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

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
doi:10.1029/95JD03631

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:14117800

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
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., CH$_4$ < 1680 ppb, CO < 70 ppb, C$_2$H$_6$ < 400 ppt, C$_3$H$_8$ < 40 ppt, NO$_x$ < 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 (CH$_3$OOH), oxides of nitrogen (i.e., NO, NO$_2$, PAN, HNO$_3$), hydrogen peroxide (H$_2$O$_2$), and ozone (O$_3$). 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 CH$_2$O, HFO, and HNO$_3$. The transport of peroxyacetyl nitrate (PAN) from the FT to the MBL exceeded the rate of HNO$_3$ production and was more than sufficient to maintain observed NO$_x$ levels without having to invoke an oceanic source for NO. The flux of NO$_2$, PAN, and HNO$_3$ was in balance with the surface deposition flux of HNO$_3$. However, the predicted rates of HNO$_3$ formation from the oxidation of NO$_2$ and HNO$_3$ entrainment from aloft were inadequate to maintain observed levels of HNO$_3$ unless HNO$_3$ was partitioned between the gas phase and a more slowly depositing aerosol phase. The estimated dry deposition flux of HNO$_3$ to the South Atlantic during TRACE A, 2-4 $\times$ 10$^9$ molecules cm$^{-2}$ s$^{-1}$, was about 10 times the annual average estimate for this region. The destruction of O$_3$ within the MBL was found to be exceeded by transport into the MBL from aloft, 6 $\pm$ 2 $\times$ 10$^{10}$ compared to 11 $\pm$ 10 $\times$ 10$^{10}$ molecules cm$^{-2}$ s$^{-1}$. The principal O$_3$ destruction process was mediated by the formation and surface deposition of H$_2$O$_2$ and CH$_2$OOH, 4 $\pm$ 4 $\times$ 10$^{10}$ and 1.1 $\pm$ 0.5 $\times$ 10$^{10}$ molecules cm$^{-2}$ s$^{-1}$. The direct loss of O$_3$ to the sea surface was estimated to be 1.7 $\pm$ 0.2 $\times$ 10$^{10}$ molecules cm$^{-2}$ s$^{-1}$. CH$_3$OOH was lost to the sea and transported into the FT from the MBL. Its first-order loss rate was estimated to be 7 $\times$ 10$^{-6}$ s$^{-1}$ for a mean MBL height of 700 m. H$_2$O$_2$ and CH$_2$O losses from the MBL were estimated at rates of 1.3 $\times$ 10$^{-5}$ s$^{-1}$ for both species. The inclusion of surface deposition improved the agreement between predicted and measured concentrations of HNO$_3$, CH$_2$OOH, H$_2$O$_2$, and CH$_2$O. However, model CH$_2$O remained significantly greater than that measured in the MBL.

Copyright 1996 by the American Geophysical Union.

Paper number 95JD03631.
0148-0227/96/95JD-03631$\times$09.00

24,221
1. Introduction

The NASA GTE Transport and Atmospheric Chemistry near the Equator—Atlantic Experiment (TRACE A) was an investigation in to the causes of high tropospheric ozone (O₃) 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 O₃ 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 O₃, light hydrocarbons, oxides of nitrogen, and a few photochemical products over the South Atlantic and western Indian Oceans. TRACE A results related to high O₃ throughout the tropospheric column are presented in companion articles [e.g., Fishman et al., this issue(b); Thompson et al., 1993; Jacob et al., this issue; Krishnamurti et al., this issue].

The remote MBL is recognized for its role in the destruction of tropospheric O₃, the antithesis of the primary TRACE A mission. Lenschow et al. [1982], Kawa and Pearson [1989], and Paluch et al. [1994] evaluated the vertical flux of O₃ 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 O₃. 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 O₃ in and above the MBL over the North Atlantic in two Lagrangian experiments near the Azores. They could not resolve net O₃ 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 O₃ 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 O₃ and H₂O₂ over diel and annual cycles at Cape Grimm, Tasmania, and showed the daytime destruction of O₃ to be accompanied by a stoichiometric increase in peroxides (most likely hydrogen peroxide and a major fraction of methylhydroperoxide). They further suggested that replacement O₃ 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 O₃ 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 O₃ 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]. Zafiriou 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 (NO₂), peroxyacetyl nitrate (PAN), and nitric acid (HNO₃) 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 HNO₃ to the ocean removes reactive nitrogen from the troposphere, thereby limiting net oxidant production, the downward flux of HNO₃ and the conversion of NO₂ to HNO₃ 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 HNO₃ 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, CH₃OOH, and CH₂O measurements have been used to validate photochemical model odd hydrogen (e.g., HO, HO₂, RO₂) 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., CH₂O, HNO₃, and H₂O₂, has often been invoked to explain these differences. The suite of the more soluble species measured in TRACE A (H₂O₂, CH₃OOH, CH₂O, HNO₃, and HFO) together with the measurements of O₃, NO, and hydrocarbons permitted us to examine this assumption and test for consistency between the deposition of species with short photochemical timescales (e.g., H₂O₂, CH₃OOH, or CH₂O) and those with longer photochemical timescales (e.g., O₃, HNO₃ 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 O₃ 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,
A was characterized by a strong thermal inversion at the top of the MBL, as noted by Mauzerall et al. [this issue]; Blake et al., this issue. Air parcel trajectories for the MBL, calculated using the procedures of Fuelberg et al. [this issue(b)], indicated sampled air masses to have come from over the ocean for at least the prior 4 days [Pickering et al., this issue]. Chemical data and air trajectories for the overlying FT indicated this air to have come from over the continental emissions. Chemical data and air trajectories for the lower atmosphere and the transport processes which we have included.

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 NO2 were measured using two-photon laser-induced fluorescence [Smyth et al., this issue]. Hydrocarbon samples (specifically ethane, ethene, propane, propene, and n-butane or C2H6, C2H4, C3H8, C3H6, and n-C4H10, respectively) were collected in stainless-steel canisters and analyzed using the techniques and procedures outlined by Blake et al. [this issue]. O3 was measured using a NO-O3 chemiluminescence method [Collins et al., this issue]. H2O2 and CH3OOH were collected in aqueous solution and analyzed using high-pressure liquid chromatography system [Lee et al., 1995]. CH2O was collected in aqueous solution using a coil collector and was analyzed by the method of Lazrus et al. [1988]. HNO3 and formic acid (HFO) 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,MBL/dt, molecules cm$^{-3}$ s$^{-1}$) is described by its local photochemical production and loss (P,M and L,MBL, molecules cm$^{-3}$ s$^{-1}$), its flux across the air-sea interface (F,AS, molecules cm$^{-2}$ s$^{-1}$), and its flux across a surface defining the top of the MBL (F,MBL, molecules cm$^{-2}$ s$^{-1}$):

$$\frac{dC_{\text{MBL}}}{dt} = P_{\text{MBL}} - L_{\text{MBL}} - F_{\text{MBL}}/Z_{\text{MBL}} - F_{\text{AS}}/Z_{\text{MBL}}$$

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.

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:

$$F_{\text{MBL}} = K_e(C_{\text{FT}} - C_{\text{MBL}})$$

where C, 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 O3 across the top of the MBL under meteorological conditions.

### Table 1: Marine Boundary Layer Cases

<table>
<thead>
<tr>
<th>Case</th>
<th>Flight</th>
<th>Julian Day</th>
<th>Start Time, sec-UT</th>
<th>Stop Time, sec-UT</th>
<th>Latitude, North</th>
<th>Longitude, East</th>
<th>Pressure, hPa</th>
<th>Wind Speed, m s$^{-1}$ ~300 m</th>
<th>Wind Speed, m s$^{-1}$ ~300 m</th>
<th>MBL Height, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5</td>
<td>268</td>
<td>56010</td>
<td>59910</td>
<td>-28.90</td>
<td>-44.10</td>
<td>973</td>
<td>18</td>
<td>13</td>
<td>450</td>
</tr>
<tr>
<td>b</td>
<td>8</td>
<td>275</td>
<td>52350</td>
<td>54570</td>
<td>-27.10</td>
<td>-42.00</td>
<td>978</td>
<td>8</td>
<td>6</td>
<td>500</td>
</tr>
<tr>
<td>c</td>
<td>e</td>
<td>8</td>
<td>275</td>
<td>55950</td>
<td>-30.03</td>
<td>-44.90</td>
<td>970</td>
<td>12</td>
<td>9</td>
<td>500</td>
</tr>
<tr>
<td>d</td>
<td>e</td>
<td>8</td>
<td>275</td>
<td>60390</td>
<td>-33.98</td>
<td>-48.30</td>
<td>977</td>
<td>12</td>
<td>9</td>
<td>500</td>
</tr>
<tr>
<td>e</td>
<td>c</td>
<td>11</td>
<td>283</td>
<td>32970</td>
<td>-23.40</td>
<td>38.85</td>
<td>983</td>
<td>8</td>
<td>6</td>
<td>600</td>
</tr>
<tr>
<td>f</td>
<td>f</td>
<td>11</td>
<td>383</td>
<td>42810</td>
<td>-35.55</td>
<td>31.30</td>
<td>993</td>
<td>8</td>
<td>6</td>
<td>600</td>
</tr>
<tr>
<td>g</td>
<td>g</td>
<td>13</td>
<td>288</td>
<td>36750</td>
<td>-6.60</td>
<td>8.75</td>
<td>978</td>
<td>5</td>
<td>4</td>
<td>900</td>
</tr>
<tr>
<td>h</td>
<td>h</td>
<td>13</td>
<td>288</td>
<td>43950</td>
<td>-19.20</td>
<td>9.00</td>
<td>979</td>
<td>8</td>
<td>6</td>
<td>700</td>
</tr>
<tr>
<td>i</td>
<td>i</td>
<td>14</td>
<td>289</td>
<td>38190</td>
<td>-6.20</td>
<td>4.05</td>
<td>979</td>
<td>4</td>
<td>3</td>
<td>1100</td>
</tr>
<tr>
<td>j</td>
<td>j</td>
<td>14</td>
<td>289</td>
<td>46350</td>
<td>-19.88</td>
<td>8.58</td>
<td>982</td>
<td>12</td>
<td>9</td>
<td>1000</td>
</tr>
<tr>
<td>k</td>
<td>k</td>
<td>15</td>
<td>292</td>
<td>51330</td>
<td>-11.67</td>
<td>2.50</td>
<td>976</td>
<td>5</td>
<td>4</td>
<td>1000</td>
</tr>
<tr>
<td>l</td>
<td>l</td>
<td>17</td>
<td>296</td>
<td>38610</td>
<td>-17.30</td>
<td>-19.70</td>
<td>984</td>
<td>7</td>
<td>6</td>
<td>500</td>
</tr>
<tr>
<td>m</td>
<td>m</td>
<td>17</td>
<td>296</td>
<td>51270</td>
<td>-20.00</td>
<td>-10.40</td>
<td>975</td>
<td>9</td>
<td>7</td>
<td>700</td>
</tr>
</tbody>
</table>
The 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 climatological values [U.S. Navy, 1978, 1976]. A typical parameterized model of Duce et al. [1991]. Air-sea transfer was take depends upon both an atmospheric transport velocity, k\(_a\), and an oceanic transport velocity, kw. This scheme required 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\(_{\text{i,FT}}\) from observations between Z\(_{MBL}\) and 4000 m. This treatment was analogous to those used by Pulich 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 hydrocarbon concentrations for the 13 cases identified. Table 3 lists MBL and FT concentrations for H\(_2\)O\(_2\), CH\(_3\)OOH, CH\(_2\)O, and CH\(_4\)O into the ocean was estimated using a deposition velocity (K\(_{e,AS}\)) times the MBL concentration:

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

The oceanic equivalent gas phase concentration in the upper ocean, C\(_{i,AS}\), was assumed to be negligible for the species listed. K\(_{e,AS}\) 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\(_2\)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\(_w\). 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 winds 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\(_2\)OOH 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.

Figure 2. Schematic of the three-layer lower-atmosphere transport model used in the marine boundary layer (MBL) chemical budget studies [after Lenschow et al., 1983].

![Figure 2](image-url)
Table 2. Light Hydrocarbon Concentrations, ppt

<table>
<thead>
<tr>
<th>Case</th>
<th>C₃H₆</th>
<th>C₂H₄</th>
<th>C₃H₈</th>
<th>C₄H₁₀</th>
<th>n-C₄H₁₀</th>
<th>i-C₄H₁₀</th>
<th>4 km to Top of MBL</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>450</td>
<td>20</td>
<td>200</td>
<td>4</td>
<td>70</td>
<td>40</td>
<td>650</td>
</tr>
<tr>
<td>b</td>
<td>330</td>
<td>5</td>
<td>25</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>320</td>
</tr>
<tr>
<td>c</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>330</td>
</tr>
<tr>
<td>d</td>
<td>340</td>
<td>6</td>
<td>30</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>320</td>
</tr>
<tr>
<td>e</td>
<td>325</td>
<td>11</td>
<td>12</td>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>500</td>
</tr>
<tr>
<td>f</td>
<td>370</td>
<td>8</td>
<td>40</td>
<td>5</td>
<td>9</td>
<td>6</td>
<td>390</td>
</tr>
<tr>
<td>g</td>
<td>325</td>
<td>15</td>
<td>12</td>
<td>5</td>
<td>2</td>
<td>&lt;1</td>
<td>410</td>
</tr>
<tr>
<td>h</td>
<td>315</td>
<td>15</td>
<td>17</td>
<td>5</td>
<td>2</td>
<td>&lt;1</td>
<td>700</td>
</tr>
<tr>
<td>i</td>
<td>310</td>
<td>11</td>
<td>10</td>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>600</td>
</tr>
<tr>
<td>j</td>
<td>290</td>
<td>11</td>
<td>14</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>550</td>
</tr>
<tr>
<td>k</td>
<td>310</td>
<td>12</td>
<td>14</td>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>500</td>
</tr>
<tr>
<td>l</td>
<td>310</td>
<td>18</td>
<td>15</td>
<td>6</td>
<td>1</td>
<td>&lt;1</td>
<td>475</td>
</tr>
<tr>
<td>m</td>
<td>320</td>
<td>21</td>
<td>13</td>
<td>5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>330</td>
</tr>
</tbody>
</table>

Table 3a. Marine Boundary Layer Concentration, ppt

<table>
<thead>
<tr>
<th>Case</th>
<th>CO, ppb</th>
<th>O₃, ppb</th>
<th>NOₓ, a</th>
<th>HNO₃</th>
<th>PAN</th>
<th>H₂O₂</th>
<th>CH₃OOH</th>
<th>HFo</th>
<th>CH₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>63</td>
<td>23</td>
<td>14</td>
<td>90</td>
<td>11</td>
<td>420</td>
<td>960</td>
<td>930</td>
<td>230</td>
</tr>
<tr>
<td>b</td>
<td>61</td>
<td>27</td>
<td>6</td>
<td>90</td>
<td>2</td>
<td>4920</td>
<td>1000</td>
<td>220</td>
<td>na</td>
</tr>
<tr>
<td>c</td>
<td>na</td>
<td>28</td>
<td>na</td>
<td>30</td>
<td>na</td>
<td>4800</td>
<td>1300</td>
<td>100</td>
<td>na</td>
</tr>
<tr>
<td>d</td>
<td>61</td>
<td>26</td>
<td>6</td>
<td>70</td>
<td>3</td>
<td>4350</td>
<td>1055</td>
<td>350</td>
<td>na</td>
</tr>
<tr>
<td>e</td>
<td>70</td>
<td>29</td>
<td>7</td>
<td>190</td>
<td>2</td>
<td>940</td>
<td>1035</td>
<td>340</td>
<td>140</td>
</tr>
<tr>
<td>f</td>
<td>61</td>
<td>30</td>
<td>9</td>
<td>150</td>
<td>7</td>
<td>690</td>
<td>620</td>
<td>540</td>
<td>na</td>
</tr>
<tr>
<td>g</td>
<td>76</td>
<td>25</td>
<td>8</td>
<td>280</td>
<td>3</td>
<td>1700</td>
<td>1380</td>
<td>770</td>
<td>na</td>
</tr>
<tr>
<td>h</td>
<td>66</td>
<td>32</td>
<td>11</td>
<td>230</td>
<td>3</td>
<td>960</td>
<td>770</td>
<td>430</td>
<td>&lt;43</td>
</tr>
<tr>
<td>i</td>
<td>65</td>
<td>29</td>
<td>9</td>
<td>190</td>
<td>2</td>
<td>1580</td>
<td>1280</td>
<td>470</td>
<td>&lt;44</td>
</tr>
<tr>
<td>j</td>
<td>61</td>
<td>22</td>
<td>11</td>
<td>150</td>
<td>1</td>
<td>1790</td>
<td>920</td>
<td>360</td>
<td>&lt;44</td>
</tr>
<tr>
<td>k</td>
<td>64</td>
<td>25</td>
<td>12</td>
<td>280</td>
<td>2</td>
<td>1180</td>
<td>1140</td>
<td>900</td>
<td>77</td>
</tr>
<tr>
<td>l</td>
<td>65</td>
<td>26</td>
<td>5</td>
<td>180</td>
<td>2</td>
<td>1010</td>
<td>1240</td>
<td>420</td>
<td>&lt;47</td>
</tr>
<tr>
<td>m</td>
<td>88</td>
<td>27</td>
<td>5</td>
<td>190</td>
<td>2</td>
<td>270</td>
<td>1580</td>
<td>420</td>
<td>&lt;47</td>
</tr>
<tr>
<td>Average</td>
<td>67</td>
<td>27</td>
<td>8</td>
<td>160</td>
<td>3</td>
<td>1900</td>
<td>1100</td>
<td>480</td>
<td>1000</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Case</th>
<th>CO, ppb</th>
<th>O₃, ppb</th>
<th>NOₓ, a</th>
<th>HNO₃</th>
<th>PAN</th>
<th>H₂O₂</th>
<th>CH₃OOH</th>
<th>HFo</th>
<th>CH₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>140</td>
<td>55</td>
<td>160</td>
<td>550</td>
<td>1100</td>
<td>4000</td>
<td>1300</td>
<td>2200</td>
<td>650</td>
</tr>
<tr>
<td>b</td>
<td>66</td>
<td>40</td>
<td>25</td>
<td>100</td>
<td>20</td>
<td>6000</td>
<td>1000</td>
<td>560</td>
<td>na</td>
</tr>
<tr>
<td>c</td>
<td>71</td>
<td>38</td>
<td>25</td>
<td>40</td>
<td>55</td>
<td>4800</td>
<td>1100</td>
<td>500</td>
<td>na</td>
</tr>
<tr>
<td>d</td>
<td>65</td>
<td>37</td>
<td>20</td>
<td>60</td>
<td>15</td>
<td>1500</td>
<td>500</td>
<td>500</td>
<td>na</td>
</tr>
<tr>
<td>e</td>
<td>90</td>
<td>55</td>
<td>50</td>
<td>250</td>
<td>160</td>
<td>1500</td>
<td>500</td>
<td>1650</td>
<td>150</td>
</tr>
<tr>
<td>f</td>
<td>73</td>
<td>45</td>
<td>25</td>
<td>110</td>
<td>60</td>
<td>300</td>
<td>400</td>
<td>650</td>
<td>na</td>
</tr>
<tr>
<td>g</td>
<td>180</td>
<td>65</td>
<td>75</td>
<td>400</td>
<td>400</td>
<td>6000</td>
<td>1900</td>
<td>4000</td>
<td>2000</td>
</tr>
<tr>
<td>h</td>
<td>95</td>
<td>55</td>
<td>65</td>
<td>400</td>
<td>100</td>
<td>1700</td>
<td>750</td>
<td>1750</td>
<td>na</td>
</tr>
<tr>
<td>i</td>
<td>155</td>
<td>58</td>
<td>65</td>
<td>350</td>
<td>350</td>
<td>4500</td>
<td>1700</td>
<td>1700</td>
<td>na</td>
</tr>
<tr>
<td>j</td>
<td>125</td>
<td>60</td>
<td>65</td>
<td>400</td>
<td>350</td>
<td>2500</td>
<td>1000</td>
<td>2000</td>
<td>na</td>
</tr>
<tr>
<td>k</td>
<td>110</td>
<td>70</td>
<td>65</td>
<td>450</td>
<td>120</td>
<td>3400</td>
<td>1400</td>
<td>2700</td>
<td>na</td>
</tr>
<tr>
<td>l</td>
<td>85</td>
<td>70</td>
<td>35</td>
<td>250</td>
<td>40</td>
<td>1100</td>
<td>650</td>
<td>650</td>
<td>na</td>
</tr>
<tr>
<td>m</td>
<td>100</td>
<td>50</td>
<td>70</td>
<td>350</td>
<td>80</td>
<td>3900</td>
<td>1300</td>
<td>900</td>
<td>130</td>
</tr>
<tr>
<td>Average</td>
<td>100</td>
<td>55</td>
<td>60</td>
<td>280</td>
<td>220</td>
<td>3200</td>
<td>1000</td>
<td>1500</td>
<td>na</td>
</tr>
</tbody>
</table>

*NOₓ is the diel-average model value based upon measured NO.

*According to the provided data, the standard deviation for each measurement is also calculated.

aNOₓ is the diel-average model value based upon measured NO.

A value of 3 was substituted for <5 in calculating the average and standard deviation.
Figure 3. Vertical profiles of $O_3$, NOx, PAN, HNO$_3$, H$_2$O$_2$, CH$_3$OOH, HFo, C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_8$, and $n$-C$_4$H$_{10}$ 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 HO$_2$ and CH$_3$OO to make H$_2$O$_2$ and CH$_3$OOH,

$$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

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

and (6) subsequent removal of H$_2$O$_2$ or CH$_3$OOH 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 ($K_{O_3,AS} = 0.026$ [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 $\sim 450 \times 10^8$ 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 $\sim 650 \times 10^8$ 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
Ozone and Hydroperoxide MBL-Column Budget

Figure 5. MBL budget of \( \text{O}_3 \), \( \text{H}_2\text{O}_2 \), and \( \text{CH}_3\text{OOH} \). Values in rectangles give the average ± s.d. (standard deviation) of the vertical fluxes for the 13 MBL cases (molecule cm\(^{-2}\) s\(^{-1}\) × 10\(^{-8}\)). Negative flux values indicate net downward movement of material and vice versa. The transfer of odd oxygen from \( \text{O}_3 \) 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 \( \text{NO}_x \) 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 \( \text{NO}_x \) concentration, was 1.4 ppb d\(^{-1}\) and corresponded to a net MBL column production of 280 \( \times 10^8 \) molecules cm\(^{-2}\) s\(^{-1}\). This represents a baseline production rate to which the contribution from net \( \text{O}_3 \) destruction should be added. The photolytic loss of \( \text{H}_2\text{O}_2 \) was approximately 3 times that of \( \text{CH}_3\text{OOH} \). The loss of \( \text{CH}_3\text{OOH} \) through its reaction with HO was about twice the loss of \( \text{H}_2\text{O}_2 \) reacting with HO. This was in agreement with prior \( \text{O}_3 \)-hydroperoxide analyses in the MBL that suggested a stoichiometric conversion of \( \text{O}_3 \) to hydroperoxides [e.g., Thompson et al., 1993; Ayers et al., 1992].

The rate of surface deposition and the net rate of \( \text{O}_3 \) photochemical destruction in the MBL, nominally 1.7 \( \times 10^{10} \) and 5 \( \times 10^{10} \) molecules cm\(^{-2}\) s\(^{-1}\), respectively, can be compared and contrasted with net \( \text{O}_3 \) production throughout the tropospheric column. Jacob et al. [this issue] has presented and discussed tropospheric column net \( \text{O}_3 \) production throughout the TRACE A study region. They gave an estimated stratospheric source of 1–3 \( \times 10^{10} \) molecules cm\(^{-2}\) s\(^{-1}\), a median net \( \text{O}_3 \) production rate of 4 \( \times 10^{10} \) molecules cm\(^{-2}\) s\(^{-1}\), and a median gross production rate of 9 \( \times 10^{11} \) molecules cm\(^{-2}\) s\(^{-1}\). The \( \text{O}_3 \) surface loss rate given above was comparable to the rate of stratospheric injection. MBL \( \text{O}_3 \) 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 \( \text{O}_3 \) production for cases d (0–8.5 km) and i (0–10.5 km) was \(-6 \times 10^{10}\) and \(-60 \times 10^{10} \) 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 \( \text{O}_3 \) production was negative with the bulk of the \( \text{O}_3 \) 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 \( \text{O}_3 \) 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 \( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \) gross production and the net \( \text{O}_3 \) 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 \( \text{O}_3 \) is balanced by the net production of the hydroperoxides.
HEIKES ET AL.: CHEMICAL BUDGETS IN THE MBL

**Figure 7.** $O_3$ production as a function of altitude for MBL cases $d$ and $i$. Dashed line, net $O_3$ production; solid square, gross $O_3$ loss rate; solid triangle, rate of $O_3 + HO$ and $O_3 + HO_2$; solid diamond, rate of $O_3 + HO$, $O_3 + HO_2$ and $O_1D + H_2O$ open square, gross $O_3$ formation rate; open triangle, rate of $NO + HO_2$; open diamond, rate of NO + HO and NO + CH$_3$OO. Net $O_3$ destruction occurs principally in the MBL and lower FT and primarily through the reaction of $O_1D$ with water vapor. Note column-integrated destruction of $O_3$.

TRACE A study region showed a similar trend with altitude but with net column $O_3$ production near zero. This indicated the South Atlantic basin was near $O_3$ steady state during the TRACE A period.

The key reactions contributing to net $O_3$ production are detailed in Figure 7. CH$_3$OO and HO$_2$ radicals contributed equally to gross $O_3$ production in the MBL. Above the MBL, HO$_2$ was diagnosed as the primary source of gross $O_3$ production. O$_1D$-H$_2O$ and O$_3$-odd H reactions were the principal $O_3$ destruction reactions with the former being greater at low altitude. In case $d$ the predominance of O$_1D$-H$_2O$ in the gross destruction of $O_3$ was limited to altitudes below 2 km and in case $i$ its predominance extended up to 7 km, as was discussed above. Gross $O_3$ production was nearly in balance with O$_3$-odd H destruction at all altitudes and it is the reaction of O$_1D$ with water which shifted the balance toward net $O_3$ destruction in these marine profiles.

### 3.2. NO – NO$_2$ – PAN – HNO$_3$

NO is required for $O_3$ production in the troposphere and its absence or very low concentration, along with H$_2$O, was responsible for net $O_3$ loss in the MBL. Even though the TRACE A MBL was depleted in NO and NO$_2$, 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 peroxyacetyl nitrate (PAN), which comprises most of the oxides of nitrogen flux, exceeded the rate of HNO$_3$ production and its transport and thermal decomposition was sufficient to maintain observed NO and NO$_2$ levels without having to invoke an oceanic source for NO. However, the predicted rate of HNO$_3$ formation from NO$_2$ and the entrainment of HNO$_3$ from aloft were significantly lower than the deposition rate of HNO$_3$ and inadequate to maintain observed levels of HNO$_3$. Figure 8 also gives lower limits for the air-sea flux of PAN and NO$_2$. These fluxes were considered of minor importance and were estimated assuming an upper limit deposition velocity of 1 cm s$^{-1}$.

The deposition of HNO$_3$ is complicated by the presence of sea-salt aerosol and its absorption of HNO$_3$ 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 HNO$_3$ and the 0.2 and 0.8 give the assumed partitioning of HNO$_3$ between gas and aerosol near the surface.
erably different than a gas. Theoretically, the partitioning of HNO$_3$ between gas and aerosol is a function of particle mass, composition, and relative humidity. A solution to the HNO$_3$-aerosol deposition problem was presented by Duce et al. [1991] and was similar to that used by Thompson and Zafiriou [1983]. Duce et al. assumed, based on shipboard and island observations, 15% of the total nitrate (HNO$_3$ 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 on 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 HNO$_3$ at 300 m in TRACE A was within the range of their total nitrate concentration. After assuming 20% of the HNO$_3$ 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 HNO$_3$ and aerosol nitrate fluxes are $6 \times 10^8$ and $10 \times 10^8$ 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 NO$_x$-HNO$_3$-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 entrainment of the oxides of nitrogen and not by surface deposition nor by photochemical oxidation of NO$_2$.

The estimated dry deposition flux of HNO$_3$ gas to the South Atlantic during TRACE A, $3 \pm 2 \times 10^8$ 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, $2 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$ [Duce et al., 1991].

### 3.3. Light Hydrocarbons, $<C_4$

The surface emission rates of hydrocarbons were estimated from their MBL concentration, reactivity with O$_3$ 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 supplies them at a rate equal to their photochemical destruction. The concentration of O$_3$ was taken from the observations and the photochemical model was used to estimate HO and NO$_3$ in the MBL. Hydrocarbon oxidation by NO$_3$ could be neglected in the TRACE A MBL. Kinetic rate constants were taken from Atkinson et al. [1993] and evaluated assuming a temperature of 20°C and a pressure of 950 hPa. The average MBL column chemical destruction rates for C$_2$H$_4$, C$_3$H$_6$, C$_2$H$_6$, C$_2$H$_8$, and n-C$_4$H$_{10}$ during TRACE A are listed in Table 4. The diel-average HO concentration was $\sim5 \times 10^6$ and the midday HO concentration was $\sim5 \times 10^6$. 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 C$_2$H$_4$ and C$_3$H$_6$ the inferred oceanic source was an order of magnitude larger than the estimated 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-C$_4$H$_{10}$, to those with an equal likelihood of an oceanic or FT source, C$_2$H$_4$, and on to those suggesting a predominantly FT source, C$_3$H$_6$. Pluss et al. [1992] estimated the oceanic flux of these hydrocarbons for the South Atlantic from surface seawater 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 C$_2$H$_4$ 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 C$_2$H$_4$ and C$_3$H$_6$ 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 reflected 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
C$_2$H$_4$ and C$_3$H$_6$ 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. CH$_2$O 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 $6 \times 10^4$ molecules cm$^{-2}$ s$^{-1}$ or $\sim 200$ 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 CH$_2$O to HFo in cloud or aerosol, as was modeled by Chameides 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, C$_2$H$_4$ or C$_3$H$_6$, since a correlation among alkenes, HFo, HAc, and CH$_2$O 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 ($17 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$, Table 4) were less than 1/2 of that required, $40 \times 10^8$ (Figure 9). A viable gas phase or aqueous photochemical source of HFo remains to be demonstrated.

The available CH$_2$O measurements within the MBL and lower FT are listed in Table 3. The CH$_2$O 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 CH$_2$O data. It was unreasonable to perform CH$_2$O budget calculations on so few cases.

The low CH$_2$O 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 CH$_2$O 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 Carlier 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 CH$_2$O 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 O$_3$ and hydroperoxides appeared to be in reasonable balance. The close correspondence between measured and model values of H$_2$O$_2$, CH$_3$OOH, and CH$_3$O$_2$ 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 O$_3$, H$_2$O$_2$, and CH$_3$OOH 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 $1.4 \times 10^{-5}$ s$^{-1}$ for HFo, HNO$_3$, CH$_3$O$_2$, and H$_2$O$_2$, and $6 \times 10^{-6}$ s$^{-1}$ for CH$_3$OOH. The surface loss rate of H$_2$O$_2$ was approximately twice its diel-average photochemical loss rate. For CH$_3$OOH, surface deposition was about 1/2 its diel-average photochemical loss rate and that for CH$_3$O$_2$ was about 1/3 its diel-average photochemical loss rate. The inclusion of

---

**Figure 9.** As in Figure 5 except for formic acid.
surface deposition in the point model reduced the instantaneous steady state values of \( \text{H}_2\text{O}_2 \), \( \text{CH}_3\text{OOH} \), and \( \text{CH}_2\text{O} \) to 1/2, 2/3, and 3/4 of their values without surface deposition. Modeled and measured concentrations of \( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \) were resolved with surface deposition, whereas model \( \text{CH}_2\text{O} \) 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 \( \text{HNO}_3 \) and an additional mechanism for converting PAN to \( \text{HNO}_3 \) is needed.

The lack of model-measurement closure in \( \text{CH}_2\text{O} \) was consistent with observations at Mauna Loa Observatory and model simulations of the chemistry of this location [Heikes, 1992; Liu et al., 1992; Heikes et al., 1996]. The \( \text{CH}_2\text{O} \) analytical method used during TRACE A was also used in a series of \( \text{CH}_2\text{O} \) 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 \( \text{CH}_2\text{O} \) there.

A HFo formation mechanism operative in the MBL has yet to be identified. The magnitudes of the missing \( \text{CH}_2\text{O} \) sink and HFo source were comparable. While intriguing, whether the missing \( \text{CH}_2\text{O} \) 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 \( \text{CH}_2\text{O} \) 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), methylhydroperoxide, oxides of nitrogen (i.e., NO, NO\(_2\), PAN, \( \text{HNO}_3 \)), 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 alkenes 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 \( \text{HNO}_3 \). 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 \( \text{HNO}_3 \) 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\(_2\), PAN, and \( \text{HNO}_3 \) was in balance with the surface deposition flux of \( \text{HNO}_3 \) and indicated balance of the oxides of nitrogen family. However, the predicted rates of \( \text{HNO}_3 \) formation and \( \text{HNO}_3 \) entrainment from aloft were inadequate to maintain observed levels of \( \text{HNO}_3 \) unless aerosol partitioning and depositional effects were included. The estimated dry deposition flux of \( \text{HNO}_3 \) 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 \( \text{O}_3 \) 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 \( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \). A direct loss of ozone to the sea surface was of secondary importance. \( \text{CH}_3\text{OOH} \) 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 \( 6 \times 10^{-5} \text{ s}^{-1} \) for a mean MBL height of 700 m. \( \text{H}_2\text{O}_2 \), HFo, \( \text{HNO}_3 \), and \( \text{CH}_2\text{O} \) losses from the MBL are estimated at rates of \( 1.4 \times 10^{-5} \text{ s}^{-1} \). Sea-salt aerosol confines the surface deposition of \( \text{HNO}_3 \). Inclusion of surface loss improved the agreement between model-predicted and measured concentrations of \( \text{HNO}_3 \), \( \text{CH}_3\text{OOH} \), \( \text{H}_2\text{O}_2 \), and \( \text{CH}_2\text{O} \) species which had been overestimated in the MBL by the photochemical point model. A strong but unknown \( \text{CH}_2\text{O} \) sink was required in addition to surface deposition to resolve model and measurements in the MBL. The missing sink of \( \text{CH}_2\text{O} \) and source of HFo were comparable.

References


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


B. Anderson, NASA Langley Research Center, Hampton, VA 23681-0001.
D. Blake, University of California, Irvine, CA 92717.
J. Bradshaw, Georgia Institute of Technology, Atlanta, GA 30332.
H. Fuelberg, Florida State University, Tallahassee, FL 32306.
B. Heikes (corresponding author), and M. Lee, Center for Atmospheric Chemistry Studies, Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882-1197. (email: zagar@notos.gso.uri.edu)

D. Jacob, Harvard University, Cambridge, MA 02138.
H. Singh, NASA Ames Research Center, Moffet Field, CA 94035.
R. Talbot, University of New Hampshire, Durham, NH 03824.
A. M. Thompson, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

(Received March 21, 1995; revised November 6, 1995; accepted November 6, 1995.)