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:

Martin K. Vollmer, Stefan Reimann (project leader), Matthias Hill, Simon A. Wyss, Lukas Emmenegger

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 hydrofluoro-carbons (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 (4^{th}) 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, 2^{nd} generation) as well as the strong GHGs hydrofluorocarbons (HFCs, 4^{th} 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, $CF_3CF=CH_2$), HFC-1234ze(E) (E-1,3,3,3-tetrafluoroprop-1-ene, *trans*-$CF_3CH=CHF$), and HCFC-1233zd(E) (E-1-chloro-3,3,3-trifluoroprop-1-ene, *trans*-$CF_3CH=CHCl$) (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.

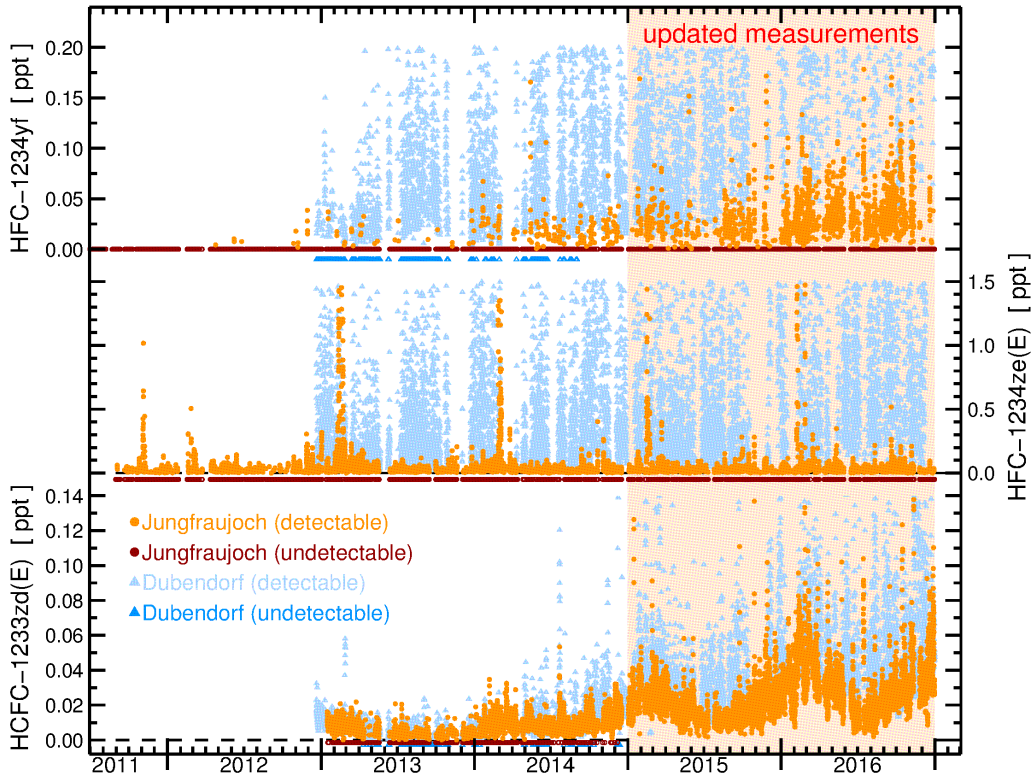

Figure 1. Atmospheric abundances of the 4th generation anthropogenic halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) at Jungfraujoch and urban Dubendorf. Undetectable mole fractions are separately shown as dark brown and dark blue symbols and are slightly shifted to negative values for better illustration. Above-detection-limit mole fractions are shown in orange and light blue whereas some of the higher abundances, particularly for Dubendorf, are not shown. Figure adopted from Vollmer et al., 2015 and updated to 2016.

HFC-1234ze(E) (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-1234ze(E) at Jungfraujoch. However, periodic measurements of laboratory air at the Sphinx observatory have not shown any elevated HFC-1234ze(E) 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

Vollmer, M. K., S. Reimann, M. Hill, D. Brunner, First observations of the fourth generation synthetic halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the atmosphere, Environ. Sci. Technol., 2703–2708, doi: 10.1021/es505123x (49), 2015.

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

Scientific publications and public outreach 2016:

Refereed journal articles and their internet access

Chirkov, M., G.P. Stiller, A. Laeng, S. Kellmann, T. von Clarmann, C.D. Boone, J.W. Elkins, A. Engel, N. Glatthor, U. Grabowski, C.M. Harth, M. Kiefer, F. Kolonjari, P.B. Krummel, A. Linden, C.R. Lunder, B.R. Miller, S.A. Montzka, J. Mühle, S. O'Doherty, J. Orphal, R.G. Prinn, G. Toon, M.K. Vollmer, K.A. Walker, R.F. Weiss, A.Wiegele, D. Young, Global HCFC-22 measurements with MIPAS: retrivval, validation, global distribution and its evolution over 2005–2012, Atmos. Chem. Phys., **16**, 3345–3368, doi:10.5194/acp-16-3345-2016, 2016. http://www.atmos-chem-phys.net/16/3345/2016/

Graziosi, F., J. Arduini, P. Bonasoni, F. Furlani, U. Giostra, A.J. Manning, A. McCulloch, S.J. O'Doherty, P.G. Simmonds, S. Reimann, M.K. Vollmer, M. Maione, Emissions of carbon tetrachloride (CCl_4) from Europe, Atmos. Chem. Phys., **16**, 12849–12859, doi:10.5194/acp-16-12849-2016, 2016.
http://www.atmos-chem-phys.net/16/12849/2016/

Helmig, D., S. Rossabi, J. Hueber, P. Tans, S.A. Montzka, K. Masarie, K. Thoning, C. Plass-Duelmer, A. Claude, L.J. Carpenter, A.C. Lewis, S. Punjabi, S. Reimann, M.K. Vollmer, R. Steinbrecher, J.W. Hannigan, L.K. Emmons, E. Mahieu, B. Franco, D. Smale, A. Pozzer, Reversal of global atmospheric ethane and propane trends largely due to US oil and natural gas production, Nature Geoscience, **9**, 490–495, doi: 10.1038/ngeo2721, 2016.
http://www.nature.com/ngeo/journal/v9/n7/abs/ngeo2721.html

Simmonds, P.G., M. Rigby, A.J. Manning, M.F. Lunt, S. O'Doherty, A. McCulloch, P.J. Fraser, S. Henne, M.K. Vollmer, J. Mühle, R.F. Weiss, P.K. Salameh, D. Young, S. Reimann, A. Wenger, T. Arnold, C.M. Harth, P.B. Krummel, L.P. Steele, B.L. Dunse, B.R. Miller, C.R. Lunder, O. Hermansen, N. Schmidbauer, T. Saito, Y. Yokouchi, S. Park, S. Li, B. Yao, L.X. Zhou, J. Arduini, M. Maione, R.H.J. Wang, D. Ivy, R.G. Prinn, Global and regional emissions estimates of 1,1-difluoroethane (HFC-152a, CH_3CHF_2) from in situ and air archive observations, Atmos. Chem. Phys., **16**, 365–382, doi:10.5194/acp-16-365-2016, 2016.
http://www.atmos-chem-phys.net/16/365/2016/

Trudinger, C.M., P.J. Fraser, D.M. Etheridge, W.T. Sturges, M.K. Vollmer, M. Rigby, P. Martinerie, J. Mühle, D.R. Worton, P.B. Krummel, L.P. Steele, B.R. Miller, J. Laube, F.S. Mani, P.J. Rayner, C.M. Harth, E. Witrant, T. Blunier, J. Schwander, S. O'Doherty, M. Battle, Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1800 inferred from ice core, firn, air archive and in situ measurements, Atmos. Chem. Phys., **16**, 11733–11754, doi:10.5194/acp-16-11733-2016, 2016.
http://www.atmos-chem-phys.net/16/11733/2016/

Vollmer, M.K., J. Mühle, C.M. Trudinger, M. Rigby, S.A. Montzka, C.M. Harth, B.R. Miller, S. Henne, P.B. Krummel, B.D. Hall, D. Young, J. Kim, J. Arduini, A. Wenger, B. Yao, S. Reimann, S. O'Doherty, M. Maione, D.M. Etheridge, S. Li, D.P. Verdonik, S. Park, G. Dutton, L.P. Steele, C.R. Lunder, T.S. Rhee, O. Hermansen, N. Schmidbauer, R.H.J. Wang, M. Hill, P.K. Salameh, R.L. Langenfelds, L. Zhou, T. Blunier, J. Schwander, J.W. Elkins, J.H. Butler, P.G. Simmonds, R.F. Weiss, R.G. Prinn, P.J. Fraser, Atmospheric histories and global emissions of halons H-1211 ($CBrClF_2$), H-1301 ($CBrF_3$), and H-2402 ($CBrF_2CBrF_2$), J. Geophys. Res. Atmos., **121**, 3663–3686, doi:10.1002/2015/2015JD024488, 2016a.
http://onlinelibrary.wiley.com/doi/10.1002/2015JD024488/abstract

Vollmer, M.K., S. Reimann, M. Hill, B. Buchmann, L. Emmenegger, Tracking new halogenated alkenes in the atmosphere, Chimia, **70**, 5, 365, doi:10.2533/chimia.2016.365, 2016. https://chimia.ch

Book sections

Buchmann B., C. Hueglin, S. Reimann, M.K. Vollmer, M. Steinbacher, and L. Emmenegger, Reactive Gases, Ozone Depleting Substances and Greenhouse Gases, in Willemse, S., and M. Furger (eds.), *From weather observations to atmospheric and climate sciences in Switzerland*, vdf Hochschulverlag AG, 361-374, 2016.

Conference papers

Reimann, S., D. Brunner, M.K. Vollmer, S. Henne, L. Emmenegger, A. Manning, Observation-Based Greenhouse Gas Emission Estimates for Policy Support and Evaluation, IG3IS side event at the annual WMO meeting, Geneva, Switzerland, June 16, 2016.

Reimann, S., D. Brunner, M.K. Vollmer, S. Henne, L. Emmenegger, A. Manning, Source Attribution of Halogenated Compounds in Support of Emission Inventories for International Agreements, ICOS yearly science meeting, Helsinki, Finland, September 27–29, 2016.

Reimann, S., M.K. Vollmer, S. Henne, D. Brunner, L. Emmenegger, A. Manning, P.J. Fraser, P.B. Krummel, B.L. Dunse, P. DeCola, O.A. Tarasova, Towards a Novel Integrated Approach for Estimating Greenhouse Gas Emissions in Support of International Agreements, AGU annual fall meeting, San Francisco, USA, December 12–16, 2016.

Data books and reports

Liang, Q., P.A. Newman, S. Reimann (Eds.), Report on the Mystery of Carbon Tetrachloride, SPARC Report N°7 WCRP-13/2016, 2016. http://www.sparc-climate.org/publications/sparc-reports/sparc-report-no7

Magazine and Newspapers articles

„Gefährliches Kältemittel in der Luft", Tages-Anzeiger, Wissen Forschungsplatz Zürich, p. 36, January 25, 2016.

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