Recent Trends in Global Emissions of Hydrochlorofluorocarbons and Hydrofluorocarbons: Reflecting on the 2007 Adjustments to the Montreal Protocol

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ABSTRACT: Global-scale atmospheric measurements are used to investigate the effectiveness of recent adjustments to production and consumption controls on hydrochlorofluorocarbons (HCFCs) under the Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) and to assess recent projections of large increases in hydrofluorocarbon (HFC) production and emission. The results show that aggregate global HCFC emissions did not increase appreciably during 2007−2012 and suggest that the 2007 Adjustments to the Montreal Protocol played a role in limiting HCFC emissions well in advance of the 2013 cap on global production. HCFC emissions varied between 27 and 29 kt CFC-11-equivalent (eq)/y or 0.76 and 0.79 GtCO$_2$-eq/y during this period. Despite slower than projected increases in aggregate HCFC emissions since 2007, total emissions of HFCs used as substitutes for HCFCs and chlorofluorocarbons (CFCs) have not increased more rapidly than rates projected [Velders, G. J. M.; Fahey, D. W.; Daniel, J. S.; McFarland, M.; Andersen, S. O. The Large Contribution of Projected HFC Emissions to Future Climate Forcing. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10949−10954] for 2007−2012. HFC global emission magnitudes related to this substitution totaled 0.51 (−0.03, +0.04) GtCO$_2$-eq/y in 2012, a magnitude about two times larger than emissions reported to the United Nations Framework Convention on Climate Change (UNFCCC) for these HFCs. Assuming accurate reporting to the UNFCCC, the results imply that developing countries (non-Annex I Parties) not reporting to the UNFCCC now account for nearly 50% of global HFC emissions used as substitutes for ozone-depleting substances (ODSs). Global HFC emissions (as CO$_2$-eq) from ODS substitution can be attributed approximately equally to mobile air conditioning, commercial refrigeration, and the sum of all other applications.

Attributing Global Hydrofluorocarbon Emissions with Atmospheric Observations
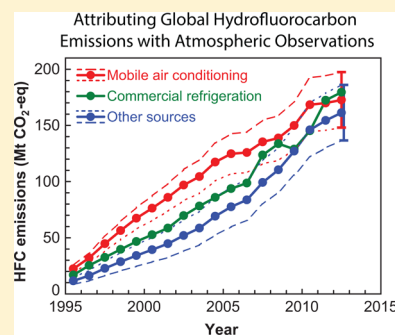
INTRODUCTION

The phase-out of ozone-depleting substances (ODSs) has involved a multistep elimination within different chemical classes guided by the adjusted and amended 1987 Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol). Hydrochlorofluorocarbons (HCFCs) are an important component to this phase out. Although one HCFC (HCFC-22) had been used prior to the Montreal Protocol, this HCFC and others introduced as replacements for chlorofluorocarbons (CFCs) were considered "transitional substances", key to a rapid phase out of the more potent CFCs. HCFC production increased rapidly in non-Article 5 Montreal Protocol Parties (developed countries) in the 1990s as production of CFCs was curtailed. But by the 2000s, HCFC production and consumption from developed countries for emissive uses was decreasing in response to Montreal Protocol controls resulting in substitution with HFCs, and, in some cases, by other economically and environmentally superior not-in-kind alternatives.[2] The atmospheric accumulation of some HCFCs slowed temporarily but accelerated shortly thereafter

when sales in developing countries of products manufactured with and containing HCFCs increased substantially.[2,3] By the mid-2000s, production and consumption of HCFCs for emissive uses in Article 5 Montreal Protocol Parties (developing countries) was increasing exponentially, approaching magnitudes reported in developed countries at their peak (in the mid-1990s) and, at that time, was not slated for control until 2016, at which point production and consumption would be capped at 2015 rates (note that "consumption" is defined in the Montreal Protocol to refer to magnitudes of chemical production plus amounts imported minus amounts exported).

In 2007, against this backdrop, the Parties to the Montreal Protocol agreed to Adjustments to the Protocol that accelerated the phase-out schedules for HCFC production and con-

Table 1. NOAA Measurement Details and Results for HCFCs and HFCs[a]

compound	analysis instrument	start date	ODP[b]	GWP[c] (100-y)	mean mixing ratio (2012) ppt[e,f]	rate of change (2010−2012) ppt/y	derived emission[d] (2012) Gg/y
Hydrochlorofluorocarbons							
HCFC-22	M1&M3	1992	0.055	1810	218.0	6.1	358
	M2	2007			218.3	6.0	358
HCFC-141b	M1&M3	1993	0.11	725	22.3	0.93	66
	M2	2007			22.3	0.99	69
HCFC-142b	M1&M3	1992	0.065	2310	21.4	0.62	27
	M2	2007			21.6	0.67	27
Hydrofluorocarbons							
HFC-134a	M1&M3	1994	0	1430	67.5	5.1	173
	M2	2007			67.5	5.0	172
HFC-152a	M1&M3	2000	0	124	6.7	0.31	54
	M2	2007			6.8	0.27	56
HFC-143a	M2	2007	0	4470	12.3	1.1	21
HFC-125	M2	2007	0	3500	11.4	1.5	41
HFC-32	M2	2007	0	675	5.1	0.7	16
HFC-227ea	M2	2007	0	3220	1.1	0.09	3
HFC-365mfc	M2	2007	0	794	0.8	0.08	6

[a]Notes. [b]ODPs (ozone depletion potentials) are reported as listed in the Montreal Protocol. [c]GWPs (100-y global warming potentials) are from Forster et al.[27] [d]Emissions are derived with a 3-box model (northern and southern hemisphere troposphere and the stratosphere) forced to match the measured tropospheric mixing ratios. [e]M1&M3 global mean surface mixing ratios are derived from results at 8 sites: South Pole (SPO, 90°S, 2837 masl (meters above sea level)); Cape Grim, Australia (CGO, 40.682°S, 144.688°E, 164 masl); American Samoa (SMO, 14.247°S, 170.564°W, 77 masl); Mauna Loa, USA (MLO, 19.5362°N, 155.5763°W, 3433 masl); Cape Kumukahi, USA (KUM, 19.516°N, 154.811°W, 39 masl); Niwot Ridge, USA (NWR, 40.1°N, 105.5°W, 3475 masl); Barrow, USA (BRW, 71.3°N, 156.6°W, 27 masl); Alert, Canada (ALT, 82.5°N, 62.3°W, 210 masl). Nearly identical results are derived if results from additional remote sites are also included: Palmer Station, Antarctica (PSA, 64.6°S, 64.0°W, 15 masl); Trinidad Head, USA (THD, 41.0°N, 124.1°W, 120 masl); Mace Head, Ireland (MHD, 53.3°N, 9.9°W, 42 masl); and Summit, Greenland (SUM, 72.6°N, 38.4°W, 3209 masl). Flask sampling frequency at most sites is 1/wk; at SPO, PSA, and SUM it is less. Results from instrument M1&M3 are obtained with a DB-5 chromatography column and temperature program starting at subambient temperatures. [f]M2 global mean surface mixing ratios are derived from results at 7 sites: SPO, CGO, SMO, MLO, KUM, THD, and BRW. Analysis is performed on about half of the flasks analyzed on M1 and M3 (∼2 pair/month), and these analyses are performed using a Gaspro chromatography column. Global surface means from both instruments are derived from the available measurements after weighting by sampling latitude.

sumption for emissive uses in both developed and developing countries. In developing countries production and consumption was capped in 2013 at average rates in 2009 and 2010, resulting in global production and consumption of HCFCs being capped beginning in 2013. While these adjustments moved forward the recovery date anticipated for the stratospheric ozone layer, they also had important implications for climate[1,4] because most HCFCs in use are potent greenhouse gases (GHGs).[5] In fact, the relatively small influence on ozone recovery timescales projected from these adjustments (<5 years)[6] suggests that reducing GHG emissions was likely an important consideration for the parties in 2007 during their deliberations.[7]

Although the 2007 Adjustments to the Montreal Protocol will allow the stratospheric ozone layer to recover sooner, their influence on the timing of ozone recovery could not be estimated precisely for three reasons. First, the adjustments did not control HCFC production and consumption for developing country uses prior to 2013, leaving open the potential for substantial increases during 2007−2013. Second, production and consumption during 2009 and 2010 would determine the size of the developing country baseline that set limits on use magnitudes from 2013 until the 2040 phaseout. Third, the timing of HCFC emission decreases are likely only loosely proportional to production magnitudes owing to the presence of a poorly quantified but substantial "bank" of produced but not-yet-emitted chemicals contained in inventories, actively used products (e.g., air conditioning and refrigeration equipment, plastic foam used for thermal insulation, and fire

extinguishers), and products in landfills where ODSs slowly leak out as they deteriorate.[8]

Furthermore, maintaining or even augmenting the GHG emission reductions achieved by the Montreal Protocol between 1987 and 2007 is not ensured by the 2007 adjustments. The net impact of the 2007 Adjustments on GHG emissions will be determined by the global warming potential (GWP) and energy efficiency of substitutes used to replace HCFCs, particularly in developing countries. If substitutes with high 100-y GWPs or low energy efficiency are used in developing countries during their future industrialization, a substantial fraction of the climate "benefit" provided by the Montreal Protocol could be offset.[1,9]

Measurements of long-lived trace gases in the remote atmosphere allow estimates of underlying global emission rates that are independent of inventory-based approaches that derive emissions from production or consumption magnitudes with many difficult-to-assess assumptions.[10−14] As a result, they allow independent globally integrated assessments of international policy measures. Here atmospheric observations of the major HCFCs and HFCs are presented through 2012 to determine if the trajectories of HCFC and HFC emissions changed after the 2007 Adjustments to the Montreal Protocol and to determine the overall influence of those changes on atmospheric ODS amounts and associated climate forcing. We discuss the implications of these results for understanding current and future emissions of HFCs, particularly in developing countries, which is made possible by considering the observation-derived emissions together with the inventory-

based emissions compiled for developed countries and countries with economies in transition (Annex I UNFCCC Parties; data available at http://unfccc.int/ghg_data/ghg_data_unfccc/items/4146.php). Finally, we estimate the relative contribution of different use categories for HFCs to recent atmospheric HFC increases.

■ EXPERIMENTAL SECTION

Atmospheric mixing ratios (pmol mol^{-1} or ppt) for three HCFCs and seven HFCs have been determined at the National Oceanographic and Atmospheric Administration (NOAA) with gas chromatography and mass spectrometry techniques from samples collected in paired glass or electropolished stainless-steel flasks at 7 to 12 remote sites across the globe since as early as 1992 (Table 1).[2,15] Replicate injection precision for most compounds has improved over time as atmospheric mixing ratios have increased and instrumentation optimized. For example, mean replicate injection precision for HFC-134a was 1.1% for flasks analyzed in 2000 and was 0.23% during 2010–2012; for HCFC-22 in 2000 it was 0.45%, and it was 0.20% during 2010–2012. For chemicals regularly measured from glass and electropolished stainless steel flasks (HCFC-22, -142b, -141b, HFC-134a, -152a, -365mfc, -227ea), measured flask pair means for all except HCFC-141b are independent of flask type (mean differences between glass and stainless steel flask pairs collected since mid-2009 are <0.15%). HCFC-141b results from glass flasks are often elevated owing to outgassing from polytetrafluoroethylene (PTFE) O-ring seals unique to those flasks. Accordingly, only HCFC-141b results from stainless steel flasks are used in this analysis. Furthermore, for all compounds considered here, differences between mixing ratios determined in simultaneously filled flasks are not measurably different in more than 90% of the flask pairs analyzed, suggesting that these HCFCs and HFCs are reliably stored in flasks prior to analysis. Consistent results are observed for the subset of compounds (HCFC-22, HCFC-141b, HCFC-142b, HFC-134a, and HFC-152a) measured on two different instruments in the NOAA Global Monitoring Division laboratory (Table 1). Although tied to the same suite of gravimetrically prepared standards, the results from these two instruments are derived with different gas chromatography columns and column-oven temperature programs and, on one instrument (M2), from only a subset of the sampled flasks (Table 1). This consistency provides additional confidence in the robustness of NOAA's analytical systems and in the ability of periodically collected flask samples to provide accurate measures of global mean surface mixing ratios, their rates of change, and global emissions magnitudes for these long-lived trace gases.

Results are referenced to suites of standards prepared in-house with gravimetric techniques at near-ambient mixing ratios. Absolute uncertainties in standard scales are estimated to be <2% based on potential errors associated with reagent purity and mass determinations; comparisons between global means derived here and those derived from independent global networks typically show differences of this magnitude or less.[20] The long-term consistency in standard scales is evaluated with repeat analyses of gravimetrically prepared standards and consideration of relative response factors measured for these standards over time and by repeat analyses of a suite of high-pressure real-air samples in aluminum and electropolished stainless-steel cylinders. Published comparisons between global annual mean mixing ratios for HCFCs and HFC-134a derived

from the NOAA sampling network and those derived by independent sampling networks (e.g., the Advanced Global Atmospheric Gases Experiment)[17] show small but consistent differences over multidecadal periods.[16]

Global emission rates are derived with a 3-box model representing hemispheric mean tropospheric mixing ratios and mean loss frequencies across the northern and southern hemispheric troposphere and stratosphere.[2] Although we consider the 3-box approach more accurate, to facilitate comparisons with previous studies, we have also included results from a 1-box model configured as used by Velders et al.[1,4] and in reports of the World Meteorological Organization (WMO)/United Nations Environment Programme (UNEP)/ NOAA/National Aeronautics and Space Administration (NASA)/European Commission (EC)-sponsored Montreal Protocol Scientific Assessment Panel (SAP).[16,18] Hemispheric mean mixing ratios are derived by weighting results at different sites by the fraction of the global troposphere represented by each site. Stratospheric loss frequencies are chosen to give steady-state stratospheric lifetimes estimated by Naik et al.,[19] and tropospheric loss frequencies (constant interannually[20]) are subsequently adjusted to yield the current best-estimate global steady-state lifetimes.[16,21] Previous studies have demonstrated that for long-lived gases, global emissions derived with box models are comparable to those derived with more sophisticated approaches.[16,22,23] The simple 1-box approach has been used extensively for deriving emissions and scenarios in the ozone SAP reports.

Ongoing measurements of some HFCs were initiated at NOAA from flasks collected at 7 sampling locations only in the mid- to late-2000s (HFC-143a, -125, -32, 365mfc, and -227ea) (see Table 1). Global atmospheric changes before 2007 were derived from the analysis of archived air samples filled at Niwot Ridge, Colorado (40°N) or in the Pacific Ocean Basin[15] in treated-aluminum cylinders and in humidified electropolished stainless-steel cylinders. As a result, larger uncertainties are associated with estimated global mixing ratios, trends, and emissions derived for these HFCs before 2007.

Methodology for Partitioning HFC Emissions among Three Different Use Categories: Mobile Air Conditioning, Commercial Refrigeration, and Other Uses. Some of the HFCs measured here are used almost exclusively in a single application and can be directly attributed to that use, while other HFCs are used in a variety of applications and are apportioned here based on publically reported data, information from chemical suppliers, and their product manufacturing customers, information from service organizations, and other expert sources.

HFC-143a is used primarily in commercial refrigeration as an ingredient in the blends R-404A (52%/44%/4% HFC-143a/ HFC-125/HFC-134a; blend compositions are by weight) and R-507A (50%/50% HFC-143a/HFC-125). R-404A is also used in some regions for industrial food processing and storage and has some additional small uses. Accordingly, total commercial HFC refrigerant emission magnitudes (T_{com}; including those from the additional industrial R-404A applications mentioned above) were estimated as the total observationally derived global emissions of HFC-143a divided by the average weight fraction of HFC-143a in these blends (0.51). Different assumptions about the relative usage of R-404A and R-507A refrigerants (0 to 100% for one or the other refrigerant) make only a small difference (± 1 Mt CO_2-eq) in the total contributions of the three sectors in this analysis. The bulk of

4441

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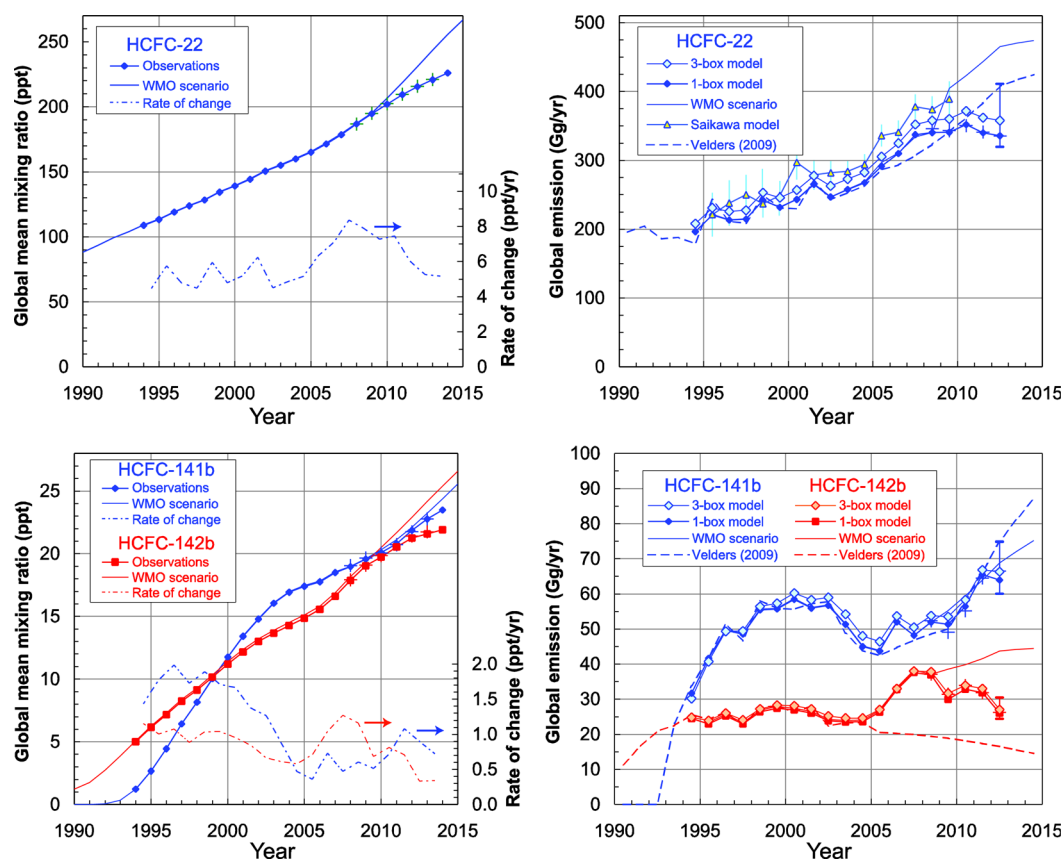
Figure 1. Left: Global mean surface mixing ratios of the three most abundant HCFCs derived from NOAA flask measurements at remote sites (◆ or ■ connected with lines); rates of change are plotted relative to the right-hand scale (dot-dashed lines; derived as annual mean differences). These results are compared with the baseline scenario from the 2010 Ozone Assessment Report ("WMO scenario").[18] Right: HCFC global emission rates derived from these flask measurements and a 3-box inverse analysis. Results from a 1-box analysis of the flask data are also provided to allow a direct comparison to the WMO baseline scenario[18] and to past and projected emissions from Velders et al.[1] ["Velders (2009)"], both of which are derived from global observations and a 1-box model. Global emissions derived from an inverse analysis of global atmospheric HCFC-22 data (including NOAA data among other networks) with a 3D model ("Saikawa model")[23] indicate a small high bias compared to the 3-box results that is due primarily to the 0.1 y shorter lifetime used in that corrigendum. In all panels, plus symbols represent global quantities derived from the subset of flasks analyzed on the second NOAA instrument (M2, see Experimental Section). Emission uncertainties are shown only for 2012 and represent only the uncertainty associated with the trace-gas lifetimes.[21]

CO_2-equivalent emissions (CO_2-eq; 1 Mt = 10^{12} g) from the commercial refrigeration sector were estimated as the total observationally derived global emissions of HFC-143a, plus emissions of HFC-125 derived as $T_{com} \times 0.47$ (the average of 0.44 and 0.5), plus emissions of HFC-134a derived as $T_{com} \times 0.02$ (the average of 0.00 and 0.04) and consideration of the appropriate 100-y GWPs.

Noncommercial (i.e., residential) HFC refrigerant emission magnitudes were included in the "other" category and were estimated by assuming atmospheric measurements of HFC-32 were indicative of emissions related to use of R-407C (23%/25%/52% HFC-32/HFC-125/HFC-134a) and R-410A (50%/50% HFC-32/HFC-125). R-407C was used as a near drop-in replacement for R-22 in new residential air conditioning equipment in the European Union and Japan until around 2006 because original equipment manufacturers were not ready then to implement R-410A, the preferred blend in North America at that time. Total emissions of R-407C associated with first-fill and servicing of air conditioning equipment were calculated by dividing global atmosphere-derived HFC-32 emissions by 0.23 through 2004; in subsequent years, this emission was held constant assuming that the total inventory of equipment emitting R-407C remained constant after that. Emissions of

HFC-125 and HFC-134a from R-407C were derived from total R-407C emissions by multiplying by their respective fractions in this blend.

Emissions of R-410A (50%/50% HFC-32/HFC-125) were estimated as the remaining emissions of HFC-32 in years after 2004 and an equivalent emission of HFC-125. R-410A is used in unitary room air conditioning systems as a primary substitute for HCFC-22, and these emissions were also included in the "other" category.

Consideration of these main refrigerant blends and emissions of other HFCs as described above accounts for 97% of summed global emissions of HFC-125 between 1995 and 2012 derived from the modeled atmospheric measurements; annual differences have averaged about 2 Gg, or about 10% of the global emission in each year. During 2011 and 2012, however, the observationally derived global HFC-125 emission has been larger by about 5 Gg, possibly because of increased recent use of R-407A (20%/40%/40% HFC-32/HFC-125/HFC-134a), R-407F (30%/30%/40% HFC-32/HFC-125/HFC-134a), and R-438A (8.5%/45%/44.2% HFC-32/HFC-125/HFC-134a) as lower-GWP substitutes for R-404A and R-507A in new and existing commercial refrigeration equipment. These additional
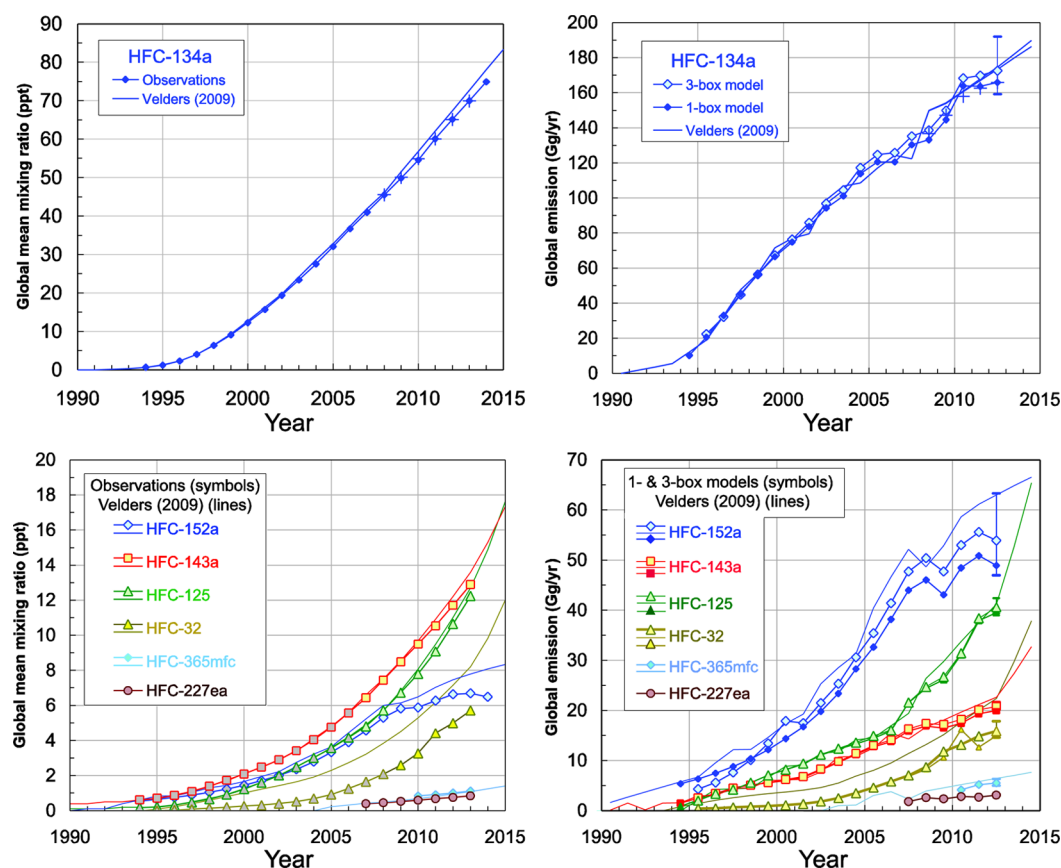
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Figure 2. Left: Global mean surface mixing ratios of the main HFCs used as substitutes for ozone-depleting substances. Mixing ratios derived from NOAA flask measurements at remote sites (lines with symbols) are overlaid on the estimates and projections from Velders et al.[1] (lines only, from both the low and high future scenarios). Gray-filled symbols represent periods when global mean mixing ratios were derived with only archived samples. Right-hand panels: HFC global annual emission rates derived from measured global means and a 3-box inverse analysis (solid points with lighter fill color connected by lines). Results from a 1-box analysis of the flask data (solid filled points connected with lines) are provided to allow a direct comparison to emissions from Velders et al.[1] (lines; derived with a 1-box approach; only high scenario results shown). Emissions derived for HFC-32 are displayed as 3 y averages to smooth noise associated with poor signal-to-noise in some measurements of this gas. For HFC-134a (the top panels), plusses are results derived with a subset of flasks analyzed on the second NOAA instrument (M2, see Experimental Section). Emission uncertainties are shown only for 2012 and represent only the uncertainty associated with the lifetimes of these gases.[21]

small HFC-125 emissions have been added to the totals attributed to commercial refrigeration.

Emissions of HFC-134a from mobile air conditioning (MAC) were estimated as accounting for 70 ± 10% of the global emissions of this chemical derived from atmospheric measurement data. This fraction is based on national inventory reporting to the UNFCCC, which suggest that most HFC-134a emissions are associated with MAC applications despite use also in building air conditioning, commercial and residential refrigeration, and metered-dose inhalers. In reporting from the US, for example, the fraction of HFC-134a emitted from MAC decreased from 76% in 2007 to 64% in 2011 (an average of 70%) (National Emission Inventory submissions available at http://unfccc.int/national_reports/annex_i_ghg_inventories/national_inventories_submissions/items/7383.php). Slightly smaller fractions (70% in 2007 decreasing to 61% in 2011) are derived when amounts reported by some other major emitting countries reporting total emissions and emissions from MACs to the UNFCCC are also considered (France, Germany, Spain, and Great Britain). The gradual decrease in this fraction over time likely represents the introduction of refrigerant blends containing HFC-134a as substitutes for HCFCs in non-MAC applications (e.g., R404A and 407C). In developing countries non-MAC uses of HFC-134a likely have even less of

the current market share because Montreal Protocol-related limits to HCFC use were only present beginning in 2013. As a result, on a global scale it is likely that during 2007−2012 the fraction of HFC-134a used in MACs relative to other applications is at least as high as suggested by the data reported to the UNFCCC.

The remaining emissions of HFC-134a and emissions of HFC-152a, HFC-365mfc, and HFC-227ea were included in the "other" category along with emissions derived for use of R-407C and R-410A, as discussed above.

■ RESULTS AND DISCUSSION

Global Atmospheric Changes Observed for HCFCs and Their Implications. Global mean surface mixing ratios of HCFCs and HFCs used as substitutes for ozone-depleting gases have increased every year in the background atmosphere throughout the measurement record (Figures 1 and 2). Measured mixing ratios at northern hemispheric sites are larger than those in the southern hemisphere (not shown), consistent with continuing anthropogenic emissions arising predominantly from the more populated northern hemisphere. The highest global mean surface mixing ratios and recent rates of increase (as ppt/y) are observed for HCFC-22 and HFC-134a.

4443

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While growth rates measured for global mean surface mixing ratios of some HCFCs were increasing before 2007,[2] since then global growth rates for two of the three most abundant HCFCs have appreciably slowed (Figure 1). The annual rate of increase observed for HCFC-22 between 2011 and 2012 was 30% slower than observed between 2007 and 2008, and, for HCFC-142b, the 2011−2012 rate of increase was 60% slower than observed between 2007 and 2008. In contrast, the atmospheric growth rate of HCFC-141b increased nearly a factor of 2 between 2007 and 2012.

These observations suggest substantial changes in global emission magnitudes for HCFCs since 2007 (Figure 1). Emissions of HCFC-22 and HCFC-142b had been increasing before 2007; since then, emissions of HCFC-22 have been nearly constant and emissions of HCFC-142b have declined by 25% (2012 vs 2008 value). Emissions of HCFC-141b had decreased slightly between 2000 and 2007 but then increased such that by 2012, they were 25% larger than those in 2008. Annual aggregate HCFC emissions increased on average by 28 Gg/y between 2004 and 2007 and by ∼2 Gg/y (or 0.5%/y) between 2007 and 2012. In 2012, global HCFC emissions amounted to 450 (−47, +65) Gg/y (0.76 GtCO$_2$-eq/y or 29 kt CFC-11-eq/y), which is indistinguishable from that reported by an independent sampling network and a 12-box model analysis [466 (−58, +107) Gg/y].[14]

The shift in the trend of aggregate global HCFC emissions observed in ∼2007 was not captured in the WMO baseline scenarios because production and consumption trends in years prior to 2007 were assumed to continue through 2012 in developing countries given that caps to total HCFC production and consumption in Article 5 Parties began only in 2013. Hence, aggregate emissions of HCFCs could have increased through 2013 even with the 2007 adjustments to the Protocol. The atmospheric observations indicate, however, that HCFC mixing ratios and summed emissions did not increase to the extent allowable during 2008−2012 (Figure 1). Specifically, while annual emissions of HCFC-22 increased by an average of 29 Gg/y between 2007 and 2012 in the WMO baseline scenario, the atmospheric data indicate that annual emissions increased over that period by <1 Gg/y on average. We estimate from these observations a 2012 global emission of HCFC-22 of 360 (−40, +50) Gg/y (340 Gg/y from the 1-box model), which is only 73% as large as assumed in the baseline scenario.[18] For HCFC-142b, the atmospheric observations indicate a slight decrease in emissions between 2007 and 2012, whereas the baseline scenario suggested emissions could remain approximately constant. For HCFC-141b, the observations indicate an increase in HCFC-141b emissions from 50 to 67 Gg/y (48 to 65 Gg/y from 1-box analysis) between 2007 and 2012, very consistent with the baseline scenario projection.

These results suggest that the 2007 Amendments to the Montreal Protocol had a measurable and environmentally favorable impact on global emissions and atmospheric mixing ratios of HCFCs well in advance of the 2013 cap on global production. Other factors such as the global economic slowdown in 2009 and improved service practices also may have contributed to slower emission increases during this period.

The recent trends in emissions derived with atmospheric measurement data are qualitatively consistent with HCFC production and consumption magnitudes reported to UNEP by the Parties to the Montreal Protocol for controlled uses (Figure 3; data available at: http://ozone.unep.org/Data_Reporting/
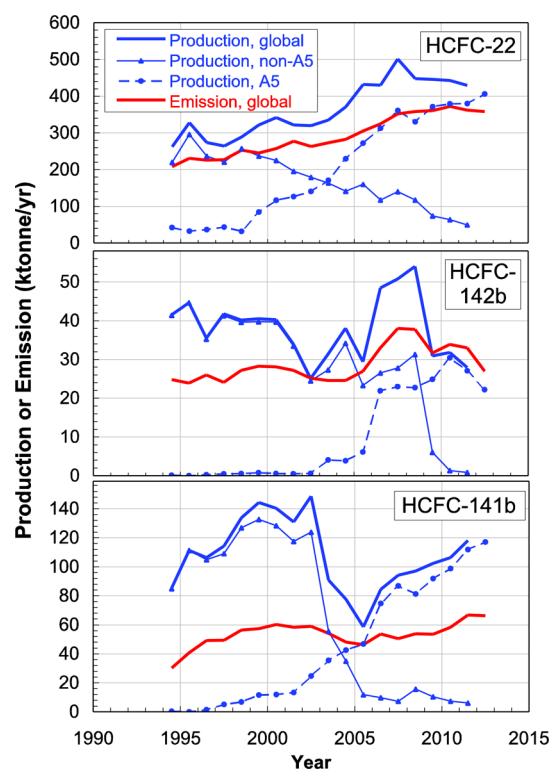

Figure 3. A comparison between global HCFC emissions derived in this work (red lines; see Figure 1) and global HCFC production magnitudes reported to UNEP (blue lines) over time. Different panels represent different chemicals. Global production is the sum of reported magnitudes from A5 parties (developing countries; dashed blue line with ●) and non-A5 parties (developed countries; thin solid blue line with ▲) for emissive uses only; production magnitudes for nonemissive uses (e.g., as feedstocks and process agents where emissions are thought to be negligible) are not included.

Data_Access/) (production of ODSs as feedstocks and process agents that are chemically transformed and not appreciably emitted to the atmosphere are not controlled).

Production magnitudes reported by compound also allow an assessment of changes in the size of produced-but-not-yet-emitted banks of HCFCs (Figure 3). These comparisons indicate that banks of HCFC-22 and HCFC-141b were still increasing by 75 and 50 Gg/y, respectively, between 2009 and 2011. This suggests annual increases of ∼3 to 5%/y in bank magnitudes for both of these chemicals (when total bank magnitudes are estimated as in Daniel et al.[18]). Fairly constant global emissions of HCFC-22 derived for a period when banks were increasing also suggest that improved service practices contributed to limiting HCFCs emissions during recent years, although it could also imply an increase in chemical inventories not associated with "in-use" chemicals. HCFC-22 in such inventories would likely not leak at rates as large as those associated with "in-use" applications.

Reported production for HCFC-142b since 2009 has been between 1 and 6 Gg/y below the observationally derived global emission rates (Figure 3). Although uncertainties on global emissions estimated from the atmospheric measurement data prevent the definitive conclusion that banks of this HCFC are currently decreasing in size, such a decrease is qualitatively consistent with the recent decline in global emission derived from the atmospheric observations. Emissions for HCFC-142b last decreased during 2002 and 2003 (Figure 1), which was also
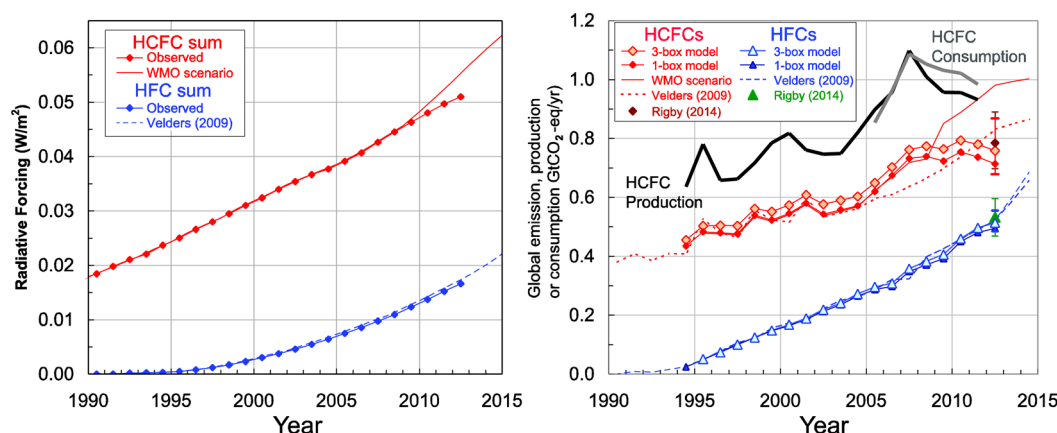
Figure 4. Aggregate direct radiative forcing (left panel) and global CO_2-eq emissions (right panel) from the HCFCs and HFCs shown in Figures 1 and 2. Emissions are derived from observations and a 3-box or 1-box inverse analysis. Emissions derived with the 1-box model allow direct comparisons to the WMO baseline scenario ("WMO scenario")[18] and estimates from Velders et al.[1] ["Velders (2009)"]. CO_2-eq emissions are derived by weighting mass emissions by 100-y GWPs (Table 1). Emission uncertainties are shown only for 2012 and represent only the uncertainty associated with the lifetimes of these gases.[21] Summed HCFC and HFC emissions derived in this work are in good agreement with those derived from independent global data and inverse modeling techniques ["Rigby (2014)"].[14] Production and consumption totals are from UNEP.
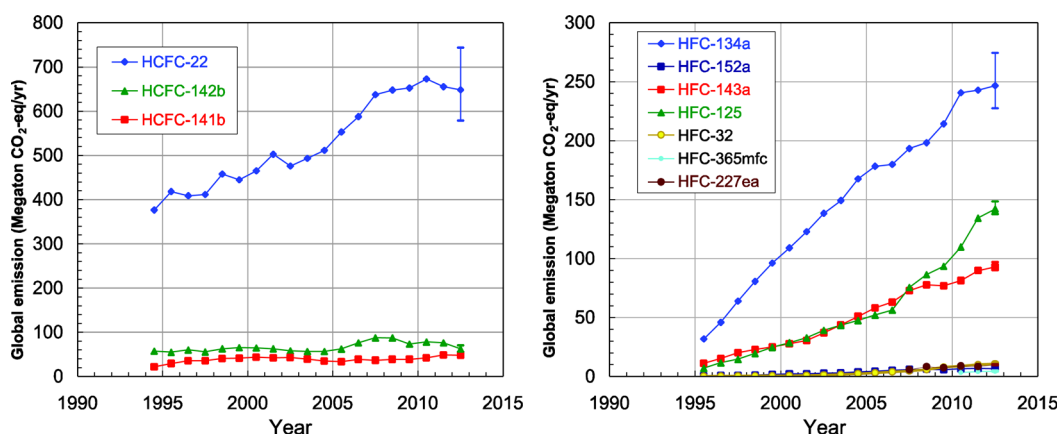

Figure 5. CO_2-eq emissions derived for individual HCFCs (left) and HFCs (right) by weighting emissions derived from NOAA observations and a 3-box inverse analysis with 100-y GWPs (Table 1). Emission uncertainties are shown only for 2012 and represent only the uncertainty associated with the lifetimes of these gases.[21]

the last time reported production was comparable to estimated global emissions.

Despite continued increases in production and consumption of HCFCs in developing countries through 2012, total aggregate HCFC production and consumption has decreased slightly since 2007 (when expressed as ODP-tons or CO_2-eq, see Figure 4) because of offsetting declines in developed country production and consumption magnitudes (Figure 3). Production of HCFCs reported for controlled uses peaked in 2007 at 41.5 ODP-kt/y and has since been between 38 and 39.7 (through 2012; n.b., 1 ODP-kt = 1 kt CFC-11-eq). Global reported consumption has been fairly constant between 41.1 and 42.6 ODP-kt/y during 2007−2012.

Because the 2013 caps on production and consumption of HCFCs in developing countries are based on average magnitudes during 2009−2010, we anticipate a reduction of 10% or more in global HCFC production in 2013 compared to 2012 provided recent trends in developed countries continue. Given the near-constant global production and emission of HCFCs since 2008 (as Gg/y, not shown) and a substantial drop in production expected for 2013, it is possible that aggregate global emissions of HCFCs have peaked and will

begin declining in the next few years. This conclusion depends in part, however, on how much HCFC is currently stored in banks.

The policy-driven changes in HCFC emissions after 2007 provided societal benefits related to stratospheric ozone and climate. Tropospheric chlorine (Cl) from HCFCs, for example, increased at a slower rate (an average of 9 ppt/y) during 2009 to 2012 than it could have, considering the existing Montreal Protocol controls (Cl from HCFCs increased at 15 ppt/y in the WMO baseline scenario). Total Cl from HCFCs in 2012 was approximately 25 ppt less than estimated for that year in the WMO baseline scenario. Furthermore, with regard to climate, total emissions of HCFCs remained virtually constant during 2007−2012 between 0.76 and 0.79 GgCO$_2$-eq/y or only 75% of the 2012 emission magnitude in the WMO scenario (Figure 4). When compared to the HCFC increases that could have occurred between 2009 and 2012 as projected in the WMO scenarios, the total avoided CO_2-eq emission during this 4 year period was 0.7 GtCO$_2$-eq. The reduced HCFC emissions also led to radiative forcing in 2012 that was 4 mW/m² less than projected in the WMO scenario (Figure 4).
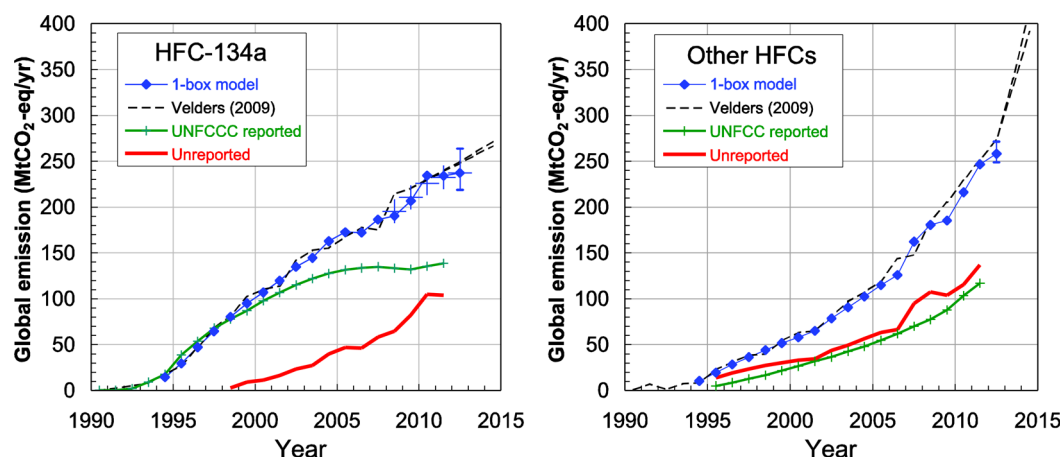
Figure 6. HFC emissions derived from NOAA global observations (blue ◆ connected by solid lines; 1-box result) are compared to the projections of Velders et al.[1] (black dashed lines; 1-box result), and those reported to the UNFCCC (green lines and plus symbols; data from http://unfccc.int/ghg_data/ghg_data_unfccc/items/4146.php) for HFC-134a alone (left) and for the aggregate sum of other HFCs used as substitutes for ozone-depleting substances (right panel, HFC-125, −143a, −32, −152a, −227ea, and −365mfc [i.e., not HFC-134a or HFC-23]). The difference between global emissions derived from NOAA atmospheric measurements (3-box result) and those reported to the UNFCCC are shown as "unreported" emissions (red lines).

Global Atmospheric Changes Observed for HFCs Used As Substitutes for ODSs and Their Implications. It is well-recognized that the phase-out of CFCs and HCFCs has the potential to cause substantial increases in the production, emission, and atmospheric mixing ratios of high-GWP HFCs.[1] Both the recent atmospheric changes measured for HCFCs, as discussed above, and relatively rapid increases in atmospheric mixing ratios observed for HFCs (Table 1; Figure 2)[12−14,16,24,25] indicate that this transition from HCFCs to HFCs is well underway. The global mean mixing ratio, rate of increase, and emissions of HFC-134a are substantially larger than those of other HFCs as a result of the direct transition from CFCs to HFC-134a in MAC and some commercial air conditioning applications while other sectors have experienced a two-step transition from CFCs to HCFCs to HFCs. Smaller absolute rates of increase are observed for mixing ratios of HFC-125, HFC-143a, and HFC-32, followed by HFC-152a, HFC-227ea, and HFC-365mfc.

HFC-134a accounts for over half of emissions (by mass) from all HFCs used as ODS substitutes, and it has accounted for most of the increase in HFC emissions over recent decades (Figure 2). The next largest contributor by mass is HFC-152a, followed by HFC-125, HFC-143a, and HFC-32 (HFC-23 is not considered here as it is not used appreciably as a substitute for ODSs). When considering HFC emission magnitudes as CO_2-eq emissions, those from HFC-134a still dominate, and among the other HFCs used as ODS substitutes only contributions of HFC-143a and HFC-125 are substantial (Figure 5). The relative influence that HFC emissions will have on climate change is determined largely by the chemical's lifetime;[26] HFCs in use today with lifetimes ranging from 5 to 47 y have 100-y GWPs of between 675 and 4470.[27] HFC-152a, in contrast, contributes relatively less to CO_2-eq emissions because its short global lifetime (1.5 y) results in a much smaller 100-y GWP (124). Hydrofluoro-olefin (HFO) alternatives to HFCs have atmospheric lifetimes of 5 to 22 days and 100-y GWPs between <1 and 6.[27] HFC-23, which is an inadvertent and unwanted byproduct of HCFC-22 production with few commercial uses, has a lifetime of 222 y and a 100-y GWP of 13856.[27]

Summed CO_2-eq emissions from HFCs used as ODS substitutes were 68% as large as summed emissions from HCFCs in 2012 (Figure 4). But while summed HCFC emissions have been fairly constant between 0.76 and 0.79 $GtCO_2$-eq/y since 2007, summed emissions of HFCs increased by 45% (or by 0.16 $GtCO_2$-eq/y) over this same period and, by 2012, had reached 0.51 (−0.03, +0.04) $GtCO_2$-eq/y.

Global HFC emission magnitudes derived from atmospheric observations are about two times larger than HFC emissions reported to the UNFCCC from Annex 1 Parties (developed countries and those with economies in transition) (Figure 6). A similar conclusion was drawn recently with atmospheric measurements from an independent sampling network;[14] comparable aggregate emission sums for HCFCs and HFCs were derived for 2012 in that work (Figure 4). The discrepancy between global, atmosphere-derived emissions and the Annex 1 inventory-based emissions suggests that HFC emissions from developing countries (non-Annex I Parties) not reporting emissions to the UNFCCC have increased rapidly over time and, by 2012, accounted for nearly 50% of global HFC emissions (Figure 6). Consistent with this finding is a report documenting large increases in production and consumption of HFCs from a non-Annex I Party (China) since 2007.[28] The HFC emissions implied for non-Annex I Parties (Figure 6) likely contain substantial uncertainty, however, as they hinge on the accuracy of the national-scale, predominantly inventory-based estimates reported to the UNFCCC.

Despite the slower than anticipated increase in HCFC emissions in recent years, emissions of HFCs used as substitutes for HCFCs and CFCs did not increase more rapidly than projected for 2008−2012[1] (Figures 2 and 6). We note a discrepancy of ∼100% (or ∼2 ppt) for HFC-32 but this likely stems from no observations being available for this chemical when Velders et al.[1] initialized their projections. The results show that HFC mixing ratios increased as projected by Velders et al. during 2007−2012 even though global economic activity slowed over this period.

How will HFC emissions change in the future? Projections from Velders et al.[1] include an increased emission rate for HFCs after 2012 when HCFC production and consumption

becomes capped for the first time in developing countries. Global annual HFC emissions increase by 0.095 ± 0.015 $GtCO_2$-eq/y between 2013 and 2017 in the Velders et al.[1] projection, which is about 2.7 times faster than the observed and projected rate of increase during 2008−2012. Given the accuracy of the Velders et al.[1] projections over the past five years, one might expect skill in projecting future emissions. The large increases in emissions projected by Velders et al.,[1] however, arise from a transition to HFCs and growth in market penetration of refrigeration and air conditioning that is just beginning in developing countries, so it is difficult to conclude that past skill in projecting emissions will also apply in the near future when use quantities could change dramatically.

Furthermore, projections by Velders et al.[1] were constructed as "business as usual" scenarios. Since then, some policy actions have been implemented and others are being considered that would influence future HFC use and emissions and their contributions to climate forcing.[29,30] If these policies successfully curtail global emissions of high-GWP HFCs, the upper limit of CO_2-eq emissions projected by Velders et al.[1] will be avoided. However, it should be noted that the high CO_2-eq emissions projected in that study were due to increasing use of HFCs in developing countries where there are currently few existing policies to limit use other than incentives for use of low GWP options under the Multilateral Fund of the Montreal Protocol. Since the publication of Velders et al.,[1] countries including Australia, the EC, Japan, and the U.S. have proposed national regulations or begun implementing controls that reduce GWP-weighted emissions of HFCs.[30−33] Significantly, companies in China and other developing countries supplying low-GWP technology to developed country export markets could offer the same products domestically. Furthermore, there is growing support,[34] including from China,[35] for proposals to amend the Montreal Protocol to phase-down HFC production and consumption as a complement to the Kyoto Protocol control of HFC emissions.

On the Contribution of Different Applications to Current HFC Emissions. Understanding the contributions of different applications to current HFC emissions can provide direction in mitigating emissions of high-GWP HFCs. Fortunately, the nature of HFCs blends used in major applications allows a rough estimate of the contributions of these applications to total HFC emissions (see Experimental Section). On the basis of emissions derived from global atmospheric changes, we find that three categories of use each account for approximately one-third of HFC emissions (as CO_2-eq): mobile air conditioning (MAC), commercial refrigeration, and the sum of all others (Figure 7).

Although the approach to estimate the relative contributions of these different use categories includes some uncertainty, it fairly accurately accounts for the emissions of HFC-125 derived from atmospheric observations. Furthermore, the results are comparable to the contributions suggested in the UNFCCC inventory for the 5 countries that report HFC emissions from these different use categories. For this subset of Annex-1 countries (France, Great Britain, Germany, Spain, and the United States), which account for approximately 60% of HFC reported emissions to the UNFCCC, the relative contributions of emissions from mobile air conditioning, commercial refrigeration, and other uses to total HFC emissions reported by these countries in the UNFCCC inventory in 2011 were 36%, 24%, and 40%, respectively.
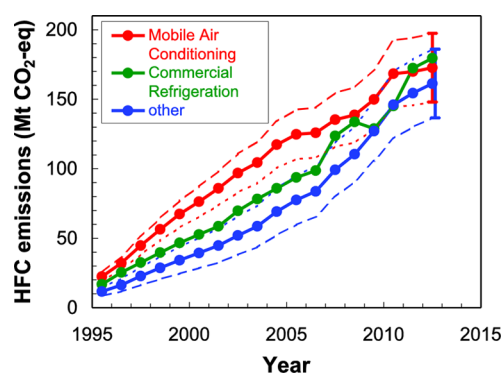

Figure 7. HFC emissions arising from the dominant applications in which they have been used over time (as CO_2-eq emissions). Values are derived from the observationally based emissions shown in Figure 2 and consideration of the relative contributions of different applications to emissions of individual HFCs (see the Experimental Section). The error bars reflect an uncertainty in the fraction of global HFC-134a emissions attributable to mobile air conditioning (MAC) of 70 ± 10%: long-dashed lines represent the result with a constant 80% of global HFC-134a emission being attributed to MAC; short-dashed lines represent a constant 60% of global HFC-134a emissions being attributed to MAC.

The substantial contribution to HFC emissions from the MAC sector suggests that efforts to mitigate MAC-related HFC emissions through improved containment and to promote the transition to alternatives with GWPs substantially smaller than HFC-134a could make a notable impact on total HFC emissions related to ODS substitution. Low-GWP alternatives to HFC-134a in MACs include HFO-1234yf (GWP <1), HFC-152a (GWP = 133), and CO_2 (GWP = 1). HFO-1234yf and HFC-152a are more energy efficient at high ambient temperatures in this application than CO_2.

■ CONCLUSION

Understanding the effectiveness of policies controlling GHGs and ODSs requires atmospheric observations of a suite of trace gases such as those provided by global sampling networks. The data from one of those networks presented here suggest that the 2007 Adjustment to the Montreal Protocol played a role in stabilizing and capping global HCFC emissions at 0.77 ± 0.01 $GtCO_2$-eq/y during 2007−2012, a time when existing controls allowed substantial increases. As a result, HCFC-associated atmospheric Cl and radiative forcing values increased more slowly than they might have, and approximately 0.7 Gt CO_2-eq of projected HCFC emissions were avoided during 2008−2012. Furthermore, aggregate global HCFC emissions could begin decreasing in the near future, given that global aggregate production, consumption, and emissions of HCFCs have not increased since 2007, the expectation of a substantial reduction (∼10%) in production and consumption from developing countries in 2013, and the history of near total global compliance with the Montreal Protocol control obligations. While summed HCFC emissions have stabilized, summed emissions of HFCs used as substitutes for HCFCs and CFCs increased by 45% during 2007−2012 and by 2012 had reached 0.51 (−0.03, +0.04) $GtCO_2$-eq/y. Although the rates of HFC emissions derived from the observations through 2012 are consistent with those projected by Velders et al.,[1] the atmospheric monitoring results do not yet allow for a refinement of the Velders et al. projections beyond 2013 principally because the developing country HCFC phase-out is

only in its initial stages. Furthermore, it is too early to predict the likelihood and stringency of a proposed amendment to the Montreal Protocol that would cap and reduce the CO_2-eq emissions of HFCs globally. Finally, new and proposed national regulations in Australia, Europe, Japan, and the United States may significantly reduce the combined atmospheric abundance of high-GWP HFCs with or without the adoption of an amendment to the Montreal Protocol related to HFCs.

We estimate that applications responsible for HFC emissions in 2012 can be divided into three, equally contributing categories: mobile air conditioning, commercial refrigeration, and the sum of all other activities. Efforts to adopt lower GWP alternatives, particularly for MAC and commercial refrigeration, have the potential to facilitate significant reductions in CO_2-eq emissions of HFCs.

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■ REFERENCES

(1) Velders, G. J. M.; Fahey, D. W.; Daniel, J. S.; McFarland, M.; Andersen, S. O. The Large Contribution of Projected HFC Emissions to Future Climate Forcing. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10949−10954.

(2) Montzka, S. A.; Hall, B. D.; Elkins, J. W. Accelerated Increases Observed for Hydrochlorofluorocarbons Since 2004 in the Global Atmosphere. *Geophys. Res. Lett.* **2009**, *36*, L03804.

(3) Andersen, S. O.; Halberstadt, M. L.; Borgford-Parnell, N. Stratospheric Ozone, Global Warming and the Principle of Unintended Consequences: An Ongoing Science and Policy Success Story. *J. Air Waste Manage. Assoc.* **2013**, *63*, 607−647.

(4) Velders, G. J. M.; Andersen, S. O.; Daniel, J. S.; Fahey, D. W.; McFarland, M. The Importance of the Montreal Protocol in Protecting Climate. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 4814−4819.

(5) *Intergovernmental Panel on Climate Change/Technology and Economic Assessment Panel, Safeguarding the Ozone Layer and Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*; Metz, B., Kuijpers, L., Solomon, S., Andersen, S. O., Davidson, O., Pons, J., deJager, D., Kestin, T., Manning, M., Meyer, L., Eds.; Cambridge University Press: N.Y., 2005; p 478.

(6) Daniel, J. S.; Velders, G. J. M.; Douglass, A. R.; Forster, P. M. D. ; Hauglustaine, D. A.; Isaksen, I. S. A.; Kuijpers, L. J. M.; McCulloch, A.; Wallington, T. J. Halocarbon Scenarios, Ozone Depletion Potentials, and Global Warming Potentials. In *Scientific Assessment of Ozone Depletion: 2006*; World Meteorological Organization: Geneva, Switzerland, 2007; p 572.

(7) *Earth Negotiations Bulletin*; Chasek, P. S., Ed.; 2007; Vol. *19*, pp 1−14.

(8) Daniel, J. S.; Velders, G. J. M.; Solomon, S.; McFarland, M.; Montzka, S. A. Present and Future Sources and Emissions of Halocarbons: Towards New Constraints. *J. Geophys. Res.* **2007**, *112*, D02301.

(9) Gschrey, B.; Schwarz, W.; Elsner, C.; Engelhardt, R. High Increase of Global F-Gas Emissions Until 2050. *Greenhouse Gas Meas. Manage.* **2011**, *1*, 85−92.

(10) Montzka, S. A.; Kuijpers, L.; Battle, M. O.; Aydin, M.; Verhulst, K. R.; Saltzman, E. S.; Fahey, D. W. Recent Increases in Global HFC-23 Emissions. *Geophys. Res. Lett.* **2010**, *37*, L02808.

(11) Miller, B. R.; Rigby, M.; Kuijpers, L. J. M.; Krummel, P. B.; Steele, L. P.; Leist, M.; Fraser, P. J.; McCulloch, A.; Harth, C.; Salameh, P.; et al. HFC-23 (CHF_3) Emission Trend Response to HCFC-22 ($CHClF_2$) Production and Recent HFC-23 Emission Abatement Measures. *Atmos. Chem. Phys.* **2010**, *10*, 7875−7890.

(12) O'Doherty, S.; Cunnold, D. M.; Miller, B. R.; Mühle, J.; McCulloch, A.; Simmonds, P. G.; Manning, A. J.; Reimann, S.; Vollmer, M. K.; Greally, B. R.; et al. Global and Regional Emissions of HFC-125 (CHF_2CF_3) from In Situ and Air Archive Atmospheric Observations at AGAGE and SOGE Observatories. *J. Geophys. Res.* **2009**, *114*, D23304.

(13) O'Doherty, S.; Rigby, M.; Mühle, J.; Ivy, D. J.; Miller, B. R.; Young, D.; Simmonds, P. G.; Reimann, S.; Vollmer, M. K.; Krummel, P. B.; et al. Global Emissions of HFC-143a (CH3CF$_3$) and HFC-32 (CH_2F_2) from In Situ and Air Archive Atmospheric Observations. *Atmos. Chem. Phys.* **2014**, *14*, 6471−6500.

(14) Rigby, M.; Prinn, R. G.; O'Doherty, S.; Miller, B. R.; Ivy, D.; Mühle, J.; Harth, C. M.; Salameh, P. K.; Arnold, T.; Weiss, R. F.; et al. Recent and Future Trends in Synthetic Greenhouse Gas Radiative Forcing. *Geophys. Res. Lett.* **2014**, *41*, 2623−2630.

(15) Montzka, S. A.; Myers, R. C.; Butler, J. H.; Elkins, J. W.; Lock, L.; Clarke, A.; Goldstein, A. H. Observations of HFC-134a in the Remote Troposphere. *Geophys. Res. Lett.* **1996**, *23*, 169−172.

(16) Montzka, S. A.; Reimann, S.; Engel, A.; Krüger, K.; O'Doherty, S.; Sturges, W. T.; Blake, D.; Dorf, M.; Fraser, P.; Froidevaux, L.; et al. Ozone-Depleting Substances (ODSs) and Related Chemicals. In *Scientific Assessment of Ozone Depletion: 2010*; World Meteorological Organization: Geneva, Switzerland, 2011; pp 516.

(17) Prinn, R. G.; Weiss, R. F.; Fraser, P. J.; Simmonds, P. G.; Cunnold, D. M.; Alyea, F. N.; O'Doherty, S.; Salameh, P.; Miller, B. R.; Huang, J.; et al. A History of Chemically and Radiatively Important Gases in Air Deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.* **2000**, *105*, 17751−17792.

(18) Daniel, J. S.; Velders, G. J. M.; Morgenstern, O.; Toohey, D. W.; Wallington, T. J.; Wuebbles, D. J.; Akiyoshi, H.; Bais, A. F.; Fleming, E. L.; Jackman, C. H.; et al. A Focus on Information and Options for Policymakers. In *Scientific Assessment of Ozone Depletion: 2010*; World Meteorological Organization: Geneva, Switzerland, 2011; pp 516.

(19) Naik, V.; Jain, A. K.; Patten, K. O.; Wuebbles, D. J. Consistent Sets of Atmospheric Lifetimes and Radiative Forcings on Climate for CFC Replacements: HCFCs and HFCs. *J. Geophys. Res.* **2000**, *105*, 6903−6914.

(20) Montzka, S. A.; Krol, M.; Dlugokencky, E.; Hall, B.; Jockel, P.; Lelieveld, J. Small Interannual Variability of Global Atmospheric Hydroxyl. *Science* **2011**, *331*, 67−69.

(21) *Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species*; Ko, M.; Newman, P.; Reimann, S.; Strahan, S., Eds.; *SPARC Report No. 6*, WCRP-15/2013.

4448

dx.doi.org/10.1021/jp5097376 | *J. Phys. Chem. A* 2015, 119, 4439−4449

(22) Saikawa, E.; Rigby, M.; Prinn, R. G.; Montzka, S. A.; Miller, B. R.; Kuijpers, L. J. M.; Fraser, P. J. B.; Vollmer, M. K.; Saito, T.; Yokouchi, Y.; et al. Global and Regional Emission Estimates for HCFC-22. *Atmos. Chem. Phys.* **2012**, *12*, 10033−10050.

(23) Saikawa, E.; Rigby, M.; Prinn, R. G.; Montzka, S. A.; Miller, B. R.; Kuijpers, L. J. M.; Fraser, P. J. B.; Vollmer, M. K.; Saito, T.; Yokouchi, Y.; et al. Corrigendum to "Global and Regional Emission Estimates for HCFC-22. *Atmos. Chem. Phys.* **2012**, *12*, 10033−10050; *Atmos. Chem. Phys.* **2014**, *14*, 4857−4858.

(24) Laube, J. C.; Martinerie, P.; Witrant, E.; Blunier, T.; Schwander, J.; Brenninkmeijer, C. A. M.; Schuck, T. J.; Bolder, M.; Röckmann, T.; van der Veen, C.; et al. Accelerating Growth of HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) in the Atmosphere. *Atmos. Chem. Phys.* **2010**, *10*, 5903−5910.

(25) Vollmer, M. K.; Miller, B. R.; Rigby, M.; Reimann, S.; Mühle, J.; Krummel, P. B.; O'Doherty, S.; Kim, J.; Rhee, T. S.; Weiss, R. F.; et al. Atmospheric Histories and Global Emissions of the Anthropogenic Hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa. *J. Geophys. Res.* **2011**, *116*, D08304.

(26) Velders, G. J. M.; Ravishankara, A. R.; Miller, M. K.; Molina, M. J.; Alcamo, J.; Daniel, J. S.; Fahey, D. W.; Montzka, S. A.; Reimann, S. Preserving Montreal Protocol Climate Benfits by Limiting HFCs. *Science* **2012**, *335*, 922−923.

(27) Forster, P.; Ramaswamy, V.; Artaxo, P.; Bernsten, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D.; Myhre, G.; et al. Changes in Atmospheric Constituents and in Radiative Forcing. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M. M. B., Miller, H. L., Jr., Chen, Z., Eds.; Cambridge Univ. Press: Cambridge, U.K., 2007; pp 130−234.

(28) Zhang, J.; Wang, C. China's hydrofluorocarbon challenge. *Nat. Clim. Change* **2014**, *4*, 943−945.

(29) Regulation (EC) No 842/2006 of the European Parliament and of the Council of 17 May 2006 on Certain Fluorinated Gases. *Official Journal of the European Union*, **2006**, *L 161*, 1−11.

(30) *Benefits of Addressing HFCs Under the Montreal Protocol*; EPA 430-R-14-005; U.S. EPA Stratospheric Protection Division: Washington, D.C., 2014.

(31) *Press Release: Council Adopts Regulation On Fluorinated Greenhouse Gases*; Council of the European Union: Brussels, April 14, 2014.

(32) *Act for Rationalized Use and Proper Management of Fluorocarbons*; Japanese Ministry of Economy, Trade and Industry: Japan, April 19, 2013.

(33) Protection of Stratospheric Ozone: Change of Listing Status for Certain Substitutes Under the Significant New Alternatives Policy Program; Proposed Rule. *Fed. Regist.* **2014**, *79*, 46126 − 46166.

(34) *Report of the Thirty-Fourth Meeting of the Open-Ended Working Group of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer*; OzL.Pro.WG.1/34/6; United National Environment Program: Paris, July 31, 2014.

(35) *The President's Climate Action Plan*; Executive Office of the President of the United States: Washington, D.C., June 2013.

(36) Xiang, B.; Patra, P. K.; Montzka, S. A.; Miller, S. M.; Elkins, J. W.; Moore, F. L.; Atlas, E. L.; Miller, B. R.; Weiss, R. F.; Prinn, R. G.; et al. Global emissions of refrigerants HCFC-22 and HFC-134a: unforeseen seasonal contributions. *Proc. Natl. Acad. Sci.*, **2014**; DOI: 10.1073/pnas.1417372111.

■ NOTE ADDED IN PROOF

Additional new information regarding factors potentially influencing emissions of HFC-134a and other refrigerant fluids are discussed in the recent study by Xiang et al.[36]