Continued increase of CFC-113a (CCl₃CF₃) mixing ratios in the global atmosphere: emissions, occurrence and potential sources

Karina E. Adcock[1], Claire E. Reeves[1], Lauren J. Gooch[1], Emma C. Leedham Elvidge[1],

Matthew J. Ashfold[2], Carl A. M. Brenninkmeijer[3], Charles Chou[4], Paul J. Fraser[5],

Ray L. Langenfelds[5], Norfazrin Mohd Hanif[1], Simon O'Doherty[6], David E. Oram[1,7],

Chang-Feng Ou-Yang[8], Siew Moi Phang[9], Azizan Abu Samah[9], Thomas Röckmann[10],

William T. Sturges[1], and Johannes C. Laube[1]

[1]Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[2]School of Environmental and Geographical Sciences, University of Nottingham Malaysia Campus, 43500 Semenyih, Malaysia
[3]Air Chemistry Division, Max Planck Institute for Chemistry, Mainz, Germany
[4]Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan
[5]Oceans and Atmosphere, Climate Science Centre, Commonwealth Scientific and Industrial Research Organisation, ~~Oceans and Atmosphere, Climate Science Centre,~~ Aspendale, Australia
[6]Department of Chemistry, University of Bristol, Bristol, UK
[7]National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[8]Department of Atmospheric Sciences, National Central University, Taipei, Taiwan
[9]Institute of Ocean and Earth Sciences, University of Malaya, Kuala Lumpur, Malaysia
[10]Institute for Marine and Atmospheric Research Utrecht, Utrecht University, Utrecht, the Netherlands

Correspondence to: Karina Adcock (Karina.Adcock@uea.ac.uk)

Abstract

Atmospheric measurements of the ozone depleting substance CFC-113a (CCl₃CF₃) are reported from ground-based stations in Australia, Taiwan, Malaysia and the United Kingdom, together with~~and~~ aircraft-based data for~~measurements in~~ the upper troposphere and lower stratosphere. Building on previous work we find that, since the gas first appeared in the atmosphere in the 1960s, global CFC-113a mixing ratios have been increasing monotonically to the present day. Mixing ratios of CFC-113a have increased by 40 % (percent) from 0.50 to 0.70 ppt (parts per trillion) in the Southern Hemisphere between the end of the previously published record in December 2012 and February 2017. We derive updated global emissions of 1.7 Gg yr⁻¹ (gigagrams per year)~~(1.3-2.4 Gg yr⁻¹)~~ on average between 2012 and 2016 using a two-dimensional model. We compare the long-term trends and emissions of CFC-113a to those of its structural isomer, CFC-113 (CClF₂CCl₂F), which still has much higher mixing ratios than CFC-113a, despite its mixing ratios and emissions decreasing since the 1990s. The continued presence of Northern Hemispheric emissions of CFC-113a is confirmed by our measurements of a persistent interhemispheric gradient in its mixing ratios, with higher mixing ratios in the Northern Hemisphere. The sources of CFC-113a are still unclear, but we present evidence that indicates large emissions in East Asia, most likely due to its use as a chemical involved in the production of hydrofluorocarbons. Our aircraft data confirm the interhemispheric gradient as well as showing mixing ratios consistent with ground-based observations and the relatively long atmospheric lifetime of CFC-113a. CFC-113a is the only known CFC for which abundances are still ~~substantially~~ increasing substantially in the atmosphere.

1. Introduction

The ozone layer in the stratosphere blocks most of the harmful solar ultraviolet radiation from reaching the Earth's surface and therefore protects human health and the environment. Chlorofluorocarbons (CFCs) are industrially produced chemicals that were commonly used as refrigerants, aerosol propellants, solvents and foam blowing agents. CFCs have negligible loss mechanisms in the troposphere and only break down when they reach the stratosphere where they are exposed to strong ultraviolet light and decompose mostly through photolysis and reaction with O^1D (Ko et al., 2013). These decomposition productscompounds act as catalysts in the destruction of ozone and they have, in combination with other chlorine and bromine containing gases, led to the formation of the ozone hole (Farman et al., 1985; Molina and Rowland, 1974). The discovery of this phenomenon motivated the `Montreal Protocol on Substances that Deplete the Ozone Layer', an international agreement to phase out the use of CFCs and other ozone depleting substances (ODSs) (UNEP, 2016a). It came into force in 1989 and, other than for a few critical use exceptions, there has been a global ban on CFC production since 2010 (UNEP, 2016a). Due to this, mixing ratios of most CFCs are now decreasing in the atmosphere and the ozone hole shows signs of recovery (Pawson et al., 2014; Solomon et al., 2016). Continued reductions in CFC mixing ratios are needed to allow the ozone layer to recover to pre-1970 levels.

Recently, mixing ratios of CFC-113a (CCl_3CF_3), the structural isomer of the well-known ozone-depleting substance CFC-113 ($CF_2ClCFCl_2$), were found to still be increasing in the atmosphere up until 2012 (Laube et al., 2014). The previously published evidence for increasing mixing ratios of CFC-113a comes from air samples collected at Cape Grim, Tasmania (41° S) and firn air data collected in Greenland (77° N) in 2008 (NEEM project) (Buizert et al., 2012; Laube et al., 2014). The firn air depth profile data, when combined with inverse modelling, provide smoothed time series of compound mixing ratios going back up to a century (Buizert et al., 2012; Laube et al., 2012). CFC-113a became detectable in the atmosphere in the 1960s (Laube et al., 2014). Cape Grim is a clean-air measurement site located in Tasmania, Australia, with air sampling/analysis activities since 1976 and the CFC-113a record derived from the Cape Grim Air Archive (1978 onwards) shows mixing ratios increasing over time with a sharp acceleration starting around 2010 (Laube et al., 2014). Global annual emissions of CFC-113a were estimated using a two-dimensional atmospheric chemistry-transport model, showing increases since the 1960s and more than doubling between 2010 and 2012, reaching 2.0 Gg yr^{-1} in 2012 (Laube et al., 2014). In addition, measurements of aircraft samples from the IAGOS CARIBIC-IAGOS observatoryproject identified an interhemispheric gradient with mixing ratios increasing from the Southern Hemisphere to the Northern Hemisphere; and the atmospheric lifetime of CFC-113a was estimated at 51 years from stratospheric research aircraft flights in late 2009 and early 2010 (Laube et al., 2014).

The origin of the emissions that cause this increase in CFC-113a mixing ratios is as yet undetermined. Some evidence of a potential connection with hydrofluorocarbon (HFC) production has been found (Laube et al., 2014) and here we use additional data to investigate this possibility further. Laube et al. (2014) reported data until 2012. This studypaper uses data that have become available since 2012 to provide an update on its global trend and emissions and to assess these in terms of our understanding of the sources of this gas and its potential impact on ozone.

2. Methods

2.1 Analytical technique

Air samples from all the campaigns discussed in this study were collected in electropolished and/or silco-treated stainless steel gas cylinders, except for the CARIBIC observatoryproject, for which samples were collected using a glass-bottle based samplers (Brenninkmeijer et al., 2007). Various pumps were used for the different sampling activities, all of which have been thoroughly tested for a large range of trace gases (Allin et al., 2015; Brenninkmeijer et al., 2007; Laube et al., 2010ab; Allin et al., 2015 and Oram et al., 2017). After collection, the samples were transported to the University of East Anglia (UEA) to be analysed on a high-sensitivity gas chromatograph coupled to a Waters AutoSpec magnetic sector mass spectrometer (GC-MS). The trace gases were cryogenically extracted and pre-concentrated. A full description of this system can be found in Laube et al. (2010ba). Analysis was partly carried out using a GS GasPro column (length ~50 m, ID 0.32 mm) and partly with

a KCl-passivated Al$_2$O$_3$Al-PLOT column (length: 50 m, ID 0.32 mm), (Laube et al., 2016). The latter analysis has been slightly modified by the addition of an Ascarite filter to remove carbon dioxide. Several tests and comparisons ensured that no significant differences in CFC-113 and CFC-113a mixing ratios were obtained regardless of the column or filter used. A possible interference could arise when measuring CFC-113a on the GS GasPro column using m/z 116.91 if concentrations of the nearby eluding HCFC-123 are high. This was the case for a small number of samples analysed for this work and those measurements were either a) repeated using the interference-free m/z 120.90, b) replaced with measurements on the KCl-passivated Al$_2$O$_3$-PLOT column, or c) excluded. The KCl-passivated Al$_2$O$_3$-PLOT column separated CFC-113 and CFC-113a well, no interferences were observed and m/z 116.91 was used for quantification. All the samples are compared to the same NOAA standard (AAL-071170) and there were routine measurements of multiple standards to exclude the possibility of mixing ratio changes in the standard over time. The samples collected in Taiwan in 2013 were also measured on the Entech-Agilent GC-MS system operating in electron ionisation (EI) mode. This consists of a preconcentration unit (Entech model 7100) connected to an Agilent 6890 GC and 5973 quadrupole MS (Leedham Elvidge et al., 2015). The calibration scale used for CFC-113a is the UEA calibration scale and for CFC-113 is the NOAA 2002 calibration scale. On a typical day, the working standard is measured five to eight times, between every two or three samples. The sample peak sizes are measured relative to the standards measured just before and after them. The working standard is used to correct for small changes in instrument response over the course of a day. The dry air mole fraction (mixing ratio) is measured and the units, parts per trillion (ppt) are used in this study as an equivalent to picomole per mole. The measurement uncertainties are calculated the same way for all measurements and represent the one sigma standard deviation. They and are based onderived as the square root of the sum of the squared uncertainties from sample repeats and repeated measurements of thean air standard on the same day.

2.2 Sampling

The following new data are presented in this study (see also Figure 1 and Table 1):

1. Laube et al. (2014) reported CFC-113a measurements from Cape Grim, Tasmania from 1978 to 2012. We nowThis paper reports four more years of CFC-113a measurements from Cape Grim, up to February 2017. From 2013 to 2017, 20 samples were collected at Cape Grim at irregular intervals of between one to five months apart. The CFC-113 mixing ratios, (1978-2017), from analyses of archived air samples collected at Cape Grim, Tasmania and analysed at the UEAAir Archive, together with NOAA flask data, and AGAGE *in situ* data are also included to compare the two isomers. CFC-113 stability in the Cape Grim Air Archive has been demonstrated in the AGAGE program for periods up to 15 years and longer (Fraser et al., 1996; CSIRO unpublished data). Most of the CFC-113 UEA Cape Grim data set was previously published in (Laube et al., (2013). Some of the earlier samples from Laube et al. (2013) and Laube et al. (2014) were reanalysed on the KCl-passivated Al$_2$O$_3$-PLOT column (length: 50 m, ID 0.32 mm). They showed very good agreement with the previous GasPro column-based measurement with comparable precisions and no detectable offset. The Cape Grim air samples were collected under background conditions with winds from the south-west, marine sector, so that sampled air masses were not influenced by nearby terrestrial sources and are representative of the extra-tropicallarge-scale Southern Hemisphere atmosphere. Details of the sampling procedure have been reported in previous publications (e.g. Fraser et al., 1999; Laube et al., 2013).

2. Tacolneston tower is a measurement site in Norfolk (Ganesan et al., 2015), and is part of the UK Tall Tower Network. Air samples were collected on a near-biweekly basis between July 2015 and March 2017 using an air inlet at 185 m.

3. Ground-based samples were collected from Bachok Marine Research Station on the northeast coast of Peninsular Malaysia in January and February 2014.

4. During the StratoClim campaign (http://www.stratoclim.org/), air samples were collected during two flights by the Geophysica high altitude research aircraft, as described in Kaiser et al. (2006), in the upper troposphere and lower stratosphere (10-20 km) over the Mediterranean on 01-Sep-/09/2016 and 06-Sep-/09/2016.

5. Air samples were collected at regular intervals at altitudes of 10-12 km during long distance flights on a commercial Lufthansa aircraft from 2009 to 2016 (Brenninkmeijer et al., 2007) on four flights between Frankfurt, Germany and Bangkok, Thailand; five flights between Frankfurt, Germany and Cape Town, South

Africa; and one flight between Frankfurt, Germany and Johannesburg, South Africa; including the four flights referred to in Laube et al. (2014) (CARIBIC project, www.caribic-atmospheric.com).

6. Four ground-based air sampling campaigns took place in Taiwan from 2013 to 2016. Between 19 and 33 air samples were collected in March and April each year. In 2013 and 2015 samples were collected from a site on the southern coast of Taiwan (Hengchun) and in 2014 and 2016 samples were collected from a site on the northern coast of Taiwan (Cape Fuguei). See also Vollmer et al. (2015), Laube et al. (2016) and Oram et al. (2017). ~~The median mixing ratios are used for the measurements made at the Taiwan sites to decrease the influence of the large spikes in CFC-113a mixing ratios that occurred during these campaigns (Section 3.2.1). All other averages are calculated using the mean.~~

2.3 Emission modelling

A two-dimensional atmospheric chemistry-transport model was used to estimate, ~~the~~ top-down, global annual emissions of CFC-113a and CFC-113 for the purpose of comparing the emissions of the two isomers. The model contains 12 horizontal layers each representing 2 km of the atmosphere and 24 equal-area zonally averaged latitudinal bands. The modelled mixing ratios for the latitude band that Cape Grim is located within (35.7° S–41.8° S) were matched as closely as possible to the observations at Cape Grim (40.7° S) by iteratively adjusting the global emissions rate until the differences between the modelled mixing ratios and the observations were minimised. For more details about the model see Newland et al. (2013); and Laube et al. (2016).

This model was previously used to estimate the global annual emissions of CFC-113a (Laube et al., 2014). We now update the ~~In this study, the~~ CFC-113a emission estimates ~~are updated~~ using an additional four years of Cape Grim measurements. The ~~and~~ CFC-113 emissions are estimated using CFC-113 mixing ratios at Cape Grim for 1978-2017 from the UEA Cape Grim dataset ~~Air Archive~~ and compared with bottom-up emissions estimates from the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, https://agage.mit.edu/data/afeas-data). The upper and lower emission uncertainties for CFC-113a and CFC-113 were determined by first calculating the uncertainty in matching the modelled mixing ratios with the observed mixing ratios using their recommended atmospheric lifetimes and secondly considering the uncertainty range in the lifetimes. The 'best fit' (minimum-maximum) steady-state lifetimes used in this study are 51 years (30 years-148 years) for CFC-113a and 93 years (82 years-109 years) for CFC-113 (Ko et al., 2013; Leedham Elvidge et al., ~~2017)~~accepted ACP). ~~For f~~urther details are provided in ~~see~~ the supplementary material.

A latitudinal distribution of emissions, with 95 % of emissions originating in the Northern Hemisphere, was assumed for both compounds. As Cape Grim is a remote ~~n isolated~~ Southern Hemispheric site the emission distribution within the Northern Hemisphere has almost no effect on the modelled mixing ratios in the latitudinal band of Cape Grim ~~is located in~~. The emission ~~s~~ distribution used for CFC-113 was assumed to be constant for the whole of the model run and ~~. This distribution~~ has been used in previous studies for similar compounds (McCulloch et al., 1994; Reeves et al., 2005; Laube et al., 2014, 2016 ~~and has been shown to reproduce the reported mixing ratios of CFC-11 and CFC-12 at Cape Grim to within 5 % uncertainty (Reeves et al., 2005)~~. For CFC-113a ~~W~~we decided to select an emission distribution ~~for CFC-113a~~ based on how well the modelled mixing ratios in the latitude band 48.6-56.4° N agreed with the observations at Tacolneston for the later part of the trend. Tacolneston can be considered to be representative of Northern Hemisphere background mixing ratios of CFC-113a for that latitude as there are no significant enhancements ~~large spikes~~ in mixing ratios (Figure 2). The emission distribution used in the CFC-113a model is the same as CFC-113 for the first 60 years (1934-1993) and then gradually shifts over the next 10 years from more northerly latitudes (36-57° N) to more southerly latitudes (19-36° N). It then remains at more southerly latitudes until the end of the run in 2017. This distribution shift is based on the assumption that CFC-113a emissions are predominantly from Europe and North America at the beginning of the model run and then shift to be coming predominantly from East Asia towards the end of the model run. There are significant enhancements in CFC-113a mixing ratios in our measurements from Taiwan indicating continued emissions in this region (Section 3.2.1) which is consistent with emissions in this latitude band in the model. The latter is also consistent with ~~our measurements from Taiwan (Section 3.2.1) and~~ previous work that ~~that~~ has found ~~that~~ emissions of ozone depleting substances shifted from more northerly Northern Hemisphere latitudes to more southerly Northern Hemisphere latitudes (Reeves et al., 2005; Montzka et al., 2009). This is likely due to developing countries, which are mostly located further south, having more time to phase out

the use of many ODSs than developed countries (Newland et al., 2013; CTOC, 2014; Fang et al., 2016). With this emissions distribution, the modelled CFC-113a mixing ratios at Tacolneston matched closely to the observations (Figure 2). It should be noted that while there is evidence that supports the emission distribution used here, there might be alternative distributions that result in equally good fits to the trends, particularly in the earlier part of the record.

2.4 Dispersion modelling

The UK Met Office's Numerical Atmospheric Modelling Environment (NAME, Jones et al. 2007), a Lagrangian particle dispersion model, was used to produce footprints of where the air sampled during the Taiwan and Malaysia campaigns (Table 1) had previously been close to the Earth's surface. The model setup related to samples collected in Taiwan in 2016 was slightly different to the setup for simulations in 2013-2015; hereafter those differences are noted in parentheses, though they have no practical implications for our findings. The footprints were calculated over 12 days by releasing batches of 60,000 (30,000 in 2016) inert backward trajectories over a 3 hour period encompassing each sample. Over the course of the 12 day travel time the location of all trajectories within the lowest 100m of the model atmosphere was recorded every 15 minutes on a grid with a resolution of 0.5625° longitude and 0.375° latitude (0.25° by 0.25° in 2016). The trajectories were calculated using three-dimensional meteorological fields produced by the UK Met Office's Numerical Weather Prediction tool, the Unified Model (UM). These fields have a horizontal grid resolution of 0.35° longitude by 0.23° latitude for the 2013 and 2014 simulations, and 0.23° longitude by 0.16° latitude for the 2015 and 2016 simulations. In all cases the meteorological fields have 59 vertical levels below ~30km. Dates in the NAME footprint maps are presented in the format yyyy-mm-dd and use UTC time.

3. Results

3.1 Long-term atmospheric trends and estimated global annual emissions of CFC-113a and CFC-113

CFC-113a ~~atmospheric~~ mixing ratios at Cape Grim were previously found to have been increasing from 1978-2012 (Laube et al., 2014, Figure 3). Since 2012, ~~CFC-113a mixing ratios at Cape Grim~~they have continued to increase from 0.50 ppt in December 2012 to 0.70 ppt in February 2017 (Figure 3). ~~Overall CFC-113a mixing ratios increased gradually until about 2010 followed by a more rapid increase.~~ Between 1978 and 2009 ~~CFC-113a mixing ratios increased on~~ the average rate of increase was~~by~~ 0.012 ppt yr^{-1}; ~~then~~ between 20~~10~~09 and 2017 the~~y~~ rate has risen threefold to ~~increased by~~ about 0.037 ppt yr^{-1} ~~i.e. more than three times the increase from the previous period~~.

Although measurements at Tacolneston were made for a shorter time period ~~at Tacolneston~~ (20 months), ~~this site~~ it also experienced ~~shows~~ an increase in CFC-113a mixing ratios of 0.03 ppt yr^{-1} over the period July 2015 to March 2017, based on start and end points (Figure 2). Furthermore, ~~the median mixing ratios of CFC-113a in Taiwan increased on average by 0.06 ppt yr^{-1} from 2013 to 2016. During~~for the CARIBIC flights the mean mixing ratios of CFC-113a increased on average, by 0.04 ppt yr^{-1} between 2009 and 2016. Overall, there is a consistent picture of a continued global increase in background mixing ratios of CFC-113a. It~~s~~ atmospheric ~~has~~burden has been increasing since the 1960s (Laube et al., 2014) and this has continued ~~to increase~~ until early 2017, implying; ~~therefore there must be~~that ongoing emissions of ~~CFC-113a~~CFC-113a exceed its rate of removal ~~into the atmosphere~~. The modelled global annual CFC-113a emissions began in the 1960s and increased steadily at an average rate of 0.02 Gg yr^{-1} yr^{-1} until they reached 0.9 Gg yr^{-1} (0.6-1.2 Gg yr^{-1}) in 2010 followed by ~~and then there was~~ a sharp increase ~~in the average growth rate~~ to 0.52 Gg yr^{-1} yr^{-1} from 2010 to 2012 when emissions were 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1}) (Figure 3). We find that between 2012 and 2016, modelled emissions were on average 1.7 Gg yr^{-1} (1.3-2.4 Gg yr^{-1}). The best model fit (minimum-maximum) suggests some minor and statistically non-significant variability between 1.6 Gg yr^{-1} (1.3-2.0 Gg yr^{-1}) in 2015 and 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1})~~Gg yr^{-1}~~ in 2012. See the supplementary material for more details.

It is instructive to look at CFC-113 to learn more about CFC-113a. The atmospheric trends of CFC-113 at Cape Grim (Figure 4) and estimated emissions ~~of CFC-113 at Cape Grim (Figure 4)~~ are very different from those of

CFC-113a. Mixing ratios of both compounds increased at the beginning of the record, but then the CFC-113 mixing ratios stabilised in the early 1990s and ~~then~~ started to decrease (Figure 4), consistent with previous observations (~~Carpenter et al., 2014;~~ Fraser et al., 1996; Montzka et al., 1999; Rigby et al., 2013; Carpenter and Reimann, 2014)~~(Montzka et al., 1999; Rigby et al., 2013; Carpenter and Reimann, 2014)~~. This trend is similar to those of many other CFCs in the atmosphere (for example CFC-11 and CFC-12, Rigby et al., 2013), but in contrast to the increasing mixing ratios of CFC-113a. Note that CFC-113a mixing ratios are still much lower~~higher~~ than those of CFC-113~~a~~ even at the end of our current record in early 2017. CFC-113 is the third most abundant CFC in the atmosphere (Carpenter and Reimann, 2014) and mixing ratios of CFC-113a are only about 1 % of CFC-113 mixing ratios in 2017. CFC-113 mixing ratios at Cape Grim measured by NOAA (https://www.esrl.noaa.gov/gmd/dv/ftpdata.html) and AGAGE (http://agage.eas.gatech.edu/data_archive/agage/) are also included in Fig. 4. There is a small offset of 2 % between the NOAA data and the current UEA Cape Grim dataset, with the UEA Cape Grim dataset being slightly higher, similar to the offset reported previously (Laube et al., 2013).

The CFC-113 model derived emissions begin in the 1940s and rapidly increase until they peak in 1989 at 25~~21.5~~ Gg yr⁻¹, after which~~then~~ they decrease ~~and in 2016, they are~~to 2.4 Gg yr⁻¹ in 2016 (Figure 4). This sharp decline ~~demonstrates~~witnesses the success of the Montreal Protocol, which came into force in 1989 and phased out the production of CFCs by 1996 in developed countries and 2010 in developing countries (UNEP, 2016a). The total cumulative emissions of CFC-113, up to the end of 2016, are 316~~34~~ Gg while the cumulative emissions of CFC-113a are 29 Gg, making the total cumulative emissions of CFC-113a less than 1 % of its isomer CFC-113. Alternatively, in the last decade, 2007-2016, cumulative emissions of CFC-113 are 3~~87~~ Gg, while for CFC-113a they are 13 Gg, ~~which is about~~ or a third ~~35 %~~ of the CFC-113 cumulative emissions ~~over this period. This indicates that as emissions of other CFCs are decreasing CFC-113a becomes relatively more important~~. Current CFC-113a emissions are ~~now~~ similar to those of CFC-113 ~~emissions~~ and could even surpass them~~become larger in the future~~ if the ~~current~~ trends continue (Figure 5).

Up until 1992, the CFC-113 emissions used in the model are the bottom-up emissions estimates from AFEAS. In the model, these emissions lead to a best-fit match to the CFC-113 observations. This shows that in the first part of the record, AFEAS report~~s~~ data ~~were~~ accurately reflecting global CFC-113 emissions. However, after 1992 the AFEAS emissions lead to lower modelled mixing ratios than the observations indicating that AFEAS was missing some emissions after 1992. Therefore, the emissions used in our study here are the AFEAS emissions up until 1992. From 1992 onwards they are based on the best model fit to the UEA Cape Grim observations. CFC-113 emissions were also derived in another study using a range of emission inventories and estimates (Rigby et al., 2013). Those~~These~~ emissions mostly agree with ~~the emissions estimated in this study~~ours within the uncertainties. ~~, and the d~~Differences are likely due to this study using different lifetimes than ~~differences in the methods used to calculate the emissions. Rigby et al. (2013) used the estimated emissions to derive the steady-state atmospheric lifetimes whereas in this study, we used the steady-state atmospheric lifetimes to derive the emissions using shorter lifetimes than in~~ Rigby et al. (2013).

The upper and lower bounds of the CFC-113 emissions in this study are derived using the 'likely' range in the CFC-113 lifetime given by SPARC ~~WMO~~ of 82-109 years (Ko et al., 2013) ~~(Carpenter and Reimann, 2014)~~. The 'possible' range of 69-138 years was also estimated by ~~(~~Ko et al., ~~(~~2013)~~Carpenter and Reimann (2014)~~, however using~~with~~ a lifetime of 138 years the modelled mixing ratios did not decrease sufficiently rapidly~~quickly enough~~ after 1990 to match the observed downwards trend in CFC-113 ~~observations~~ even in the absence of~~with no~~ emissions. ~~This indicates that the maximum possible lifetime of CFC-113 is somewhere between 109 years and 138 years.~~ We can use the observed decrease in CFC-113 mixing ratios from 2003 onwards to calculate a decay time (lifetime at zero emissions). For long lived gases with stratospheric sinks, such as CFC-113, the decay time and steady state lifetime are very similar differing by no more than 2 % (Ko et al., 2013). Setting the emissions to zero from 2003 onwards and adjusting the lifetime so that the model reproduce~~d~~ the CFC-113 mixing ratios at Cape Grim, suggests the ~~maximum~~ lifetime for CFC-113 is 110 years. By assuming zero emissions, this lifetime is a maximum value, since any source of CFC-113 would have to be balanced by a shorter lifetime. Combining the measurement and model errors as described in the supplementary material gives an error of 5.7 %. Accounting

290 for the 2 % error introduced by assuming the decay time is the same as the steady state lifetime gives are overall error of 6 %. ~~and a~~Applying this to the lifetime gives a maximum lifetime of 110 ± 76 years. For comparison, we also calculated the maximum lifetime from the observed rate of decrease in CFC-113 mixing ratios at Cape Grim between 2003 and 2017 using the continuity equation and assuming no sources of CFC-113 (Supplementary material, Section 2). The agreement was good giving a maximum lifetime of 113 ± 54 years. It should be noted

295 that CFC-113 is not the focus of this study, but we do find that emissions of it persist until 2017, which leaves room for~~enables~~ the possibility that some of the recent emissions of CFC-113a are related to CFC-113 emissions, possibly through HFC production or agrochemical production (see Section 4) ~~–~~similar to findings for other isomeric CFCs (Laube et al., 2016).

3.2 Global distributions of CFC-113a

300 ### 3.2.1 Enhancement above background mixing ratios

Many of the CFC-113a mixing ratios observed in~~at~~ Taiwan (light blue stars ~~dots~~, Figure 5~~6~~) are significantly higher than at the other locations considered in this study. The background mixing ratios consistently increase through this period from about 0.4 ~~ppt~~ to about 0.7 ppt whereas the highest Taiwan samples have mixing ratios of up to 3 ppt. These enhancements~~large spikes~~ in mixing ratios in all four years of the Taiwan campaigns indicate

305 continued emissions in this region, most likely continental East Asia.

~~These enhancements in CFC-113a mixing ratios are likely due to emissions of this compound in East Asia.~~ To determine the region(s) of emissions~~origin~~ more accurately NAME footprints were~~are~~ used (Figure 7~~6~~a-g). In general, when there are the ~~enhancements~~spikes in CFC-113a mixing ratios then the ~~usually occur when the~~ NAME footprints usually show that the air most likely came from the boundary layer over eastern China or the

310 Korean Ppeninsula as shown in (a), (c), (d), and (g) for example. In contrast,~~Whereas~~ the footprints in (b), (e) and (f) are examples of samples with lower CFC-113a mixing ratios and correspondingly there is very little influence from eastern China or the Korean Ppeninsula. ~~In (b) and (e), the air is coming from the north, between the eastern coast of China and the Korean peninsula, and in (f) the air mass originates predominantly from over the Pacific Ocean.~~ However, we recognise the limitations of our relatively sparse dataset which prevents us from pinpointing

315 the source region(s) further.

The mixing ratios in Taiwan are very variable indicating nearby source region(s) whereas Cape Grim and Tacolneston mixing ratios are much less variable. Therefore, the Taiwan measurements are better suited to investigate correlations that might shed further light on potential sources. After investigating correlations of CFC-113a with a over 50 ~~range of~~ other halocarbons in samples from Taiwan we found CFC-113a mixing ratios

320 correlate well ($R^2 > 0.750$) in multiple years with those of CFC-113 and HCFC-133a (CH_2ClCF_3) indicating a possible link between the sources of these compounds (Table 2). There is a great deal of variability in mixing ratios in the Taiwan samples. CFC-113a correlates well with CFC-113 in 2013 and 2014, but shows almost no correlation in 2015 and a slightly decreased correlation coefficient in 2016 (Table 2, Figure 7~~8~~). In contrast, HCFC-133a strongly correlates with CFC-113a in the first three years (Table 2). The tropospheric lifetime of

325 HCFC-133a is 4-5 years (McGillen et al., 2015) and its ~~HCFC-133a~~ mixing ratios have varied in recent ~~over the last few~~ years. They increased in 2012/2013 and decreased~~then the trend reversed and~~ in 2014/2015~~, they decreased~~ (Vollmer et al., 2015). ~~Then a~~According to our latest data from Cape Grim, in 2016~~,~~ they began increasing again. Large changes in emissions are needed to produce such a~~this~~ variable trend but the causes of ~~it is currently unclear what is causing~~ these changes are still unclear (Vollmer et al., 2015).

330 CFC-113a mixing ratios in many of the samples collected at~~from~~ Bachok, Malaysia (grey crosses ~~dots~~, Figure 6~~5~~) are also enhanced above background levels although not to the same degree~~as much~~ as the Taiwan samples, ~~. The mixing ratios~~they range from 0.68 ppt to 1.00 ppt. The higher mixing ratios also have their origin in East Asian air masses being transported rapidly to the tropics by the East Asian winter monsoon circulation (Ashfold et al., 2015; Oram et al., 2017). Figure 9~~8~~ shows an example NAME footprint from a sample collected in January 2014

335 that is representative for many other events.~~.~~

The Tacolneston samples (yellow diamonds ~~dots~~, Figure 6~~5~~) show no significant enhancements ~~large spikes~~ in CFC-113a mixing ratios. This indicates the absence of regional ~~that Tacolneston is not located close to any~~ sources ~~of CFC-113a and therefore~~in this part of the UK ~~does not have large sources of CFC-113a~~. Due to this and the relatively long lifetime of CFC-113a Tacolneston can be considered to be representative of Northern Hemisphere background mixing ratios of ~~CFC-113a~~CFC-113a for that latitude. Both sites in Taiwan and also Tacolneston are Northern Hemisphere sites and although the Taiwan sites have many enhancements ~~large spikes~~ in CFC-113a mixing ratios there are some samples with background mixing ratios. For example, in spring 2016, the only period for which these datasets overlap, the lowest CFC-113a mixing ratio in Taiwan is 0.70 ppt on 24 ~~Mar-/03/20~~Mar/2016 (Figure 7~~6~~e). The closest Tacolneston sample to this is on 04 ~~Apr-/04/20~~Apr/2016 with a CFC-113a mixing ratio of 0.71 ppt. This shows that Taiwan can encounter mixing ratios at background levels of CFC-113a. However, many of the air samples collected in Taiwan show mixing ratios of CFC-113a above background levels, indicating~~suggesting~~ that enhanced levels of CFC-113a are generally widespread across this region.

3.2.2 Interhemispheric gradient of CFC-113a

For the period when measurements were made at both Cape Grim and Tacolneston (from July 2015 to February 2017), the Tacolneston mixing ratios were almost exclusively higher (though often indistinguishable within uncertainties) generally ~~higher~~ than the Cape Grim mixing ratios (Figure 5~~6~~-inset). On average Cape Grim mixing ratios are 0.055 ± 0.024 ppt lower~~higher~~ than Tacolneston mixing ratios. This shows that there is an interhemispheric gradient with higher CFC-113a mixing ratios in the Northern Hemisphere as would be expected for a compound emitted primarily in the Northern Hemisphere. This ~~interhemispheric~~ gradient is further supported by data from the six CARIBIC flights between~~from~~ Germany and~~to~~ South Africa for ~~between~~ 2009 ~~and~~ 2016. The CARIBIC samples (purple circles~~dots~~, Figure 6) from the 2016 flight coincide temporally with the Tacolneston and the Cape Grim samples in Fig. 6~~5~~ and confirm the observation of higher mixing ratios in the Northern Hemisphere (filled purple circles~~dots~~) and lower mixing ratios in the Southern Hemisphere (unfilled purple circles~~dots~~). Also see Fig. S1a in the supplementary material.

Laube et al. (2014) already~~also~~ found an interhemispheric gradient in CFC-113a using four of these CARIBIC flights 2009-2011 and furthermore discovered~~they found~~ that the increasing trend of CFC-113a at Cape Grim, lagged behind the increasing trend inferred from the firn air samples, collected to a depth of 76 metres, from Greenland, in the Northern Hemisphere. As the firn air measurements in the Laube et al. (2014) study were collected in Greenland between 14-30 July 2008, the surface measurements will be representative of atmospheric mixing ratios at that time. They will also be representative of background Northern Hemispheric CFC-113a mixing ratios for that latitude as the Greenland firn air location was isolated from any large industrial areas with potential sources of CFC-113a. Figure 6~~5~~ includes the three measurements closest to the surface (brown crosses ~~dots~~) although they are so close together that they appear to be one cross~~dot~~ in the F~~f~~igure and the average mixing ratio of the three samples is 0.44 ± 0.01 ppt.

Overall, these measurements demonstrate that there is an interhemispheric gradient in CFC-113a with higher mixing ratios in the Northern Hemisphere. This persistent interhemispheric difference indicates ongoing emissions of CFC-113a in the Northern Hemisphere with~~or~~ higher emissions in the Northern Hemisphere compared to the Southern Hemisphere. Similar interhemispheric gradients have been found for other CFCs (Liang et al., 2008), as CFCs are almost exclusively produced by industrial processes and most industrial production (and consumption) takes place in the Northern Hemisphere.

3.2.3 Measurements of CFC-113a in the stratosphere

Nearly all A~~a~~ir samples ~~are usually~~ collected during~~on the~~ CARIBIC flights represent~~at~~ cruising altitudes of 10-12 km, which for samples over northern India, during four flights going from Germany to Thailand (green diamonds~~dots~~, Figure 6~~5~~) would be near~~at~~ the tropopause. Thei~~r~~ ~~measurements should thus be representative of the~~ mixing ratios should be representative ~~of compounds~~ for air masses ~~just~~ prior to entering the tropical tropopause region~~layer (TTL)~~ which is the main entrance region to the stratosphere (Fueglistaler et al., 2009). For the flight on 9 ~~Nov-/11/~~Nov/2013, there is some enhancement above background mixing ratios over South-East Asia (Figures 6~~5~~, S1b). We speculate that T~~t~~his is likely due to air being transported from East Asia into the tropics via

cold surges and then being transported up into the upper troposphere via convection (Oram et al., 2017). This means that the uplift mechanism in this region could potentially enhance concentrations of long-lived ODSs entering the stratosphere as compared to the 'background' clean air ground-based abundances that are normally used to derive such inputs (Carpenter and Reimann, 2014). The mechanism has already been proven to exist for shorter-lived gases (Oram et al., 2017) and we see very similar patterns transporting elevated mixing ratios of CFC-113a to the tropics very rapidly (within days) during a time of increased convective uplift.

The Geophysica flights reach altitudes of 20 km and so ~~take~~ samples ~~of~~ lower stratospheric air. The Geophysica 2009-2010 flights (pink squares~~dots~~) and the Geophysica 2016 flights (orange squares~~dots~~) begin at background mixing ratios and then decrease (Figure 6~~5~~). During the 2016 flights, for example, measurements start at 10 km altitude where mixing ratios are 0.71 ppt and go up to 20 km where the mixing ratios are 0.36 ppt. In comparison to this, ground level measurements made at the Northern Hemisphere site, Tacolneston, had an average CFC-113a mixing ratio in 2016 of 0.72 ppt. In general, mixing ratios decrease as the aircraft ascends, mainly~~. This is~~ because air at higher altitudes will have taken longer to travel there and therefore is older and CFC-113a at higher altitudes has experienced photolytic decomposition. For more information about the Geophysica flights see the supplementary material.

4. Possible sources of CFC-113a

CFCs are entirely anthropogenic in origin. ~~It is therefore likely that there is a continuing industrial process~~This means that there are processes ~~(s)~~ either producing or involving CFC-113a that lead~~s~~ to continuing emissions of substantial amounts of this compound ~~into the atmosphere~~, especially in East Asia. Whilst the Montreal Protocol has banned the production and consumption of CFCs, there are exemptions including the use of ODSs as chemical feedstocks, chemical intermediates and fugitive emissions ~~. Whilst feedstock usage has to be reported to the United Nations Environment Programme (UNEP), these data are not publicly available~~ (UNEP, 2016a). A~~lso~~ the Montreal Protocol does not require isomers to be reported separately, ~~so~~ CFC-113 and CFC-113a may be reported together. ~~Furthermore, the use of ODSs as intermediate species and trace amounts of fugitive emissions do not have to be reported. Therefore, possible sources for the increase in CFC-113a mixing ratios include its use as a chemical feedstock, chemical intermediates, and fugitive emissions as well as unsanctioned production (Laube et al., 2014).~~

The strong correlations of CFC-113a with CFC-113 and HCFC-133a in Taiwan (Section 3.2.1) suggest that they are involved in the same production pathways or that their production facilities are co-located. The~~re is an~~ absence of a correlation between CFC-113a and CFC-113 in 2015 in ~~Taiwan~~Taiwan and in ~~is not what we would expect based on their source type (industry) and lifetimes. In~~ addition, the overall mixing ratios in 2015 appear to be lower than in the other years and have fewer large enhancements~~spikes~~ (Figure 8~~7~~). This could be because in general less air was arriving from China/Korea in 2015, which is indicated by the NAME footprints (Supplementary material, Section 5). Regions in ~~China~~China and /Korea we~~re the areas we~~ found to be the most likely locations~~source~~ of CFC-113a emissions. Alternatively, the varying correlations in different years between CFC-113a and CFC-113 could ~~indicate that there is more than one process emitting CFC-113a in East Asia, or variability in the process or in the amount of leaking of gases. This may~~ be an indication of two or more independent sources of CFC-113a. CFC-113 feedstock use decreased by over 50 % in 2015 due to one producer, which is also a user choosing not to produce CFC-113 in 2015 and reducing in-house inventories instead (Maranion et al., 2017). If this were the process leading to correlated emissions of CFC-113a and CFC-113 it~~this~~ may explain their lack of correlation in 2015.

One possible source of CFC-113a is from HFC production, specifically, of HFC-134a (CH_2FCF_3) and HFC-125 (CF_3CHF_2), as both may involve CFC-113a in their production process. ~~There are two main routes for making HFC-134a (Manzer, 1990).~~ One of the pathways for production of HFC-134a ~~The first~~ begins with CFC-113 being isomerised to form CFC-113a, which is then fluorinated to produce CFC-114a (CF_3CCl_2F), the latter is then hydrogenated to produce HFC-134a (Manzer, 1990; Rao et al., 1992; Bozorgzadeh et al., 2001; ~~Manzer, 1990;~~ Maranion et al., 2017~~; Rao et al., 1992~~). Another ~~The other~~ production method involves the reaction of hydrogen

fluoride with trichloroethylene to form HCFC-133a and HFC-134a (Manzer, 1990; McCulloch and Lindley, 2003; Shanthan Rao et al., 2015). The process for manufacturing HFC-125 involves the starting materials of either HCFC-123 or HCFC-124. CFC-113a, CFC-113 and HCFC-133a can be formed as by-products when HCFC-123 and HCFC-124 are fluorinated and recycled during the process that forms HFC-125 (Kono et al., 2002; Takahashi et al., 2002).

435

If there were ~~any~~ leaks in the system or venting of gases was practiced during these processes, this could lead to enhanced mixing ratios of CFC-113a and strong correlations with its isomer CFC-113 and HCFC-133a. HFC production should be contained and not involve ~~no~~ fugitive emissions to the atmosphere. However, the Chemicals Technical Options Committee (CTOC) 2014 report suggests there may be small leaks, depending on the quality of the system, ranging between 0.1 % and 5 % of the feedstock used. The CTOC reported that a leak rate of about 1.6 % would be needed if all CFC-113a and HCFC-133a in the atmosphere had come from their use as feedstock in the production of HFC-134a, HFC-125 and HFC-143a, which is within the previous range (CTOC, 2014). HFC-143a is produced using HCFC-133a so it was included in the CTOC estimate but CFC-113a is not involved in its production so it is not included in this study (CTOC, 2014).

440

445

~~Observed~~ HFC-134a and HFC-125 mixing ratios are not well correlated with those of CFC-113a, CFC-113 or HCFC-133a, except for HFC-125 in 2016 that has a good correlation with CFC-113a (Table 2). We would not necessarily expect them to be well correlated as most of the emissions of the HFCs are usually related to their uses rather than their production. ~~For example, as HFC-134a is used in mobile air conditioning units and in refrigeration, we would expect a significant component of HFC-134a emissions to be related to automobile use.~~ CFC-114a is also part of the production process of HFC-134a (Manzer, 1990), and can be another by-product during HFC-125 production (Kono et al., 2002; Takahashi et al., 2002). CFC-114a was only measured in 2015 and 2016 in Taiwan and was strongly correlated with CFC-113a in 2015 but not in 2016. This inconsistent correlation does not help to define further the source of CFC-113a. Furthermore HCFC-123 mixing ratios are not well correlated with CFC-113a, CFC-113 or HCFC-133a in any year in Taiwan but HCFC-124 mixing ratios are well correlated in 2015 with CFC-113a (Table 2) and with HCFC-133a (R^2=0.791). This strong correlation with HCFC-124 points to HFC-125 production being the dominant source in 2015.

450

455

~~On the one hand, the Cape Grim dataset shows that CFC-113a and CFC-113 have very different atmospheric trends (Figures 3, 4) but on the other hand, the Taiwan dataset shows that the isomers are mostly strongly correlated (Figure 7). This is not necessarily a contradiction because, close to sources the two compounds would still be correlated, but the emissions are low in absolute numbers for CFC-113 so it is globally still decreasing. In Sect. 3.1 we concluded that there was possibly a small amount of continued emissions of CFC-113 to maintain the observed atmospheric mixing ratios. This would be consistent with either a source from banks and/or release in conjunction with CFC-113a.~~

460

As discussed above, eastern China and/or the Korean Ppeninsula are the most likely source~~s~~ regions for~~of~~ the elevated mixing ratios of CFC-113a observed in Taiwan, and the HFC industry in China has been growing rapidly in recent years (Fang et al., 2016). In China in 2013, productions of 118 Gg yr^{-1} of HFC-134a and 78 Gg yr^{-1} of HFC-125 were reported (Fang et al., 2016). Most industry in China is located on the eastern coast and the majority of HFC manufacturers are in the three eastern provinces of Shanghai, Zhejiang and Jiangsu. There are also HFC-134a and HFC-125 production plants in Japan, South Korea and Taiwan but the majority are located in China. The HFC production plants located in Taiwan could influence the mixing ratios at both the sites in Taiwan ~~and as we do not know where they are located,~~ which ~~this~~ introduces an additional uncertainty. ~~We suggest that the CFC-113a emissions in the atmosphere originate predominantly from HFC production; however, there is currently insufficient data available to conclude this with high confidence.~~

465

470

Alternatively, there is an official exemption in the Montreal Protocol for the use of CFC-113a as an "agrochemical intermediate for the manufacture of synthetic pyrethroids", (UNEP, 2003) probably because it is used to make the insecticides cyhalothrin and tefluthrin (Brown et al., 1994; Jackson et al., 2001; Cuzzato and Bragante, 2002~~; Jackson et al., 2001~~). In addition CFC-113 is a feedstock used to make trifluoroacetic acid (TFA) and pesticides (Maranion et al., 2017). ~~In addition~~ CFC-113a is an intermediate in this process and these production processes are used in India and China and so this could also be a source in this region (Maranion et al., 2017). Furthermore

475

480

HCFC-133a is also used to manufacture TFA and agrochemicals although the process involving HCFC-133a is not related to the process involving CFC-113a (Rüdiger et al., 2002; Maranion et al., 2017).

Furthermore, CFC-113a is potentially present as an impurity in CFC-113 and the emissions of CFC-113a could be from CFC-113 banks. We saw in Sect. 3.2 that estimated emissions of CFC-113a began in the 1960s and HFC production did not become a large-scale industry until much later, so there must have been another source of CFC-113a during that earlier part of the record. In Sect. 3.1 we concluded that there was possibly a small amount of continued emissions of CFC-113 to maintain the observed atmospheric mixing ratios. This would be consistent with either a source from banks and/or release in conjunction with CFC-113a.

To summarise we have identified four possible sources of CFC-113a: agrochemical production, HFC-134a production, HFC-125 production and an impurity in CFC-113. The correlations indicate that HFC production is the dominant source in the East Asian region however; there is currently insufficient data available to conclude this with high confidence. Overall, the sources of CFC-113a emissions are still uncertain and further evidence is needed to quantify and pinpoint them. However, the likely sources we have found do not necessarily indicate a breach of the treaty as the use of CFCs as intermediates in the production of other compounds are permitted under the Montreal Protocol.

5. Conclusions

There is a continued global increasing trend in CFC-113a mixing ratios based on a number of globally distributed sampling activities giving a consistent picture. CFC-113a mixing ratios at Cape Grim, Australia increased since the previous study from 0.50 ppt in December 2012 to 0.70 ppt in February 2017. The derived emissions were still significantly above 2010 levels and were on average 1.7 Gg yr^{-1} (1.3-2.4 Gg yr^{-1}) between 2012 and 2016. Additionally, CFC-113a mixing ratios vary globally and our findings confirm an interhemispheric gradient with mixing ratios decreasing from the Northern Hemisphere to the Southern Hemisphere. No significant emissions of CFC-113a occur in the UK but strong sources exist in East Asia. There are multiple possible sources of CFC-113a emissions and correlation analysis suggests the emissions might be associated with the production of HFC-134a and HFC-125.

The background abundances of CFC-113a reported here are currently small (<1.0 ppt) in comparison to the most common CFC, CFC-12 which has declining atmospheric mixing ratios of ~510 ppt in 2017 (NOAA, 2017). Therefore, the contribution of CFC-113a to stratospheric ozone depletion is comparably small and is not yet a cause for major concern. While its increase in recent years has been considerable in percentage terms, it would have to continue increasing at this rate for several centuries before it reaches the atmospheric mixing ratios of the major CFCs in the 1990s. For example, a constant emission of 2 Gg yr^{-1} for CFC-113a yields a steady-state global mixing ratio of about 3.2 ppt. In 2016, HFCs were added to the Montreal Protocol and under the new amendment HFC consumption will be phased down in the coming decades (UNEP, 2016b). Therefore, if this phase down schedule is successful and the main source of CFC-113a is indeed from HFC production, then CFC-113a atmospheric mixing ratios should stop increasing in the future. However, whilst it seems likely, it is still not clear whether HFC production is actually the main source of global CFC-113a emissions and whilst CFC-113a emissions have appeared to be stable in recent years this does not mean that they will not increase in the future. Further investigation and continued monitoring is needed to assess future changes and ensure the continued effectiveness of the Montreal Protocol. When What is required is continuous measurements of CFC-113a in the East Asia region become available . With such data the magnitude and origins of East Asian CFC-113a emissions cancould be quantified.

In the past, it was assumed that isomers of CFCs had similar uses, sources and trends and therefore it was not necessary to report them separately. However, in this study, we have found that the isomers CFC-113a and CFC-113 continue to have different trends in the atmosphere and in their emissions. Recently CFC-114a (CF$_3$CCl$_2$F) and CFC-114 (CClF$_2$CClF$_2$) were also found to have different trends and sources (Laube et al., 2016). If policy-makers wish to limit the impacts of individual isomers, then Therefore, we recommend that atmospheric

observational data on individual CFC isomers should be reported to UNEP wherever possible. In addition, the increase in CFC-113a demonstrates that the use of ODSs as chemical feedstock or intermediates is becoming relatively more important as the use of ODSs for direct applications decreases. If policy-makers target zero emissions of CFCs, then they might consider regulating these uses of ODSs. used as chemical feedstock or intermediates might need to start being regulated by the Montreal Protocol as the use of ODSs for direct applications decreases, the use of ODSs as chemical feedstock or intermediates is becoming relatively more important.

6. Data availability

All data have been made publicly available in the supplement.

Competing interests. The authors declare that they have no conflict of interest.

References

Allin, S. J., Laube, J. C., Witrant, E., Kaiser, J., McKenna, E., Dennis, P., Mulvaney, R., Capron, E., Martinerie, P., Röckmann, T., Blunier, T., Schwander, J., Fraser, P. J., Langenfelds, R. L. and Sturges, W. T.: Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air, Atmos. Chem. Phys., 15(12), 6867–6877, doi:10.5194/acp-15-6867-2015, 2015.

Ashfold, M. J., Pyle, J. A., Robinson, A. D., Meneguz, E., Nadzir, M., Phang, S. M., Samah, A. A., Ong, S., Ung, H. E., Peng, L. K., Yong, S. E., Harris, N. R. P. and Ashfold, M.: Rapid transport of East Asian pollution to the deep tropics, Atmos. Chem. Phys, 15, 3565–3573, doi:10.5194/acp-15-3565-2015, 2015.

Bozorgzadeh, H., Kemnitz, E., Nickkho-Amiry, M., Skapin, T. and Winfield, J. M.: Conversion of 1,1,2-trichlorotrifluoroethane to 1,1,1-trichlorotrifluoroethane and 1,1-dichlorotetrafluoroethane over aluminium-based catalysts, J. Fluor. Chem., 107, 45–52 [online] Available from: http://ac.els-cdn.com/S002211390000350X/1-s2.0-S002211390000350X-main.pdf?_tid=3845707e-7053-11e7-a009-00000aacb360&acdnat=1500889019_2ab62e1f092b19b11e78f0a630956a69 (Accessed 24 July 2017), 2001.

Brenninkmeijer, C. A. M., Crutzen, P., Boumard, F., Dauer, T., Dix, B., Ebinghaus, R., Filippi, D., Fischer, H., Franke, H., Frieß, U., Heintzenberg, J., Helleis, F., Hermann, M., Kock, H. H., Koeppel, C., Lelieveld, J., Leuenberger, M., Martinsson, B. G., Miemczyk, S., Moret, H. P., Nguyen, H. N., Nyfeler, P., Oram, D., O'sullivan, D., Penkett, S., Platt, U., Pupek, M., Ramonet, M., Randa, B., Reichelt, M., Rhee, T. S., Rohwer, J., Rosenfeld, K., Scharffe, D., Schlager, H., Schumann, U., Slemr, F., Sprung, D., Stock, P., Thaler, R., Valentino, F., Van Velthoven, P., Waibel, A., Wandel, A., Waschitschek, K., Wiedensohler, A., Xueref-Remy, I., Zahn, A., Zech, U. and Ziereis, H.: Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system, Atmos. Chem. Phys., 7, 4953–4976, doi:10.5194/acp-7-4953-2007, 2007.

Brown, S. M., Glass, J. C. and Sheldrake, G. N.: Preparation of 1,1,1,trichlorotrifluoroethane, UK Patent

575   Application, GB2269381A, [online] Available from:
https://patents.google.com/patent/GB2269381A/en?q=%22CFC-
113a%22,trichlorotrifluoroethane,CCl3CF3&q=cyhalothrin,Lambda-
cyhalothrin,C23H19ClF3NO3&q=tefluthrin,C17H14ClF7O2&q=C07C17%2F10, 1994.

Buizert, C., Martinerie, P., Petrenko, V. V., Severinghaus, J. P., Trudinger, C. M., Witrant, E., Rosen, J. L.,
580   Orsi, A. J., Rubino, M., Etheridge, D. M., Steele, L. P., Hogan, C., Laube, J. C., Sturges, W. T., Levchenko, V.
A., Smith, A. M., Levin, I., Conway, T. J., Dlugokencky, E. J., Lang, P. M., Kawamura, K., Jenk, T. M., White,
J. W. C., Sowers, T., Schwander, J. and Blunier, T.: Gas transport in firn: Multiple-tracer characterisation and
model intercomparison for NEEM, Northern Greenland, Atmos. Chem. Phys., 12, 4259–4277, doi:10.5194/acp-
12-4259-2012, 2012.

585   Carpenter, L. J., Reimann, S., (Lead Authors), Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube,
J. C. and Yvon-Lewis, S. A.: Chapter 1: Update on Ozone-Depleting Substances (ODSs) and Other Gases of
Interest to the Montreal Protocol, in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research
and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland., 2014.

Chemicals Technical Options Committee (CTOC): Montreal Protocol on Substances that Deplete the Ozone
590   Layer Report of the Chemicals Technical Options Committee 2014 Assessment Report. [online] Available from:
http://ozone.unep.org/Assessment_Panels/TEAP/Reports/CTOC/, 2014.

Cuzzato, P. and Bragante, L.: Process to obtain CFC-113a from CFC-113, United States Patent, US Patent
6,791,001 B2, [online] Available from:
https://patentimages.storage.googleapis.com/pdfs/164b296774fb119c06f0/US20020151755A1.pdf (Accessed 9
595   March 2017), 2002.

Fang, X., Velders, G. J. M., Ravishankara, A. R., Molina, M. J., Hu, J. and Prinn, R. G.: Hydrofluorocarbon
(HFC) Emissions in China: An Inventory for 2005-2013 and Projections to 2050, Environ. Sci. Technol., 50(4),
2027–2034, doi:10.1021/acs.est.5b04376, 2016.

Farman, J. C., Gardiner, B. G. and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal
600   ClOx/NOx interaction, Nature, 315, 207–210, doi:10.1038/315207a0, 1985.

Fraser, P., Cunnold, D., Alyea, F., Weiss, R., Prinn, R., Simmonds, P., Miller, B. and Langenfelds, R.: Lifetime
and emission estimates of 1,1,2-trichlorotrifluorethane (CFC-113) from daily global background observations
June1982-June 1994, J. Geophys. Res., 101(D7), 12585–12599, 1996.

Fraser, P., Oram, D., Reeves, C., Penkett, S. and McCulloch, A.: Southern Hemisphere halon trends (1978-
605   1998) and global halon emissions, J. Geophys. Res, 104(D13), 15985–15999, doi:10.1029/1999JD900113,
1999.

Fueglistaler, S., Dessler, A. E., Dunkerton, T. J., Folkins, I., Fu, Q. and Mote, P. W.: Tropical Tropopause
Layer, Rev. Geophys., 47, RG1004, doi:10.1029/2008RG000267, 2009.

Ganesan, A. L., Manning, A. J., Grant, A., Young, D., Oram, D. E., Sturges, W. T., Moncrieff, J. B. and O
610   'Doherty, S.: Quantifying methane and nitrous oxide emissions from the UK and Ireland using a national-scale
monitoring network, Atmos. Chem. Phys, 15, 6393–6406, doi:10.5194/acp-15-6393-2015, 2015.

Jackson, A. R., Doyle, S. J., Moorhouse, K. and Gray, T.: Chlorination Process, United States Patent, US Patent
6,229,057 B1, [online] Available from:
https://patentimages.storage.googleapis.com/00/8d/59/58d47ee41c4baf/US6229057.pdf (Accessed 24 July
615   2017), 2001.

Jones, A., Thomson, D., Hort, M. and Devenish, B.: The U.K. Met Office's Next-Generation Atmospheric
Dispersion Model, NAME III, in Air Pollution Modeling and Its Application XVII, edited by C. Borrego and
A.-L. Norman, pp. 580–589, Springer US., 2007.

Kaiser, J., Engel, A., Borchers, R. and Röckmann, T.: Probing stratospheric transport and chemistry with new
620   balloon and aircraft observations of the meridional and vertical N_2O isotope distribution, Atmos. Chem. Phys.,
6(11), 3535–3556, doi:10.5194/acp-6-3535-2006, 2006.

Ko, M. K. W., Newman, P. A., Reimann, S. and Strahan, S. E., Eds.: SPARC Report on Lifetimes of

Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, SPARC Office. [online] Available from: http://www.sparc-climate.org/publications/sparc-reports/, 2013.

625 Kono, S., Yoshimura, T. and Shibanuma, T.: Process for producing 1,1,1,2,2-pentafluoroethane, United States Patent, US Patent 6,392,106 B1, [online] Available from: https://patentimages.storage.googleapis.com/96/18/bb/1942c2e2d57286/US6392106.pdf (Accessed 5 September 2017), 2002.

630 Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Sturges, W. T., Braß, M. and Röckmann, T.: Fractional release factors of long-lived halogenated organic compounds in the tropical stratosphere, Atmos. Chem. Phys. Atmos. Chem. Phys., 10, 1093–1103, doi:10.5194/acp-10-1093-2010, 2010ba.

Laube, J. C., Martinerie, P., Witrant, E., Blunier, T., Schwander, J., Brenninkmeijer, C. A. M., Schuck, T. J., Bolder, M., Röckmann, T., Van Der Veen, C., Bönisch, H., Engel, A., Mills, G. P., Newland, M. J., Oram, D. E., Reeves, C. E. and Sturges, W. T.: Accelerating growth of HFC-227ea (1,1,1,2,3,3,3- heptafluoropropane) in 635 the atmosphere, Atmos. Chem. Phys., 10(13), 5903–5910, doi:10.5194/acp-10-5903-2010, 2010ba.

Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Sturges, W. T., Braß, M. and Röckmann, T.: Fractional release factors of long-lived halogenated organic compounds in the tropical stratosphere, Atmos. Chem. Phys. Atmos. Chem. Phys., 10, 1093–1103, doi:10.5194/acp-10-1093-2010, 2010b.

Laube, J. C., Hogan, C., Newland, M. J., Mani, F. S., Fraser, P. J., Brenninkmeijer, C. A. M., Martinerie, P., 640 Oram, D. E., Röckmann, T., Schwander, J., Witrant, E., Mills, G. P., Reeves, C. E. and Sturges, W. T.: Distributions, long term trends and emissions of four perfluorocarbons in remote parts of the atmosphere and firn air, Atmos. Chem. Phys., 12(9), 4081–4090, doi:10.5194/acp-12-4081-2012, 2012.

Laube, J. C., Keil, A., Bönisch, H., Engel, A., Röckmann, T., Volk, C. M. and Sturges, W. T.: Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important 645 source gases, Atmos. Chem. Phys, 13, 2779–2791, doi:10.5194/acp-13-2779-2013, 2013.

Laube, J. C., Newland, M. J., Hogan, C., Brenninkmeijer, C. A. M., Fraser, P. J., Martinerie, P., Oram, D. E., Reeves, C. E., Röckmann, T., Schwander, J., Witrant, E. and Sturges, W. T.: Newly detected ozone-depleting substances in the atmosphere, Nat. Geosci., 7(March), 10–13, doi:10.1038/NGEO2109, 2014.

Laube, J. C., Hanif, N. M., Martinerie, P., Gallacher, E., Fraser, P. J., Langenfelds, R., Brenninkmeijer, C. A. 650 M., Schwander, J., Witrant, E., Wang, J.-L., Ou-Yang, C.-F., Gooch, L. J., Reeves, C. E., Sturges, W. T. and Oram, D. E.: Tropospheric observations of CFC-114 and CFC-114a with a focus on long-term trends and emissions, Atmos. Chem. Phys, 16, 15347–15358, doi:10.5194/acp-16-15347-2016, 2016.

Leedham Elvidge, E. C., Oram, D. E., Laube, J. C., Baker, A. K., Montzka, S. A., Humphrey, S., O'Sullivan, D. A. and Brenninkmeijer, C. A. M.: Increasing concentrations of dichloromethane, CH_2Cl_2, inferred from 655 CARIBIC air samples collected 1998-2012, Atmos. Chem. Phys., 15(4), 1939–1958, doi:10.5194/acp-15-1939-2015, 2015.

Leedham Elvidge, E. C., Bönisch, H., Brenninkmeijer, C. A. M., Engel, A., Fraser, P. J., Gallacher, E., Langenfelds, R., Mühle, J., Oram, D. E., Ray, E. A., Ridley, A. R., Röckmann, T., Sturges, W. T., Weiss, R. F. and Laube, J. C.: Evaluation of stratospheric age-of-air from CF_4, C_2F_6, C_3F_8, CHF_3, HFC-125, HFC-227ea and 660 SF_6; implications for the calculations of halocarbon lifetimes, fractional release facto, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-748, 2018.

Liang, Q., Stolarski, R. S., Douglass, A. R., Newman, P. A. and Nielsen, J. E.: Evaluation of emissions and transport of CFCs using surface observations and their seasonal cycles and the GEOS CCM simulation with emissions-based forcing, J. Geophys. Res. Atmos., 113(14), 1–15, doi:10.1029/2007JD009617, 2008.

665 Manzer, L. E.: The CFC-Ozone Issue: Progress on the Development of Alternatives to CFCs, Science., 249(4964), 31–35, doi:10.1126/science.249.4964.31, 1990.

Maranion, B., Pizano, M. and Woodcock, A.: Montreal Protocol on Substances that Deplete the Ozone Layer, Report of the UNEP Technology and Economic Assessment Panel, Volume 1, Progress Report, May 2017, Nairobi, Kenya. [online] Available from: http://conf.montreal-protocol.org/meeting/oewg/oewg-670 39/presession/Background-Documents/TEAP-Progress-Report-May2017.pdf (Accessed 19 September 2017), 2017.

McCulloch, A. and Lindley, A. A.: From mine to refrigeration: A life cycle inventory analysis of the production of HFC-134a, Int. J. Refrig., 26, 865–872, doi:10.1016/S0140-7007(03)00095-1, 2003.

675 McCulloch, A., Midgley, P. M. and Fisher, D. A.: Distribution of emissions of chlorofluorocarbons (CFCs) 11, 12, 113, 114 and 115 among reporting and non-reporting countries in 1986, Atmos. Environ., 28(16), 2567–2582, doi:10.1016/1352-2310(94)90431-6, 1994.

McGillen, M. R., Bernard, F., Fleming, E. L. and Burkholder, J. B.: HCFC-133a (CF_3CH_2Cl): OH rate coefficient, UV and infrared absorption spectra, and atmospheric implications, Geophys. Res. Lett., 42(14), 6098–6105, doi:10.1002/2015GL064939, 2015.

680 Molina, M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, Nature, 249, 810–812, doi:10.1038/249810a0, 1974.

Montzka, S. A., Bulter, J. H., Elkins, J. W., Thompson, T. M., Clarke, A. D. and Lock, L. T.: Present and future trends in the atmospheric burden of ozone-depleting halogens, Nature, 398, 690–694, 1999.

Montzka, S. A., Hall, B. D. and Elkins, J. W.: Accelerated increases observed for hydrochlorofluorocarbons
685 since 2004 in the global atmosphere, Geophys. Res. Lett., 36(3), 1–5, doi:10.1029/2008GL036475, 2009.

National Oceanic and Atmospheric Administration (NOAA): GMD Data Archive, [online] Available from: ftp://ftp.cmdl.noaa.gov/hats/cfcs/cfc12/combined/HATS_global_F12.txt (Accessed 24 April 2017), 2017.

Newland, M. J., Reeves, C. E., Oram, D. E., Laube, J. C., Sturges, W. T., Hogan, C., Begley, P. and Fraser, P. J.: Southern hemispheric halon trends and global halon emissions, 1978-2011, Atmos. Chem. Phys., 13(11),
690 5551–5565, doi:10.5194/acp-13-5551-2013, 2013.

Oram, D. E., Ashfold, M. J., Laube, J. C., Gooch, L. J., Humphrey, S., Sturges, W. T., Leedham-Elvidge, E., Forster, G. L., Harris, N. R. P., Mead, M. I., Samah, A. A., Phang, S. M., Ou-Yang, C.-F., Lin, N.-H., Wang, J.-L., Baker, A. K., Brenninkmeijer, C. A. M. and Sherry, D.: A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons, Atmos. Chem. Phys, 175194, 11929–11941, doi:10.5194/acp-17-11929-2017,
695 2017.

Pawson, S., Steinbrecht, W., (Lead Authors), Charlton-Perez, A. J., Fujiwara, M., Karpechko, A. Y., Petropavlovskikh, I., Urban, J. and Weber, M.: Chapter 2: Update on global ozone: Past, present, and future, in Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland., 2014.

700 Rao, M. V. N., Weigert, F. J. and Manzer, L. E.: Catalytic Process for Producing CCl_3CF_3, United States Patent, US Patent 5,120,883, [online] Available from: https://patentimages.storage.googleapis.com/07/5c/92/7117da778942ae/US5120883.pdf, 1992.

Reeves, C. E., Sturges, W. T., Sturrock, G. A., Preston, K., Oram, D. E., Schwander, J., Mulvaney, R., Barnola, J.-M. and Chappellaz, J.: Trends of halon gases in polar firn air: implications for their emission distributions,
705 Atmos. Chem. Phys, 5, 2055–2064, doi:10.5194/acp-5-2055-2005, 2005.

Rigby, M., Prinn, R. G., 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 CH_3CCl_3 using atmospheric trends, Atmos. Chem. Phys, 13, 2691–2702, doi:10.5194/acp-13-2691-2013, 2013.

710 Rüdiger, S., Gross, U., Shekar, S. C., Rao, V. V., Sateesh, M. and Kemnitz, E.: Studies on the conversion of 1,1,1-trichlorotrifluoroethane, chloro-2,2,2-trifluoroethane, and 1,1,1-trifluoroethane by catalytic oxidation, hydrolysis and ammonolysis, Green Chem., 4(6), 541–545, doi:10.1039/B206098C, 2002.

Shanthan Rao, P., Narsaiah, B., Rambabu, Y., Sridhar, M. and Raghavan, K. V.: Catalytic processes for fluorochemicals: Sustainable alternatives, in Industrial Catalysis and Separations: Innovations for Process
715 Intensification, edited by K. V Raghavan and B. M. Reddy, pp. 407–435, Apple Academic Press, Toronto., 2015.

Solomon, S., Ivy, D. J., Kinnson, D., Mills, M. J., Neely III, R. R. and Schmidt, A.: Emergence of healing in the Antarctic ozone layer, Science., 353(6296), 269–274, doi:10.1126/science.aae0061, 2016.

Takahashi, K., Kono, S. and Shibanuma, T.: Manufacturing method for fluorine-containing ethane, United
States Patent, US Patent 6,455,745 B1, [online] Available from:
https://patentimages.storage.googleapis.com/pdfs/945d53805f1b12c0c1e5/US6455745.pdf (Accessed 9 March
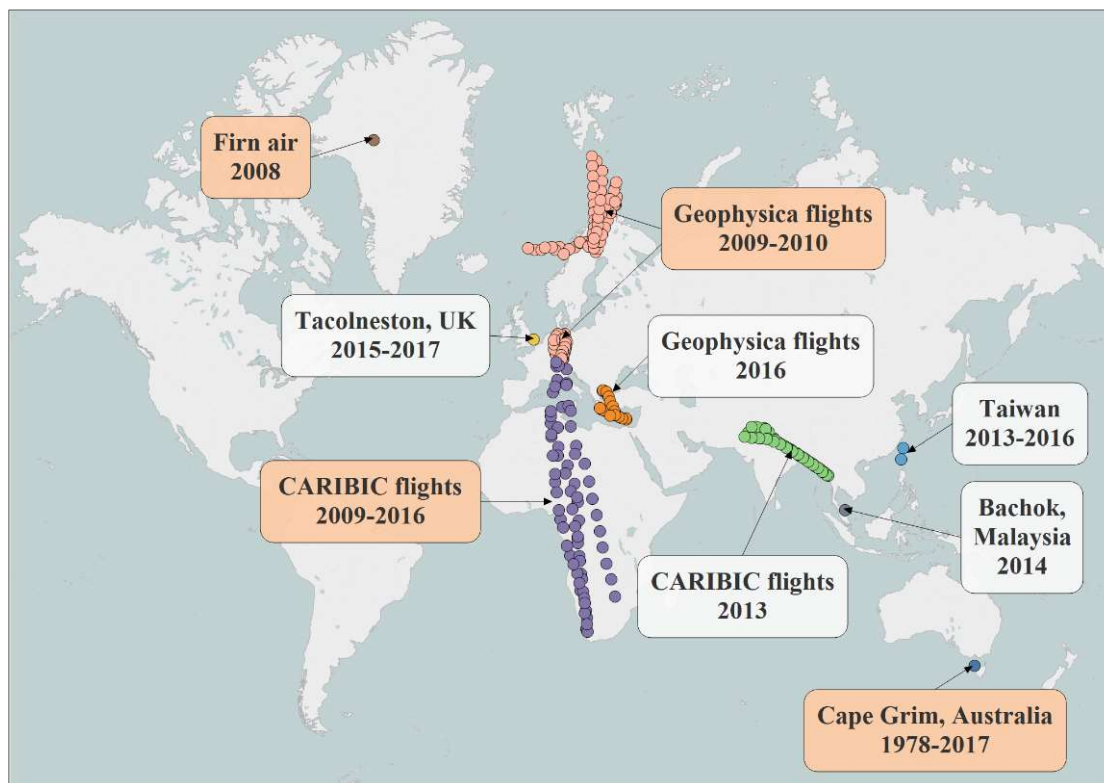2017), 2002.

United Nations Environment Programme (UNEP): Fifteenth Meeting of the Parties to the Montreal Protocol on
Substances that Deplete the Ozone Layer, Nairobi, 10-14 November 2003, New Ozone-Depleting Substances
that have been Reported by the Parties, UNEP/OzL.Pro.15/INF/2, [online] Available from:
http://www.42functions.eu/new_site/en/meetings/mop/mop15-index.php (Accessed 18 October 2017), 2003.

United Nations Environment Programme (UNEP): Amendment to the Montreal Protocol on Substances that
Deplete the Ozone Layer Decision XXVII/1, UNEP/OzL.Pro.28/CRP/10. [online] Available from:
http://conf.montreal-protocol.org/meeting/mop/mop-28/final-report/English/Kigali_Amendment-English.pdf
(Accessed 18 July 2017a), 2016.

United Nations Environment Programme (UNEP): Twenty-Eighth Meeting of the Parties to the Montreal
Protocol on Substances that Deplete the Ozone Layer, Kigali, 10–14 October 2016, Decision XXVIII/1 Further
Amendment of the Montreal Protocol. [online] Available from:
http://ozone.unep.org/sites/ozone/files/Publications/Handbooks/Montreal-Protocol-English.pdf (Accessed 21
July 2017b), 2016a.

United Nations Environment Programme (UNEP): Amendment to the Montreal Protocol on Substances that
Deplete the Ozone Layer Decision XXVII/1, UNEP/OzL.Pro.28/CRP/10. [online] Available from:
http://conf.montreal-protocol.org/meeting/mop/mop-28/final-report/English/Kigali_Amendment-English.pdf
(Accessed 18 July 2017), 2016b.

Vollmer, M. K., Rigby, M., Laube, J. C., Henne, S., Siek, T., Gooch, L. J., Wenger, A., Young, D., Steele, L. P.,
Langenfelds, L., Brenninkmeijer, C. A. M., Wang, J., Wyss, S. A., Hill, M., Oram, D. E., Krummel, P. B.,
Schoenenberger, F., Zellweger, C., Fraser, P. J., William, T., Doherty, S. O. and Reimann, S.: Abrupt reversal of
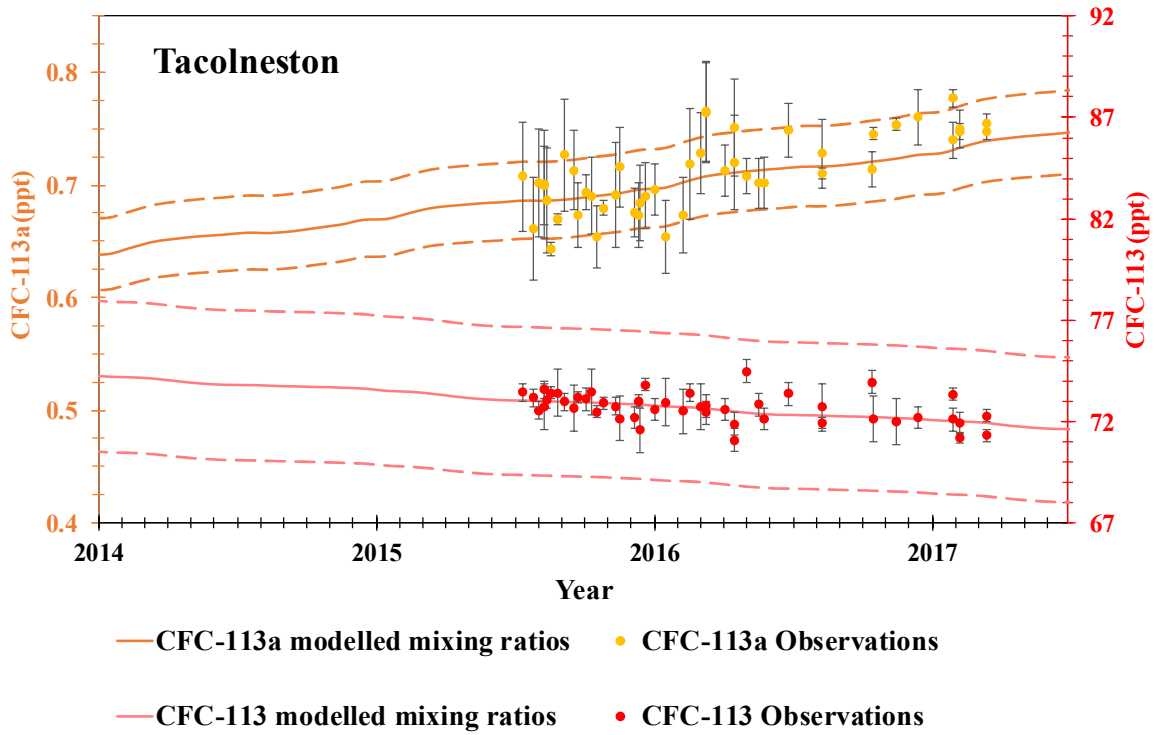HCFC-133a (CF_3CH_2Cl) in the atmosphere, Geophys. Res. Lett., 1–9, doi:10.1002/2015GL065846, 2015.

Figure 1. Sampling locations used in this study. Those locations that have been added since Laube et al. (2014)
are in white. Those shaded orange featured in, or have been extended since, the Laube et al. paper.

Table 1. Air sampling campaigns from which atmospheric CFC-113a mixing ratios were measured, including the data published in Laube et al. (2014).

Sampling campaign	Location	Longitude and Latitude	Dates	No. of samples	Nature of data
NEEM	Greenland	77.445° N, 51.066° W 2484m a.s.l.	14-Jul-~~/07/~~2008–30-Jul-~~/07/~~2008	3 closest to the surface	Firn air surface data
Cape Grim	Tasmania, Australia	40.683° S, 144.690° E	(07-Jul-~~/07/~~1978) 14-Mar-~~/03/~~2013–23-Feb-~~/02/~~2017	66 ~~in~~ total, 20 new	Southern Hemisphere ground-based site
Taiwan	East Asia	Hengchun, 22.0547° N, 120.6995° E, (2013, 2015) Cape Fuguei, 25.297° N, 121.538° E, (2014, 2016)	2013–2016	2013: 19 2014: 24 2015: 23 2016: 33	Northern Hemisphere ground-based sites
Tacolneston Tower	Norfolk, United Kingdom	52.3104° N, 1.0820° E	13-Jul-~~/07/~~2015–16-Mar-~~/03/~~2017	47	Northern Hemisphere tall tower site
Bachok Marine Research Station	Bachok, Malaysia	6.009° N, 102.425° E	20-Jan-~~/01/~~2014–03-Feb-~~/02/~~2014	16	Tropical ground-based site
Geophysica flights 2009-2010	North Sea	76-48° N, 28-0° E	30-Oct-~~/10/~~2009– 02-Feb-~~/02/~~2010	98	Research aircraft
Geophysica flights 2016	Mediterranean Sea	33-41° N, 22-32° E	01-Sep-~~/09/~~2016 06-Sep-~~/09/~~2016	23	Research aircraft
CARIBIC flights	Germany to South Africa	48° N-30° S, 6-19° E	27-Oct-~~/10/~~2009 28-Oct-~~/10/~~2009 14-Nov-~~/11/~~2010 20-Mar-~~/03/~~2011 10-Feb-~~/02/~~2015 13-Jan-~~/01/~~2016	14 7 13 14 15 7	Commercial aircraft

CARIBIC flights	Germany to Thailand	32-17° N, 70-97° E	21-Feb-/02/2013	14	Commercial aircraft
			21-Mar-/03/2013	7	
			09-Nov-/11/2013	14	
			05-Dec-/12/2013	14	
				14	

750

CFC-113a modelled mixing ratios   ● CFC-113a Observations
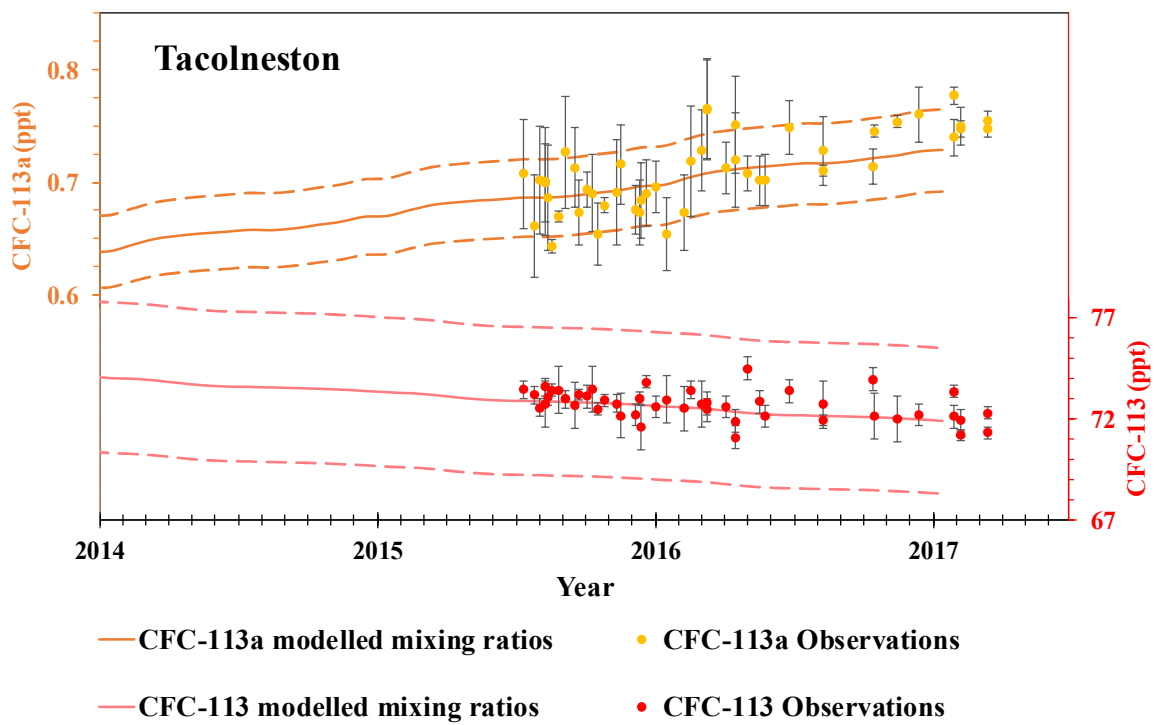
CFC-113 modelled mixing ratios   ● CFC-113 Observations

Figure 2. CFC-113a and CFC-113 modelled and observed mixing ratios at Tacolneston. The error bars represent the 1σ standard deviation. The modelled uncertainties are 5 % and are based on the model reproducing the reported mixing ratios of CFC-11 and CFC-12 at Cape Grim to within 5 % uncertainty (Reeves et al., 2005).
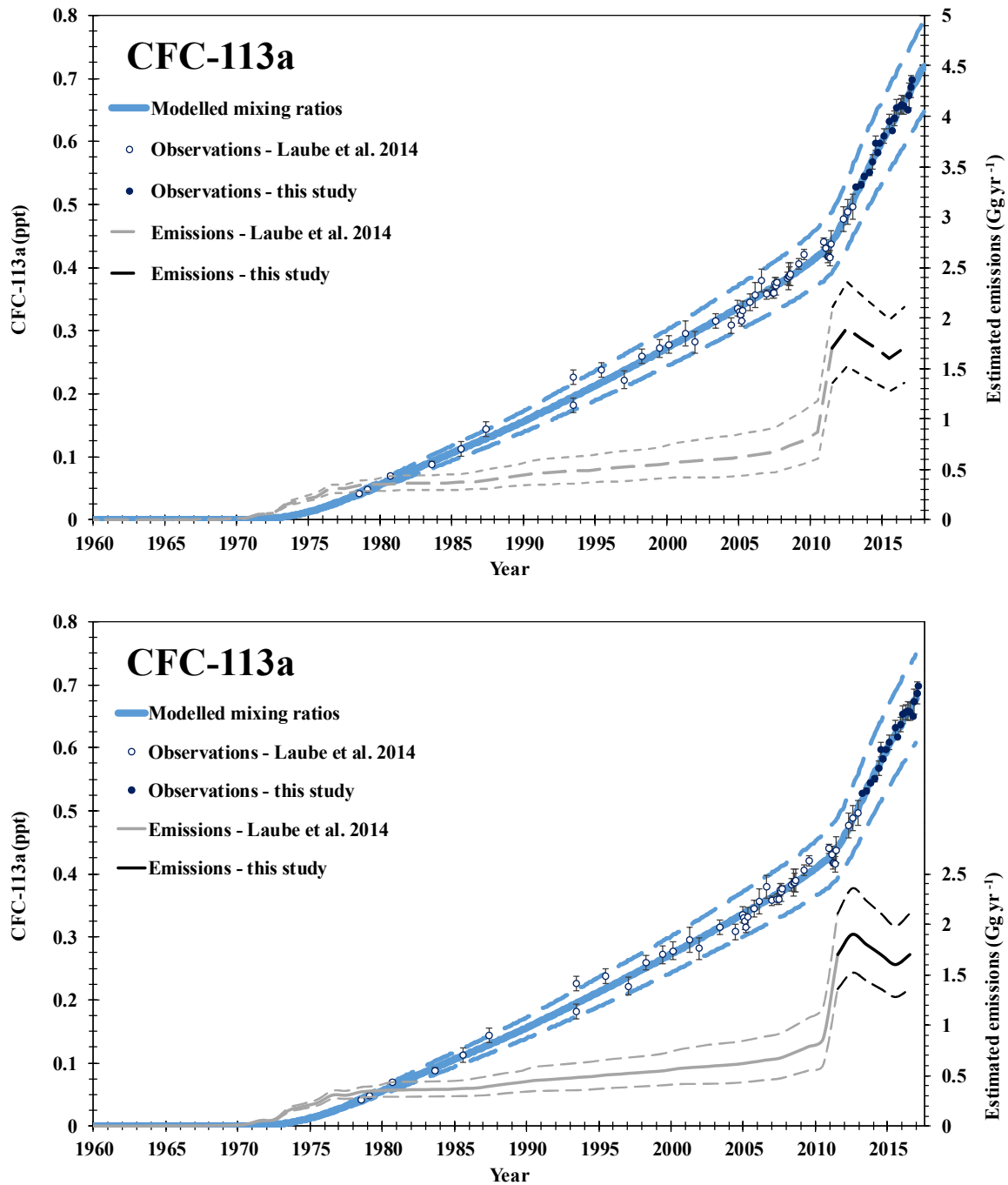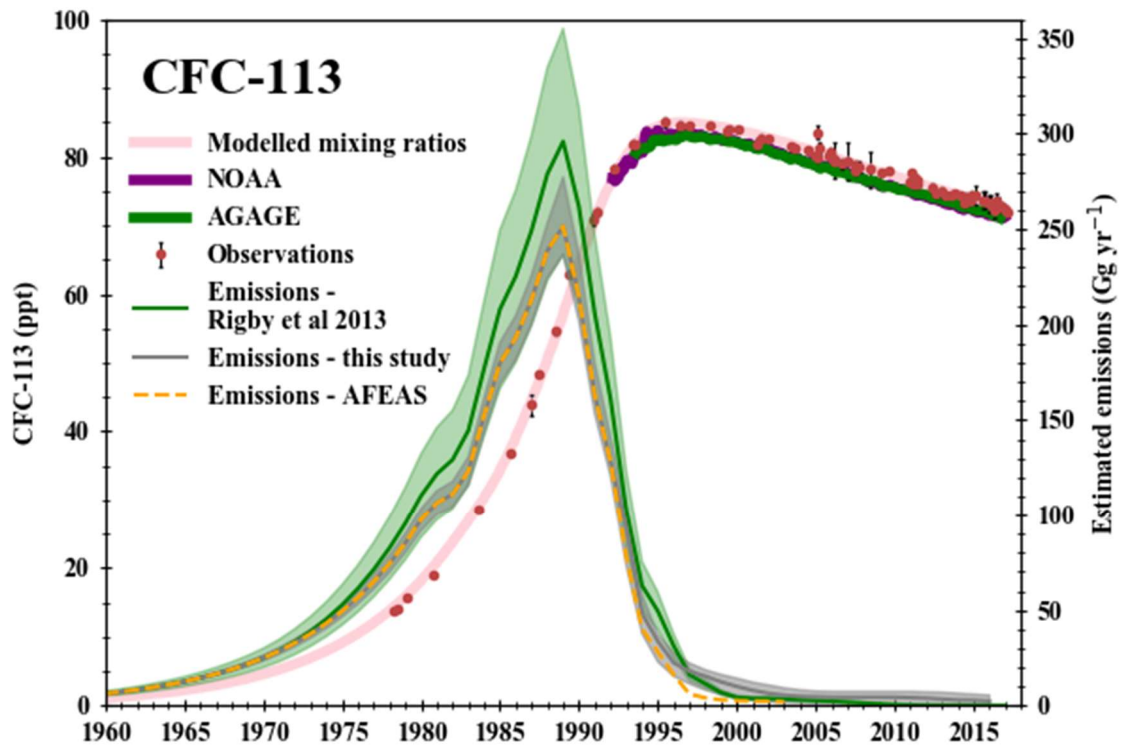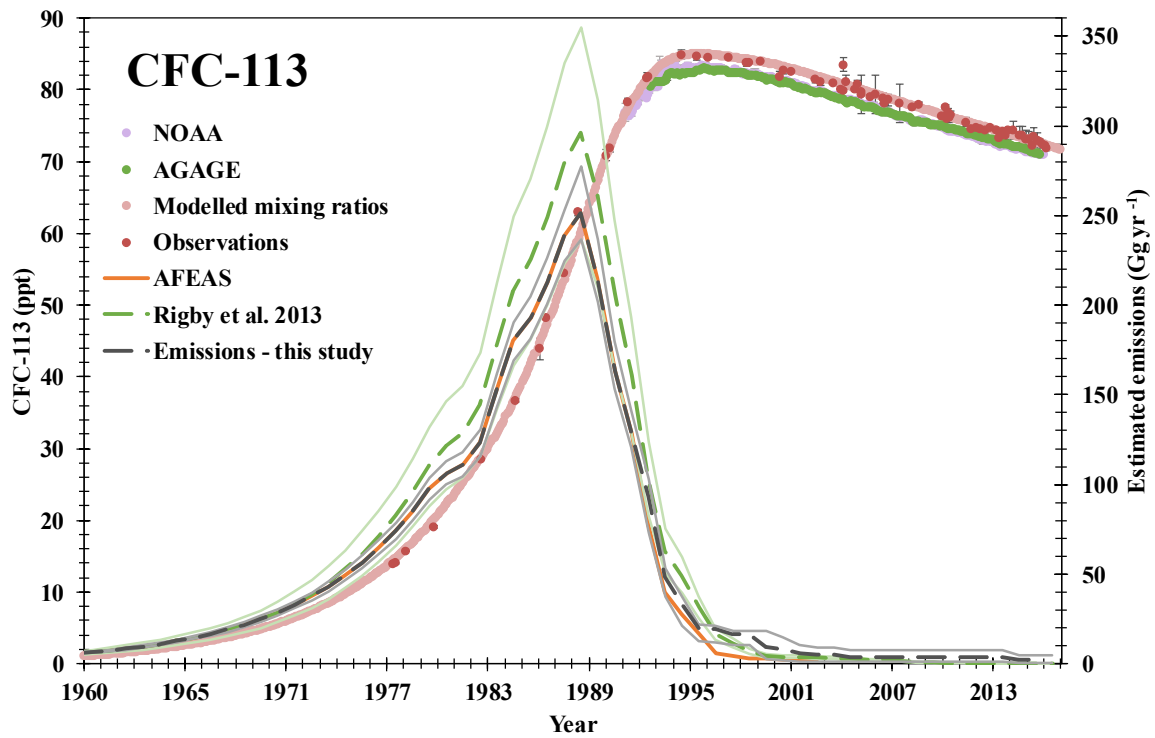
Figure 3. CFC-113a modelled and observed mixing ratios at Cape Grim 1960-2017 and estimated global annual emissions of CFC-113a. The observations are from July 1978-February 2017 with 1σ standard deviations as error bars. Data prior to 04-Dec-/12/2012 is from Laube et al. (2014). The blue solid line represents the modelled mixing ratios with uncertainties (dashed blue line). The dashed black and grey lines represent the modelled 'best fit' emissions with uncertainties (short-dashed). The method used for calculating the upper and lower emission bounds is in the supplementary material.
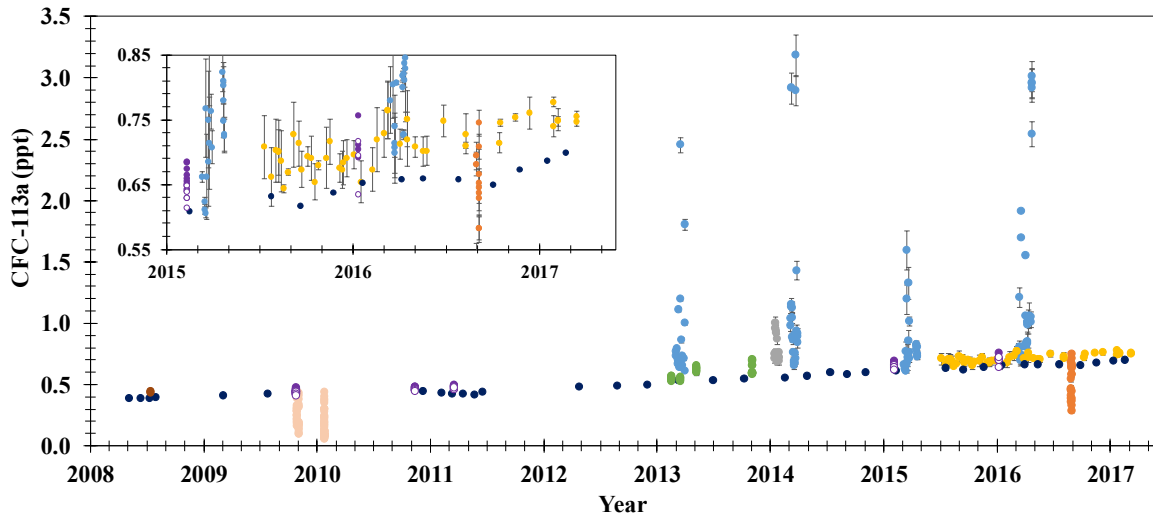
Figure 4. CFC-113 modelled and observed mixing ratios at Cape Grim 1960-2017 and estimated global annual emissions of CFC-113. The observations are from Cape Grim, Tasmania, July 1978-February 2017 with 1σ standard deviations as error bars. Also for comparison are the NOAA and AGAGE CFC-113 mixing ratios at Cape Grim and previous emissions estimates from AFEAS and Rigby et al. (2013) (based on AGAGE in situ

data) with 'likely' uncertainties (green lines). The dashed black line shows the modelled 'best fit' emissions with uncertainties (grey lines). The method used for calculating the upper and lower emission bounds is in the supplementary material.
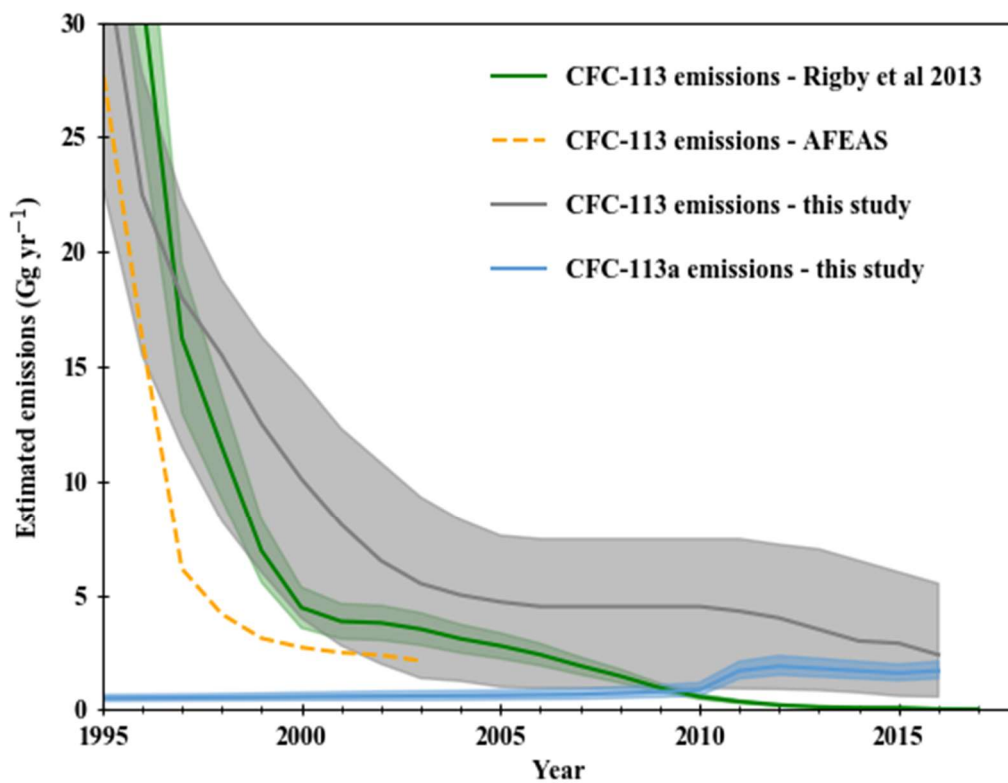
Figure 5. CFC-113 emissions from this study, AFEAS and Rigby et al 2013 and CFC-113a emissions from this study 1995-2016 with uncertainties.
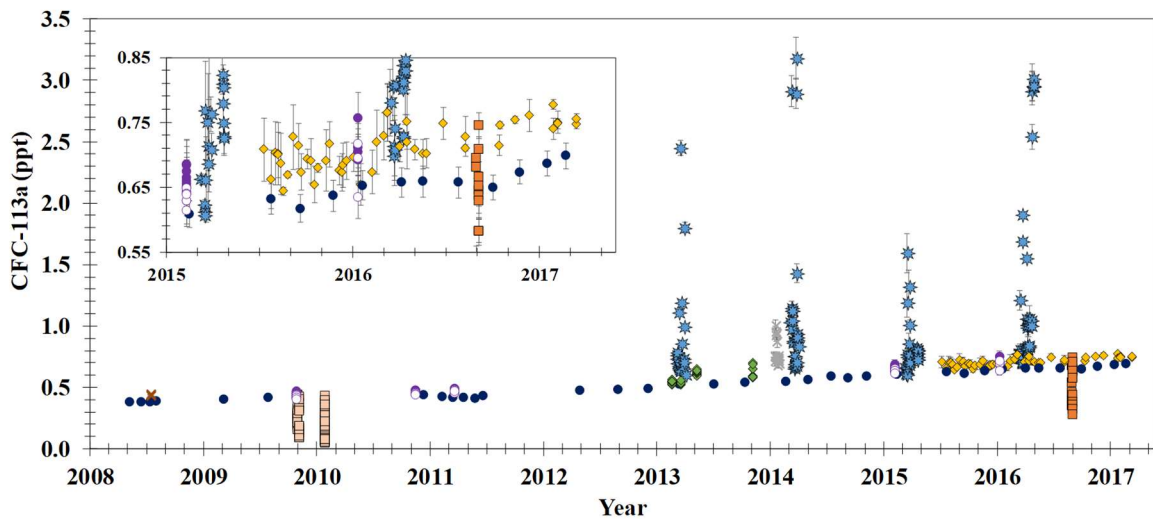
Figure 65. CFC-113a mixing ratios 2008-2017 from all the sources presented in this study with an inset of the period 2015-2017 to give an enlarged view of the Tacolneston data. The error bars represent the 1σ standard deviation.
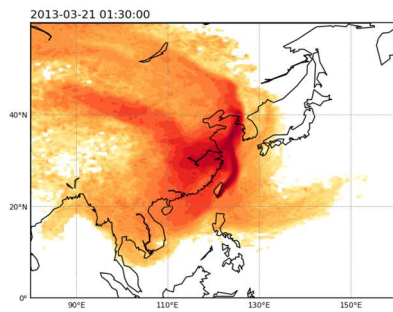
(a)   21-Mar-/03/2013

(b)   22-Mar-/03/2014
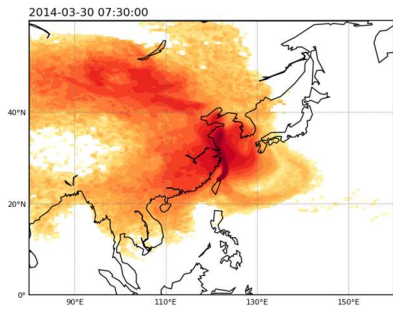
(c)   30-Mar-/03/2014
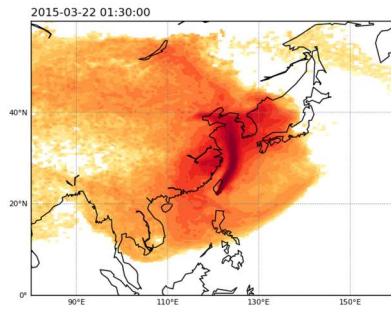
(d)   22-Mar-/03/2015
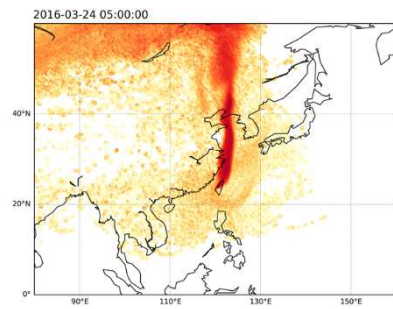
(e)   24-Mar-/03/2016
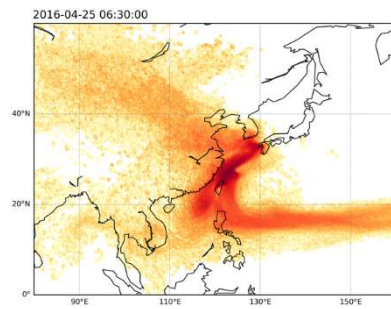
(f)   25-Apr-/04/2016
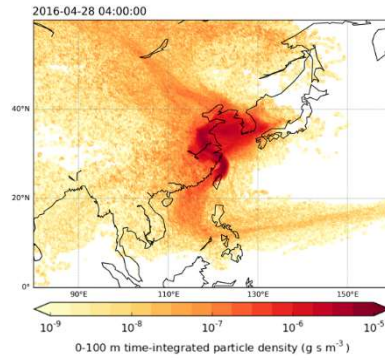
(g) 28-~~Apr- /04/~~2016

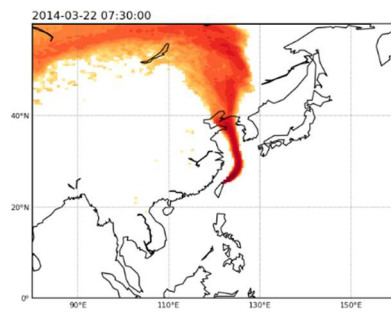Figure 7~~6~~. NAME footprints derived from 12-day backward simulations and showing the time integrated density of particles below 100 m altitude for the approximate times when samples were collected during the Taiwan campaign. (a), (c), (d) and (g) are examples of one enhanced CFC-113a mixing ratio in each year. (f) is the sample taken just before (g) when the air was coming from a different direction and the mixing ratio of CFC-113a was much lower. (b) and (e) are also examples of samples with lower CFC-113a mixing ratios. Arrows in Fig. 8~~7~~ show the mixing ratios of CFC-113a for these NAME footprints. For the rest of the NAME footprints see the supplementary material.
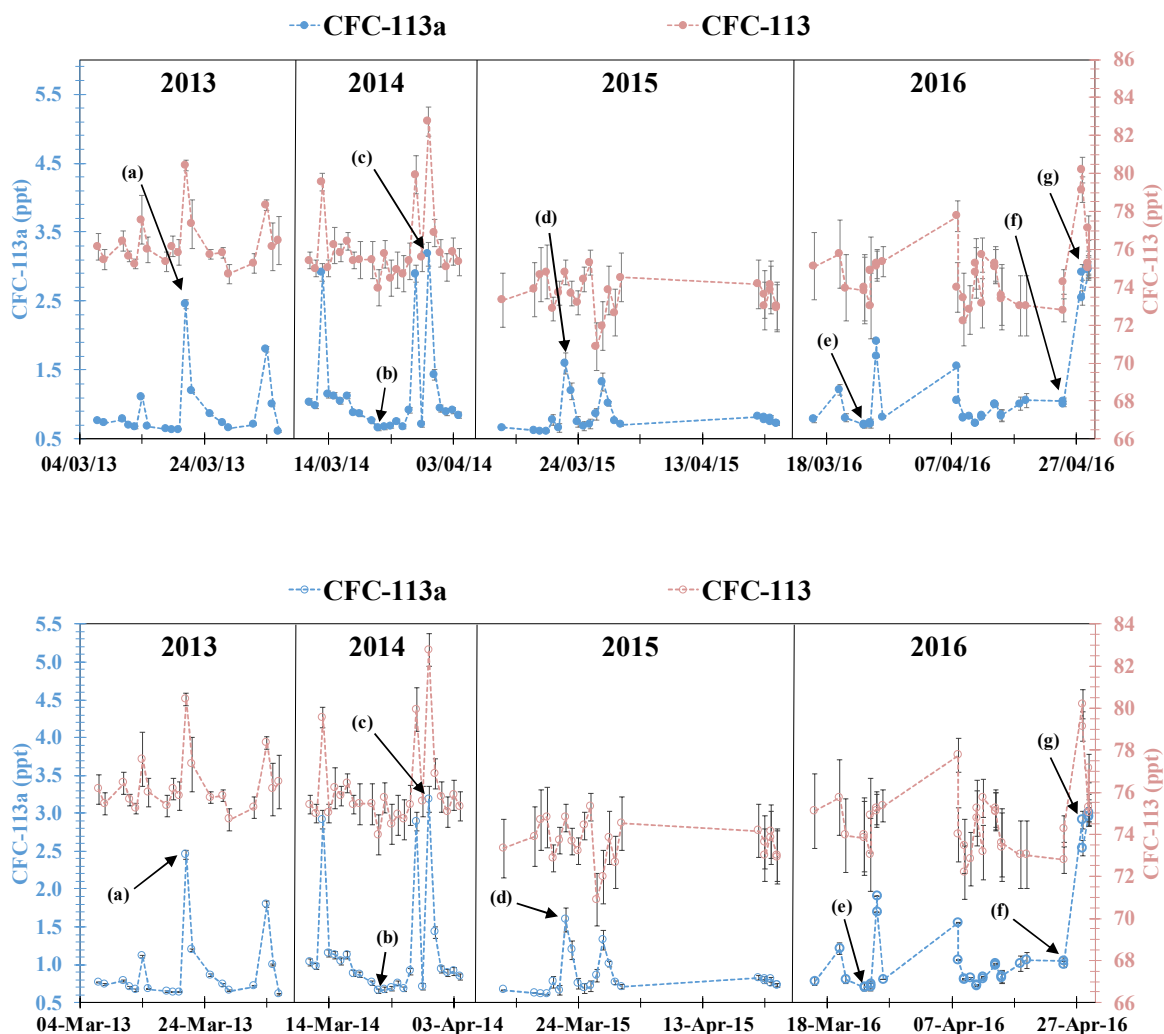
810

Figure 87. CFC-113a and CFC-113 mixing ratios observed in Taiwan in March and April 2013-2016. Arrows show the mixing ratios of CFC-113a that relate to the NAME footprints shown in Fig. 67. The error bars represent the 1σ standard deviation.

Table 2. Squared pearson correlations (R^2) of CFC-113a mixing ratios with other compounds in Taiwan 2013-
815   2016.

	2013	2014	2015	2016
CFC-113	0.866	0.909	0.013	0.429
HCFC-133a	0.923	0.923	0.891	0.637
HFC-134a	0.001	0.055	0.010	–
HFC-125	0.319	0.219	0.016	0.850
CFC-114a	–	–	0.754	0.386
HCFC-123	–	0.013	0.217	0.202
HCFC-124	–	0.537	0.833	0.078
No. of data points	19	24	23	33
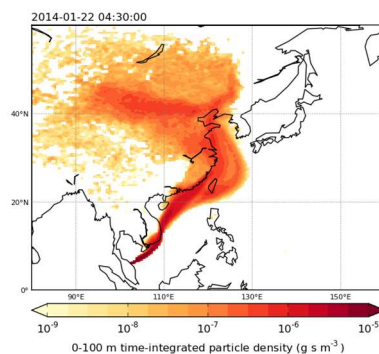
Figure 98. NAME footprint derived from 12-day backward simulation and showing the time integrated density of particles below 100 m altitude on 22 Jan /01/2014 during a period of elevated CFC-113a mixing ratios at Bachok, Malaysia.

Interactive comment on "Continued increase of CFC-113a (CCl$_3$CF$_3$) mixing ratios in the global atmosphere: emissions, occurrence and potential sources" by Karina E. Adcock et al.

Anonymous Referee #1

Received and published: 15 December 2017

Review for Adcock et al., Continued increase of CFC-113a (CCl3CF3) mixing ratios in the global atmosphere: emissions, occurrence and potential sources

The authors provide updated data sets for CFC-113a from various observation platforms and use these to update global abundances and emissions. These show that after a rapid increase in CFC-113a emissions in approximately 2010, they have now leveled off. Interhemispheric gradients and pollution events at the Asian stations are presented. Potential sources of CFC-113a are discussed, which however remain speculative.
The paper is an informative and useful update on a compound, little is known about. This study adds to other recent studies of newly-discovered compounds with no purposeful end use, and shows the necessity to distinguish the two isomers in order to de-tangle their stories.

The paper is well written and understandable, but could benefit from some consolidating of information, in particular in the sections where the potential sources are discussed.

The topic is well researched and the authors have done a good job in bringing the many data sets together. The supplement adds more information and data are made available. This paper is well suited for publication in ACP and I have only minor comments, which, once thoroughly handled, should make this acceptable for publication.

1. Introduction: A brief discussion on the loss mechanisms of CFC-113a would be helpful to understand the cycling of this compound through the atmosphere, in particular for the discussion on CFC-113a in the stratosphere.

We agree with the reviewer that a brief discussion on the loss mechanisms would be helpful and we have added a sentence explaining the loss mechanisms of CFCs in general to the introduction (lines 47-49). We thought it would fit better in the introduction if we talked about the loss mechanisms of CFCs in general rather than CFC-113a specifically.

"CFCs have negligible loss mechanisms in the troposphere and only break down when they reach the stratosphere where they are exposed to strong ultraviolet light and decompose mostly through photolysis and reaction with O^1D (Ko et al., 2013)."

2. p. 2, l. 77: What kind of pumps were used for the various sampling sites?

We agree with the reviewer that information of the kinds of pumps used would be a good idea. Various pumps were used for the different sampling activities and they have been described in previous articles: Cape Grim (Allin et al., ACP, 2015); Taiwan, Tacolneston and Bachok (Oram et al., 2017); Geophysica (Laube et al., ACP, 2010 (Fractional Release…)); CARIBIC (Brenninkmeijer et al., 2007).

This sentence was added to the methods section (lines 84-86)

"Various pumps were used for the different sampling activities, all of which have been thoroughly tested for a large range of trace gases (e.g. Brenninkmeijer et al., 2007; Laube et al., 2010; Allin et al., 2015 and Oram et al., 2017)."

3. p. 2, l. 84: Please elaborate more on the use of different methods (chromatography columns) particularly to give insight which samples / batches of samples were measured one way or the other.

We agree with the reviewer that more information of the different columns should be added. We have added the Cape Grim CFC-113a and CFC-113 measurements on the GS GasPro column (length ~50 m, ID 0.32 mm) and the KCl-passivated Al_2O_3-PLOT column (length: 50 m, ID 0.32 mm) to the spreadsheet in the supplementary material. A range of Cape Grim samples were reanalysed on the AlPLOT column and showed very good agreement with the previous GasPro column-based measurement with comparable precisions and no apparent offset. We have also added two tables to the supplement spreadsheet: one for the Taiwan measurements and one for all the other samples showing which columns were used for which measurements.

Some of the samples collected in Taiwan in 2013 were also measured on another GC-MS. HCFC-133a, HFC-134a & HFC-125 were measured on the Entech GCMS. Some information about this instrument was added to the methods section (lines 101-103).

"The samples collected in Taiwan in 2013 were also measured on the Entech-Agilent GC-MS system operating in electron ionisation (EI) mode. This consists of a preconcentration unit (Entech model 7100) connected to an Agilent 6890 GC and 5973 quadrupole MS (Leedham Elvidge et al., 2015)."

4. p. 2, l. 86: Primary calibration scale: Describe, or refer to the literature, on how the primary reference material was produced (how many primary standards, at what ppt level), and what

the estimated accuracy is. Was the CFC-113a pure or contaminated with CFC-113? Accuracy of the NOAA calibration scale for CFC-113.

We believe all of this information is already available and it is not necessary to add it to the paper. For CFC-113a all of the requested information was published in Laube et al., 2014 who reported the first measurements of this compound in the atmosphere. For CFC-113, which we are reporting on a NOAA scale, all of the information is publicly available from the NOAA ESRL websites. NOAA calibration scales are internationally widely recognised and Laube et al., 2013 demonstrated that UEA measurements of CFC-113 on samples collected at Cape Grim match respective NOAA observations of that gas quite closely and over several decades with a small offset.

5. p. 2, l. 89: How did the repeated standard measurements feed into the calculation? Were these referenced against other standards, or were chromatographic peak sizes assumed constant over a day? How many standards were measured per day?

We have added these sentences to the methods section (lines 105-107)

"On a typical day, the working standard is measured five to eight times, between every two or three samples. The sample peak sizes are measured relative to the standards measured just before and after them. The working standard is used to correct for small changes in instrument response over the course of a day."

As described in the manuscript (lines 109-111), the repeated standard measurements feed into the calculation as follows: "The measurement uncertainties are calculated the same way for all measurements and represent one sigma standard deviation. They are based on the square root of the sum of the squared uncertainties from sample repeats and repeated measurements of an air standard on the same day."

6. p. 2, Methods. If not published previously, please provide a few more analytical details. How well do CFC-113 and CFC-113a separate on the two columns used, which fragments were measured? If available, provide a spectrum of CFC-113a; how well does it compare with one from the literature? If some ions were used for both isomers, what were their sensitivities if scaled to the same mole fraction on the MS used for this study? Does 'pure' CFC-113 normally have CFC-113a impurities or vice versa? Provide any other information that can be useful for comparison with other networks, which may not be able to separate the two isomers (this could all be in the supplement).

Almost all available information on GasPro column-based measurements has already been published in Laube et al., 2014. We only add here that a possible interference could arise when measuring CFC-113a on that column using m/z 116.91 if concentrations of the nearby eluding HCFC-123 are high. This was the case for a small number of samples analysed for this work and those measurements were either a) repeated using the interference-free m/z 120.90, b) replaced with measurements on the other column, or c) excluded. The KCl-passivated Al_2O_3-PLOT column separated CFC-113 and CFC-113a well, we observed no interferences and used m/z 116.91 for quantification. We have added this information to the methods section (lines 94-99). Whether pure CFC-113 normally contains CFC-113a impurities would require diluting and analysing multiple samples from multiple companies which exceeds the scope of this study. We would however be very open to carry out a direct intercomparison experiment if approached.

7. p. 3, l. 95: How many CGAA samples were added, were these equally spaces over the 2012 –
    2017 period. Were some of the earlier samples from Laube et al., 2014 re-analyzed and if so,
    how did these agree with the present study?

We added this sentence to the methods section (line 116-117)

"From 2013 to 2017, 20 samples were collected at Cape Grim at irregular intervals of between one
to five months apart."

Some of the earlier samples from Laube et al 2013 and Laube et al 2014 were re-analysed on the
KCl-passivated Al_2O_3-PLOT column (length: 50 m, ID 0.32 mm). They showed very good agreement
with the previous GasPro column-based measurement with comparable precisions and no apparent
offset. We have added this information to the methods section (lines 122-124). We have added the
Cape Grim CFC-113a and CFC-113 measurements on the GS GasPro column (length ~50 m, ID 0.32
mm) and the KCl-passivated Al_2O_3-PLOT column (length: 50 m, ID 0.32 mm) to the spreadsheet in the
supplementary material.

8. p. 3, l. 109: Which is day and which is month in the xx/zz/yyyy date description. This can be
    rather confusing (and seems to be reversed in the supplementary tables), why not spell out the
    month(s), like e.g. p. 7 l. 290? This confusing style re-appears throughout the document.

We agree with the reviewer and all the dates in the article and in the supplementary material have
been changed to the format dd-mmm-yyyy. We have not changed the date format in the NAME
model figures but have added a sentence to the methods section (lines 208-209) that says "Dates in
the NAME footprint maps are presented in the format yyyy-mm-dd and use UTC time."

9. p. 3, l. 124: The very first mentioning of CFC-113 here without any prior motivation for this
    leaves the reader confused.

We refer the reviewer to the abstract, which states that "We compare the long-term trends and
emissions of CFC-113a to those of its structural isomer, CFC-113 ($CClF_2CCl_2F$), which still has much
higher mixing ratios than CFC-113a, despite its mixing ratios and emissions decreasing since the
1990s."

We also modified the first sentence in this section (lines 150-151) to:

"A two-dimensional atmospheric chemistry-transport model was used to estimate, top-down, global
annual emissions of CFC-113a and CFC-113 for the purpose of comparing the emissions of the two
isomers."

10. p. 3, l. 125: Even though explained in details in the cited references, please provide a couple of
    sentences describing this model. Are the emissions derived from an inversion, was a prior used?

For this comment we mostly moved information from the supplementary material into the paper to
give a more detailed description of the model (lines 151-156).

"The model contains 12 horizontal layers each representing 2 km of the atmosphere and 24 equal-
area zonally averaged latitudinal bands. The modelled mixing ratios for the latitude band that Cape
Grim is located within (35.7° S–41.8° S) were matched as closely as possible to the observations at
Cape Grim (40.7° S) by iteratively adjusting the global emissions rate until the differences between

1000   the modelled mixing ratios and the observations were minimised. For more details about the model
        see Newland et al. (2013); and Laube et al. (2016).”

        11. p. 3, l. 127: What is the UEA Air Archive?

1005   We have changed the sentence (lines 117-119):

        “The CFC-113 mixing ratios (1978-2017) from analyses of archived air samples collected at Cape
        Grim, Tasmania and analysed at the UEA, together with NOAA flask data, and AGAGE *in situ* data are
        also included to compare the two isomers.”
1010
        In addition, all later references to the “UEA Air Archive” have been changed to the “UEA Cape Grim
        data set”.

        12. p. 3, l. 126: Have the CFC-113 mixing ratios been published previously, or are these
1015   measurements part of the present study?

        Most of the UEA Cape Grim CFC-113 mixing ratios were published in Laube et al., 2013, which also
        included the aforementioned comparison to NOAA measurements from the same site.

1020   We have added this sentence to the methods section (lines 121-122)

        “Most of the CFC-113 UEA Cape Grim data set was previously published in (Laube et al., 2013).”

        13. By reading this sentence it is not a priori clear if AFEAS has also provided bottom-up emissions
1025   for CFC-113a.

        AFEAS has not provided bottom-up emissions for CFC-113a. That part of the sentence refers only to
        CFC-113. We have now separated it into two sentences (lines 157-162).

1030   “We now update the CFC-113a emission estimates using an additional four years of Cape Grim
        measurements. The CFC-113 emissions are estimated using CFC-113 mixing ratios at Cape Grim for
        1978-2017 from the UEA Cape Grim dataset and compared with bottom-up emissions estimates
        from the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS,
        https://agage.mit.edu/data/afeas-data).”
1035
        14. p. 3, l. 131: What do the authors mean by ‘isolated’?

        We agree with reviewer and have replaced the word in question with the more appropriate
        “remote” (line 169).
1040
        15. p. 3, l. 138: Please explain why Tacolneston can be considered of NH background air given that
             there is apparently a gradient of CFC-113a in the NH. The absence of pollution events at
             Tacolneston may make this site representative for background air at that latitude at most. See
             similar issue p. 6 l. 268. ‘Spikes’ is a rather confusing term.
1045
        We agree with the reviewer and have changed this sentence (lines 177-178):

        “Tacolneston can be considered to be representative of Northern Hemisphere background mixing
        ratios of CFC-113a **for that latitude** as there are no **significant enhancements** in mixing ratios (Figure
1050   2).”

In addition, all later references to "spikes" have been changed to "enhancements".

16. p. 4, l. 141. I am not convinced about the shift to more southerly latitudes. Is this an assumption that was made, or a result of the model? If the former, on what basis is this assumption founded? If the latter, how can a model using Cape Grim data give such detailed results about the NH distribution, particularly when apparently Cape Grim is insensitive to the NH distribution as stated on p. 3, l. 133? The mentioning of Tacolneston observations here is confusing also, how could these be used to determine the NH latitudinal distribution over decades if there are only a few years of measurements? Also the comparison to Taiwan seems inappropriate if the authors use median values for that site rather than a 'Taiwan background'. Overall there seem to be too many degrees of freedom here to be able to pin-point such a detailed evolution of NH latitudinal gradients.

We agree with the reviewer that there are many degrees of freedom here, which is why we state at the end of the paragraph that "It should be noted that while there is evidence that supports the emission distribution used here, there might be alternative distributions that result in equally good fits to the trends, particularly in the earlier part of the record." (lines 192-194). We also note, however, that for the later part of the trend (which is the main focus of this manuscript) the assumed emission distribution gives the best match to NH mixing ratios both in Tacolneston and in Taiwan. We would also like to point out that medians are mentioned nowhere in this paragraph, when we mention "measurements from Taiwan" we mean that there are significant enhancements in CFC-113a mixing ratios in Taiwan indicating continued emissions so it is not unreasonable to move emissions to this latitude band in the model. We have modified this sentence (lines 184-186):

"There are significant enhancements in CFC-113a mixing ratios in our measurements from Taiwan indicating continued emissions in this region (Section 3.2.1) which is consistent with emissions in this latitude band in the model."

17. p. 4, l. 171 (Overall : : :) Is this sentence necessary?

We agree with the reviewer that this sentence is not necessary and we have deleted this sentence and modified the next sentence (lines 216-218):

"Between 1978 and 2009 the average rate of increase was 0.012 ppt yr^{-1}; then between 2010 and 2017 the rate had risen 3-fold to about 0.037 ppt yr^{-1}."

18. p. 4, l. 176: Is the 0.03 ppt/yr increase a result of the model or some other kind of fit?

The first measurement at Tacolneston was 0.71 ppt on 13-Jul-15 at 11:03 and the most recent measurement for which we have a CFC-113a mixing ratio is 0.76 ppt on 16-Mar-17 at 16:30. The calculation is the difference between these two values (0.76-0.71=0.05ppt) divided by 20 (because there are 20 months between these two measurements) to give an increase per month. Then this is multiplied by 12 to give an average increase per year of 0.03 ppt.

We have changed the sentence (lines 219-221):

"Although measurements at Tacolneston were made for a shorter time period (20 months), it also experienced an increase in CFC-113a mixing ratios of 0.03 ppt yr^{-1} over the period July 2015 to March 2017 **based on start and end points** (Figure 2)."

19. The mentioning of 0.06 ppt/yr for Taiwan is somewhat missleading as it makes the reader believe that mixing ratios have grown more rapidly there, but isn't the Taiwan growth most likely tagged with a large uncertainty given the fact that the authors take the median values rather than deriving a real 'background' record for Taiwan.

We agree with the reviewer, we do not have enough data to reliably derive background trends. We have deleted the sentence about Taiwan. We has also deleted the sentence explaining the median average in the methods section (lines 146-148) because it is the only place the Taiwan median is used.

"the median mixing ratios of CFC-113a in Taiwan increased on average by 0.06 ppt yr^{-1} from 2013 to 2016."

"The median mixing ratios are used for the measurements made at the Taiwan sites to decrease the influence of the large spikes in CFC-113a mixing ratios that occurred during these campaigns (Section 3.2.1). All other averages are calculated using the mean."

20. p. 4 l. 182: The presentation of the result would evolve less confusing if the emissions were first mentioned before rates of growth of these emissions are discussed. Also, the mentioning of an average of 1.7 Gg/yr does not say anything about the variability of the emissions in these years (There is not a single mentioning of emissions for a specific year). It would be helpful to learn how much they varied in these years, by e.g. giving the range of emission for these few years. I presume that the numbers in parentheses are some uncertainty ranges, or are these the ranges they vary over that time?

The variations between years were not included because they are not statistically significant but we have now included them. We have also edited this section to include some more information on estimated emissions in specific years (lines 227-233).

"The modelled global annual CFC-113a emissions began in the 1960s and increased steadily at an average rate of 0.02 Gg yr^{-1} yr^{-1} until they reached 0.9 Gg yr^{-1} (0.6-1.2 Gg yr^{-1}) in 2010 followed by a sharp increase to 0.52 Gg yr^{-1} yr^{-1} from 2010 to 2012 when emissions were 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1}) (Figure 3). We find that between 2012 and 2016, modelled emissions were on average 1.7 Gg yr^{-1}. The best model fit (minimum-maximum) suggests some minor and statistically non-significant variability between 1.6 Gg yr^{-1} (1.3-2.0 Gg yr^{-1}) in 2015 and 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1}) in 2012. See the supplementary material for more details."

The model was run three times: once for the most likely emissions, once for the smallest possible emissions and once for the largest possible emissions. These are the values in parentheses. How the three versions of emissions were calculated is explained in the supplementary material and we have added an explanation of how the modelled uncertainties are calculated to the methods section (lines 162-166).

21. p. 5, l. 185: Can this 2% offset (using the same primary calibration scale) be related that perhaps NOAA measures the combined CFC-113a/CFC-113 isomers?

The 2% has remained approximately the same over time which means it's unlikely to be caused by combining CFC-113a and CFC-113 because their mixing ratios have been changing over time and

therefore the offset would most likely change as well. The offset is most likely due to analytical uncertainties when transferring calibration scales between labs. We decided not to include this in the paper as it is just speculation and the offset has been discussed in Laube et al., 2013.

22. Also, there does not seem to be a description anywhere on how the NOAA scale for CFC-113 was adopted, and what the propagation uncertainties of this procedures might be.

The working standard was directly purchased from NOAA and the analytical uncertainty provided by NOAA was 0.4 %. This does however not include the uncertainty of the NOAA calibration scale itself, which is currently not quantifiable as the content of CFC-113a in all standards is unknown. CFC-113a does have however a distinctly different EI mass spectrum to CFC-113, so it is unlikely that the CFC-113 used for the NOAA calibration would contain a large fraction of CFC-113a. It might however be enough to explain a 2 % offset, but the confirmation of that is outside the scope of this paper.

23. Which way is the offset, which network reports higher values?

We added more information into this sentence to say that UEA is the one with the higher mixing ratios (lines 246-248).

"There is a small offset of 2 % between the NOAA data and the current UEA Cape Grim dataset, **with the UEA Cape Grim dataset being slightly higher**, similar to the offset reported previously (Laube et al., 2013)."

24. p. 5, l. 200: It would be very informative to see a graphical comparison of the emissions for the two compounds over the last years, for example by adding those of CFC-113 to Fig 3, or to somewhere plot the ratio of the CFC-113a/CFC-113 emissions.

We agree with the reviewer and have created a new figure with all the CFC-113 emission estimates and the CFC-113a emission estimates from 1995 to 2016. This figure serves two purposes: 1) It makes the differences between the CFC-113 emission estimates for more recent years easier to see and 2) It graphically compares the CFC-113 and CFC-113a emission estimates for the last few years.

25. p. 5, l. 211: This is confusing, if the AFEAS data are used as the CFC-113 emissions in the model, then the sentence that follows does not make sense. Do the authors perhaps mean that the modeled emissions agree closely with the AFEAS bottom-up emissions?

We agree with the reviewer that the current wording is potentially misleading and have added a sentence to the text to make this clearer (lines 266-267).

"Therefore, the emissions used in our study here are the AFEAS emissions up until 1992. From 1992 onwards they are based on the best model fit to the UEA Cape Grim observations."

26. Fig. 4: colors are very hard to distinguish, for example, colors for NOAA and modelled mixing ratios seem the same. Also, filled circles don't appear as such due to their close proximities. Dashed lines appear as dash-dotted in the legend. The matching of modeled and AFEAS data is perplexing – are AFEAS data used as prior? In which year does AFEAS end, 2000; it is not possible to see this on the graph? I see only one green Rigby uncertainty line. Are the uncertainties shown for the present study based on the 'likely' or 'possible' range (p. 5 l. 22) or something else?

We agree with the reviewer and have changed the figure. The colours of the NOAA observations have been changed to a darker purple. The filled circles have been changed to lines. The legend has been changed so the emissions appear as dashes. The AFAES data is used as prior up until 1992 so they are the same as this study until then and then they diverge. This study has higher emissions after 1992 and AFEAS ends in 2003. The differences in the emissions estimates are not clear for the later years because they appear so close together on the graph. We have created a new figure with the CFC-113 and CFC-113a emission estimates for 1995-2016 to make graphical comparison clear. The lower Rigby uncertainty line is very close to this study's lower uncertainty line, which is why it is difficult to see. We have changed the emissions uncertainties to a filled area to make this clearer. We also changed the axis range of the observations to move them down slightly so they do not overlap with the emissions as much. The uncertainties for the present study are for the likely range. We have added the word "likely" to the figure caption.

27. p. 5, l. 221: Lifetime work was really done by SPARC, it might be better to cite that work.

We agree with the reviewer and have changed the reference to the SPARC 2013 report.

28. p. 5, l. 234: Do you mean 'related to CFC-113 emissions from (old) banks, i.e impurities of CFC-113a in CFC-113? This would not agree with their historic emission ratios. Please clarify.

We agree with the reviewer that this is not clear. We do not mean "related to CFC-113 emissions from old banks". We mean "related to co-emission from HFC production or agrochemical production as discussed in section 4". We have edited this sentence to be more specific (line 295).

"It should be noted that CFC-113 is not the focus of this study, but we do find that emissions of it persisted until 2017, which leaves room for the possibility that some of the recent emissions of CFC-113a are related to CFC-113 emissions, **possibly through HFC production or agrochemical production (see Section 4)** similar to findings for other isomeric CFCs (Laube et al., 2016)."

29. p. 6, l. 243: I suggest to phrase the other way: When there are spikes, then the NAME model : : :.

We agree with the reviewer and have rephrased this sentence (lines 305-308):

"In general, when there are enhancements in CFC-113a mixing ratios then the NAME footprints usually show that the air most likely came from the boundary layer over eastern China or the Korean Peninsula as shown in (a), (c), (d), and (g) for example."

30. p. 6, l. 252: Were compounds other than those listed in Table 2 also looked at?

Yes, compounds other than those listed in Table 2 were also looked at. Only the ones that we considered relevant are included in Table 2 and discussed in the text. We have edited this sentence to say that over 50 halocarbons were measured in samples from Taiwan (lines 316-319).

"After investigating correlations of CFC-113a with **over 50** other halocarbons in samples from Taiwan we found CFC-113a mixing ratios correlate well (R^2>0.750) in multiple years with those of CFC-113 and HCFC-133a (CH_2ClCF_3) indicating a possible link between the sources of these compounds (Table 2)."

31. p. 6, l. 277: 'generally': Does this mean that this was not always the case and that some Cape Grim results were higher than Tacolneston. From Fig 5 inset, it is not easy to see this.

Cape Grim is not always higher than Tacolneston. There is one data point in January 2016 when Cape Grim is higher and other measurements when the error bars overlap. The Tacolneston and Cape Grim measurements were not collected on the same days as each other so to compare them we used the dates which were closest to each other timewise.

We have changed the word in the text from "generally" to "almost exclusively (though often indistinguishable within uncertainties)", (lines 348-349).

32. Is the dark filled circle at the beginning of 2016 at _0.75 ppt from Cape Grim (with uncertainties smaller than the plotting symbol)?

The uncertainties were not smaller than the plotting symbol they just were not included. We thank the reviewer for spotting this omission. We have now changed the figure to include the uncertainties.

33. l. 279: replace 'higher' by 'lower'.

We have replaced the word "higher" with "lower".

34. p. 7, l 289: It is unclear, if only the three surface samples were used here for the interhemispheric comparison, or a historic reconstruction of the NH based on more samples. If only the surface samples were use, the mentioning of 'trend' is not adequate.

The interhemispheric comparison is from a historic reconstruction of 16 firn air samples collected at depths down to 76 metres. Only the three surface measurements were included in the figure to compare to other atmospheric measurements.

We have edited the sentence to make this clearer (lines 358-361):

"Laube et al. (2014) already found an interhemispheric gradient in CFC-113a using four of these CARIBIC flights 2009-2011 and furthermore discovered that the increasing trend of CFC-113a at Cape Grim, lagged behind the increasing trend inferred from the firn air samples, **collected to a depth of 76 metres**, from Greenland, in the Northern Hemisphere."

35. Also, Greenland firn air samples are here declared as 'representative of background Northern Hemisphere CFC-113a mixing ratio', which (similar to the same statement for Tacolneston) seems to be in contradiction to the assumption of latitudinal gradients in the NH.

We agree with the reviewer and have changed this sentence (lines 363-365):

"They will also be representative of background Northern Hemispheric CFC-113a mixing ratios **for that latitude** as the Greenland firn air location was isolated from any large industrial areas with potential sources of CFC-113a."

36. The samples are hard to see in Fig. 5, perhaps but a year in the legend for 'Greenland (surface)'.

We agree with the reviewer and have changed the legend from Greenland (surface) to Greenland 2008 (surface).

37. p. 7, l. 319: What is the 's' in parentheses?

1305   We have changed "process(s)" to "processes" (lines 399-401):

"This means that there are **processes** either producing or involving CFC-113a that lead to continuing emissions of substantial amounts of this compound, especially in East Asia."

1310   38. p. 8, l. 334: I disagree with the statement on l. 333 ff, that the absence of a correlation is not what we would expect. Before, the authors rightly state, that the correlation between CFC-113 and CFC-113a may derive from co-located factories (this is a rather likely scenario, as there are large centers of industrial activities in China). Taiwan may simply see air from places where CFC-113 and CFC-113a factories are not co-located,

1315

We agree with the reviewer and have changed this sentence to remove the part which says there the absence of a correlation is not what we would expect (lines 411-414).

"There is an absence of a correlation between CFC-113a and CFC-113 in 2015 in Taiwan and in
1320   addition, the overall mixing ratios in 2015 appear to be lower than in the other years and have fewer large enhancements (Figure 8)."

39. p. 8, l. 347: I am having difficulties to derive from Manzer 1990, that the CFC-113a route is a main pathway. It appears that he showed many pathways graphically, and listed two examples
1325   of potential pathways, neither of which was via CFC-113a. In contrast, Maranion et al., seem to suggest this route, but without backing it up with literature.

One of the pathways Manzer 1990 listed was production of HFC-134a via CFC-114a. CFC-113a can be used to make CFC-114a as shown in Manzer 1990 (Fig 3). We have changed the wording of this
1330   section so it no longer states this is one of the main routes but now states that it is one of the pathways for production of HFC-134a (line 426). We have also added in addition references in this section that also mention production of HFC-134a via CFC-113a. We also took the opportunity to add in additional references in other parts of this section to provide more references for the production methods of HFC-134a and HFC-125 and for the use of CFC-113a to produce insecticides (line 475).
1335

40. References: Laube et al., 2014: Captial 'A' For Brenninkmeijer, C. A. M.; Manzer, 1990. Reverse intials; Rigby et al., 2013: Correct Muhle

We have corrected these mistakes. The reference list is written using the Mendeley reference
1340   manager so these changes will not appear as tracked changes in the document.

41. Fig. 2: Limiting the y axes labels to the range of the data would greatly help in distinguishing the two data sets. Are these error bars now also including some uncertainties of the standard measurements, as indicated in the main text?
1345

We agree with the reviewer and have limited the y axes labels to the range of the data.

All the error bars including the ones in figure 2 are calculated the same way and include the uncertainty in the standard measurements for the day they were measured. How the error bars are
1350   calculated is described in the methods section (lines 109-111). The explanation is not included in every figure as we thought it would make all the figure captions unnecessarily long.

We have changed the methods section to explicitly say that we calculate the uncertainties the same way for all measurements.
1355

"The measurement uncertainties are calculated the same way for all measurements and represent one sigma standard deviation. They are based on the square root of the sum of the squared uncertainties from sample repeats and repeated measurements of an air standard on the same day."

1360   42. Fig. 3: Similar comment as for Fig 2 for the right y-axis: Label ticks only in range where data are. For the mean emissions, a solid line rather than a dashed line would help to see the apex better. Date 04/12/2012 not apriori clear, which is month and which is day. Legend shows light blue filled circles but these can't be seen in the plot. Suggest to replace these by lines for the model results.

1365

We agree with the reviewer and have change the axis labels, and tick marks. The mean emissions have also been changed to a solid line. We also changed the emissions uncertainties to a larger dashed line. We changed the date format to 04-Dec-2012 and we changed the filled circles to a blue line.

1370

43. Consider to somehow show the CFC-113 emissions for the last decades in a different form, such that they could be compared to the CFC-113a emissions in Fig. 3 (perhaps add them there).

We agree with the reviewer and have created a new figure with all the CFC-113 emission estimates
1375   and the CFC-113a emission estimates from 1995 to 2016. This figure serves two purposes: 1) It makes the differences between the CFC-113 emission estimates for more recent years easier to see and 2) It graphically compares the CFC-113 and CFC-113a emission estimates for the last few years.

1380   44. Fig. 5: It is very difficult to distinguish the various sampling sets. Please improve figure.

We agree with the reviewer and have changed the figure so the data points are larger and are different shapes.

1385   45. Fig. 7: There seem to be no error bars on the CFC-113a measurements.

There are error bars they are just really small.

We have changed the colour of the error bars to a darker grey, changed the circles to no fill so the
1390   error bars underneath them can be seen and changed the axis of the CFC-113a and CFC-113 mixing ratios so the CFC-113a error bars are more stretched out.

46. Fig. 8: Why was this particular measurement chosen? There seem to be many elevated CFC-113a shown in Fig. 5.

1395

This was an example that was representative for many other occasions. We have changed the sentence referring to this figure to explicitly say that it was representative for many other events (lines 332-333).

1400   "Figure 9 shows an example NAME footprint from a sample collected in January 2014 **that is representative for many other events.**"

47. SI Tables: Emissions are calculated for 2017 based on 2 samples only for Jan and Feb 2017. This is almost certainly biased and I suggest to omit presenting model results for 2017.

1405

We agree with the reviewer and have removed the 2017 emissions from the figures and the supplementary material.

48. Consider complementing tables with information's on calibration scales used for the various compounds and data sets.

We agree with the reviewer and have added calibration scales to the Taiwan sheet in the spreadsheet in the supplementary material as Taiwan is the location with all the additional halocarbon measurements.

Interactive comment on "Continued increase of CFC-113a (CCl$_3$CF$_3$) mixing ratios in the global atmosphere: emissions, occurrence and potential sources" by Karina E. Adcock et al.

Anonymous Referee #2
Received and published: 21 December 2017

This paper updates and advances our understanding of CFC-113a in the global atmosphere, its lifetime, regions contributing emissions, and potential sources. The continued increase is interesting and important to document and understand, especially given the accelerated increase that appears to be continuing after being initially documented in an earlier paper. It is nice to see the broad range of measurement locations and information they supply. The paper is mostly sound, although there are a few sections where some reconsideration of results is warranted and where some improvement in the writing is needed. But after these issues are addressed, the paper likely would be appropriate for publication.

1. Issues to consider: As the authors note, the impact of these emissions on the ozone layer to date is minor. Suggesting that more CFC-113a might make it to the stratosphere than is indicated by surface means is a conclusion whose importance can only be speculated about (line 309-312). It is not a conclusion based on data presented here so doesn't seem appropriate to include. Geophysica results from the stratosphere are indicated as starting at background levels and decreasing above; in other words, entirely consistent with background mole fractions at Earth's surface.

We have modified this section to explicitly state that this is speculation (line 381) and have added an additional sentence (lines 385-387).

"The mechanism has already been proven to exist for shorter-lived gases (Oram et al., 2017) and we see very similar patterns transporting elevated mixing ratios of CFC-113a to the tropics very rapidly (within days) during a time of increased convective uplift."

2. Related to this, it seems important to mention in the text that a constant emission of 2 Gg/yr for a chemical with a 50-yr lifetime yields a steady-state global mole fraction of 5 ppt (15 ppt of Cl for CFC-113a). This helps the reader to objectively understand the significance of these results compared to the contribution of other chemicals including CFCs in a much more meaningful way than a comparison of cumulative emissions since 2007, for example (lines 206-209). Undoubtedly CFC-113a emissions could increase, but the potential for this is constrained by the

1455   cause of the increasing emissions and, for that fraction associated with HFC production, the Kigali Amendment.

We agree with the reviewer and have included this sentence in the conclusion (lines 510-511).

1460   "For example, a constant emission of 2 Gg yr^{-1} for CFC-113a yields a steady-state global mixing ratio of about 3.2 ppt."

3. Potential sources for CFC-113a emissions should be considered in light of the fact that emissions were fairly small until 2010, and then increased to a new value and have been essentially
1465   constant since. It is my view that this step change in emissions is primarily why this paper is worth publishing in ACP. It provides a strong hint as to which process likely caused this step change (at the least it reduces the likelihood of some causes) and is important to consider in gauging the likelihood of emissions increasing in the future. At the present time this section (4) rambles a bit and would benefit from significant tightening.
1470
We agree with the reviewer and have edited section 4 to make it more concise.

In the first paragraph the details of possible exceptions to the Montreal Protocol have been shortened. Also, the discussion of the possible causes of variations in CFC-113a and CFC-113
1475   correlations has been shortened. We have removed the example of HFC-134a in mobile air conditioning. We have also removed the paragraph about the differences in the correlations of CFC-113a and CFC-113 between Cape Grim and Taiwan. We moved the last two sentences from this paragraph into the paragraph about CFC-113 source banks. We removed the concluding sentence from the HFC paragraph and moved some of it to the concluding paragraph.
1480
4. On the upper lifetime limit derived for CFC-113 based on the observed rate of change of CFC-113. Some consideration or discussion of steady-state lifetimes vs lifetimes at zero emissions is required here before such a conclusion is made. These are two different quantities that have different values. For CFC-113, I expect its lifetime in the presence of zero emissions to be slightly
1485   shorter than one derived at SS. See papers by Prather on this topic, and consider calculating the difference in your model to determine if an upper limit to a SS lifetime is inconsistent or not with the observationally-derived value upper limit (assuming E=0).

The SPARC Lifetime Report (Ko et al., 2013) discusses the differences between steady state lifetimes
1490   and decay times (lifetimes at zero emissions) based on the work of Prather and others. Whilst the decay time can differ from the steady state lifetime (Prather 1994) this difference can be very small, especially for long-lived gases with constant stratospheric sinks. Specifically, this difference is no more than 2% for gases with lifetimes greater than 10 years. CFC-113 is a long-lived gas, with a stratospheric sink and a likely steady state lifetime of around 82-109 years. The decay time should
1495   therefore be very similar to the steady state lifetime and any difference is relatively small compared to the overall uncertainty in the steady state lifetimes.

Ko, M. K. W., Newman, P. A., Reimann, S. and Strahan, S. E., Eds.: SPARC Report on Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, SPARC Office. [online] Available from: http://www.sparc-climate.org/publications/sparc-reports/, 2013.

1500   Prather, M. J., Lifetimes and eigenstates in atmospheric chemistry, *Geophys. Res. Lett., 21,* 801-804, 1994.

We have added the following text to section 3.1 of the paper:

"We can use the observed decrease in CFC-113 mixing ratios from 2003 onwards to calculate a decay time (lifetime at zero emissions). For long lived gases with stratospheric sinks, such as CFC-113, the decay time and steady state lifetime are very similar, differing by no more than 2 % (Ko et al., (2013). …. Accounting for the 2 % error introduced by assuming the decay time is the same as the steady state lifetime gives are overall error of 6 %. Applying this to the lifetime gives a maximum lifetime of 110 ± 7 years."

We have added the following text to section 2 of the supplementary information where we calculate the lifetime of CFC-113 by using the change in its mixing ratios at Cape Grim and a rearrangement of the chemical continuity equation:

"Accounting for the possible 2 % difference between the decay time and steady state lifetime gives an overall range of 113 ± 5 years."

5. Line 438-440. A suggestion that new regulatory mechanisms might need to be added to the Montreal Protocol is made in the conclusion. This statement diminishes the objective nature of the data and discussion included in the paper. Policy is made with consideration of a broad range of costs and benefits, and you cannot begin to cover this complex and multifaceted discussion in a paper about atmospheric changes. If you want to comment on policy, consider doing it with an "if...then" construction. And in this case, if policy-makers wanted to require absolutely zero emissions of CFCs, then they might consider doing x,y, and z.

We agree with the reviewer and have edited this section to turn it into an 'if…then' construction (lines 524-529).

"If policy-makers wish to limit the impacts of individual isomers, then atmospheric observational data on individual CFC isomers should be reported to UNEP wherever possible. In addition, the increase in CFC-113a demonstrates that the use of ODSs as chemical feedstock or intermediates is becoming relatively more important as the use of ODSs for direct applications decreases. If policy-makers target zero emissions of CFCs, then they might consider regulating these uses of ODSs."

6. The discussion of section 4 in the supplement is not useful without explicitly considering the changes over time in tropospheric entry values. Without this, the section adds little to the paper.

We agree with the reviewer and have added a discussion of the stratospheric mixing ratios to the supplement (lines 92-97).

"The Geophysica 2016 highest CFC-113a mixing ratio was 0.75 ± 0.02 ppt. The Tacolneston mixing ratio at this time was 0.72 ± 0.01 ppt. In 2009-2010 the Geophysica highest mixing ratio was 0.44 ± 0.01 ppt and at this time the Cape Grim mixing ratio was 0.43 ± 0.01 ppt. The highest mixing ratios observed in both campaigns agree quite well (within uncertainties) with tropospheric background mixing ratios at the time and can therefore be considered as representative of stratospheric entrance mixing ratios."

7. Other items. How was calibration consistency maintained throughout time and across the different missions?

We have added this sentence to the methods section (lines 99-101):

1550 "All the samples are compared to the same NOAA standard (AAL-071170) and there were routine measurements of multiple standards to exclude the possibility of mixing ratio changes in the standard over time."

8. Figure 3, mention blue solid and dashed lines in caption.
1555

We have added this sentence to the caption:

"The blue solid line represents the modelled mixing ratios with uncertainties (dashed blue line)."

1560 9. p. 2, line 89-91, uncertainties are mentioned, but these are not the uncertainties used in the modeling, which are discussed in the supplement but not the section on modeling. I'd suggest that this appear somewhere in the main text.

We have edited and moved a section in the supplement into the 2.3 emission modelling section in
1565 the main paper (lines 162-166).

"The upper and lower emission uncertainties for CFC-113a and CFC-113 were determined by first calculating the uncertainty in matching the modelled mixing ratios with the observed mixing ratios using their recommended atmospheric lifetimes and secondly considering the uncertainty range in
1570 the lifetimes. The best fit (minimum-maximum) steady-state lifetimes used in this study are 51 years (30 years-148 years) for CFC-113a and 93 years (82 years-109 years) for CFC-113 (Ko et al., 2013; Leedham-Elvidge et al. accepted, ACP)."

10. On uncertainties in CFC-113 calibration arising from co-elution of CFC-113a. Consider doing the
1575   atmospheric measurement community a favor by discussing the relative magnitude of
         interference that an analyst might have in measuring CFC-113 given co-elution of CFC-113a at
         the different ions these chemicals have in common (perhaps a simple table in the supplement?).
         This would be very helpful, and easy to add, I imagine, given that you are in a unique position to
         supply this important information that to first order would be independent of mass spec
1580   instrument being used.

This is unfortunately not easy to add as we are not measuring all those ions. This would also require detailed information of the setup of the different analytical systems to be compared such as GC columns, retention times, potential interferences, differences in ionisation due to different mass
1585 spectrometers (e.g. source vacuum, chemical used for mass axis calibration) and unknown quantities of CFC-113a in primary calibration standards. This would exceed the scope of this manuscript. We would however be very open to carry out a direct intercomparison experiment if approached.

11. Lines 133-136 and 150-152. This doesn't make sense. Fitting well data at CGO wouldn't say much
1590   about the accuracy of and emission distribution in the lower SH and throughout the NH.

We agree with the reviewer and have deleted this part of the sentence:

"and has been shown to reproduce the reported mixing ratios of CFC-11 and CFC-12 at Cape Grim to
1595 within 5 % uncertainty (Reeves et al., 2005)"

12. Lines 217, Confusing phrasing. Ultimately, global emission magnitudes derived from observations depend on the lifetime used, and you used different lifetimes than others.

1600   We agree with the reviewer and have modified this sentence (lines 270-273):

"Differences are likely due to this study using different lifetimes than Rigby et al. (2013)."

1605   13. Paragraph starting on line 251. First part: make this a discussion of variability in mole fractions and not just mole fractions. This makes your point valid and will help later when you are discussing differences in trends vs short-term variability in the UK vs Cape Grim. Second point: mention the HCFC-133a lifetime.

1610   We agree with the reviewer and have added this sentence (lines 314-316):

"The mixing ratios in Taiwan are very variable indicating nearby source region(s) whereas Cape Grim and Tacolneston mixing ratios are much less variable. Therefore, the Taiwan measurements are well suited to investigate correlations that might shed further light on potential sources."

1615

We also have added this sentence (lines 322-323):

"The tropospheric lifetime of HCFC-133a is 4-5 years (McGillen et al., 2015)"

1620

     14. Para starting on line 265 (also line 291). Assertions are made that are not valid here or that extend limited results to broader context without justification (was Tacolneston sensitive to emissions from all UK source regions? Why would results from this site be representative of the NH? They might be proportional to that quantity, but not necessarily quantitatively the same).
1625   These are weakness to the paper that aren't needed and could be easily avoided.

We agree with the reviewer and have changed these sentences (lines 335-338), (lines 363-365):

"This indicates the absence of regional sources of CFC-113a in **this part of the UK**. Due to this and
1630   the relatively long lifetime of CFC-113a Tacolneston can be considered to be representative of Northern Hemisphere background mixing ratios of CFC-113a **for that latitude**."

"They will also be representative of background Northern Hemispheric CFC-113a mixing ratios **for that latitude** as the Greenland firn air location was isolated from any large industrial areas with
1635   potential sources of CFC-113a."

List of all relevant changes

- Line 15: author affiliation edited
1640

Abstract

- Line 27: "and" changed to "together with"
- Line 28: "data for" changed to "measurements in" and "lower" inserted
- Line 32: "(1.3-2.4 Gg yr^{-1})" deleted and "(gigagrams per year)" inserted
1645 - Line 42: "substantially" moved

1. Introduction

- Line 45: "most of the" and "solar" inserted

- Line 47: "CFCs have negligible loss mechanisms in the troposphere and only break down when they reach the stratosphere where they are exposed to strong ultraviolet light and decompose mostly through photolysis and reaction with O^1D (Ko et al., 2013)." Inserted
- Line 50: "compounds" changed to "decomposition products"
- Line 71: "IAGOS-CARIBIC project" changed to "CARIBIC-IAGOS observatory"
- Line 75: "as" inserted

- Line 78: "study" changed to "paper"

2. Methods

2.1 Analytical technique

- Line 84: "project" changed to "observatory"

- Line 85: "a glass-bottle sampler" changed to "glass bottle samplers"
- Line 85: "Various pumps were used for the different sampling activities, all of which have been thoroughly tested for a large range of trace gases (Brenninkmeijer et al., 2007; Laube et al., 2010a; Allin et al., 2015 and Oram et al., 2017)." Inserted
- Line 91: "Laube et al. (2010)" changed to "Laube et al. (2010b)"

- Line 92: "Al-PLOT" changed to "Al_2O_3-PLOT"
- Line 95: "A possible interference could arise when measuring CFC-113a on the GS GasPro column using m/z 116.91 if concentrations of the nearby eluding HCFC-123 are high. This was the case for a small number of samples analysed for this work and those measurements were either a) repeated using the interference-free m/z 120.90, b) replaced with measurements on the KCl-passivated Al_2O_3-PLOT column,

  or c) excluded. The KCl-passivated Al_2O_3-PLOT column separated CFC-113 and CFC-113a well, no interferences were observed and m/z 116.91 was used for quantification. All the samples are compared to the same NOAA standard (AAL-071170) and there were routine measurements of multiple standards to exclude the possibility of mixing ratio changes in the standard over time. The samples collected in Taiwan in 2013 were also measured on the Entech-Agilent GC-MS system operating in electron ionisation (EI)

  mode. This consists of a preconcentration unit (Entech model 7100) connected to an Agilent 6890 GC and 5973 quadrupole MS (Leedham Elvidge et al., 2015)." Inserted
- Line 106: "On a typical day, the working standard is measured five to eight times, between every two or three samples. The sample peak sizes are measured relative to the standards measured just before and after them. The working standard is used to correct for small changes in instrument response over the course of a

  day." Inserted
- Line 110: "are calculated the same way for all measurements and" inserted
- Line 111: "the" deleted and "and are derived as" changed to "They are based on"
- Line 112: "an" changed to "the"

2.2 Sampling

- Line 115: "This paper reports" changed to "We now report"
- Line 117: "From 2013 to 2017, 20 samples were collected at Cape Grim at irregular intervals of between one to five months apart." Inserted
- Line 118: parentheses inserted around "1978-2017"
- Line 118: "UEA Air Archive" changed to "analyses of archived air samples collected at Cape Grim,

  Tasmania and analysed at the UEA, together with"
- Line 119: "in situ" italicised
- Line 120: "CFC-113 stability in the Cape Grim Air Archive has been demonstrated in the AGAGE program for periods up to 15 years and longer (Fraser et al., 1996; CSIRO unpublished data). Most of the CFC-113 UEA Cape Grim data set was previously published in Laube et al. (2013). Some of the earlier samples from

  Laube et al. (2013) and Laube et al. (2014) were reanalysed on the KCl-passivated Al_2O_3-PLOT column (length: 50 m, ID 0.32 mm). They showed very good agreement with the previous GasPro column-based measurement with comparable precisions and no detectable offset." Inserted
- Line 128: "large-scale" changed to "extra-tropical" and "atmosphere" deleted
- Line 132: "air" inserted

1700 • Line 137: "lower" inserted, "01/09/2016 and 06/09/2016" changed to "01-Sep-2016 and 06-Sep-2016"

• Line 147: "The median mixing ratios are used for the measurements made at the Taiwan sites to decrease the influence of the large spikes in CFC-113a mixing ratios that occurred during these campaigns (Section 3.2.1). All other averages are calculated using the mean." Deleted

1705 **2.3 Emission modelling**

• Line 151: "the top down" changed to ", top down,"

• Line 152: "for the purpose of comparing the emissions of the two isomers. The model contains 12 horizontal layers each representing 2 km of the atmosphere and 24 equal-area zonally averaged latitudinal bands. The
1710 modelled mixing ratios for the latitude band that Cape Grim is located within (35.7° S–41.8° S) were matched as closely as possible to the observations at Cape Grim (40.7° S) by iteratively adjusting the global emissions rate until the differences between the modelled mixing ratios and the observations were minimised. For more details about the model see Newland et al. (2013); and Laube et al. (2016)." Inserted

• Line 159: "In this study" changed to "We now update" and "are updated" deleted

1715 • Line 161: "Air Archive" changed to "Cape Grim dataset"

• Line 163: "The upper and lower emission uncertainties for CFC-113a and CFC-113 were determined by first calculating the uncertainty in matching the modelled mixing ratios with the observed mixing ratios using their recommended atmospheric lifetimes and secondly considering the uncertainty range in the lifetimes. The 'best fit' (minimum-maximum) steady-state lifetimes used in this study are 51 years (30 years-148 years) for
1720 CFC-113a and 93 years (82 years-109 years) for CFC-113 (Ko et al., 2013; Leedham Elvidge et al., accepted ACP)." Inserted

• Line 168: "For further details see" changed to "Further details are provided in"

• Line 170: "isolated" changed to "remote"

• Line 172: "of" inserted and "is located in" deleted

1725 • Line 172: "emission" changed to "emissions"

• Line 173: "This distribution" deleted, "and" inserted

• Line 174: "and has been shown to reproduce the reported mixing ratios of CFC-11 and CFC-12 at Cape Grim within 5 % uncertainty (Reeves et al., 2005)." Deleted

• Line 175: "For CFC-113a" moved

1730 • Line 177: "for the later part of the trend" inserted

• Line 179: " for that latitude" inserted

• Line 179: "large spikes" changed to "significant enhancements"

• Line 185: "There are significant enhancements in CFC-113a mixing ratios in our measurements from Taiwan indicating continued emissions in this region (Section 3.2.1) which is consistent with emissions in this latitude
1735 band in the model." Inserted

• Line 187: "also" inserted, "our measurements from Taiwan (Section 3.2.1) and" deleted

• Line 188: "that" moved

2.4 Dispersion modelling

1740 • Line 210: "Dates in the NAME footprint maps are presented in the format yyyy-mm-dd and use UTC time." Inserted

3. Results

3.1 Long-term atmospheric trends and estimated global annual emissions of CFC-113a and CFC-113

1745 • Line 214: "atmospheric" deleted, "to be" changed to "to have been"

• Line 215: "CFC-113a mixing ratios at Cape Grim" changed to "they"

• Line 216: "Overall CFC-113a mixing ratios increased gradually until about 2010 followed by a more rapid increase." Deleted

- Line 217: "CFC-113a mixing ratios increased on average by" changed to "the average rate of increase was"
- Line 218: "then" deleted, "2009" changed to "2010", "they increased by" changed to "the rate has risen threefold to"
- Line 219: "i.e. more than three times the increase from the previous period." Deleted
- Line 221: "at Tacolneston" moved, "period" inserted, "this site" changed to "it"
- Line 222: "shows" changed to "experienced"
- Line 223: "based on start and end points" inserted
- Line 223: "the median mixing ratios of CFC-113a in Taiwan increased on average by 0.06 ppt yr^{-1} from 2013 to 2016. During" deleted
- Line 224: "for" inserted
- Line 226: "It has" changed to "Its atmospheric burden has"
- Line 227: "this has" inserted, "to increase" deleted
- Line 227: "therefore there must be" changed to "implying that"
- Line 228: "exceed its rate of removal" inserted, "into the atmosphere" deleted
- Line 229: "began in the 1960s and" inserted
- Line 230: "they reached 0.9 Gg yr-1 (0.6-1.2 Gg yr-1) inserted
- Line 230: "and then there was" changed to "followed by"
- Line 231: "in the average growth rate" deleted
- Line 231: "when emissions were 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1})" inserted
- Line 233: "(1.3-2.4 Gg yr^{-1})" deleted
- Line 233: "(minimum-maximum)" inserted
- Line 234: "1.6 Gg yr^{-1} (1.3-2.0 Gg yr^{-1}) in 2015 and 1.9 Gg yr^{-1} (1.5-2.4 Gg yr^{-1}) in 2012. See the supplementary material for more details." inserted
- Line 236: "of CFC-113 at Cape Grim (Figure 4)" moved
- Line 239: "then" deleted
- Line 240: "Fraser et al., 1996" inserted
- Line 243: "CFC-113" and "CFC-113a" moved, "higher" changed to "lower"
- Line 249: "with the UEA Cape Grim dataset being slightly higher" inserted
- Line 251: "251.5" changed to "252"
- Line 252: "then" changed to "after which", "and in 2016, they are 2.4 Gg yr^{-1}" changed "to 2.4 Gg yr^{-1} in 2016"
- Line 254: "demonstrates" changed to "witnesses"
- Line 256: "3163" changed to "3164"
- Line 258: "37" changed to "38"
- Line 259: "which is about 35%" changed to "or a third"
- Line 259: "over this period" deleted
- Line 260: "This indicates that as emissions of other CFCs are decreasing CFC-113a becomes relatively more important." Deleted
- Line 260: "Current" inserted
- Line 261: "CFC-113a emissions are now similar to CFC-113 emissions and could even become larger in the future if the current trends continue." Changed to "Current CFC-113a emissions are similar to those of CFC-113 and could even surpass them if the trends continue (Figure 5).
- Line 265: "In the model, these emissions lead to a best-fit match to the CFC-113 observations." Inserted
- Line 266: "AFEAS reports were" changed to "AFEAS report data"
- Line 269: "Therefore, the emissions used in our study here are the AFEAS emissions up until 1992. From 1992 onwards they are based on the best model fit to the UEA Cape Grim observations." Inserted
- Line 271: "These" changed to "Those", "the emissions estimated in this study" changed to "ours"
- Line 272: "and the differences are likely due to differences in the methods used to calculate the emissions. Rigby et al. (2013) used the estimated emissions to derive the steady state atmospheric lifetimes whereas in this study, we used the steady state atmospheric lifetimes to derive the emissions using shorter lifetimes than in Rigby et al. (2013)" changed to "Differences are likely due to this study using different lifetimes than Rigby et al. (2013)."
- Line 278: "WMO" changed to "SPARC", "(Carpenter and Reimann, 2014)" changed to "(Ko et al., 2013)

- Line 279: "(Carpenter and Reimann, 2014)" changed to "(Ko et al., 2013)
- Line 280: "with" changed to "using"
- Line 280: "quickly enough" changed to "sufficiently rapidly"
- Line 281: "observed" inserted, "observations" deleted, "with no emissions" changed to "in the absence of emissions"
- Line 282: "This indicates that the maximum possible lifetime of CFC-113 is somewhere between 109 years and 138 years." Deleted
- Line 283: "We can use the observed decrease in CFC-113 mixing ratios from 2003 onwards to calculate a decay time (lifetime at zero emissions). For long lived gases with stratospheric sinks, such as CFC-113, the decay time and steady state lifetime are very similar differing by no more than 2 % (Ko et al., 2013)." Inserted
- Line 286: "reproduced" changed to "reproduces"
- Line 287: "maximum" deleted
- Line 287: "By assuming zero emissions, this lifetime is a maximum value, since any source of CFC-113 would have to be balanced by a shorter lifetime." Inserted
- Line 289: "Accounting for the 2 % error introduced by assuming the decay time is the same as the steady state lifetime gives are overall error of 6 %." Inserted
- Line 291: "110 ± 6" changed to "110 ± 7"
- Line 294: "113 ± 4" changed to "113 ± 5"
- Line 295: "enables" changed to "leaves room for"
- Line 297: "possibly through HFC production or agrochemical production (see Section 4)" inserted

3.2 Global distributions of CFC-113a

3.2.1 Enhancement above background mixing ratios

- Line 301: "at Taiwan" changed to "observed in Taiwan", "light blue dots" changed to "light blue stars", "Figure 5" changed to "Figure 6"
- Line 302: "considered" inserted
- Line 303: "ppt" deleted
- Line 304: "large spikes" changed to "enhancements"
- Line 205: "most likely continental East Asia" inserted
- Line 306: "These enhancements in CFC-113a mixing ratios are likely due to emissions of this compound in East Asia." Deleted
- Line 307: "origin" changed to "emissions", "are" changed to "were", "Figure 6" changed to "Figure 7"
- Line 308: "when there are" inserted, "the spikes" changed to "enhancements", "then the" inserted, "usually occur when the" deleted
- Line 309: "usually" inserted
- Line 310: "peninsula" changed to "Peninsula", "as shown" inserted, "Whereas" changed to "In contrast"
- Line 311: "correspondingly" inserted
- Line 312: "peninsula" changed to "Peninsula"
- Line 312: "In (b) and (e), the air is coming from the north, between the eastern coast of China and the Korean peninsula, and in (f) the air mass originates predominantly from over the Pacific Ocean." Deleted
- Line 316: "The mixing ratios in Taiwan are very variable indicating nearby source region(s) whereas Cape Grim and Tacolneston mixing ratios are much less variable. Therefore, the Taiwan measurements are better suited to investigate correlations that might shed further light on potential sources." Inserted
- Line 319: "a range of" changed to "over 50", "samples from" inserted
- Line 321: "There is a great deal of variability in mixing ratios in the Taiwan samples." Inserted
- Line 323: "Figure 7" changed to "Figure 8"
- Line 324: "The tropospheric lifetime of HCFC-133a is 4-5 years (McGillen et al., 2015)" inserted
- Line 325: "HCFC-133a" changed to "and its"
- Line 325: "over the last few years" changed to "in recent years"
- Line 326: "then the trend reversed and" changed to "decreased", "they decreased" deleted
- Line 327: "Then" deleted

- Line 328: "this" changed to "such a"
- Line 328: "it is currently unclear what is causing these changes" changed to "the causes of these changes are still unclear"
- Line 330: "from" changed to "at", "grey dots" changed to "grey crosses", "Figure 5" changed to "Figure 6"
- Line 331: "as much" changed "to the same degree"
- Line 331: "The mixing ratios" changed to "they"
- Line 332: "East Asia" changed to "East Asian air masses"
- Line 334: "Figure 8" changed to "Figure 9"
- Line 335: "that is representative for many other events" inserted
- Line 336: "yellow dots" changed to "yellow diamonds", "Figure 5" changed to "Figure 6", "large spikes" changed to "significant enhancements"
- Line 337: "that Tacolneston is not located close to any sources of CFC-113a and therefore" changed to "the absence of regional sources"
- Line 338: "in this part of" inserted, "does not have large sources of CFC-113a" deleted
- Line 340: "for that latitude" inserted
- Line 341: "large spikes" changed to "many enhancements"
- Line 343: "24/03/16" changed to "24-Mar-2016
- Line 344: "Figure 6" changed to "Figure 7", "04/04/16" changed to "04-Apr-2016"
- Line 347: "suggesting" changed to "indicating"

3.2.2 Interhemispheric gradient of CFC-113a

- Line 350: "generally higher" changed to "almost exclusively higher (though often indistinguishable within uncertainties)"
- Line 351: "Figure 5" changed to "Figure 6"
- Line 352: "higher" changed to "lower"
- Line 354: "interhemispheric" deleted
- Line 355: "data from" inserted, "from Germany to South Africa between 2009 and 2016" changed to "between Germany and South Africa for 2009-2016"
- Line 356: "purple dots" changed to "purple circles, Figure 6"
- Line 357: "Fig. 5" changed to "Fig.6"
- Line 358: "dots" changed to "circles"
- Line 359: "dots" changed to "circles"
- Line 360: "also" changed to "already"
- Line 361: "they found" changed to "discovered"
- Line 362: "collected to a depth of 76 metres" inserted
- Line 366: "for that latitude" inserted
- Line 367: "Figure 5" changed to "Figure 6", "dots" changed to "crosses"
- Line 368: "dot" changed to "cross", "figure" changed to "Figure"
- Line 372: "or" changed to "with"

3.2.3 Measurements of CFC-113a in the stratosphere

- Line 377: "Nearly all" inserted, "are usually" deleted, "on the" changed to "during", "at" changed to "represent"
- Line 379: "dots" changed to "diamonds", "Figure 5" changed to "Figure 6", "at" changed to "near"
- Line 379: "The measurements should thus be representative of the mixing ratios of compounds just" changed to "Their mixing ratios should be representative for air masses"
- Line 381: "layer" changed to "region"
- Line 382: "9/11/2013" changed to "9-Nov-2013"
- Line 383: "Figure 5" changed to "Figure 6", "We speculate that" inserted

- Line 387: "The mechanism has already been proven to exist for shorter-lived gases (Oram et al., 2017) and we see very similar patterns transporting elevated mixing ratios of CFC-113a to the tropics very rapidly (within days) during a time of increased convective uplift." Inserted
- Line 391: "take samples of stratospheric air" changed to "sample lower stratospheric air"
- Line 392: "dots" changed to "squares"
- Line 393: "Figure 5" changed to "Figure 6"
- Line 396: "mainly" inserted, "This is" deleted

4. Possible sources of CFC-113a

- Line 401: "It is therefore likely that there is a continuing industrial process(s)" changed to "This means that there are processes"
- Line 402: "leads" changed to "lead"
- Line 403: "into the atmosphere" deleted
- Line 405: "chemical intermediates and fugitive emissions" inserted
- Line 405: "Whilst feedstock usage has to be reported to the United Nations Environment Programme (UNEP), these data are not publicly available" deleted
- Line 406: "Also" changed to "As"
- Line 407: "so" deleted
- Line 408: "Furthermore, the use of ODSs as intermediate species and trace amounts of fugitive emissions do not have to be reported. Therefore, possible sources for the increase in CFC-113a mixing ratios include its use as a chemical feedstock, chemical intermediates, and fugitive emissions as well as unsanctioned production (Laube et al., 2014)." Deleted
- Line 413: "The absence" changed to "There is an absence"
- Line 414: "is not what we would expect based on their source type (industry) and lifetimes" deleted
- Line 416: "spikes changed to "enhancements", "Figure 7" changed to "Figure 8"
- Line 418: "China/Korea were the areas" changed to "Regions in China and Korea"
- Line 419: "source" changed to "locations"
- Line 420: "indicate that there is more than one process emitting CFC-113a in East Asia, or variability in the process or in the amount of leaking of gases. This may" deleted
- Line 424: "this" changed to "it"
- Line 427: "may" inserted, "There are two main routes for making HFC-134a (Manzer, 1990)" deleted
- Line 428: "One of the pathways for production of HFC-134a" inserted, "The first" deleted
- Line 430: "Rao et al., 1992; Bozorgzadeh et al., 2001; Maranion et al., 2017" inserted
- Line 431: "The other" changed to "Another"
- Line 436: "any" deleted, "was practiced" inserted
- Line 439: "no" changed to "not"
- Line 446: "Observed" deleted
- Line 449: "For example, as HFC-134a is used in mobile air conditioning units and in refrigeration, we would expect a significant component of HFC-134a emissions to be related to automobile use." Deleted
- Line 458: "On the one hand, the Cape Grim dataset shows that CFC-113a and CFC-113 have very different atmospheric trends (Figures 3, 4) but on the other hand, the Taiwan dataset shows that the isomers are mostly strongly correlated (Figure 7). This is not necessarily a contradiction because, close to sources the two compounds would still be correlated, but the emissions are low in absolute numbers for CFC-113 so it is globally still decreasing. In Sect. 3.1 we concluded that there was possibly a small amount of continued emissions of CFC-113 to maintain the observed atmospheric mixing ratios. This would be consistent with either a source from banks and/or release in conjunction with CFC-113a." deleted
- Line 465: "and/" inserted, "peninsula" changed to "Peninsula", "sources of" changed to "source regions for"
- Line 471: "and as we do not know where they are located" deleted
- Line 472: "this" changed to "which"
- Line 472: We suggest that the CFC-113a emissions in the atmosphere originate predominantly from HFC production; however, there is currently insufficient data available to conclude this with high confidence.
- Line 477: "Jackson et al., 2001; Cuzzato and Bragante, 2002" inserted
- Line 478: "In addition" moved

1955 • Line 486: "In Sect. 3.1 we concluded that there was possibly a small amount of continued emissions of CFC-113 to maintain the observed atmospheric mixing ratios. This would be consistent with either a source from banks and/or release in conjunction with CFC-113a."
• Line 492: "however; there is currently insufficient data available to conclude this with high confidence."

1960 **5. Conclusions**

• Line 508: "declining" inserted
• Line 509: "yet" deleted
• Line 510: "major" deleted
• Line 512: "For example, a constant emission of 2 Gg yr^{-1} for CFC-113a yields a steady-state global mixing
1965 ratio of about 3.2 ppt." inserted
• Line 517: "and whilst CFC-113a emissions have appeared to be stable in recent years this does not mean that they will not increase in the future." Inserted
• Line 520: "What is required is" changed to "When"
• Line 521: "become available" inserted, "With such data" deleted
1970 • Line 522: "could" changed to "can"
• Line 526: "Therefore, we recommend that" changed to "If policy-makers wish to limit the impacts of individual isomers, then"
• Line 527: "should" inserted
• Line 529: "ODSs used as chemical feedstock or intermediates might need to start being regulated by the
1975 Montreal Protocol as the use of ODSs for direct applications decreases, the use of ODSs as chemical feedstock or intermediates is becoming relatively more important." Changed to "the use of ODSs as chemical feedstock or intermediates is becoming relatively more important as the use of ODSs for direct applications decreases. If policy-makers target zero emissions of CFCs, then they might consider regulating these uses of ODSs."

1980 **Acknowledgements**

• Line 539: "(CARIBIC-IAGOS)" inserted

Figures and Tables

• Table 1: all dates changed to dd-mmm-yyyy format
1985 • Figure 2: axis and tick marks changed and 2017 emissions removed
• Figure 3: axis and tick marks changed, the modelled mixing ratios changed from filled circles to a line, the 'best-fit' emissions changed from dashed line to a solid line, 2017 emissions and modelled mixing ratios removed, in the figure caption "04/12/2012" changed to "04-Dec-2012", "The blue solid line represents the modelled mixing ratios with uncertainties (dashed blue line)." Inserted
1990 • Figure 4: NOAA observations colour changed, filled circles changed to lines, emissions in legend changed to dashes, emissions uncertainties changed to a filled area, axis range of the observations changed, 2017 emissions and modelled mixing ratios removed and "likely" inserted into the figure caption
• Figure 5: new figure, caption: "CFC-113 emissions from this study, AFEAS and Rigby et al 2013 and CFC-113a emissions from this study 1995-2016 with uncertainties."
1995 • Figures after Figure 5 renumbered
• Figure 6: error bars added, size and shape of data points changed
• Figure 7: all dates changed to dd-mmm-yyyy format
• Figure 8: axis changed, colour of error bars changed, colour of data points changed, all dates changed to dd-mmm-yyyy format
2000 • Figure 9: date changed to dd-mmm-yyyy format