RECENT TRENDS of INORGANIC CHLORINE and HALOGENATED SOURCE GASES above the JUNGFRAUJOCH and KITT PEAK STATIONS DERIVED from HIGH-RESOLUTION FTIR SOLAR OBSERVATIONS

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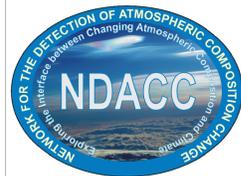(2) NASA-Langley Research Center, Hampton, VA, USA
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1. INSTRUMENTATION, SITES AND OBSERVATIONAL DATABASES

- We use solar observations from state-of-the-art Fourier Transform Infrared (FTIR) spectrometers operated under clear-sky conditions at the high-altitude International Scientific Station of the Jungfraujoch (ISSJ, 46.5ºN, 8.0ºE, 3580m a.s.l.) and at the Kitt Peak National Solar Observatory (KPNSO, 31.9ºN, 111.6ºW, 2090m a.s.l.). These sites are part of the Network for the Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org).

- High-resolution (0.003 to 0.009 cm^{-1}) IR absorption solar spectra relevant to the present study have been recorded regularly either with MCT or INSB detectors, using a suite of optical filters which, altogether, cover the 2 to 16 micron spectral range. The earliest measurements are available from KPNSO (1977) while regular recording of FTIR spectra started in 1984 at ISSJ.

- About two dozen atmospheric species are actually retrieved from the ground-based FTIR ISSJ observations. In the present study, we have focused on a suite of long-lived halogenated species: HCl, ClONO$_2$, CCl$_3$F (CFC-11), CCl$_2$F$_2$ (CFC-12), CHClF$_2$ (HCFC-22), CCl$_4$ and SF$_6$.

Target species	Limits (cm^{-1})
HCl	2925.740 – 2926.060
ClONO$_2$	779.300 – 780.600 then 780.050 – 780.355
CCl$_3$F	830.000 – 860.000
CCl$_2$F$_2$	922.500 – 923.600
CHClF$_2$	828.750 – 829.400
CCl$_4$	785.000 – 807.000
SF$_6$	947.800 – 948.150

TABLE 1. Microwindows used in the ISSJ retrievals.

2. RETRIEVAL STRATEGY AND TREND DETERMINATION

- All retrievals have been performed either with the SFIT-1 or the SFIT-2 algorithms which allow to retrieve total columns of the target gases. Moreover, information on their vertical distributions with altitude can generally be derived when using SFIT-2 which implements the Optimal Estimation Method formalism of Rodgers [1].

- The retrievals have been performed in carefully selected microwindows encompassing well characterized features of the target species, seeking also for minimum absorptions by other telluric gases or solar lines. Table 1 lists the microwindows used for each species.

- Line parameters are from recent HITRAN spectroscopic compilations [e.g. 2], augmented with pseudoline parameters fitted to the measured cross sections of CFC-11, -12, HCFC-22, CCl$_4$, SF$_6$ and ClONO$_2$, by G.C. Toon (NASA-Jet Propulsion Laboratory). Balloon-, space-based measurements or model simulations are used as a priori information for the target and interfering species.

- Annual trends have been determined with a tool developed by one of us [3]. The statistical analysis employs a bootstrap re-sampling method to determine the long-term change and intra-annual variability affecting the time series as well as the confidence levels associated to the retrieved quantities. All the uncertainties provided in this communication correspond to the 95% confidence interval.

- The function fitted to the various time series is a combination of a linear component and of a 3rd order Fourier series, i.e.:

$$F(t,b) = c_0 + c\,(t-t_0) + b_1 \cos 2\Pi(t-t_0) + b_2 \sin 2\Pi(t-t_0) + b_3 \cos 4\Pi(t-t_0) + b_4 \sin 4\Pi(t-t_0) + b_5 \cos 6\Pi(t-t_0) + b_6 \sin 6\Pi(t-t_0)$$

where c_0 is the concentration at the reference time t_0 for the linear component (deseasonalized data), and c is the annual trend.

BACKGROUND INFORMATION: EVOLUTION OF CHLORINE IN THE ATMOSPHERE AND THE MONTREAL PROTOCOL

- Chlorine atoms participate to stratospheric ozone depletion through the ClO$_x$ catalytic cycle first described by Molina and Rowland in 1974. Moreover, heterogeneous reactions taking place on polar stratospheric clouds also contribute to important ozone loss.

- Most of the atmospheric sources of chlorine are of anthropogenic origin. In particular, the long-lived CFCs -which are also potent greenhouse gases- have been significant contributors to the buildup of Cl. They were massively released to the atmosphere, following intensive use in many industrial and domestic applications. Then, their progressive photolysis frees Cl and F atoms in the lower stratosphere.

- The Montreal Protocol (1987) on substances that deplete ozone has set up and reinforced through Amendments and Adjustments a phase-out schedule for the production of all important chlorine- and bromine- bearing source gases, among which: CFCs, HCFCs, Halons, CCl$_4$, CH$_3$CCl$_3$.

- As a result of these progressive bans, emissions of chlorinated source gases have been drastically reduced and the global concentration of tropospheric chlorine has peaked in 1993. In turn, the concentration of stratospheric chlorine has reached its maximum in 1996-1997, it is now slowly decreasing.
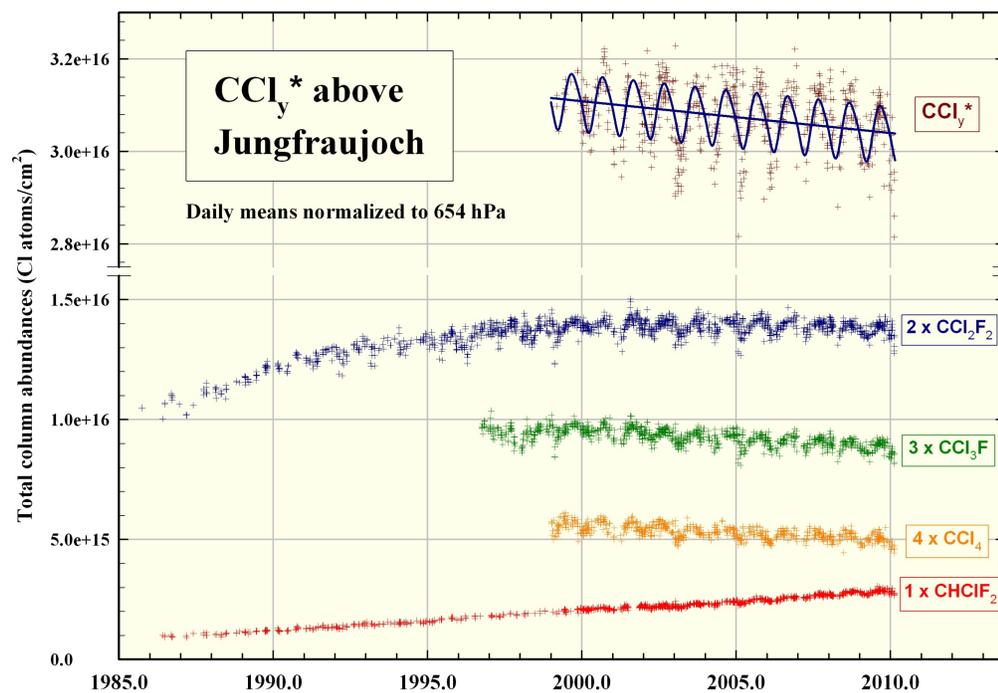
FIGURE 1. Temporal evolution of the long-lived chlorinated source gases retrieved from the Jungfraujoch observational data base, weighted by the number of Cl atoms in each species (notice the vertical scale break). Data points correspond to daily means normalized to 654 hPa. The upper data set is the sum of the individual contributions, for days with simultaneous measurements available. It is noted CCl$_y$* since it does not represent the total organic chlorine in the atmosphere, with two significant contributors missing (CH$_3$Cl and CFC-113). Altogether, the four species retrieved from ISSJ observations correspond to ~72% of the total CCl$_y$ budget for the year 2004 [4]. The seasonal signals seen in most time series essentially result from the tropopause height changes throughout the year.
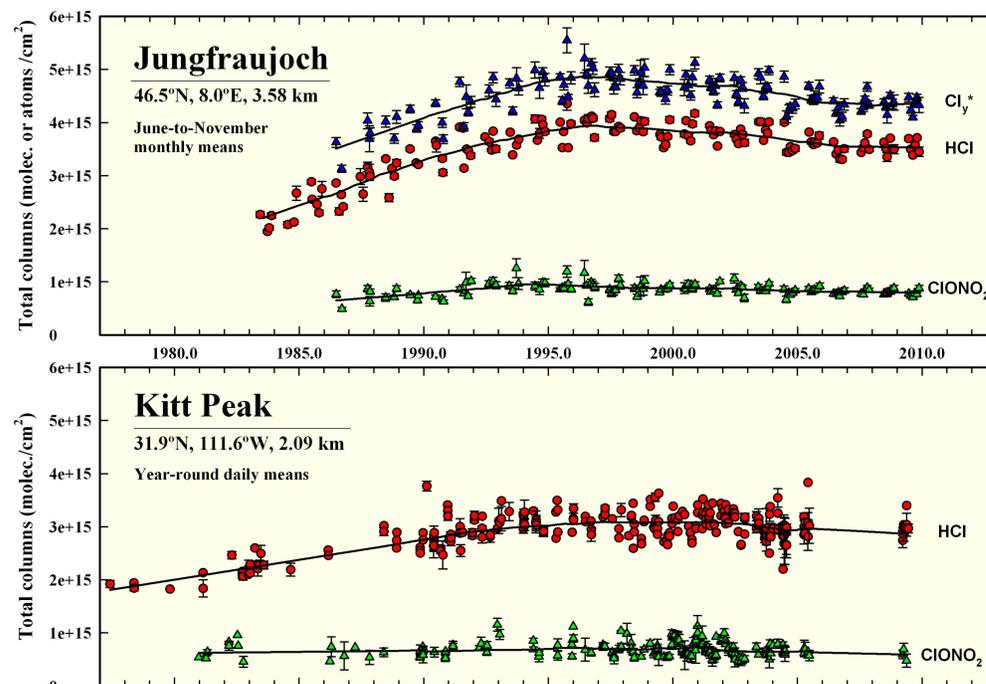
FIGURE 2.

Upper frame: Jungfraujoch time series of monthly mean total columns of HCl (red circles), ClONO$_2$ (green triangles) and their summation (blue triangles) which is a good proxy of the total inorganic chlorine, since these two reservoirs represent ~92% of Cl$_y$ at mid-latitude, in absence of chlorine activation [5]. Error bars correspond to the standard deviations around the monthly means. Only June to November months are reproduced here since they are less affected by variability resulting from meridional transport and subsidence events occurring essentially during winter-springtime. Continuous thick curves correspond to non-parametric least square fits to the monthly means, they help appraising the temporal evolution of the loadings of inorganic chlorine at mid-latitude.

Lower frame: Time series of daily mean total columns of HCl (red circles) and ClONO$_2$ (green triangles) above Kitt Peak. There is no data available in the 2006-2008 time frame due to a prolonged instrumental failure.

Overall: the data sets indicate that after a buildup in chlorine which lasts until about 1996-1997, at mean rates larger than 3%/yr, we have then observed a decrease in inorganic chlorine. Post-peak trend values are listed in Table 2, they are compared to data derived from modeled time series produced by KASIMA [6] for the two stations under investigations here.

TABLE 2.

Table 2 lists all trend values derived from the available Jungfraujoch and Kitt Peak daily mean time series, in terms of annual total column (Cl or F atoms/cm^2) or percent change. The time periods considered are 2001-2010 for the source gases, 1996-2009 for the reservoirs. We also provide in green trend values derived from KASIMA runs (1996-2008) performed for both sites, for the reservoir species. For Jungfraujoch and to avoid the impact of sampling, only model data coincident with measurements are included in the trend evaluations. For Kitt Peak, there is much less measurement days and model data are not available for 2009; hence the trend evaluations for the KASIMA runs were performed considering all synthetic data (see values between brackets).

CCl$_y$* is decreasing slowly, at a rate of -0.20%/yr. The largest negative contribution of CFC-11 is actually balanced by the accumulation of HCFC-22 (+8.7x10^{13} Cl atoms/cm^2 per year) whose partial ban by the Montreal Protocol has only started in 2005.

Sulfur hexafluoride (SF$_6$) is targeted by the Kyoto Protocol since it is a very strong greenhouse gas with an atmospheric lifetime of more than 3000 yr. Both the ISSJ and KPNSO time series indicate a steady increase of that species, with annual changes of about 0.40x10^{13} molec./cm^2 (with actual total columns larger than 1.0x10^{14} molec./cm^2 at both sites).

For inorganic chlorine, all trend values are consistent for the two sites when accounting for their associated uncertainties, and significant decreases are observed for HCl and ClONO$_2$. In all cases however, KASIMA modeled data predict statistically lower rates of decline and causes for this discrepancy are currently under investigation (see also EGU2010-8100 by Ruhnke et al).

		Jungfraujoch (46.5ºN)		Kitt Peak (31.9ºN)	
Annual changes for halogenated source gases, over 2001 -2010					
		10^{13} atoms/cm^2	%	10^{13} atoms/cm^2	%
CFC-11		-7.89 ± 0.54	-0.83 ± 0.06	--	--
CFC-12		-2.04 ± 0.61	-0.15 ± 0.04	--	--
CCl$_4$		-5.97 ± 0.50	-1.09 ± 0.09	--	--
HCFC-22		+8.70 ± 0.15	+4.22 ± 0.07	--	--
CCl$_y$		**-6.02 ± 1.67**	**-0.19 ± 0.05**	--	--
SF$_6$ [1988-2010]		+2.22 ± 0.06	+14.0 ± 0.40	+2.40 ± 0.60	+29 ± 7
Annual changes for inorganic chlorine, over 1996 -2009					
HCl	FTIR	-3.59 ± 0.42	-0.87 ± 0.10	-1.74 ± 1.08	-0.55 ± 0.34
	KASIMA	-0.96 ± 0.35	-0.29 ± 0.11	[-0.86 ± 0.11]	[-0.34 ± 0.04]
ClONO$_2$	FTIR	-0.91 ± 0.27	-0.90 ± 0.27	-0.96 ± 0.62	-1.27 ± 0.82
	KASIMA	-0.55 ± 0.16	-0.72 ± 0.21	[-0.31 ± 0.04]	[-0.57 ± 0.08]
Cl$_y$	FTIR	**-4.80 ± 0.72**	**-0.93 ± 0.14**	--	--
	KASIMA	**-1.67 ± 0.60**	**-0.41 ± 0.15**	--	--

Rem.: Annual percent changes are computed using 2001, 1996 or 1988 total columns as reference (c_0) for the chlorinated source gases, the Cl$_y$ species or SF$_6$, respectively.

References

[1] Rodgers, C.D., Characterisation and error analysis of profiles derived from remote sensing measurements, J. Geophys. Res., 95, 5587-5595, 1990.
[2] Rothman, L.S. et al., The HITRAN 2008 molecular spectroscopic database, J. Quant. Spectrosc. Radiat. Transfer, 110, 533-572, 2008.
[3] Gardiner, T. et al., Trend analysis of greenhouse gases over Europe measured by a network of ground-based remote FTIR instruments, Atmos. Chem. Phys., 8, 6719-6727, 2008.
[4] Chapter 1 of Scientific Assessment of Ozone Depletion, WMO-Report No 50, 2006.
[5] Zander, R. et al., The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations, Geophys. Res. Lett., 23, 2357-2360, 1996.
[6] Kouker, W. et al., The Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA), Version 2, Fzk Technical-Report Nr 6278, Karlsruhe, Germany, 1999.

Jungfraujoch 46.5ºN, 8.0ºE, 3.58 km — June-to-November monthly means — Cl$_y$* / HCl / ClONO$_2$

Kitt Peak 31.9ºN, 111.6ºW, 2.09 km — Year-round daily means — HCl / ClONO$_2$

CCl$_y$* above Jungfraujoch — Daily means normalized to 654 hPa — CCl$_y$* / 2 x CCl$_2$F$_2$ / 3 x CCl$_3$F / 4 x CCl$_4$ / 1 x CHClF$_2$