

Halogenated greenhouse gases at Jungfrauoch

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1 Project description

Halogenated synthetic greenhouse gases (GHGs) and ozone-depleting substances (ODSs) have been monitored at Jungfrauoch 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-CO₂ 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, which are based on emission factors and industry information (import / export / manufacture). Furthermore, the measurements help to track global trends of ODSs and GHGs in the “background” air. Measurements at Jungfrauoch comprise a suite of more than 50 halogenated organic compounds, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), perfluorocarbons (PFCs), SF₆, and hydrofluorocarbons (HFCs), which are regulated under the Montreal Protocol on Substances That Deplete the Ozone Layer and the Kyoto Protocol. Additional 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).

2 Focus of this year’s report: Naturally occurring brominated compounds

Given the large selection of compounds we measure within this project, we traditionally pick some selected groups of trace gases on which we elaborate in more detail for the annual reports. While in the last report we presented brominated compounds, which are controlled under the Montreal Protocol and mainly synthetic in origin, we here present measurements of brominated compounds, which have both natural and anthropogenic sources. This includes four compounds: Methyl bromide (CH₃Br), dibromomethane (CH₂Br₂), bromoform (CHBr₃) and the newly-measured bromoethane (ethyl bromide, C₂H₅Br).

Table 1: Climate metrics for brominated natural compounds.

Compound	Atmospheric lifetime ^{a,b}	ODP ^a	GWP ^{a,c}	Abundance at JFJ (ppt) ^d
CH ₃ Br	0.8 yr	0.57	2	6.6–7.0
CH ₂ Br ₂	147 d	3–4	1	0.7–1.2
CHBr ₃	13 d	1–5	≪1	0.6–1.3
C ₂ H ₅ Br	50 d	<0.46	<1	0.11–0.18

^a (Burkholder et al. 2022)

^b WMO 2022 total lifetime

^c GWP over a 100-yr time span

^d for 2024. Dry air mole fraction in picomol mol⁻¹

Measurements of the four compounds at Jungfrauoch are shown in Figure 1 along with the exemplary records of two other European AGAGE stations, those for Mace Head (east coast of Ireland) and Tacolneston (UK). Although measurements are available for much longer, we chose to include only the last 10 years in Figure 1 to better visualize some details. In fact, Jungfrauoch measurements for CH₃Br, CH₂Br₂ and CHBr₃ are available for the entire ‘Medusa-GCMS’ period (2008–present), while CH₃Br was measured within the entire HALCLIM/CLIMGAS programs, including 2000–2008 using an older measurement technology.

CH₃Br is a first generation (Class I) Montreal Protocol compound, which was intensively used in the past for fumigation in agriculture and disinfection of grain and other food storage silos as well as other pesticide applications such as in international shipping. The substance is still permitted for use in very specialized application in some countries under the rules for QPS (quarantine and pre-shipment) fumigants. Efforts to phase out this strong ozone-depleting substance has led to a global decline from 9 ppt in the 1990s to currently 6.5–7 ppt. Global direct anthropogenic emissions (from QPS) are estimated at 10 kton yr⁻¹, while the total emissions are at 130 kton yr⁻¹. These significant emissions are largely due to natural sources, particularly production from marine algae. The records at Mace Head and Tacolneston (Figure 1) are dominated by ‘events’ from such marine emissions. Most other AGAGE stations with a marine ‘window’ in their advection footprint show similarly large and frequent emissions. In contrast, at Jungfrauoch, a land-locked station, such ‘pollution events’ are generally absent.

CH₂Br₂ and CHBr₃ emissions are predominantly from nat-

ural sources, such as macroalgae and phytoplankton. Their global emissions are considerable, with a high uncertainty of the estimated source strength ($150\text{--}820\text{ kt Br yr}^{-1}$). Their atmospheric lifetimes towards degradation is short (Table 1). Both compounds are reacting relatively quickly with the OH radical, which results in the pronounced seasonal cycle seen at Jungfraujoch. For both compounds, there is no trend in the AGAGE records over the approximately 20 years of measurements. The record for CHBr_3 at Jungfraujoch is interrupted from 2015–2020 due to some measurement difficulties. CHBr_3 is one of the lowest-boiling-point compounds measured in the network, which can lead to difficulties in its adsorption and desorption on the preconcentration cold traps.

Jungfraujoch is the AGAGE site holding the record in first measurements of newly detected compounds. While bromoethane has been measured in the past during shorter campaigns, it is now measured continuously at a few AGAGE sites, lead by Jungfraujoch. Little is known about this compound, but literature suggests both natural and anthropogenic sources (Carpenter et al. 1999; Low et al. 2003). Our first measurements seem to confirm this. Pollution events at Mace Head are occasionally high, and generally, abundances are higher than at Jungfraujoch. However, there are also some pollution events detected at Jungfraujoch which are not seen in CH_2Br_2 or CHBr_3 . The measurements shown in Figure 1d are preliminary. Longer storage-effect studies and more intercomparison measurements are needed for the calibration standards used in this project. While most calibration standards used so far suggest stability of bromoethane over longer periods, there are some standards that show drift in the bromoethane concentration. Also, our measurements of flask samples from Antarctica, which occasionally exhibit high bromoethane concentrations, show instability (based on duplicate sampling). Clearly, the compound is still on an explorative level and needs more research before more quantitative analysis can be pursued. Nevertheless, primary calibration is available through dilution of a commercially-obtained reference gas, allowing us to report mole fractions on an Empa-BOC-2023 primary calibration scale. Based on this calibration, we find seasonally varying bromoethane concentration of $0.08\text{--}0.18\text{ ppt}$ at Jungfraujoch, while those at Mace Head and Tacolneston are generally higher ($0.20\text{--}0.25\text{ ppt}$). These estimates are in agreement with the few measurements available in the literature (Carpenter et al. 1999; Low et al. 2003). The importance of bromoethane for the stratospheric ozone depletion is unclear but depends to a large extent on its atmospheric lifetime. While this is listed as 50 days in the latest WMO Ozone Assessment report (Burkholder et al. 2022), estimates by Hossaini et al. (2012), based on atmospheric observations, are at ≈ 18 days at the earth's surface and up to ≈ 183 days in the tropical tropopause layer. If the latter holds, bromoethane could potentially be a significant source of bromine to the stratosphere.

It is worthwhile noting that measurements of other naturally-occurring brominated compounds, such as CBrClCF_2 , CH_2BrCl , CHBrCl_2 and CHBr_2Cl , have remained explorative, and although some of these compounds are present in the atmosphere above Jungfraujoch, no efforts have so far been made to provide continuous and quantitative measurements. Also, while the fully fluorinated and chlorinated methanes (CF_4 , CCl_4) are abundant in the global atmosphere, CBr_4 appears to be absent. Despite some (admittedly rare) literature citations about algal production of CBr_4 , acquisition of this

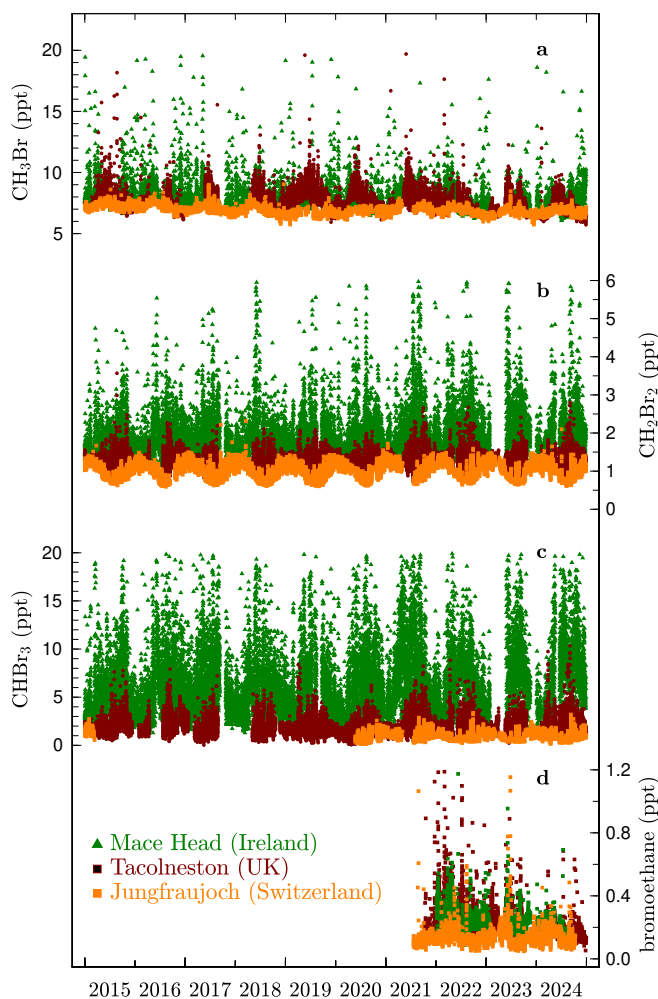


Figure 1: High-resolution (ca 2-hourly) records of the four brominated compounds CH_3Br , CH_2Br_2 , CHBr_3 , and $\text{C}_2\text{H}_5\text{Br}$ at Jungfraujoch (Switzerland), Mace Head (UK), and Tacolneston (UK) for 2015–2024. For better visualization of the Jungfraujoch record, pollution events at Mace Head are cut at the upper tick mark levels.

compound's fragments on the Jungfraujoch Medusa over the past 10 years has not revealed any detectable GCMS signal.

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Empa: <http://empa.ch/web/s503/climate-gases>.

Collaborating partners / networks

ACTRIS – Aerosol, Clouds, and Trace Gases Research Network.
Advanced Global Atmospheric Gases Experiment (AGAGE).
URL: <https://www-air.larc.nasa.gov/missions/agage/>.
Bundesamt für Umwelt (BAFU) / Federal Office for the Environment (FOEN).
EMEP – European Monitoring and Evaluation Programme.
GAW – Global Atmosphere Watch.
ICOS – Integrated Carbon Observation System Research Infrastructure.
IG3IS – Integrated Global Greenhouse Gas Information System.
Institut d’Astrophysique et de Géophysique, Université de Liège.
Korea Polar Research Institute.
Swiss National Air Pollution Monitoring Network.
University of Bristol.
World Meteorological Organisation (WMO).

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