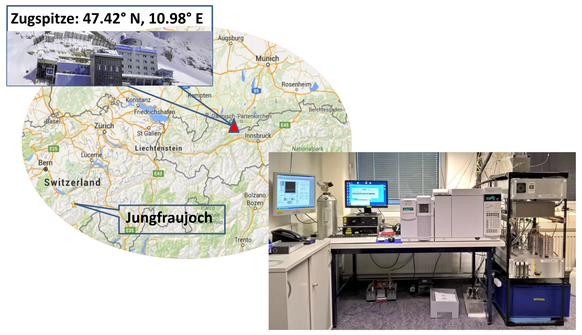
Halogenated Trace Gases and Volatile Organic Compounds at the Global Atmosphere Watch Global Observatory Schneefernerhaus/Zugspitze, Germany

Wei Wang[1], Jacques Hueber[1], Abigale J. Curtis[1], Cédric Couret[2], Ludwig Ries[2], Detlev Helmig[1]

[1]Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA. [2]German Environment Agency, Global Atmosphere Watch Observatory Zugspitze/Hohenpeissenberg, Platform Zugspitze at Environment Research Station Schneefernerhaus, Germany

Introduction: Halocarbons and hydrocarbons (C2 - C8) are being monitored at the German GAW Global Station Zugspitze/Hohenpeissenberg, 2670 m a.s.l., Germany. At the Zugspitze summit, atmospheric monitoring has been performed since the late 1970's. In 1998, measurements for the United Nation's Global Atmosphere Watch program (GAW) moved to the environmental research station Schneefernerhaus, ~300 m below the summit, where they support the study of greenhouse gases, reactive gases and aerosols. In 2013, an automated, remotely controlled gas chromatography/mass spectrometry (GC/MS) analytical system was installed for the monitoring of chlorofluorocarbon and other halocarbon trace gases. Monitoring of volatile organic compounds (VOC) was added in 2015. Ozone depleting and climate-change related organic traces have been monitored for more than a decade at a network of ground-based stations within the Advanced Global Atmospheric Gases Experiment (AGAGE) program following the Montreal and Kyoto protocols, which primarily rely on MEDUSA GC/MS measurement systems. The GC/MS at Zugspitze is a much simplified instrument, providing a lower maintenance and lower cost option for the long-term monitoring of these species.



Brief description of the operation: The instrument contains two main components, a custom-built pre-concentration inlet system and an Agilent GC/MS. The inlet system is controlled by a Labview program that also acquires and stores the metadata. It is synchronized with the GC/MS system where Agilent ChemStation software is used for instrument control and data acquisition. Both systems are primarily accessed and remotely operated from our Boulder offices. On-site tests, maintenance, and other instrument work are mainly covered by two scheduled site visits each year. Local technical staff provide support when needed. Ambient samples are taken daily at 2:00 AM local time, followed by measurements of a standard and zero air. Samples (volume = 2.8 L) are dried to a dew point of -45°C and pre-concentrated onto an adsorbent trap containing Carboxen 1000 and Carboxen 1016 at -40°C. Analytes are then injected onto the GC column by flash heating. Over 70 compounds are identified and routinely monitored; of these, 53 are quantified based on availability of standards. Analytes include compounds regulated by the Montreal Protocol, such as CFC-11, CFC-12, CCl_4, HCFC-22, HFC-134a and HFC-152a. Monitored VOCs include C2-C6 alkanes, alkenes, benzene, toluene and o-xylene. Most of the halocarbons are quantified based on a NOAA standard (certification, August 2014), and a few quantifications (PFC-116, HFC-143a, HFC-125, CFC-115 and CFC-114) are based on an older NOAA standard that was reanalyzed at the University of Bristol in 2012. A NIST standard (August, 2015) is used to quantify the hydrocarbons.

List of compounds monitored at Zugspitze. Those with standards available for quantification are indicated in **bold**. The compounds in *italic* are very often below the detection limit.

CFC-11	**CCl4**	**i-pentane**
CFC-113	**methyl chloroform**	**1-pentene**
CFC-114	**perchloroethylene**	**isoprene**
CFC-115	**methyl bromide**	trans-2-pentene
CFC-12	**CH2Br2**	cis-2-pentene
CFC-13	**CHBr3**	**n-pentane**
	methyl iodide	2-methylpentane
H-1211		3-methylpentane
H-1301	**PFC-116**	**hexane**
H-2402	PFC-218	**benzene**
	PFC-318	cyclohexane
HCFC-22	**SF6**	**n-heptane**
HCFC-124	SO2F2	**toluene**
HCFC-141b	**COS**	**iso-octane**
HCFC-142b		**octane**
	ethene	*ethylbenzene*
HFC-125	**ethane**	*m-xylene*
HFC-134a	**propene**	***o-xylene***
HFC-143a	**propane**	*1,2,4-trimethylbenzene*
HFC-152a	**i-butane**	*1,3,5-trimethylbenzene*
HFC-245fa	**iso-butene**	
HFC-365mfc	1,3-butadiene	methanol
	1-butene	ethanol
methyl chloride	trans-2-butene	acetaldehyde
CH2Cl2	**n-butane**	methyl formate
chloroform	cis-2-butene	actone

Results: Presented here are the time series of preliminary results of the ambient mixing ratios for a few selected compounds. The data quality of some compounds, such as H-1301, may be improved by better integration methods, which have been implemented but not yet applied to some of the data. Compared with results from the nearby Jungfraujoch/Switzerland AGAGE site, some halocarbons, such as CFC-11, CFC-115, HCFC-22, HFC-134a and CH_2Cl_2, show good agreement in the absolute values of the mixing ratios, seasonal cycles, day-to-day variabilities, as well as the long-term rates of change. Other compounds, including CFC-12, H-1301, H-1201, methyl chloride and methyl bromide, agree well in seasonality and long-term trends, but have a significant difference in their absolute mixing ratios. Bias in the calibration standards used in obtaining these results at both sites is likely the cause for this discrepancy, and needs to be investigated. Lastly, compounds HCFC-141b and HCFC-142b show a high abundance with highly enhanced concentrations. Air leaking from within the station building is the most likely reason because the sample intake is situated only 4 meters above the building terrace and regular lab air tests have shown large enhancements of both compounds in indoor air. This problem is currently being addressed by installing a new sampling line with the inlet much further away from the station building. The hydrocarbon results show seasonal cycles that are in agreement with other global background observations.

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