

Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation

Stefan Reimann, Daniel Schaub, Konrad Stemmler, Doris Folini, Matthias Hill, Peter Hofer, and Brigitte Buchmann

Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland

Peter G. Simmonds, Brian R. Grealley, and Simon O'Doherty

School of Chemistry, University of Bristol, Bristol, UK

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[1] At the high Alpine site of Jungfraujoch (3580 m asl), 23 halogenated greenhouse gases are measured quasi-continuously by gas chromatography-mass spectrometry (GCMS). Measurement data from the years 2000–2002 are analyzed for trends and pollution events. Concentrations of the halogenated trace gases, which are already controlled in industrialized countries by the Montreal Protocol (e.g., CFCs) were at least stable or declining. Positive trends in the background concentrations were observed for substances which are used as CFC-substitutes (hydrofluorocarbons, hydrochlorofluorocarbons). Background concentrations of the hydrofluorocarbons at the Jungfraujoch increased from January 2000 until December 2002 as follows: HFC 134a ($\text{CF}_3\text{CH}_2\text{F}$) from 15 to 27 ppt, HFC 125 (CF_3CHF_2) from 1.4 to 2.8 ppt, and HFC 152a (CHF_2CH_3) from 2.3 to 3.2 ppt. For HFC 152a, a distinct increase of its concentration magnitude during pollution events was observed from 2000 to 2002, indicating rising European emissions for this compound. Background concentrations of all measured compounds were in good agreement with similar measurements at Mace Head, Ireland. On the other hand, peak concentrations were significantly higher at the Jungfraujoch. This finding is due to the proximity to potent European sources, foremost in southern Europe. The average ratio of halocarbons versus carbon monoxide (CO) concentrations above their baseline values was used to estimate source strengths for the part of Europe which most influences the Jungfraujoch during pollution events. HFCs emission estimates from Jungfraujoch tend to be higher than figures at Mace Head (Ireland) from the end of the 1990s, which either reflects the increased use of these compounds or the closer location of Jungfraujoch to major southern European sources. Transport of polluted European boundary layer air masses to the high Alpine site was observed especially during frontal passages, foehn events, and thermal lifting of air masses in summer. The measurement data during the periods when the Jungfraujoch was under the influence of the polluted boundary layer were used in combination with concurrent air mass trajectories to allocate above baseline halocarbon concentrations to specific European source regions. **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** halocarbons, greenhouse gases, trajectory statistics

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1. Introduction

[2] Halocarbons are important industrial substances with a wide variety of applications such as refrigeration, foam blowing, and fire extinction [Midgley and McCulloch,

1999]. Halocarbons are greenhouse gases, and they contribute to global warming depending on their emission, their atmospheric lifetime, and their infrared-absorption properties [Intergovernmental Panel on Climate Change (IPCC), 2001; Sihra et al., 2001]. Regarding their environmental impact, these substances can further be divided into two main groups. The first group consists of halocarbons responsible for the

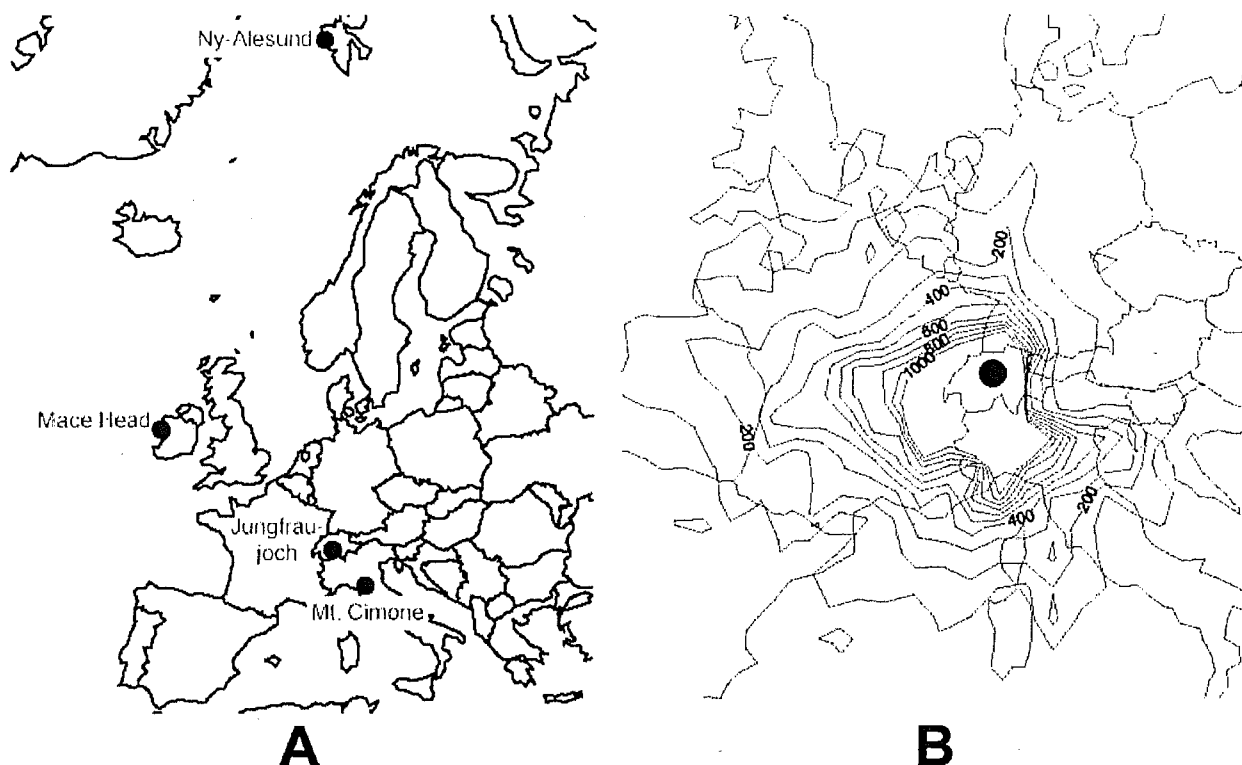


Figure 1. (a) Geographical setting of the Jungfraujoch station in Europe together with the other sites of the SOGE program. (b) Contour plot of a residence time analysis using trajectories arriving at the Jungfraujoch. Numbers indicate the total counts of trajectory time steps in the respective grid cell in 2000–2002. Trajectories were only counted if the distance between the trajectory height and the model surface was less than 120–200 hPa (depending on the season). The plot shows the mean flow regime of PBL air to the site indicating the most PBL events coming from western, southern, and southeastern direction.

depletion of stratospheric ozone, i.e., chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), bromine-containing halocarbons (Halons, CH_3Br), and long-lived chlorinated solvents. These substances are regulated in the Montreal Protocol and are due to be phased out worldwide. The second group combines halocarbons with fluorine as the only halogen, i.e., hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6). These substances do not have a direct effect on stratospheric ozone but contribute to global warming and were therefore included into the Kyoto Protocol. Halocarbons in total are responsible for about 14% of the radiative forcing by anthropogenic greenhouse gases [IPCC, 2001]. Although this contribution is set to fall, because of the reduction in the atmospheric concentrations of CFCs (following their phase-out under the Montreal Protocol), other halocarbons might contribute significantly to future climate change, if they were released in sufficient quantities.

[3] At the high Alpine site of Jungfraujoch (3580 m asl), halogenated greenhouse gases have been measured quasi-continuously since January 2000 by gas chromatography-mass spectrometry (GCMS). It is the highest site worldwide to host this kind of measurement. The Jungfraujoch is a station in the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) and is included in the Swiss National Air Pollution Monitoring Network (NABEL). Within NABEL, other air pollutants such as NO_x , ozone, CO, and particles are also continuously

measured. Furthermore, measurements by Fourier Transform Infrared Spectroscopy (FTIR) of some of the halogenated greenhouse gases (SF_6 , CFC 12, HCFC 22) and other substances related to global change have been performed routinely at the Jungfraujoch for many years [Mahieu *et al.*, 1997; Rinsland *et al.*, 2000; Zander *et al.*, 2002].

[4] During extended periods, the Jungfraujoch is decoupled from the tropospheric boundary layer below and can be used as a background site [Zanis *et al.*, 2000]. On the other hand, transport of polluted boundary layer air to the height of the Jungfraujoch occurs periodically because of meteorological transport connected with the passage of fronts, foehn winds, or thermally driven convection during anticyclonic periods in summer [Forrer *et al.*, 2000; Lugauer *et al.*, 1998]. In particular, the thermal lifting in summer has been the subject of various research activities related to aerosol climatology [Baltensperger *et al.*, 1997; Lugauer *et al.*, 2000; Nyeki *et al.*, 2000]. Together with other authors [Prevot *et al.*, 2000; Forrer *et al.*, 2000; Zellweger *et al.*, 2002], these studies concluded that this is a key process for mixing boundary layer air into the free troposphere in mountain regions.

[5] The continuous measurements of halocarbons at the Jungfraujoch are a part of the EU project SOGE (System for Observation of Halogenated Greenhouse Gases in Europe) with the aims to determine trends of halocarbons and to estimate the spatial distribution and strength of their European sources. Within SOGE, fully intercalibrated in situ data

have been measured since 2001 with an almost identical technique at four European background stations (i.e., Mace Head, Ireland; Ny-Ålesund, Spitsbergen; Jungfraujoch, Switzerland; and Monte Cimone, Italy; see Figure 1a).

[6] Within Europe, the site at Mace Head, which is also part of the AGAGE program (Advanced Global Atmospheric Gases Experiment), has the longest data record. At this site, estimates of European halocarbon emissions down to the regional scale have already been made using observations coupled with state-of-the-art meteorological transport models [Simmonds *et al.*, 1998; Ryall *et al.*, 2001; Manning *et al.*, 2003].

[7] For this purpose also, the site of Jungfraujoch is well situated in the middle of Europe, i.e., one of the most important source regions for anthropogenic pollution worldwide. With the new measurements at the Jungfraujoch presented here, the spatial resolution of European emission estimates can be improved and uncertainties due to long-range transport of air masses over different source regions can be reduced. In combination with the other European background sites, these measurements can potentially be used as a tool for independent validation of emission figures submitted as National Communications to the United Nations Framework Convention on Climate Change (UNFCCC).

[8] In this study we show results of long-term continuous measurements of halocarbons at the high Alpine station of Jungfraujoch, Switzerland (3580 m asl), from January 2000 until December 2002. The analyses are focused on HFCs 125, 134a, and 152a, and on HCFC 141b, whose background concentrations have considerably increased in the last few years [Simmonds *et al.*, 1998; Prinn *et al.*, 2000; Montzka *et al.*, 1999]. Time series of these halocarbons are analyzed during meteorological conditions, when the site is influenced by polluted boundary layer air masses. During these periods, the average ratio of halocarbons versus carbon monoxide (CO) concentrations above the baseline was used to estimate the source strength of these gases from the regions of Europe which most influence the site during pollution events.

[9] Finally, we use a statistical trajectory model to connect measurement data of halocarbons at the Jungfraujoch with meteorological information. This information is used to assess the impact of different European source regions to the observations of atmospheric halocarbons.

2. Experimental

2.1. High Alpine Site of Jungfraujoch

[10] The Jungfraujoch (3580 m asl) is situated in the northern part of the Swiss Alps and belongs to the first topographical barrier for the frequent westerly winds in Central Europe. The site is situated on a prominent rock formation at the saddle between the summits of Jungfrau (4158 m asl) and Moench (4099 m asl). Its location is relatively remote for Central European conditions, with the villages of Grindelwald and Wengen both in 8 km horizontal and 2.5 km vertical distance. Because of its isolated and elevated position, the station is only weakly influenced by local anthropogenic sources. In contrast to Mace Head and other background sites, where the wind sector gives a good proxy for the influence by polluted air masses, conditions at this high elevated site in the middle of an important anthropogenic source region exhibit some peculiarities.

Table 1. Substances Analyzed With ADS-GCMS From 2000 Until 2002 at the Jungfraujoch

Name	Chemical Formula
<i>Montreal Protocol Regulated Halocarbons</i>	
Chlorofluorocarbons (CFCs)	
CFC 11	CCl ₃ F
CFC 12	CCl ₂ F ₂
CFC 113	C ₂ Cl ₃ F ₃
CFC 114	C ₂ Cl ₂ F ₄
CFC 115	C ₂ ClF ₅
Hydrochlorofluorocarbons (HCFCs)	
HCFC 22	CHClF ₂
HCFC 142b	C ₂ H ₃ ClF ₂
HCFC 141b	C ₂ H ₃ Cl ₂ F
HCFC 124	C ₂ HClF ₄
Halon and others	
halon 1211	CBrClF ₂
halon 1301	CBrF ₃
tetrachloromethane	CCl ₄
methyl chloroform	C ₂ H ₃ Cl ₃
methyl bromide	CH ₃ Br
<i>Kyoto Protocol Regulated Halocarbons</i>	
Hydrofluorocarbons (HFCs)	
HFC 125	C ₂ HF ₅
HFC 134a	C ₂ H ₂ F ₄
HFC 152a	C ₂ H ₄ F ₂
<i>Non-Regulated Halocarbons and Hydrocarbons</i>	
halogenated solvents and naturally occurring compounds	
methyl chloride	CH ₃ Cl
methyl iodide	CH ₃ I
dichloromethane	CH ₂ Cl ₂
chloroform	CHCl ₃
trichloroethene	C ₂ HCl ₃
tetrachloroethene	C ₂ Cl ₄
non-halogenated hydrocarbons	
n-butane	C ₄ H ₁₀
isobutane	C ₄ H ₁₀
n-pentane	C ₅ H ₁₂
isopentane	C ₅ H ₁₂
hexane	C ₆ H ₁₄
benzene	C ₆ H ₆
toluene	C ₇ H ₈

Thus pollution events occur mainly during the following meteorological events: frontal transport, thermally driven vertical transport, and south foehn (section 3). Background conditions normally occur when the site is influenced by downward advection of air masses representative of upper tropospheric conditions.

[11] A residence time analysis [Ashbaugh, 1983] of trajectories influenced by boundary layer air masses has been performed and the resulting contour plot is shown in Figure 1b, which indicates the number of trajectory time steps in the respective grid cell during periods with boundary layer contact. Boundary layer influence was assumed if the distance between the trajectory height and the model surface was less than 120 (winter) or 200 hPa (summer). The plot shows that the mean flow regime of polluted boundary layer air masses to the site is coming from western, southern, and southeastern direction, with practically no influence from eastern Europe. This behavior can be explained by the main wind direction in western Europe and the influence of the foehn, a strong wind crossing the Alps, which is further discussed in section 3.3.

[12] Furthermore, Figure 1b indicates which source regions of Europe are most likely to contribute substantial

emissions to the Jungfrauoch site. Contributions to the pollution events can be seen from a region referred to the central western Europe (i.e., Switzerland, eastern France, southern Germany, and northern Italy) in section 4 and 5. Estimates from other parts of Europe are hindered by dilution processes during transport (e.g., from the United Kingdom and Spain) and by low occurrence of transport from the respective area (e.g., eastern Europe and northern Europe).

2.2. Analytical Technique

[13] Every 4 hours, 23 individual halocarbons and selected nonhalogenated hydrocarbons (Table 1) were automatically analyzed by GCMS (Agilent, 5793N). Substances from 2 L of air were preconcentrated on a micro trap (automated adsorption-desorption system, ADS), filled with three different adsorbents. This preconcentration unit was developed by the University of Bristol [Simmonds *et al.*, 1995] and has been in operation at Mace Head (Ireland) and Cape Grim (Tasmania) in the AGAGE network for several years [Prinn *et al.*, 2000]. During adsorption of halocarbons, the trap was cooled to -50°C by means of a triple-stage Peltier element. Subsequently, compounds were desorbed by fast inductive heating of the micro trap to 235°C and were transferred into the gas chromatograph by an uncoated silanized fused silica capillary without further cryofocusing. Chromatographic separation was achieved with a $120\text{ m} \times 0.32\text{ mm}$ CP-SIL 5CB capillary column (Chrompack) with film thickness of $5\text{ }\mu\text{m}$. The temperature program started at 37°C and reached 180°C within 51 min. The individual compounds were quantified by single ion mass spectrometry of selected characteristic ions, and their individual chromatographic retention times.

[14] Each ambient air measurement was bracketed with calibration runs using real-air standards with concentrations representative of the Northern Hemispheric background. These standards were prepared by compressing ambient air at Mace Head (Ireland) in 35-L SUMMA-treated canisters (Essex, U.S.A.) with a specially cleaned scuba diving pump (RIX, SA-3, U.S.A.). For substances measured within AGAGE (i.e., CFCs and other substances regulated within the Montreal Protocol) [Prinn *et al.*, 2000], this air was calibrated against a standard (SIO98) from Scripps Institution of Oceanography. For all the other halocarbons (HFC, HCFCs, chlorinated solvents), the air was calibrated against a diluted standard from Bristol University, propagated from a gravimetrically prepared primary standard with a stated accuracy of $\pm 1\%$ (Linde Gases, Stoke-on-Trent, UK) [Simmonds *et al.*, 1998]. Nonhalogenated hydrocarbons were calibrated against a 30-component standard in the lower ppb range (National Physical Laboratory (NPL), UK).

2.3. Background Determination

[15] The time-dependent background concentration, $c^b(t)$, was determined as the local linear regression of those measurements, m^b , which lie within 1 standard deviation of $c^b(t)$. Note that this implies that we had to determine both m^b and $c^b(t)$. The standard deviation for the measurements was taken from the bracketing air standards, which can be regarded as air measurements without emissions. For the local linear regression, we used the function "loess" from the statistics package "R" [Hastie *et al.*, 2001] with a parameter "span = 0.09,"

which corresponds to a local time window of about 90 days. To determine both the background, $c^b(t)$, and the set of measurements, m^b , from which it is calculated, we proceeded iteratively. We started from the entire set of measurements, m_0^b , and calculated a first guess, $c_0^b(t)$, for the background concentration as the local linear regression to this data. We then determined a subset of measurements, m_1^b , by omitting those data points which do not lie within a distance of $c_0^b(t)$. For this subset, m_1^b , we then again calculated a background concentration, $c_1^b(t)$. We continued this iteration until two subsequent subsets of measurements, m_n^b and m_{n+1}^b , were identical. Finally, we calculated the net difference by subtracting the background, $c^b(t)$, from the measured data and taking the mean over all the data points.

2.4. Statistical Trajectory Model

[16] From January 2000 until July 2001, backward trajectories for the Jungfrauoch were computed twice a day (arrival time: 0000 and 1200 UTC; length: 48 hours) by the Swiss Meteorological Institute MeteoSwiss. After July 2001, three-dimensional (diabatic) trajectories have been calculated 6 times a day (0000, 0400, 0800, 1200, 1600, and 2000 UTC). For this purpose, the 3-dimensional TRAJEC model [Fay *et al.*, 1995] from the German Weather Service (DWD) has been used. Wind fields have been provided by the Swiss Model (horizontal resolution of 14 km) and since July 2001 by the improved alpine Local Model (aLMo, horizontal resolution of 7 km). The arrival point of the trajectories was positioned 100 m above the model surface. To compensate for complex flow regimes at the mountain site, we used not only the trajectory arriving at the accurate location but also four trajectories being displaced by $\pm 7\text{ km}$ in latitude and $\pm 7\text{ km}$ in longitude, respectively.

[17] For our analyses, we combined these trajectories with measured concentrations at the Jungfrauoch. This procedure has often been chosen in order to identify potential source regions of pollutants. One of the first approaches was developed by Ashbaugh [1983]. Thereby accumulated residence times of the trajectories in grid cells were calculated and transport of air masses to the measurement site was revealed by contour plots. Since then, many variations of the original approach have been developed [Cheng *et al.*, 1993; Stohl and Kromp-Kolb, 1994; Hopke *et al.*, 1995; Lucey *et al.*, 2001]. In this study we applied the method of Seibert *et al.* [1994], which, in contrast to other methods, allows a consideration of significant and insignificant structures in the resulting field.

[18] The domain of the calculated trajectories was superimposed with a $0.22^{\circ} \times 0.22^{\circ}$ grid. For these grid cells, the mean concentrations were calculated after the approach of Seibert *et al.* [1994], using the following formula:

$$\overline{C_{mn}} = \frac{1}{\sum_{a=1}^M \tau_{mna}} \sum_{a=1}^M (c_a) \tau_{mna},$$

where $\overline{C_{mn}}$ is a relative measure of potential source region strength, m , n are indices of the horizontal grid, a is the index of the trajectory, M is the total number of trajectories, c_a is the concentration (minus the background concentration) measured during arrival of trajectory a , and

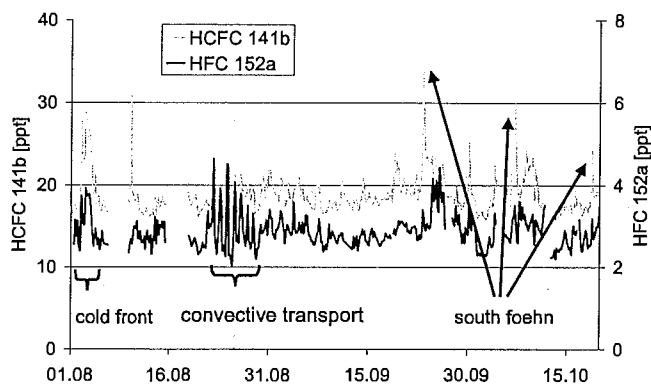


Figure 2. Time series of HFC 152a and HCFC 141b during August and October 2001, showing typical weather phenomena influencing mixing ratios of halocarbons at the Jungfraujoch.

τ_{mna} is the residence time (or the number of trajectory time steps, respectively) of the trajectory a spent over grid cell m, n . We only regarded air masses as influenced by emissions at ground level if the difference between the pressure at the height of the trajectory and the surface pressure did not exceed a value between 120 hPa (in winter) and 200 hPa (in summer).

[19] For minimizing errors arising from inconsistent data, only grid cells with more than 12 over-passing trajectories were taken into consideration. To allow for possible errors in the track of the trajectories and random variations in the calculated concentration field, a nine-point filter smoothing was applied.

[20] A high $\overline{C_{mn}}$ -value for a specific grid cell m, n means that over-passing air masses are on average associated with high concentrations at the receptor site. However, because measured concentrations are distributed equally to all grid cells passed by the appropriate trajectory, the approach used is susceptible to underestimation of spatial gradients of the true emission field [Stohl, 1996]. Other constraints are that only one measurement site was used, and similar weather patterns decreased the amount of independent information. Thus the area referred to central western Europe in section 2.1 makes the largest contribution to pollution events observed at the Jungfraujoch; conversely, important European source

regions like the United Kingdom and eastern Europe are insufficiently depicted.

3. Case Studies of Atmospheric Transport of Halocarbons to the Jungfraujoch

[21] In this section we investigate the behavior of halocarbon mixing ratios during selected meteorological conditions, which are typical for transport of air masses from the polluted boundary layer to the high Alpine region. For the discussion of the variability of the measured trace gas concentrations with respect to meteorological transport, a representative 2 months period from August to October, inclusive, in 2001 was selected (Figure 2). HFC 152a and HCFC 141b have been chosen to visualize the effects of the different transport processes.

[22] Higher concentrations of HFC 152a are normally seen when transport is from the north of the Alps, whereas for HCFC 141b elevated concentrations are mainly seen in air arriving from south of the Alps (see section 5). Major pollution events during this time period were caused by the passing of a cold front on 2 and 3 August, by thermally driven transport between 21 and 29 August, which led to diurnal cycles of concentrations, and by south foehn events on 23 September and 7 and 20 October.

3.1. Frontal Transport

[23] In midlatitudes, fronts are important mechanisms for tropospheric vertical mixing [Cotton *et al.*, 1995; Donnell *et al.*, 2001]. Connected with fronts are conveyor belts, which lift air masses from the boundary layer into the middle or even upper troposphere [Browning, 1985]. Pronounced differences in the chemical composition of air masses have been found connected with frontal transport across Europe [Bethan *et al.*, 1998]. This behavior is also present for the halocarbons at the Jungfraujoch.

[24] Following a distinct period of fine weather at the end of July 2001, a cold front crossed central Europe and reached the Alps in the afternoon of 2 August. The cold front remained at the Alpine range during 3 August, with daytime temperature at the Swiss plateau decreasing by 10°C. On 4 August, a following cold front overflowed the Alps. As illustrated in Figure 3, halogenated trace gases show a distinct increase in their concentrations during this meteorological event. The correlated behavior of the differ-

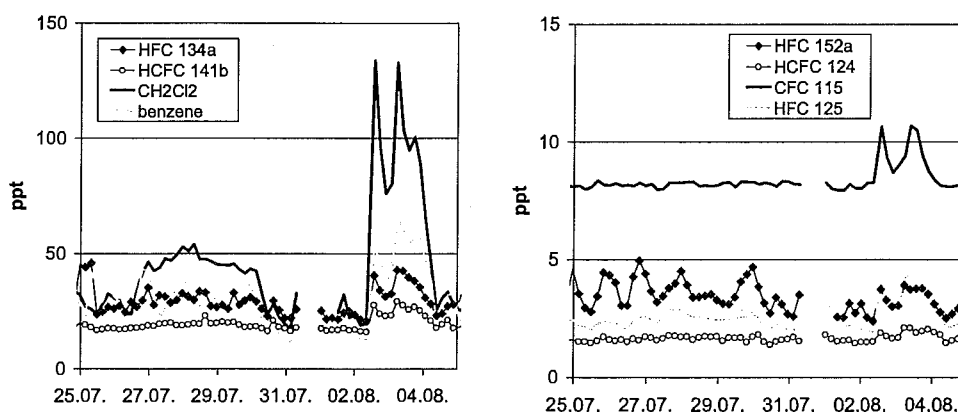


Figure 3. From 2 August until 4 August 2001, passage of a cold front leads to elevated concentrations caused by transport of polluted boundary layer air to the Jungfraujoch.

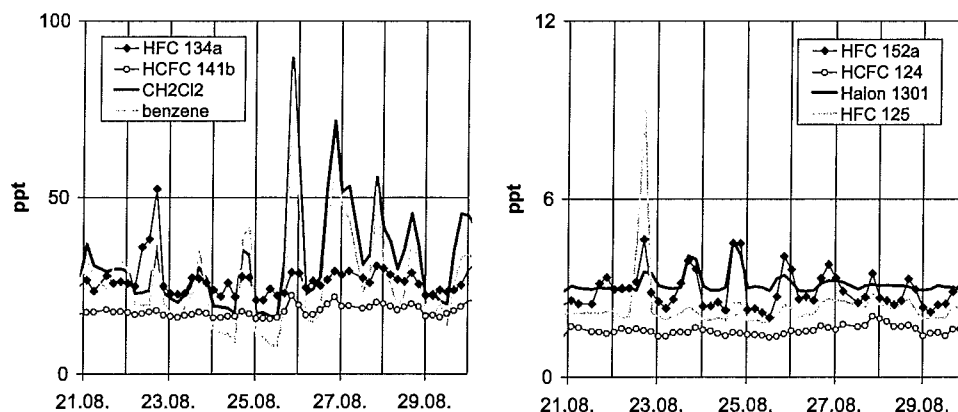


Figure 4. From 22 August until 29 August 2001, convective transport during a stable anticyclonic period over Europe leads to transport of air masses to the height of the Jungfraujoch. From 25 August to 27 August, the site is influenced by air from the southern parts of the Alps; on the other days, influence is from the north.

ent compounds indicates that well-mixed air masses from a larger source region have been advected simultaneously to the monitoring site at Jungfraujoch.

3.2. Thermally Driven Vertical Transport

[25] Occasionally, halogenated trace gases at the Jungfraujoch show distinct diurnal cycles with rising concentrations in the afternoon and low concentrations during night and morning (Figure 4). These diurnal cycles are predominately observed during anticyclonic periods in summer and are caused by the mountain circulation which develops during calm days with high solar radiation [Stull, 1988]. This thermally induced lifting has been observed to transport polluted boundary layer air to the height of the alpine peaks [Lugauer et al., 1998; Forrer et al., 2000; Zellweger et al., 2000; Prevot et al., 2000].

[26] In our example of 21 August to 29 August 2001, a stable fine weather period prevailing over central Europe caused the observed diurnal cycles in the halocarbon concentrations. From 21 August to 25 August, light

synoptic winds from the northeast lead to the incursion of halocarbons from the industrialized Swiss Plateau, resulting in high values at the Jungfraujoch on 22 August for HFC 125, and HFC 152a. On 25 and 26 August the wind direction changed to south, which led to elevated diurnal cycles for the chlorinated solvent CH_2Cl_2 and HCFC 141b. These substances could either be advected from regions south of the Alps or from the southwest of Switzerland.

3.3. South Foehn

[27] The foehn phenomenon of the Alps has been widely studied [Barry, 1992]. Thereby, humid air masses are advected to the Alps and are forced to ascent the slopes. Subsequent condensation, precipitation, and adiabatic heating during the descent in the lee lead to warm and dry winds called foehn. At the Jungfraujoch, advection of polluted air masses from industrialized areas adjacent to the alpine area (e.g., Po-valley) can be observed during foehn events [Forrer et al., 2000; Seibert et al., 1998].

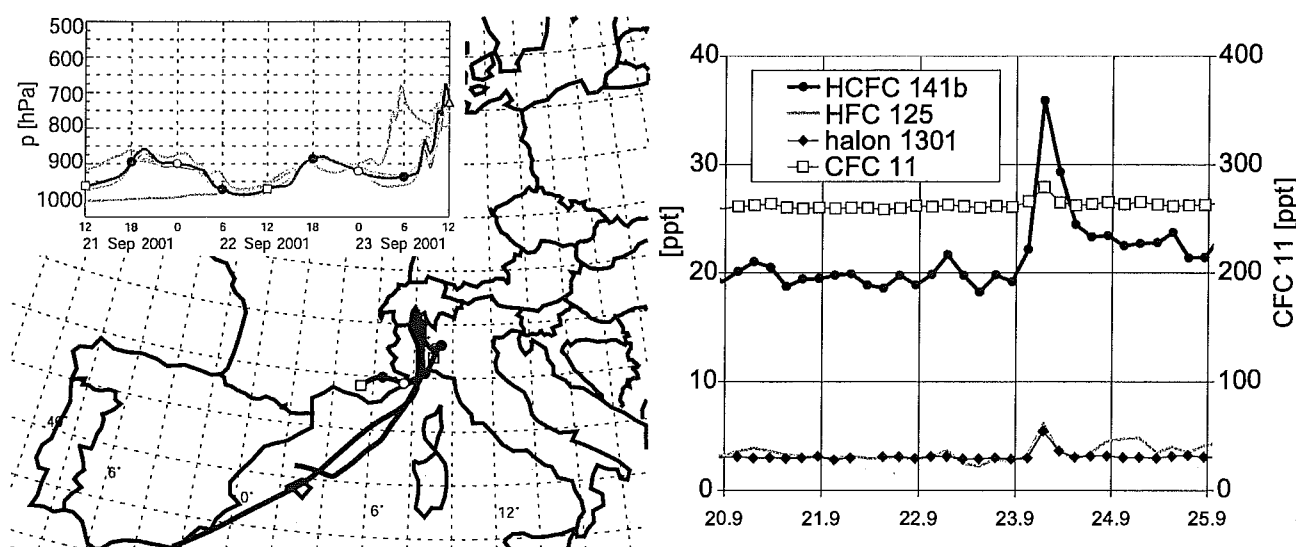


Figure 5. On 23 September 2001, the trajectory indicates that the Jungfraujoch is influenced by south foehn, transporting polluted boundary layer air masses from the Po-Valley. This is indicated by a steep rise of concentrations of halocarbons advected from Italy.

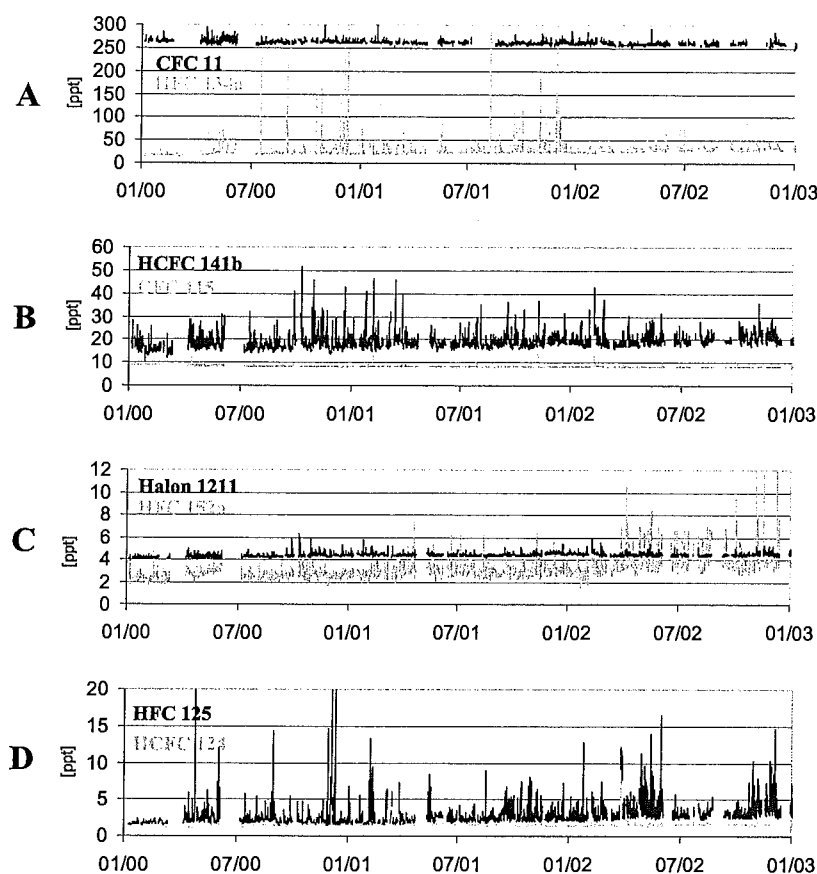


Figure 6. Time series of selected halogenated trace gases at the Jungfraujoch from 2000 until 2002. (a) CFC 11(black); HFC 134a (shaded). (b) HCFC 141b (black); CFC 115 (shaded). (c) halon 1211(black); HFC 152a(shaded). (d) HFC 125(black); HCFC 124(shaded).

[28] On 23 September the Jungfraujoch was influenced by a south foehn situation (Figure 5). The 2-day backward trajectories indicate that the air masses during this particular event originate from ground levels in the Po-Valley (northern Italy) and were lifted according to the topography. Many compounds with potentially high source strengths in the Po valley, for example HCFC 141b, show a distinct pollution peak at the Jungfraujoch during this event.

4. Data Series and Regional European Emission Estimates

[29] This section provides an overview and a discussion of the time series of halocarbons measured at the Jungfraujoch. Furthermore, concentrations above the background are used to estimate European emissions of the halocarbons.

The resulting figures have to be considered as an approximate estimate as they are centered on central western Europe, due to the limited range of trajectories reaching the Jungfraujoch (Figure 1b). Continuous measurements of the halocarbons listed in Table 1 have been performed since the beginning of 2000. In the work presented here we focus the analyses on the time series of HFCs and HCFCs in the period between January 2000 and December 2002. The background concentrations of these substances have increased considerably in the latest years [Prinn *et al.*, 2000], reflecting their growing use as substitutes for ozone-depleting halocarbons (e.g., CFCs) within various technical applications. Data series for the years 2000 until the end of 2002 of HFCs 134a ($\text{CF}_3\text{CH}_2\text{F}$), 125 (CF_3CHF_2), and 152a (CHF_2CH_3) and of HCFCs 141b (CFCl_2CH_3) and 124 (CF_3CHFCl) are shown in Figure 6. For comparison

Table 2. Background Mixing Ratios and Their Trends From January 2000 Until December 2002 for Selected Halocarbons^a

Compound	Background Mixing Ratio, ppt		Trend of Background Mixing Ratio January 2000 to December 2002		Measurement Precision (2σ)
	January 2000	December 2002	ppt/Year	Percent per Year	
HFC 125	1.4	2.8	0.47	+22%	13.4%
HFC 134a	15	27	4.0	+19%	2.4%
HFC 152a	2.3	3.2	0.3	+11%	12.4%
HCFC 141b	14	18	1.33	+8%	4.0%
CFC 11	263	260	-1.0	-0.4%	1.2%
CFC 12	536	540	1.33	+0.2%	1.8%

^aAdditionally, the precision of the measurement is shown.

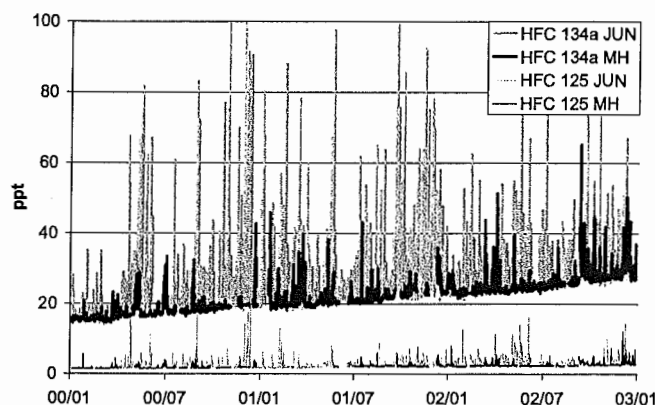


Figure 7. Comparison of the time series of HFC 134a and HFC 125 at the Jungfraujoch (JUN) and at Mace Head, Ireland (MH).

and discussion, we also include selected CFCs, for example, CFC 11 (CFC1₃), CFC 115 (CF₂ClCF₃), and halon 1211 (CF₂ClBr).

[30] The time series of the individual compounds in Figure 6 show that compounds differ with respect to the magnitude and to the frequency of pollution events monitored at the Jungfraujoch. For example, CFCs (e.g., CFC 11 and CFC 115; Figures 6a and 6b, respectively) and halons (e.g., halon 1211; Figure 6c) show only minor deviations from the tropospheric background concentrations, with occasionally elevated concentrations, representing emissions from outdated installations. On the other hand, the widely used HCFCs and HFCs show pollution events with elevated concentrations up to several hundred ppt (i.e., HFC 134a and to a lesser degree, HCFC 141b).

[31] For data analysis, we compared the behavior of the tropospheric background concentrations (section 2.3) of different halocarbons (Table 2). Thereby, growth rates of about 20% per year were found for HFC 125 and HFC 134a. For HFC 152a and HCFC 141b, these figures were in the range of 10% per year, whereas nearly stable values were seen for CFC 12 (+0.2%/year) and CFC 11 (−0.4%/year).

[32] For all the halocarbons discussed, excursions from the baseline are higher at the Jungfraujoch compared with the more remote European background site of Mace Head. As an example, observations of HFC 134a and HFC 125 recorded at the Jungfraujoch and at Mace Head (Ireland) are compared in Figure 7. It is obvious that at the Jungfraujoch, pollution

events show much higher mixing ratios for both gases. Nevertheless, background concentrations are increasing at nearly identical rates at the two sites.

[33] Table 3 reports the average excursion above the background concentration for individual compounds. This is regarded as a measure for European emissions transported to the Jungfraujoch. We are aware of the fact that our estimates are biased toward central western Europe as this is the region which mostly influences the air masses sampled at Jungfraujoch. Therefore, we see our European emission estimates as being complementary to those of Ryall *et al.* [2001] and Manning *et al.* [2003] from analysis of measurements at Mace Head. Combining analyses from the two stations has the potential to provide a more complete picture of European emissions. For estimation of the source strengths of halocarbons in Europe, their average concentration above the background was divided by the average carbon monoxide concentration above the background (i.e., 43.13 $\mu\text{g}/\text{m}^3$ at Jungfraujoch from 2000 to 2002) and multiplied with the European emission estimate of carbon monoxide of 30,499 Gg/year in 2001 (EMEP, <http://webdab.emep.int>) (Table 3). Thereby the assumption was made that the sources of CO and of halocarbons were colocated. This was justified by the facts that both classes of gases are anthropogenically emitted and that air masses transported to the site from the polluted boundary layer are normally well mixed prior to their arrival at the high Alpine site.

[34] European emissions of halocarbons have been estimated from measurements at Mace Head [Ryall *et al.*, 2001; Manning *et al.*, 2003] using a meteorological dispersion model. Estimates from Jungfraujoch and Mace Head are compared below with differences being discussed in terms of source strength and source allocation. However, the limitations of the representability of Jungfraujoch and of Mace Head measurements have to be taken into consideration, with estimates from Mace Head having restricted meaningfulness in southern Europe and Jungfraujoch, with limitations discussed in section 2.1 and representativity biased to the area around the site shown in Figure 1b.

4.1. HFC 134a (CF₃CH₂F)

[35] The tropospheric background concentration of HFC 134a has increased steadily from 15 ppt in January 2000 to 27 ppt at the end of 2002, reflecting the widespread use of this compound. The yearly increase in background mixing ratio is nearly 20% (Table 2), which is somewhat lower than the global growth rate of more than 25% in 1999/2000

Table 3. Estimation of European Emissions of Selected Halocarbons at Jungfraujoch, by Comparing the Average Concentration Above the Background Relative to Carbon Monoxide (CO)

Compound	Average of Measured Mixing Ratio Above Background (2000–2002)		Estimated European Emission From Jungfraujoch 2000–2002, ^a Gg/year	Estimated European Emission From Mace Head 1998, ^b Gg/year
	ppt	ng/m ³		
HFC 125	0.6	2.9	2.2 ± 1.0	1.5
HFC 134a	7.5	31.4	23.6 ± 1.7	9.6
HFC 152a	0.4	1.1	0.8 ± 0.7	0.4
HCFC 141b	2.5	11.9	9.0 ± 2.1	11.0

^aFor CO, the average mixing ratio above the background was 43.13 $\mu\text{g}/\text{m}^3$ at Jungfraujoch (2000–2002). The European emission of CO in 2001 (30,499 Gg) (EU15 and Switzerland) was taken from EMEP (<http://webdab.emep.int>). The range for the emission estimate represents 2 σ from real-air standard measurements.

^bRyall *et al.* [2001].

[World Meteorological Organization (WMO), 2002]. With an estimated lifetime of about 14 years [IPCC, 2001], HFC 134a is relatively stable in the atmosphere, resulting in a considerable accumulation potential. In fact, HFC 134a is the most widely used HFC, mainly replacing applications of CFC 12 (CF_2Cl_2) as a cooling agent in refrigerators and in automotive air conditioners. According to the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, www.afeas.org), in 2001 over 80% of the world-wide sales of HFC 134a fall into this category. The remaining quantity is used approximately equally between blowing of closed cell foams and various short-term applications, like aerosol propellants and open cell foam blowing [Midgley and McCulloch, 1999; McCulloch et al., 2003].

[36] Besides the permanent losses during operation of refrigerators and air condition units, considerable amounts of HFC 134a may be released instantaneously during filling or servicing or because of major defects of equipment using this substance. Accordingly, considerable loss rates of around 150 g/year per unit have been estimated in the case of automotive air conditioners [Siegl et al., 2002].

[37] At the Jungfraujoch, elevated concentrations of HFC 134a are often linked with air masses being advected to the site by strong winds from southern direction (foehn). This mountain-induced meteorological process advects polluted air masses from one of the most densely industrialized regions of Europe (i.e., Po-valley, northern Italy) to the height of the Jungfraujoch.

[38] Our estimate for European emissions of HFC 134a of 23.6 ± 1.7 Gg/year (Table 3) exceeds that of HFCs 125 and 152a by roughly a factor of 10 and 30, respectively. Our figure for 2000–2002 emissions is considerably higher than the European emission estimate from Mace Head in 1998 (i.e., 9.6 Gg/year; Table 3). A portion of this difference is due to the enhanced world-wide emissions of this compound between 1998 and 2000–2002. Thus AFEAS reports an increase of global emissions from 54 Gg/year in 1998 to 95 Gg/year in 2001 (+76%), which explains about half of the relative enhancement of +146% between emission estimates based on Mace Head and Jungfraujoch observations. Furthermore (detailed in section 5), northern Italy has the potential to be a very potent source region in Europe for HFC 134a. The location of Jungfraujoch relatively close to northern Italy could explain a significant part of the difference.

4.2. HFC 125 (CF_3CHF_2)

[39] For HFC 125, an increase of the background concentration from 1.4 to 2.8 ppt has been observed between January 2000 and December 2002 at Jungfraujoch (Table 2). The observed trend of 22% increase per year is identical with global figures from WMO [2002]. HFC 125 is mainly used in HFC-refrigerant blends, often together with HFC 134a. Occasionally, very high concentrations of HFC 125 up to 25 ppt can be observed during events, when air from northern Italy is advected to the site. Generally, HFC 125 is not as widely used as HFC 134a, and therefore its atmospheric mixing ratio is still relatively low. However, owing to its long lifetime of 29 years [IPCC, 2001], there is considerable potential for accumulation of this substance. Our estimate for the European emission of this compound in 2000–2002 is 2.2 ± 1.0 Gg/year, which is about 10% of our European estimate for HFC 134a. In comparison to esti-

mates from Mace Head in 1998 (1.5 Gg/year), the European emission appears to be quite stable in the most recent years.

4.3. HFC 152a (CHF_2CH_3)

[40] For HFC 152a, a substantial increase of the background concentration from 2.3 ppt in January 2000 to 3.2 ppt in December 2002 has been observed at the Jungfraujoch (Table 2). The resulting yearly increase of 11% in this period is in good agreement with the global increase of 12% in 1999–2000 [WMO, 2002]. HFC 152a is mainly used as a blowing agent for insulation foams. With its high reactivity toward OH and its tropospheric lifetime of ~ 1.5 years, HFC 152a is quite reactive compared with the other halogenated compounds discussed here and is, therefore, less prone to accumulation in the atmosphere. In addition to the rising background concentrations, average excursions above the baseline have risen between 2000 and 2002 from 0.20 ppt to 0.77 ppt. This indicates an increasing use of this substance in Europe during the 3 years of monitoring.

[41] Our average estimate for the European HFC 152a emission in the years 2000–2002 is 0.8 ± 0.7 Gg/year (Table 3). In comparison to estimates from Mace Head in 1998, our numbers for 2000–2002 are more than 2 times higher on average; however, the precision of the measurements allowed no statistically sound proof of increase. However, as rising peak values could be seen for HFC 152a in our measurements at the end of the data series, we conclude that the considerable increase in the use of this substance explains most of the difference of the two emission estimates.

4.4. HCFC 141b (CFCl_2CH_3)

[42] An increase of the background concentration of HCFC 141b from 14 ppt in January 2000 to 18 ppt in December 2002 has been observed at the Jungfraujoch (Table 2). HCFC 141b is used extensively as a foam-blowing agent, replacing the banned CFC 11. Instantaneous emissions occur during the manufacturing of the foam, followed by a much slower release during aging. Because of its regulation under the Montreal Protocol, emissions are expected to decrease in the coming years.

[43] AFEAS estimated its emissions in 2001 at 63 Gg per year world wide (with the omission of China, India, Russia, and Korea), with only minor growth rates in the latest years. In fact, the production for this substance seems to have peaked with production estimates for 2001 being lower than in the preceding years. This could be an effect of industries shifting to chlorine-free HFCs or halogen-free alternatives for foam blowing due to the Montreal Protocol. A further indication of the already ongoing replacement of HCFC 141b is the finding that at Jungfraujoch the yearly increase of the background concentration in 2000–2002 was only 8%, in comparison with global increases of 15% in 1999–2000 [WMO, 2002]. However, our estimation of 9.0 ± 2.1 Gg/year (Table 3) for the European source strength of HCFC 141b between 2000 and 2002 was still within the range of 11 Gg/year estimated from Mace Head in 1998. This indicates that still considerable emissions occur, presumably from already installed equipment.

5. Assessment of European Source Regions

[44] Emissions from different regions of central western Europe contribute to the observed elevated concentrations

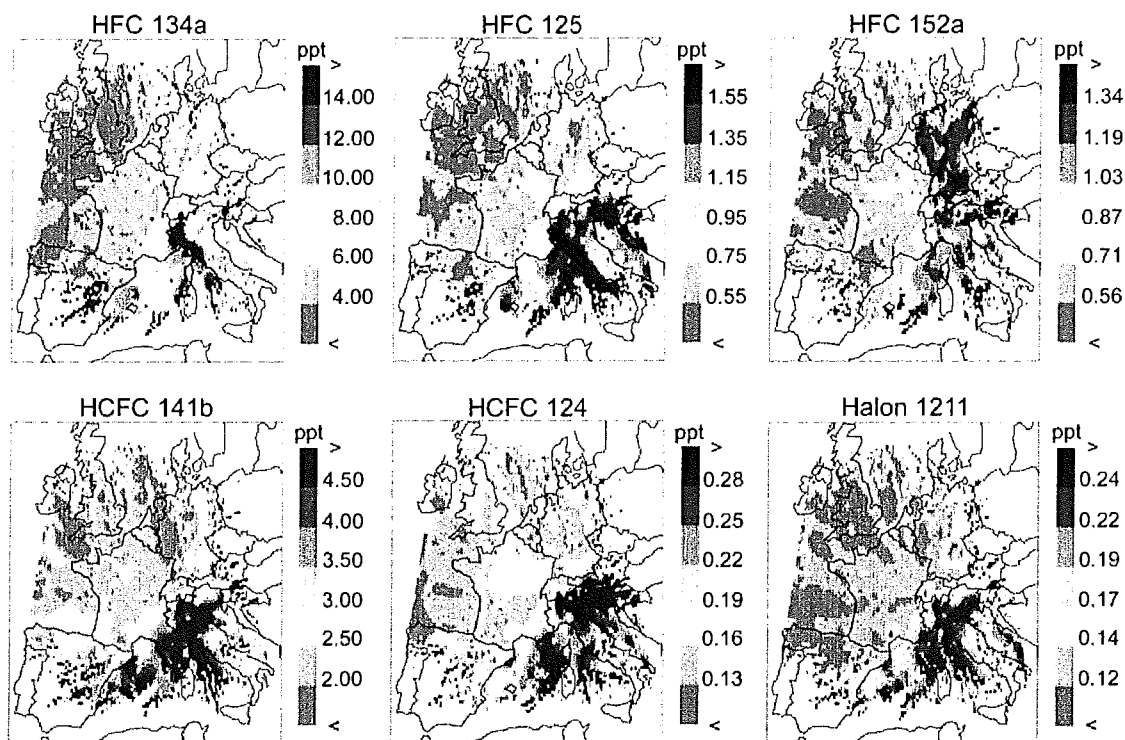


Figure 8. Potential source regions resulting from trajectory statistics of HFCs 134a, 125, and 152a, HCFCs 141b and 124, and halon 1211 for the years 2000 until 2002. Units indicate averaged concentrations above the baseline, linked to trajectories that were in the boundary layer when they passed over the respective grid cell.

of halogenated greenhouse gases at the Jungfraujoch. In this section, potential source regions are investigated by combining measurements at the Jungfraujoch with a statistical trajectory model (section 2.4), using meteorological information provided by the Swiss Meteorological Institute (MeteoSwiss). All measurement data from January 2000 to December 2002 have been combined with their appropriate trajectories to perform a source allocation. Owing to the restricted representativity of the Jungfraujoch (section 2.1), the resulting pictures are biased toward central western Europe. They should, therefore, be regarded as indicative, showing only potential source regions. Especially from France the signal is rather low, which could be due to the fact that if air masses are advected to the site from this part of Europe, transport is normally fast, with low total residence time within the polluted boundary layer.

[45] In Figure 8, results of trajectory statistics for some representative halogenated greenhouse gases are shown. Deduced from our model, southern Europe could be a very potent source region for all halocarbons. This seems to be reasonable, since northern Italy is a heavily industrialized area, where industries with known emissions of halocarbons are situated (e.g., installation of air conditioning units, for both mobile and stationary purposes). For HFC 134a and HFC 125, Germany and the eastern part of France were found to be potential source regions in the north of Jungfraujoch, although their contribution to pollution events at Jungfraujoch was smaller than from the southern direction.

[46] For HFC 152a, a different picture was observed. Highest concentrations for this compound were measured when air masses from Germany were advected to the

Jungfraujoch. Deduced from our study, we see a quite homogeneous distribution over Germany, with hot spots at locations with higher population density (e.g., the city of Munich and the Ruhr valley). Although some emissions seemed to occur in Italy, southern Europe was not as important a source for HFC 152a as for the two other HFCs discussed above. The HFC 152a source in Germany was also seen by Ryall *et al.* [2001] and is probably due to the fact that the foam blown with this substance is predominately used in Germany. However, sources to the south of our measurement site gained in importance during the course of the 3-year measurement period.

[47] Results of the trajectory statistics showed that for HCFC 141b the most important sources were located in southern Europe, particularly in Italy. Elevated emissions were also observed associated with trajectories originating from eastern Germany. As about one third of the source strength for this compound is known to be instantaneous emissions during the production of foams (AFEAS), foam blowing is likely to contribute to this distribution.

[48] For HCFC 124, the most important potential source regions were situated south of the Alps, and to a lesser extent in France and Germany. Highest values of the trajectory statistics occurred at the eastern edge of the model domain, suggesting potential sources in southeastern Europe.

[49] Halon 1211 is at the moment being phased out within the Montreal Protocol. Nevertheless, higher concentrations advected to the Jungfraujoch could still be seen from southern Europe and eastern Germany. For the other parts of the modeling domain, the distribution of the potential sources was quite homogeneous. Installed fire extinguisher

units, with both diffusive emissions and accidental releases, are expected to be the main source of this substance in the atmosphere.

6. Conclusions

[50] Halogenated greenhouse gases have been measured quasi-continuously in the years 2000–2002 at the high Alpine site of Jungfraujoch (Switzerland). Elevated concentrations representing transport of polluted boundary layer air masses have been shown to be considerable for HFCs and HCFCs, which have been introduced as replacement compounds for banned CFCs. Growth rates in the atmosphere of up to 20% for the replacement compounds represent their losses from use in many industrial and domestic applications, such as refrigeration and foams.

[51] Potential source regions in central western Europe could be detected for individual halogenated greenhouse gases by applying trajectory statistics. Although the results are only indicative, most of the halogenated greenhouse gases seem to have potent sources in northern Italy. On the other hand, substantial emissions of HFC 152a could also be observed from Germany.

[52] The site at Jungfraujoch is very different from the site in Mace Head. Because of its height, it is in principle a background site, but due to the proximity to potent source regions, it is much more influenced by anthropogenic activities. Therefore the fraction of polluted events is much higher as in Mace Head, which, for example, makes it more difficult to define an independent baseline.

[53] In future, the combined analysis of measurement data from the Jungfraujoch with other SOGE network stations could ultimately lead to an adequate picture of European emissions. Such analysis of in situ monitoring could prove to be a valuable method to validate emission figures of halocarbons from individual European regions and assess compliance with the international protocols (Montreal, Kyoto).

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- B. Buchmann, D. Folini, M. Hill, P. Hofer, S. Reimann, D. Schaub, and K. Stemmler, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland. (brigitte.buchmann@empa.ch; doris.folini@empa.ch; matthias.hill@empa.ch; peter.hofer@empa.ch; stefan.reimann@empa.ch; daniel.schaub@empa.ch; konrad.stemmler@empa.ch)
- B. R. Grealley, S. O'Doherty, and P. G. Simmonds, School of Chemistry, University of Bristol, Bristol BS8 1TS, UK. (brian.grealley@bristol.ac.uk; s.odoherty@bristol.ac.uk; p.simmonds@bristol.ac.uk)