

Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

A Division of the Swiss Chemical Society

Tracking New Halogenated Alkenes in the Atmosphere

Martin K. Vollmer*, Stefan Reimann, Matthias Hill, Brigitte Buchmann, and Lukas Emmenegger

*Correspondence: Dr. M. K. Vollmer, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, E-mail: martin.vollmer@empa.ch

Keywords: Gas chromatography/mass spectrometry · Greenhouse gases · Ozone depletion · HFC-1234yf

Many halogenated trace gases in the atmosphere are potent stratospheric ozone-depleting substances and greenhouse gases. For many of them, international regulations on their usage and emissions are in place such as the Montreal and Kyoto Protocols. Consequently, over the last decades some compound classes were phased out from usage while others were newly introduced.

At Jungfraujoch we started world-wide first measurements of newly-produced halogenated alkenes (also referred to as hydrofluoroolefins, HFOs), a subgroup of the hydrofluorocarbons (HFCs). These compounds were recently marketed for replacing currently-used HFCs in refrigeration, foam blowing, and as solvents. In comparison to currently-used HFCs, halogenated alkenes have shorter atmospheric lifetimes (days vs years) and lower Global Warming Potentials (GWP_{100} , <10 vs 100s to 1'000s).

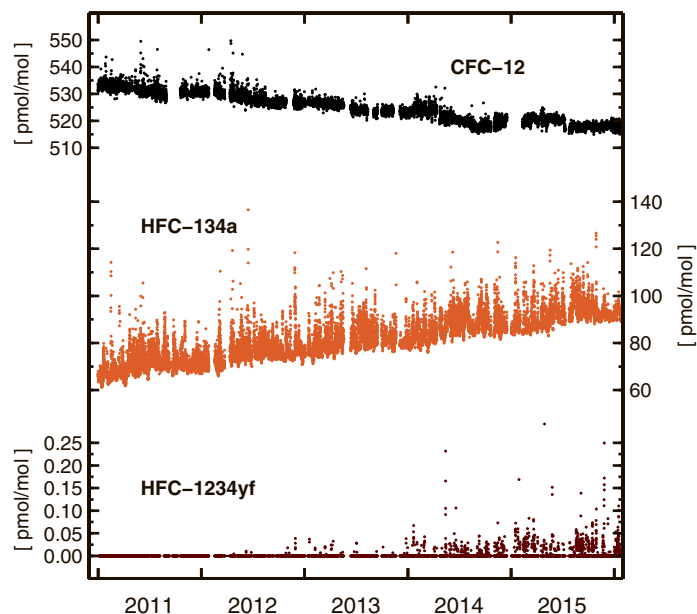
We measure HFC-1234yf (2,3,3,3-tetrafluoroprop-1-ene), HFC-1234ze(E) (E-1,3,3,3-tetrafluoroprop-1-ene), and HCFC-1233zd(E) (E-1-chloro-3,3,3-trifluoroprop-1-ene) along with ~50 other halogenated trace gases using gas chromatography coupled with quadrupole mass spectrometry (GC-MS) in selected ion mode. Every two hours, a fully-automated ambient air measurement is conducted and bracketed by similar calibration measurements using whole air working standards, which are linked to absolute calibration standards. Two liters of sample are preconcentrated on cold traps held at -150°C . The traps are subsequently heated to 100°C to release the compounds of interest into the GC-MS.

An example is the highly-debated replacement of HFC-134a



High-altitude research station Jungfraujoch, Switzerland. Image source: jungfrau.ch

(1,1,1,2-tetrafluoroethane) by HFC-1234yf as refrigerant in mobile air conditioners. We have captured the phase-in of HFC-1234yf usage within the air-mass footprint at Jungfraujoch, which covers large parts of



Time series at Jungfraujoch of three generation refrigerants used in mobile air conditioning. HFC-1234yf (2,3,3,3-tetrafluoroprop-1-ene), a newly marketed compound, is still undetectable (<0.003 picomol/mol) in most air samples arriving at the site.

Europe. At the same time we track the phase-out of the oldest generation refrigerant CFC-12 (dichlorodifluoromethane) and we monitor the currently used HFC-134a in the atmosphere.

A widespread use of HFC-1234yf and other halogenated alkenes may be expected in the near future. While the short atmospheric lifetimes of these halogenated alkenes are favorable from a climate perspective, little is currently known about the fate of the decay products of these compounds.

Continuous atmospheric monitoring of halogenated alkenes is necessary to estimate regional emissions and distribution patterns of these compounds and their decay products in the atmosphere.

Acknowledgements

We acknowledge funding by the Federal Office for the Environment (FOEN), the Swiss National Science Foundation (SNF) and support by the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG).

Received: March 11, 2016

References

- M. K. Vollmer, S. Reimann, M. Hill, D. Brunner, *Environ. Sci. Technol.* **2015**, *49*, 2703.
 M. K. Vollmer, T. S. Rhee, M. Rigby, D. Hofstetter, M. Hill, F. Schoenenberger, S. Reimann, *Geophys. Res. Lett.* **2015**, *42*, 1606.
 F. Schoenenberger, M. K. Vollmer, M. Rigby, M. Hill, P. J. Fraser, P. B. Krummel, R. L. Langenfelds, T. S. Rhee, T. Peter, S. Reimann, *Geophys. Res. Lett.* **2015**, *42*, 7817.
 M. K. Vollmer, M. Rigby, J. C. Laube, S. Henne, T. S. Rhee, L. J. Gooch, A. Wenger, D. Young, L. P. Steele, R. L. Langenfelds, C. A. M. Brenninkmeijer, J.-L. Wang, C.-F. Ou-Yang, S. A. Wyss, M. Hill, D. E. Oram, P. B. Krummel, F. Schoenenberger, C. Zellweger, P. J. Fraser, W. T. Sturges, S. O'Doherty, S. Reimann, *Geophys. Res. Lett.* **2015**, *42*, 8702.

Can you show us your analytical highlight?

Please contact: Dr. Veronika R. Meyer, Unterstrasse 58, CH-9000 St. Gallen
 Tel.: +41 71 222 16 81, E-mail: VRMeyer@bluewin.ch