

Fifteen Years-Trend Characteristics of Key Stratospheric Constituents Monitored by FTIR above the Jungfraujoch.

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Introduction

Since 1989, the International Scientific Station of the Jungfraujoch (ISSJ) in the Swiss Alps (46.5° N, 8.0° E, 3580 m asl) is an accepted site of the northern midlatitude primary Alpine station of the NDSC (Network for the Detection of stratospheric Change). This acceptance resulted from earlier monitoring activities by ULg of a large number of atmospheric constituents that demonstrated the power of infrared spectrometric solar observations to characterize the chemical composition of both the troposphere and the stratosphere [1]. Within the NDSC frame, special attention has been devoted to monitoring species primarily concentrated in the stratosphere where one of the past decades' concerns has been the quantification and the understanding of the ozone layer depletion. The protection and recovery of the latter have been and remain the main drivers of the phase-out scenarios imposed by the Montreal Protocol (1987) and its subsequent Amendments upon important chlorine-bearing source gases with large ozone depletion potentials.

Data Bases and Analysis

The key stratospheric constituents about which we report long-term trends here include HCl, ClONO₂, HNO₃, NO₂, NO, HF, COF₂ and O₃. The related data bases consist of vertical column abundances (VCAs, expressed in number molecules per square cm) derived from infrared solar observations made at ISSJ, primarily with very high-resolution, broad-band Fourier transform spectrometers. The VCAs are determined by nonlinear least-squares fittings between observed and calculated spectral intervals encompassing characteristic absorptions of the individual target gases, using the SFIT-1.09 algorithm developed by Rinsland et al. [e.g.,2]. Inputs to these fittings include: (i) most realistic volume mixing ratio profiles for both the target and the interfering gases; (ii) spectroscopic line parameters taken from recent line parameter compilations [e.g., 3]; (iii) daily P-T model atmospheres obtained from the National Centers for Environmental Prediction (NOAA, Washington, D.C., USA), and (iv) instrumental parameters characterizing the individual observations.

An excerpt of the Liège total data sets is reproduced in Figure 1. It shows daily mean VCAs during the last decade for the eight molecules listed above, as well as for the long-lived source gas N₂O used as tracer of atmospheric circulation and dynamics. Within that context, it can be noticed that the low N₂O columns observed during the first months of 1999 anti-correlate with high columns of ClONO₂ and with record high values of O₃, HNO₃, HCl, HF and COF₂, thus clearly indicating significant intrusions of Arctic polar air over Europe during that period; this was confirmed upon inspection of back-trajectory maps produced by the ECMWF and accessed via NILU.

The data displayed in Fig. 1 have been normalized for a mean local pressure of 654 hPa. They allow to produce budget estimates of inorganic chlorine, Cl_y (to better than 92% by combining HCl and ClONO₂ columns), inorganic fluorine, F_y (to better than 98% based on HF and COF₂), and daytime NO_y (to nearly 96% when including HNO₃, NO, NO₂ and ClONO₂); trends of these budgets will be reported here as well.

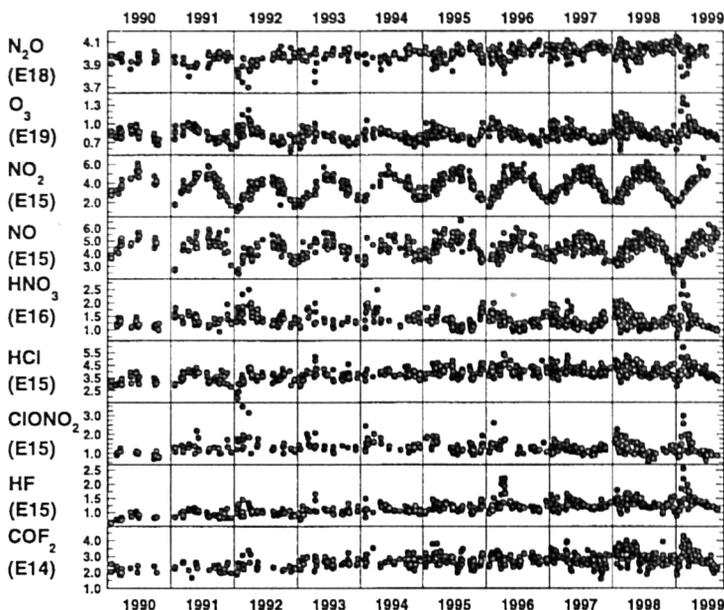


Figure 1. Sample data from 1990 to present, excerpted from the Liège data base of daily VCAs accumulated since the mid-1980s for more than 20 atmospheric gases. The values between parentheses are the multiplicative base ten exponents associated to the displayed VCAs.

Trend Characteristics

As short-term variability, seasonal- and inter-annual modulations are frequently present in the data sets (see Fig. 1), mean trend characteristics can only be derived when the time base is sufficiently long, so that the former can be properly identified and be dealt with in a quantified approach. Noticeable in Fig. 1 is the fact that most short-term variability occurs during the winter-spring months (December-May), so that secular trend determinations often are better defined by considering the summer-fall data only (June-November). In addition, we have calculated monthly mean columns in order to mitigate the impact of months with very different observation densities. With these considerations in mind (which would not be applicable if evaluating mass loadings), we have fitted the data points of HCl and ClONO₂ with polynomial functions of orders 5 and 2, respectively (see thin curves in Figure 2) to “visualize” the smooth, overall evolution of their trends. Further taking into account pre-1983 HCl column measurements to constrain the fittings, rates of change over successive time intervals have been evaluated as reported in Table 1. The Cl_y atom rate of change resulting from the summation of our HCl and ClONO₂ measurements, complemented by a ClO model background for northern mid-latitudes is also shown in Fig. 2 and documented in Table 1. The observed stabilization and initial slowing down of its loading is an unambiguous proof that the Montreal Protocol and its Amendments have been properly implemented and applied; the peak load of Cl_y identified around 1995-97 is consistent with the maximum concentration of organic chlorine (CCl_y) observed between 1992-93 by *in situ* ground-level measurement networks [4].

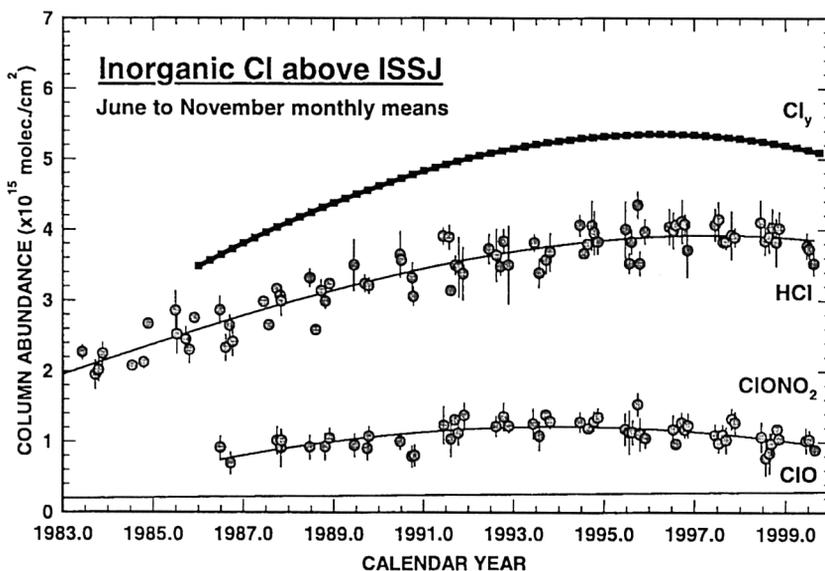


Figure 2. The evolution of the burdens of HCl and ClONO₂ above ISSJ based on June to November monthly mean VCAs. The reported Cl_y includes a ClO background load derived from model calculations.

Fluorine does not contribute to ozone depletion, because F atoms released from the photo-dissociation of fluor-bearing sources are quickly sequestered into carbonyl compounds (COF₂ and COClF) and subsequently into the ultimate reservoir HF which is very stable in the stratosphere. The primary interest in monitoring the inorganic fluorine (F_y) is as a surrogate of the amounts of its precursors (mainly the long-lived CFCs and HCFCs) having been photo-dissociated. The trends derived for HF, COF₂ and the related F_y are also reported in Table 1. The slightly smaller rate of growth during the recent years results from the relative loading mix of regulated CFCs and HCFC- and HFC-type substitutes.

Since last reported [5], the daytime burdens of the main reactive nitrogen species that are being monitored above ISSJ (i.e., HNO₃, NO, NO₂ and ClONO₂) have continued to show their characteristic variability and seasonal modulation (see Fig. 1). While ClONO₂ has been characterized before, the other compounds show relatively little long-term changes over the period 1986 to present. The corresponding NO_y budget has undergone a mean 1986-98 rate of change equal to $+(0.1 \pm 0.2) \%$ /yr, which is statistically insignificant, but remains consistent with the mean rate of increase found for its primary source gas N₂O over the same time interval [6]. Rates of change of NO_y and of its individual compounds are given in Table 1.

The mean rate of decrease derived from the 1984 to 1998 VCAs of O₃ above ISSJ is found equal to $-(0.35 \pm 0.2) \%$ /yr. This is significantly lower than the mean trend reported earlier for the period 1984-1995 [7, 8], i.e., $-(0.75 \pm 0.15) \%$ /yr; the cause is an observed O₃ column increase of $+(1.0 \pm 0.3) \%$ /yr after 1994 which is primarily due to specific atmospheric circulation characteristics that affected meridional transport in the northern hemisphere during the recent past years.

Species	Periods				Column	Remarks
	1984-85	1986-90	1991-95	1996-98	1998	
HCl	7.0 ± 4.5	5.6 ± 1.5	2.4 ± 0.8	-0.1 ± 0.8	4.03×E15	trends based on June-Nov. monthly means
ClONO ₂		5.8 ± 1.8	0.8 ± 1.9	-5.0 ± 2.5	1.05×E15	same
Cl _y		5.7	2.0	-1.0	-	same
HF	7.7 ± 4.0	6.5 ± 1.8	4.7 ± 1.0	3.0 ± 1.4	1.23×E15	trends based on June-Nov. monthly means
COF ₂		3.3 ± 1.6	2.8 ± 1.3	2.5 ± 1.4	2.80×E14	same
F _y		5.7	4.1	2.8	-	same
HNO ₃		← -3.9 ± 1.5	-0.2 ± 0.3 0.0 ± 1.5	→ 0.2 ± 1.0	1.28×E16	slightly lower columns after 1995 indicative; poorly defined
NO ₂		← 3.9 ± 1.3	0.7 ± 0.3 3.3 ± 1.0	→ 0.0 ± 1.0	3.74×E15	Pinatubo influence in 1992-94 same
NO		← 2.9 ± 1.0	0.1 ± 0.2 1.3 ± 0.8	→ -1.9 ± 1.1	4.30×E15	trend statistically insignificant low values in winter 1998-99
NO _y		← -1.2 ± 1.3	0.1 ± 0.2 0.6 ± 1.0	→ -1.0 ± 0.8	-	trend statistically insignificant indicative; poorly defined
O ₃		← -1.5 ± 1.0	-0.35±0.2 -0.8 ± 0.7	→ 0.6 ± 1.0	8.15×E18	1984-95 trend was twice as negative indicative, but col. increase since 1994

Table 1. Summary of timely rates of change expressed in %/yr of VCAs derived from remote solar observations at the Jungfraujoch for a series of compounds discussed in this paper. All uncertainties correspond to one standard deviation. Mean 1998 columns are included for information.

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