Vertical transport rates in the stratosphere in 1993 from observations of CO\textsubscript{2}, N\textsubscript{2}O and CH\textsubscript{4}.

Steven C. Wofsy, Kristie A. Boering, Bruce C. Daube, Jr., and Michael B. McElroy
Division of Applied Science and Department of Earth and Planetary Science, Harvard University, Cambridge, Massachusetts

Max Loewenstein and James R. Podolske
NASA Ames Research Center, Moffett Field, California

James W. Elkins, Geoffrey S. Dutton and David W. Fahey
National Oceanic and Atmospheric Administration, Boulder, Colorado

Abstract. Measurements of CO\textsubscript{2}, N\textsubscript{2}O and CH\textsubscript{4} are analyzed to define hemispheric average vertical exchange rates in the lower stratosphere from November 1992 to October 1993. Effective vertical diffusion coefficients were small in summer, \( \leq 1 \text{ m}^2\text{s}^{-1} \) at altitudes below 25 km; values were similar near the tropopause in winter, but increased markedly with altitude. The analysis suggests possibly longer residence times for exhaust from stratospheric aircraft, and more efficient transport from 20 km to the middle stratosphere, than predicted by many current models. Seasonally-resolved measurements of stratospheric CO\textsubscript{2} and N\textsubscript{2}O provide significant new constraints on rates for global-scale vertical transport.

Introduction

Future high speed civil transports (HSCTs) are expected to inject H\textsubscript{2}O and nitrogen oxides into the stratosphere. The residence time for the exhaust in the stratosphere will determine the magnitude of the associated perturbation to atmospheric chemistry. Residence times for stratospheric gases are currently estimated using observations of radioactive and volcanic debris, mostly in particular form. These data reflect stratospheric transport rates only for particular single-point injections in the past.

To predict the impact of HSCTs, we must understand rates for meridional dispersion and vertical transport of exhaust continuously emitted over the globe. Boering et al. [this issue] documented the propagation through the stratosphere of seasonal cycles and long-term trends in tropospheric CO\textsubscript{2} [Keeling et al., 1989; Conway et al., 1988], relative to N\textsubscript{2}O. Here we use data for N\textsubscript{2}O, CO\textsubscript{2}, and CH\textsubscript{4} obtained from the ER-2 during SPADE to derive seasonally-resolved rates for vertical exchange in 1992-93, averaged over midlatitudes in the Northern hemisphere stratosphere, and we discuss implications for predicted impacts of HSCTs.

Conceptual framework

Concentrations of stratospheric trace gases fluctuate with latitude, altitude, and time. However, variations for long-lived species are usually correlated [Ehhalt et al., 1983]; scatterplots of one tracer concentration against another give compact curvilinear relationships, often uniform on global scales [e.g., Fahey et al., 1990]. Plumb and Ko [1992] argued that compact global relationships arise by advection of trace species in the global residual circulation, modified by quasi-isentropic mixing by planetary-scale waves that propagate from the troposphere in winter [cf. Holton, 1986, Mahlman et al., 1986; Plumb and Mahlman, 1987; Schoeberl and Hartmann, 1991]. If quasi-isentropic mixing were much faster than non-conservative processes, isopleths for long-lived tracers would be parallel and transport of one tracer relative to another could be represented as a flux \((F_Z)\) in one dimension, normal to the isopleths,

\[
F_Z = -K(Z^*) \frac{\partial \sigma}{\partial Z^*}, \quad \text{where} \quad K(Z^*) = \left[ \frac{(\gamma^2-K_{zz})^2}{K_{yy}} + K_{za} \right]_o.
\]

Here \( \sigma \) is the tracer mole fraction, \( \chi \) the stream function, and \( K \) a mixing tensor along \((y,z)\), the meridional and vertical directions, respectively. Brackets denote the global average on an isopleth and \( Z^* = 7/\text{ln}(1000/p) \) \((\text{km})\), \( p \) isopleth pressure \((\text{mb})\) is the isopleth pressure altitude at a specified reference latitude.

The data conform closely to this idealized model. Scatterplots of CO\textsubscript{2} [Boering et al. this issue] and CH\textsubscript{4} vs. N\textsubscript{2}O were remarkably compact. Seasonal and interannual variations of CO\textsubscript{2} propagated uniformly upward from the troposphere (seasonal changes for CH\textsubscript{4} were undetectable when compared with earlier measurements [see Schauffler et al., 1993]). Hence we use Eq. (1) with data for CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}O to derive mean rates for vertical transport in the stratosphere over the domain of the observations \((15-60^\circ N)\), analogous to early "eddy-diffusion" models [Lettu, 1951; Colegrove et al., 1965; Wofsy and McElroy, 1973; Hunten, 1975]. Here the CO\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2}O coordinate system eliminates effects of variance due to reversible displacements of the tracer fields [Ehhalt et al., 1983], allowing us to exploit these displacements to infer tracer distributions above flight altitudes.

**Mean \( K(Z^*) \) for 1992-93**

We derive \( K(Z^*) \) by integrating the continuity equation,

\[
\frac{\partial C}{\partial t} = \frac{1}{p} \frac{\partial}{\partial Z^*} \left[K(Z^*) \frac{\partial C}{\partial Z^*} \right] = 0, \quad (2)
\]

\[
K(Z^*) = \left[ \frac{\partial C}{\partial N_2O} \frac{\partial N_2O}{\partial Z^*} \right]^{-1} \times (3)
\]

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Here \( C = CH_4 + CO_2 \), and the last term (with \( H = 6 \) km) approximates the flux at \( Z^* = Z^*_{\text{top}} \). Eq. 3 was evaluated using data for \( \Delta CO_2/\Delta N_2O \) and \( \Delta CO_2(N_2O)/\Delta t \) [Fig. 2, Boering et al., this issue], and \( \Delta CH_4/\Delta N_2O = 0.0043 \) ppm/ppb. A profile for \( N_2O(Z^*) \) was adopted from data for 24±4° (Fig. 1b), the reference latitude chosen to approximate global mean photolysis rates for \( N_2O \). The profile for \( N_2O(Z^*) \) from Fig. 1b was used to derive \( K(Z^*) \) for 42 > \( Z^* > 30 \) km, the interval with 70% of the \( N_2O \) gradient, using Eq. 3 with \( \Delta C(N_2O(Z^*))/\Delta t \) replaced by \( \Lambda \) from Eq. (4) below. Including \( CH_4 \) increases vertical gradients by ~15%, with little effect on time derivatives, hence, neglect of \( CO_2 \) from \( CH_4 \) oxidation would give \( K(Z^*) \) about 15% too large.

Profiles of \( K(Z^*) \) (Fig. 1a) show a bottleneck just above the tropopause, implied by slow propagation of the seasonal oscillation. The fall minima and spring maxima for \( CO_2 \) require 4-7 months to propagate 2-3 km, i.e. from the tropopause to \( N_2O = 300 \) ppb. The bottleneck was inferred also in early studies of transport of heat, nuclear bomb debris, \( CH_4 \) and \( N_2O \) [e.g. Holton, 1986; Wofsy and McElroy, 1973; Hunten, 1975], from steep gradients observed just above the tropopause. The increase of \( K(Z^*) \) above the tropopause in winter is implied by the rise in \( CO_2 \) for \( N_2O < 200 \) ppb; very slow vertical exchange at these levels is indicated in summer by virtually unchanged \( CO_2 \) from May to November.

The composite profile adopted for \( N_2O \) is not constrained to be consistent with the \( CO_2:N_2O \) relationships in SPADE. Figure 2a shows consistent solutions for \( CO_2(Z^*) \) from Eq. (2) and for \( N_2O \) from

![Figure 1a. Vertical profiles of \( K(Z^*) \): summer (open □) and winter (filled □) using Eq. 3 and data for \( CO_2 \), \( CH_4 \), and \( N_2O \) (\( Z^* > 26 \) km); solid line, using satellite data for \( N_2O(Z^*) \) (\( Z^* > 30 \) km); dotted line, interpolated values.](image1)

![Figure 1b. Vertical profile of \( N_2O \) for 15-25N. The line is a fit (locally-weighted least squares, "lowess") to data: \( Z^* > 30 \) km, satellite observations November, 1992 [CLAES/UAARS, A. Roche and J. Mergenthaler, private communication, 1994; ATMOS/ATLAS, M. Gunson, private communication, 1994]; 30 > \( Z^* > 20 \) km, tropical balloon data [Goldan et al., 1981]; \( Z^* < 20 \) km, ER-2, 20-28N, on dates indicated. Dotted lines show \( N_2O \) computed from the 1-D model, using \( K(Z^*) \) from Eq. (3) and with 0.5x this value("0.5xK_{\text{dir}}").](image2)

\[
\frac{\partial N_2O}{\partial t} - \frac{1}{p} \frac{\partial}{\partial Z^*} \left[ K(Z^*) \frac{\partial N_2O}{\partial Z^*} \right] = \Lambda \cdot N_2O . \tag{4}
\]

Here we set tropospheric \( N_2O \) to 325 ppb, as given by the ER-2 ATLAS instrument. We set \( CO_2 \) at the bottom boundary to the mean of surface data from Mauna Loa and Samoa [T. Conway, private communication, 1994], delayed by 1 month to allow for tropospheric mixing, which approximates \( CO_2 \) observations just above the tropopause (Fig. 2b). In Eq. (4), \( \Lambda = J_{N_2O} + k_3[O(\Delta)] \) for 15N at equinox, \( J_{N_2O} \) is the photolysis rate (sec⁻¹), and \( k_3 \) is the rate constant for...
The calculation commenced in 1982. The initial CO$_2$-N$_2$O relationship was specified by subtracting 15 ppm CO$_2$ (the global mean increase in the decade) from the observations for November 1992. Winter and summer profiles for K(Z*)$_{alt}$ (Fig. 1a), or 0.5xK(Z*)$_{alt}$, were repeated each year.

Observed CO$_2$-N$_2$O relationships are bracketed by models using 1x and 0.5xK(Z*)$_{alt}$ (Fig. 2a). The 1-D model simulates observed propagation of the CO$_2$ signal through the lower stratosphere remarkably well (using N$_2$O as the vertical coordinate), with the best fit for K(Z*)=0.5xK(Z*)$_{alt}$ (Fig. 2b), and it projects changes observed in early 1994. Details of N$_2$O-CO$_2$ variations near the tropopause (290<N$_2$O<325 ppb) are not clearly delineated; these data were obtained on ascent near the tropopause (290<N$_2$O<325 ppb) are not clearly delineated; these data were obtained on ascent.

Values for N$_2$O are somewhat lower than observed for the profile of K(Z*) giving the best fit to CO$_2$-N$_2$O data (Fig. 1b). This difference likely reflects errors in the specified vertical profile for N$_2$O, leading to an inaccurate global mean vertical flux of N$_2$O. The discrepancy contributes uncertainty to estimates of the rate of upward spread of HSCT exhaust; it could be resolved by extending measurements of CO$_2$, CH$_4$, and N$_2$O to the middle stratosphere.

A recent 3-D model [Hall and Prather, 1993] simulated the mean difference between stratospheric and tropospheric CO$_2$, however, CO$_2$ evolved uniformly vs N$_2$O through the year, lacking the observed seasonal asymmetry. The model gave qualitatively correct gradients near the tropopause, but finer vertical resolution (<0.5 km, vs 3 km in the model) is needed for detailed comparison.

NO$_x$ from stratospheric aviation

The concentration of NO$_x$ was computed by solving

\[
\frac{\partial \text{NO}_x}{\partial t} - \frac{1}{\rho} \frac{\partial}{\partial Z^*} (\rho K(Z^*) \frac{\partial \text{NO}_x}{\partial Z^*}) = P(N_2O(Z^*)) - \beta(\text{NO}_x)^2
\]

(6)

where P(N$_2$O(Z*)) denotes production of odd nitrogen by (5a) or by aircraft, and $\beta(\text{NO}_x)^2$ is the sink for NO$_x$.

\begin{align*}
\text{NO} + \text{hv} &\rightarrow \text{N} + \text{O} \\
\text{N} + \text{O}_2 &\rightarrow \text{NO} + \text{O} \\
\text{N} + \text{NO} &\rightarrow \text{N}_2 + \text{O}
\end{align*}

(7)

averaged along an N$_2$O isopleth. Solutions to (6) reproduce observed correlations for N$_2$O-NO$_x$ (Figure 3a) [e.g., Loewenstein et al., 1993], virtually independent of K(Z*)

Figure 3b shows computed springtime perturbations in NO$_x$ produced by hypothetical HSCTs injecting NO$_x$ at Z*=20 km for 10 years at a rate of 1.45x10$^6$ cm$^{-2}$s$^{-1}$, 60% of total fleet emissions for the Mach 2.4/EI 15 fleet scenario [Baughcum et al., 1993] (to approximate northern hemisphere cruise input at cruise). Results are shown from the AER 2-D model [Ko and Douglass, 1993] for the full scenario, averaged over the Northern hemisphere.

At altitudes higher than injection, ∆NO$_x$ in 2-D models is smaller than in 1-D models, because exhaust does not spread uniformly along N$_2$O isopleths, giving rise to a local maximum in flight corridors. It is presently not clear if the 1-D model represents a global mean, as envision by Plumb and Ko [1992], or if the tropics represent a distinct regime essentially uncoupled from midlatitudes. Data for CO$_2$, CH$_4$, N$_2$O and NO$_x$ are presently scarce or nonexistent for altitudes above 20 km, preventing confident prediction of ∆NO$_x$ above flight levels; this is highly significant due to the enhanced reactivity of NO$_x$ at high altitudes.

Conclusions

Temporal variations of tropospheric CO$_2$, relative to N$_2$O and CH$_4$, provide a unique signal for determining rates for transport in the lower and middle stratosphere. Seasonally-resolved data for CO$_2$, N$_2$O and NO$_x$ are needed above 20 km to define rates for vertical advection and quasi-isentropic mixing, and fine-scale data near the tropopause are needed to define rates for transport in the key "bottleneck" region. Interannual variations, rates for interhemispheric exchange, and possible effects of the quasi-biennial oscillation need to be investigated. The present analysis shows that systematic tracer measurements over a period of years promise to help resolve these issues, providing essential constraints on models used to predict impacts of future HSCTs.

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Kristie A. Boering, Bruce C. Daube, Jr., Michael B. McElroy, and Steven C. Wofsy, Division of Applied Science and Department of Earth and Planetary Science, Harvard University, Cambridge, MA 02138


Max Loewenwein and James R. Podolske, NASA-Ames Research Center, Moffett Field, CA 94035

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