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Key Points:

- Trifluoroacetic acid (TFA) production from long-lived chlorofluorocarbon replacements has increased ~3.5-fold between the years 2000 and 2022
- Model comparisons to ice core records suggest that long-lived fluorinated gases are the major source of TFA in the Arctic
- HFO-1234yf, a low-global-warming potential refrigerant is an important atmospheric TFA source in recent years at lower latitudes

Supporting Information:

Supporting Information may be found in the online version of this article.

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Growth in Production and Environmental Deposition of Trifluoroacetic Acid Due To Long-Lived CFC Replacements and Anesthetics

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Abstract Trifluoroacetic acid (TFA) is a persistent pollutant with potential long-term effects on the environment and on health. Recent studies using ice core records report large increases (up to tenfold) in Arctic TFA deposition since the 1970s, and trends suggest long-lived chlorofluorocarbon (CFC) replacements may be a major source. Here, we use a chemical transport model to examine the global TFA budget arising from CFC replacements–hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs)–and inhalation anesthetics. Global TFA deposition from these sources increased ~3.5-fold from 6.8 (5.9–7.6) Gg/yr in 2000 to 21.8 (18.6–25.0) Gg/yr in 2022, with cumulative deposition reaching 335.5 Gg. We find HCFC-123, HCFC-124, and HFC-134a account for most modeled TFA production and that long-lived CFC replacements account for virtually all of the observed Arctic deposition trend. At lower latitudes, our analysis supports the recent emergence of hydrofluoroolefins (HFOs) as a TFA source. We conclude that increased TFA monitoring is required.

Plain Language Summary Trifluoroacetic acid (TFA) is an emerging contaminant known as a "forever chemical" because of its long lifetime in the environment. Some fluorinated gases are known to break down to TFA in the atmosphere, but their importance is not well understood. This study uses a global atmospheric model to quantify the contribution of fluorinated refrigerant gases and inhalation anesthetics to environmental TFA deposition. We find that TFA production from these sources has increased ~3.5 fold between the years 2000 and 2022. Comparisons of our model results to measurements suggest that these fluorinated gases are the major source of TFA in the Arctic, but that in the more industrialized Northern Hemisphere mid-latitude regions additional sources are likely to contribute. Our findings support the need for increased monitoring of TFA.

1. Introduction

Trifluoroacetic acid (TFA, CF_3COOH), the shortest chain perfluorocarboxylic acid (PFCA), is a pollutant of emerging concern because of its potential health and environmental risks. It is accumulating in environmental media including soils, crops, and surface water, where remediation is challenging (Arp et al., 2024). Ultrashort-chain PFCAs (C2-C3) account for a high proportion of the environmental fluorine mass balance (Chen et al., 2019; Hartz et al., 2023; Lan et al., 2020). Yet research into their long-term effects on humans and the biosphere is less extensive than into long-chain PFCAs (Brendel et al., 2018). The high environmental levels and persistence of TFA result in continuous, potentially irreversible exposure (Ellis, Mabury, et al., 2001, Ellis, Hanson, et al., 2001), leading to proposals to designate TFA a "planetary boundary threat" (Arp et al., 2024). TFA has been detected in significant concentrations in human blood serum, reproductive cells (Duan et al., 2020), and plants (Boutonnet et al., 1999). The European Chemicals Agency (ECHA) classifies TFA as harmful to aquatic life with long-lasting effects; it is proposed for classification as a reprotoxicant, Persistent, Mobile, Toxic, and

Very Persistent, Very Mobile substance (ECHA, 2024). Based on limited available toxicological data, current environmental levels are below known safe thresholds (Neale et al., 2025) but the regulation of TFA under the precautionary principle may be warranted while the understanding of TFA impacts continues to develop (e.g., Cousins et al., 2019).

Despite growing concerns over TFA, its atmospheric budget remains poorly quantified and there is an urgent need for improved quantification of TFA sources. It is believed that any chemical with a -C-CF_3 moiety has the potential to form TFA (>5,000,000 compounds; Kim et al., 2025) and those with sufficient volatility could be atmospheric sources (Freeling & Björnsdotter, 2023). First- and second-generation CFC-replacement gases, namely hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), undergo long-range atmospheric transport and may oxidize to TFA (Kanakidou et al., 1995). Although their phase out is currently underway due to the Montreal Protocol and its amendments, the atmospheric abundances of a number of HCFCs and HFCs are still increasing (Laube & Tegtmeier, 2023). Other known atmospheric sources include inhalation anesthetics used in human and farm animal anesthesia, fluorotelomer alcohols (FTOHs), fluoropolymer thermolysis, and hydrofluoroolefins (HFOs)/hydrochlorofluoroolefins (HCFOs)—the latest generation of ultra-low Global Warming Potential (GWP) refrigerants (Ellis, Mabury, et al., 2001, Ellis, Hanson, et al., 2001, 2004; Henne et al., 2012). Non-atmospheric TFA sources to the hydrosphere and pedosphere include pesticides, landfill leachate, and industrial wastewater (Garavagno et al., 2024). Contrary to previous thinking, a recent critical review by Joudan et al. (2021) found insufficient evidence for a natural TFA source.

There is growing evidence for increasing global TFA deposition, including significant increases in TFA concentrations measured in surface waters (Cahill, 2022; Zhai et al., 2015) and precipitation (Freeling et al., 2020). Ice cores from remote Arctic regions show a tenfold increase in TFA deposition since the 1990s (Pickard et al., 2020). However, a gap remains between measured TFA deposition and modeled sources. One modeling study found that TFA production from FTOHs could only explain a fraction of deposition to ice cores (Thackray et al., 2020) and it is hypothesized that CFC replacements are likely the major source of TFA in the Arctic (Pickard et al., 2020). This hypothesis is based on temporal correspondence between Arctic ice core records of TFA deposition and the estimated time-varying production rate of TFA from CFC replacements. However, this has yet to be assessed with a global atmospheric chemistry model. Previous global model studies of TFA from HCFCs and HFCs are more than 25 years old (Kanakidou et al., 1995; Kotamarthi et al., 1998), so a reassessment is required using updated models and chemistry and considering the latest trends in source gases.

Here, we implement a detailed chemical scheme describing TFA production from long-lived CFC replacements in a chemical transport model (CTM) and evaluate the global TFA budget over the period 2000 to 2022. Model trends in TFA deposition are compared to ice core records (Hartz et al., 2023; Pickard et al., 2020) and precipitation concentrations (Freeling et al., 2020) to interpret the observed long-term trends and to infer the significance of CFC replacements as sources of TFA to the environment.

2. Model and Methods

We have used the Frontier Research System for Global Change version of the University of California Irvine (FRSGC/UCI) CTM. The model is extensively evaluated and shown to reproduce key features of tropospheric chemistry and transport well (e.g., Ryan & Wild, 2021; Wild et al., 2004). Here, the model was forced using meteorology from the European Centre for Medium-Range Weather Forecasts Integrated Forecasting System (IFS; cycle 38r1) and was run at a horizontal resolution of 1.9° × 1.9°, with a 2-year spin-up to allow oxidants to reach steady state. Monthly NOx, CO, and non-methane volatile organic compound emissions from anthropogenic and biogenic sources were prescribed using the most recent Copernicus Atmosphere Monitoring Service inventories, CAMS-GLOB-ANT v6.2 (Soulie et al., 2024) and CAMS-GLOB-BIO v3.1 (Sindelarova et al., 2022). Fire emissions were taken from the GFED4S inventory (van der Werf et al., 2017).

Three HCFCs (123, 124, 133a), six HFCs (134a, 227ea, 143a, 245fa, 365mfc, 43-10mee), and four anesthetics were added to the model (Table S1 in Supporting Information S1). Surface concentrations of these TFA source gases were specified annually (Text S1 in Supporting Information S1), using zonal mean fields derived from surface measurements (Figures S1 and S2 in Supporting Information S1), including from the global AGAGE network (Prinn et al., 2018). The atmospheric chemistry of the HCFCs/HFCs considered has been studied experimentally and the mechanisms are generally well constrained (e.g., Calvert et al., 2008; Franklin, 1993; Hayman et al., 1994). Detailed tropospheric degradation schemes for each gas were added to the model (Tables S2–S4; Text S2 in Supporting Information S1; Abusallout et al., 2022; Atkinson et al., 2008; Burkholder et al., 2020; Maricq et al., 1994; Møgelberg et al., 1995, 1996; Nielsen et al., 1994; Wallington et al., 1996; Zellner et al., 1994). Oxidation to TFA is initiated by hydroxyl (OH) radicals (the rate-determining step), and proceeds via $CF_3C(O)X$ intermediates (X = F, Cl, H), which are converted through in-cloud hydrolysis to TFA, or may undergo reaction with OH, or photolysis. In-cloud removal for the $CF_3C(O)X$ species is parameterized following Wild et al. (1996) and depends on species solubility, hydrolysis rate (Table S5 in Supporting Information S1), and cloud liquid water content (taken from the meteorological fields). Wet and dry deposition of TFA and its precursors were parameterized using Henry's law constants (Table S6 in Supporting Information S1) from Sander (2023). Stratospheric loss of TFA and its precursors was parameterized using a first-order loss rate above the tropopause set to match the corresponding tracer profiles from the TOMCAT/SLIMCAT stratospheric CTM (Chipperfield, 2006; Hossaini et al., 2024).

A total of seven CTM experiments were performed, covering the period 2000 to 2022. These included a run incorporating the processes detailed above (BASE), and six sensitivity experiments. To investigate the sensitivity to chemical formation of TFA, run SIMPLE-chem applied a single step chemistry to produce $CF_3C(O)X$ with yields specified from the literature (Table S1 in Supporting Information S1). The solubility of TFA and the solubility and hydrolysis rates of its $CF_3C(O)X$ precursors are highly uncertain. To explore the effect of this on TFA deposition, runs BASE-MAX and BASE-MIN applied upper and lower limits of Henry's law constants from the literature (Tables S5 and S6 in Supporting Information S1). BASE-LOWRES was run at lower resolution (2.8° × 2.8°) to explore the sensitivity of model results to horizontal resolution. Run BASE-EMIS compared the concentration-driven approach to a fully emissions driven run (see Text S3 in Supporting Information S1; Crippa et al., 2024). Finally, BASE-AN followed the BASE run but included four additional TFA source gases: halothane, isoflurane, desflurane and sevoflurane (Figure S3 in Supporting Information S1). These gases have principally been used as inhalation anesthetics (e.g., Vollmer, Rhee, et al., 2015) and have non-negligible TFA yields (Table S1 in Supporting Information S1). The modeled lifetimes of all TFA source gases (Table S1 in Supporting Information S1) are in good agreement with the compilation of Burkholder and Hodnebrog (2022).

In the subsequent discussion, molar TFA yields are presented and were calculated using the approach outlined in Text S4 in Supporting Information S1. TFA rainfall concentrations were estimated by dividing the modeled wet TFA deposition by the model rainfall for each grid-box. When comparing the model to measurements, the mean ± one standard deviation of a central grid-box and the eight surrounding boxes was reported to characterize the spatial representation error at regional scale.

3. Results and Discussion

3.1. Global Budget of TFA and Its Precursors

Modeled TFA production from HCFCs and HFCs shows a marked increase over our study period (Figure 1a), with global production ~3.5 times higher in 2022 (21.3 Gg) than in 2000 (6.3 Gg). Despite the phase-out first agreed in a 1992 amendment to the Montreal Protocol, HCFCs (123, 124, 133a) provide an important, albeit declining, TFA source (~68% of total production in 2000; 19% in 2022). Figure 1a also highlights the growing importance of HFCs, which replaced HCFCs, and for which a phase-down has only more recently been agreed via the 2016 Kigali Amendment to the Protocol. Notably, high emissions of HFC-134a (Simmonds et al., 2017) has led it to becoming the dominant TFA source in our study (~28% of production in 2000; 69% in 2022), despite its relatively low TFA yield (9%). In 2020, we estimate TFA production from HFC-134a at 13.8 Gg, which is within the estimated 10–30 Gg range for 2020 reported by Daniel and Reimann (2022). Although relatively minor, the other HFCs considered (HFC-143a, HFC-227ea, HFC-245fa, HFC-365mfc, and HFC-4310mee) and anesthetics collectively accounted for 3.7 Gg (17%) of TFA production in 2022 and their cumulative effects warrant consideration. Several other HFCs are also known TFA sources (e.g., Madronich et al., 2023) but were not included here due to either insufficient observations with which to constrain the model (e.g., HFC-236ea and HFC-245ea) or very low rates of TFA formation (e.g., HFC-236fa). The chemistry of HFC-125 is highly uncertain but using the range of yields (1%–10%) reported by Madronich et al. (2023), we estimate a possible additional 0.3–2.5 Gg of TFA in 2022. The HCFCs/HFCs considered here are well-mixed and TFA production

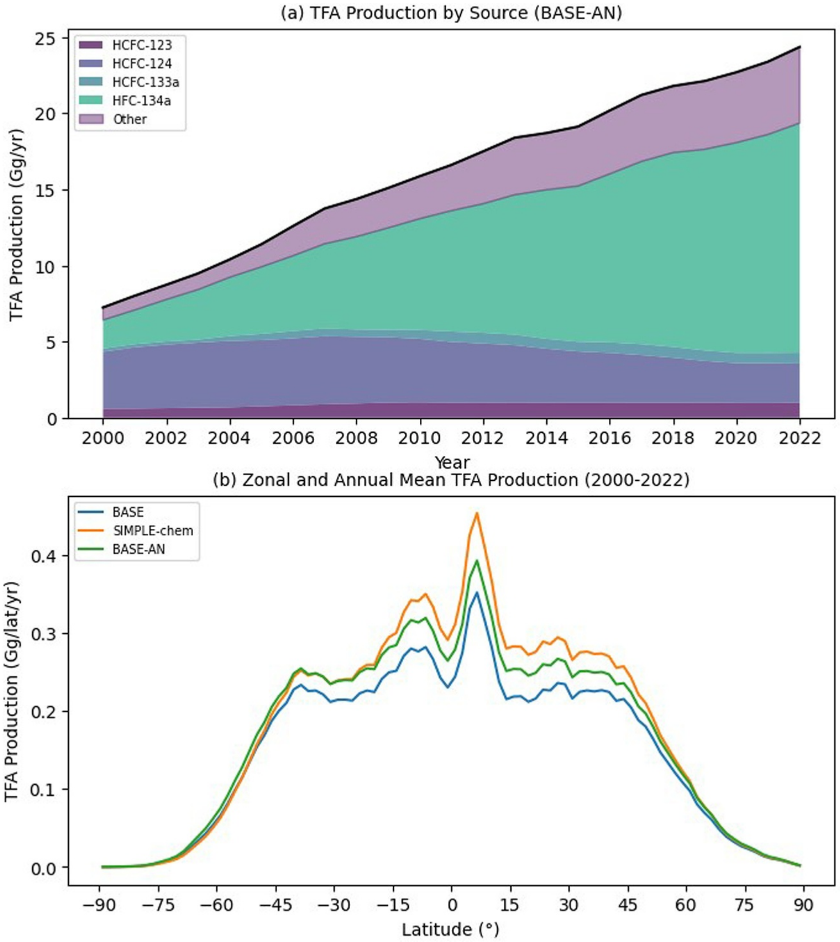

Figure 1. Modeled annual (a) global trifluoroacetic acid (TFA) production rate (Gg/yr) from run BASE-AN, and (b) variation of TFA production rate per 1.9° latitude band. Panel (b) results are averaged over 2000–2022 and also include runs BASE, SIMPLE-chem and BASE-AN.

maximizes in the tropics (Figure 1b), where their OH-initiated removal and the hydrolysis of $CF_3C(O)X$ products to TFA, are both relatively fast (Kanakidou et al., 1995).

The contribution of individual source gases to TFA production depends on their abundance, lifetime, and overall TFA yield. TFA yields (mean of 2000–2022) vary widely (2%–95%) and are comparable to literature values (see Table S1 in Supporting Information S1). Annual changes in meteorology and background chemical composition were found to have very little impact on these yields (standard deviation of yields was $\leq 0.1\%$). The yields depend on the fate of the $CF_3C(O)X$ intermediates; $CF_3C(O)X$ hydrolysis leads to TFA production, though competes with non-TFA forming removal processes (Table S7 in Supporting Information S1). Modeled TFA yields from $CF_3C(O)X$ intermediates were 94%, 49%, and 10% for $X = F$, Cl, and H, respectively. Inclusion of the photolysis loss pathway for $CF_3C(O)Cl$ reduced its yield of TFA from >90% reported in previous modeling studies (Kotamarthi et al., 1998) to 49% which is in alignment with the 38.6% loss from photolysis reported by Hayman et al. (1994). $CF_3C(O)H$ exhibited a TFA yield of 10%, with reported yields ranging from 1% to 10% (Campbell et al., 2021; Sellevåg et al., 2004; Sulbaek Andersen et al., 2023). There has been considerable recent interest in the photolysis of $CF_3C(O)H$ due to the production of the potent greenhouse gas HFC-23 (e.g.,Hoomissen et al., 2025; Thomson et al., 2024). The Henry's Law constant for $CF_3C(O)H$ is not well characterized and constitutes a substantial uncertainty in its removal. In this study, a photolysis quantum yield of 0.17 was applied based on Pérez-Peña et al. (2023) and the Henry's law constant was assumed equal to that of $CF_3C(O)F$.

The importance of using a full chemistry mechanism is demonstrated by the SIMPLE-Chem results (Figure 1b), which showed on average a 14% larger TFA production rate compared to BASE (see Table S8 in Supporting

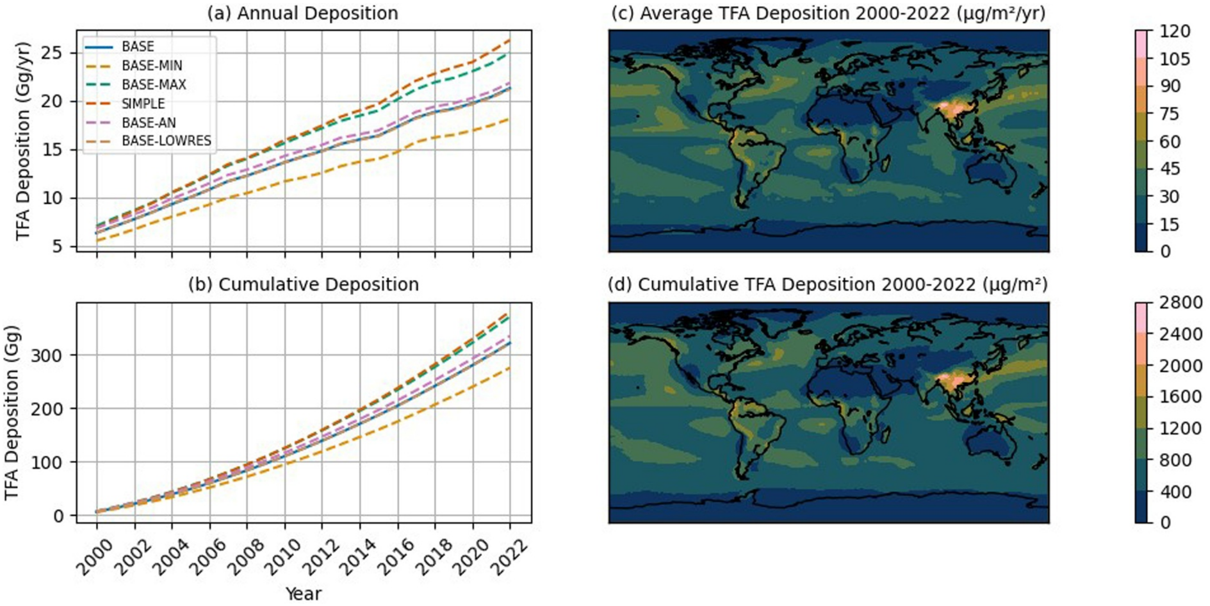

Figure 2. Modeled (a) annual global trifluoroacetic acid deposition (Gg/yr), (b) corresponding cumulative deposition (Gg), (c) spatial distribution of deposition (µg/m^2/yr) averaged over the period 2000 to 2022, and (d) corresponding cumulative (µg/m^2) deposition in run BASE. Deposition quantities are the sum of wet and dry deposition.

Information S1). This arises because SIMPLE-Chem uses prescribed yields based on laboratory studies whereas pressure and temperature dependent yields are explicitly calculated in BASE. Deposition processes that can affect yields are also included.

The anesthetic gases collectively produced 0.7–1.0 Gg/yr of TFA (Figure 2a), but their contribution beyond 2014 remains uncertain. Apart from halothane, which was phased out in the 1970s, the atmospheric abundances of the anesthetics have increased between 2000 and 2014 (Figure S3 in Supporting Information S1), and given their continued use will likely continue increasing. An update only exists for desflurane, which showed a modest increase in mole fraction from 0.30 ppt in 2014 to 0.37 ppt in 2020 (Laube & Tegtmeier, 2023). Our approach of fixed concentrations beyond 2014 is therefore a conservative estimate. Another key factor that affects TFA production is the model tropospheric OH field and hence lifetimes of the HCFC/HFC source gases. The configuration of the FRSGC/UCI CTM used here produces a CH_4 chemical lifetime against OH oxidation of 10.2 years which is within the observation-based estimate of 11.2 (±1.3) years reported by Prather et al. (2012). Uncertainty in OH is thus not expected to strongly bias our results.

The global atmospheric lifetime of TFA is 2 days (see budget terms in Table S7 in Supporting Information S1), calculated as the ratio of its global burden to its global sink. Modeled TFA sinks are wet deposition (partial lifetime of 3 days), dry deposition (6 days), and OH oxidation (58 days). The absolute and relative importance of wet and dry deposition is expected to differ between models, due to different parameterizations of deposition and the assumptions made. While the focus of previous TFA modeling studies differ, our results are broadly consistent in showing a greater role of wet over dry deposition (e.g., David et al., 2021; Holland et al., 2021). Further measurements of both wet and dry deposition fluxes would be beneficial to improve these estimates. Our modeled chemical lifetime of TFA is in reasonably good agreement with the 80 days reported by Wild et al. (1996).

3.2. Spatial and Temporal Trends in TFA Deposition

Annual global TFA deposition (Figure 2a) increased significantly in run BASE from 6.3 Gg/yr in 2000 to 21.3 Gg/yr in 2022 (Mann-Kendall $p < 0.05$, slope = 0.67, variance = 1434, $z = 6.7$), with cumulative deposition reaching 321.7 Gg in 2022 (Figure 2b). Henry's law constants for TFA and its precursors vary by two orders of magnitude in the literature, so sensitivity tests were used to establish an uncertainty range for TFA deposition (Figure S4 in Supporting Information S1). BASE-MAX/MIN each altered TFA deposition by ~14% with respect to BASE. $CF_3C(O)X$ in-cloud hydrolysis is fast (hours), so large differences in Henry's law constants have a

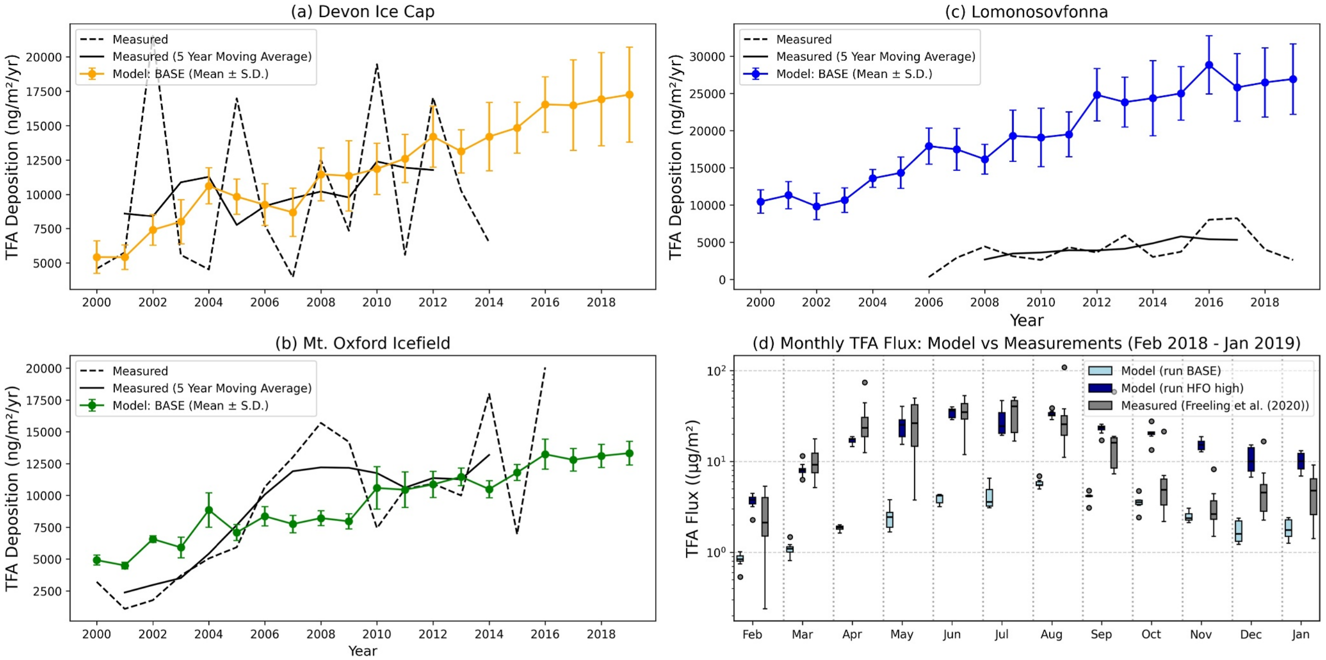

Figure 3. Modeled versus observed trifluoroacetic acid (TFA) deposition rate (ng/m^2/yr) at (a) Devon ice cap, (b) Mt. Oxford icefield and (c) Lomonosovfonna. (d) Comparison of monthly average modeled TFA deposition flux (μg/m^2) with and without inclusion of HFO-1234yf (high emissions) to flux derived from measured TFA concentrations in Germany 2018/19 (Freeling et al., 2020).

comparatively small impact on deposition. Assuming the same uncertainty range, global TFA deposition from BASE-AN was 6.8 (5.9–7.6) Gg/yr in 2000 rising to 21.8 (18.6–25.0) Gg/yr in 2022, with cumulative deposition reaching 335.5 Gg. We found that lower model resolution (run BASE-LOWRES) also made little difference to the global deposition total, but changed the results spatially (see Section 3.3).

The short atmospheric lifetime of TFA (~2 days) means that deposition patterns closely follow chemical production, both spatially and temporally (Figure S5 in Supporting Information S1). Deposition fluxes demonstrate clear seasonal cycles, reflecting seasonality in TFA production (from OH-initiated oxidation of precursors), and precipitation rates. Seasonality in fluxes is most prominent in the Northern Hemisphere (NH), especially in the Arctic, and is much weaker in the Southern Hemisphere (SH). These seasonal cycles align with observations reported in previous monitoring studies of TFA in rainwater and ice (Freeling et al., 2022; Hartz et al., 2024). The meteorological factors mentioned above also modulate the spatial distribution of TFA, which shows a strong latitudinal dependence. Deposition is highest in the tropics and midlatitudes, and lowest in polar regions (Figure S5 in Supporting Information S1). There is a notable hotspot of TFA deposition in China associated with high OH and substantial rainfall which merits focused monitoring (Figure 2d). The emissions-driven approach (run BASE-EMIS) produces a comparable magnitude of TFA deposition but shifts some deposition from the tropics to midlatitudes (Figure S6 in Supporting Information S1).

3.3. Significance of CFC Replacements

Modeled Arctic deposition fluxes were compared to measured values inferred from ice core records from the Mt. Oxford (82.2°N, 73.0°W) and Devon (75.2°N, 82.7°W) Icecaps in Nunavut, Canada (Pickard et al., 2020), and Lomonosovfonna (78.5°N, 17.3°E) in Svalbard (Hartz et al., 2023). These data sets are valuable because they are the only historical records over the long study period, and because the absence of point sources of TFA here means that measured TFA is primarily from atmospheric sources. However, deposition at the poles is considerably lower than global average TFA production and deposition (e.g., Figures 2c and 2d) and large interannual variability may confound any assessment of long-term trends. Despite this, the model captures the Devon and Mt. Oxford records well (Figures 3a and 3b), implying that CFC replacements are the primary source of TFA deposition to Arctic regions and corroborating the suggestion of Pickard et al. (2020). Modeled TFA deposition at Lomonosovfonna exceeds the measured flux (Figure 3c) and is also higher than the model latitudinal average (see

Figure S7 in Supporting Information S1). Lomonosovfonna is an ice cap located in north/central Spitsbergen at an altitude of ∼1,200 masl, but experiences seasonal melt, more so than the Canadian ice caps located at a similar altitude (Koerner, 1997). Seasonal snow/firn melt may result in the redistribution of organic anions like TFA, with possible loss from surface snow layers due to meltwater percolation. Therefore, when comparing to deposition inferred from ice cores it should be noted that the ice core may represent accumulation rather than deposition at the time (Grannas et al., 2013). The TFA deposition inferred from the ice core records may carry large errors, but these are not reported. A full quantitative comparison is given in Table S9 in Supporting Information S1. The results are sensitive to model resolution, with 16% higher Arctic TFA deposition (2% higher in the hotspot at 20–30°N, 90–110°E) in run BASE-LOWRES compared to BASE associated with more diffusive and therefore faster transport at lower resolution, demonstrating the importance of high spatial resolution when comparing to measurements in the Arctic (see Figure S7 in Supporting Information S1).

The model outputs were also compared to observed rainwater concentrations of TFA (see Table S10 in Supporting Information S1), which provide comparisons for lower latitudes, but are too sparse in time and location to estimate temporal trends (Björnsdotter et al., 2021; Scott et al., 2006; Taniyasu et al., 2008; Wang et al., 2014). Generally, the model rainwater TFA concentrations were at the low end of the reported ranges of 4–1,800 ng/l (see Figure S8 in Supporting Information S1). Modeling rainfall magnitudes and distributions is difficult, but we suggest that the gap could be explained by the proximity of the rainwater measurements to midlatitude sources of shorter-lived TFA precursors that have a smaller emission footprint than HCFC/HFCs (e.g., HFOs, FTOHs, fluoropolymer thermolysis, and/or fluorinated pesticides). To explore this, an additional sensitivity test was performed which included HFO-1234yf and a fixed yield of 100% for the $CF_3C(O)F$ precursor. The EU mobile air-conditioning (MAC) Directive banned the use of refrigerants with a GWP of >150 in new vehicles from 2017, and thus HFO-1234yf has now largely replaced HFC-134a (Pabon et al., 2020). Emissions of HFO-1234yf from MAC systems in Europe, USA, China, India, and the Middle East for the year 2020 were prescribed based on "low" and "high" literature estimates (Text S5 in Supporting Information S1; Taddonio, 2021; Wang et al., 2018). This increased global TFA production in 2020 by 31% (low) and 187% (high) compared with the BASE run. The calculated HFO-1234yf lifetime was ∼13 days, in good agreement with the 12 days reported by Daniel and Reimann (2022).

The effect of HFO-1234yf inclusion is shown in Figure 3d where the results are compared to the seasonally-resolved TFA deposition flux data set of Freeling et al. (2020). The latter is based on measurements at eight sites across Germany in 2018/19. While the magnitude of HFO-1234yf emissions is uncertain due to its relatively recent uptake and detection in the atmosphere (Vollmer, Reimann, et al., 2015), its addition considerably decreases the gap between modeled and measured fluxes of TFA in Germany, highlighting that HFO-1234yf is important for NH midlatitude deposition (see also Figure S9 in Supporting Information S1). The modeled high-emissions scenario predicts wintertime deposition well, but spring and summer deposition fluxes remain lower than measured fluxes. It is not possible to conclusively attribute this bias here but the influence of unknown sources is a plausible factor. The model does not include a chlorine atom (Cl) sink of HFO-1234yf which could reduce its lifetime in regions with elevated Cl concentrations and therefore increase TFA production (Papadimitriou et al., 2011). The combined uncertainty from modeled wet deposition flux, model precipitation amounts, and measured precipitation concentrations likely also contribute to the disparity. This could be reduced in future by undertaking more widely distributed rainwater concentration measurements, and experimental efforts to constrain the uncertainty in the solubility of TFA.

While the impact of HFOs (especially HFO-1234yf) on regional TFA levels is currently in the spotlight (e.g., Behringer et al., 2021), our results highlight the importance of HCFCs and HFCs as a global source since the early 2000s. Based on model-derived yields and lifetimes (Table S1 in Supporting Information S1) and the full range of HFC concentrations projected under the shared socio-economic pathways reported by Meinshausen et al. (2020), we calculate that TFA production from HFCs in 2050 will be between 6.7 Gg/yr (SSP1-1.9) and 42.5 Gg/yr (SSP5-8.5; see Table S11 in Supporting Information S1). Under these scenarios, peak annual TFA production from HFCs could be anywhere between 2025 and 2100, so HFCs could remain an important TFA source well into the future. While the future trajectory of HFCs in the atmosphere will depend on adherence to the Kigali Amendment and other factors (Velders et al., 2022), their phase-down may ultimately be accompanied by increased future TFA production if HFOs, with relatively high TFA yields, are the principal low-GWP replacements (e.g., Holland et al., 2021). Notably, this includes continued replacement of HFC-134a (TFA yield

∼9%; Table S1 in Supporting Information S1) with HFO-1234yf (yield 100%), with TFA production from the latter projected to rise to 340–490 Gg/yr in 2050 (Daniel & Reimann, 2022).

3.4. Environmental Implications

A comparison of modeled annual average precipitation concentrations in the period 2000–2010 versus 2012–2022 shows higher rainfall concentrations occurring more frequently in the latter period (Figure S10 in Supporting Information S1). The highest monthly modeled rainwater concentration is 39 μg/l in 2022 in Central Africa, excluding points with <0.1 mm/day rainfall. This exceeds the lowest reported Predicted No Effect Concentration to date of 0.12 μg/l (Xie et al., 2019) and the German drinking water health target value (10 μg/l). However, the potential of TFA to accumulate in the environment, as well as dilution in water bodies, means that rainwater concentrations are not representative of environmental concentrations (Russell et al., 2012). Monitoring and multimedia environmental fate modeling using updated TFA deposition fluxes are required to determine environmental TFA concentrations, particularly given the large projected increase in TFA from HFO-1234yf. The transboundary nature of TFA pollution raises environmental justice issues; deposition reaches all regions of the globe including "pristine" locations at the poles and areas with lower emissions receive a disproportionate amount of TFA deposition. These findings underscore the need for coordinated international efforts to reduce global emissions.

4. Conclusions

This study quantifies TFA production from long-lived precursors (HCFCs, HFCs and inhalation anesthetics) which are well-mixed and allow TFA deposition to occur in remote regions. We show that HCFCs and HFCs alone can explain most of the observed Arctic TFA deposition trend. Globally, we estimate a ∼3.5-fold increase in TFA deposition from HCFCs and HFCs from 2000 to 2022. At midlatitudes, our analysis also supports the emergence of HFO-1234yf as an important, and likely growing, component of the atmospheric TFA budget. Up-to-date measurements of TFA-forming sources gases, including the anesthetics and additional HFCs (236ea and 245ea), and constraint on global HFO emissions would benefit assessment of the TFA budget. Similarly, more spatially extensive and continuous TFA monitoring programmes, including deposition and rainfall quantities, extending into the tropics and SH would help to constrain models and reduce uncertainties. Overall, the results presented here support the growing literature around the increasing production of highly persistent TFA and thus its potential to be a planetary boundary threat (Arp et al., 2024).

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data for the source gas mixing ratios is publicly available at the following sites. AGAGE data (Prinn et al., 2018) can be downloaded at https://www-air.larc.nasa.gov/missions/agage/data. Data for HCFC-123 from (Wofsy et al., 2017) can be downloaded from https://doi.org/10.3334/CDIAC/HIPPO_012. CMIP6PLUS data is available at https://esgf-node.llnl.gov/search/input4mips/. Measurement data for TFA is available in the following publications and their supplements. Devon and Mt Oxford icefields: (Pickard et al., 2020), Lomonsovfonna: (Hartz et al., 2023), and German rainwater: (Freeling et al., 2020). Python code used for figures and analysis, and model output files are available with open access on Zenodo (Hart, 2025a, 2025b).

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