The Evolution of Inorganic Chlorine above the Jungfraujoch Station: an update

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Abstract. Within the frame of the NDSC, the total vertical column abundances of HCl and $ClONO_2$, by far the two most important inorganic chlorine reservoirs at northern mid-latitudes, have been further monitored above the Jungfraujoch station (Swiss Alps, 46.5ºN, 8.0ºE, 3580m a.s.l.), by analyzing infrared solar absorption spectra recorded with very high-resolution Fourier spectrometers. The mean temporal evolution of the sum of their monthly mean abundance time series indicates that the total stratospheric inorganic chlorine loading (Cl_y) has decreased slowly (-0.7±0.3%/yr, 1σ) since it peaked in late 1996, at the limit of being statistically significant at the 2σ level. Comparison with model calculations and with the evolution of surface total organic chlorine will also be discussed.

Context

Following the demonstration of the important role played by stratospheric chlorine in the ozone layer depletion, a special effort has been devoted to the monitoring of anthropogenic chlorine bearing source gases (among which the man-made CFCs and HCFCs) and to species resulting from their photo-dissociation in the stratosphere. These monitoring activities were and remain essential to assess the efficiency of the phase out scenarios imposed by the Montreal Protocol (1987) and its subsequent Amendments and Adjustments upon important halogenated source gases with large ozone depletion potentials, with the ultimate aim of reducing the inorganic chlorine loading in the stratosphere.

Since the formalization of the NDSC (Network for the Detection of Stratospheric Change, http://www.ndsc.ws) in 1989, the International Scientific Station of the Jungfraujoch (46.5ºN, 8.0ºE, 3580 m a.s.l.; hereafter ISSJ) has been an essential component of the Network's primary Alpine station to monitor the state of the atmosphere at northern mid-latitudes, hosting very high-resolution Fourier transform spectrometers maintained by the University of Liège to perform year-round infrared observations. Under clear sky conditions, solar spectra reveal usable signatures of over two dozen atmospheric species among which many (i.e. CCl_2F_2, CCl_3F, CCl_4, $CHClF_2$, HCl and $ClONO_2$) are of direct relevance to the subject dealt with here.

In this contribution, we present the updated ISSJ total column time series of the two most important inorganic chlorine reservoirs in the absence of chlorine activation: HCl (hydrogen chloride) and $ClONO_2$ (chlorine nitrate). Their long-term evolutions are compared with those from (1) 2-D model calculations performed for northern mid-latitudes and (2) total organic chlorine measured at the surface by the AGAGE network.

Observational data

A subset of available IR spectra recorded at ISSJ since the mid-eighties has been considered in the present investigation. Selected microwindows encompassing HCl and $ClONO_2$ spectral absorption features have been analyzed consistently to determine total vertical column abundances of these species above the observing site. Details on the algorithms, spectroscopic line parameters and ancillary data adopted in the retrievals can be found in appendix A2 of Rinsland et al. [2003].

To avoid the significant variability frequently affecting measurements performed during the winter-spring periods (which primarily results from meridional transport of air masses), the time series reported here have been limited to the June to November months. Figure 1 reproduces the monthly mean total vertical column time series of HCl and $ClONO_2$, respectively as empty circles and triangles. Error bars represent the random errors (estimated at 5 and 20 % respectively for HCl and $ClONO_2$ single measurements) divided by the square root of the number of averaged measurements. Monthly mean total inorganic chlorine columns (reproduced by filled triangles and noted Cl_y) are obtained by summing the HCl and $ClONO_2$ contributions. Based on ATMOS observations, it has been shown that the chlorine reservoirs not included here (e.g. ClO, HOCl) amount to at most 8% of total inorganic

chlorine at northern mid-latitudes [Zander et al., 1996], so that the sum of HCl and $ClONO_2$ can be considered as a good surrogate for Cl_y. Thick continuous lines represent the nonparametric least-square fits to the various monthly means time series, with 20% weighting (which corresponds to smoothing over about 3 years).

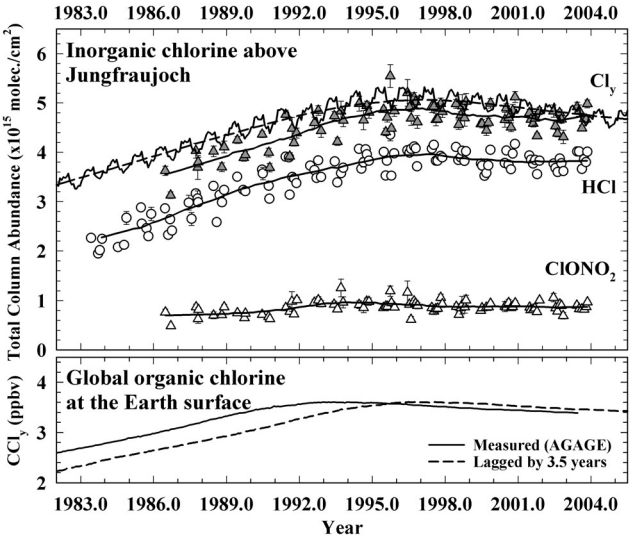

Figure 1. June to November monthly mean total column abundances of HCl, $ClONO_2$ and their summation, Cl_y, above the Jungfraujoch station are reproduced in the top panel. The upper trace corresponds to the sum of the HCl and $ClONO_2$ columns calculated by the 2-D model. The lower panel displays the evolution of total surface organic chlorine based on measurements performed by the AGAGE network. For further details, see text.

2-D model runs have been performed for all chlorine reservoirs, based on the evolution of the relevant source gas concentrations characterized by past measurements and by the predicted "Ab baseline" scenario. A brief description of the model and assumptions made for the present runs can be found in section 6 of Rinsland et al. [2003], and references therein. Year round results obtained for ($HCl+ClONO_2$) at 47ºN are displayed in Fig. 1 (upper trace).

Additionally, the temporal evolution of global surface total organic chlorine (CCl_y) based on AGAGE measurements is shown in the lower frame of Fig. 1. Related information is given in O'Doherty et al. [2003].

Discussion

After a steady increase at a mean rate of 3.8%/yr during the 1986-1993 period, the Cl_y loading above ISSJ has begun a progressive stabilization, with a maximum observed during the second half of 1996. Since then, a slight Cl_y decrease has been observed over the 1997-2003 period, at a mean yearly rate close to -0.7%. The latter, however, is at the limit of being statistically significant at the 95% confidence level, mainly because of noticeable inter-annual variability affecting the monthly mean total columns of HCl and $ClONO_2$, even during the quietest summer-fall months considered here.

Overall, the above findings are in very good agreement with the 2-D model calculations which, after smoothing of the seasonal variations (see upper dashed curve in the top frame of Fig. 1), also reveal a Cl_y peak during the second half of 1996. The model predicts a 12-14% decrease in 2010 relative to the maximum [Rinsland et al., 2003] which, even if a bit faster, is commensurate with our post 1996 observations. The model calculations further indicate that on average, the sum of the HCl and $ClONO_2$ columns corresponds to 91% of Cl_y, in very good agreement with ATMOS budget evaluations [Zander et al., 1996].

The Cl_y long-term evolution is also consistent with the temporal development of the surface organic chlorine loading, when accounting for a time delay of about 3.5 years for tropospheric air to propagate and mix into the mid-latitude stratosphere. After peak occurrence in 1993, CCl_y also exhibits a slow decrease of ~0.7%/yr, in excellent agreement with the Cl_y observations and model calculations reported here.

Conclusions

With respect to recent studies, this update confirms the stabilization of inorganic chlorine at northern mid-latitudes, followed by a slow decrease, in good agreement with surface measurements of organic chlorine and with model calculations. This further demonstrates the appropriateness and proper implementation of the phase out scenarios adopted by the Montreal Protocol and its subsequent enforcements. However, given the marked natural dynamics and variability characterizing the atmosphere, further measurements will be necessary to improve the statistical significance of the of the Cl_y decrease above Europe.

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