Recent Characteristic Budgets of Inorganic Chlorine and Fluorine above the Jungfraujoch Station

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Within the frame of NDSC (Network for the Detection of Stratospheric Change)-related monitoring activities conducted at the International Scientific Station of the Jungfraujoch (ISSJ, Swiss Alps, 46.5 °N, 8.0 °E, 3580 m a.s.l.), long-term investigations of the inorganic chlorine (Cl) and fluorine (F) budgets have been pursued during the last years. They are based on the analysis of high-resolution infrared solar spectra, recorded with grating and Fourier transform state-of-the-art spectrometers. Nonlinear least squares fittings of synthetic spectra to the observations are performed over selected intervals, encompassing characteristic absorptions of HCl, $ClONO_2$, HF and COF_2; this allows the retrieval of their total vertical column abundances (VCAs) above ISSJ. Description of the data and error analysis method can be found in Rinsland et al. [1] while ISSJ instrumentation is described in Delbouille and Roland [2].

The following steps explain how the total inorganic Cl burden above the Jungfraujoch station has been evaluated : (i) monthly averaged VCAs of HCl and $ClONO_2$ determined for the months of June to November have been selected, in order to avoid significant variability occurring during the winter-spring time (see transport discussion hereafter); these monthly mean VCAs are respectively reproduced by filled circles and filled triangles in Figure 1; in both cases, vertical bars represent one standard deviation around the monthly means. In step (ii), second order polynomial fits have been applied to both datasets described above (see corresponding thick lines in Fig. 1), their associated 2-σ confidence ranges are given by the thin dotted curves. The two fits present negative second order derivatives, suggesting an attenuation in both species' trends. Based on the polynomial fits, the HCl rates of increase referred to 1986.5 and 1994 correspond respectively to 7.2 %/yr and 2.7 %/yr. In step (iii), ClO columns computed by AER Inc. (Cambridge, MA, USA; M. Ko, private communication) have been added to the $ClONO_2$ and HCl ones, to complete the inorganic Cl burden evolution above ISSJ during the last fifteen years (see upper thick curve in Fig. 1); the ClO averaged contribution to the total inorganic Cl budget amounts to about 5.5 %, in excellent agreement with the value of 5.7 % derived by Zander et al. [3] and based on a 1985 Cl inventory at 30 °N. In the same study, evaluation of the contributions of species such as HOCl, COClF, which are not included in the present work, indicate that they account for at most 2 % of total inorganic Cl.

Timely total Cl trends have been calculated for 1986 and 1994, they are respectively equal to 7.7 %/yr and 2.6 %/yr, which correspond to yearly increases of 2.8 and 1.4×10^{14} Cl atoms/cm^2 (the maximum Cl trends above ISSJ occurred around the mid-1980s); this significant slowing down results from the phase-out of CFCs (their photodissociations constitute the primary source of inorganic Cl in the stratosphere) by the Montreal protocol and its amendments. In particular, drastic decrease in CFC-11 and CFC-12 releases to the atmosphere are reported by AFEAS (see AFEAS-1996 report [4]), indicating that their actual releases are back to their early 1950 levels. In situ measurements confirm that the global CFC-11 ground-level concentration is already decreasing, while that of CFC-12 has significantly leveled off (see, e.g., Montzka et al. [5]). Extrapolation of the second order polynomial function representing the total Cl in Fig.1 indicates that its maximum above ISSJ

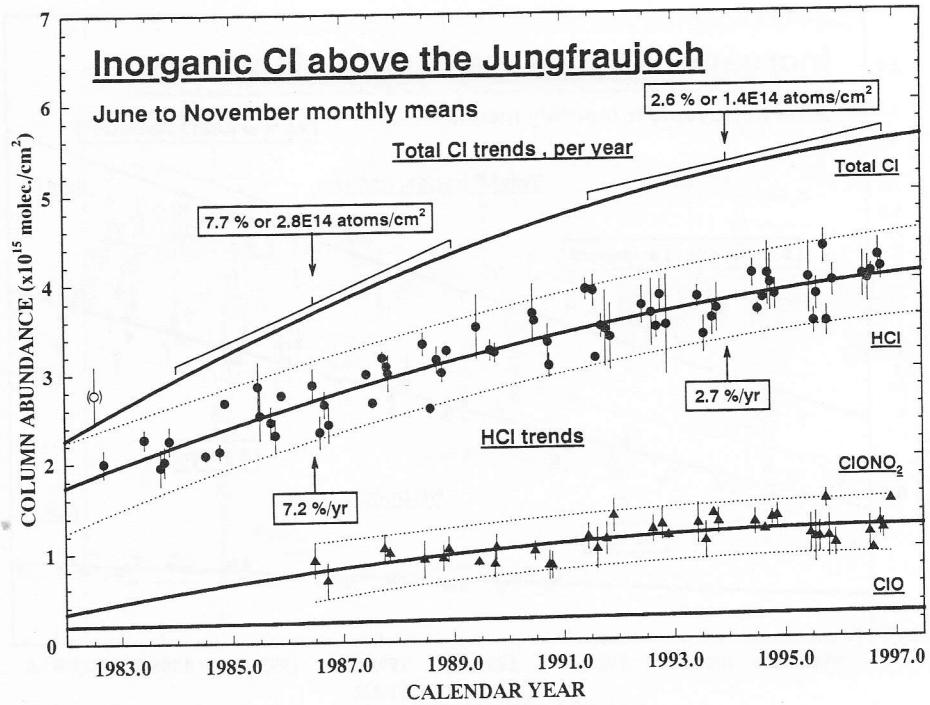

Figure 1. Total inorganic Cl burden evolution above the Jungfraujoch station during the last fifteen years. High column observed in July 1982 is believed to be biased by the El Chichon volcanic eruption of March-April 1982.

may occur between years 2000 and 2003.

The above procedure has further been adopted to determine the total inorganic F burden above ISSJ. In Figure 2, June to November HF monthly averaged VCAs are reproduced by dots and COF_2 VCAs by triangles; both datasets are fitted by a second order polynomial function (see corresponding thick curves) which present positive curvatures, thus indicating mean steady burden increases of these two gases above ISSJ. Error bars correspond to the standard deviation around the monthly means; dotted lines reproduce the 2-σ confidence range. The upper thick curve displays the total inorganic fluorine burden above ISSJ, obtained by summing the HF and two times the COF_2 columns read off the two lower curves. Missing species, e.g. COClF, account for at most 2 % of the total budget (Zander et al. [3]). Timely total F increases calculated for 1986 and 1994 are equal to 6.2 %/yr and 4.5 %/yr respectively, which correspond to yearly inorganic F increases of respectively 6.4 and 6.8×10^{13} F atoms/cm^2. The latter values indicate that the F deposition in the atmosphere has remained constant over the period investigated here, which is qualitatively anticipated when considering the replacement of the CFCs by other "fluorinated" species such as HCFCs and HFCs.

Beside long-term trend evaluations described in the previous paragraphs, effects of latitudinal transport on VCAs measured above the ISSJ mid-latitudinal site have also been identified (see also De Mazière et al. ; Demoulin et al. ; Patton Walsh et al. in this volume). In Figure 3, the ratios between HCl and HF daily average VCAs obtained over the last 6.5 years are reproduced by open and filled circles. The overall tendency is given by a two iterations-linear fit to the data; its decrease results from the relative evolutions of HF and HCl; the corresponding 99 % confidence range is represented by the dotted lines. All ratios falling below this range are reproduced by filled circles. These latter, as well as a few ones found above the high limit of the range, are considered to result from unusual atmospheric

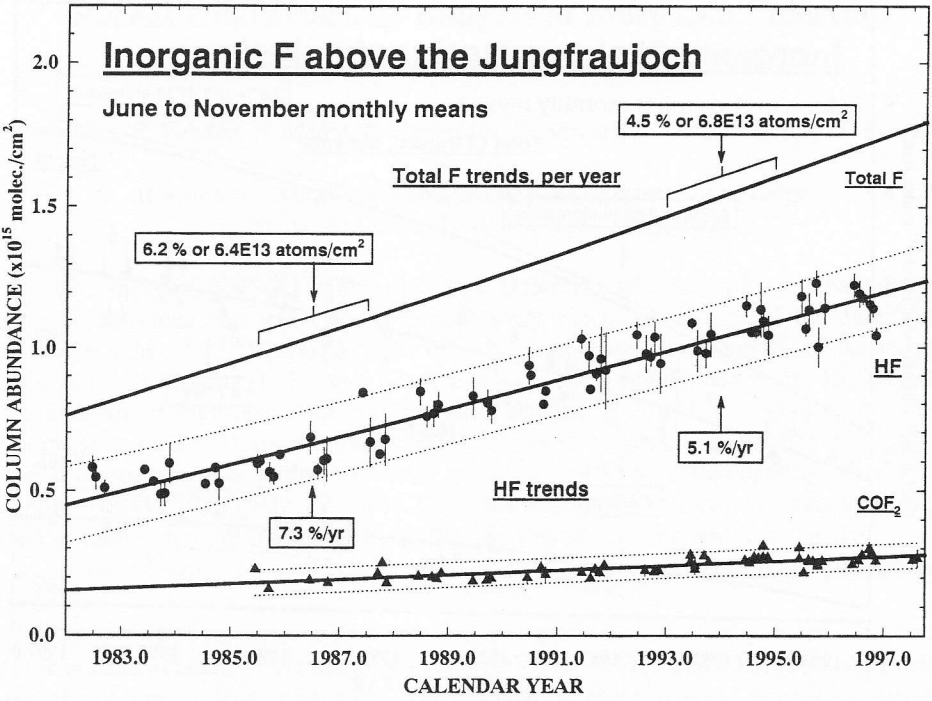

Figure 2. Total inorganic F burden evolution above the Jungfraujoch station during the last fifteen years.

circulation situations. The extremely low ratios, observed during the winter 1992, primarily results from heterogeneous conversion of HCl in the presence of stratospheric aerosol clouds associated with the major volcanic eruption of Mt. Pinatubo in June 1991; this is confirmed by record high values of $ClONO_2$ noticed during this period (on February 19th 1992, the $ClONO_2$ column, equal to 3.45×10^{15} molec./cm^2, even exceeded that of HCl (3.33×10^{15} molec./cm^2)). In late January 1994, the circulation situation reversed completely within one day : on January 30th, back-trajectory ECMWF-maps (provided by the European Centre for Medium-Range Weather Forecasts via NILU) indicate that the airmasses were originating from sub-tropical regions, with expected air enriched in HCl (relatively to HF); the corresponding high ratio, equal to 3.93, is well noticed on Fig. 3; potential vorticity (PV) at noon is 25.59 (PV Units = 10^{-6} Km^2/kgs) for the 475K level (similar sub-tropical air intrusions have also been observed twice in February 1996). The next day, circulation brought vortex-type airmasses above the Jungfraujoch station and the ratio fell to 2.64, with a PV value near 33 PVU at the same level. Low ratio episodes have further been observed in mid-February, late March and mid-April of 1996. Despite a PV at 475 K of 22 PVU, the February 15 event is indicative of some chlorine activation, with HCl and $ClONO_2$ VCAs respectively equal to 3.38 and 2.57×10^{15} molec./cm^2, which correspond to deviations from the expected values of –15 % for HCl and near 100 % for $ClONO_2$. In March and April, the situation was somewhat different when low HCl/HF ratios were correlated with the presence above ISSJ of vortex-type air-masses. Noticeable were the record high values of HF and HCl VCAs, while $ClONO_2$ columns were some 33 % above normal; PV at 475 K extended from 37 to 40 PVU. Analysis of PV- and back-trajectory ECMWF-maps confirm the north-south meridional transports that prevailed at this time. On the basis of more recent ISSJ measurements made during the winter and spring time of 1996-97, it appears that less transport activity occurred : only three datapoints (April 12, May 2 and 3) are found slightly below the 99 % normal

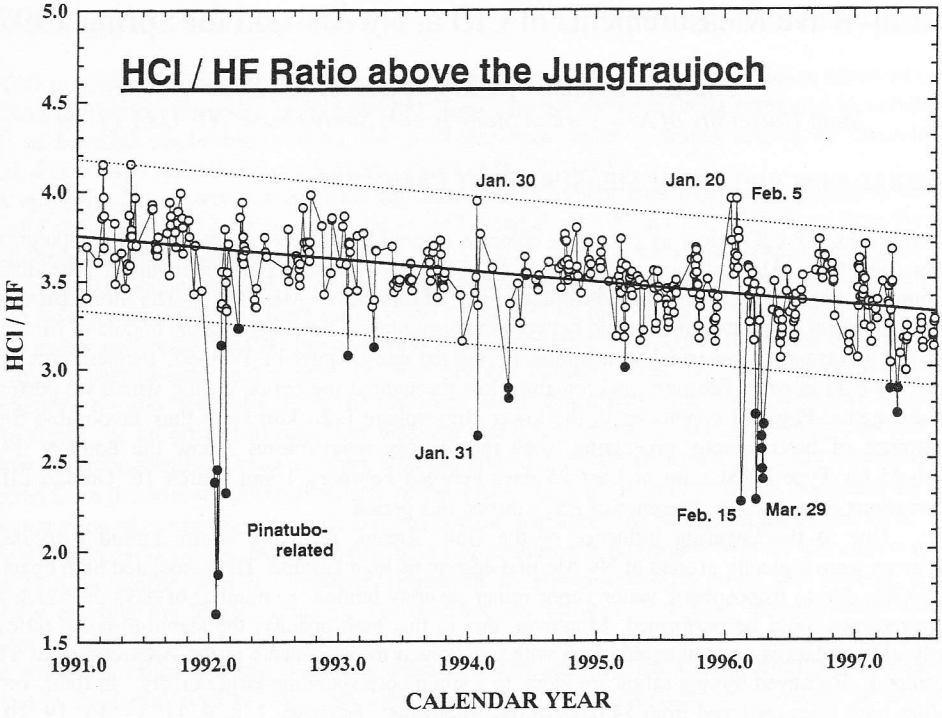

Figure 3. All datapoints correspond to the HCl/HF ratios observed above ISSJ during the last 6.5 years. Filled circles, which fall below the 99 % confidence range determined after two successive, 2-σ linear fits, are associated with peculiar atmospheric circulation situations.

"climatology" limit.

ACKNOWLEDGEMENTS

Acknowledgment is made for the financial contributions from the Belgian organizations FNRS and OSTC, Brussels, and from the CEC, Brussels. We thank M. De Mazière, J. Granville, O. Hennen (BIRA/IASB) and R. Blomme (KSB) who participated in some observational campaigns at ISSJ. We further thank the Stiftungsrat of the Jungfraujoch and the University of Liège for supporting the facilities needed to perform both the observations and their analysis.

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