Observationally-derived Fractional Release Factors, Ozone Depletion Potentials, and Stratospheric Lifetimes of Four Long-Lived CFCs: CFC-13 ($CClF_3$), CFC-114 ($C_2Cl_2F_4$), CFC-114a (CF_3CCl_2F), and CFC-115 (C_2ClF_5)

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Abstract. The longer an Ozone Depleting Substance (ODS) remains in the stratosphere, the longer it will be available for the process of ozone depletion. We present improved policy-relevant parameters: Fractional Release Factors (FRFs), Ozone Depletion Potentials (ODPs), and stratospheric lifetimes, for four understudied long-lived chlorofluorocarbons (CFCs): CFC-13 ($CClF_3$), CFC-114 ($CClF_2CClF_2$), CFC-114a (CCl_2FCF_3), and CFC-115 (C_2ClF_5). Previous estimates for the stratospheric lifetimes of these compounds were derived using model and laboratory-based kinetic studies. This study instead uses stratospheric observational data, and correlations between FRFs and lifetimes, to semi-empirically and independently determine the steady-state stratospheric lifetimes of these compounds.

Our newly derived stratospheric lifetime estimates are 315 (287-331) yr for CFC-13 (~~300+~~315 years shorter than previous estimates), 190 (176-201) yr for CFC-114 (similar to previous estimates~~1 year shorter than previous estimates~~), 81 (76-87) yr for CFC-114a (26~~5.7~~ years shorter), and 369 (328-435) yr for CFC-115 (295 years shorter). For CFC-13 and CFC-115 this is outside the uncertainty ranges of previously published estimates. This suggests that these two compounds may have had greater emissions than previously thought, in order to account for their abundance. We calculated FRFs and ODSs for the four CFCs of interest: CFC-13 (FRF = 0.07, ODP = 0.4), CFC-114 (FRF = 0.12, ODP = 0.5), CFC-114a (FRF = 0.31, ODP = 0.52), and CFC-115 (FRF = 0.06, ODP = 0.27). Providing new and updated lifetimes, FRFs and ODPs for these compounds, will help improve future estimates of their tropospheric emissions and their potential ~~resulting~~to damage ~~to~~ the stratospheric ozone layer.

1 Introduction

Due to ~~their destructive effect on the ozone layer, Chlorofluorocarbons (CFCs) needed to be phased-out and the resultant reduced emissions needed to be monitored via atmospheric observations to assess the success or otherwise of the phase-out policies. In order to do this~~the destructive effect of chlorofluorocarbons (CFCs) on the ozone layer, an international agreement, the Montréal Protocol on Substances that Deplete the Ozone Layer, was developed to phase out the use of Ozone Depleting Substances (ODS). The Montréal Protocol was finalised in 1987, and later strengthened by amendments. It banned the production and use of CFCs in developed countries from 1996, and developing countries from 2010 (UNEP, 2016, 2017). The resultant reduced emissions need to be monitored via atmospheric observations to assess the success or otherwise of the phase-out policies.

~~. Annual growth rates are in situ measurements from both NOAA (gml.noaa.gov/dv/site) and AGAGE (https://www-air.larc.nasa.gov/missions/agage/) for CFC-11, CFC-12, and CFC-113. Annual growth rates for CFC-13 and CFC-115 were from in situ measurements by AGAGE (https://www-air.larc.nasa.gov/missions/agage/). CFC-114 and CFC-114a needed to be quantified separately, so were taken from the University of East Anglia (UEA) and Forschungszentrum Jülich (FZJ) flask sampling for CFC-114, and CFC-114a (NOAA and AGAGE's CFC-113 measurements are also likely be a mixture of CFC-113 and CFC-113a). Values are to the same significant figures as they are listed in their original source.~~

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The 'atmospheric residence time' (or 'lifetime') of a compound, refers to the average time spent by a molecule of that compound in the atmosphere, between the time that it leaves its source and the time it encounters a sink. As CFCs are inert in the troposphere this paper focuses on their stratospheric steady-state lifetime (defined as when the burden does not change, i.e. when sources balance sinks). The stratospheric lifetime of a compound provides a measure of ~~tells one at a glance approximately~~ how long that compound will remain in the stratosphere, and available for ozone depletion. Knowing this is necessary for calculations of ozone recovery~~,~~ and evaluating a compound's potential risk to stratospheric ozone. The primary removal mechanisms for the CFCs examined here take~~s~~ place in the stratosphere through reaction with excited atomic oxygen ($O^{(1D)}$) and via photolysis from ultraviolet (UV) rays, though there is also a less dominant removal mechanism in the mesosphere via Lyman -α photolysis (Vollmer et al., 2018).

Air parcels will experience different conditions during transit, and this mixing process is complex, therefore an individual air parcel will not have a single age, instead it will be composed of the different ages of its components. This results in a 'spectrum of ages' (Strunk *et al.*, 2000; Engel *et al.*, 2002), and a 'mean age of air' which is the average transport time since the air parcel entered the stratosphere, primarily through the tropical tropopause (Holton, 1990). Fractional Release Factors (FRFs) are the fraction of a species that has been disassociated into its reactive (and thus ozone-depleting) form (Solomon et al., 1992) over a set number of years (here 3 and 5 years mean age) after being injected into the stratosphere. FRF is a useful metric for evaluating how quickly compounds disassociate; compounds with a high FRF will disassociate faster, doing more damage to the ozone in the short term, but for a smaller time period. Compounds with a low FRF may do less damage over the short term~~,~~ but will remain available for ozone depletion much longer.

To calculate FRFs, this paper uses the ~~new~~ time-independent, loss-weighted method defined in Ostermöller et al., (2017), which accounts for time-lag.

$$\xcancel{ODP_i = \left(\alpha n_{Br,i} + n_{Cl,i}\right) \frac{f_i}{f_{CFC_{11}}} \frac{\tau_i}{\tau_{CFC_{11}}} \frac{M_{CFC_{11}}}{M_i} \frac{1}{3}}$$

~~***Equation 1***~~

~~Equation 3 is the full equation for calculation of ODPs. Where i is the gas of interest; α is the bromine efficiency factor (redundant in this case as the CFCs do not contain bromine), n is the number of chlorine (or bromine) atoms in molecule; f is the FRF; τ is the atmospheric lifetime (in this case the stratospheric steady-state lifetime); and M is the molecular weight.~~

~~).~~

There is a wealth of research on the most abundant CFCs (CFC-11, CFC-12, and CFC-113) (Cunnold *et al.*, 1986; Golombek *et al.*, 1989; Prinn *et al.*, 2000, 2018; Minschwaner *et al.*, 2012; Ko *et al.*, 2013; Allin *et al.*, 2015; Rigby *et al.*, 2019). However, many CFCs with lower atmospheric abundances have not been as well studied, and this paper focuses on four of them: CFC-13, CFC-114, CFC-114a, and CFC-115. The most abundant CFCs (CFC-11, CFC-12 and CFC-113) had annual mole fractions (near the surface) in 2020 of ~224 ppt, ~497 ppt and ~69 ppt respectively, while the four compounds studied all have total atmospheric abundances of less than 20 ppt (Laube et al., 2022) (Table 1). ~~(). With estimated stratospheric lifetimes considerably longer than those of the most abundant CFCs, once these compounds enter the atmosphere it will take centuries for them to be fully removed, and even small emissions are sufficient to maintain an increase in abundance.~~ 1 represents the current state of knowledge for this paper's compounds of interest, along with the three most abundant CFCs for comparison. This paper presents updated estimates for the stratospheric lifetimes, FRFs, and ODPs of: CFC-13, CFC-114, CFC-114a, and CFC-115.

~~: Compounds used~~1: Previously published data for the compounds considered in this ~~report,~~study, presented here for reference and to enable direct comparison with ~~their~~the results of this work. *The table lists molecular formulae,* **~~abundance, change~~***abundances, changes in abundance between 2019- and 2020, stratospheric lifetimes*~~, **lifetime uncertainty, Ozone Depletion Potentials, and Fractional Release Factors**~~ *and associated uncertainties, ozone depletion potentials (ODPs), and fractional release factors (FRFs) (Burkholder et al., 2022; Daniel et al., 2022; Laube et al., 2022).* ~~**Fractional Release Factors are derived using the time independent method detailed in** *(Engel et al., 2018).*~~ *Annual growth rates are based on in situ measurements from both NOAA (https://gml.noaa.gov/dv/site~~(gml.noaa.gov/dv/site)~~) and -AGAGE (https://www-air.larc.nasa.gov/missions/agage/~~(https://www-air.larc.nasa.gov/missions/agage/)~~) for CFC-11, CFC-12, and CFC-113~~. Annual growth rates~~ , and from just AGAGE measurements for CFC-13 and CFC-115~~ were from in situ measurements by AGAGE (https://www-air.larc.nasa.gov/missions/agage/).~~. CFC-114 and CFC-114a ~~needed to be~~were quantified separately~~, so were taken~~ using flask measurements from the University of East Anglia (UEA) and Forschungszentrum Jülich (FZJ~~) flask sampling for CFC-114, and CFC-114a~~), (NOAA and AGAGE~~'s~~ CFC-113 measurements ~~are also~~ likely ~~be a mixture of~~include contributions from both CFC-113 and CFC-113a). ~~Values~~All values are reported to the same significant figures as ~~they are listed~~ in their original ~~source. All data in this table has been previously published, and represents~~sources and represent the current state of knowledge ~~regarding~~for these compounds~~, and is here for easy reference so that this paper's findings can be easily compared to previously published data.~~ .*

Table 1: **Previously published data for the compounds considered in this study, presented here for reference and to enable direct comparison with the results of this work.** ***The table lists molecular formulae, abundances, changes in abundance between 2019 and 2020, stratospheric lifetimes and associated uncertainties, ozone depletion potentials (ODPs), and fractional release factors (FRFs) (Burkholder et al., 2022; Daniel et al., 2022; Laube et al., 2022). Annual growth rates are based on in situ measurements from both NOAA (https://gml.noaa.gov/dv/site) and AGAGE (https://www-air.larc.nasa.gov/missions/agage/) for CFC-11, CFC-12, and CFC-113, and from just AGAGE measurements for CFC-13 and CFC-115. CFC-114 and CFC-114a were quantified separately using flask measurements from the University of East Anglia (UEA) and Forschungszentrum Jülich (FZJ), (NOAA and AGAGE CFC-113 measurements likely include contributions from both CFC-113 and CFC-113a). All values are reported to the same significant figures as in their original sources and represent the current state of knowledge for these compounds.***

Compound	Formula	Atmospheric abundance, 2020, ppt	Change (2019-2020), ppt yr^{-1}	Stratospheric Lifetime, (yr)	Lifetime Uncertainty, (1σ)	Ozone depletion potential (ODP)	Fractional Release Factor (FRF)
CFC-11	CCl_3F	224	-2.2a/-2.5b	55	± 22%	1	0.47
CFC-12	CF_2Cl_2	497.2	-3.9a/-4.2b	103	± 15%	0.75	0.24
CFC-113	$CClCF_3$	68.9	-0.5a/-0.7b	94.5	± 17%	0.82	0.3
CFC-13	$CClF_3$	3.32	0.04a	-*	-*	0.3	-*
CFC-114	CCl_2FCClF_2	16.3	-0.01c	191	± 12%	0.53	0.13
CFC-114a	CCl_2FCClF_2	1.11	0.02c	106.7	± 22%	0.72	-*
CFC-115	CF_3CClF_2	8.7	0.03a	664	± 17%	0.45	0.007

a. AGAGE b. NOAA. c. UEA/FZJ. *. Data does not appear in Burkholder et al., (2022).

~~represents the current state of knowledge for this paper's compounds of interest, along with the three most abundant CFCs for comparison. This paper presents updated estimates for the stratospheric lifetimes, FRFs, and ODPS of: CFC-13, CFC-114, CFC-114a, and CFC-115.~~

Previous estimates for these compounds have relied heavily on laboratory-based kinetics experiments and model estimates (Ravishankara et al., 1993; Newman et al., 2007; Waugh et al., 2007; Burkholder et al., 2020). ~~In this paper we use in situ measurements, taken onboard the high-altitude research aircraft M55 Geophysica, in order to derive updated metrics for these compounds.~~ In the current literature, the estimated stratospheric lifetime of CFC-115 is 664 (±113) years~~.~~, and CFC-13 lacks a stratospheric lifetime in Burkholder et al., (2022) but has a total atmospheric lifetime listed as 630 years. The estimated lifetime of CFC-114 is 191 (±23) years and the estimated lifetime range of CFC-114a is 82–133 years. Currently there is a dearth of measurement-based lifetime estimates for either CFC-114 or CFC-114a, aside from the lab-based kinetics from Davis et al., (2016). The Laube et al., (2016)~~'s~~ estimate of 82-133 years for CFC-114a was not based on observational data, it was based on that reported in Davis et al., (2016), (which used the GSFC 2-D model and UV absorption spectra to estimate the lifetime), and the uncertainty range was assumed. In this paper we use in situ measurements, taken onboard the high-altitude research aircraft M55 Geophysica, in order to derive updated metrics for these compounds.

~~Introducing the ODSs in focus, CFC-13's main sources are~~CFC-13 is primarily associated with **low-temperature refrigeration,** ~~some~~with additional **minor sources in aluminium** ~~plants, and is potentially~~production. It may also be **generated** ~~as a result of~~ during **plasma destruction of CFC-12 (Vollmer et al., 2018**~~), as well as potentially being~~) and can be **present as** an **impurity in CFC-12 due to over-fluorination during** ~~production~~manufacture **(Murphy et al., 2002**~~) . In~~). Between **2016** ~~CFC-13's~~ and 2020, the **global tropospheric abundance** ~~was~~of CFC-13 increased from **3.0 ppt**~~, and its~~ to 3.3 ppt, corresponding to a **growth rate** ~~was 0.03 ppt yr-1 (Vollmer et al., 2018). By 2020 atmospheric abundance had increased to 3.32 ppt, and its growth rate was~~ of **0.04 ppt yr**~~-1 (). CFC-13 is one of the few CFCs for which sources continue to outweigh sink processes.~~ $^{-1}$ (Table 1).

CFC-115 is a known by-product of HFC-125 production~~, it was~~ and has **also** been **used as a refrigerant, as an aerosol propellant and to a lesser extent as a dielectric fluid (Fisher et al., 1993). From 2016 to 2020, the global tropospheric abundance of CFC-115**~~,~~ **increased from 8.5 ppt to 8.7 ppt, with a growth rate of 0.03 ppt yr^{-1} (Vollmer et al., 2018).**

Both CFC-114 and CFC-114a were used primarily as blowing agents and aerosol propellants. In addition**, CFC-114 was** ~~also used heavily~~employed **as a refrigerant and** ~~had uses~~ **in heat-**~~pumps~~pump applications**, while CFC-114a was used in polyolefin foams.** ~~From~~Between **2016** ~~to~~and **2020, the global tropospheric abundance of CFC-114** ~~rose~~increased **from 15.0 ppt to 16.3 ppt**~~, though the~~ ; although, its **growth rate is now negative** ~~(~~ (**−0.01 ppt yr**~~$^{-1}$) (Engel, M. Rigby, *et al.*, 2018).~~ $^{-1}$). From 2016 to 2020, the global tropospheric abundance of **CFC-114a** ~~had~~increased from 1.0 ppt to 1.1 ppt, with **a growth rate of -0.02 ppt yr^{-1}** ~~and global abundance of 1ppt in 2016 (Engel, M. Rigby, *et al.*, 2018), by 2020 CFC-114a had a positive growth rate (0.02 ppt yr^{-1}), and an abundance of 1.11 ppt ().~~(Table 2).

~~It should be noted that uses data from UEA/FZJ flask measurements for CFC-114 and CFC-114a, rather than from AGAGE (https://www-air.larc.nasa.gov/missions/agage) in situ measurements, as UEA/FZJ were able to quantify the isomers separately (Laube et al., 2022). There are difficulties to independently detect each isomer; this is because the two isomers have virtually identical boiling points, making gas-chromatographic separation difficult. They also have similar mass spectra, further complicating their individual analysis and detection using mass spectrometric techniques. The two isomers also likely have different molar responses on the detectors used (electron capture detector or mass spectrometer) and those may change over time (Laube et al., 2016). In addition, historically gravimetric calibrations were only prepared for the major isomer, CFC-114, and the "pure" CFC-114 used may have also contained CFC-114a. Because of these problems~~It is difficult to measure CFC-114 and CFC-114a separately (Laube et al., 2016). So**, the two isomers are frequently reported as a somewhat ill-defined sum, with the assumption that CFC-114a accounts for approximately 10% of the total (Carpenter et al., 2014). However, Laube et al., (2016), using a chromatographic system that can separate the isomers, found this to be an overestimate, and that the assumption that the ratio between the two isomers remained constant was incorrect due to changing atmospheric rise/decline rates of the two isomers (see also Western et al., (2023)).** Therefore, Table 1 uses data from UEA/FZJ flask measurements for CFC-114 and CFC-114a, rather than from AGAGE (https://www-air.larc.nasa.gov/missions/agage) in situ measurements, as UEA/FZJ were able to quantify the isomers separately (Laube et al., 2022).

Understanding ~~how quickly~~ both the rate at which an ozone-depleting substance (ODS) is removed from the atmosphere ~~(using their~~ quantified by its fractional release factor (FRF) and stratospheric steady-state lifetime~~),~~ and ~~how strongly a compound depletes ozone (its~~ the strength of its ozone-depleting effect, expressed by its ozone depletion potential (ODP~~)~~), is ~~vital~~essential for accurately estimating ozone recovery. This paper ~~sets out to supply~~provides updated FRFs, stratospheric lifetimes, and ODPs for CFC-13, CFC-114, CFC-114a, and CFC-115 ~~using~~based on in situ atmospheric measurements. ~~First this paper details how samples were collected~~Section 2 describes the sample collection (Sect. ~~)~~2.1), sample preparation and ~~the methods by which these samples were prepared and analysed~~instrumental analysis (Sect. ~~). Then~~2.2), and a comparison of the ~~samples the~~ tropospheric background ~~trend is performed, additionally providing an independent verification of the~~ trends with data ~~in~~presented by Vollmer et al~~.~~,. (2018) ~~data~~ (Sect. ~~).~~2.3). The methods section ~~is concluded~~concludes with a detailed ~~explanation~~description of the lifetime-FRF method used to estimate stratospheric lifetimes (Sect. ~~). We then present our findings in three sections; firstly~~2.4). Section 3 presents the results, including newly derived stratospheric lifetimes and FRFs ~~for our compounds of interest~~ (Sect. ~~), notably we find that CFC-13~~3.1) and ~~CFC-115 have statistically longer lifetimes than previously estimated. Secondly we present our newly derived ODPs, none of which overlap within the uncertainties with previous~~updated ODP estimates (Sect. ~~). Thirdly we explore what effect these revised lifetimes and ODPs would have on~~ 3.2), followed by an assessment of the implications of these revisions for emissions estimates, ~~presenting revised estimates~~ updated from Western et al~~.~~,. (2023),~~.~~ ~~Finally,~~ ~~Section 4~~ along with discussing discusses the broader implications of ~~our~~these findings for ozone depletion and emission estimates~~,~~ and ~~explores possible~~considers potential sources ~~for increased~~of the observed emissions ~~of these compounds. The paper concludes with a concise summary of all findings and their implications in Sect. .~~

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2 Methods

2.1 Sample Collection

In this paper we used whole air samples collected on board the high-altitude research aircraft M55 Geophysica during three campaigns. The flights in Oberpfaffenhofen, Bavaria, Germany in 2009 (OB09) and Kiruna, Sweden in 2010 (KIR10), were part of the RECONCILE campaign (Von Hobe et al., 2013). The 2011 flight in Kiruna, Sweden (KIR11), was part of the ESSenCe campaign, which itself was a part of the ESA project PremierEx (Kaufmann et al., 2013). The Kalamata, Greece campaign in 2016 (KAL16) and the Kathmandu, Nepal 2017 (KAT17) ~~campaigns~~campaign were part of the StratoClim EU project (Johansson et al., 2020; Adcock et al., 2021; Lee et al., 2021~~) were part of the StratoClim EU project.~~).

2.2 Sample Preparation and instrumental analysis

~~After the samples~~Samples were collected in the stratosphere ~~stored in~~by filling canisters ~~in~~following the ~~manner~~protocol described ~~in~~by Adcock et al. (2021) and were subsequently transported to the ~~central lab at the~~ University of East Anglia (UEA~~), UK,~~) for analysis. The samples underwent cryogenic pre-concentration then were analysed via a gas chromatography mass spectrometry system (GC-MS), using the method detailed in (Laube *et al.*, 2016, 2020; Adcock *et al.*, 2018, 2021; Leedham-Elvidge *et al.*, 2018). In short, the samples were first dried by passing through a magnesium perchlorate ($Mg(ClO_4)_2$) drying tube, then cryogenically trapped by passing through a stainless steel sample loop packed with Hayesep D absorbent which was immersed in a cold bath (made up of a dry-ice and ethanol mixture) at ~-78 °C, in order to give quantitative retention and release. The sample loop was then submerged in boiling water, heating it to near 100 °C, thus providing immediate and complete desorption of the analytes. Separation was accomplished using an Agilent 6890 Gas Chromatograph, which ~~is~~was connected to a high-sensitivity Waters AutoSpec tri-sector mass spectrometer.

Samples were analysed on two different GC columns: ~~the~~an Agilent GS GasPro column with a unique bonded silica (~~silican Dioxidesilicon~~silicon dioxide) PLOT column (length ~50 m, ID 0.32 mm) and ~~the ‘Al-Plot’~~ an Agilent KCl-passivated Al_2O_3-PLOT column with an aluminium oxide ($Al_{2}0_{3}$) deactivated by potassium chloride stationary phase (length: 50 m, ID 0.32 mm, called the Al-Plot here). Of particular relevance to this study, the Al-Plot column is capable of separating CFC-114 and CFC-114a. Samples from the Oberpfaffenhofen 2009 campaign were only measured on the GasPro column, all other samples were measured on both columns. The measurements from both columns agreed within the uncertainty range, with the exception of KIR11’s Al-Plot data which was distorted due to CO_2 build up on the column, and KAT17 where the tail of the large peak for CO_2 partially obscured the small CFC-13 peak. These samples were excluded from the analysis detailed in Sect~~.~~ion 3.

2.3 Comparison to tropospheric background trend

A reliable tropospheric background trend is a ~~vital part of~~critical component in calculating entry mixing ratios, and ~~from these, fractional release factors. The archived~~ consequently, Fractional Release Factors (FRF). In this study, archived air samples from the Kennaook/Cape Grim Observatory (CGO~~) tropospheric trend series used here is updated to 2018 from Laube et al., (2016) for CFC-114 and CFC-114a. For CFC-13 and CFC-115 it is unpublished. In this study we use the~~), analysed at the UEA, are used to derive these trends. The CGO time series~~, which~~ has been ~~proven~~demonstrated to be of high quality for multiple species (Laube *et al.*, 2013, 2016; Leedham-Elvidge *et al.*, ~~2018), and is here compared to the~~ 2018). CGO tropospheric time series for CFC-114 and CFC-114a were previously published ~~trend of the same location from Vollmer et al., (2018), thus also acting as an independent verification of the trends presented in Vollmer et al., (2018). The archived CGO air is believed to contain a trace gas record representative of unpolluted southern hemisphere air, and thus is a useful means of determining a trend, largely free of large regional pollution events which might obscure it. The~~ in Laube et al., (2016) and are extended here to 2018. Although the CGO data set ~~(analysed at UEA)~~ is from the ~~southern hemisphere, and it has been demonstrated by~~Southern Hemisphere, Leedham-Elvidge et al., ~~(2018) that a CGO trend shifted by 0.5 years represents the mixing ratios present in the upper troposphere in the tropics (where most air enters the stratosphere) very well~~(2018) showed that, for long-lived compounds~~, as these~~ that are inert in the troposphere~~.~~, a CGO trend shifted by 0.5 years provides a good representation of mixing ratios in the tropical upper troposphere, where most air enters the stratosphere.

~~The~~ Independent measurements of CGO tropospheric background ~~trend analysed at UEA (Laube et al., 2013, 2016; Leedham-Elvidge et al., 2018), was compared to data from the same station as Vollmer et al., (2018).~~trends have been published by Vollmer et al., (2018), allowing a comparison with the UEA-derived trends to verify the UEA calibration scales. The UEA calibration standards have been used successfully for a number of compounds (Laube et al., 2016; Adcock et al., 2020, 2021)~~,~~. ~~h~~However, the ~~UEA~~ calibration scales for CFC-115 and CFC-13 were developed in the 1990s, and have not been updated, ~~so it was important to verify whether the scales are comparable with~~whereas Vollmer et al., (2018) ~~which~~ used a much more regularly maintained scale. Vollmer et al. (2018) did not distinguish between the CFC-114 and CFC-114a~~, and so the data for~~ isomers; therefore UEA measurements of these ~~two compounds are presented as~~species were combined into 'ΣCFC-114', which are~~is~~ combined-isomer measurements~~ a weighted sum~~. ~~The weights are unknown, and depend on the choice of ions used for the combined measurement. Laube et al., (2016) showed that the ratio between CFC-114/CFC-114a has~~While this approach is not ~~remained constant over time. Thus we do not know the precise ratio~~ideal, it represents the most appropriate comparison available. This analysis also provides an independent verification of ~~CFC-114/CFC-114a in~~ the trends reported by Vollmer et al~~ data.~~ ., (2018).

~~A~~For both the Vollmer et al. (2018) and UEA CGO datasets, simple linear ~~correlation~~regressions (without offset) ~~was~~were calculated ~~(~~separately~~) for both the Vollmer et al., (2018) and the UEA CGO data (in each case~~ by correlating mixing ratio ~~was correlated~~ with date (Figure 1~~, as seen in), and comparison~~). Comparisons of these ~~linear correlations was~~regressions were used to derive a conversion factor~~“~~, x~~” with~~, that minimised the ~~lowest~~ residual sum of squares (RSS~~)~~ (), which were CFC-13=0.11, CFC-115=0.11, and ΣCFC-114=0.81~~), to attempt to make UEA measurements compatible with Vollmer et al., (2018).~~. Applying ~~this simple~~the resulting conversion factors (CFC-13=0.8, CFC-115=0.953), ~~the two data sets line up closely~~brings the UEA and Vollmer et al., (2018) datasets into closer agreement for CFC-13 (Fig. 1a~~),~~) and CFC-115 (Fig. 1b). ~~Our CFC-114 and CFC-114a data were combined, in order to be comparable to Vollmer et al., (2018). Looking at Fig. c~~For ΣCFC-114, the use of a conversion factor (of 1.0234), does largely bring the ~~Laube et al., (2016)~~UEA data into line with the Vollmer et al., (2018~~),~~) data, though the overlap is not perfect~~. This fits the Laube et al., (2016) conclusion that CFC-114 and CFC-114a have varying ratios and should be examined separately.~~ (Fig. 1c). As Vollmer et al. ~~does~~(2018) did not separate the individual isomers, ~~our~~the UEA and Vollmer et al., (2018) data ~~does~~are not necessarily ~~have~~expected to correlate~~ to theirs. The fact~~. Nevertheless, the observed correlation indicates that ~~it indeed does, shows that~~the Vollmer et al. ~~presents~~(2018) dataset provides a reasonable approximation ~~to~~of the ~~sum of~~combined CFC-114 and CFC-114a~~, although they are not able to observe~~ abundance, despite being unable to capture the changing trend of CFC-114a (Western et al., 2023~~)~~), as the ~~sum~~combined signal is dominated by CFC-114.

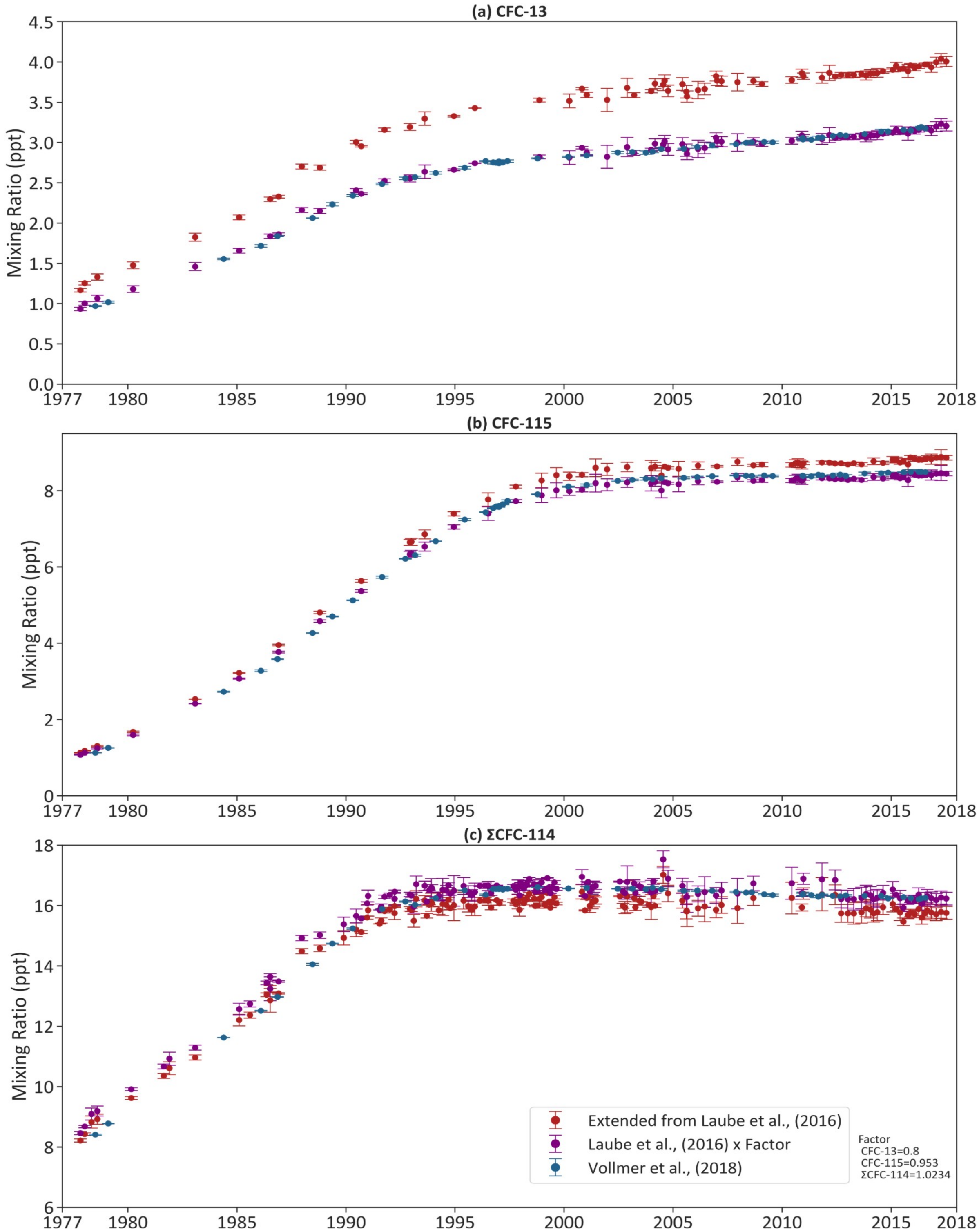

Figure 1: Tropospheric mixing ratios (~~MR) (~~ppt) from samples collected at -the Cape Grim observatory for CFC-13 (a), CFC-115 (b), and ΣCFC-114 (c), plotted against the date (year). (Conversion factor was 0.8 for CFC-13, 0.953 for CFC-115 and 1.0234 for ΣCFC-114). Error bars use instrument precision to 1 sigma.

2.4 Stratospheric lifetimes to Fractional Release Factor (FRF) correlation

There are a number of ways the stratospheric lifetime of a compound can be derived (Ko *et al.*, 2013). These include model simulations (Montzka *et al.*, 1999; Butchart *et al.*, 2006; Lee *et al.*, 2011; Rigby *et al.*, 2013), satellite data (Ko *et al.*, 1991; Minschwaner *et al.*, 2012; Brown *et al.*, 2013), lab-based kinetics experiments (Burkholder et al., 2020), and by examining the relationship between tracer-tracer or tracer-mean age (Plumb et al., 1992, 1996).

The stratospheric lifetime and FRF of a compound are related~~;~~ since the halocarbons within an air mass experienced similar transport pathways~~, there will be a correlation between their dry molar mixing ratio or abundances ~~(Plumb, 2007). Using the correlation between lifetime and FRF, for compounds with well documented values, it is possible to estimate the lifetime of additional (less well documented) compounds, using their FRF at the same mean age (Kloss et al., 2014). FRFs at 3 and 5 years mean age are used here, in order to reflect the average transit time of stratospheric air to the mid (3 years) and high latitudes~~. This is a rough approximation as the age of air even in mid latitudes will reach 5 years if samples are taken at high enough altitude. ~~ (5 years).

Leedham-Elvidge et al., (2018) calculated mean ages and FRFs for 10 compounds. This study used the same air samples, instruments, mean ages, and method (for sample collection, analysis, and the generation of FRFs), as Leedham-Elvidge et al., (2018), with the exception of the KAL16 and KAT17 campaigns, for which ~~we took ~~mean ages were taken from Adcock et al., (2021). Using the time-independent method detailed in Ostermöller et al., (2017), we then calculated the entry mixing ratios for CFC-13, CFC-114, CFC-114a, and CFC-115, for the five campaigns (OB09, KIR10, KIR11, KAL16, and KAT17). Entry mixing ratios are an estimate of the mixing ratio of a compound at the point it entered the stratosphere. By comparing these entry mixing ratios and the observed (partially-dissociated) mixing ratios in the stratosphere, it is possible to estimate what fraction of the compound has disassociated since entering the stratosphere using Eq. (2) (which is a simplified equation calculating Fractional Release Factors using entry and observed mixing ratios). Using this method FRFs for each sample in every campaign were generated.

$$FRF = \left(\mathit{Entry\ Mixing\ Ratio} - \mathit{Observed\ Mixing\ Ratio}\right) / \mathit{Entry\ Mixing\ Ratio}$$

Equation 2

The FRFs from the five campaigns were combined together. This was~~To derive an estimate for the uncertainty, we calculated the FRF using the mean and the upper and lower limits of the measured mixing ratios and mean ages, in similar fashion to Laube et al., (2020). This was also~~ necessary as each campaign had a limited number of samples and some campaigns did not measure certain compounds. ~~Another concern was that~~Also, the KAL16 and KAT17 campaigns sampled relatively young air; the greatest mean ages recorded were 3.02 and 2.53 years mean age respectively.

To derive an estimate for the uncertainty, we calculated the FRF using the mean and the upper and lower limits of the measured mixing ratios and mean ages, in similar fashion to Laube et al., (2020). ~~With such low mean ages, using the FRF-mean age correlation to derive FRFs at 3 and 5 years mean age for these campaigns individually, would require extrapolation beyond the existing data which produces unreliable results. Therefore using the combined~~Then, using the **combined data set for each compound, FRF was plotted against mean age and a 2nd order polynomial trendline was** ~~plotted~~determined **through the data (see Fig. 2).**

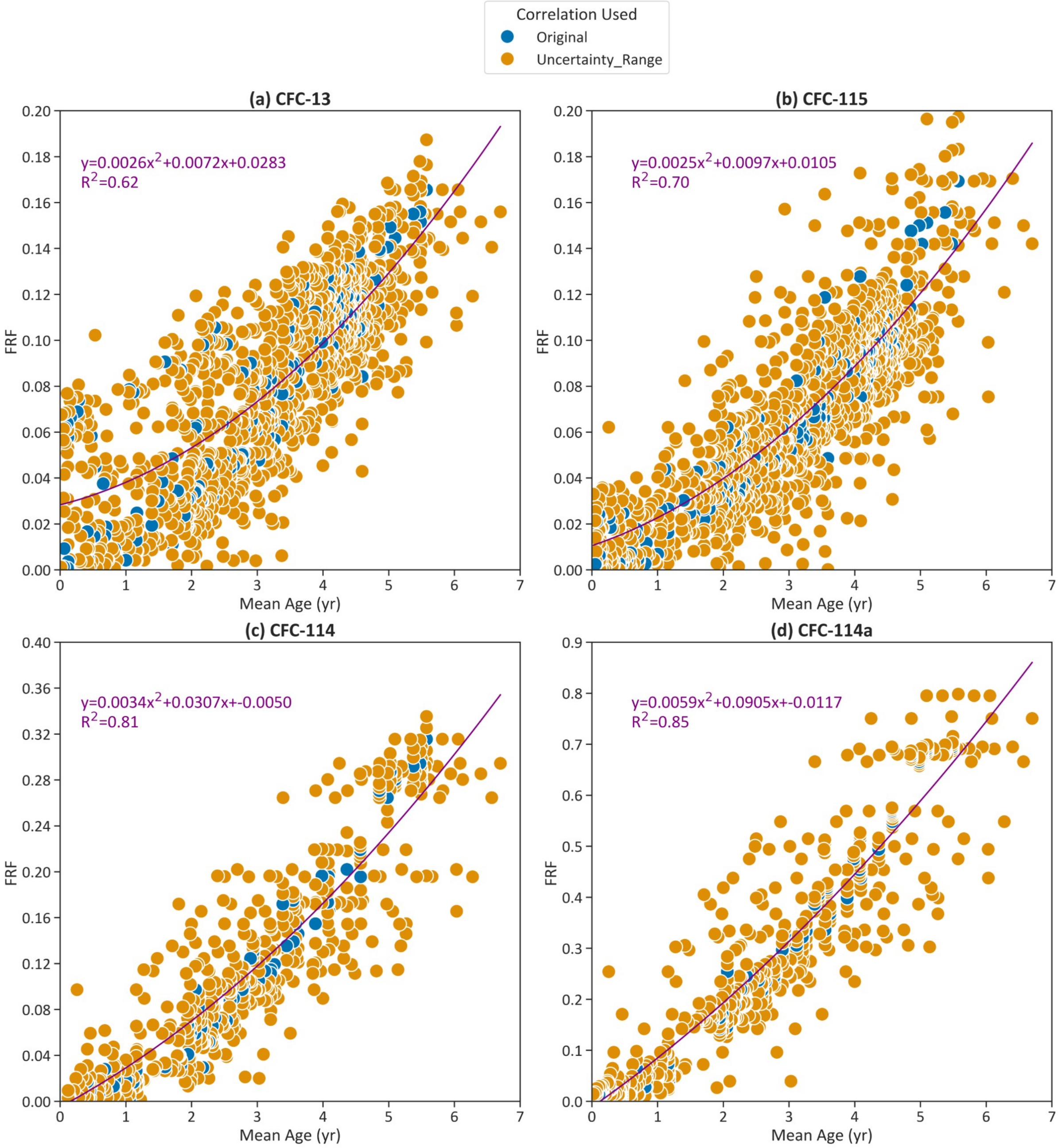

Figure 2 : Fractional Release Factors (FRF) plotted against Mean Age (yr) for all flights (expanded to 5n, uncertainty range), for all compounds. A 2nd order polynomial trendline is plotted through the data set, and both the equation of the line and the R2 value is shown. The trendline is not forced to zero as FRFs do not need to be zero in the extra-tropical tropopause.

The ~~2nd-~~second-**order polynomial trendline shown in Fig.** 2 **was chosen** ~~because of~~to capture **the non-linearities in** ~~the~~ **stratospheric transport and chemistry**~~, which has been observed~~ **previously** ~~(~~observed by **Newman et al**~~.,~~. **(2007**~~;~~) and **Laube et al**~~.,~~. **(2010). The longer-lived compounds**, **CFC-13 and CFC-115** ~~have~~, exhibit **a slight** positive **offset, with the y-intercept above** ~~0, meaning there is~~zero, indicating **a mismatch between** the **measured abundance**s **and the tropospheric trend.** A similar offset was reported by **Adcock et al**~~.,~~. **(2021**~~) also saw an offset between background trends for certain compounds and actual mixing ratios, due~~), attributed **to the Asian Monsoon providing efficient transport pathways for air containing elevated levels of tropospheric gases. In** ~~short~~Fig. 2a and 2b, **the** observed **offset** ~~seen in Fig. a&b~~ **reflects differences in** the **transport pathways experienced by** the sampled **air parcels** ~~sampled and~~ compared with **those experienced by the CGO trend. The** potential **influence of th**~~e~~is **offset was investigated**~~,~~ **and** ~~accounting for the offset~~incorporating it **did not** ~~change the results to a~~produce **statistically significant** ~~degree~~changes in the results**.**

The trend-line was used to calculate the FRF at 3 and 5 years mean age for each compound, and a bootstrapping program (Barreto & Howland, 2010) was used to test the robustness of the polynomial’s estimate. The results gave a list of 2000 predictions, and the frequency at which these estimations occurred. In order to exclude extreme outliers from this the top and bottom 2.5% were excluded, leaving 95% of all predictions for FRF at 3 and 5 years mean age.

From the bootstrapping results~~ of this bootstrap,~~ FRFs at 3 and 5 years mean age (including uncertainty range) were derived (see Table 2). This was done for all four compounds of interest~~,~~ and ~~included~~also SF_6 which does not have estimates of FRF available. The compounds studied in Leedham-Elvidge et al., (2018) had stratospheric lifetimes largely in the order of 200 years or less. SF_6 was included because without a longer-lived compound with both known FRF and lifetime, a correlation between FRF and lifetime drawn from these compounds alone cannot be extrapolated to provide lifetime estimates for longer lived compounds.~~ However, the~~

The lifetime of SF_6 is subject to some dispute. Engel et al., (2018) notes that the widely used value of 3200 years (Ravishankara et al., 1993) may be a substantial overestimate. Kovács et al., (2017) estimated an average lifetime of 1,278 (1120-1475) years using model data, while Ray et al., (2017) estimated a lifetime of 850 (580-1400) years using observations of SF_6 in the Arctic polar vortex. Ravishankara et al., (1993) lists a lower limit for the lifetime of SF_6 as 580 years, so the range of 580-3200 years encompasses the estimates of both Ray et al., (2017) and Kovács et al., (2017). Kouznetsov et al., (2020) used a model study which gave a range for SF_6's lifetime between 600 and 2900 years, while Loeffel et al., (2022) proposed a value of 2100 years (1900-2600 years range). As there is growing evidence that the 3200 years figure is an overestimate, this paper will focus primarily on Ray's estimate of 850 years stratospheric lifetime, and Kovac's 1278 years stratospheric lifetime estimate for SF_6. The estimate for Kouznetsov et al., (2020) gave too wide a spread of possible lifetime for SF_6, for this method to be practical. Loeffel et al., (2022) was a modelling paper, does not focus on defining the lifetime of SF_6, and the lifetimes listed are time-dependant lifetimes and varied over the spread of the simulation. For the calculations in this paper, equilibrium steady-state lifetimes are required, so lifetimes listed in Loeffel et al., (2022) are not used. Calculations for both the Ray et al., (2017) and Kovács et al., (2017) lifetime estimates were performed, for FRFs at both 3 and 5 years mean age, and they are included in Figs. 4a&b. When calculating FRFs for SF_6 two campaigns were excluded: KIR10 as it could have captured SF_6 depleted mesospheric air due to the polar vortex (Ray *et al.*, 2017), and KAL17 as this campaign contained elevated trace gas levels from the highly polluted air masses transported by the Asian Monsoon (Adcock et al., 2021).

This paper uses the FRFs and stratospheric lifetimes (including their uncertainty ranges), for a number of well-studied compounds (SF_6, HCFC-141b, HCFC-142b, HCFC-22, CFC-12, CFC-113, CFC-11, H1301, CCl_4, CH_3CCl_3, H1211), found in Leedham-Elvidge et al., (2018) and Burkholder et al., (2022). All the lifetime estimates in Leedham Elvidge et al. are dependent on the uncertainties of the same age of air, as well as on that of CFC-11. With these lifetimes and FRFs a trendline was plotted and the resulting correlation was used to generate predicted lifetimes for our compounds of interest. Different trendline functions were tested to see which best fitted the data, and the 'power' trendline ($y = cx^b$) was the best fit. ~~This was the fit function with the lowest degree of freedom that produces robust results; the 'power' trendline function gives the smoothest fit while still retaining a robust goodness of fit.~~. This correlation considered the uncertainty in both the FRFs and stratospheric lifetimes. ~~For this reason,~~ T~~t~~he calculations were performed using the 'power' trendline, using (separately) both the FRFs and lifetimes from Leedham-Elvidge et al~~.,~~. (2018) and using those listed in Burkholder et al~~.,~~. (2022). The resulting correlations (using FRFs at 3 years mean age) can be seen in Figs. 4 a&b. This was done using (separately) ~~-~~both SF_6 lifetimes of 850 years and 1278 years. In order to account for the lifetime uncertainty ranges of these compounds, this trendline was bootstrapped as described previously, in order to derive the ~~-8~~eight different lifetime estimates for each compound (Fig. 5).

The method of calculating time-independent FRFs used in Section. 2.4 is able to correct for changes in the tropospheric trends of the CFCs, however it cannot account for changes in tropical upwelling. This is because the lifetimes calculated are steady-state lifetimes, and rely on the atmosphere to remain in a certain state. If the atmosphere changes, such as with a drastic change in tropical upwelling, then a new steady state would eventually be reached, with a new corresponding steady-state lifetime. There is evidence that stratospheric circulation is changing, and in turn affecting the lifetimes of long-lived tracer gases (Prather et al., 2023). . It can be argued that the current observed N_2O lifetime changes are relatively small and, for the four long-lived CFCs examined here, it could be expected to be well within the uncertainties that we derive. So, while this method cannot completely account for the effect of upwelling, the lifetimes presented in Sect. 3.1, still represent a significant improvement to previous estimates.

This paper uses the FRFs and stratospheric lifetimes, for a number of well-studied compounds, found in Leedham-Elvidge et al. (2018) and Burkholder et al. (2022).

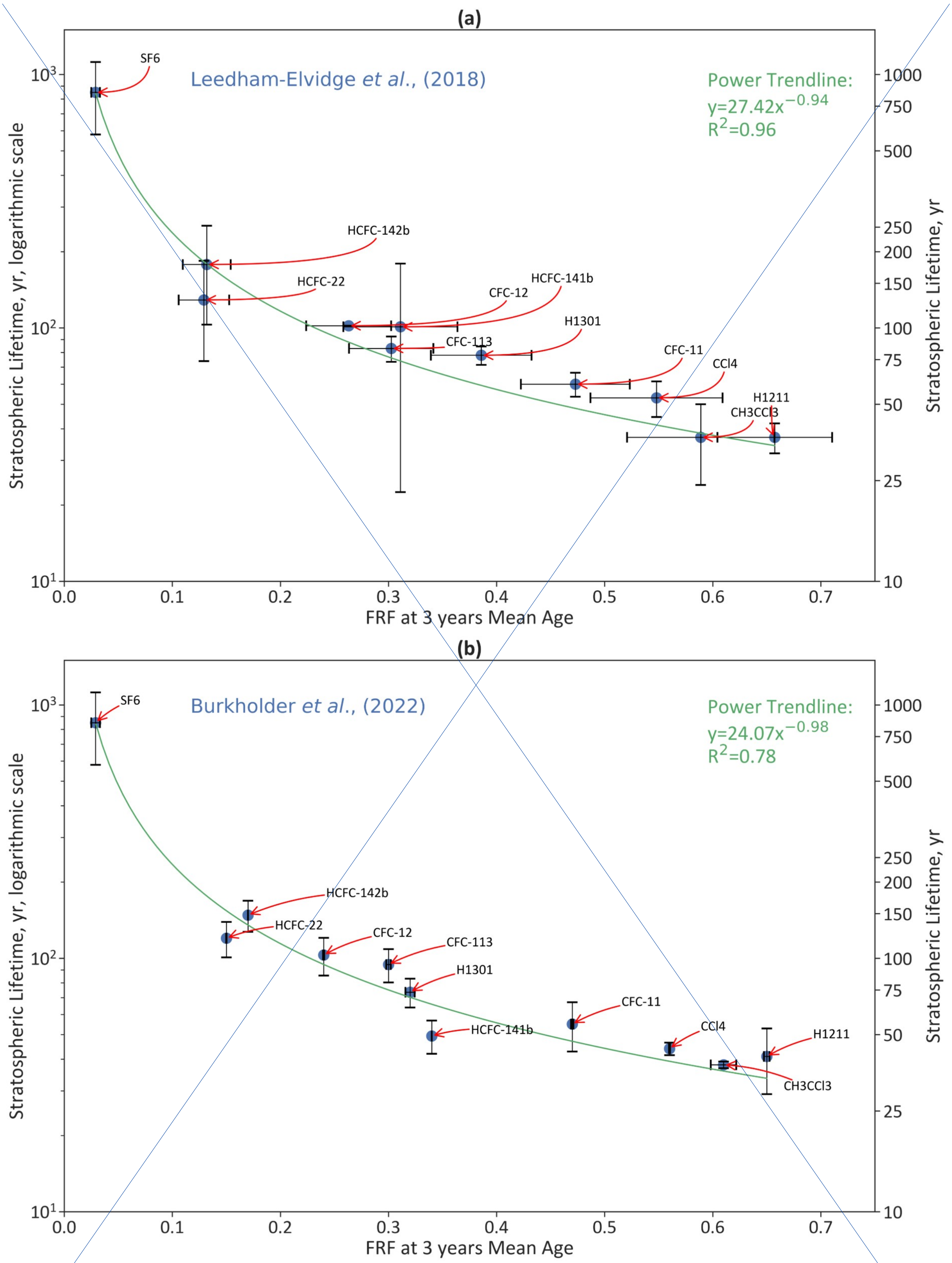

Figure 3; Plotting FRF at 3 years mean ages against Lifetime (yr) for mid latitude. FRFs, lifetimes, and lifetime uncertainties from(a) Leedham-Elvidge et al., (2018), and (b) Burkholder et al., (2022). With the exception of SF$_6$, where the lifetime from Ray et al., (2017) is used. FRF uncertainties were derived from instrument precision and the uncertainty range generated by the bootstrapping procedure. Some compounds (notably SF$_6$) have small enough uncertainty ranges that they are hard to distinguish. No uncertainty values were provided for CCl$_4$'s lifetime estimate, so it is missing the y-error bar. Included in the plot are the 'power' trendline and R^2 value.

In the case of HCFC-141b, Leedham-Elvidge et al. (2018) estimated 101 (64-221) years for the stratospheric lifetime, while Burkholder et al. (2022) lists a stratospheric lifetime of 49.4 years stratospheric lifetime. The

FRFs listed in Burkholder et al. (2022) are taken from Engel et al. (2018) and Leedham-Elvidge et al. (2018) uses the same time-independent method as Engel. et al. (2018). Engel et al. (2018) lists FRFs at 5.5 years rather than the 5 years used with the Leedham-Elvidge et al. (2018) data. Burkholder et al. (2022) primarily uses lifetime estimate for the compounds in question from the 2013 SPARC lifetime report (Ko et al., 2013), which relied upon kinetics and modelling data. There are two exceptions; HCFC-142b which used the lifetime estimate from Papanastasiou et al. (2018) and CCl_4 which used the 2016 SPARC report (Liang et al., 2016). It is worth noting that the stratospheric lifetimes of many compounds are subject to substantial uncertainty, which is something this paper hopes to improve.

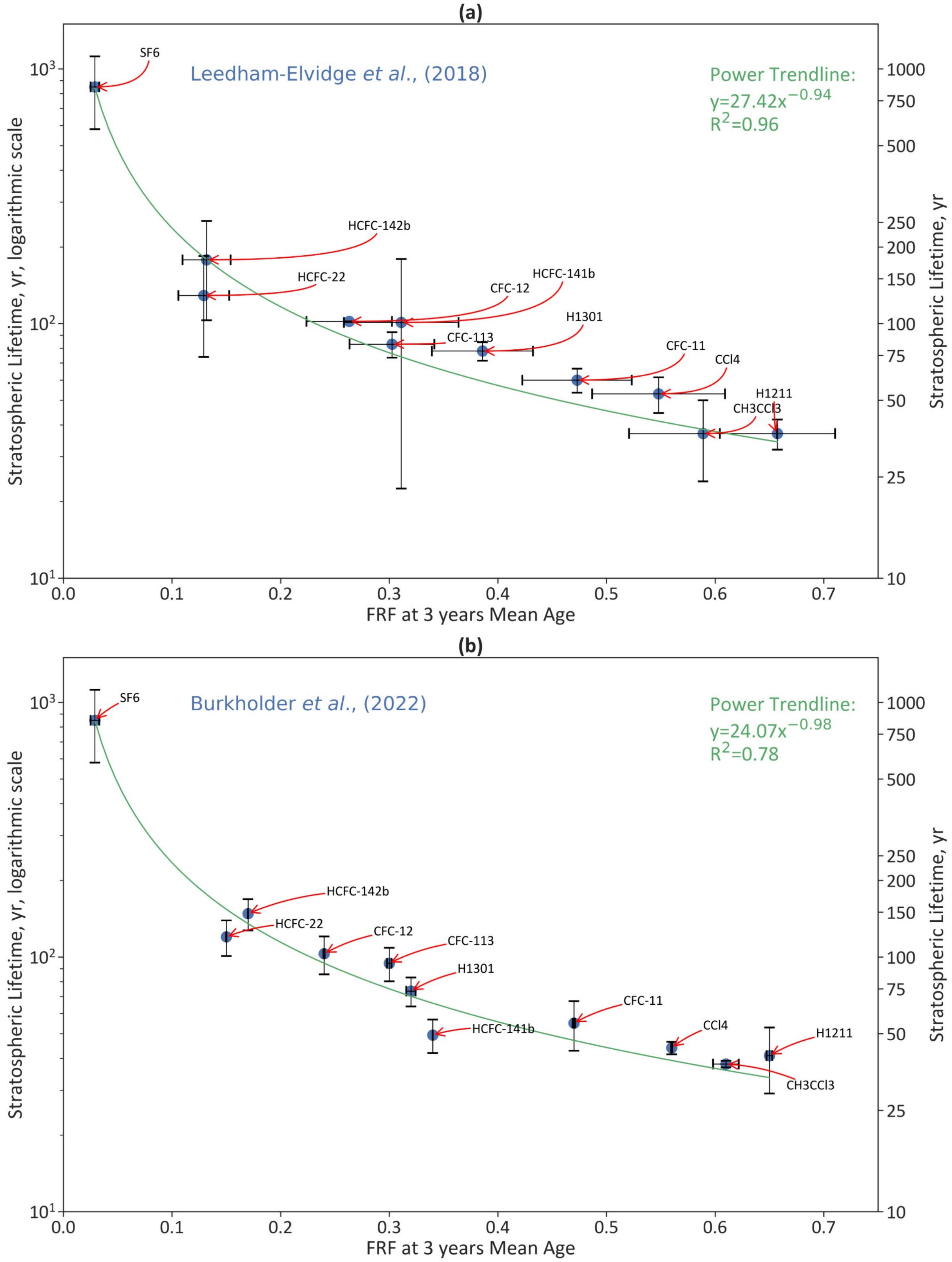

Figure 4; Plotting FRF at 3 years mean ages against Lifetime (yr) for mid latitude. FRFs, lifetimes, and lifetime uncertainties from(a) Leedham-Elvidge et al., (2018), and (b) Burkholder et al., (2022). With the exception of SF_6, where the lifetime from Ray et al., (2017) is used. FRF uncertainties were derived from instrument precision and the uncertainty range generated by the bootstrapping procedure. Some compounds (notably SF_6) have small enough uncertainty ranges that they are hard to distinguish. No uncertainty values were provided for CCl_4's lifetime estimate, so it is missing the y-error bar. Included in the plot are the 'power' trendline and R^2 value.

All methods have weaknesses. Models rely on parametrisations, and require accurate transport and chemistry inputs, which may be incomplete (Ko *et al.*, 2013). Satellites may be unable to resolve less abundant trace gases. Lab-based kinetics experiments may not be able to differentiate isomers (such as CFC-114/CFC-114a, see Vollmer et al., (2018)). This paper uses a version of the tracer-mean age method, which does rely on some assumptions; notably that the lifetimes of the compounds used in this correlation are robust. It also relies on observational data being of high quality. While no method is perfect, expanding the range of methods used can cover gaps left by other methods, and build a more robust understanding of compound lifetimes.

~~This paper uses the FRFs and stratospheric lifetimes, for a number of well-studied compounds, found in Leedham-Elvidge et al., (2018) and Burkholder et al., (2022). In the case of HCFC-141b, Leedham-Elvidge et al., (2018) estimated 101 (64-221) years for the stratospheric lifetime, while Burkholder et al., (2022) lists a stratospheric lifetime of 49.4 years stratospheric lifetime. The FRFs listed in Burkholder et al., (2022) are taken from Engel et al., (2018) and Leedham-Elvidge et al., (2018) uses the same time-independent method as Engel. et al. (2018). Engel et al., (2018) lists FRFs at 5.5 years rather than the 5 years used with the Leedham-Elvidge et al., (2018) data. Burkholder et al., (2022) primarily uses lifetime estimate for the compounds in question from the 2013 SPARC lifetime report (Ko et al., 2013), which relied upon kinetics and modelling data. There are two exceptions; HCFC-142b which used the lifetime estimate from Papanastasiou et al., (2018) and~~ ~~CCl_4 which used the 2016 SPARC report (Liang et al., 2016). It is worth noting that the stratospheric lifetimes of many compounds are subject to substantial uncertainty, which is something this paper hopes to improve.~~

[3] Results

2.5[3.1] Fractional Release Factors and Stratospheric Lifetime Estimates

Table 2 shows that the FRF at 3 years mean age for CFC-114a (0.313 ±0.015) is similar to (but greater than) that of CFC-12 (0.24 ±0.000528) (Engel *et al.*, 2018)(Table 1), which would constrain the CFC-114a lifetime to the lower end of the reported range. This is feasible: the CFC-12 lifetime is 102 years (±15.5 yr~~),~~), while the CFC-114a lifetime is 82-133 years (Table 1). We can also compare CFC-114, whose FRF at 3 years mean age was found to be 0.121 (±0.007) and has an estimated lifetime of 191 years (±23 yr), to HCFC-22 which has an estimated FRF at 3 years mean age of 0.13, and lifetime of 129 (94-204) years in Leedham-Elvidge et al., (2018) and 120 years in Burkholder et al., (2022). Hence, HCFC-22 and CFC-114 have similar FRFs at 3 years mean age, and comparable lifetimes.

Table 2: Fractional Release factors for this paper's compounds of interest. Includes both FRFs at 3 and 5 years mean ages, and their uncertainty range. Compared to previous ~~Time~~ time-independent FRF estimates from Engel et al., (2018), as cited in Burkholder et al. (2022).

Compound	FRF at 3 years Mean Age	FRF at 5 years Mean Age	Previous Estimates (FRF at 3 years Mean Age)
CFC-13	0.071 (±0.003)	0.126 (± 0.003)	N/A
CFC-114	0.121 (±0.007)	0.227 (± 0.012)	0.13 (± 0.00014)
CFC-114a	0.313 (±0.015)	0.571 (± 0.026)	N/A
CFC-115	0.060 (± 0.002)	0.118 (±0.005)	0.07 (±0.00032)
SF_6	0.029 (±0.002)	0.046 (±0.005)	N/A

In Table 2 we see that for the two compounds where we have previous estimates for FRF at 3 years mean age (CFC-114 and CFC-115), the newly derived estimates are lower than the previously derived estimates. For CFC-13 and CFC-114a, FRFs at 3 years mean age are not listed in Burkholder et al. (2022), so this data represents an expansion of our knowledge of these compounds.

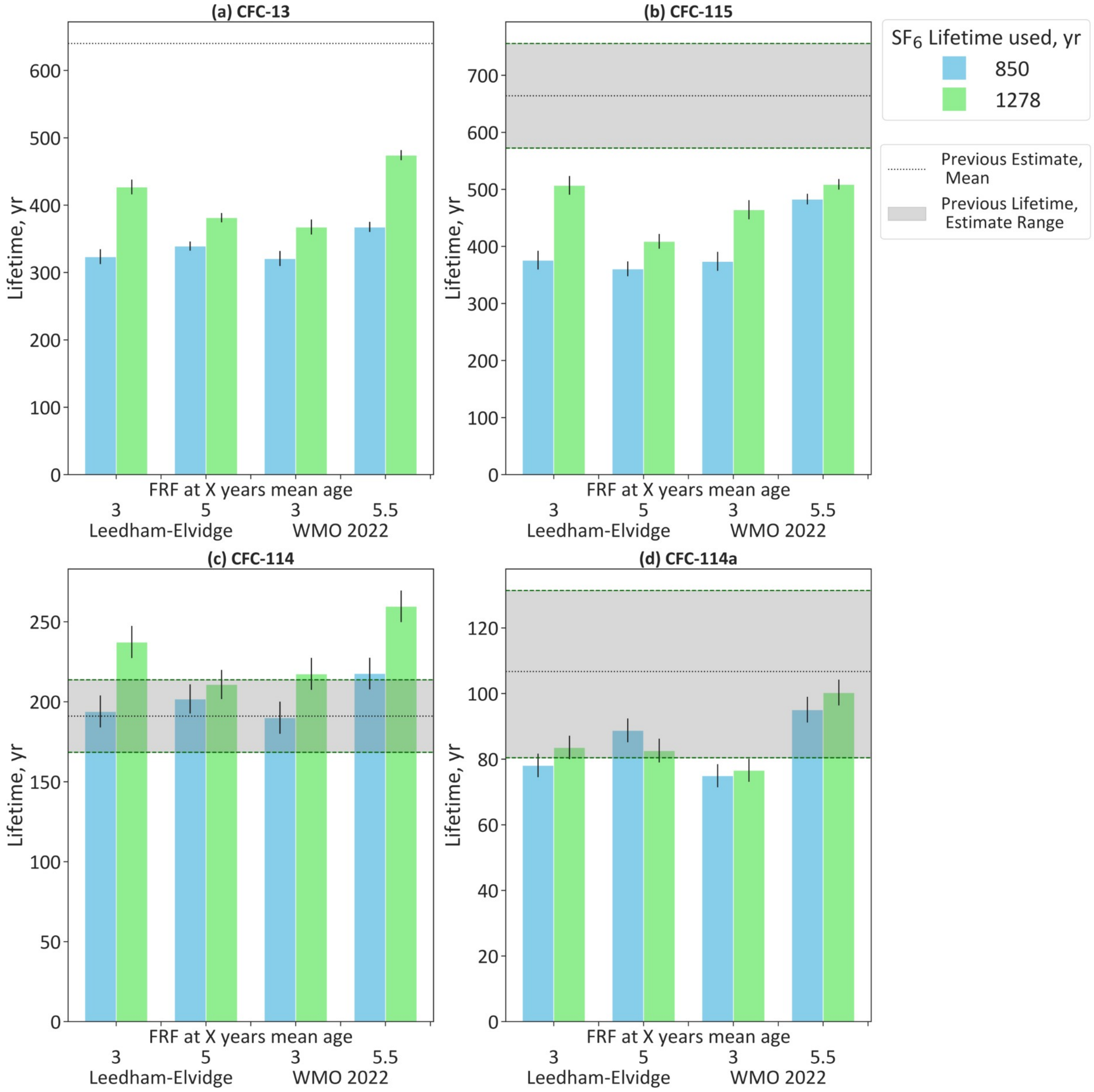

Figure 5: Newly estimated stratospheric lifetimes for each compound, using the correlation between FRF at X years mean age (3 or 5/5.5 years) and lifetimes of well -studied compounds taken either from Leedham-Elvidge et al., (2018) or Burkholder et al. (2022) (labelled as WMO 2022 in Figure). These are compared to previous lifetime estimates in Burkholder et al., (2022). Uncertainty range unavailable in Burkholder et al., (2022) for CFC-13. As the lifetime of SF_6 is disputed, two different correlations were used, one containing the lifetime estimates of 850 years from Ray et al., (2017), and one using the lifetime estimate of 1278 years from Kovács et al., (2017). Error bars are to 2 sigma uncertainty. Uncertainty range unavailable in Burkholder et al., (2022) for CFC-13.

In Fig. 5, the newly estimated stratospheric lifetimes for both CFC-13 and CFC-115 are substantially lower than the previous estimates (see Table 1). This is outside the uncertainty range for CFC-115, though no uncertainty was provided for the previous CFC-13 lifetime estimate, so we cannot definitively state this is outside the uncertainty range. However, this does strongly suggest that previous stratospheric lifetime estimates for these compounds are a significant overestimate.

The longer-lived CFC-13 and CFC-115 both showed greater variation in their estimated lifetime, depending on which SF_6 lifetime was used, when compared to the shorter-lived CFC-114 and CFC-114a. As can be seen in Figs. 4 a&b, SF_6 was the longest-lived compound in the correlation by a substantial margin. Without other compounds within this lifetime range, changes to its lifetime would have a more pronounced effect on estimated lifetimes of compounds with lifetimes between that of SF_6 and HCFC-142b (the longest lived of the other compounds used in the correlation). As there were many compounds with comparatively shorter lifetimes, this portion of the trendline is better constrained, and so CFC-114 and CFC-114a would be less affected by which lifetime estimate for SF_6 was used. This is seen in Fig. 5 c&d as most lifetime estimates for CFC-114 and CFC-114a are within the range of their previous lifetime estimate (Table 1).

2.6[3.2] Ozone Depletion Potentials

The newly derived FRFs at 3 and 5 years mean age, and the newly derived lifetimes for these compounds were utilised to calculate ODPs (using Equation 3), and the results can be seen in Table 3.

$$ODP_i = \left(\alpha n_{Br,i} + n_{Cl,i}\right) \frac{f_i}{f_{CFC_{11}}} \frac{\tau_i}{\tau_{CFC_{11}}} \frac{M_{CFC_{11}}}{M_i} \frac{1}{3}$$

Equation 3

Equation 3 is the equation for calculation of ODPs. Where *i* is the gas of interest; α is the bromine efficiency factor (redundant in this case as the CFCs do not contain bromine), *n* is the number of chlorine (or bromine) atoms in the molecule; *f* is the FRF; τ is the atmospheric lifetime (in this case the stratospheric steady-state lifetime); and M is the molecular weight.

Table 3: The ~~C~~compounds, their ODP values listed in Burkholder et al~~.,~~. (2022), and their newly estimated ODP values using FRFs at ~~at~~ 3 and 5 years mean age.

Compound	Burkholder et al., 2022	Newly estimated; using FRFs at 3 years mean age	Newly estimated; using FRFs at 5 years mean age
CFC-13	0.3	0.38 (0.36-0.39)	0.34 (0.34-0.35)
CFC-114	0.53 (±0.02)	0.48 (0.45-0.5)	0.46 (0.43-0.48)
CFC-114a	0.72	0.53 (0.5-0.55)	0.49 (0.47-0.51)
CFC-115	0.45 (±0.01)	0.25 (0.25-0.27)	0.26 (0.24-0.27)

ODPs derived using FRFs at 3 years and those using FRFs at 5 years agree within their respective uncertainty ranges, with the exception of CFC-13 for which the uncertainties do not quite overlap. None of the newly derived ODPs overlap with those listed in Burkholder et al~~.,~~. (2022), though CFC-114 is the closest.

2.7[3.3] Effect on Emissions Estimates

If the stratospheric lifetimes of these compounds are significantly shorter than previously believed, then this would suggest that historic emissions must have been higher than previously estimated in order to account for the compounds' abundance. This paper includes updated data from Western et al~~.,~~. (2023), which used the averaged lifetimes derived here (Table 1), and the results can be seen in Fig. 6.

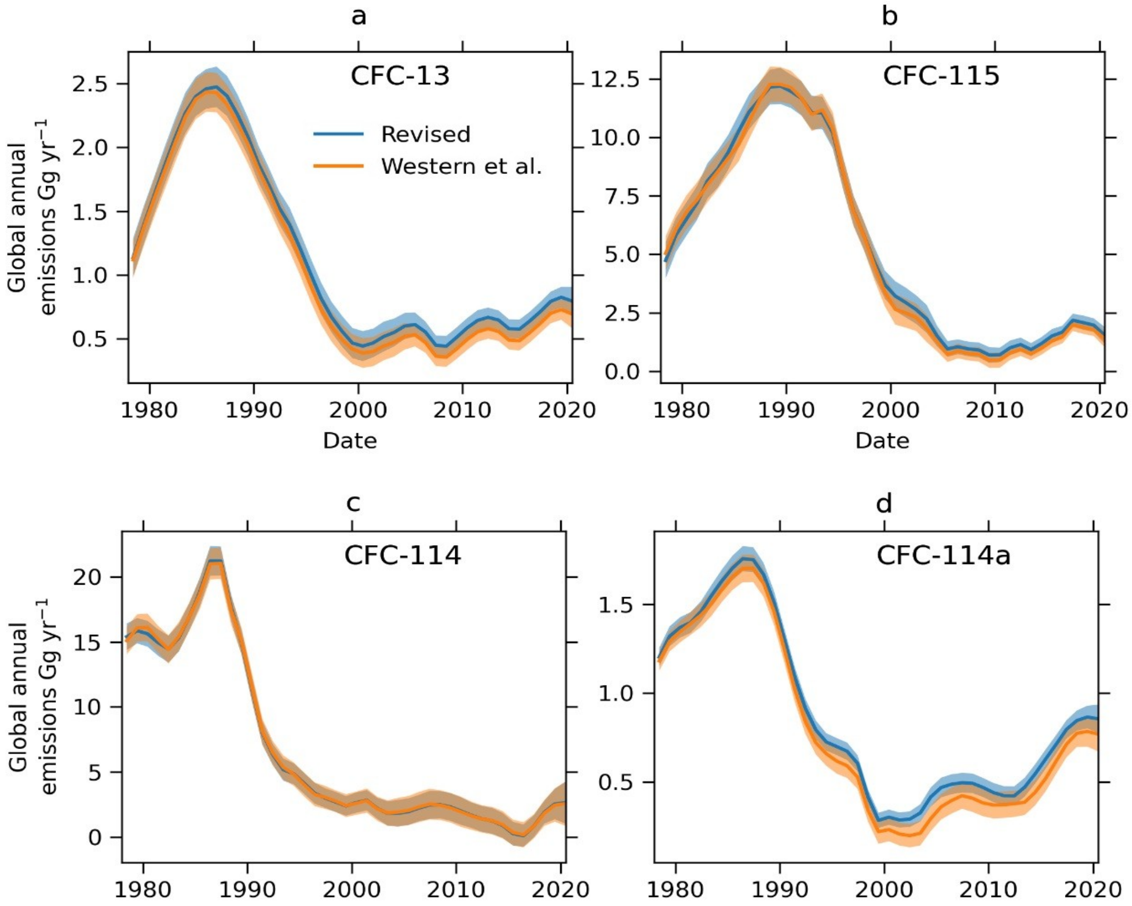

Figure 6: The emissions estimates for all four compounds, showing the original emissions estimates from Western et al~~,~~. (2023) and revised estimates that use the revised lifetime estimates from Table 4.

As expected, between 2000 and 2020, emission estimates are higher when using the revised lifetimes compared to the previously estimated lifetimes, with the exception of CFC-114 (whose lifetime estimate did not change significantly) (Fig. 6). This represented an increase in average emissions for CFC-13 of 17% (±3%), CFC-114a of 20% (±8%), and CFC-115 of 19% (±5%). CFC-114 saw only a -0.07% change (±8%). The uncertainty range is broad and overlaps for all compounds, however it is clear that longer stratospheric lifetimes would result in higher emissions.

~~Discussions~~

The question remains whether these increased global emission estimates for CFC-13 and CFC-115 are due to release from long-term banks, or from new emissions. Estimates of bank emissions vary widely as they are estimated using different techniques which utilise incomplete or imprecise information (TEAP, 2009). Lickley et al., (2022) argues that production assumptions for several CFCs (including CFC-115 but not CFC-13) have a low bias stemming from under-reporting, leading to published bank estimates that also have a low bias, and thus banks are likely to be larger than previously assumed. This is consistent with Section 3.3 where the decreased lifetimes estimated in Sect 3.1 resulted in greater estimated emissions.

Emissions from aluminium smelters (CFC-13) and impurities of CFC-115 in the refrigerant HFC-125 did not fully account for the lingering global emissions found in atmospheric observations. Western et al., (2023) found that CFC-115 emissions are probably the result of the production of hydrofluorocarbons, and that CFC-13 emissions can be the result of deliberate plasma arc destruction of CFC-12. Bourguet et al., (2024) argues that unreported feedstock production for HFCs may be responsible for higher than expected emissions of CFC-114 and CFC-115. Vollmer et al., (2018) and Western et al. (2023) found that growth rates for both CFC-13 and CFC-115 were significantly larger than would have been predicted based on zero emissions. Shorter lifetimes for these two compounds would require greater emissions than previously assumed in order to account for their atmospheric abundance, which is consistent with this paper's findings. Lickley et al., (2022) found a discrepancy for CFC-115 in which the modelled mole fraction increased through the simulation period (1960-2020), which is in contrast to observed real world mole fractions which were comparatively constant. This is qualitatively consistent with the results shown in Fig. 6, where emissions estimates using the new, shorter lifetime, are greater than those derived using the previously estimated lifetime.

3[4] Conclusion

In this paper we used in situ data to investigate four relatively long-lived CFCs: CFC-13, CFC-114, CFC-114a, and CFC-115. These are important because due to their long lifetimes they will be present in the atmosphere longer and thus contribute to ozone depletion for longer. This paper presents newly derived (using in situ data) policy relevant metrics for these compounds ~~().~~ (Table 5).

This study derived updated steady-state stratospheric lifetimes for these compounds (Sect.3.1), and in the case of CFC-13 and CFC-115 these were substantially lower than previous estimates. With such lower lifetimes, emissions for these compounds would need to be substantially greater in order to account for the compounds' abundance. Sect.3.3 shows that this is indeed the case, with the greatest effect seen for the longer lived compounds (where the lifetimes have been more significantly revised). While this study suggests that emissions of CFC-13 and CFC-115 are likely to be higher than those previously estimated, at present it is not certain if these additional emissions are the result of long-term banks, or new production of the compounds, either deliberately, or as a by-product of other processes.

This paper also ~~presents newly derived~~derives new FRFs and ODPs for these compounds~~,~~ using observational data. Sect. 3.1 presents newly derived FRFs; ~~the two compounds for which FRFs at 3 years mean age are listed in Burkholder et al., (2022),~~ CFC-114 and CFC-115 were found to have lower FRFs than previously assumed~~.~~ (Burkholder et al., 2022). CFC-13 and CFC-114a did not have ~~FRFs at 3 years mean age listed in Burkholder et al., (2022), so this paper's findings can help fill that~~ previously published FRFs, and therefore the results presented here address this gap. In terms of ODPs, Sect. 3.2 found that none of the compounds studied here had ODPs that overlapped Burkholder et al., (2022) within the uncertainties. CFC-13 had a larger ODP than previously estimated, while CFC-114, CFC-114a, and CFC-115 had smaller ODPs.

Emissions of the four long-lived CFCs discussed here have been increasing in recent years, despite a phase-out of the production of CFCs in 2010. The new metrics derived in this work will assist to further investigate the sources and impacts of these ongoing emissions. For example, Lickley et al., (2022) shows that long-term 'banks' are likely to be greater than previous estimates had suggested~~,~~ and ~~suggests~~indicates that production of ODSs was higher than previously reported. In order to accurately assess these banks, accurate lifetimes for the compounds of interest are required. The new estimates for lifetimes found in along with the method for using in situ data to determine lifetime described in Sect. 2.4 should aid ~~aid~~ in accounting for these banks. This in turn should assist in efforts to evaluate ongoing compliance with the Montreal Protocol.

Table 4. The ~~C~~compounds, their newly estimated stratospheric lifetimes (yr), FRFs, and ODPs.

Compound	Newly Estimated Stratospheric Lifetime, yr	Newly Estimated FRF	Newly Estimated ODP
CFC-13	315 (287-331)	0.071 (±0.003)	0.38 (0.36-0.39)
CFC-114	190 (176-201)	0.121 (±0.007)	0.48 (0.45-0.5)
CFC-114a	81 (76-87)	0.313 (±0.015)	0.53 (0.5-0.55)
CFC-115	369 (328-435)	0.06 (±0.002)	0.25 (0.25-0.27)

~~While this study suggests that emissions of CFC-13 and CFC-115 are likely to be higher than those previously estimated, at present it is not certain if these additional emissions are the result of long-term banks, or new production of the compounds, either deliberately, or as a by-product of other processes.~~

Supplementary data

Supplementary data for this paper includes: The Cape Grim Observatory background trend (date and mixing ratio), as measured at UEA, for CFC-13, CFC-114, CFC-114a, and CFC-115. The mean ages, mixing ratios, and respective uncertainties for the four compounds studied, for all ~~5~~five Geophysica flights. The updated emissions estimates from Western et al., (2023) for all four compounds. This supplementary data can be found at: https://zenodo.org/records/16736497

Author Contributions

ET wrote the article and conducted most of the analysis of the overall dataset. JCL, KEA, and ELE, conducted most of the sample measurements, and worked together with ET to calculate the mean ages and fractional release factors. JCL and WTS coordinated activities for the University of East Anglia (UEA) related to the StratoClim aircraft campaigns. PJF, RL and DEO organised the collection of samples from the Cape Grim Monitoring Station. TR coordinated the operation a whole air sampler on the research aircraft to collect the air samples used in this study. LMW calculated updated (from Western et al., (2023)) emissions estimates using this paper's newly estimated stratospheric lifetimes. JM and PK were the key contacts at AGAGE~~,~~ and contributed substantially to the scientific discussions surrounding this article, and the process of writing it. HB provided help in analysis of the dataset. ~~-~~Valuable comments on the manuscript were provided by all authors, in addition to helpful discussion and insights throughout the study process.

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

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