

Tropical entrainment time scales inferred from stratospheric N₂O and CH₄ observations

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Abstract. Simultaneous *in situ* measurements of N₂O and CH₄ were made with a tunable diode laser spectrometer (ALIAS II) aboard the Observations from the Middle Stratosphere (OMS) balloon platform from New Mexico, Alaska, and Brazil during 1996 and 1997. We find different compact relationships of CH₄ with N₂O in the tropics and extra-tropics because mixing is slow between these regions. Transport into the extra-tropics from the tropics or the polar vortex leads to deviations from the normal compact relationship. We use measured N₂O and CH₄ and a simple model to quantify entrainment of mid-latitude stratospheric air into the tropics. The entrainment time scale is estimated to be 16 (+17, -8) months for altitudes between 20 and 28 km. The fraction of tropical air entrained from the extra-tropical stratosphere is 50% (+18%, -30%) at 20 km, increasing to 78% (+11%, -19%) at 28 km.

Introduction

Historically, long-lived tracers have been used to determine the large-scale circulation of the stratosphere because they are conserved during atmospheric motions that are fast compared to chemical production or loss. Brewer [1949] and Dobson [1956] utilized H₂O and column O₃ as passive tracers to infer that air enters the stratosphere at the tropical tropopause, is transported poleward, and returns to the troposphere at middle and high latitudes. More recently, CH₄ and N₂O have been studied because of their long photochemical lifetimes in the lower stratosphere, ranging from centuries at the tropopause to roughly 4 years and 1 year, respectively, at 10 hPa. Both gases are produced at the Earth's surface and photochemically removed in the stratosphere. CH₄ is predominantly removed in the troposphere, but is nearly homogenized there by rapid mixing. Early measurements of these gases [e.g., Fabian *et al.*, 1981; Jones and Pyle, 1984] showed stratospheric isopleths sloping downward and poleward, as expected from the Brewer-Dobson model of stratospheric circulation. These measurements also showed temporal and spatial variations that were well-correlated

for CH₄ and N₂O, implying that they represented only small-scale motions [Ehhalt *et al.*, 1983]. Therefore, plots of one tracer versus another should remove effects of small-scale dynamics, and can be used to infer larger-scale air motions.

Two tracers with long photochemical time scales relative to the time scale for quasi-horizontal mixing are said to be in "slope equilibrium," which means their functional relationship is independent of location along the surface of fastest mixing [Plumb and Ko, 1992]. Such tracers are expected to exhibit a compact correlation (i.e., small variance from a well-defined relationship). If, in addition, the photochemical time scales are longer than vertical transport time scales, then the tracers are expected to have a linear relationship [Plumb and Ko, 1992]. However, if mixing is slow between two latitudes with different photochemical environments, then the tracer vs. tracer relationship will depend on latitude, as observed in the tropical and extra-tropical lower stratosphere [e.g., Murphy *et al.*, 1993; Volk *et al.*, 1996]. Such observations led Plumb [1996] to develop the so-called "tropical pipe" model of stratospheric circulation, in which the tropical stratosphere is isolated from the extra-tropics. However, tracer observations indicate that the barrier is permeable to transport between the tropics and mid-latitudes [e.g., Avallone and Prather, 1996; Minschwaner *et al.*, 1996; Volk *et al.*, 1996; Schoeberl *et al.*, 1997; Hall and Waugh, 1997; Mote *et al.*, 1998].

Tracer observations can be used to infer the time scale for mid-latitude stratospheric air to be transported back into the tropical stratosphere, which we define here as the "entrainment" time scale. Previous studies concluded that the mean entrainment time scale is approximately 12 to 18 months at 20 km and that about 50% of the tropical air at 21 km had been entrained from mid-latitudes [Minschwaner *et al.*, 1996; Volk *et al.*, 1996]. In this paper, we present new, high-precision observations of stratospheric N₂O and CH₄ and use them to quantify the entrainment time scale in the lower and middle stratosphere.

Balloon Observations of N₂O and CH₄

The Aircraft Laser Infrared Absorption Spectrometer II (ALIAS II) has measured *in situ* N₂O and CH₄ mixing ratios on flights of the Observations from the Middle Stratosphere (OMS) balloon platform from New Mexico (34°N, 104°W), Alaska (65°N, 148°W), and Brazil (7°S, 39°W). ALIAS II uses tunable diode lasers to measure N₂O and CH₄ by infrared absorption spectroscopy [Webster *et al.*, 1994]. During balloon ascent and descent, air flows freely through an open-path multipass cell (61.8 m optical path) suspended outside the gondola. Measurements of both gases have an estimated 5% precision and 5% accuracy relative to calibration standards provided by the National Oceanic and Atmospheric Administration (NOAA)

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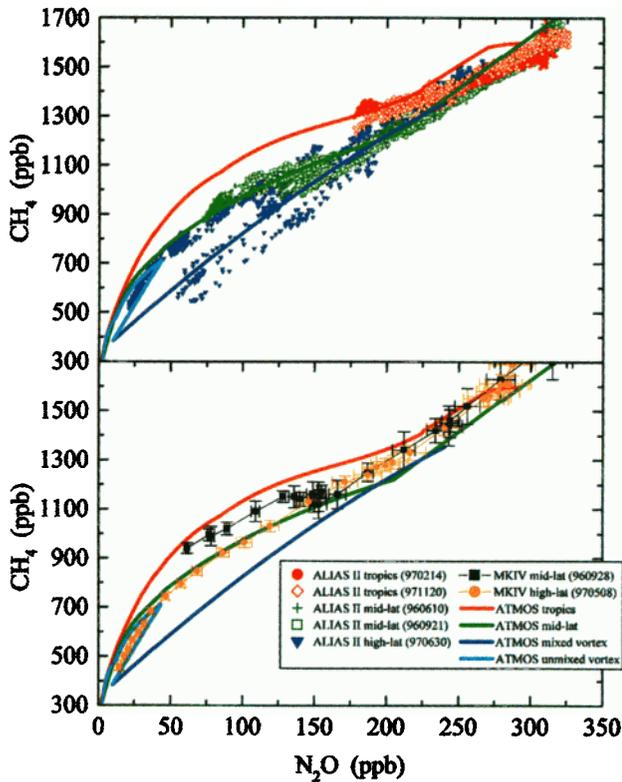


Figure 1. CH_4 vs. N_2O volume mixing ratios. For $\text{N}_2\text{O} < 230$ ppb, the CH_4 vs. N_2O relationship in the tropics is different from the extra-tropics due to the subtropical transport barrier. Mixing between polar vortex and extra-vortex air creates a unique high-latitude CH_4 vs. N_2O relationship for two vortex remnants and the ATMOX mixed vortex curve. ATMOX curve fits are from *Michelsen et al.*, [1998].

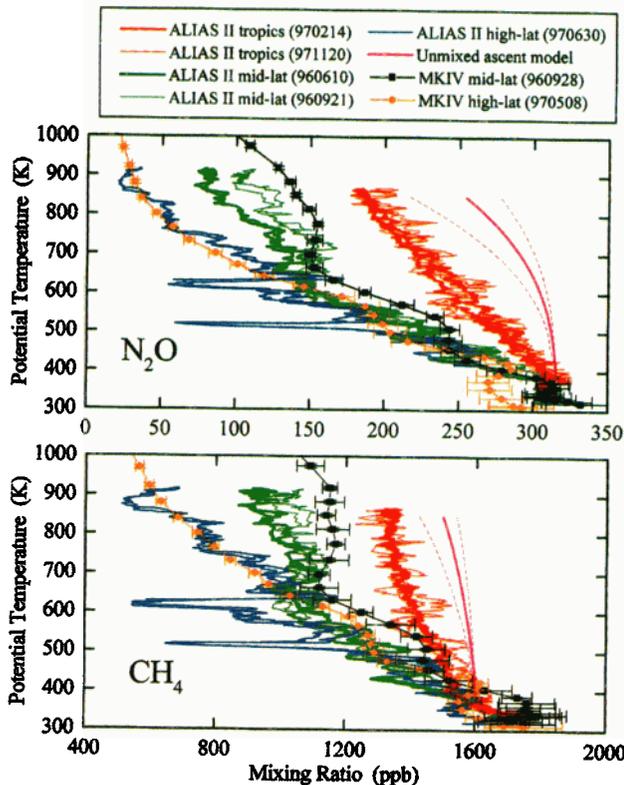


Figure 2. Vertical profiles of N_2O and CH_4 . Measured tropic mixing ratios are significantly lower than predicted by the unmixed ascent model (pink line with 1 st. dev. error range) due to entrainment of extra-tropical air. This model is constrained by 315 ppb N_2O and 1600 ppb CH_4 at the tropical tropopause. The two thin layers of low mixing ratios at high latitudes correspond to the polar vortex remnants of Fig. 1.

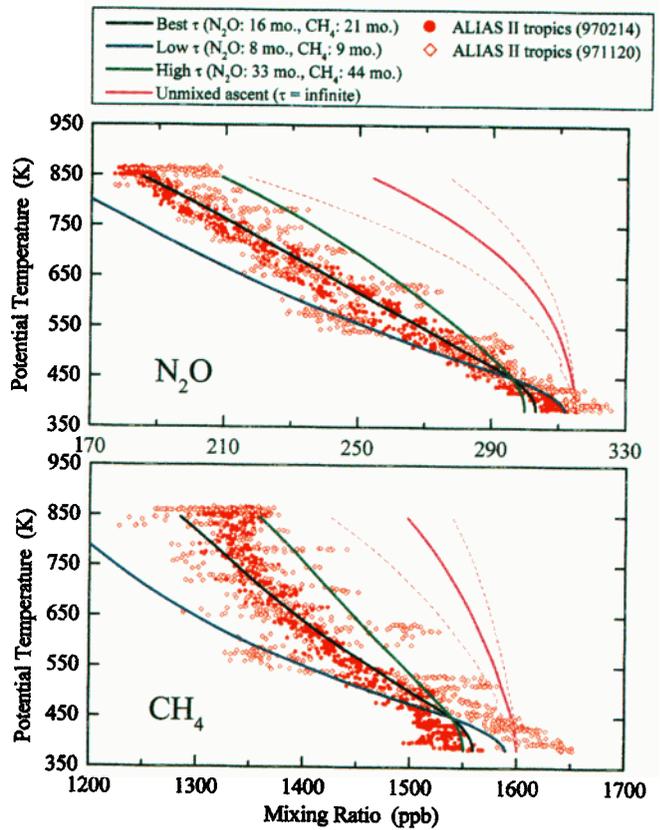


Figure 3. Vertical profiles of tropical N_2O and CH_4 . Lines are tracer profiles predicted by the entrainment model with constant values of τ_{TN} . The black line is the best fit to the data. The entrainment model is constrained by the mean mixing ratios of N_2O and CH_4 at 450 K (the unmixed ascent model is described in Fig. 2).

Climate Monitoring and Diagnostics Laboratory (CMDL). Simultaneous measurements of pressure p and temperature T are used to calculate potential temperature, $\theta = T(1000/p)^\kappa$, where $\kappa = 0.286$. The following analysis uses data obtained during both ascent and descent (200 to 9 hPa).

CH_4 and N_2O mixing ratios are highly correlated in the ALIAS II observations (Fig. 1). For $230 < \text{N}_2\text{O} < 310$ ppb, CH_4 and N_2O have the same linear, compact relationship at all latitudes due to their long photochemical lifetimes in the lower stratosphere, as observed previously [e.g., *Collins et al.*, 1993]. However, for $\text{N}_2\text{O} < 230$ ppb, the tropical CH_4 vs. N_2O relationship deviates from the extra-tropical relationship. A similar separation in CH_4 vs. N_2O relationships has been recorded by the Atmospheric Trace Molecule Spectroscopy (ATMOX) instrument aboard the space shuttle [*Michelsen et al.*, 1998] (Fig. 1). This separation demonstrates that there is some degree of a barrier between the tropical and mid-latitude stratosphere, to be quantified in the next section.

At mid-latitudes, ALIAS II CH_4 and N_2O have a compact relationship at all altitudes measured (up to 30 km), in agreement with ATMOX. For $\text{N}_2\text{O} > 150$ ppb, the JPL MkIV interferometer [*Toon*, 1991] has measured similar CH_4 and N_2O at mid-latitudes (Fig. 1). However, for $\text{N}_2\text{O} < 150$ ppb, the mid-latitude MkIV relationship of the 960928 (yymmdd) flight lies between the ATMOX mid-latitude and tropical curves, presumably because the air has come from the tropics recently and has not mixed

completely with the background mid-latitude reservoir. This feature corresponds to higher mixing ratios of CH₄ and N₂O above 25 km ($\theta > 630$ K), as shown in Fig. 2. Such features have often been measured at mid-latitudes by MkIV, ALIAS II (960921), and others [e.g., Kondo *et al.*, 1996], and are manifestations of outflow from the tropics.

At high latitudes, the CH₄ vs. N₂O relationship measured by ALIAS II (970630) is similar to the MkIV relationship (970508) and the ATMOS mid-latitude relationship due to rapid meridional transport within the extra-tropics. ATMOS measurements outside the polar vortex confirm this observation [Michelsen *et al.*, 1998]. However, ALIAS II intercepted two narrow layers with anomalously low mixing ratios centered at $\theta \approx 515$ K (20.4 km) and 615 K (24.0 km) (Fig. 2). At these altitudes, such low mixing ratios could only be associated with remnants of the Arctic polar vortex. These remnants are not evident in the MkIV high latitude data measured on 970508 because the flight occurred prior to the breakup of the vortex. All of the high latitude ALIAS II data that fall below the cluster of mid-latitude data in Fig. 1 are from these layers and their partially mixed edges. These data are similar to the Arctic vortex CH₄ vs. N₂O relationship of ATMOS because both are mixing lines between mid-latitude lower stratospheric air and descended vortex air.

Tropical Model

We now examine the tropical and mid-latitude ALIAS II data to determine entrainment time scales. For a given potential temperature, N₂O and CH₄ mixing ratios are considerably higher in the tropics than in the extra-tropics (Fig. 2) because tropical air has spent considerably less time in the stratosphere and thus has experienced less photochemical loss. The mean profiles of N₂O and CH₄ are similar for both tropical flights, so we assume that they are representative of the tropics.

We calculate the time scale for entrainment of mid-latitude air into the tropics by comparing measured tropical mixing ratios to values calculated by a simple tropical model allowing for photochemical loss, vertical advection, and entrainment from mid-latitudes. This technique is described in detail by Minschwaner *et al.* [1996]. For an air parcel ascending in the tropics with isentropic entrainment of extra-tropical air, the continuity equation is given by:

$$Q(\partial\chi/\partial\theta) = -L\chi - \gamma\chi + (\chi_{MID} - \chi)/\tau_{IN} \quad (1)$$

where Q is $(\partial\theta/\partial t)$ calculated with a radiative model constrained by zero net mass flux through a global pressure surface [Rosenlof, 1995], χ is the tropical mixing ratio, χ_{MID} is the mid-latitude mixing ratio at the same potential temperature, $L\chi$ is the local photochemical loss rate, $\gamma\chi$ is the long-term growth rate, and τ_{IN} is the time scale for entrainment of mid-latitude air into the tropical stratosphere. A representative mean tropical profile of Q was obtained by averaging over tropical latitudes (9.5°S - 9.5°N), all seasons (July 1995 - June 1997), and all longitudes. Long-term growth rates are included because stratospheric air has a time lag with respect to air at the tropopause. These growth

rates are global averages of recent tropospheric trends in data collected by the NOAA CMDL global network [Elkins and Dlugokencky, unpubl.].

Photochemical loss includes removal of N₂O by photolysis and reaction with O(¹D), and removal of CH₄ by reaction with OH, O(¹D), and Cl. Twenty four hour average photolysis rates were calculated with a radiative transfer model using measured temperature and O₃ profiles (JPL O₃ measurements from 0 to 30 km, and satellite-based climatology above 30 km) [Salawitch *et al.*, 1994; Minschwaner *et al.*, 1993]. The photochemical model was initialized with measured CH₄, N₂O, and H₂O. NO_y was inferred from the November 1994 ATMOS tropical relationship with N₂O [M. R. Gunson, pers. comm., 1998]. Cl_y (total inorganic chlorine) and Br_y (total inorganic bromine) were inferred from CFC-11 measured by the NOAA Lightweight Airborne Chromatograph Experiment (LACE) [Elkins *et al.*, 1996] and also from measurements of organic source gases [Wamsley *et al.*, 1998]. Twenty four hour average concentrations of OH, O(¹D), and Cl were calculated with this photochemical model [Salawitch *et al.*, 1994] using reaction rates and absorption cross sections from DeMore *et al.* [1997]. We assume 20% uncertainty in the N₂O photolysis rate, reaction rate uncertainties from DeMore *et al.* [1997], 20% uncertainty in radical concentrations, 40% uncertainty in Q for $p < 50$ hPa, and 60% uncertainty in Q for $50 < p < 90$ hPa.

In the limit of infinite τ_{IN} , equation (1) represents vertical advection in the tropics with no mixing in from the extra-tropics, and is solved to obtain unmixed ascent profiles (Fig. 2). Measured tropical N₂O and CH₄ decrease significantly faster with altitude than predicted by this model, so entrainment of extra-tropical stratospheric air is required to explain the measured mixing ratios [e.g., Avallone and Prather, 1996; Minschwaner *et al.*, 1996; Volk *et al.*, 1996].

N₂O and CH₄ are modeled to estimate the time scale, τ_{IN} , for entrainment of mid-latitude air into the tropics. Equation (1) is solved numerically for χ at each θ level and τ_{IN} is varied to achieve the best fit with the observations. The two tracers can be reproduced over a wide range of θ with a constant τ_{IN} (Fig. 3). For N₂O, τ_{IN} is 16 (+17, -8) months for altitudes between 20 and 28 km (450 K $< \theta < 770$ K). For CH₄, τ_{IN} is 21 (+23, -9) months between 20 and 27 km (450 K $< \theta < 690$ K). At lower altitudes, the model cannot match the data unless τ_{IN} is smaller. For N₂O, τ_{IN} is approximately 6 (+11, -4) months between the tropical tropopause and 20 km (380 K $< \theta < 450$ K). The error bars, dominated by the uncertainty in Q , are large enough that we cannot rule out a single time scale independent of altitude. These time scales are similar to previous results [Minschwaner *et al.*, 1996; Volk *et al.*, 1996; Mote *et al.*, 1996], but we note that there is better agreement with time scales derived from previous balloon measurements of N₂O than from satellite data [Minschwaner *et al.*, 1996].

Following Minschwaner *et al.* [1996], we calculate the fraction, $\zeta(\theta)$, of tropical air entrained from the extra-tropical stratosphere:

$$\zeta(\theta) = 1 - \exp\left[-\int_{\theta_0}^{\theta} (1/\tau_{IN} Q) d\theta\right] \quad (2)$$

where $\theta_0 = 385$ K and τ_{IN} is set equal to the two constant values determined above for N₂O. The vertical profile of ζ , shown in Fig. 4, indicates that most entrainment into the tropics occurs in the lower stratosphere. The percentage of tropical air entrained

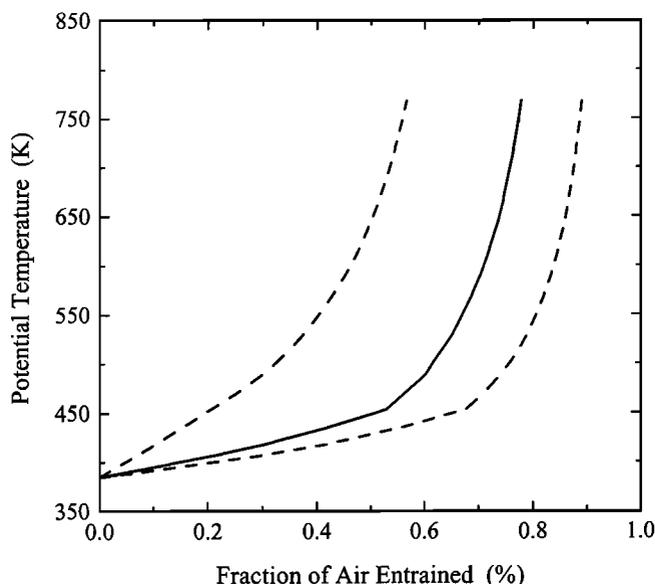


Figure 4. Fraction of extra-tropical air entrained into the tropical stratosphere corresponding to the best estimates of τ_{IV} and Q (dashed lines show range of uncertainty).

from the extra-tropics is 50% (+18%, -30%) at 20 km ($\theta = 500$ K), increasing to 78% (+11%, -19%) at 28 km ($\theta = 770$ K). These percentages are similar to those found by Minschwaner *et al.* [1996] and Volk *et al.* [1996].

In situ observations of N_2O and CH_4 reported here show distinct compact relationships for the tropics and extra-tropics. We have used a simple model of the tropical upwelling region to quantify the time scale and fraction of entrainment of mid-latitude air into the tropics. Our results have important implications for calculated trends of mid-latitude ozone [e.g., Volk *et al.* 1996] as well as the altitude and latitude distribution of NO_y released by future fleets of supersonic aircraft. Once in the tropical stratosphere, NO_y is efficiently lofted to higher altitudes where perturbations to ambient levels of NO_y lead to greater loss of O_3 . The CH_4 vs. N_2O relationships, entrainment time scales and fraction of entrained air provide important empirical constraints for evaluating multi-dimensional models used to calculate the effects of anthropogenic gases on the global O_3 distribution.

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