

Name of research institute or organization:

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**Empa, Swiss Federal Laboratories for Materials Science and Research**

Title of project:

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Halogenated Greenhouse Gases at Jungfraujoch

Project leader and team:

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Project description:

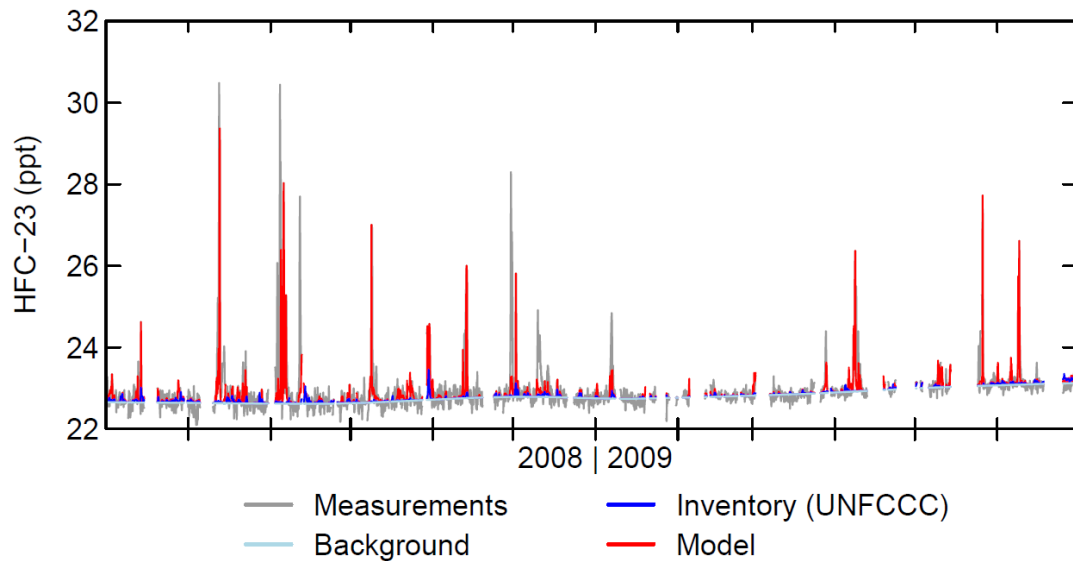
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Anthropogenic halogenated compounds (halocarbons) are strong greenhouse gases, and many of them also deplete stratospheric ozone, which is why international treaties such as the Montreal and the Kyoto Protocols have been negotiated to control the usage of these compounds. Halocarbons have been continuously measured at Jungfraujoch since 2000 with a gas chromatography / mass spectrometry. By linking these observations with calculations from an atmospheric transport model, the emission sources over Central Europe can be allocated and quantified, which provides a unique tool to independently check for compliance with the Montreal and the Kyoto Protocols.

In 2008, the original adsorption-desorption system (ADS) was replaced by a new-generation instrument (“Medusa”), which enables the detection of a larger number of compounds and with higher accuracy and temporal resolution. Amongst the new measured compounds, trifluoromethane (HFC-23,  $\text{CHF}_3$ ) is of particular interest due to its long atmospheric lifetime of ~270 years and its high global warming potential (GWP) of 14800 on a 100-yr timescale. While HFC-23 has also some limited use as fire-extinguisher, it is primarily produced unintentionally during the manufacture of HCFC-22 ( $\text{CH}_2\text{F}_2$ , a feedstock during polymer production, e.g. PTFE: Teflon®), from where it might be released to the atmosphere.

As shown in Figure 1, the HFC-23 observations at Jungfraujoch are characterized by the frequent occurrence of distinct pollution events, where concentrations suddenly increase by up to 7 ppt (parts per trillion;  $1 \times 10^{-12}$ ). To investigate the origin of these events, the Lagrangian particle dispersion model FLEXPART was employed, providing a 5-day backwards history of the air masses arriving at the Jungfraujoch. This analysis showed that increased HFC-23 concentrations at Jungfraujoch were primarily linked to air transport from Northern Italy, indicating that a HCFC-22 production plant in Northern Italy is responsible for the HFC-23 variations observed at Jungfraujoch.

To further quantify HFC-23 emissions over Western Europe, the Jungfraujoch data were combined with observations from Mace Head (Ireland), and a Bayesian optimization technique was applied to provide an estimate for the annual mean HFC-23 emissions over Europe. This analysis clearly confirmed that the six European HCFC-22 production sites (located in Belgium, France, Germany (2x), Italy and the United Kingdom) are by far the most important source for HFC-23 emissions in Europe.



**Figure 1.** Time series of HFC-23 at Jungfraujoch between July 2008 – July 2009. Observations are shown in grey, model predicted concentrations based on the officially reported emission data from the UNFCCC are shown in dark blue, optimized model predicted concentrations are coloured red. Light blue line indicates the background concentration.

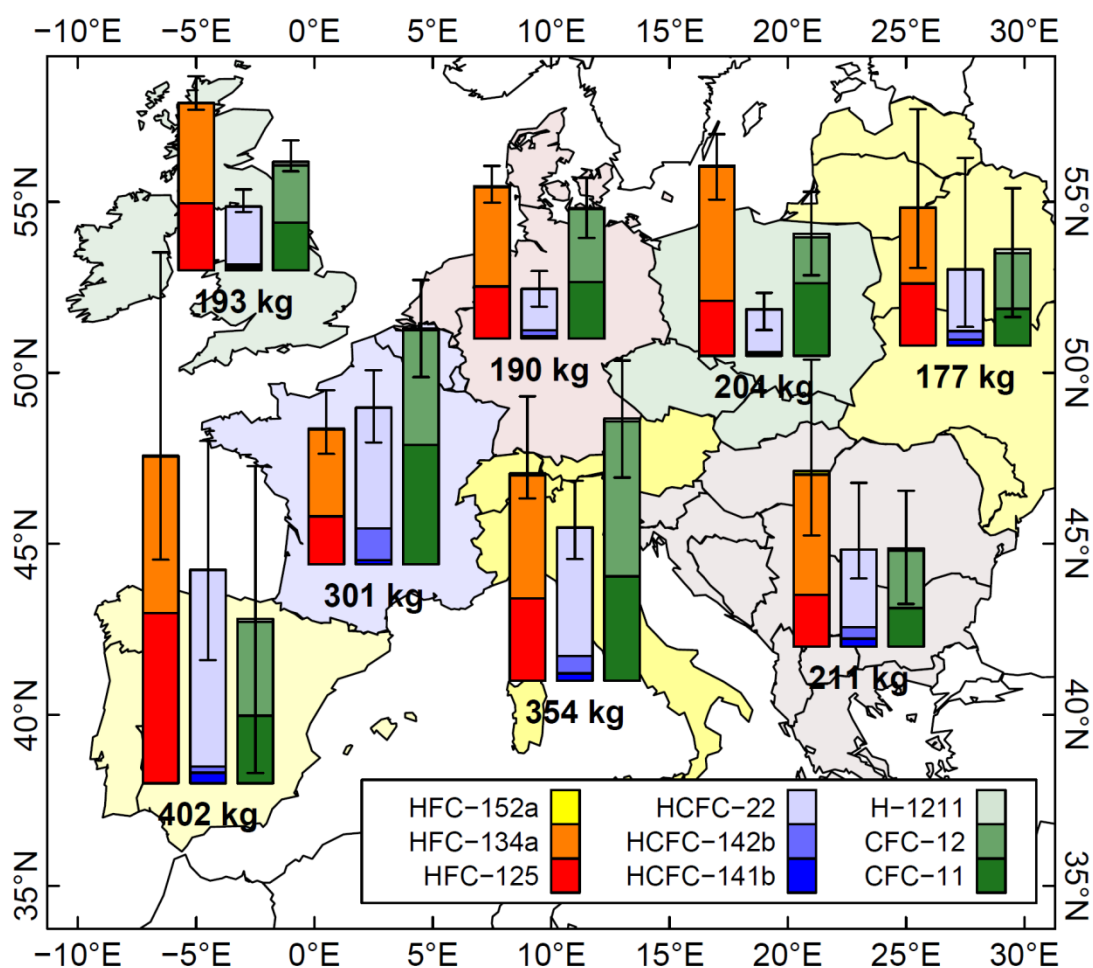
As the Bayesian inversion only yields the temporal averaged emission field, a second inversion method was developed, also taking into account the temporal variations of HFC-23 emissions originating from the six European HCFC-22 production plants. In this method, referred to as the “point source analysis”, all observed HFC-23 variability at Jungfraujoch and Mace Head was attributed to one of the HCFC-22 plants, yielding a set of short-term emission estimates from which an annual estimate could be derived for each of the plant individually.

Within the last 20 years, HFC-23 emissions from HCFC-22 production have been reduced substantially, which can be primarily related to the fact that most of the produced HFC-23 is nowadays collected and burned instead of being released to the atmosphere. However, this process is never complete and a small fraction of the produced HFC-23 still escapes to the atmosphere. Our inversion results indicate that this amount is generally underestimated by the inventories. Especially large discrepancies between our estimates and the officially reported numbers are found for Italy, which reports no HFC-23 emissions from the HCFC-22 production (the reported 2.6 t/yr are attributed to releases from fire extinguishers). Albeit the exact emission number is difficult to estimate (ranging between 26 and 56 t/yr), our results clearly indicate that HFC-23 emissions from HCFC-22 manufacture are the principal emission source in Italy, too, and the official inventory should therefore be adjusted accordingly.

Due to the elevated location in the middle of Europe, Jungfraujoch is influenced by air masses from many parts of western and central Europe, including Switzerland, Germany, northern Italy, France, northern Spain, the Benelux countries, and western Austria. This enables the emission quantification of a large number of halocarbons for all these regions using the Jungfraujoch data only. In combination with measurements from other observation sites, the Jungfraujoch data can even help to constrain

halocarbon emissions of entire Europe except Scandinavia. This is illustrated in Figure 2, which shows the inversely estimated per capita emissions of three groups of halocarbons for eight geographical regions in Europe. The estimates are based on observations from Jungfraujoch, Mace Head, Monte Cimone (Italy) and K-Puszt (Hungary), and are derived using the same Bayesian inversion technique already discussed above. As becomes apparent from Figure 2, the per capita emissions of the first and second generation halocarbons, the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs), tend to be higher in Western Europe compared to Eastern Europe, which may be explained by the delayed technological development and hence a less rigid usage of CFCs in Eastern Europe compared to Western Europe. For the newest generation halocarbons, the hydrofluorocarbons (HFCs), the estimated per capita emissions are comparable throughout Europe, indicating a similar usage of halocarbons in Europe nowadays.

On average, the total per capita halocarbon emissions in Europe amount to 246 kg CO<sub>2</sub> equivalents per year, which is similar to estimates for China (although the fractionation amongst the three groups of halocarbons is different there), but approximately 3 times lower than current estimates for the United States.



**Figure 2.** Average per capita halocarbon emissions per region in 2009, weighted by their GWPs. Numbers below the bars indicate total aggregated emissions in kilograms of CO<sub>2</sub> equivalents per capita and year.

Key words:

Ozone-depleting compounds, greenhouse gases, chlorofluorocarbons (CFCs) hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), 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)  
UK Met Office

Scientific publications and public outreach 2011:

**Refereed journal articles and their internet access**

Bond, S. W., Vollmer, M. K., Steinbacher, M., Henne, S. and Reimann, S. Atmospheric molecular hydrogen (H<sub>2</sub>): observations at the high-altitude site Jungfraujoch, Switzerland. *Tellus B* 63(1): 64-76, 2011.

Brunner, D., Henne, S., Keller, C.A., Reimann, S., Vollmer, M.K., O'Doherty, S., Maione, M.: An extended Kalman-filter for regional scale inverse emission estimation, *Atmos. Chem. Phys. Discuss.*, 11, 29195–29249, 2011.

Giostra, U., Furlani, F., Arduini, J., Cava, D., Manning, A. J., O'Doherty, S. J., Reimann, S. and Maione, M. The determination of a “regional” atmospheric background mixing ratio for anthropogenic greenhouse gases: A comparison of two independent methods. *Atmospheric Environment* 45(39): 7396-7405, 2011.

Keller, C.A., Brunner, D., Henne, S., Vollmer, M.K., O'Doherty, S., Reimann, S.: Evidence for under-reported Western European emissions of the potent greenhouse gas HFC-23, *Geophys. Res. Lett.*, 38, L15808, 2011.

Keller, C.A., Hill, M., Vollmer, M.K., Henne, S., Brunner, D., Reimann, S., O'Doherty, S., Arduini, J., Maione, M., Ferenczi, Z., Haszpra, L., Manning, A.J., Peter, T.: European emissions of halogenated greenhouse gases inferred from atmospheric measurements, *Environ. Sci. Technol.*, doi:<http://dx.doi.org/10.1021/es202453j>.

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., Grealley, B. R., Hill, M., Leist, M., Wenger, A., Prinn, R. G. Atmospheric histories and global emissions of the anthropogenic hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa, *J. Geophys. Res.*, 116, D08304, 2011.

Yver, C. E., Pison, I. C., Fortems-Cheiney, A., Schmidt, M., Chevallier, F., Ramonet, M., Jordan, A., Søvde, O. A., Engel, A., Fisher, R. E., Lowry, D., Nisbet, E. G., Levin, I., Hammer, S., Necki, J., Bartyzel, J., Reimann, S., Vollmer, M. K., Steinbacher, M., Aalto, T., Maione, M., Arduini, J., O'Doherty, S., Grant, A., Sturges, W. T., Forster, G. L., Lunder, C. R., Privalov, V., Paramonova, N., Werner, A., Bousquet, P.: A new estimation of the recent tropospheric molecular hydrogen budget using atmospheric observations and variational inversion, *Atmos. Chem. Phys.*, 11, 3375-3392, 2011.

### **Book sections**

Bond S.W., Alvarez, R., Reimann, S., Weilenmann, M., Buchmann, B., Co-Authors “Hydrogen emissions to the atmosphere from industry and transportation” (Teil 4, Seiten 96-127) from the book: Transition to Hydrogen Pathways Towards Clean Transportation, Wokaun, A., Wilhelm, E. (Eds.), Verlag Cambridge University Press, Copyright 2011, ISBN 978-0-521-19288-0 (Print).

### **Conference papers**

Keller, C.A., Hill, M., Ferenczi, Z., Haszpra, L., Conen, F., Brunner, D., Reimann, S. First measurements of a suite of halogenated greenhouse gases over Eastern Europe, European Geophysical Union, Vienna, 3 – 8 April 2011.

Keller, C.A. Unreported HFC-23 emissions from Italy. 43th Meeting of AGAGE scientists and Cooperating Networks, Bristol, 22-26 May 2011.

Reimann, S., Vollmer, M. K. HFOs: The new kid in town – Measurements at the onset of the first industrial production. 43th Meeting of AGAGE scientists and Cooperating Networks, Bristol, 22-26 May 2011.

Reimann, S., Brunner, D., Keller, C.A., F-gas emissions through inverse modeling, GMES conference, Copenhagen, 13 October 2011.

Reimann, S., Vollmer, M., Velders, G., Rigby, M., O'Doherty, S. Comparison of measurement-based global emission estimates of halocarbons with emission scenarios used in international assessments, Non-CO<sub>2</sub> greenhouse gases (NCGG-6), Amsterdam, 2-4 November 2011.

Reimann, S., Vollmer, M.K., Brunner, D., Henne, S. Replacement of ozone-depleting methyl bromide (CH<sub>3</sub>Br) with the radiatively active sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) for pest control, Non-CO<sub>2</sub> greenhouse gases (NCGG-6), Amsterdam, 2-4 November 2011.

Reimann, S. Vollmer, M.K., Replacement compounds all over, talk at the 44th Meeting of AGAGE scientists and Cooperating Networks, La Jolla, California, US, 29 November-02 December 2011.

Reimann, S., Brunner, D., Vollmer, M.K., Henne, S., Maione, M., Arduini, I., Miller, M., Phasing-out of methyl bromide (CH<sub>3</sub>Br) and usage of sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) for pest control in Europe, AGU, San Francisco, US, 05-09 December 2011.

Vollmer, M. K. and AGAGE team. Atmospheric Observations and emission patterns of the foam blowing compounds CFC-11, HCFC-141b, HFC-365mfc, and HFC-245fa, CAWCR 5th annual workshop, Atmospheric Composition Observation and Modelling and the Cape Grim Annual Science Meeting, Melbourne, 15-17 November 2011.

### **Edited books**

Montzka, S. A. and Reimann, S., Ozone depleting substances (ODSs) and related chemicals, Chapter 1, in: Scientific Assessment of ozone depletion, 2010, Global Ozone Research and Monitoring Project – Report No. 52, World Meteorological Organization, Geneva, 2011.

### **Theses**

Keller, C.A. Assessment of European non-CO<sub>2</sub> greenhouse gas emissions from continuous measurements and transport models, PhD thesis, ETH Zurich, Diss. ETH No. 20094, 2011.

**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 Jungfrauojoch (HALCLIM-4). Empa project No 201'203, 2. Zwischenbericht, 30. Juni 2011.  
<http://www.bafu.admin.ch/luft/00649/01960/>

**Magazine and Newspapers articles**

Italien trickst bei Treibhausgas, Tagesanzeiger, 19 August 2011.

Emission unterschätzt, NZZ, 19 August 2011.

La Svizzera accusa l'Italia: non dice la verità sui gas serra, Corriere della Sera (IT), 21 August 2011.

Der grosse Betrug mit HFC-23, Klimaretter.info, 22 August 2011.

Super greenhouse gas HFC-23 vented in Europe as millions are spent on face HFC-23 credits abroad, Environmental investigation agency (EIA), 24 August 2011.

Les Etats européens sous estiment leurs émissions de certains gaz à effet de serre, Le Monde, 27 August 2011.

Nederland probeert met dubieuze kunstgrepen Kyoto te halen, de Volkskrant (NLD), 27 August 2011.

„Bratpfannen heizen das Klima auf“, Beobachter Natur, Ausgabe: 20/11, 2011.

**Radio and television**

Reimann, S., Radio interview: 80 years of research at Jungfrauojoch, DRS 1, 1. July 2011

Reimann, S., Radio interview: HFC-23 Emissions in Europe, DRS 4, 19 August 2011

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