Comparisons between ACE-FTS and ground-based measurements of stratospheric HCl and $ClONO_2$ loadings at northern latitudes

E. Mahieu, R. Zander, and P. Duchatelet
Institute of Astrophysics and Geophysics, University of Liège, Liège, Belgium

J. W. Hannigan and M. T. Coffey
Optical Techniques Project, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA

S. Mikuteit, F. Hase, and T. Blumenstock
IMK-ASF, Forschungszentrum Karlsruhe, Karlsruhe, Germany

A. Wiacek, K. Strong, and J. R. Taylor
Department of Physics, University of Toronto, Toronto, Ontario, Canada

R. L. Mittermeier and H. Fast
Meteorological Service of Canada, Downsview, Ontario, Canada

C. D. Boone, S. D. McLeod, K. A. Walker, and P. F. Bernath
Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

C. P. Rinsland
NASA-Langley Research Center, Hampton, Virginia, USA

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[1] We report first comparisons of stratospheric column abundances of hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$) derived from infrared solar spectra recorded in 2004 at selected northern latitudes by the spaceborne Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS) and by Fourier transform infrared (FTIR) instruments at the NDSC (Network for Detection of Stratospheric Change)-affiliated sites of Thule (Greenland), Kiruna (Sweden), Jungfraujoch (Switzerland), and Egbert and Toronto (Canada). Overall, and within the respective uncertainties of the independent measurement approaches, the comparisons show that the ACE-FTS measurements produce very good stratospheric volume mixing ratio profiles. Their internal precision allows to identify characteristic distribution features associated with latitudinal, dynamical, seasonal and chemical changes occurring in the atmosphere. **Citation:** Mahieu, E., et al. (2005), Comparisons between ACE-FTS and ground-based measurements of stratospheric HCl and $ClONO_2$ loadings at northern latitudes, *Geophys. Res. Lett.*, *32*, L15S08, doi:10.1029/2005GL022396.

1. Introduction

[2] The investigation of the Earth's atmosphere from space in 1985 by the ATMOS (Atmospheric Trace MOlecule Spectroscopy) high-resolution FTIR spectrometer was a pioneering milestone towards global studies of atmospheric gases [*Farmer*, 1987]. Operated in solar occultation mode on the Space Shuttle, ATMOS returned profiles of more than 30 species through the free troposphere and the stratosphere, including key species of the nitrogen-, chlorine-, and fluorine families [*Russell et al.*, 1988; *Zander et al.*, 1992]. The subsequent ATMOS missions in 1992, 1993 and 1994 allowed further studies of atmospheric variability and decadal changes [e.g., *Gunson et al.*, 1996; *Irion et al.*, 2002]. Within the framework of the chlorine family study, it became clear that HCl and $ClONO_2$ are the main gases contributing to the inorganic chlorine loading in the stratosphere [*Zander et al.*, 1992, 1996]. Ten years later, the ACE-FTS instrument (abbreviated hereafter as ACE), which was successfully launched on 12 August 2003, is building on this heritage [*Bernath et al.*, 2005]. With a nominal 2-year lifetime, ACE has the capability to produce a much larger, more consistent set of global observations. The ACE Version 1.0 (V1) data derived so far from observations performed since February 2004 corroborate this capability.

[3] The aim of this work is to evaluate the performance of ACE in measuring HCl and $ClONO_2$ volume mixing ratio (vmr) profiles throughout the stratosphere. It is based on comparisons of integrated burdens of these gases above 15 km altitude derived from selected ACE occultations and from solar observations at 5 ground-based, NDSC-affiliated sites located in the northern hemisphere. All analyses are based on HCl (1-0)-band transitions near 3μm and on the ν_4-band Q branch of $ClONO_2$ at 780.22 cm^{-1}, using spectroscopic parameters

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Table 1. NDSC Sites and Institutions Involved

Sites and Institutions Involved	Latitude	Longitude	Data Contributed
Thule – NCAR, USA	76.5°N	68.7°W	HCl and $ClONO_2$
Kiruna – FZK, Germany	67.8°N	20.4°E	HCl and $ClONO_2$
Jungfraujoch – ULg, Belgium	46.5°N	8.0°E	HCl and $ClONO_2$
Egbert – MSC, Canada	44.2°N	79.8°W	HCl
Toronto – U. Toronto, Canada	43.7°N	79.4°W	HCl

recommended in the 2001 and 2004 versions of the HITRAN compilation (see http://www.hitran.com).

2. Observational Data Sets Involved

[4] The ACE mission has been in its science operational mode since February 2004. The present investigation was restricted to partial column abundances above 15 km to ensure that only stratospheric air was sampled and that a large number of occultations with altitude coverage down to that level could be evaluated reliably for both gases. We have focused on all ACE-V1 sunsets located in 3 latitudinal zones encompassing the NDSC sites listed in Table 1.

[5] Table 2 gives details on the periods during which ACE occultations occurred in each selected zone and their numbers for each target gas. The adoption of 5-degree wide zones at higher latitudes was motivated by the fact that variability is generally larger in polar regions as compared to middle latitudes.

[6] The overall characteristics of the ACE retrieved vmr profiles for HCl and $ClONO_2$ during March 2004 is exemplified in Figure 1. The error bars include both retrieval uncertainties as well as contributions resulting from longitudinal inhomogeneities that occur in any zonal band. These mean zonal profiles are consistent with expectations [e.g., *Zander et al.*, 1996, Figure 1] in terms of the peak concentrations and altitude locations for $ClONO_2$ and the overall height distributions for HCl. The latter show features in the 30–45 km altitude range reflecting an increased winter contribution of ClO to the inorganic chlorine loading at higher latitudes [*Michelsen et al.*, 1996], and demonstrate the good relative sensitivity of the ACE observations. The ground-based data consist of daily mean column abundances of HCl and $ClONO_2$ derived from solar spectra recorded at the participating sites and analyzed with retrieval codes allowing to produce total and partial column abundances of both species. Retrieval codes include SFIT1 (for Egbert) SFIT2 (for Thule, Jungfraujoch and Toronto) and PROFFIT (for Kiruna), which have been described previously [e.g., *Rinsland et al.*, 2003; *Hase et al.*, 2004]. While SFIT2 and PROFFIT allow the retrieval of information on vertical distributions of gases, SFIT1 only scales a priori profiles by single multiplicative factors over the entire atmosphere. Partial columns derived with SFT1 therefore, may be less representative of the current state of the atmosphere. The column-averaging kernels for HCl and $ClONO_2$ show poor sensitivity in the troposphere [*Rinsland et al.*, 2003]; this is an additional argument for restricting comparisons with ACE to partial columns above 15 km. The a priori stratospheric distribution profiles of HCl adopted at most sites result from over a decade-long monitoring of that gas by HALOE (Halogen Occultation Experiment [see *Russell et al.*, 1996]). *McHugh et al.* [2005] have shown that the ACE mean upper stratospheric concentrations of HCl are systematically larger than the HALOE ones by 10 to 20%. However, Jungfraujoch tests with both HALOE and ACE profiles as a priori indicate that the retrieved partial columns of HCl differ by less than 2%, the values with ACE as a priori being the lowest.

3. Stratospheric Column Comparisons

[7] Figures 2 and 3 reproduce the 15 to 100 km partial column abundances, respectively, for HCl and for $ClONO_2$, derived from ACE occultations that occurred between March and October 2004 in the 3 latitudinal zones centered on Thule (Figures 2A and 3A), on Kiruna (Figures 2B and 3B), and on the Jungfraujoch, Egbert and Toronto sites (Frames C). We have focused here on same-day ground-based measurements with ACE occultations that occurred in these zones within 500 km longitude distance from the relevant site. ACE measurements were performed in the 5-degree wide latitudinal zone centered on Thule only during March 2004. Both HCl and $ClONO_2$ stratospheric columns (Figures 2A and 3A) show large scatter which results from strong vortex activity in the Arctic polar region during February and March 2004 (R. Ruhnke, Forschungszentrum Karlsruhe; private communication, 2004). Observations were carried out regularly at Thule between 7 and 31 March 2004. Good coincidences occurred on 4 days for HCl and 5 days for $ClONO_2$, with respectively, 6 and 7 ACE occultations meeting the "same day, <500 km" criterion. Related details are summarized in Table 3 and visualized in the inserts of Figures 2A and 3A. The largest differences among the ACE/Thule partial column ratios are 8% for HCl and 21% for $ClONO_2$. These values are well within the estimated one-sigma partial column uncertainties for HCl

Table 2. Overview of ACE Sunset Occultations Considered Here

Latitudinal Zones Centered On (Site(s))	Target Gases	Numbers of Occultations for Each Target Gas During Observation Periods in Months Given			Total Occults. Per Zone
		March 2004	June 2004	July 2004	
74°–79°N (Thule)		07-14/03/04	-	-	
	HCl	69	-	-	69
	$ClONO_2$	69	-	-	69
65°–70°N (Kiruna)		18-21/03/04	-	05-15/07/04	
	HCl	36	-	50	86
	$ClONO_2$	36	-	49	85
40°–50°N (Jungfraujoch+ Egbert+Toronto)		27-30/03/04	27-29/06/04	25-28/07/04	
	HCl	29	12	25	66
	$ClONO_2$	29	14	24	67

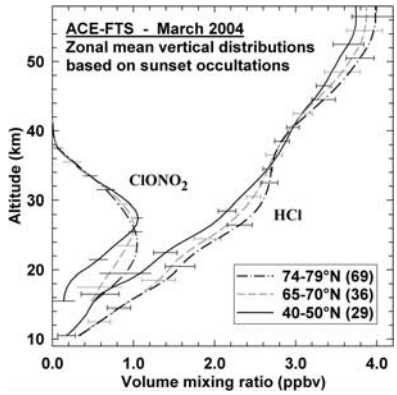

Figure 1. Zonal mean vmr profiles for HCl and $ClONO_2$ derived from ACE sunset occultations observed during March 2004 in 3 latitudinal zones indicated in the figure legend. The error bars drawn at discrete altitudes correspond to the standard deviation of the observations around the mean.

and $ClONO_2$, viz respectively 5–8% and 15–25% for ACE, and 4–8% and 12–25% for the ground-based retrievals. Notice that the average of the ACE/Thule ratios is equal to 1.04 for HCl and 0.99 for $ClONO_2$, which indicates a remarkable internal consistency of the sets of coincident measurements. The abnormally low ratio of $ClONO_2$ on 11 March 2004 cannot be rejected on the basis of ACE spectrometric quality criteria; it deserves further investigations relating detailed ACE observing geometries and local atmospheric inhomogeneities, which are evident in potential vorticity (PV) maps for that day in the latitudinal zone centered on Thule.

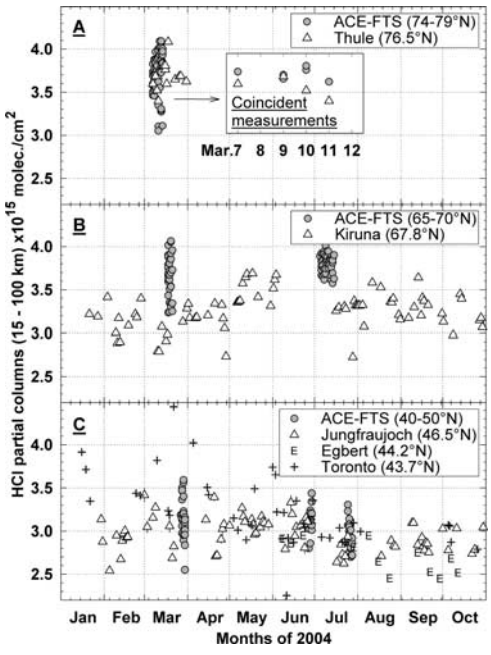

Figure 2. Comparison of HCl partial column abundances from 15 to 100 km altitude, derived from ACE sunset occultations and from ground–based FTIR solar observations. The ACE measurements were selected according to 3 latitudinal zones encompassing (A) Thule, (B) Kiruna, and (C) the Jungfraujoch, Egbert and Toronto sites. For details, see text.

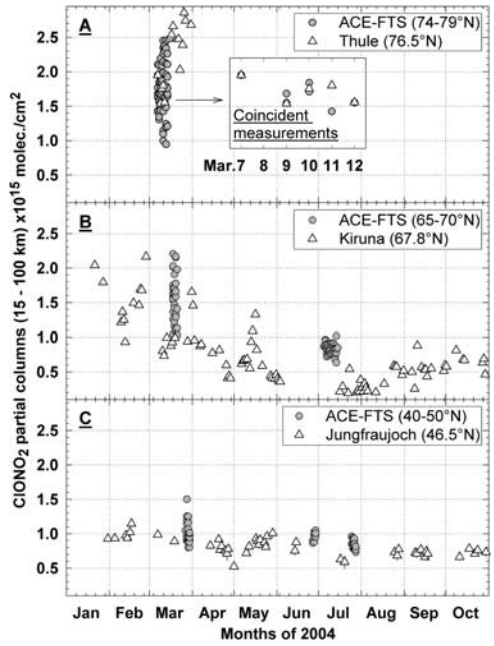

Figure 3. Same as Figure 2, but for $ClONO_2$, with Figure 3c including only data from the Jungfraujoch.

[8] Figures 2B and 3B reproduce, respectively, the 15–100 km HCl and $ClONO_2$ columns derived from the ACE sunset occultations in the latitudinal zone 65° to 70°N during March and July 2004, and those retrieved from FTIR observations at Kiruna between January and October 2004. The ACE data from March show a large dispersion in the columns (similar to that observed in the Thule zone), whose quantitative explanation will also require further local investigations in relation with the polar stratospheric vortex location. The ACE data from July cluster very nicely together, indicating little atmospheric perturbation in that latitudinal zone during summer time. The extremes in these clusters suggest that the ACE precision in retrieving partial columns is better than ±5% for HCl and ±18% for $ClONO_2$ at the one-sigma level. The sum of the means of these HCl and $ClONO_2$ clusters indicates an inorganic chlorine loading (considered as [HCl] + [$ClONO_2$]) above 15 km, equal to 4.60×10^{15} molecules cm^{-2}, which is commensurate with the findings reported for Kiruna in mid-2001 by *Rinsland et al.* [2003]. There are currently no ACE occultations in the database that occur within 500 km and 1 day of ground-based observations for both target gases at Kiruna. However, partial column measurements of $ClONO_2$ on 19 March 2004 by ACE (SS3237, 140 km distant from Kiruna) and at Kiruna, are respectively equal to 1.22 and 0.99×10^{15} molecules cm^{-2}, thus within the combined uncertainty of both measurement approaches. At first glance, there is some inconsistency in the July $ClONO_2$ partial columns by ACE and at Kiruna, with the latter being lower with respect to ACE by some 75%. This difference, which is well outside of the combined

Table 3. Correlative Stratospheric Column Abundance Measurements (15–100 km) for Thule in March 2004[a]

Day in 03/04	Occultation Nr. (and Δ in km)[b]	HCl Columns			$ClONO_2$ Columns		
		ACE	Ground	Ratio[c]	ACE	Ground	Ratio[c]
07	SS3063 (250)	3.73	3.60	1.04	1.95	1.95	1.00
09	SS3092 (444)	3.66	3.69	0.99	1.68	1.54	1.09
	SS3093 (222)	3.70	3.69	1.00	1.55	1.54	1.01
10	SS3107 (350)	3.76	3.52	1.07	1.71	1.76	0.97
	SS3108 (280)	3.81	3.52	1.08	1.84	1.76	1.05
11	SS3122 (250)	3.62	3.40	1.06	1.42	1.80	0.79
12	SS3137 (180)	3.74	-	-	1.56	1.56	1.00

[a]All column values in units $\times 10^{15}$ molecules cm^{-2}.
[b]Δ is distance from 30 km tangent point occultation to Thule site.
[c]Ratio ACE/Ground.

uncertainties, needs to be explained and may require assimilation of field measurements in multidimensional chemistry-transport models with high spatial resolution. Notice here that the mean total $ClONO_2$ column abundance above Kiruna in July–August 2004 is the lowest ever recorded in this database since 1996 [S. Mikuteit, private communication, 2004].

[9] Figures 2C and 3C refer to the 40° to 50°N latitudinal zone. ACE sunset occultations have been observed in March, June and July 2004 (Table 2), and relatively regular ground-based observations of HCl have been made throughout the year at Jungfraujoch, Egbert, and Toronto. As there are no ACE and ground-based observations meeting the "same day, <500 km" criteria, some more general considerations are made for this zone. When discarding the six highest ACE column measurements in March (observations through polar air having moved to middle latitudes over various longitudinal areas; R. Ruhnke, private communication, 2004), there is reasonably good agreement with all nearest partial columns measured at the Jungfraujoch and some at Toronto. Notice that the apparent high outliers in the Toronto database have been checked for their proper spectral fitting, and that correlations with the HF tracer indicate that they resulted from intrusions of polar air above Toronto. The pairs of highest HCl partial columns observed by ACE in June and July occurred over Canada and are commensurate with measurements performed in Toronto and Egbert within a few days. Overall, the combined June and July measurements are in very good agreement at the 1-σ level. Despite some noticeable scatter in the data points, the various datasets show a general decrease between March and August, which is characteristic of the mid-latitude seasonal variation of the HCl loading. Linear fits to the individual ACE, Jungfraujoch and Toronto datasets over that period (Egbert was discarded, as measurements only started in June 2004) return slopes, respectively equal to -1.61, -1.75, and -2.15×10^{12} molecules cm^{-2} d^{-1}, thus nearly parallel. Relative to ACE, the column differences for July 2004 are equal to −2.3% for the Jungfraujoch, and +6.3% for Toronto. These differences are also within the uncertainties of the individual datasets. Figure 3C displays the partial columns of $ClONO_2$ derived from ACE occultations and from observations at the Jungfraujoch. Except for one outlier at the end of March (which corresponds to occultation SS3366 that was sounding through a strong $ClONO_2$-enriched polar air intrusion over Siberia on 28 March 2004; R. Ruhnke, private communication, 2004), the 3 sets of ACE measurements are relatively compact. Linear fits to both $ClONO_2$ datasets indicate that, on average, the Jungfraujoch partial columns are 15% lower than the ACE ones. While remaining within the uncertainty of both measurement approaches, this difference deserves further consideration regarding consistency in retrieval input parameters.

4. Summary and Conclusions

[10] This initial evaluation of ACE-V1 measurements of HCl and $ClONO_2$ has demonstrated that the related spectral absorption features observed by ACE from space produce very good vmr profiles above 15 km altitude. The ACE measurement sensitivity has allowed the identification of characteristic distribution features associated with geographical, dynamical, seasonal, and chemical changes occurring in the atmosphere. When tight coincidence in time and location is achieved, very good agreement is found between ACE and ground-based loadings of HCl and $ClONO_2$ above 15 km altitude in restricted latitudinal zones of the Northern Hemisphere. In the present exercise, this has only been met on a few occasions around the Thule site. When relaxed coincidence criteria are applied, good agreement is generally achieved at northern mid-latitudes, although systematic differences between some data sets need to be given further consideration, especially with regard to possible local PV perturbations.

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P. F. Bernath, C. D. Boone, S. D. McLeod, and K. A. Walker, Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada. (bernath@uwaterloo.ca; cboone@acebox.uwaterloo.ca; sdmcleod@uwaterloo.ca; kwalker@acebox.uwaterloo.ca)

T. Blumenstock, F. Hase, and S. Mikuteit, IMK-ASF, Forschungszentrum Karlsruhe, P.O. Box 3640, 76021 Karlsruhe, Germany. (thomas.blumenstock@imk.fzk.de; frank.hase@imk.fzk.de; sabine.mikuteit@imk.fzk.de)

M. T. Coffey and J. W. Hannigan, Optical Techniques Project, Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80303, USA. (coffey@ncar.ucar.edu; jamesw@ncar.ucar.edu)

P. Duchatelet, E. Mahieu, and R. Zander, Institute of Astrophysics and Geophysics, University of Liège, 17 Allée du 6 Août – Bât. 5a, 4000 Liège, Belgium. (p.duchatelet@ulg.ac.be; emmanuel.mahieu@ulg.ac.be; r.zander@ulg.ac.be)

H. Fast and R. L. Mittermeier, Meteorological Service of Canada, 4905 Dufferin Street, Downsview, ON M3H5T4, Canada. (hans.fast@ec.gc.ca; richard.mittermeier@ec.gc.ca)

C. P. Rinsland, NASA Langley Research Center, Mail Stop 401A, Hampton, VA, USA. (c.p.rinsland@larc.nasa.gov)

K. Strong, J. R. Taylor, and A. Wiacek, Department of Physics, University of Toronto, 60 St. George Street, Toronto, ON, M5S 1A7, Canada. (strong@atmosp.physics.utoronto.ca; jeff@atmosp.physics.utoronto.ca; aldona@atmosp.physics.utoronto.ca)