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Key Point:

• First observations of HCFC-31 in the atmosphere

Supporting Information:

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Abstract We report the first multiyear atmospheric record of HCFC-31 (CH₂CIF), based on flask samples and in situ analyses of air from both hemispheres. Although HCFC-31 has never been produced in large amounts, observed mole fractions in the Northern Hemisphere increased from 2000 onward, reaching 170 ppq (parts per quadrillion, 10^{-15}) in 2011–2012 before decreasing rapidly. By combining our observations with a two-dimensional atmospheric chemistry-transport model, we infer an increase in global emissions from 240 t yr⁻¹ in 2000 to 840 t yr⁻¹ in 2011–2012, followed by a relatively fast decline to 570 t yr⁻¹ in 2014. Emissions of HCFC-31 originate most probably from intermediate product release during the manufacturing process of HFC-32 (CH₂F₂). The rapid decline in recent years could be due to changes in production methods rather than declines in diffusive sources such as landfills or HCFC-31 contaminations in merchandised HFC-32.

1. Introduction

Hydrochlorofluorocarbons (HCFCs) are a class of anthropogenic chemicals, used mainly in refrigeration and foam blowing. They were produced initially as chemicals for specific applications and later as replacement compounds to facilitate the phaseout of chlorofluorocarbons (CFCs), which have a large ozone depletion potential (ODP). CFCs were identified as agents to catalyze stratospheric ozone destruction in the early 1970s [Molina and Rowland, 1974] and were banned from emissive usage under the Montreal Protocol, after the discovery of a severe thinning of the ozone layer over Antarctica [Farman et al., 1985]. HCFCs have at least one C-H bond, which makes them susceptible to oxidation by hydroxyl radicals (OH) in the troposphere, resulting in a large fraction being destroyed before reaching the stratospheric ozone layer [Carpenter et al., 2014]. Due to their chemical structure, containing both hydrogen and chlorine, HCFCs are denoted as transition substitutes and are also regulated by the Montreal Protocol. In developed countries, production and consumption are still allowed under certain restrictions, while in developing countries, they were not restricted until 2013 [Braathen et al., 2012], resulting in an accelerated accumulation of HCFCs in the atmosphere during the past decades [Montzka et al., 2009, 2015]. The most abundant HCFCs in the atmosphere are HCFC-22 (CHCIF₂), HCFC-141b (CH₃CCI₂F), and HCFC-142b (CH₃CCIF₂). In 2012, they reached mole fractions of 219.8 ppt (parts per trillion, 10^{-12}), 22.5 ppt, and 22.0 ppt, respectively, in the global background atmosphere [Carpenter et al., 2014]. In addition to these abundant HCFCs, there are a number of minor HCFCs, such as HCFC-133a (C₂H₂CIF₃) [Laube et al., 2014] and HCFC-225ca (C₃HCl₂F₅) [Kloss et al., 2014], which were observed recently in the current atmosphere or in archived air samples. Despite the Montreal Protocol regulations for developed countries, most of these HCFCs are still increasing in the troposphere, due to the allowed, growing use in developing countries.

The topic of this study is HCFC-31 (chlorofluoromethane, CH_2CIF), for which we provide the first measurements in the global atmosphere. Little is known about this compound. Even though HCFC-31 has been used in two refrigerant blends (R-505 and R-506) [*Agarwal et al.*, 2002], it has never been produced industrially in large amounts due to its flammable and carcinogenic character [*Balsiger et al.*, 2005; *DFG*, 2014; *Höhener et al.*, 2003]. HCFC-31 is an intermediate in the synthesis of HFC-32 (CH_2F_2) [*Clemmer et al.*, 2002; *Shantan Rao et al.*, 2015; *Wismer*, 2003], a widely used refrigerant. Further, it is a known product of the anaerobic degradation of CFC-11 (CCl_3F) and was found in emissions from landfills [*Balsiger et al.*, 2005; *Scheutz et al.*, 2007a, 2010a, 2010b; *Scheutz and Kjeldsen*, 2003].

©2015. American Geophysical Union. All Rights Reserved. HCFC-31 is removed from the atmosphere by the reaction with OH [*Bhatnagar and Carr*, 1996; *Charmet et al.*, 2013], resulting in a total lifetime of 1.2 years [*Carpenter et al.*, 2014]. It has a radiative efficiency of $0.08 \text{ Wm}^{-2} \text{ ppb}^{-1}$ and a resulting 100 year greenhouse warming potential (GWP) of 83, with an uncertainty of ±30% [*Charmet et al.*, 2013]. HCFC-31 contains chlorine and is therefore listed in the Montreal Protocol as an ozone-depleting substance, with an ODP of 0.02 [*Braathen et al.*, 2012].

In this paper, we present the first atmospheric records of HCFC-31 based on measurements in archived air samples from various northern hemispheric and southern hemispheric locations and in situ measurements at a Northern Hemisphere urban and a Southern Hemisphere remote observation site. To quantify global emissions from the observations, the atmospheric abundances are compared to the results of an atmospheric chemistry-transport model. Furthermore, we discuss potential sources and their possible contribution to global emissions.

2. Methods

2.1. Measurements

To reconstruct past abundances of HCFC-31, we use three different sets of samples for our analysis. For the Northern Hemisphere, the samples consist of air collected in canisters from various remote sites, filled during periods with relatively clean air (when the mole fractions of various compounds, including HCFC-31, are similar to those measured in background air) between 2000 and 2014. Additional northern hemispheric information is gained from air samples collected aboard the Korean research vessel "Araon" during the SHIPPO-2012 expedition, on a transect through the North Pacific from Incheon (South Korea) to Nome (Alaska, USA) (June 2012 to August 2012) [*Park and Rhee*, 2015]. To track the atmospheric history in the Southern Hemisphere, we analyzed air samples from the South Korea Antarctic station King Sejong, located on the Barton Peninsula (King George Island; 62°13'S, 58°47'W), as part of a long term flask sampling program [*Vollmer et al.*, 2011]. The record was complemented by eight archived air samples, collected at Cape Grim (Tasmania) (December 2012 to September 2014), to increase data availability during the reversal in the Southern Hemisphere and to overlap the records from King Sejong and Cape Grim [*Langenfelds et al.*, 1996, 2014]. Most of the above-mentioned samples are the same as those used by *Vollmer et al.* [2015], and more detailed sample information can be found there and in our supporting information.

We also measured HCFC-31 continuously, using Medusa gas chromatograph mass spectrometer (GCMS) technology (see section 2.2) [*Miller et al.*, 2008]. One in situ measurement system is operating at Dübendorf, a suburban site near Zurich (Switzerland). The intercepted air masses at this site can potentially be affected by direct anthropogenic emissions of halogenated greenhouse gases from the surrounding areas. Another Medusa-GCMS system is located at the Cape Grim Baseline Air Pollution Station, operated by the Australian Bureau of Meteorology. However, data availability is sporadic at these stations due to chromatographic interferences on aged columns (see below). We complemented our intermittent in situ record at Dübendorf with biweekly flask sampling. Sample pairs were collected on the rooftop of the laboratory building into electropolished stainless steel canisters at ~4 bar using an oil-free diaphragm pump (KNF-N-022-ANE, Neuberger).

2.2. Analytical Setup

Flask sample analyses were carried out at Empa (Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland), using a Medusa sample preconcentration unit which is coupled to a gas chromatograph (GC, Agilent 6890 N) mass spectrometer (MS, Agilent 5975MS) [*Miller et al.*, 2008]. The Medusa is equipped with Hayesep-D packed cold traps, which are cooled to -160° C for preconcentration and heated to $\sim 100^{\circ}$ C for desorption. To enhance peak size and allow for better measurement precision, most flasks were analyzed by trapping 4L of sample, compared to a standard volume of 2L for routine continuous ambient air monitoring measurements. Preconcentrated samples are chromatographically separated on a 25 m × 0.32 mm internal diameter Agilent CP-Porabond Q column with 5 µm film thickness before detection on a selected ion mode quadrupole MS. This system has been used for both HCFC-31 flask measurements and continuous in situ measurements of air from the laboratory building rooftop in Dübendorf.

We identified HCFC-31 on our Medusa-GCMS system by scanning diluted subsamples of a commercial reference multicomponent gas mixture (Carbagas, Switzerland) for the mass/charge (m/z) ratio pattern of

the most abundant mass fragments from published mass spectra. On our Empa Medusa-GCMS we found HCFC-31 eluting at ~1170 s (in the vicinity of perfluorocarbon PFC-318 ($c-C_4F_8$) and CFC-12 (CCI_2F_2)). It was identified in the mass spectrum based on its most abundant mass fragments m/z 68 as target ion for quantification and m/z 70 as qualifier ion.

During the aging of the chromatographic column, the retention time of HCFC-31 increases faster (5 s over 10 months) compared to the initially later eluting CFC-12 (3.7 s over 10 months). Over time, the two compounds interfere until eventually they completely coelute. All ion fragments of HCFC-31 are also present in CFC-12 on our MS, which has only limited mass resolution (the CH_2^{35} ClF fragment with a m/z of 67.98 is unique for HCFC-31 but cannot be resolved from the CFC-12 fragment C^{37} ClF with a m/z of 67.96). Because of this limitation, we lose the capability to detect HCFC-31 in instruments with aged columns, and consequently, in situ observations, using the same column, are only possible for approximately 10 months. However, HCFC-31 is integrated by peak height, and data are flagged for chromatograms with significant peak overlap such that during the initial use of a new chromatographic column, the measurement integrity of HCFC-31 is not affected by the column aging. Ambient air data availability for the Empa Medusa-GCMS is January–October 2013 and November 2014 to July 2015. On the Cape Grim Medusa-GCMS, measurements are available from October 2014 to April 2015.

For the correction of short-term drifts of MS response, a working standard ("quaternary standard") is measured after each two canister air sample measurements or after each in situ measurement, respectively. These quaternary standards are ambient air compressed into internally electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA) at Rigi-Seebodenalp (Switzerland), using an oil-free diving compressor (SA-6, Rix Industries, USA) or with cryogenic methods at Cape Grim (Tasmania) [*Langenfelds et al.*, 1996]. The mean measurement precision (1 σ) for HCFC-31 is 2.8% for northern hemispheric flask samples after 2008, with atmospheric mole fractions larger than ~100 ppq. Older samples with lower abundances have a mean measurement precision (1 σ) of 5.7%. Southern hemispheric flask samples with mole fractions below ~100 ppq during the whole sampling period have been measured with a mean precision (1 σ) of 4.7%. The mean measurement precision for in situ measurements is somewhat lower at 6.0% (1 σ), because only 2 L samples are trapped during standard operation of the Medusa-GCMS.

There are no commercial reference standards for HCFC-31 in the low mole fraction range of our observations. This required us to produce our own primary standard by dilution of a commercial ppm (parts per million, 10^{-6}) standard to a mole fraction of ~2 ppt, which defines our "Empa-2013 primary calibration scale," to which all the data of this study are referenced. The accuracy for "Empa-2013" is estimated to be ±6%; the overall uncertainty of our reported results is estimated to be ±8% and includes the calibration scale uncertainty, a small uncertainty (~1%) due to the propagation of standards and the analytical precisions outlined above.

Further laboratory tests were conducted to ensure measurement integrity. Experiments were conducted on the Empa Medusa-GCMS to check for potential system nonlinearity. They confirmed that our Medusa-GCMS system behaves linearly in the mole fraction range of interest and within measurement uncertainties for HCFC-31 and no systematic biases could be observed. The tests also showed trap breakthrough volumes > 6 L, from which we conclude no sample loss despite the enhanced sample size during this study. The lowest detectable HCFC-31 mole fraction on our Medusa is 14 ppq (2 L samples, 3 times the amplitude of noise) suggesting that even though we are working with very low abundances, we operate well above our detection limits. Our instrument was also free of blank and memory effects well within the detection limits. The stability of HCFC-31 during storage was examined by repeated measurements of a number of samples within a timeframe of 1.5 years. The observed mole fraction differences were random in sign and smaller than the combined measurement uncertainty. We therefore start from the premise that HCFC-31 is stable in the canisters used during this study, and trends in mole fractions originate from changes in the troposphere and are not storage artifacts.

2.3. Modeling

Global HCFC-31 mole fractions and emission estimates are derived from the AGAGE (Advanced Global Atmospheric Gases Experiment) 12-box model [*Cunnold et al.*, 1983; *Rigby et al.*, 2013]. The model divides the Earth's atmosphere into four latitudinal boxes with boundaries at 30°S, the equator and 30°N and three vertical boxes, divided at 500 hPa and 200 hPa. For this study, we prescribed a stratospheric partial lifetime

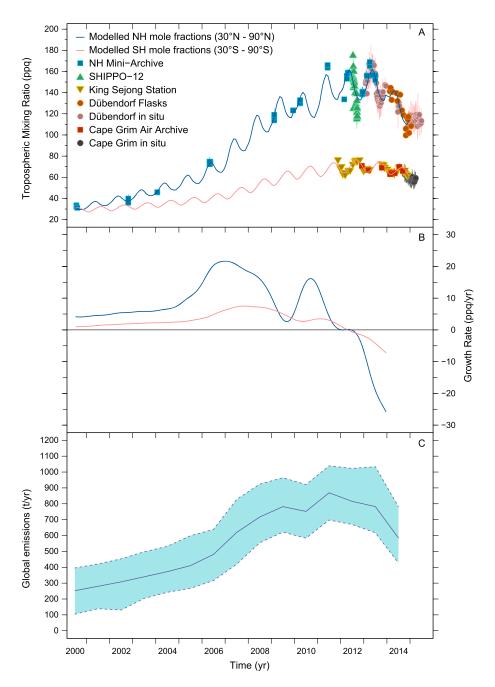


Figure 1. (a) Atmospheric record of HCFC-31 (CH₂CIF). Vertical bars: measurement precision $(\pm 1\sigma)$ for flask measurements, often smaller than the symbol size, and $\pm 1\sigma$ for in situ measurements, referring to weekly means. Solid lines: dry air mole fractions from the AGAGE 12-box model for the model surface boxes 30°N to 90°N (in blue) and 30°S to 90°S (in red). (b) Growth rates derived from Figure 1a for dry air mole fractions in the model surface boxes. (c) Model-derived global emissions in t yr⁻¹.

of 35 years [*Carpenter et al.*, 2014] and used OH reaction rates from *Sander et al.* [2011], which, when combined with mean global OH mole fractions from *Rigby et al.* [2013], lead to an overall lifetime of 1.3 years in the model. There is some uncertainty about the lifetime of this species in the literature [*Carpenter et al.*, 2014]. Therefore, we assumed a potential \pm 20% uncertainty in our lifetime estimates, which is approximately twice the discrepancy between the 2011 and 2014 World Meteorological Organization assessments. This uncertainty is propagated through to our derived emissions (following *Rigby et al.* [2014]).

The AGAGE 12-box model has been used extensively for inverse modeling of global emissions using background atmospheric measurements [*Rigby et al.*, 2011, 2013; *Vollmer et al.*, 2015]. In order to derive emissions, a Bayesian

approach was used, based on independent a priori estimates of the rate of change of emissions [*Rigby et al.*, 2011]. Due to the absence of inventory information on HCFC-31, we initiated the model with a prescribed a priori emissions growth rate of 0 ± 0.5 kt yr⁻² from 2000 to 2014.

3. Results and Discussion

3.1. Observations

Measurements of atmospheric HCFC-31 abundances are shown in Figure 1a. The records show early northern midlatitude dry air mole fractions of ~30 ppq in 2000 and a distinct rise until 2011–2012, peaking at ~170 ppq. After 2012, measured mole fractions decreased to ~110 ppq in early 2015. Results from our northern Pacific air samples [*Park and Rhee*, 2015] correspond well with the northern hemispheric record, although we observe some variability in these samples. HCFC-31 mole fractions are lower for air advected over the remote Southern Pacific, while there is evidence for higher mixing ratios in air directly advected from the Asian continent. These observations are consistent with similar findings for other anthropogenic trace gases in the same samples [*Vollmer et al.*, 2015]. In the Southern Hemisphere, mole fractions of HCFC-31 are lower, which is indicative of predominantly northern hemispheric emissions. While mean dry air mole fractions in Antarctic air samples from 2012 are ~70 ppq, Cape Grim in situ data from November 2014 to March 2015 drop to ~60 ppq, suggesting a rapid decrease also in the Southern Hemisphere.

The atmospheric history of HCFC-31 was reproduced using the derived emission estimates from the AGAGE 12-box model (see section 3.2 below) by running the model in forward mode. The modeled mole fractions agree well with measured values, and the seasonal cycle is accurately captured. Maximum model-derived growth rates in the 2000–2007 period were ~25 ppq yr⁻¹ (Figure 1b). Then the northern hemispheric trend slowed down substantially in 2007–2008, followed by another period of increased growth rates in 2008–2011. After reaching the above mentioned northern midlatitudinal peak values of ~170 ppq in 2012, the model replicates the surprisingly quick and clear reversal of growth rates (Table 1). The delay of the maximum in the southern hemispheric record, compared to that in the Northern Hemisphere, is ~1 year and corresponds to the typical time scale for interhemispheric tracer transport [*Jacob*, 1999].

At the suburban site in Dübendorf, we observe a strong seasonal cycle of HCFC-31. Our modeling shows, that this reflects the seasonal variability of OH, the primary sink for HCFC-31, which has a maximum in summer and a minimum in winter [*Bhatnagar and Carr*, 1996; *Spivakovsky et al.*, 2000].

3.2. Emissions and Potential Sources

The emission estimates, inferred by the AGAGE 12-box model, are shown in Figure 1c. First observations of changes in the tropospheric mixing ratio in 2000 translate to modeled global emissions of 240 tyr^{-1} (±170 t yr⁻¹). Beginning in 2004, we observe an increase of up to 30% per year in global emissions. Emissions stabilize between 2008 and 2012, with peak emissions of around 840 tyr^{-1} (±90 t yr⁻¹). In 2012, the emission increase stops and reverses in a sharp manner, decreasing by 30% to 570 t yr⁻¹ (±110 t yr⁻¹) in 2014. From 2000–2014, a global time-integrated total of 8000 t of HCFC-31, with a global climate forcing equivalent to ~700 kt of CO₂, were emitted.

Besides direct synthesis, which has never been carried out in large amounts, there are, to the best of our knowledge, two methods capable of releasing HCFC-31 into the atmosphere. An average of ~75% of CFC-11, formerly used as blowing agent, is still contained in insulation foam when products are shredded at the end of their operational life span [*Scheutz et al.*, 2007b]. It is known that in methanogenic, strongly reducing environments, prevalent in deeper layers of shredded waste landfills, CFC-11 can be dechlorinated, producing HCFC-31 [*Balsiger et al.*, 2005; *Scheutz et al.*, 2007a, 2010a; *Scheutz and Kjeldsen*, 2003]. While most of the reduced compounds are oxidized in shallower, aerobic layers, low emissions of HCFC-31 ($0.006 \text{ gm}^{-2} \text{ d}^{-1}$) were detected during a field study at a Danish waste facility [*Scheutz et al.*, 2010b]. While we cannot exclude a contribution of HCFC-31 emissions from landfills, the rapid decline in global emissions from 2013 onwards is inconsistent with gradual changes expected from landfill emissions. Therefore, only a minor contribution from this source is presumed for the measured HCFC-31 mole fractions in the atmosphere.

A more plausible explanation is emissions of HCFC-31 related to the production and use of HFC-32, a popular, non-ozone depleting substance used in mixtures such as R-407 and R-410 as substitute for phased-out

Table 1. Mean Global Mole Fractions (Reported as Dry Air Mole Fractions in Parts Per Quadrillion, 10^{-15}), Their Uncertainties (16%/84% Percentiles), Annual Growth Rates, Emissions, and Emission Uncertainties (16%/84% Percentiles) for HCFC-31 (CH₂ClF) Derived From Observations Using the AGAGE 12-Box Model

Year	Mole Fraction (ppq)	MF_Uncertainty (ppq)	Growth Rates (ppq yr ⁻¹)	Emissions (t yr ⁻¹)	E_Uncertainties (t yr ⁻¹)
2000	27	23/32	0	252	104/395
2001	29	20/44	2	280	139/421
2002	32	24/44	3	308	130/453
2003	35	28/40	3	340	204/498
2004	38	30/49	3	372	242/532
2005	42	26/63	3	410	267/599
2006	48	40/56	6	481	316/639
2007	58	44/66	10	620	419/827
2008	69	57/76	12	717	555/924
2009	79	72/84	10	782	621/964
2010	84	78/89	4	752	583/921
2011	90	84/97	6	869	698/1039
2012	93	88/99	3	815	669/1023
2013	92	87/98	-1	782	617/1034
2014	83	78/88	-9	584	426/781

refrigerants. In developed countries, major consumption of HFC-32 started around 2000, while the rapid increase of HFC-32 use in developing countries started around 2005 (G. Velders, National Institute for Public Health and the Environment, RIVM, unpublished data, 2015), resulting in estimated global emissions of $21,000 \pm 11,000 \text{ tyr}^{-1}$ in 2012 [O'Doherty et al., 2014]. To produce HFC-32, methylene chloride (CH₂Cl₂) or HCFC-22 (CHF₂Cl) is reacted with hydrogen fluoride (HF) or hydrogen (H₂), whereupon HFC-32 is extracted from the reactor effluent, comprising HFC-32, unreacted feedstock substances, HF or H₂, HCl, and HCFC-31 as an intermediate substance [*Frischknecht*, 1999; *Wismer*, 2003]. However, assuming good factory practice, unreacted CH₂Cl₂ or CHF₂Cl and HCFC-31 are fully recovered during the extraction process and reinjected into the production chain (M. McFarland, DuPont, personal communication, 2015).

The rapid reversal of the estimated global emissions of HCFC-31 points to a shutdown of sources that were under direct and immediate human control and less likely to diffusive sources related to banked HCFC-31, stored in equipment or other reservoirs. We speculate that a significant fraction of past HCFC-31 emissions resulted from factory release during HFC-32 synthesis under potentially poorly optimized production conditions. Our observed rapid decline in these emissions would consequently be a result of improvements in the synthesis at one or a few factories, an overall reduction of their HFC-32 production, or both. Our hypothesis is supported by the absence of any known purposeful significant end user application of HCFC-31, which could otherwise have a similar effect on the tropospheric mole fraction, once halted from release to the atmosphere.

There is a strikingly parallel behavior between the atmospheric records and derived emissions of HCFC-31 and HCFC-133a, a recently discovered compound, which also has no known significant end user applications [*Laube et al.*, 2014]. A reversal of atmospheric abundances and emissions was also found for HCFC-133a, over a similar period as for HCFC-31 (M. K. Vollmer, personal communication, 2015). This finding supports the hypothesis of *Laube et al.* [2014] that an earlier interruption of the HCFC-133a increase in the atmosphere might be due to changes in production plants, presumably some of those for the synthesis of HFC-134a, HFC-125, or HFC-143a, where HCFC-133a is an intermediate product.

If HCFC-31 is an impurity in merchandised HFC-32, then the two would be coemitted during the leakage of installed HFC-32. While atmospheric abundances and inferred emissions have also grown for HFC-32 during the growth period of HCFC-31 [*O'Doherty et al.*, 2014], we propose that the reversal we find for HCFC-31 is inconsistent with this scenario. HFC-32 emissions continue to grow and the compound is built into refrigeration systems for which a sudden prevention of leakage is unrealistic. Also, our measurement program at urban Dübendorf includes HFC-32 for which we find large pollution events. However, simultaneously occurring pollution events for HCFC-31 are absent from this record, suggesting no significant impurities of HCFC-31 in the HFC-32 installed within the air mass footprint of our station. Measurements of potential

HCFC-31 impurities in various HFC-32 products would lead to an improved understanding of such a HCFC-31 source, but it would be a difficult and an elaborate task due to the large number of plants and the poorly traceable distribution.

4. Conclusion

We present the first measurements of HCFC-31 in the global background atmosphere. Although HCFC-31 has never been produced in large amounts, we observe a distinct increase in the tropospheric mixing ratio between 2000 and 2012. While the contribution to global radiative forcing and stratospheric ozone depletion is small for HCFC-31 alone, the collective effects of all HCFCs are significant [*Hodnebrog et al.*, 2013; *Montzka et al.*, 2009, 2015], calling for high-accuracy measurements in accordance with the Montreal Protocol and its amendments.

HCFC-31 is produced as an intermediate during the synthesis of HFC-32, a popular alternative used in mixtures for the replacement of ozone-depleting refrigerants. Due to the relatively rapid variations that we infer in global emissions of HCFC-31, we expect a limited number of industrial emitters to be the most plausible source for a large fraction of the measured HCFC-31.

Minor additional contributions can originate from the production of HCFC-31 during the anaerobic depletion of CFC-11 (e.g., in landfills) or the release of HCFC-31 as an unintended contamination in merchandised HFC-32. However, we do not find evidence of significant coemission of HCFC-31 and HFC-32 in observations at the Dübendorf station, where HFC-32 pollution events regularly occur, but coincident elevated HCFC-31 is absent.

The discovery of HCFC-31 in the global background atmosphere during this study and other examples of recently found, nonreported substances [*Kloss et al.*, 2014; *Laube et al.*, 2014; *Vollmer et al.*, 2015], highlights the necessity of a continuous top-down monitoring of feedstock, intermediates, and products, even if production processes are designed not to lead to such emissions. Therefore, HCFC-31 should be further monitored to ensure that its decline continues and additional efforts are needed to isolate the specific emission sources. Further, the ongoing search for previously unidentified chemicals in the atmosphere should be encouraged.

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