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Intercomparison of ATMOS, SAGE II, and ER-2 observations in Arctic vortex and extra-vortex air masses during spring 1993

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Abstract. We have compared measured abundances of NO_y, O_3, H_2O, CH_4, HCl, and N_2O from ATMOS and aerosol from SAGE II from inside and outside the Arctic vortex with *in situ* observations from the SPADE aircraft campaign in April/May 1993. When the distinction between vortex and extra-vortex air is taken into account, SPADE measurements of NO_y, O_3, H_2O, CH_4, HCl, and aerosol abundances, correlated with [N_2O], demonstrate excellent agreement with ATMOS and SAGE II data. Observations of low [HCl] and high [$ClNO_3$] inside the vortex by ATMOS and low [HCl] in vortex fragments by ALIAS suggest that vortex-influenced air masses maintained unusually high levels of [$ClNO_3$] throughout spring 1993.

Introduction

As part of the ATLAS-2 (AT-2) space shuttle mission of 8-16 April 1993, ATMOS, a high resolution Fourier transform spectrometer, measured vertical profiles of a number of trace species inside and outside the Arctic vortex. The SAGE II satellite instrument measured aerosol extinction profiles inside and outside the vortex two weeks earlier. As the lower stratospheric vortex broke up in late April [*Manney et al.*, 1994a], vortex air was transported to lower latitudes, where it was encountered during the SPADE ER-2 aircraft campaign in the five weeks following the AT-2 mission. A large fraction of the air sampled during SPADE showed tracer characteristics indicating a strong influence by the vortex [*Waugh et al.*, 1997]. Distributions of species in the majority of these air masses were thus not representative of midlatitude air, and data intercomparisons must account for the photochemical histories of the air masses in which the measurements were made.

One method for identifying recent air mass histories relies on back-trajectory or contour-advection calculations [*Newman et al.*, 1996; *Waugh et al.*, 1997]. An alternative approach entails sorting data by differences in correlations of long-lived tracers [*Waugh et al.*, 1997; *Michelsen et al.*, 1998]. In spring 1993, [NO_y], [O_3], [H_2O], [CH_4], and [HCl] were lower, relative to [N_2O], and aerosol abundances were higher, inside the vortex than outside ([χ] ≡volume mixing ratio of species χ). We have identified the SPADE data most consistent with midlatitude correlations of long-lived tracers and compared these data with extra-vortex observations from ATMOS and SAGE II. We have also selected the SPADE data most strongly influenced by the vortex for comparison with ATMOS and SAGE II vortex measurements. The remote and *in situ* data sets demonstrate excellent agreement when the distinction between vortex and extra-vortex air masses is taken into account.

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Remote and *in situ* measurements

During AT-2 ATMOS measured mixing ratios (with estimated accuracy) of O_3 (6%), N_2O (5%), H_2O (6%), CH_4 (5%), NO_y (15%), $ClNO_3$ (20%), and HCl (5%) at sunrise at latitudes of 60-70°N and altitudes of 16-80 km [*Abrams et al.*, 1996]. SAGE II similarly acquired vertical profiles of visible aerosol extinction from which surface area densities (SA) were derived [*Thomason et al.*, 1997]. *In situ* measurements of species abundances made during SPADE included those of O_3 (3%) from a dual-channel UV photometer [*Proffitt and McLaughlin*, 1983], N_2O (3-5%), CH_4 (10%), and HCl (5-7%) from a tunable diode laser (TDL) spectrometer [*Webster et al.*, 1994a], N_2O (10%) from a second TDL system [*Loewenstein et al.*, 1990], NO_y (10%) from a chemiluminescence instrument [*Fahey et al.*, 1990], H_2O (5-10%) from two Lyman-α hygrometers [*Kelly et al.*, 1989; *Hintsa et al.*, 1994], and aerosols (35%) from two instruments that detect laser light scattered from particles [*Brock et al.*, 1993]. These measurements were made during 11 flights at altitudes of 15-20 km and latitudes of 34-45°N (with two excursions south to 15°N and two north to 60°N). We have used SPADE stratospheric data from 34-45°N, including flights of 23, 26, 30 April and 1, 3, 6, 7, 11, 12, 14, 18 May 1993.

N_2O is a convenient and commonly used tracer against which to correlate other long-lived species. During SPADE, experimental uncertainties were significant for measurements of [N_2O] made by both TDL instruments, ATLAS and ALIAS. For ALIAS (1σ) absolute accuracy is estimated to have been ~3-5% and precision error ~1-5%. ATLAS demonstrated 0.5% precision and a nominal accuracy of 5%, but experienced technical difficulties that limited the accuracy and contributed a positive bias when temperature was changing rapidly during flight, particularly when the instrument was exposed to low temperatures (tropopause temperatures were as low as 201 K during SPADE). To avoid ambiguities in distinguishing vortex from extra-vortex air associated with these instrumental uncertainties, we sorted the SPADE data based on tracer correlations that are independent of [N_2O]. As described below, using [NO_y], [O_3], [H_2O], and [CH_4] observations, measurements from

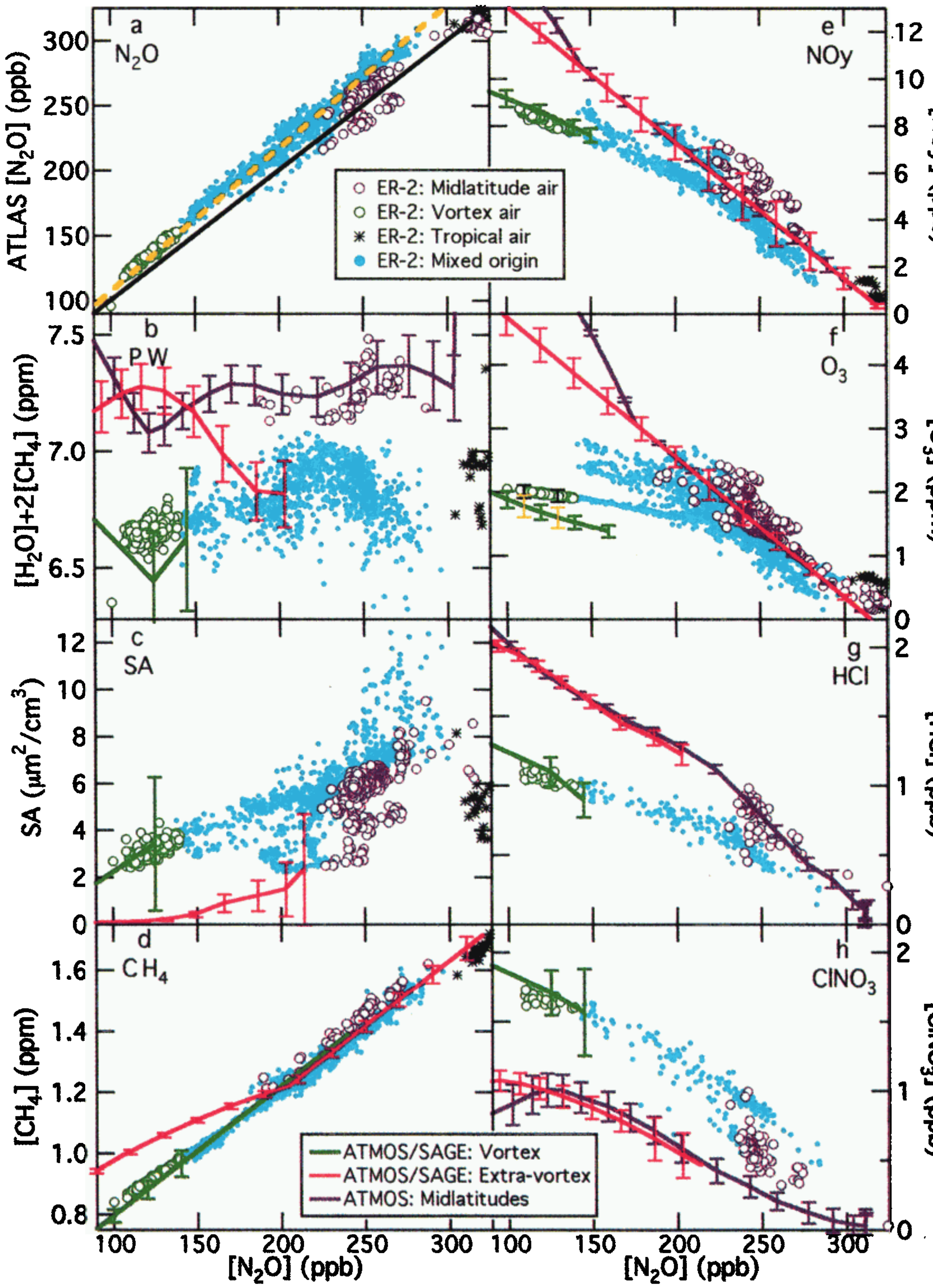

Figure 1. ATLAS $[N_2O]$ is plotted against ALIAS $[N_2O]$ (a), and correlations from ATMOS, SAGE II, and SPADE are shown relative to $[N_2O]$ for $[H_2O]+2[CH_4]$ (b), SA (c), $[CH_4]$ (d), $[NO_y]$ (e), $[O_3]$ (f), [HCl] (g), and $[ClNO_3]$ (h). Lines with 1σ error bars show data from ATMOS/AT-2 (SAGE II for SA) for vortex and high latitude extra-vortex regions and data from ATMOS/AT-3 for midlatitudes. Symbols represent SPADE observations from nominal midlatitude, tropical (from 3 May, 15-19°N), and vortex-influenced air masses.

midlatitude air masses were selected from the 15,347 (10 s) data points acquired in the stratosphere between 34 and 45°N. The remainder appears to have been influenced by vortex and possibly tropical air.

Once sorted, the data were averaged by flight and category (midlatitude or vortex-influenced) in groups of 5-10 points within 20 ppb O_3 bins. Averaging the sorted data reduces the random error for the ALIAS $[N_2O]$ measurements to <2% and yields a more precise and accurate measure of $[N_2O]$ (than provided by the raw data from either ALIAS or ATLAS) against which to correlate other species. Fig. 1a shows ATLAS versus ALIAS $[N_2O]$. Many of the points lie close to the dashed line

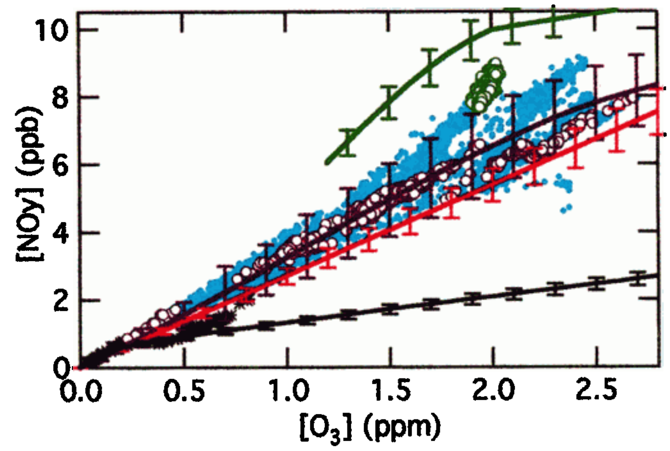

Figure 2. Measurements of $[NO_y]$ are shown relative to $[O_3]$ for ATMOS/AT-2 and -3 and SPADE. Lines with 1 σ error bars show data from ATMOS; symbols represent observations made during SPADE, color-coded as in Fig. 1.

(slope=1.1), showing that the ALIAS measurements tend to be systematically lower than those of ATLAS by ~10% for this data set. The discrepancies between the instruments appear correlated with the magnitude, duration, and frequency of temperature and pressure changes experienced by the ER-2 during flight, suggesting that the differences may in part result from the temperature-dependent bias in the ATLAS data set.

Air masses were identified as midlatitude air if potential water (PW≡$[H_2O]$+2$[CH_4]$) exceeded 7.1 ppm (purple circles, Fig. 1b). In the lower stratosphere ($[N_2O]$>100 ppb) PW is expected to be conserved outside the tropics and in the absence of precipitation of polar stratospheric cloud (PSC) particles, as shown by the ATMOS midlatitude case from the ATLAS-3 (AT-3) mission (4-12 Nov 1994) in Fig. 1b. ATMOS/AT-2 measurements show that PW was ~0.7 ppm lower inside the vortex than outside in spring 1993. The magnitude of this deficit in PW is comparable to other observations of Arctic vortex dehydration [e.g., *Fahey et al.*, 1990]. In Jan/Feb 1993, vortex temperatures were low enough for Type II (water ice) PSC formation [*Manney et al.*, 1994b], and removal of water vapor may have occurred by PSC sedimentation. The deficit in PW may alternatively be explained by descent of air from the mesosphere, where H_2O is lost via photolysis. In either case, the ATMOS vortex observations are consistent with SPADE $[CH_4]$ and $[H_2O]$ measurements for air that has been previously determined to have originated in the vortex [*Newman et al.*, 1996; *Waugh et al.*, 1997]. (These data are not consistent with simultaneous measurements of $[H_2O]$ made by the Harvard instrument, for which PW>7.4 ppm for vortex air.)

In addition to excluding dehydrated vortex air via this classification for midlatitude air masses, selecting measurements for which PW exceeds 7.1 ppm excludes tropical air since $[H_2O]$ was in the negative phase of its seasonal cycle at altitudes accessed by the ER-2 [*Hintsa et al.*, 1994]. In the tropics the average value of PW measured is ~0.5 ppm lower than the nominal midlatitude value (asterisks, Fig. 1b).

Several flights were missing measurements of $[CH_4]$ or $[H_2O]$, making it impossible to sort these data based on PW. Fig. 2 shows that ATMOS data demonstrate distinct correlations between $[NO_y]$ and $[O_3]$ inside and outside the vortex [*Michelsen et al.*, 1998]. A midlatitude correlation derived from ATMOS/AT-3 lies in between the vortex and extra-vortex curves and is remarkably consistent with the SPADE observations identified as midlatitude air based on PW (purple circles). The separation between the correlation for mid- and high latitudes may result from mixing of high latitude air with air from the tropics. Since the tropical correlation (black line and asterisks) is separated significantly from the extra-tropical correlations, even a small amount of tropical air will lead to a modification of the correlation. If $[CH_4]$ or $[H_2O]$ were not available, midlatitude air was identified by the midlatitude correlation of $[NO_y]$ with $[O_3]$ established from other flights. If $[NO_y]$ was also unavailable, data were likewise sorted by the midlatitude $[CO_2]$:$[O_3]$ correlation.

Approximately 37% of the data were identified as nominal midlatitude air. If measurements missing PW and $[NO_y]$ (~30% of the data set) are excluded from the analysis, nominal midlatitude air accounts for 26% of the remainder. Excluding flights from 11 and 12 May, only 14% of the SPADE data set is classified as midlatitude air. The results of the sorting and averaging procedure are shown in all panels of Fig. 1. The ER-2 data are plotted relative to ATLAS $[N_2O]$ when ALIAS data were unavailable and against ALIAS $[N_2O]$ otherwise.

Results and discussion

In order to demonstrate the consistency among species and between data sets, we have highlighted (green circles) the SPADE observations that fall closest to the ATMOS $[NO_y]$:$[O_3]$ vortex correlation and thus have the most vortex character. In each panel of Fig. 1 these ER-2 "vortex" data are in quantitative agreement with the ATMOS vortex correlation (green lines), and the ER-2 nominal midlatitude data (purple circles) are in good agreement with the ATMOS mid- (purple lines) and high latitude (pink lines) correlations. The additional scatter for the SPADE mixed air masses (blue dots) results from mixtures of air masses with different tracer characteristics. Fig. 1c demonstrates similarly good agreement between SA from SAGE II and SPADE observations. Mean values of SAGE II SA are plotted against those of ATMOS $[N_2O]$ for measurements made inside and outside the vortex. The lower stratospheric vortex appeared to remain well intact during the two weeks between the SAGE II and ATMOS observations [*Santee et al.*, 1996], and the exchange of air between the vortex and extra-vortex regions was thus limited. Furthermore, variations in the mean vortex temperature, which can lead to changes in aerosol characteristics, were minimal over this time period [*Manney et al.*, 1994b]. The distinction between the vortex and extra-vortex correlations can be attributed to descent of air, followed by particle regeneration, in the vortex. The amount of water required to account for the particle abundance observed in the vortex could be responsible for only ~2% of the dehydration shown in Fig. 1b and thus cannot account for the PW deficit.

The separation between the vortex and extra-vortex $[CH_4]$:$[N_2O]$ correlations (Fig. 1d) is caused by photochemical modification of the tracer characteristics at high altitudes followed by descent of this air within the vortex and mixing with extra-vortex air in the spring [*Michelsen et al.*, 1998]. This process is similarly responsible for the distinct vortex and extra-vortex correlations observed for $[NO_y]$:$[N_2O]$ (Fig. 1e); the apparent 25-30% loss of NO_y inside the vortex is explained by descent of air from altitudes (>30 km) at which NO_y is rapidly photochemically lost. (If the PW deficit had resulted from PSC sedimentation, these particles must have contained little nitrate.) High altitude photochemistry and descent can partially account for differences between vortex and extra-vortex $[O_3]$:$[N_2O]$ (Fig. 1f); additional differences are caused by photochemical ozone loss in the lower vortex during the winter [e.g., *Manney et al.*, 1994b]. These processes do not explain the discrepancy between the ATMOS and ER-2 vortex observations of $[O_3]$ for $[N_2O]$>100 ppb. Accounting for total (systematic and random) error (5% for SPADE and 10% for ATMOS, black and yellow bars) barely brings the measurements into agreement for $[N_2O]$<120 ppb. Nevertheless, distinctions between the vortex and extra-vortex correlations collectively demonstrate the extent of vortex dehydration, particle regeneration following descent and sedimentation, methane oxidation and NO_y destruction at high altitudes followed by descent, and ozone loss by a combination of photochemistry and descent.

The distinction between vortex and extra-vortex air masses is also apparent for HCl (Fig. 1g) and $ClNO_3$ (Fig. 1h). These species abundances had been influenced by chemistry occurring in the vortex during the winter and spring. In the initial recovery period following PSC activation of these species, Cl_y had been partitioned predominantly into $ClNO_3$ by the reaction of ClO with NO_2 [*Santee et al.*, 1996]. In mid-April $[ClNO_3]$ was still higher than [HCl] by as much as 75% below 20 km inside the vortex; outside the vortex [HCl] exceeded $[ClNO_3]$.

As with the long-lived tracers described above, the ER-2 [HCl] vortex and midlatitude data are consistent with the corresponding ATMOS observations. ATMOS $[ClNO_3]$ observations demonstrate similarly good agreement with values of $[ClNO_3]$ inferred from the ER-2 measurements of [HCl], $[N_2O]$, and $[CH_4]$ (i.e., $[ClNO_3]\approx[Cl_y]$-[HCl], where $[Cl_y]$ was derived from $[N_2O]$ and $[CH_4]$ via the relation given by *Woodbridge et al.* [1995]). These results imply that vortex air maintained high levels of $[ClNO_3]$ and low levels of [HCl] throughout late April and early May when it was encountered by the ER-2.

During SPADE, the abundance of HCl measured at midlatitudes was frequently a factor of two lower than expected based on the results of models assuming photochemical steady state for local conditions encountered by the ER-2 [*Salawitch et al.*, 1994; *Webster et al.*, 1994b]. In addition, *in situ* measurements of $[ClNO_3]$ were not available during SPADE, and values of $[ClNO_3]$ inferred from measured [ClO], [NO], and $[O_3]$ are a factor of ~4 too low to account for the remaining Cl_y [*Stimpfle et al.*, 1994]. The data shown in Figs. 1g and h suggest that $[ClNO_3]$ comprised a significantly higher fraction of Cl_y than predicted or inferred. The inability of models to reconcile these results indicates large uncertainties in the current understanding of Cl_y and NO_y chemistry for elevated aerosol levels.

Recent remote and *in situ* observations of [HCl] and $[ClNO_3]$ yield Cl_y partitioning expected for extra-vortex/midlatitude air ([HCl]>$[ClNO_3]$), a closed Cl_y budget, and agreement with models assuming photochemical steady state [*Michelsen et al.*, 1996; *Sen et al.*, submitted]. These data were obtained at low aerosol levels and/or high temperatures; the results may thus have little bearing on understanding the chlorine chemistry during SPADE, for which temperatures were frequently below 210 K, aerosol loading was 3-8 times non-volcanic values, and much of the air had originated in the vortex.

Conclusions

Measurements of $[NO_y]$, $[O_3]$, $[H_2O]$, $[CH_4]$, [HCl], SA, and $[N_2O]$ made during SPADE are quantitatively consistent with ATMOS and SAGE II observations from inside and outside the Arctic vortex in spring 1993. These observations confirm that $[NO_y]$, $[O_3]$, $[H_2O]$, $[CH_4]$, and [HCl] were lower, and SA was higher (relative to $[N_2O]$), in vortex air masses than in midlatitude air masses. The results also suggest that $[ClNO_3]$ in vortex-influenced air was higher than predicted by photochemical models for conditions encountered in spring 1993.

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