On the Emissions of HCFCs and CFCs Potentially Related to HFC Production

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Based on the Montreal Protocol on Substances That Deplete the Ozone Layer there is a general ban on the use of chlorofluorocarbons (CFCs) since 2010, and an ongoing phase-out for hydrochlorofluorocarbons (HCFCs). The regulations are in place for 'emissive' use and essentially apply to end-products in refrigeration, foam blowing, fire retardants and as solvents. The regulations do not apply to the use of these chemicals as feedstock or process agents. Leakage of CFCs and HCFCs process agents during production of hydrofluorocarbons (HFCs) may lead to detectable changes in the atmosphere.

Recent studies have shown the presence of HCFC-133a (CF_3CH_2Cl) and HCFC-31 (CH_2ClF) in the atmosphere, two compounds, for which no purposeful use is known. Speculations are in place on their atmospheric presence from emissions during HFC manufacture. We present updated atmospheric records of HCFC-133a and HCFC-31 and derive emissions based on the AGAGE (Advanced Global Atmospheric Gases Experiment) 12-box model. HCFC-133a atmospheric abundances and emissions have reversed multiple times over the past decades. In contrast, HCFC-31 has declined over the past years to ~0.1 ppt (parts-per trillion, nmol/mol) in the northern hemisphere.

We also provide evidence for increased growth of CFCs, in particular CFC-115. An atmospheric history for this compound is derived from archived air samples and *in situ* measurements at AGAGE stations. 12-box model calculations show a decline in the global growth rates of CFC-115 from a maximum of 0.45 ppt/yr in the late 1980s to 0.005 ppt/yr in 2009 but a re-increasing growth to 0.02 ppt/yr in the last years. If we assume this increase to be solely due to a change in emissions then these are globally increasing from ~0.6 kt/yr in 2009 to ~0.9 kt/yr in 2015. A source of CFC-115 is identified as impurity in the refrigerant HFC-125 for which CFC-115 is an intermediate in one possible production path. Also, high-resolution CFC-115 measurements from the Asian AGAGE stations show increasing pollution events (frequency and magnitutde) advected to the sites over the past years. The records are used in a FLEXPART regional model simulation to identify source regions of CFC-115 emissions. Our analysis shows 'hot-spot' emissions from the Asian mainland, which may explain some of the enhanced atmospheric growth.

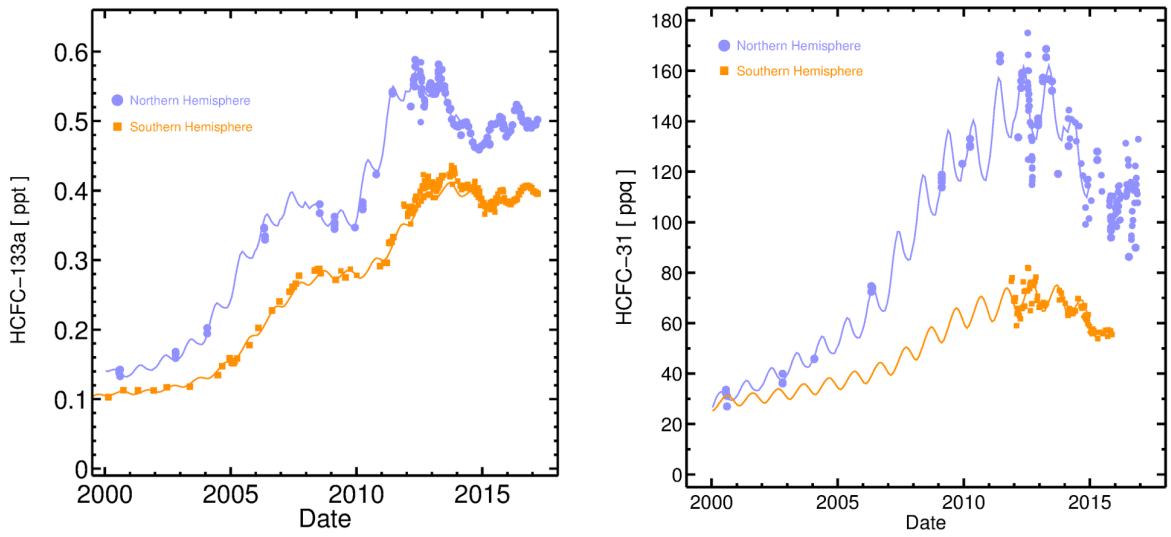

Figure 1. Atmospheric records of HCFC-133a (left) and HCFC-31 (right) (updated from Vollmer et al., 2015 and Schoenenberger et al., 2015)