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# Global increase of ozone-depleting chlorofluorocarbons from 2010 to 2020

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## Abstract

The production of chlorofluorocarbons (CFCs) that would ultimately be released to the atmosphere was banned globally in 2010 under the Montreal Protocol. Here we use measurements combined with an atmospheric transport model to show how atmospheric abundances and emissions of five CFCs increased between 2010 and 2020 – contrary to the goals of the phase-out. The Montreal Protocol allows CFC production for use as a feedstock to produce other chemicals. Emissions of CFC-113a, CFC-114a and CFC-115 likely arise during the production of hydrofluorocarbons, which have replaced CFCs for many applications. The drivers behind increasing emissions of CFC-13 and CFC-112a are more uncertain. The combined emissions of CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115 increased from 1.6 ± 0.2 to 4.2 ± 0.4 ODP-Gg $yr^{1}$ (CFC-11 equivalent ozone-depleting potential) between 2010 and 2020. The anticipated impact of these emissions on stratospheric ozone recovery is small. However, ongoing emissions of the five CFCs of focus may negate some of the benefits gained under the Montreal Protocol if they continue to rise. Additionally, the climate impact of the emissions of these CFCs needs to be considered, as their 2020 emissions are equivalent to 47 ± 5 Tg of $CO_2$.

## Main text

Chlorofluorocarbons (CFCs) are industrially produced compounds that were commonly used as refrigerants, aerosol propellants, solvents, and foam-blowing agents. An increasing abundance of CFCs in the atmosphere was the primary driver behind stratospheric ozone depletion and the Antarctic ozone hole. In response, nations agreed that the production of CFCs that would ultimately be released to the atmosphere (dispersive uses) would be phased out globally by 2010. Examples of dispersive uses of CFCs are aerosol sprays, foam blowing agents or as a refrigerant. The phase-out has avoided substantial additional depletion of the stratospheric ozone layer[1,2] and global warming, as long-lived CFCs have global warming potentials many thousand times that of carbon dioxide over a 100-year time horizon[3,4].

Global emissions of several gases have increased despite controls imposed on their production under the Montreal Protocol on Substances that Deplete the Ozone Layer. Emissions of CFC-11 increased after its global phase-out in 2010, which was attributed to CFC-11 production and use that was not reported, as required, under the Montreal Protocol[5,6]. Since 2017, emissions of HCFC-141b, the primary replacement for CFC-11 for foam blowing, have been increasing even though its production phase-down is underway. The increase is possibly due to the disposal of appliances with foam containing HCFC-141b. Increasing or persistent emissions of several other CFCs[7–9] and HCFCs[10,11] have been attributed, at least in part, to their production as feedstock or as an intermediate/by-product during production of other compounds, such as hydrofluorocarbons (HFCs). Feedstocks are the raw materials used to produce another compound and are often assumed to be near-fully converted into the target compound. While the Montreal Protocol does not ban the use of chemicals as feedstocks or emission of some by-products, it does encourage best efforts to reduce emissions.

Here, we focus on five CFCs with few, or no, known current uses: CFC-13 ($CClF_3$), CFC-112a ($CClF_2CCl_3$), CFC-113a ($CF_3CCl_3$), CFC-114a ($CF_3CCl_2F$), and CFC-115 ($CF_3CClF_2$), which have atmospheric lifetimes ranging from 52-640 years[12,13]. We present measurement-based atmospheric abundance time series of the five CFCs, from which we derive global emissions using a model of global atmospheric transport. The atmospheric abundances and emissions of all five CFCs have increased since the phase-out for dispersive use of CFCs in 2010, resulting in a modest impact on stratospheric ozone and a substantial contribution to climate change. Whilst little to none of these gases are expected to exist in old appliances or building foams, CFC-113a, CFC-114a and CFC-115 are known feedstocks, intermediates, or by-products during the production of other chemicals. The most notable target chemicals are the two most common HFCs, HFC-134a and HFC-125, whose production has rapidly increased since 2010[14]. There are no known current uses for CFC-112a and CFC-13. CFC-13 emissions are known to occur during the deliberate plasma arc destruction of CFC-12[15], and CFC-112a had been used as a feedstock for fluorovinyl ether production[16]. CFC-13 was previously used as a low-temperature refrigerant and CFC-112a as a solvent. However, like other CFCs in dispersive uses, these emissions should have ceased in 2010.

## Increasing global abundances and emissions

Atmospheric mole fractions of CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115 have been previously reported[8,9,17,18] and are updated here. Abundances of CFC-13 and CFC-113a had been increasing throughout their published measurement record (1950s to 2017), while had been increasing throughout their published measurement record (1960s to 2017), while those of CFC-115 had started to increase again after a period of near-zero growth in the 2000s. For CFC-114a, global mole fractions had stabilised in the early 2000s, and for CFC-112a they had started to decrease around that time. Our new results focus on the decade from 2010 to 2020 (Figure 1), after CFCs were phased out globally for dispersive uses. Most notable is that the mole fractions of CFC-112a and CFC-114a started to increase around 2013, and the growth of CFC-113a accelerated around 2016. In 2020, all five gases were at their highest abundance since direct measurement-based records began (1978 for all gases, except CFC-112a, which began in 1999. Records before 1978 are based on measurements of air extracted from polar firn rather than air collected in situ), as abundances of both CFC-13 and CFC-115 continued to increase. Furthermore, atmospheric abundances of CFC-112a and CFC-113a were growing faster in 2020 than at any point in their atmospheric records. For CFC-13 and CFC-115, two independent measurement networks support the record-high mole fraction in 2020 (see supplementary Fig S1 and its caption for a more detailed discussion, and Fig S2 for additional independent measurements of CFC-13 and CFC-115). For CFC-112a, CFC-113a, and CFC-114a it is worth noting that their isomers (CFC-112, CFC-113 and CFC-114), which are present in the atmosphere at larger abundances in all three cases, have continued to decrease in abundance throughout 2010-2020 (Figure S3).

Combined global emissions of CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115 increased from 1.6 ± 0.2 to 4.2 ± 0.4 ODP-Gg yr$^{-1}$ (ODP-Gg, mass weighted by their CFC-11 equivalent ozone depleting potential) between 2010-2020 (Figure 2). The mean growth rate of these emissions is around 0.3 ODP-Gg yr$^{-1}$ per year. Global emissions of CFC-11 increased between 2008-2012 and 2014-2018[5,19], and were attributed to unreported production. The increase in global emissions between 2010-2020 of the five CFCs reported here (expressed as ODP-Gg yr$^{-1}$) is around a fifth of the global increase in CFC-11. In terms of impact on climate, the five CFC emissions derived for 2020 are equivalent to 47 ± 5 Tg yr$^{-1}$ $CO_2$-eq in 2020 (around 150% of London's $CO_2$ emissions in 2018[20] based on 100-year global warming potentials). In 2020, combined emissions of CFC-112a, CFC-113a and CFC-114a (3.1 ± 0.4 ODP-Gg yr$^{-1}$) may have exceeded that of their isomers CFC-112, CFC-113 and CFC-114 (1.3 ± 14.1 ODP-Gg yr$^{-1}$, Figs. S3 and S4), albeit with large uncertainty. In 2020, ODP emissions of CFC-113a were the largest of the five gases (2.5 ± 0.4 ODP-Gg yr$^{-1}$), followed by CFC-13 (0.7 ± 0.1 ODP-Gg yr$^{-1}$), CFC-114a (0.6 ± 0.1 ODP-Gg yr$^{-1}$), CFC-115 (0.4 ± 0.1 ODP-Gg yr$^{-1}$) and CFC-112a (0.1 ± 0.03 ODP-Gg yr$^{-1}$). In terms of the global warming potentials of the emissions, CFC-115 emissions were highest (14.3 ± 3.6 Tg yr$^{-1}$ $CO_2$-eq), followed by CFC-113a (14.0 ± 2.2 Tg yr$^{-1}$ $CO_2$-eq), CFC-13 (12.0 ± 1.9 Tg yr$^{-1}$ $CO_2$-eq), CFC-114a (6 ± 0.8 Tg yr$^{-1}$ $CO_2$-eq) and CFC-112a (0.1 ± 0.03 Tg yr$^{-1}$ $CO_2$-eq). Figure S3 shows emissions for individual CFCs and its caption gives more details about their changes.

## CFC production as feedstock, intermediates or by-products

Previous work has linked emissions of CFC-113a and CFC-115 to the production of HFC-125, a compound used primarily in refrigeration and air conditioning in rapidly increasing quantities in recent years[8,9,17,21]. CFC-113a and CFC-115, along with CFC-114a[22], are considered 'undesirable by-products' during HFC-125 production, which may account for at least some of the observed emissions. During HFC-125 production, up to ~1.1% by mass of the perchloroethylene (PCE, $C_2Cl_4$) feedstock may end up as CFC-113a, ~3.3% as CFC-114a and ~3.3% as CFC-115, depending on the production route[22]. Estimates of global HFC-125 production increased from around 95 to 205 Gg yr$^{-1}$ between 2010-2020[14]. These estimates of HFC production use the mean of the upper and lower estimates of a scenario of compliance with the Kigali Amendment[14] (Figure S5), which aims to phase out most HFC production, and is likely an underestimate of true HFC production for 2020. We use the estimated HFC-125 production and derived CFC emissions, minus their values in 2010, to approximate the ratio of CFC emissions to HFC production. Since 2010, CFC-115 emissions represent ~1.3%, CFC-113a ~2.1% and CFC-114a ~0.2% of HFC-125 production by mass. The timing and trajectory of the increase in CFC-113a and CFC-115 emissions follows that of HFC-125 production in countries under Article 5 of the Montreal Protocol (developing countries) since 2006 (see Figure S5). Estimates of leakage rates for feedstock production vary substantially. A previous worst-case scenario for emissions due to by-product leakage during HFC production was 1.6%[23], yet typical leakage during fluorochemical production has also been estimated to be as high as 4%[24] (with a 95% uncertainty range of 0.1-20%). If undesirable by-products are formed during HFC-125 production, and not properly captured or destroyed, by-product leakage may explain at least some of the increasing emissions of CFC-113a, CFC-114a and CFC-115 over the past decade. The ratio of derived CFC emissions rates to HFC production supports the hypothesis of CFC leakage during HFC production.

In addition to being possible by-products in HFC-125 production, CFC-113a and CFC-114a are intermediates in a production pathway of HFC-134a. HFC-134a is the most abundant HFC in the atmosphere, and is used primarily in mobile air conditioning, with estimated global consumption increasing from 237 to 321 Gg yr$^{-1}$ between 2010 and 2020[14] (Figure S5). Emissions above 2010 levels for CFC-113a and CFC-114a are equivalent to around 3.5% and 0.3% of HFC-134a production, or 1.2% and 0.1% of combined HFC-125 and HFC-134a production. Leakage from feedstock usage of CFC-113a to produce trifluoroacetic acid (TFA), pesticides and the hydrofluoroolefin HFO-1336mzz may also contribute to the emissions[25] but there are no published estimates of the produced quantities of these target substances. HFO-1336mzz will replace some HFCs with very high global warming potentials, and its production has the potential to continue long into the future.

The hydrochlorofluorocarbon HCFC-133a is another undesirable by-product of HFC-125 production (up to 1.3% of PCE), and its emissions were previously attributed to HFC-125 and HFC-134a production[10,11,17,25]. Persistent emissions of HCFC-133a give supporting evidence for intermediate/by-product leakage during HFC production. However, emissions of HCFC-133a do not exhibit the same continuously increasing trend as the associated CFCs, which may suggest that not all sources of CFC and HCFC emissions are common during HFC production. Additionally, emissions of HCFC-132b, also an intermediate/by-product of HFC-134a production, have increased from near zero in 2000 to around 1 Gg yr$^{-1}$ in 2019[11]. Emissions of HCFC-31 have persisted, but have not increased, since 2010[11] and are associated with the production of HFC-32. HFC-32 is used with HFC-125 in the common refrigerator blend R-410A. Production of HFC-32 and HFC-125 for R-410A is positively correlated, although this correlation may not hold for production-related emissions of by-product gases.

If the Kigali Amendment to the Montreal Protocol had been universally ratified in 2016, production of HFC-134a was projected to be around 8% smaller in 2030 than in 2020[14]. To date, full ratification has not been achieved. However, even under this ideal scenario, HFC-125 production is still projected to increase by 18% between 2020 and 2030. If HFC-125 production

production is still projected to increase by 13% between 2020 and 2030. If HFC-125 production alone is the source of CFC-113a, CFC-114a and CFC-115 emissions, and similar leakage rates continue, further increases in emissions of these CFCs are likely over the next decade even under universal ratification of the Kigali Amendment as HFC production continues to increase. Emissions of CFC-113a, CFC-114a and CFC-115 could reach around 4 ODP-Gg $yr^{-1}$ in 2030, using average projected HFC-125 production assuming universal ratification of the Kigali Amendment[14] and our estimated leakage rates. If emissions of CFCs from feedstock use continue to rise, the ozone depletion associated with HFC and HFO production will continue to increase.

## Uncertain drivers behind CFC-13 and CFC-112a

CFC-13 may be produced during the deliberate plasma arc destruction of CFC-12 refrigerants from old appliances[15]. Reported consumption of all CFCs to the United Nations Environment Programme (UNEP) has been negative since 2011[26], meaning that CFCs are being destroyed globally. However, there is no information on the quantities of CFC-12 destroyed using plasma arc destruction versus other destruction methods, and thus the interconversion levels and eventual emissions of CFC-13 are unclear. Previous work has excluded aluminium smelters as a significant source of global emissions of CFC-13[9]. CFC-13 may be a by-product during the production of CFC-11[9]. Unreported production of CFC-11 occurred during the period 2013-2018[6], and thus CFC-13 may have been inadvertently produced. However, unlike global emissions of CFC-11, which dropped rapidly after 2018[19], emissions of CFC-13 continue through 2020, suggesting a different dominant source.

The source of the renewed emissions of CFC-112a is unknown and we can only speculate qualitatively on a possible resurgence of use as a solvent or a feedstock for fluorovinyl ether production[16].

## Significance for the Montreal Protocol

The trajectory of recently increasing emissions of CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115 is counter to the goal of the production phase-out for dispersive uses, which was completed in 2010 (Figure 2 and S4). The global annual rate of growth in the abundance of CFC-112a, CFC-114a and CFC-115 has accelerated rapidly since 2010. The rate of increase of the global abundance of CFC-113a has twice rapidly risen over the same period. Meanwhile, growth in the abundance of CFC-13 has continued to fluctuate since 2010 following an overall increasing trend. At present, the impact on stratospheric ozone is modest. Cumulative emissions of CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115 between 2010-2020, relative to 2010 levels, could result in around a 0.002% loss in global stratospheric ozone, or 0.01% for the Antarctic Spring (following ref.[27]). These emissions equate to an integrated ozone depletion of around 1.1 DU years[28]. However, if current trends continue or, as has already occurred twice for CFC-113a during 2010-2020, accelerate further, these influences would be larger and offset some of the progress made under the Montreal Protocol. Previous work has identified East Asia as a source of CFC-113a and CFC-115 emissions[8,11]. Updated regional emission estimates of CFC-13 and CFC-115 may better constrain the magnitudes of the increasing trends and their contributing emissions sources (CFC-13 and CFC-115 have wider measurement coverage than CFC-112a, CFC-113a and CFC-114a, see Methods).

Ozone-depleting substances used as feedstocks and produced as by-products are not subject to the same controls on production as those for so-called dispersive use under the Montreal Protocol. As such, there is no current barrier to future use in the synthesis of chemicals. In the absence of further evidence, it is likely that the rapidly rising emissions of the long-lived ozone-depleting CFCs identified here are from processes not subject to current controls under the Montreal Protocol.

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## Online Methods

### *Measurements*

Measurements of CFCs have been made by multiple organisations from air sampled at 14 distinct measurement sites spanning the globe (83°N-90°S). Measurements of CFC-112, CFC-112a, CFC-113, CFC-113a, CFC-114 and CFC-114a are based on background air collected at

112a, CFC-113, CFC-113a, CFC-114 and CFC-114a are based on background air collected at Cape Grim, Tasmania, Australia, 40.7°S, 144.7°E, as part of the Cape Grim Air Archive. Analysis was performed at the University of East Anglia (UEA) and Forschungszentrum Jülich (FZJ). CFC-115 and CFC-13 measurements were made as part of the Advanced Global Atmospheric Gases Experiment (AGAGE)[29] at Mace Head, Ireland, 53.3°N, 9.9°W, Jungfraujoch, Switzerland, 46.5°N, 8.0°E, Trinidad Head, California, USA, 41.0°N, 124.1° W, Cape Matatula, American Samoa, 14.2°S, 170.6°W and Cape Grim. Additionally, CFC-13 was measured by AGAGE at Ragged Point, Barbados, 13.2°N, 59.4°W, but CFC-115 measurements at this site were not used due to CFC-115 contamination from a leaking air conditioning unit containing HFC-32 and HFC-125. AGAGE CFC-13 and CFC-115 measurements were used to derive emissions. CFC-13 and CFC-115 were also measured in samples of background air collected as part of the National Oceanic and Atmospheric Administration (NOAA) measurement network from the sites Alert, Canada, 82.5°N, 62.5°W, Summit, Greenland, 72.6°N, 38.4°W, Barrow, USA, 71.3°N, 156.6°W, Mace Head, Ireland, 53.3°N, 9.9°W, Trinidad Head, USA, 41.0°N, 124.1° W, Niwot Ridge, USA, 40.1°N, 105.6°W, Cape Kumukahi, USA, 19.6°N, 154.9°W, Mauna Loa, USA, 19.5°N, 155.6°W, Cape Matatula, American Samoa, 14.2°S, 170.6°W, Cape Grim, Australia, 40.7°S, 144.7°E and Palmer Station, Antarctica, 64.8°S, 64.1°W for CFC-13. CFC-115 was also measured at South Pole, Antarctica, 90.0°S, 24.8°W, in addition to the measurement sites for CFC-13.

On AGAGE and NOAA analytical systems, air sample measurements were bracketed by those of calibrated tanks of compressed whole air. Tanks from NOAA[30] and AGAGE[29] are calibrated against standards established through accepted gravimetrically derived methods. Cylinders from UEA/FZJ are calibrated against volumetric standards, where primary standards are based on a two-step static dilution in pure $N_2$, which have been shown to compare well with gravimetrically derived calibration scales[10,17]. The calibration standards serve as reference links to the respective scales established at UEA (CFC-112, CFC-112a, CFC-113, CFC-113a, CFC-114, CFC-114a), NOAA (CFC-13, and CFC-115), and within AGAGE (CFC-115) and at the Swiss Federal Institute of Metrology, METAS (for CFC-13 AGAGE measurements).

At UEA/FZJ, air samples were analysed using 200-300 ml of air and systems based on cryogenic preconcentration at -78°C followed by gas chromatography coupled with mass spectrometry (GC-MS). UEA/FZJ secondary standards have been obtained from NOAA from air collected at Niwot Ridge, Colorado, USA (40.0542° North, 105.5889° West, 3538.00 masl). For more information on the measurement system see refs.[8,18,31]. CFC-112, -112a, -113, -113a, -114, and -114a measurements were performed on an Agilent 6890 GC coupled to a Waters AutoSpec triple-sector MS[8,17,18]. Two of the GC-MS systems were used for the analysis of the Cape Grim air archive[32] and flask samples in this work, one at UEA and one newly established at FZJ. The respective time series overlap for several years and show excellent agreement for all species with similar uncertainties and no indications of any offset. Uncertainties are derived from the square root of the sum of the squared 1-sigma standard deviations of the working standard and the sample repeats, which were, on average, 4.1% (CFC-112a), 2.9% (CFC-113a) and 1.3% (CFC-114a) between 2000 and 2020. The different chromatographic setup of these analytical systems[17,18] enables the separation of CFC isomers, which is crucial for the derivation of isomer-independent trends and emissions.

AGAGE in situ measurements of CFC-13 and CFC-115 in ~2 L air samples were made using

Medusa GC-MS instruments. These are cryogenic pre-concentration systems coupled with a gas chromatograph (GC, Agilent, USA) and a quadrupole mass selective detector (MSD, Agilent, USA)[33,34]. The mass spectrometers were upgraded at several AGAGE sites in the 2011-2013 time frame resulting in improved precisions[9] for CFC-13 from ~1.5% (1-sigma) to ~1%. CFC-115 precisions were ~0.8-0.4% (with only small improvements following the mass spectrometer upgrades). Ambient air and reference gas measurements were alternated resulting in ~12 fully calibrated samples per day[29]. The same kind of instruments were used to measure archived air samples (also typically ~2 L) collected as part of the Cape Grim Air Archive at Cape Grim[35] at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and at the Scripps Institution of Oceanography (SIO)[36]. Measurements of CFC-13 are reported on the METAS-2017 primary calibration scale and measurements of CFC-115 on the SIO-05 scale as parts per trillion (ppt) dry-air mole fractions[9]. Secondary and tertiary AGAGE calibration standards are compressed clean air samples filled in the wintertime during stormy conditions at La Jolla (recent) or Trinidad Head (past), California. Quaternary standards were either also filled at these sites or near individual measurement stations[29]. AGAGE measurements of archived air samples and in situ data are representative of both background and polluted air, and therefore were filtered with statistical methods to remove outliers and pollution events to produce monthly means from the high frequency measurements[37].

The data provided from the NOAA network (Fig. S2) were obtained from flask-air samples collected in paired stainless-steel flasks at approximately weekly intervals and sent to the NOAA Boulder lab for analysis. Measurements of these flask samples were done using two different customised GC–MS instruments: a GC-MS for CFC-13 and CFC-115, operating from 2014 onwards identified as ‘Perseus’ (typical sample volume of 0.5L), and an additional GC-MS instrument for CFC-115, from 2010 to 2015 identified as ‘M2’ (typical sample volume of 0.2L)[38,39]. For CFC-115, M2 data were scaled to the measurements made on the Perseus GC-MS instrument using the mean value of the contemporaneous hemispheric-averaged values obtained when both instruments were operational (2014-2015; M2 data were scaled up by 4.19%). For CFC-13 and CFC-115, the NOAA measurements are reported in parts per trillion (ppt) relative to compressed whole air standards, referenced as the NOAA-2016-PR1-CFC13 and NOAA-2016-PR1-CFC115 scales, respectively. These standards are high pressure cylinders filled with compressed clean air from Niwot Ridge, Colorado, USA (40.0542° North, 105.5889° West, 3538.00 masl) when winds are from the westerly direction, which is the clean air sector. The NOAA-2016-PR1-CFC13 scale is positively offset relative to the AGAGE METAS-2017 scale by 4.5% ± 0.7%, determined by comparison of spatially and temporally co-located sampling from 2015-2021 at 4 sites (Mace Head, Cape Grim, Cape Matatula, and Trinidad Head). For CFC-115, the NOAA-2016-PR1-CFC115 scale is positively offset by 0.56% ± 0.27% relative to the AGAGE SIO-05 scale, using the same method as for CFC-13.

### *Emission modelling*

Emissions were estimated using measurements of dry-air mole fraction and a model of global atmospheric transport

[40,41]. The estimation procedure follows a Bayesian approach modified from refs.[42,43]. The Bayesian approach involves inferring emissions from the measurements of dry-air mole fraction by means of an affine relationship between emissions and atmospheric mole fraction, considering the associated uncertainties, and a prior constraint on the emissions. The affine relationship is derived using the model of atmospheric transport.

Atmospheric transport is simulated using a 12-box model[44], which divides the atmosphere into four semi-hemispheric zonal boxes (at 30° N and S) and vertically at 500 and 200 hPa (approximately representing the planetary boundary layer height and tropopause). Transport is seasonally averaged and repeats annually.

Measurements of dry-air mole fraction are averaged into monthly means, which are assumed to be representative of the semi-hemisphere surface box in which the measurement station is situated. Measurements from the AGAGE network were filtered to remove measurements not representative of background conditions using a statistical filter[45] before averaging.

A prior constraint is placed on the year-to-year growth in emissions, where the 1-sigma standard deviation in the growth is set equal to 20% of the mean a priori emissions over the inversion period (5% for CFC-114a). Due to the lack of information on emissions, a priori emissions of CFC-112a were somewhat arbitrarily assumed to be 0.05 Gg $yr^{-1}$ each year. CFC-113a and CFC-114a were assumed to be 1 Gg $yr^{-1}$ each year. Changing the a priori emissions by a factor of two had very little impact on the derived emissions ($\lesssim$5% of the mean estimate) and does not change any conclusions drawn. CFC-115 a priori emissions were taken from ref.[9] (reaching a maximum of 12.7 Gg $yr^{-1}$ in 1992), and CFC-13 a priori emissions were assumed to be one-seventh of CFC-115, following an earlier comparison of production estimates[9].

Reported emissions are the maximum a posteriori (MAP) estimates through minimisation of a cost function[43]. In this work the minimisation used an iterative procedure (L-BFGS-B algorithm[46]), which was constrained to ensure only positive emissions. Random uncertainties were calculated by assuming linearity around the MAP estimate (i.e., Gaussian uncertainties), and additional systematic uncertainties were included due to errors in measurement calibration scales (3%), model transport error (1%) and atmospheric lifetime. Systematic uncertainties were found by random sampling the posterior covariance matrix, including the additional error terms. Lifetime errors are defined on the inverse lifetime, and are assumed to be 20, 55, 80, 20 and 20% for CFC-13, CFC-112a, CFC-113a, CFC-114a and CFC-115, respectively[17,47].

Our work does not consider interannual changes to large-scale dynamics, which are known to impact emissions estimates of CFCs derived from atmospheric observations

[19,48,49]. However, the sustained 10 years of increasing emissions presented here far exceeds that of, for example, the mean period of the quasi-biennial oscillation of the direction of the zonal wind in the tropical lower stratosphere (~28 months[50]). Errors in the year-to-year variability between emissions of CFCs may be introduced when changes to large-scale dynamical features of the atmosphere are neglected, but we are confident that the long-term trends are robust.

### *Derivation of global mean mole fractions and growth rates*

Semi-hemispheric mole fractions were modelled using the derived emissions in each semi-hemisphere using the box-model approach described in the Emissions Modelling section and the affine relationship between emissions and mole fraction. The reported global mole fractions are the averages of the derived semi-hemispheric mole fractions for measurements from AGAGE and UEA/FZJ. Measurements of CFC-112, CFC-112a, CFC-113, CFC-113a, CFC-114 and CFC-114a were only made from air samples from Cape Grim in the southernmost semi-hemisphere. Therefore, derived global mole fractions in other semi-hemispheres are fully inferred from measurements in one semi-hemisphere. The additional uncertainty in the emission estimates arising from using measurements from only one semi-hemisphere is reflected by the uncertainty quantified using the Bayesian methodology. Such an approach has previously been used extensively to derive global emissions and mole fraction estimates of CFCs[8,17,18]. Mole fraction growth rates are calculated as an annual growth rate per month, which is smoothed over an approximately 18-month window using a Kolmogorov–Zurbenko (KZ) filter[51]. The estimated global and hemispheric mole fractions from the NOAA record are weighted by the cosine of the latitude of the measurement site locations, from which the annual mean is taken.

### *Atmospheric lifetimes and metrics for ozone depletion and climate impact*

The ozone-depleting potential (ODP) is a metric to assess the ability of a gas to deplete ozone in the stratosphere and is calculated relative to that of CFC-11 (which has an ODP of 1). Both the ODP and atmospheric lifetimes of CFCs have been taken from ref.[12], as the most recent estimates. Global warming potentials over a 100-year time-horizon (GWP-100) have since been updated using newly available absorption spectra, revised atmospheric lifetimes[12] and methodology to calculate radiative efficiencies, and we refer to ref.[13] for these values. CFC-13 has an assumed ODP of 1.0 and is a potent greenhouse gas, with a GWP-100 17,200 times that of $CO_2$. Its steady-state atmospheric lifetime is estimated at 640 years, with the dominant sink being reaction with $O(^1D)$. CFC-112a has an ODP of 0.86 and a GWP-100 of 3,740, with an atmospheric lifetime estimate of 52 years. The atmospheric sink of CFC-113a is primarily due to stratospheric photolysis, giving an atmospheric lifetime of 55 years, an ODP of 0.73 and a GWP-100 of 4,140. The primary $O(^1D)$ sink results in a CFC-114a atmospheric lifetime of 105 years, an ODP of 0.72 and a GWP-100 of 7,850. CFC-115 has an atmospheric lifetime of 540 years, an ODP of 0.26 and a GWP-100 of 10,200. ODPs for CFC-112, CFC-113 and CFC-114 were estimated to be 0.98, 0.815 and 0.5, respectively, and GWPs were 4,880, 6,900 and 9,990, respectively. The integrated ozone depletion was calculated using an empirical formula[28] considering the total chlorine emissions and assuming that all loss occurs in the stratosphere.

## Data Availability

AGAGE data are available at http://agage.mit.edu/data/agage-data (last access: 16 November 2022) and https://doi.org/10.15485/1841748[52]. NOAA atmospheric observations are available at https://gml.noaa.gov/aftp/data/hats/PERSEUS/ and https://gml.noaa.gov/aftp/data/hats/cfcs/ (last access: 16 November 2022). All inputs to the 12-box model and the resultant estimated emissions, mole fractions and their growth rates are available at https://github.com/lukewestern/py12box_laube (last access: 16 November 2022) or https://doi.org/10.5281/zenodo.7388012 [53], which also contains measurements analysed at UEA/FZJ.

## Code Availability

The 12-box model and the inverse method used to quantify emissions are available via GitHub, https://github.com/mrghg/py12box (last access: 16 November 2022) and https://github.com/mrghg/py12box_invert (last access: 16 November 2022), or Zenodo (https://doi.org/10.5281/zenodo.6857447 [54] and https://doi.org/10.5281/zenodo.6857794 [55]). Additional code to prepare inputs are available at https://github.com/lukewestern/py12box_laube (last access: 16 November 2022) or https://doi.org/10.5281/zenodo.7388012 [53].

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## Author contributions statement

LMW and JCL conceived and designed the study. MKV, PBK, KEA, PJF, CMH, RLL, SAM, JM, SO'D, DEO, SR, IV, RFW, DY and JCL provided measurement data and analysis. Emissions modelling was designed and performed by LMW and MR. LMW led the writing of the manuscript with contributions from all authors.

## Competing interests statement

The authors declare no competing interests.

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## Figures

## Figures

**Figure 1:** Surface dry-air mole fractions and growth rates for (a) CFC-13, (b) CFC-112a, (c) CFC-113a, (d) CFC-114a and (e) CFC-115 from the year 2000 through 2020. Circles show

CFC-113a, (d) CFC-114a and (e) CFC-115 from the year 2000 through 2020. Circles show measured monthly mean mole fractions and lines are the model estimated mean mole fractions, with the colours indicating the semi-hemisphere in which the measurement or modelled estimate was made. Uncertainties (1 sd) are only shown for the global mean mole fractions and growth rates by the grey shading.

**Figure 2:** Global mean annual emissions of CFC-13, CFC-112a, CFC-113a, CFC-114a, and CFC-115 from 2000 to 2020. Emissions are weighted by their (a) ozone depleting potential and (b) global warming potential over a 100-year time horizon (see text).

## Extended Data Figures

**Extended Data Figure S1:** Surface dry-air mole fractions and growth rates for CFCs with increasing abundances. Surface dry-air mole fractions and growth rates are shown for (a) CFC-13, (b) CFC-112a, (c) CFC-113a, (d) CFC-114a and (e) CFC-115 for the available direct atmospheric record (i.e., excluding trends derived from firn air) from 1978 through 2020 (1999 through 2020 for CFC-112a). Circles show measured monthly mean mole fractions and lines are the model estimated mole fractions, with the colours indicating the semi-hemispheric modelled estimate in which the measurement was made. Uncertainties (1 sd) are shown by the grey shading and are only shown for the global mean mole fractions and growth rates. Details on previously published records can be found in refs.

[8,9,17,18]. CFC-13 abundances have increased continuously since 1978. The CFC-13 growth rate was rapid in the 1980s, slowed to 0.015 ppt yr$^{-1}$ in 2000, and subsequently increased over the next two decades. From 2010 to 2020, CFC-13 increased by 9% from 3.04 ppt to 3.31 ppt (3.44, ppt in 2020 using the NOAA record, only available since 2014; see Figure S2). CFC-112a has the lowest abundance of the five CFCs. Its abundance was declining in the early 2000s, but rapidly grew from 2010 to 2020 by 19% from 0.066 ppt to 0.078 ppt. The CFC-113a abundance grew since 1978 at a rate less than 0.02 ppt yr$^{-1}$ until 2010, but from 2010 to 2020 it grew by 141% from 0.43 ppt to 1.02 ppt. CFC-114a growth rates were rapidly accelerating prior to 1990, then dropped to near zero between 1998-2003, after which they accelerated again. Between 2010 and 2020 CFC-114a increased by 9% from 1.03 ppt to 1.13 ppt. Similar to CFC-13 and CFC-114a, CFC-115 abundances also grew rapidly prior to the 1990s, but the timing is different. CFC-115 growth dropped to close to zero between 2005-2011, after which its growth rate again slowly increased. From 2010 to 2020, CFC-115 abundance grew by 4% from 8.38 ppt to 8.71 ppt (growing from 8.42 to 8.75 ppt from 2010 to 2020, or by 4%, using the NOAA record, Figure S2).

**Extended Data Figure S2:** (a) CFC-13 and (b) CFC-115 hemispheric monthly means (circles) and the annual global mean (black line) derived from measurements from the NOAA network. See the caption of Fig S1 for a discussion of these data.

**Extended Data Figure S3:** As Figure S1 but for (a) CFC-112, (b) CFC-113 and (c) CFC-114. CFC-112, CFC-113 and CFC-114 are structural isomers of CFC-112a, CFC-113a and CFC-114a, respectively. Note that the measurement approach at UEA/FJZ can measure the major isomers alone as opposed to the NOAA or AGAGE measurements of these gases (see methods), where these gases are reported as a sum of the paired isomers. It was previously assumed that the isomers are co-produced and therefore co-emitted into the atmosphere. However, mole fractions of CFC-112 ($CCl_2FCCl_2F$) and CFC-113 ($CClF_2CCl_2F$) have been declining continuously since 1996, and those of CFC-114 ($CClF_2CClF_2$) have declined, or been indistinguishable from zero growth, since 1998.

**Extended Data Figure S4:** Annual global mean emissions for (a) CFC-112, (b) CFC-112a, (c) CFC-113, (d) CFC-113a, (e) CFC-114, (f) CFC-114a, (g) CFC-13 and (h) CFC-115. Shading shows the 1-sigma standard deviation uncertainty. Emissions are in units of gigagrams by mass of the substance released. CFC-113a emissions have grown fastest, with a 244% increase in emissions between 2010-2020 (2.5 ± 0.4 ODP-Gg yr

$^{-1}$ in 2020). Emissions of CFC-112a increased by 169% over the same period, although the 2020 emissions are modest at 0.10 ± 0.03 ODP-Gg yr$^{-1}$ in 2020, compared to 0.6 ± 0.07 ODP-Gg yr$^{-1}$ for CFC-114a, which increased by 108%. Emissions of CFC-115 were at a minimum in 2009-2010 (0.1 ± 0.1 ODP-Gg yr$^{-1}$), before rapidly rising to 0.5 ± 0.1 ODP-Gg yr$^{-1}$ in 2017, and slightly falling to 0.4 ± 0.1 ODP-Gg yr$^{-1}$ in 2020 (2010-2020 increase of 192%). CFC-115 emissions are still substantially smaller than at its peak of around 3 ODP-Gg yr$^{-1}$ in the late 1980s and early 1990s. CFC-13 emissions in 2019 (0.7 ± 0.1 ODP-Gg yr$^{-1}$) were at their highest of this millennium (0.5 ± 0.1 ODP-Gg yr$^{-1}$ in 2010 and 0.7 ± 0.1 ODP-Gg yr$^{-1}$ in 2020), again contrasting with a rapid decline since its emissions peaked in the 1980s, and representing a 41% increase in emissions between 2010-2020.

**Extended Data Figure S5:** Comparison of HFC production and CFC emissions which may be associated with HFC production. The production of HFC-125 (a) and HFC-134a (b) is shown by the blue shading for Article 5 countries and orange shading for non-Article 5 countries. The composite of these two shading blocks shows total global production (without any metric of uncertainty). The estimates of HFC production assumes that all countries have ratified the Kigali Amendment, which to date would underestimate HFC production, and the values displayed are the mean of the lower and upper estimates from ref.[14]. The production quantity is shown on the left axis. Mean global emissions are shown for CFC-115 (pink), CFC-113a (green) and CFC-114a (dark orange) by dotted lines and the shading around the line shows the 1-sigma standard deviation uncertainties in the emissions. The right axis displays the emission values for CFCs by mass. CFC-113a, CFC-114a and CFC-115 are known by-products of HFC-125 production (panel a), and CFC-113a and CFC-114a are a feedstock and intermediate, respectively, in one of the production pathways to HFC-134a (panel b).