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:

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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 more than 50 compounds, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs and $SF_6$), and hydrofluorocarbons (HFCs), which are regulated under the Montreal and Kyoto Protocols, and additional compound classes such as e.g. hydrofluoroolefines (HFOs) and 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 2017 activities we chose to present an update for the halogenated inhalation anesthetics halothane and three fluranes. These are used in human and animal clinical applications from where they escape to the atmosphere. We first introduced results on these compounds in the atmosphere in the 2014 HFSJG report and in Vollmer et al. (2015), based on the world-wide first measurements of these four anesthetics. The presented 3-year update extends the published measurements to 2017 in the Northern Hemisphere based on in-situ measurements from Jungfraujoch, and to 2016 in the record from the Korean Antarctic station King Sejong (South Shetland Islands), where Empa runs a flask sampling program in collaboration with the Korea Polar Research Institute (KOPRI). While all four anesthetics have continued to be measured at these two locations, desflurane is now additionally measured routinely around the globe within the AGAGE network.

Halothane ($CF_3CHClBr$, halon-2311, atmospheric lifetime of 1 year) was intensively used in the 1960s and 1970s but is now replaced in most developed countries. Fluranes (fluorinated ethers) have been popular replacements and three of them are presently used globally in large quantities. These are isoflurane ($CF_3CHClOCHF_2$), desflurane ($CF_3CHFOCHF_2$), and sevoflurane ($(CF_3)_2CHOCH_2F$), with atmospheric lifetimes of 3.2 yr, 14 yr, and 1.1 yr, respectively. These compounds have significant Global Warming Potentials (GWPs) and hence contribute to the human-induced increase in the radiative forcing of the atmosphere.

Atmospheric abundances of halothane have continued to decline since the start of our record in 2000, and have now reached record-low levels in the lower ppq range (dry air mole fraction in femtomol $mol^{-1}$, $10^{-15}$) as is shown in Figure 1. The air reaching the Jungfraujoch contained ~11 ppq of halothane in 2017 and exhibited a pronounced seasonality due to the

seasonally varying OH molecule, with which halothane undergoes its major removal reaction. Abundances in the atmosphere above Antarctica at King Sejong are even lower than at Jungfraujoch, reaching ~8 ppq in 2016 (batch samples for 2017 not analyzed yet). The north-south gradient indicated by the difference between the two stations, demonstrates that the compound is still released to the atmosphere with predominantly Northern Hemisphere sources. The extremely low mole fractions for this compound, to our knowledge unprecedented in any in-situ measurements of halogenated greenhouse gases, create an analytical challenge. With its measurements close to analytical detection, halothane is likely not measureable anymore in the near future without any additional analytical efforts.

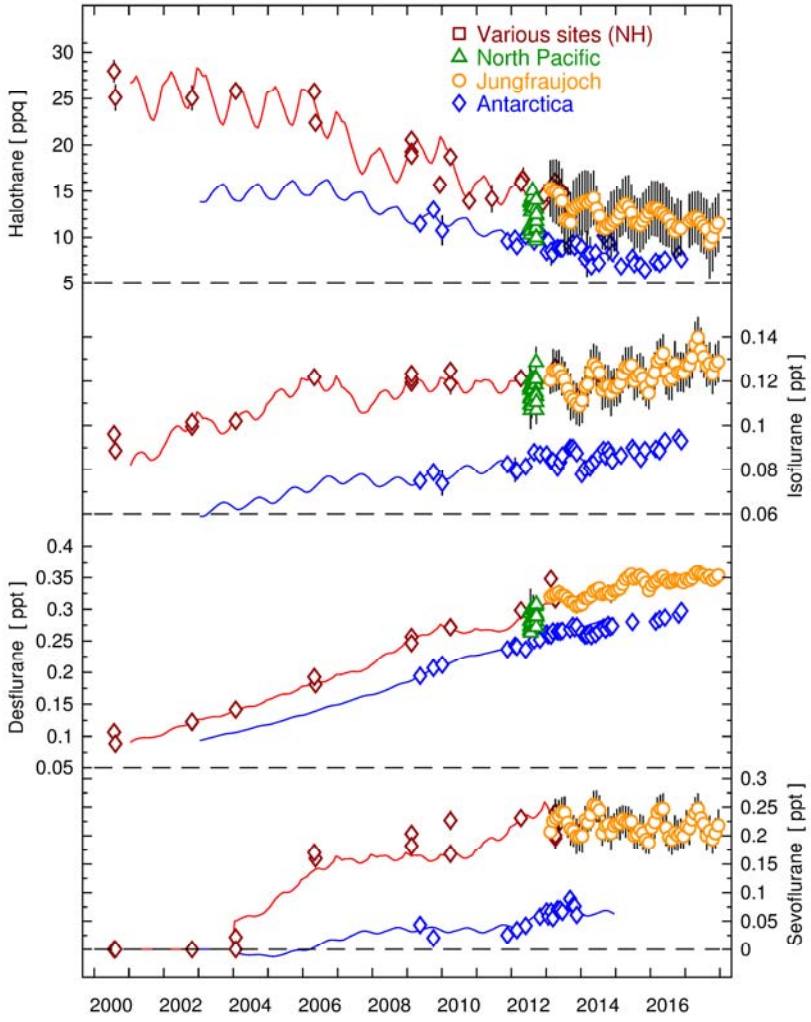


*Figure 1. Atmospheric abundances of the four inhalation anesthetics halothane (halon-2311) and the fluorinated ethers isoflurane, desflurane and sevoflurane. The update to Vollmer et al. (2015) contains new data from Jungfraujoch and the Korean Antarctic Station King Sejong (3 years each). Earlier data also include archived air samples from various sites in the Northern Hemisphere (NH), and a latitudinal gradient from samples collected aboard the Korean icebreaker R/V Araon. The Jungfraujoch data are background-filtered monthly means and the vertical bars are the 1-σ standard deviation of these monthly means. Vertical bars for the flasks samples represent the reproducibility (1 σ) from repeated measurements. When not shown, these are smaller than the plotting symbols. Solid lines are from an earlier model representation (Vollmer et al., 2015) and not updated here. Recent sevoflurane measurements from Antarctica are deemed unreliable and are therefore omitted here.*

Isoflurane, which is also used in animal medicine, has continued to increase in the past three years reaching a monthly mean of 0.13 ppt (picomol $mol^{-1}$, $10^{-12}$) at Jungfraujoch in 2017 and with an Antarctic record that lags in abundance. Similarly, desflurane, the longest-lived and

most climate-active of all three fluranes, has continued to grow, with a yearly mean mole fraction of 0.35 ppt at Jungfraujoch in 2017. Again, desflurane in the Antarctic record is comparably lower. These observations indicate ongoing emissions of isoflurane and desflurane with predominantly Northern Hemisphere sources. By contrast, the abundance of sevoflurane at Jungfraujoch has remained relatively stable over the past few years (0.22 ppt), indicating that emissions match destruction at a global level of ~1'200 t $yr^{-1}$ (Vollmer et al., 2015). Analytical difficulties prevent us from updating the Antarctic record for this compound. A summary of the yearly mean abundances of the four anesthetics is given in Table 1.

| | 2013 | 2014 | 2015 | 2016 | 2017 |
|---|---|---|---|---|---|
| Halothane (ppq) | 13.5 | 12.6 | 12.4 | 12.1 | 11.3 |
| Isoflurane (ppt) | 0.118 | 0.119 | 0.122 | 0.123 | 0.130 |
| Desflurane (ppt) | 0.317 | 0.324 | 0.344 | 0.345 | 0.352 |
| Sevoflurane (ppt) | 0.220 | 0.225 | 0.212 | 0.216 | 0.219 |

*Table 1. Atmospheric abundances of four inhalation anesthetic at Jungfraujoch. Yearly means are derived from in-situ measurements (16 samples per day), and averaged from monthly means background-filtered data (deemed representative of broad atmospheric regions). Results are based on the Empa-2013 primary calibration scales for these compounds.*

Desflurane measurements have also been introduced into the in-situ measurement program of AGAGE (Figure 2). The compound is now measured at most stations (on a 2-hourly frequency) and results are fully inter-calibrated through the central calibration laboratory at the Scripps Institution of Oceanography (UCSD, San Diego), based on the Empa-2013 primary calibration scale. Mole fraction at Cape Matatula (American Samoa) and Cape Grim (Tasmania), both sites influenced by Southern Hemisphere air, are lower compared to the Northern Hemisphere sites. Pollution events are absent at Cape Matatula, but the occasional arrival of pollution events at Cape Grim (from the Melbourne area) demonstrates the use of this compound in Australia. Similarly, the field sites Mace Head (Ireland), Gosan (Jeju Island, Korea), and Jungfraujoch (Switzerland) also exhibit occasional pollution events, while the records at Zeppelin (Spitsbergen) and Ragged Point (Barbados) are limited to background levels. Ultimately, the urban sites Aspendale (Melbourne), La Jolla (San Diego), and Dübendorf (Zürich) show large and frequent pollution events, reflecting the frequent use of this anesthetic in these urban environments (e.g. in operation theatres).

Measurements of all four inhalation anesthetics have continued to deliver important information on these compounds. They demonstrate the global presence of these anthropogenic compounds due to their continued emissions and their relative longevity. Efforts are now in place to use the high-resolution measurements from the AGAGE sites to improve our quantitative understanding of the distribution and emissions of desflurane to the atmosphere, within the air mass footprint of these stations.

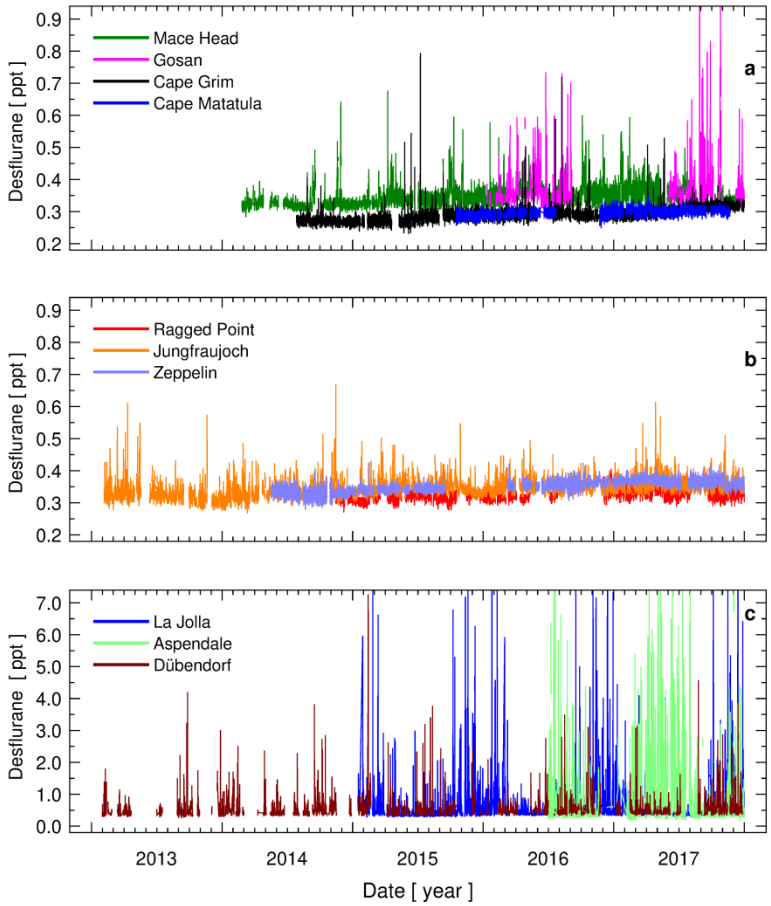


*Figure 2. Atmospheric abundances of the inhalation anesthetic desflurane ($CF_3CHFOCHF_2$) from in-situ measurements at AGAGE (Advanced Global Atmospheric Gases Experiment) stations. All results are expressed as dry air mole fractions in ppt (picomol $mol^{-1}$). Remote stations are shown in panels a and b, urban stations are shown in panel c (note the 10-fold change in the y-axis range).*

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Key words:

Halogenated ozone-depletion substances (ODSs), greenhouse gases (GHGs), F-gases, anesthetics, fluranes

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 2017:

## Refereed journal articles and their internet access

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## Conference papers

Reimann, S., M.K. Vollmer, D. Brunner, L. Emmenegger, A. Manning, P.L. DeCola, O. Tarasova, Towards a Novel Integrated Approach for Estimating Greenhouse Gas Emissions in Support of International Agreements, NOAA ESRL Global Monitoring Conference, Boulder, Colorado, USA, May 23–24, 2017.

Reimann, S., Evolution and Observations of Ozone Depleting Substances, Symposium for the 30th Anniversary of the Montreal Protocol, Paris, France, September 19–20, 2017.

Vollmer, M.K., M. Rigby, C.M. Trudinger, L. P. Steele, J. Mühle, S. Henne, S. Park, AGAGE+ Team, On the Emissions of HCFCs and CFCs Potentially Related to HFC Production, NOAA ESRL Global Monitoring Conference, Boulder, Colorado, USA, May 23–24, 2017.

## Magazine and Newspapers articles

„Kältemittel in der Atmosphäre --- Eine neue Chemikalie für Auto-Klimaanlagen birgt auch Probleme", Frankfurter Rundschau, May 8, 2017.

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