



First appearance and rapid growth of anthropogenic HFC-245fa (CHF₂CH₂CF₃) in the atmosphere

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[1] We capture the first atmospheric appearance of HFC-245fa (CHF₂CH₂CF₃), a new foam blowing agent. Our results from the high-altitude observatory at Jungfraujoch, Switzerland, show a rapid growth of this substance in the northern hemispheric troposphere from 0.28 ppt in July 2004 to 0.68 ppt at the end of 2005, which corresponds to an overall increase of >90% per year. By combining our observations with an atmospheric 3-box model we estimate a southern hemispheric trend for this trace gas which we compare to observations at southern hemisphere mid-latitudes. We also estimate a global HFC-245fa emissions increase from 2100–2400 tonnes in 2003 to 5100–5900 tonnes in 2005. Pollution episodes are relatively rare at Jungfraujoch compared to other hydrofluorocarbons thereby confirming the limited use of HFC-245fa in Europe. Back trajectory analysis reveals the largest potential European sources of HFC-245fa in northern Italy and northeastern Spain. **Citation:** Vollmer, M. K., S. Reimann, D. Folini, L. W. Porter, and L. P. Steele (2006), First appearance and rapid growth of anthropogenic HFC-245fa (CHF₂CH₂CF₃) in the atmosphere, *Geophys. Res. Lett.*, 33, L20806, doi:10.1029/2006GL026763.

1. Introduction

[2] The use of ozone-depleting substances has been regulated by the Montreal Protocol and its subsequent amendments because of their negative impact on the earth's atmosphere. Among these substances are the chlorofluorocarbons (CFCs), first regulated in the late 1980s, and now exhibiting stable or decreasing concentrations in the background atmosphere [Prinn *et al.*, 2000; Montzka and Fraser, 2003]. Alternatives to the CFCs are the hydrochlorofluorocarbons (HCFCs), which are also restricted under the Montreal Protocol, and which were introduced as transition substances to a subsequent third generation of non-ozone-depleting compounds, the hydrofluorocarbons (HFCs).

[3] In the rigid-foam sector, the consumption of CFC-11 (CCl₃F) has been successfully phased-out in industrialized countries and is due for global phase-out by 2010. It has been replaced mainly by HCFC-141b (CH₃CCl₂F).

While this substance is heavily used in the developing countries, many of the industrialized countries are now in the process of phasing it out. As a consequence the concentrations of this trace gas have stabilized in the atmosphere [Derwent *et al.*, 2006]. Among the replacements for HCFC-141b are the two market-competing non-ozone-depleting HFCs, HFC-365mfc (CH₃CF₂CH₂CF₃, 1,1,1,3,3-pentafluorobutane), and HFC-245fa (CHF₂CH₂CF₃, 1,1,1,3,3-pentafluoropropane). HFC-365mfc is currently produced in a single plant (Tavaux, France) and exclusively marketed in Europe. Measurements of this compound at Jungfraujoch over the past 3 years have shown increasing background concentrations and frequent pollution events, many of which were traced to the site of production using back trajectory analysis (K. Stemmler *et al.*, European emissions of HFC-365mfc, a chlorine-free substitute for the foam blowing agents HCFC-141b and CFC-11, submitted to *Environmental Science and Technology*, 2006). HFC-245fa is also produced in a single plant (Geismar, Louisiana, USA) and predominantly marketed in North America. Mass production of this compound started in August 2002 (unpublished data). Partially due to temporary production shortages for HFC-365mfc, HFC-245fa entered the European market in 2004. Because the production and sales figures are confidential and unknown to us, we are currently unable to estimate the global or regional emissions using a sales-based bottom-up analysis. Based on CFC and HCFC replacement and emission scenarios, global emissions of HFCs in the foam blowing sector could reach 70 kton yr⁻¹ by 2010 [McCulloch, 1999] presumably with HFC-245fa being responsible for a significant fraction of these emissions.

[4] HFC-245fa is removed from the atmosphere by reaction with hydroxyl radicals and its respective lifetime is 7.4–7.6 yr [Orkin *et al.*, 1996; Ko *et al.*, 1999]. This is currently the only known significant removal process of this compound from the atmosphere. This HFC is a significant greenhouse gas with a greenhouse warming potential of 950–1020 over a 100 year time frame [Ko *et al.*, 1999; Montzka and Fraser, 2003, Table 1.6]. HFCs are one of the classes of chemicals considered by the Kyoto Protocol.

[5] The purpose of this paper is to present the first record of the emergence of HFC-245fa in the background atmosphere based on continuous measurements at the high-altitude Jungfraujoch observatory (46°33'N, 7°59'E) located at 3580 m.a.s.l. in the Swiss Alps. Due to its unique location within Europe, this site receives both clean background and polluted boundary layer air depending on meteorological conditions [e.g., Forrer *et al.*, 2000]. Measurements of halogenated trace gases from Jungfraujoch combined with atmospheric transport models have been

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used in the past to deduce Swiss and European emissions of these compounds [Reimann *et al.*, 2004].

2. Methods

2.1. Analysis

[6] At Jungfraujoch fully automated *in-situ* measurements of halogenated trace gases have been made since 2000 [Reimann *et al.*, 2004] using gas-chromatograph mass-spectrometry (Agilent 6890 and 5793N) with a custom-built preconcentration system [Simmonds *et al.*, 1995] to allow for sample trapping of 2 L of air for each measurement. Halogenated compounds are collected on a microtrap at -50°C and thermally desorbed at $\sim 240^{\circ}\text{C}$. They are then chromatographically separated on a 120 m \times 0.32 mm I.D. CP-SIL 5CB capillary column (Chrompack) with 5 μm film thickness, and detected using single-ion mode quadrupole mass spectrometry. The HFC-245fa elution time was determined using a high-concentration reference gas and is quantified using the $\text{C}_3\text{H}_3\text{F}_4^+$ m/z 115 mass fragment. The $\text{C}_3\text{H}_2\text{F}_5^+$ m/z 133 mass fragment was also detectable, but less abundant, in our high-concentration reference gas. It is not detectable on our instruments in current air samples. Measurements of this trace gas began in early 2004 but the results before July 2004 were rejected mainly because of poor measurement precision due to the low abundance of HFC-245fa in the atmosphere.

[7] Air sample measurements take 2 hrs each and are bracketed by working standard measurements to determine and correct for instrumental drift. These working standards are prepared by compressing ambient air into 35 L electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA), by means of a modified oil-free compressor (model SA-3, RIX, California, USA), or using cryogenic filling techniques. The trace gas concentrations of these working standards for the trace gases are referenced against a secondary standard, which is discussed in the following section. The mean precision (1σ) of our Jungfraujoch air measurements is 9% as determined from the precision of the working standard measurements. Air samples from the mid-latitudes of the southern hemisphere were collected in 2.5 L internally electropolished stainless steel flasks. The precision of these measurements is 10% as determined from duplicate flask samples. The detection limit based on a signal-to-noise height ratio of 3 is ~ 0.18 ppt. Based on measurements of older air in canisters, where no baseline change was detectable at the elution time of HFC-245fa, we estimate any potential natural occurrence of this gas to be < 0.06 ppt in today's atmosphere.

2.2. Calibration Scale

[8] In the absence of any calibration scale for HFC-245fa in the ambient air concentration range, our measurements were linked to a gravimetrically prepared multi-component reference gas (Apel-Riemer Environmental Inc., Denver, Colorado, USA) with a nominal HFC-245fa concentration of 24.9 ppb molar (parts-per-billion or 10^{-9}). For this purpose a secondary standard was prepared by dynamic dilution of this reference gas with synthetic air. The synthetic air was purified using a trap (charcoal and molecular sieve 13X) cooled in a dry-ice ethanol slurry, to remove any potential traces of HFC-245fa which may have remained

undetected when first determining the purity of the synthetic air. The dilution was prepared by mixing the two components in a previously evacuated 35L stainless steel canister, spiked with 0.6 ml of H_2O and later immersed in a liquid nitrogen bath to maintain a sub-ambient pressure in the canister. The gases were sequentially passed through high-accuracy venturi flowmeters (molbloc, DH Instruments, Phoenix, Arizona) while monitoring the individual cumulative flows. A back-pressure regulator was fitted downstream of each flowmeter to ensure a constant pressure gradient across these units and to operate the devices in their optimal pressure range. 243 ml of the high-concentration reference gas were mixed with ~ 1200 L of synthetic air to produce a secondary standard HFC-245fa concentration of 5.22 ppt molar (parts-per-trillion, 10^{-12}). This defines our "Empa-2005" calibration scale on which we report our results presented in this paper. Measurements of n-butane, which was also present in the reference gas and diluted by the same fraction as HFC-245fa, showed agreement within $< 1\%$ when compared to an alternative reference gas (National Physical Laboratory, UK). We take this as an independent confirmation of the integrity of the dilution procedure for which we estimate an uncertainty well below 1%. The uncertainty of the HFC-245fa concentration in the original reference gas is given as 5%. From this we assign an accuracy of $\sim 6\%$ to the Empa-2005 calibration scale for HFC-245fa and, because of propagating measurement uncertainties between the standards, we estimate an overall accuracy of 10–15% for our atmospheric measurements.

3. Atmospheric Record and Budget

3.1. Observations

[9] The results for the HFC-245fa measurements at Jungfraujoch are shown in Figure 1 from mid 2004 to early 2006. In order to deduce an atmospheric background trend we have iteratively filtered the data. In each iteration step a trend is determined using a robust local regression smoothing technique (rloess, matlab) with a span of 90 days. Then the subset of data is selected which encompassed the original data within a band of $\pm 2\sigma$ of the currently estimated trend. Data outside this band are rejected. This procedure was repeated 4 times, when no further data points were rejected. Finally we define the background measurements as the final smoothed record $\pm 2\sigma$ of the last iteration using the 70% of the original data retained during the filtering. The monthly mean background values are listed in auxiliary material Table S1¹.

[10] Mean HFC-245fa background concentrations increased from 0.28 ppt in July 2004 to 0.68 ppt at the end of 2005, resulting in an overall rate of increase for this period of ~ 0.27 ppt yr^{-1} or $\sim 95\%$ yr^{-1} . The record shows a few pollution events in 2004 and early 2005 but fewer towards the end of the record. We speculate that this enhanced frequency and magnitude of pollution is linked to the increased regional use of HFC-245fa during temporary production shortages of the more widely used HFC-365mfc in Europe. The atmospheric record also shows events when HFC-245fa concentrations were low (e.g., Figure 1, period D). Using back trajectory analysis such events could

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/gl/2006gl026763>.

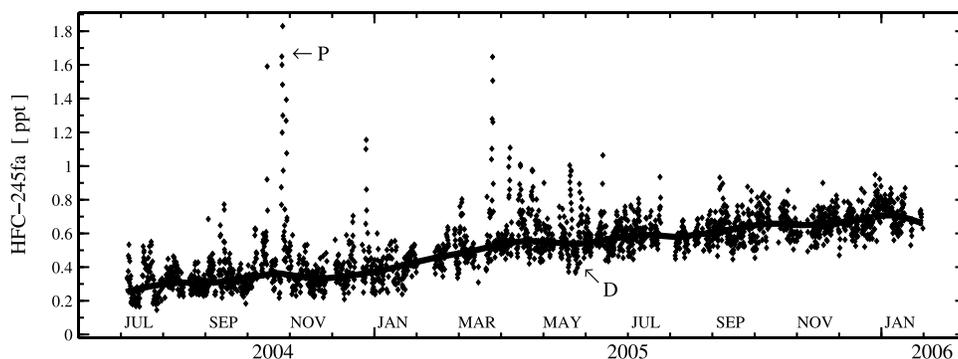


Figure 1. Atmospheric mixing ratios (ppt, molar) of HFC-245fa at Jungfraujoch. The solid line represents the mean background concentrations. Measurement results indicated by “P” and “D” show the most pronounced pollution and low-concentration events, respectively.

be traced to arrival of air masses which had been decoupled from the polluted boundary layer for longer periods of time.

[11] We have also analyzed air flask samples collected during clean air conditions in Australia at Cape Schanck (38°S, 145°E) and subsamples of the Cape Grim (41°S, 145°E) air archive (auxiliary material Table S1). Based on observations of other halogenated trace gases in the SH [e.g., Thompson *et al.*, 2004] we are confident that the HFC-245fa concentrations in these samples closely represent the mean mid-latitude SH tropospheric values at the time of their collection. A sample from December 2004 yielded undetectable concentrations, while samples from July 2005 and January/February 2006 showed concentrations of 0.19 ppt and ~0.24 ppt, respectively.

3.2. Southern Hemisphere Trend

[12] In order to better understand the current atmospheric budget of HFC-245fa we have used a 3-box model of the atmosphere consisting of the two tropospheric hemispheres and the stratosphere. For the sake of clarity we have divided our modelling into two steps. In the first step we have calculated the southern hemisphere (c_{SH}) and the stratospheric (c_{ST}) HFC-245fa trends from our Jungfraujoch observations, which we have assumed represent the northern hemisphere (c_{NH}):

$$dc_{SH}/dt = k_{TT}(c_{NH} - c_{SH}) + k_{ST}c_{ST} - k_{TS}c_{SH} - k_{OH}c_{SH} \quad (1)$$

$$dc_{ST}/dt = k_{TS}(c_{NH} + c_{SH})/2 - k_{ST}c_{ST} \quad (2)$$

[13] We chose an intertropospheric exchange rate coefficient $k_{TT} = 1/1.7 \text{ yr}^{-1}$, which we adopt from Levin and Hesshaimer [1996] based on box model results using SF₆ and ⁸⁵Kr. Compared to exchange coefficients used in three-dimensional transport models, this value is relatively low but it takes into account the deficiencies inherent in a simple box model [Levin and Hesshaimer, 1996; Jacob *et al.*, 1987]. We further assumed a transport coefficient from the stratosphere to the troposphere of $k_{ST} = 1/1.4 \text{ yr}^{-1}$ and that the troposphere contains 83% of the atmosphere’s total mass, yielding a transport coefficient from the troposphere to the stratosphere $k_{TS} = 0.17 k_{ST}$ [Warneck, 2000]. For the destruction of HFC-245fa by OH we used a rate coefficient $k_{OH} = 0.13 \text{ yr}^{-1}$ [Orkin *et al.*, 1996; Ko *et al.*, 1999]. We

have neglected SH HFC-245fa emissions because there are very few (industrialized) countries in the SH which have replaced HCFC-141b consumption with HFC-245fa (unpublished data). We have extrapolated the Jungfraujoch record back in time to a zero concentration at the start of the mass production of HFC-245fa in August 2002 using an exponential fit. The model was run with a time step of 0.01 yr. This first calculation results in a SH HFC-245fa concentration of ~0.29 ppt at the end of 2005, as shown in Figure 2. The modeled stratospheric concentrations for the same time are at undetectable levels for our measurement technique.

[14] These SH model estimates are 15%–20% higher than the corresponding flask sample observations. This discrepancy is likely related to our assumptions that the Jungfraujoch record is representative for the NH and that the flask sample results are representative for the SH. Neglecting a vertical HFC-245fa gradient in the atmosphere is somewhat included in our choice of a low k_{TT} [Levin and Hesshaimer, 1996]. However, Jungfraujoch lies at ~46°N and is therefore in a latitude band with typically high

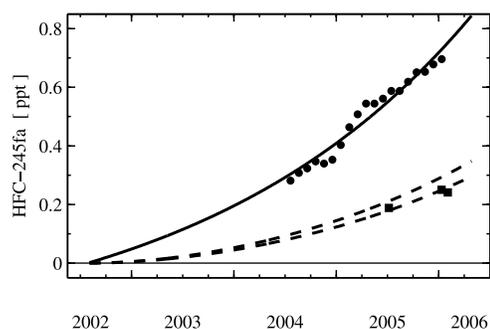


Figure 2. Model results for the southern hemisphere (SH) HFC-245fa concentrations. The filled circles are monthly means based on the Jungfraujoch record, the solid thick line is an exponential fit through these data and through the start time of HFC-245fa production. The filled squares are the results from SH flasks samples (another sample in late 2004 was below the limit of detection). The upper dashed line represents the modeled SH concentration and the lower dashed line is the same model result but using mean northern hemisphere concentrations which are 15% lower than the background concentrations at Jungfraujoch.

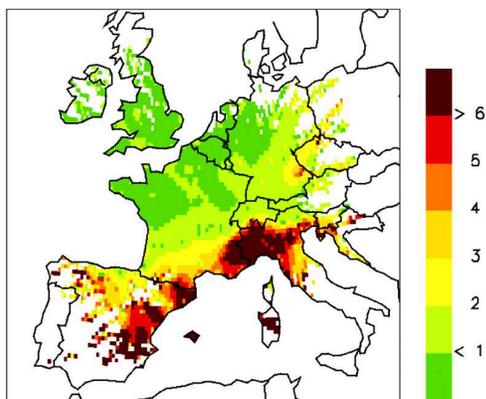


Figure 3. Source regions for potential HFC-245fa emissions in Europe. Units for the color codes are relative to the dark-green, representing the lowest emissions. White areas are excluded from this analysis as they are either oceans or areas from which too few trajectories reach Jungfraujoch.

concentrations of anthropogenic tracers. For example, results for SF₆ [Maiss *et al.*, 1996; Levin and Hesshaimer, 1996] in the 1990s show that even with its relatively low interhemispheric gradients of less than 20%, the mean northern hemispheric concentrations were ~5% lower than typical concentration at the latitude of Jungfraujoch. Also, for the fast-growing HFCF-141b in the early 1990s, when concentrations at stations >40°N were double those in the SH, air samples from 19.5°N showed concentrations ~25% lower than those from latitudes >40°N [Montzka *et al.*, 1994]. For HFC-245fa, where Jungfraujoch concentrations are more than 130% higher than those in the SH, it is to be expected that the northern lower latitudes are considerably depleted in HFC-245fa. Therefore, the Jungfraujoch background concentrations are expected to significantly exceed the NH tropospheric mean. In analogy the Cape Grim and Cape Schanck samples results may underestimate the mean SH tropospheric HFC-245fa concentration. The SH low latitudes are expected to be enriched in HFC-245fa compared to these sampling sites because of the mixing in from the north. Best agreement between the modeled and observed SH concentrations would result if we used a NH mean concentration which is 15% lower than the Jungfraujoch background concentrations. Alternatively, model and observations would also better agree if we chose $k_{TT} = 1/2.2 \text{ yr}^{-1}$.

3.3. Top-Down Emission Estimates

[15] In the second modeling step we estimated the HFC-245fa NH emissions using our observations and the same transport coefficients and OH sink as in the first step. Because we assume negligible SH emissions our results equal total emissions to the atmosphere:

$$E = m_{NH} (dc_{NH}/dt + k_{TT} (c_{NH} - c_{SH}) - k_{ST} c_{ST} + k_{TS} c_{NH} + k_{OH} c_{NH}) \quad (3)$$

where m_{NH} is the mass of the NH troposphere. These calculations result in emissions of ~600 tonnes for the period Aug–Dec 2002, 2400 tonnes for 2003, 4000 tonnes for 2004, and 5900 tonnes for 2005. We regard these results

as upper limits. If we assume that the mean NH concentrations are 15% lower than the Jungfraujoch background, in order to match the SH model results and observations, then the above emission figures are reduced by ~15%. We treat this as a lower bound of our emission estimates. Unfortunately, there are no production-based estimates available with which to compare our results.

3.4. Source Regions of European Emissions

[16] Using our atmospheric HFC-245fa record in combination with a statistical trajectory model we have deduced a map of potential sources of European emissions covering the period of our observations (Figure 3). Our analysis is based on the approach by Seibert *et al.* [1994] and explained more in detail by Reimann *et al.* [2004] for the specific use with data from Jungfraujoch. The map in Figure 3 shows relative source strengths for regions of Europe which are within the footprint of Jungfraujoch. There are potential biases in this analysis due to the nature of the trajectory analysis and pollution identification. Close-by pollution yields higher concentrations at the Jungfraujoch than the same pollution would have from a more distant source, because of dilution effects, which are neglected in this method. As a consequence, emissions from closer sources tend to be overestimated. Nevertheless, this analysis shows that the largest emissions are likely to have occurred in northern Italy and northeastern Spain. The relatively high emissions from Spain agree well with industry-based information (W. Schwarz, personal communication, 2006) on the intensive use of HFC-245fa in this region of Europe. The relatively very low emissions from the northern and western sectors are a unique feature when compared to emissions maps for other halogenated trace gases [e.g., Reimann *et al.*, 2004; Derwent *et al.*, 2006].

4. Conclusions

[17] We present the first long-term measurements of HFC-245fa in the background atmosphere where our Jungfraujoch record captures the onset of measurable concentrations in the NH troposphere. Our model results for the SH show higher concentrations than the corresponding measured flask samples. These estimates suggest that the Jungfraujoch concentrations are significantly higher than the northern hemispheric mean concentrations. More measurements and improved modeling should help to further our understanding of the atmospheric fate of HFC-245fa. The so far insignificant SH emissions of this compound, along with other new substances such as HFC-365mfc, will provide a unique opportunity to study interhemispheric transport or southern hemisphere OH concentrations once more long-term atmospheric measurements from both hemispheres become available.

[18] **Acknowledgments.** We thank the station personnel at Jungfraujoch for their continuous on-site support, and the International Foundation High Altitude Research Stations Jungfraujoch and Gornegrat (HFSJG) for providing the infrastructure. We also acknowledge technical assistance by Matthias Hill and advice on mass flow measurements by Bernhard Niederhauser (METAS). This work is funded by the Swiss Federal Office for the Environment (FOEN). It is also carried out under the auspices of System for Observations of greenhouse Gases in Europe (SOGE). Members of SOGE and of the Advanced Global Atmospheric Gases Experiment (AGAGE) are acknowledged for their continuous

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References

- Derwent, R. G., P. G. Simmonds, B. R. Gready, S. O'Doherty, A. Manning, A. McCulloch, S. Reimann, D. Folini, and M. K. Vollmer (2006), The phase-in and phase-out of European emissions of HCFC-141b and HCFC-142b under the Montreal Protocol: Evidence from observations at Mace Head, Ireland and Jungfraujoch, Switzerland from 1994–2004, *Atmos. Environ.*, in press.
- Forer, J., R. Rüttimann, D. Schneider, A. Fischer, B. Buchmann, and P. Hofer (2000), Variability of trace gases at the high-alpine site Jungfraujoch caused by meteorological transport processes, *J. Geophys. Res.*, *105*, 12,241–12,251.
- Jacob, D. A., M. J. Prather, S. C. Wofsy, and M. McElroy (1987), Atmospheric distribution of ^{85}Kr simulated with a general circulation model, *J. Geophys. Res.*, *92*, 6614–6626.
- Ko, M., R.-L. Shia, N.-D. Sze, H. Magid, and R. G. Bray (1999), Atmospheric lifetime and global warming potential of HFC-245fa, *J. Geophys. Res.*, *104*, 8173–8181.
- Levin, I., and V. Heshaimer (1996), Refining of atmospheric transport model entries by the globally observed passive tracer distributions of $^{85}\text{krypton}$ and sulfur hexafluoride (SF_6), *J. Geophys. Res.*, *101*, 16,745–16,755.
- Maiss, M., L. P. Steele, R. J. Francey, P. J. Fraser, R. L. Langenfelds, N. B. A. Trivett, and I. Levin (1996), Sulfur hexafluoride—A powerful new atmospheric tracer, *Atmos. Environ.*, *30*, 1621–1629.
- McCulloch, A. (1999), CFC and halon replacements in the environment, *J. Fluorine Chem.*, *100*, 163–173.
- Montzka, S. A., and P. J. Fraser (2003), Controlled substances and other source gases, in *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project, Rep. 47*, pp. 1.2–1.83, World Meteorol. Org., Geneva.
- Montzka, S. A., R. C. Myers, J. H. Butler, and J. W. Elkins (1994), Early trends in the global tropospheric abundance of hydrochlorofluorocarbon-141b and 142b, *Geophys. Res. Lett.*, *21*, 2483–2486.
- Orkin, V. L., R. E. Huie, and M. J. Kurylo (1996), Atmospheric lifetimes of HFC-143a and HFC-245fa: Flash photolysis resonance fluorescence measurements of the OH reaction rate constants, *J. Phys. Chem.*, *100*, 8907–8912.
- Prinn, R. G., et al. (2000), A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, *105*, 17,751–17,792.
- Reimann, S., D. Schaub, K. Stemmler, D. Folini, M. Hill, P. Hofer, B. Buchmann, P. G. Simmonds, B. Gready, and S. O'Doherty (2004), Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, *J. Geophys. Res.*, *109*, D05307, doi:10.1029/2003JD003923.
- Seibert, P., H. Kromp-Kolb, U. Baltensperger, D. T. Jost, M. Schwikowski, A. Kasper, and H. Puxbaum (1994), Trajectory analysis of aerosol measurements at high alpine sites, in *Transport and Transformation of Pollutants in the Troposphere*, edited by P. M. Borrell, pp. 689–693, SPB Acad., Hague, Netherlands.
- Simmonds, P. G., S. O'Doherty, G. Nickless, G. A. Sturrock, R. Swaby, P. Knight, J. Ricketts, G. Woffendin, and R. Smith (1995), Automated gas chromatograph mass spectrometer for routine atmospheric field measurements of the CFC replacement compounds, the hydrofluorocarbons and hydrochlorofluorocarbons, *Anal. Chem.*, *67*(4), 717–723.
- Thompson, T. M., et al. (Eds.) (2004), Halocarbons and other atmospheric trace species, Summary Rep. 27, pp. 115–135, NOAA Clim. Monit. and Diag. Lab., Boulder Colorado.
- Warneck, P. (2000), *Chemistry of the Natural Atmosphere, Intern. Geophys. Ser.*, vol. 71, 927 pp., Academic Press, New York.
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