

Latitude Variations of Stratospheric 'Trace Gases

(i. C. Toon, J.-F. Blavier, and J.T. Szeto

Jet Propulsion Laboratory, California Institute of Technology

Abstract. We present vertical column abundances of H_2O , N_2O , HNO_3 , NO_2 , O_3 , 111° , 1 ICl , and ClNO_2 determined from solar absorption spectra measured by the JPL MkIV interferometer from the NASA DC-8 aircraft. These observations, taken in 1987 and 1992, covered latitudes ranging from 85°S to 85°N . Although most gases display latitude symmetry, large asymmetries in H_2O , HNO_3 , and O_3 are apparent, which can be ascribed to processes enhanced by the colder Antarctic winter temperatures.

The Observations

The JPL MkIV interferometer, a Fourier Transform Infrared (FTIR) spectrometer designed specifically for atmospheric remote measurements (Leon, 1991), was out of a dozen instruments installed on the NASA DC-8 aircraft to participate in the Airborne Antarctic Ozone Experiment (AAOI) in 1987 and the two Airborne Arctic Stratosphere Experiments (AASI) in 1989 and 1992. For all of these observations the spectrometer was operated in solar absorption mode, i.e. viewing direct sunlight. During these three campaigns, over 50 flights were conducted, the majority over the polar regions. The MkIV results from these individual campaigns have already been published (Toon et al., 1989 & 1992 a,b). In this paper we attempt a synthesis of the results obtained in the 1987 and 1992 campaigns.

The observations from AAOI were all made south of 30°S in September 1987, while those from AASI were all made north of 30°S in January, February and March 1992. The average observation pressure of the Arctic measurements (210 mbar) was close to that from the Antarctic (225 mbar). An important consideration when interpreting these data is that the latitudes we sampled extended poleward with the sun throughout each measurement campaign. In fact, in Jan. 1992 no observations could be made north of 70°N because the sun simply was not up yet. So care must be exercised not to mis-interpret seasonal variations as latitude trends or vice versa. No observations from the 1989 Arctic campaign are presented in this paper, because their rather limited range of sampled latitudes are already covered by the more extensive 1992 observations.

Data Reduction

Each individual spectrum covered the entire $650\text{-}5400 \text{ cm}^{-1}$ spectral region simultaneously at 0.02 cm^{-1} resolution (30 cm optical path difference). Spectra were averaged in groups of 4 to 12 before analysis. Each averaged spectrum therefore represents 3-9 minutes of observation. Averaging reduces the labor of analysis and provides a smaller uncertainty in

the retrieved burdens.

The data were analyzed by the same method as was described by Toon et al. (1992a): A least squares spectral fitting algorithm adjusted the assumed volume mixing ratio (vmr) profile of the gas of interest until the line-by-line calculation best matched the observed spectrum. The precision of the retrieved burdens was then estimated from the quality of the spectral fit. For many of these gases multiple spectral intervals were used to determine the amount of gas (e.g. for HCl five separate lines were used), in which case the value plotted is the weighted mean.

Discussion

1 Hydrofluoric Acid

Figure 1 illustrates the HF burdens measured at various latitudes. The larger HF burdens observed in the north merely reflect the 40% increase in HF which has occurred over the 4½ years between the Sept. 1987 Antarctic observations and the early 1992 Arctic measurements. Since the vmr of HF increases with altitude, upwelling in the tropics reduces its burden, whereas over the polar regions descent enhances its burden. Hence, the poleward increase of HF is a consequence of the stratospheric circulation and is predicted by 2-D photochemical models e.g. Kaye et al (1991).

The large (factor of 2) variability in HF burdens observed at mid- to high-northern latitudes can be attributed to the irregular shape of the Arctic winter vortex. By contrast, the Antarctic winter vortex is much more symmetrical about the pole and so the relationship between HF burden and latitude is more consistent in the south.

Since the abundances of many chemically active, stratospheric gases have strong contrasts across the vortex edge, it is important when illustrating their spatial distributions not to smear their structure by using an inappropriate spatial ordinate. This is especially true in the northern hemisphere where the vortex edge can occur anywhere from 55°N to 85°N. Many workers have therefore used potential vorticity (PV) as a measure of vortex penetration. After examining the measured burdens of long-lived tracers (e.g. N_2O) we found that we obtained tighter correlations with HF than PV. This is not surprising because the HF was measured simultaneously with the other gases and so many internal systematic errors cancel. Moreover, uncertainties in the calculation of PV are completely avoided. We therefore decided to use HF as our measure of vortex penetration and express the HF amount as an "Effective Latitude" defined by the equation

$$\text{HF} = \text{PCOL} \times [1 - 0.88 \times \cos^{3/2}(\text{Eff. Lat})]$$

where the coefficient PCOL (the polar column) was 2.1×10^{15} molec. cm^{-2} in early 1992 and 1.5×10^{15} molec. cm^{-2} in Sept. 1987, consistent with an 8% annual rate of HF increase. These curves, shown superimposed over the appropriate latitudes in Figure 1, gives a reasonable fit to the measured HF column abundance. This expression differs qualitatively from that used by Mankin and Coffey (1983) in that our gradient is zero at the poles. We find this physically

more appealing than having a maximum gradient at the poles, and it also fits our observations better.

So for the remainder of the figures illustrating latitudinal distributions of gases the northern hemisphere data have been plotted versus this effective latitude, which can differ by up to 15° from the actual latitude. The position of the vortex edge, expressed in effective latitude (65°N), is much more consistent than in actual latitude, and therefore facilitates the identification of intra-extra vortex contrasts.

Water Vapor

Figure 2 illustrates the observed latitudinal distribution of H_2O . Since H_2O is highly abundant in the lower atmosphere, changes in aircraft altitude will change its burden. To help minimize such artifacts, we have, therefore divided the H_2O burdens by the aircraft pressure. The resulting mean (pressure weighted) volume mixing ratios above the observed (denoted mva) are more reliable indicators of atmospheric composition than the burdens themselves.

The tropical H_2O abundances were very large due to the fact that the DC-8 aircraft could not fly above 12 km altitude, which was well below the tropical tropopause. The mid-latitude H_2O abundances were also occasionally elevated by tropospheric H_2O . In the polar regions, however, the observations were always performed from above the tropopause and therefore reveal the true behavior of the stratospheric H_2O . Figure 2 reveals a gradual poleward increase of H_2O from 4 to 5 ppmv in the north. Inside the Antarctic vortex, H_2O abundances were much lower, 3.0 to 3.5 ppm, due to freeze-out during the winter when temperatures fell below the frost point.

Nitrous Oxide.

N_2O is a long-lived tracer whose vmr generally decreases with altitude. The stratospheric circulation therefore increases its column abundance in the tropics and reduces it in the polar regions. Like H_2O , the N_2O burdens were divided by the observation pressure to remove artifacts arising from changes in aircraft altitude. As expected, the N_2O vmrs peak in the tropics and are a minimum in the polar regions. The Arctic N_2O abundances are lower than those observed over Antarctica, implying more descent in the north.

Nitric Acid

Figure 2 illustrates that in the northern hemisphere the HNO_3 latitude variation complements that of N_2O . This is not surprising because N_2O is the main source of HNO_3 and merely indicates that the HNO_3 distribution is governed mainly by transport. The one exception to this was the low HNO_3 burdens observed on Jan. 19 1992 at an effective latitude of 44°N . These are due to temporary NAT formation above the aircraft as synoptically forced air moved poleward and upward, an event already described by Toon et al. (1993).

Inside the Antarctic vortex the HNO_3 was depleted to a small fraction of what one might have expected based on the N_2O abundances. In fact, some of the Antarctic HNO_3 burdens were 10 times smaller than those measured at the

same latitude. in the north. This depletion is believed to be caused by freeze-out and sedimentation of HNO_3 (denitrification). This belief is supported by Figure 3 which illustrates the Arctic and Antarctic HNO_3 burdens plotted versus temperature at the 440 K level (about 20 km altitude) above the aircraft. The low latitude observations have been omitted from this figure. The 1987 Antarctic points can be identified by their larger symbol size. The results reveal a sharp decline in HNO_3 as the temperatures fall more than 2.00 K. Although the Arctic temperatures never fell as low as those in the Antarctic, in instances where they overlap there is excellent consistency in the HNO_3 burdens, supporting the conclusion that cold temperatures are solely responsible for the HNO_3 depletion.

Nitrogen Dioxide

in both polar regions NO_2 was highly depleted compared with measurements at other latitudes and seasons. This is believed to be due to both heterogeneous conversion of N_2O_5 to HNO_3 and to the presence of large amounts of ClO which converts any remaining NO_2 into ClNO_2 . In the north we observed (Figure 2) a slight increase in NO_2 burdens between Jan. 1992 ($0.3 \times 10^{15} \text{ molec.cm}^{-2}$) and Feb. 1992 ($0.5 \times 10^{15} \text{ molec.cm}^{-2}$) and then a faster increase into March 1992 ($1.0 \times 10^{15} \text{ molec.cm}^{-2}$). By contrast, the NO_2 burdens inside the Antarctic vortex in Sept. 1987 (0.6×10^{15}) were substantially smaller than the corresponding month (March) in the north, and did not exhibit a significant secular increase. This contrast may be explained by two facts: (i) denitrification inside the Antarctic vortex prevented recovery of NO_2 from photolysis of HNO_3 , and (ii) substantial concentrations of ClO still existed inside the Antarctic vortex in Sept. 1987, whereas by March 1992 ClO was virtually all gone in the north. The large differences in the NO_2 burdens at 30°S and 25°S arise simply from the fact that the former was a sunset measurement whereas the latter was a sunrise.

Chlorine Nitrate

In the Antarctic the characteristic "collar" of high ClNO_2 columns can be seen in Figure 2. This is due to mixing of ClO -rich air inside the vortex with NO_2 -rich air from outside the vortex. In the north the "collar" was abnormally small in Jan. 1992 due to increased heterogeneous processing of ClNO_2 , which resulted from the increased aerosol loading and the unusually cold temperatures on days when we made observations at the vortex edge (normally temperatures are only cold enough for PSC processing deep inside the arctic vortex). As the solar insolation increased during Feb. 1992, and NO_2 abundances rose, the ClO inside the vortex rapidly became converted into ClNO_2 , first at the vortex edge and then deeper inside. By March the largest ClNO_2 columns were to be found well inside the vortex, where ClNO_2 became the main reservoir of inorganic chlorine, exceeding HCl by a factor of 2. Inside the Arctic vortex, the ClNO_2 burdens increased by a factor 5 between Jan. and Mar. 1992. Note that no such recovery of ClNO_2 was observed in the south, presumably insufficient HNO_3 remained at the appropriate altitudes.

Hydrochloric Acid

In the absence of heterogeneous processes one would expect a minimum in HCl at the equator and maxima at the poles. What we actually observed (Figure 2) was a widespread depletion inside the Antarctic vortex, due to heterogeneous conversion of HCl and ClNO₂ into ClO. In the north, where the PSC processing events were more sporadic and less thorough, we observed large variations of HCl even inside the vortex. In freshly processed air (e.g. Jan. 1992) the HCl depletions approached those observed over Antarctica. However, in the Arctic the losses of HCl were not as ubiquitous as was observed over Antarctica.

In February and March 1992, the recovery of HCl around 60°N is evident, however, at higher latitudes the recovery of HCl was much slower. The appearance that at high Arctic latitudes HCl was never as low as over Antarctica is erroneous; it is probably an artifact of our inability to make solar observations deep inside the vortex in January, when temperatures were at their coldest.

Ozone

Figure 2 illustrates tropical O₃ burdens of around 6 x 10¹⁸ molec.cm⁻² (225 Dobson Units). In the northern hemisphere a substantial poleward increase of O₃ was observed, as might be expected from the stratospheric circulation.

In the southern hemisphere the O₃ column decreased south of 60°S, due to destruction by Cl atoms. In fact, by comparing the early and late Sept. 1987 symbols, the O₃ column can be seen to have decreased during Sept. 1987.

Interestingly, the 1992 Arctic O₃ burdens fall into two branches, with the larger values observed over Alaska and Canada (up to 400 DU) where the lower stratospheric temperatures were warm, and the smaller values over Europe where it was colder. While the proximity of the Aleutian anticyclone (and the descent within it) frequently give rise to large ozone burdens and warm temperatures over Alaska and Canada, the low ozone burdens over Europe in 1992 were unprecedented. It seems unlikely that the cause was solely chemical (either catalytic destruction of O₃ or heterogeneous conversion of CO₂ to HF) because the air we sampled over Alaska was usually re-sampled over Europe a few days later (with much lower O₃/HF ratios). It is more likely that the low ozone over Europe was mainly due to a persistent pattern of lower stratospheric uplift which reduced the O₃ burden more than that of HF simply because the HF resides at a higher effective altitude than O₃.

Summary

Column abundances of H₂O, N₂O, HNO₃, NO₂, O₃, HF, HCl, and ClNO₂ were determined from solar absorption spectra measured by the JPL MkIV interferometer from the NASA DC-8 aircraft during the 1987 AAOJ and 1992 AASIS2 campaigns. These observations, taken on 26 different flights, covered latitudes ranging from 85°S to 85°N. The asymmetry in the latitude distribution of HF is consistent with a 8%/year secular increase during the 4½ year interval between the southern and northern measure-

ments. The latitude distribution of N_2O shows slightly less in the north, which is consistent with somewhat more subsidence in the north. Asymmetries in the latitude distributions H_2O , HNO_3 , and O_3 are much larger than can be attributed to transport effects, and can only be the result of chemical and physical processes enhanced by the colder Antarctic winter temperatures.

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References

- Kaye, J. A., A.R. Douglass, C.H. Jackman, and R.S. Stolarski, Two-Dimensional Model Calculation of Fluorine-Containing Reservoir Species in the Stratosphere, *J. Geophys. Res.*, 96, 12,865-12,881, 1991.
- Mankin, W. G., and M.T. Coffey, Latitudinal Distributions and Temporal Changes of Stratospheric HCl and HF, *J. Geophys. Res.*, 88, 10,776-10,784, 1983.
- Teon, G. C., The JPL MkIV Interferometer, *Optics and Photonics News*, 2, 19-2.1, 1991.
- Teon, G. C., C.B. Farmer, L.L. Lowes, P.W. Schaper, J.-F. Blavier, and R.H. Norton, Infrared Aircraft Measurements of the Stratospheric Composition Over Antarctica During September 1987, *J. Geophys. Res.*, 94, 16,571-16,596, 1989.
- Teon, G. C., C.B. Farmer, P.W. Schaper, L.L. Lowes, and R.H. Norton, Composition Measurements of the 1989 Arctic Winter Stratosphere by Airborne Infrared Solar Absorption Spectroscopy, *J. Geophys. Res.*, 97, 7,939-7,961, 1992a.
- Toon, G. C., J.-F. Blavier, J.N. Solario, and J.T. Szeto, Airborne Observations of the 1992 Arctic Winter Stratosphere by FTIR Solar Absorption Spectroscopy, *SPH Proceedings*, 1715, 457-467, 1992b.
- Toon, O., B. Browell, B. Gary, L.L. Lait, J.J. Livingston, P. Newman, R. Pueschel, P. Russell, M. Schoeberl, (L.L. Teon, W. Traub, L.L. J. Valero, H. Selkirk, J. Jordan, Heterogeneous Reaction Probabilities, Solubilities, and the Physical State of Cold Volcanic Aerosols, *Science*, 261, 1136-1140

G.C. Teon, J.-F. Blavier, and J. Szeto, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA, 91109
(toon@mark4sun.jpl.nasa.gov)

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Figure 1. H^+ burdens plotted vs. observation latitude. In this figure and all which follow, a different symbol has been adopted for each observation day number (e.g. 43 = Feb. 12). See text for explanation of 'curves,

Figure 2. Abundances of N_2O , HNO_3 , H_2O , NO_2 , ClNO_2 , HCl , and O_3 plotted vs. Latitude (effective in North, actual in South).

Figure 3. HNO_3 burdens plotted vs. the 440 K temperature.

Fig. 1

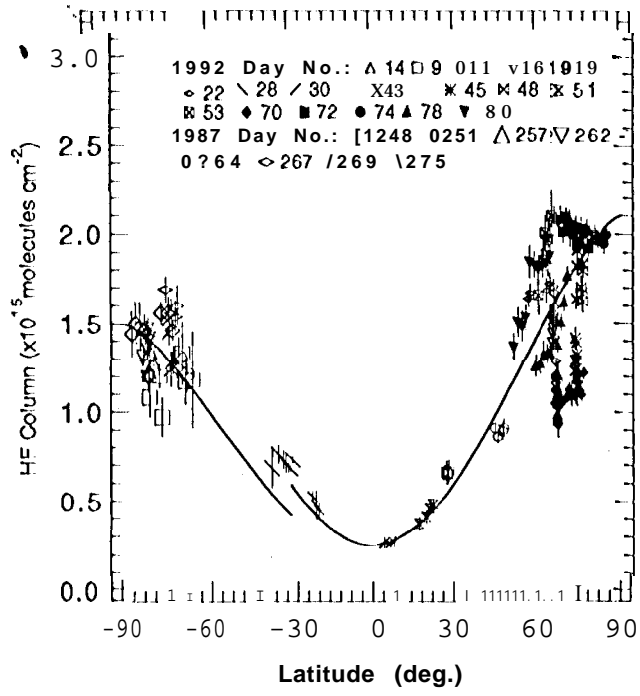


Fig. 2

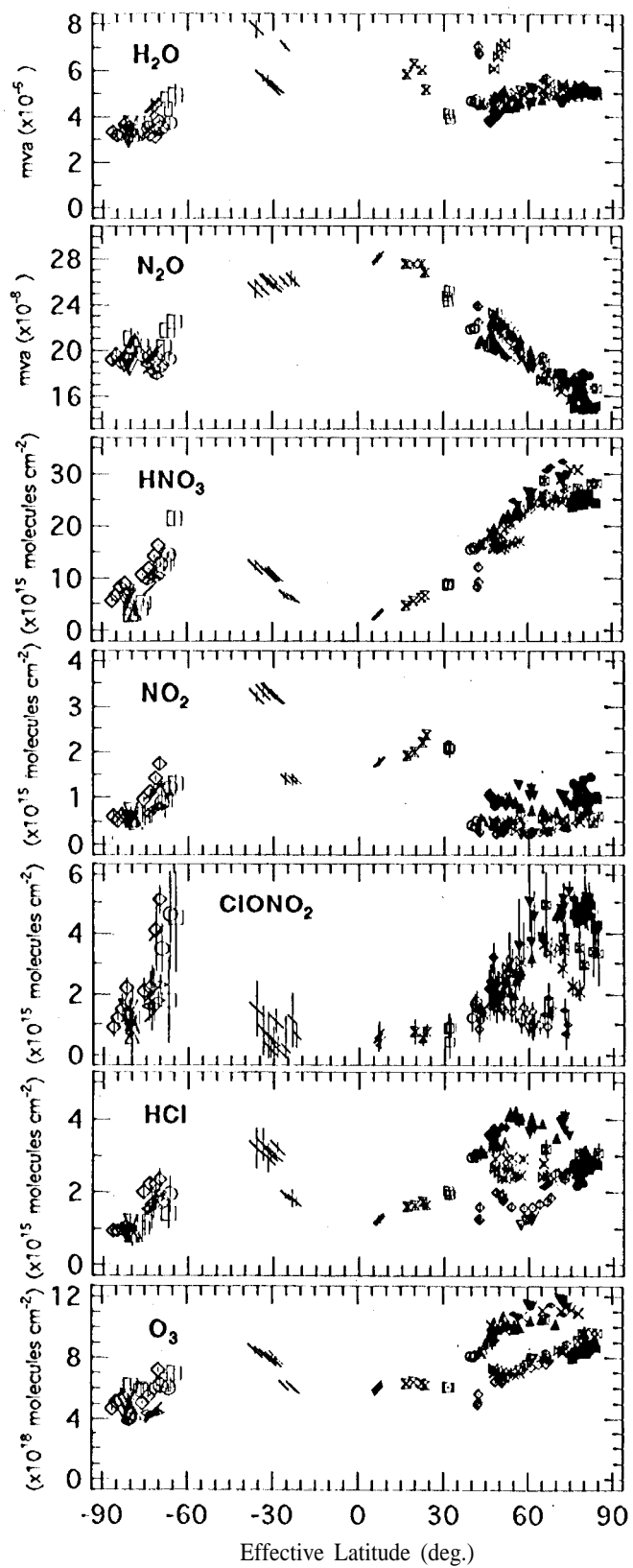


Fig. 3

