Halogenated greenhouse gases at Jungfraujoch

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1. Project description

Halogenated ozone-depleting substances (ODSs) and greenhouse gases (GHGs) have been monitored at Jungfraujoch since 2000 under the project “HALCLIM”, which was extended into “CLIMGAS-CH” in 2018. These measurements are combined with atmospheric transport models for identifying and quantifying national and regional emissions of non-CO2 greenhouse gases (Switzerland and neighboring countries). For the synthetic greenhouse gases, which are the focus of this report, 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 Protocol on Substances That Deplete the Ozone Layer, and the Kyoto Protocol, 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 analysis by gas chromatography mass spectrometry (GC-MS) techniques.

For the 2018 activities we chose to present an update on the HFCs measured at Jungfraujoch. HFCs are used in refrigeration, as foam blowing compounds, solvents and fire retardants. These compounds serve as replacements for the chlorine- and bromine-containing CFCs, HCFCs, and halons, which have been regulated under the Montreal Protocol for their capacity to destroy stratospheric ozone. HFCs, being free of chlorine and bromine, are however very potent greenhouse gases and have so far been included in the Kyoto Protocol under the United Nations’ Framework Convention on Climate Change (UNFCCC).

HFCs were recognized as some of the fastest growing compounds in the atmosphere with the potential of a future significant contribution of the greenhouse gas radiative forcing of the atmosphere. A proposition to phase down HFCs within the framework of the Montreal Protocol lead to multi-year negotiations resulting in the 2016 Kigali Amendment to the Protocol, which came into force on 1 January 2019. Under this Amendment, a reduction of the use of HFCs by >80% is foreseen by 2030. By the end of 2018, ~65 countries have ratified the Amendment.

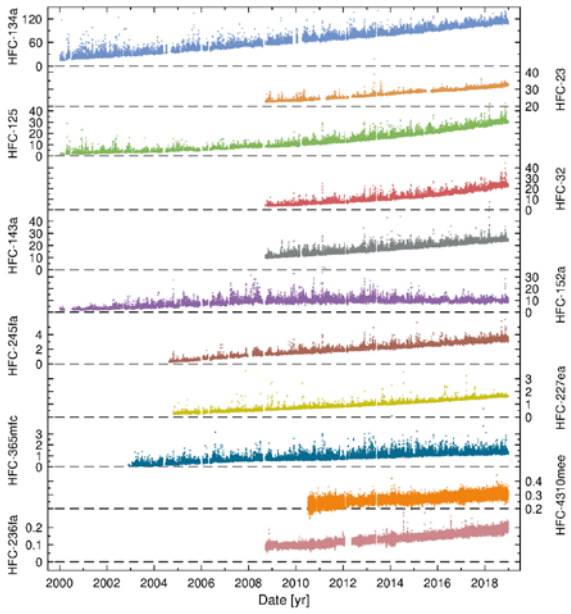

Figure 1. Records of hydrofluorocarbons (HFCs) measured at Jungfraujoch. Compounds are arranged according to their end-of-2018 abundances with the most abundant compound (HFC-134a) at the top. Abundances are expressed as dry air mole fraction in ppt (parts-per-trillion, pmol mol^{-1}). Records start at different times due to different times of introduction into the measurement program, in particular with the change to Medusa-GCMS technology in early 2008.

HFCs have been observed in the atmosphere by several networks including AGAGE (Figure 1). Records at Jungfraujoch reveal the general long-term trends of these HFCs as well as pollution events, which are advected from source regions to this site. At Jungfraujoch, measurements of the refrigerants HFC-134a and HFC-125 and the blowing agent HFC-152a began in 2000 using an ADS-GC-MS system (Simmonds et al., 1995). Later, the world-wide first measurements of the foam blowing agents HFC-245fa and HFC-365mfc, and the fire retardant HFC-227ea were made at Jungfraujoch. With the change to a Medusa-GC-MS system (Miller et al., 2008) at Jungfraujoch in 2008, measurements of more HFCs became possible. The very powerful greenhouse gases HFC-23 and the refrigerant HFC-236fa (pioneering measurements at Jungfraujoch) were added as well as the refrigerants HFC-32 and HFC-143a. Ultimately, the solvent HFC-4310mee was added to the measurement program in 2010.

Table 1. Hydrofluorocarbons (HFCs) measured at Jungfraujoch.

	Chemical Formula	Atm. Lifetime [yr] a)	GWP-100 a)	Radiative Efficiency [Wm^{-2} ppb^{-1}] b)	Abundance at JFJ end 2018
HFC-134a	CH_2FCF_3	14	1'300	0.16	110
HFC-23	CHF_3	230	12'400	0.18	32
HFC-125	CHF_2CF_3	31	3'200	0.23	30
HFC-32	CH_2F_2	5.4	680	0.11	23
HFC-143a	CF_3CH_3	51	4'800	0.16	24
HFC-152a	CH_3CHF_2	1.6	140	0.10	9.5
HFC-245fa	$CHF_2CH_2CF_3$	7.9	860	0.24	3.3
HFC-227ea	CF_3CHFCF_3	36	3'400	0.26	1.6
HFC-365mfc	$CH_3CF_2CH_2CF_3$	8.7	800	0.22	1.3
HFC-236fa	$CF_3CH_2CF_3$	240	8'100	0.24	0.20
HFC-4310mee	$CF_3CHFCHFCF_2CF_3$	16	1'700	0.42	0.31

a) Lifetimes and Global Warming Potentials (GWP) 100-yr according to WMO Ozone Assessment 2014

b) From Hodnebrog et al., (2017)

By the end of 2018, atmospheric abundances for HFC-134a were highest (110 ppt) of all HFCs measured at Jungfraujoch and pollution events continued to be large and frequent. The compound is used in stationary refrigeration systems and in mobile air conditioners (MAC), but efforts are taken to replace this compound by HFOs, in particular in the MAC sector. Similarly, HFC-125, HFC-32, and HFC-143a (often used in blends) were >20 ppt each by the end of 2018, and their frequent pollution events demonstrate the widespread usage of these compounds. Resulting from emissions in the foam-blowing sector, abundances of HFC-245fa and HFC-365mfc are comparably low. HFC-152a, with a relatively low atmospheric lifetime (1.6 yr), is the only HFC that has stopped growing in the atmosphere. Its stabilized abundance indicates that global sinks and sources are currently balanced. HFC-23, which has its major source as unintentional by-product in the HCFC-22 production, is continuing to grow in the atmosphere after large efforts for its factory-level destruction under the Clean Development Mechanism within the Kyoto Protocol have ceased. There are virtually no pollution events recorded for the two minor HFCs HFC-236fa (lifetime 240 yr) and HFC-43-10mee, suggesting that there is little usage in the part of Europe, which is usually "seen" from Jungfraujoch. The cumulative mole fraction of all eleven HFCs has reached 240 ppt at the end of 2018 (Figure 2a).

HFCs absorb long-wave radiation and contribute to global warming. Their absorption efficiencies vary and are expressed as Radiative Efficiency (RE) in W m^{-2} ppb^{-1} (parts-per-billion, nmol mol^{-1} mole fraction). Using updated RE from Hodnebrog et al. (2013), we calculate the radiative forcing of the HFCs (Figure 2b). The relative accounting of the individual HFCs changes slightly compared to the mole fractions, with that of HFC-125 increasing relative to HFC-134a, due to its larger RE. The cumulative radiative forcing of all measured HFCs amounts to 0.04 W m^{-2}. This compares with 0.37 W m^{-2}, for all synthetic greenhouse gases combined, and with ~2 W m^{-2} for CO_2 (AGAGE-internal calculations). Consequently, the radiative forcing of the HFCs is currently still very small. However, the growth of these compounds in the atmosphere is very rapid. Calculations by Velders et al. (2009) show that global HFC emissions in 2050 could be equivalent to 9–19% (CO_2-eq. basis) of projected global CO_2 emissions in a business-as-usual scenario and contribute to a radiative forcing equivalent to that from 6–13 years of CO_2 emissions near 2050. It is however expected that this rapid growth of HFCs will significantly slow down under the phase-out program of the Kigali Amendment to the Montreal Protocol.

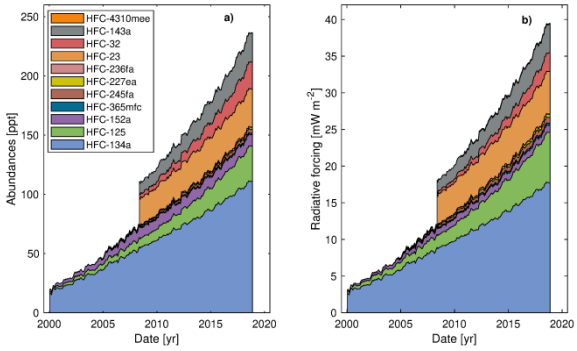

Figure 2. Stacked records of abundances (a) and radiative forcing (b) for eleven hydrofluorocarbons (HFCs) measured at Jungfraujoch. Calculations are based on monthly means of background data (results deemed representative of broad atmospheric regions far from emission sources). Stacking is arranged according to record lengths with the shortest records at the top.

The HFCs measured at Jungfraujoch are all part of the 'Annex-F' compound list of the Kigali Amendment. However, the list contains an additional seven compounds, which are currently not measured at Jungfraujoch, or, to the best of our knowledge, anywhere else. The 'missing' compounds are mainly isomeric forms of those measured. Little is known about technical measurement details for these compounds, their potential presence in the atmosphere, and their atmospheric fate. Clearly, more research is needed to fill this gap.

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Collaborating partners / networks

Bundesamt für Umwelt (BAFU) / Federal Office for the Environment (FOEN)
Advanced Global Atmospheric Gases Experiment (AGAGE)
University of Bristol
Korea Polar Research Institute
ACTRIS – Aerosol, Clouds, and Trace Gases Research Network
NABEL – Swiss National Air Pollution Monitoring Network
Institut d'Astrophysique et de Géophysique, Université de Liège
World Meteorological Organisation (WMO)
EMEP – European Monitoring and Evaluation Programme
GAW – Global Atmosphere Watch
ICOS – Integrated Carbon Obervation System Research Infrastructure
IG3IS – Integrated Global Greenhouse Gas Information System

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