



## RESEARCH LETTER

10.1002/2017GL074388

## Key Points:

- Atmospheric data indicate substantial declines in United States emissions of ozone-depleting substances owing to the Montreal Protocol
- The emission decline is also substantial compared to the decline in total emissions of CO<sub>2</sub> and other major greenhouse gases
- Spatial distribution and seasonality of derived emissions for ozone-depleting gases and hydrofluorocarbons are consistent with their uses

## Supporting Information:

- Supporting Information S1

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## Citation:

Hu, L., et al. (2017), Considerable contribution of the Montreal Protocol to declining greenhouse gas emissions from the United States, *Geophys. Res. Lett.*, 44, 8075–8083, doi:10.1002/2017GL074388.

Received 31 MAY 2017

Accepted 20 JUL 2017

Published online 14 AUG 2017

## Considerable contribution of the Montreal Protocol to declining greenhouse gas emissions from the United States

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**Abstract** Ozone depleting substances (ODSs) controlled by the Montreal Protocol are potent greenhouse gases (GHGs), as are their substitutes, the hydrofluorocarbons (HFCs). Here we provide for the first time a comprehensive estimate of U.S. emissions of ODSs and HFCs based on precise measurements in discrete air samples from across North America and in the remote atmosphere. Derived emissions show spatial and seasonal variations qualitatively consistent with known uses and largely confirm U.S. Environmental Protection Agency (EPA) national emissions inventories for most gases. The measurement-based results further indicate a substantial decline of ODS emissions from 2008 to 2014, equivalent to ~50% of the CO<sub>2</sub>-equivalent decline in combined emissions of CO<sub>2</sub> and all other long-lived GHGs inventoried by the EPA for the same period. Total estimated CO<sub>2</sub>-equivalent emissions of HFCs were comparable to the sum of ODS emissions in 2014, but can be expected to decline in the future in response to recent policy measures.

### 1. Introduction

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) have been widely used as refrigerants, foam-blowing agents, aerosol propellants, fire retardants, and solvents. CFCs were first identified as capable of destroying stratospheric ozone in 1974 [Molina and Rowland, 1974], and their production and consumption have been controlled since the late 1980s under the Montreal Protocol on Substances that Deplete the Ozone Layer and its adjustments and amendments (hereafter, Montreal Protocol). HCFCs have been used extensively as temporary replacements for CFCs, with ozone-depleting potentials (ODPs) 1 to 2 orders of magnitude smaller than CFCs [Daniel et al., 2011; Harris et al., 2014]. A 1992 amendment to the Montreal Protocol controlled production and consumption of HCFCs beginning in 2004, while HFCs have been phased in as substitutes for both CFCs and HCFCs because they do not contain ozone-depleting chlorine and bromine.

CFCs, HCFCs, and HFCs are also potent greenhouse gases (GHGs) with global warming potentials (GWPs) hundreds to tens of thousand times greater than CO<sub>2</sub> on a 100 year time horizon [Daniel et al., 2011; Harris et al., 2014; Myhre et al., 2013]. The total direct radiative forcing from all CFCs, HCFCs, and HFCs currently in the atmosphere amounts to roughly 18% of that from anthropogenically derived CO<sub>2</sub> [Myhre et al., 2013; Rigby et al., 2014] and would have been substantially larger in the absence of mitigation by the Montreal Protocol [Velders et al., 2007, 2012]. While it is clear that the Montreal Protocol has protected ozone and has likely helped to mitigate the ongoing increase in planetary radiative forcing [Solomon et al., 2016; Velders et al., 2012; World Meteorological Organization (WMO), 2014], its overall climate benefit is being offset by rapidly growing worldwide use and emission of HFCs having high GWPs [Velders et al., 2009, 2012]. To

preserve the direct climate benefit of the Montreal Protocol, the Parties to the Protocol have recently agreed to limit future production and consumption of HFCs [*The Kigali Amendment*, 2016].

Implementation of the Montreal Protocol in the U.S. has been achieved largely through the U.S. Clean Air Act. This led to near-complete phaseout of the production and consumption of CFCs for dispersive uses beginning in 1996 and a 95% decline of HCFC production since peak production in 1998 [*Ozone Secretariat*, 2016]. In contrast, the consumption of HFCs has grown rapidly in the U.S. over the past two decades [*U.S. Environmental Protection Agency*, 2016; *Velders et al.*, 2015]. Rapid expansion of HFC use has likely resulted in increased emissions, but actual HFC emissions in the U.S. remain poorly constrained. For example, estimated U.S. emissions of HFCs in the Emissions Database for Global Atmospheric Research (EDGAR) were more than a factor of 2 larger than reported by the U.S. Environmental Protection Agency (EPA) for all HFCs combined for 2010 [*U.S. Environmental Protection Agency*, 2016] (Figure S1) and 5–10 times larger for some individual gases (e.g., HFC-143a and HFC-125). Given such large discrepancies, atmosphere-derived estimates of U.S. emissions provide an important independent measure of emissions and their changes over time.

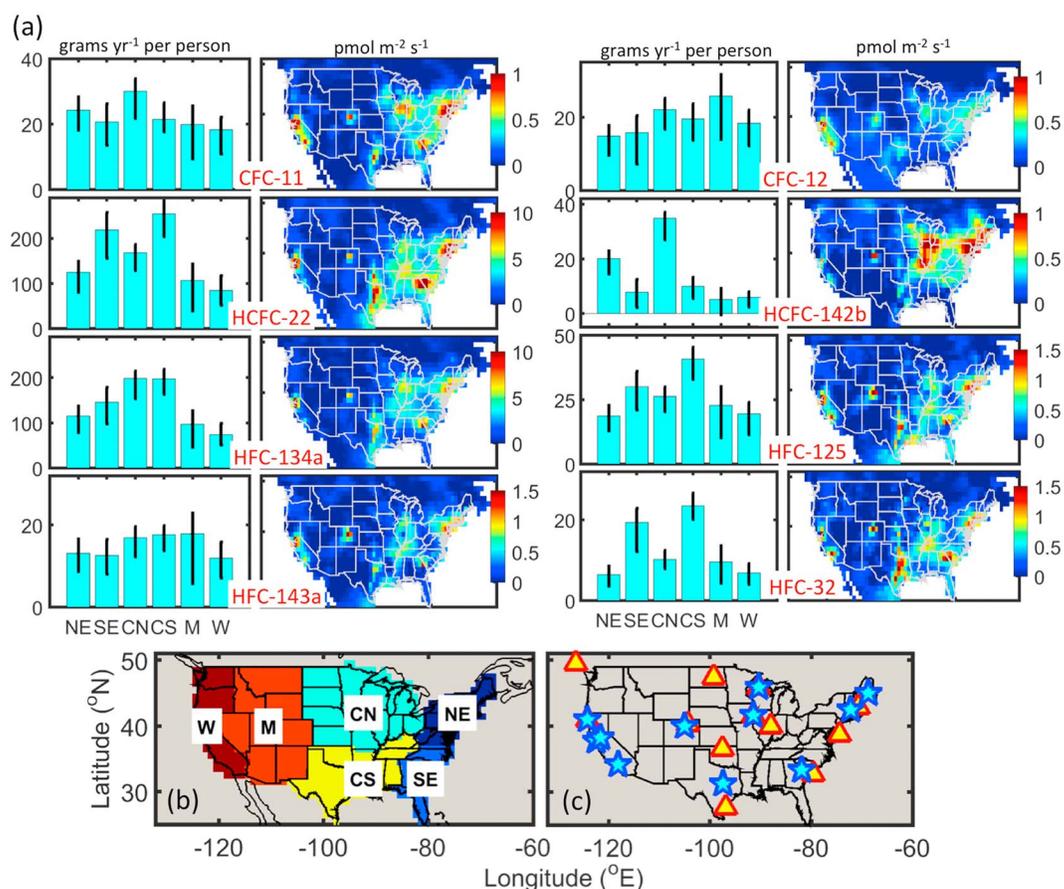
Here we estimate U.S. emissions of the three most abundant CFCs (CFC-11, CFC-12, and CFC-113), two HCFCs (HCFC-22 and HCFC-142b) and six HFCs (HFC-134a, HFC-125, HFC-143a, HFC-32, HFC-227ea, and HFC-365mfc) with well-quantified uncertainties for the period 2008 to 2014. These estimates are based on regional inverse modeling of atmospheric mole fractions as measured in air collected over the U.S. and in the remote atmosphere from an extensive ground- and aircraft-based flask air sampling network maintained by the National Oceanic and Atmospheric Administration (NOAA) and cooperative institutions [*Hu et al.*, 2016, 2015] (Figure 1 and Figure S2 in the supporting information). The results are used to provide measurement-based estimates of the overall influence of the Montreal Protocol on U.S. emissions of ozone depleting and greenhouse gases.

## 2. Methodology

Atmospheric measurements of long-lived trace gases (including CFCs, HCFCs, and HFCs) have been made with high accuracy and high precision from flask air samples collected at 37 sites across a wide range of latitude, longitude, and altitude over North America since 2008 and at remote sites around the globe since the early 1990s (i.e. Figures 1 and S2 and [*Elkins et al.*, 1993; *Hall et al.*, 2014; *Hu et al.*, 2016, 2015; *Montzka et al.*, 1999, 1996, 2015]) (See Text S1 in the supporting information for more measurement and calibration details.). Those include 15 airborne sampling locations, where vertical profiles of the atmosphere were sampled at 9–12 different altitudes once or twice per month, and 22 ground-based sites, where air samples were collected approximately daily from tall towers within North America or weekly from remote areas around the globe. The long-term, multilocation, multialtitude air sampling enables us to characterize temporal and spatial (both vertical and horizontal) variations in mole fractions of ozone depleting substances (ODSs) and their substitutes in the remote atmosphere and throughout the U.S.

Monthly  $1^\circ \times 1^\circ$  gridded emissions were determined from the observations using Lagrangian atmospheric transport models (i.e., HYSPLIT-NAM12 and WRF-STILT) and a Bayesian inverse modeling technique following methods of *Hu et al.* [2015] and *Hu et al.* [2016] and as detailed in the supporting information Texts S2–S5 (Additional information on Bayesian inverse modeling and their applications can be found in, e.g., *Brunner et al.* [2012], *Lunt et al.* [2015], *Maione et al.* [2014], *Manning et al.* [2003], *Rodgers* [2000], and *Stohl et al.* [2009]). Grid-scale emissions and their error covariance were further aggregated across space and time to derive monthly and annual totals by region and for the nation. In the Lagrangian regional framework, the individual trace gas observations are treated as enhancements, calculated as the difference between mole fractions measured in the lower atmosphere (0–3 km above ground) over the U.S. and those in background air not affected by recent emissions. As is common for underconstrained inverse problems, the Bayesian method requires an initial or “prior” guess of emission distributions and magnitudes. Prior emissions are then adjusted to obtain posterior emissions estimates that best represent the observed atmospheric enhancements given model-data mismatch errors and prior emission errors that are both determined by maximum likelihood estimation [*Hu et al.*, 2015; *Michalak et al.*, 2005] (Text S4).

To evaluate the influence of the prior guess on the posterior emissions estimates, we considered a wide range of prior emissions magnitude, seasonality, and distribution (e.g., ranging from seasonalized “population-based” emissions to constant emissions over space and time (“flat”) as described in the supporting



**Figure 1.** (a) Annual average emissions derived from a “flat” prior distribution (contour maps) and regional per capita emissions of CFCs, HCFCs, and HFCs averaged over 2008 to 2014 (bar charts) from the regions identified and labeled in (b): northeast (NE), southeast (SE), central north (CN), central south (CS), mountain (M), and west (W). (c) Emissions are derived from flask-air measurements made at ground (blue stars) and aircraft (yellow triangles) sites. Note that different color scales are used for emission maps of different compounds in Figure 1a. Regional emissions and their uncertainties were derived from multiple inversions as described in Text S5 and were used (with 2012 U.S. population) to obtain regional per capita emissions and emission uncertainties.

information Text S5). In addition to posterior emissions uncertainties associated with (1) prior emissions, we also considered posterior emissions uncertainties associated with (2) systematic errors related with the choice of atmospheric transport and mixing model, (3) uncertainty in trace gas mole fractions in background air, (4) choices of state vectors (parameters to be solved, i.e., emissions or scaling factors of emissions), and (5) changes in air-sampling locations and frequencies between 2008 and 2014, as discussed in *Hu et al.* [2016]. Stated uncertainties correspond to the full range of emissions estimates for a subset of inversion runs that best represent the atmospheric observations, as detailed in the supporting information Text S5.

To allow a comparison with inventory-based national greenhouse gas emissions reported by the U.S. EPA and the United Nations Framework Convention on Climate Change (UNFCCC), CO<sub>2</sub>-equivalent (CO<sub>2</sub>e) emissions were computed with 100 year GWPs from the Inter-governmental Panel on Climate Change Fourth Assessment Report. Where appropriate, ODP-weighted emissions were calculated with ODP values listed in the original Montreal Protocol.

### 3. Results

#### 3.1. Spatial Distribution and Seasonality of Derived Emissions

Annual emissions patterns and regional totals of derived CFC, HCFC, and HFC emissions are given in Figure 1. Consistently higher emissions were obtained from more populated areas for all gases (Figures 1 and S3), as

expected for man-made chemicals emitted solely as a result of anthropogenic activity. The emission distributions derived using the flat prior also make clear that the broad-scale distribution of emissions was determined primarily by the observations themselves and not the assumed prior distribution (Figures 1 and S3). Spatial patterns and seasonal variations of emissions derived for individual compounds also agree well with qualitative expectations. For example, we derived higher per capita emissions for chemicals used as blowing agents in building insulation foams (CFC-11, HCFC-142b, and HFC-365mfc) in the northern states (Figure 1), where higher thermal resistance materials are recommended in wood-framed houses [U.S. Department of Energy, 2016]. In southeastern and central south states, where a higher percentage of homes are air-conditioned [U.S. Energy Information Administration, 2011], derived per capita emissions of HCFC-22, HFC-125, and HFC-32 used in residential air conditioning (A/C) were higher than elsewhere (Figure 1). HFC-134a, which is the most abundant HFC in the atmosphere, is used primarily in mobile A/C. Derived per capita emissions of HFC-134a display similar regional patterns as refrigerants used in residential A/C, except in the central north region where the per capita emission was comparable to that in southern regions (Figure 1). This distribution may stem from additional use of HFC-134a in refrigeration and as a foam-blowing agent in building insulation in northern regions [U.S. Environmental Protection Agency, 2016].

In addition to specific regional patterns, we observed consistent year-to-year seasonal cycles in national-scale emissions for chemicals used primarily in A/C, i.e., HFC-134a, HCFC-22, HFC-125, and HFC-32 (Figure S4), with larger emissions derived for summer than for winter. Although seasonal variations in emissions of HCFC-22 and HFC-134a have been inferred in previous studies [Hu *et al.*, 2015; Xiang *et al.*, 2014], seasonal amplitudes of emissions obtained here (a factor of 1.5–2) are smaller than suggested on a global scale (a factor of 2–3) [Xiang *et al.*, 2014]. A nonnegligible seasonal cycle was also derived for emissions of CFC-11 (Figure S4), perhaps due to the remaining use of CFC-11 in large building A/C systems (such as chilled-water systems) [U.S. Environmental Protection Agency, 2016]. No discernable seasonality was derived for HFC-143a, a halocarbon used primarily in commercial refrigeration systems that operate year round rather than seasonally (in the refrigerant blends R-404A (HFC-143a/HFC-125/HFC-134a: 52%/44%/4% by mass) and R-507 (HFC-143a/HFC-125: 50%/50% by mass)) (Figure S4).

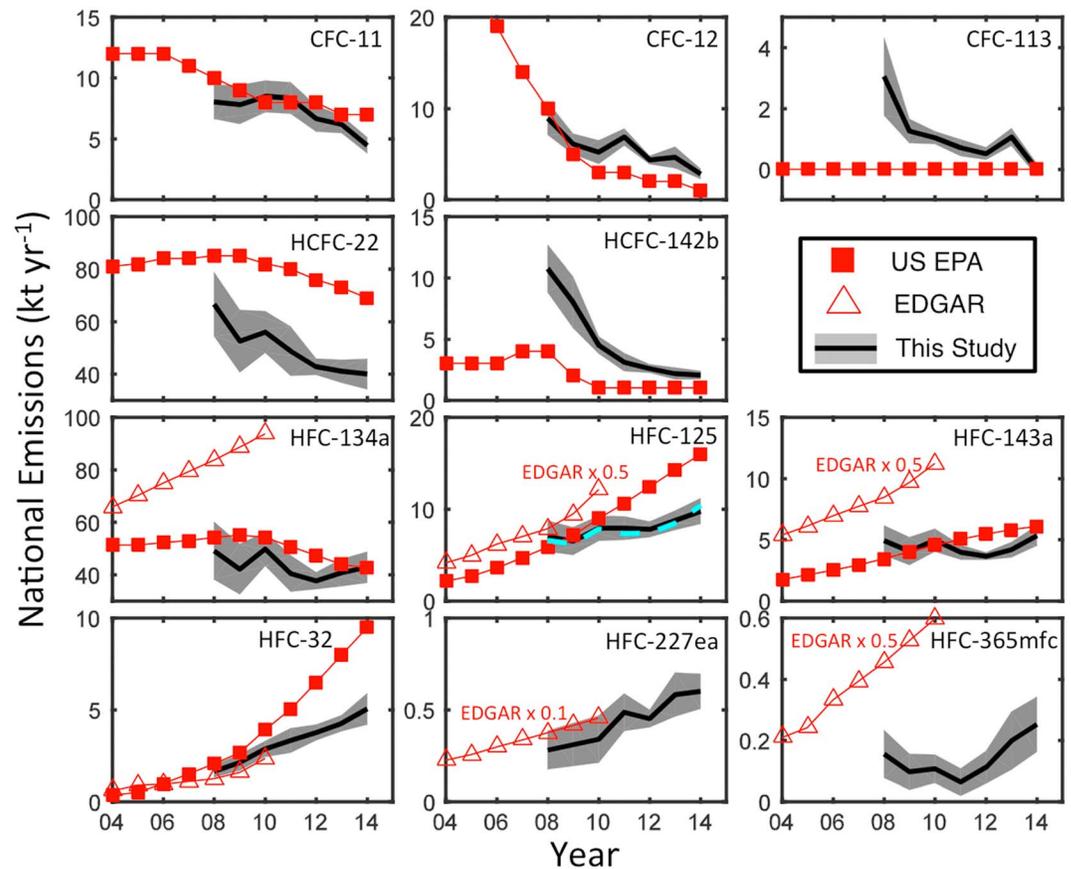
## 3.2. Emissions and Emission Trends

### 3.2.1. ODSs

The U.S. was historically the largest producer of CFCs, accounting for 50 to 70% of world production in the 1960s–1970s [Quinn *et al.*, 1986]. Reported U.S. production and consumption of CFCs fell from 320 ODP-kt yr<sup>-1</sup> in 1989 to near zero in 1996 (Figure S5). According to a market-based analysis by the EPA (14), U.S. emission of CFCs decreased rapidly over this period but lagged the phaseout of production and consumption significantly, and was still 8 ODP-kt yr<sup>-1</sup> (0.1 GtCO<sub>2</sub>e yr<sup>-1</sup>) in 2014 (Figure S5). Emission magnitudes and trends for the ODP-weighted aggregated emissions of CFCs we estimated from atmospheric observations for the period 2008 to 2014 are nearly identical to the EPA estimates (Figure S5).

Both the inventory and atmosphere-based estimates suggest that the decline of aggregated CFC emissions was dominated by reduced emissions of CFC-12, although U.S. emissions of the CFC-11 and CFC-113 also declined over this period (Figures 2, 3, S5, and S6). Differences among trends for individual CFCs are primarily due to differences in their past applications and the size and composition of their associated “banks” (reserves of chemicals used in old equipment, foams, or other products that have not yet escaped to the atmosphere) [Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (IPCC/TEAP), 2005; Montzka *et al.*, 2011]. CFC-12 was used predominantly in mobile A/C and refrigeration, whereas CFC-11 was used primarily as a blowing agent in insulation foams. Banks of refrigeration and air conditioning are estimated to have larger leak rates but shorter leakage lifetimes (15–30 years) than banks of foams (leakage lifetimes of 15–80 years) [Alternative Fluorocarbons Environmental Acceptability Study, 2005; Gamlen *et al.*, 1986; Godwin *et al.*, 2003; IPCC/TEAP, 2005]. For CFC-113, the EPA inventory suggests near-zero emissions (<0.5 kt yr<sup>-1</sup>) after 1996, whereas our atmosphere-based estimates indicate above zero emissions at least until 2014 (Figures 2 and S6).

HCFCs are transitional substitutes for CFCs and are used primarily in stationary A/C, refrigeration and foam-blowing applications [IPCC/TEAP, 2005]. Unlike CFCs, for which consistent emissions were obtained from inventory- and atmosphere-based methods, HCFC emissions derived from atmospheric data differ substantially from EPA estimates (Figures 2 and S6). Emissions of HCFC-22 are currently larger than all other ODSs.

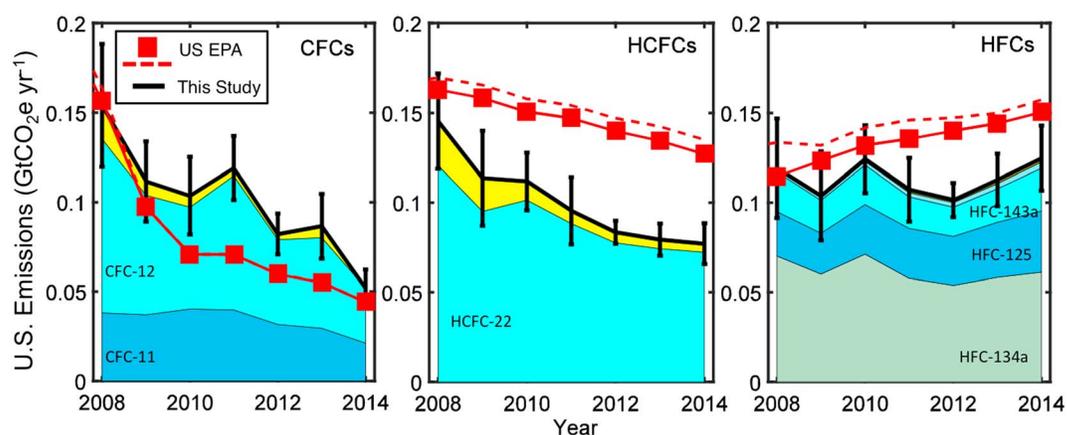


**Figure 2.** U.S. annual national emissions of CFCs, HCFCs, and HFCs derived from this study (black lines with gray shading indicating emission ranges computed from multiple inversions as detailed in Text S5), reported from inventories by the EPA (red squares) and by EDGAR (unfilled red triangles). The sum of measurement-derived HFC-143a and HFC-32 emissions (a cyan dashed line) is shown relative to HFC-125 emissions. These measurement-based emission results are tabulated in Table S1.

Our atmosphere-derived emissions are 20 (10–40) % lower than the EPA-reported emissions in 2008 (this study: 67 (54–79)  $\text{kt yr}^{-1}$ ; EPA: 85  $\text{kt yr}^{-1}$ ) and 40 (30–50) % lower in 2014 (this study: 40 (34–46)  $\text{kt yr}^{-1}$ ; EPA: 69  $\text{kt yr}^{-1}$ ). The atmosphere-based estimates indicate a decline of ~40% from 2008 to 2014, about twice as large as that reported by the EPA [U.S. Environmental Protection Agency, 2016]. A  $^{14}\text{CO}_2$ -tracer-ratio-based study using atmospheric data from only the northeastern U.S. [Miller et al., 2012], and a global inversion analysis using some of the same data considered here [Saikawa et al., 2012] both noted similar discrepancies with respect to EPA estimates (Figure S6). For HCFC-142b, the atmosphere-derived emission in 2008 of 11 (9–13)  $\text{kt yr}^{-1}$  was about 3 times larger than reported by the EPA, but decreased to levels comparable to EPA estimates by 2014 (1–2  $\text{kt yr}^{-1}$ ) (Figures 2 and S6). In compliance with the Montreal Protocol, reported U.S. production and consumption of HCFCs declined by 95% from the early 2000s to 2014 (Figure S7). HCFC emissions estimated by the EPA continued to rise gradually until 2008, and thereafter gradually declined (Figure S7). Our atmosphere-derived HCFC emissions (for HCFC-22 and HCFC-142b only) also indicate declining emissions from 2008 to 2014, but at a rate (–1.1 to –1.8 ODP- $\text{kt yr}^{-1}$ ) about 2 times faster than estimated by the EPA (Figure S7).

### 3.2.2. HFCs

In contrast to significantly declining emissions of ODSs, emissions of most HFCs are increasing (Figures 2 and S8). The prominent exception is HFC-134a, a substitute for CFC-12 in mobile A/C. Within the U.S., this transition began in 1992 with full penetration of HFC-134a into newly manufactured car A/C in 1994 [U.S. Environmental Protection Agency, 2016]. Correspondingly, emissions of HFC-134a estimated by the EPA increased dramatically after 1992, peaked in 2009, and decreased thereafter, in good agreement with our

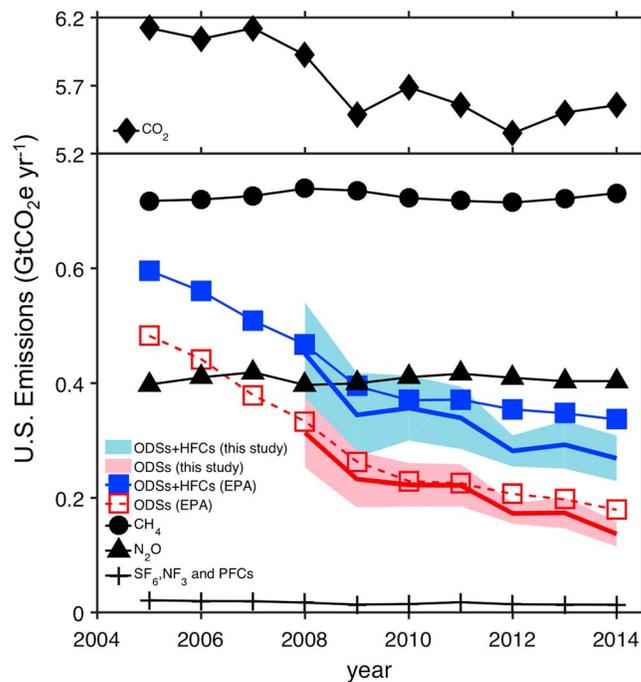


**Figure 3.** Aggregate CO<sub>2</sub>-equivalent emissions of CFCs (CFC-11, CFC-12, and CFC-113), HCFCs (HCFC-22 and HCFC-142b), and HFCs (HFC-134a, HFC-125, HFC-143a, HFC-32, HFC-365mfc, and HFC-227ea) from the U.S. derived in this study (black lines with error bars) and reported by the EPA (red squares connected with solid lines). Red dashed lines represent EPA emissions augmented by EPA-estimated emissions of chemicals not included in the atmosphere-based analyses (CFCs (CFC-115), HCFCs (HCFC-141b, HCFC-123, and HCFC-124), or HFCs (HFC-23, HFC-236fa)). Error bars for national aggregates were computed from multiple inversions, as described in Text S5 and are expressed as CO<sub>2</sub>-equivalent emissions.

atmosphere-based estimates (Figures 2 and S8). The emission decrease during 2008–2014 was likely due to reduced amounts of refrigerant installed in newly manufactured vehicles [U.S. Environmental Protection Agency, 2016]. Note that HFC-134a emissions derived here are 5–10 kt yr<sup>-1</sup> (10–20%) lower than we reported in a previous study covering the period 2008–2012 (when using the same transport models and background mole fractions) [Hu *et al.*, 2015] (Figure S8). This difference is primarily the result of including additional data at 1–3 km above ground level (agl) in the current analysis (Text S3). This addition improves the simulation of aircraft data at 0–1 km agl (used in both studies) and thus likely provides more accurate emissions estimates overall (Figure S10).

HFC-125 and HFC-143a are the third and fourth most abundant HFCs in the global atmosphere (after HFC-134a and HFC-23, [Carpenter *et al.*, 2014]) and have 100 year GWPs greater than 1000. Both have been used since the mid-1990s in refrigerant blends (R-404A (HFC-143a/HFC-125/HFC-134a: 52%/44%/4% by mass) and R-507 (HFC-143a/HFC-125: 50%/50% by mass)) to replace CFC-12 and HCFC-22 in commercial refrigeration. In addition, HFC-125 has been used since 2005 with HFC-32 in R-410A (HFC-32/HFC-125: 50%/50% by mass) to replace HCFC-22 in residential A/C [U.S. Environmental Protection Agency, 2016]. Like HCFC-22, measurement-derived emissions of HFC-125 and HFC-32 are smaller than reported in the inventory (Figure 2). Emission increases derived for HFC-125 and HFC-32 for 2008–2014 (a 0.5 kt yr<sup>-1</sup> per year increase, on average) are a factor of 3 smaller than the increases reported by the EPA, implying better refrigerant containment and/or slower market penetration of new residential A/C than assumed in the EPA's market-based inventory model [Godwin *et al.*, 2003]. Smaller emissions increases might also reflect retrofitting of old HCFC A/C units with refrigerant blends that contain less HFC-32 and HFC-125 by mass, such as R-407C (HFC-32/HFC-125/HFC-134a: 23%/25%/52% by mass) [Honeywell, 2016]. Furthermore, we note that the derived national emissions of HFC-125 are approximately equal to the sum of HFC-143a and HFC-32 emissions (Figure 2). This may reflect the predominant uses of these gases in refrigerant blends mentioned above, which have one-to-one mass ratios between HFC-125 and HFC-143a or HFC-32 within the U.S. For other minor HFCs (e.g., HFC-227ea and HFC-365mfc), our results indicate growth of emissions over the past 7 years, but at substantially smaller rates than reported by the EDGAR inventory (Figures 2 and S8).

Emissions of HFCs by sector were estimated using the atmosphere-based magnitudes derived here, sectoral emission fractions reported by the EPA [U.S. Environmental Protection Agency, 2016], and a method described by Montzka *et al.* [2015] (see also Text S6 for more detailed method description). Estimated sectoral emissions indicate that emissions from mobile A/C accounted for one half of total CO<sub>2</sub>-equivalent emissions of HFCs in the U.S. in 2008 (Figure S9); by 2014, the contribution of mobile A/C to HFC emissions was about one third of the total (Figure S9). Overall, emissions of HFCs remained approximately constant over this period, with decreased emissions from mobile A/C during 2008–2014 being largely offset by increasing emissions from



**Figure 4.** Aggregate CO<sub>2</sub>-equivalent emissions of major GHGs from the U.S. reported by the EPA (points connected with lines) [U.S. Environmental Protection Agency, 2016] and derived from this study (lines bounded by combined uncertainties from Figure 3). The atmosphere-based emissions shown here are augmented by EPA estimates for gases not measured in the present work (approximately 0.01–0.03 GtCO<sub>2</sub>e yr<sup>-1</sup> from CFC-115, HCFC-141b, HCFC-123, HCFC-124, HFC-23, and HFC-236fa).

atmosphere-derived aggregate CO<sub>2</sub>-equivalent emissions of HFCs from the U.S. are consistent with EPA-reported emissions within estimated uncertainties, suggesting that the increasing divergence between global HFC emissions derived from atmospheric observations and emissions reported to the UNFCCC by the EPA does not stem from inaccuracies in U.S. reporting [Lunt *et al.*, 2015; Montzka *et al.*, 2015; Rigby *et al.*, 2014].

Derived total CO<sub>2</sub>-equivalent emissions of CFCs, HCFCs, and HFCs decreased from 0.42 (0.33–0.51) GtCO<sub>2</sub>e yr<sup>-1</sup> in 2008 to 0.25 (0.21–0.29) GtCO<sub>2</sub>e yr<sup>-1</sup> by 2014 (Figure 4). In 2008, the U.S. emissions of ODSs and ODS substitutes were comparable to the national anthropogenic emissions of N<sub>2</sub>O reported by the EPA, and more than half of reported national anthropogenic emissions of CH<sub>4</sub>. By 2014, aggregated emissions of these halocarbons had decreased below national anthropogenic N<sub>2</sub>O emissions and were one third of national anthropogenic CH<sub>4</sub> emissions (Figure 4). Overall, aggregated CO<sub>2</sub>-equivalent emissions of ODSs and substitute chemicals have decreased 40% between 2008 and 2014 as a result of the Montreal Protocol and national regulations, while U.S. emissions of the main non-CO<sub>2</sub> GHGs (e.g., CH<sub>4</sub> and N<sub>2</sub>O) have remained nearly constant (Figures 3 and 4).

The estimated reduction of ODS emissions alone (i.e., excluding HFCs) is 0.17 (0.13–0.19) GtCO<sub>2</sub>e yr<sup>-1</sup> from 2008 to 2014, confirming the impression from inventory-based estimates that declines in ODS emissions have been substantial relative to decreases in other GHG emissions in recent years. Indeed, our estimated decline equates to ~50 (35–61)% of the decline in aggregate emissions of all other long-lived GHGs inventoried by the EPA over the same period [U.S. Environmental Protection Agency, 2016]. Adding the change suggested by EPA's inventory from 2005 to 2008 (0.15 GtCO<sub>2</sub>e yr<sup>-1</sup>) (Figure 4), the total reduction in ODS emissions from 2005 to 2014 is ~0.32 GtCO<sub>2</sub>e yr<sup>-1</sup>, amounting to ~60% of emission reductions achieved for other GHGs over the same time interval. Projecting the rate of reduction from 2008 to 2014 forward, ODS emissions could decline by an additional ~0.13 GtCO<sub>2</sub>e yr<sup>-1</sup> by 2025.

The overall climate impact of the Montreal Protocol in the future will also be determined by emissions of HFCs. Past U.S. HFC emission increases estimated here for some HFCs are not expected to continue. In fact,

residential A/C and foams, which increased by 11% and 3% from 2008 to 2014, respectively (relative to the total HFC emissions) (Figure S9).

#### 4. Discussion

Our results suggest that total CO<sub>2</sub>-equivalent emissions of CFCs decreased by two thirds from 2008 to 2014 (from 0.15 (0.12–0.19) GtCO<sub>2</sub>e yr<sup>-1</sup> to 0.05 (0.04–0.06) GtCO<sub>2</sub>e yr<sup>-1</sup>), while the total emissions of HCFCs decreased by about one half over the same period (from 0.15 (0.12–0.17) GtCO<sub>2</sub>e yr<sup>-1</sup> to 0.08 (0.07–0.09) GtCO<sub>2</sub>e yr<sup>-1</sup>) (Figure 3). For HFCs used as substitutes for both CFCs and HCFCs, aggregate emissions changed negligibly (i.e., within estimated year-to-year errors) from 2008 to 2014 (Figure 3). The large declining trends of CFC and HCFC emissions and increasing trends of emissions of many HFCs over the U.S. are indicative of the progress made in the U.S. in replacing ODSs with HFCs and other ozone-friendly chemicals. Furthermore, the

the U.S. EPA's Significant New Alternatives Policy (SNAP) program and the 2016 Kigali amendment of the Montreal Protocol controlling the use and production of HFCs may result in reductions of HFC emissions of  $0.07\text{--}0.09\text{ GtCO}_2\text{e yr}^{-1}$  [Greenblatt and Wei, 2016; U.S. Department of State, 2016]. Hence, the overall influence of the Montreal Protocol on U.S. GHG emissions decline from 2005 to 2025 can now be expected to be as large as  $\sim 0.5\text{ GtCO}_2\text{e yr}^{-1}$ . This is equivalent to  $\sim 25\text{--}30\%$  of the GHG emission reduction target previously identified in the U.S. Intended Nationally Determined Contributions (INDCs) to the 2015 UNFCCC 21st Conference of Parties (COP-21) in Paris ( $1.64\text{--}2.07\text{ GtCO}_2\text{e yr}^{-1}$  or a  $26\text{--}28\%$  reduction compared to 2005 values [Greenblatt and Wei, 2016; U.S. Environmental Protection Agency, 2016]). Only gases of the Kyoto Protocol, namely  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , HFCs, perfluorocarbons,  $\text{NF}_3$ , and  $\text{SF}_6$  were considered in the U.S. INDCs. Our results underscore the presence of significant GHG emission reductions related to the Montreal Protocol in addition to those achieved from gases included in the Kyoto Protocol and the historic COP-21 agreement.

### Acknowledgments

This work was supported in part by NOAA Climate Program Office's AC4 program. Support for tower operations in California were provided by the California Energy Commissions Natural Gas program and the California Air Resources Board, and the U.S. Department of Energy, Biological and Environmental Research Program at Lawrence Berkeley National Laboratory under U.S. Department of Energy contract DE-AC02-05CH11231. L.H. thanks E. Saikawa for providing HCFC-22 prior and posterior emissions from her global inversion study. We also thank other colleagues in the NOAA/ESRL Global Monitoring Division and at cooperative institutes for their ongoing efforts to maintain the long-term flask air sampling network. All data used in this study are available through the NOAA/ESRL Global Monitoring Division website (<https://www.esrl.noaa.gov/gmd/>) and ftp site (<ftp://ftp.cmdl.noaa.gov/hats/>). Modeling parameters and results not given here will be made available upon request.

### References

- Alternative Fluorocarbons Environmental Acceptability Study (2005), *Production, Sales, and Atmospheric Release of Fluorocarbons Through 2003*, Arlington, Va.
- Brunner, D., S. Henne, C. A. Keller, S. Reimann, M. K. Vollmer, S. O'Doherty, and M. Maione (2012), An extended Kalman-filter for regional scale inverse emission estimation, *Atmos. Chem. Phys.*, *12*(7), 3455–3478, doi:10.5194/acp-12-3455-2012.
- Carpenter L. J., et al. (2014), Ozone-depleting substances (ODSs) and other gases of interest to the Montreal Protocol, Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project—Report No. 55, chap. 1, World Meteorological Organization, Geneva, Switzerland.
- Daniel, J. S., et al. (2011), *A Focus on Information and Options for Policymakers*, 516 pp., World Meteorological Organization, Geneva, Switzerland.
- Elkins, J. W., T. M. Thompson, T. H. Swanson, J. H. Butler, B. D. Hall, S. O. Cummings, D. A. Fishers, and A. G. Raffo (1993), Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12, *Nature*, *364*(6440), 780–783.
- Gamlen, P. H., B. C. Lane, P. M. Midgley, and J. M. Steed (1986), The production and release to the atmosphere of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  (chlorofluorocarbons CFC 11 and CFC 12), *Atmos. Environ.*, *20*(6), 1077–1085, doi:10.1016/0004-6981(86)90139-3.
- Geels, C., et al. (2007), Comparing atmospheric transport models for future regional inversions over Europe—Part 1: Mapping the atmospheric  $\text{CO}_2$  signals, *Atmos. Chem. Phys.*, *7*(13), 3461–3479, doi:10.5194/acp-7-3461-2007.
- Gerbig, C., S. Körner, and J. C. Lin (2008), Vertical mixing in atmospheric tracer transport models: Error characterization and propagation, *Atmos. Chem. Phys.*, *8*(3), 591–602, doi:10.5194/acp-8-591-2008.
- Godwin, D. S., M. M. Van Pelt, and K. Peterson (2003), Modeling Emissions of High Global Warming Potential Gases, 12th International Emission Inventory Conference - "Emission Inventories - Applying New Technologies", San Diego, Calif.
- Greenblatt, J. B., and M. Wei (2016), Assessment of the climate commitments and additional mitigation policies of the United States, *Nat. Clim. Change*, *6*, 1090–1093, doi:10.1038/nclimate3125.
- Hall, B. D., et al. (2014), Results from the international halocarbons in air comparison experiment (IHALACE), *Atmos. Meas. Tech.*, *7*(2), 469–490, doi:10.5194/amt-7-469-2014.
- Harris, N. R. P., D. J. Wuebbles, J. S. Daniel, J. Hu, L. J. M. Kuijpers, K. S. Law, M. J. Prather, and R. Schofield (2014), Scenarios and information for policymakers, Chapter 5 in *Scientific Assessment of Ozone Depletion: 2014. Global Ozone Research and Monitoring Project - Report No. 55*, World Meteorological Organization, Geneva, Switzerland.
- Honeywell (2016), R-22 replacement in residential air conditioning.
- Hu, L., et al. (2015), U.S. emissions of HFC-134a derived for 2008–2012 from an extensive flask-air sampling network, *J. Geophys. Res. Atmos.*, *120*, 801–825, doi:10.1002/2014JD022617.
- Hu, L., et al. (2016), Continued emissions of carbon tetrachloride from the United States nearly two decades after its phase out for dispersive uses, *Proc. Natl. Acad. Sci. U.S.A.*, *113*(11), 2880–2885, doi:10.1073/pnas.1522284113.
- Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel (2005), *Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, 488 pp., Cambridge Univ. Press, Cambridge, U. K., and New York.
- Lunt, M. F., et al. (2015), Reconciling reported and unreported HFC emissions with atmospheric observations, *Proc. Natl. Acad. Sci. U.S.A.*, *112*(19), 5927–5931, doi:10.1073/pnas.1420247112.
- Maione, M., et al. (2014), Estimates of European emissions of methyl chloroform using a Bayesian inversion method, *Atmos. Chem. Phys.*, *14*(18), 9755–9770, doi:10.5194/acp-14-9755-2014.
- Manning, A. J., D. B. Ryall, R. G. Derwent, P. G. Simmonds, and S. O'Doherty (2003), Estimating European emissions of ozone-depleting and greenhouse gases using observations and a modeling back-attribution technique, *J. Geophys. Res.*, *108*(D14), 4405, doi:10.1029/2002JD002312.
- Masarie, K. A., and P. P. Tans (1995), Extension and integration of atmospheric carbon dioxide data into a globally consistent measurement record, *J. Geophys. Res.*, *100*, 11,593–11,610, doi:10.1029/95JD00859.
- Michalak, A. M., A. Hirsch, L. Bruhwiler, K. R. Gurney, W. Peters, and P. P. Tans (2005), Maximum likelihood estimation of covariance parameters for Bayesian atmospheric trace gas surface flux inversions, *J. Geophys. Res.*, *110*, D24107, doi:10.1029/2005JD005970.
- Miller, J. B., et al. (2012), Linking emissions of fossil fuel  $\text{CO}_2$  and other anthropogenic trace gases using atmospheric  $^{14}\text{CO}_2$ , *J. Geophys. Res.*, *117*, D08302, doi:10.1029/2011JD017048.
- Molina, M. J., and F. S. Rowland (1974), Stratospheric sink for chlorofluoromethanes: Chlorine atom-catalysed destruction of ozone, *Nature*, *249*(5460), 810–812.
- Montzka, S. A., J. H. Butler, J. W. Elkins, T. M. Thompson, A. D. Clarke, and L. T. Lock (1999), Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, *398*(6729), 690–694.
- Montzka, S. A., J. H. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, A. D. Clarke, L. T. Lock, and J. W. Elkins (1996), Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, *272*(5266), 1318–1322, doi:10.1126/science.272.5266.1318.

- Montzka, S. A., E. J. Dlugokencky, and J. H. Butler (2011), Non-CO<sub>2</sub> greenhouse gases and climate change, *Nature*, 476(7358), 43–50.
- Montzka, S. A., M. McFarland, S. O. Andersen, B. R. Miller, D. W. Fahey, B. D. Hall, L. Hu, C. Siso, and J. W. Elkins (2015), Recent trends in global emissions of hydrochlorofluorocarbons and hydrofluorocarbons: Reflecting on the 2007 adjustments to the Montreal Protocol, *J. Phys. Chem. A*, 119(19), 4439–4449, doi:10.1021/jp5097376.
- Myhre, G., et al. (2013), *Anthropogenic and Natural Radiative Forcing*, Cambridge Univ. Press, Cambridge, U. K., and New York.
- Ozone Secretariat (2016), ODS Production and Consumption in ODP Tonnes. [Available at <http://ozone.unep.org/en/data-reporting/data-centre>.]
- Quinn, T. H., K. A. Wolf, W. E. Mooz, J. K. Hammitt, T. W. Chesnutt, and S. Sarma (1986), *Projected US, Emissions, and Banks of Potential Ozone-Depleting Substances*, N-2282-EPA, The Rand Corporation, Santa Monica, Calif.
- Rigby, M., et al. (2014), Recent and future trends in synthetic greenhouse gas radiative forcing, *Geophys. Res. Lett.*, 41, 2623–2630, doi:10.1002/2013GL059099.
- Rodgers, C. D. (2000), *Inverse Methods for Atmospheric Sounding*, World Sci., Tokyo.
- Saikawa, E., et al. (2012), Global and regional emission estimates for HCFC-22, *Atmos. Chem. Phys.*, 12, 10,033–10,050, doi:10.5194/acp-12-10033-2012.
- Solomon, S., D. J. Ivy, D. Kinnison, M. J. Mills, R. R. Neely, and A. Schmidt (2016), Emergence of healing in the Antarctic ozone layer, *Science*, doi:10.1126/science.aae0061.
- Stohl, A., et al. (2009), An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, *Atmos. Chem. Phys.*, 9(5), 1597–1620, doi:10.5194/acp-9-1597-2009.
- Tans, P. P., T. J. Conway, and T. Nakazawa (1989), Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide derived from surface observations and an atmospheric transport model, *J. Geophys. Res.*, 94, 5151–5172, doi:10.1029/JD094iD04p05151.
- The Kigali Amendment (2016), The amendment to the Montreal Protocol agreed by the twenty-eighth meeting of the parties, Kigali.
- U.S. Department of Energy (2016), Insulation. [Available at <http://energy.gov/energysaver/insulation>.]
- U.S. Department of State (2016), 2016 Second Biennial Report of the United States of America Under the United Nations Framework Convention on Climate Change.
- U.S. Energy Information Administration (2011), Residential Energy Consumption Survey (RECS).
- U.S. Environmental Protection Agency (2016), Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2014, U.S. Environmental Protection Agency, 1200 Pennsylvania Ave., N. W., Washington, D. C.
- Velders, G. J. M., S. O. Andersen, J. S. Daniel, D. W. Fahey, and M. McFarland (2007), The importance of the Montreal protocol in protecting climate, *Proc. Natl. Acad. Sci. U.S.A.*, 104(12), 4814–4819, doi:10.1073/pnas.0610328104.
- Velders, G. J. M., D. W. Fahey, J. S. Daniel, M. McFarland, and S. O. Andersen (2009), The large contribution of projected HFC emissions to future climate forcing, *Proc. Natl. Acad. Sci. U.S.A.*, 106(27), 10,949–10,954, doi:10.1073/pnas.0902817106.
- Velders, G. J. M., A. R. Ravishankara, M. K. Miller, M. J. Molina, J. Alcamo, J. S. Daniel, D. W. Fahey, S. A. Montzka, and S. Reimann (2012), Preserving Montreal protocol climate benefits by limiting HFCs, *Science*, 335(6071), 922–923.
- Velders, G. J. M., D. W. Fahey, J. S. Daniel, S. O. Andersen, and M. McFarland (2015), Future atmospheric abundances and climate forcings from scenarios of global and regional hydrofluorocarbon (HFC) emissions, *Atmos. Environ.*, 123, 200–209, doi:10.1016/j.atmosenv.2015.10.071.
- World Meteorological Organization (WMO) (2014), *Scientific Assessment of Ozone Depletion: 2014*, World Meteorological Organization, Geneva, Switzerland.
- Xiang, B., et al. (2014), Global emissions of refrigerants HCFC-22 and HFC-134a: Unforeseen seasonal contributions, *Proc. Natl. Acad. Sci. U.S.A.*, 111(49), 17,379–17,384, doi:10.1073/pnas.1417372111.