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Global Emissions of Perfluorocyclobutane (PFC-318, c-C$_4$F$_8$) Resulting from the Use of Hydrochlorofluorocarbon-22 (HCFC-22) Feedstock to Produce Polytetrafluoroethylene (PTFE) and related Fluorochemicals

5 Jens Mühle[1*], Lambert J. M. Kuijpers[2], Kieran M. Stanley[3], Matthew Rigby[4], Luke M. Western[4], Jooil Kim[1], Sunyoung Park[5], Christina M. Harth[1], Paul B. Krummel[6], Paul J. Fraser[6], Simon O'Doherty[3], Peter K. Salameh[1], Roland Schmidt[1], Dickon Young[3], Ronald G. Prinn[7], Ray H. J. Wang[8], and Ray F. Weiss[1]

[1]Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, 92093, USA
10 [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
15 [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 Muhle (jmuhle@ucsd.edu)

Abstract

Emissions of the potent greenhouse gas perfluorocyclobutane (c-C$_4$F$_8$, PFC-318, octafluorocyclobutane) into the global
20 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$_4$F$_8$ is a known by-product, causing a significant fraction of global c-C$_4$F$_8$ emissions. We find a global emission factor of ~0.003 kg c-C$_4$F$_8$ per kg of HCFC-22 FS pyrolyzed. Mitigation of these
25 c-C$_4$F$_8$ 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$_4$F$_8$ 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$_4$F$_8$ emissions.

1 Introduction

30 Perfluorocyclobutane (c-C$_4$F$_8$, 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

al., 2021). Mühle et al. (2019) reported that global atmospheric emissions of c-C_4F_8 began in the late-1960s, reaching a plateau of ~1.2 Gg yr^{-1} during late-1970s to the late-1980s, followed by a decline to a plateau of ~0.8 Gg yr^{-1} during the early-1990s to early-2000s, and then increased sharply reaching ~2.2 Gg yr^{-1} in 2017. Emissions of c-C_4F_8 from developed

35   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

40   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 ~56% of global c-C_4F_8 emissions to specific regions with significant emissions from Eastern China (~32%), Russia (~12%), and India

45   (~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;

50   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

55   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.

60   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

65   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$_4$F$_8$ emissions are dominated by c-C$_4$F$_8$ by-product emissions from the production of TFE/HFP, PTFE and related fluoropolymers and fluorochemicals.

2 Methods

2.1 Atmospheric observations of c-C$_4$F$_8$ and inverse modeling of global emissions

70   We have extended the 1970-2017 AGAGE in situ c-C$_4$F$_8$ atmospheric measurement record used by Mühle et al. (2019) and produced updated global emissions through 2020. For this we used measurements of c-C$_4$F$_8$ 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);

75   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$_4$F$_8$ 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).
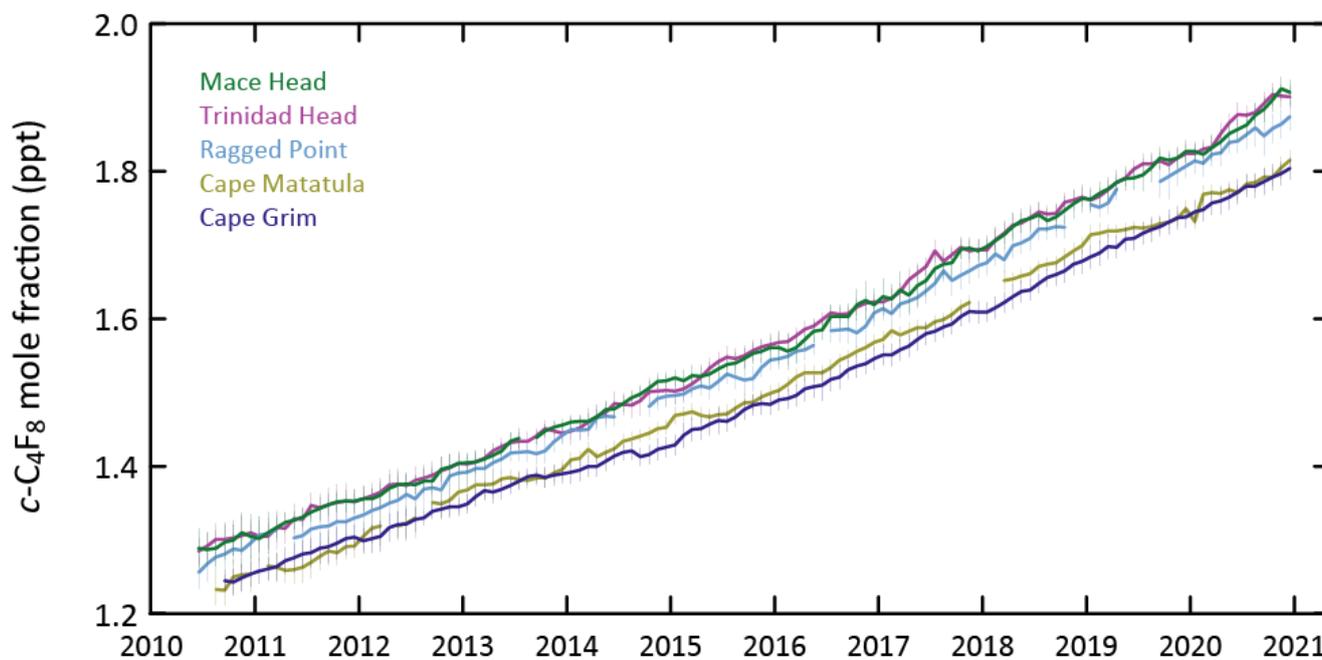
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Figure 1 Pollution free monthly mean mole fraction calculated from in situ c-C$_4$F$_8$ measurements at five AGAGE sites using the AGAGE statistical method (Cunnold et al., 2002) (https://agage.mit.edu/data/agage-data).

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In situ data were filtered with the AGAGE statistical method to remove pollution events (Cunnold et al., 2002). Fig. 1 shows
85 the continued increase of pollution free monthly mean c-C_4F_8 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
90 c-C_4F_8 lifetime is set to infinity. Details of this inversion are given in Rigby et al. (2014) and Mühle et al. (2019).

	c-C_4F_8 emissions (Gg yr^{-1}, 1 σ)	HCFC-22 feedstock (FS) production (Gg yr^{-1}, ktonnes yr^{-1})			
	global	non-A5 (developed) countries[a]	A5 (developing) countries[a]	China Only[b]	Global (non-A5 + A5)[a]
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[c]		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[c]		135.3
2001	0.74 (0.61 - 0.93)	152.4	0.3[c]		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	166.1	368.5

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-C_4F_8 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.

[a]UNEP (2021). [b]See Table 4-1 TEAP (2020). HCFC-22 FS production data for China before 2008 is not publicly available. [c]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.
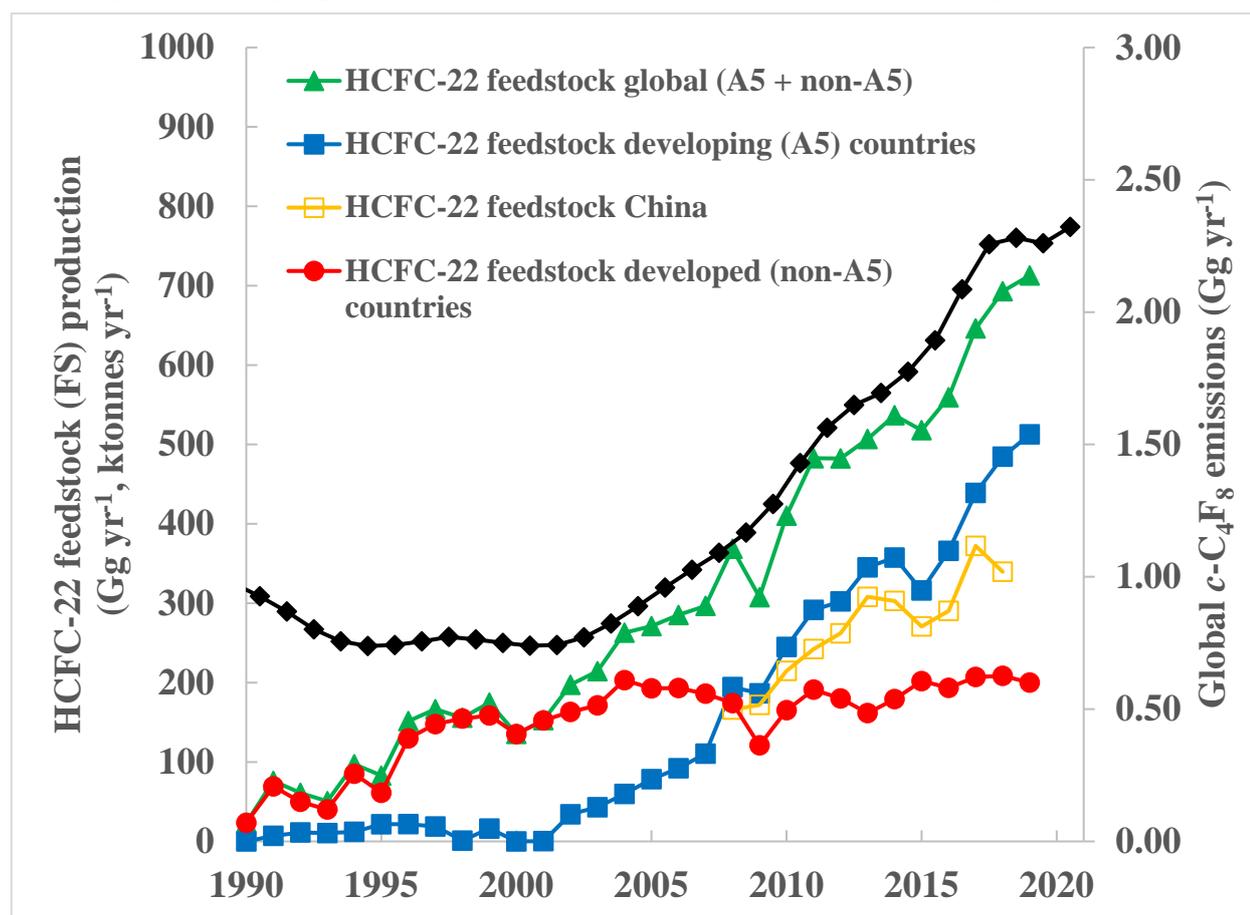
2.2 HCFC-22 feedstock (FS) production data

To investigate if the chemical relationship between HCFC-22 pyrolysis and c-C_4F_8 by-product (as discussed in the introduction) results in a correlation between HCFC-22 feedstock (FS) production and c-C_4F_8 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.

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110 In agreement with Mühle et al. (2019), our updated global inversion results show that c-C_4F_8 emissions were relatively stable at ~0.8 Gg yr^{-1} in the early-1990s to early-2000s. However, in 2002 c-C_4F_8 emission growth resumed, reaching levels not seen before, with a relatively steady increase to 2.26 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 Gg yr^{-1} in 2020 (however, differences between the 2017-2020 emissions are not statistically significant). In comparison,

115 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-C_4F_8 emissions.

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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.

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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

130   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).
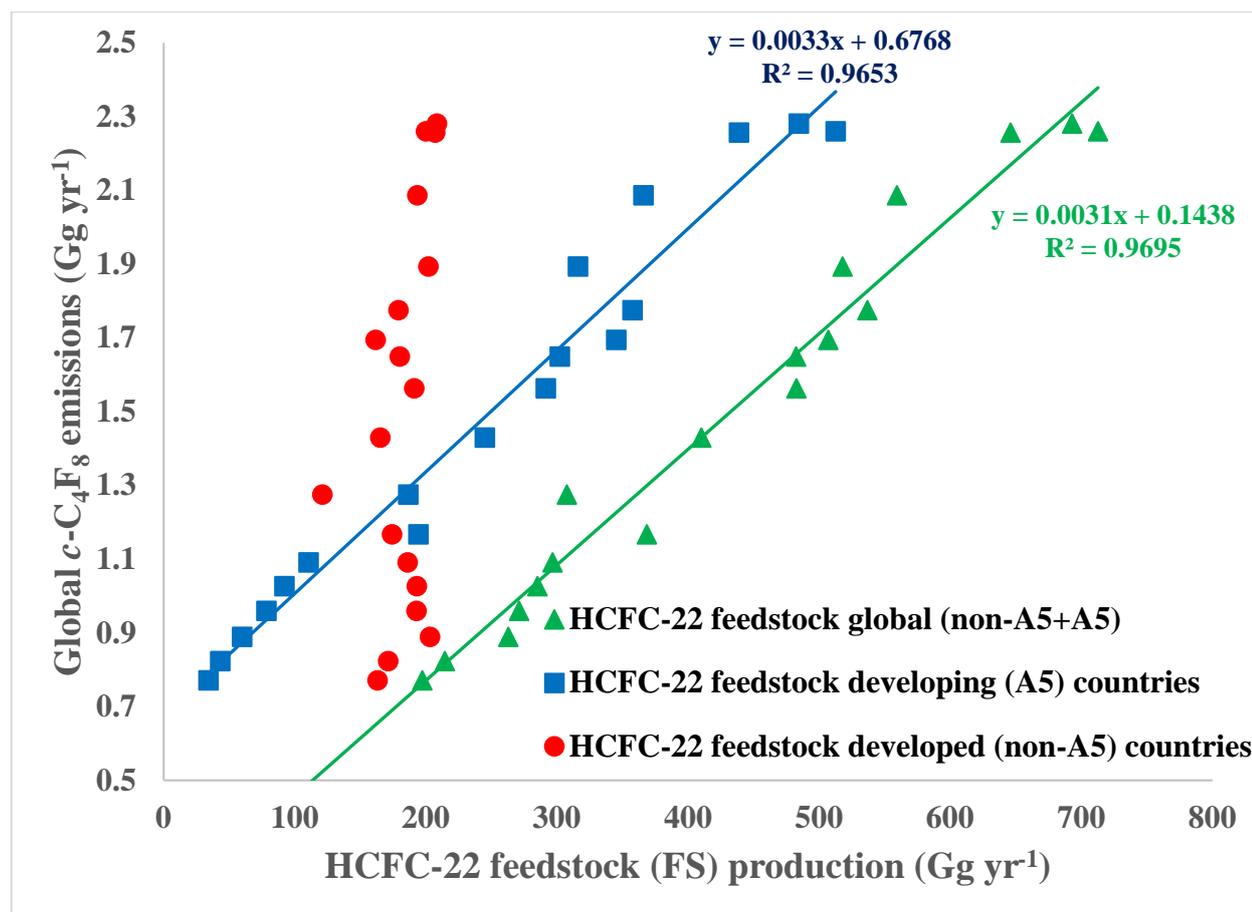
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Figure 3 The relationship between A5 (developing), non-A5 (developed) countries and total global HCFC-22 feedstock (FS) production and global c-C_4F_8 (PFC-318) emissions (2002-2019).

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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-C_4F_8 route; products include sulfentrazone 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 c-C_4F_8 emissions and HCFC-22 FS use supports our hypothesis that current

145 global emissions of c-C_4F_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 ± 0.0002 kg c-C_4F_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 c-C_4F_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-C_4F_8 route. The EF is similar with 0.0031 ± 0.0001 kg/kg, but it is unclear whether this indicates that facilities in

150 non-A5 countries that pyrolyze HCFC-22 to produce TFE/HFP also emit c-C_4F_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 c-C_4F_8 emissions ($R^2 = 0.16$, p = 0.1, Fig. 3, 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 c-C_4F_8 emissions, thus hardly affecting the correlation with the A5

155 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 c-C_4F_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% c-C_4F_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, c-C_4F_8 emissions

160 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 c-C_4F_8 by-product emissions, an EF of 0.0052 ± 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

165 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 c-C_4F_8 emissions in recent years and subtract these from total global emissions. From an investigation of the correlation of the remaining c-C_4F_8 emissions against HCFC-22 FS production in A5 countries, we find the same EF (0.0031 ± 0.0001 kg/kg) as for A5 countries determined earlier, but a negative offset (-0.21 ± 0.05 Gg yr^{-1} c-C_4F_8). This negative offset indicates that the subtracted estimates of non-A5 c-C_4F_8 emissions were too high, and thus that

170 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.

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Questions also remain about China's c-C_4F_8 emissions. Dividing the c-C_4F_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

175 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-C_4F_8 emissions are larger than those determined for eastern China as several Chinese facilities that likely emit c-C_4F_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.

180 4 Summary and Conclusions

Mühle et al. (2019) concluded that significant fractions of global 2016 c-C_4F_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

185 which c-C_4F_8 is a known by-product. In this investigation, we find that this chemical relationship between the HCFC-22 pyrolysis and c-C_4F_8 by-product leads to tight correlations between a) HCFC-22 FS production in A5 (developing) countries and global c-C_4F_8 emissions and between b) total global HCFC-22 FS production and global c-C_4F_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-C_4F_8 as by-product. Our results support the hypothesis that current global c-C_4F_8 emissions are mostly

190 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-C_4F_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-C_4F_8 by-product formation, which, unless recovered or recycled, may lead to c-C_4F_8 emissions. Historically, similar c-C_4F_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

195 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-C_4F_8 at similar rates. Atmospheric measurements covering c-C_4F_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-C_4F_8 emissions. Similarly, more atmospheric measurements and/or data are needed to determine

200 whether c-C_4F_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-C_4F_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 ($CHCl_3$). Emissions of HFC-23 contribute unnecessarily to the carbon footprint of HCFC-22 industry despite technical solutions, regulations, and financial incentives

205 (e.g., Stanley et al., 2020). 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. 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
215 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
220 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.

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