Perfluorocyclobutane (PFC-318, *c*-C_4F_8) in the global atmosphere

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REVISED Supplemental text, figures, and tables ONLY

Details on data quality assurance for the measurements of archived air samples of the extra-tropical Southern Hemisphere (SH, Cape Grim Air Archive, CGAA) and extra-tropical Northern Hemisphere (NH)

To reconstruct the atmospheric history of *c*-C_4F_8 in the extra-tropical SH, 41 unique CGAA samples (collected 1978–2009, Langenfelds et al., 2014) were measured at CSIRO in 2011 (Ivy et al., 2012). Three CGAA tanks were measured at the beginning, in the middle, and towards the end of the measurements at CSIRO, with agreements within typical precisions or better (0.01–0.02 ppt). In addition, 8 SH samples were measured at SIO which were sub-sampled from CGAA parent tanks (fill dates 1986–2008, 0.60–1.17 ppt) into evacuated stainless steel (SS) tanks (4.5 L, Essex Industries, USA) with a vacuum manifold and pressure regulator shown not to produce any *c*-C_4F_8 artefacts. They were measured at SIO on Medusa 7 to take advantage of the more sensitive MSD and to evaluate the agreement with Medusa 9 measurements at CSIRO. Four of these CGAA subsamples measured at SIO agreed within precisions (delta mole fractions, Δx = 0.00–0.01 ppt, ratio = 1.0047, R^2 = 0.9994) with their CGAA parents measured at CSIRO, 2 subsamples showed a larger differences (0.018 and 0.027 ppt). The measurements of the seventh subsample and its CGAA parent were rejected, perhaps due to problems during the subsampling or with the parent tank. While we did not measure the CGAA parent of the eighth subsample at CSIRO, we found agreement (Δx = 0.01 ppt) with another CGAA tank of similar air age (Δt = 63 days) measured at CSIRO. Four additional SH samples (fill dates 1995–2010, 0.84–1.25 ppt) were measured at SIO. Three were also in very good agreement with CGAA samples of similar fill date measured at CSIRO (Δx < 0.006 ppt, Δt = 7–23 days) and one showed a larger difference (Δx = 0.05 ppt).

To reconstruct the atmospheric history in the extra-tropical NH, 126 unique air samples mostly filled at SIO and THD (1973–2016) were measured at SIO. Additionally, 3 NH samples (filled in 1980 and 1999) were measured at CSIRO. Two of these tanks measured at CSIRO were filled together at SIO in 1999 with 2 tanks measured at SIO and the agreement is excellent (Δx = <0.007 ppt). The third tank, filled in 1980 at Cape Meares, Oregon, agreed within 0.034 ppt with another NH tank (filled at SIO within 9 days) measured at SIO. Despite this larger difference,

the overall good agreement of NH and SH samples measured at SIO and CSIRO shows that measurements on the involved instruments were comparable and that calibration scales were properly propagated.

Details on the production of HFO-1234yf from HCFC-22 with potential *c*-C_4F_8 by-product emissions

The hydrofluoroolefin HFO-1234yf ($CF_3CF=CH_2$) is a fourth generation refrigerant replacing HFC-134a in mobile air conditioning (MAC) (Vollmer et al., 2015). It can be produced starting out with similar chemistry that is used for the production of PTFE/FEP, that is the pyrolysis of HCFC-22 to TFE and HFP (Lim et al., 2017), with *c*-C_4F_8 as a by-product that may be vented to the atmosphere. Even though this route to produce HFO-1234yf is not continuous, requiring several batch operations, it is the preferred route in China and India due to the existing large scale HCFC-22, TFE, and HFP production capacities. Honeywell has licensed Navin Fluorine International (NFIL, Surat, Gujarat, India) in 2016 to produce HFO-1234yf (www.coolingpost.com/world-news/honeywell-licences-r1234yf-production-in-india, accessed 2019/07/01). This facility is one of the PTFE producing facilities shown in Fig. 9 in Western India. Honeywell has also licensed the Juhua Group Corporation in China in 2016 to produce HFO-1234yf (www.springerprofessional.de/betriebsstoffe/honeywell-laesst-1234yf-auch-in-china-produzieren/10062482, accessed 2019/07/01, German, translate.google.com). The likely location of this HFC-1234yf production in China corresponds to one or both of to the two Juhua Group Corporation PTFE production facility shown in Fig. 7 in Zhejiang province. Other facilities licensed by Honeywell to produce HFO-1234yf using this route with potential *c*-C_4F_8 emissions may exist in East Asia, but any such production is relatively recent and cannot explain historic *c*-C_4F_8 emissions.

Lim, S., Kim, M. S., Choi, J.-W., Kim, H., Ahn, B. S., Lee, S. D., Lee, H., Kim, C. S., Suh, D. J., Ha, J.-M., and Song, K. H.: Catalytic dehydrofluorination of 1,1,1,2,3-pentafluoropropane (HFC-245eb) to 2,3,3,3-tetrafluoropropene (HFO-1234yf) using in-situ fluorinated chromium oxyfluoride catalyst, Catalysis Today, 293-294, 42-48, 10.1016/j.cattod.2016.11.017, 2017.

Vollmer, M. K., Reimann, S., Hill, M., and Brunner, D.: First Observations of the Fourth Generation Synthetic Halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the Atmosphere, Environ. Sci. Technol., 49, 5, 2703-2708, 10.1021/es505123x, 2015.

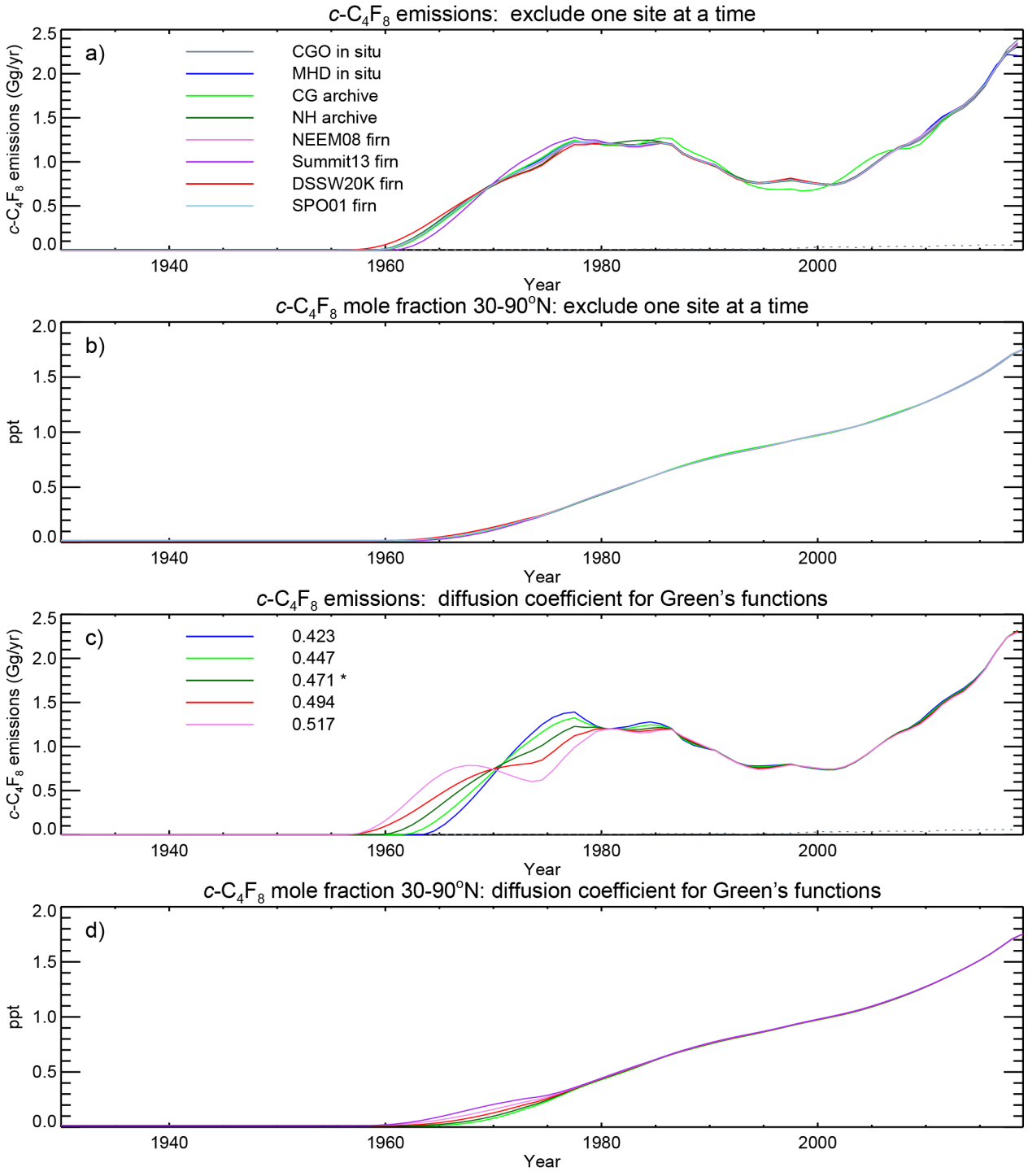


Figure S3. Sensitivity tests with the CSIRO inversion for removal of individual data subsets and uncertainty in the diffusion coefficient: a) inferred emissions with one firn site or in situ or archive part of the atmospheric record in each hemisphere left out at a time; b) same as a but inferred mixing ratios; c) inferred emissions for different values of the diffusion coefficient of *c*-C_4F_8 relative to CO_2, with values from -10 % to +10 %; d) same as c but inferred mixing ratios.

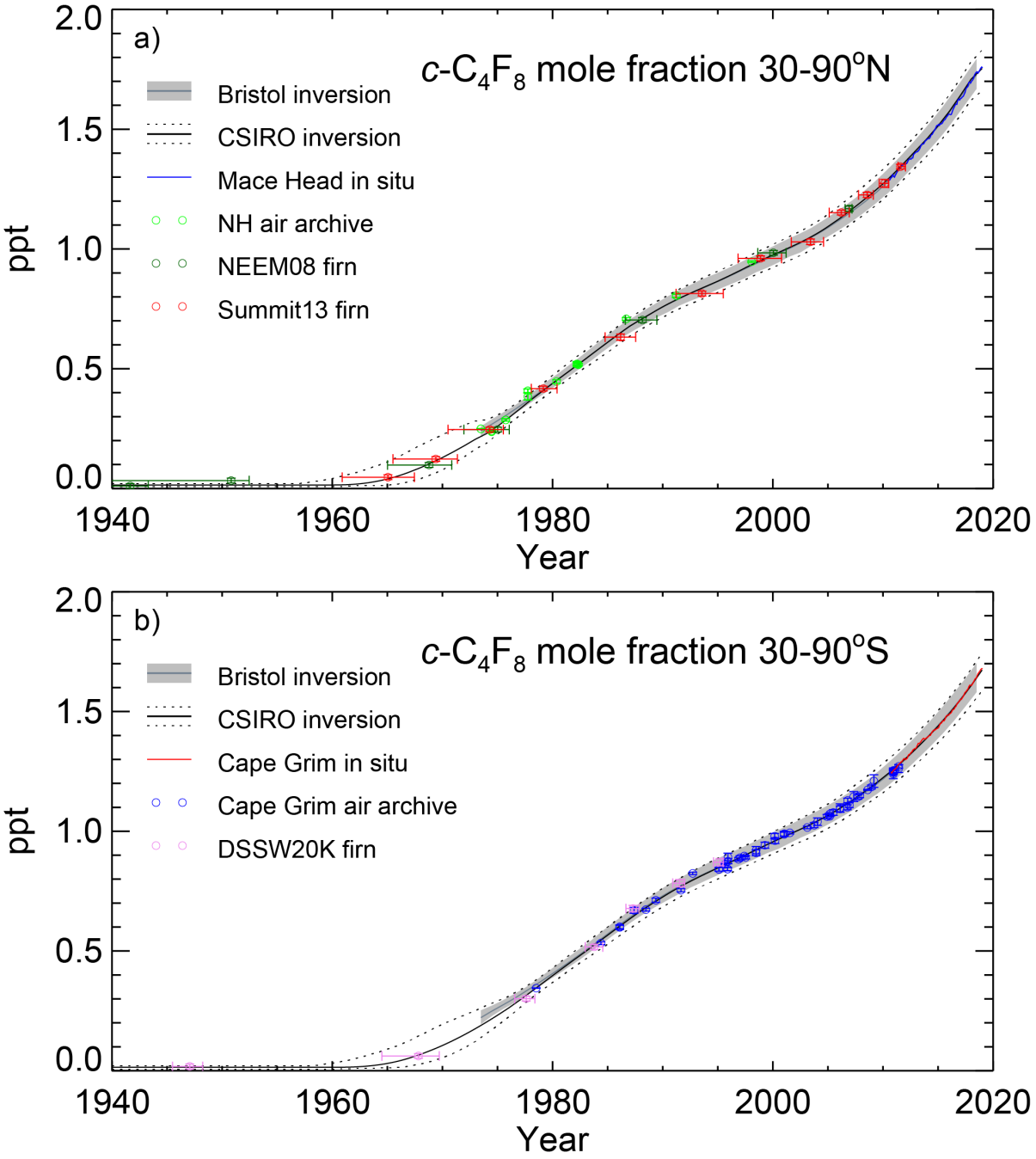


Figure S7. *c*-C_4F_8 extra-tropical mole fractions (ppt) reconstructed by the UB (grey line) and CSIRO (black line) inversions are shown with 2σ uncertainty bands (grey band and black dotted line, respectively) and the underlying in situ (pollution removed monthly means), archive, and firn air data: a) for 30-90°N MHD in situ (blue line), NH archive (light green circles), and the NH firn sites NEEM08 (dark green circles) and Summit13 (red circles); (b) for 30-90°S CGO in situ (red line), the Cape Grim air archive (CGAA, blue circles), and the SH firn site DSSW20K (pink circles); Firn samples are plotted against mean ages (before 1965) or effective ages (after 1965) with 2σ uncertainties as horizontal error bars. Vertical error bars represent precisions for archive and firn data. Uncertainties in monthly means for in situ data have been omitted for clarity (they are shown in Fig. 1).

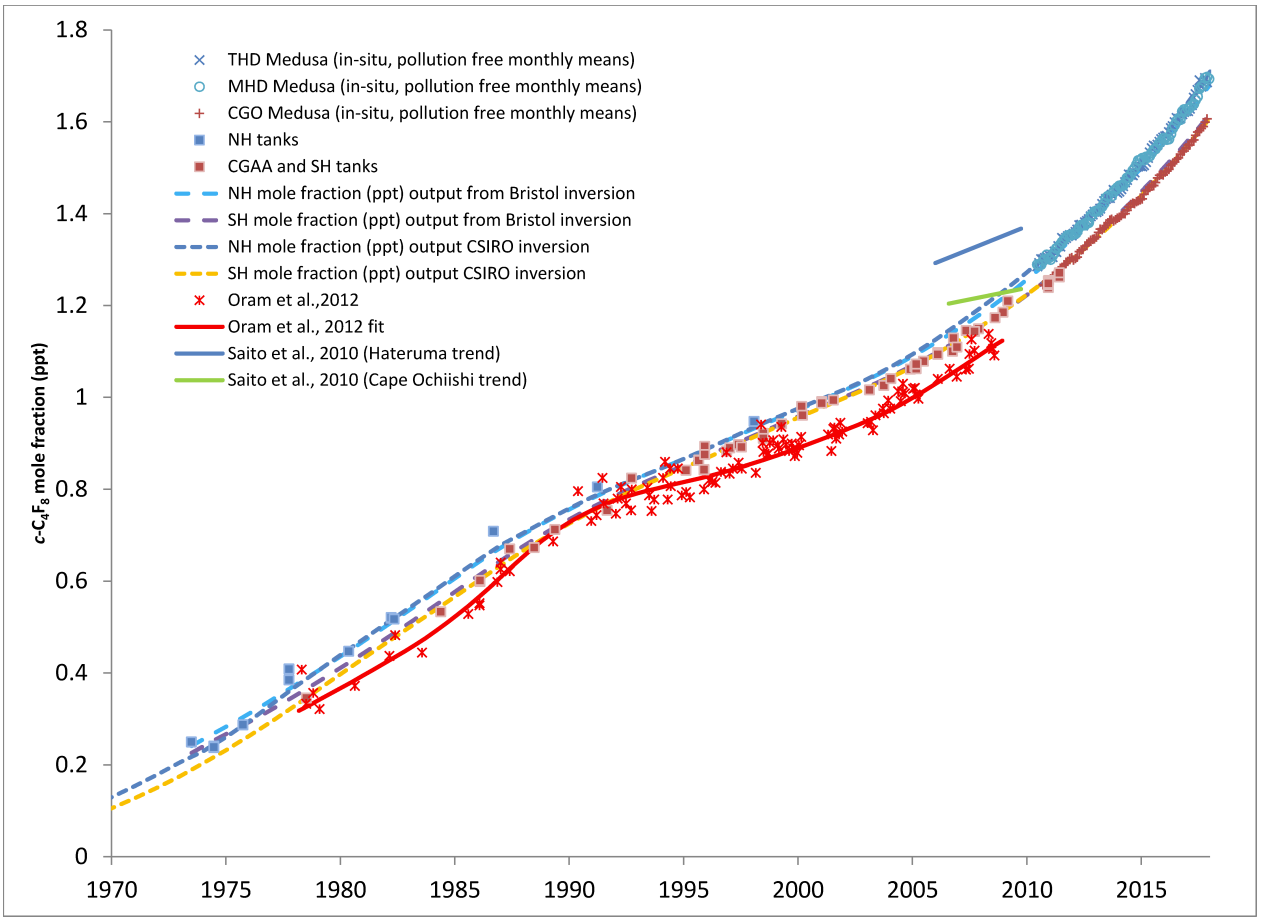


Figure S8. *c*-C_4F_8 mole fractions reconstructed here for the Northern (NH) and Southern Hemisphere (SH) compared to results from Oram et al., 2012 (SH only) and Saito et al., 2010. Measured *c*-C_4F_8 mole fractions from THD, MHD, and CGO Medusa (in situ, pollution-free monthly means, blue crosses and blue circles (NH), red pluses (SH) and NH (blue squares) and CGAA and SH tanks (red squares) are shown together with results from the Bristol (AGAGE 12-box, light blue (NH) and purple (SH) long dashes) and CSIRO (dark blue (NH) and orange (SH) short dashes) inversions. *c*-C_4F_8 mole fractions from Oram et al., 2012 (CGAA/SH only, red stars and red solid line) and Saito et al., 2010 (Hateruma island, blue solid line, Cape Ochiishi, green solid line, both NH) are shown for comparison.

Oram, D. E., Mani, F. S., Laube, J. C., Newland, M. J., Reeves, C. E., Sturges, W. T., Penkett, S. A., Brenninkmeijer, C. A. M., Röckmann, T., and Fraser, P. J.: Long-term tropospheric trend of octafluorocyclobutane (*c*-C_4F_8 or PFC-318), Atmos. Chem. Phys., 12, 1, 261-269, 10.5194/acp-12-261-2012, 2012.

Saito, T., Yokouchi, Y., Stohl, A., Taguchi, S., and Mukai, H.: Large emissions of perfluorocarbons in East Asia deduced from continuous atmospheric measurements, Environ. Sci. Technol., 44, 11, 4089-4095, 10.1021/es1001488, 2010.

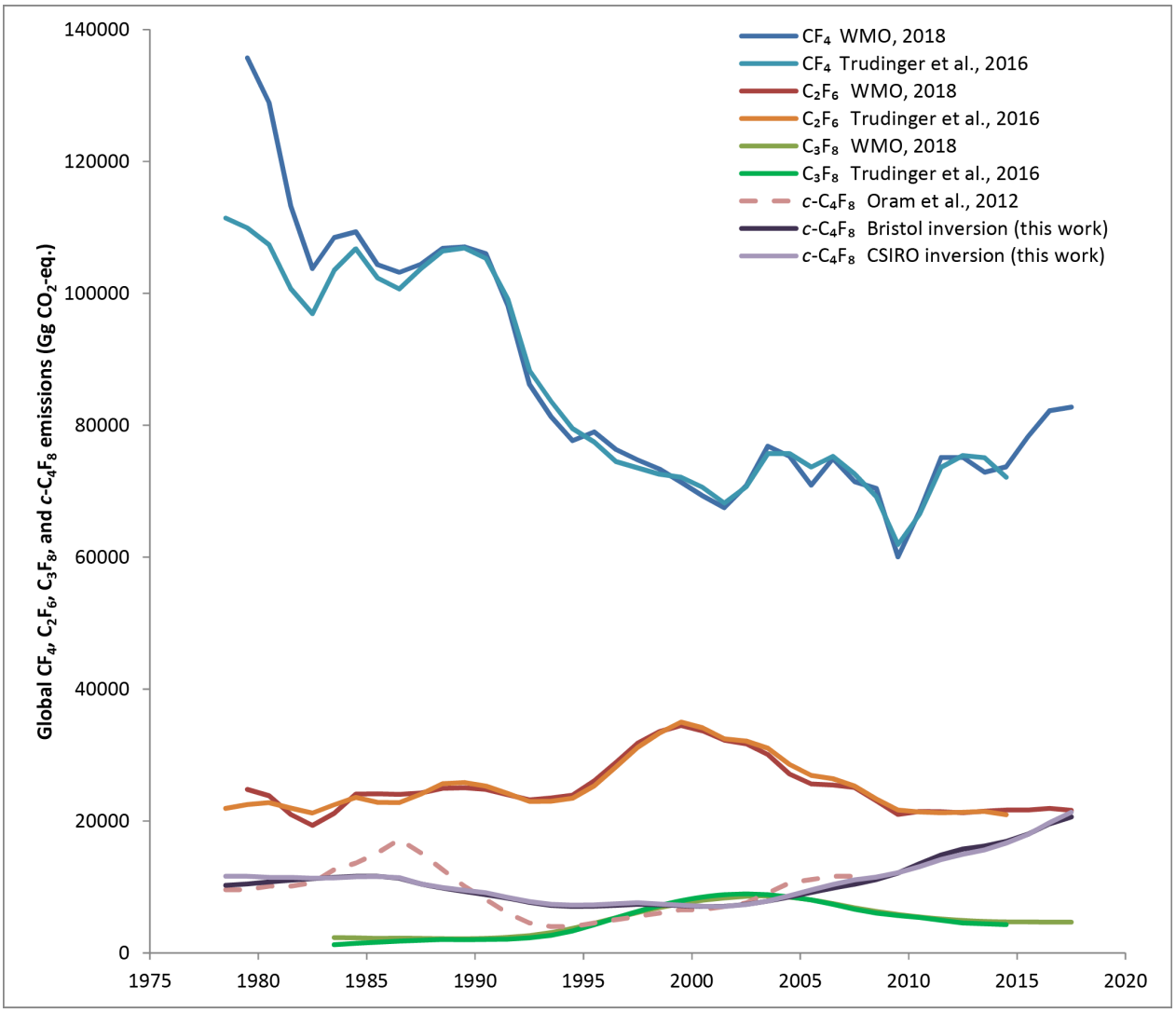


Figure S9. Global emissions of CF_4, C_2F_6, C_3F_8, and *c*-C_4F_8 expressed as carbon dioxide equivalent emissions (CO_2-eq.) emissions (using GWP_{100} of 6,630, 11,100, 8,900, and 9,540, respectively, Burkholder et al., 2018) (1.000.000 Gg CO_2-eq. = 1 billion tonnes CO_2-eq.). In 2017, *c*-C_4F_8 emissions have reached 0.021 billion tonnes of CO_2-equivalent compared to 0.083, 0.022, and 0.005 billion tonnes of CO_2-eq. for CF_4, C_2F_6, and C_3F_8.

Burkholder, J. B. (Lead Author)., Hodnebrog, Ø., and Orkin, V. L. (Contributors).: Appendix A: Summary of Abundances, Lifetimes, Ozone Depletion Potentials (ODPs), Radiative Efficiencies (REs), Global Warming potentials (GWPs), and Global Temperature ChanGe Potentials (GTPs), in: Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project–Report No. 58, World Meteorological Organization, Geneva, Switzerland, 2018.

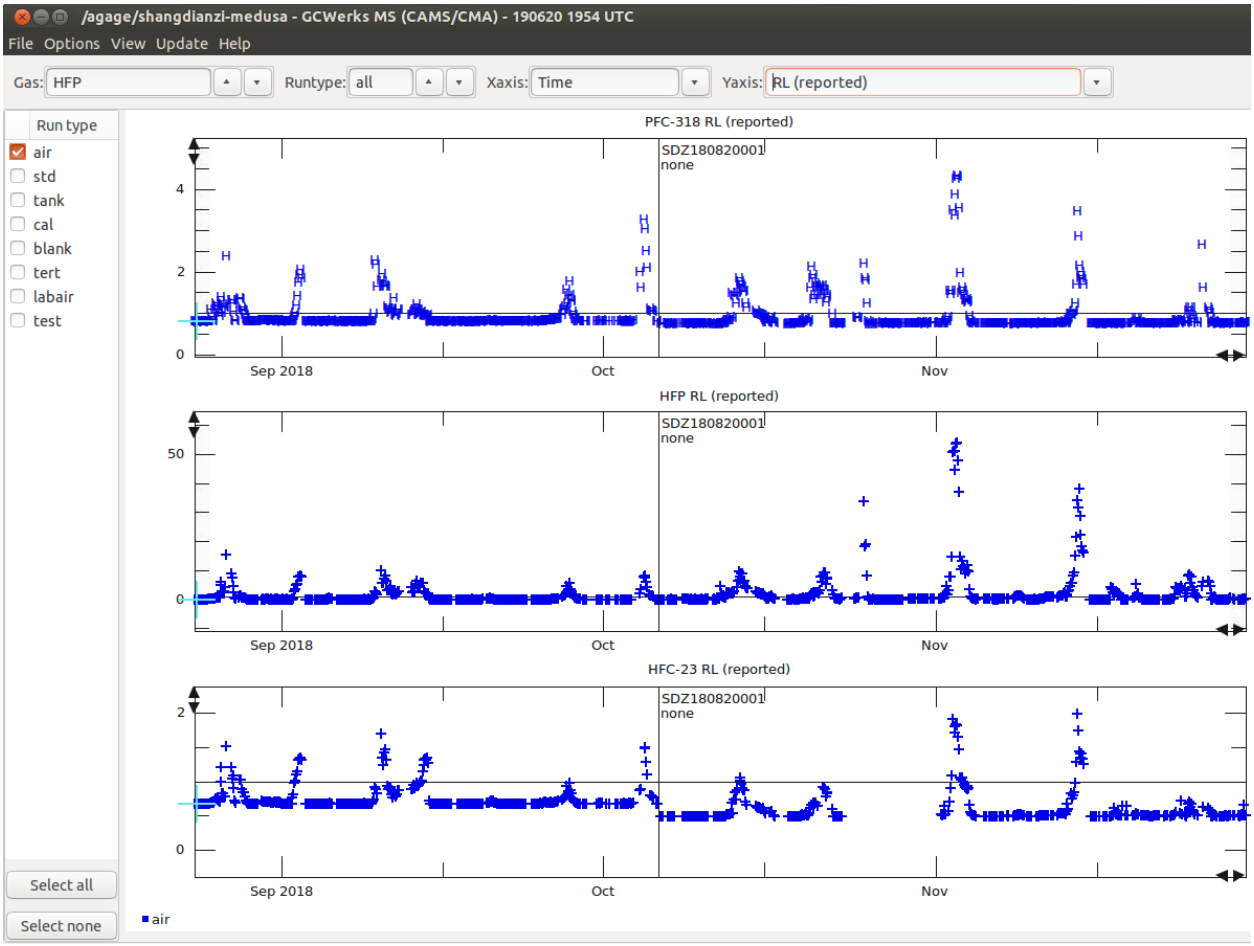
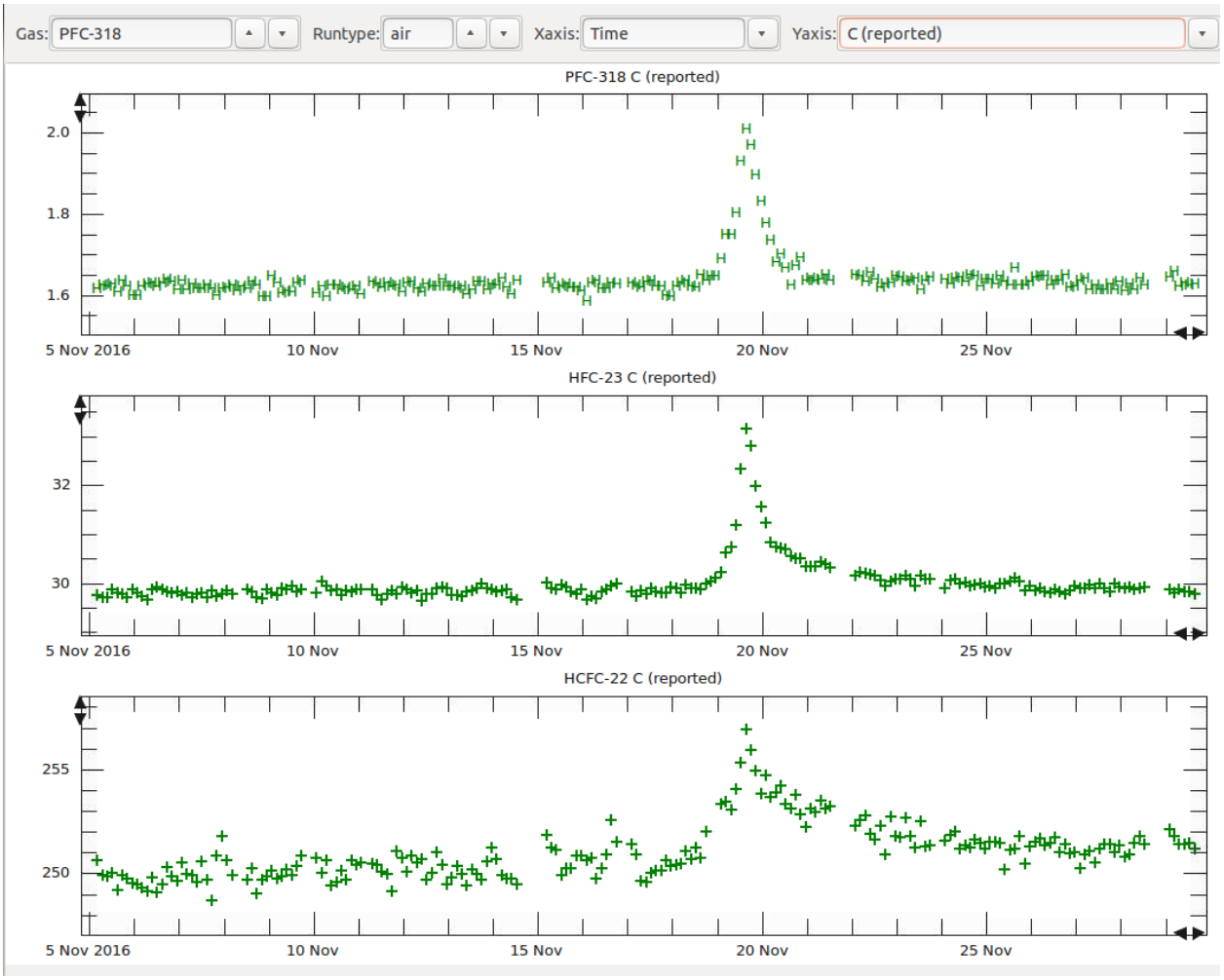


Figure S12. Area responses of ambient air samples relative to those of the working standard (RL (reported)) for *c*-C_4F_8 (PFC-318), HFP (hexafluoropropylene), and HFC-23 measurements at SDZ.

HFP (hexafluoropropylene) is measured on m/z 131 and 150. On the Porabond Q column it elutes after HFC-125 and before CFC-115. We confirmed its identify with a spike of ~10 ppt HFP (87,422 area counts) at SIO. The working standard used at the time contained ~0.03–0.04 ppt HFP (270–380 area counts). Ambient air samples contained ~0.01 ppt HFP (98–123 area counts), just around estimated detection limit of ~0.01 ppt (3 times baseline noise). The low abundance in the working standards led to poor precisions of ~20%. From Nov. 2018 until present, ambient air at SIO typically showed 0–0.5 times (0–150 area counts) the response of the working standard used (reaching a few times to 2.5 times), indicating continuing miniscule ambient mixing ratios. HFP measurements at Aspendale (ASA) have not been calibrated, but the peak responses in ambient air from Feb. 2017 until present were almost always small (0–300 area counts), indicating similarly small ambient mixing ratios as at SIO. Occasional small pollution events have been observed at ASA, see Section 5.3.3. HFP measurements at GSN and SDZ were not calibrated, but several working standards showed significant peak responses (up to 2,500 and 4,000 area counts, respectively). From Aug. 2018 until present, HFP pollution events at SDZ always coincided with *c*-C_4F_8 and HFC-23 pollution events. Figure S12 shows examples of the good correlations observed among PFC-318 (*c*-C_4F_8), HFP, and HFC-23.

Figure S15. PFC-318 (c-C_4F_8), HFC-23, and HCFC-22 mixing ratios in ambient during the largest PFC-318 pollution event at ZEP.



The best correlation was observed between PFC-318 and HFC-23 mixing ratios (C (reported)). Other compounds, such as HCFC-22 (shown above), CFC-13, CH_2Cl_2, $CHCl_3$, or TCE showed weaker correlations. Most other halogenated compounds showed no obvious correlations.

Table S3. Estimates of global PTFE market share by region

	2012[%]	2015[+]	2015[+]	2015[#]	2015[#]
North America	31 %	10 %	10 %	see RoW	
Europe	21 %	14 %	14 %	see RoW	
Asia Pacific (Total)	36 %	62 %		78 %	
China			53 %		67 %
Japan			9 %		11 %
Rest of World (RoW, Total)	12 %	14 %		22 %	22 %
India			8 %		
Russia			6 %		
Total	100 %	100 %	100 %	100 %	100 %

[%]Polytetrafluoroethylene (PTFE), Market Analysis, www.grandviewresearch.com, accessed Oct. 2018.

RoW is comprised of India and Russia.

[+]Polytetrafluoroethylene (PTFE), A Global Market Overview, www.industry-experts.com, accessed Jul. 2018.

RoW is comprised of India and Russia.

[#]www.qianzhan.com/analyst/detail/220/170629-c33a2ca7.html, accessed Dec. 2018 (Chinese, translate.google.com).

RoW is comprised of North America, Europe, India, and Russia.

In 2015, PTFE production in China was estimated to account for 53 - 67% of global PTFE production.

Table S4. Estimates of global PTFE market share by company

	2012[%]		2015[#]
DuPont	31.0 %	Dupont (Global incl. China)	13 %
Daikin	14.0 %	Daikin (Global incl. China)	13 %
Solvay	11.5 %	Solvay (China)	4 %
3M	9.0 %	3M	4 %
Others	31.0 %	Shangdong Dongyue Group	20 %
		Others (China)	30 %
		Others (Global excl. China)	11 %
Arkema SA	5.5 %		
Gujarat Fluorochemicals Ltd.	3.5 %		
		Asahi Glass (Japan)	5 %
Total	100.0 %		100 %

[%]Polytetrafluoroethylene (PTFE), Market Analysis, www.grandviewresearch.com, accessed Oct. 2018

[#]www.qianzhan.com/analyst/detail/220/170629-c33a2ca7.html, accessed Dec. 2018 (Chinese, translate.google.com).

DuPont incl. Chemours, Solvay incl. Solexis, 3M incl. Dyneon, and Asahi Glass incl. AGC.