

European Emissions of HFC-365mfc, a Chlorine-Free Substitute for the Foam Blowing Agents HCFC-141b and CFC-11

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HFC-365mfc (1,1,1,3,3-pentafluorobutane) is an industrial chemical used for polyurethane foam blowing. From early 2003, HFC-365mfc has been commercially produced as a substitute for HCFC-141b, whose use in Europe has been banned since January 2004. We describe the first detection of HFC-365mfc in the atmosphere and report on a 2 year long record at the high Alpine station of Jungfraujoch (Switzerland) and the Atlantic coast station of Mace Head (Ireland). The measurements at Jungfraujoch are used to estimate the central European emissions of HFC-365mfc, HCFC-141b, and CFC-11. For HFC-365mfc, we estimate the central European emissions (Germany, France, Italy, Switzerland, The Netherlands, Belgium, and Luxembourg) in 2003 and 2004 as 400–500 tonnes year⁻¹. These emissions are about one-third lower on a per capita basis than what we estimate from the Mace Head measurements for the total of Europe. The estimated emissions of HCFC-141b for central Europe are higher (i.e., 7.2–3.5 ktonnes year⁻¹) with a decreasing trend in the period from 2000 to 2004. Residual emissions of CFC-11 are estimated at 2.4–4.7 ktonnes year⁻¹ in the same time period. The Po Valley (northern Italy) appears to be a main source region for HFC-365mfc and for the former blowing agents HCFC-141b and CFC-11. In 2004, the emissions of HFC-365mfc arose from a wider region of Europe, which we attribute to an increased penetration of HFC-365mfc into the European market.

Introduction

Cellular polymers are widely used as insulation foams and packaging materials. They are made by introducing a blowing

agent into a liquid polymer to produce a cellular structure. Historically, chlorofluorocarbons (CFCs) were used as blowing agents, in particular, CFC-11 (CCl₃F) was widely used for polyurethane (PU) and phenolic foams (1). Because the CFCs have been linked to the destruction of stratospheric ozone, there has been a worldwide phase-out of these compounds under the Montreal Protocol and its amendments. In the European Union, the use of CFC-11 as a foam blowing agent has been prohibited since 1995. The major replacement compound for CFC-11 was hydrochlorofluorocarbon-141b (HCFC-141b, CH₃CCl₂F). This compound has always been considered as an interim substitute, as it still has significant ozone-depleting properties. Commercialization of HCFC-141b started in the early 1990s. Presently, developed countries seek to eliminate HCFC usage. In Europe, all HCFC-141b usage in foams was eliminated progressively from 2000 leading to the complete ban on January 1, 2004. Depending on the specific application, the following substitutes for CFC-11 and HCFC-141b are currently used for PU-foams: pentanes, H₂O/CO₂, or hydrofluorocarbons (HFCs). HFCs are specifically selected for applications where good thermal insulation properties or non-flammability are necessary. HFCs are not ozone-depleting, but they are considered as greenhouse gases, which fall under the Kyoto Protocol.

To satisfy the new demand for HFCs as foam blowing agents, the chemical industry recently started commercial production of suitable compounds. These new compounds are HFC-365mfc (CF₃CH₂CF₂CH₃), which is produced as a replacement of HCFC-141b mainly for the European market, and HFC-245fa (CF₃CH₂CF₂H), its American counterpart (2). The first pilot scale production of HFC-365mfc started at the end of 1996, and a larger pilot plant, with a capacity of several hundred tonnes per year, began operation in January 2000, to allow application tests by plastic foam producers. In January 2003, a commercial scale plant with a nominal yearly capacity of 15 000 tonnes became operational (3) in the eastern part of France.

Experimental Procedures

Measurement Sites. High Alpine Station Jungfraujoch. Jungfraujoch (3580 m above sea level) is situated in the northern part of the Swiss Alps (see Figure 4) and belongs to the first topographical barrier for the frequent westerly winds in central Europe. Its location is relatively remote, with the nearest villages more than 8 km in horizontally and 2.5 km in vertically distant and is only weakly influenced by local anthropogenic sources. Therefore, it can be used to monitor pollutant emissions from a wider area surrounding the Alps. The emission source regions, which have a detectable impact on the measurements at Jungfraujoch, have been investigated by Reimann et al. (4). It was concluded that emissions from an integrated area in central Europe including Switzerland, northern Italy, France, southern and western Germany, the Benelux countries, and to limited extent northeastern parts of Spain could be observed at Jungfraujoch.

Atlantic Coast Station Mace Head. The Mace Head station (5 m above sea level) is located on the Atlantic coast of Ireland and at the western fringe of Europe (see Figure 4). Mace Head is predominantly influenced by westerly winds and by the succession of frontal systems originating from the Atlantic Ocean, but quite often also by easterly and southerly winds advecting air from Europe. The latter air masses normally lead to pollution events for the halocarbons originating from distant emission sources in western Europe. The Mace Head station has a long history in measuring halogenated trace

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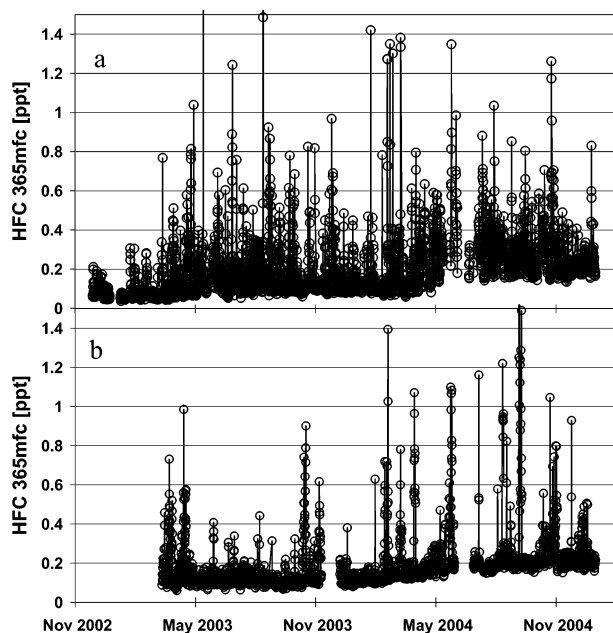


FIGURE 1. Time series of HFC-365mfc at Jungfraujoch (a) and Mace Head (b) for 2003 and 2004. The panels show the atmospheric mixing ratios of the compounds as dry air mixing ratios in parts per trillion (ppt, 10^{-12}).

gases within the ALE/GAGE/AGAGE-networks (5) and in the estimation of European emissions for these gases (6–8).

Sampling and Analysis. The analyses of HFC-365mfc, HCFC-141b, and CFC-11 were performed in situ on an automated gas chromatograph equipped with a mass selective detector (GC-MS, Agilent 5793N). The analytes were pre-concentrated using a custom-built adsorption–desorption system (9). Such instruments are in operation at Mace Head (Ireland) and Cape Grim (Tasmania) in the AGAGE network since 1994 and have been described previously (5). A detailed description of the analyses and their calibration is provided in the Supporting Information for this paper.

Meteorological Analysis. For the retrieval of potential central European source regions for the foam blowing agents from the Jungfraujoch measurements, a trajectory statistical approach has been employed as described previously (4). The method is based on 2 day backward trajectories derived from wind fields provided by the weather prediction models of MeteoSwiss. As a second model approach, we employ simulations based on the Lagrangian Particle Dispersion Model (LPDM) developed by the German Weather Service (10). The LPDM was used in backward mode (11) to map air mass origins for all measurement intervals at Jungfraujoch.

The emission estimates from the Mace Head data series have been performed using the UK Met Office’s dispersion model NAME. This model has been used in various studies to simulate the transport of pollutants to Mace Head (6–8, 12) and is detailed in refs 6–8 and 12. A more detailed description of these model approaches is given in the Supporting Information for this paper.

Results

Figure 1 shows the observed time series of HFC-365mfc at Jungfraujoch from December 2002 to December 2004 and at Mace Head from March 2003 to December 2004. The background mixing ratios of HFC-365mfc were still very low at the end of 2002, about 50 ppq (ppq: parts per quadrillion, 10^{-15}). We estimate the background mixing ratio here by the mean of the lowest 20% of the observed concentrations in each quarter of a year (see Supporting Information Table S2 for the comparison of the background concentrations at

Jungfraujoch and at Mace Head). If we assume that this background mixing ratio is representative for the global atmosphere, then this corresponds to a total mass of 1360 tonnes of HFC-365mfc in the atmosphere. This is an upper limit because the majority of emissions occurred in the Northern Hemisphere, and hence, the concentrations in the Southern Hemisphere and in the stratosphere could be lower due to the restricted transport across the tropopause and across the tropical convergence zone. If we assume that no HFC-365mfc existed in the Southern Troposphere or in the stratosphere, but its concentration was 50 ppq in the Northern Troposphere, our lowest estimate of the amount of HFC-365mfc in the atmosphere at the end of 2002 corresponds to 600 tonnes.

A global burden of 600–1360 tonnes could be in line with the producers’ statement (3) of a pilot plant production of several hundred tonnes per year in 2000, 2001, and 2002. If any additional continuous natural source of HFC-365mfc exists, its worldwide emissions strength would be very limited (<130 tonnes year $^{-1}$) according to the low mixing ratio of 50 ppq observed at the beginning of 2003 and an atmospheric lifetime of 9.9 years (13) for HFC-365mfc.

The background concentration of the Northern Hemisphere has risen from 50 ppq at the end of 2002 to ~85 ppq at the end of 2003 and to ~175 ppq at the end of 2004. In May and June 2004, only few data were collected at the Jungfraujoch due to technical problems with the GC-MS. This partly masks a strong concentration increase between the beginning of April and the beginning of July. We observe a similar concentration step also in April and May 2003. Therefore, it appears that the background concentration of HFC-365mfc rises in steps with strong increases during spring and much less increases during the rest of the year. We also observed this behavior over many years for other HFCs (HFCs-134a, -125, and -152a) and document this in Figure S3 (Supporting Information) for HFC-134a in comparison with HFC-365mfc. The increase observed in the Mace Head data series is smoother and occurs between February and May 2004. We relate this short-term deviation of the two data series to recently emitted amounts of HFCs, which are not completely mixed in the troposphere. The two stations are located in quite a different environment (high Alpine vs Atlantic coast) and sample air from very different altitudes, which could be the reason for such differences. The frequency of elevated concentrations of HFC-365mfc at Jungfraujoch increased significantly from late 2002 (Figure 1). We attribute this finding to the increasing emissions of HFC-365mfc after commercialization. At Mace Head, elevated concentrations were less frequent due to its remote location on the Atlantic coast. However, strong emission signals are observed at Mace Head in cases where the air masses sampled are from local or continental regions.

The background concentration of CFC-11 measured at Jungfraujoch has decreased slowly over the past 5 years (Figure 2), due to the successful reduction of its global emissions as a result of the Montreal Protocol (1, 14, 15). On the other hand, current observations show that there are still residual emissions occurring within central Europe. This is evident from the concentration fluctuations observed at Jungfraujoch, which are similar in magnitude to those observed for HCFC-141b. For HCFC-141b, the background concentration increased from 2000 to 2004. However, the frequency and magnitude of pollution events decreased at Jungfraujoch from 2000 to 2004, implying a reduction in emissions in Europe.

Emission Estimates for Central Europe. Exploration of the Jungfraujoch Data Series. To estimate the emissions of the foam blowing agents from central Europe, the observed emissions at Jungfraujoch were compared to the emissions of a reference compound, for which independent emission

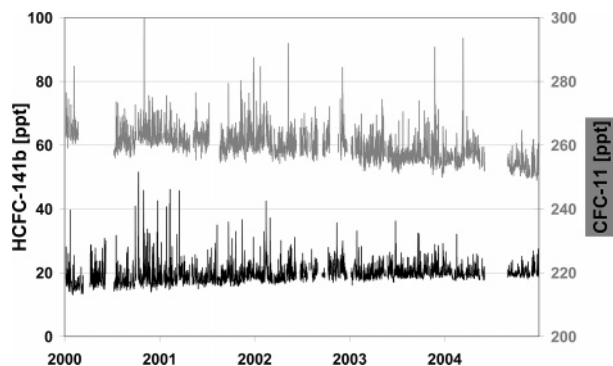


FIGURE 2. Time series of HCFC-141b (black line, left y-axis) and CFC-11 (gray line, right y-axis) at the Jungfraujoch from January 2000 until December 2004.

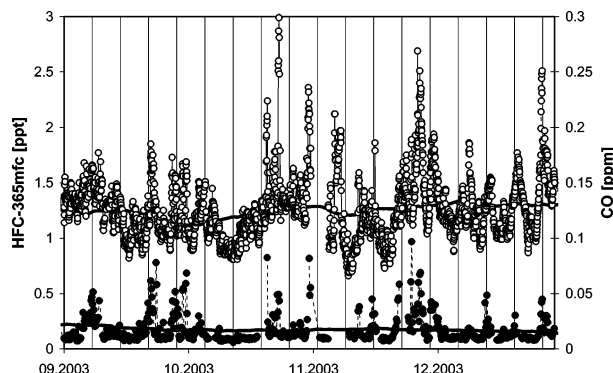


FIGURE 3. Data series for a 4 month period (September 2003 to December 2003) of HFC-365mfc (●) and carbon monoxide (○). The data series illustrate the short-term variation of the measured concentrations in comparison with the 30 day running mean concentrations (solid lines).

estimates exist. Here, we use carbon monoxide (CO) as the reference compound and base our estimate on the CO emission data reported in the UNECE/EMEP emission database(16) for the individual European countries.

The magnitude of the short-term variation of the concentrations of HFC-365mfc, HCFC-141b, and CFC-11 and of the reference compound is used as a measure for their relative

emission strengths. This variation originates from the varying influences from the emission source regions surrounding the Alps and unpolluted air on the measurements, which depend on the meteorological situation. The pollution situation at Jungfraujoch changes rapidly, and the influences of polluted air normally persists for a few hours to a few days. The magnitude of the short-term variation is expressed by the average absolute deviation of each measurement from its surrounding 30 day running mean concentration. The running mean is simultaneously used to detrend the data series. Figure 3 shows a 4 month section of the data series of HFC-365mfc and CO to visualize the short-term fluctuations of the concentrations around the 30 day running mean. A corresponding plot for HCFC-141b and CFC-11 is given in the Supporting Information (Figure S2). To quantify the influence of the time window used to calculate the running mean, we performed a sensitivity analysis using also 7 and 60 day windows. The emission estimates based on this procedure are summarized in Table 1 for the central European countries (aggregated emissions for Germany, France, Italy, Switzerland, and the Benelux countries, i.e., the countries whose emissions have the biggest influence on the measurement at Jungfraujoch).

Not only the varying influence of European emission sources but also the imprecision of the GC-MS measurements leads to a variation in the determined concentrations. To quantify the variation caused by the measurement imprecision, we express this variation separately by the same method but based on the calibration gas injections, which are executed before and after each measurement (e.g., every 4 h during routine operation). A high fraction of variation by analytical imprecision prevents firm emission estimation by the described method. As shown in Table 1, the variation caused by the analytical imprecision is a substantial fraction of the total variation in the CFC-11 measurement series. For CFC-11, this is due to its high background concentration, which demands a highly precise measurement to be able to detect the comparatively small concentration variations due to the emissions. In Table 1, we corrected our emission estimates for CFC-11 by assuming that the variation caused by the analytical imprecision and by the varying influence of the emission sources behaves additively (i.e., we subtracted the variation caused by the measurement imprecision from the total observed concentration variation).

TABLE 1. Characteristics of the Measurement Series of the Halogenated Foam Blowing Agents HFC-365mfc, HCFC-141b, and CFC-11 and of Carbon Monoxide at Jungfraujoch

	2000	2001	2002	2003	2004
HFC-365mfc					
background mixing ratio (ppt)				0.074	0.141
av short-term variation in the observation (ppt)				0.086	0.090
variation caused by measurement imprecision (ppt)				0.007	0.007
estimated central European emissions (ktonnes year ⁻¹) ^a				0.44 (0.42 – 0.45)	0.43 (0.43 – 0.50)
HCFC-141b					
background mixing ratio (ppt)	15.1	16.6	17.5	18.3	18.5
av short-term variation in the observation (ppt)	2.3	1.8	1.6	1.3	0.9
variation caused by measurement imprecision (ppt)	0.15	0.16	0.18	0.10	0.10
estimated central European emissions (ktonnes year ⁻¹) ^a	6.4 (6.3 – 7.4)	7.2 (7.2 – 7.3)	5.3 (5.2 – 5.3)	5.3 (5.2 – 5.4)	3.5 (3.5 – 4.0)
CFC-11					
background mixing ratio (ppt)	259.0	258.3	257.3	255	253.1
av short-term variation in the observation (ppt)	2.3	1.8	2.2	2.1	1.6
variation caused by measurement imprecision (ppt)	1.6	1.2	1.1	1.1	0.6
estimated central European emissions (ktonnes year ⁻¹) ^a	2.4 (1.9 – 2.7)	2.8 (2.2 – 3.0)	3.8 (3.2 – 3.8)	4.7 (4.0 – 4.8)	4.1 (4.1 – 4.7)
carbon monoxide					
av short-term variation in the observation (ppb)	29	18	21	17	17
reported central European emissions (ktonnes year ⁻¹)	19010	17900	16850	16440	(15400) ^b

^a Aggregated emissions for Germany, France, Italy, Switzerland, The Netherlands, Belgium, and Luxembourg. The range given in parentheses is the range of results obtained when 7, 30, and 60 day running means are used in the estimation procedure (see text). ^b The value for the central European CO emission for 2004 has not been reported yet. The given value is an extrapolation of the recent emission trend.

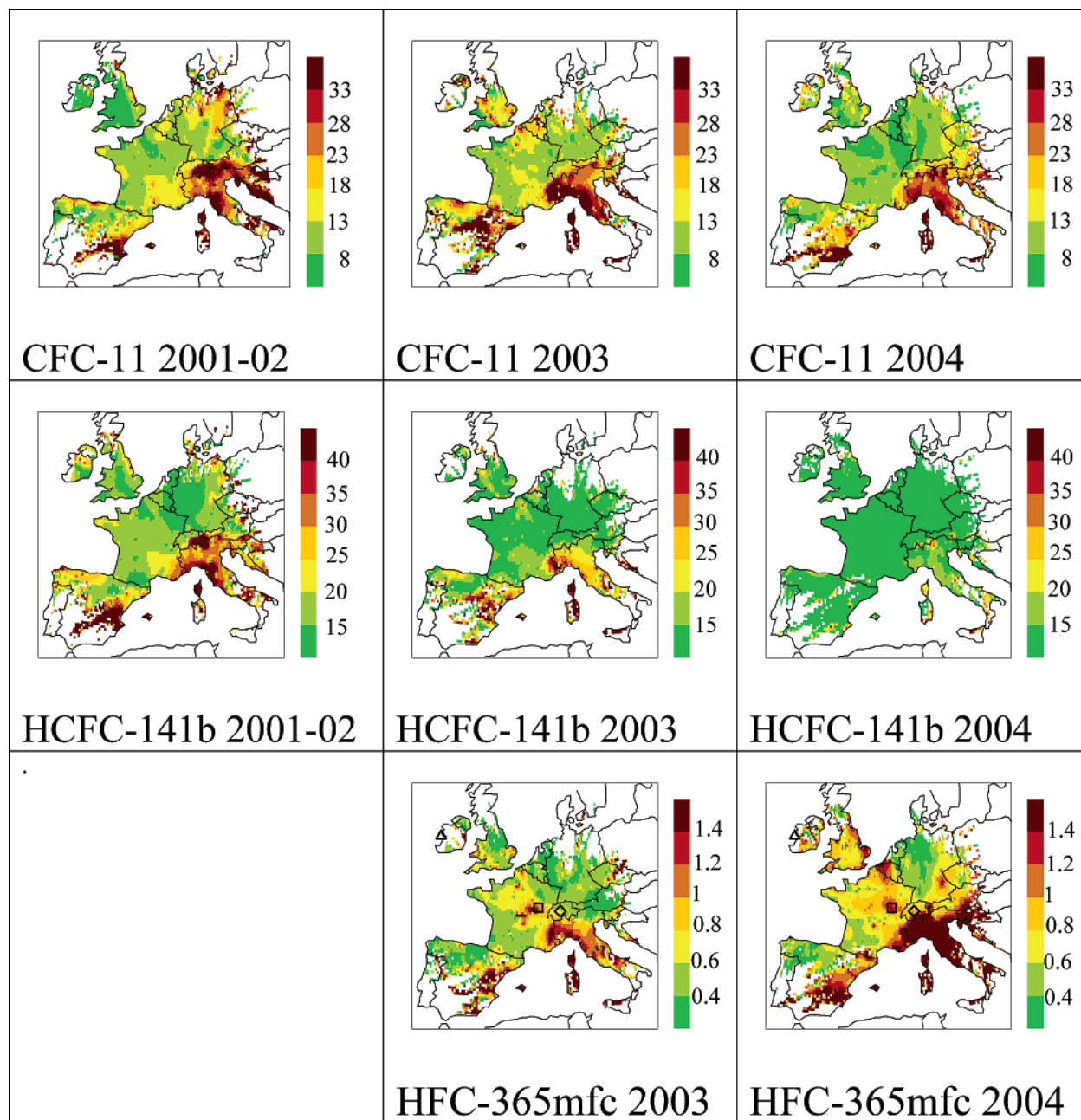


FIGURE 4. Potential source regions resulting from trajectory statistics for CFC-11, HCFC-141b, and HFC-365mfc for 2001–2004 at Jungfraujoch. In the plot for HFC-365mfc, the symbols indicate following locations: (Δ) Mace Head Station; (\diamond) Jungfraujoch Station; and (\square) production plant for HFC-365mfc. The units for the potential source strength are arbitrary.

The central European emissions of CFC-11 estimated in this paper can be compared to the emissions estimated by Manning et al. (6). They estimated the CFC-11 emissions for some central European countries in 1995–2000 based on the measurements at Mace Head. Their combined emission estimate for Germany, France, and the Benelux countries is 3.5 ktonnes year⁻¹. Our estimate of 2.4–4.7 ktonnes year⁻¹ for 2000–2004 covers additionally Italy and Switzerland and therefore comprises a 1.4 times larger population and is in reasonable agreement with the estimate based on the Mace Head measurements for the preceding years. These data imply that substantial European emissions of CFC-11 persist even a decade after their production ban in Europe. These emissions are further confirmed by a long-term monitoring program (1994–2000) in the agglomeration of Zürich, Switzerland (17), which showed that the CFC-11 emissions decreased slower than the emissions of other prominent

Montreal Protocol regulated gases, like the solvents 1,1,1-trichloroethane, CFC-113, and the refrigerant and aerosol propellant CFC-12.

When extrapolating our Jungfraujoch-based emission estimates for HCFC-141b to the European Union (EU-15; ~30000 ktonnes year⁻¹ CO emissions (16); EU-15 stands for the 15 pre-2004 EU member states), we calculate about 10 ktonnes year⁻¹ for 2000–2002. By comparison, O’Doherty et al. (7) determined the EU-15 emissions based on the measurements at Mace Head using the NAME model. They reported emissions of 7–8 ktonnes year⁻¹ in 2000–2002. The same authors also estimated HCFC-141b emissions based on reported industry data and determined the EU-15 emissions as 13 ktonnes year⁻¹ in 1999–2001.

The emissions of HFC-365mfc are about 1 order of magnitude lower than those for HCFC-141b and CFC-11. A reason for the higher emissions of the banned compounds

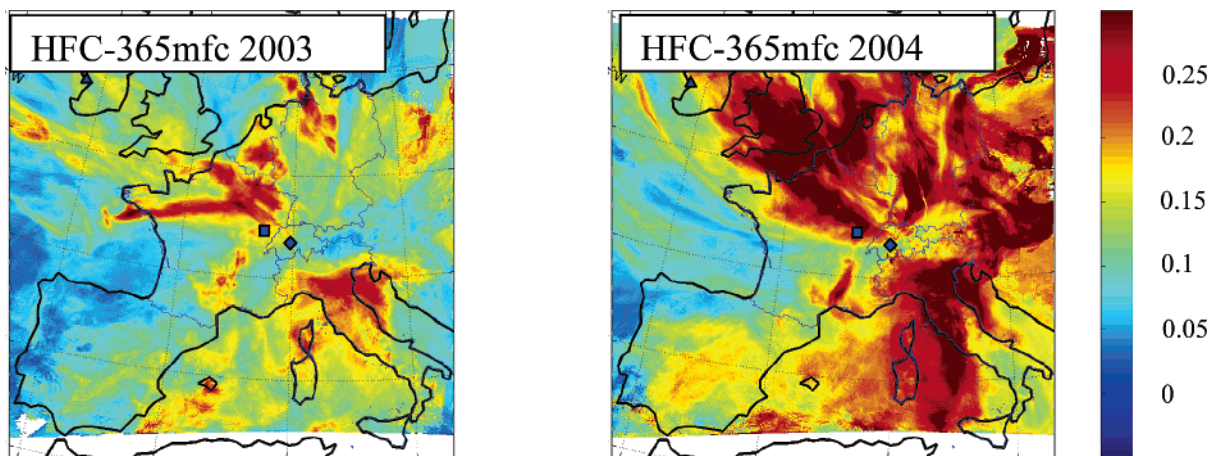


FIGURE 5. Potential European source regions resulting from Lagrangian particle dispersion model backward calculations for the HFC-365mfc measurement at Jungfraujoch in 2003 (left panel) and in 2004 (right panel). The blue symbols indicate the following locations (\blacktriangle): Mace Head Station; (\blacklozenge): Jungfraujoch Station; (\blacksquare): Production plant for HFC-365mfc. The units for the potential source strength are arbitrary.

may be that emissions of blowing agents from closed cell foams occur at different stages in the life of a foam (1, 18): (i) during manufacture, (ii) during use, when the blowing agent diffuses slowly from the foam, and (iii) during disposal. For CFC-11 and HCFC-141b, the observed emissions can be attributed to the diffusive losses from installed foams and to the losses at disposal. For HCFC-141b, also emissions from foam production were contributing before 2004. For HFC-365mfc, the amount of installed foams is still very small, and presently, the main emissions are likely to occur from production losses during foam blowing.

Exploration of the Mace Head Data Series. For HFC-365mfc, we also explored the Mace Head data series by employing the NAME model for a quantitative emission estimation. This direct inverse emission modeling technique eliminates the uncertainties of introducing the reference emissions of CO. The NAME model is not suitable for the Jungfraujoch measurement due to its low resolution of the complex Alpine topography. As can be seen in Figure 1b, the emission estimation from the Mace Head data is based on a much smaller number of European pollution events. From the Mace Head data, we estimate the integral emissions of HFC-365mfc for a larger region in Europe [15°W, 16°E and 40°N, 60°N, which is inhabited by a approximately 1.5 times larger population (325 million in 1990 (19)) than the central European region modeled from Jungfraujoch] being 970–1080 and 1060–1200 tonnes in 2003 and in 2004, respectively. Therefore, the emissions per capita are estimated approximately 50% higher by the Mace Head approach than estimated from the Jungfraujoch data. This may be partially related to substantial emissions from the British Isles, which are not included in the Jungfraujoch estimate, but probably this reflects the general accuracy of our emission estimations.

Distribution of Emission Source Regions in Europe. Potential Source Regions Derived from the Jungfraujoch Data Series. Figure 4 shows the results of the trajectory statistics for CFC-11, HCFC-141b, and HFC-365mfc. For CFC-11 and HCFC-141b, the source apportionment is shown for the measurement from 2001 to 2002 and additionally for the years 2003 and 2004 separately, to allow a better comparison with the plots for HFC-365mfc, which are only available for 2003 and 2004. As can be seen in Figure 4, in general, the trajectory plots indicate that sources are unequally distributed within Europe. The plots represent a back attribution of the measured concentrations along a given trajectory to the source regions affecting the measurement. Therefore, the plots indicate only the general direction from where the majority of the pollution events originate; however,

the distance of these potential source regions can be determined only with low accuracy. For CFC-11 and HCFC-141b, the trajectory analysis identifies the heavily industrialized Po Valley as the most likely source region. Corsica and Sardinia appear as source regions on the plots as well, but this is most likely an artifact because the air masses originating from this direction also pass over the Po Valley, where they pick up the emissions. The plot also indicates source regions in Spain, but we judge the allocation of these source regions as uncertain as the data density is low and the results could be distorted by closer lying emission sources. For HCFC-141b, the emissions decrease throughout 2001–2004. This decrease is discussed more comprehensively by Derwent et al. (20).

The trajectory plot for HFC-365mfc for 2003 shows a source region located, as for CFC-11 and HCFC-141b, in a southern direction, most likely in the Po Valley. This collocation of the source regions is not unexpected, as all three compounds are used for the same applications, and therefore, the same industries or consumers could be responsible for the emissions of these gases. For HFC-365mfc, there appears to be another source region located in the eastern part of France. This region has so far not been recognized as a potential source region for any man-made halocarbon measured at the Jungfraujoch (4). This source region matches the location of the production plant for HFC-365mfc (see Figures 4 and 5 for the exact location). It is likely that these observed emissions arise from losses during the production and handling of this compound. In general, the production of a foam blowing agent is not considered to be a major contributor to its total emissions into the atmosphere, as at this stage an effective containment of the compound is easier to achieve than during the blowing, processing, or disposal of the foams. The observed emissions of HFC-365mfc from the production area are therefore expected to be less prominent in the future if the compound finds wide acceptance by foam producing companies within Europe. In the trajectory plot for the year 2004, we find an even more distinct emission of HFC-365mfc south of the Alps and also potential sources in Germany and the Benelux countries. This is a strong indication that HFC-365mfc has penetrated the foam blowing market in wide areas of central Europe. There also appears to be source regions in Great Britain and Spain, but we judge the allocation of these source regions as uncertain as they are likely distorted by closer lying emission sources.

Principally, the applied trajectory model contains only a simplified description of the meteorological transport and

does not account for the dispersion of air masses during transport from the source regions to the measurement station. A potential model error resulting from this simplification might be an unequal representation of source regions lying in different directions and distances from Jungfraujoch. To detect such an artifact, the source distribution of HFC-365mfc was also calculated using the backward simulations of a Lagrangian Particle Dispersion Model (LPDM). The resulting statistics are shown in Figure 5. The source regions in northern Italy and in eastern France are also well-represented by the LPDM approach in 2003. Therefore, it appears that the apportionment of the major source regions for HFC-365mfc by the trajectory statistics is not strongly biased by statistical differences in the meteorological transport from the two directions. In 2004, the LPDM plot shows a much wider distribution of the emissions of HFC-365mfc, both south and north of the Alps, as indicated by the trajectory statistics.

Discussion of the Present European Emissions of Fluorinated Foam Blowing Agents. The measured foam blowing agents act as greenhouse gases, and the banned CFC-11 and HCFC-141b additionally act as ozone-depleting chemicals. Therefore, these compounds fall under the Kyoto Protocol (HFC-365mfc) and the Montreal Protocol (CFC-11 and HCFC-141b), respectively. For CFC-11, the measurements establish that despite its production ban in 1995, substantial emissions of this compound still persist within Europe. This is likely to be related to the long banking times of blowing agents in foams with service lives between 12 and 50 years depending on the type of foam (1). In their worldwide survey, McCulloch et al. (1) estimated the annual released fractions of the banked amounts as about 0.04. For HCFC-141b, the European emissions declined rapidly during the European phase-out years 2000–2003; this is a strong indication that the measures have been successful (20). The fast decline is explainable by the phase-out of the foam blowing with HCFC-141b, a process that leads to significant in situ emissions. As this compound has only been produced since 1990, the amounts estimated (21) to be banked in closed cell foams are considerably lower (676 ktonnes worldwide in 2002) than for CFC-11 (1073 ktonnes in 1994). Assuming the same release rate for banked HCFC-141b, one expects that there will be lower future residual emissions of HCFC-141b than we presently observe for CFC-11. For HFC-365mfc, the emissions during the first 2 years of commercial production stayed significantly lower than the emissions of HCFC-141b at the beginning of its European phase-out. This indicates that HFC-365mfc has only partially replaced HCFC-141b and that other alternative non-fluorinated blowing agents are also being increasingly used. This meets with projections of the future usage of HFCs in the foam blowing market (18, 22), concluding that HFCs will be limited to only some of the applications where CFCs and HCFCs were utilized, with HFCs replacing less than 50% of the HCFCs and less than 25% of the CFCs on a weight basis.

We estimate the combined emissions of the three foam blowing agents from Germany, France, Italy, Switzerland, and the Benelux countries as amounting to between 1500 and 2500 ktonnes of CO₂ equivalents per year (2000–2004). This is a minor fraction (0.6–1.0%) of the total greenhouse gas emissions (CO₂, CH₄, N₂O, and F-gases) of 2 550 000 ktonnes of CO₂ equivalents these countries estimate in their Kyoto Protocol reports in 2002.

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Supporting Information Available

Detailed description of chemical and meteorological analyses. Estimated background concentrations of HFC-365mfc at Jungfraujoch and Mace Head. Calibration curves for the GCMS analysis of HFC-365mfc. Data series for a 4 month period of HCFC-141b and CFC-11 at Jungfraujoch. Comparison of the data series of HFC-134a and HFC-365mfc at the Jungfraujoch. This material is available free of charge via the Internet at <http://pubs.acs.org>

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