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Chemical characteristics of continental outflow over the tropical South Atlantic Ocean from Brazil and Africa

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Abstract. The chemical characteristics of air parcels over the tropical South Atlantic during September - October 1992 are summarized by analysis of aged marine and continental outflow classifications. Positive correlations between CO and CH_3Cl and minimal enhancements of C_2Cl_4 and various chlorofluorocarbon (CFC) species in air parcels recently advected over the South Atlantic basin strongly suggest an impact on tropospheric chemistry from biomass burning on adjacent continental areas of Brazil and Africa. Comparison of the composition of aged Pacific air with aged marine air over the South Atlantic basin from 0.3 to 12.5 km altitude indicates potential accumulation of long-lived species during the local dry season. This may amount to enhancements of up to two-fold for C_2H_6, 30% for CO, and 10% for CH_3Cl. Nitric oxide and NO_x were significantly enhanced (up to ~1 part per billion by volume (ppbv)) above 10 km altitude and poorly correlated with CO and CH_3Cl. In addition, median mixing ratios of NO and NO_x were essentially identical in aged marine and continental outflow air masses. It appears that in addition to biomass burning, lightning or recycled reactive nitrogen may be an important source of NO_x to the upper troposphere. Methane exhibited a monotonic increase with altitude from ~1690 to 1720 ppbv in both aged marine and continental outflow air masses. The largest mixing ratios in the upper troposphere were often anticorrelated with CO, CH_3Cl, and CO_2, suggesting CH_4 contributions from natural sources. We also argue, based on CH_4/CO ratios and relationships with various hydrocarbon and CFC species, that inputs from biomass burning and the northern hemisphere are unlikely to be the dominant sources of CO, CH_4, and C_2H_6 in aged marine air. Emissions from urban areas would seem to be necessary to account for the distribution of at least CH_4 and C_2H_6. Over the African and South American continents an efficient mechanism of convective vertical transport coupled with large-scale circulations conveys biomass burning, urban, and natural emissions to the upper troposphere over the South Atlantic basin. Slow subsidence over the eastern South Atlantic basin may play an important role in establishing and maintaining the rather uniform vertical distribution of long-lived species over this region. The common occurrence of values greater than 1 for the ratio CH_3OOH/H_2O_2 in the upper troposphere suggests that precipitation scavenging effectively removed highly water soluble gases (H_2O_2, HNO_3, HCOOH, and CH_3COOH) and aerosols during vertical convective transport over the continents. However, horizontal injection of biomass burning products over the South Atlantic, particularly water soluble species and aerosol particles, was frequent below 6 km altitude.

1. Introduction

Field measurements of biomass fire emissions in the tropics have been sparsely scattered over tropical forest and savanna regions of Brazil and the continent of Africa during the last decade. The scope of these studies has been limited geographically and also chemically to a small suite of species at each location. These studies show greatly enhanced local mixing ratios of tropospheric CO, CO_2, CH_4, HCOOH, CH_3COOH, NO, selected nonmethane hydrocarbons, particulate elemental species such as P, S, Cl, Mg, K, Ca, graphitic (soot) C, and organic carbon [*Leslie,* 1981; *Greenberg et al.,* 1984; *Cachier et al.,*

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1985, 1989; *Andreae et al.*, 1988; *Kirchhoff et al.*, 1990, 1994; *Helas et al.*, 1992; *Rudolph et al.*, 1992]. Estimates suggest that these emissions are important on various scales, ranging from causing regional air pollution problems [*Kirchhoff et al.*, 1990] to being a significant global source of tropospheric species [*Crutzen et al.*, 1979; *Andreae et al.*, 1988; *Crutzen and Andreae*, 1990].

The environmental consequences of biomass fires are diverse. Denitrification during biomass burning, where as much as 50% of the fuel nitrogen is released as N_2 [*Kuhlbusch et al.*, 1991], may cause sizable loss of fixed nitrogen from tropical ecosystems [*Crutzen and Andreae*, 1990]. Burning emissions of some C, N, and S compounds leads to production of acidic gases, and these subsequently cause acid rainfall [*Lacaux et al.*, 1992]. Release of smoke particles from biomass fires may provide copius amounts of cloud condensation nuclei, and therefore play a role in cloud formation and precipitation in the tropics [*Crutzen and Andreae*, 1990; *Cachier and Ducret*, 1991].

Perhaps one of the most important consequences of biomass fire emissions is widespread photochemical production of O_3 coupled with its coincident rapid transport. This phenomenon has been observed in the tropics on regional [*Andreae et al.*, 1992; *Kirchhoff et al.*, 1990, 1994] to hemispheric scales [*Fishman et al.*, 1991]. In addition, the seasonality and large-scale influence of biomass fire emissions in the southern hemisphere appears to be evident in the annual cycles of CO and CH_4 [*Fishman et al.*, 1991].

Together these observations suggest that a large-scale, comprehensive investigation of biomass fire emissions should be conducted in the southern hemisphere concentrating on the influence of fires occurring in Brazil and southern Africa during the local dry season. The NASA TRACE A (Transport and Chemistry Near the Equator - Atlantic) airborne expedition in September - October 1992 provided a unique database to address many of the important issues related to these particular fire emissions. This paper summarizes the chemical characteristics of air parcels exported from the South American and African continents out over the South Atlantic and Indian Oceans during the local dry season. We argue that the polluted composition of these air parcels was largely biased by biomass fire emissions on both continents and that this source is a major cause of hemispheric scale air pollution. The impact of these emissions on tropospheric chemical cycles in the southern hemisphere is the focus of companion papers [*Heikes et al.*, this issue; *Jacob et al.*, this issue; *Kirchhoff et al.*, this issue; *Olson et al.*, this issue].

2. Experiment

The TRACE A expedition was conducted aboard the NASA Ames DC-8 research aircraft. Transit and intensive site science missions composed 19 flights, each averaging 8 hours in duration and covering the altitude range of 0.3-12.5 km. In this paper we utilize data obtained over the South Atlantic and Indian Oceans, centered in the geographic grid bounded by 5°N - 35°S latitude and 41°E to 55°W longitude. A map of this region with the flight tracks over the tropical South Atlantic superimposed on it is shown in Figure 1. The aircraft base of operations for these missions progressed from (1) Recife (one mission) to Brasilia (three missions), and then to Rio de Janerio (one mission) in Brazil; (2) Johannesburg (three missions) in South Africa; (3)

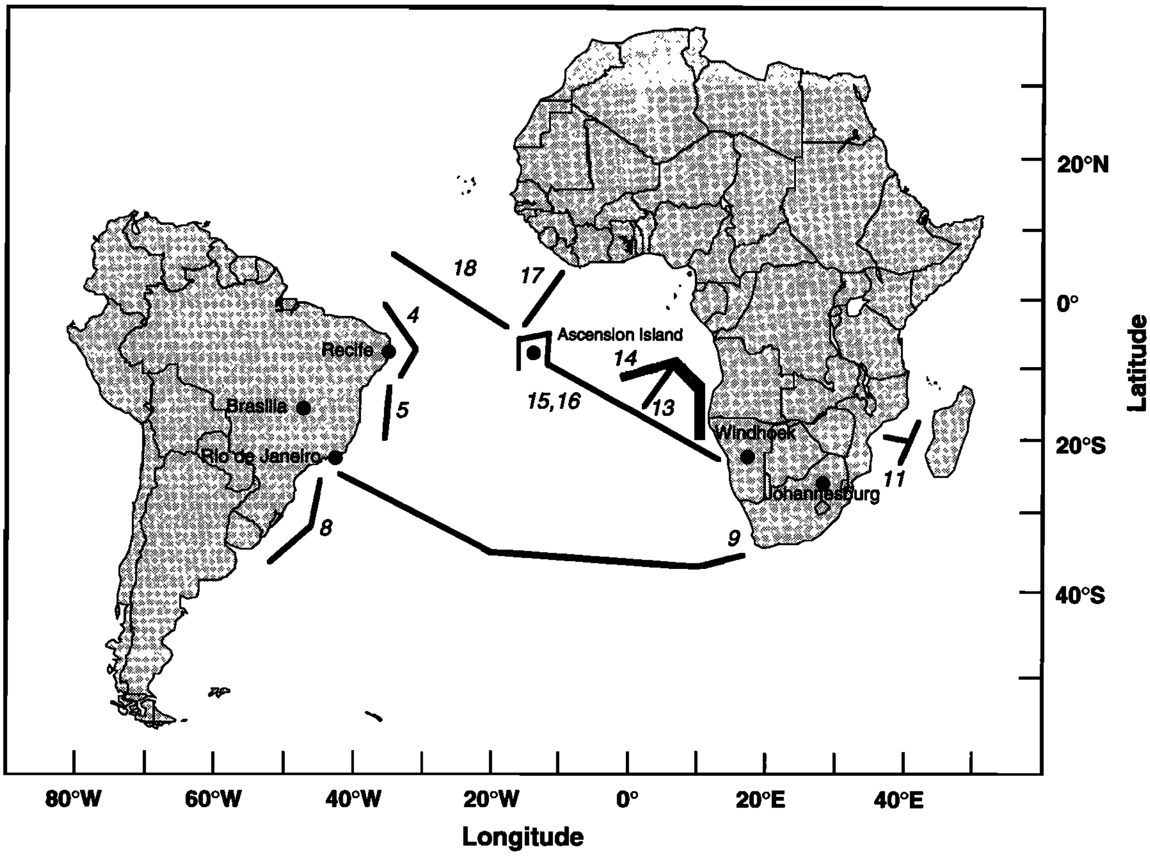


Figure 1. Map of the (TRACE A) study area with the DC-8 flight paths over the tropical South Atlantic Ocean superimposed. Solid lines depict aircraft flight tracks and associated numbers indicate the particular mission. Bases of DC-8 operation are also shown.

Windhoek (four missions) in Namibia; and finally (4) Ascension Island (two missions) in the central tropical South Atlantic.

The overall scientific rationale and description of the individual aircraft missions is described in the TRACE A overview paper [*Fishman et al.*, this issue]. The salient features of the large-scale meteorological regime are provided by *Bachmeier and Fuelberg* [this issue]. Since we present a broad description of the observed chemical composition of air parcels in continental outflow conditions, it is impractical to provide the details here for the individual species measurements. Instead, the philosophy adopted for TRACE A was to present measurement-specific details in the mission overview paper [*Fishman et al.*, this issue]. To summarize the chemistry of continental outflow, 29 individual gas phase species were selected plus aerosol number density information binned in the 0.12- to 3.1-μm-diameter range. The chemical composition of the atmospheric aerosol was not determined during TRACE A. Due to questions regarding the exact suite of compounds being measured by current total reactive nitrogen (NO_y) instruments [*S.T. Sandholm, et al.*, Comparison of N_xO_y budgets from NASA's ABLE-3, PEM-W, and TRACE-A measurement programs: An update, *J. Geophys. Res.*, submitted, 1996], we use the sum of the species-specific measurements to represent NO_y (ΣNO_{yi} = nitric oxide [NO] + nitrogen dioxide [NO_2] + nitric acid [HNO_3] + peroxyacetylnitrate [PAN].

3. Formulation of Continental Outflow Data Set

3.1. Meteorological Basis

The detailed synoptic meteorological scheme leading to outflow of South American and African continental air masses over the South Atlantic and Indian Oceans is described elsewhere [*Pickering et al.*, 1994; *Garstang et al*, this issue; *Bachmeier and Fuelberg*, this issue]. This section provides a brief description of the large-scale flow regime which established the general environmental conditions for outflow of continental air parcels to the marine atmosphere.

Prior to the TRACE A mission, relatively few details were known about the atmospheric flow patterns over the tropical South Atlantic Ocean. This region is under the general influence of slow subsidence, as evidenced by the clear skies and sparce precipitation. A major oceanic anticyclone is located near 30 °S which tends to dominate the flow in the TRACE A study area. This feature is sufficiently large that it can sweep air from over Brazil or Africa to the central tropical South Atlantic in 2 - 3 days [*Krishnamurti et al.*, 1993]. Weaker cyclonic and anticyclonic circulations are located over Africa that transport air parcels either to the east over the Indian Ocean or westward to the tropical South Atlantic Ocean. Anticyclonic flow over southcentral Brazil is confined by the origraphic feature of the Andes Mountains on the west, so most of the air exits the continent to the southeast. The NASA DC-8 aircraft sampled each of these persistent continental outflow regimes during the TRACE A expedition.

3.2. Measurement Database

Extensive processing of final archived data was required to obtain the data products utilized in our analysis here. Because of the diversity in measurement time resolutions for the species of interest, merged data products were used on various timescales. The principal database was 90-s averaged data that corresponded to the highest resolution NO_x (NO + NO_2) measurements. The measurements of faster response instruments (e.g., meteorological parameters, aerosol number density, and species including O_3, CO, CO_2, CH_4, and N_2O) were averaged to coincide with the 90-s time base. Merged data products on various time resolutions were used for species with time resolutions longer than 90 s (i.e., acidic gases, peroxides, peroxyacetylnitrate, hydrocarbons, and halocarbons).

3.3. Classification of the Database

Isentropic back trajectories were used to identify time intervals on constant altitude flight legs where the sampled air parcels had recently (<1 - 5 days) passed over continental areas of Brazil or southern Africa [*Bachmeier and Fuelberg*, this issue]. The chemical characteristics of continental outflow are captured in this air mass classification. A second major data group was compiled which contained air parcels from over the ocean that had not passed over continental areas within the past 5 days. These data represent the aged marine air classification. For both air mass classifications, data were included for altitude changes of 3 km or less where the chemistry (as indicated mainly by NO, CO, and C_2H_6) was uniform. Data obtained during spirals was not used here due to heterogeneity in air masses and practical limitations imposed by the vertical density of trajectories. Air parcels of primarily stratospheric composition were also eliminated from the data groups using N_2O, which has a uniform tropospheric mixing ratio of 308 - 312 parts per billion by volume (ppbv). A cutoff mixing ratio of 308 ppbv and above was used to distinguish tropospheric from stratospheric (<308 ppbv) air.

Two outflow data sets were developed, one for air parcels sampled over the western South Atlantic and the other for the eastern basin near Africa. This latter set included data obtained over the Indian Ocean during one flight between Africa and Madagascar. For some analyses here, the outflow and aged marine data sets were divided into three altitude bands: 0 - 4.9 km, 5 - 9.9 km, and 10 - 13 km. These altitude breakdowns provided chemical depictions of air masses in the lower, middle, and upper troposphere. The rationale for these divisions was based on the fact that above 10 km altitude the air parcels had distinctly different chemistry than below this level; thus these data comprised one group and the region below 10 km was split evenly into two more groups. For most species this provided an approximately equal distribution of data between the two lower-altitude bins.

4. Characteristics of Air Parcels Over the Tropical South Atlantic

4.1. Aged Marine Air Parcels

The aged marine classification represents air parcels that have not been recently (< 5 days) influenced by continental emissions. The chemistry of this classification is summarized in Table 1. The most aged air parcels appear to be contained below 5 km altitude, as evidenced by the smallest mixing ratios there of NO, C_2H_6, C_3H_8, C_2H_2, and lowest ratio values of C_2H_2/CO and C_3H_8/C_2H_6. In the marine boundary layer the sampled air parcels had trajectories leading typically back to high latitudes over the South Atlantic. These air parcels probably had been over the ocean for a week or two, based on mixing ratios in the 65 ppbv range for CO and 300-400 pptv for C_2H_6. Deposition to the surface ocean would also deplete many species. A detailed discussion of the processes affecting the chemistry of the marine boundary layer is in a companion paper [*Heikes et al.*, this issue].

Within the aged marine air classification, several species showed a trend of increased mixing ratio with altitude (Figure 2). The most dramatic increase was above 10 km. Air parcels in the 10 to 13-km range appear to show a combustion influence based on the increased mixing ratios of C_2H_6, C_3H_8, and C_2H_2 compared to those at lower altitudes. Halocarbon industrial tracers did not follow the trend exhibited by these hydrocarbon species, but CH_3Cl did. The CH_3Cl enhancement is evidence for a biomass

Table 1. Mixing Ratios of Principal Species Measured in Aged Marine Air Over the Tropical South Atlantic Ocean

	0 – 4.9 km					5 – 9 9 km					10 – 13 km				
Species	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	13	9.5	10	1.9-89	203	49	51	30	1.6-353	366	174	127	114	7.6-805	549
NO_x	43	22	38	14-129	158	68	56	57	17-533	215	182	133	121	1.2-908	549
HNO_3	191	131	61	8.0-566	159	85	66	63	14-383	173	65	33	45	14-180	254
PAN	62	86	25	1.0-461	87	181	92	179	27-559		198	72	186	76-429	175
ΣNO_{yi}	219	158	187	98-170	183	195	128	164	103-658	280	256	167	201	102-1163	487
O_3	42	14	39	21-80	373	58	14	57	32-101	468	71	13	70	40-102	685
CO	76	12	72	60-100	368	82	11	83	59-104	452	86	8	87	63-102	677
CH_4	1687	11	1683	1663-1720	369	1704	13	1703	1673-1736	432	1716	10	1717	1684-1742	677
CO_3	355.0	0.78	354.9	352 5-357.5	349	354.6	0.77	574.7	351.9-356.5	443	354.0	1.1	353.9	349.9-356.9	626
N_2O	309.6	0.43	309.0	308.7-311 1	191	309.9	0.48	309.5	308.4-311.1	295	310.0	0.47	309.9	308.0-311.0	532
C_2H_2/CO	0.18	0.07	0 11	0.11-0.40	191	0 22	0 09	0.15	0.11-0.53	191	0.26	0 06	0.18	0.12-0.45	225
C_3H_8/C_2H_6	0.06	0.08	0.03	0.02-0 56	213	0.08	0.05	0.05	0 02-0.26	203	0.50	0.33	0 25	0 11-0.96	242
C_2H_6	397	102	313	286-854	214	537	195	425	287-1448	203	642	188	590	383-1773	248
C_3H_8	24	32	15	7 1-339	214	51	53	35	7.1-369	202	73	55	60	19-484	246
C_2H_2	60	27	38	27-164	213	80	37	60	33-324	203	88	23	72	42-159	248
C_2H_4	13	15	16	2-184	168	9	8	4	2-69	139	9	3	7	3-22	186
CH_3Cl	616	23	613	549-668	215	634	30	629	579-812	203	652	40	644	618-857	248
C_2Cl_4	3.5	1.9	2.6	2.3-27	200	3 0	0.95	2.9	0.3-8.5	171	3.0	0.71	2.9	0.9-5.1	219
CFC-11	259.5	3.4	259.9	248.5-265.8	202	260.1	4.2	260.0	245.7-268.5	174	260.7	2.7	260.5	250.7-268.9	221
CFC-12	489.0	4.4	488.3	479.4-507.6	210	491.0	4.4	490.7	483.2-504.2	172	494.7	3.3	494.5	488.4-506.1	219
CFC-113	78.8	1 2	78.8	75.6-81.1	202	78.3	1.6	78.0	75.3-86.6	175	79.0	1.7	79.0	72.7-87.9	221
CH_3CCl_3	124	6.7	124	102-134	210	122	5.2	122	98-137	173	123	5 8	122	106-135	215
CCl_4	101	2.4	101	85-106	215	98	4.6	98	72-110	203	97	6	96	71-106	246
C_6H_6	14	10	12	3.1-110	212	13	8.7	12	2 5-61	175	13	6.7	12	2.8-37	221
HCOOH	516	313	415	10-1554	146	693	415	595	175-1876	169	576	282	550	93-1589	253
CH_3COOH	1023	612	850	13-2550	113	1355	595	975	426-4112	119	1363	682	1095	490-2977	139
H_2O_2	1784	1160	915	103-6051	228	549	443	475	84-3552	265	131	93	75	34-543	294
CH_3OOH	623	268	308	37-1439	219	161	115	125	15-840	236	46	48	25	7.5-376	162
CH_2O	116	55	65	52-247	31	58	17	55	36-95	12	85	56	65	39-284	67
Aerosols	143	201	54	7.3-1680	338	51	64	26	1.7-616	443	23	16	16	3.4-65	627

Mixing ratios are stated in parts per trillion by volume (pptv); except for CO, CH_4, N_2O and O_3 that are in parts per billion by volume (ppbv), and CO_2 in parts per million by volume (ppmv); s.d. states the 1 standard deviation. C_2H_2/CO ratio is stated in pptv/ppbv; and aerosols are stated in number per cubic centimeter for 0.12– to 3 1-µm diameter range.

burning influence on the chemistry of aged air at altitudes above the marine boundary layer [*Crutzen et al.*, 1979; *Crutzen and Andreae*, 1990].

Further evidence for a combustion signal in the aged marine air parcels comes from comparison of these data to those obtained during mission 8 (see Figure 1) where trajectories indicated air of Pacific origin was sampled south of Brazil. The air parcels sampled on mission 8 had very uniform chemistry, with mean mixing ratios of NO_x of 18 pptv, 325 pptv of C_2H_6, 45 pptv of C_2H_2, 600 pptv of CH_3Cl, and 65 ppbv of CO. The composition and backward trajectories for these air parcels indicated that they had probably been over the Pacific Ocean without contacting emissions from continental areas for at least 10 days [*Gregory et al.*, 1996].

Comparison of mission 8 data with values for aged marine air suggests the possibility that emissions from biomass burning may have elevated the mixing ratios of many species in the general background air (called aged marine here) over the tropical South Atlantic. This may reflect gradual accumulation of longer-lived species during the local dry season, since our measurements occurred at the latter stage of it. Convective transport of polluted air from low to high altitude over the continents most likely explains the high-altitude enhancements of some species [*Kleinman and Daum*, 1991; *Pickering et al.*, 1992, this issue]. Colder temperatures and low OH concentration would increase species lifetimes once they were in this region [*Jacob et al.*, this issue].

The elevated mixing ratios of NO and NO_x in the 10-to 13-km altitude range stand out from the rest of the chemistry of these aged air parcels. There does not appear to be strong evidence for recent (<5 days) combustion inputs to these air parcels. Indeed, median mixing ratios of most species are indicative of moderately aged air [*Singh and Zimmerman*, 1992]. Poor correlations ($r^2 <$ 0.3) between NO (or NO_x) and CO or CH_3Cl suggest a different source for the NO other than biomass burning. In addition, data presented in the next section of this paper shows that NO and NO_X mixing ratios in the upper troposphere were not significantly different in aged marine and continental influenced air masses.

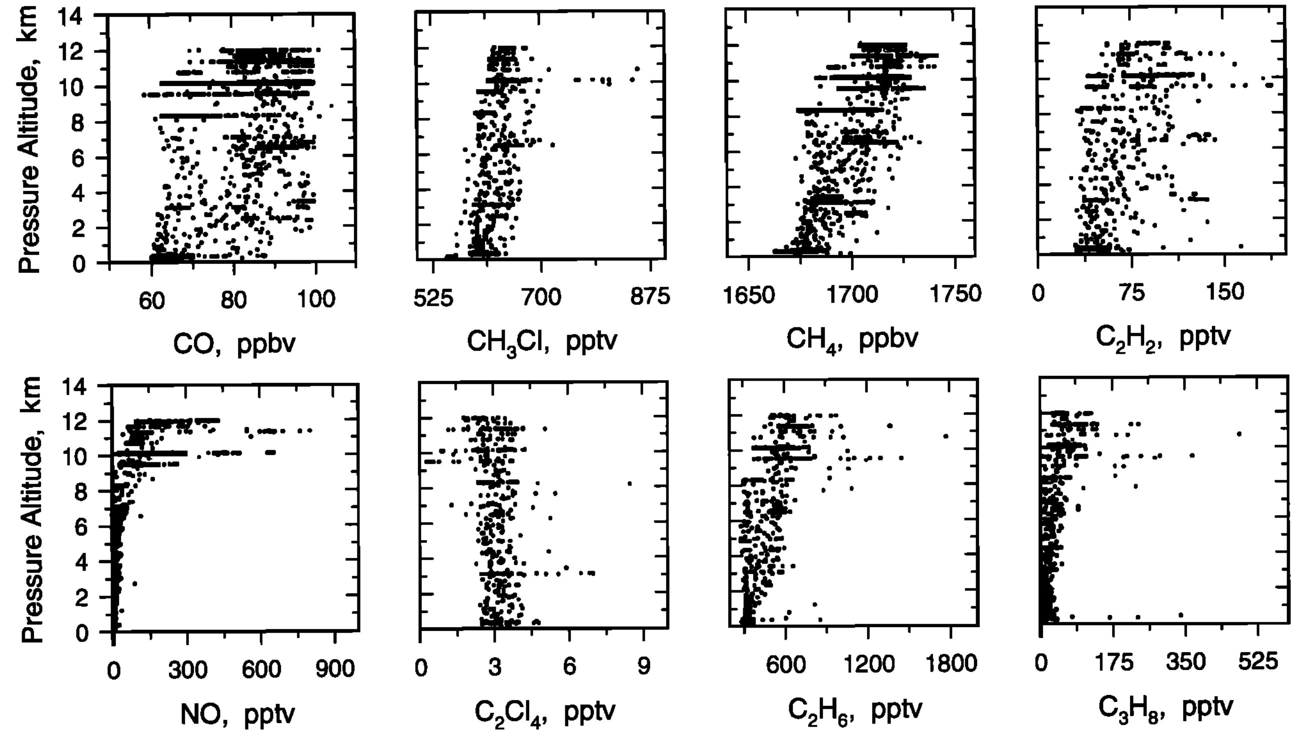


Figure 2. Vertical distribution of selected species in aged marine air over the tropical South Atlantic Ocean.

This is further evidence for important sources of NO_x besides biomass burning. Note that while NO mixing ratios approached 1 ppbv, CO remained at less than 100 ppbv (Figure 2). Two potential sources of NO that would not provide significant amounts of other tropospheric species (e.g., CO) are jet aircraft emissions and lightning. In the TRACE A study area it is likely that lightning is an important source of NO in the middle-to-upper troposphere [*Smyth et al.*, this issue].

4.2. Continental Outflow Air Parcels

The chemical characteristics of the continental outflow air parcels over the western and eastern basins of the tropical South Atlantic are summarized in Tables 2 and 3, respectively. The vertical distribution of selected species is shown in Figures 3 and 4. The composition of the outflow air parcels on both sides of the South Atlantic was similar, but there were some subtle differences. At low altitude over the western basin the industrial tracer C_2Cl_4 showed significant isolated enhancement (up to 87 pptv) relative to aged marine air (≈3 pptv, Table 1). Note that corresponding enhancements in chlorofluorocarbon species (CFCs) were not observed. The air mass back trajectories indicated that these anthropogenic emissions probably originated from the urbanized east coast region of Brazil that extends from Recife south to the Rio de Janeiro/São Paulo area. It is likely that emissions from this urban region contributed to species enhancements observed in air parcels at 0 - 5 km altitude east of Brazil. In contrast, direct industrial emissions appear to have had minimal impact on the air parcels sampled over the eastern basin of the tropical South Atlantic, as industrial tracer compounds were not enhanced above their mixing ratio median value in aged marine air.

Hydrocarbon species are valuable tracers that can be used to study photochemical and atmospheric transport processes [*McKeen and Liu*, 1993]. The ratio of shorter- to longer-lived species is particularly useful in this respect. Here we use the ratios C_2H_2/CO and C_3H_8/C_2H_6 to facilitate comparisons of various air parcels. For an [OH] of 1 x 10^6 molecules cm^{-3}, a reasonable value for the TRACE A study area [*Jacob et al.*, this issue], C_2H_2 and C_3H_8 have atmospheric lifetimes near 2 weeks compared to about 2 months for CO and C_2H_6.

On the average, the value of the ratio C_2H_2/CO was greater over the western basin compared to the eastern basin. This suggests that outflow air parcels sampled over the western basin contained more recent emissions, especially below 5 km altitude. In Brazil, biomass burning was occurring in the savannas located several hundred kilometers inland, and the largest urban areas are located right along the coast. Emissions from both of these sources could easily be swept off the coast out over the western South Atlantic within a day or so.

The situation in southern Africa was not conducive to such direct outflow of polluted air parcels [*Garstang et al.*, this issue]. Here the fires were centered in the middle or eastern portions of the continent (e.g., in Zambia). Emissions from this area would need a day or two just to reach the western coast of Africa which is located at an elevation of about 1100 m. Furthermore, air parcels appear to become periodically entrained in circular flow patterns over southern Africa for days at a time [*Garstang et al.*, this issue].

As the emissions are advected off the African coast over the eastern basin of the South Atlantic at an altitude greater than 1 km, their transport into the marine boundary layer is usually hindered by a thick stratocumulus cloud deck. This persistent stratus deck extends over a significant amount of the basin's eastern area [*Thompson et al.*, 1993]. The marine boundary layer typically contained quite aged marine air with elevated mixing ratios of some species (e.g., HNO_3) that appeared to originate by downward infiltration from the polluted region above the stratus deck [*Heikes et al.*, this issue].

The vertical distributions of the combustion products CO, ΣNO_{yi}, C_2H_6, and CH_3Cl over the western South Atlantic were relatively constant above 2 km altitude (Figure 3). Mixing ratios of CO, ΣNO_{yi}, and C_2H_6 were elevated roughly two-fold over their median values in aged marine air, while CH_3Cl was

Table 2. Mixing Ratios of Principal Species Measured in Continental Outflow Over the Western South Atlantic Ocean

	0 – 4.9 km					5 – 9.9 km					10 – 13 km				
Species	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	30	16	22	11-102	41	160	129	91	15-559	116	107	26	100	4.5-175	121
NO_x	94	40	67	57-220	39	109	47	103	40-218	27	142	41	117	4 0-274	121
HNO_3	458	97	455	215-566	23	47	13	46	32-96	47	40	13	43	26-96	67
PAN	531	265	520	262-1151	16	288	242	256	71-1538	42	380	182	402	120-1119	50
ΣNO_{y}	779	395	761	148-1775	27	366	237	306	116-1634	80	316	206	203	100-1147	115
O_3	50	5	50	25-67	61	64	11	64	47-88	145	76	11	77	55-97	169
CO	147	18	146	89-184	59	102	33	92	55-189	145	110	31	98	70-173	168
CH_4	1702	6	1702	1688-1712	59	1713	9.9	1712	1695-1736	140	1721	8.2	1721	1701-1748	168
CO_3	357.7	0.75	357 6	355 5-359 4	56	355.5	1 3	355 3	353.0-359 0	125	355.2	1.0	355.0	353.5-358.2	163
N_2O	310.1	0.39	309.8	308 8-310.9	37	310.3	0.38	310 2	309.2-310.9	39	310.3	0.36	310.2	309.1-311.0	119
C_2H_2/CO	2.7	1.3	2.6	1.1-6.9	47	1 6	0.72	1.5	0.66-3.4	58	1.2	0.51	0.98	0 74-2 5	28
C_3H_8/C_2H_6	0.13	0.16	0.09	0.08-1.1	47	0.11	0.06	0.09	0.01-0.26	60	0.12	0 03	0 10	0.08-0.17	28
C_2H_6	774	147	748	403-1111	51	756	251	792	384-1448	58	922	232	908	641-1372	28
C_3H_8	106	127	78	26-919	51	97	81	73	7.5-369	58	111	56	123	54-239	28
C_2H_2	433	138	390	94-874	51	181	119	140	37-499	58	141	103	171	60-413	28
C_2H_4	79	77	46	7-363	51	25	37	16	2-178	51	13	13	7	3-47	25
CH_3Cl	666	21	667	592-702	51	655	35	638	602-731	58	662	37	656	618-763	28
C_2Cl_4	7.4	13	3.5	2.9-87	51	2.6	1 4	3.2	1 1-5.0	58	3.0	2 4	3.1	1 0-10	28
CFC-11	252.0	2.2	252.1	245 9-257.1	51	253.9	2.6	253.2	250.1-265 7	58	258.9	4.0	258.0	250.7-266.3	28
CFC-12	488.7	4.4	486.6	481.2-507 6	51	488.3	3.1	488.0	483.1-498.1	58	494.1	4 5	493.5	486 4-503.7	28
CFC-113	76.5	0.72	76.3	74.5-78.6	51	76.7	0.85	76 5	75.3-80.8	58	78.7	1.2	78.3	75.7-80.4	28
CH_3CCl_3	123	3.6	122	110-140	51	120	4.7	121	106-134	58	123	4.2	122	116-130	28
CCl_4	99	1.8	99	92-103	51	96	5.0	97	72-100	58	97	3.8	98	88-102	28
C_6H_6	80	23	73	16-164	51	22	28	12	2.4-114	53	16	20	8.8	2.8-69	28
HCOOH	1802	266	1847	1502-2369	23	418	95	385	215-611	47	253	174	220	93-708	67
CH_3COOH	1995	162	1983	1765-2373	23	1139	360	1080	615-2086	47	704	163	650	490-1117	66
H_2O_2	4935	2519	3396	716-11,418	40	442	1595	335	84-14,297	80	338	376	250	85-1569	87
CH_3OOH	857	152	727	581-1196	40	94	154	80	16-840	62	175	150	135	15-393	46
CH_2O	387	119	402	214-721	22	105	130	75	36-402	8	75	29	60	43-179	48
Aerosols	975	542	977	118-3050	61	43	81	24	9 4-822	145	62	82	53	12-902	169

Mixing ratios are stated in parts per trillion by volume (pptv); except for CO, CH_4, N_2O and O_3 that are in parts per billion by volume (ppbv); and CO_2 in parts per million by volume (ppmv), s.d. states the 1 standard deviation. C_2H_2/CO ratio is stated in pptv/ppbv; and aerosols are stated in number per cubic centimeter for 0.12– to 3.1-μm diameter range

enhanced about 10%. There was good correlation between mixing ratios of CO and CH_3Cl (Figure 5), indicative of a biomass burning source for the combustion products in these air parcels.

An interesting feature of the data was the low CO and CO_2 but elevated CH_4 mixing ratios in some air parcels sampled at high altitude. Overall, there was a vertical gradient in the mixing ratio of CH_4 of +2.3 ppbv km^{-1} over the South Atlantic basin [*Bartlett et al.*, this issue]. A possible explanation would be convective transport from ground level to the upper troposphere of air parcels from over a large wetland area such as the Pantanal in southwestern Brazil. Aged Pacific air parcels flowing down the eastern slope of the Andes (low CO) could accumulate CH_4 released from natural methanogenic processes while CO_2 would be consumed by photosynthetic activity. Air mass back trajectories commonly originated over southwestern Brazil, and convective activity was frequent [*Pickering et al.*, this issue]. Furthermore, the longitudinal distribution of CH_4 over the South Atlantic basin suggests that CH_4 inputs were greater from South America than from Africa [*Bartlett et al.*, this issue].

Another indication that convective activity might be involved comes from the NO and NO_x data. Mixing ratios of NO and NO_x were quite elevated (100 - 250 pptv) in near-surface air parcels apparently influenced by natural biogenic processes [*Harris et al.*, this issue; *Levine et al.*, this issue]. Lightning could also have contributed to the elevated mixing ratios of NO and NO_x at high altitude, preserving the characteristically low mixing ratios of CO.

Compared to the western basin of the tropical South Atlantic, a fairly extensive sampling of continental outflow was obtained over the eastern basin (Figure 4). As was found over the western basin, mixing ratios of CO and CH_3Cl were correlated for CH_3Cl mixing ratios in the range 600 - 700 pptv (Figure 5). The reason for the departures from the primary relationship between these species is unclear, particularly since smoldering fires have high emissions of both CO and CH_3Cl [*Lobert et al.*, 1991; *Blake et al.*, this issue]. The data in the divergent arms of the plots shown in Figure 5 are from several different flights and altitudes. Thus they are not confined to a single flight or air parcel.

The vertical distribution of combustion-derived insoluble species over the eastern basin indicates that the tropospheric column from 2 to 13 km was predominately fumigated with biomass fire emissions. Natural biospheric sources might also be important for alkene species, especially C_2H_4 [*Rudolph et al.*,

Table 3. Mixing Ratios of Principal Species Measured in Continental Outflow Over the Eastern South Atlantic Ocean

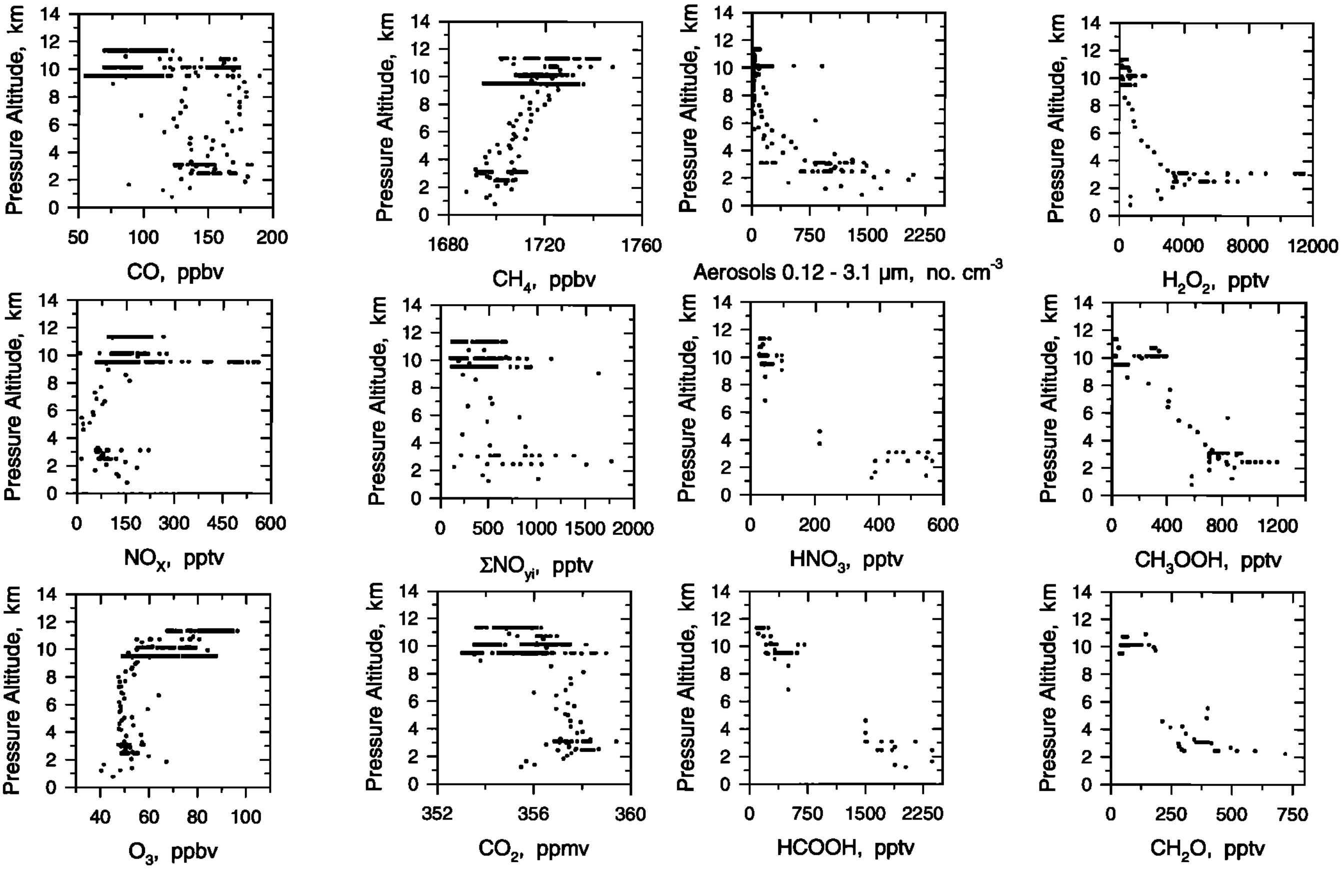
	1 5 – 4 9 km					5 – 9 9 km					10 – 13 km				
Species	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N	Mean	s.d.	Median	Range	N
NO	22	10	19	12-37	101	51	41	37	14-353	160	200	140	135	19-805	676
NO_x	71	25	59	37-136	93	98	66	54	40-533	107	221	145	151	19-942	670
HNO_3	411	168	445	152-973	67	119	55	140	14-271	57	71	31	85	14-180	342
PAN	294	336	230	10-1488	34	302	163	300	85-1123	48	249	160	265	82-2184	230
ΣNO_{yi}	588	334	522	213-2113	66	368	185	338	100-1123	75	335	207	277	99-2376	466
O_3	61	6 2	63	47-80	122	74	12	73	55-102	186	73	14	71	44-105	867
CO	129	42	108	80-198	122	101	15	99	75-140	180	99	15	95	69-150	860
CH_4	1699	6 0	1701	1684-1719	122	1710	9 1	1706	1694-1732	165	1717	7 3	1717	1696-1741	857
CO_2	356.8	2.3	356 6	353.3-360.0	116	355 3	0 76	355 3	353 0-358 1	170	354 5	1.3	354.4	349.9-357.8	812
N_2O	309.9	0.31	310.1	309 4-310.8	58	309.8	0.39	309.8	308.5-310 8	161	310.0	0.58	310.0	308.0-310.9	713
C_2H_2/CO	1.1	0.60	1.0	0.51-2.1	56	1.2	0.23	1.1	0.71-1.8	82	1.2	0 25	1.1	0.61-2.0	359
C_3H_8/C_2H_6	0.05	0.02	0.06	0.02-0.09	56	0.08	0 02	0.07	0.04-0.16	85	0.10	0.04	0.10	0.05-0.27	362
C_2H_6	574	170	635	430-1015	56	669	152	720	441-982	61	683	146	710	394-1773	362
C_3H_8	31	23	35	8.2-79	56	59	29	48	25-134	61	69	44	55	27-484	362
C_2H_2	140	117	160	39-388	56	120	40		61-246	61	121	40	125	53-246	362
C_2H_4	19	20	30	3-81	53	10	9	12	3-66	46	9	3	9	3-22	274
CH_3Cl	648	26	655	615-716	56	668	31	660	610-812	61	667	43	670	621-880	362
C_2Cl_4	3.3	0 50	3.1	2.4-4.2	49	3.0	0.40	3 0	2.1-4.1	43	3.0	0.60	2.9	1.6-5.1	340
CFC-11	259.9	2.3	258.8	255.2-264.0	56	261 3	2 6	260 5	256.8-267.3	52	260.2	2.5	260.1	254.6-268.9	340
CFC-12	491.6	3.7	492.0	485.6-503.5	56	492 6	3 0	493.1	485.0-497.9	52	493.9	3.4	495.0	485.0-506.1	340
CFC-113	79.9	0.71	78 9	77 9-81.7	56	79.3	0.97	79 1	77.2-81 2	52	78.8	1.6	79 0	72.7-87.9	340
CH_3CCl_3	129	2.9	130	121-134	56	125	3.7	125	117-133	50	122	7 4	123	71-135	340
CCl_4	103	1 3	101 5	100-106	56	100	3 9	102 2	84-106	61	97	8 8	97.6	71-105	362
C_6H_6	30	30	20	6 6-124	55	20	7 5	22	7.2-41	58	17	7 7	17	4.5-51	317
HCOOH	2187	1838	1560	230-6966	61	905	554	677	304-3581	57	638	281	675	238-3664	342
CH_3COOH	2785	2554	2155	487-12,254	61	2834	1603	2530	767-7793	57	2788	1630	2250	658-9213	342
H_2O_2	2940	2147	617	28-7818	79	481	451	329	26-2412	85	108	94	93	10-498	376
CH_3OOH	828	441	668	13-1547	80	105	79	65	10-523	85	55	63	48	13-376	233
CH_2O	132	89	92	5.0-323	32	40	32	53	6.0-83	7	87	73	69	5.0-284	34
Aerosols	520	472	175	7.5-1457	94	68	50	51	7.3-294	151	23	17	14	3 4-115	727

Mixing ratios are stated in parts per trillion by volume (pptv); except for CO, CH_4, N_2O and O_3 that are in parts per billion by volume (ppbv), and CO_2 in parts per million by volume (ppmv); s.d. states the 1 standard deviation C_2H_2/CO ratio is stated in pptv/ppbv; and aerosols are stated in number per cubic centimeter for 0.12– to 3 1-μm diameter range.

1992]. Previous observations from the space shuttle identified the South Atlantic region as having elevated CO mixing ratios of 80 - 100 ppbv at this time of the year [*Newell et al.*, 1988]. The TRACE A airborne measurements appear to confirm the suspicions of *Newell et al.* [1988] that biomass burning is the source of much of the enhanced tropospheric CO during the austral springtime.

Within plume layers coming directly off the African continent, there were significant enrichments of the water-soluble gases H_2O_2, CH_3OOH, CH_2O, HCOOH, CH_3COOH, and HNO_3. This characteristic was also prevalent in the air parcels sampled over the western basin. Outflow plumes coming off southern Africa were typically centered around 4 km altitude. This feature is illustrated in Figure 6 using observations obtained on mission 14 flown over the eastern South Atlantic basin. The relatively small mixing ratios of NO and NO_x (< 100 pptv) and large ratios of HNO_3 (≤1000 pptv) indicate photochemical aging of these plumes of the order of a few days. Nitric acid usually comprised 70% or more of the ΣNO_{yi} in these plumes. Mixing ratios of O_3 within the plumes were usually less than 70 ppbv compared to up to 105 ppbv in air parcels over the South Atlantic. Peroxide and carboxylic acid species commonly approached or exceeded 10 ppbv within the plume layers. Previous measurements of carboxylic acids over the Congo region of Africa during the dry season indicated an important biomass burning source for these species [*Helas et al.*, 1992]. It appears that a similar argument can be made for the peroxide species [*Heikes et al.*, 1996].

A noticeable characteristic of the chemistry over the tropical South Atlantic was the elevated mixing ratios of water-soluble gases and aerosol particles (0.12- to 3.1-μm diameter) below 6 km compared to above this altitude (Figures 3c and 4c). Insoluble and/or long-lived (i.e., atmospheric lifetime >1 month) gases showed a much more uniform distribution from 1 to 12.5 km altitude (Figures 3a, 3b, 4a, and 4b). A possible explanation for this is that the transport of species to the middle-to-upper troposphere over the continents occurred primarily in wet convective systems where soluble gases and aerosol particles were effectively scavenged. The outflow at altitudes below 6 km appeared to be largely coupled to synoptic flow patterns and the



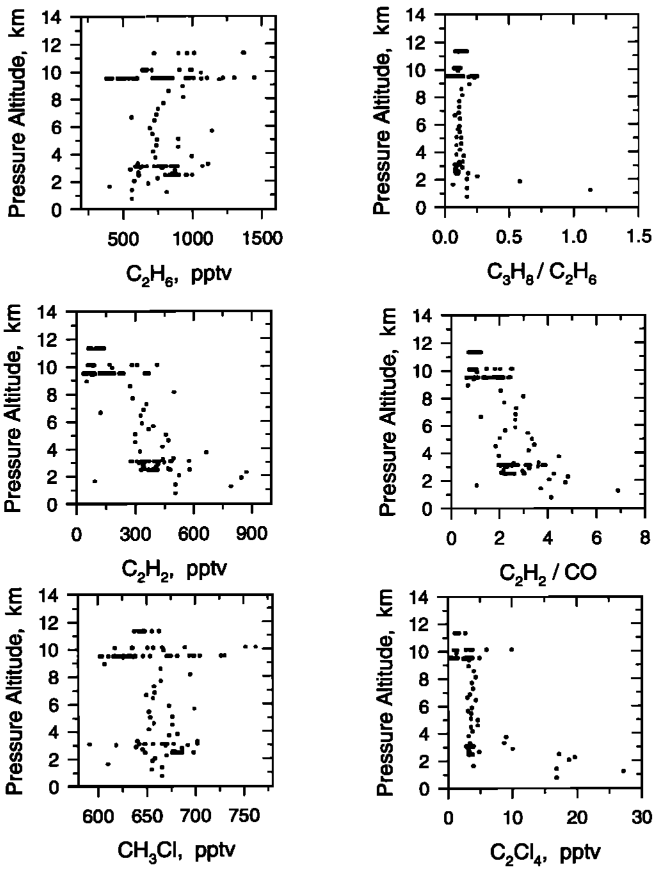
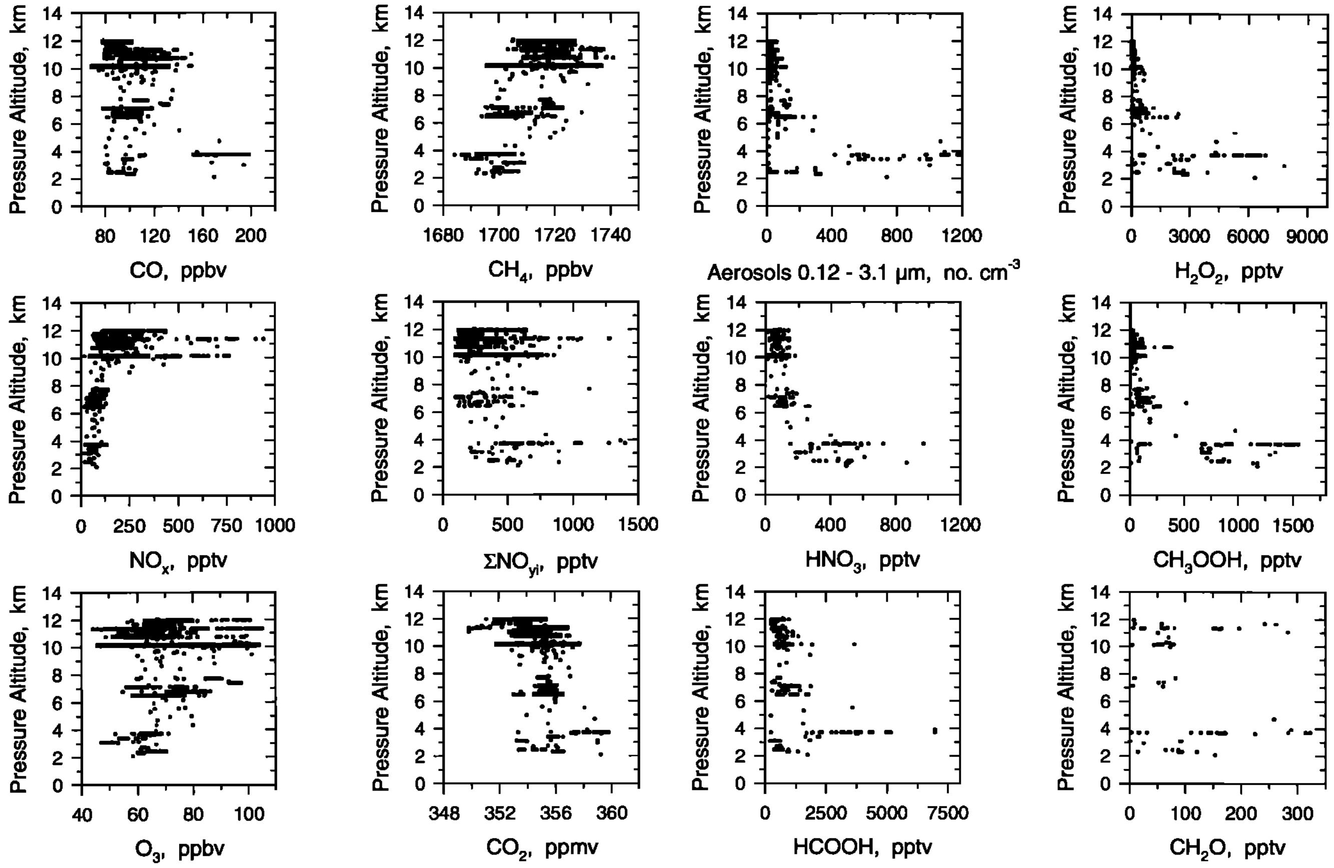


Figure 3. Vertical distribution of selected species in continental outflow air masses over the western South Atlantic Ocean: primary species; hydrocarbon, halocarbon, and ratios (C_2H_2/CO is stated in parts per trillion by volume/parts per billion by volume(pptv/ppbv); water-soluble species and aerosols.

general lofting of fire plumes into the prevailing offshore wind regimes over Brazil and Africa.

The ratio CH_3OOH/H_2O_2 can be a potentially useful diagnostic to identify air parcels influenced by precipitation scavenging during the previous 1- to 2-day period. For timescales longer than this, atmospheric mixing and photochemical production processes can significantly alter the ratio values. Retaining this caveat, ratio values greater than 1 are suggestive of preferential removal of H_2O_2 by precipitation due to its greater solubility in water than CH_3OOH [*Heikes*, 1992]. The vertical distribution of the ratio is shown in Figure 7. It is apparent that values greater than 1 were common in the upper troposphere over the South Atlantic (≈80 %), lending support to the idea of wet removal of soluble species over the continents. Precipitation over the South Atlantic is quite sparse [*Elliott and Reed*, 1984], and what does occur probably has minimal effect on species at 6- to 12-km altitudes. We conclude that significant continental outflow of soluble gases and aerosol particles was confined to the lower troposphere.

Various meteorological analyses relevant to the TRACE A experiment show that dynamics are likely to play an important role in the distribution of tropospheric species over the tropical South Atlantic and especially in the generation of the eastern basin O_3 maxima [*Krishnamurti et al.*, this issue]. The same transport phenomena also appear to be key in elevating NO_x mixing ratios in this same region [*Smyth et al.*, this issue]. The



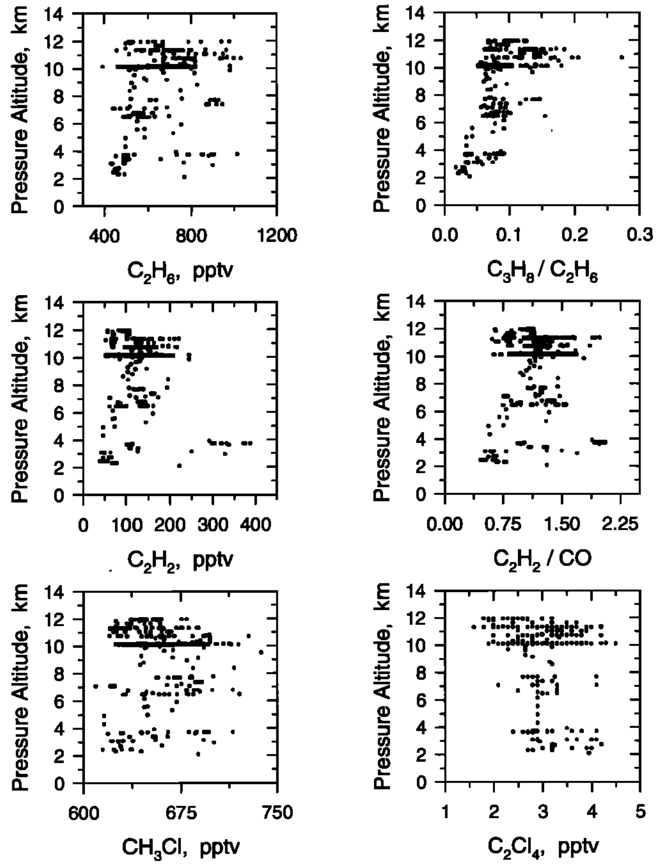


Figure 4. Vertical distribution of selected species in continental outflow air masses over the eastern South Atlantic Ocean: primary species; hydrocarbon, halocarbon, and ratios (C_2H_2/CO is stated in pptv/ppbv); water-soluble species and aerosols.

convergence of air parcels in the upper troposphere over the eastern basin of the tropical South Atlantic appears to be driven by large-scale circulations bringing air to this region from over Brazil, central and southern Africa, and even the Asian monsoon area [*Krishnamurti et al.*, this issue].

Slow subsidence over the eastern South Atlantic basin promotes clear skies and an environment conducive to photochemical activity [*Krishnamurti et al.*, 1993]. This subsidence undoubtedly plays a role in establishing and maintaining the rather uniform vertical distribution of long-lived species over this whole region. Horizontal injection of additional biomass burning products from the African continent, including water-soluble species and aerosol particles, is frequent below 6 km altitude. The deposition of aerosol particles and gaseous species like HNO_3 may provide important nutrient inputs to oligotrophic South Atlantic and Indian Ocean surface waters [*Moody et al.*, 1991]. Nitrogen is often a limiting nutrient in marine ecosystems [*Paerl*, 1985, 1993], and biomass burning emissions from the African continent are known to be especially nitrogen rich [*Delmas*, 1982].

5. Aged Marine Air at 10-13 km Altitude: A Closer Look

Nearly 50% of the air parcels sampled during TRACE A were classified as aged marine. These air parcels thus contributed in an important way to the large-scale chemistry of the troposphere over the tropical South Atlantic. Of particular interest is an

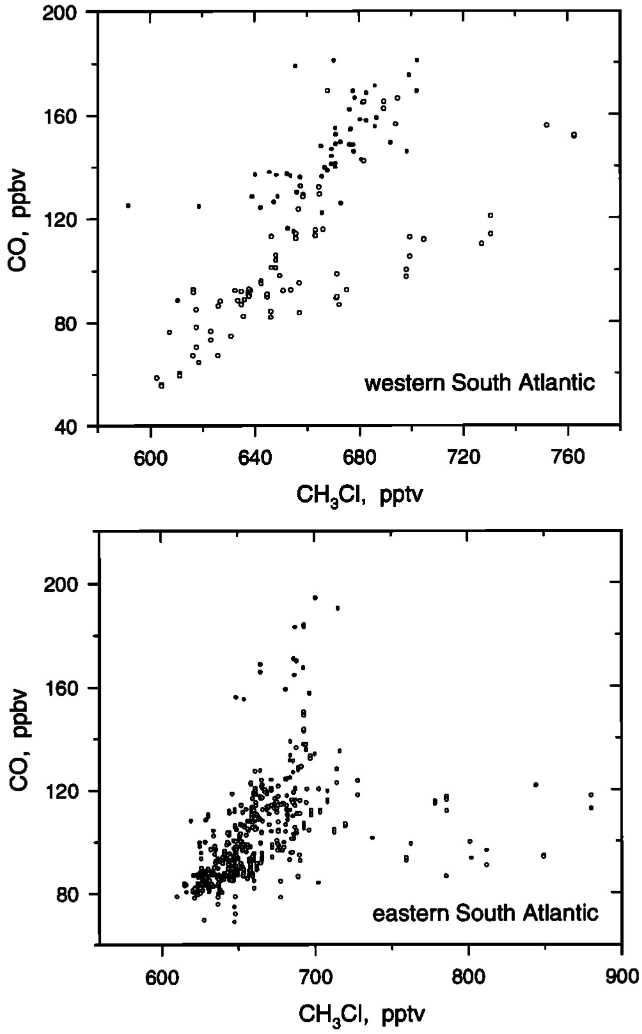


Figure 5. Relationship between CO and CH_3Cl in continental outflow air masses over the tropical South Atlantic Ocean. The solid circles refer to data obtained at 0 - 5.9 km altitude and the open circles 6 - 12 km. These correlations are evidence for a biomass burning source.

assessment of species sources in the 10- to 13-km altitude range. Values of the ratios C_2H_2/CO and C_3H_8/C_2H_6 indicated that these air parcels were the least processed (i.e., source emissions influenced the least by photochemical aging and mixing process [*McKeen and Liu,* 1993]). It appears that subsidence then mixes these high-altitude air parcels downward producing compositionally similar but more processed air parcels (indicated by lower C_2H_2/CO and C_3H_8/C_2H_6 ratios) at lower altitudes.

The latitudinal distribution of selected species illustrates the dramatic influence on the chemistry from the convergence of various air parcels at high altitude over the tropical South Atlantic (Figure 8). These data were obtained at 10 km altitude during a transist flight between Ascension Island and Puerto Rico (Figure 1, mission 18). The sharp gradient in the mixing ratio of various species indicates that the Intertropical Convergence Zone (ITCZ) was crossed near 10 °N. In the southern hemisphere the enhanced mixing ratios of CO, PAN, C_2H_2, and CH_3Cl are indicative of a large-scale influence of biomass fire emissions. The increased mixing ratios of CH_4 and C_2Cl_4 in the northern hemisphere are presumably driven by larger sources there [*Steele et al.,* 1992; *Blake et al.,* 1996].

Close examination of the southern hemispheric data shown in Figure 8 suggests that this latitudinal survey crossed through several continental plumes of combustion-related emissions with parcels of air corresponding to our aged marine classification sampled in between. Within these plumes there was good correlation among CO, CH_4, PAN, C_2H_2, and CH_3Cl. Backward trajectories indicated that the various plumes sampled on mission 18 had originated from over Africa or South America. Eventually, these plume features should disappear as they photochemically age and are turbulently mixed and diluted to form aged marine air over the tropical South Atlantic.

We explored various sources of species in high-altitude aged marine air parcels using a geographic depiction of the mixing

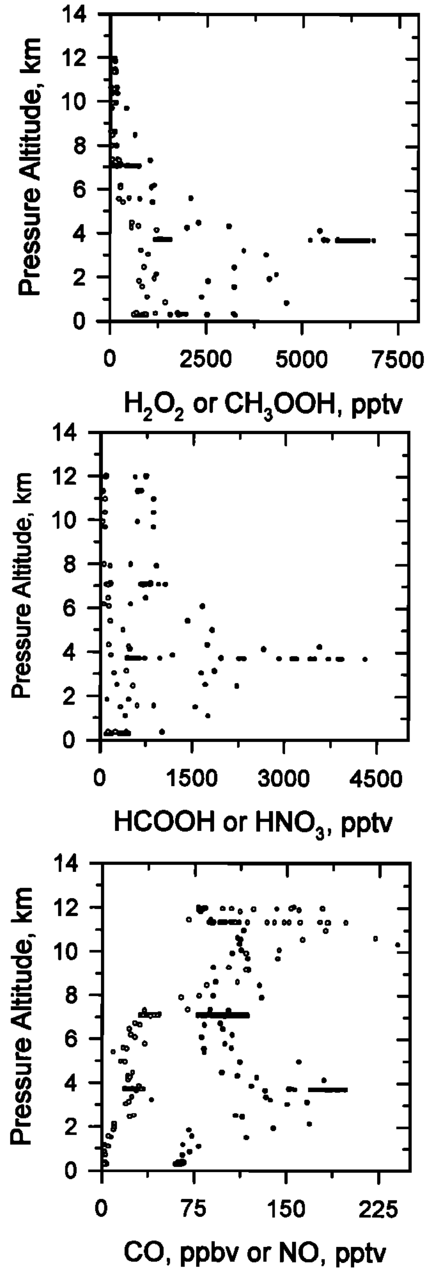


Figure 6. Vertical distribution of selected species in continental outflow air masses sampled during a spiral over the eastern South Atlantic basin on mission 14 (see Figure 1 for location). First species listed on each plot are shown by a solid circle and the second species as an open circle.

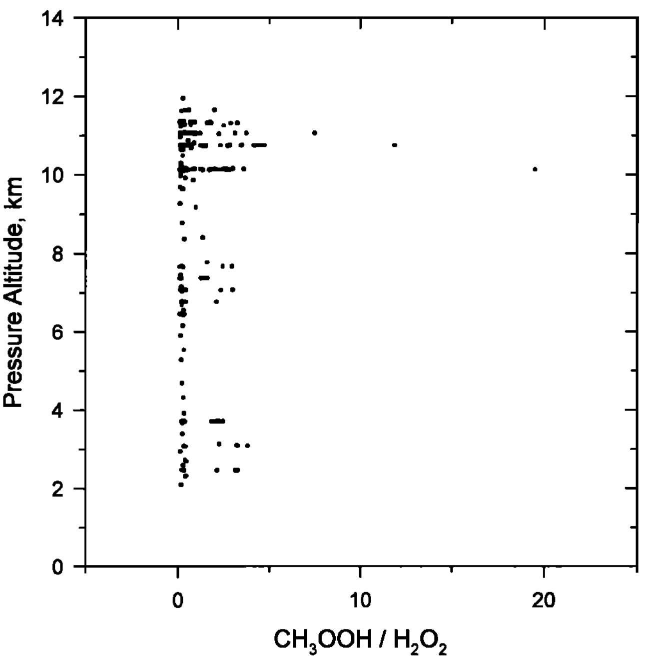


Figure 7. Distribution of the ratio CH_3OOH/H_2O_2 as a function of altitude in continental outflow air masses over the South Atlantic basin. Ratio values greater than 1 are indicative of air masses where H_2O_2 was preferentially removed by precipitation.

ratio as a function of latitude (Figure 9). Most species showed a rather uniform latitudinal distribution, demonstrating remarkable consistency in the composition of the high-altitude air parcels. The feature of depressed mixing ratios of some species (e.g., CO, CH_4, and CO_2) in the 20° - 25° latitude band may be related to stratospheric inputs or it simply may reflect very aged tropospheric air. These data were not removed from the aged marine classification by our filtering process for stratospheric air, but they typically exhibited N_2O mixing ratios around 308 ppbv.

The latitudinal data also exhibit several other notable characteristics. For example, O_3 mixing ratios showed an increasing trend that progressed from the equator to midlatitudes. Thus the in situ data suggest that the average mixing ratio of O_3 in the vicinity of Ascension Island (Figure 1) was less than those observed off southern Africa (near Namibia, Angola, or Mozambique). Such details of the distribution of O_3 are discussed in great detail in numerous companion papers in this issue.

Another feature of the high-altitude aged air over the tropical South Atlantic was the repetitive occurrence of large mixing ratios of NO (Figure 10). The mean lifetime of NO is estimated to be about 3.5 days at this altitude [*Jacob et al.*, this issue]. This suggests that NO must be frequently replenished in high altitude air parcels to maintain a median mixing ratio of 130 pptv (Table 1). It is unclear if the NO is replenished from biomass fire emissions, lightning, or recycled reactive nitrogen (Figure 10); [*Jacob et al.*, this issue; *Smyth et al.*, this issue].

Data were not obtained above 9 km altitude during mission 8 when aged Pacific air was sampled. However, the zenith-looking data for O_3 and aerosols obtained remotely by the UV-DIAL (differential absorption lidar) system indicated that the uniform chemistry sampled below 9 km altitude probably extended up to at least 12 km [*Browell et al.*, this issue]. In addition, during the initial leg of the mission 9 transit flight from Rio de Janeiro to Johannesburg we sampled aged Pacific air at 10 km altitude. These data are shown in Figure 9 at a latitude of about 36° and CO mixing ratios <75 ppbv (data at bottom left corner of each plot). The composition of this aged Pacific air was very similar to the aged South Atlantic air sampled in the marine boundary on numerous missions [*Heikes et al.*, this issue]. These air parcels thus define the chemistry of the "clean" aged air feeding into the tropical South Atlantic basin at all altitudes.

Comparison of this "clean" aged air with our aged marine classification indicates that source contributions to it must be frequent or large enough to maintain significantly enhanced mixing ratios of long-lived species over the South Atlantic. If biomass fire emissions were a dominant source of species at high

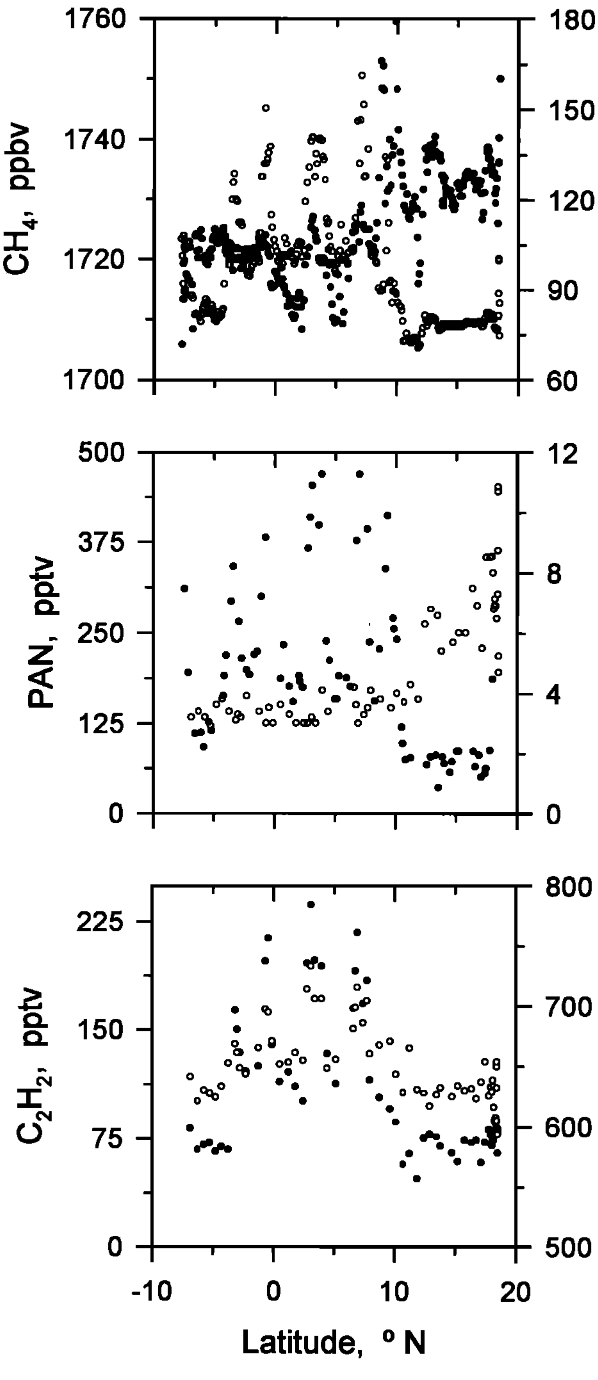


Figure 8. Latitudinal distribution of selected species at 10 km altitude between Ascension Island and Puerto Rico. Intertropical convergence zone was crossed near 10 °N, as evidenced by the sharp change in mixing ratio of the various species. Species shown on the left-hand side of plots are indicated by solid circles and those on the right-hand side by open circles.

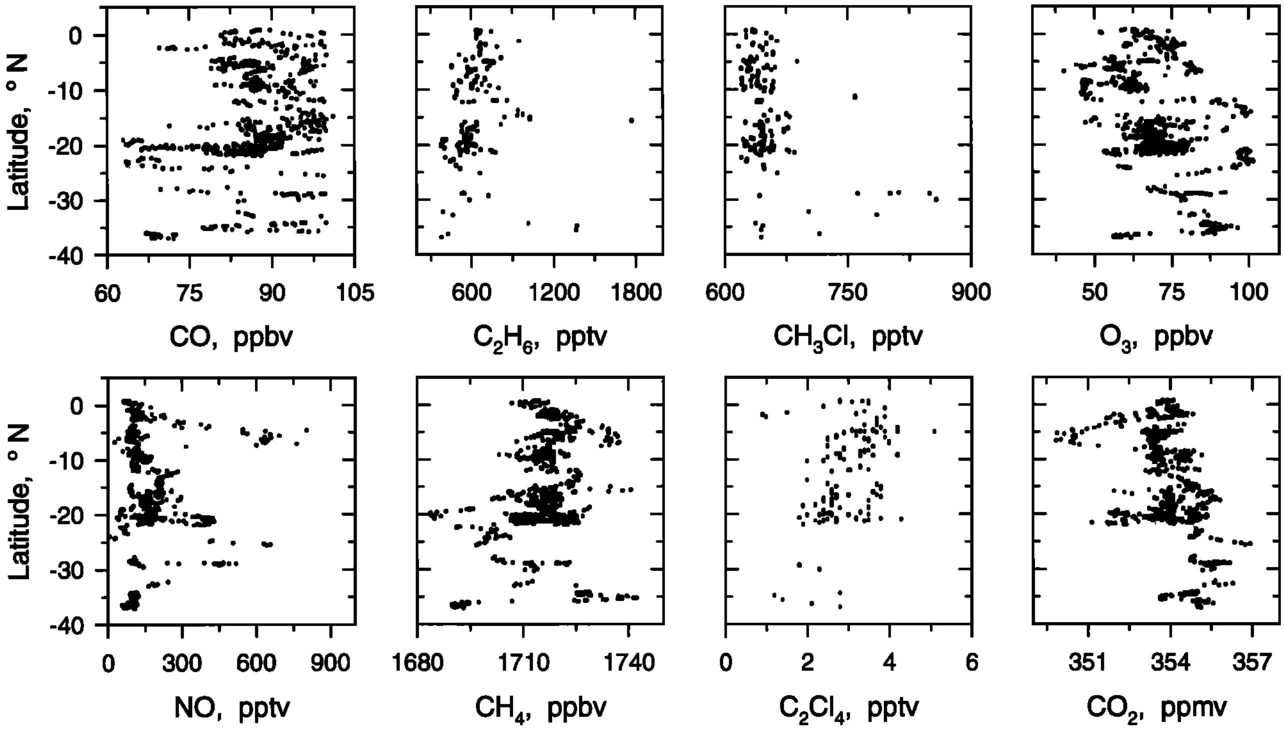


Figure 9. Latitudinal distribution of selected species at 10 -13 km altitude in aged marine air over the tropical South Atlantic Ocean.

altitude over the South Atlantic, the aged marine classification may reflect the net cumulative effect of the 1992 local dry season. Satellite observations indicated that the occurrence of biomass fires in Brazil and Africa was rapidly diminishing over the time span of the TRACE A expedition [*Fishman et al.*, this issue].

There does not appear to be a straightforward method to identify definitively the sources of species in aged marine air over the South Atlantic. Backward trajectories indicated that the air parcels typically originated over all parts of central South America or Africa north of the equator (Figure 11). Dynamical studies also showed this, plus a possible teleconnection with the Indian monsoon region of southern Asia [*Krishnamurti et al.*, this issue]. This opens a wide spectrum of source possibilities for many species, that include emissions from biomass fires, urban areas, wetlands, tropical forests, rice paddies (Southeast Asia), and air transported across the ITCZ from the northern hemisphere. Once air parcels carrying materials from various sources

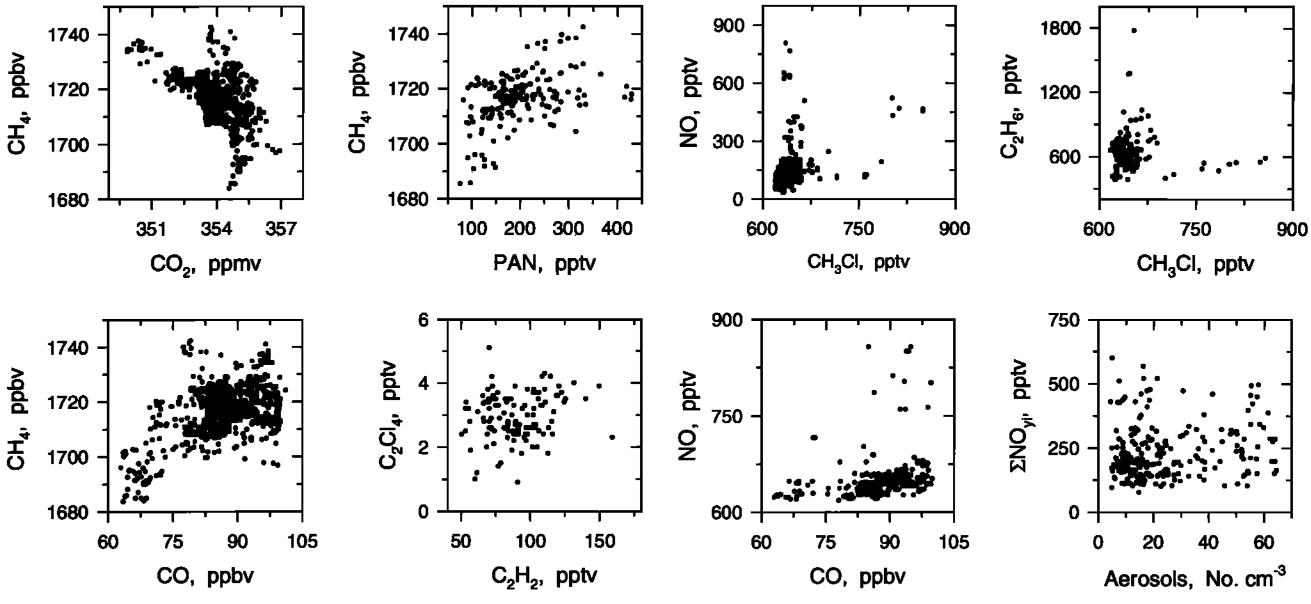


Figure 10. Relationship between selected species at 10 - 13 km altitude in aged marine air over the tropical South Atlantic Ocean.

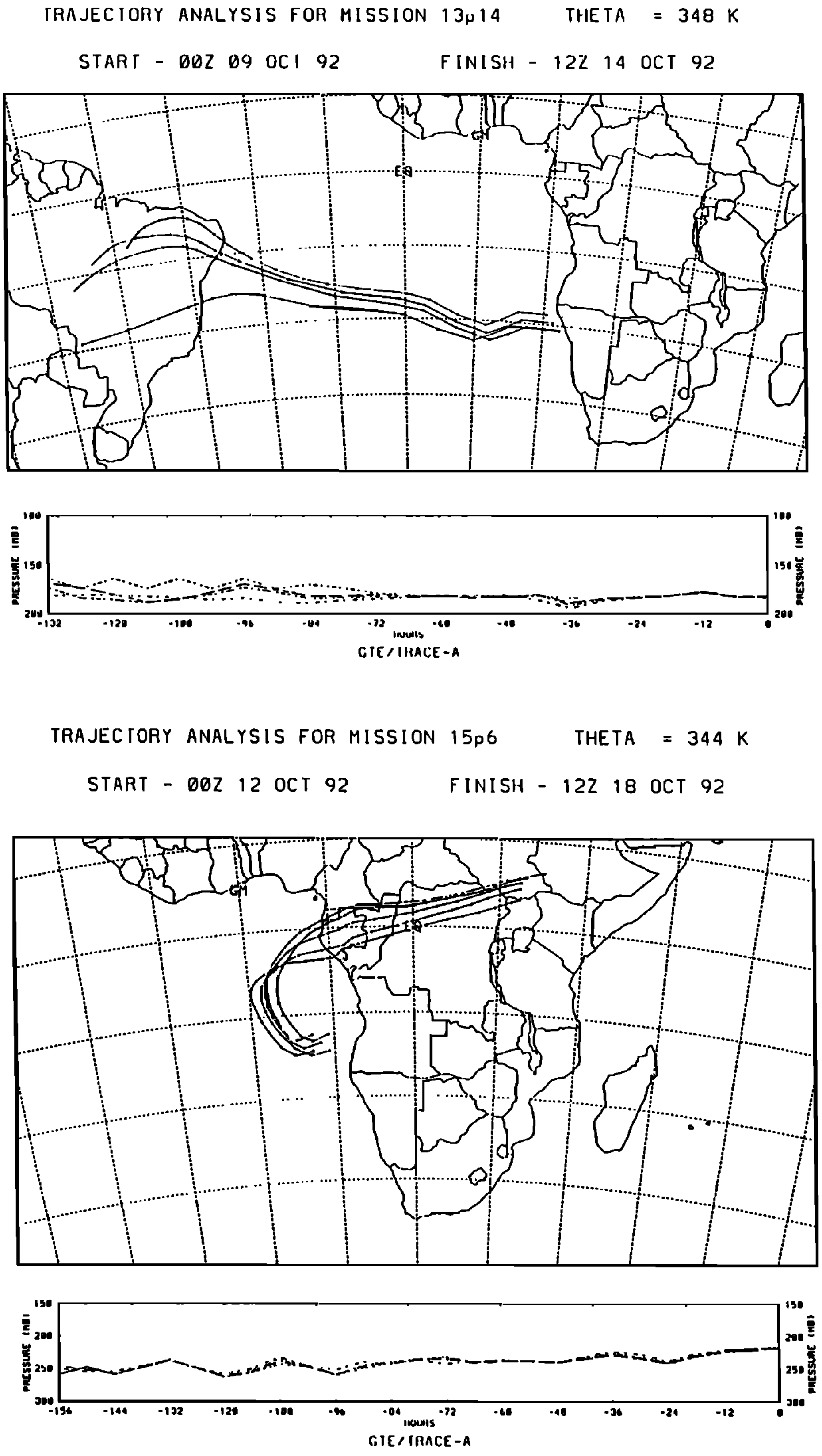


Figure 11. Typical isentropic backward trajectories for air masses sampled at 10 -13 km altitude over the western basin of the tropical South Atlantic Ocean. Trajectories originating over Brazil indicated that air masses had passed over a mixture of tropical forest, wetland, and savanna ecosystem types. Over Africa the air masses appeared to pass over equatorial tropical forest and wetland regions only. Air masses rarely passed over the savanna regions in southern Africa where satellite observations indicated that biomass fires were concentrated [*Fishman et al.*, this issue].

are mixed and diluted in the atmosphere, it is very difficult to deconvolute the various chemical signatures. The aged marine air over the South Atlantic basin exemplifies this problem.

Correlations between various species in high-altitude air parcels were weak ($r \leq 0.5$) or nonexistent (Figure 10). For example, there appears to be a positive but very general correlation between ΣNO_{yi} and aerosol number density ($r = 0.41$). No other species, including NO_x, HNO_3 or PAN, showed even a hint of a correlation with aerosol number density. Since aerosol composition was not measured, it is not known if the relationship was driven by nitrate aerosols. Aerosol number densities >10 cm^{-3} (0.12- to 3.1-µm diameter) are quite enhanced for the southern hemispheric upper troposphere. Both the TRACE A and ABLE 2A (Atmospheric Boundary Layer Experiment - Amazon Basin dry season) data show that in the absence of pollution plumes free tropospheric aerosol concentrations are <5 cm^{-3} [*Gregory et al.*, 1990]. In the boundary layer over Brazil and Africa we observed aerosol concentrations as large as 5 x 10^3 cm^{-3} under conditions of heavy fumigation by biomass fire emissions. Aerosol and ΣNO_{yi} concentrations also approached this magnitude near large urban areas in Brazil and Africa.

Methane appeared to show signs of a positive correlation with combustion products (CO and PAN plots) and also an anticorrelation with natural biogenic indicators (CO_2 plot, CH_4 emissions, and CO_2 uptake). To evaluate the potential for emissions from biomass fires to support the CH_4 enhancements at high altitude, we used median values from Table 1 and emission ratios summarized by *Crutzen and Andreae* [1990]. Comparison of the median mixing ratios of CH_4 and CO at 10 - 13 km altitude (1717 and 87 pbbv, respectively) with mean values (1680 and 65 ppbv, respectively) in aged Pacific (mission 8) and South Atlantic marine boundary layer air yields enhancements of 37 and 22 ppbv respectively. This enhancement gives a molar ratio of 1.7 mol CH_4/mol CO compared to a biomass fire emission ratio of about 0.1 [*Crutzen and Andreae,* 1990]. We conclude from this estimate that significant inputs from sources other than biomass fires are needed to explain the CH_4 enhancement at high altitude.

While natural CH_4 sources in tropical regions are known to be substantial [*Cicerone et al.*, 1988], they would have to be very large to have affected the entire middle-to-upper troposphere over the tropical South Atlantic basin. Ground-based studies in South America and Africa have not uncovered unusually large natural CH_4 emissions from these regions [*Bartlett et al.*, 1988, 1990; *Tathy et al.*, 1992].

Emissions from urban areas, however, can be quite enriched in CH_4 [*Harriss et al.*, 1994]. The southeastern coast of Brazil is highly urbanized, and this is a potentially large source region for anthropogenic emissions. There is also a high density (≥12) of coal-fired steam-generating plants located in South Africa. The burning of fossil fuels in these plants constitutes a large combustion source, as they represent the third largest anthropogenic sulfur input to the southern hemisphere troposphere [*Spiro et al*, 1992]. There are also numerous smelter operations located in the Katanga province of northern Zambia (M. O. Andreae, personal communication, 1995).

These anthropogenic sources might explain the substantial enhancement of C_2H_6 (and other species) and its poor correlation with CH_3Cl (Figure 10) at high altitude. We base our argument on comparisons of C_2H_6 and CO, two insoluble species with similar atmospheric lifetimes. The ratio C_2H_6/CO directly over (≤1 km) active savanna fires in Brazil (mission 6) and Zambia (mission 10) had a value of about 6.0 (pptv/ppbv). Based on the median values given in Table 1 (590 pptv and 87 ppbv), the ratio in the upper troposphere over the South Atlantic basin (12.1) was twice that observed in the biomass fire regions. In both cases we subtracted background values of 65 ppbv for CO and 325 pptv for C_2H_6, their mean mixing ratio in aged Pacific and South Atlantic marine boundary layer air. This comparison suggests that sources besides biomass fire emissions contributed to the significant C_2H_6 enhancements over the South Atlantic basin.

In the high-altitude air parcels there was little direct evidence for an influence on the chemistry from urban emissions. Generally, C_2Cl_4 and CH_3CCl_3 are excellent tracers of urban (industrial) emissions [*Blake et al.*, 1995]. Over the South Atlantic basin these species rarely deviated from mixing ratios indicative of aged marine air (≈3 pptv C_2Cl_4 and 123 pptv CH_3CCl_3). Only in air parcels sampled directly downwind of Brazil's urban southeastern coast did we see enhancements in halocarbon species (Figure 3b) [*Blake et al.*, this issue]. Based on these few data, it is hard to tell if Brazilian urban areas are significant sources of halocarbon species. It could be the case that halocarbon species are only slightly enriched in these urban air parcels; mixing processes could then reduce halocarbon mixing ratios to near background values by the time the air parcels are ventilated into upper troposphere. This could explain the poor correlations observed between halocarbon species and combustion products (Figure 10).

It is possible that some of the species enhancements (e.g., CH_4) in the upper troposphere were related to inputs of northern hemispheric air parcels. During transit flights 4 and 18 we observed a molar ratio of ≈21 for CH_4/CO in the region 10° - 20 °N, just north of the ITCZ at 10 km altitude. Median values in aged marine air at 10 - 13 km altitude give a value of 20 for this ratio (Table 1), indicative of northern hemispheric air. However, other comparisons provide evidence against a northern hemispheric CH_4 source. The transit flight data (missions 4 and 18) documented an upper tropospheric gradient in CH_4 of ≈10 ppbv between the northern (1730 ppbv) and the southern hemispheres (1720 ppbv SH), or a north-south difference of -0.6%. Coincident interhemispheric differences in other long-lived species were significantly greater (e.g., C_2H_6 +10%, CH_3CCl_3 +12%, CO +15%, and C_2Cl_4 -70%). Thus the relative interhemispheric amounts of various hydrocarbon and halocarbon species are inconsistent with the idea of the northern hemisphere being the principal source of CO, CH_4 or C_2H_6 in aged marine air over the South Atlantic basin.

6. Conclusion

The positive correlations between CO and CH_3Cl and minimal enhancements of C_2Cl_4 and various CFCs in air parcels recently advected over the South Atlantic basin strongly suggest an impact on tropospheric chemistry due to continental outflow of biomass burning emissions from Brazil and Africa. The composition of aged marine air also appeared to be affected, as it exhibited an accumulation over the local dry season reflected in enhancements of up to two-fold for C_2H_6, 30% for CO, and 10% for CH_3Cl. Median mixing ratios of NO and NO_x were significantly enhanced (up to ~1 ppbv) above 10 km altitude and poorly correlated with CO and CH_3Cl. It appears that in addition to biomass burning, lightning or recycled reactive nitrogen may be an important source of NO_x in the upper troposphere over the South Atlantic.

Methane exhibited a monotonic increase in altitude from ~1690 to 1720 ppbv in both aged marine and continental outflow air masses. The largest mixing ratios in the upper troposphere were often anticorrelated with CO, CH_3Cl, and CO_2, suggesting CH_4 contributions from natural sources. Based on CH_4/CO ratios and relationships with various hydrocarbon and CFC species, it appears that inputs from biomass burning and the northern hemisphere cannot explain the distribution of CO, CH_4, or C_2H_6 in aged marine air. It would seem necessary to invoke emissions from urban areas to account for their distributions.

An efficient transport mechanism consisting of deep vertical convection over Brazil and Africa coupled with large-scale circulations conveys continental emissions to the upper troposphere over the South Atlantic basin. The resultant geographic distribution of long-lived species is remarkably constant at 10 - 13 km altitude. Slow subsidence over the eastern South Atlantic basin undoubtedly plays an important role in maintaining the compositionally similar but more processed air parcels residing from 2 to 10 km altitude. The common occurrence of values greater than 1 for the ratio CH_3OOH/H_2O_2 in the upper troposphere suggests that precipitation scavenging effectively removed highly water soluble gases (H_2O_2, HNO_3, HCOOH, and CH_3COOH) and aerosols during vertical convective transport over the continents. However, horizontal injection of biomass burning products over the South Atlantic, particularly water soluble species and aerosol particles, was frequent below 6 km altitude. These biomass fire products then appear to filter through the extensive stratocumulus cloud deck covering this oceanic region into the marine boundary layer. Here they should be efficiently deposited to the surface ocean, where inputs of atmospheric nitrogen and other nutrient species may have important implications for this oligotrophic marine ecosystem.

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References

Andreae, M. O., et al., Biomass burning and associated haze layers over Amazonia, *J. Geophys. Res.*, *93*, 1509-1527, 1988.

Andreae, M. O., A. Chapuis, B. Cros, J. Fontan, G. Helas, C. Justice, Y. J. Kaufman, A. Minga, and D. Nganga, Ozone and Aitken nuclei over equatorial Africa: Airborne observations during DECAFE 88, *J. Geophys. Res.*, *97*, 6137-6148, 1992.

Bachmeier, S., and H. E. Fuelberg, A meteorological overview of the TRACE A period, *J. Geophys. Res.*, this issue.

Bartlett, K. B., P. M. Crill, D. I. Sebacher, R. C. Harriss, J. O. Wilson, and J. M. Melack, Methane flux from the central Amazonian floodplain, *J. Geophys Res.*, *93*, 1571-1582, 1988.

Bartlett, K. B., P. M. Crill, J. A Bonassi, J. E. Richey, and R. C. Harriss, Methane flux from the Amazon River floodplain: Emissions during rising water, *J. Geophys. Res.*, *95*, 16,773-16,788, 1990.

Bartlett, K. B., G. W. Sachse, J. E. Collins, Jr., and R. C. Harriss, Methane in the tropical South Atlantic: Sources and distribution during the late dry season, *J. Geophys. Res.*, this issue.

Blake, D. R., T. -Y. Chen, T. W. Smith Jr., C. J. -L. Wang, O. W. Wingenter, N. J. Blake, F. S. Rowland, and E. W. Mayer, Three-dimensional distribution of NMHCs and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-WEST A), *J. Geophys. Res.*, *100*, 1763-1778, 1996.

Blake, D. R., N. J. Blake, B. C. Sive, T. -Y. Chen, F. S. Rowland, J. E. Collins Jr., G. W. Sachse, and B. E. Anderson, Biomass burning emissions and vertical distribution of atmospheric methyl halides and gases in the South Atlantic region, *J. Geophys. Res*, this issue.

Browell, E. V., et al., Ozone and aerosol distributions and air mass characteristics over the South Atlantic basin during the burning season, *J. Geophys. Res.*, this issue.

Cachier, H., and J. Ducret, Influence of biomass burning on equatorial African rains, *Nature*, *352*, 228-230, 1991.

Cachier, H., P. Buat-Menard, M. Fontugne, and R. Chesselet, Source terms and source strengths of the carbonaceous aerosol in the tropics, *J. Atmos. Chem.*, *3*, 469-489, 1985.

Cachier, H., M. P. Bremond, and P. Buat-Menard, Carbonaceous aerosols from different tropical biomass burning sources, *Nature*, *340*, 371-373, 1989.

Cahoon, D. C., Jr., B. J. Stocks, J. S. Levine, W. R. Cofer III, and K. P. O'Neill, Seasonal distribution of African savanna fires, *Nature*, *359*, 812-815, 1992.

Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, *2*, 299-327, 1988.

Crutzen, P.J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669-16778, 1990.

Crutzen, P. J., L. E. Heidt, J. P. Krasnec, and W. H. Pollock, Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl and COS, *Nature*, *282*, 253-256, 1979.

Delmas, R., On the emission of carbon, nitrogen and sulfur in the atmosphere during bushfires in intertropical savannah zones, *Geophys. Res. Lett.*, *9*, 761-764, 1982.

Elliott, W. P., and R. K. Reed, A climatological estimate of precipitation for the world ocean, *J. Clim. Appl. Meteorol.*, *23*, 434-439, 1984.

Fishman, J., K. Fakhruzzaman, B. Cros, and D. Nganga, Identification of widespread pollution in the southern hemisphere deduced from satellite analyses, *Science*, *252*, 1693-1696, 1991.

Fishman, J., J. M. Hoell Jr., R. D. Bendura, V. W. J. H. Kirchhoff, R. J. McNeal Jr.,, NASA GTE TRACE A experiment (September - October 1992): Overview, *J. Geophys. Res.*, this issue.

Garstang, M., P. D. Tyson, R. Swap, M. Edwards, P Kållberg, and J. A. Lindesay, Horizontal and vertical transport of air over southern Africa, *J. Geophys. Res.*, this issue.

Greenberg, J. P., P. R. Zimmerman, L. Heidt, and W. Pollock, Hydrocarbon and carbon monoxide emissions from biomass burning in Brazil, *J. Geophys. Res.*, *89*, 1350-1354, 1984.

Gregory, G. L., E. V. Browell, and L. S. Warren, Amazon Basin ozone and aerosol: Wet season observations, *J. Geophys. Res.*, *95*, 16,903-16,912, 1990.

Gregory, G. L., A. S. Bachmeier, D. R. Blake, B. G. Heikes, D. C. Thornton, J. D. Bradshaw, and Y. Kondo, Chemical signatures of aged Pacific marine air: Mixed layer and free troposphere as measured during PEM-WEST A, *J. Geophys. Res.*, *101*, 1727-1742, 1996.

Harris, G. W., et al., Airborne observations of strong biogenic NO_x emissions from the Namibian savanna at the end of the dry season, *J. Geophys. Res.*, this issue.

Harriss, R. C., G. W. Sachse, J. E. Collins Jr., L. Wade, K. B. Bartlett, R. W. Talbot, E. V. Browell, L. A. Barrie, G. F. Hill, and L. G. Burney, Carbon monoxide and methane over Canada: July - August 1990, *J. Geophys. Res.*, *99*, 1659-1669, 1994.

Heikes, B. G., Formaldehyde and hydroperoxides at Mauna Loa observatory, *J. Geophys. Res.*, *97*, 18,001-18,013, 1992.

Heikes, B. G., et al., Hydrogen peroxide and methylhydroperoxide distributions related to ozone and odd hydrogen over the North Pacific in the fall of 1991, *J. Geophys. Res.*, *101*, 1891-1905, 1996.

Heikes, B., M. -H. Lee, D. Jacob, R. Talbot, and J. Bradshaw, Ozone-hydroper oxides, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic, *J. Geophys Res.*, this issue.

Helas, G., H. Bingemer, and M. O. Andreae, Organic acids over equatorial africa: Results from DECAFE 88, *J Geophys. Res.*, *97*, 6187-6193, 1992

Jacob, D. J., et al., Origin of ozone and NO_x in the Atlantic basin in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin, *J. Geophys. Res.*, this issue.

Kirchhoff, V. W. J. H., and R. A. Rasmussen, Time variations of CO and O_3 concentrations in a region subject to biomass burning, *J. Geophys. Res.*, *96*, 10,899-10,909, 1990.

Kirchhoff, V. W. J. H., and E. V. A. Marinho, Layer enhancements of tropospheric ozone in regions of biomass burning, *Atmos. Environ.*, *28*, 69-74, 1994.

Kirchhoff, V. W. J. H., J. R. Alves, F. R. da Silva, and J. Fishman, Observations of ozone concentrations in the Brazilian cerrado during the TRACE A field expedition, *J. Geophys. Res*, this issue.

Kleinman, L. I., and P. H. Daum, Vertical distribution of aerosol particles, water vapor, and insoluble trace gases in convectively mixed air, *J. Geophys. Res.*, *96*, 991-1005, 1991.

Krishnamurti, T. N., H. E. Fuelberg, M. C. Sinha, D. Oosterhof, E. L. Bensman, and V. B. Kumar, The meteorological environment of the tropospheric ozone maximum over the tropical South Atlantic Ocean, *J. Geophys. Res.*, *98*, 10,621-10,641, 1993.

Krishnamurti, T. N., M. C. Sinha, M. Kanamitsu, D. Osterhof, H. Fuelburg, R. Chatfield, D. J. Jacob, and J. Logan, Passive tracer transports relevant to the TRACE A experiment, *J. Geophys. Res.*, this issue.

Kuhlbusch, T. A., J. M. Lobert, P. J. Crutzen, and P. Warneck, Molecular nitrogen emissions from denitrification during biomass burning, *Nature*, *351*, 135-137, 1991.

Lacaux, J. P., R. Delmas, G. Kouadio, B. Cros, and M. O. Andreae, Precipitation chemistry in the Mayombe Forest of equatorial Africa, *J. Geophys. Res.*, 97, 6195-6206, 1992.

Leslie, A. C D., Aerosol emissions from forest and grassland burning in the southern Amazon Basin and central Brazil, *Nucl. Instrum. and Method ,181*, 345-351, 1981.

Levine, J. S., et al., Biogenic soil emissions of nitric oxide (NO) and nitrous oxide (N_2O) from savanna in South Africa: The impact of wetting and burning, *J. Geophys. Res.*, this issue.

Lobert, J. M., D. H. Scharffe, W. -M. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning - Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 289-304, The MIT press, Cambridge, Mass., 1991.

McKeen, S. A., and S. C. Liu, Hydrocarbon ratios and photochemical history of air masses, *Geophys. Res. Lett.*, *20*, 2363-2366, 1993.

Moody, J. L., A. A. P. Pszenny, A. Gaudry, W. C. Keene, J. N. Galloway, and G. Polian, Precipitation composition and its variability in the southern Indian Ocean: Amsterdam Island, 1980-1987, *J. Geophys. Res.*, *96*, 20,769-20,786, 1991.

Newell, R. E., S. T. Shipley, V. S. Connors, and H. G. Reichle Jr., Regional studies of potential carbon monoxide sources based on space shuttle and aircraft measurements, *J. Atmos. Chem.*, *6*, 61-81, 1988.

Olson, J. R., J. Fishman, V. W. J. H. Kirchhoff, D. Nganga, and B. Cros, An analysis of the distribution of O_3 over the southern Atlantic region, *J. Geophys. Res.*, this issue.

Paerl, H. W., Enhancement of marine primary production by nitrogen-enriched acid rain, *Nature*, *315*, 747-749, 1985.

Paerl, H. W., Emerging role of atmospheric nitrogen deposition in coastal eutrophication: Biogeochemical and trophic perspectives, *Can. J. Aquat. Sci.*, *50*, 2254-2269, 1993.

Pickering, K. E., A. M. Thompson, J. R. Scala, W. Tao, and J. Simpson, Ozone production potential following convective redistribution of biomass burning emissions, *J. Atmos. Chem.*, *14*, 297-313, 1992.

Pickering, K. E., A. M. Thompson, D. P. McNamara, and M. R. Schoeberl, An intercomparison of isentropic trajectories over the South Atlantic, *Mon. Weather Res.*, *122*, 864-879, 1994.

Pickering, K. E., et al., Convective transport of biomass burning emissions over Brazil during TRACE A, *J. Geophys Res* , this issue.

Rudolph, J , A. Khedim, and B Bonsang, Light hydrocarbons in the tropospheric boundary layer over tropical Africa, *J. Geophys. Res.*, *97*, 6181-6186, 1992.

Singh, H. B., and P. B. Zimmerman, Atmospheric distribution and sources of nonmethane hydrocarbons, in *Gaseous Pollutants: Characterization and cycling*, edited by J. O. Nriagu, pp. 177-235, John Wiley, New York, 1992.

Smyth, S., et al., Factors influencing the upper free tropospheric distribution of reactive nitrogen over the South Atlantic during the TRACE A experiment, *J. Geophys Res.*, this issue.

Spiro, P. A., D. J. Jacob, and J. A. Logan, Global inventory of sulfur emissions with 1° x 1° resolution, *J. Geophys. Res.*, *97*, 6023-6036, 1992.

Steele, L. P., E. J. Dlugokencky, P. M. Lang, P. P. Tans, R. C. Martin, and K. A. Masarie, Slowing down of the global accumulation of atmospheric methane during the 1980s, *Nature*, *358*, 313-316, 1992.

Tathy, J. P., B. Cros, R. A. Delmas, A. Marenco, J. Servant, and M. Labat, Methane emission from flooded forest in central Africa, *J. Geophys. Res.*, *97*, 6159-6168, 1992.

Thompson, A. M., K. E. Pickering, D. P. McNamara, R. D. Peters, Effect of marine stratocumulus on TOMS ozone, *J. Geophys. Res.*, *98*, 23,051-23,057, 1993.

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