Stratospheric influences on the tropospheric seasonal cycles of nitrous oxide and chlorofluorocarbons

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Received 29 April 2004; revised 23 August 2004; accepted 17 September 2004; published 21 October 2004.

[1] The stratospheric influence on the tropospheric seasonal cycles of N_2O, CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 (CCl_2FCClF_2) is investigated using observations from the AGAGE global trace gas monitoring network and the results of the Whole Atmosphere Community Climate Model (WACCM). WACCM provides the basis for a number of predictions about the relative amplitudes of N_2O and CFC seasonal cycles and about the relative magnitude and phasing of seasonal cycles in the northern and southern hemispheres. These predictions are generally consistent with observations, suggesting that the stratosphere exerts a coherent influence on the tropospheric seasonal cycles of trace gases whose primary sinks are in the stratosphere. This stratospheric influence may complicate efforts to validate estimated source distributions of N_2O, an important greenhouse gas, in atmospheric transport model studies. *INDEX TERMS:* 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions. **Citation:** Nevison, C. D., D. E. Kinnison, and R. F. Weiss (2004), Stratospheric influences on the tropospheric seasonal cycles of nitrous oxide and chlorofluorocarbons, *Geophys. Res. Lett.*, *31*, L20103, doi:10.1029/2004GL020398.

1. Introduction

[2] Nitrous oxide (N_2O), an important long-lived greenhouse gas, is produced by microbial activity in soils and oceans. N_2O destruction occurs almost entirely in the stratosphere, by photolysis and oxidation. In the last century, the atmospheric N_2O concentration has increased sharply, due primarily to an enhancement of the microbial source associated with human agriculture [*Mosier et al.*, 1998]. There is still considerable uncertainty in the magnitude, distribution and relative importance of the various surface sources, both natural and anthropogenic, of N_2O [*Bouwman et al.*, 1995].

[3] Atmospheric transport models (ATMs) provide a tool for evaluating the current understanding of global N_2O sources. The temporal and spatial distribution of atmospheric N_2O predicted by ATMs, run with specified surface sources, can be validated against observations at global trace gas monitoring stations. Past evaluations of N_2O sources in ATMs have revealed poor matches between modeled and observed seasonal cycles. ATMs predict maximum N_2O mixing ratios in summer at northern hemisphere sites, where N_2O sources are dominated by soil microbial emissions [*Bouwman and Taylor*, 1996]. In contrast, the observed seasonal cycles of N_2O are generally minimum in summer in the northern hemisphere (Figure 1).

[4] CFCs are useful independent tracers for understanding N_2O seasonal cycles because they have similar stratospheric loss mechanisms to N_2O, but are entirely man-made compounds with better known and less complex surface sources. Thanks to their phase-out in response to the Montreal Protocol, CFC atmospheric mixing ratios started to level off or even decline in the 1990s and their interhemispheric gradients decreased sharply [*Montzka et al.*, 1999; *Prinn et al.*, 2000]. Although some surface sources remain, observed CFC seasonal cycles at tropospheric monitoring stations since the mid to late 1990s should primarily reflect atmospheric dynamical influences.

[5] A number of studies have examined the observed seasonal variations in atmospheric CFCs and/or N_2O. These studies have generally attributed seasonality to tropospheric transport processes, e.g. interhemispheric exchange [*Prather et al.*, 1987; *Prinn et al.*, 2000]. However, some studies have speculated that the stratosphere may contribute to the observed tropospheric summer minima in N_2O [*Bouwman and Taylor*, 1996; *Levin et al.*, 2002]. The purpose of this paper is to examine the stratospheric hypothesis, using a combination of models and observations. Our strategy is to compare the results of a 3-dimensional atmospheric model to observed N_2O and CFC seasonal cycles at tropospheric monitoring stations.

2. Methods

2.1. AGAGE Data

[6] Atmospheric concentrations of N_2O, CFC-11, CFC-12, and CFC-113 are measured every 40 minutes by gas chromatography at Mace Head, Ireland (53N, 10W), Trinidad Head, California (41N, 124W), and Cape Grim, Tasmania (41S, 145E) as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) program [*Prinn et al.*, 2000]. The relative precisions of the individual measurements range from about 0.03% for N_2O to about 0.3% for CFC-113. Monthly mean values are based on

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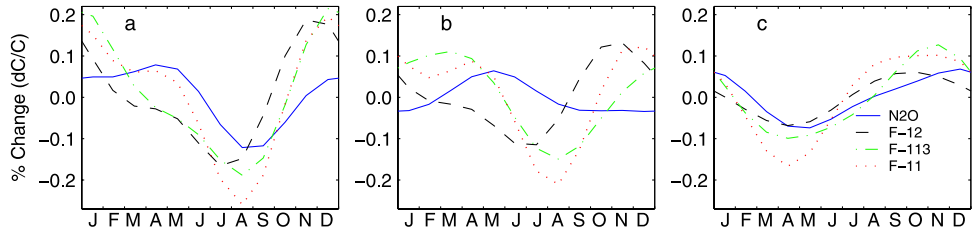

Figure 1. Normalized seasonal cycles of CFC-11, CFC-12, CFC-113, and N_2O. Seasonal residuals are the detrended harmonic fits to 8–10 years of monthly mean AGAGE data. a) Mace Head, b) Trinidad Head, c) Cape Grim.

order 10^3 measurements with pollution events removed. To derive seasonal cycles at each AGAGE station, the 8–10 year monthly mean data sets were fit to a function consisting of a 3rd order polynomial plus 4 harmonics. The optimal fit was determined by least squares regression and the polynomial component was subtracted to remove the secular trend. The remaining harmonic component is assumed to reflect the seasonal cycle (Figure 1).

2.2. WACCM Model

[7] WACCM is a comprehensive chemical-dynamical model of the atmosphere [*Sassi et al.*, 2002; *Forkman et al.*, 2003]. For the current study, WACCM Version 2 was run for 13 years with interannually variable meteorology, $2.0 \times 2.5^\circ$ horizontal resolution, and 66 pressure levels spanning altitudes from Earth's surface to the thermosphere (140 km). Fixed, uniformly distributed CFC-11, CFC-12 and N_2O mixing ratios were imposed at the lowest model level and were held constant through the 13 year run. (CFC-113 was not included.) The residual seasonal cycles in the 3 trace gases were calculated by subtracting the annual mean at each gridpoint. Due to the uniform lower boundary conditions, the seasonal cycles result purely from stratospheric chemistry and stratospheric and/or tropospheric dynamics. Because the restoring influence of the fixed boundary suppresses the seasonal cycles at the model's lowest layers, all tropospheric results are presented at the 700 mb level.

3. Results and Discussion

3.1. AGAGE Data

[8] The detrended harmonic fits to the observed N_2O and CFC data reveal distinct seasonal cycles at each of the mid-latitude AGAGE stations (Figure 1). The magnitude of the seasonal change is small, corresponding to only a fraction of a percent of the absolute mixing ratios. The N_2O, CFC-11, -12 and -113 harmonic fits have generally well correlated seasonal minima, although CFC-12 consistently leads the other two CFCs by ~1 month (Figure 1). At Cape Grim, all four species have minima in April–May. In the northern hemisphere, all have minima in July–August at Mace Head. At Trinidad Head, the CFCs have coordinated July–Aug minima, but N_2O is constant from August to January with a peak in May. The Trinidad Head N_2O maximum most likely reflects the influence of the strong local coastal upwelling source, which peaks in spring-summer [*Lueker et al.*, 2003]. The correlation in the seasonal minima of N_2O and the CFCs suggests a common driving mechanism, while the differences between the N_2O and CFC maxima suggest additional influences from surface N_2O sources.

[9] A consistent pattern at all three stations is that the seasonal peak-to-trough amplitudes (normalized by the mean annual atmospheric mixing ratios at each station) decrease in the following order CFC-11 > CFC-113 > CFC-12 ≈ or > N_2O (Table 1, Figure 1). Another feature of the harmonic fits is that for all CFCs, the amplitude of the seasonal cycle is larger in the northern hemisphere than at comparable latitudes in the southern hemisphere. In addition, the CFC minima occur 2–3 months earlier at northern stations, i.e., in summer rather than autumn, as at Cape Grim (Figure 2).

3.2. WACCM Results

[10] WACCM predicts a strong seasonal cycle in the northern polar lower stratosphere, which is caused by the winter downwelling of CFC- and N_2O-depleted air from the middle and upper stratosphere. A similar cycle occurs in the southern polar lower stratosphere, but with about half the amplitude (Figure 3). The stronger northern hemisphere signal is attributed to the rougher surface topography and consequent greater planetary wave-breaking activity in the northern hemisphere, which drives a stronger meridional circulation and weakens the zonal-mean wind circulation (i.e., polar vortex) [*Holton et al.*, 1995; *Appenzeller et al.*, 1996].

[11] Another feature of the stratospheric meridional circulation is that wintertime downwelling is stronger but

Table 1. Normalized Seasonal Cycle Amplitudes CFC-11:CFC-113:CFC-12:N_2O

Station	Observed	WACCM2
Cape Grim (41S)	1.0:0.84:0.48:0.53	No coherent cycles
Trinidad (41N)	1.0:0.78:0.74:0.29	1.0:N/A:0.79:0.73
Mace Head (53N)	1.0:0.89:0.78:0.44	1.0:N/A:0.70:0.61
Canonical $\tau_X/\tau_{F\text{-}11}$ lifetime ratios	1.0: 0.52: 0.45: 0.38	

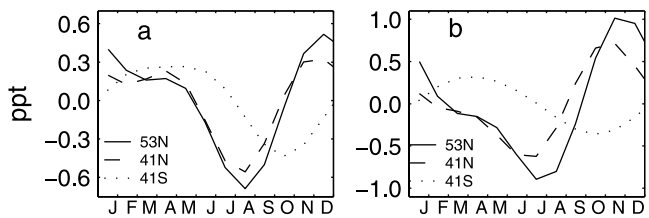

Figure 2. Mace Head, Trinidad Head and Cape Grim seasonal cycles. The Cape Grim data have been shifted 6 months to facilitate the examination of interhemispheric asymmetry. a) CFC-11, b) CFC-12.

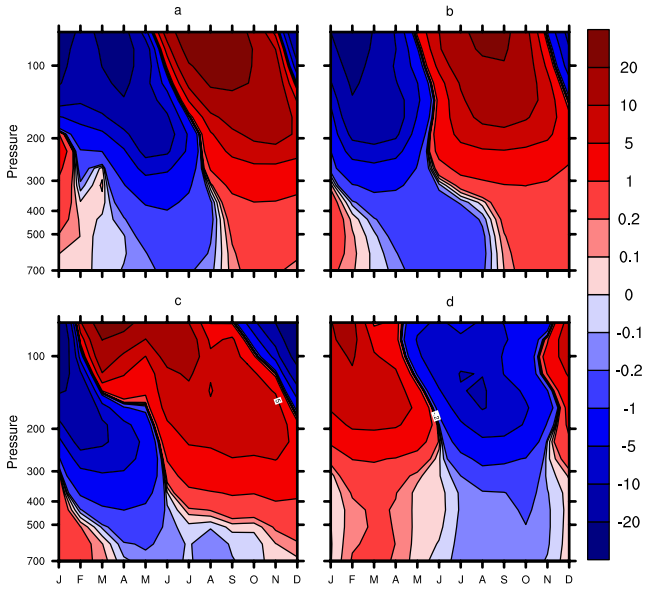

Figure 3. Pressure vs. month cross section of the WACCM N_2O seasonal residual, showing the apparent propagation of the stratospheric signal to the troposphere. Seasonal residuals are calculated by subtracting the annual mean from the monthly mean mixing ratio at each model grid point. Zonal average at a) 70–80N, b) 40–50N, c) 70–80S, d) 40–50S. Contour scale (in ppb) is irregular.

diminishes earlier in the northern hemisphere [*Garcia et al.*, 1992]. In the north, downwelling into the polar region begins in autumn and continues through late winter/early spring. Occasional disturbances facilitate exchange and mixing of northern vortex air with midlatitude air throughout the downwelling season. The final vortex breakup generally occurs around March, at which point N_2O and CFC mixing ratios begin to recover. In contrast, in the southern hemisphere, weaker wave breaking and the strong polar vortex over Antarctica inhibit meridional mixing and downwelling. The polar vortex remains largely isolated throughout the winter, which delays mixing of polar stratospheric air with midlatitudes. The final warming does not occur until late November, allowing N_2O and the CFCs to continue their decline well into late spring [*Waugh et al.*, 1999].

[12] In the WACCM lower stratosphere, the northern polar and mid-latitude N_2O seasonal cycles are at a minimum in February–March and appear to propagate into the troposphere, with ~4 months delay, creating June–July minima in N_2O and CFC mixing ratios at 700 mb (Figures 3a and 3b). The main delay in propagation appears to occur above the tropopause at polar latitudes but below the tropopause at mid-latitudes. The phasing and amplitude of the 700 mb WACCM cycles at northern midlatitudes agree well with CFC-12 surface observations and somewhat less well with CFC-11 surface observations (Figures 4a and 4b). The reasonable agreement between model and observations suggests that the observed summer minima can be plausibly explained as a stratospheric signal.

[13] In the Southern Hemisphere, the WACCM polar seasonal cycle in the lower stratosphere is weaker than in the north and is minimum in December–January, ~1 month later than the observed November minimum. The polar signal appears to propagate into the troposphere with ~5 months delay, resulting in May–June 700 mb N_2O and CFC minima at southern high latitudes (Figure 3c). At southern mid-latitudes, the lower stratospheric seasonal cycle appears unrelated to the polar cycle and only it propagates weakly to the troposphere (Figure 3d).

[14] Because the WACCM southern hemisphere stratospheric seasonal cycle is weaker, its propagation down to the troposphere may be less reliable and more sensitive to uncertainties in model dynamics. However, one might speculate, based on WACCM results in the northern hemisphere and at southern polar latitudes, that autumn minima in the surface seasonal cycles of N_2O and the CFCs would be expected at southern mid-latitudes if the polar cycle were to propagate coherently equatorward and down to the troposphere, with 4–5 months delay. Thus, the later breakup of the southern polar vortex relative to the northern vortex, and hence delayed propagation of the stratospheric downwelling signal, provides a possible explanation for the observed interhemispheric asymmetry noted above in the phasing of the surface CFC cycles. Alternatively, if southern hemisphere seasonal cycles are driven primarily by the combination of north-south surface gradients and seasonal variations in interhemispheric transport, the fixed uniform boundary conditions in WACCM may explain the model's failure to reproduce the observed seasonality at Cape Grim (Figure 4c).

3.3. Stratospheric Lifetimes and Tropospheric Seasonal Amplitudes

[15] The atmospheric lifetimes of the 4 species considered in this study can be ranked from shortest to longest as CFC-11 (45 years) < CFC-113 (85 years) < CFC-12 (100 years) < N_2O (120 years) [*Prather et al.*, 2001]. The normalized seasonal amplitudes observed at tropospheric monitoring stations decrease in exactly this order (Figure 1

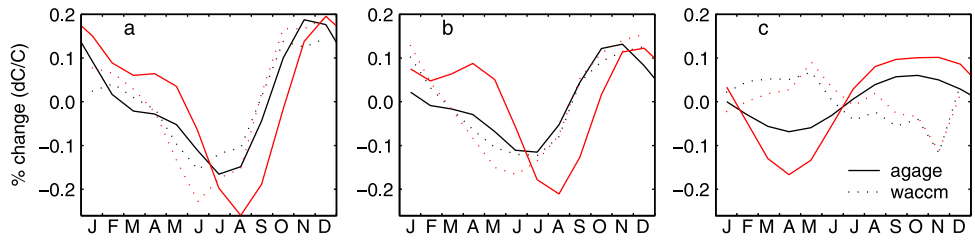

Figure 4. Dotted lines are WACCM 700mb CFC-11 (red) and CFC-12 (black) seasonal cycles. Solid lines are AGAGE observations a) Mace Head, b) Trinidad Head, c) Cape Grim.

and Table 1). A simple explanation for this pattern involves the relative atmospheric lifetimes of the species. A shorter atmospheric lifetime means a sharper depletion with height in the stratosphere due to photochemical destruction. As a result, stratospheric meridional downwelling creates the greatest seasonal variability in CFC-11, the shortest lived of the 4 species.

[16] Stratospheric tracer correlation theory provides a framework for examining the relative lifetimes of long-lived trace gas species whose primary sinks are in the stratosphere [*Plumb and Ko*, 1992; *Volk et al.*, 1997]. According to theory, a cross plot of two such species collapses to a compact curve whose slope near the tropopause reflects the relative atmospheric lifetimes of the two species [*Plumb and Ko*, 1992]. At northern high latitudes, the near-tropopause correlation slopes derived from WACCM N_2O vs. CFC crossplots correspond closely to ratio of the model CFC-11:CFC-12:N_2O (1:0.63:0.52) seasonal amplitudes at 700 mb. This is not unexpected, given that other potential causes of tropospheric seasonality (e.g., interhemispheric gradients) are suppressed in the model design. Notably, however, the model correlation slopes are larger than what one would predict (1:0.45:0.38) based on the inverse ratios of the canonical atmospheric lifetimes of N_2O and the CFCs (Table 1) [*Prather et al.*, 2001].

[17] At the gridpoints corresponding to the midlatitude AGAGE stations, the WACCM 700 mb seasonal amplitudes decrease consistently in the order CFC-11 > CFC-12 > N_2O, but do not agree quantitatively with either the model near-tropopause correlation slopes or the inverse ratios of the canonical atmospheric lifetimes. The model CFC-12:CFC-11 seasonal amplitude ratios do, however, agree reasonably well with AGAGE observations at Trinidad Head and Mace Head, with both model and observations showing ratios of 0.70 to 0.79 (Table 1). In the case of the observations, the discrepancy with canonical lifetime ratios could be caused by an additional tropospheric influence, e.g., winter trapping of air in the surface boundary layer over the North American and Eurasian continents [*Barrie and Hoff*, 1984], although it is unclear that the model would capture this influence.

[18] Modeled and observed N_2O:CFC-11 normalized seasonal amplitude ratios are generally not consistent. Since surface sources may exert strong competing influences on N_2O seasonal cycles, one would not expect the observed amplitude ratios to agree with the results of WACCM. On the other hand, modeled N_2O:CFC ratios provide a possible methodology for correcting observed N_2O cycles for stratospheric influences: CFC seasonal cycles, scaled by modeled N_2O:CFC ratios, or by observed near tropopause N_2O-CFC correlation slopes, could be subtracted from N_2O cycles to correct for the stratospheric influence (C. D. Nevison et al., Southern Ocean ventilation inferred from seasonal cycles of atmospheric N_2O and O_2/N_2 at Cape Grim, Tasmania, submitted to *Tellus*, 2004). However, additional tropospheric influences on observed N_2O:CFC seasonal amplitude ratios must be sorted out before this approach can be applied with confidence.

4. Conclusions

[19] The WACCM model helps lay out the basis for a number of testable predictions about the influence of the stratospheric meridional circulation on the tropospheric seasonal cycles of N_2O and the CFCs. Our analysis of observed N_2O and CFC data at tropospheric monitoring stations suggests that the following predictions are consistent with observations:

[20] 1) Tropospheric seasonal cycles amplitudes increase with decreasing atmospheric lifetime, due to greater sensitivity to stratospheric downwelling.

[21] 2) Summer minima in tropospheric N_2O and CFCs in the Northern Hemisphere, which result from the propagation of springtime lower stratospheric minima down to the troposphere, with ~4 months lag time.

[22] 3) Stronger seasonal cycles in the northern hemisphere vs. the southern hemisphere due to the stronger downwelling branch of the Brewer-Dobson circulation.

[23] 4) Earlier minima in the northern hemisphere due to the earlier break-up of the northern polar vortex.

[24] The body of evidence presented above suggests that the stratosphere influences the seasonal tropospheric cycles of CFCs and N_2O in a coherent manner. This conclusion has important implications for the greenhouse and ozone-modulating gas N_2O, whose global sources are not well understood. However, the following caveats apply: First, our model does a poor job of representing observed seasonal cycles in the Southern Hemisphere. Second, both observed and modeled seasonal amplitude ratios generally do not agree with the inverse ratios of canonical atmospheric lifetimes, as one might predict from stratospheric tracer correlation theory. Our study highlights the need for better understanding of stratosphere-troposphere exchange and of the relative influence of stratospheric and tropospheric dynamics on the tropospheric seasonal cycles of long-lived tracers.

[25] **Acknowledgments.** We thank P. Fraser, C. Harth, S. O'Doherty, L. Porter, R. Prinn, P. Salameh, P. Simmonds, G. Spain and W. Snible for their many contributions to the AGAGE station measurements used in this paper, NASA for their support of the AGAGE program, and Rolando Garcia and 2 anonymous reviewers for helpful comments. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation.

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