

Name of research institute or organization:

Empa, Swiss Federal Laboratories for Materials Testing and Research

Title of project:

Halogenated greenhouse gases at Jungfraujoch

Project leader and team:

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Project description:

Halogenated ozone-depleting substances (ODS) and greenhouse gases (GHG) have been monitored at Jungfraujoch since 2000. 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 immediately 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 ODS 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' compounds, the hydrofluorocarbons (HFCs).

In February 2008, the 'Adsorption-Desorption System' (ADS) gas chromatograph mass spectrometer (GCMS) at Jungfraujoch was replaced by a new system with improved sample preparation capabilities, the 'Medusa' GCMS. While generally improving measurement precisions and frequencies, several new compounds have also been added to the zoo of about 45 compounds currently investigated.

For this year's report we provide an example of the measurements of four fully fluorinated compounds and elaborate a little on the use of modeling tools using the example of the GHG hydrofluorocarbon-134a (HFC-134a) a cooling agent mainly used in mobile air conditioners (cars).

Perfluorated compounds are characterized by extremely long lifetimes in the atmosphere. In Fig 1 we show preliminary data of time series (of Medusa-GCMS measurements only) for 3 stations, Jungfraujoch (Switzerland), and the AGAGE stations Mace Head (east coast of Ireland) and Cape Grim (west coast of Tasmania, Australia). Sulfur hexafluoride (SF₆) is predominantly used in the electric industry as an electric insulator in high-voltage switch gear. Its global emissions are several kilotons per year and combined with its very long atmospheric lifetime of 3200 years, this compounds experiences a fast increase in the global background concentrations. It has the largest of all Greenhouse Warming Potentials (GWPs) of all substances measured, 22'000 based on a 100-yr timescale (i.e. 22'000 times more effective than CO₂). There is a significant difference between the northern hemisphere (NH) sites and the southern hemisphere (SH) site which is reflecting the much larger NH emissions. Regional pollution episodes are detected mainly at Mace Head and Jungfraujoch while Cape Grim is predominantly influenced by clean air and only

occasionally under the influence of the main continent's effluent (Melbourne). PFC-116 (C_2F_6) and PFC-218 (C_3F_8) are used in the semi-conductor industry. Their global increase in absolute concentrations is smaller compared to SF_6 but in relative terms, that of PFC-218 is approximately the same as SF_6 ($\sim 4.5\% \text{ yr}^{-1}$). PFC-116 has a very long atmospheric lifetime of 10'000 yrs, and that of PFC-218 is 2'600 yrs. However the longest-lived anthropogenic trace gas is CF_4 with a lifetime estimated at $\sim 50'000$ yrs. The Jungfraujoch record of CF_4 is still short due to instrumental problems which were solved at the end of 2009. Despite the remoteness of aluminium smelters, which are the dominant emitters of CF_4 , there is an indication of detection of CF_4 -polluted air arriving at Jungfraujoch. More measurements are necessary in order to better understand this compound's potential in tracing air masses back to specific locations such as the few European aluminium-processing plants.

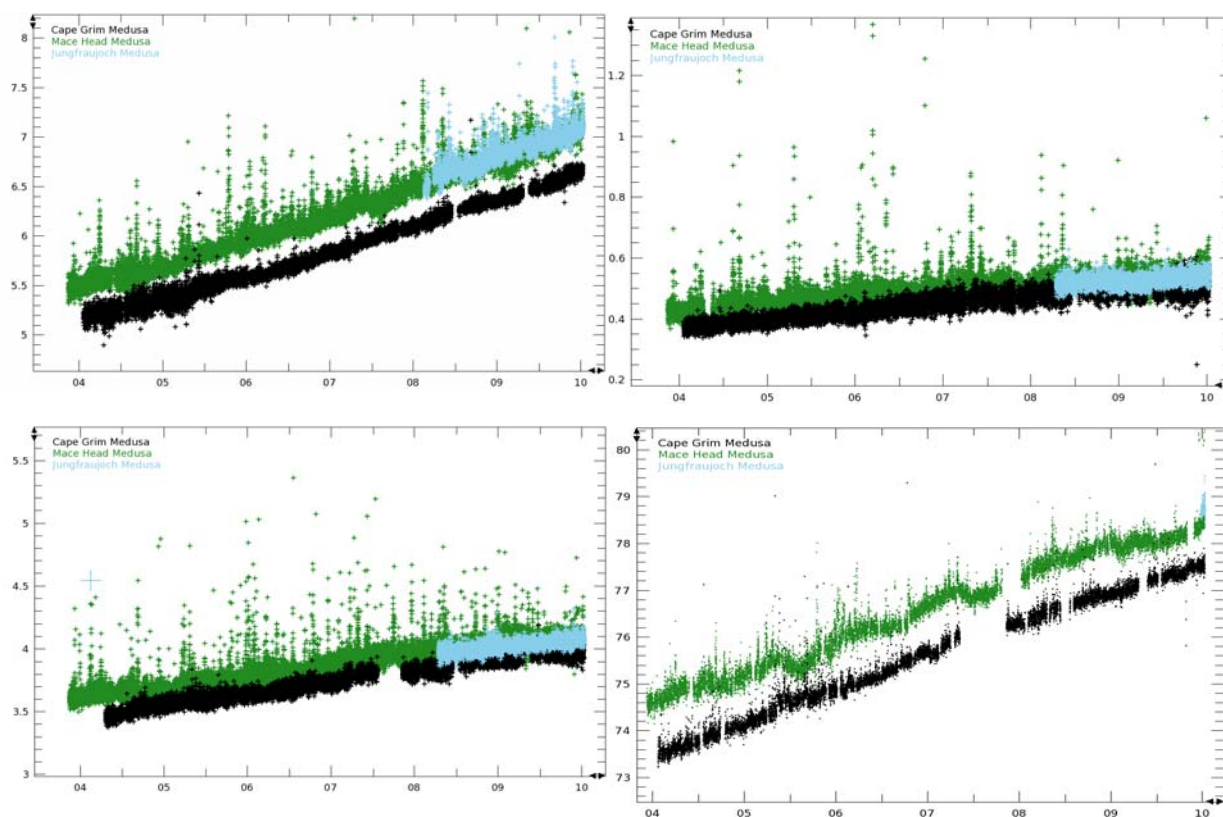


Figure 1: Tropospheric mixing ratios for a selection of 4 compounds over a total time period measured by the GCMS-Medusa at Jungfraujoch (Switzerland, in light blue), Mace Head (Ireland, in green), and Cape Grim (Australia, in black). The mixing ratios are given as dry-air mole fractions in parts-per-trillion (ppt, 10^{-12}). Upper left: SF_6 , upper right: PFC-218, lower left: PFC-116, lower right CF_4 .

Quantitative emission estimates are conducted using various techniques but can mainly be divided into two categories. 'Bottom-up' emission estimates are those based on release data given on industry statistics, and of information on 'banking' (storing before releasing, e.g. foaming agents in ageing foam). These 'bottom-up' estimates can be validated by 'top-down' techniques which are based on atmospheric observations. Top-down techniques are for example carbon monoxide (CO)-bootstrapping or ^{222}Rn bootstrapping (both not further discussed here) or by

sophisticated modeling approaches. These can be, for example, based on Lagrangian Particle Dispersion Models.

Our recent work has delivered some improved inversion techniques using statistical-mathematical Kalman-filter techniques. An example of a distribution of HFC-134a for a short time period is given in Fig. 2 based on the observations at Jungfraujoch. For HFC-134a during the observational period in May 2008, emission centers were found in the south of Jungfraujoch (Po-Valley), in northern France and some parts of Germany. More research is conducted on these techniques including rigorous calibration and testing by applying it to the CO for which the European bottom-up emission estimates are believed to be known to a fair degree of accuracy.

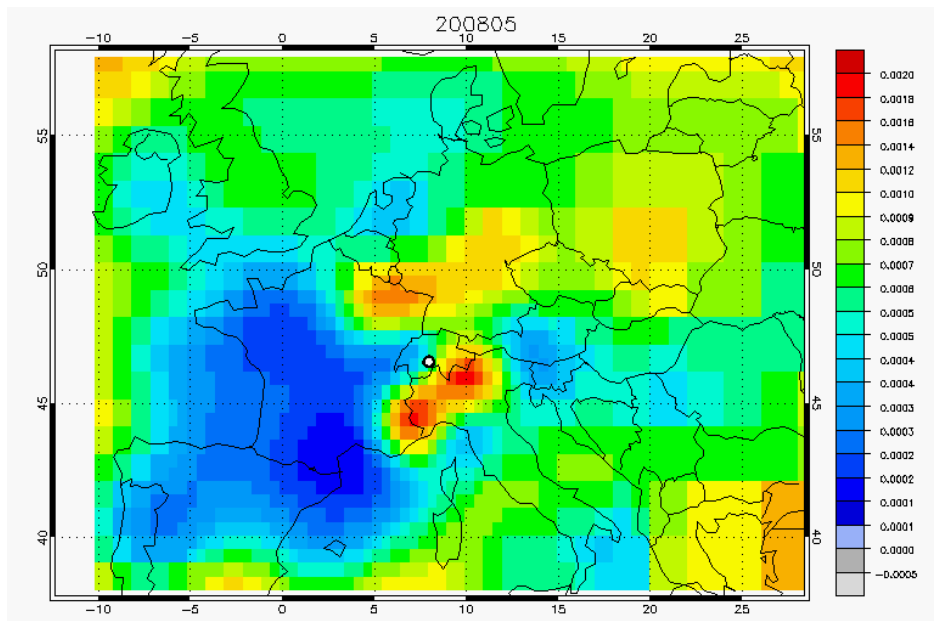


Figure 2: Distribution of emission of HFC-134a [ppt/sec] in May 2008 as estimated by the Kalman filter from measurements at the high-alpine station Jungfraujoch, Switzerland. Source D. Brunner, American Geophysical Union Fall meeting 2009.

Key words:

Ozone-depleting compounds, greenhouse gases, 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)

Scientific publications and public outreach 2009:

Refereed journal articles and their internet access

Cui J., M. Sprenger, J. Staehelin, A. Siegrist, M. Kunz, S. Henne, M. Steinbacher, 2009. Impact of stratospheric intrusions and intercontinental transport on ozone at Jungfraujoch in 2005: comparison and validation of two Lagrangian approaches.

Atmospheric Chemistry and Physics, **9**, 3371-3383. <http://www.atmos-chem-phys.net/9/3371/2009/acp-9-3371-2009.html>

Lanz V. A., C. Hueglin, M. K. Vollmer, M. Steinbacher, S. Henne, J. Staehelin, B. Buchmann, S. Reimann, 2009. Statistical analysis of anthropogenic non-methane VOC variability at a European background location (Jungfrauoch, Switzerland). Atmospheric Chemistry and Physics, **9**, 3445-3459. <http://www.atmos-chem-phys.net/9/3445/2009/acp-9-3445-2009.html>

Parker A. E., P. S. Monks, K. P. Wyche, J. M. Balzani Lööv, J. Staehelin, S. Reimann, G. Legreid, M. K. Vollmer, M. Steinbacher, 2009. Peroxy radicals in the summer free troposphere: Seasonality and heterogeneous loss. Atmospheric Chemistry and Physics, **9**, 1989-2006. <http://www.atmos-chem-phys.net/9/1989/2009/acp-9-1989-2009.html>

Vollmer, M. K., Zhou, L. X., Grealley, B. R., Henne, S., Yao, B., Reimann, S., Stordal, F., Cunnold, D. M., Zhang, X. C., Maione, M., Zhang, F., Huang, J. and Simmonds, P. G., 2009. Emissions of ozone-depleting halocarbons from China. Geophysical Research Letters **36** (15), L15823, doi:10.1029/2009GL038659. <http://www.agu.org/journals/gl/gl0915/2009GL038659/>

Stohl, A., Seibert, P., Arduini, J., Eckhardt, S., Fraser, P., Grealley, B. R., Lunder, C., Maione, M., Mühle, J., O'Doherty, S., Prinn, R. G., Reimann, S., Saito, T., Schmidbauer, N., Simmonds, P. G., Vollmer, M. K., Weiss, R. F. and Yokouchi, Y., 2009. An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons. Atmospheric Chemistry and Physics **9**(5): 1597-1620. <http://www.atmos-chem-phys.net/9/1597/2009/acp-9-1597-2009.html>

O'Doherty, S., Cunnold, D. M., Miller, B. R., Mühle, J., McCulloch, A., Simmonds, P. G., Manning, A. J., Reimann, S., Vollmer, M. K., Grealley, B. R., Prinn, R. G., Fraser, P. J., Steele, L. P., Krummel, P. B., Dunse, B. L., Porter, L. W., Lunder, C. R., Schmidbauer, N., Hermansen, O., Salameh, P. K., Harth, C. M., Wang, R. H. J., Weiss, R. F. Global and regional emissions of HFC-125 (CHF₂CF₃) from in situ and air archive atmospheric observations at AGAGE and SOGE observations. Journal of Geophysical Research **114** D23304, doi:10.1029/2009JD012184. <http://www.agu.org/journals/jd/jd0923/2009JD012184/>

Conference papers

Bond, S. W., M. K. Vollmer, M. Steinbacher, S. Reimann, Direct and remote H₂ measurements — recent results from Empa, EUROHYDROS 3rd annual meeting, Helsinki, Finland, June 03 – 04, 2009.

Brunner, D., S. Henne, M. K. Vollmer, S. Reimann, A new emission estimation approach based on Lagrangian Particle Dispersion Modeling and Kalman-filter based inversion, American Geophysical Union, San Francisco, December 12 – 14, 2009.

Buchmann, B., Gas-Programme @ Jungfrauoch - Trend Analysis, Early Warning, Benefit for International Treaties and Programmes, ZAMG Sonnblick symposium, Wien, Austria, October 22, 2009

Buchmann, B., S. Reimann, M. K. Vollmer, M. Steinbacher, M. Hill, D. Brunner, C. Hüglin, Gas-Programme @ Jungfrauoch - Trend Analysis, Early Warning, Benefit for International Treaties and Programmes, GAW2009 Symposium, Geneva, Switzerland, May 04 – 08, 2009.

Buchmann, B., Identification and Quantification of Anthropogenic Air Pollutants, Colloquium MeteoSchweiz, Payerne, Switzerland, June 09, 2009.

Henne, S., D. Brunner, J. Klausen, B. Buchmann, Long-range Transport and Its Impact on Trace Gas Variability at Selected GAW Stations, EGU General Assembly, Vienna, Austria, April 19 - 24, 2009.

Henne, S., D. Brunner, J. Klausen, B. Buchmann, Multi-year simulation of carbon monoxide and methane applying a novel Lagrangian concept, American Geophysical Union, San Francisco, December 12 – 14, 2009.

Jalkanen, L., S. Gilge, S. Henne, L. Ries, S. Reimann, M. K. Vollmer, J. Klausen, GAW Mountain Observatories in Detection of Atmospheric Change, International Conference on Mountains as Early Indicators of Climate Change, Padua, Italy, April 17 -18, 2009.

Keller, C. A., D. Brunner, M. K. Vollmer, M. Steinbacher, M. Schürmann, F. Conen, S. Reimann, Halogenated greenhouse gas emissions over Central Europe inferred from ambient air measurements and 222-Rn activity, GEIA-ACCENT Open Conference, Oslo, Norway, October, 26 – 28, 2009.

Keller, C., D. Brunner, M. K. Vollmer, F. Conen, S. Reimann, Top-down estimation of halogenated greenhouse gas emissions using Radon as tracer, Fifth International Symposium on Non-CO₂ Greenhouse Gases (NCGG-5), Wageningen, The Netherlands, June 30 – July 03, 2009.

Laube, J. C., C. A. M. Brenninkmeijer, A. Engel, S. A. Montzka, E.G. Nisbet, K. P. Shine, M. Steinbacher, W. T. Sturges, A systematic search for unknown halocarbons in the troposphere and stratosphere: Overview and first results of the CLEARFOGG project, EGU General Assembly, Vienna, Austria, April 19 - 24, 2009.

Reimann, S., D. Brunner, S. Henne, M. K. Vollmer, C. Keller, A. J. Manning, S. O'Doherty, P. G. Simmonds, S. Montzka, Global and regional emission estimation using halocarbon measurements at background sites, Non-CO₂ Greenhouse Gases (NCGG-5), Wageningen, The Netherlands, June 30 – July 03, 2009

Steinbacher, M., EUROHYDROS - A European Network for Atmospheric Hydrogen Observations and Studies: Calibration, quality assurance and data management, EUROHYDROS 3rd annual meeting, Helsinki, Finland, June 03 – 04, 2009.

Steinbacher, M., Greenhouse Gas Measurements and Related Modelling at Jungfrauoch – Empa's Activities, Workshop on Greenhouse Gases in Northern Italy / Switzerland, Ispra, Italy, June 23, 2009.

Steinbacher, M., M. K. Vollmer, S. Henne, D. Brunner, C. Hueglin, S. Reimann, In-situ CH₄ observations at the high-Alpine site Jungfrauoch, Fifth International Symposium on Non-CO₂ Greenhouse Gases (NCGG-5), Wageningen, The Netherlands, June 30 – July 03, 2009.

Steinbacher, M., Ground-based in-situ observations of oxides of nitrogen: experience from the Swiss National Air Pollution Monitoring Network, Experts Workshop on Oxides of Nitrogen, Hohenpeissenberg, Germany, October 08 – 09, 2009.

Steinbacher, M., S. Henne, D. Brunner, M. K. Vollmer, S. Reimann, European source allocations and emission estimates for CH₄ derived from in-situ observations at Jungfrauoch, GEIA-ACCENT Open Conference, Oslo, Norway, October, 26 – 28, 2009.

Vollmer, M. K., S. Reimann, AGAGE team, SOGE team, New HFCs update (HFCs-245fa, 227ea, 236fa, 365mfc) and other new compounds such as c-C4F8, 40th meeting of AGAGE scientists and collaborating networks, La Jolla, CA, 26 – 29 Oct 2009.

Zellweger, C., C. Hüglin, J. Klausen, M. Steinbacher, M. K. Vollmer, B. Buchmann, Inter-comparison of carbon monoxide measurements with four techniques at the GAW site Jungfraujoch, GAW 2009 workshop, Geneva.

Data books and reports

Empa and BAFU, Kontinuierliche Messung von halogenierten Treibhausgasen auf dem Jungfraujoch (HALCLIM-3), Schlussbericht 2009, Technical report, Empa Project 201'203, December 2009.

Magazine and Newspapers articles

Unabhängige Überwachung der Emissionen, Interview with scientist Stefan Reimann, Empa and Martin Heimann, MPI Jena, in ‚Wissen‘, NZZ am Sonntag, 6. December 2009, p. 70.

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