Fourth Generation Anthropogenic Halogenated Greenhouse Gases

M.K. Vollmer and S. Reimann

Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland;
41-58-765-42-42, E-mail: martin.vollmer@empa.ch

Halogenated greenhouse gases are typically categorized into 'generations' of compound classes following the evolution of the regulatory phases and their properties related to climate. Ozone-Depletion Substances (ODSs) are the first two generations with the CFCs (chlorofluorocarbons) and halons (fully halogenated compounds) defining the first generation and the HCFCs (hydrochlorofluorocarbons, partially halogenated compounds) defining the second generation. Both these are generally regulated under the Montreal Protocol. They were followed by the F-gases, typically long-lived HFCs (hydrofluorocarbons) and PFCs (perfluorocarbons), which have no chlorine and bromine but are usually compounds with high radiative forcing and hence included in the regulations of the Kyoto Protocol. Here we present first measurements of a fourth generation of halogenated trace gases (halogenated alkenes, HFOs), which are now under mass production and have started to appear in our atmosphere.

Their development was mainly driven by regulatory requirements (foremost the European F-gas regulation) to reduce the use of potent fluorinated greenhouse gases by compounds with much lower global warming potentials (GWPs). Partially-halogenated short-lived (weeks) propenes are part of the 4th generation. These are the here-discussed HFC-1234yf (HFO-1234yf, $CF_3CF{=}CH_2$), which is now installed in mobile air conditioners, HFC-1234ze(E) (trans-$CF_3CH{=}CHF$), used as refrigerant and foam-blowing compound, and HCFC-1233zd(E) (trans-$CF_3CH{=}CHCl$), which is used as a solvent. While not detectable for the first years of the measurements, we now find increasing abundances and pollution events at the high-altitude (3500 m) Jungfraujoch and the urban Duebendorf (Switzerland) sites (Figure 1).

The three compounds discussed here have short lifetimes (order of weeks). This is a beneficial feature from the climate perspective as their rapid removal from the atmosphere will likely result in a smaller accumulation compared to the previous generations. However, there are challenges that will require attention. Foremost is the necessity for a profound understanding of their decay products and the fate of these. For example, it is well known that HFC-1234yf decays to trifluoroacetic acid, a problematic environmental substance for ecosystems. Also the short lifetimes will bring new challenges to the modeling community when assessing the global distributions and top-down-derived emissions.

Because their lifetimes are of similar size as some of the atmospheric transport processes, these compounds may be of help to better understand air mass distributions once a better measurement network and a better understanding of their source distributions becomes available.

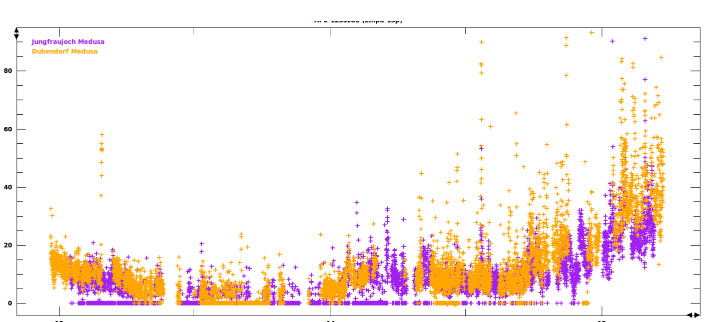

Figure 1. HCFC-1233zd(E) (trans-$CF_3CH{=}CHCl$) at Jungfraujoch (violet) and Dubendorf (yellow) for 2013 – March 2015. Y-axis is dry air mole fraction in ppq (parts-per-quadrillion, 10-15). Many of the early measurements yielded undetectable mole fractions and a seasonal cycle is apparent (lifetime 26 –46 days). Mole fraction started to increase rapidly at the end of 2014.