# 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 as part of the 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, which are the focus of this report, the "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 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 (Miller et al., 2008).

For the 2019 activities we present an update on the chlorofluorocarbons (CFCs) measured at Jungfraujoch. This choice was triggered by several globally significant findings on CFC emissions over the last few years, which moved this class of compound back in focus after more than a decade of expectable atmospheric trends with little scientific excitation.

CFCs were used in refrigeration, foam blowing and as solvents. They are the most potent stratospheric ozone depletion substances (ODSs) and part of Class 1 regulated compounds of the Montreal Protocol on Substances that Deplete the Ozone Layer. A phase-out of the production of these compounds for end-use applications started in the mid 1990s and has led to a complete global ban on production in 2010. CFCs are long-lived in the atmosphere and, combined with their high radiative efficiencies, they are also some of the most potent greenhouse gases (Table 1). Their ban makes the Montreal Protocol a significant climate change mitigation treaty.

Three CFCs have distinctly higher abundances in the atmosphere compared to others. CFC-12 (dichlorodifluoromethane) is the most abundant CFC (Table 1, Fig. 1) and was predominantly used as a refrigerant in the past. CFC-11 (trichlorofluoromethane) was predominantly used for foam blowing, and ∑CFC-113 (trichlorotrifluoroethane) was a solvent. Minor CFCs are CFC-13 (chlorotrifluoromethane), ∑CFC-114 (dichlorotetrafluoroethane) and CFC-115 (chloropentafluoroethane), all three mainly used in specialized refrigeration.

*Table 1. Chlorofluorocarbons (CFCs) measurements at Jungfraujoch.*

| | Chemical Formula | Atmos. Lifetime (yr) [a)] | ODP [a)] | GWP-100 [a)] | Abundance at JFJ end 2019 (ppt) |
|---|---|---|---|---|---|
| CFC-11 | $CCl_3F$ | 52 | 1.0 | 5'200 | 226 |
| CFC-12 | $CCl_2F_2$ | 102 | 0.73-0.81 | 10'300 | 503.5 |
| CFC-13 | $CClF_3$ | 640 | 1.0 | 13'900 | 3.3 |
| ∑CFC-112[b,c)] | $CCl_4F_2$ | 64/52 | 0.98/0.86 | 4'370/3'460 | - |
| ∑CFC-113[c)] | $C_2Cl_3F_3$ | 93/55 | 0.82/0.73 | 6'080/3'750 | 69.7 |
| ∑CFC-114[c)] | $CCl_2F_4$ | 189/105 | 0.50/0.72 | 8'580/6'670 | 16.3 |
| CFC-115 | $C_2ClF_5$ | 540 | 0.26 | 7'310 | 8.73 |

a) Lifetimes, Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) 100-yr according to WMO Ozone Assessment 2018

b) Measurements not yet calibrated

c) Combined measurements of both isomers for each chemical. The second numbers denote the properties of the rare isomers.

Trichlorotrifluoroethane and dichlorotetrafluoroethane, each have one isomer, which is atmospherically less important (CFC-113a (1,1,1-trichlorotrifluoroethane) and CFC-114a (1,1-dichlorotetrafluoroethane), respectively. Due to their similar chemical properties compared to their main isomers, an analytical distinction of the two is not possible for most measurement techniques, including the one used in our studies, and hence the measurements combine both isomers. This has led to the 'Sigma' notation ∑CFC-113 and ∑CFC-114 for our measurement technique and reporting. Isomer distinction for these chemicals is possible for some analytical techniques, which were used to demonstrate that the atmospheric abundance of CFC-113a contributes 1 % to ∑CFC-

113 (Adcock et al., 2018) and CFC-114a 7% to ∑CFC-114 (Laube et al., 2016) in the present troposphere. At Jungfraujoch, most of the CFCs have been measured since 2000 within HALCLIM/CLIMGAS-CH. However, since superior measurement techniques have been installed in 2008 (Medusa-GCMS, Miller et al., 2008) we limit the reporting of these compounds to this period only. Measurement results from Jungfraujoch, 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.

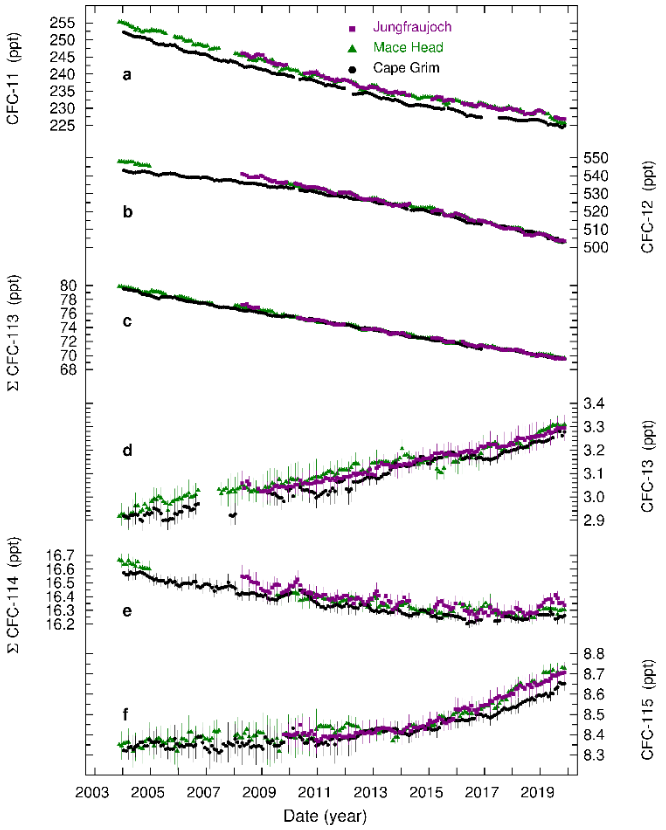


*Figure 1. Records of chlorofluorocarbons (CFCs) measured at Jungfraujoch (47 °N), Mace Head (Ireland, 53 °N), and Cape Grim (Tasmania, 41 °S). Background observations (observations deemed representative for a large region) are binned into monthly means and the vertical bars are 1-sigma std dev of that mean. The three major CFCs CFC-11, CFC-12, and ∑CFC-113 (panels a–c) are declining in the atmosphere. However, CFC-11 was recently found to not decline as rapidly as predicted, leading to findings on large illegal CFC-11 production and a violation of the Montreal Protocol in China (Montzka et al., 2018, Rigby et al., 2019). Minor CFCs (CFC-13, ∑CFC-114, and CFC-115) are also not declining as rapidly as expected, however the source for their lingering emissions is currently unclear. Abundances are expressed as dry air mole fraction in ppt (parts-per-trillion, pmol mol$^{-1}$). Records are shown from the start of Medusa-GCMS measurement technology only.*

Atmospheric abundances of the three major CFCs have levelled in the 1990s/early 2000s and have slowly declined since (Fig. 1a–c). Global emissions, derived from these observations, have generally also declined. However, a recent study found that atmospheric observations of CFC-11 has not declined as rapidly as predicted, and global emissions have increased again (Montzka et al, 2018), by 13±5 Gg yr$^{-1}$ for the period 2012–2017. A follow-up study using high-resolution observations, in particular from the AGAGE Korean site Gosan, revealed that a large fraction of these “new” emissions stemmed from China (Rigby et al., 2019). These findings, together with the discovery by the Non-government Organization EIA (Environmental Investigation Agency) of illegal CFC-11 use in the foam blowing sector in China pointed to a violation of the Montreal Protocol.

A recent study on the minor CFCs from the AGAGE network has revealed some additional disturbing findings (Vollmer et al., 2018). CFC-13, for the first time in AGAGE referenced to a sound primary calibration scales (Guillevic et al., 2018), and fully inter-calibrated among the AGAGE stations and archived air measurement sets, allowed for a reconstruction of the full history of this CFC. Continued growth of CFC-13 was demonstrated for this long-lived compound (lifetime 640 yr, Fig. 1d), and a detailed analysis showed that emissions have not declined in recent decades, although they were expected to. For ∑CFC-114, atmospheric abundances have slowly declined, but not as rapidly as would have been expected given the ban on this substance (Fig. 1e). Global emissions, as derived from these observations, showed no decline over the past decades. CFC-115, again a long-lived compound (540 yr), recently showed a clear increase in atmospheric abundances and a corresponding increase in emissions (Vollmer et al., 2018, Fig 1f). Finally, Laube et al., 2016 showed increasing global abundances and emissions of CFC-114a over the past decade, and Adcock et al., 2018, came to the same conclusions for CFC-113a, showing the largest relative growth of all CFCs observed in the atmosphere. Similarly to CFC-11, it was shown that the majority of the emissions of all these minor CFCs predominantly originate from East Asia.

The lack of declining emissions for the three minor CFCs and for the rare isomers CFC-113a and CFC-114a remains a puzzle so far. Hypotheses are put forward that these compounds may be emitted as intermediate product / byproduct during the production of other fluorocarbons, most likely that of hydrofluorocarbons (HFCs). If this was the case, then their treatment under the Montreal Protocol is different compared to compounds with end-use applications. In the case of byproduct emissions, the Montreal Protocol urges the Parties to take steps to minimize such emissions (UNEP 2017).

In conclusion, atmospheric CFC 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. None of the examples on increasing global emissions shown here was captured by the reporting scheme under the Montreal Protocol. 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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**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

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