# Halogenated greenhouse gases at Jungfraujoch

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**1. Project description**

Halogenated synthetic greenhouse gases (GHGs) and ozone-depleting substances (ODSs) have been monitored at Jungfraujoch since 2000 as part of the FOEN/BAFU-funded 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-$CO_2$ greenhouse gases (Switzerland and neighboring countries). For the synthetic greenhouse gases these "top-down" (observation-based) estimates are used to support "bottom-up" estimates of the national reporting authorities, that 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), $SF_6$, and hydrofluorocarbons (HFCs), which are regulated under the Montreal Protocol on Substances That Deplete the Ozone Layer and the Kyoto Protocol. Additionally measured compounds are hydrofluoroolefines (HFOs), fluorinated anesthetics, halogenated hydrocarbons and hydrocarbons. Most of these compounds are core substances measured by the AGAGE program (Advanced Global Atmospheric Gases Experiment), of which Empa is a partner. Individual measurements are conducted on 2 L of sampled air and using a gas chromatograph-mass spectrometer (GC-MS) analytical technique (Miller et al., 2008).

For the 2022 activities we present an update on the hydrochloro-fluorocarbons (HCFCs) measured at Jungfraujoch. This choice was triggered by the discovery of a new HCFC and by globally significant findings on HCFC emissions over the last few years, which moved this class of compounds back in focus after more than a decade of atmospheric trends with little scientific excitation.

HCFCs are the second-generation entirely anthropogenic halo-carbons, designed in the 1990s as interim replacements of the CFCs, the first-generation ozone-depletion Substances (ODSs), used in refrigeration, foam blowing and as solvents. HCFCs are also ODSs, because they still contain chlorine, but their potential to destroy stratospheric ozone is significantly smaller because of their reduced atmospheric lifetimes compared to the CFCs. HCFCs are Class II regulated compounds of the Montreal Protocol on Substances that Deplete the Ozone Layer. Similar to the CFCs, a phase-out of the production of these compounds for end-use applications started in the late 1990s, leading to a complete global ban on production and consumption for emissive use by 2030. HCFCs are also potent greenhouse gases, but again, less powerful than CFCs (Table 1).

For the interpretations of HCFCs and their atmospheric trends, it is important to note that emissions of these substances can also originate from feedstock, by-products, and intermediate products in the fluorocarbon industry. These sources are also included in the Montreal Protocol but their regulation is different. In contrast to a complete ban for ODS production for emissive end-use, HCFC feedstock, by-products, and intermediate products are not banned but their emissions must be kept at minimum.

Three of these HCFCs have distinctly higher abundances in the atmosphere (Table 1, Fig. 1). HCFC-22 (chlorodifluoromethane) is the most abundant HCFC. It was predominantly produced for use in refrigeration and polymer production. HCFC-141b (1,1-dichloro-1-fluoroethane) was predominantly produced for foam blowing, and HCFC-142b (1-chloro-1,1-difluoroethane) for refrigeration and foam blowing. Of those HCFCs that are present in the atmosphere at minor mole fractions we here report on HCFC-124 (1-chloro-1,2,2,2-tetrafluoroethane), used in specialized refrigeration applications. The other three HCFCs, HCFC-133a (2-chloro-1,1,1-tri-fluoroethane), HCFC-132b (1-chloro-2-chloro-2,2-difluoroethane), and HCFC-31 (chlorofluoromethane) are not known for any purposeful end-use. There are other HCFCs present in the atmosphere, but these are currently not measured at Jungfraujoch, or no calibration has yet been applied.

At Jungfraujoch, the first four of the HCFCs listed in Table 1 have been measured within the entire HALCLIM/CLIMGAS-CH period (2000 – present). However, we limit the reporting of these compounds to the period of the superior Medusa-GCMS technology (Fig. 1). Jungfraujoch indoor air and the originally used inlet for halocarbons are highly contaminated with HCFC-22 and HCFC-142b banked in old foam. This has prevented us from making reliable measurements until the halocarbon air inlet was moved to the ridge ~80 m east of the visitor terrace. For this reason, our Jungfraujoch records for these two compounds are limited to 2012 − present. In addition to Jungfraujoch, the HCFC records for Mace Head (Ireland) and Cape Grim (Tasmania) are shown in Fig. 1. The atmospheric mole fractions were statistically filtered to extract background conditions, thereby removing pollution events (data,

which are not deemed representative for a large region), and are binned into monthly means. Our interpretation below is thus representative for hemispheric-scale results.

*Table 1. Hydrochlorofluorocarbons (HCFCs) measurements at Jungfraujoch (HCFC-31 excluded).*

| | Chemical Formula | Atmos. Lifetime (yr) [a] | ODP [a] | GWP-100 [a] | Abundance at JFJ end 2022 (ppt) |
|---|---|---|---|---|---|
| HCFC-22 | $CHClF_2$ | 12 | 0.024–0.034 | 1'780 | 258 |
| HCFC-141b | $CCl_2FCH_3$ | 9.4 | 0.069–0.102 | 800 | 26.0 |
| HCFC-142b | $CClF_2CH_3$ | 18 | 0.023–0.057 | 2'070 | 22.6 |
| HCFC-124 | $CClFCF_3$ | 5.9 | 0.022 | 530 | 0.93 |
| HCFC-133a | $CH_2ClCF_3$ | 4.6 | 0.019 | 355 | 0.55 |
| HCFC-132b | $CH_2ClCClF_2$ | 3.5 | 0.038 | 320 | 0.19 |
| HCFC-31 | $CH_2ClF$ | 1.2 | 0.019 | 65 | 0.12[b] |

a) Lifetime, Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) 100-yr according to WMO Ozone Assessment 2018

b) In the northern hemisphere in 2020

The northern hemisphere abundances of the HCFCs shown in Fig. 1, as represented by the Jungfraujoch and Mace Head stations, are elevated compared to the southern hemisphere (represented by Cape Grim) because of the predominantly northern hemisphere sources of these compounds. Seasonal variations in the records are caused by seasonality in the OH radical, which is one of the two major removal mechanism (stratospheric photolysis being the other).

In recent years, the abundances of the three major HCFCs, HCFC-22, HCFC-141b, and HCFC-142b have levelled, as a consequence of emission reductions, following the international ban on these compounds. However, emission reductions have been delayed and slow, primarily because of the enormous amounts of these compounds stored in equipment (banks), from which they gradually leak to the atmosphere. For HCFC-22, the last two years represent a historic mark for its reversal in the northern hemisphere mole fractions. HCFC-141b has shown puzzling records over the last decades. Stabilizations, reversals and re-rise have been observed in the 1990s (not shown in Fig. 1), but also in the past decade. The renewed increase in the last few years after a minimum in 2018 is caused by increasing emissions, the origin of which is unclear (Western et al., 2022). Speculations reach from intermediate/by-product emissions in new fluorocarbons production to illegal 'new' production for emissive end-use in the foam-blowing sector, similar to that found for CFC-11 (Montzka et al, 2018, Rigby et al., 2019).

HCFC-124 is a minor HCFC, which was primarily used as refrigerant in niche applications. Its multi-decadal decline in the atmosphere was expected based on the phase-out regulations. However, this decline has stopped about 3 years ago and mole fractions have levelled because of stable or increasing emissions. The source of this new HCFC-124 production is unclear. While there are possible fluorocarbon production routes involving HCFC-124 as an intermediate compound, renewed illegal production for direct use in emissive applications cannot be excluded.

HCFC-133a, HCFC-132b, and HCFC-31 were recently discovered in the atmosphere (Laube et al., 2014, Vollmer et al., 2015, Schoenenberger et al., 2015, Vollmer et al., 2021). In-situ measurements of the former two were first conducted at Jungfraujoch and later included in the measurement program of the AGAGE network with ~11 global monitoring stations. HCFC-31 measurements require instrumental alterations from the routine program and hence this compound is not measured continuously. However, based on flask samples collected at Dübendorf for this very purpose, piggy-bag analyses on archived air samples and a Swiss-Korean Antarctic sampling program, Empa has reconstructed the history of HCFC-31 (and older parts of the records of HCFC-132b and HCFC-133a) by laboratory analysis (Fig. 1).

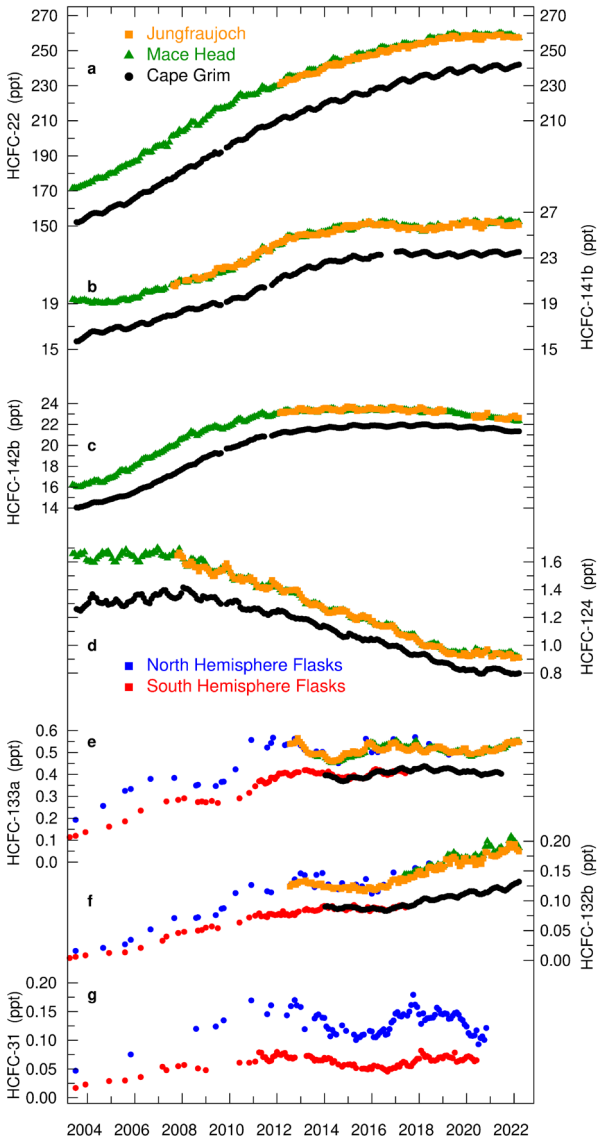


*Figure 1. Records of hydrochlorofluorocarbons (HCFCs) measured at Jungfraujoch (47 °N), Mace Head (Ireland, 53 °N), and Cape Grim (Tasmania, 41 °S), complemented with measurements from flask samples collected in both hemispheres. In situ background observations (observations deemed representative for a large region) are binned into monthly means. Abundances are expressed as dry air mole fraction in ppt (parts-per-trillion, pmol mol$^{-1}$). The records are limited to analytical periods with Medusa-GCMS measurement technology.*

There is no known purposeful use of these three minor HCFCs, but their appearance as intermediate substances are plausible and documented. HCFC-133a, and most likely HCFC-132b, are both intermediates in the production of the Generation-3 hydrofluorocarbon (HFC) HFC-134a (1,1,1,2-tetrafluoroethane), a widely used refrigerant. However, the atmospheric records shown in Fig. 1 and their underlying emissions do not linearly correlate with the monotonically increasing production of HFC-134a, except perhaps for HCFC-132b in recent years. A possible explanation for the lack of

such correlation might be that the 'cleanliness' of HFC-134a production is strongly factory dependent, with potentially a few factories creating a dominant share of HCFC-133a and HCFC-132b emissions.

HCFC-31 is believed to be emitted as an intermediate substance in the production pathway for HFC-32 (difluoromethane), another popular refrigerant. Again, while global HFC-32 demand has been monotonically increasing over the last decades, no correlation to the abundances and underlying emissions of HCFC-31 seems to be apparent.

In conclusion, atmospheric HCFC measurements, which for decades have shown predictable results, became a focus of attention in the last few years due to unexpected changes in their atmospheric abundances and inferred emissions. The records presented here lead to a surprising number of questions on the sources and fluxes of these HCFCs. Jungfraujoch and other AGAGE in-situ measurements contain a wealth of information on regional emissions, particularly in the active Asian region. These high-resolution measurements can help to explore the mysteries found in the global records for several of these HCFCs.

None of the examples on increasing global emissions shown here were captured by the reporting scheme under the Montreal Protocol. In fact, there are no country reports on HCFC-133a, HCFC-132b, or HCFC-31. This demonstrates the power and need of observations to support bottom-up based emission estimates. Ultimately, the halogen loading to the stratosphere and hence the evolution of the ozone hole are driven by the abundance of the CFCs, not their (reported) emissions, thereby further supporting the need for long-term global measurements.

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**Internet data bases**

http://empa.ch/web/s503/climate-gases
https://www.bafu.admin.ch/bafu/en/home/topics/air/publications-studies/studies.html

**Collaborating partners / networks**

Bundesamt für Umwelt (BAFU) / Federal Office for the Environment (FOEN)
Advanced Global Atmospheric Gases Experiment (AGAGE): https://agage.mit.edu/
University of Bristol
Korea Polar Research Institute
CSIRO Oceans and Atmosphere
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

**Scientific publications and public outreach 2022**

**Refereed journal articles and their internet access**

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