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Ozone, hydroperoxides, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic

Brian Heikes, Meehye Lee, Daniel Jacob, Robert Talbot, John Bradshaw, Hanwant Singh, Donald Blake, Bruce Anderson, Henry Fuelberg, and Anne M. Thompson

Abstract. The NASA GTE TRACE A mission sampled air over the South Atlantic and western Indian Oceans. Thirteen flight legs were flown within the marine boundary layer (MBL). The MBL was typically the cleanest air sampled (e.g., CH₄ < 1680 ppb, CO < 70 ppb, C₂H₆ < 400 ppt, C₃H₈ < 40 ppt, NOₓ < 15 ppt, and midday NO < 5 ppt) but was overlain by polluted air. The photochemistry of the MBL was influenced by oceanic emissions, surface deposition, and entrainment of pollutants from aloft. Chemical budgets were constructed for several species in the MBL in order to investigate these effects and are presented for ethane, ethylene, propane, propylene, n-butane, formic acid (HFO), methylhydroperoxide (CH₃OOH), oxides of nitrogen (i.e., NO, NO₂, PAN, HNO₃), hydrogen peroxide (H₂O₂), and ozone (O₃). A photochemical point model was used to evaluate local chemical production and loss. An entrainment model was used to assess material exchange between the lower free troposphere (FT) and the MBL and a resistance deposition model was used to evaluate material exchange across the air-sea interface. The results suggested the ocean to be the source of measured alkenes in the MBL and to be the most likely source of the shorter-lived alkanes: propane and n-butane. Ethane was the only hydrocarbon for which input from aloft may have exceeded its photochemical destruction. The estimated hydrocarbon sources from the ocean were in agreement with prior analyses. Transport from the lower FT together with surface loss could not account for measured concentrations of CH₂O, HFO, and HNO₃. The transport of peroxyacetyl nitrate (PAN) from the FT to the MBL exceeded the rate of HNO₃ production and was more than sufficient to maintain observed NOₓ levels without having to invoke an oceanic source for NO. The flux of NOₓ, PAN, and HNO₃ was in balance with the surface deposition flux of HNO₃. However, the predicted rates of HNO₃ formation from the oxidation of NO₂ and HNO₃ entrainment from aloft were inadequate to maintain observed levels of HNO₃ unless HNO₃ was partitioned between the gas phase and a more slowly depositing aerosol phase. The estimated dry deposition flux of HNO₃ to the South Atlantic during TRACE A, 2-4 × 10⁹ molecules cm⁻² s⁻¹, was about 10 times the annual average estimate for this region. The destruction of O₃ within the MBL was found to be exceeded by transport into the MBL from aloft, 6 ± 2 × 10¹⁰ compared to 11 ± 10 × 10¹⁰ molecules cm⁻² s⁻¹. The principal O₃ destruction process was mediated by the formation and surface deposition of H₂O₂ and CH₃OOH, 4 ± 4 × 10¹⁰ and 1.1 ± 0.5 × 10¹⁰ molecules cm⁻² s⁻¹. The direct loss of O₃ to the sea surface was estimated to be 1.7 ± 0.2 × 10¹⁰ molecules cm⁻² s⁻¹. CH₂O losses to the sea and transported into the FT from the MBL. Its first-order loss rate was estimated to be 7 × 10⁻⁶ s⁻¹ for a mean MBL height of 700 m. H₂O₂ and CH₃O losses from the MBL were estimated at rates of 1.3 × 10⁻⁵ s⁻¹ for both species. The inclusion of surface deposition improved the agreement between predicted and measured concentrations of HNO₃, CH₂O, H₂O₂, and CH₃O. However, model CH₂O remained significantly greater than that measured in the MBL.
1. Introduction

The NASA GTE Transport and Atmospheric Chemistry near the Equator—Atlantic Experiment (TRACE A) was an investigation into the causes of high tropospheric ozone ($O_3$) concentrations observed over the South Atlantic in the months of September and October [Fishman et al., 1990, this issue(a)]. The TRACE A study area included the continents of South America and Africa and the South Atlantic and western Indian Oceans. The experiment occurred in September and October 1992. The NASA DC-8 aircraft was used as a platform to measure $O_3$ and the distribution of key-related species throughout the entire depth of the troposphere. On 7 of the 19 flights a total of 13 legs were flown in the marine boundary layer (MBL). We present in this paper MBL chemical budgets for $O_3$, light hydrocarbons, oxides of nitrogen, and a few photochemical products over the South Atlantic and western Indian Oceans. TRACE A results related to high $O_3$ throughout the tropospheric column are presented in companion articles [e.g., Fishman et al., this issue(b); Thompson et al., this issue; Jacob et al., this issue; Krishnamurti et al., this issue].

The remote MBL is recognized for its role in the destruction of tropospheric $O_3$, the antithesis of the primary TRACE A mission. Lenschow et al. [1982], Kawo and Pearson [1989], and Paluch et al. [1994] evaluated the vertical flux of $O_3$ at the top of the MBL and within the MBL. They showed the MBL over the Gulf of Mexico and the eastern North Pacific to be a sink for tropospheric $O_3$. Ozone loss was postulated to be the result of photochemical destruction and ozone destruction/absorption at the ocean's surface. Noone et al. [1995] examined $O_3$ in and above the MBL over the North Atlantic in two Lagrangian experiments near the Azores. They could not resolve net $O_3$ production from surface deposition and entrainment. Modeling studies by Liu et al. [1983] and Thompson et al. [1993] have shown the net destruction of ozone in the MBL to be photochemically mediated with $O_3$ replacement from the overlying free troposphere (FT). These chemical models were applied to observations from the equatorial Pacific Ocean, where nitric oxide (NO) concentrations were less than a few ppt. Ayers et al. [1992] and Ayers et al. [1995] examined the correlation of $O_3$ and $H_2O_2$ over diel and annual cycles at Cape Grim, Tasmania, and showed the daytime destruction of $O_3$ to be accompanied by a stoichiometric increase in peroxides (most likely hydrogen peroxide and a major fraction of methylhydroperoxide). They further suggested that replacement $O_3$ was mixed into the MBL from aloft, while the peroxides were lost to the ocean's surface. The TRACE A measurements and photochemical model results permitted an evaluation of the rate and mechanism of net $O_3$ production in the MBL over the South Atlantic under similar low NO conditions.

Several investigations have attempted to evaluate the oceanic flux of hydrocarbons into the atmosphere and their impact on atmospheric chemistry, particularly $O_3$ and hydroxyl (HO). A combination of atmospheric measurements, seawater measurements, air-sea exchange rates, and photochemical models have been used to infer hydrocarbon fluxes over the equatorial Pacific [Donahue and Prinn, 1993; Thompson et al., 1993], the North and South Pacific [Lamontagne et al., 1974], the Atlantic [Rudolph and Johnsen, 1990; Plass et al., 1992], the Indian Ocean [Bonsang et al., 1988], and in the remote marine atmosphere [Donahue and Prinn, 1990]. Bonsang et al. [1991] made hydrocarbon measurements up to an altitude of 1600 m from which they investigated both oceanic emissions and MBL-FT exchange at an island site in the South Pacific. Nevertheless, measurements and oceanic flux estimates remain sparse in time and location over the ocean. Although few in number, the evaluated oceanic hydrocarbon emissions span orders of magnitude. A combination of model results and measurements are applied below in an investigation of the relative contribution of FT-MBL exchange and oceanic emissions in establishing hydrocarbon concentrations in the MBL over the South Atlantic.

Oxides of nitrogen along with hydrocarbons are central to defining oxidant species and their concentrations in the atmosphere. The remote MBL is one of the few regions of the world wherein noontime NO levels below 5 ppt are consistently found [McFarland et al., 1979; Torres and Thompson, 1993]. Zafirou and McFarland [1981] and Torres and Thompson [1993] proposed a weak photolytic source of atmospheric NO from nitrate rich ocean waters. TRACE A NO concentrations in the MBL were also below 5 ppt under daylight conditions [Smyth et al., this issue]. NO, nitrogen dioxide ($NO_2$), peroxyacetylinitrate (PAN), and nitric acid ($HNO_3$) were typically observed to increase in going from the MBL to the FT [Singh et al., this issue], which suggested that the downward flux of nitrogen oxides could be an important source of MBL nitrogen oxides in the TRACE A study location.

While the deposition of $HNO_3$ to the ocean removes reactive nitrogen from the troposphere, thereby limiting net oxidant production, the downward flux of $HNO_3$ and the conversion of $NO_2$ to $HNO_3$ in the MBL has important biological implications. Biological productivity in the oligotrophic ocean is considered to be limited by the availability of fixed nitrogen and the atmosphere may be a source of this macronutrient [Duce et al., 1991]. The TRACE A oxides of nitrogen data allowed estimates of the flux of $HNO_3$ to the South Atlantic to be made and allowed a reexamination of earlier estimates of the air-sea input of fixed nitrogen over this region.

Hydrogen peroxide, $CH_3OOH$, and $CH_2O$ measurements have been used to validate photochemical model odd hydrogen (e.g., HO, $HO_2$, $RO_2$) chemistry through the comparison of observed and predicted concentrations. The comparisons with airborne data above the boundary layer are in agreement within stated measurement and kinetic uncertainties [Jacob et al., this issue; Crawford et al., 1995]. However near the Earth's surface, models and measurements diverge with the models typically indicating higher values than observed [Lowe and Schmidt, 1983; Thompson et al., 1993; Crawford et al., 1995; Jacob et al., this issue], and surface deposition of the more highly soluble species, e.g., $CH_2O$, $HNO_3$, and $H_2O_2$, has often been invoked to explain these differences. The suite of the more soluble species measured in TRACE A ($H_2O_2$, $CH_3OOH$, $CH_2O$, $HNO_3$, and $HFO$) together with the measurements of $O_3$, NO, and hydrocarbons permitted us to examine this assumption and test for consistency between the deposition of species with short photochemical timescales (e.g., $H_2O_2$, $CH_3OOH$, or $CH_2O$) and those with longer photochemical timescales (e.g., $O_3$, $HNO_3$, or $HFO$). These data and their analysis provide additional constraints on the models and, if successful, place greater confidence in other model products (e.g., HO or net $O_3$ production).

2. Methodology

The location of the TRACE A MBL flight legs is shown in Figure 1. Specific MBL cases are identified by lowercase letters. Capital letters indicate aircraft bases of operation: A,
Ascension Island; J, Johannesburg; Re, Recife; Ri, Rio de Janeiro; W, Windhoek. The lower atmosphere during TRACE A was characterized by a strong thermal inversion at the top of the MBL, at which the specific humidity ($q$) of the air decreased markedly. Often, the MBL was capped by stratus clouds which are a prominent feature of the South Atlantic MBL. The height of the MBL ($Z_{MBL}$) was defined by the temperature inversion and decrease in $q$ and encompassed the marine stratus and cumulus clouds. A combination of dropsonde data (see discussion by Fuelberg et al. [this issue(a)]), differential absorption lidar (DIAL) data [Browell et al., this issue], and aircraft observations were used to establish $Z_{MBL}$.

Air parcel trajectories for the MBL, calculated using the procedures of Fuelberg et al. [this issue(b)], indicated sampled air masses to have been over the ocean for at least the prior 4 days. Further, the concentrations of NO, CO, CH$_4$, and other chemical data suggested it to be relatively unimpacted by recent continental emissions. Chemical data and air trajectories for the overlying FT indicated this air to have come from over the continents within the past 1 to 2 days [Pickering et al., this issue], and the chemical data suggested that it contained partially processed continental biomass and industrial emissions [Talbot et al., this issue; Mauzerall et al., 1996; Blake et al., this issue].

Table 1 lists the MBL cases, locations, times, MBL height ($Z_{MBL}$), and other chemical data.

The complete suite of chemical and meteorological measurements made onboard the DC-8 during TRACE A is listed by Fishman et al. [this issue(a)]. Specific chemical measurements used in this study are presented briefly below. Nitric oxide and NO$_2$ were measured using two-photon laser-induced fluorescence [Smyth et al., this issue]. Hydrocarbon samples (specifically ethane, ethene, propane, propene, and $n$-butane or C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$, C$_2$H$_6$, and $n$-C$_4$H$_{10}$, respectively) were collected in stainless-steel canisters and analyzed using the techniques and procedures outlined by Blake et al. [this issue]. O$_3$ was measured using a NO-O$_3$ chemiluminescence method [Collins et al., this issue]. H$_2$O$_2$ and formic acid (HFA) were collected in aqueous solution and analyzed using a high-pressure liquid chromatography system [Lee et al., 1995]. CH$_2$O was collected in aqueous solution using a coil collector and was analyzed by the method of Lazrus et al. [1988]. HNO$_3$ and formic acid (HFA) were collected in aqueous solution using mist chambers and analyzed by ion chromatography [Talbot et al., this issue].

A slab model [after Lenschow et al., 1982] was used to analyze MBL chemical budgets. In this model, the time rate of change of a chemical constituent in the MBL slab ($dC_{i,MBL}/dt$, molecules cm$^{-3}$ s$^{-1}$) is described by its local photochemical production and loss ($P_{i,MBL}$ and $L_{i,MBL}$, molecules cm$^{-3}$ s$^{-1}$), its flux across the air-sea interface ($F_{i,AS}$, molecules cm$^{-2}$ s$^{-1}$), and its flux across a surface defining the top of the MBL ($F_{i,MBL}$, molecules cm$^{-2}$ s$^{-1}$):

$$dC_{i,MBL}/dt = P_{i,MBL} - L_{i,MBL} - F_{i,MBL}/Z_{MBL} - F_{i,AS}/Z_{MBL}$$

where $i$ denotes a specific chemical species. Horizontal advection was assumed to be negligible on the timescale of a day or 3, which was of the order of the chemical relaxation times of the species listed above. Figure 2 shows a schematic of the lower atmosphere and the transport processes which we have included.

The flux at the top of the MBL is represented by an entrainment velocity ($K_e$) times the difference in concentration between the FT and MBL:

$$F_{MBL} = K_e(C_{i,FT} - C_{i,MBL})$$

where $C_i$ has units of molecules cm$^{-3}$. $K_e$ was assumed to be equal to 0.5 cm s$^{-1}$ and was estimated from the work of Lenschow et al. [1982], Kawa and Pearson [1989], Paluch et al. [1994], and Bretherton and Siems [1994], describing the flux of O$_3$ across the top of the MBL under meteorological conditions.
wind speed was 7 m s\(^{-1}\). At 7 m s\(^{-1}\) the resulting deposition velocity for CH\(_3\)OOH is 0.5 cm s\(^{-1}\) and is 0.88 cm s\(^{-1}\) for the wind speed (nominally 300-m elevation), assuming a logarithmic wind profile and the parameterization given by Wu [1995]. Ke was taken to be independent of the wind speed and concentrations at 10-m elevation. The parameterized model of Duce et al. [1991]. Air-sea transfer was taken depends upon both an atmospheric transport velocity, k\(_a\), and oceanic equivalent gas phase concentration in the upper ocean, C\(_{i,AS}\), was assumed to be negligible for the species listed. K\(_{i,AS}\) was evaluated using the simplified thin-film parameterized model of Duce et al. [1991]. Air-sea transfer was assumed to be limited by atmospheric turbulence for all but the ocean was estimated using a deposition velocity (K\(_{i,AS}\)) times the MBL concentration:

\[
F_{i,AS} = K_{i,AS}(C_{i,MBL} - C_{i,AS})
\]

The oceanic equivalent gas phase concentration in the upper ocean, C\(_{i,AS}\), was assumed to be negligible for the species listed. K\(_{i,AS}\) was evaluated using the simplified thin-film parameterized model of Duce et al. [1991]. Air-sea transfer was assumed to be limited by atmospheric turbulence for all but CH\(_3\)OOH, which has a significantly lower solubility in water [O'Sullivan et al., 1995], than the other species. Hence its uptake depends upon both an atmospheric transport velocity, k\(_a\), and an oceanic transport velocity, k\(_o\). This scheme required the wind speed and concentrations at 10-m elevation. The 10-m wind speed has been calculated from aircraft-measured wind speed (nominally 300-m elevation), assuming a logarithmic wind profile and the parameterization given by Wu [1995].

These wind speeds are listed in Table 1 and were nearly identical to climatological values [U.S. Navy, 1978, 1976]. A typical wind speed was 7 m s\(^{-1}\). At 7 m s\(^{-1}\) the resulting deposition velocity for CH\(_2\)O is 0.5 cm s\(^{-1}\) and is 0.88 cm s\(^{-1}\) for the other gases. Thompson and Lenschow [1984] showed through a modeling investigation that the concentration of a soluble gas (e.g., HNO\(_3\)) at 10-m height is within a few percent of its concentration at 100 m or higher and the concentrations at 300 m have been used without modification to calculate surface fluxes. The assumptions related to surface fluxes could be compromised if flow separation has developed (C. S. Bretherton, personal communication) and the estimated fluxes would then reflect upper limit values. Flow separation is associated with relative deep and mature MBLs, which are characterized by marine cumulus clouds. The bulk of the MBL cases here were overlain by marine stratus, which suggested a continuous MBL flow regime connecting the surface flux layer to the MBL cloud layer. Hence the assumptions above appeared reasonable.

The diel-average photochemical point model of Jacob et al. [this issue] was used to evaluate local MBL chemistry (i.e., F\(_{i,MBL}\) and L\(_{i,MBL}\)). Parameterizations of vertical fluxes, such as those just described, are not included in the model. Odd oxygen (sum of O\(_3\), O, NO\(_2\), HNO\(_4\), 2'NO\(_3\), and 3'N\(_2\)O\(_5\)), H\(_2\)O\(_2\), CH\(_2\)OH, and HNO\(_3\) production rates were calculated along with the concentrations of HO, perhydroxyl (HO\(_2\)), H\(_2\)O\(_2\), CH\(_2\)OH, CH\(_2\)O, HNO\(_3\), NO\(_2\), and PAN. The model calculations were performed using a merged time series of the aircraft data indexed to the NO sample times [see Jacob et al., this issue]. The availability of hydrocarbon measurements limited the number of points which could be explicitly simulated, and in order to enhance the number of model-measurement points, the model was run assuming fixed background hydrocarbon concentrations [Jacob et al., this issue].

The MBL chemical concentrations were taken from the NO-merged product for consistency with the photochemical point model [Jacob et al., this issue] or, if available, directly from actual observations entirely within the MBL. However, estimating lower FT concentrations was more difficult. Individual species measurements were made with different instrument duty cycles and at variable intervals. This, together with the aircraft ascent/descent rate nominally 7 m s\(^{-1}\), made it necessary to infer C\(_{i,FT}\) from observations between Z\(_{MBL}\) and 4000 m. This treatment was analogous to those used by Falch et al. [1994] and Wang and Albrecht [1994], wherein they used mean concentrations between Z\(_{MBL}\) and a reference height to calculate material fluxes at the MBL. Table 2 lists the MBL and FT hydrocarbon concentrations for the 13 cases identified. Table 3 lists MBL and FT concentrations for H\(_2\)O\(_2\), O\(_3\), CO, CH\(_2\)OH, CH\(_3\)OH, H\(_2\)O\(_2\), CH\(_2\)OH, and CH\(_2\)O. Figures 3 and 4 show vertical profiles for these species for cases d and i from flights 8 and 14 off the coasts of Brazil and Gabon. Species variation within the MBL and during descent and ascent at each end of a MBL leg are illustrated by these figures. The dashed line shows the height of the MBL.

The species examined were chosen because of their relevance to photochemistry in the MBL and to check for consistency among measurements, photochemical model results, and transport models. They represent a mix of species with different aqueous solubilities, sources, and photochemical lifetimes.

3. Results

3.1. \(O_3 - H_2O_2 - CH_3OOH\)

According to current understanding, destruction of ozone in the MBL is thought to proceed through the following se-
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Table 3a. Marine Boundary Layer Concentration, ppt

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^aNO_x is the diel-average model value based upon measured NO.
^bA value of 3 was substituted for <5 in calculating the average and standard deviation.

Table 3b. Four Kilometers to Marine Boundary Layer Concentrations, ppt

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<th>Case</th>
<th>CO, ppb</th>
<th>O_3, ppb</th>
<th>NO_x,^a</th>
<th>HNO_3</th>
<th>PAN</th>
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<td>1000</td>
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<tr>
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<td>160</td>
<td>300</td>
<td>1800</td>
<td>450</td>
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</table>

^aNO_x is the diel-average model value based upon measured NO.
Figure 3. Vertical profiles of O₃, NOₓ, PAN, HNO₃, H₂O₂, CH₃OOH, HFO, C₂H₆, C₃H₈, C₄H₁₀, and n-C₄H₁₀ for MBL case d off the coast of southern Brazil. The dashed horizontal line indicates MBL height. Descent, ascent, and MBL leg data are shown with lines connecting consecutive points in time. Table 1 lists MBL cases.

(5) dismutation of HO₂ and CH₃OO to make H₂O₂ and CH₃OOH,

\[ 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

\[ \text{HO}_2 + \text{CH}_3\text{OO} \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \]

and (6) subsequent removal of H₂O₂ or CH₃OOH via surface deposition or reaction with HO. This is schematically shown in Figure 5. The rates shown indicate averages and standard deviations for 12 of the 13 cases (case c was not included because of the aircraft's short duration in the MBL and the consequent absence
of key species measurements). The loss of O$_3$ in the remote atmosphere proceeded primarily through hydroperoxide formation, with a smaller contribution ascribable to surface deposition ($K_{O_3,\text{depol}} = 0.026$ [Kawa and Pearson, 1989]). Note that the loss of O$_3$ in the MBL was more than compensated for by the transport of O$_3$ into the MBL from aloft. This MBL-column excess was on average $\sim 450 \times 10^9$ molecules cm$^{-2}$ s$^{-1}$, which for a mean column height of 700 m corresponded to an O$_3$ increase of 1.5 ppb d$^{-1}$. The MBL-column O$_3$ loss rate was $\sim 650 \times 10^9$ molecules cm$^{-2}$ s$^{-1}$, which corresponded to 2.2 ppb d$^{-1}$ and gave a mean O$_3$ MBL lifetime of 12 days.

The hydroperoxide budget is also shown in Figure 5. Figure 6 demonstrates the 1:1 relationship between ozone destruction and hydroperoxide production predicted by the model for all of the cases (more than 13 points are shown due to the fact that some legs had more than one calculable model point). This result for the MBL represented a unique combination of very low nitrogen oxide concentrations and moderate to high water
Figure 5. MBL budget of O₃, H₂O₂, and CH₂OOH. Values in rectangles give the average ± s.d. (standard deviation) of the vertical fluxes for the 13 MBL cases (molecule cm⁻² s⁻¹ x 10⁻⁸). Negative flux values indicate net downward movement of material and vice versa. The transfer of odd oxygen from O₃ to the hydroperoxides is shown for the MBL by the dashed rectangle and vertical line. Values in ellipses give the average ± s.d. of the species concentration (ppb) for the free troposphere (FT) and MBL.

vapor concentrations. The total NOₓ concentration was less than 15 ppt and the specific humidity (q), was >5 g kg⁻¹ for all cases. The minimum hydroperoxide production rate in humid air, q > 5, regardless of NOₓ concentration, was 1.4 ppb d⁻¹ and corresponded to a net MBL column production of 280 × 10⁸ molecules cm⁻² s⁻¹. This represents a baseline production rate to which the contribution from net O₃ destruction should be added. The photolytic loss of H₂O₂ was approximately 3 times that of CH₂OOH. The loss of CH₂OOH through its reaction with HO was about twice the loss of H₂O₂ reacting with HO. This was in agreement with prior O₃-hydroperoxide analyses in the MBL that suggested a stoichiometric conversion of O₃ to hydroperoxides [e.g., Thompson et al., 1993; Ayers et al., 1992].

The rate of surface deposition and the net rate of O₃ photochemical destruction in the MBL, nominally 1.7 × 10¹⁰ and 5 × 10¹⁰ molecules cm⁻² s⁻¹, respectively, can be compared and contrasted with net O₃ production throughout the tropospheric column. Jacob et al. [this issue] has presented and discussed tropospheric column net O₃ production throughout the TRACE A study region. They gave an estimated stratospheric source of 1–3 × 10¹⁰ molecules cm⁻² s⁻¹, a median net O₃ production rate of 4 × 10¹⁰ molecules cm⁻² s⁻¹, and a median gross production rate of 9 × 10¹¹ molecules cm⁻² s⁻¹. The O₃ surface loss rate given above was comparable to the rate of stratospheric injection. MBL O₃ production can be compared with the rest of the tropospheric column and is illustrated for cases d and i in Figure 7. The vertically integrated net O₃ production for cases d (0–8.5 km) and i (0–10.5 km) was ~6 × 10⁸ and ~60 × 10⁸ molecules cm⁻² s⁻¹. Case d was representative of profiles at cases a–f, h, j, and k. Cases i and g were similar to each other. Cases l and m went unanalyzed due to the absence of key species measurements throughout the column. Over the ocean, net O₃ production was negative with the bulk of the O₃ destroyed within or just above the MBL. The highest destruction rates in cases i (Figure 7 (right)) and g (not shown) were just above a marine stratus cloud deck, were due to the resulting significant enhancement of O₃ photolysis rates, and were associated with some of the highest hydroperoxide concentrations recorded. The median profile presented by Jacob et al. [this issue] and representing the

Figure 6. Relationship between H₂O₂ and CH₂OOH gross production and the net O₃ production for all modeled points in the MBL. The solid line shows the least squares linear fit through the data. The slope of the line is ~1.0 and the coefficient of determination is 0.83. The photochemical destruction of O₃ is balanced by the net production of the hydroperoxides.
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ß L(O3)
ß 03 + HOx
ß O3+HOx
& O1D+H20
[
] P(O3)
z HO2+NO
o CH3OO+NO
& HO2+NO
x Net 03

Case d, Flight 8

Case i, Flight 14,
ß 03 + HOx
ß 03+HOx ::
& O1D-H20
DP(O3) m.'
z HO2+NO,
:: >
o CH3OO+NO
& HO2+NO :
xNet03 :: am.
ß ac : A
ß x ß i
ß x ß
ms t

Figure 7. O₃ production as a function of altitude for MBL cases d and i. Dashed line, net O₃ production; solid square, gross O₃ loss rate; solid triangle, rate of O₃ + HO and O₃ + HO₂; solid diamond, rate of O₃ + HO, O₃ + HO₂ and O₁D + H₂O; open square, gross O₃ formation rate; open triangle, rate of NO + HO₂; open diamond, rate of NO + HO₂ and NO + CH₃OO. Net O₃ destruction occurs principally in the MBL and lower FT and primarily through the reaction of O¹D with water vapor. Note column-integrated destruction of O₃.

TRACE A study region showed a similar trend with altitude but with net column O₃ production near zero. This indicated the South Atlantic basin was near O₃ steady state during the TRACE A period.

The key reactions contributing to net O₃ production are detailed in Figure 7. CH₂OO and HO₂ radicals contributed equally to gross O₃ production in the MBL. Above the MBL, HO₂ was diagnosed as the primary source of gross O₃ production. O¹D-H₂O and O₃-odd H reactions were the principal O₃ destruction reactions with the former being greater at low altitude. In case d the predominance of O¹D-H₂O in the gross destruction of O₃ was limited to altitudes below 2 km and in case i its predominance extended up to 7 km, as was discussed above. Gross O₃ production was nearly in balance with O₃-odd H destruction at all altitudes and it is the reaction of O¹D with water which shifted the balance toward net O₃ destruction in these marine profiles.

3.2. NO – NO₂ – PAN – HNO₃

NO is required for O₃ production in the troposphere and its absence or very low concentration, along with H₂O, was responsible for net O₃ loss in the MBL. Even though the TRACE A MBL was depleted in NO and NO₂, there was still considerable movement in the oxides of nitrogen from the lower FT to the MBL and on into the ocean. This is shown schematically in Figure 8. The downward transport of peroxyacetylnitrate (PAN), which comprises most of the oxides of nitrogen flux, exceeded the rate of HNO₃ production and its transport and thermal decomposition was sufficient to maintain observed NO and NO₂ levels without having to invoke an oceanic source for NO. However, the predicted rate of HNO₃ formation from NO₂ and the entrainment of HNO₃ from aloft were significantly lower than the deposition rate of HNO₃ and inadequate to maintain observed levels of HNO₃. Figure 8 also gives lower limits for the air-sea flux of PAN and NO₂. These fluxes were considered of minor importance and were estimated assuming an upper limit deposition velocity of 1 cm s⁻¹.

The deposition of HNO₃ is complicated by the presence of sea-salt aerosol and its absorption of HNO₃ vapor [Thompson and Zafiriou, 1983; Duce et al., 1991]. The deposition rate of aerosol varies as a function of particle size and can be consid-

Figure 8. As in Figure 5 except for oxides of nitrogen. Concentrations are in ppt. Dashed arrows and ellipses indicate the unresolved involvement of aerosols in the deposition of HNO₃ and the 0.2 and 0.8 give the assumed partitioning of HNO₃ between gas and aerosol near the surface.
was about 10 times the annual average estimate for this region.

from their MBL concentration, reactivity with O3 and HO, and

Atlantic during TRACE A, 3 _+ 2 x 10^9 molecules cm^-2 s^-1, [Duce et al., 1991].

ment of the oxides of nitrogen and not by surface deposition

balance the MBL NOx-HNO3-PAN system and the oxide of

Duce et al. assumption. Their cruise track is shown by the

dashed line on Figure 1. The Papenbrock et al. gas and aerosol

Figure 1). Their data are also listed in Table 4. The TRACE A
diel-average HO concentration was ~1.5 x 10^6 and the midday HO
collection. For C2H4 and C3H6 the inferred oceanic source was an order of magnitude larger than the esti-
minated by the inclusion in their "base case" of the significantly

Duce et al. assumed, based on shipboard and island observa-
tions, 15% of the total nitrate (HNO3 plus aerosol nitrate) in
the MBL to be in the gas phase and the remainder to be

distributed on the sea-salt aerosol. A mean aerosol deposition
velocity of 0.3 cm s^-1 was also assumed. Papenbrock et al. [1992] presented data from a cruise in the South Atlantic
during September and October 1988, which showed 10–20% of
the total nitrate to be in the gas phase, consistent with the
Duce et al. assumption. Their cruise track is shown by the
dashed line in Figure 1. The Papenbrock et al. gas and aerosol
concentrations (measured at a height 20 m above the ocean),
ranged from <30–70 ppt to 40–700 ppt, respectively, and the
HNO3 at 300 m in TRACE A was within the range of their
total nitrate concentration. After assuming 20% of the HNO3
measured at 300 m remains as a gas, the remainder absorbs
onto aerosols, and the aerosol deposition rate is 0.3 cm s^-1,
then the resultant HNO3 and aerosol nitrate fluxes are 6 x 10^8
and 10 x 10^8 molecules cm^-2 s^-1. The effect of aerosol is
indicated in Figure 8 by the dashed boxes, ellipses, and arrows.
These fluxes represent lower limits only, since we did not
measure and have not included aerosol nitrate at 300 m in the
MBL flux estimates. The inclusion of aerosol effects puts in
balance the MBL NOx-HNO3-PAN system and the oxide of
nitrogen family appears to be near steady state. In TRACE A
the deposition of nitrate appears to be limited by the entrain-
ment of the oxides of nitrogen and not by surface deposition
nor by photochemical oxidation of NOx.

The estimated dry deposition flux of HNO3 gas to the South
Atlantic during TRACE A, 3 ± 2 x 10^8 molecules cm^-2 s^-1,
was about 10 times the annual average estimate for this region.
The aerosol and gas deposition estimate was comparable to the
deposition rate for all nitrate-containing species, 2 x 10^8 mol-
ecules cm^-2 s^-1 [Duce et al., 1991].

3.3. Light Hydrocarbons, <C4

The surface emission rates of hydrocarbons were estimated
from their MBL concentration, reactivity with O3 and HO, and
rate of entrainment from aloft, as was done by Donahue and
Prinn [1990]. In this scheme the MBL hydrocarbon species are
assumed to be in steady state such that the ocean or FT sup-
plies them at a rate equal to their photochemical destruction.
The concentration of O3 was taken from the observations and
the photochemical model was used to estimate HO and NO3 in
the MBL. Hydrocarbon oxidation by NO3 could be neglected
in the TRACE A MBL. Kinetic rate constants were taken from
Atkinson et al. [1993] and evaluated assuming a temperature of
20ºC and a pressure of 950 hPa. The average MBL column
chemical destruction rates for C2H4, C2H6, C2H8, C3H8, and
n-C4H10 during TRACE A are listed in Table 4. The diel-
average HO concentration was ~1.5 x 10^6 and the midday HO
concentration was ~5 x 10^6. The oceanic sources implied by
the chemical destruction rates should be reduced by an amount
equal to the FT-MBL entrainment rates, which are listed in
Table 4, and the differences yield refined estimates of the
oceanic emission rates. For C2H4 and C3H6 the inferred ocean-
ic source was an order of magnitude larger than the esti-
mated FT source, clearly demonstrating the ocean as the
source of these compounds. There was a progression in the
alkanes from those indicating a predominantly oceanic source,
n-C4H10 to those with an equal likelihood of an oceanic or FT
source, C2H8, and on to those suggesting a predominantly FT
source, C2H6. Papenbrock et al. [1992] estimated the oceanic flux of
these hydrocarbons for the South Atlantic from surface sea-
water and lower MBL measurements (cruise track is shown in
Figure 1). Their data are also listed in Table 4. The TRACE A
lower-limit rate for C2H4 was comparable to theirs, but our
estimated oceanic fluxes for the other species were 2–4 times
their flux estimates. Donahue and Prinn [1990] determined hydrocarbon fluxes for the remote MBL from their own model
analysis and from the measurements of Bonsang et al. [1988] and
Lamontagne et al. [1974]. Their C2H4 and C2H6 flux estimates
were significantly greater (~10 times) than those given here
and their alkane fluxes were similar in magnitude but
higher (approximately a factor of 2–4). The high rates re-
lected the inclusion in their "base case" of the significantly
higher atmospheric hydrocarbon concentrations reported by
Bonsang et al. as compared to others [Singh and Zimmerman,
1992]. Donahue and Prinn [1993] calculated ocean fluxes of

<table>
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<th>Species</th>
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<th>C2H6</th>
<th>C2H8</th>
<th>C3H8</th>
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<td>10</td>
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</table>

In molecules cm^-2 s^-1 x 10^-6.

*Only 5 of 13 MBL cases have data in both MBL and FT.

*Calculated by Donahue and Prinn [1990] from the data of Bonsang et al. [1988] and Lamontagne et al. [1974].

*GSFC one-dimensional model results for a TRACE A MBL simulation. The model is described by

Thompson et al. [1993], but the kinetic rate constants and photophysical parameters have been updated per

Atkinson et al. [1993].
C₂H₄ and C₃H₆ for the equatorial Pacific based upon their own seawater and atmospheric concentrations and measured winds. Their flux estimates were comparable to those reported here and by Plass et al. Thompson et al. [1993] also calculated hydrocarbon flux estimates for SAGA 3 using the Goddard Space Flight Center (GSFC) one-dimensional photochemical model. Their flux estimates are higher than those of Donahue and Prinn [1993]. This result was due, in part, to matching different hydrocarbon data sets [Donahue and Prinn, 1993; Atlas et al., 1993], differences in model mechanisms and differences in model HO. The GSFC one-dimensional model was applied to the TRACE A MBL data and yielded alkene fluxes, which were of the same order as the point model but gave much higher fluxes for the alkanes. These flux estimates are listed in Table 4.

3.4. CH₂O and Formic Acid — HFO

In TRACE A, HFO was significantly greater in the lower FT than in the MBL due to the transport of continental emissions [Talbot et al., this issue]. Figure 9 shows the HFO MBL budget. The FT-MBL flux of HFO is approximately 1/2 of the MBL deposition flux of HFO. This suggests an in situ source of HFO of the order of 6 × 10⁴ molecules cm⁻² s⁻¹ or ~200 ppt d⁻¹.

Tokos [1989] proposed HFO to have a photochemical source, based upon his observations of its diel cycle in the MBL over the Atlantic in the summer of 1988. He suggested a likely mechanism was heterogeneous photochemical conversion of CH₂O to HFO in cloud or aerosol, as was modeled by Chaimeides and Davis [1983] and Jacob [1986]. Arlander et al. [1990] also noted a diel cycle in HFO and postulated that it arose from either vertical transport phenomena or sunlight-driven activity (photochemistry and biological activity). Heterogeneous photochemistry was stated by them to be unable to yield sufficient HFO. Talbot et al. [1990, 1995a] and Keene et al. [1995] have also shown that aqueous chemistry cannot explain observations of HFO in the Amazonian dry and wet seasons nor in the fall at Shenandoah National Park. Arlander et al. [1990] concluded that a more likely MBL source was the gas phase ozonolysis of alkenes, C₂H₄ or C₃H₆, since a correlation among alkenes, HFO, HAc, and CH₂O was observed. In TRACE A, however, the above diagnosed oceanic emission rates for these compounds and those from Plass et al. [1992] would be insufficient to support HFO production via their oxidation. The upper limit total oceanic emissions of alkenes (17 × 10⁶ molecules cm⁻² s⁻¹, Table 4) were less than 1/2 of that required, 40 × 10⁶ (Figure 9). A viable gas phase or aqueous photochemical source of HFO remains to be demonstrated.

The available CH₂O measurements within the MBL and lower FT are listed in Table 3. The CH₂O instrument duty cycle, 10 min of measurements followed by 10 min of background, and the short residence time of the aircraft in the MBL, often <5 min, combined to reduce the number of MBL cases with CH₂O data. It was unreasonable to perform CH₂O budget calculations on so few cases.

The low CH₂O concentrations were striking and significantly below (factors of 2–10) those predicted by the photochemical model. Jacob et al. [this issue] have discussed this discrepancy in terms of gas phase mechanisms and measurement uncertainty. The inclusion of a surface loss process in the point model brought its predicted concentrations down slightly, a few tens of percent, but nowhere near the factors of 2 to 3 required. The CH₂O concentrations of cases a and e, 230 and 170 ppt, respectively, were comparable to (1) the cleaner air data of Lowe and Schmidt [1983] from a cruise near the Brazilian coast in October and November 1980, (2) the South Atlantic clean air data reported by Cartier et al. [1990] from a cruise in October 1988, and (3) the very clean air measurements of Arlander et al. [1990] over the Indian Ocean near western Australia. However, the values below the detection limit, nominally 45 ppt, for cases h, i, j, l, and m were well below these measurements. The latter measurements imply either measurement uncertainty was greater than realized or a process related to CH₂O formation or loss is absent from the model.

4. Discussion

The simple FT-MBL and surface flux models and the photochemical point model provided a framework from which to discuss the chemical budgets of ozone, hydroperoxides, oxides of nitrogen, and hydrocarbons. The MBL budgets of O₃ and hydroperoxides appeared to be in reasonable balance. The close correspondence between measured and model values of H₂O₂, CH₃OOH, and CH₂O above the MBL indicated that the photochemical model chemical mechanisms and kinetic rate constants captured the odd hydrogen and odd oxygen chemistry of the FT [Jacob et al., this issue]. The O₃, H₂O₂, and CH₃OOH MBL measurements and model results, including MBL flux estimates, suggested that this result applied in the MBL as well. The estimated surface deposition velocity together with a mean MBL height yield pseudo-first-order loss rates of 1.4 × 10⁻⁵ s⁻¹ for HFO, HNO₃, CH₃OH, and H₂O₂, and 6 × 10⁻⁶ s⁻¹ for CH₃OOH. The surface loss rate of H₂O₂ was approximately twice its diel-average photochemical loss rate. For CH₃OOH, surface deposition was about 1/2 its diel-average photochemical loss rate and that for CH₃OH was about 1/3 its diel-average photochemical loss rate. The inclusion of
surface deposition in the point model reduced the instantaneous steady state values of H$_2$O$_2$, CH$_3$OOH, and CH$_2$O to 1/2, 2/3, and 3/4 of their values without surface deposition. Modeled and measured concentrations of H$_2$O$_2$ and CH$_3$OOH were resolved with surface deposition, whereas model CH$_2$O remains significantly greater than the measured values. In total, the oxides of nitrogen family was balanced in the MBL, but this required the inclusion of gas-aerosol partitioning for HNO$_3$ and an additional mechanism for converting PAN to HNO$_3$ is needed.

The lack of model-measurement closure in CH$_2$O was consistent with observations at Mauna Loa Observatory and model simulations of the chemistry of this location [Heikes et al., 1992; Liu et al., 1992; Heikes et al., 1996]. The CH$_2$O analytical method used during TRACE A was also used in a series of CH$_2$O methods comparisons at Mauna Loa Observatory [Heikes et al., 1996]. It consistently gave results which were the same (within estimated instrumental precision) or higher in value than the other measurements. Hence it was considered to provide an upper limit to ambient CH$_2$O there.

A HFO formation mechanism operative in the MBL has yet to be identified. The magnitudes of the missing CH$_2$O sink and HFO source were comparable. While intriguing, whether the missing CH$_2$O sink and HFO source are related and whether this relationship was a consequence of the low NO environment may have been fortuitous and cannot be firmly established here. However, the role of heterogeneous chemistry on CH$_2$O and HFO in a cloud-impacted MBL is the subject of future work.

5. Conclusions

Chemical budgets were constructed for several species in the MBL and presented for ethane, ethylene, propane, propylene, n-butane, formic acid (HFO), methlyhydroperoxide, oxides of nitrogen (i.e., NO, NO$_2$, PAN, HNO$_3$), hydrogen peroxide, and ozone. A diel-average photochemical point model was used to evaluate local photochemical production and loss of these species. An entrainment model was used to estimate material exchange between the lower free troposphere and MBL and a resistance deposition model was used to calculate material exchange across the air-sea interface. The results suggested the ocean to be the source of measured alkanes in the MBL and that the ocean is the most likely source of the shorter-lived alkanes: propane and n-butane with a smaller contribution from the FT. The estimated hydrocarbon sources from the ocean were in agreement with prior analyses. Transport from the lower FT together with surface loss could not account for measured concentrations of HFO and HNO$_3$. A photochemical source of HFO is needed in the MBL. The transport of PAN from the FT to the MBL exceeds the rate of NO$_2$ oxidation to HNO$_3$ and was more than sufficient to maintain observed NO$_2$ levels without having to invoke an oceanic source for NO. The total flux of the sum of NO$_x$, PAN, and HNO$_3$ was in balance with the surface deposition flux of HNO$_3$ and indicated balance of the oxides of nitrogen family. However, the predicted rates of HNO$_3$ formation and HNO$_3$ entrainment from aloft were inadequate to maintain observed levels of HNO$_3$ unless aerosol partitioning and depositional effects were included. The estimated dry deposition flux of HNO$_3$ to the South Atlantic during TRACE A was about 10 times the annual average estimate for this region and comparable to the deposition rate for all nitrate-containing species. The destruction of O$_3$ within the MBL was more than balanced by transport from aloft. The principal destruction process was through photochemical reactions and mediated by the formation and surface deposition of H$_2$O$_2$ and CH$_3$OOH. A direct loss of ozone to the sea surface was of secondary importance. CH$_3$OOH loss to the sea surface and its transport into the FT from the MBL was estimated to occur at a first-order loss rate of 6 x 10$^{-6}$ s$^{-1}$ for a mean MBL height of 700 m. H$_2$O$_2$, HNO$_3$, and CH$_3$O losses from the MBL are estimated at rates of 1.4 x 10$^{-5}$ s$^{-1}$. Sea-salt aerosol confounds the surface deposition of HNO$_3$. Inclusion of surface loss improved the agreement between model-predicted and measured concentrations of HNO$_3$, CH$_3$OOH, H$_2$O$_2$, and CH$_2$O species which had been overestimated in the MBL by the photochemical point model. A strong but unknown CH$_2$O sink was required in addition to surface deposition to resolve model and measurements in the MBL. The missing sink of CH$_2$O and source of HFO were comparable.

References


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