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Key Points:

- 2012 global tropospheric abundance of HFC-43-10mee is 0.21 ppt
- 2012 growth rate is 15 ppq yr⁻¹, and emission rate is 1.13 Gg yr⁻¹
- \bullet CO2 equivalent emissions of 1.9 Tg yr $^{-1}$ are comparable to HFC-365mfc and HFC-236fa

Supporting Information:

- Readme
- Figure S1
- Figure S2
- Figure S3
- Table S1
- Table S2
- Table S3
- Text S1

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HFC-43-10mee atmospheric abundances and global emission estimates

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Abstract We report in situ atmospheric measurements of hydrofluorocarbon HFC-43-10mee ($C_5H_2F_{10}$; 1,1,1,2,2,3,4,5,5,5-decafluoropentane) from seven observatories at various latitudes, together with measurements of archived air samples and recent Antarctic flask air samples. The global mean tropospheric abundance was 0.21 ± 0.05 ppt (parts per trillion, dry air mole fraction) in 2012, rising from 0.04 ± 0.03 ppt in 2000. We combine the measurements with a model and an inverse method to estimate rising global emissions—from 0.43 ± 0.34 Gg yr⁻¹ in 2000 to 1.13 ± 0.31 Gg yr⁻¹ in 2012 (~1.9 Tg CO₂-eq yr⁻¹ based on a 100 year global warming potential of 1660). HFC-43-10mee—a cleaning solvent used in the electronics industry—is currently a minor contributor to global radiative forcing relative to total HFCs; however, our calculated emissions highlight a significant difference from the available reported figures and projected estimates.

1. Introduction

The hydrofluorocarbon (HFC) HFC-43-10mee ($C_5H_2F_{10}$; 1,1,1,2,2,3,4,5,5,5-decafluoropentane), composed of a mixture of the diastereomers erythro-CF₃CHFCHFC₂F₅ and threo-CF₃CHFCHFC₂F₅, was introduced in the mid-1990s for cleaning applications in the electronics industry. It replaces compounds whose consumptions are controlled under the Montreal Protocol [*United Nations Environment Program*, 1987], namely CCl₂FCClF₂ (CFC-113), CH₃CCl₃ (methyl chloroform), and CH₃CCl₂F (HCFC-141b), and is an alternative to perfluorinated compounds (PFCs), which have global warming potentials (GWPs) >8000 [*U.S. Environmental Protection Agency*, 2001]. It also replaces some uses of PFCs and CFC-113 as a solvent for lubricants applied to computer hard disks and other minor applications. An estimated lifetime of 16.1 years, together with a radiative efficiency of 0.4 W m⁻² ppb⁻¹, leads to a calculated 100 year global warming potential (GWP₁₀₀) for HFC-43-10mee of 1660 [*Daniel et al.*, 2011]. Thus, it has potential to make a contribution to the Earth's radiative budget and is controlled under the Kyoto Protocol [*United Nations Framework Convention on Climate Change*, 1997].

As a class of compounds, emissions and atmospheric abundances of the HFCs have been projected to increase substantially in the coming decades [*Velders et al.*, 2009, 2013]. As a result of these projections, consideration is being given to limit future HFC consumption by including HFCs in the Montreal Protocol [*United Nations Environment Program*, 2013; *U.S. Environmental Protection Agency*, 2013]. The abundances of most major long-lived HFCs have now been quantified in the atmosphere and "top down" emission estimates inferred (e.g., *Miller et al.* [2010]); however, HFC-43-10mee is an exception. Atmospheric measurements are vital in providing an independent verification of reported and/or estimated emission rates [*Weiss and Prinn*, 2011], and in this study we provide the first observations of HFC-43-10mee. We present measurements of archived air samples from the two hemispheres and frequent in situ air measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE) beginning in 2010, together with flask samples from

Antarctica from 2010 to 2012. We use an atmospheric chemistry transport model and inverse method to derive global emissions, and average abundances and growth rates, in order to understand the significance of HFC-43-10mee in the atmosphere.

2. Methods

2.1. Instrumentation and Measurement

We used the "Medusa" preconcentration gas chromatography–mass spectrometry (GC-MS) system to measure the dry air mole fraction of HFC-43-10mee from both ambient air and archived air samples [*Miller et al.*, 2008; *Arnold et al.*, 2012]. Northern Hemisphere (NH) archived air samples, which were collected at Trinidad Head, California (41.05° N, 124.15° W), were measured at the Scripps Institution of Oceanography (SIO), University of California, San Diego (La Jolla, CA, USA). Southern Hemisphere (SH) archived air samples, collected at the Cape Grim Baseline Air Pollution Station (40.68° S, 144.69° E) [*Krummel et al.*, 2007], were measured at the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Division of Marine and Atmospheric Research (CMAR) (Aspendale, Australia) as part of a study previously described [*Ivy et al.*, 2012]. Ivy *et al.* [2012] used a Medusa fitted with a GasPro capillary column (60 m × 0.32 mm ID, Agilent Technologies) for an improved resolution of the PFCs, rather than the PoraBOND Q column (25 m × 0.32 mm ID, Agilent Technologies) used as the main column in all other Medusas. Samples were also measured using a Medusa at Empa, Switzerland, from flasks collected at the South Korean Antarctic station King Sejong, King George Island, South Shetland Islands (62.2° S, 58.8° W), maintained by the Korea Polar Research Institute [*Vollmer et al.*, 2011].

Each Medusa measurement cycle lasts 60–65 min, and each sample is bracketed by analyses of a compressed reference gas, resulting in a calibrated ambient air measurement every 120–130 min [Miller et al., 2008; Arnold et al., 2012]. For archive samples, at least three separate measurements were made, and the measurement error was estimated as the standard deviation (s.d.) of these replicate analyses. Typically, the mass spectrometer (MS) (Agilent 5975 or 5973) is set to continuously acquire the relevant ions (single-ion mode) during elution of specific compounds. HFC-43-10mee was typically acquired with a target ion of mass to charge ratio (m/z) 183 $(C_4H_2F_7^+)$ and a qualifier ion of 133 m/z $(C_3H_2F_5^+)$ or 119 m/z $(C_2F_5^+)$. The MS response with the 119 m/z fragment was ~1.8 times larger than that with either the 183 or 133 m/z fragments; however, for real air samples, the 119 or 133 m/z fragments had more poorly defined or variable baselines (Figure S1 in the supporting information). Under a Medusa setup with the PoraBOND Q column, the threo isomer eluted at 458 s and the erythro at 449 s—between CFC-11 at 424 s and CFC-113 at 489 s. With a GasPro column substituted for the PoraBOND Q, the threo isomer eluted at 796 s and the erythro at 745 s—later than both CFC-11 at 583 s and CFC-113 at 675 s. The PoraBOND Q and GasPro performed equally well in terms of chromatogram quality. The evidence for the integrity of samples collected and the methodology for measurement is presented in Text S1 and Figure S2 in the supporting information, including the data to test the linearity of instrument response across a range of mole fractions and volumes sampled (Figure S3 in the supporting information).

2.2. Calibration

A primary gravimetric standard was prepared at SIO to identify and quantify HFC-43-10mee using the Medusa. This standard was prepared in 2010 (SIO-2010 scale) together with the PFCs C_4F_{10} , C_5F_{12} , C_6F_{14} , C_7F_{16} , and C_8F_{18} , following the bootstrap method by stepwise dilution [*Prinn et al.*, 2000], with nitrous oxide (N₂O) used as the bootstrap gas and using high-purity (>98%) HFC-43-10mee (SynQuest Laboratories, USA). The PFCs only were recalibrated in 2012 (SIO-2012 scale) by making four additional standards for each of the five gases [*lvy et al.*, 2012]. The average uncertainty on the calibration of these four PFC standards was 6.6 ± 1.6% (1 s.d.), which includes the reproducibility after preparation and measurement, an assessment of reagent purity, and consideration of possible handling losses/gains during preparation. The average difference between the independently prepared SIO-2010 and SIO-2012 calibration scales for the five PFCs was 7.6 ± 3.8% (1 s.d.). Thus, given the closeness of the two scales for the PFCs, we are confident that the use of the SIO-2010 scale is appropriate for this first study of HFC-43-10mee, and based on the difference found for the PFCs between SIO-2010 and SIO-2012, we assign an uncertainty on this primary calibration of 8%.

In order for HFC-43-10mee's total atmospheric abundance to be quantified via measurement of only the major isomer, we needed to demonstrate that the relative proportion of the two isomers was constant

Table 1. Percentage of Threo Isomer in HFC-43-10mee Mixture With Associated 1 σ Uncertainties				
Sample Description	GC–Flame Ionization Detector	Manufacturer's Range ^a	Medusa GC-MS ^b	
Ambient air sample (this study) Artificial whole air standard (this study)		85-90	83.8 ± 1.7 82.71 ± 0.07	
Pure sample (Chen et al. [2010])	88			

^aAs given by the supplier of the sample used to make our primary standard (C. Deigl, SynQuest Laboratories, 2010). ^bThe ratio measured by our Medusa GC-MS is possibly inaccurate; however, given that the measured ratios for all the samples in this study (both the artificial standard used for calibration, archived samples, and ambient air samples) are identical within the measurement precision, we were able to calculate the total HFC-43-10mee atmospheric mole fractions based on the routine measurement of the threo isomer only.

between standards and samples. The MS detector relative response of the threo isomer to the erythro isomer was within the measurement precision for both the synthetic dilution made from a pure purchased aliquot and a recent ambient air sample (Table 1). Thus, the measurement of the higher-abundance threo isomer was sufficient for the calibration of air measurements for total HFC-43-10mee. We found that the ratio of the isomers in a selection of atmospheric samples from 2004 to present day is constant; however, the absence of reliable measurements of the erythro isomer in samples collected prior to 2004 means that we could only infer this same ratio for older samples. The reported ratios of isomers we give in Table 1 reveal a significant difference with the estimated ratio from the manufacturer (provided by C. Deigl, SynQuest Laboratories, 2010) and to other measurements [*Chen et al.*, 2010]. This could be due to the fact that the two isomers elute into the MS at different times when the MS has developed a different sensitivity, or that the isomers have slightly different fragmentation patterns in the MS, or that there are discrepancies in the isomer ratio of the synthesized HFC-43-10mee.

2.3. Modeling and Inversion Calculation

For the inversion, we computed the sensitivity of atmospheric mole fractions to global emissions using the AGAGE 12-box model [*Cunnold et al.*, 1997; *Rigby et al.*, 2013]. This model has been successfully implemented in recent studies to simulate the atmospheric behavior of other long-lived anthropogenic species [*O'Doherty et al.*, 2009; *Miller et al.*, 2010; *Mühle et al.*, 2010; *Vollmer et al.*, 2011; *Arnold et al.*, 2013; *Rigby et al.*, 2014]. Sinks for HFC-43-10mee include reaction with the hydroxyl radical (OH) in the troposphere [*Zhang et al.*, 1992; *Schmoltner et al.*, 1993; *Chen et al.*, 2010] and stratospheric loss [*Naik et al.*, 2000]. Chen *et al.* [2010] recently reported that the two diastereomers of HFC-43-10mee have identical lifetimes in the troposphere due to reaction with OH (the dominant sink), therefore ruling out the need to consider the two diastereomers separately in terms of global atmospheric chemistry. The lifetime of HFC-43-10mee is currently reported at 16.1 years [*Montzka et al.*, 2011], which is short compared to many other halogenated compounds, such as the longest-lived HFC (HFC-23), with a total atmospheric lifetime of 228 years [*SPARC*, 2013]. We used an atmospheric lifetime due to reaction with OH in the troposphere of 17.9 years and a stratospheric lifetime of 157 years [*Montzka et al.*, 2011]. The model transport parameters, and OH concentrations (previously determined) are seasonally varying and interannually repeating [*Prinn et al.*, 2005].

Given that emission rates of HFCs are often significantly undereported [*Rigby et al.*, 2014], and as our atmospheric measurements are sparse prior to 2010, we utilized a growth-based Bayesian inverse method to optimally derive global emissions [*Rigby et al.*, 2011]. Instead of using absolute a priori emission rates, this method uses the more reliably understood year-to-year growth in emissions, thus largely eliminating the sensitivity of the a posteriori emission rates to the often poorly estimated independent estimates. The Emissions Database for Global Atmospheric Research (EDGAR) v4.2 was used as the source of a priori emissions growth rates in this study [*European Commission, Joint Research Centre/Netherlands Environmental Assessment Agency*, 2013]. This database has published global emissions based on summed estimates from just three countries: Canada, France, and Austria from 1994 to 2008 (France and Austria since 1990). The inversion calculation included years 1985 to 2013, with initial modeled atmospheric mole fractions before this time assumed to be zero.

We calculated an a priori annual growth rate of emissions using EDGAR and assigned the maximum growth rate as the uncertainty to each annual growth rate. From 2008 onward, when EDGAR v4.2 did not provide estimates, the growth rate was assumed constant. The total observational uncertainty used in the inversion

Year	Mole Fraction (ppt)	Mole Fraction Growth Rate (ppq yr $^{-1}$)	Emission Rate (Gg yr $^{-1}$)
1997	0.022 ± 0.034	3.8 ± 2.8	0.26 ± 0.35
1998	0.028 ± 0.032	2.6 ± 2.9	0.30 ± 0.35
1999	0.033 ± 0.034	6.5 ± 3.1	0.35 ± 0.35
2000	0.041 ± 0.034	9.5 ± 2.5	0.43 ± 0.34
2001	0.052 ± 0.035	11.2 ± 3.1	0.53 ± 0.33
2002	0.063 ± 0.036	11.2 ± 2.7	0.63 ± 0.32
2003	0.074 ± 0.037	11.1 ± 2.6	0.73 ± 0.31
2004	0.085 ± 0.036	12.7 ± 2.1	0.83 ± 0.31
2005	0.101 ± 0.036	18.6±1.9	0.93 ± 0.31
2006	0.119 ± 0.037	16.7 ± 1.9	1.02 ± 0.30
2007	0.135 ± 0.036	15.2 ± 3.1	1.10 ± 0.29
2008	0.150 ± 0.034	14.8 ± 2.5	1.15 ± 0.29
2009	0.165 ± 0.035	14.4 ± 2.4	1.17 ± 0.29
2010	0.179 ± 0.037	15.0 ± 3.2	1.16 ± 0.29
2011	0.195 ± 0.040	16.7 ± 3.6	1.14 ± 0.29
2012	0.211 ± 0.046	15.1 ± 3.2	1.13±0.31

Table 2. Average Global Tropospheric HFC-43-10mee Dry Air Mole Fractions, Mole Fraction Growth Rates, and Global Emissions Flux, Together With Associated 1 σ Uncertainties for Each

method was calculated as the square root of the sum of the following squared errors: errors resulting from sampling frequency, measurement-model mismatch, measurement precision, and scale propagation [*Chen and Prinn*, 2006]. The sampling frequency error was estimated as the variability in the in situ monthly mole fractions divided by the square root of the number of observations, with scaled values applied to the archive measurements. The measurement-model mismatch error, which provides an estimate of how well the measured value reflects what the model is trying to simulate, was estimated from the observed variability of the in situ measurements within each month with a scale factor applied for estimating the error on the archive samples. Precisions on the air samples were estimated from the bracketing standard measurements, and precisions on archive samples were calculated directly from the multiple repeat measurements. The scale propagation error was calculated by considering the typical measurement precision at each step of the calibration from the primary standard to the working standard.

Following the *Prinn et al.* [2005] Monte Carlo approach, uncertainties in the optimally derived emissions due to model systematic uncertainties were simulated by repeating the inversion using randomly perturbed model parameters and the model OH concentrations within the estimated ranges of their systematic uncertainties. The elements of the measurement vector were also randomly perturbed by $\pm 8\%$ (1 σ , normal distribution assumed) to simulate uncertainty in the calibration scale. The inversion was carried out 1000 times using 1000 alternative sensitivity matrices and measurement vectors constructed from the randomly perturbed parameters in the model and calibration scale, respectively. The uncertainty associated with the average emissions from the 1000 inversions was combined with the inherent uncertainty from the inversion to produce the final 1 σ uncertainties for the global emission estimates.

To estimate the annual average global tropospheric mixing ratios and related uncertainties (Table 2), the model was run 1000 times using the annual emissions with normal distributions based on the associated uncertainties derived from the inversions. Each run produced modeled mole fractions for the lower troposphere in each of the latitudinal semihemispheres. The growth rates and associated uncertainties were calculated similarly using the first derivative of each of the 1000 model outputs fitted with a cubic spline curve.

3. Results and Discussion

In situ measurements of HFC-43-10mee started in the NH in mid-2010 at Trinidad Head, USA; Mace Head, Ireland; Jungfraujoch, Switzerland; Zeppelin, Norway; and Ragged Point, Barbados, with SH measurements beginning at Cape Grim, Australia in August 2010 and more recently at Cape Matatula, Samoa, in February 2013. In Figure 1, we show the monthly means of the data—following a statistical filter algorithm— representative of the well-mixed atmosphere in that latitudinal band [O'Doherty et al., 2001; Cunnold et al.,



Figure 1. Time series of atmospheric HFC-43-10mee (in parts per trillion dry air mole fraction) using monthly mean mixing ratios calculated from in situ measurements of the Advanced Global Atmospheric Gases Experiment that were filtered to remove pollution episodes. The vertical bars denote the 1 s.d. of the monthly means, and for clarity, only those from the Cape Grim data have been included—the standard deviation of the monthly means at other sites are similar. Mass spectrometer upgrades were made at the Trinidad Head, Mace Head, Ragged Point, Cape Matatula, and Cape Grim observatories during 2012–2013, which are visible in the Cape Grim record shown here as a decrease in the standard deviation of the monthly means starting in August 2012. Modeled mole fractions are from the AGAGE 12-box model using the optimized emissions as input (shown in Figure 3 as black line).

2002]. For the length of the in situ record (i.e., since 2010), a hemispheric gradient is observed (~0.03 ppt) between the measurements at the high northern latitude sites and Cape Grim, and a difference between at least three of the four semihemispheric latitudinal bands is also clear. A significant improvement in precisions is observed in the middle of 2012 for measurements at Cape Grim (Figure 2), which is also evident in the calculated monthly averages (Figure 1). This change in precisions resulted from a mass spectrometer upgrade on the Medusa instruments from the Agilent 5973 to the Agilent 5975C, which produced improved signal-to-noise ratios for low-abundance compounds. Mass spectrometer upgrades were also made at the Trinidad Head, Mace Head, Ragged Point, and Cape Matatula observatories during 2012–2013. Figure 2 includes measurements from samples filled at King Sejong (Table S1 in the supporting information), Antarctica, giving an independently measured verification of the in situ SH record.

Significant pollution episodes for HFC-43-10mee were not evident at the observatories used in this study except at Mace Head, where measurements over 0.6 ppt have been observed on <10 occasions over 3 years. Measurements at SIO of up to 10 ppt have been observed during certain meteorological conditions that occur in the winter months; however, understanding the possible local or regional sources of pollution detected at SIO's urban site is beyond the scope of this work.

Based on the archived air samples (Tables S2 and S3 in the supporting information), Figure 3 shows the atmospheric history of HFC-43-10mee. The earliest detection of HFC-43-10mee was from a Trinidad



Figure 2. In situ measurements (made every 120–130 min) of HFC-43-10mee (in parts per trillion dry air mole fraction) from Cape Grim, Australia (black dots), together with flask samples from King Sejong, Antarctica (open circles). Measurements from Mace Head, Ireland (gray dots), are shown for comparison.

Head sample in February 1999 at 36 ± 2 parts per quadrillion (ppg) (1 s.d.) and in the SH at Cape Grim in February 2000 at 30 ± 13 ppg (Figure 3). Since then, the abundance has risen over sixfold (with the growth rate peaking in 2005 at 19 ppq yr^{-1}) to the monthly mole fractions on June 2013 of 0.240 ± 0.012 ppt (1 s.d. of 263 measurements) at Trinidad Head and 0.208 ± 0.008 ppt (252 measurements) at Cape Grim. Measurements continue to be made by AGAGE, and the calculated monthly mole fraction data from this time forward will be released on a six-monthly basis to the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/).



Figure 3. (top) Full time series of atmospheric HFC-43-10mee mole fractions (in parts per trillion dry air mole fraction) showing the monthly averaged data from the in situ measurements of the four semihemispheres (see Figure 1) and from measurements of Northern Hemisphere and Southern Hemisphere archived air samples (see Tables S2 and S3 in the supporting information). Vertical bars on the archive measurements are calculated as the total measurement uncertainty, which includes measurement error and the ability of the measurement to reflect well-mixed air. The most recent archive samples in which HFC-43-10mee could not be detected are indicated by the red (NH) and blue (SH) solid rectangles within the shaded gray region representing the estimated detection limit. Trends were calculated using the AGAGE 12-box model with emissions from the inversion as input. (bottom) Top down HFC-43-10mee emissions estimated optimally using the atmospheric measurements and independent emission growth rates (calculated from EDGAR v4.2) as constraints. The shaded area represents the 1σ uncertainty band for the optimized emissions. Emissions used in the Representative Concentration Pathways (RCP3-PD, RCP4.5, and RCP6) by Meinshausen et al. [2011] are shown in red (available online at www.pik-potsdam.de/~mmalte/rcps).

A modeled time series of monthly mole fractions in the lower troposphere for the Earth's four latitudinal semihemispheres is plotted alongside recent in situ measurements in Figure 1. Only the extratropical semihemispheres were plotted for the full time series in Figure 3. Annual average global mole fractions have risen from below 0.05 ppt in 2000 to just above 0.2 ppt in 2012, with the global average annual growth rate remaining relatively constant at ~15 ppg since 2007 (Table 2). Using the atmospheric histories to constrain emissions, Figure 3 shows the global annual emissions of HFC-43-10mee. Annual emission rates have risen from year to year between 2000 and 2008, from 0.43 ± 0.34 Gg yr⁻¹ to $1.15 \pm 0.29 \text{ Gg yr}^{-1}$ (1 σ uncertainties), with a plateauing of emissions thereafter (Table 2 and Figure 3). This change in the emission growth rate has not been investigated in terms of changes in production, supply, or end use practices. The current emission rate of ~1.15 Gg yr⁻¹ equates to ~1.9 Tg CO₂-eq yr⁻¹ (CO₂-equivalents based on a GWP₁₀₀ of 1660). This is within the range of estimates $(1-2 \text{ Tg CO}_2\text{-eq yr}^{-1}, \text{ based on a})$ GWP₁₀₀ of 1590) made in a special Intergovernmental Panel on Climate Change report in 2005 projecting for the year 2015 [Intergovernmental Panel on Climate Change, 2005]. The projections made in the Special Report on Emissions Scenarios (SRES) significantly overestimated HFC-43-10mee emissions [Intergovernmental Panel on Climate Change, 2000]. The emissions from SRES were used as the basis in calculating the greenhouse gas concentrations for the Representative Concentration Pathways (RCPs)

[*Meinshausen et al.*, 2011], and are displayed in Figure 3 alongside our calculated emissions. The current atmospheric burden of HFC-43-10mee has been significantly overestimated: Between 2001 and 2010, the emission growth rate used for calculating the RCP greenhouse gas concentrations is significantly higher than our estimate. In 2010, however, the predicted emission rate growth decreases to a level comparable to the average we observe from a large proportion of the atmospheric record (0.1 Gg yr⁻² between 1999 and 2007). We therefore suggest that whatever feature was driving the rapid growth in the SRES emission projections to 2010 should be revised downward.

4. Conclusions

We present the first atmospheric measurements of HFC-43-10mee and show that the global atmospheric abundance of this greenhouse gas has risen since its first appearance, reaching a mean concentration in the global background troposphere of 0.21 ± 0.05 ppt during mid-2012. The atmospheric growth rate and emission rate however have plateaued since 2008 at ~15 ppq yr⁻¹ and ~1.15 Gg yr⁻¹, respectively. In terms of CO₂ equivalents based on a GWP₁₀₀ of 1660, the 2012 HFC-43-10mee emission rate equates to ~1.9 Tg CO₂-eq yr⁻¹. This emission rate is comparable to two other low-abundance HFCs, HFC-365mfc, and HFC-236fa, with emissions in 2010 of ~2.3 Tg CO₂-eq yr⁻¹ and ~1.1 Tg CO₂-eq yr⁻¹, respectively [*Vollmer et al.*, 2011]. Atmospheric measurements of HFC-43-10mee will continue within the AGAGE program over the coming years in order to assess its future emission rates and impact on radiative forcing.

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