Name of research institute or organization:  
**Empa, Swiss Federal Laboratories for Materials Science and Technology**

Title of project:  
Halogenated Greenhouse Gases at Jungfraujoch

Part of this programme:  
AGAGE

Project leader and team:  
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Project description:  
Halogenated ozone-depleting substances (ODSs) and greenhouse gases (GHGs) have been monitored at Jungfraujoch since 2000. These measurements are combined with atmospheric transport models for identifying and quantifying national and regional emissions (Switzerland and neighboring countries). The "top-down" (observation based) estimates are then used to support "bottom-up" estimates of the national reporting authorities, which are based on industry information (import/export/manufacture). Furthermore, the measurements help to track global trends of ODSs and GHGs in the "background" air. Measurements at Jungfraujoch comprise a suite of over 50 compounds, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs and SF$_6$), and hydrofluorocarbons (HFCs), which are regulated under the Montreal and Kyoto Protocols, and additional halogenated hydrocarbons. Most of these compounds are core-substances measured by the AGAGE program (Advanced Global Atmospheric Gases Experiment), of which Empa is a partner. Measurements are conducted with 2 liters of air and using gas chromatography mass spectrometry techniques.

For the 2016 activities we chose to present an update for the HFOs (hydrofluoro-olefines) introduced in the last year’s report. The newly-added observations deliver a wealth of new information and results in this active field. HFOs, which are fluorinated alkenes (carbon double bonds) are the youngest (4th) generation of anthropogenic compounds used in refrigeration, as foam-blowing substances, and as solvents. They are intended to replace the strong ODSs chlorofluorocarbons (CFCs, first generation) and hydrochlorofluorocarbons (HCFCs, 2nd generation) as well as the strong GHGs hydrofluorocarbons (HFCs, 4th generation). While these HFOs have short atmospheric lifetimes (days to a few months) and hence are favoured from a climate perspective, their atmospheric decay products (in particular trifluoro-acetic acid, TFA) are of environmental concern in water and soil.

Based on measurements at Jungfraujoch and urban Dubendorf, Empa has published the world-wide first measurements of the three most-widely used HFOs in ambient air, HFC-1234yf (or HFO-1234yf, 2,3,3,3-tetrafluoroprop-1-ene, CF$_3$CF=CH$_2$), HFC-1234ze(E) (E-1,3,3,3-tetrafluoroprop-1-ene, trans-CF$_3$CH=CHF), and HCFC-1233zd(E) (E-1-chloro-3,3,3-trifluoroprop-1-ene, trans-CF$_3$CH=CHCl) (Vollmer et al., 2015).

HFC-1234yf has virtually been absent from ambient air at Jungfraujoch for the first years of measurements (Fig. 1). However during the last two years, this compound has been frequently detected at Jungfraujoch despite its short atmospheric lifetime (10 – 16 days), with abundances up to ~0.2 ppt (mole fraction, parts-per-trillion, 10$^{-12}$). Also, while some of the measurements at Dubendorf showed undetectable mole fraction (~0.004 ppt) in 2013 – 2014, HFC-1234yf was present in all air samples in 2015 – 2016. These results suggest that HCFC-1234yf is now used even more widely than in the first years of observations. The main use of
this compound is as refrigerant in mobile air conditioners. Most new cars are now equipped with a HFC-1234yf.

HFC-1234yf (lifetime 0.5 – 1 month) has become a widely-used foam-blowing agent and refrigerant. Measurements at Dubendorf have revealed largely elevated mole fractions since measurements began in 2013 and those from Jungfraujoch have shown detectable mole fractions in an increasing percentage of all samples over the past years. Earlier-noted peculiarly strong pollution events at Jungfraujoch have continued to appear over a few days in late winter of each year (see Fig. 1). The magnitude of these pollution events have raised concern about a potential local source of HFC-1234yf at Jungfraujoch. However, periodic measurements of laboratory air at the Sphinx observatory have not shown any elevated HFC-1234yf above the levels measured in the air drawn from the outside. Nevertheless, a temporary local source cannot be excluded (such as would occur during yearly maintenances or checks, e.g. fire detection systems). However, an investigation with the Jungfrau Railways has not revealed any known potential use of this compound. These yearly re-occurring large pollution events currently remain unexplained.

HCFC-1233zd(E) differs from the other two compounds as it is a compound also containing chlorine hence it is an ODS. However, given its short lifetime (1 – 1.5 months) its ozone-depletion potential is very small. Measurements of HCFC-1233zd(E) started only in in 2013, significantly later than those of the other two compounds mentioned in the present report. Measurements from both Jungfraujoch and Dubendorf showed very small abundances of this compound in the first two years of observations (~0.02 ppt) and the absence of pollution...
events. These observations suggested the absence of usage within the footprint of Jungfraujoch and Dubendorf but with longer-range transport of this compound to these sites. In the last two years, some pollution events have now been detected at Dubendorf and Jungfraujoch but still to a significantly lesser extent compared to HFC-1234yf and HFC-1234ze(E). It currently remains unclear where in Europe this compound is used and what its main applications are (most likely solvent and foam-blowing applications). Nevertheless, HCFC-1233zd(E) has likely become more widely used on a global scale. This is evident from the enhanced background mole fractions observed at Jungfraujoch and Dubendorf – this compound has been present at detectable levels in all samples over the past two years. Also, there is a strong seasonality in the background record, which is due to the seasonality in the hydroxyl radical acting as the main sink for HCFC-1233zd(E). The pronounced seasonality compared to HFC-1234yf and HFC-1234ze(E) is a further indication of the absence of close-by sources.

Measurements of all three HFOs have continued to deliver important information on these compounds. Efforts are now in place to extend these measurements to other AGAGE sites to improve our understanding of the distribution and quantitative use of these compounds in Europe and other populated parts of the world.

References

Key words:
Halogenated ozone-depletion substances (ODSs), greenhouse gases (GHGs), F-gases, hydrofluoroolefines (HFOs)

Internet data bases:
http://empa.ch/web/s503/climate-gases
https://agage.mit.edu/

Collaborating partners/networks:
Bundesamt für Umwelt (BAFU) / Federal Office for the Environment (FOEN)
Global Atmosphere Watch (GAW), World Meteorological Organization (WMO)
Advanced Global Atmospheric Gases Experiment (AGAGE)
ACTRIS – Aerosol, Clouds, and Trace Gases Research Network
Korea Polar Research Institute (KOPRI)
University of Bristol, UK

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