Global Emissions of Perfluorocyclobutane (PFC-318, $c$-$C_4F_8$) Resulting from the Use of Hydrochlorofluorocarbon-22 (HCFC-22) Feedstock to Produce Polytetrafluoroethylene (PTFE) and related Fluorochemicals

Jens Mühle, Lambert J. M. Kuijpers, Kieran M. Stanley, Matthew Rigby, Luke M. Western, Jooil Kim, Sunyoung Park, Christina M. Harth, Paul B. Krummel, Paul J. Fraser, Simon O’Doherty, Peter K. Salameh, Roland Schmidt, Dickon Young, Ronald G. Prinn, Ray H. J. Wang, and Ray F. Weiss

1 Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, 92093, USA
2 A/gent Consultancy BV, 95CF+9M Venlo, The Netherlands
3 Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt, Frankfurt, 60438, Germany
4 School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK
5 Department of Oceanography, Kyungpook National University, Daegu, 41566, Republic of Korea
6 Climate Science Centre, CSIRO Oceans and Atmosphere, Aspendale, Victoria, 3195, Australia
7 Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA
8 School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, 30332, USA

Correspondence to: Jens Mühle (jmuhle@ucsd.edu)

Abstract

Emissions of the potent greenhouse gas perfluorocyclobutane ($c$-$C_4F_8$, PFC-318, octafluorocyclobutane) into the global atmosphere inferred from atmospheric measurements have been increasing sharply since the early 2000s. We find that these inferred emissions are highly correlated with the production of hydrochlorofluorocarbon-22 (HCFC-22, CHClF$_2$) for feedstock (FS) uses, because almost all HCFC-22 FS is pyrolyzed to produce (poly)tetrafluoroethylene ((P)TFE, Teflon) and hexafluoropropylene (HFP), a process in which $c$-$C_4F_8$ is a known by-product, causing a significant fraction of global $c$-$C_4F_8$ emissions. We find a global emission factor of ~0.003 kg $c$-$C_4F_8$ per kg of HCFC-22 FS pyrolyzed. Mitigation of these $c$-$C_4F_8$ emissions, e.g., through process optimization, abatement, or different manufacturing processes, such as electrochemical fluorination, could reduce the climate impact of this industry. While it has been shown that $c$-$C_4F_8$ emissions from developing countries dominate global emissions, more atmospheric measurements and/or detailed process statistics are needed to quantify country to facility level $c$-$C_4F_8$ emissions.

1 Introduction

Perfluorocyclobutane ($c$-$C_4F_8$, PFC-318, octafluorocyclobutane, CAS 115-25-3) is a potent greenhouse gas (GHG) with global warming potential of 10,200 on a 100-year timescale (GWP$_{100}$) based on a lifetime estimate of 3200 years (Forster et
Mühle et al. (2019) reported that global atmospheric emissions of $c$-$C_4F_8$ began in the late-1960s, reaching a plateau of $\sim 1.2$ Gg yr$^{-1}$ during late-1970s to the late-1980s, followed by a decline to a plateau of $\sim 0.8$ Gg yr$^{-1}$ during the early-1990s to early-2000s, and then increased sharply reaching $\sim 2.2$ Gg yr$^{-1}$ in 2017. Emissions of $c$-$C_4F_8$ from developed countries are regulated and reported under the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC). However, these reports from developed countries to UNFCCC only account for a small fraction of global emissions of $c$-$C_4F_8$ inferred from atmospheric measurements (Mühle et al., 2019), similar to the emissions gaps observed for other synthetic GHGs (e.g., Montzka et al., 2018; Mühle et al., 2010; Stanley et al., 2020). This emissions gap results partly from emissions in developing countries, which do not have to be reported to UNFCCC and are therefore missing, and/or from uncertainties in emissions reported by developed countries. To understand the sources of recent global $c$-$C_4F_8$ emissions, Mühle et al. (2019) used Bayesian inversions of atmospheric $c$-$C_4F_8$ measurements made at sites of the Advanced Global Atmospheric Gases Experiment (AGAGE, Prinn et al., 2018) in East Asia and Europe and from an aircraft campaign over India. For 2016, these limited regional measurements allowed Mühle et al. (2019) to allocate $\sim 56\%$ of global $c$-$C_4F_8$ emissions to specific regions with significant emissions from Eastern China ($\sim 32\%$), Russia ($\sim 12\%$), and India ($\sim 7\%$). Spatial patterns of these regional $c$-$C_4F_8$ emissions were roughly consistent with facilities that produce polytetrafluoroethylene (PTFE, Teflon) and related fluoropolymers and the necessary precursor monomers tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), which are produced via the pyrolysis of hydrochlorofluorocarbon-22 (HCFC-22, CHClF$_2$). $c$-$C_4F_8$, essentially the dimer of TFE, is one of several by-products/intermediates of this process (Chinoy and Sunavala, 1987; Broyer et al., 1988; Gangal and Brothers, 2015; Harnisch, 1999; Ebnesajjad, 2015). Process control and optimization to reduce the formation of $c$-$C_4F_8$ and other by-products are complex, and under unsuitable conditions $c$-$C_4F_8$ by-production could be as high as $14\%$ (Ebnesajjad, 2015). On the other hand, Murphy et al. (1997) demonstrated that co-feeding several percent of $c$-$C_4F_8$ to the HCFC-22 feed could reduce additional $c$-$C_4F_8$ formation to less than $0.5\%$ of the combined TFE and HFP yield, thus increasing combined TFE and HFP yield to more than $96\%$. But they also stated that perfect process control may be impractical. In 2018, one of China’s largest TFE producer confirmed $c$-$C_4F_8$ by-product formation (Mühle et al., 2019). Unless $c$-$C_4F_8$ is recovered or recycled, excess $c$-$C_4F_8$ may therefore be emitted to the atmosphere, consistent with the observations. Historically, similar $c$-$C_4F_8$ by-product venting occurred in the US and Europe (Mühle et al., 2019), unnecessarily increasing the carbon footprint of this industry. Note that Ebnesajjad (2015) and e.g. Mierdel et al. (2019) discuss research into the use of electrochemical fluorination (ECF) which may offer significantly reduced by-product formation rates in addition to energy savings and overall waste reduction. Closely related to $c$-$C_4F_8$ (as a by-product of HCFC-22 pyrolysis) is hydrofluorocarbon-23 (HFC-23, CHF$_3$), also a strong GHG, which has long been known to be a by-product of the actual production of HCFC-22 from chloroform (CHCl$_3$), that is often vented to the atmosphere, unnecessarily increasing the carbon footprint of this industry, despite technical solutions, regulations, and financial incentives (e.g., Stanley et al., 2020). Here we show that global emissions of $c$-$C_4F_8$ since 2002 are highly correlated with the amount of HCFC-22 produced for feedstock (FS) uses, because almost all this FS HCFC-22 is pyrolyzed to produce TFE/HFP, a process with $c$-$C_4F_8$ as a
known by-product. This supports the hypothesis that recent global $c$-$C_4F_8$ emissions are dominated by $c$-$C_4F_8$ by-product emissions from the production of TFE/HFP, PTFE and related fluoropolymers and fluorochemicals.

2 Methods

2.1 Atmospheric observations of $c$-$C_4F_8$ and inverse modeling of global emissions

We have extended the 1970-2017 AGAGE in situ $c$-$C_4F_8$ atmospheric measurement record used by Mühle et al. (2019) and produced updated global emissions through 2020. For this we used measurements of $c$-$C_4F_8$ by “Medusa” gas chromatographic systems with quadrupole mass selective detection (GC/MSD) (Arnold et al., 2012; Miller et al., 2008) from five AGAGE stations: Mace Head, Ireland (MHD, 53.3°N, 9.9°W); Trinidad Head, USA (THD, California, 41.0°N, 124.1°W); Ragged Point, Barbados (RPB, 13.2°N, 59.4°W); Cape Matatula, American Samoa (SMO, 14.2°S, 170.6°W); Cape Grim, Australia (CGO, Tasmania, 40.7°S, 144.7°E). Ambient air and reference gas measurements are alternated resulting in up to 12 fully calibrated samples per day (Prinn et al., 2018). Reference gases are supplied by the Scripps Institution of Oceanography (SIO) and all $c$-$C_4F_8$ data are reported on the SIO-14 calibration scale in parts per trillion (ppt) dry-air mole fractions. Daily reference gas measurement precisions are ~0.01–0.02 ppt (~1–2%); for more details see Mühle et al. (2019).

Figure 1 Pollution free monthly mean mole fraction calculated from in situ $c$-$C_4F_8$ measurements at five AGAGE sites using the AGAGE statistical method (Cunnold et al., 2002) (https://agage.mit.edu/data/agage-data).
In situ data were filtered with the AGAGE statistical method to remove pollution events (Cunnold et al., 2002). Fig. 1 shows the continued increase of pollution free monthly mean c-C₄F₈ mole fractions in the global atmosphere. The data were then used in conjunction with the AGAGE 12-box two-dimensional model (Rigby et al., 2013) and a Bayesian inverse method to update global emissions (Table 1 and Fig. 2). The model describes the transport and loss of trace gases in the global atmosphere and calculates mole fractions in each model box with latitudinal divisions at 30°S, 0° and 30°N and pressure divisions at 500 and 200 hPa. Model transport parameters are varied seasonally but repeated annually. In the model the c-C₄F₈ lifetime is set to infinity. Details of this inversion are given in Rigby et al. (2014) and Mühle et al. (2019).

| Year | c-C₄F₈ emissions (Gg yr⁻¹, 1 σ) | HCFC-22 feedstock (FS) production (Gg yr⁻¹, ktonnes yr⁻¹) |
|------|-------------------------------|----------------------------------------------------------|
|      | global (developed) countries  | non-A5 (developing) countries | A5 | China Only | Global (non-A5 + A5) |
| 1990 | 0.93 (0.76 - 1.11)            | 23.3                        | 0.0 |            | 23.3 |
| 1991 | 0.87 (0.71 - 1.03)            | 69.2                        | 7.0 |            | 76.2 |
| 1992 | 0.80 (0.65 - 0.97)            | 49.9                        | 11.2|            | 61.1 |
| 1993 | 0.76 (0.59 - 0.93)            | 40.1                        | 10.5|            | 50.6 |
| 1994 | 0.74 (0.57 - 0.89)            | 85.2                        | 12.1|            | 97.3 |
| 1995 | 0.74 (0.57 - 0.90)            | 61.2                        | 21.7|            | 82.9 |
| 1996 | 0.76 (0.61 - 0.91)            | 129.8                       | 21.7|            | 151.5 |
| 1997 | 0.77 (0.63 - 0.89)            | 147.7                       | 18.8|            | 166.5 |
| 1998 | 0.76 (0.61 - 0.90)            | 154.7                       | 1.1 |            | 155.7 |
| 1999 | 0.75 (0.60 - 0.89)            | 158.5                       | 16.2|            | 174.7 |
| 2000 | 0.74 (0.61 - 0.89)            | 135.2                       | 0.1 |            | 135.3 |
| 2001 | 0.74 (0.61 - 0.93)            | 152.4                       | 0.3 |            | 152.7 |
| 2002 | 0.77 (0.63 - 0.97)            | 163.1                       | 34.2|            | 197.3 |
| 2003 | 0.82 (0.66 - 0.97)            | 171.3                       | 43.1|            | 214.4 |
| 2004 | 0.89 (0.75 - 1.06)            | 203.1                       | 59.8|            | 262.9 |
| 2005 | 0.96 (0.83 - 1.14)            | 192.8                       | 78.3|            | 271.1 |
| 2006 | 1.03 (0.91 - 1.20)            | 193.1                       | 92.1|            | 285.2 |
| 2007 | 1.09 (0.95 - 1.23)            | 186.1                       | 110.5|           | 296.6 |
| 2008 | 1.17 (1.03 - 1.30)            | 174.2                       | 194.3|           | 368.5 |
| Year | c-C4F8 Emissions | Production | Emissions | Production | Production |
|------|-----------------|------------|-----------|------------|------------|
| 2009 | 1.28 (1.13 - 1.43) | 121.0      | 186.6     | 171.9      | 307.6      |
| 2010 | 1.43 (1.30 - 1.58) | 165.2      | 244.9     | 214.7      | 410.2      |
| 2011 | 1.56 (1.46 - 1.71) | 191.1      | 291.6     | 242.2      | 482.7      |
| 2012 | 1.65 (1.54 - 1.77) | 180.1      | 302.2     | 262.2      | 482.4      |
| 2013 | 1.69 (1.58 - 1.82) | 161.7      | 345.3     | 308.0      | 506.9      |
| 2014 | 1.77 (1.68 - 1.92) | 179.2      | 357.6     | 302.9      | 536.8      |
| 2015 | 1.89 (1.79 - 2.04) | 201.9      | 316.0     | 270.7      | 517.9      |
| 2016 | 2.09 (1.97 - 2.24) | 193.4      | 365.9     | 290.3      | 559.4      |
| 2017 | 2.26 (2.13 - 2.39) | 207.1      | 438.9     | 372.3      | 646.0      |
| 2018 | 2.28 (2.16 - 2.43) | 208.5      | 484.5     | 339.7      | 693.0      |
| 2019 | 2.26 (2.11 - 2.40) | 200.1      | 512.6     | 712.7      |            |
| 2020 | 2.32 (2.16 - 2.48) |           |           |            |            |

**Table 1** Global c-C4F8 emissions determined from AGAGE atmospheric measurements and hydrochlorofluorocarbon-22 (HCFC-22) feedstock (FS) production from United Nations Environment Programme (UNEP) and Technology and Economic Assessment Panel (TEAP) reports.

- UNEP (2021).
- See Table 4-1 TEAP (2020).
- HCFC-22 FS production data for China before 2008 is not publicly available.
- China accounted for >90% of A5 HCFC-22 production during 1991 to 2007, but did not report for 1998, 2000, and 2001 to UNEP, leading to the low A5 values for these years.

### 2.2 HCFC-22 feedstock (FS) production data

To investigate if the chemical relationship between HCFC-22 pyrolysis and c-C4F8 by-product (as discussed in the introduction) results in a correlation between HCFC-22 feedstock (FS) production and c-C4F8 emissions, we compiled HCFC-22 FS production statistics (Table 1 and Fig. 2). While production of HCFC-22 for such presumed non-emissive FS uses are not regulated by the Montreal Protocol on Substances that Deplete the Ozone Layer (MP), various types of data, including FS production, are reported by countries (parties) to the United Nations Environment Programme (UNEP) under Article 7 of the MP. Specifically, HCFC-22 FS production data for MP Article 5 (A5, developing) countries and non-Article 5 (non-A5, developed) countries were used here (UNEP, 2021). Additionally, HCFC-22 FS production data for China were taken from Table 4.1 in the TEAP (2020) report for 2008 to 2018; this report contains data used for the determination of the funding requirement for the Multilateral Fund (MLF) for the implementation of the MP. It also lists totals for A5 countries which show small inconsistencies with the UNEP (2021) data, probably due to recent updates.
3 Results and Discussion

In agreement with Mühle et al. (2019), our updated global inversion results show that \( c\text{-C}_4\text{F}_8 \) emissions were relatively stable at \( \sim 0.8 \text{ Gg yr}^{-1} \) in the early-1990s to early-2000s. However, in 2002 \( c\text{-C}_4\text{F}_8 \) emission growth resumed, reaching levels not seen before, with a relatively steady increase to \( 2.26 \text{ Gg yr}^{-1} \) in 2017 (Table 1 and Fig. 2, black diamonds). Here, we find a stabilization at this emission level from 2017 to 2019, followed by a possible resumed increase in emission growth to \( 2.32 \text{ Gg yr}^{-1} \) in 2020 (however, differences between the 2017-2020 emissions are not statistically significant). In comparison, global HCFC-22 production for feedstock (FS) uses has increased relatively steadily since the early 1990s, initially driven by FS production in non-A5 (developed) countries (Fig. 2, red circles). This non-A5 growth slowed down in the early-2000s and non-A5 HCFC-22 FS production has been relatively stable since then. The global growth in HCFC-22 FS production since 2002 has been driven by the increase in production in A5 (developing) countries (Fig. 2, blue squares), dominated by China (Fig. 2, open orange squares). This is the time frame of a steady increase of inferred global \( c\text{-C}_4\text{F}_8 \) emissions.

Figure 2: HCFC-22 feedstock (FS) production (Gg yr\(^{-1}\)). Global HCFC-22 FS production (green triangles) is the sum of HCFC-22 FS production in non-A5 (developed, red circles) and A5 (developing, blue squares) countries. Since about 2002, the increasing trend of global HCFC-22 FS production is dominated by growth in A5 countries, particularly China (orange open squares), while HCFC-22 FS production in non-A5 countries has been relatively stable.
We find a strong correlation between HCFC-22 FS production in A5 (developing) countries and inferred global \( c-C_4F_8 \) emissions \((R^2 = 0.97, p < 0.01)\) (Fig. 3, blue squares and fit, 2002-2019). While HCFC-22 FS production itself does not lead to \( c-C_4F_8 \) by-production and emissions (HFC-23 is by-produced in this process and emitted, Stanley et al. (2020)), the fact that 98-99% of global HCFC-22 FS production is used to produce TFE (~87%) and HFP (~13%), to in turn produce PTFE and related fluoropolymers and fluorochemicals, causes the observed strong correlation with HCFC-22 FS production. This would probably not be the case if a significant fraction of HCFC-22 FS production were used for other processes without \( c-C_4F_8 \) by-production and emissions. Note that the HCFC-22 to TFE route (with \( c-C_4F_8 \) by-product) can also be used to produce HFC-225 isomers and hydrofluoroolefin HFO-1234yf \((CF_3-CF=CH_2)\) (Sherry et al., 2019), with HFO-1234yf being the preferred replacement for HFC-134a \((CF_3-CFH_2)\) in mobile air conditioning (MAC).

**Figure 3** The relationship between A5 (developing), non-A5 (developed) countries and total global HCFC-22 feedstock (FS) production and global \( c-C_4F_8 \) (PFC-318) emissions (2002-2019).
Current industry knowledge is that less than 2% of HCFC-22 FS produced is used in reactions that do not involve the TFP/HFP/c-\(\text{C}_4\text{F}_8\) route; products include sulfentrazole herbicide, pantoprazole pharmaceutical, isoflurane and desflurane anesthetics, as well as high-purity HFC-23 to manufacture iodotrifluoromethane, halon-1301 and from this fipronil pesticide. The observed post-2001 correlation between \(\text{c-}\text{C}_4\text{F}_8\) emissions and HCFC-22 FS use supports our hypothesis that current global emissions of \(\text{c-}\text{C}_4\text{F}_8\) are dominated by HCFC-22 FS use to produce TFE/HFP and related products. The correlation indicates an emission factor (EF) of \(0.0033 \pm 0.0002\) kg \(\text{c-}\text{C}_4\text{F}_8\) emitted per kg of HCFC-22 produced for FS use (to produce TFE/HFP). We also find a strong correlation between global HCFC-22 FS production and global \(\text{c-}\text{C}_4\text{F}_8\) emissions \((R^2 = 0.97, p < 0.01,\) green triangles and fit, 2002-2019), again because almost all HCFC-22 FS produced globally is used in the TFE/HFP/c-\(\text{C}_4\text{F}_8\) route. The EF is similar with \(0.0031 \pm 0.0001\) kg/kg, but it is unclear whether this indicates that facilities in non-A5 countries that pyrolyze HCFC-22 to produce TFE/HFP also emit \(\text{c-}\text{C}_4\text{F}_8\) with a similar EF as facilities in A5 countries do. The reason is that HCFC-22 FS use in non-A5 (developed, see Fig. 2, red circles) countries has been essentially stable since the early 2000s. This leads to a very weak correlation with global \(\text{c-}\text{C}_4\text{F}_8\) emissions \((R^2 = 0.16, p = 0.1,\) red circles, 2002-2019) and essentially causes a change in the offset rather than the slope of the correlation of combined A5 plus non-A5 (global) HCFC-22 FS production with \(\text{c-}\text{C}_4\text{F}_8\) emissions, thus hardly affecting the correlation with the A5 HCFC-22 FS production component (with the slope being the resulting EF).

Note that the EFs of \(~0.003\) kg/kg or \(~0.3\%\) (by weight) of \(\text{c-}\text{C}_4\text{F}_8\) emitted per HCFC-22 FS used are similar to the optimal production conditions explored by Murphy et al. (1997) of less than 0.5% \(\text{c-}\text{C}_4\text{F}_8\) by-product of the combined TFE and HFP yield (excluding other by-products).

From 1996 to 2001, before the start of any significant production of HCFC-22 for FS uses in A5 countries, \(\text{c-}\text{C}_4\text{F}_8\) emissions and non-A5 HCFC-22 FS production were relatively stable (Fig. 2). Assuming that all of the HCFC-22 produced for FS uses in non-A5 countries was pyrolyzed to TFE/HFP with \(\text{c-}\text{C}_4\text{F}_8\) by-product emissions, an EF of \(0.0052 \pm 0.0004\) kg/kg could be calculated, which is larger than the EF for A5 (developing) countries (or the total global) in recent years. However, it cannot be excluded that other sources, such as the semi-conductor industry, caused emission during this timeframe (but see the small emissions from the semiconductor producing countries Japan and South Korea in Mühle et al., 2019) or that EF reductions have occurred since then. Still, if we multiply this EF with the HCFC-22 FS production in non-A5 countries we could estimate non-A5 country \(\text{c-}\text{C}_4\text{F}_8\) emissions in recent years and subtract these from total global emissions. From an investigation of the correlation of the remaining \(\text{c-}\text{C}_4\text{F}_8\) emissions against HCFC-22 FS production in A5 countries, we find the same EF \((0.0031 \pm 0.0001\) kg/kg) as for A5 countries determined earlier, but a negative offset \((0.21 \pm 0.05\) Gg yr\(^{-1}\) \(\text{c-}\text{C}_4\text{F}_8\)). This negative offset indicates that the subtracted estimates of non-A5 \(\text{c-}\text{C}_4\text{F}_8\) emissions were too high, and thus that an EF of \(0.0052\) kg/kg (from 20 years ago) may not be applicable to today’s non-A5 country HCFC-22 FS production. Ultimately, atmospheric measurements covering more facilities that pyrolyze HCFC-22 and/or detailed mass balance statistics would be needed to determine EFs for A5 and non-A5 countries, and how EFs may differ from facility to facility.
Questions also remain about China’s $c\text{-C}_4\text{F}_8$ emissions. Dividing the $c\text{-C}_4\text{F}_8$ emissions for eastern China of 0.67 ± 0.13 (~32% of global emissions, Mühle et al., 2019) for 2016/2017 by the HCFC-22 FS production reported by China for these years (Table 1), results in an EF of 0.0021 ± 0.0003 kg/kg. This is lower than the EF determined for non-A5 countries (or the total global) in recent years, which seems unlikely, as total A5 country HCFC-22 FS production is dominated by China (Fig. 2). Most probably, total Chinese $c\text{-C}_4\text{F}_8$ emissions are larger than those determined for eastern China as several Chinese facilities that likely emit $c\text{-C}_4\text{F}_8$ are outside of the inversion domain used in Mühle et al. (2019). More measurements would be needed to answer this question and similar questions for other parts of the world.

### 4 Summary and Conclusions

Mühle et al. (2019) concluded that significant fractions of global 2016 $c\text{-C}_4\text{F}_8$ emissions occurred in eastern China, Russia, and India and that spatial emission patterns were roughly consistent with facilities that produce tetrafluoroethylene (TFE) and/or hexafluoropropylene (HFP) and from these polytetrafluoroethylene (PTFE, Teflon) and related fluoropolymers and fluorochemicals. TFE and HFP are produced via the pyrolysis of hydrochlorofluorocarbon-22 (HCFC-22), a process in which $c\text{-C}_4\text{F}_8$ is a known by-product. In this investigation, we find that this chemical relationship between the HCFC-22 pyrolysis and $c\text{-C}_4\text{F}_8$ by-product leads to tight correlations between a) HCFC-22 FS production in A5 (developing) countries and global $c\text{-C}_4\text{F}_8$ emissions and between b) total global HCFC-22 FS production and global $c\text{-C}_4\text{F}_8$ emissions (both from 2002 to 2019). These correlations arise as ~98% of the HCFC-22 FS production is used to produce TFE and HFP via HCFC-22 pyrolysis, with $c\text{-C}_4\text{F}_8$ as by-product. Our results support the hypothesis that current global $c\text{-C}_4\text{F}_8$ emissions are mostly due to avoidable by-product venting during the production of TFE/HFP, PTFE and related fluoropolymer and fluorochemicals. Emission factors are estimated to be ~0.003 kg $c\text{-C}_4\text{F}_8$ emitted per kg of HCFC-22 FS (to produce TFE and HFP) or ~0.3% (by weight). In 2018, one of the largest TFE producer in China confirmed $c\text{-C}_4\text{F}_8$ by-product formation, which, unless recovered or recycled, may lead to $c\text{-C}_4\text{F}_8$ emissions. Historically, similar $c\text{-C}_4\text{F}_8$ by-product venting occurred in the US and Europe, unnecessarily increasing the carbon footprint of this industry. Due to the relatively stable HCFC-22 FS production in non-A5 (developed) countries since 2002, it is not possible to determine whether facilities that pyrolyze HCFC-22 to TFE/HFP in non-A5 (developed) and A5 countries (developing) currently emit $c\text{-C}_4\text{F}_8$ at similar rates. Atmospheric measurements covering $c\text{-C}_4\text{F}_8$ emissions from more HCFC-22 pyrolyzing facilities in non-A5 and in A5 countries and/or detailed mass balance statistics would be needed to investigate this further and to determine contributions of other countries to global $c\text{-C}_4\text{F}_8$ emissions. Similarly, more atmospheric measurements and/or data are needed to determine whether $c\text{-C}_4\text{F}_8$ emissions for eastern China (~32% of global emissions, Mühle et al., 2019) should be revised upwards for all of China.

Closely related to emissions of $c\text{-C}_4\text{F}_8$ are emissions of hydrofluorocarbon-23 (HFC-23), also a strong GHG, which has long been a known by-product of the actual production of HCFC-22 from chloroform (CHCl₃). Emissions of HFC-23 contribute unnecessarily to the carbon footprint of HCFC-22 industry despite technical solutions, regulations, and financial incentives...
Similarly, we have shown strong evidence that use of HCFC-22 feedstock for pyrolysis to TFE/HFP to produce fluoropolymers and related fluorochemicals likely cause most of the global $c$-$C_4F_8$ emissions. To reduce overall global GHG emissions of this industry, further efforts to mitigate $c$-$C_4F_8$ and HFC-23 emissions should be considered, e.g., through process optimization, abatement, or different manufacturing processes such as electrochemical fluorination.

### Data and code availability

AGAGE data is available from [http://agage.mit.edu/data/agage-data](http://agage.mit.edu/data/agage-data). AGAGE 12-box model code can be made available upon request by contacting MR.

### Author contributions

Measurements and/or oversight for measurement collection were provided by JM, KMS, JK, SP, CMH, PBK, SOD, RS, and DY. CMH provided and maintained the gravimetric SIO calibration scale for $c$-$C_4F_8$. RHJW processed the AGAGE data and produced pollution free monthly mean $c$-$C_4F_8$ abundances. MR and LMW performed model analysis. PKS wrote the GCWerks software to control the instruments, acquire the data, collect the data from all stations, and perform calculations necessary to provide calibrated end results. JM conceptualized the work, analysed the data, visualized the data, and wrote the manuscript with contributions from LJMK and all other co-authors. LJMK provided most valuable insight into industrial processes and collected UNEP data. RGP and RFW acquired the main funding for this work.

### Competing interests

The authors declare that they have no conflict of interest.

### Acknowledgments

Overall operation of the AGAGE network, including the measurements at Mace Head, Trinidad Head, Cape Matatula, Ragged Point, and Cape Grim were supported by National Aeronautics and Space Administration grants (nos. NNX16AC96G and NNX16AC97G to SIO and NNX16AC98G to MIT). Additional funding was provided by the Department for Business, Energy & Industrial Strategy (BEIS) Contract 1537/06/2018 (to the University of Bristol for Mace Head) and the National Oceanic and Atmospheric Administration (NOAA, contract 1305M319CNRMJ0028 to the University of Bristol for Ragged Point). We thank the Commonwealth Scientific and Industrial Research Organisation (CSIRO, Australia) and the Bureau of Meteorology (Australia) for their ongoing long-term support and funding of the Cape Grim station and the Cape Grim science program. S. Park and operations of the Gosan station on Jeju Island, South Korea...
were supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (no. 2020R1A2C3003774). L. J. M. Kuijpers was supported by A/agent. M. Rigby and L. M. Western were supported by UK Natural Environment Research Council grants NE/S004211/1, NE/V002996/1 and NE/N016548/1. We are indebted to the staff and scientists at AGAGE and other sites for their continuing contributions to produce high-quality measurements of atmospheric trace gases.

References

Arnold, T., Mühle, J., Salameh, P. K., Harth, C. M., Ivy, D. J., and Weiss, R. F.: Automated measurement of nitrogen trifluoride in ambient air, Anal. Chem., 84, 4798–4804, https://doi.org/10.1021/ac300373e, 2012.

Broyer, E., Bekker, A. Y., and Ritter, A. B.: Kinetics of the pyrolysis of chlorodifluoromethane, Ind. Eng. Chem. Res., 27, 208-211, https://doi.org/10.1021/ie00073a039, 1988.

Chinoy, P. B. and Sunavala, P. D.: Thermodynamics and kinetics for the manufacture of tetrafluoroethylene by the pyrolysis of chlorodifluoromethane, Ind. Eng. Chem. Res., 26, 1340-1344, https://doi.org/10.1021/ie00067a013, 1987.

Cunnold, D. M., Steele, L. P., Fraser, P. J., Simmonds, P. G., Prinn, R. G., Weiss, R. F., Porter, L. W., O’Doherty, S., Langenfelds, R. L., Krummel, P. B., Wang, H. J., Emmons, L., Tie, X. X., and Drugokencky, E. J.: In situ measurements of atmospheric methane at GAGE/AGAGE sites during 1985-2000 and resulting source inferences, J. Geophys. Res., 107, ACH 20-21-20-18, https://doi.org/10.1029/2001JD001226, 2002.

Ebnesajjad, S.: 6 - Preparation of Tetrafluoroethylene and Other Monomers, in: Fluoroplastics (Second Edition), 1 ed., William Andrew Publishing, Oxford, 48-75, https://doi.org/10.1016/B978-1-4557-3199-2.00006-9, 2015.

Forster, P., T. Storelvmo (Coordinating Lead Authors), Armour, K., Collins, W., Dufresne, J.-L., Frame, D., Lunt, D. J., Mauritzen, T., Palmer, M. D., Watanabe, M., Wild, M., and H. Zhang (Lead Authors): The Earth’s energy budget, climate feedbacks, and climate sensitivity, in: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Chapter 7, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2021.

Gangal, S. V. and Brothers, P. D.: Perfluorinated Polymers, in: Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Hoboken, New Jersey, https://doi.org/10.1002/B978-1-4557-3199-2.00006-9, 2015.

Harnisch, J.: Reactive Fluorine Compounds, in: Reactive Halogen Compounds in the Atmosphere Vol. 4 Part E, The Handbook of Environmental Chemistry, Springer Berlin/Heidelberg, 81-111, https://doi.org/10.1007/10628761_3, 1999.

Mierdel, K., Jess, A., Gerdes, T., Schmidt, A., and Hintzer, K.: Energy and Resource Efficient Production of Fluoroalkenes in High Temperature Microreactors, ChemEngineering, 3, https://doi.org/10.3390/chemengineering0304007, 2019.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., and Simmonds, P. G.: Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80, 1536-1545, https://doi.org/10.1021/ac702084k, 2008.

Montzka, S. A., G.J.M. Velders (Lead Authors), Krummel, P. B., Mühle, J., Orkin, V. L., Park, S., Shah, N., H. Walter-Terrinoni (Coauthors), Bernath, P., Boone, C., Hu, L., Kurylo, M. J., Elvidge, E. L., Maione, M., Miller, B. R., O’Doherty,
S., Rigby, M., Simpson, I. J., Vollmer, M. K., R.F. Weiss (Contributors), Kuijpers, L. J. M., and W.T. Sturges (Review Editors): Hydrofluorocarbons (HFCs) (Chapter 2), in: Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project–Report No. 58, World Meteorological Organization, Geneva, Switzerland, 2018.

Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Greally, B. R., Rigby, M., Porter, L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O’Doherty, S., Fraser, P. J., Simmonds, P. G., Prinn, R. G., and Weiss, R. F.: Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, Atmos. Chem. Phys., 10, 5145-5164, https://doi.org/10.5194/acp-10-5145-2010, 2010.

Mühle, J., Trudinger, C. M., Western, L. M., Rigby, M., Vollmer, M. K., Park, S., Manning, A. J., Say, D., Ganesan, A., Steele, L. P., Ivy, D. J., Arnold, T., Li, S., Stohl, A., Harth, C. M., Salameh, P. K., McCulloch, A., O’Doherty, S., Park, M. K., Jo, C. O., Young, D., Stanley, K. M., Krummel, P. B., Mitrevski, B., Hermansen, O., Lunder, C., Evangelou, N., Yao, B., Kim, J., Hmiel, B., Buizert, C., Petrenko, V. V., Arduini, J., Maione, M., Etheridge, D. M., Michalopoulou, E., Czerniak, M., Severinghaus, J. P., Reimann, S., Simmonds, P. G., Fraser, P. J., Prinn, R. G., and Weiss, R. F.: Perfluorocyclobutane (PFC-318, c-C4F8) in the global atmosphere, Atmos. Chem. Phys., 19, 10335-10359, https://doi.org/10.5194/acp-19-10335-2019, 2019.

Murphy, P., Schleinix, H., and Van Bramer, D.: Synthesis of tetrafluoroethylene, Patent 5,672,784, September 30, 1997.

Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A. L., Gasore, J., Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M., Lunder, C. R., Maione, M., Manning, A. J., Miller, B. R., Mitrevski, B., Mühle, J., O’Doherty, S., Park, S., Reimann, S., Rigby, M., Saito, T., Salameh, P. K., Schmidt, R., Simmonds, P. G., Steele, L. P., Vollmer, M. K., Wang, R. H., Yao, B., Yokouchi, Y., Young, D., and Zhou, L.: History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE), Earth Syst. Sci. Data, 10, 985-1018, https://doi.org/10.5194/essd-10-985-2018, 2018.

Rigby, M., Prinn, R. G., O’Doherty, S., Miller, B. R., Ivy, D., Mühle, J., Harth, C. M., Salameh, P. K., Arnold, T., Weiss, R. F., Krummel, P. B., Steele, L. P., Fraser, P. J., Young, D., and Simmonds, P. G.: Recent and future trends in synthetic greenhouse gas radiative forcing, Geophys. Res. Lett., 41, 2623-2630, https://doi.org/10.1002/2013gl059099, 2014.

Rigby, M., Prinn, R. G., O’Doherty, S., Montzka, S. A., McCulloch, A., Harth, C. M., Mühle, J., Salameh, P. K., Weiss, R. F., Young, D., Simmonds, P. G., Hall, B. D., Dutton, G. S., Nance, D., Mondeel, D. J., Elkins, J. W., Krummel, P. B., Steele, L. P., and Fraser, P. J.: Re-evaluation of the lifetimes of the major CFCs and CH3CCl3 using atmospheric trends, Atmos. Chem. Phys., 13, 2691-2702, https://doi.org/10.5194/acp-13-2691-2013, 2013.

Sherry, D., Nolan, M., Seidel, S., and Andersen, S. O.: HFO-1234yf: An Examination of Projected Long-Term Costs of Production, 2019.

Stanley, K. M., Say, D., Mühle, J., Harth, C. M., Krummel, P. B., Young, D., O’Doherty, S. J., Salameh, P. K., Simmonds, P. G., Weiss, R. F., Prinn, R. G., Fraser, P. J., and Rigby, M.: Increase in global emissions of HFC-23 despite near-total expected reductions, Nature Commun., 11, 397, https://doi.org/10.1038/s41467-019-13899-4, 2020.

TEAP: Technology and Economic Assessment Panel, May 2020, Volume 3, Assessment of the Funding Requirement for the Replenishment of the Multilateral Fund for the Period 2021-2023, Nairobi, Kenya, 108, https://ozone.unep.org/system/files/documents/TEAP_decision XXXI-1 replenishment-task-force-report may2020.pdf, 2020.

UNEP: Data on HCFC-22 production as reported under Article 7 by parties to the Montreal Protocol, 1989-2019, United Nations Environment Programme, Ozone Secretariat, Nairobi, Kenya, 2021.