ATMOS/ATLAS-3 Measurements of Stratospheric Chlorine and Reactive Nitrogen Partitioning Inside and Outside the November 1994 Antarctic Vortex

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Abstract. Partitioning between HCl and $ClONO_2$ and among the main components of the reactive nitrogen family (NO, NO_2, HNO_3, $ClONO_2$, N_2O_5, and HO_2NO_2) has been studied inside and outside the Antarctic stratospheric vortex based on ATMOS profiles measured at sunrise during the 3-12 November 1994 ATLAS 3 shuttle mission. Elevated lower stratospheric HCl mixing ratios with a peak of ~2.9 ppbv, 10^{-9} parts per volume) near 500 K potential temperature (~19 km), were measured inside the vortex. Maximum $ClONO_2$ mixing ratios of ~1.2, ~1.4, and ~0.9 ppbv near 700 K (~25 km) were measured inside, at the edge, and outside the vortex, respectively. Model calculations reproduce the higher levels of HCl and NO_x ($NO+NO_2$) inside the lower stratospheric vortex (both driven by low O_3). The high HCl at low O_3 results from chemical production of HCl via the reaction of enhanced Cl with CH_4, limited production of $ClONO_2$, and the descent of inorganic chlorine from higher altitudes.

Introduction

The critical role of active chlorine in the winter and springtime catalytic destruction of stratospheric O_3 in polar regions has been well established through ground-, aircraft-, and satellite-based measurements [cf. World Meteorological

Organization (WMO), 1995, Chapt. 3]. Reactive nitrogen is also important- in polar O_3 losses, especially in the Antarctic where it is irreversibly removed over large portions of the vortex through the sedimentation of polar stratospheric cloud particles [Fahey et. al., 1990], Low levels of reactive nitrogen inhibit the formation of $C\ell ONO_2$ when sunlight returns in spring, thereby allowing active chlorine to persist and catalytic O_3 destruction *to* continue inside the vortex [e.g. , Brune et al., 1991].

A primary objective of the Atmospheric Laboratory for Applications and Science (ATLAS)-3 shuttle mission from 3-12 November 1994, was to obtain sets of volume mixing ratio (VMR) profiles at high southern latitudes during the photochemical recovery phase of the Antarctic ozone hole. We report here Atmospheric Trace MOlecule Spectroscopy (ATMOS) observations of inorganic chlorine and reactive nitrogen species inside and outside the vortex. A photochemical model was used to interpret the measurements.

Observations and Spectral Analysis

The ATMOS/ATLAS -3 Antarctic measurements were recorded during sunrises between 64.5°s and 72.4°S latitude [Gunson et al., 1996]. The measurements reported here were obtained by combining spatially and temporally coincident observations with filters 3 (1580-3420 cm^{-1}) and 12 (625-1400 cm^{-1}). The 6 principal components of the reactive nitrogen (NO_y) family, NO, NO_2, HNO_3, $C\ell ONO_2$, N_2O_5, and HO_2NO_2, plus $HC\ell$ and N_2O were measured.

Diurnal corrections were included in the NO and NO_2 retrievals presented here [Newchurch et al., 1996]. Random error bars, which vary with altitude and species, are shown in the plots. Total systematic errors were 5% ($HC\ell$), 20% ($C\ell ONO_2$), NO (5%), NO_2 (6%), and N_2O_5 (15%) [Gunson et. al., 1996].

Results

Figure 1 presents an overview of the Antarctic measurements of [HCl] (top) and [$ClONO_2$] (bottom) (where [x] denotes the species VMR) plotted versus longitude and potential temperature (θ). Longitude is a useful coordinate because the measurements were recorded over a narrow latitude range, and the vortex remained at similar longitudes throughout the mission (--240° to 315°E) [Manney et al., 1996]. The vortex is apparent in the [N_2O] contours overlayed in both panels.

Above 900 K, no [HCl] variations with longitude are apparent.. Zonal mean [HCl] decreased from 3.35±0.42 ppbv at 2000 K (-50 km) to 3.09±0.17 ppbvat 1550 K (-44 km), and 2.73±0.09 ppbv at 1000 K (-34 km). Error limits denote standard deviations of the measurements. Below 800 K (-28 km), [HCl] in the vortex was systematically higher than outside. A shallow minimum in [HCl] occurred inside the vortex at 725 K (-26 km) followed by a sharp rise to a maximum of -2.9 ppbv at 500 K (--19 km). [HCl] remained elevated inside the vortex at least down to 400 K (--15 km).

Peak [$ClONO_2$] occurred at -700 K (25 km) at all longitudes. Maximum values, ‘1.4 ppbv, were measured at the vortex edge, as compared to ‘1.2 ppbv inside and 0.9 ppbv outside the vortex. The [$ClONO_2$] decline below its peak was much sharper inside the vortex than outside. Inside and outside VMRS were equal at 550 K (-21 km); below 450 K (-17 km), [$ClONO_2$] in the vortex interior was <0.1 ppbv.

Table 1 lists mean [HCl] and [$ClONO_2$] profiles measured in the interior and outside the vortex. The classifications are based on scaled potential vorticity (sPV) derived with -PV in the southern hemisphere so that values increase toward the vortex center. The criteria for classification are reported by Rinsland et al. [1996]. Gradients in sPV suggest that the vortex extended down to at least 375 K [Abrams et al. 1996].

The ATMOS/ATLAS-3 lower stratospheric measurements inside the vortex contrast

3.35±0.42 ppbv at 2000 K, where all other components are minor contributors [Zander et al., 1996], demonstrates the consistency of the ATMOS measurements. The minimum inside-to-outside the vortex O_3 ratio 0.16 occurred at 395 K (-15 km) where $[O_3]$=89±29 ppbv inside the vortex.

Fig. 3 illustrates measurements of NO, NO_2, HNO_3, and N_2O_5. Measurements obtained outside the vortex (upper panel) show that HNO_3 and NO_x ($NO+NO_2$) were the most abundant NO_y components in the middle and lower stratosphere. The ratio $[HNO_3]/[NO_y]$ increases at lower θ, reaching 85% at 400 K (-15 km). In the vortex interior (lower panel) NO_x and HNO_3 each account for -50% of NO_y below 700 K (-25 km).

A photochemical model [Salawitch et al., 1994] was used to compute the partitioning of inorganic chlorine and reactive nitrogen for the sets of ATMOS measurements in Figs. 2 and 3. The calculations were constrained by the ATMOS profiles of temperature, pressure, $[O_3]$, $[H_2O]$, $[CH_4]$, $[C_2H_6]$, $[NO_y]$, [CO], and total inorganic chlorine (Cly) estimated from the sum of $[ClONO_2]$ and [HCl]. Aerosol surface area profiles were taken from correlative SAGE 11 measurements (G. K. Yue and L. W. Thomason, private communication, 1995).

Two sets of model calculations were performed. In the first, reaction rates and absorption cross sections from DeMore et al. [1994] were assumed. In the second, the data of DeMore et al. [1994] were again assumed except for modifications deduced from reanalysis of laboratory reaction rate data and comparisons between model calculations and ATMOS arctic, northern midlatitude, and tropical inorganic chlorine measurements [Michelsen et al., 1996]. For the present study, the most important change is the inference of a branching ratio of 7% for the ClO+OH reaction, leading to production of HCl.

The model calculations in Figs. 2 and 3 reproduce the main features of the measurements, highlighted by elevated [HCl] and $[NO_x]/[NO_y]$, both driven by low

$[O_3]$, and very low $[N_2O_5]$ at all altitudes inside the vortex. The low $[N_2O_5]$ inside relative to outside the vortex is a consequence of the difference in the lengths of the night. For the air sampled inside the vortex, the stratospheric solar zenith angle never drops below 92°, preventing the nighttime buildup of $[N_2O_5]$. The outside-the-vortex occultations were recorded -40 equatorward, where the night was ~4 hours 1 ong, allowing $[N_2O_5]$ to accumulate rapidly in darkness.

The inorganic chlorine measurements inside the vortex arc better reproduced by the modified model calculations (labeled revised) than by the standard run (labeled JPL94) based on the data of DeMore et al. [1994]. The improvements, which are largest near 700 K (-25 km), are consistent with a more extensive analysis of ATMOS HCl and $ClONO_2$ measurements [Michelsen et al., 1996]. The differences between the two sets of calculations for the outside-the-vortex case are smaller, and therefore, it is not possible to distinguish between the two sets of model results given the measurement uncertainties.

The comparisons in Fig. 3 show several systematic discrepancies: (1) the $[NO_2]/[NO]$ ratio in the lower stratosphere was underpredicted by up to 50% both inside and outside the vortex, (2) $[N_2O_5]$ was overpredicted outside the vortex above 800 K, and (3) the $[NO_x]/[NO_y]$ ratio was underpredicted in the lower stratosphere both inside and outside the vortex. These differences are being investigated in the context of the larger set of ATMOS measurements.

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Table 1. ATMOS Antarctic HCl and $ClONO_2$ VMRS (ppbv) versus θ Inside and Outside the Vortex[a]

	[HCl]		[$ClONO_2$]	
θ (K)	Inside	Outside	Inside	Outside
750-800	2.34	1.98(12)	0.94(18)	0.89(30)
700-750	2.20(10)	1.79(9)	1.22(13)	0.93(20)
650-700	2.32(14)	1.68(7)	1,20(17)	0.90(15)
600-650	2.49(21)	1.60(10)	1.22(17)	0.85(17)
575-600	2.51(38)	1.63(4)	1.04(10)	0.89(13)
550-575	2.64(19)	1.57(8)	0.87(13)	0.82(10)
525-550	2.63(36)	1.38(14)	0.64(10)	0.74(11)
500-525	2.71 (38)	1.32(17)	0.49(10)	0.60(3)
475-500	2.90(9)	1.23(12)	0.30(9)	0.49(8)
450-475	2.79(22)	1.17(15)	0.18(8)	0.35(8)
425-450	2.73(49)	0.95(16)	0.10(8)	0.21(10)
400-425	2.11 (72)	1,07(58)	0.06(51)	--

[a] Measurements arc classified as inside the vortex if sPV>2, outside if sPV< 1. Units arc 10^{-4} s-l, Values in parenthesis are VMR standard deviations in units of the last quoted digit.

Figure 1

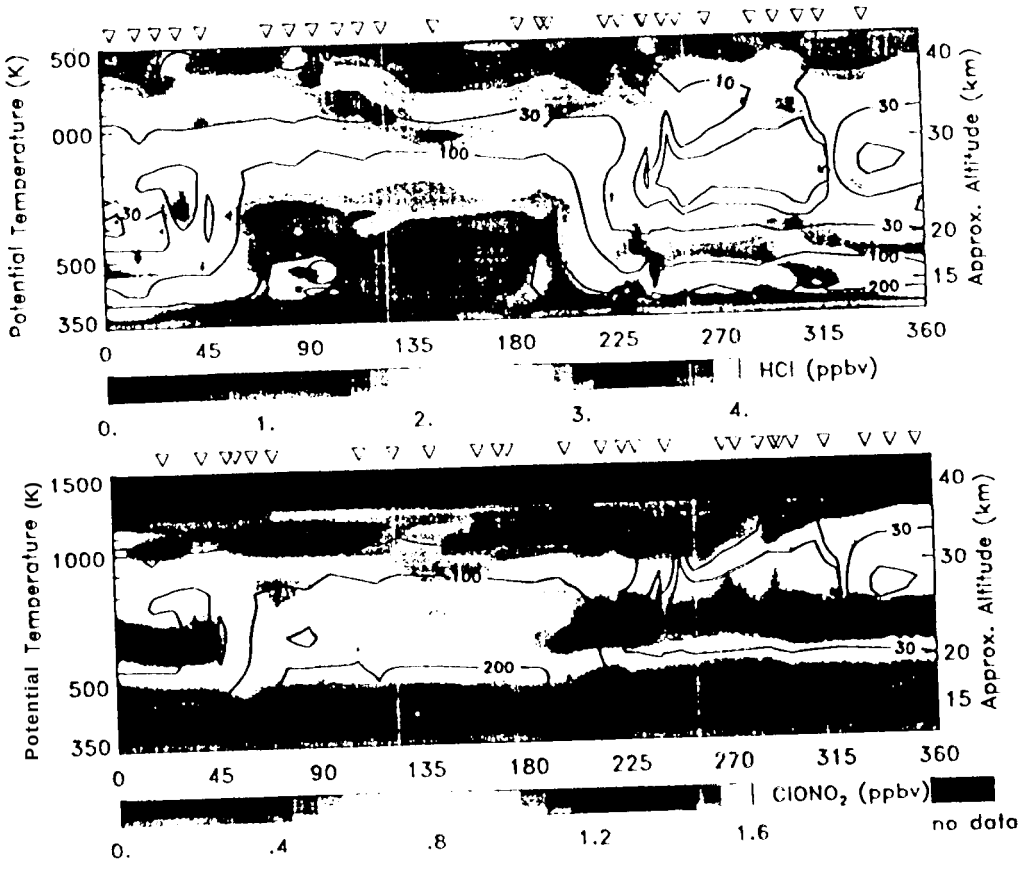
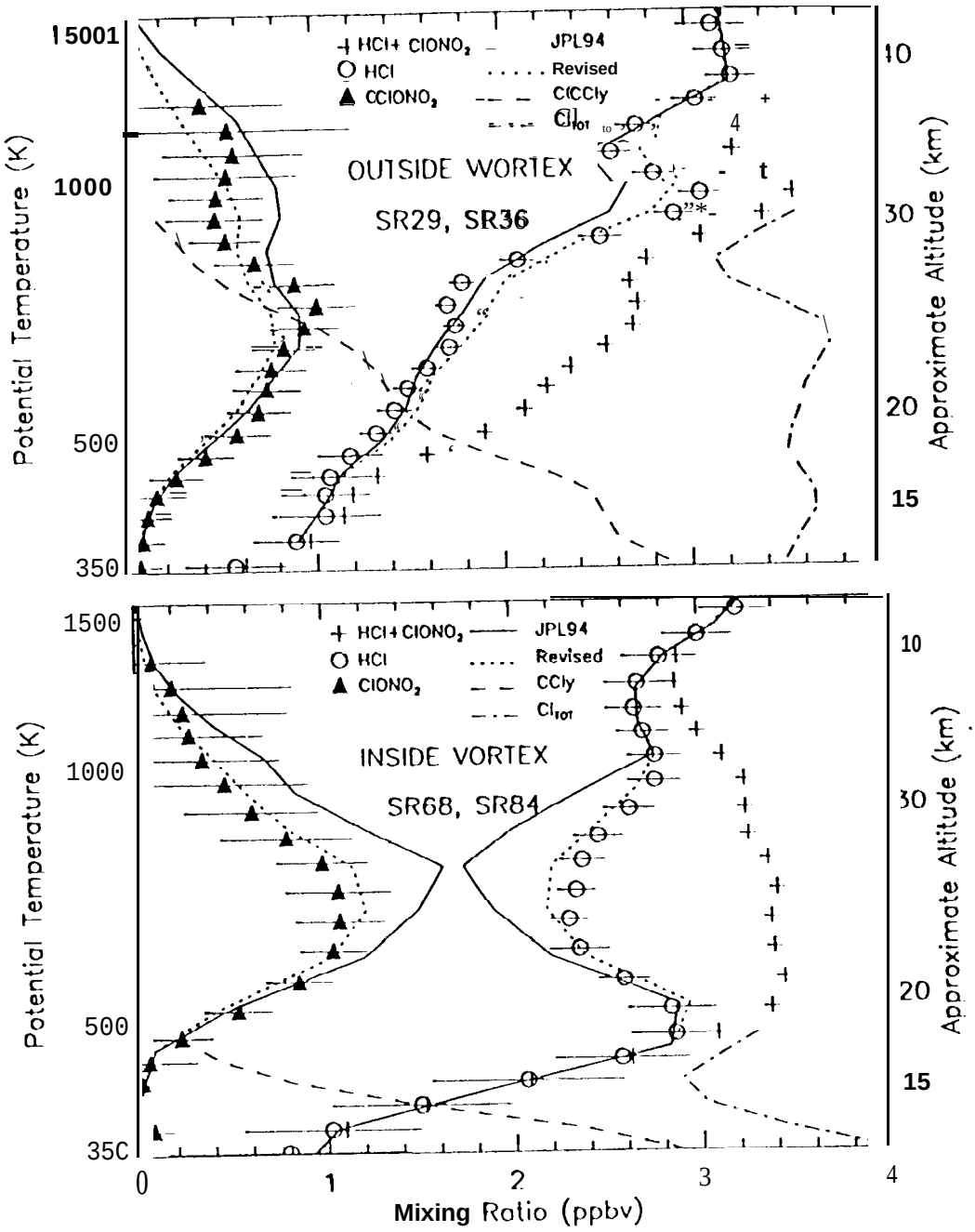

Potential Temperature (K)
500
000
500
350
10
30
100
200
0
45
90
135
180
225
270
315
360
Approx. Altitude (km)
40
30
20
15
HCl (ppbv)
0.
1.
2.
3.
4.
1500
1000
500
350
ClONO2 (ppbv)
no data
.4
.8
1.2
1.6

Figure 2


15001
1000
500
350
Potential Temperature (K)
HCl+ ClONO2
HCl
ClONO2
JPL94
Revised
CCCly
Cltot
OUTSIDE VORTEX
SR29, SR36
10
30
20
15
Approximate Altitude (km)
1500
1000
500
350C
INSIDE VORTEX
SR68, SR84
0
1
2
3
4
Mixing Ratio (ppbv)