Atmospheric circulation changes identified thanks to ground-based FTIR monitoring of hydrogen chloride (HCl)

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Monitoring the success of the Montreal Protocol on substances that deplete stratospheric ozone is one of the primary tasks of the NDACC network. Among the various techniques involved, giving access to numerous relevant parameters, the ground-based FTIR instruments contribute significantly by providing total and partial columns of key tropospheric and stratospheric constituents. Indeed, high-resolution solar infrared spectra contain the signatures of a suite of halogenated organic source gases. The current list includes CFC-11, CFC-12, HCFC-22, HCFC-142b, CCl_4, CF_4, SF_6 (e.g., Krieg et al., 2005; Zander et al., 2008; Rinsland et al., 2012; Mahieu et al., 2013a; Mahieu et al., 2014a) and efforts are ongoing to expand this list. In addition, the respective evolutions of the inorganic chlorine and fluorine loadings in the stratosphere are also accessible to this technique through observations of the main reservoirs, i.e. hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$), hydrogen fluoride (HF) and carbonyl fluoride (COF_2). Time series and trends of all these species have been reported and analyzed in successive studies, notably allowing characterising from the ground the rapid increase of inorganic chlorine (Cl_y) in the Earth's stratosphere (e.g., Zander et al., 1987; Rinsland et al., 1991, 1996; Reisinger et al., 1995), following large emissions of anthropogenic halogenated source gases during the 1970s to 1990s. Later, studies involving several NDACC ground-based FTIR stations provided evidence for a stabilisation of HCl and $ClONO_2$ around the mid-1990s (Rinsland et al., 2003), and then a near-global characterisation of the Cl_y decrease at rates close to 1%/yr in both hemispheres at 17 sites between 80°N and 78°S (Kohlhepp et al., 2012).

Recently, Mahieu et al. (2013b) concentrated on the post-peak evolution of HCl using the latest observations available from the Jungfraujoch station (Swiss Alps, 46.5°N) and from a composite satellite partial column time series based on infrared solar occultation measurements performed by HALOE (Halogen Occultation Experiment, onboard UARS; Russell et al., 1993) until 2005 and by ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer, onboard SCISAT; Bernath et al., 2005) from 2004 onwards. Although this study confirmed for the 1997-2007 time period the amplitude of the downward trend determined by Kohlhepp et al. (2012), both the ground-based and satellite data sets revealed a significant re-increase (at the 2σ level of uncertainty) of the HCl reservoir in the Northern Hemisphere mid-latitude stratosphere after 2007. This feature was unexpected given the well documented and smooth decrease of total organic chlorine in the troposphere (e.g. WMO 2010, 2011). At that time it was possible to exclude that a change in the partitioning among the main inorganic chlorine reservoirs was responsible for the HCl upturn since the Jungfraujoch time series combining HCl and $ClONO_2$ columns also exhibited a significant increase of Cl_y after 2007. Possible causes for this HCl upturn include a change in atmospheric circulation or the substantial contribution of new unknown chlorine-bearing source gases to the organic chlorine budget monitored by the AGAGE and NOAA/ESRL in situ networks.

These observations and questions stimulated a follow up study including data from other NDACC stations to check whether the recent HCl increase was a global atmospheric feature. We also

used the GOZCARDS satellite data set (merging measurements of HALOE, ACE-FTS and Aura/MLS; Froidevaux et al., 2013) in order to confirm the ground-based observations and to get information on the altitude range where the changes were taking place as well as simulations by the state-of-the-art 3-D chemistry transport models SLIMCAT and KASIMA (Kohlhepp et al., 2012).

The paper reporting about these investigations has recently been published in Nature (Mahieu et al., 2014b) and the main findings are as follows:

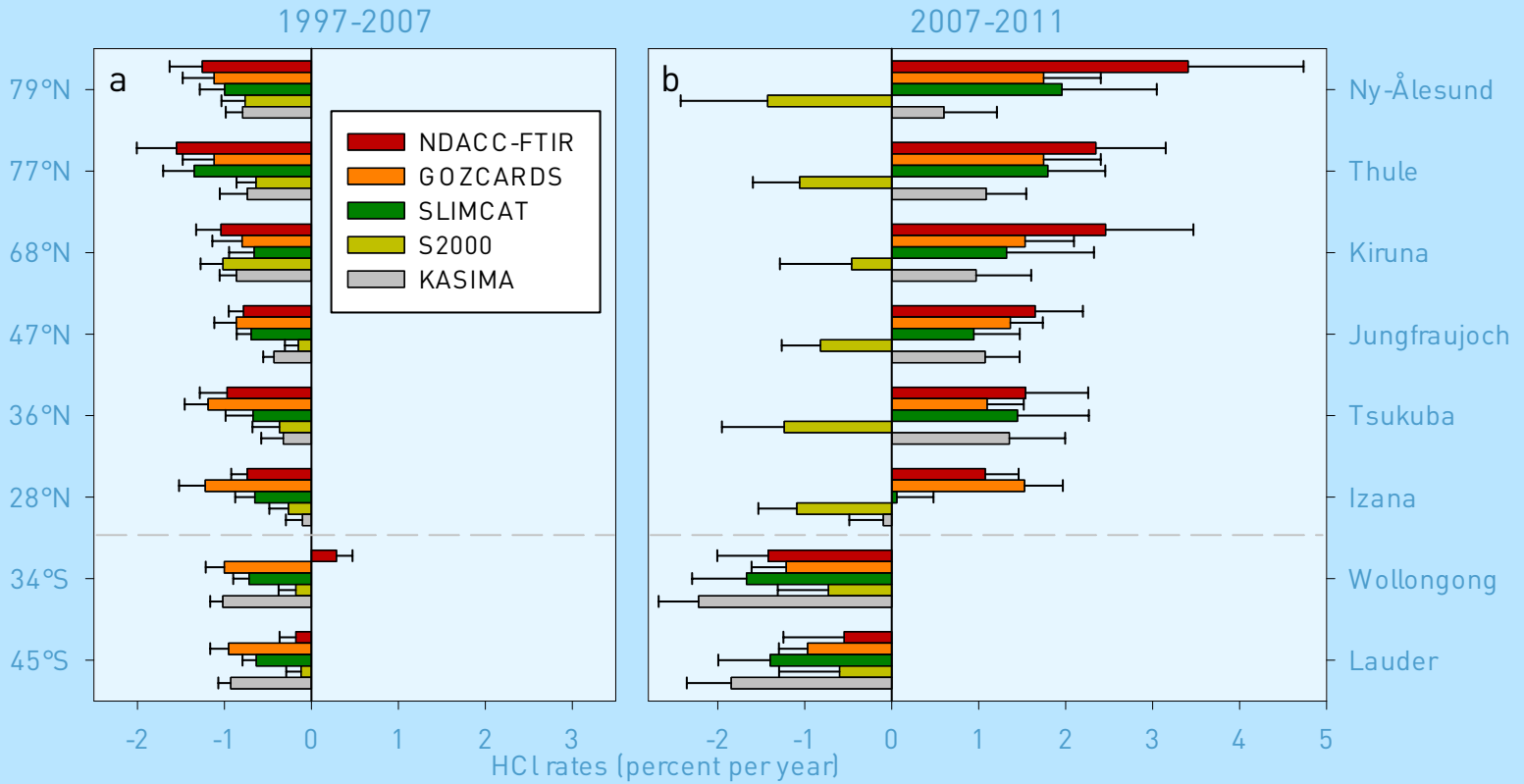

Figure 1. HCl relative rates of changes in %/yr determined for the 1997-2007 (panel a) and 2007-2011 (panel b) time periods, from the various observational and modeled data sets (see colour key for their identification) at eight NDACC stations and latitudes. The error bars correspond to the 2σ level of uncertainty (from Mahieu et al., doi:10.1038/nature13857, 2014b).

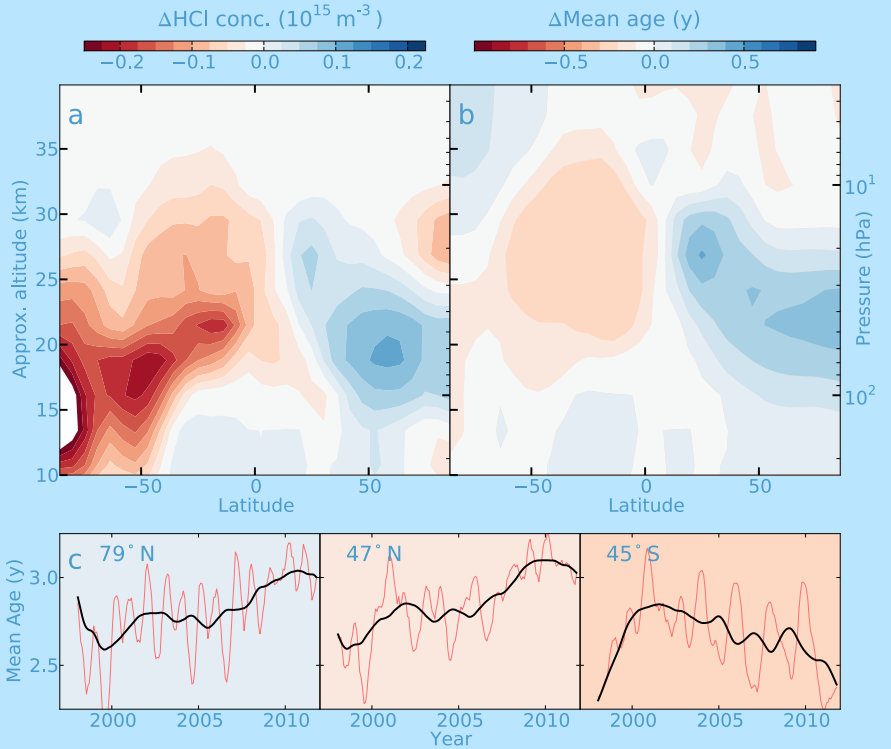

Figure 2. Mean differences of the HCl concentration (panel a) and age-of-air (panel b) between 2010/2011 and 2005/2006 as a function of altitude and latitude, as derived from the standard SLIMCAT run (from Mahieu et al., doi:10.1038/nature13857, 2014b).

- As shown in Figure 1a, HCl negative rates of changes are found at the eight NDACC sites for 1997-2007 (in red), in agreement with the satellite data (in orange); SLIMCAT and KASIMA model simulations using ERA-Interim meteorology and surface source gases mixing ratios from the WMO A1 scenario confirm these trends in sign and amplitude (in green and grey, respectively).
- For 2007-2011, we observed a contrasting situation, with NDACC, GOZCARDS, SLIMCAT and KASIMA showing significant increases of HCl in the Northern Hemisphere, at rates up to 3%/yr, while the various data sets consistently show HCl decreases in the Southern Hemisphere.
- A dedicated SLIMCAT run (denoted S2000, light green) used constant 6-hourly winds of 2000, from 2000 onwards, to study the impact of atmospheric dynamics. Clearly, this run does not produce the HCl increase in the Northern Hemisphere (Fig. 1b) and since the only difference between the standard and S2000 SLIMCAT run resides in the meteorological forcings, we conclude that these are responsible for the HCl upturn.

Stratospheric circulation changes have been evaluated using an indicator of mean age-of-air available in both models as an idealised tracer with a linearly increasing tropospheric mixing ratio. Figure 2 shows the spatial distribution of the HCl concentration and mean age-of-air changes between 2005/2006 and 2010/2011, as derived from the standard SLIMCAT run. These plots indicate an obvious asymmetry between both hemispheres, with a clear correlation in the lower stratosphere between the HCl increase/decrease over the time period under investigation and a slower/faster Brewer-Dobson circulation.

The slower and specific transport pathways followed by the air masses over the recent years in the Northern Hemisphere has allowed a longer exposure to strong ultraviolet radiation responsible of the photolysis of the source gases, ultimately resulting in a larger relative conversion into the reservoir species.

The most important point is that by combining the NDACC observations with state-of-the-art CTM simulations, we can conclude that the recent HCl increase which occurred in the Northern Hemisphere over 2007-2011 does not

result from rogue emissions of chlorinated source gases. Hence, the Montreal Protocol is well on track and will lead to an overall reduction of the stratospheric chlorine abundance required to ensure ozone recovery in the decades to come. Our study also underlines the constant need for reliable long-term monitoring of the stratospheric composition, both from the ground and from space.

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