

Name of research institute or organization:

Empa, Swiss Federal Laboratories for Materials Science and Technology

Title of project:

Halogenated Greenhouse Gases at Jungfrauoch

Project leader and team:

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

Project description:

Halogenated ozone-depleting substances (ODSs) and greenhouse gases (GHGs) have been monitored at Jungfrauoch since 2000. These measurements are combined with atmospheric transport models for identifying and quantifying national and regional emissions (Switzerland and neighboring countries). These "top-down" estimates are then used to verify "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 Jungfrauoch comprise a suite of over 50 compounds, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs and SF₆), 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 this 2014 report we present recent results on the detection of new halogenated compounds in the atmosphere. One of our focal points is the search for compounds, which have not been measured up to present, or which are believed to be newly manufactured by industry and released to the atmosphere. In 2012 we performed a detailed search for new compounds, some of which we began measuring in 2013 at Jungfrauoch and at the urban station Dubendorf. Among these compounds were the two inhalation anesthetics halothane and desflurane. Halothane (CF₃CHClBr, halon-2311) is an anesthetics that was introduced to clinical surgery in the 1950s and widely used until the 1970s before it was gradually phased-out due to medical side effects (halothane hepatitis). Fluorinated ethers (fluranes), such as enflurane, isoflurane sevoflurane and desflurane, were used as replacements. Desflurane (CF₃CHFOCHF₂, HFE-236ea2) is a very stable anesthetics, both in terms of metabolism during application (<0.1% metabolized) and atmospheric degradation (14 years lifetime).

We analysed halothane and desflurane in archive air samples of the northern hemisphere and in flasks collected from Antarctica (Korean station King Sejong) as part of our ongoing collaboration with the Korea Polar Research Institute (KOPRI). In addition, in-situ continuous (2-hourly) measurements were started at Jungfrauoch and Dubendorf. Halothane is present in the atmosphere at very low dry air mole fractions (mid-parts-per-quadrillion (ppq), 10⁻¹⁵ and declining. A pronounced seasonality is observed, which is due to the seasonality of the major degradation process (OH). Desflurane, in contrast, has grown from 150 to 330 ppq over the fourteen-year record. Both compounds are detectable in Antarctic air with a temporal delay compared to the northern hemisphere — an indication of predominantly northern hemisphere sources.

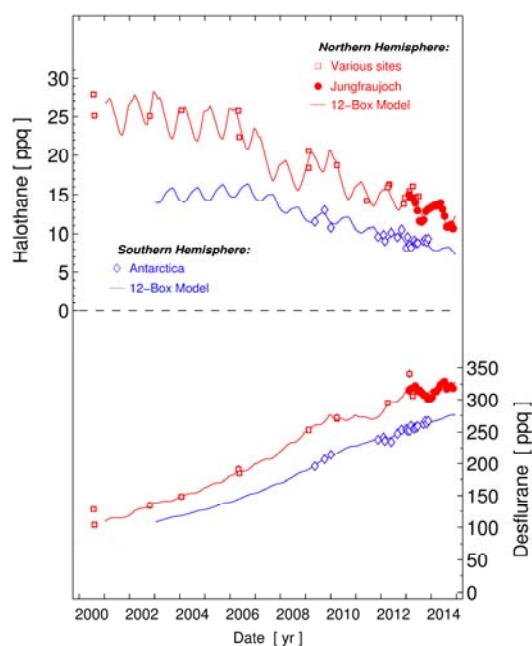


Figure 1. The inhalation anesthetics halothane (CF_3CHClBr , halon-2311) and desflurane ($\text{CF}_3\text{CHFOCHF}_2$, HFE-236ea2) in air samples from the northern and southern hemisphere. Halothane has been phased out from usage in most countries while desflurane is one of the widely used replacement anesthetics. As a consequence of this consumption pattern, halothane (atmospheric lifetime ~ 1 year) is declining in the atmosphere while desflurane (lifetime 14 years) has been steadily increasing since 2000 (oldest samples measured). Adopted from Vollmer et al., 2015 (GRL, in review).

The observations were simulated using the AGAGE (Advanced Global Atmospheric Gases Experiment) 12-box two-dimensional model of transport and chemistry. This model was combined with the observation to estimate emissions using a Bayesian methodology. Because of its comparably large Greenhouse Warming Potential, desflurane is the dominant of the two compounds in terms of CO_2 -equivalent emissions and has increased to ~ 2.5 mio t CO_2 -eq globally. While these emissions are relatively small compared to those caused by other human activities, it adds to the basket of the many anthropogenic halogenated compounds and raises the question of potential alternative anesthetics with less climate impact.

Key words:

Halogenated ozone-depletion substances (ODS), greenhouse gases (GHG), F-gases, hydrofluorocarbons (HFCs)

Internet data bases:

<http://empa.ch/abt503>

<http://agage.eas.gatech.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)
InGOS – Integrated non- CO_2 Greenhouse gas Observing System
ACTRIS – Aerosol, Clouds, and Trace Gases Research Network
Korea Polar Research Institute (KOPRI)
University of Bristol, UK

Scientific publications and public outreach 2014:

Refereed journal articles and their internet access

Arnold, T., D.J. Ivy, C.M. Harth, M.K. Vollmer, J. Mühle, P.K. Salameh, L.P. Steele, P.B. Krummel, R.H.J. Wang, D. Young, C.R. Lunder, O. Hermansen, T.-S. Rhee, M. Rigby, J. Kim, S. Reimann, S. O'Doherty, P.J. Fraser, P.G. Simmonds, R.G. Prinn, and R.F. Weiss, HFC-43-10mee atmospheric abundances and global emission estimates, *Geophys. Res. Lett.*, **41**, 6, 2228–2235, doi: 10.1002/2013GL059143, 2014.
<http://onlinelibrary.wiley.com/doi/10.1002/2013GL059143/pdf>

Bader, W., T. Stavrou, J.-F. Muller, S. Reimann, C.D. Boone, O. Flock, B. Bovy, B. Franco, B. Lejeune, C. Servais, and E. Mahieu, Long-term evolution and seasonal modulation of methanol above Jungfraujoch (47°N, 8.0°E): Optimisation of the retrieval strategy comparison with simulations and observations, *Atmos. Meas. Tech.*, **7**, 3861–3872, doi: 10.5194/amt-7-3861-2014, 2014.
<http://hdl.handle.net/2268/168055>

Hall, B. D., A. Engel, J. Muhle, J. W. Elins, F. Artuso, E. Atlas, M. Aydin, D. Blake, E.-G. Brunke, S. Chiavarini, P. J. Fraser, J. Happell, P. B. Krummel, I. Levin, M. Loewenstein, M. Maione, S. A. Montzka, S. O'Doherty, S. Reimann, G. Rhoderick, E. S. Saltzman, H. E. Scheel, L. P. Steele, M. K. Vollmer, R. F. Weiss, D. Worthy, and Y. Yokouchi, Results from the International Halocarbon in Air Comparison Experiment (IHALACE), *Atmospheric Measurement Techniques*, **7**, 469–490, doi: 10.5194/amt-7-469-2014, 2014.
<http://www.atmos-meas-tech.net/7/469/2014/amt-7-469-2014.html>

Liang, Q., P.A. Newman, J.S. Daniel, S. Reimann, B. Hall, G. Dutton, and L.J.M. Kuijpers, Constraining the carbon tetrachloride (CCl₄) budget using its global trend and inter-hemispheric gradient, *Geophys. Res. Lett.*, **41**, 14, 5307–5315, doi: 10.1002/2014GL060754, 2014.
<http://onlinelibrary.wiley.com/doi/10.1002/2014GL060754/pdf>

Mahieu, E., R. Zander, G. C. Toon, M. K. Vollmer, S. Reimann, J. Muhle, W. Bader, B. Bovy, B. Lejeune, S. Servais, P. Demoulin, G. Roland, P. F. Bernath, C. D. Boone, K. A. Walker, and P. Duchatelet, Spectrometric monitoring of atmospheric carbon tetrafluoride (CF₄) above the Jungfraujoch station since 1989: evidence of continued increase but at a slowing rate, *Atmospheric Measurement Techniques*, **7**, 333–344, doi: 10.5194/amt-7-333-2014, 2014.
<http://hdl.handle.net/2268/154767>

Maione, M., F. Graziosi, I. Arduini, F. Furlani, U. Giostra, D.R. Blake, P. Bonasoni, X. Fang, S.A. Montzka, S. O'Doherty, S. Reimann, A. Stohl, and M.K. Vollmer, Estimates of European emissions of methyl chloroform using a Bayesian inversion method, *Atmos. Chem. Phys.*, **14**, 9755–9770, doi: 10.5194/acp-14-9755-2014, 2014.
<http://www.atmos-chem-phys.net/14/9755/2014/acp-14-9755-2014.html>

O'Doherty, S., M. Rigby, J. Mühle, D.J. Ivy, B.R. Miller, D. Young, P.G. Simmonds, S. Reimann, M.K. Vollmer, P.B. Krummel, P.J. Fraser, L.P. Steele, B. Dunse, P.K. Salameh, C.M. Harth, T. Arnold, R.F. Weiss, J. Kim, S. Park, S. Li, C. Lunder, O. Hermansen, N. Schmidbauer, L.X. Zhou, B. Yao, R.H.J. Wang, A.J. Manning, and R. G. Prinn, Global emissions of HFC-143a (CH₃CF₃) and HFC-32 (CH₂F₂) from in situ and air archive atmospheric observations, *Atmos. Chem. Phys.*, **14**, 9249–9258, doi: 10.5194/acp-14-9249-2014, 2014.
<http://www.atmos-chem-phys.net/14/9249/2014/acp-14-9249-2014.html>

Conference papers

Reimann, S., Non-CO₂ greenhouse gas measurements for trend analysis and international protocols, Spawning the Atmosphere Measurements Workshop, Bern, Switzerland, January 22-23, 2014.

Reimann, S., Ground-based Networks for Measuring Ozone- and Climate-Related Trace Gases, Ozone research Management meeting, WMO, Geneva, Switzerland, May, 2014.

Reimann, S., Real-World Verification of Methyl Bromide (CH₃Br) Phase-Out in Europe and its partial replacement with sulfuryl fluoride (SO₂F₂), AGU Fall meeting, San Francisco, USA, December, 2014.

Schoenenberger, F., HCFC-31: A new kid in town..., 49th Meeting AGAGE Scientists and Cooperating Networks, Ascona, Switzerland, April 26 – May 2, 2014.

Vollmer, M., Modern Inhalation Anesthetics in the Global Atmosphere, 49th Meeting AGAGE Scientists and Cooperating Networks, Ascona, Switzerland, April 26 – May 2, 2014.

Vollmer, M., First Observations of 4th generation synthetic halocarbons in the atmosphere: HFC-1234yf (CH₃CF=CH₂), HFC-1234ze(E) (trans-CF₃CH=CHF), and HCFC-1233zd(E) (trans-CF₃CH=CHCl), 50th Meeting AGAGE Scientists and Cooperating Networks, La Jolla, California, USA, December 8 – 13, 2014.

Vollmer, M., Observations of Greenhouse Gases from Jungfraujoch, Switzerland, Symposium on Atmospheric Chemistry and Physics, Steamboat Springs, Colorado, USA, August 11 – 15, 2014.

Vollmer, M., Modern Inhalation Anesthetics — Potent Greenhouse Gases in the Global Atmosphere, Non-CO₂ Greenhouse Gases Conference 7, Amsterdam, The Netherlands, November 5 – 7, 2014.

Data books and reports

Carpenter, L. J. and S. Reimann (Lead Authors), J. B. Burkholder, C. Clerbaux, B. D. Hall, R. Hossaini, J. C. Laube, S. A. Yvon-Lewis, Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project — Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014.

Reimann, S., M. K. Vollmer, D. Brunner, M. Steinbacher, M. Hill, L. Emmenegger, Kontinuierliche Messung von Nicht-CO₂-Treibhausgasen auf dem Jungfraujoch (HALCLIM-5), Empa/BAFU Progress report 2014-2, 2014. www.bafu.admin.ch/luft/00612/00625/11899/index.html

Magazine and Newspapers articles

SRF, Fernsehen, Interview für „10 vor 10“, Reimann, S.: Ozonloch: FCKW-Verbot zeigt Wirkung, 10.09.2014.

RTS, Radio, La reconstitution de la couche d'ozone est en bonne voie, selon l'ONU, 10.09.2014.

SRF, Radio Interview für SRF4, SRF1, Reimann, S.: Die Ozonschicht erholt sich, 11.09.2014.

Neue Zürcher Zeitung, Ozonbericht der Vereinten Nationen – der Ozonschicht geht es besser, 11.09.2014.

20 Minuten, Was gut fürs Ozonloch ist, schadet dem Klima, 11.09.2014.

St. Galler Tagblatt, Das Ozonloch stagniert, aber Ersatz schadet, 11.09.2014.

Tages-Anzeiger, der Bund, Baiser Zeitung, Erfolgsgeschichte mit Nebenwirkung, 12.09.2014.

La Liberté, La couche d'ozone en bonne voie de se rétablir, 11.09.2014.

Address:

Empa
Laboratory for Air Pollution/Environmental Technology
Ueberlandstrasse 129
CH-8600 Dübendorf

Contacts:

Dr. Martin K. Vollmer
Tel.: +41 58 765 4242
Fax: +41 58 765 1122
e-mail: martin.vollmer@empa.ch
URL: <http://www.empa.ch/abt503>