Name of research institute or organization:

Empa, Swiss Federal Laboratories for Materials Science and Research

Title of project:

Halogenated Greenhouse Gases at Jungfraujoch

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 using gas-chromatography mass spectrometric (GC-MS) measurement techniques. The measurements aim at several purposes. Most importantly, these measurements help to identify regional pollution of these substances and build the basis for a quantitative estimate of regional emissions, using atmospheric transport models to identify the origin of the polluted air masses. The measurements also aid at defining global background concentrations (air not recently polluted) in combination with other similar observations around the globe. These measurements also help to identify 'new' substances. Due to the restriction on the uses of ODSs within the Montreal Protocol (e.g. the chlorofluorocarbons, CFCs), new replacement chemicals are being produced by the industry. Some of these substances are greenhouse gases, particularly the '3rd generation' replacement compounds, the hydrofluorocarbons (HFCs).

For this year's report we present the Jungfraujoch results in a global perspective. For the past decade, Empa has collaborated on an international level with institutes with similar interests and activities. The Jungfraujoch measurements are embedded in the European observation network SOGE (System for Observations of Greenhouse Gases in Europe, 4 stations), AGAGE (Advanced Global Atmospheric Gases Experiment, 5 stations) other affiliated stations with in-situ measurements (Gosan, Korea, and Shangdianzi, China) and flask sampling programs from Antarctica. One of the key issues of such international collaboration is to provide an instrument calibration scheme that allows for the results to be reported on unified calibration scales. This allows for direct comparison of the results, a prerequisite in a study like the one described below.

Jungfraujoch is the observatory where the first in-situ measurements were conducted world-wide, of a group of new compounds used by the industry. These are HFCs used in replacement of HCFCs and CFCs. The first two are the foam blowing compounds HFC-365mfc ($CH_3CF_2CH_2CF_3$) and HFC-245fa ($CHF_2CH_2CF_3$), used as replacement for HCFC-141b which is undergoing a world-wide phase-out. They were used in the developed countries, HFC-365mfc predominantly in Europe, and HFC-245fa in North America. These two compounds were first produced in industrial quantities in the early 2000. First measurements of these compounds yielded bearily detectable signals on the GC-MS in 2003, but soon the signals increased, reflecting a growing concentration in the atmosphere.

Many years after these initial measurements, these compounds are ubiquitously abundant in the atmosphere, they have reached the pristine atmosphere in Antarctica. They are now measured by all network partners. Figure 1 shows the monthly means of the records from the in-situ measurement sites. These results are filtered for 'background' air, i.e. the regional pollution events detected at the many sites were removed from this analysis (a completely different subject). The results show the rapid increases to nearly 1 ppt (parts-per-trillion, 10^{-12}, dry air mole fraction) as well as the typical interhemispheric gradient caused by the predominantly northern hemispheric emissions.

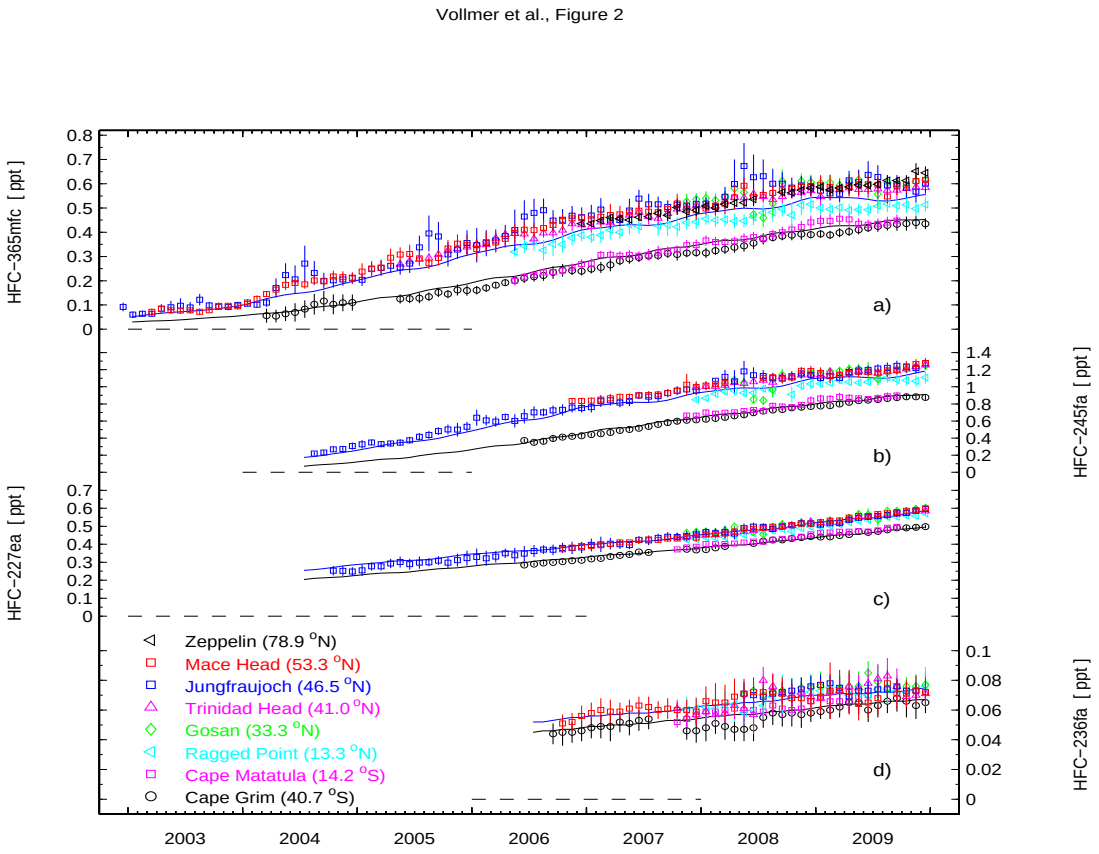

Figure 1: Atmospheric records of the hydrofluorocarbons (HFCs) HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa at selected monitoring stations. Background (pollution events removed) monthly means (and std as vertical bars) are given in concentration units of ppt (parts-per-trillion, 10^{-12}, dry air mole fraction). Figure taken from Vollmer et al., (in review).

In Figure 1, the abundances of two other HFCs are also shown. This is HFC-227ea (CF_3CHFCF_3) used in fire extinguishers and metered dose inhalers such as asthma sprays, and HFC-236fa ($CF_3CH_2CF_3$), used in fire extinguishers and in specialized cooling equipment. These two substances are not permitted for use in Switzerland due to their long atmospheric lifetimes vs OH destruction (40 yr for HFC-227ea and 240 yr for HFC-236fa).

Vollmer et al., Figure 4

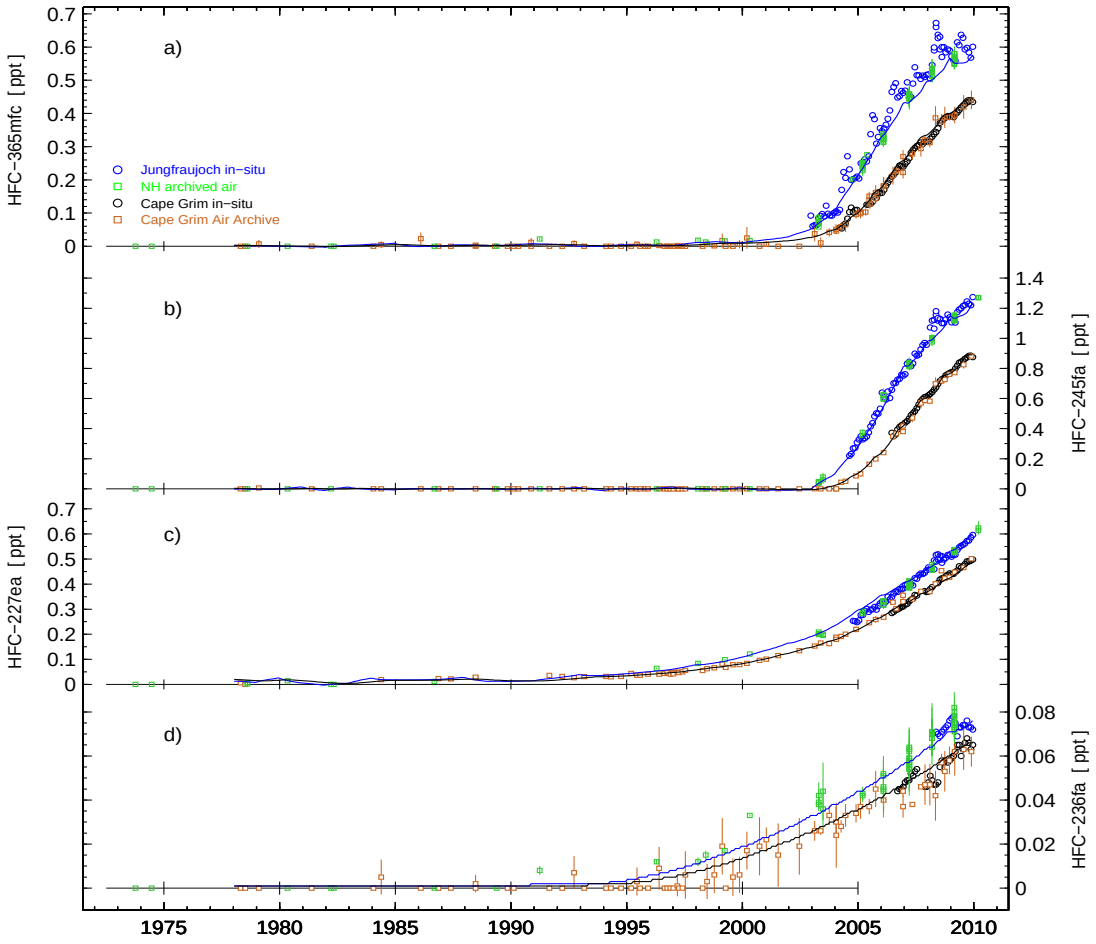

Figure 2: Atmospheric histories of the hydrofluorocarbons (HFCs) HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa in-situ measurements (Jungfraujoch and Cape Grim) and from archived air samples collected in the southern hemisphere (Cape Grim) and in the northen hemisphere (various sites). Figure taken from Vollmer et al., (in review).

To extend the history of these compounds back in time, archived air samples were also measured. Unlike in paleo-climatology, our measurement techniques and the extremely low abundances of these substance inhibit the measurements of these compounds for air enclosed as bubbles in ice cores. Instead, our archived air measurements derive from air collected in large quantities (into steel containers) at Cape Grim (Tasmania, Australia) since the 1970s. These precious air samples were also analysed for the four compounds of interests here. The results are shown in Fig. 2 along with results from measurements of other archived air samples of the northern hemisphere. The results show in an impressive manner the absence of HFC-365mfc and HFC-245fa from the global atmosphere until the early 2000s, when their abundances started to increase rapidly. The Jungfraujoch in-situ measurements, also shown in this Fig. 2, were started shortly after these compounds' onsets in the atmosphere. By contrast, HFC-227ea and HFC-236fa appear in the global atmosphere

about 1 decade or more earlier. This is a reflection of an earlier start of their uses. This is almost certainly caused by the fact that HFC-227ea and HFC-236fa were direct replacements of the halons used in fire extinguishing and banned in the early phases of the Montreal Protocol (1990s). By comparison, in the foam-blowing sector, the earliest compounds used (CFCs, mainly CFC-11) were replaced by intermediate foaming compounds (HCFCs, mainly HCFC-141b) and only the phase-out of the HCFCs called for HFCs in this industrial sector: HFC-365mfc and HFC-245fa production began. From the absence of all four compounds in the earlier record one can conclude that they are of purely anthropogenic origin and that nature has not produced these compounds, at least not during the past decades.

The wheels of new compound production has not stopped with these four HFCs. Industry is already experimenting with new substances to meet new needs and to follow regulations on the use of these climate-active compounds. Most of these are not detectable in the atmosphere yet. As they will slowly appear in the atmosphere, and being detected at Jungfraujoch and other sites, they may provide yet another tool to investigate global emission pattern and atmospheric transport patterns.

Key words:

Ozone-depleting compounds, greenhouse gases, hydrofluorocarbons, Montreal Protocol, Kyoto Protocol

Collaborating partners/networks:

Bundesamt für Umwelt (BAFU) / Federal Office for the Environment (FOEN)
Global Atmosphere Watch (GAW)
SOGE (System for Observations of Halogenated Greenhouse Gases in Europe)
AGAGE (Advanced Global Atmospheric Gases Experiment)
Korea Polar Research Institute (KOPRI)

Scientific publications and public outreach 2010:

Refereed journal articles and their internet access

Vollmer, M. K., Miller, B. R., Rigby, M., Reimann, S., Mühle, J., Krummel, P. B., O'Doherty, S., Kim, J., Rhee, T. S., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Salameh, P. K., Harth, C. M., Wang, R. H. J., Steele, L. P., Young, D., Lunder, C. R., Hermansen, O., Ivy, D., Arnold, T., Schmidbauer, N., Kim, K.-R., Greally, B. R., Hill, M., Leist, M., Wenger, A., Prinn, R. G., Atmospheric histories and global emissions of the anthropogenic hydrofluorocarbons (HFCs) HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa, J. Geophys. Res., in review

Yver, C., Pison, I., Fortems-Cheiney, A., Schmidt, M., Bousquet, P., Ramonet, M., Jordan, A., Søvde, A., Engel, A., Fisher, R., Lowry, D., Nisbet, E., Levin, I., Hammer, S., Necki, J., Bartyzel, J., Reimann, S., Vollmer, M. K., Steinbacher, M., Aalto, T., Maione, M., Arduini, I., O'Doherty, S., Grant, A., Sturges, W., Lunder, C. R., Privalov, V., Paramonova, N., A new estimation of the recent tropospheric molecular hydrogen budget using atmospheric observations and variational inversion, Atmos. Chem. Phys. Discuss., 10, 28963-29005, 2010.
http://www.atmos-chem-phys-discuss.net/10/28963/2010/acpd-10-28963-2010.pdf

Rigby, M. Mühle, J., Miller, B. R., Prinn R. G., Krummel, P. B., Steele, L. P., Fraser, P. J., Salameh, P. K., Harth, C. M., Weiss, R. F., Greally, B. R., O'Doherty, S., Simmonds, P. G., Vollmer, M. K., Reimann, S., Kim, K., Kim, K. R.,

Wand, H. J., Dluogencky, E. J., Dutton, G. S., Elkins, J. W., History of atmospheric SF_6 from 1973 – 2008, Atmos. Chem. Phys. **10**, 10305 – 10320.
http://www.atmos-chem-phys.net/10/10305/2010/acp-10-10305-2010.pdf

Stohl, A., J. Kim, S. Li, S. O'Doherty, J. Mühle, P. K. Salameh, T. Saito, M. K. Vollmer, D. Wan, R. F. Weiss, B. Yao, Y. Yokouchi, L. X. Zhou, 2010. Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., **10**, 3545 – 3560.
http://www.atmos-chem-phys.net/10/3545/2010/acp-10-3545-2010.pdf

Xiao, X., R. G. Prinn, P. J. Fraser, P. G. Simmonds, R. F. Weiss, S. O'Doherty, B. R. Miller, P. K. Salameh, C. M. Harth, P. B. Krummel, L. W. Porter, J. Mühle, B. R. Greally, D. Cunnold, R. Wang, S. A. Montzka, J. W. Elkins, G. S. Dutton, T. M. Thompson, J. H. Butler, B. D. Hall, S. Reimann, M. K. Vollmer, F. Stordal, C. Lunder, M. Maione, J. Arduini, and Y. Yokouchi, 2010. Optimal estimation of the surface fluxes of methyl chloride using a 3-D global chemical transport model, Atmos. Chem. Phys. , **10**, 5515-5533.
http://www.atmos-chem-phys.net/10/5515/2010/acp-10-5515-2010.pdf

Book sections

Montzka, S. A. and Reimann, S., Ozone depleting substances (ODSs) and related chemicals, Chapt. 1, in: Scientific Assessment of ozone depletion, 2010, Global Ozone Research and Monitoring Project – Report number xxx, World Meteorological Organization, Geneva, 2011.

Conference papers

Steinbacher M., C. Zellweger, and C. Hueglin, Continuous in-situ CH_4 and CO_2 Observations at Jungfraujoch using Cavity Ring Down Spectroscopy, Swiss Global Change Day, Bern, 20 April 2010.

Keller, C. A., D. Brunner, M. K. Vollmer, S. O'Doherty, A. Manning, and S. Reimann, Halogenated Greenhouse Gas Emissions Inferred from Ambient Air Measurements and 222Rn, European Geophysical Union, Vienna, 3 – 7 May 2010.

Henne, S., D. Brunner, J. Klausen, B. Buchmann, Inter-Annual Variability of CO and CH_4 Observations Interpreted by a Global Lagrangian Transport Model, European Geophysical Union, Vienna, 3 – 7 May 2010.

Henne, S., D. Brunner, J. Klausen, B. Buchmann, Inter-Annual Variability of CO and CH_4 Observations Interpreted by a Global Lagrangian Transport Model, NOAA ESRL Global Monitoring Annual Meeting, Boulder, Colorado, 18 – 19 May 2010.

Reimann, S., C. A. Keller, D. Brunner, M. K. Vollmer, S. O'Doherty, A. Manning, Top-Down Validation of European Halocarbon Emission Inventories, NOAA ESRL Global Monitoring Annual Meeting, Boulder, Colorado, 18 – 19 May 2010.

Buchmann, B., Reactive Gases and Greenhouse Gases at the GAW site Jungfraujoch, Earth Observation Programme Board, Jungfraujoch, 28 May 2010.

Buchmann, B., Integrated Carbon Observation System, Status Switzerland, ICOS Stakeholder Meeting, Helsinki, 31 May – 2 June 2010.

Vollmer, M. K., et al., Atmospheric Histories and Global Emissions of the Anthropogenic Hydrofluorocarbons (HFCs) HFC-365mfc, HFC-245fa, HFC-227ea,

and HFC-236fa, 41st Meeting of AGAGE scientists and Cooperating Networks, Beijing 7 – 11 June 2010.

Keller, C. A., D. Brunner, M. K. Vollmer, S. Henne, and S. Reimann, Allocation and Trends of Halogenated Hydrocarbon Emissions in Europe as Observed from Jungfraujoch, Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Interlaken, 8 – 10 June 2010.

Keller, C. A., M. K. Vollmer, D. Brunner, F. Conen, and S. Reimann, Halogenated Greenhouse Gas Emissions inferred from Ambient Air Measurements and Radon-222 at Jungfraujoch, Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Interlaken, 8 – 10 June 2010.

Steinbacher, M., D. Brunner, S. Henne, M. K. Vollmer, S. Reimann, In-situ Methane Observations at Jungfraujoch: European Source Allocations and Emission estimates, Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Interlaken, 8 – 10 June 2010.

Steinbacher, M., B. Schwarzenbach, B. Buchmann, C. Hueglin, Continuous in-situ Air Quality Measurements at Jungfraujoch as Part of the Swiss National Air Pollution Monitoring Network (NABEL), Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Interlaken, 8 – 10 June 2010.

D. Brunner, S. Henne, J. Klausen, and B. Buchmann, A Global Lagrangian Model to Study Trace Gas Variability and Long Range Transport, Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Interlaken, 8 – 10 June 2010.

M. Steinbacher, S. Reimann, M. K. Vollmer, M. Hill, C. Hueglin, VOC Observations Within the Swiss National Air Pollution Monitoring Network, 3rd WMO/GAW expert meeting on global observations of VOCs, Helsinki, 29 – 30 June 2010.

Vollmer, M. K., Atmospheric Halogenated Trace Gases – Automated Measurements using Gas Chromatography – Mass Spectrometry (GC – MS), Agilent Forum, Basel, 7 – 8 September 2010.

Reimann, S., and M. K. Vollmer, Hydorfluoroolefines (HFOs): Measured before produced, AGAGE 42nd Meeting of AGAGE scientists and Cooperating Networks, Melbourne, 8 – 11 November 2010

Theses

Bond, S. W. Sources and Sinks of Hydrogen in the Atmosphere during Transition to Hydrogen-based Transportation. PhD Thesis, ETH Zurich, 2010.

Data books and reports

Reimann, S., M. K. Vollmer, D. Brunner, M. Steinbacher, M. Hill, A. Wenger, C. Keller, and B. Buchmann, Kontinuierliche Messung von halogenierten Treibhausgasen auf dem Jungfraujoch (HALCLIM-4). Empa project No 201'203, 1st Interim Report, 21 October 2010. Available at:
http://www.bafu.admin.ch/luft/00649/01960/

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