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

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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 peroxyacetylnitrate (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 x 10^9 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 x 10^10 compared to 11 +/- 10 x 10^10 molecules cm^-2 s^-1. The principal O3 destruction process was mediated by the formation and surface deposition of H2O2 and CH3OOH, 4 +/- 4 x 10^10 and 1.1 +/- 0.5 x 10^10 molecules cm^-2 s^-1. The direct loss of O3 to the sea surface was estimated to be 1.7 +/- 0.2 x 10 molecules cm^-2 s^-1. CH3OOH was lost to the sea and transported into the FT from the MBL. Its first-order loss rate was estimated to be 7 x 10^-6 s^-1 for a mean MBL height of 700 m. H2O2 and CH2O losses from the MBL were estimated at rates of 1.3 x 10^-5 s^-1 for both species. The inclusion of surface deposition improved the agreement between predicted and measured concentrations of HNO3, CH3OOH, H2O2, and CH2O. However, model CH2O remained significantly greater than that measured in the MBL.