Vertical transport rates in the stratosphere in 1993 from observations of CO₂, N₂O and CH₄.

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Abstract. Measurements of CO₂, N₂O and CH₄ 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, ≤ 1 m²/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 CO₂ and N₂O provide significant new constraints on rates for global-scale vertical transport.

Introduction

Future high-speed civil transports (HSCTs) are expected to inject H₂O 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 particulate 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 CO₂ [Keeling et al., 1989; Conway et al., 1988], relative to N₂O. Here we use data for N₂O, CO₂, and CH₄ 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; Schoebel and Hartmann, 1991]. If quasi-isentropic mixing was 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 (F₂z) in one dimension, normal to the isopleths,

\[ F_{2z} = -K(Z^*) \frac{d\sigma}{dz^*}, \quad \text{where} \]

\[ K(Z^*) = \frac{(\gamma^2-K_{22}^z)^z}{K_{yy}}. \]  

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 \( Z^* = \gamma 10^3/(1000/p) \) (km), \( p \) isopleth pressure (mb) is the isopleth pressure altitude at a specified reference latitude.

The data conform closely to this idealized model. Scatterplots of CO₂ [Boering et al. this issue] and CH₄ vs. N₂O were remarkably compact. Seasonal and interannual variations of CO₂ propagated uniformly upward from the troposphere (seasonal changes for CH₄ were undetectable when compared with earlier measurements [see Schauffler et al., 1993]). Hence we use Eq. (1) with data for CO₂, CH₄, and N₂O to derive mean rates for vertical transport in the stratosphere over the domain of the observations (15-60N), analogous to early "eddy-diffusion" models [Lettau, 1951; Colegrove et al., 1965; Wofsy and McElroy, 1973; Hunten, 1975]. Here the CO₂/CH₄/N₂O 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,

\[ \frac{dC}{dt} = \frac{1}{p} \frac{\partial}{\partial z^*} \left[ K(Z^*) p \frac{\partial C}{\partial z^*} \right] = 0, \]  

\[ K(Z^*) = \left[ \int \frac{dC}{dN_2O} \frac{dN_2O}{dz^*}^{-1} \right] \times z-z^*. \]
Here \( C = CH_4 + CO_2 \), and the last term (with \( H=6 \) km) approximates the flux at \( Z^* \geq Z^*_\text{top} \). 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±8 [Fig. 1b], the reference latitude chosen to approximate global mean photolysis rates for \( N_2O \). The profile for \( N_2O(Z^*) \) was used to derive \( K(Z^*) \) for 42 > \( Z^* \geq 30 \) km, the interval with 70% of the \( N_2O \) gradient, using Eq. 3 with \( \partial(N_2O(Z^*))/\partial t \) 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

\[
\frac{dN_2O}{dt} = \frac{1}{p} \frac{\partial}{\partial Z^*} \left( K(Z^*) p \frac{dN_2O}{dZ^*} \right) = \Lambda N_2O. \tag{4}
\]

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), \( \Lambda = J_{N_2O} + k_s[O^D(D)] \) for 15N at equinox, \( J_{N_2O} \) is the photolysis rate (sec\(^{-1}\)), and \( k_s \) is the rate constant for
The calculation commenced in 1982. The initial CO₂-N₂O relationship was specified by subtracting 15 ppm CO₂ (the global mean increase in the decade) from the observations for November 1992. Winter and summer profiles for K(Z*)_per (Fig. 1a), or 0.5xK(Z*)_des, were repeated each year.

Observed CO₂-N₂O relationships are bracketed by models using 1x and 0.5xK(Z*)_des (Fig. 2a). The 1-D model simulates observed propagation of the CO₂ signal through the lower stratosphere remarkably well (using N₂O as the vertical coordinate), with the best fit for K(Z*)=0.55xK(Z*)_des (Fig. 2b), and it projects changes observed in early 1994. Details of N₂O-CO₂ variations near the tropopause (290<N₂O<325 ppb) are not clearly delineated: these data were obtained on ascent near the tropopause (290<N₂O<325 ppb) are not clearly delineated: these data were obtained on ascent and descent, adversely affecting the diode laser spectrometer.

Values of N₂O are somewhat lower than observed for the profile of K(Z*) giving the best fit to CO₂-N₂O data (Fig. 1b). This difference likely reflects errors in the specified vertical profile for N₂O, leading to an inaccurate global mean vertical flux of N₂O. The discrepancy contributes uncertainty to estimates of the rate of upward spread of HSCT exhaust; it could be resolved by extending measurements of CO₂, CH₄, and N₂O to the middle stratosphere.

A recent 3-D model [Hall and Prather, 1993] simulated the mean difference between stratospheric and tropospheric CO₂, however, CO₂ evolved uniformly vs N₂O 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.

**NOₓ from stratospheric aviation**

The concentration of NOₓ was computed by solving

\[ \frac{\partial \text{NO}_x}{\partial t} = \frac{1}{p} \frac{\partial}{\partial Z} (p K(Z*) \frac{\partial \text{NO}_x}{\partial Z}) - \text{P}(\text{N}_2\text{O}(Z*)) - \beta(\text{NO}_x)^2 \]  

(6)

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

\[ \text{NO} + \text{hv} \rightarrow \text{N} + \text{O} \]  

(7a)

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \]  

(7b)

\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \]  

(7c)

averaged along an N₂O isopleth. Solutions to (6) reproduce observed correlations for N₂O-NOₓ (Figure 3a) [e.g., Loewenstein et al., 1993], virtually independent of K(Z*)..

Figure 3b shows computed springtime perturbations to NOₓ produced by hypothetical HSCTs injecting NOₓ at \( Z^* = 20 \) km for 10 years at a rate of 1.45x10⁶ cm⁻²s⁻¹, 60% of total fleet emissions for the Mach 2.4/EI 15 fleet scenario [Baughcum et al., 1993] (to approximate northern hemisphere cruise-level inputs). Each summer, excess NOₓ accumulated near 20 km, then spread to higher altitudes, or was removed to the troposphere, in winter. The maximum \( \text{NO}_x \) perturbation near 20 km (0.5xK(Z*)_des) was ~7 ppb (Fig. 3b), 60% larger than predicted by most 2-D models. Values for \( \Delta \text{NO}_x \) are insensitive to K(Z*) above, and proportional to K(Z*) below, the injection altitude (see curve for 1xK(Z*)_des, Fig. 3b). The perturbation is reduced by 50% for injection just 2 km lower (at \( Z^* = 18 \) km).

**Conclusions**

Temporal variations of tropospheric CO₂, relative to N₂O and CH₄, provide a unique signal for determining rates for transport in the lower and middle stratosphere. Seasonally-resolved data for CO₂, N₂O, and NOₓ 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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