RECENT EVOLUTION of STRATOSPHERIC INORGANIC CHLORINE (Cl_y) INFERRED from LONG-TERM GROUND-BASED FTIR OBSERVATIONS of HCl and $ClONO_2$

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1. INSTRUMENTATION AND STATIONS INVOLVED

- High-resolution Fourier Transform Infrared (FTIR) spectrometers allow to record broadband solar absorption spectra, year-round, under clear-sky conditions.
- The FTIR instruments involved here are operated at two primary sites of the Network for Detection of Atmospheric Composition Change (NDACC, formerly NDSC, visit http://www.ndacc.org) at northern and southern mid-latitudes. Sites coordinates and database time-span are detailed in the following table.

NDACC-Site	Latitude	Longitude	Altitude a.s.l.	Relevant and regular observations available from
Jungfraujoch	46.5°N	8.0°E	3580 m	1984 onwards
Lauder	45.0°S	169.7°E	370 m	1990 onwards

Rem: For both sites, earlier historical measurements are available at least for HCl.

2. LONG-TERM OBSERVATIONS AND MODELING

- Microwindows encompassing spectral absorption features of the two most important inorganic chlorine reservoirs, i.e. HCl (hydrogen chloride) and $ClONO_2$ (chlorine nitrate), have been consistently analyzed to retrieve their total vertical column abundances. For details on the retrievals and adopted line parameters, consult Appendix A of [1].
- Monthly mean total vertical column time series of HCl and $ClONO_2$ are reproduced in FIGURE 1 as red circles and green triangles. For Jungfraujoch, error bars represent the random errors (conservatively estimated at 5 and 20%, respectively for HCl and $ClONO_2$ single measurements) divided by the square root of the number of averaged individual columns. For Lauder, error bars correspond to the standard deviations around the monthly means.
- Inorganic chlorine (Cl_y) total columns (see blue triangles) are obtained by summing up the HCl and $ClONO_2$ contributions. Based on ATMOS and ACE-FTS chlorine budget evaluations (see e.g. [2] and [3]), it has been shown that these two reservoir species contribute to at least 92% of total inorganic chlorine at mid-latitudes; the sum of HCl and $ClONO_2$ is therefore a good surrogate for Cl_y.
- Enhanced variability is frequently observed at the Jungfraujoch during the winter-spring periods (primarily resulting from meridional transport of airmasses), time series used here for long-term trend evaluations have therefore been limited to the relatively quite June to November months. For Lauder, year-round monthly means are displayed and used in the analyses.
- The monthly mean time series reported here have been compared with 3-D CTM KASIMA model calculations performed by IMK Karlsruhe. In these model runs, the temporal evolution of the relevant source gas concentrations (primarily the CFCs and HCFCs) are characterized by past tropospheric measurements and by the predicted "Ab baseline" scenario [4]. A thorough description of the KASIMA model is available from [5] and [6].

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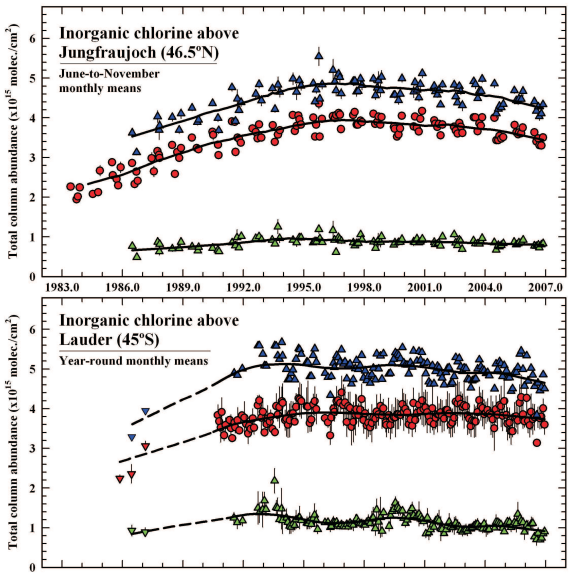

FIGURE 1. Time series of total vertical column abundances of HCl (red circles), $ClONO_2$ (green triangles) and their summation, Cl_y (blue triangles), above Jungfraujoch and Lauder. Running mean calculations reproduced by thick continuous lines help appraising the long-term evolution of each species.

References

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3. COMPARISONS WITH KASIMA

- For both sites, comparisons indicate that KASIMA underestimates HCl and $ClONO_2$ total columns by about 25% and 30%, on average. FIGURE 2 reproduces observational and modeled monthly mean total column time series after scaling of the KASIMA data. KASIMA monthly means were computed by selecting days for which observations were available.
- In the case of the Jungfraujoch, these comparisons further show that the model nicely captures the HCl evolution, including inter-annual variability, with the exception of the first years. For $ClONO_2$, its overall development is also well reproduced, although KASIMA failed to mimic the enhanced columns around 1992.
- For Lauder, KASIMA is able to reproduce the seasonal and long-term evolutions of HCl, including some extreme measurements in 1996 and 2006. Contrarily, the 3-D model fails to match the significantly high $ClONO_2$ columns recorded in the early and late 1990s; in addition the modeled seasonal cycle is generally too strong with maxima larger than the observations.

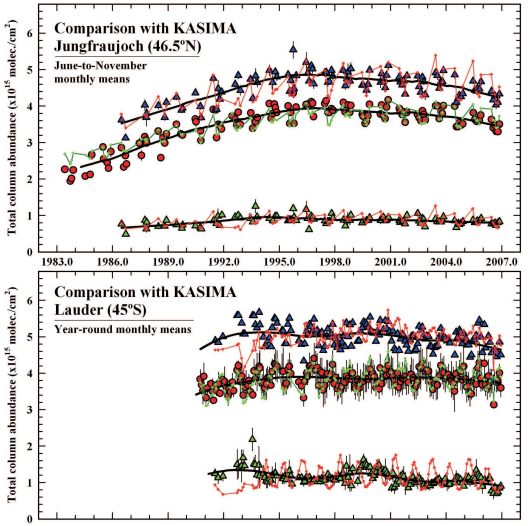

FIGURE 2. Comparisons between observational and modeled monthly mean total vertical column abundances of HCl, $ClONO_2$ and Cl_y, for Jungfraujoch (upper frame) and Lauder (lower frame). KASIMA monthly means are reproduced by interconnected red or green dots.

4. TREND EVALUATIONS OVER RECENT YEARS FOR INORGANIC CHLORINE

- After a steady increase until around the mid-1990s, the Cl_y loading has begun a progressive stabilization. Since then, a slight decrease has been observed over the 1997-2006 and 2000-2006 time periods, respectively for Jungfraujoch and Lauder.
- Mean decreasing rates have been determined by linear fits to the observed and modeled Cl_y time series. For Jungfraujoch, we found a mean yearly rate of [-1.1±0.2]%/yr (1-sigma), in agreement with the one deduced from Lauder, i.e. [-1.0±0.3]%/yr. Corresponding decreasing rates of change based on model simulations are equal to [-0.6±0.3] and [-1.3±0.2]%/yr, respectively for Jungfraujoch and Lauder. In both cases, these latter numbers agree with observational trends reported above when accounting for the 1-sigma level of uncertainty.