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


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 CH3Cl and minimal enhancements of C2C14 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 C2H6, 30% for CO, and 10% for CH3Cl. Nitric oxide and NO2 were significantly enhanced (up to ~1 part per billion by volume (ppbv)) above 10 km altitude and poorly correlated with CO and CH3Cl. In addition, median mixing ratios of NO and NO2 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 NO2 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, CH3Cl, and CO2, suggesting CH4 contributions from natural sources. We also argue, based on CH4/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, CH4, and C2H6 in aged marine air. Emissions from urban areas would seem to be necessary to account for the distribution of at least CH4 and C2H6. 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 CH3OOH/H2O2 in the upper troposphere suggests that precipitation scavenging effectively removed highly water soluble gases (H2O2, HNO3, HCOOH, and CH3COOH) 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, CO2, CH4, HCOOH, CH3COOH, NO, selected nonmethane hydrocarbons, particulate elemental species such as P, S, Cl, Mg, Ca, graphitic (soot) C, and organic carbon [Leslie, 1981; Greenberg et al., 1984; Cachier et al.,...
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\textsubscript{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 lead to production of acidic gases, and these subsequently cause acid rainfall [Lacaux et al., 1992]. Release of smoke particles from biomass fires may provide copious 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\textsubscript{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\textsubscript{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 Janeiro (one mission) in Brazil; (2) Johannesburg (three missions) in South Africa; (3)
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 outflow conditions 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 (NOx) instruments [S.T. Sandholm, et al., Comparison of NOx budget 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 NOx (ΣNOx = nitric oxide [NO] + nitrogen dioxide [NO2] + nitric acid [HNO3] + peroxyacetyl nitrate [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 sparse 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]. Weeker 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 southeastern Brazil is confined by the orographic 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 NOx (NO + NO2) measurements. The measurements of faster response instruments (e.g., meteorological parameters, aerosol number density, and species including O3, CO, CO2, CH4, and N2O) 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, peroxyacetyl nitrate, 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 South Atlantic 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 NOx, CO, and C2H6) 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 N2O, 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 NOx, C2H6, C3H8, C2H2 and lowest ratio values of C2H5/CO and C4H9/C2H6. 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 C2H6. 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 C2H5, C3H8, and C2H2 compared to those at lower altitudes. Halocarbons and industrial tracers did not follow the trend exhibited by these hydrocarbon species, but CH3Cl did. The CH3Cl enhancement is evidence for a biomass
Andreae, the marine boundary layer [Crutzen and Daum, 1991; Picketing et al., 1992, this issue]. Poor correlations (r < 0.3) between NO (or NOx) and CO or CH3Cl 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 NOx mixing ratios in the upper troposphere were not significantly different in aged marine and continental influenced air masses.

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 species lifetimes once they were in this region [Jacob et al., 1991] indicated that they had probably been over the Pacific Ocean (<5 days) combustion inputs to these air parcels. Indeed, elevated mixing ratios of many species in the general composition and backward trajectories for these air parcels aged air parcels. There does not appear to be strong evidence for biomass burning influence on the chemistry of aged air at altitudes above the marine boundary layer [Crutzen et al., 1979; Crutzen and Andreae, 1990].

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 NOx 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 < 0.3) between NO (or NOx) and CO or CH3Cl 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 NOx mixing ratios in the upper troposphere were not significantly different in aged marine and continental influenced air masses.
This is further evidence for important sources of NOx besides biomass burning. Note that while NO mixing ratios approached 1 pptv, 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 C2Cl4 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 C2H2/CO and C2H4/C2H6 to facilitate comparisons of various air parcels. For an [OH] of $1 \times 10^6$ molecules cm$^{-2}$, a reasonable value for the TRACE A study area [Jacob et al., this issue], C2H2 and C2H4 have atmospheric lifetimes near 2 weeks compared to about 2 months for CO and C2H6.

On the average, the value of the ratio C2H2/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., HNO3) 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, $\sum$NOy, C2H4, and C2H6 over the western South Atlantic were relatively constant above 2 km altitude (Figure 3). Mixing ratios of CO, $\sum$NOy, and C2H6 were elevated roughly two-fold over their median values in aged marine air, while CH3Cl was
enhanced about 10%. There was good correlation between mixing ratios of CO and CH$_3$Cl (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 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$_2$ data. Mixing ratios of NO and NO$_2$ 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$_2$ 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$_3$Cl were correlated for CH$_3$Cl 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$_3$Cl [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$_2$H$_4$ [Rudolph et al.,...
Table 3. Mixing Ratios of Principal Species Measured in Continental Outflow Over the Eastern South Atlantic Ocean

<table>
<thead>
<tr>
<th>Species</th>
<th>Mean (ppbv)</th>
<th>s.d.</th>
<th>Median (ppbv)</th>
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<td>CFC-II</td>
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<td>445</td>
<td>152-973</td>
<td>67</td>
</tr>
<tr>
<td>PAN</td>
<td>294</td>
<td>336</td>
<td>230</td>
<td>10-1488</td>
<td>34</td>
</tr>
<tr>
<td>ΣNO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>588</td>
<td>334</td>
<td>522</td>
<td>212-2113</td>
<td>66</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6</td>
<td>6.2</td>
<td>63</td>
<td>47-80</td>
<td>122</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>129</td>
<td>42</td>
<td>108</td>
<td>80-198</td>
<td>122</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1699</td>
<td>6.0</td>
<td>1701</td>
<td>1684-1719</td>
<td>122</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>356.8</td>
<td>2.3</td>
<td>356.6</td>
<td>353.3-360.0</td>
<td>116</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>103</td>
<td>1.3</td>
<td>101.5</td>
<td>100-106</td>
<td>56</td>
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<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30</td>
<td>30</td>
<td>20</td>
<td>6.6-124</td>
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<td>HCHO</td>
<td>2187</td>
<td>1838</td>
<td>1560</td>
<td>230-6966</td>
<td>61</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;C=O</td>
<td>2785</td>
<td>2554</td>
<td>2155</td>
<td>487-12,254</td>
<td>61</td>
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<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2940</td>
<td>2147</td>
<td>617</td>
<td>28-7818</td>
<td>59</td>
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<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>828</td>
<td>441</td>
<td>668</td>
<td>13-1547</td>
<td>80</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>132</td>
<td>89</td>
<td>92</td>
<td>5.0-323</td>
<td>32</td>
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<tr>
<td>Aerosols</td>
<td>520</td>
<td>472</td>
<td>175</td>
<td>7.5-1457</td>
<td>49</td>
</tr>
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</table>

Mixing ratios are stated in parts per trillion by volume (pptv), except for CO, CH<sub>4</sub>, N<sub>2</sub>O and O<sub>3</sub> that are in parts per billion by volume (ppbv), and CO<sub>2</sub> in parts per million by volume (ppmv); s.d. states the 1 standard deviation. CH<sub>2</sub>OH/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<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>2</sub>O, HCHO, CH<sub>3</sub>COOH, and HNO<sub>3</sub>. 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<sub>x</sub> (< 100 pptv) and large ratios of HNO<sub>3</sub> (<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<sub>x</sub> in these plumes. Mixing ratios of O<sub>3</sub> 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 [Heikes et al., 1992]. It appears that a similar argument can be made for the peroxyde 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
general lofting of fire plumes into the prevailing offshore wind regimes over Brazil and Africa.

The ratio CH$_3$OOH/H$_2$O$_2$ 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$_2$O$_2$ by precipitation due to its greater solubility in water than CH$_3$OOH [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].

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$_3$H$_6$/CO is stated in parts per trillion by volume/parts per billion by volume(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 HNO₃ 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
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, CH₄, PAN, C₂H₂, and CH₃Cl. 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 turbulent 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 assessment of species sources in the 10- to 13-km altitude range. Values of the ratios C₂H₂/CO and C₃H₈/C₂H₆ 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 C₂H₂/CO and C₃H₈/C₂H₆ 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 10⁰ N. In the southern hemisphere the enhanced mixing ratios of CO, PAN, C₂H₂, and CH₃Cl are indicative of a large-scale influence of biomass fire emissions. The increased mixing ratios of CH₄ and C₂Cl₂ in the northern hemisphere are presumably driven by larger sources there [Steele et al., 1992; Blake et al., 1996].

Figure 5. Relationship between CO and CH₃Cl 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.

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.
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, CH₄, and CO₂) 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 N₂O mixing ratios around 308 ppbv.

The latitudinal data also exhibit several other notable characteristics. For example, O₃ 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 O₃ 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 O₃ 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 O₃ 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 7. Distribution of the ratio CH₃OOH/H₂O₂ 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 H₂O₂ was preferentially removed by precipitation.

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

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 ≤ 0.5) or nonexistent (Figure 10). For example, there appears to be a positive but very general correlation between ΣNOx and aerosol number density (r = 0.41). No other species, including NO2, HNO3, 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 ABL (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 10⁴ cm⁻³ under conditions of heavy fumigation by biomass fire emissions. Aerosol and ΣNOx 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 plumes) and also an anticorrelation with natural biogenic indicators (CO2, CO, CH4 emissions, and CO2 uptake). To evaluate the potential for emissions from biomass fires to support the CH4 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 CH4 and CO at 10 - 13 km altitude (1717 and 87 ppbv, 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 CH4/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 CH4 enhancement at high altitude.

While natural CH4 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 CH4 emissions from these regions [Bartlett et al., 1988, 1990; Tathy et al., 1992].

Emissions from urban areas, however, can be quite enriched in CH4 [Harries 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 fuel 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 CH4 (and other species) and its poor correlation with CH4Cl (Figure 10) at high altitude. We base our argument on comparisons of CH4 and CO with CH4Cl over 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 ppbv for CH4 to 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 CH4 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, C2H4, CH3CCL, and CH4Cl 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 CH4Cl, and 123 pptv CH4Cl2). 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., CH4) 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 CH4/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 have a value of 20 for this ratio (Table 1), indicative of northern hemispheric air. However, other comparisons provide evidence against a northern hemispheric source. The transit flight data (missions 4 and 18) documented an upper tropospheric gradient in CH4 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., C2H6 +10%, CH3CCl +12%, CO +15%, and C2Cl4 -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, CH4, or CH4Cl in aged marine air over the South Atlantic basin.

6. Conclusion

The positive correlations between CO and CH4Cl and minimal enhancements of C2H4Cl 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 C2H6, 30% for CO, and 10% for CH4Cl. Median mixing ratios of NO and NO2 were significantly enhanced (up to ~1 ppbv) above 10 km altitude and poorly correlated with CO and CH4Cl. It appears that in addition to biomass burning, lightning or recycled reactive nitrogen may be an important source of NO 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, CH4Cl, and CH4, suggesting CH4 contributions from natural sources. Based on CH4/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, CH4, or CH4Cl 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 CH2O/H2O in the upper troposphere suggests that precipitation scavenging effectively removed highly water soluble gases (H2O2, HNO3, HCOOH, and CH2COOH) 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 5 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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