. Hydrocarbon data indicated that the biomass burning pollution layers were 1–3 weeks old. The O_3/CO enhancement ratio was typically greater than 1, consistent with chemical production of O_3 and chemical decay of CO during aging. Back–trajectory analyses and 3–dimensional transport simulations showed that most of the layers originated from fires in Africa and South America and were transported to the South Pacific by strong westerly flow at subtropical latitudes (Fuelberg *et al.*, 1998). A few of the layers could have originated from fires in Indonesia and Australia. Flights along the west coast of South America also showed some fresh biomass burning plumes originating from that continent and transported westward in the trade winds.

Figure 9 shows the relationship between O_3 and CO concentrations observed for the ensemble of DC–8 flights out of Tahiti and Easter Island during PEM–Tropics A. The data at 4–8 km show a remarkable positive correlation, implying that biomass burning influence extends beyond the obvious enhanced layers to make a major contribution to the regional O_3 budget. The same positive correlation is also found at 8–12 km, although some stratospheric influence (high O_3, low CO) is also apparent in data south of Easter Island. At 0–4 km the correlation disappears, which can be attributed to rapid chemical loss of O_3 in this region of the atmosphere.

5. The Role of OH

The role of OH in controlling tropospheric chemistry is well established from laboratory kinetic studies and models. However, direct measurements of OH in clean background air, free of complex organic reactions,

where the critical controlling species for OH, as well as OH itself, have been simultaneously measured have proven to be quite elusive. The problem is rendered even more difficult by the fact that the most credible tests of models require measurements extending from daylight into twilight and night.

As noted above, the direct measurement of OH on the P3–B during PEM–Tropics A by Mauldin *et al.* (1998a) were highly successful. The tropical marine environment sampled during this mission was ideal for a photochemical experiment based on OH detection. Understanding this setting is essential for a comprehensive understanding of global HO_x chemistry. In PEM–Tropics A, a Lagrangian type sampling strategy was employed which enabled the first near–continuous set of observations to be recorded over a substantial fraction of a diel cycle (see Figure 5). The concentrations of OH are seen ranging from sunrise values near 10^5 cm^{-3} to high noon maximum values of $8x10^6$ cm^{-3}. Using concurrently measured values of the key controlling species to constrain model calculations, the agreement between model simulations and observations was found to range from 5 to 20%. This suggests that for the tropical MBL, the mechanisms in current models are representative of those operating in the real atmosphere.

The OH data also have provided the basis for a detailed examination of several other important aspects of HO_x photochemistry. Among these is the role of OH in the oxidation cycle of biogenic sulfur.

6. Sulfur Chemistry

The PEM campaigns have had a significant focus on sources of atmospheric sulfur compounds. During PEM–West A, Thornton *et al.* (1996) reported that SO_2 exhibited a marked increase in concentration with altitude owing to two major sources. One is the long range transport of northern hemispheric anthropogenic emissions injected by convection over Asia. The other is emissions from the Mt. Pinatubo volcanic eruption in June 1991 into the stratosphere followed by injections of stratospheric air back into the troposphere.

No clear gradient in SO_2 was observed in the upper troposphere during PEM–West B, and the concentrations of SO_2 also were significantly lower than in PEM–West A (Thornton *et al.*, 1997). Thornton *et al.* (1997) also concluded that during PEM–West A and B the oxidation of DMS, on average, was a relatively insignificant source of SO_2 in the free troposphere. However, of some interest was one particular observation by Thornton *et al.* (1997) and Talbot *et al.* (1997) in which there was a coincidence of elevated concentrations of DMS, SO_2, NO and CN. This observation was recorded above 9 km in the tropical convergence zone during PEM–West B and supports earlier observations by Clarke (1993) showing the production of new particles at high altitude from natural sulfur sources.

Direct measurements of OH during PEM–Tropics A (Mauldin *et al.*, 1998a) made possible more quantitative evaluations of the natural sulfur cycle. Of special interest was the oxidative cycle for DMS, the largest natural sulfur source globally, and the largest single sulfur source over much of the world's oceans (Andreae *et al.*, 1985, Bates *et al.*, 1992). For this vast region, therefore, DMS oxidation also represents the largest source of sulfate aerosol and, hence, cloud condensation nuclei (CCN). The latter play a major role in defining the radiative properties of clouds and therefore represent a critical component in efforts to understand climate forcing by aerosols (Charlson *et al.*, 1987). The results from PEM–Tropics A have significantly improved our understanding of the basic chemical processes involved in the conversion of DMS to sulfate and the formation of new particles.

During the equatorial PEM–Tropics A Lagrangian experiment, simultaneous measurements of OH, DMS, SO_2, methanesulfonic acid (MSA(g)), H_2SO_4(g), methanesulfonate (MS), and non–seasalt sulfate (NSS), as well as critical meteorological parameters, permitted one of the most intensive examinations yet of the detailed chemical processes involved. As shown in Figure 5, the decrease in DMS following sunrise is consistent with the diel cycle of OH, the latter being a major oxidizing species for DMS. Concomitant with the decrease in DMS, there also is seen a major increase in SO_2. Model simulations using these data suggest that the oxidation of DMS by OH was responsible for 90 to 95% of the SO_2 produced from DMS, and that for the boundary layer this was the dominant source of SO_2 (Davis *et al.*, 1998; Thornton *et al.*, 1998).

An internally consistent picture involving SO_2 also was developed showing that only a small fraction of this species is lost to the ocean's surface. Most of the SO_2 forms NSS but the oxidation pathway primarily involves heterogeneous reactions, including in–cloud processes. Far more surprising was the finding that MS in the boundary layer was also entirely derived from heterogeneous in–cloud processes (Davis *et al.*, 1998). Although details are still lacking, it appears that the nature of the heterogeneous chemical processes for these two DMS end products is quite different. This raises an interesting question concerning the use of the frequently cited MS/NSS ratio for sulfur source apportionment purposes for marine regions of the world.

Farther to the East, near the coasts of Costa Rica and

Panama, a quite different boundary layer sulfur experiment was performed. Unique to this setting was the presence of a very active ITCZ in the near vicinity of a coastal shelf, where there was high biological productivity and release of significant DMS. This was an ideal setting for examining the evolution of the natural sulfur cycle under conditions where aerosol surface area was minimized from precipitation scavenging. In fact, the measured surface area was more than an order of magnitude less than typically found for the MBL. Observed H_2SO_4(g) levels were also higher by nearly the same amount (Mauldin *et al.*, 1998b). This setting allowed the formation of new ultrafine particles, a process never recorded before in the MBL, but detected in PEM–Tropics A. A combination of observations and modeling showed that this nucleation event was a direct result of oxidation processes occurring within the natural sulfur cycle, starting with the oxidation of DMS via OH to produce SO_2 (Clarke *et al.*, 1998). Equally significant was the finding that classical binary nucleation theory failed to predict this event without the use of a very large "tuning factor". This may point to a deficiency in classical theory or, we suspect more likely, to alternative mechanisms, e.g., ternary nucleation.

What is quite clear is that this unique observation of a tropical nucleation event will provide a solid experimental foundation from which new theories can be tested. Thus, the outcome of these new observations should have a significant impact on our understanding of the relationship between aerosols and global climate change.

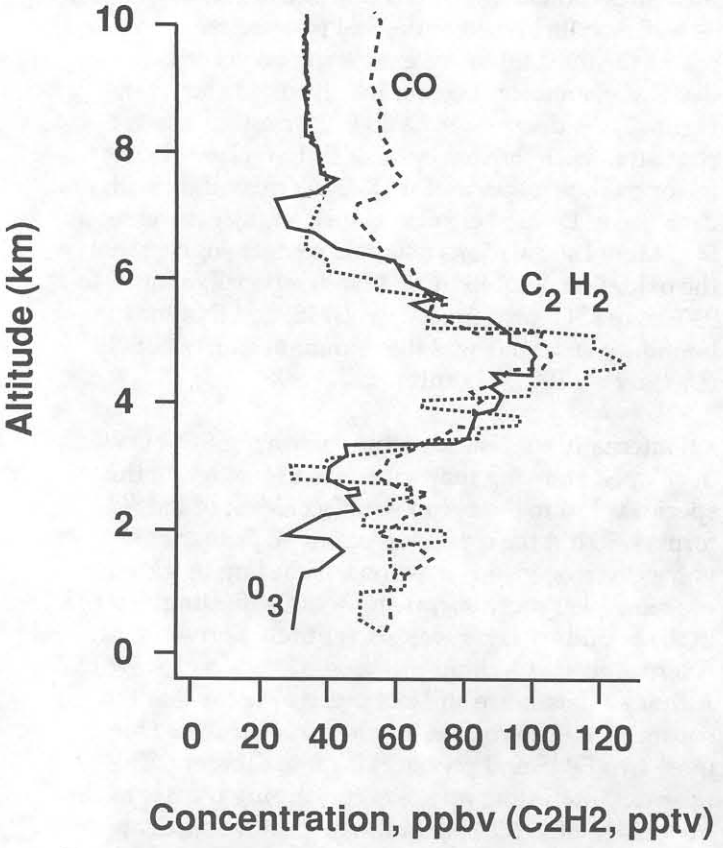

Figure 8. *In situ* profiles of selected tracer species measured in a descent through a biomass burning plume encountered near Tahiti.

7. Asian Outflow

The PEM–West missions investigated the chemical composition of the western Pacific atmosphere under different seasonal regimes of outflow from the Asian continent. The meteorological differences between PEM–West A and B can be characterized by the position and strength of the Japan Jet and the location of the Pacific High (Merrill *et al.* , 1997). During PEM–West A, the Japan Jet tended to be weaker and positioned more northerly than during the PEM–West B. As a result, PEM–West A was characterized by more inflow of marine and southern hemispheric air into the mid–tropical latitudes, accompanied by extensive vertical mixing along a typhoon storm track that ran roughly parallel with the Asian coast. The continental outflow into the lower troposphere tended to be limited to latitudes above 40°N.

In contrast, the PEM–West B period was characterized by enhanced continental outflow throughout the study region. During PEM–West B, at latitudes >20°N, high velocity strong westerlies transported Asian pollutants thousands of kilometers from the coast within 2 to 3 days after passage of a cold front. The pollutants were generally confined to below 6 km during PEM West B. Stronger convective events during PEM–West A transported pollutants to the upper troposphere and then strong westerlies carried them out to the Pacific basin (Blake *et al.*, 1996; Liu *et al.*, 1996). The implication of quick transport is that Asian outflow, enhanced in pollutants, arrives at remote ocean sites relatively "fresh" in terms of potential for photochemistry—a very important finding (Newell *et al.*, 1997; Crawford *et al.*, 1997a).

Three independent methodologies were employed to classify air masses: the backward trajectory method (Gregory *et al.*, 1996; Talbot *et al.*, 1996, 1997), the tracer signature method (Browell *et al.*, 1996; Blake *et al.*, 1997), and the hydrocarbon ratio method (Smyth *et al.*, 1996). For example, Blake *et al.* (1997) demonstrated that in both mid–latitude (>25°N) and low–latitude (<25°N) regions, the anthropogenic non–methane hydrocarbon (NMHCs) mixing ratios in the upper troposphere during PEM–West A were discernibly higher than those observed during PEM–West B. This is particularly significant because the NMHCs in the lower troposphere tend to have seasonal maxima in winter or early spring (near the time of PEM–West B)

because of the lower concentration of OH during the winter. In addition, the observed distributions of NMHCs and CO indicated clearly that the upper tropospheric distributions of trace species with photochemical lifetimes of about a week or longer were strongly influenced by air masses that originated in the upwind regions of Asia, i.e., Europe and beyond (Liu *et al.*, 1996; Smyth *et al.*, 1996; McKeen *et al.*, 1996).

The question of the outflow from continents and the chemical evolution of the outflow is expected to become increasingly urgent as the population rises and the economic activity increases on a per capita basis in the emerging and developing world, and it will be a major focus of future experiments.

8. The Next Mission

The next GTE mission, PEM–Tropics B, will be conducted in January–April 1999 as a sequel to PEM–Tropics A. It will involve two aircraft, the DC–8 and P–3B, operating out of Hawaii, Christmas Island, Tahiti, Fiji, and Easter Island. January–April is the wet season of the southern tropics, and biomass burning influence is then minimal (Kirchhoff *et al.*, 1991; Olson *et al.*, 1996); burning during that time of year is concentrated in the northern tropics. PEM–Tropics B will thus provide an important complement to PEM–Tropics A. Ozonesonde data at Fiji, Tahiti, and Easter Island indicate lower O_3 levels in January–April than in September–October, and none of the high O_3 layers (>80 ppbv) that are observed in September–October. Surface O_3 at Samoa is at its seasonal minimum, averaging only 10 ppbv (Oltmans and Komhyr, 1986). The large–scale minimum of tropospheric O_3 over the Equatorial Pacific (Routhier *et al.*, 1980; Piotrowicz *et al.*, 1991) is particularly extensive in January–April, stretching from the western Pacific warm pool to South America (Fishman *et al.*, 1990). Some biomass burning influence could still be present during PEM–Tropics B due to long–range transport from the northern tropics. Asian outflow circulating around the Pacific High also could provide a source of trace gases over the Equatorial Pacific (Merrill *et al.*, 1985; Merrill, 1989). Lightning over Oceania will be near its seasonal maximum during the PEM–Tropics B period (Turman and Edgar, 1982).

The objectives of PEM–Tropics B extend beyond those of PEM–Tropics A to include focused studies of (1) fast photochemical processes involving the HO_x radical family (HO_x = OH + H + peroxy radicals), (2) the cause of the large–scale ozone minimum over the western equatorial Pacific, (3) vertical transport by deep convection in the SPCZ and ITCZ, (4) the scavenging of gases and aerosols associated with deep convection and gas to aerosol conversion in convective outflow, and (5) the processes controlling photochemistry and aerosol formation beneath the trade wind inversion.

In PEM–Tropics B, OH and HO_2 measurements will be made aboard both the P–3B and the DC–8 aircraft, enabling not only a repeat of the crucial boundary layer tests of the basic photochemical model of OH formation and loss but also measurements of OH in the upper free troposphere. Recent studies (Jaegle *et al.*, 1997; McKeen *et al.*, 1997, Prather and Jacob, 1997; Wennberg *et al.*, 1998) have pointed out that photolysis of acetone, peroxides, and formaldehyde transported up from the lower troposphere must be invoked to explain observed OH levels. PEM–Tropics B will allow a close examination of this hypothesis, because it will measure the suspected precursors, along with OH and other atmospheric constituents that play a major role in OH chemistry.

9. Challenges and Plans for the Future

Considerable progress has been made in the development of aircraft instrumentation over the past two decades, but much more needs to be done. A top priority is the development of an ensemble of reliable, sensitive, and fast instruments for the full suite of major nitrogen species (Crosley, 1996). Further work is needed to improve the capabilities of OH and peroxy radical measurements, and an intercomparison mission for these species should be conducted in the future. Other important gas phase species for which current aircraft instrumentation is inadequate include NH_3, CH_2O, and other carbonyl compounds. Improved instrumentation for measuring the microphysical and chemical properties of aerosols is also needed. Chemical flux measurement capabilities by eddy correlation are presently limited to a handful of species (CO_2, CH_4, O_3, CO) and should be extended to others.

There are two missions under consideration for 2001, the next opportunity for a large–scale experiment. Both deal with the broad questions of the impact of important source regions on the global atmosphere.

One of the two candidate missions to follow PEM–Tropics B is TRACE–B (TRAnsport and Chemistry near the Equator—Brazil). Plans for this mission have been developed in two GTE workshops and a white paper is available (Jacob *et al.*, 1995). The goal of TRACE–B would be to understand the contribution of Amazonia to the global atmospheric budgets of greenhouse gases, aerosols, and oxidants, and to determine the related implications of rapid development and exploitation of natural resources in the region. It would be conducted as part of the Large–

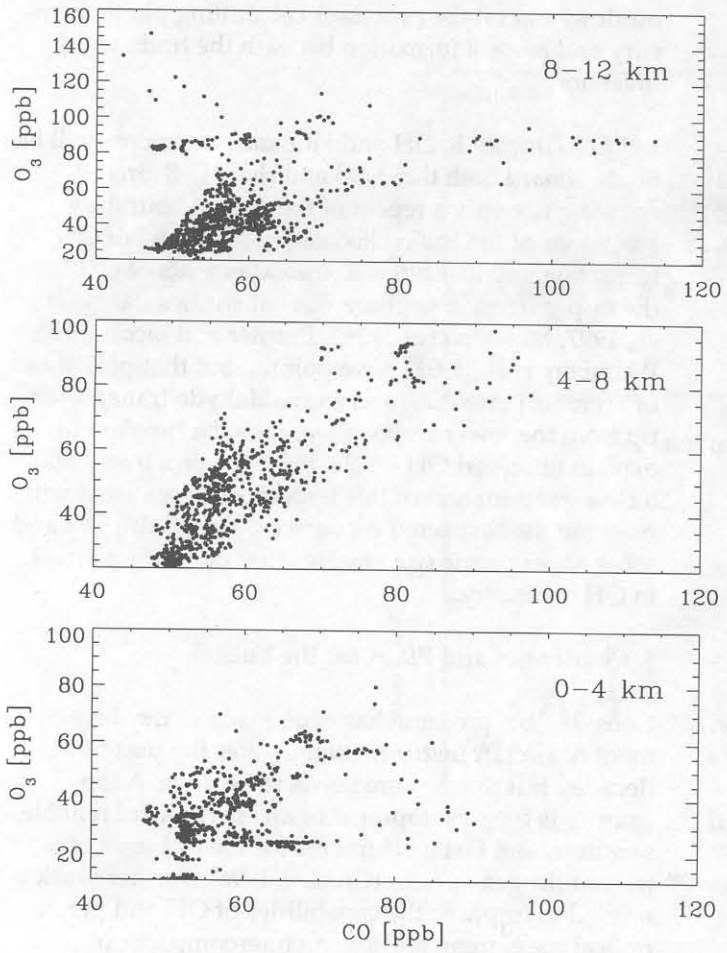

Figure 9. Relationship of O_3 and CO concentrations at different altitudes measured in sorties out of Tahiti and Easter Island during PEM–Tropics A in September 1996.

Scale Biosphere–Atmosphere Experiment in Amazonia (LBA), an ongoing international program aimed at improving knowledge of the regional moisture, energy, biogeochemical, and trace gas budgets and their perturbation by human activity. To minimize the influence of biomass burning, a January–March time frame would be optimal for TRACE–B. The data collected in TRACE–B, in combination with the continuous ground–based biogeochemical measurements conducted independently as part of LBA, would allow investigation of spatial variations of trace gas fluxes along ecosystem gradients, of atmospheric budgets of trace species over the scale of the Amazon Basin, and of long range transport across Basin boundaries.

The other candidate mission is TRACE–P (TRAnsport and Chemical Evolution over the Pacific). Plans for this mission were developed at a recent GTE workshop and a white paper is available (Jacob *et al.*, 1998). The goal of TRACE–P is to determine the chemical and physical evolution of the outflow of natural and anthropogenic gases and aerosols from the Asian continent to the western Pacific. TRACE–P would respond to strong interest in the scientific community to better understand the extent of Asian influence on global atmospheric chemistry. Compared to the two other major industrialized regions of the world (North America and Europe), far less is known of emissions from eastern Asia and of the chemistry of the Asian outflow. The mix of anthropogenic and natural emissions is expected to differ substantially from that in the more developed countries of North America and Europe. As a result, the chemical composition and evolution of the continental outflow may be quite different. The anthropogenic contribution is expected to increase sharply during the next decade.

A decision between these two candidate missions for the year 2001 will be made in an *ad hoc* mission planning workshop to be held late in 1998 or early in 1999.

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Comment and Reply

Comment on "Sulfate Versus Carbonaceous Materials on the East Coast of the United States: Results from TARFOX"

H. Rodhe (Stockholm University, Sweden), T. Bates (NOAA/PMEL, USA), R. Charlson (Univ. of Washington, USA), J. Heintzenberg (Inst. for Tropospheric Research, Germany), and B. Huebert (Univ. of Hawaii, USA (Received 7 May 1998.)

In the January 1998 issue of the IGAC*tivities* News letter—later copied in the March 1998 Global Change Newsletter of IGBP—Peter Hobbs reported on results from the Tropospheric Aerosol Radiation Forcing Observational Experiment (TARFOX) carried out off the East Coast of the U.S. in July 1996. His conclusion was that carbonaceous aerosol dominated the aerosol optical depth over a vertical column from the surface to 3 km elevation and that such aerosol would then also dominate the aerosol radiative forcing in this region. We commend Hobbs for having contributed to the collection and analysis of a valuable set of data and appreciate his plea for more attention to be placed on atmospheric concentration of carbonaceous aerosol material in future measurement programs. However, we think that he is too quick to jump to conclusions regarding the contribution of such aerosol to radiative forcing.

IPCC carefully defines 'radiative forcing' as the perturbation (in general anthropogenic) in the net irradiance at the tropopause level. In the case of the carbonaceous material a substantial fraction is likely to be due to natural sources which should then not be included in the forcing estimate. For sulfate, on the other hand, many studies have shown that anthropogenic sources greatly exceed natural ones in the region of the TARFOX study. Therefore, we believe that Hobbs' use of the term radiative forcing is misleading.

Another important question, not adequately addressed by Hobbs, is the contribution to the optical depth of the cations and water associated with the sulfate. Sulfate normally occurs in molecular forms ranging from pure sulfuric acid to ammonium sulfate. In the latter case the mass of the sulfate ion accounts for only 72% of the total molecular mass. Furthermore, given the high hygroscopicity of sulfuric acid and sulfate salts compared to that of most organic molecules, it seems likely that the largest part of the water reported by Hobbs is associated with the sulfate. Both ionic and hygroscopic effects increase the relative importance of sulfate compared to that of organic aerosol components in radiative forcing.

Given also the substantial uncertainties in the measurements of the airborne carbonaceous material, we do not think that there is convincing evidence for Hobbs' conclusion that such material is more important than sulfate for radiative forcing at this site.

Reply

P.V. Hobbs (Univ. of Washington, USA) (Received 12 May 1998)

"Although I am fully convinced of the truth of the views given in this volume..., I by no means expect to convince experienced naturalists whose minds are stocked with a multitude of facts all viewed, during a long course of years, from a point of view directly opposite to mine."

Charles Darwin
Origin of Species

"When paradigms enter, as they must, into a debate about paradigm choice, their role is necessarily circular. Each group uses its own paradigm to argue in that paradigm's defense."

Thomas S. Kuhn
The Structure of Scientific Revolutions

My brief article in the IGAC*tivities* NewsLetter summarized some of the interesting and surprising results that have emerged so far from TARFOX. Details of these results are given by Hegg *et al.* (1997) and Novakov *et al.* (1997), to which papers the reader is referred for more information.

Only two substantive and interrelated points are raised by Rodhe *et al.* The first concerns the distribution of the condensed water between the sulfate and organic aerosol. This issue was discussed by Hegg *et al.* Even if a very generous hygroscopic (or humidification) scattering factor of 3 is assumed for sulfate, wet sulfate contributed less than 50% to the measured column optical depths in TARFOX. If a more reasonable hygroscopic scattering factor for sulfate of 2 is used, wet sulfate contributed less than 30% to the column optical depths. The second point concerns the impact of the cations, supposedly associated with sulfate, on the "sulfate" mass scattering efficiency. Rodhe *et al.* apparently still advocate a model for the atmospheric aerosol for which there is diminishing support (see Hegg *et al.*, 1994).
We can all agree that improvements are needed in the measurements of carbonaceous materials. However, as discussed in some detail by Novakov *et al.*, we adopted a very conservative approach in deriving the concentrations of carbonaceous materials from the thermal evolution technique used in TARFOX. Consequently, the concentrations of carbonaceous materials may well have been greater than those used in our analyzes. It is quite unlikely that they were less.

The only other issue raised by Rodhe *et al.* concerns semantics. As is commonly done, we have used the term "aerosol radiative forcing" to refer to the perturbation in the net irradiance at the tropopause level produced by all of the aerosol in a vertical column. The TARFOX results provide information on how this perturbation was divided between sulfates and carbonaceous materials on the East Coast of the United States during the period of our field study. We have not attempted to address the more difficult problem of determining the relative contributions of natural and anthropogenic sources to these two materials, although we did point out that a significant fraction of the carbonaceous aerosol is probably natural.

Finally, neither Hegg *et al.*, Novakov *et al.*, nor I have claimed that there is "convincing evidence" that carbonaceous materials are more important than sulfate in radiative forcing. I repeat the last sentence of the conclusion to my article in the January 1998 IGAC*tivities* NewsLetter: "While one data set collected in one location is by no means definitive, it indicates that much more attention needs to be placed on carbonaceous materials in the atmosphere, and that measurements similar to those obtained in TARFOX should be made in other airsheds around the world."

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Correction

In the article, "The Budget of Methane from Rice Fields" by H.-U. Neue and R. Sass published in the previous issue of this newsletter (No. 12), the units for seasonal emission of methane in Table 2 (p. 6) should have read: kg CH_4 ha^{-1}.

Announcements

IGAC Tracegas Merger (ITM) Open Meeting

23 August 1998
Seattle, Washington, USA

At its last meeting held in Nagoya, Japan, the IGAC Scientific Council decided to modify the overall structure of IGAC. The motivation was to refocus IGAC's Activities around a limited number of scientific themes instead of the original mostly geographic structure. A proposal was made to combine the current Activities BATGE, HESS, RICE, TRAGEX that have been working on terrestrial biosphere-atmosphere trace gas exchange. This proposal will be discussed on 23 August 1998 during the CACGP/IGAC Symposium on Global Atmospheric Chemistry in Seattle, Washington, USA. Interested experts will have the opportunity to join efforts and consolidate the proposed merger into a new IGAC Activity. The main thrust of the ITM meeting is to bring the terrestrial biosphere-atmosphere trace gas community together to discuss the merger and propose to the IGAC Scientific Council:

- a science plan
- structure, name, and mode of operation
- implementation plan for the period 1999-2003
- members and Conveners of a Coordinating Committee

All interested persons are invited to participate. For further information contact:

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For information about the CACGP/IGAC Symposium see: http://saga.pmel.noaa.gov/cacgp98/

Lesovedenie Now Available in English Translation

Beginning in 1998 the journal *Russian Forest Sciences (Lesovedenie)* is being published in English translation. This journal is the primary source for information about Russian forest ecology. Articles by authors from Russia, the Commonwealth of Independent States, and Eastern Europe describe the results of recent research and research methodology and review various problems of forest science.

Authors analyze ecosystems and their ecology in terms of their structure and biodiversity, the interrelations of separate components, primary and secondary biological productivity, feeding and water element cycles, carbon cycles, vegetation successions, typology of ecosystems, modeling of ecological processes and the influence of anthropogenic factors (fires, cuttings and chemical emissions). In addition, the journal publishes articles on boreal, temperate, and broad-leaf forests and the role of Russian forests in global climate change. The use of aerospace methods for forest monitoring receives special emphasis. Many articles are devoted to research on separate forest-forming species (more than sixty of which have been found in the forests of Russia).

The journal also includes works on ecology, ecophysiology, genetics and selection, dendrometry of some species and genera, on forestry (cutting, forest reproduction, planting, etc.), forest pathology and protection, wood resources, and analysis of other biological resources.

For further information or to subscribe to this scientific journal contact:

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IGAC Directory of Data on the Chemical Composition of the Atmosphere

Initiated in March of 1997, IGAC's index of locator information for data on atmospheric chemical composition archived in various locations around the world now has more than 60 listings and continues to grow. It is available on:

http://web.mit.edu/afs/athena.mit.edu/org/i/igac/www/datadirec.html

All scientists who make field measurements of atmospheric composition are encouraged to contribute to this index and make it an increasingly useful resource for the community.

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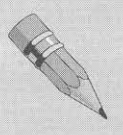
Please return to the IGAC Core Project Office by mail or email the information to: igac@mit.edu



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