# The evolution of the inorganic fluorine budget since the mid-1980s based on FTIR measurements at northern mid-latitudes


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## 1. Databases and methodology

In this work, we define the total inorganic ($F_y$*) and total organic ($CF_y$) fluorine as follow:

$$F_y^* = [HF] + 2 \times [COF_2] \quad (1)$$

$$CF_y = [CFC\text{-}11] + 2 \times [CFC\text{-}12] + 3 \times [CFC\text{-}113] + 4 \times [CFC\text{-}114] + 5 \times [CFC\text{-}115] + 2 \times [HCFC\text{-}22] + [HCFC\text{-}141b] + 2 \times [HCFC\text{-}142b] + 2 \times [H\text{-}1211] + 3 \times [H\text{-}1301] \quad (2)$$

where the brackets designate the total (or partial) vertical abundance of a given species, where CFC-, HCFC- and H- stand for ChloroFluoroCarbon, HydroChloroFluoroCarbon and Halon, respectively and where each fluorine species is weighted by the number of its fluorine atoms.

| Data set | Description | Location | Products[a] | Covered time span for this study |
|---|---|---|---|---|
| FTIR | Ground-based solar IR absorption observations | Jungfraujoch station (46.5°N, 8°E, 3580m) | HF, $COF_2$ | March 1984 – December 2010 |
| KASIMA | 3-D Chemical Transport Model | Data simulated for the Jungfraujoch | HF, $COF_2$ | January 1985 – December 2010 |
| SLIMCAT | 3-D Chemical Transport Model | Data simulated for the Jungfraujoch | HF, $COF_2$ | January 1985 – July 2010 |
| HALOE v19 | Satellite observations by solar occultations | [41-51]°N latitude belt | HF [15-35] | October 1991 – September 2004 |
| ACE-FTS v3 | Satellite observations by solar occultations | [41-51]°N latitude belt | HF [15-55], $COF_2$ [15-35] | March 2004 – September 2010 |

[a] Provide the name of gases for which total columns are derived. For satellite data, only partial columns are available. The altitude ranges of these partial columns are specified in kilometers between the brackets, for each molecule.

**Table 1** - Some characteristics of the five datasets used in our inorganic fluorine inventory.

COClF was not included in our inorganic inventory as its detection from ground-based FTIR measurements at Jungfraujoch is problematic, principally due to strong interferences with water vapor. Such exclusion does not constitute a critical issue since HF and $COF_2$ altogether represent an excellent proxy - denoted here by $F_y$* - for inorganic fluorine at northern mid-latitudes ( see panel #2).

All datasets involved in our fluorine inventory are presented in Table 1. According to Eq. (1), HF and $COF_2$ (when available) daily mean time series have been summed over the 1985-2010 time period to produce inorganic fluorine $F_y$* data sets. An example of corresponding FTIR monthly mean time series is displayed in Figure 1. For both KASIMA and SLIMCAT CTMs, we have considered HF and $COF_2$ modeled daily values for all coincident day with FTIR observations. For satellite data, individual observations recorded in the [41-51]°N latitude belt have been selected and averaged to produce daily mean partial column time series, whose altitude ranges are provided in Table 1. No time coincident criterion with FTIR data has been applied, in order to maximize the number of data available for the trend analysis. The time periods covered by the sattelite observations are also shorter, as specified in the last column of Table 1.

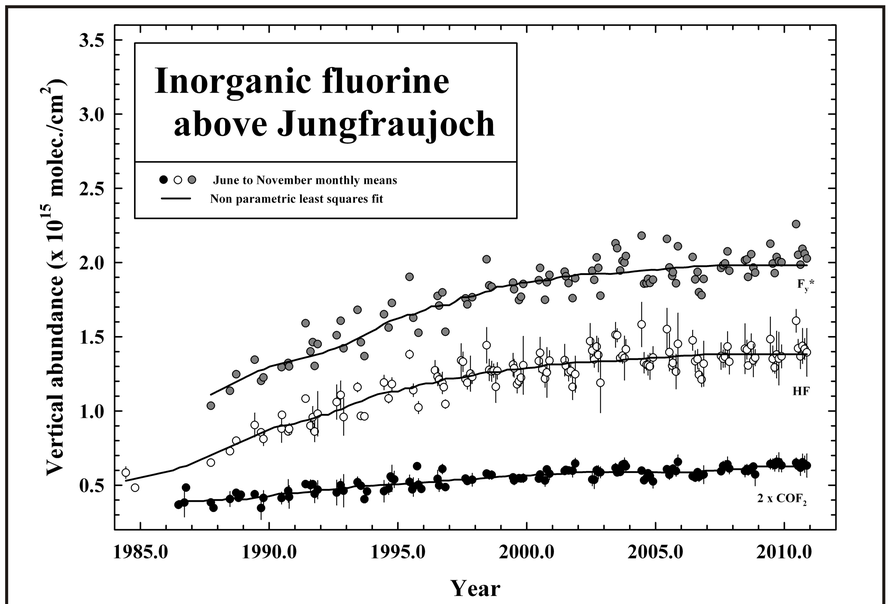


**Figure 1** - Time series of monthly mean total vertical column abundances of 2 x $COF_2$ (black dots), HF (white dots) and their sum $F_y$* (grey dots) derived from FTIR measurements at Jungfraujoch between 1984 and 2010. Only measurements from June to November are shown to avoid the significant variability observed during winter and spring. The black curves through each time series represent non-parametric least squares fits, in order to better appraise their temporal evolutions. For the two lower time series, error bars are 1-σ standard deviation around monthly mean values. The retrieval strategies used to derive the HF and $COF_2$ time series are described in Duchatelet et al. [2010] and Duchatelet et al. [2009], respectively.

## 2. Trend analysis

Trend values for four successive time periods (namely 1985-1995, 1995-2000, 2000-2005 and 2005-2010) have been deduced from FTIR, model and space daily mean time series (produced by following the method described in panel #1) by using a bootstrap resampling approach [Gardiner et al., 2008]. For each time period, trends expressed in relative values are plotted in Figure 2.

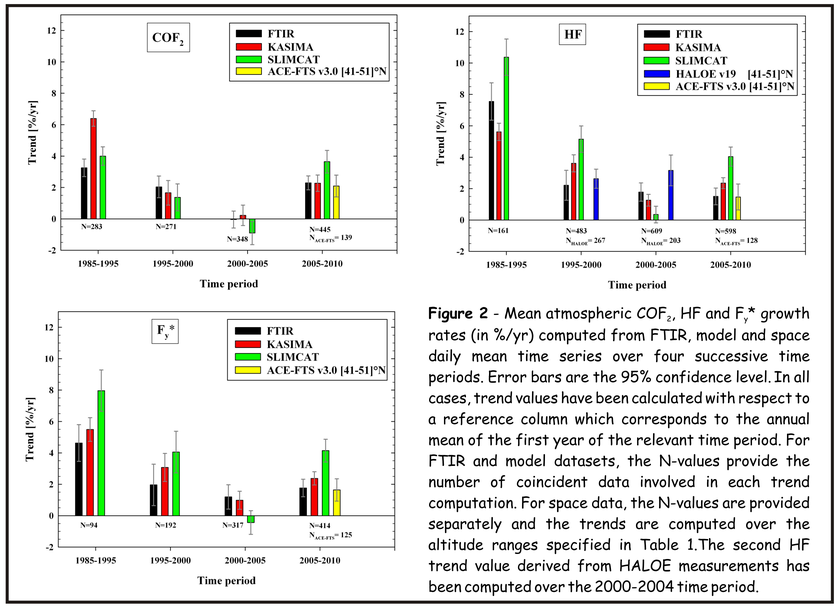


**Figure 2** - Mean atmospheric $COF_2$, HF and $F_y$* growth rates (in %/yr) computed from FTIR, model and space daily mean time series over four successive time periods. Error bars are the 95% confidence level. In all cases, trend values have been calculated with respect to a reference column which corresponds to the annual mean of the first year of the relevant time period. For FTIR and model datasets, the N-values provide the number of coincident data involved in each trend computation. For space data, the N-values are provided separately and the trends are computed over the altitude ranges specified in Table 1.The second HF trend value derived from HALOE measurements has been computed over the 2000-2004 time period.

The FTIR trend values reproduced on the two top panels of Figure 2 indicate a significant slowing in the mean accumulation rates of both $COF_2$ and HF until 2005. For $COF_2$, this decrease is particularly obvious during the 2000-2005 time period. Over the last five years, our FTIR data further show a significant rise in the linear trend of this gas, at a mean rate close to the value that prevailed ten years before (i.e. about 2.3 %/yr). The trend analysis of our FTIR data set further shows a stabilization in the HF growth rate during the last ten years, at about 1.6 %/yr.

We further notice that the important changes observed in the $COF_2$ rate of growth during the last ten years do not significantly impact the $F_y$* trend, which remains quite constant since the beginning of this century at about 1.5 %/yr. That is explained by the fact that the $COF_2$ contribution to total inorganic fluorine is low with respect to HF. Indeed, based on our FTIR data set, we have deduced partitioning values for HF and $COF_2$ close to 65% and 30%, respectively, these values remaining significantly unchanged during the last twenty-five years.

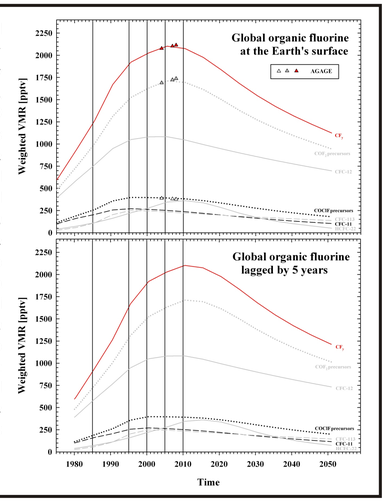


**Figure 3** - Top panel: global temporal evolution of the most abundant halogenated source gases, weighted by the number of F atoms in each species, according to A1 emission scenario of WMO [2007]. The $COF_2$ and COClF precursors curves correspond to the sum of the relevant individual contributions (not all displayed here, for clarity). The total organic fluorine $CF_y$ curve has been computed according to Eq. (2). These three latter curves are compared to corresponding amounts derived from AGAGE surface measurements (colored triangles). Bottom panel: same curves as in the top panel, but lagged by 5 years to take into account the atmospheric transport. In both panels, the vertical black solid lines delimit the successive time periods considered in our trends computation.

It appears from bottom panel of Figure 3 that during the three first time periods under investigation, the stratospheric increase rate of the $COF_2$ precursors slows significantly, as a direct consequence of the Montreal Protocol. Such a behavior qualitatively explains the significant slowing observed in the rates of growth of $COF_2$ during the corresponding time period. Between 2005 and 2010, the A1 emission scenario predicts a stratospheric increase for $COF_2$ precursors that remains almost unchanged with respect to the previous time period, probably because the stabilization or the decline of the most abundant CFCs is partially compensated by the increase of substitute products such as HCFC-22. This is however inconsistent with the significant rise observed in recent $COF_2$ trend values reported in Figure 2. This difference could perhaps partially result from the fact that recent HCFC-22 growth is more rapid that the one assumed in the A1 emission scenario [WMO, 2010], as also highlighted when comparing A1 curves with AGAGE measurements (see the two upper curves of top panel of Figure 3). According to A1 curves, the almost unchanged growth rate in the stratospheric $CF_y$ loading during the last ten years lets suggest a similar behavior for the total inorganic fluorine $F_y$ and also for HF (considering the dominant contribution of this fluorine reservoir to $F_y$) as indeed observed from the recent FTIR and ACE-FTS trend values. Anyway, the recent $COF_2$ re-increase definitely needs to be understood with the help of additional numerical model simulations.


**References**

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