CHAPTER 2

HYDROFLUOROCARBONS (HFCs)

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CHAPTER 2

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SCIENTIFIC SUMMARY

The Montreal Protocol is an international agreement designed to heal the ozone layer. It outlines schedules for the phase-out of ozone-depleting substances (ODSs) such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), chlorinated solvents, halons, and methyl bromide. As a result of this phase-out, alternative chemicals and procedures were developed by industry for use in many applications including refrigeration, air-conditioning, foam-blowing, electronics, medicine, agriculture, and fire protection. Hydrofluorocarbons (HFCs) were used as ODS alternatives in many of these applications because they were suitable substitutes and they do not contain ozone-depleting chlorine or bromine; in addition, most HFCs have smaller climate impacts per molecule than the most widely used ODSs they replaced. Long-lived HFCs, CFCs, and HCFCs, however, are all potent greenhouse gases, and concerns were raised that uncontrolled future use of HFCs would lead to substantial climate warming.

As a result of these concerns, HFCs were included as one group of greenhouse gases for which emissions controls were adopted by the 1997 Kyoto Protocol under the 1992 United Nations Framework Convention on Climate Change (UNFCCC). Consequently, developed countries (those listed in Annex I to this Convention, or "Annex I" Parties) supply annual emission estimates of HFCs to the UNFCCC.

Since the Kyoto Protocol only specified limits on the sum of all controlled greenhouse gases, emissions of HFCs were not explicitly controlled. However, following the Kyoto Protocol, some countries enacted additional controls specifically limiting HFC use based on their global warming potentials (GWPs). Ultimately the Kigali Amendment to the Montreal Protocol was agreed upon in 2016, and this Amendment supplies schedules for limiting the production and consumption of specific HFCs. Although the radiative forcing supplied by HFCs is currently small, this Amendment was designed to ensure that the radiative forcing from HFCs will not grow uncontrollably in the future. The Kigali Amendment will come into force at the start of 2019. HFC concentrations are currently monitored through atmospheric measurements. All HFCs with large abundances are monitored, as are most with small abundances.

Most HFCs that are emitted to the atmosphere are intentionally produced for use in a variety of applications that were once dependent on ODSs. An exception is HFC-23, which is emitted to the atmosphere primarily as a by-product of HCFC-22 production. HFC-23 is also unique in that it has a substantially longer atmospheric lifetime and higher GWP than nearly all other HFCs. As a result, the Kigali Amendment includes different control schedules for HFC-23 production than for other HFCs. To date, HFC-23 emissions have been partially abated in developed countries through regulations or voluntary measures and in developing countries with assistance from the UNFCCC's Clean Development Mechanism (CDM).

- **Atmospheric mole fractions of most currently measured HFCs are increasing in the global atmosphere at accelerating rates, consistent with expectations based on the ongoing transition away from use of ozone-depleting substances.**

  - **HFC-134a remained the most abundant HFC in the atmosphere**, reaching a global mean surface mole fraction of nearly 90 ppt in 2016. Its rate of increase averaged 5.6 ± 0.2 ppt yr^{-1} (7.3 ± 0.2 % yr^{-1}) during 2012–2016, which is about 0.6 ppt yr^{-1} faster than the mean increase for 2008–2012.

  - **The next four most abundant HFCs in 2016 were HFC-23, HFC-125, HFC-143a, and HFC-32.** Their global mean surface mole fractions in 2016 were 28.9 ppt, 20.4 ppt, 19.2 ppt, and 11.9 ppt, respectively. Mole fractions of these HFCs increased during 2012–2016 by an average of 1.0 ppt yr^{-1} for

HFC-23, 2.1 ppt yr^{-1} for HFC-125, 1.5 ppt yr^{-1} for HFC-143a, and 1.6 ppt yr^{-1} for HFC-32; for all of these gases, these rates are faster than the average growth rates reported for 2008–2012 in the last Assessment.

○ **Global mole fractions of most HFCs increased through 2016 at rates similar to those projected in the baseline scenario of the last Assessment**, despite the fact that this scenario was created nearly a decade ago. The HFCs for which mole fractions are increasing substantially less rapidly than originally projected include HFC-152a, HFC-365mfc, and HFC-245fa.

● **Radiative forcing from measured HFCs continues to increase; it currently amounts to 1% of the total forcing from all long-lived greenhouse gases.** The radiative forcing arising from measured atmospheric mole fractions of HFCs totaled 0.030 W m^{-2} in 2016, up by 36% from 0.022 W m^{-2} in 2012; HFC-134a accounted for 47% of this forcing in 2016, while the next largest contributors were HFC-23 (17%), HFC-125 (15%) and HFC-143a (10%). Total HFC radiative forcing in 2016 accounted for ~10% of the 0.33 W m^{-2} supplied by ODSs (**see Chapter 1**), and 1.0% of the 3 W m^{-2} supplied by all long-lived GHGs combined, including CO_2, CH_4, N_2O, ODSs and HFCs.

● **Global emissions of nearly all measured HFCs continue to increase; they currently amount to ~1.5% of total emissions from all long-lived greenhouse gases (CO_2, CH_4, N_2O, and long-lived halocarbons) in CO_2-equivalent emissions.** As derived from atmospheric observations, total emissions of HFCs increased by 23% from 2012 to 2016 and summed to 0.88 (± 0.07) GtCO$_2$-eq yr^{-1} in 2016; this increase outpaced decreases in CO_2-eq emissions from CFCs and HCFCs. These CO_2-eq HFC emissions stem primarily from four gases: HFC-134a (34% of total), HFC-125 (24% of total), HFC-23 (18% of total), and HFC-143a (16% of total). HFC CO_2-eq emissions were comparable to those of CFCs (0.8 ± 0.3 GtCO$_2$-eq yr^{-1}) and HCFCs (0.76 ± 0.11 GtCO$_2$-eq yr^{-1}) in 2016.

● **HFC emissions estimated from the combination of inventory reporting and atmospheric observations indicate that the HFC emissions originate from both developed and developing countries.** Large differences are observed between global total emissions derived from atmospheric observations and the totals reported to the UNFCCC. These differences arise primarily because only developed (Annex I) countries are obligated to report HFC emissions to the UNFCCC. When summed, these reported HFC emissions account for less than half of the global total inferred from observations (as CO_2-eq emissions).

● **Annual global emissions of HFC-23 derived from atmospheric measurements have varied substantially in recent years. This variability is mostly consistent with expectations based on reported HCFC-22 production and reported and estimated HFC-23 emissions.** This long-lived HFC is emitted to the atmosphere primarily as a by-product of HCFC-22 production. HFC-23 emissions, after reaching a low of ~10 Gg yr^{-1} (0.13 GtCO$_2$-eq yr^{-1}) 2009–2010, owing in part to destruction in developing countries facilitated under the UNFCCC's Clean Development Mechanism (CDM), increased and subsequently peaked at ~14 Gg yr^{-1} (0.18 GtCO$_2$-eq yr^{-1}) in 2013–2014. The mean global emission rate over 2013–2014 is slightly higher than that derived for 2005–2006, when CDM-facilitated destruction had yet to be fully implemented. Global emissions estimated from observations for 2015 and 2016 dropped below the 2013–2014 peak; emissions in 2016 were 12.3 ± 0.7 Gg yr^{-1} (0.16 GtCO$_2$-eq yr^{-1}), or approximately 2 Gg yr^{-1} below those in 2014. New controls put in place under the Kigali Amendment mandate HFC-23 by-product destruction, to the extent practicable, beginning in 2020. These controls are expected to limit future emissions and thus slow or reverse atmospheric concentration increases of this potent greenhouse gas.

● **Some next-generation substitute chemicals with very low GWPs (unsaturated HCFCs and unsaturated HFCs, also known as hydrofluoroolefins, or HFOs) have now been detected in ambient air, consistent with the transition to these compounds being underway**. Unsaturated HFCs and HCFCs are replacement compounds for some long-lived HCFCs and HFCs. Because unsaturated HFCs have short atmospheric

lifetimes (days) and GWPs typically less than 1 they are not included as controlled substances in the Kigali Amendment to the Montreal Protocol. Very low mole fractions (typically below 1 ppt) of two unsaturated HFCs (HFC-1234yf and HFC-1234ze(E)) have been measured at a continental background European site.

- **Global adherence to the HFC phasedown schedule of the 2016 Kigali Amendment to the Montreal Protocol would substantially reduce future projected global HFC emissions.** Emissions are projected to peak before 2040 and decline to less than 1 $GtCO_2$-eq yr^{-1} by 2100. Only marginal increases are projected for CO_2-eq emissions of the low-GWP alternatives despite substantial projected increases in their emission mass. The estimated avoided HFC emissions as a result of this Amendment is 2.8–4.1 $GtCO_2$-eq yr^{-1} emissions by 2050 and 5.6–8.7 $GtCO_2$-eq yr^{-1} by 2100. For comparison, total CH_4 emissions in 2100 are projected to be 7.0 and 25 $GtCO_2$-eq yr^{-1} in the RCP-6.0 and RCP-8.5 scenarios, respectively, and total N_2O emissions in 2100 are projected to be 5.0 and 7.0 $GtCO_2$-eq yr^{-1} in these same scenarios.

- **The 2016 Kigali Amendment to the Montreal Protocol, assuming global compliance, is expected to reduce future radiative forcing due to HFCs by about 50% in 2050 compared to the forcing from HFCs in the baseline scenario.** Currently (in 2016), HFCs account for a forcing of 0.025 W m^{-2} not including 0.005 from HFC-23; forcing from these HFCs was projected to increase up to 0.25 W m^{-2} by 2050 (excluding a contribution from HFC-23) with projected increased use and emissions in the absence of controls. With the adoption of the Kigali Amendment, a phasedown schedule has been agreed for HFC production and consumption in developed and developing countries under the Montreal Protocol. With global adherence to this Amendment in combination with national and regional regulations that were already in place in, e.g., Europe, the USA, and Japan, along with additional recent controls in other countries, future radiative forcing from HFCs is projected to reach 0.13 W m^{-2} by 2050 (excluding HFC-23), or about half the forcing projected in the absence of these controls.

- **The Kigali Amendment and national and regional regulations are projected to reduce global average warming in 2100 due to HFCs from 0.3–0.5°C in a baseline scenario to less than 0.1°C.** If the global production of HFCs were to cease in 2020, the surface temperature contribution of HFC emissions would stay below 0.02°C for the whole 21st century. The magnitude of the avoided temperature increase due to the provisions of the Kigali Amendment is substantial in the context of the 2015 UNFCCC Paris Agreement, which aims to limit global temperature rise to well below 2.0°C above pre-industrial levels and to pursue further efforts to limit the temperature increase to 1.5°C.

- **Improvements in energy efficiency in refrigeration and air-conditioning equipment during the transition to low-GWP alternative refrigerants can potentially double the climate benefits of the HFC phasedown of the Kigali Amendment.** The conversion from equipment using HFC refrigerants with high GWPs to refrigerants with lower GWPs, which will most likely result from the Kigali Amendment, provides an opportunity to consider other technological improvements that offer additional climate benefits. The total climate impact related to refrigerant use and associated emissions is not only associated with the radiative properties and lifetime of the refrigerant, but also with CO_2 emissions resulting from the energy used by the equipment over its entire life cycle. The use of a refrigerant with a lower GWP than the currently-used HFCs (i.e., following the Kigali Amendment) offers the opportunity to redesign equipment and improve its energy efficiency. For example, a 30% improvement in the energy efficiency of the global stock of mini-split air conditioners (the most widely used air conditioning systems today) in 2030 would provide a climate benefit comparable to replacing the mix of current HFC refrigerants commonly used in this application (which have GWPs averaging about 2,000) with a mix of alternatives that have GWPs of less than about 5 to about 700. An energy efficiency improvement of 30% is estimated to be technically and economically feasible and cost-effective in many economies.

- **Some HFCs degrade in the environment to produce trifluoroacetic acid (TFA), a persistent toxic chemical. The environmental effects of this source of TFA are currently small and are expected to remain negligible over the next decades.** Atmospheric degradation of HFC-1234yf, a replacement compound for some long-lived HCFCs and HFCs, produces TFA. Potential impacts beyond a few decades of this TFA source could require future evaluation due to the environmental persistence of TFA and uncertainty in future emissions of HFC-1234yf and other HFCs that produce TFA upon degradation.

- **Improvements in the understanding of reaction rates have been incorporated into revised lifetime estimates for saturated and unsaturated HFCs.** Most of these changes are small, although lifetimes of HFC-245cb ($CF_3CF_2CH_3$), octafluorocyclopentene (*cyclo*-$CF=C_4F_7$-), *(E)*-HFC-1214yc (*(E)*-$CF_3CH=CHCF_3$), and *(E)*-HFC-1438mzz (*(E)*-$CF_3CH=CHC_2F_5$) were noticeably changed because the relevant reaction rate information has become available for the first time. Lifetimes for a few HFCs considered here remain estimates based on either analogy with similar compounds or structure–activity relationships.

2.1 SUMMARY OF FINDINGS FROM PREVIOUS ASSESSMENTS

Information pertaining to HFCs was included in Chapter 1 and Chapter 5 of the 2014 Assessment report. That Assessment reported that tropospheric mole fractions of HFCs continued to increase, adding to the warming of Earth's climate. The radiative forcing supplied by HFCs in 2012, the last year assessed in that report, was small compared to that from CFCs and HCFCs, but projections suggested the potential for significant increases in HFC-associated warming in the future. Furthermore, the documented climate benefits achieved by the Montreal Protocol through reductions in the production and emission of CFCs and HCFCs might be substantially offset if emissions of the substitute HFCs were allowed to continue unabated. The sum of HFC emissions in 2012 had reached 0.72 ± 0.05 GtCO$_2$-equivalent yr^{-1} (for CO$_2$-eq considering a 100-yr time horizon) after having increased by nearly 7% yr^{-1} from 2008 to 2012. This total was similar to the magnitude of emissions from CFCs (0.9 ± 0.3 GtCO$_2$ yr^{-1}) and HCFCs (0.78 ± 0.10 GtCO$_2$-eq yr^{-1}) for 2012. This total included a global emission of approximately 0.16 ± 0.01 GtCO$_2$-eq yr^{-1} from the potent greenhouse gas HFC-23 (CHF$_3$), which is emitted primarily as a by-product during the production of HCFC-22 and not as a result of use in industrial applications and products. Although global emissions of this HFC had decreased from 2005 to 2009, they increased after 2009 and by 2012 were ~40% above the minimum recorded for 2009.

2.2 INTRODUCTION

Hydrofluorocarbons have been used in refrigeration, air conditioning, thermal insulating foam, and miscellaneous applications since the 1990s, replacing the CFCs and HCFCs that were traditionally used in these applications. The first widespread HFC use was of HFC-134a beginning in the early 1990s, as a substitute for CFC-12 in mobile air conditioning (Montzka et al., 1996; Oram et al., 1996; Andersen et al., 2013). Within a decade most mobile air conditioners used this HFC (Papasavva et al., 2009), and this remains true today. With the global CFC phase-out in 2010 and the ongoing HCFC phase-out, the use of HFCs has increased substantially, not only for various refrigeration and air conditioning applications, but also as foam blowing agents, as medical aerosols, and to a lesser extent as cleaning, etching, and fire-fighting agents. As was true for ODSs, emissions of HFCs follow production and consumption with a delay of months to decades, depending on the type of application in which the HFCs are used.

HFCs do not contain ozone-depleting chlorine or bromine, but are potent greenhouse gases (Harris and Wuebbles et al., 2014). To ensure that radiative forcing from the substitute HFCs does not offset climate gains provided by the Montreal Protocol phase-out of CFCs and HCFCs, Parties to the Montreal Protocol agreed to an Amendment in Kigali, Rwanda in October 2016, to include some HFCs as controlled substances and to phase down their production and consumption (GWP-weighted) in coming decades (UNEP, 2016a; for a list of controlled HFCs, see footnote to **Table 2-1** [or HFCs with asterisks in **Table 2-2**]). The Kigali Amendment will enter into force on January 1, 2019, since more than 20 Parties have ratified, accepted, or approved this Amendment. Limiting climate change is not the primary goal of the 1985 Vienna Convention for the Protection of the Ozone layer, but climate change considerations are addressed in this Convention. Limiting climate change was also a contributing factor to the 2007 Adjustment of the Montreal Protocol for an accelerated HCFC phase-out (UNEP, 2007).

Since 1997, HFCs have been included in the Kyoto Protocol to the United Nations Framework Convention on Climate Change as one group among many greenhouse gases for which emissions overall should be reduced by up to 8% in the period 2008–2012 by some developed countries relative to baseline levels (mostly the year 1990). HFC emissions were not directly controlled by the Kyoto Protocol, however, since controls applied to the sum of all greenhouse gases.

Table 2-1. Base level and phasedown schedule for production and consumption of controlled HFCs[1], expressed as CO_2-eq, under the Kigali Amendment to the Montreal Protocol (UNEP, 2016a).

	Developing Countries*		Developed Countries*
	A5 Group 1 Countries[2]	**A5 Group 2 Countries**[3]	**Non-A5 Countries**[4]
Base level:	Average HFCs 2020–2022 plus 65% of HCFC base level	Average HFCs 2024–2026 plus 65% of HCFC base level	Average HFCs 2011–2013 plus 15% of HCFC base level[5]
Freeze:	2024	2028	-
1st step:	2029: 10% reduction	2032: 10% reduction	2019: 10% reduction
2nd step:	2035: 30% reduction	2037: 20% reduction	2024: 40% reduction
3rd step:	2040: 50% reduction	2042: 30% reduction	2029: 70% reduction
4th step:			2034: 80% reduction
Plateau:	2045: 80% reduction	2047: 85% reduction	2036: 85% reduction

* In the UNFCCC, developing countries are referred to as "non-Annex I" countries, and developed countries are referred to as "Annex I countries."

[1] HFCs controlled by the Kigali Amendment include: HFC-23, HFC-134, HFC-134a, HFC-143, HFC-245fa, HFC-365mfc, HFC-227ea, HFC-236cb, HFC-236ea, HFC-236fa, HFC-245ca, HFC-43-10mee, HFC-32, HFC-125, HFC-143a, HFC-41, HFC-152, HFC-152a. This Amendment also specifies that emissions of HFC-23 generated during production of HCFCs or HFCs be destroyed to the extent practicable beginning January 2020.

[2] Group 1: Article 5 (developing) countries not part of Group 2. Article 5 of the Montreal Protocol.

[3] Group 2: Article 5 (developing) countries: Bahrain, India, the Islamic Republic of Iran, Iraq, Kuwait, Oman, Pakistan, Qatar, Saudi Arabia and the United Arab Emirates.

[4] Non-A5 countries, also referred to as A2 countries (developed). Article 2J of the Montreal Protocol.

[5] For Belarus, Russian Federation, Kazakhstan, Tajikistan, Uzbekistan 25% HCFC component of base level and different initial two steps (1) 5% reduction in 2020 and (2) 35% reduction in 2025. Article 2J of the Montreal Protocol.

Note: Non-Article 5 (developed) and UNFCCC Annex I (developed) countries include all EU-28 countries, Australia, Belarus, Canada, Iceland, Japan, Liechtenstein, Monaco, New Zealand, Norway, the Russian Federation, Switzerland, Ukraine, and the USA. Further, non-Article 5 countries are Andorra, Azerbaijan, the Holy See, Israel, Kazakhstan, San Marino, Tajikistan, and Uzbekistan. Turkey is solely an Annex I country.

In previous Assessments, observed concentrations, derived emissions, and atmospheric effects of HFCs were discussed together with those of ozone-depleting substances. In this Assessment, issues related to HFCs are covered in this separate chapter, with the main foci being updating observations of HFC atmospheric mole fractions and understanding what they imply for emissions on global to regional scales; determining if the observed mole fraction changes are consistent with expectations and emission magnitudes reported to UNFCCC and elsewhere; quantifying the associated climate- and environmental-related effects arising from HFC emissions and associated atmospheric changes; and considering how these influences might change in the future, especially in light of controls on HFC production and consumption specified in the Kigali Amendment to the Montreal Protocol.

With respect to climate influences, increases in radiative forcing resulting from recent increases in HFC atmospheric mole fractions are documented in this chapter. For HFCs with lifetimes longer than 1 year (e.g., those that are well mixed in the lower atmosphere), radiative forcing is linearly proportional to global mean surface mole fractions and the efficiency of the particular HFC in trapping outgoing terrestrial radiation (i.e., its radiative efficiency; see **Table A-1**). Total emission rates are also derived from these global-scale observations with consideration of lifetime-determined loss rates (**Table 2-2**) in an inverse budget analysis performed with box models (**see Box 1-1**). Emission magnitudes are considered here on a mass basis and with mass emissions weighted by 100-yr GWPs to enable an assessment of integrated radiative forcing supplied by an HFC emission relative to an equivalent CO_2 emission over a 100-year time horizon

(CO$_2$-eq emissions, **Figure 2-1; Table 2-2**). GWPs associated with a 20-year time horizon are also tabulated, but they are not considered further in this chapter.

Determining if atmospheric concentrations of ODSs or HFCs are changing as expected has always been an important remit for authors of this Assessment. For HFCs, this task is facilitated by the reporting by developed countries (Annex I Parties) to the UNFCCC of national emission magnitudes derived from country-specific analyses of production, imports, sales, exports, and use. For HFC-23, emission estimates for developing countries derived from information collected by the Montreal Protocol's Multilateral Fund[1] are also considered. In this chapter, these inventory-based HFC emission totals are compared to national and global totals derived from atmospheric data on both a compound-specific and aggregate basis. Factors contributing to differences between UNFCCC-reported and observation-derived emissions for individual HFCs are discussed; they include inaccuracies in methods for deriving emissions from atmospheric mole fraction measurements, inaccuracies in emissions reporting by Annex I (developed) countries, reporting emissions as aggregated mixes of HFCs or HFCs and perfluorocarbons (PFCs), and the potential for significant emissions from non-Annex I (developing) countries not obligated to report their HFC emissions to the UNFCCC[2]. Recent inverse analyses of atmospheric measurements made in the USA and Europe provide a means to assess UNFCCC inventory reporting from these regions. Similar observations from other regions are also considered and add to our understanding of emission magnitudes from countries not required to report emissions to the UNFCCC.

In **Chapter 6** of this Assessment, as in related chapters in previous Assessments, scenarios are constructed for ODS concentrations in the future as part of the

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[1] The Multilateral Fund (MLF) for the implementation of the Montreal Protocol was established in 1991 to assist developing countries (Article 5 countries) to meet their Montreal Protocol commitments. Financial contributions to the MLF come from developed countries (non-Article 5 countries).

[2] UNFCCC Parties listed in Annex I (as amended in 1998) include all the developed countries in the Organization for Economic Cooperation and Development, it also includes Economies in Transition, which are characterized as national economies in the process of changing from a planned economic system to a market economy. By default, other countries are referred to as non-Annex I countries.

Assessment itself, since such scenarios are usually not available in the literature. Also consistent with previous Assessments, new HFC scenarios have not been constructed here or in **Chapter 6**. Instead, projections of HFC use and emission magnitudes are taken from the literature and are discussed in this chapter. These scenarios were created based on data available at the time they were created, and they have not been updated to consider the most recent observational data. As a result, discrepancies between projected and observed HFC concentrations and emissions are apparent in years after the scenarios were created.

Discussions in this chapter extend those presented in specific chapters of the most recent Intergovernmental Panel on Climate Change (IPCC) assessment report (Hartmann, Tank, and Rusticucci et al., 2013; Myhre and Shindell et al., 2013) by updating observed mixing ratios and associated radiative forcings through 2016. Laboratory kinetic data published since that time are considered in providing updated lifetime estimates. Furthermore, the scenarios discussed here are based on more recent analyses, whereas those in the IPCC report are from the Representative Concentration Pathways (RCPs) scenarios (Meinshausen et al., 2011).

2.3 ATMOSPHERIC OBSERVATIONS AND DERIVED EMISSION ESTIMATES

2.3.1 Global HFC Concentration Changes and Estimated Emissions on Regional to Global Scales

Atmospheric abundances of HFCs are regularly measured throughout the global atmosphere by a few surface-based measurement networks at remote sites, by aircraft, and by satellite-borne instruments (**Figure 2-2** and **Table 2-3**). These results imply substantial emissions of HFCs on a global scale, when independently-determined atmospheric removal rates (or lifetimes) are considered (**Figure 2-1; Table 2-2**). Emission rates are also derived on regional spatial scales using trace-gas measurements in non-remote regions (see **Box 1-1**). These results can provide estimates of region-specific HFC emissions that are independent of inventory-based approaches used in reporting to UNFCCC. Regional emission rates are typically derived from data analysis methods such as inter-species correlation and inverse modeling. Regional emission estimates typically have larger relative uncertainties

Table 2-2. Trace gas lifetimes for selected halocarbons: partially fluorinated alkanes, partially fluorinated olefins, and perfluorinated olefins.

Industrial Designation of Chemical Name	Chemical Formula	Total Lifetime,[a] WMO-2014 (years, unless otherwise indicated)	Total Lifetime,[b,c] this Assessment (years, unless otherwise indicated)	Radiative Efficiency[d] (W m^{-2} ppb^{-1})	GWP at Given Time Horizon, this Assessment		Notes
					20-yr	100-yr	
Hydrofluorocarbons							
HFC-23 **	CHF_3	228	228	0.18	11,085	12,690	1
HFC-32 **	CH_2F_2	5.4	5.4	0.11	2,530	705	1
HFC-41 **	CH_3F	2.8	2.8	0.02	430	116	1
HFC-125 **	CHF_2CF_3	31	30	0.23	6,280	3,450	1
HFC-134 **	CHF_2CHF_2	9.7	10	0.19	3,625	1,135	1
HFC-134a **	CH_2FCF_3	14	14	0.16	3,810	1,360	1
HFC-143 **	CH_2FCHF_2	3.5	3.6	0.13	1,250	340	1
HFC-143a **	CH_3CF_3	51	51	0.16	7,050	5,080	1
HFC-152 **	CH_2FCH_2F	146 days (114–335 days)	172 days	0.04	64	17	1, b
HFC-152a **	CH_3CHF_2	1.6	1.6	0.10	545	148	1
HFC-161	CH_3CH_2F	66 days (51–154 days)	80 days	0.02	20	6	1, b
HFC-227ca	$CF_3CF_2CHF_2$	28.2	30	0.27	5,260	2,865	2
HFC-227ea **	CF_3CHFCF_3	36	36	0.26	5,250	3,140	1
HFC-236cb **	$CH_2FCF_2CF_3$	~13	13.4	0.23	3,540	1,235	1
HFC-236ea **	CHF_2CHFCF_3	11.0	11.4	0.30	4,190	1,370	1
HFC-236fa **	$CF_3CH_2CF_3$	222	213	0.24	6,785	7,680	1
HFC-245ca **	$CH_2FCF_2CHF_2$	6.5	6.6	0.24	2,530	720	1
HFC-245cb	$CF_3CF_2CH_3$	47.1	39.9	0.24	6,340	4,000	1
HFC-245ea	$CHF_2CHFCHF_2$	3.2	3.3	0.16	880	240	1
HFC-245eb	$CH_2FCHFCF_3$	3.2	3.2	0.20	1,070	290	1
HFC-245fa **	$CHF_2CH_2CF_3$	7.9	7.9	0.24	2,980	880	1
HFC-263fb	$CH_3CH_2CF_3$	1.1	1.1	0.10	250	68	1
HFC-272ca	$CH_3CF_2CH_3$	2.6	~9	0.07	1,580	480	3
HFC-281ea	CH_3CHFCH_3	23 days (19-46 days)	27 days	–	–	–	1, b
HFC-329p	$CHF_2CF_2CF_2CF_3$	~30	32	0.31	4,720	2,630	4
HFC-338pcc	$CHF_2CF_2CF_2CHF_2$	12.9	13.5	–	–	–	1
HFC-356mcf	$CH_2FCH_2CF_2CF_3$	1.2	1.2	–	–	–	1

HFC-356mff	$CF_3CH_2CH_2CF_3$	8.3	8.5	–	–	–	1
HFC-365mfc **	$CH_3CF_2CH_2CF_3$	8.7	8.9	0.22	2,660	810	1
HFC-43-10mee **	$CF_3CHFCHF-CF_2CF_3$	16.1	17.0	0.359	3,770	1,470	1, 19
HFC-458mfcf	$CF_3CH_2CF_2CH_2CF_3$	22.9	23.8	–	–	–	1
HFC-55-10mcff	$CF_3CF_2CH_2CH_2-CF_2CF_3$	7.5	7.7	–	–	–	1
HFC-52-13p	$CHF_2CF_2CF_2-CF_2CF_2CF_3$	32.7	35.2	–	–	–	5
HFC-72-17p	$CHF_2(CF_2)_6CF_3$		23.8	–	–	–	6
Fluorinated Olefinic HFCs – indicated here as HFOs							
HFO-1123	$CHF=CF_2$	–	1.5 days	0.0019	<1	<1	1, 7, b
HFO-1132a	$CH_2=CF_2$	4.0 days (3.0–5.7 days)	4.6 days	0.004	<1	<1	1, b
HFO-1141	$CH_2=CHF$	2.1 days (1.4–3.1 days)	2.5 days	0.002	<1	<1	1, b
HFO-1234ye(E)	(E)-$CHF=CFCHF_2$	<5 days	<5 days	–	–	–	8, b
HFO-1234ye(Z)	(Z)-$CHF=CFCHF_2$	<5 days	<5 days	–	–	–	8, b
HFO-1225ye(E)	(E)-$CF_3CF=CHF$	4.9 days (3.7–6.9 days)	5.7 days	0.01	<1	<1	1, b
HFO-1225ye(Z)	(Z)-$CF_3CF=CHF$	8.5 days (6.2–12 days)	10 days	0.02	<1	<1	1, b
HFO-1234ze(E)	(E)-$CF_3CH=CHF$	16.4 days (12.8-24 days)	19 days	0.04	4	<1	1, b
HFO-1234ze(Z)	(Z)-$CF_3CH=CHF$	10.0 days	10 days	0.02	1	<1	9, b
HFO-1234yf	$CF_3CF=CH_2$	10.5 days (8.4–16 days)	12 days	0.02	1	<1	1
HFO-1261zf	$CH_2FCH=CH_2$	0.7 days (0.5–1.0 days)	0.8 days	–	–	–	1, b
HFO-1234yc	$CF_2=CFCH_2F$	~2 days	~2 days	–	–	–	8, b
HFO-1225zc	$CF_2=CHCF_3$	~2 days	~2 days	–	–	–	8, b
HFO-1234zc	$CF_2=CHCHF_2$	<5 days	<5 days	–	–	–	8, b
HFO-1336mzz(E)	(E)-$CF_3CH=CHCF_3$	(16–30 days)	122 days	0.13	60	16	10, b
HFO-1336mzz(Z)	(Z)-$CF_3CH=CHCF_3$	(16–32 days)	27 days	0.07	6	2	1, b
HFO-1243zf	$CHCF_3=CH_2$	7.6 days (5.5–11 days)	9 days	0.01	<1	<1	1, b
HFO-1345fz	$CHC_2F_5=CH_2$	7.9 days (5.8–11.4 days)	9 days	0.01	<1	<1	1, b
HFO-1438mzz(E)	(E)-$CF_3CH=CHCF_2CF_3$	(16–30 days)	~122 days	–	–	–	11, b
HFO-1447fz	$CH_2=CHCF_2CF_2CF_3$	(6–10 days)	9 days	–	–	–	12, b

HFO-1549fz 1H,1H,2H-Perfluorohexene	$CHC_4F_9=CH_2$	7.6 days	9 days	0.03	<1	<1	13, b
HFO-174-13fz 1H,1H,2H-Perfluoro-1-octene	$CHC_6F_{13}=CH_2$	7.6 days	9 days	0.03	<1	<1	13, b
HFO-194-17fz 1H,1H,2H-Heptadecafluoro-1-decene	$CHC_8F_{17}=CH_2$	7.6 days	9 days	0.03	<1	<1	13, b
HFO-1438ezy(E)	(E)-$(CF_3)_2CFCH=CHF$		43 days	0.34	42	11	14, b
Perfluorinated Olefins							
PFC-1114	$CF_2=CF_2$	1.1 days (0.7–1.6 days)	1.2 days	0.002	<1	<1	1, b
PFC-1216	$CF_3CF=CF_2$	4.9 days (3.3–7.1 days)	5.5 days	0.01	<1	<1	1, b
Perfluoro buta-1,3-diene	$CF_2=CFCF=CF_2$	1.1 days (0.8–1.6 days)	1.1 days	0.003	<1	<1	1, b
Perfluoro but-1-ene	$CF_3CF_2CF=CF_2$	6 days	6 days	0.02	<1	<1	15, b
Perfluorobut-2-ene (isomer blend: 71% (E) and 29% (Z))	$CF_3CF=CFCF_3$				4.8	1.3	16
(E)-Perfluro-2-butene	(E)-$CF_3CF=CFCF_3$	–	22 days	0.05	3.6	1.0	1, b
(Z)-Perfluro-2-butene	(Z)-$CF_3CF=CFCF_3$	–	35 days	0.07	7.8	2.1	1, b
Perfluoro (2-methyl-2-pentene)	$(CF_3)_2C=CFCF_2CF_3$	–	192 days	–	–	–	1, b
Fluorinated Cycloolefins							
3,3,4,4-Tetrafluro-cyclobut-1-ene 1H,2H-Tetrafluro cyclobutene	cyclo-$CH=CHCF_2CF_2$-		84 days	0.09	37	10	17, b
2,3,3,4,4-Pentafluoro cyclobut-1-ene 1H-Pentafluoro-cyclobutene	cyclo-$CH=CFCF_2CF_2$-		270 days	0.19	214	58	17
Hexafluorocy-clobutene	cyclo-$CF=CFCF_2CF_2$-		1.2	0.25	420	110	17

Octafluorocyclo-pentene	*cyclo*-CF=CFCF$_2$CF$_2$CF$_2$-	31 days	1.05	0.27	300	82	18

Table Heading Footnotes:

Although the designation HFC is applicable to both saturated and unsaturated chemicals, it is used to refer only to partially fluorinated alkanes in this table. Partially fluorinated unsaturated compounds, hydrofluoroolefins, are designated as HFO in this table for easier identification.

** Those HFCs listed as controlled substances in Annex F of the Kigali Amendment to the Montreal Protocol. Additional reporting requirements were adopted at the 29th Meeting of the Parties of the Montreal Protocol (Decision XXIX/12) on consideration of HFCs not listed as controlled substances. This decision requested that production and consumption of HFCs with GWPs higher than the smallest GWP listed in Annex F also be reported to the Ozone Secretariat for informational purposes.

[a] Total lifetime, τ_{HFC}, reported in the 2014 Assessment (indicated as "WMO-2014"; Carpenter and Reimann et al., 2014).

[b] Lifetimes for VSLSs (values given in days) are calculated relative to the methyl chloroform (MCF) partial lifetime due to reaction with OH with the same procedure that is used for long-lived gases. Local lifetimes for VSLSs will depend on the season and location of the emission. Nevertheless, the characteristic values are within the range of likely lifetimes for an emission between the equator and midlatitudes. More detailed modeling is required to derive VSLS lifetimes associated with emission from a specific region and season. A representative range of local lifetimes taken from the 2014 Assessment (Carpenter and Reimann et al., 2014) (**Tables 1-5** and **1-11**) is given in parentheses where available.

[c] Italicized values indicate estimated lifetimes when no experimental data on OH reactivity is available.

[d] Radiative efficiency values are taken from recommendations given in Hodnebrog et al. (2013) based on a literature review of experimental data and a reanalysis of this information, unless another source is specified in notes to the table.

Lifetime Footnotes:

[1] OH reaction rate constant was taken from JPL Publication 15-10 (Burkholder et al., 2015b).

[2] OH reactivity assumed the same as CHF$_2$CF$_3$ (HFC-125).

[3] OH reactivity calculated using the structure activity relationships of DeMore (DeMore, 1996) assuming an E/R of 1700 K.

[4] OH reactivity calculated using the room-temperature rate constant reported by Young et al. (2009a) assuming an E/R of 1700 K, which is similar to that of CHF$_2$CF$_3$.

[5] OH reactivity taken from the IUPAC (Ammann et al., 2017) recommendation.

[6] OH reaction rate constant was taken from Chen et al. (2011).

[7] Radiative metrics calculated using the infrared spectrum from Baasandorj and Burkholder (2016).

[8] No experimental data were available for OH reaction rate constants, so lifetimes were estimated based on reactivity trends of fluorinated ethenes and propenes.

[9] OH reaction rate constant was taken from Zhang et al. (2015).

[10] The atmospheric lifetime and radiative efficiency were calculated using the kinetic and infrared data reported by Baasandorj et al. (2018).

[11] OH reactivity assumed the same as (E)-CF$_3$CH=CHCF$_3$.

[12] OH reactivity assumed the same as CH$_2$=CHCF$_3$.

[13] OH reactivity was recommended by JPL Publication 15-10 based on the room temperature rate constant reported by Sulbaek and Andersen et al. (2005) assuming E/R of -170, which is similar to that of CH$_2$=CHCF$_3$.

[14] OH reaction rate constant and radiative efficiency values were taken from Papadimitriou and Burkholder (2016).

[15] OH reactivity calculated using the room temperature OH rate constant reported by Young et al. (2009b) assuming E/R of -415 K, which is similar to that of CF$_3$CF=CF$_2$.

[16] Industrial Perfluorobut-2-ene is a mixture of two stereo-isomers, *(E)*-Perfluoro-2-butene and *(Z)*-Perfluoro-2-butene, with the ratio of ~71% and ~29%, respectively. Atmospheric lifetimes of individual isomers are given in **Table 2-2**.

   GWP of the mixture was calculated based on estimated GWPs of individual isomers for each time horizon. The radiative efficiency recommended by Hodnebrog et al. (2013) for CF$_3$CF=CFCF$_3$ was used to estimate this parameter for each stereo-isomer, after corresponding corrections to account for its dependence upon lifetimes of the individual stereo-isomers.

[17] OH reaction rate constant was taken from Jia et al. (2013). Radiative efficiency was taken from Jia et al. (2013), and lifetime given here includes the correction suggested by Hodnebrog et al. (2013).

[18] OH reaction rate constant was taken from Zhang et al. (2017). Radiative efficiency was taken from Zhang et al. (2017) and lifetime given here includes the correction suggested by Hodnebrog et al. (2013).

[19] Radiative efficiency was taken from Le Bris et al. (2017).
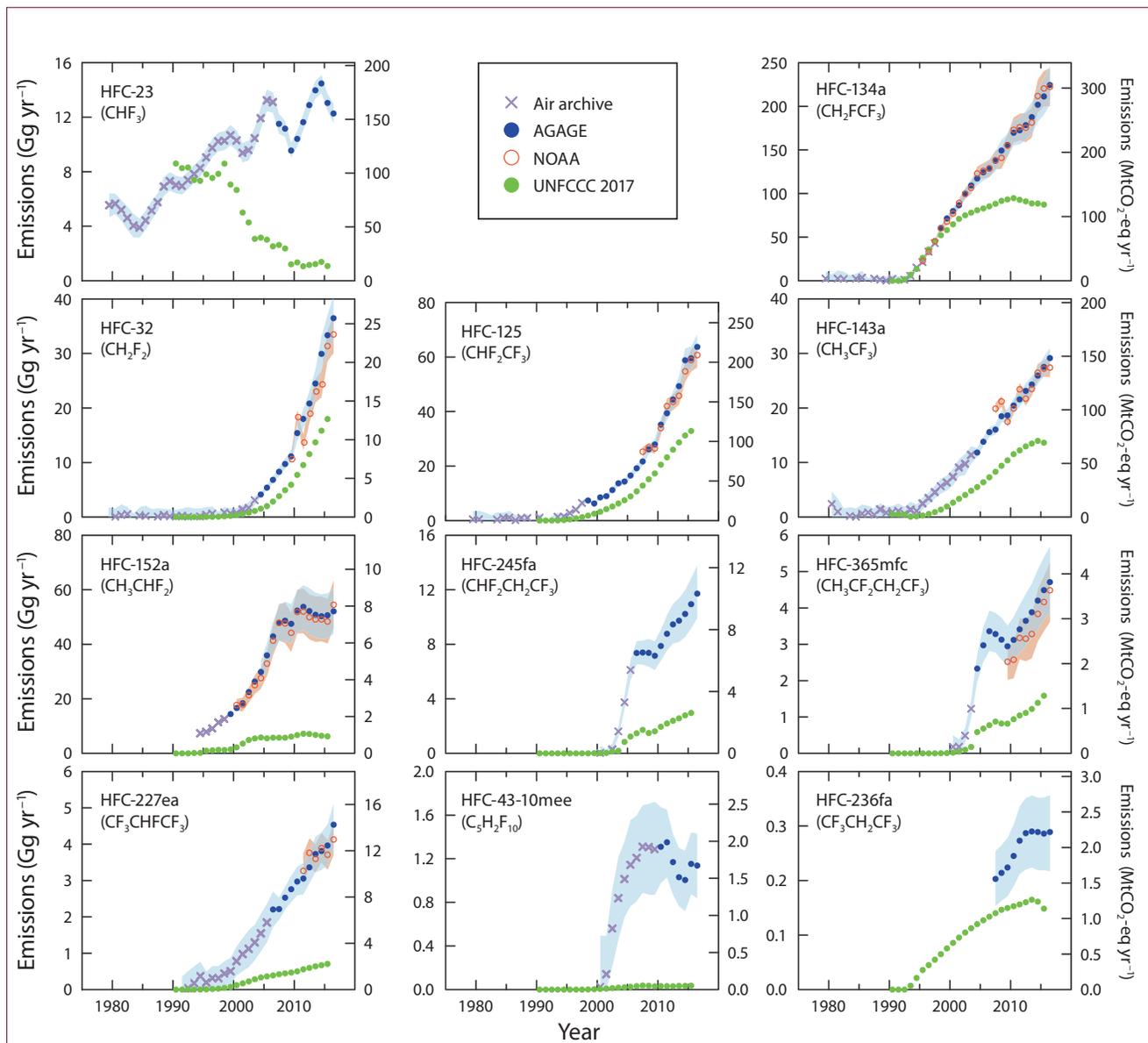
Figure 2-1. Total global emissions estimated from a budget analysis of atmosphere measurements at remote sites (those in **Figure 2-2**) compared to total emissions reported to UNFCCC (2017). Atmospheric measurement-based emissions are derived with a 12-box model and the lifetimes in **Table 2-2**; the methods and model used here are discussed by Rigby et al. (2014). Emissions are presented in units of Gg compound yr^{-1} on the left-hand axis, and the right-hand axis has been scaled by chemical-specific 100-yr GWPs (**Table 2-2**) to indicate emission magnitudes in MtCO$_2$-eq yr^{-1} (1 Mt = 10^{12} g). Shaded regions represent 1 standard deviation in global emissions derived from measured mole fractions and a 12-box model (Rigby et al., 2014). Uncertainties in mole fractions and their model representation are propagated through to the posterior emissions estimates using a Bayesian framework. These uncertainties are augmented by lifetime and calibration scale uncertainties following Rigby et al. (2014). The model uses interannually repeating meteorology and, therefore, errors may be underestimated for periods with large circulation changes, although this will likely affect short-term (e.g., annual) variations more than long-term trends.
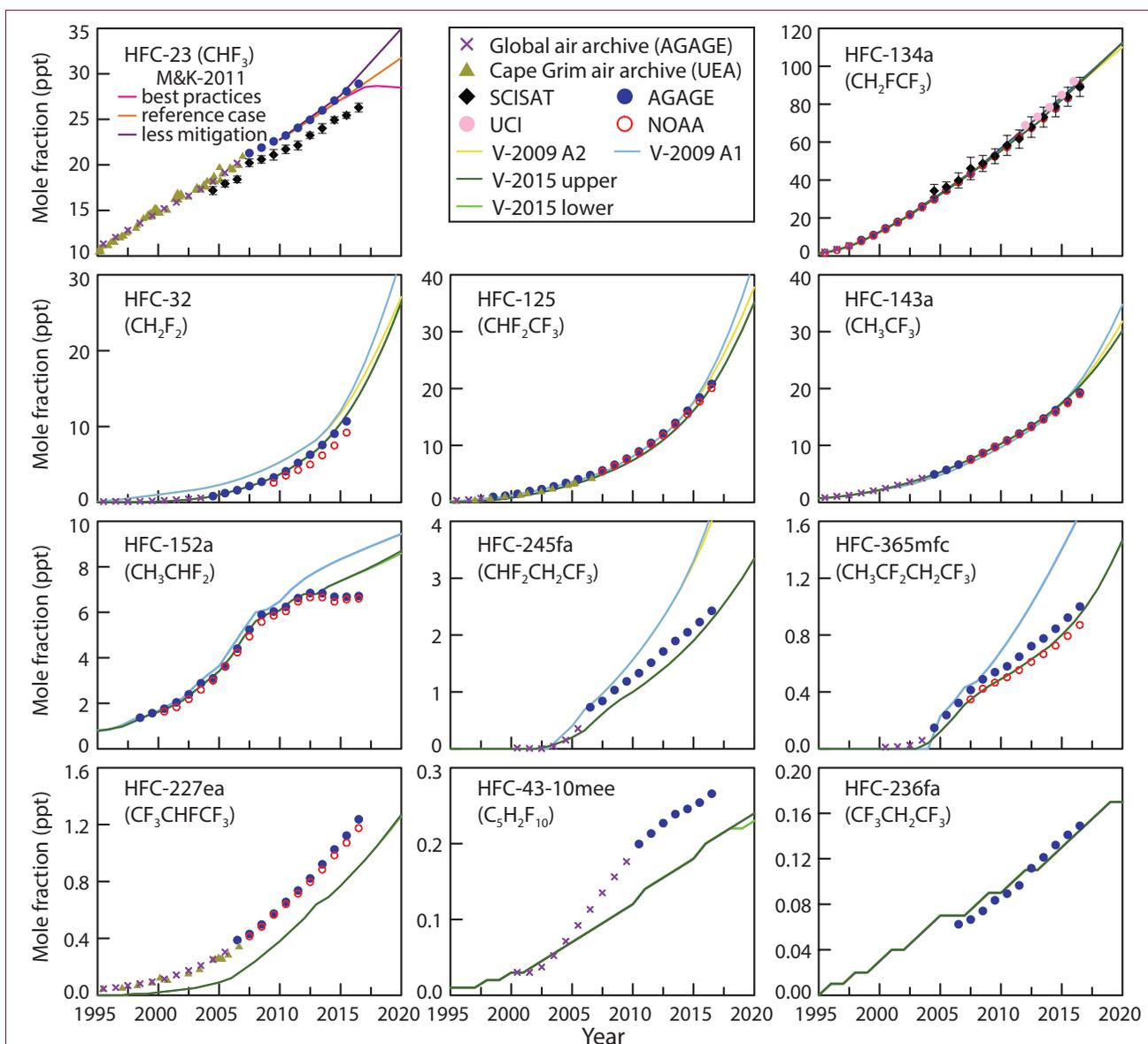
Figure 2-2. Annual mean mole fractions of HFCs and recent projections. Shown are global means estimated from in-situ instrumentation at five remote sites (AGAGE, dark blue filled circles) and independent estimates derived from weekly flasks filled at 8 remote sites (NOAA, open red circles). Global means for HFC-134a from quarterly sampling in the Pacific Basin are also shown (pink filled circles; UCI = the University of California at Irvine; Simpson et al., 2014). Global means derived from air archives in both hemispheres (AGAGE, purple crosses) (Arnold et al., 2014; O'Doherty et al., 2014; Rigby et al., 2014; Simmonds et al., 2016; Simmonds et al., 2018; Vollmer et al., 2011) are calculated using a 12-box model (Cunnold et al., 1983; Rigby et al., 2013). Results reported for the southern hemisphere from analyses of the Cape Grim Air Archive only are also shown (UEA data, khaki triangles; Oram et al., 1998; Leedham Elvidge et al., 2018). Results from satellite absorption retrievals (SCISAT) represent upper troposphere-lower stratosphere means averaged from 60°N to 60°S (black diamonds; Nassar et al., 2006; Harrison et al., 2012). Uncertainties on these satellite retrievals represent statistical variability in the data used in the averaging and do not include any systematic errors. Also shown are projections for global means that were considered in the previous Ozone Assessment (V-2009 = Velders et al., 2009; Carpenter and Reimann et al., 2014) and updated projections based on observations through 2012 (V-2015 = Velders et al., 2015; M&K-2011 = Miller and Kuijpers, 2011). Data are updates to published measurement records (see **Table 2-1** for sources not mentioned here).

Table 2-3. Global surface mean mole fractions of hydrofluorocarbons estimated from ground-based air sampling networks.

Chemical Formula	Common or Industrial Name	Annual Mean Mole Fraction (ppt)			Change (2015–2016)		Network, Method
		2012	2015	2016	ppt yr^{-1}	% yr^{-1}	
CHF_3	HFC-23	24.9	28.1	28.9	0.8	2.9%	AGAGE, in situ (Global)
CH_2F_2	HFC-32	6.28	10.7	12.6	1.9	18%	AGAGE, in situ (Global)
		4.97	9.18	11.2	2.0	22%	NOAA, flasks (Global)
CHF_2CF_3	HFC-125	12.1	18.4	20.8	2.4	13.0%	AGAGE, in situ (Global)
		11.7	17.7	20.1	2.4	13.4%	NOAA, flasks (Global)
CH_2FCF_3	HFC-134a	67.7	83.3	89.3	6.0	7.2%	AGAGE, in situ (Global)
		67.5	83.4	89.6	6.1	7.4%	NOAA, flasks (Global)
		68.9	84.9	92.1	7.2	8.5%	UCI, flasks, (global)
CH_3CF_3	HFC-143a	13.4	17.7	19.3	1.6	9.2%	AGAGE, in situ (Global)
		13.2	17.4	19.0	1.6	9.0%	NOAA, flasks (Global)
CH_3CHF_2	HFC-152a	6.84	6.68	6.72	0.03	0.5%	AGAGE, in situ (Global)
		6.65	6.57	6.61	0.04	0.6%	NOAA, flasks (Global)
$CHF_2CH_2CF_3$	HFC-245fa	1.71	2.23	2.43	0.20	8.9%	AGAGE, in situ (Global)
$CH_3CF_2CH_2CF_3$	HFC-365mfc	0.72	0.92	1.00	0.08	8.4%	AGAGE, in situ (Global)
		0.61	0.79	0.87	0.08	9.9%	NOAA, flasks (Global)
CF_3CHFCF_3	HFC-227ea	0.82	1.12	1.24	0.11	10.2%	AGAGE, in situ (Global)
		0.80	1.07	1.17	0.10	9.6%	NOAA, flasks (Global)
$CF_3(CHF)_2CF_2CF_3$	HFC-43-10mee	0.23	0.25	0.27	0.01	4.6%	AGAGE, in situ (Global)
$CF_3CH_2CF_3$	HFC-236fa	0.11	0.14	0.15	0.01	5.7%	AGAGE, in situ (Global)

Notes:
Stated mole fractions represent independent estimates of global surface means determined by different observational networks at different sampling locations; annual values represent calendar year means. Absolute changes (ppt yr^{-1}) are calculated as the difference in annual means; relative changes (% yr^{-1}) are that same difference relative to the 2015 value. Small differences between values from previous Assessments are due to changes in calibration scale and methods for estimating global mean mole fractions from a limited number of sampling sites. These observations are updated from the following sources: Montzka et al., 1996; Miller et al., 2008; Miller et al., 2010; Vollmer et al., 2011; Arnold et al., 2014; Rigby et al., 2014; Simpson et al., 2014; Montzka et al., 2015; Simmonds et al., 2016, 2017, 2018. They are available at http://agage.mit.edu/ (for AGAGE data); at http://www.esrl.noaa.gov/gmd/dv/site/ (for NOAA data); and at http://ps.uci.edu/~rowlandblake/research_atmos.html (for UCI data). Global mean estimates from AGAGE are calculated using atmospheric data and a 12-box model (Cunnold et al., 1983; Rigby et al., 2013). AGAGE calibrations are as specified in CDIAC (2016) and related primary publications. NOAA-determined values are directly estimated from measurements made at 8 to 12 remote surface sites with cosine-of-latitude weighting.

than global-scale emission estimates. Uncertainties associated with regional-scale inverse analyses, for example, include the inversion setup, the assumed priors, the uncertainty assumed for those priors and for the observations, the geographic extent of the sampling network, and sampling frequency, among other parameters. Furthermore, some emission estimates are derived from observations that have limited spatial coverage and limited sensitivity to emissions across an entire region of interest (countrywide, for example) or incomplete coverage across all seasons. While uncertainties in regional-scale emission estimates would ideally encompass all of these factors, this is often not

feasible as this entails estimating uncertainties in parameters with insufficient objective information.

2.3.1.1 HFC-134a (CH_2FCF_3)

HFC-134a remains the most abundant HFC in the global atmosphere and has the largest annual growth rate and emission. The global annual mean mole fraction reached 89.5 ppt in 2016, up from 67.7 ppt in 2012 (AGAGE and NOAA data; UCI results over this period are ~3% higher; **Table 2-3**). The rate of increase averaged 5.6 ± 0.2 ppt yr^{-1} (7.3 ± 0.2% yr^{-1}) during 2012–2016, which is about 0.6 ppt yr^{-1} larger than the

mean increase for 2008–2012, as reported in the last Assessment. This observed increase in global mole fraction is similar to that projected nearly a decade ago (Velders et al., 2009) and more recently (Velders et al., 2015); it is also consistent with the largest increases projected in the Representative Concentration Pathways (RCPs), namely RCP8.5 (**Figure 2-2**; Carpenter and Reimann et al., 2014; Velders et al., 2009; Meinshausen et al., 2011).

Mixing ratios of HFC-134a have been estimated from the ACE-FTS instrument on board SCISAT for recent years (updates to Nassar et al., 2006) using updated absorption cross sections (Harrison, 2015). The upper tropospheric annual means derived for HFC-134a from SCISAT are very consistent with mean mole fractions measured by the surface networks; differences between results from SCISAT and the surface networks are much smaller than the uncertainties associated with the satellite retrievals. Rates of change in HFC-134a mixing ratios determined for 2012–2016 from these independent measurements systems are also consistent, with 7.0 ± 0.8 % yr^{-1} derived from annual changes in SCISAT results, 7.3 ± 0.1 % yr^{-1} derived from NOAA data, and 7.2 ± 0.2 % yr^{-1} derived from AGAGE data (**Figure 2-2**).

Globally, HFC-134a contributed a radiative forcing (RF) of 14.3 mW m^{-2} in 2016. This is the largest radiative forcing contributed by any other HFC or other fluorinated gas (i.e., PFCs, SF$_6$, SO$_2$F$_2$, and NF$_3$; see **Chapter 1**). The mean rate of increase has been slightly larger over the past 4 years (5.4–5.8 ppt yr^{-1}) than

during 2008–2012 (4.9–5.1 ppt yr^{-1}). HFC-134a has been used as a substitute for CFC-12 since the mid-1990s in mobile air conditioning (MAC), in stationary refrigeration and air conditioning, in metered-dose inhalers, and in foam-blowing applications; it has also been used as a fire suppressant and for dry etching. Due to its high GWP (**Table 2-2**), controls on HFC-134a use have been adopted in some sectors in the E.U., USA, Japan, and other countries (see **Section 2.5.1**). Refrigerants with substantially lower GWPs such as HFC-1234yf and HFC-1234ze(E), among others, are starting to replace HFC-134a in various applications (see below) (UNEP, 2017a).

Total global emissions of HFC-134a estimated from a budget analysis of measured mole fractions at remote sites increased nearly linearly from 177 ± 17 Gg yr^{-1} in 2012 to 223 ± 22 Gg yr^{-1} in 2016 (**Figure 2-1**; update from Rigby et al., 2014; Montzka et al., 2015; Simmonds et al., 2017; AGAGE and NOAA data). Global emissions have increased by an average of 10 Gg yr^{-1} since 2008, faster than emissions of any other HFC. Global emissions derived with different modeling frameworks (but these same network data) are consistent with the emissions derived here (Fortems-Cheiney et al., 2015; Lunt et al., 2015; Xiang et al., 2014).

The total global emissions derived for HFC-134a from atmospheric observations are over two times larger than total emissions reported to UNFCCC from Annex I countries (see **Figure 2-3**). Furthermore, this emission gap has become larger over time; the
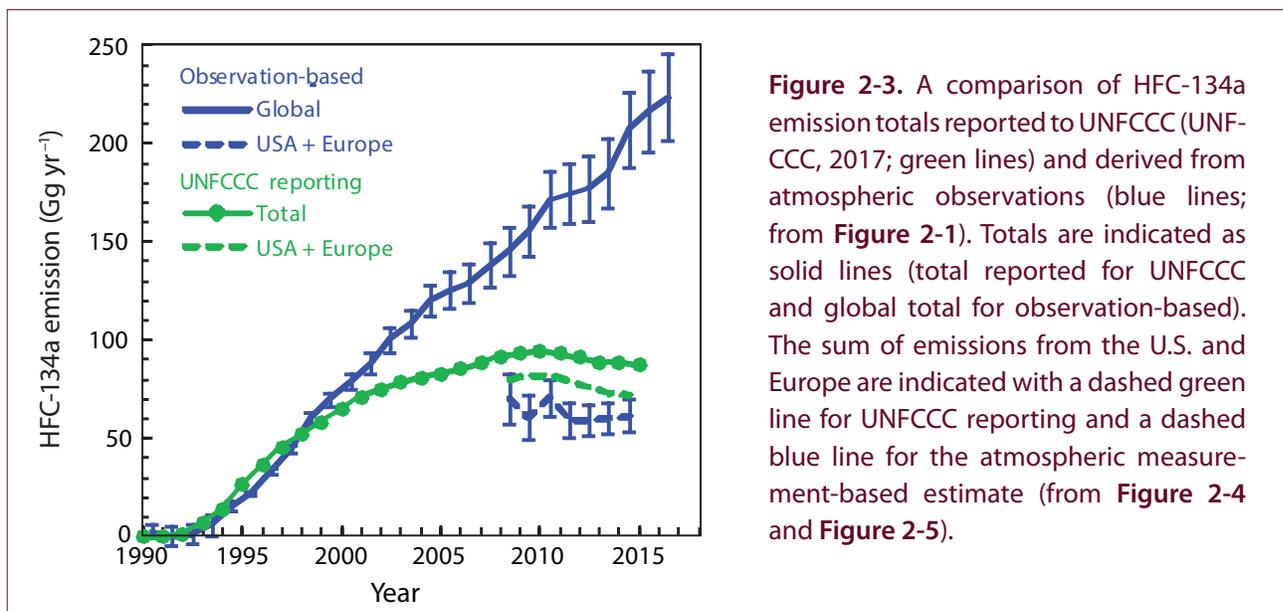
Figure 2-3. A comparison of HFC-134a emission totals reported to UNFCCC (UNFCCC, 2017; green lines) and derived from atmospheric observations (blue lines; from **Figure 2-1**). Totals are indicated as solid lines (total reported for UNFCCC and global total for observation-based). The sum of emissions from the U.S. and Europe are indicated with a dashed green line for UNFCCC reporting and a dashed blue line for the atmospheric measurement-based estimate (from **Figure 2-4** and **Figure 2-5**).

HFC-134a totals reported to UNFCCC have decreased slightly since 2010, in contrast to the increases derived for global total emissions from the atmospheric data (**Figure 2-1** and **Figure 2-3**).

The difference between UNFCCC reporting and atmosphere-based global total emission is not likely from underreporting of emissions from the USA and Europe, the two regions that account for most (~80%) emissions reported to the UNFCCC (**Figure 2-3**). Regional emissions derived from inverse modeling analysis of measurements within the USA and Europe suggest that the inventory-based reporting from these regions is accurate or slightly high (Graziosi et al., 2017; Hu et al., 2017; Say et al., 2016) (**Figure 2-4, Figure 2-5**). A similar conclusion was derived for HFC-134a

from all Annex I countries from an inverse modeling analysis of measurements at globally-distributed sites (Lunt et al., 2015). For 2014, emissions of HFC-134a from the USA and Europe summed together were 71 Gg yr^{-1} in UNFCCC reporting, and they were 61 ± 8 Gg yr^{-1} from inversion-based modeling analyses of atmospheric observations. The observation-based emissions derived for the USA totaled 43 ± 6 Gg yr^{-1} (Hu et al., 2017) and for Europe totaled 18 ± 6 yr^{-1} (Graziosi et al., 2017) in 2014. Other inversion-based analyses of atmospheric data in Europe suggest European HFC-134a emissions that are consistent with those derived in Graziosi et al. for 2009 (Keller et al., 2012); they are between 9 and 16 Gg yr^{-1} higher in other years (Brunner et al., 2017 for 2011; and Fortems-Cheiney et al., 2015 for multiple years). Slightly higher European emissions
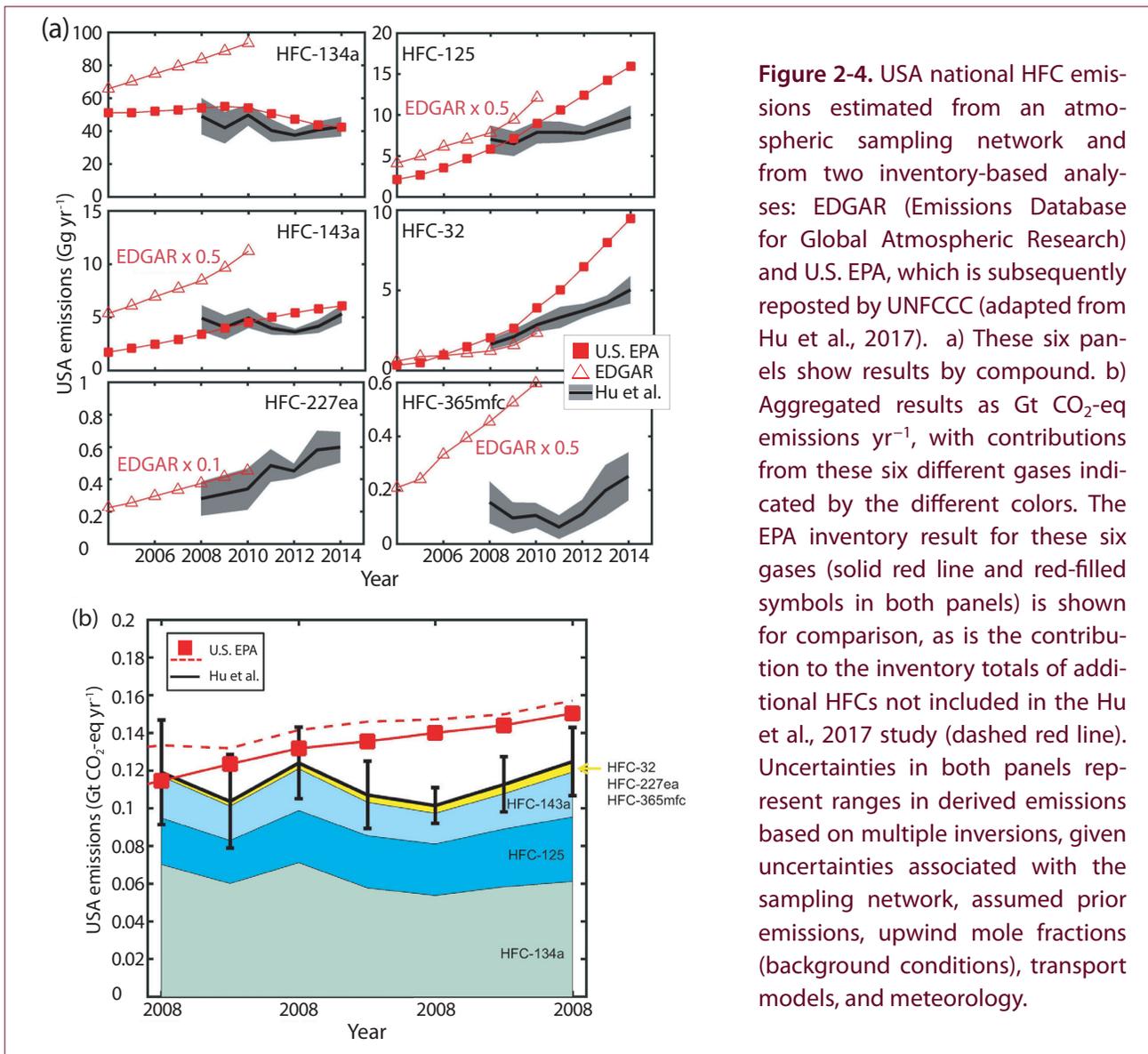
Figure 2-4. USA national HFC emissions estimated from an atmospheric sampling network and from two inventory-based analyses: EDGAR (Emissions Database for Global Atmospheric Research) and U.S. EPA, which is subsequently reposted by UNFCCC (adapted from Hu et al., 2017). a) These six panels show results by compound. b) Aggregated results as Gt CO$_2$-eq emissions yr^{-1}, with contributions from these six different gases indicated by the different colors. The EPA inventory result for these six gases (solid red line and red-filled symbols in both panels) is shown for comparison, as is the contribution to the inventory totals of additional HFCs not included in the Hu et al., 2017 study (dashed red line). Uncertainties in both panels represent ranges in derived emissions based on multiple inversions, given uncertainties associated with the sampling network, assumed prior emissions, upwind mole fractions (background conditions), transport models, and meteorology.
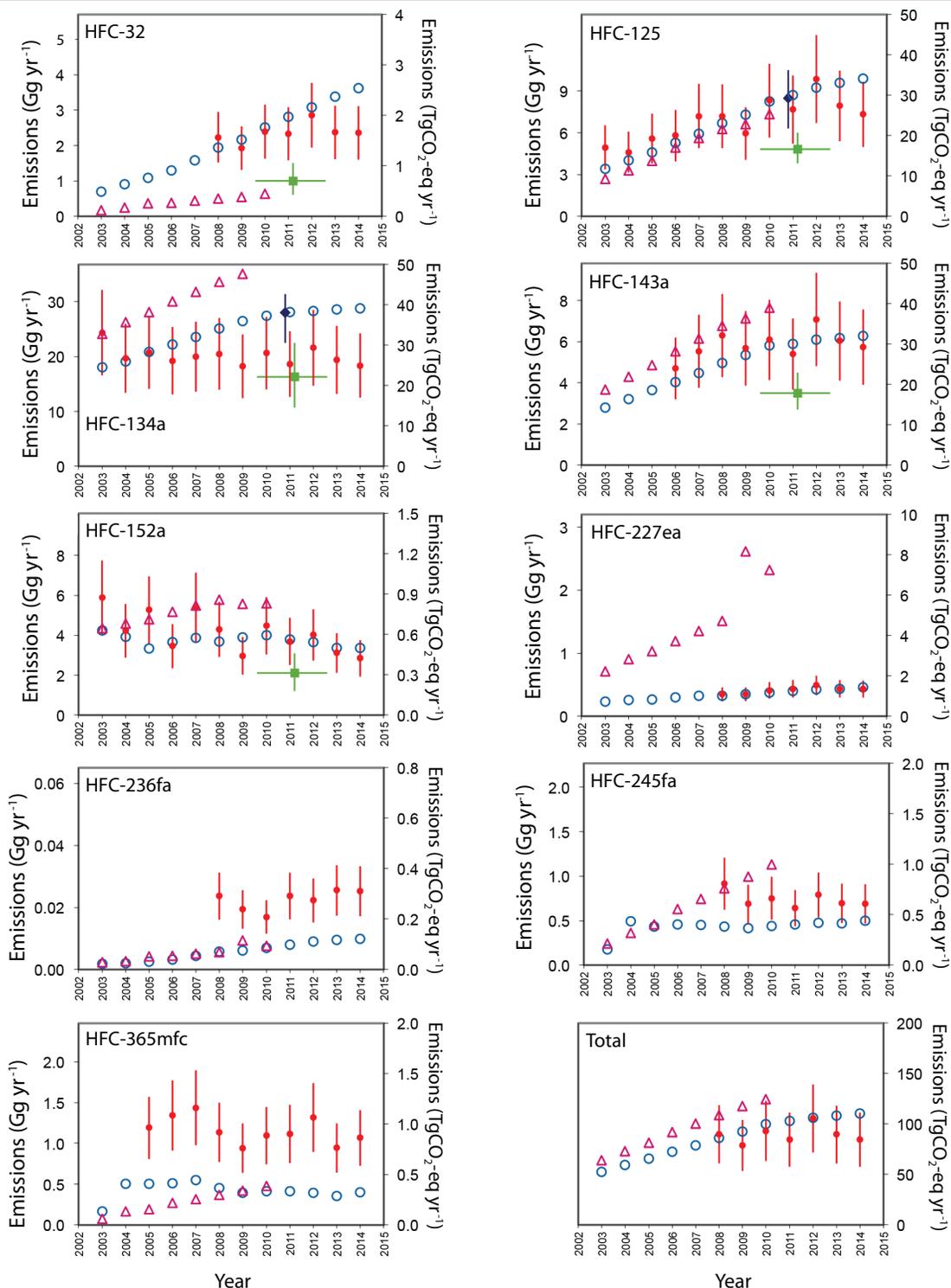
Figure 2-5. Emissions of nine HFCs from the European geographic domain, and related uncertainties, from January 2003 to December 2014. Emissions are given in Gg yr^{-1} (left axis) and in TgCO$_2$-eq yr^{-1} (right axis). The lower right panel (labeled "total") shows aggregated CO$_2$-eq emissions yr^{-1} from the nine HFCs. Emissions derived from atmospheric measurements are given as red filled circles: Graziosi et al. (2017); green filled squares: Lunt et al. (2015); and dark blue filled diamonds: Brunner et al. (2017). Emissions derived from inventories are shown as light blue unfilled circles (UNFCCC) and purple unfilled triangles (EDGAR v4.2 FT2010). Note that Lunt et al. (2015) and Brunner et al. (2017) data are shifted slightly in time for clarity; the Lunt et al. data are a 3-yr average and the Brunner et al. (2017) data refer to a smaller domain. Note that 100 Tg = 0.1 Gt.

of HFC-134a would make the sum of European and USA emissions more consistent with reporting to the UNFCCC (**Figure 2-3**). The only other recent analysis of USA emissions based on USA observations (Fortems-Cheiney et al., 2015) suggests between 10 and 20 Gg yr^{-1} larger emissions than derived in Hu et al. for the overlapping years of 2008–2010, but these higher values may be less representative of the USA total as they are derived from observations at a smaller number of USA sites.

Most of the remaining HFC-134a emissions reported to the UNFCCC (20% of reported total) come from Canada, Japan, Australia, and Russia and have ranged from 1.5 to 4 Gg yr^{-1} per country in recent years. Of these countries, atmosphere measurement-based estimates are available for Japan and Australia. Japanese emissions during 2008 have been estimated at 3.1 ± 0.2 Gg yr^{-1} in one study (Stohl et al., 2010) and 4.7 (4.5–5) Gg yr^{-1} in another (Li et al., 2011); emissions during 2010-2012 were estimated at 3.7 (0.6–7.4) Gg yr^{-1} in one study (Lunt et al., 2015) and between 2.1 and 4.3 Gg yr^{-1} in another (Saito et al., 2015). These estimates are not significantly different from the 2.5 to 2.9 Gg yr^{-1} reported to UNFCCC by Japan in these years, although higher amounts were inferred for 2010 in one study (12 ± 2 Gg yr^{-1}; Fortems-Cheiney et al., 2015). Atmosphere-based estimates for Australia for 2006 (4.5 Gg yr^{-1}; Stohl et al., 2009) indicate comparable emissions to Japan's, but they are higher than the 1.9 Gg reported by Australia to UNFCCC for that year.

The absence of substantial underestimates in national emissions reported to UNFCCC, as is implied from the above discussion, indicates that the factor of approximately two difference (> 100 Gg^{-1}) between totals reported to UNFCCC and atmosphere-based global totals likely stems from significant emissions of HFC-134a from non-reporting countries (i.e., non-Annex I, developing countries). Regional atmospheric studies in Asia support this conclusion. Emissions for 2008 from East Asia were estimated to be 15–20 Gg yr^{-1} (based on values from Li et al., 2011 of 15.2 [12.5–18.6] Gg yr^{-1} and from Stohl et al., 2010 of 19.2 ± 2.5 Gg yr^{-1}). Atmosphere-based estimates suggest that emissions from China accounted for 8–13 Gg of these East Asian HFC-134a emissions during 2008 (based on estimates of 8.3 [6.2–11] Gg yr^{-1} from Li et al., 2011, 8.7 [6.5–12] Gg yr^{-1} from Kim et al., 2010, and 12.9 ± 1.7 Gg yr^{-1} from Stohl et al., 2010). Emissions at the higher end of

this range were derived for 2010-2012 (12 [5–21] Gg yr^{-1} in Lunt et al., 2015). Based on emissions derived from atmospheric observations, South Korea has accounted for approximately 1–3 Gg yr^{-1} of HFC-134a in recent years (1.5–2.2 Gg yr^{-1} for 2008 [Stohl et al., 2010 and Li et al., 2011] and (1.83 [0.58-3.13] Gg yr^{-1} for 2010-2012 [Lunt et al., 2015]).

An analysis of HFC production and consumption in China also indicates significant Chinese emissions of HFC-134a and suggests increasing emissions over time with 9.2–11 Gg in 2008 and 33 Gg in 2013 (Su et al., 2015 and Fang et al., 2016). These results and the atmosphere measurement-based estimates, however, suggest that emissions from China account for less than half of the difference between global emissions and totals reported to UNFCCC from Annex I countries (**Figure 2-6**). As such, they imply that significant emissions of HFC-134a, perhaps as much of 30% of the global total, are currently arising from non-Annex I countries other than China that are not required to report HFC emissions to the UNFCCC.

2.3.1.2 HFC-23 (CHF$_3$)

HFC-23 is emitted into the atmosphere primarily as a by-product from over-fluorination during HCFC-22 production; much smaller emissions are associated with HFC-23 use as feedstock for halon-1301 production, in semiconductor fabrication (plasma etching and chamber cleaning), in very low-temperature refrigeration, and in specialty fire suppression systems (Miller et al., 2010; Montzka et al., 2010; Oram et al., 1998; Simmonds et al., 2018; US EPA, 2017).

Atmospheric mole fractions of HFC-23 continue to increase in the global atmosphere and reached 28.9 ppt in 2016 (up from 25 ppt in 2012; AGAGE data only; **Table 2-3**). This global abundance accounted for 5.2 mW m^{-2} in 2016, the second largest radiative forcing of all individual HFCs and other F-gases (PFCs, SF$_6$, NF$_3$, SO$_2$F$_2$, SF$_5$CF$_3$; see **Chapter 1**). The HFC-23 global mole fraction increased by 0.83 ppt yr^{-1} (2.9% yr^{-1}) in 2015–2016, similar to the 0.9 ppt yr^{-1} increase measured for 2011–2012 (Carpenter and Reimann et al., 2014), but less than the peak rate of 1.1 ppt yr^{-1} observed during 2014. The average rate of increase for 2012–2016 was 1.0 ppt yr^{-1}, which is slightly faster than the 0.8 ppt yr^{-1} reported in the previous Assessment for 2008–2012. In recent years, observed global mole
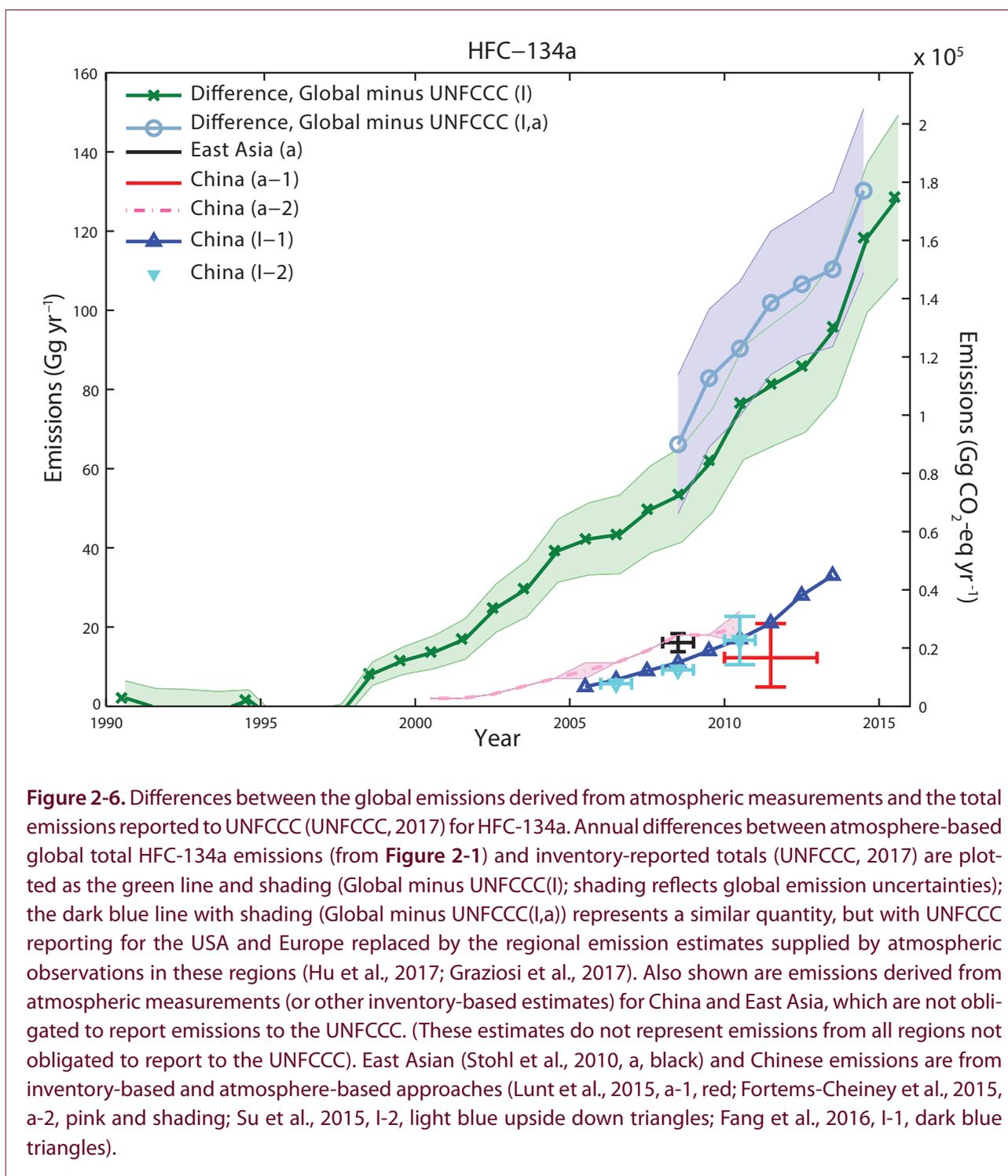
Figure 2-6. Differences between the global emissions derived from atmospheric measurements and the total emissions reported to UNFCCC (UNFCCC, 2017) for HFC-134a. Annual differences between atmosphere-based global total HFC-134a emissions (from **Figure 2-1**) and inventory-reported totals (UNFCCC, 2017) are plotted as the green line and shading (Global minus UNFCCC(I); shading reflects global emission uncertainties); the dark blue line with shading (Global minus UNFCCC(I,a)) represents a similar quantity, but with UNFCCC reporting for the USA and Europe replaced by the regional emission estimates supplied by atmospheric observations in these regions (Hu et al., 2017; Graziosi et al., 2017). Also shown are emissions derived from atmospheric measurements (or other inventory-based estimates) for China and East Asia, which are not obligated to report emissions to the UNFCCC. (These estimates do not represent emissions from all regions not obligated to report to the UNFCCC). East Asian (Stohl et al., 2010, a, black) and Chinese emissions are from inventory-based and atmosphere-based approaches (Lunt et al., 2015, a-1, red; Fortems-Cheiney et al., 2015, a-2, pink and shading; Su et al., 2015, I-2, light blue upside down triangles; Fang et al., 2016, I-1, dark blue triangles).

fractions of HFC-23 are also consistent with the largest emissions projected in the RCPs, which are in RCP8.5 (Meinshausen et al., 2011).

Mixing ratios of HFC-23 have been estimated over time from the ACE-FTS instrument on board the SCISAT satellite (Harrison et al., 2012) using updated absorption cross sections (Harrison, 2013). The upper tropospheric means are approximately 2 ppt below those estimated from surface-based data (AGAGE), although the relative rate of change averaged over 2012–2016 from the two independent measurements is not significantly different ($3.1 \pm 0.8\%$ yr^{-1} from SCISAT versus $3.8 \pm 0.6\%$ yr^{-1} from AGAGE) (**Figure 2-2**).

Total global HFC-23 emissions derived from a budget analysis of measured mole fractions at remote sites show gradual increases before 1999 and then substantial variations, with minima in 2001–2002 and in 2009–2010 and maxima in 2005–2006 and 2013–2014. Derived peak emissions were 14.5 ± 0.7 Gg yr^{-1} in 2014, and have since decreased, with 12.3 ± 0.7 Gg yr^{-1} estimated for 2016 (**Figure 2-1**, Simmonds et al., 2018).

A comparison between atmospheric measurement-based global emission estimates and Annex I country totals reported to UNFCCC shows fairly good consistency during 1990–1995 (**Figure 2-1**). After 2000, however, UNFCCC totals decrease and atmospheric measurement-derived global emissions increase. UNFCCC totals were between 1 and 1.5 Gg yr^{-1} for 2009–2015 while measurement-based global emission totals ranged between 9.5 and 15 Gg yr^{-1}. This difference increased concurrently with the substantial increases in HCFC-22 production and associated HFC-23 emission from developing countries not required to report HFC emissions to the UNFCCC (i.e., non-Annex I countries) (Miller et al., 2010; Montzka et al., 2010; Simmonds et al., 2018).

Inventory-based emissions of HFC-23 from countries not obligated to report emissions to the UNFCCC are derivable from information provided to the Montreal Protocol's Multilateral Fund (MLF) by these countries (UNEP, 2017b; Simmonds et al., 2018). These inventory emissions of HFC-23 are estimated in some countries and, in others, are derived from a combination of country-based reporting of HCFC-22 production for all uses, HFC-23 production rates, and quantities of HFC-23 destroyed or otherwise transformed as feedstock.

The sum of inventory-based emissions derived from reporting to the UNFCCC and estimated using the information collected by the Montreal Protocol's MLF fairly closely tracks the wide swings in global emissions derived from atmospheric mole fraction measurements (**Figure 2-7**), although emissions in a few years (e.g., 2008, 2013, and 2015) are significantly underestimated by these inventories (Simmonds et al., 2018). This overall consistency suggests that the inventory-derived HFC-23 emissions associated with HCFC-22 production are fairly accurately estimated (within ± 2 Gg in total) in both developed and developing countries.

This consistency also provides an understanding of HFC-23 emission changes over the past decade. The minimum in emissions centered around 2009–2010 stems from a significant decrease in the ratio of HFC-23 emission relative to HCFC-22 production (E_{23}/P_{22}) (**Figure 2-7**), which was primarily the result of HFC-23 destruction facilitated by the UNFCCC's CDM projects (Miller et al., 2010; Montzka et al., 2010). The subsequent increase in HFC-23 emissions after 2010 appears to be the result of increases in total HCFC-22 production and slight increases in the E_{23}/P_{22} ratio as the CDM projects were terminated. The ~2 Gg decrease in annual emissions after 2014 is associated with slightly reduced total HCFC-22 production as dispersive-use production was capped in 2013, although a much larger emission decline was expected in 2015 from inventory reporting than is apparent in the measurement-derived emission estimate for that year. The decline in reported emissions in 2015 is due primarily to a drop in the reported E_{23}/P_{22} ratio (**Figure 2-7**).

The inventory-based reporting totals also suggest a significant shift in regions emitting HFC-23 in the past. Emissions were primarily from the USA, Russia, the UK, and Japan during the early 1990s. Since 2009, however, between 84% and 89% of global HFC-23 emissions have come from China, which is consistent with China being the largest producer of HCFC-22 in recent years in reporting to the UN Environment Ozone Secretariat (UNEP, 2017b; Simmonds et al., 2018).

Independent evidence for substantial HFC-23 emissions from non-Annex I countries in recent years comes from a number of observational studies, although measurements have not been conducted near all developing countries reporting HFC-23 emission (i.e., Argentina, China, India, Mexico, North Korea, and Venezuela). Emissions from China, for example, were estimated for 2008 from observations in eastern Asian countries and different data analysis methods and range between 6 and 12 Gg yr^{-1} (based on estimates from Stohl et al. [2010] of 6.2 ± 0.7 Gg yr^{-1}, Fang et al., [2015] of 6.2 ± 0.6 Gg yr^{-1}, Li et al. [2011] of 10 (7.2–13) Gg yr^{-1}, and Kim et al. [2010] of 12 (8.6–15) Gg yr^{-1}). The lower end of this range is in good agreement with the inventory-based estimates provided to the MLF from China of 5.7 Gg yr^{-1} for 2008 (UNEP, 2017b; Simmonds et al., 2018). For comparison, total global emissions derived from
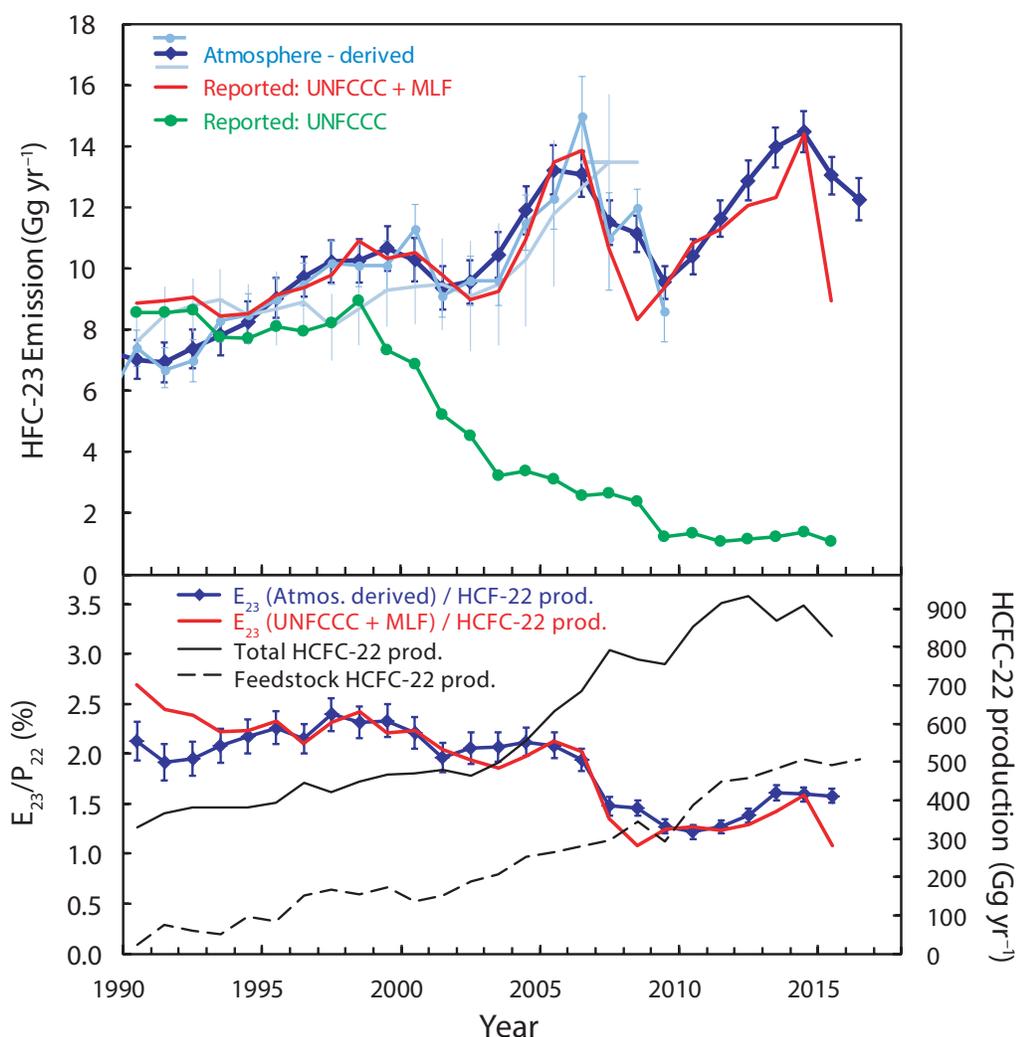
Figure 2-7. *Top panel:* Emissions of HFC-23 derived from atmospheric measurements (blue lines) and inventories (red and green lines). Measurement-based emissions are derived from analyses of southern-hemispheric firn air (light-blue line; Montzka et al., 2010), a southern-hemispheric air archive before 2007 coupled with ongoing results from multiple sites during 2007–2009 (light blue circles; Miller et al., 2010), and from a combination of air-archive, firn air, and ongoing measurements (dark blue diamonds; Simmonds et al., 2018). Uncertainties are one standard deviation of estimates. Inventory results are from Annex I reporting to UNFCCC (green line with filled circles; UNFCCC, 2017) and from the sum of reporting to UNFCCC and to the Montreal Protocol's Multilateral Fund (MLF; red line, Simmonds et al., 2018). *Bottom panel:* the ratio of HFC-23 emissions relative to HCFC-22 production for all uses (E_{23}/P_{22} by mass, left-hand axis; with emissions being the total from inventories (red) or global magnitudes estimated from atmospheric measurements and their uncertainty (blue line) from the upper panel, and total global HCFC-22 production reported for all uses (black line; right-hand axis) and for feedstock only (black dashed line; right-hand axis).

measured atmospheric changes at remote sites was 11.2 ± 0.6 Gg yr^{-1} in 2008.

By 2012, atmospheric measurement-based analyses indicated that HFC-23 emissions from China accounted for at least two-thirds of global HFC-23 emissions. Atmospheric observations in that year suggest Chinese emissions of 8.8 ± 0.8 Gg yr^{-1} (Fang et al., 2015) compared to the 10.8 Gg yr^{-1} estimate provided to the MLF (UNEP, 2017b; Simmonds et al., 2018), while the atmosphere measurement-based global estimate in 2012 was 12.9 ± 0.7 Gg yr^{-1} and UNFCCC

Annex I reporting totaled 1.2 Gg yr^{-1}. A small fraction of the global emission arises from other non-Annex I countries such as South Korea and Taiwan (Stohl et al., 2010; Li et al., 2011; Fang et al., 2015), ~0.1–0.2 Gg yr^{-1} in 2008 (compared to the estimates derived from information provided to the MLF of less than 0.1 Gg yr^{-1} for South Korea). Analyses of atmospheric observations also indicate that emissions from Japan were ~0.2–0.3 Gg yr^{-1} in 2008 (Stohl et al., 2010; Li et al., 2011; Fang et al., 2015), somewhat larger than the 0.04 Gg yr^{-1} reported to UNFCCC, while European emissions (Keller et al., 2011; Simmonds et al., 2018) are similar or slightly larger than the UNFCCC submission values.

2.3.1.3 HFC-32 (CH$_2$F$_2$), HFC-125 (CHF$_2$CF$_3$), HFC-143a (CH$_3$CF$_3$)

Global mean mole fractions of HFC-32, HFC-125, and HFC-143a continue to rise in the atmosphere primarily because these chemicals are used as HCFC substitutes in major refrigeration blends (HFC-125 also has a minor application for fire protection) (O'Doherty et al., 2014; Montzka et al., 2015; Simmonds et al., 2015, 2017; US EPA, 2017). In 2016, average global mean mole fractions were 11.9 (11.2–12.6) ppt for HFC-32, 20.4 (20.1–20.8 ppt) for HFC-125, and 19.2 (19.0–19.3) ppt for HFC-143a (NOAA and AGAGE data; **Table 2-3**). These mole fractions are approximately twice the 2012 values for HFC-32 and HFC-125, and are 50% higher for HFC-143a. Mole fractions of these HFCs increased during 2012–2016 by an average of 1.6 ppt yr^{-1} for HFC-32, 1.5 ppt yr^{-1} for HFC-143a, and 2.1 ppt yr^{-1} for HFC-125. These rates are considerably larger than measured during 2008–2012 as reported in the previous Assessment, by a factor of 1.7 for HFC-32 and HFC-125, and by a factor of 1.2 for HFC-143a.

The mole fraction increases observed for these gases since 2007 are similar to the scenario projections discussed in the previous Assessment (**Figure 2-2**; Carpenter and Reimann et al., 2014; Velders et al., 2009) and to those in newer scenarios (Velders et al., 2015), although projected HFC-32 mole fractions were slightly higher than observed.

The radiative forcings associated with these 2016 global mole fractions were 1.31 (1.23–1.39) mW m^{-2} from HFC-32, 4.70 (4.62–4.79) mW m^{-2} from HFC-125, and 3.06 (3.04–3.09) mW m^{-2} from HFC-143a.

Total global emissions of these three HFCs derived from a budget analysis of measured mole fractions at remote sites continue to increase, with estimates for 2016 of 35 ± 4 Gg yr^{-1} for HFC-32, 62 ± 5 Gg yr^{-1} for HFC-125 and 28 ± 2 Gg yr^{-1} for HFC-143a. These were higher than their 2012 emissions of 20 Gg yr^{-1}, 44 Gg yr^{-1}, and 22 Gg yr^{-1}, respectively (**Figure 2-1**; update from O'Doherty et al., 2009, 2014; Rigby et al., 2014; Lunt et al., 2015; Montzka et al., 2015; and Simmonds et al., 2017). In 2014, the global emission estimates for each of these three gases were about two times higher than the corresponding UNFCCC totals from reporting countries.

As was true for HFC-134a, the difference between UNFCCC reporting and atmosphere-based global total emission for these three gases is not likely from underreporting of emissions from the USA and Europe, the two regions that account for most emissions reported to UNFCCC (~83–90%). Regional emission magnitudes derived from measurements within the USA and Europe suggest that the inventory-based reporting from these regions is accurate or even overestimated. In Europe, atmosphere-based emissions estimated for these gases have been consistent with values reported to UNFCCC in most recent years; an exception is that UNFCCC reporting for HFC-32 has increased above the atmosphere-based estimates in the most recent years (**Figure 2-5**) (Graziosi et al, 2017; Brunner et al., 2017). A similar divergence is observed in the USA for HFC-32 and HFC-125, with the UNFCCC inventory increasing faster than atmosphere-based estimates (**Figure 2-4**); this divergence is less pronounced for HFC-143a. For Japan, both atmosphere-based estimates (Saito et al., 2015; Lunt et al., 2015) and UNFCCC reporting suggest Japanese emissions are < 2 Gg yr^{-1} for each of these gases.

The absence of substantial underestimates in national emissions reported to UNFCCC for these three HFCs indicates that the factor of approximately two difference in reporting totals versus atmosphere-based global totals likely stems from significant emissions from developing countries not required to report their emissions to UNFCCC (non-Annex I). This conclusion has also been reached in an analysis of production estimates and market demand in developing countries, based on the Montreal Protocol phase-out schedules for ODSs (Fang et al., 2016; Zhang and Wang, 2014; Velders et al., 2015).

Emissions estimates based on atmospheric measurements in East Asia confirm substantial HFC-32 emissions from non-Annex I countries. Averaged over 2010–2012, Chinese emissions of HFC-32 were estimated to be 7.0 (4.9–9.2) Gg yr^{-1} and those from South Korea were estimated at 0.43 (0.1–0.52) Gg yr^{-1} (Lunt et al., 2015). These Chinese emissions are larger than the mean emissions estimated for the USA of 3.3 ± 0.5 Gg yr^{-1} (Hu et al., 2017) or for Europe of 2.5 ± 0.9 Gg yr^{-1} (Graziosi et al., 2017) during these same years. They also are significantly larger than those from Japan (0.5–0.7 Gg yr^{-1}) (Lunt et al., 2015; Saito et al., 2015).

Consideration of HFC-32 production and consumption magnitudes along with use patterns has allowed inventory-based emission estimates in China. This analysis suggests emissions of 12 Gg yr^{-1} of HFC-32 in 2013 and 7.7 Gg yr^{-1} for 2010–2012 (Fang et al., 2016), consistent with the atmosphere-based regional estimate from Lunt et al. quoted above (7.0 [4.9–9.2] Gg yr^{-1} for 2010–2012). These results suggest that substantial emissions of HFC-32 have arisen from China as a result of the phase-out of ODSs and that

these Chinese emissions explain most if not all of the difference between global estimates and totals being reported to UNFCCC for this chemical (**Figure 2-8**).

Atmosphere-based studies also suggest substantial emissions of HFC-125 from non-Annex I countries (**Figure 2-9**). Emissions from China averaged over 2010–2012 were 5.7 (4.0–7.7) Gg yr^{-1}, and those from South Korea were substantially smaller (0.5 [0.3–0.7] Gg yr^{-1}; Lunt et al., 2015). By comparison, average emission during this period was estimated to be 7.9 ± 1.2 Gg yr^{-1} from the USA (Hu et al., 2017) and 8.6 ± 2.7 Gg yr^{-1} from Europe (Graziosi et al., 2017). Smaller emissions of 0.8 (0.3–1.5) Gg yr^{-1} were estimated from Japan for 2010–2012 (Lunt et al., 2015).

Consideration of HFC-125 production and consumption magnitudes along with use patterns has allowed inventory-based emission estimates in China. This analysis suggests emissions of 6.3 Gg yr^{-1} averaged over 2010–2012 and 12 Gg yr^{-1} of HFC-125 in 2013 (Fang et al., 2016), consistent with the atmosphere-based regional estimate from Lunt et al. (2015). While these

Figure 2-8. As in **Figure 2-6**, but for HFC-32. Here Chinese emissions are from inventory-based (Fang et al., 2016; I-1, blue triangles) and atmosphere-based (Lunt et al., 2015, a-1, yellow) estimates.

Figure 2-9. As in **Figure 2-8**, but for HFC-125.
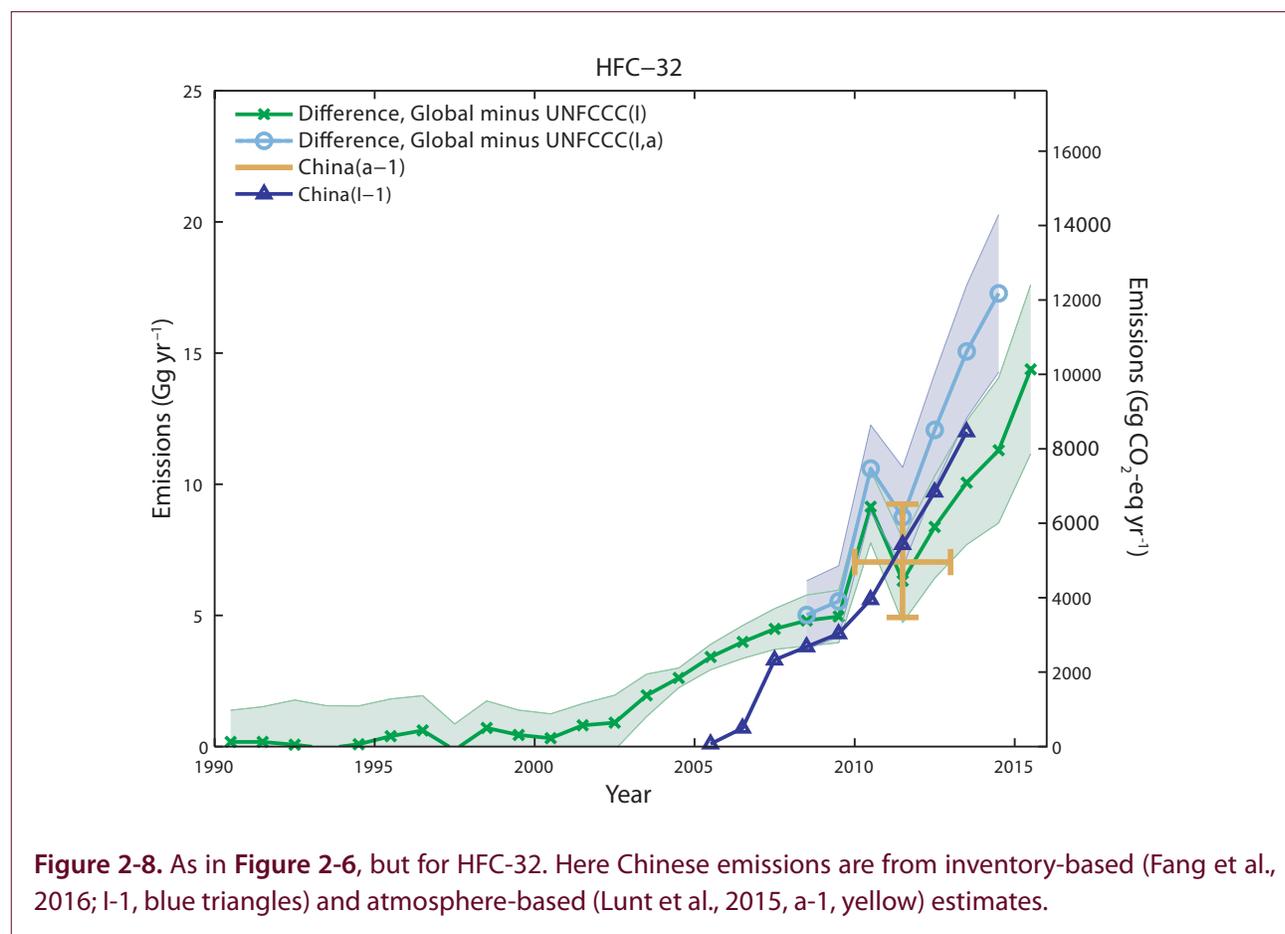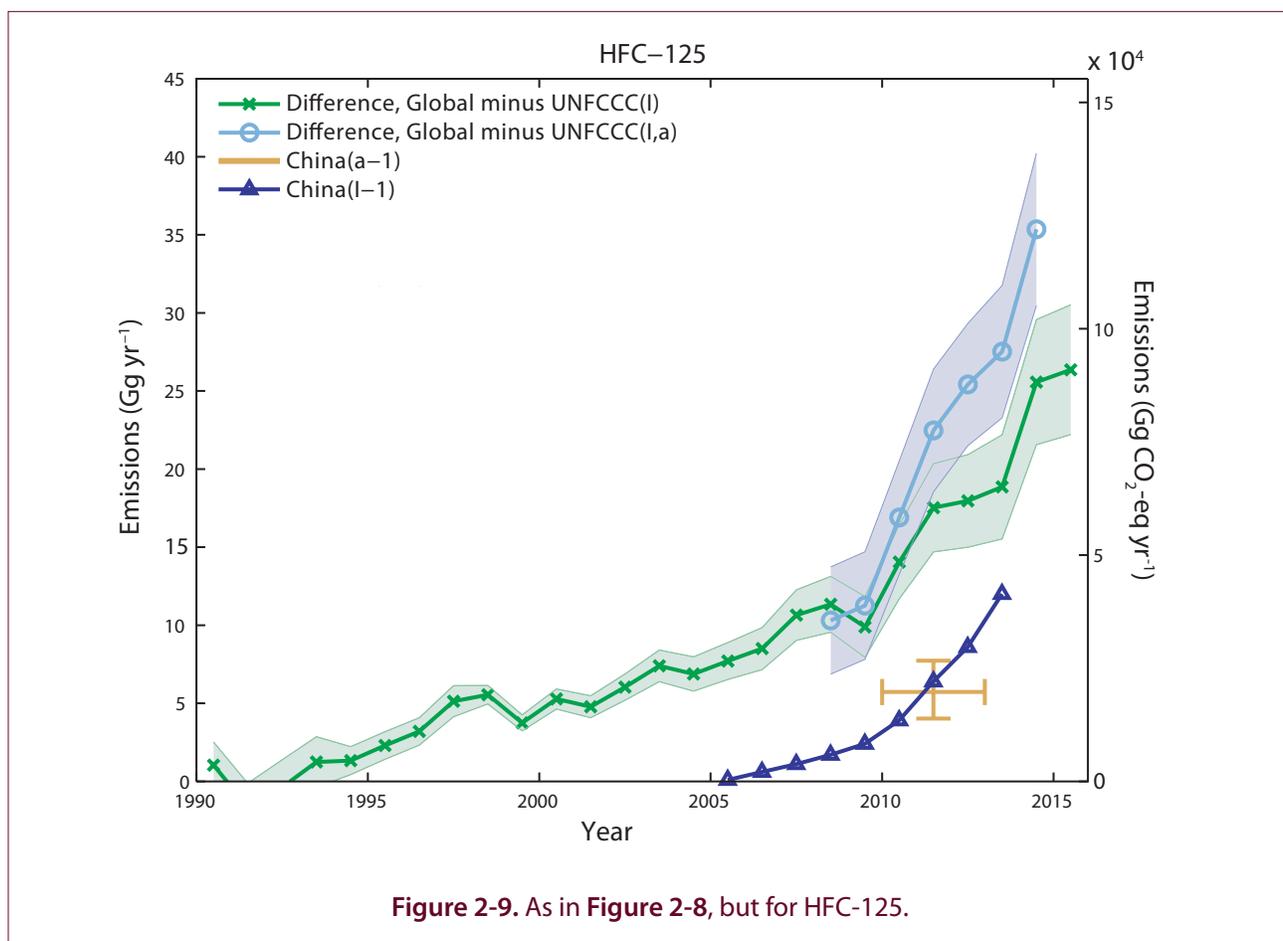
results indicate increasing emissions of HFC-125 from China during the phase-out of ODSs, they also demonstrate that Chinese emissions explain only approximately half of the difference between global emissions of HFC-125 and totals reported to UNFCCC (**Figure 2-9**). This difference suggests substantial emissions of HFC-125 from other non-Annex I countries not required to report emissions to the UNFCCC.

Atmosphere-based studies also suggest substantial emissions of HFC-143a from non-Annex I countries (**Figure 2-10**). Emissions from China averaged over 2010–2012 were 2.1 (1.3–3.1) Gg yr^{-1}, and those from South Korea were 0.13 (0.06–0.21) Gg yr^{-1} (Lunt et al., 2015). By comparison, during this period emissions of 4.2 ± 0.7 Gg yr^{-1} were estimated from the USA (Hu et al., 2017) and 6.2 ± 2.1 Gg yr^{-1} from Europe (Graziosi et al., 2017). Smaller emissions were estimated from Japan (0.3 [0.1–0.6] Gg yr^{-1}) and S.E. Australia (0.2 [0.1–0.5] Gg yr^{-1}) for 2010–2012 (Lunt et al., 2015).

Consideration of HFC-143a production and consumption magnitudes along with use patterns has allowed

inventory-based emission estimates in China. This analysis suggests Chinese emissions of 3 Gg yr^{-1} of HFC-143a in 2012 (Fang et al., 2016), consistent with the atmosphere-based regional estimate from Lunt et al. (2015), likely as a result of the phase-out of ODSs. As was true for HFC-125, Chinese emissions account for less than half of the difference between global estimates and totals being reported to UNFCCC for HFC-143a (**Figure 2-10**).

2.3.1.4 HFC-152a (CH$_3$CHF$_2$)

The global annual average HFC-152a mole fraction has varied relatively little over the past 4 years, between 6.5 and 6.8 ppt (AGAGE and NOAA data; 6.8 ppt was measured in 2012; Carpenter and Reimann et al., 2014). This is notably different from projections, which have suggested HFC-152a mole fractions would increase over time (**Figure 2-2**; Carpenter and Reimann et al., 2014; Velders et al., 2009, 2015). The global abundance in 2014 contributed a radiative forcing of 0.67 mW m^{-2}, relatively little compared to the HFCs discussed above. HFC-152a is used as a foam-blowing agent,

Figure 2-10. As in **Figure 2-8**, but for HFC-143a.
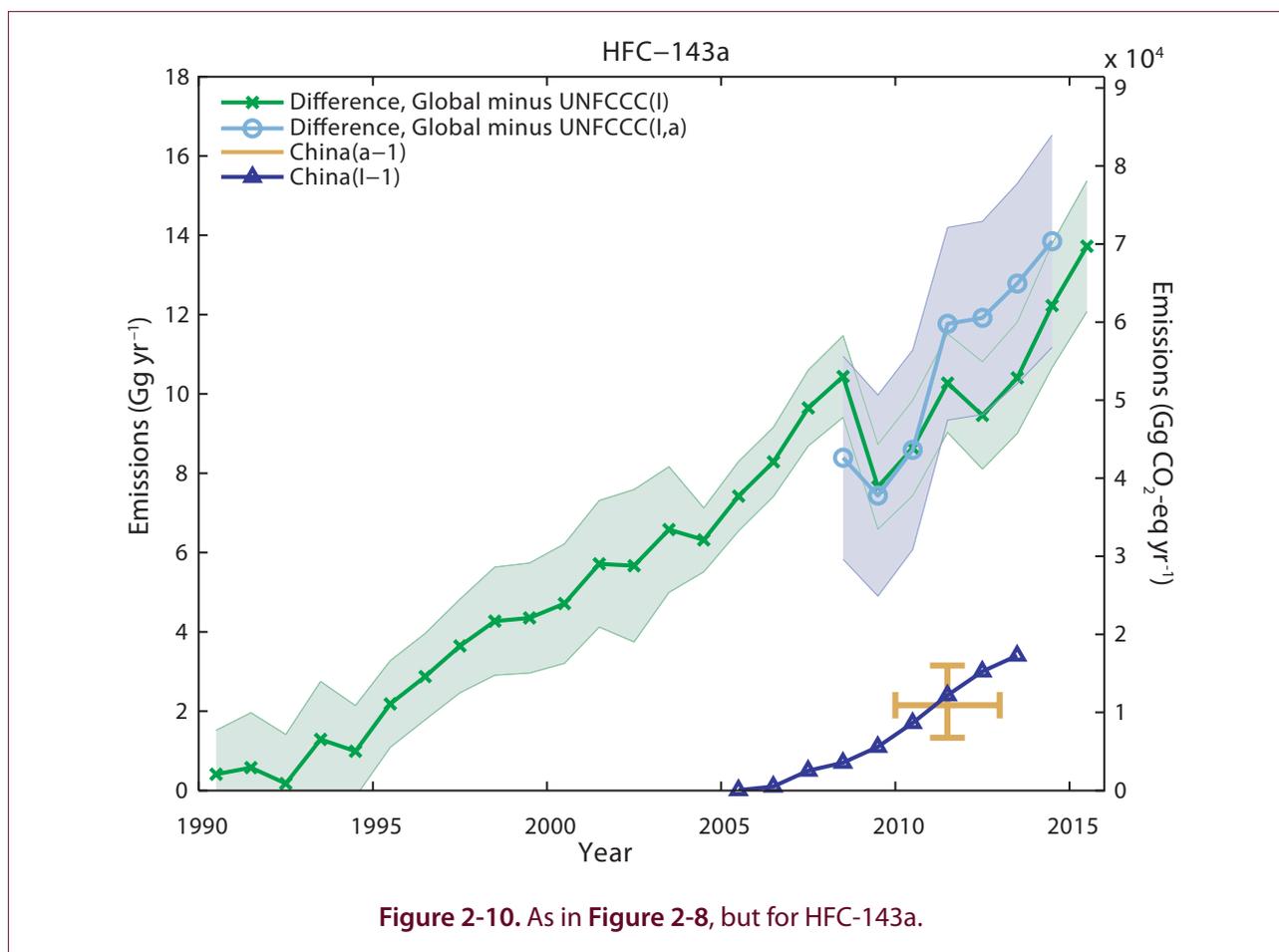
aerosol propellant, and in some refrigeration blends to replace CFCs, HCFCs, and recently HFC-134a in automobile air conditioners (Simmonds et al., 2016; UNEP, 2017a; US EPA, 2017).

Total global HFC-152a emission derived from a budget analysis of measured mole fractions at remote sites was 53 Gg yr^{-1} in 2016, not appreciably different from the 51 ± 8 Gg yr^{-1} estimated for all years since 2010 (**Figure 2-1**, update from Rigby et al., 2014, Lunt et al., 2015, Montzka et al., 2015 and Simmonds et al., 2016). While HFC-152a emissions are larger than most other HFCs, its impact on atmospheric concentrations and climate is relatively small because its lifetime (1.6 yr) and associated GWP (100-yr GWP = 148) are small compared to most other HFCs whose production and consumption is also controlled by the Kigali Amendment to the Montreal Protocol.

HFC-152a emissions reported to UNFCCC account for only 10 to 15% (6 to 7 Gg yr^{-1} for 2009–2015) of the global totals derived from measured atmospheric changes in the remote atmosphere. A likely reason for

this large difference is that emissions of HFC-152a from the USA are not included in UNFCCC totals considered here and displayed in **Figure 2-1**. This is because emissions totals of HFC-152a are only reported by the U.S. Environmental Protection Agency (EPA) to the UNFCCC together with other chemicals (HFC-227ea, HFC-245fa, HFC-43-10mee, some hydrofluoroolefins (HFOs), and some minor PFCs) owing to confidentiality issues. If half of the 10.7 MtCO$_2$-eq total reported by the USA for this mix in 2015 was due to emissions of HFC-152a, it would account for approximately 36 Gg yr^{-1} of HFC-152a emission, or most of the ~45 Gg difference shown in **Figure 2-1** between reported and atmosphere measurement-derived estimates in recent years.

Atmospheric observations from limited regions using different modeling/inversion techniques provide evidence for substantial USA HFC-152a emissions in recent years: 10–15 Gg yr^{-1} in 2005–2006 (Stohl et al., 2009), 25 (11–50) Gg yr^{-1} in 2004–2009 (Miller et al., 2012), 32 ± 4 Gg yr^{-1} in 2008 (Barletta et al., 2011), 28

(23–33) Gg yr^{-1} in 2007–2009 and 32 (25–39) Gg yr^{-1} in 2010–2012 (Lunt et al., 2015; Simmonds et al., 2016).

HFC-152a emissions from Europe have been estimated at 2.9 Gg yr^{-1} in 2009 (Keller et al., 2012), 4.1–7.5 Gg yr^{-1} in 2007–2012 (Lunt et al., 2015; Simmonds et al., 2016), and an average of 4.1 ± 1.0 Gg yr^{-1} over 2003–2014, with a slight decreasing trend over this period (Graziosi et al., 2017; uncertainty represents 1 standard deviation of annual estimates). These magnitudes and the decreasing trend are consistent with values reported to UNFCCC over this period (Graziosi et al., 2017).

Evidence exists for substantial HFC-152a emissions from countries not required to report emissions to the UNFCCC. Atmospheric measurements in eastern Asia suggest emissions of ~5 Gg yr^{-1} (Stohl et al., 2010) and 6.8 Gg yr^{-1} (Li et al., 2011) in 2008, 6.2 (5–9) Gg yr^{-1} in 2007–2009 and 7.0 (5–10) Gg yr^{-1} in 2010–2012 (Lunt et al., 2015; Simmonds et al., 2016). A sizable fraction of these eastern Asian emissions arises from China, with estimates of 2.0–2.9 Gg yr^{-1} in 2010–2011 (Yao et al., 2012) and 3.4–5.7 Gg yr^{-1} in 2004–2005 (Yokouchi et al., 2006) and 2008 (Kim et al., 2010; Stohl et al., 2010).

2.3.1.5 HFC-245fa (CHF$_2$CH$_2$CF$_3$), HFC-365mfc (CH$_3$CF$_2$CH$_2$CF$_3$), HFC-227ea (CF$_3$CHFCF$_3$), HFC-236fa (CF$_3$CH$_2$CF$_3$)

HFC-245fa and HFC-365mfc (normally blended with HFC-227ea to reduce flammability) replace HCFC-141b in polyurethane structural foam blowing, and they have potential uses in solvent applications and medical aerosols; HFC-245fa is also used in small quantities in centrifugal chillers (Vollmer et al., 2006; Stemmler et al., 2007; Laube et al., 2010; UNEP, 2010; Vollmer et al., 2011; UNEP, 2016b). The global mean mole fraction of both gases continues to steadily increase. The global mean estimated for HFC-245fa (AGAGE data) for 2016 was 2.4 ppt, up from 1.7 ppt in 2012, with an annual increase of +0.2 ppt yr^{-1} (8.9% yr^{-1}) from 2015 to 2016 (**Table 2-3**). For HFC-365mfc, networks report a global average of 0.94 (0.87–1.00) ppt, up from 0.67 ppt in 2012, with a growth rate of +0.08 ppt yr^{-1} (9.2% yr^{-1}) (NOAA and AGAGE data; **Table 2-3**).

HFC-227ea and HFC-236fa are used as fire retardants to replace halon-1211 and halon-1301; HFC-227ea is also used in mixtures with other HFCs as a propellant in metered-dose inhalers and in blends with HFC-365mfc in polyurethane foam blowing; HFC-236fa is also used as a coolant in specialized applications (UNEP, 2010; Vollmer et al., 2011; UNEP, 2014b, 2016b; US EPA, 2017). Global mean mole fractions of both compounds are relatively small but continue to increase steadily in the atmosphere. For 2016, a global average of 1.21 (1.17–1.24) ppt is estimated for HFC-227ea, up from 0.81 ppt in 2012 (NOAA and AGAGE data). The global mean estimated for HFC-236fa in 2016 was 0.15 ppt (AGAGE data), up from 0.11 ppt in 2012. Growth rates were 0.11 ppt yr^{-1} (9.9% yr^{-1}) for HFC-227ea and 0.01 ppt yr^{-1} (8.9% yr^{-1}) for HFC-236fa in 2015–2016 (**Table 2-3**). In 2016, the radiative forcings from these four HFCs were still very small with 0.58 mW m^{-2} from HFC-245fa, 0.21 mW m^{-2} from HFC-365mfc, 0.31 mW m^{-2} from HFC-227ea, and 0.04 mW m^{-2} from HFC-236fa.

Increases projected for global mole fractions of HFC-227ea and HFC-236fa have been fairly accurate over time, whereas those for HFC-245fa and HFC-365mfc were initially overestimated (**Figure 2-2**; Carpenter and Reimann et al., 2014; Velders et al., 2009, 2015) because of the lack of observations and production statistics for these HFCs being available when the initial projections were developed.

Total global emissions derived from a budget analysis of measured mole fractions at remote sites have increased nearly linearly in recent years for HFC-245fa (from 9.5 ± 1.5 Gg yr^{-1} in 2012 to 11.7 ± 1.9 Gg yr^{-1} in 2016), HFC-365mfc (from 3.4 ± 0.7 Gg yr^{-1} in 2012 to 4.6 ± 0.9 Gg yr^{-1} in 2016), and HFC-227ea (from 3.6 ± 0.4 Gg yr^{-1} in 2012 to 4.3 ± 0.5 Gg yr^{-1} in 2016). By contrast, HFC-236fa emissions have remained at 0.29 ± 0.07 Gg yr^{-1} since 2012 (**Figure 2-1**, update from Vollmer et al., 2011, Rigby et al., 2014 and Montzka et al., 2015).

Emissions reported to UNFCCC for these HFCs account for only a small fraction of global totals inferred from measurements at remote sites (**Figure 2-1**). Some of these discrepancies may arise because several countries report significant CO$_2$-eq emissions of "unspecified mix of HFCs" and "unspecified mix of HFCs and PFCs", likely due to confidentiality concerns. For example, the U.S. National Inventory Reports specifies that the latter category includes HFC-227ea and HFC-245fa emissions.

Few regional emission estimates exist for these four HFCs, and they only explain a small fraction of global emissions.

HFC-245fa emissions in 2014 from Europe were estimated to be 0.7 ± 0.5 Gg yr^{-1} from observations at European sites (Graziosi et al., 2017) compared to ~10 Gg yr^{-1} globally in that year. An inventory-based analysis suggests Chinese emissions of 0.07 Gg yr^{-1} in 2009 (Fang et al., 2016) compared to ~7 Gg yr^{-1} globally in that year.

HFC-365mfc emissions in 2014 were estimated to be 1.1 ± 0.4 Gg yr^{-1} from Europe (Graziosi et al., 2017) and 0.25 ± 0.1 Gg yr^{-1} from the USA (Hu et al., 2017), based on observations in these regions, compared to ~4 Gg yr^{-1} globally in that year. For 2008, Li et al. (2011) estimated East Asian emissions of 0.2–0.3 Gg yr^{-1} based on atmospheric measurements in that region, mostly from Japan, compared to global estimates of ~3 Gg yr^{-1} in that year.

HFC-227ea emissions in 2014 were estimated at 0.6 ± 0.1 Gg yr^{-1} from the USA (Hu et al., 2017) and 0.4 ± 0.2 Gg yr^{-1} from Europe (Graziosi et al., 2017) based on atmospheric measurements in those regions, compared to ~3.9 Gg yr^{-1} globally for that year. For 2009, Fang et al. (2016) estimated 0.5 Gg yr^{-1} from China based on an analysis of inventories and markets, compared to the global estimate of ~2.8 Gg yr^{-1} for that year.

HFC-236fa emissions in 2014 were 0.025 ± 0.019 Gg yr^{-1} from Europe compared to ~0.29 Gg yr^{-1} globally for that year (Graziosi et al., 2017).

2.3.1.6 HFC-43-10mee (CF$_3$CHFCHFCF$_2$CF$_3$)

HFC-43-10mee is used for cleaning applications in the electronics industry where it replaces CFC-113, methyl chloroform, and HCFC-141b; it is also used in aerosol sprays and is an alternative to PFCs in certain applications (Arnold et al., 2014; UNEP, 2016b; Le Bris et al., 2017). It continues to slowly accumulate in the atmosphere. In 2016, a global mean mole fraction of 0.27 ppt was measured, slightly up from 0.23 ppt in 2012, with a very small growth rate of 0.01 ppt yr^{-1} (4.6% yr^{-1}) in 2015–2016 (AGAGE data only; **Table 2-3**). In 2016, the resulting radiative forcing was still small at 0.10 mW m^{-2} relative to the other HFCs discussed here. Total global emissions derived from a budget analysis of measured mole fractions at remote sites were 1.1 ± 0.3 Gg yr^{-1} in 2016 and have not increased appreciably since 2007 (**Figure 2-1**, update from Arnold et al., 2014).

2.3.2 Summed Radiative Forcing and CO$_2$-eq Emissions Attributable to HFCs

The contribution to climate change from the atmospheric concentration of a long-lived trace gas at a particular point in time is expressed as a radiative forcing (Myhre and Shindell et al., 2013). Radiative forcing from all HFCs in the atmosphere approximately doubled over the past decade, reaching 30 mW m^{-2} in 2016 (**Figure 2-11**); this climate warming influence is 36% larger than the 22 mW m^{-2} reported for 2012 in the last Assessment (Carpenter and Reimann et al., 2014). Nearly half (47%) of the radiative forcing from HFCs in 2016 is attributable to HFC-134a; the next three largest contributors are HFC-23, HFC-125, and HFC-143a, which together account for 42% of the total. Total radiative forcing from HFCs in 2016 accounted for ~10% of the 0.33 W m^{-2} from ODSs (**see Chapter 1**), and it was approximately 1.0% of the 3 W m^{-2} supplied in recent years by all long-lived GHGs combined, including CO$_2$, CH$_4$, N$_2$O, ozone-depleting substances, and HFCs (Myhre and Shindell et al., 2013; more recent values are posted at: https://www.esrl.noaa.gov/gmd/aggi/aggi.html).

The time-integrated radiative forcing supplied from the emission of a given HFC includes consideration of the persistence or lifetime of HFCs. The GWP is the metric commonly used to express the time-integrated forcing from the emission of a trace gas relative to the forcing arising from the equivalent emission of CO$_2$ over a given time interval. One-hundred years is often the time interval considered, although GWPs considered over shorter time intervals (e.g., 20-yr GWPs) are substantially larger for all HFCs except one, HFC-23 (see **Table 2-2**). CO$_2$-eq emissions of HFCs have increased over time (**Figure 2-12**) and totaled 0.88 ± 0.07 GtCO$_2$-eq yr^{-1} emissions in 2016, up 23% from the 0.72 ± 0.05 GtCO$_2$-eq yr^{-1} estimated for 2012 (Carpenter and Reimann et al., 2014). HFC-134a accounted for 0.30 ± 0.03 GtCO$_2$-eq yr^{-1} in 2016, or 34% of the CO$_2$-eq emissions from all HFCs considered here. The next three largest contributors were HFC-125 (0.21 ± 0.02 GtCO$_2$-eq yr^{-1}), HFC-143a (0.14 ± 0.01 GtCO$_2$-eq yr^{-1}), and HFC-23 (0.16 ± 0.01 GtCO$_2$-eq yr^{-1}); these
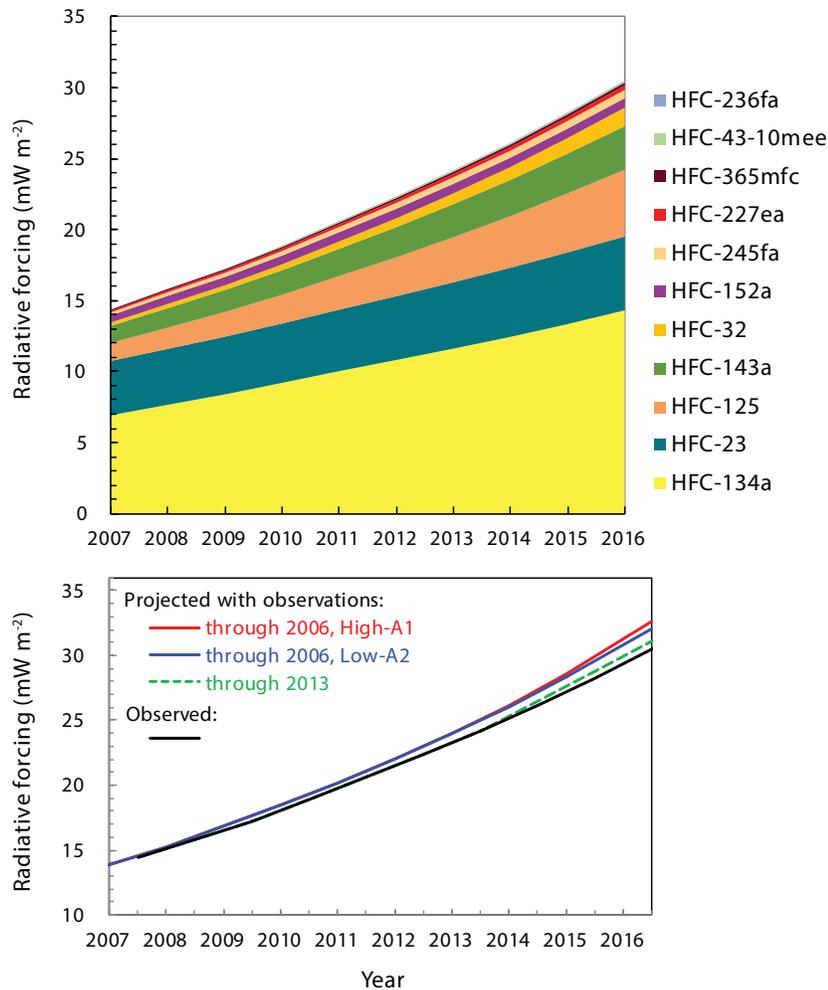
Figure 2-11. *Upper panel:* Radiative forcing supplied by individual HFCs and their sum during the past decade based on observed global mole fractions and their change over time (as given in **Figure 2-2**). These forcings are derived by multiplying measured mole fractions by radiative efficiencies (**Tables 2-1** and **2-2**). *Lower panel:* the overall observed increase in summed radiative forcing from HFCs in the upper panel (black line) was slightly less rapid than was projected nearly a decade ago based on observations through the end of 2006 and a market analysis done at that time (high and low projections from baseline scenarios in Velders et al., 2009; see **Section 2.5**). This projection analysis was updated in 2015 based on observations through 2013 (Velders et al., 2015; high and low projections overlay one another on this time scale). Radiative forcings for HFCs are derived assuming pre-industrial concentrations of zero ppt, which is consistent with the atmospheric measurement records and no known natural sources of HFCs.

top four contributors accounted for 93% of total CO_2-eq yr^{-1} emissions from HFCs in 2016.

In 2016, HFC CO_2-eq emissions were comparable to those of CFCs (0.8 ± 0.3 GtCO$_2$-eq yr^{-1}) and HCFCs (0.76 ± 0.11 GtCO$_2$-eq yr^{-1}; see **Chapter 1**), and the emissions of these HFCs represent ~1.5% of the sum all emissions from long-lived greenhouse gases in recent years (CO_2, CH_4, N_2O, and halocarbons; Montzka et al., 2011, updated).

2.3.3 Comparison of Recent Observed Changes Versus Projections Made in the Past

Large increases in emissions, mole fractions, and radiative forcing from HFCs were projected for the future before an amendment to the Montreal Protocol was agreed in Kigali in 2016 (Velders et al., 2009; Gschrey et al., 2011; Velders et al., 2015; UNEP, 2014c; see **Section 2.3**). Atmospheric measurements through
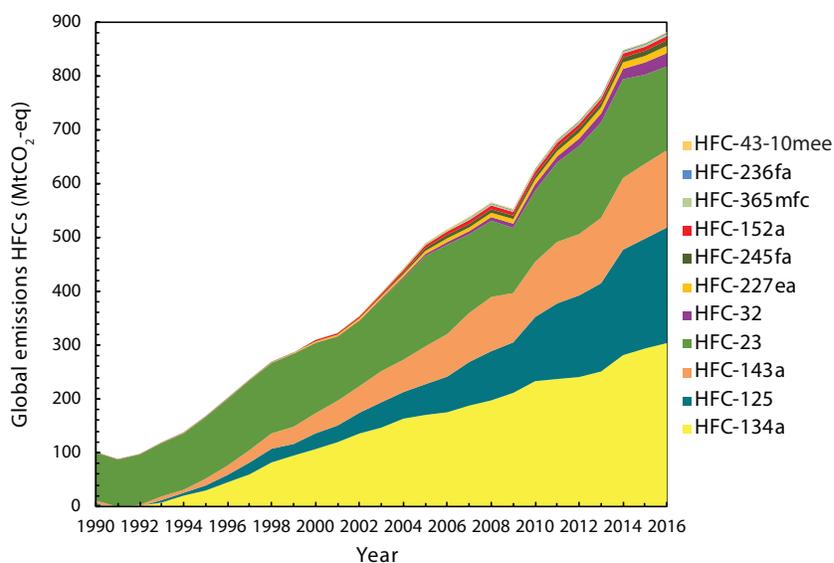
Figure 2-12. Global emissions of HFCs (MtCO$_2$-eq) derived from a budget analysis of global observations (see **Figure 2-1**; mean of AGAGE & NOAA network results when both are available) using the AGAGE 12-box model (Rigby et al., 2016). Emissions are weighted by 100-yr GWP to consider the heating supplied by these chemicals integrated over a 100-yr period relative to an equivalent emission of CO$_2$.

2016 show that mole fractions of most HFCs increased over the previous decade at rates similar to those projected in a baseline scenario created nearly a decade earlier based on an analysis of atmospheric data and market trends through 2006 (Velders et al., 2009). This baseline scenario has been updated to include data through 2012 (Velders et al., 2015). This consistency is noted for those HFCs currently contributing the most to radiative forcing and CO$_2$-eq emissions (**Figures 2-1 and 2-2**). Some less abundant HFCs (e.g., HFC-152a, HFC-245fa, and HFC-365mfc) have increased substantially more slowly than was projected. As a result, radiative forcing from the sum of HFCs used as ODS substitutes (i.e., not including HFC-23) increased slightly more slowly than in the baseline projections created nearly a decade ago (**Figure 2-11**).

These results indicate that mole fractions and emissions for most HFCs have continued to change in a fairly predictable manner during the global phase-out of CFC and HCFC production and consumption. These projections included a slowdown in the HFC emission increases from non-Article 5 countries (also referred to as Article 2 countries or Parties to the Montreal Protocol) and, beginning in the mid-2000s, significant contributions from Article 5 countries that were projected to increase substantially after the 2013

cap on global HCFC production. These projections did not include country- and region-specific controls that were introduced or were being considered during that decade (see **Section 2.5.1.2**), except the 2006 EU MAC directive (EU, 2006), and this likely explains in part the slightly slower increases in summed radiative forcing from HFCs in observations compared to projections in **Figure 2-11**. While production and consumption of some HFCs are capped in the future by controls outlined in the Kigali Amendment (see **Section 2.5.1.3** and **Table 2-1**), they may temporarily increase in some countries in the future, particularly those countries for which caps on production and consumption limit these quantities beginning in 2024 or 2028 based on baseline magnitudes determined for future years (e.g., 2020–2022 or 2024–2026, depending on developing country Group; **Table 2-1**).

2.3.4 Aggregate Sums of HFC Emissions Reported to the UNFCCC and Contributions from Non-Reporting Countries

Throughout **Section 2.3**, substantial differences were noted for all HFCs between total emissions reported to the UNFCCC and global total emissions estimated from atmospheric data. Those differences have
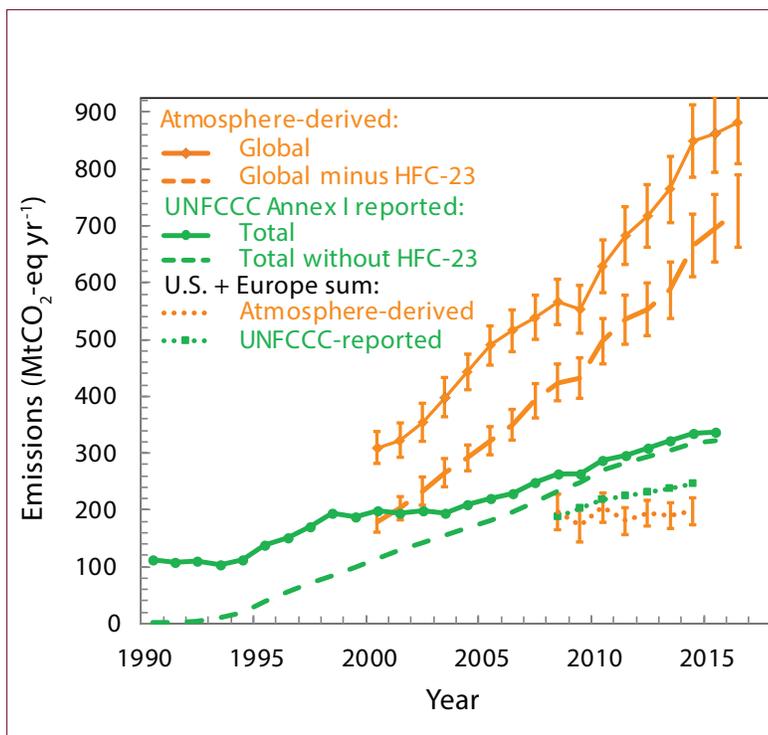
Figure 2-13. Summed HFC emissions, expressed as CO_2-eq, reported to UNFCCC (UNFCCC 2017) and based on atmospheric measurements, for the global and for the sum of the U.S. and European regions. (Global emission values from **Figure 2-1**; measurement-based regional estimates for the U.S. and Europe are taken from **Figure 2-4** and **Figure 2-5**). Sums including emissions of HFC-23 (solid lines) and without HFC-23 (dashed lines) are shown. Uncertainties on global estimates represent one standard deviation of estimates (see **Figure 2-1**); Uncertainties on regional estimates are approximate, based on the range and standard deviation quoted in the original sources (Graziosi et al., 2017 and Hu et al., 2017).

continued to grow over time for most gases (**Figure 2-1**) and in the aggregate of total HFC emission (**Figure 2-13**). On a CO_2-eq basis, aggregate HFC emissions reported to the UNFCCC in 2015, the latest year for which UNFCCC reporting is available, accounted for only 39% of the total global HFC emissions derived from global atmospheric mole fraction changes measured in the remote atmosphere; this value increases to 46% if emissions of only those HFCs used as ODS substitutes are considered (i.e., not HFC-23) (**Figure 2-13**).

Inverse analyses of atmospheric measurements made in the USA and in Europe suggest aggregate HFC emissions from these regions may actually be somewhat lower (by 10 to 20% in recent years, excluding HFC-23 emissions) than the totals reported to UNFCCC. Given that HFC emissions from the USA and Europe accounted for over 80% of total HFC emission reported to the UNFCCC for 2015 (excluding HFC-23; **Figure 2-13**), it is unlikely that inaccurate emission reporting from Annex I countries explains the increasing gap between global emissions derived from atmospheric data and totals reported to UNFCCC.

The dramatic increase in this emission gap over time is consistent with substantial increases in HFC use in developing countries not obligated to report emissions

to the UNFCCC, as had been projected (Velders et al., 2009, 2015; Gschrey et al., 2011). Inverse analyses of atmospheric measurements of HFCs in East Asia support this conclusion (see **Section 2.3.1**). Furthermore, for some HFCs, such as HFC-23 and HFC-32, emissions from China or East Asia explain most, if not all, of the unreported emissions (see **Figures 2-7 and 2-8**). For other HFCs (HFC-134a, HFC-125, and HFC-143a), emissions from China or East Asia account for only a fraction of unreported emissions (see **Figures 2-9 and 2-10**).

2.3.5   Next Generation Substitutes

2.3.5.1 HFC-1234yf ($CF_3CF=CH_2$) AND HFC-1234ze*(E)* (*(E)*-$CF_3CH=CHF$)

Unsaturated HFCs, also known as hydrofluoroolefins (HFOs), are being used as substitutes for higher GWP-HFCs in a number of applications. Given their short lifetimes and small GWPs, they are not included as controlled substances in the Kigali Amendment to the Montreal Protocol. HFC-1234yf and HFC-1234ze(E) are hydrofluoroolefins with estimated tropospheric OH-lifetimes of 12 days and 19 days, respectively, (**Table 2-2**) and 100-yr GWPs of less than 1 (Hodnebrog et al., 2013). HFC-1234yf has been identified as the main replacement for HFC-134a in MAC

Table 2-4. Composition of HFC blends referenced in this chapter

HFC Blend	Composition	100-yr GWP *
R-404A	44% HFC-125, 52% HFC-143a, 4% HFC-134a	4,210
R-407A	20% HFC-32, 40% HFC-125, 40% HFC-134a	2,070
R-407C	23% HFC-32, 25% HFC-125, 52% HFC-134a	1,730
R-407F	30% HFC-32, 30% HFC-125, 40% HFC-134a	1,790
R-410A	50% HFC-32, 50% HFC-125	2,080
R-446A of L-41 or L-41-1	68% HFC-32, 29% HFC=1234ze(E), 3% isobutane	480
R-447A or L-41-2	68% HFC-32, 3.5% HFC-125, 28.5 HFC-1234ze(e)	600
R-448A	26% HFC-32, 26% HFC-125, 20% HFC-1234yf, 21% HFC-134a, 7% HFC-1234ze(E)	1,370
R-449A	24.3% HFC-32, 24.7% HFC-125, 25.3% HFC-1234yf, 25.7% HFC-134a	1,370
R-449B	25.2% HFC-32, 24.3% HFC-125, 23.2% HFC-1234yf, 27.3% HFC-134a	1,390
R-450A	58% HFC-1234ze(E), 42% HFC-134a	570
R-452B or DR55	67% HFC-32, 7% HFC-125, 26% HFC-1234yf	715
R-459A or ARM71a	68% HFC-32, 26% HFC-1234yf, 6% HFC-1234ze(E)	480
R-513A	56% HFC-1234yf, 44% HFC-134a	600
DR5	72.5% HFC-32, 27.5% HFC-1234yf	510
L-41a	73% HFC-32, 15% HFC-1234yf, 12% HFC-1234ze(E)	515
L-41b	73% HFC-32, 27% HFC-1234ze(E)	515
ARM70a	50% HFC-32, 10% HFC-134a, 40% HFC-1234yf	490
D2Y60	40% HFC-32, 60% HFC-1234yf	282
HPR2A	76% HFC-32, 6% HFC-134a, 18% 1234ze(E)	615
HPR1D	60% HFC-32, 6% CO_2, 34% HFC-1234ze(E)	425

* 100-yr GWPs (Global Warming Potentials from this assessment) are calculated as the global warming influence of this gas relative to that by an equivalent mass emission of CO_2. See additional text in the Introduction.

systems in Europe, the USA (US EPA, 2017), and other countries, although use in developing countries may be limited because of current high production costs (UNEP, 2017a). HFC-1234ze(E) could replace HFC-134a for extruded polystyrene foam blowing (possibly in blends) and perhaps in metered-dose inhalers if toxicology, flammability, and cost concerns can be addressed (US EPA, 2017; UNEP, 2017a). Both compounds are also being investigated for use in refrigeration blends with saturated HFCs to replace fluids with high GWPs (UNEP, 2017a); various blends have been found to be non-flammable and acceptable for

use (R-448A, R-449A, R-449B, R-450A, R-513A) even in domestic applications (US EPA, 2015b; 2016). See **Table 2-4** for the composition of HFC blends.

The first ambient-air measurements of these new olefinic HFCs were reported by Vollmer et al. (2015) from two sites in Switzerland (**see Figure 2-14**). In 2011, HFC-1234yf was undetectable at the high-altitude Jungfraujoch observatory, but by mid-2016 observed mole fractions were often in the 0.02–0.20 ppt range; higher values were observed at the urban Dübendorf site where they were often in the 1–4 ppt

Figure 2-14. The emergence of HFC-1234yf and HFC-1234ze(e) in the atmosphere at two European sites, the mountaintop site Jungfraujoch (3,580 meters above sea level) and the urban Dübendorf site (updated from Vollmer et al., 2015). Different colors indicate results from different sites. Results at or below the detection limit (~0.003 ppt) are plotted at 0.003 ppt. By mid-2016, 1 to 4 ppt of HFC-1234yf and ~1 ppt of HFC-1234ze(E) were regularly observed at Dübendorf, with pollution events containing up to 20 ppt of HFC-1234ze(E), suggesting that it is more prevalently used in this region.

range. HFC-1234ze(E) has been observed in most samples since the beginning of dedicated ongoing observations. By mid-2016, ~0.025 ppt was commonly observed at Jungfraujoch and ~1 ppt at Dübendorf, where pollution events containing up to 20 ppt of this HFC have been seen, suggesting more prevalent use of HFC-1234ze(E) in this region (Vollmer et al., 2015).

2.4 ATMOSPHERIC CHEMISTRY OF HFCs

2.4.1 New Developments on Loss Rates and Lifetimes

HFCs are removed from the atmosphere mainly by their reactions with hydroxyl radicals (OH) in the troposphere. The residence times of HFCs in the atmosphere determined by reaction with tropospheric OH, τ_{HFC}^{OH}, are derived from the corresponding lifetime of

methyl chloroform, CH_3CCl_3, (Spivakovsky et al., 2000) as described in previous Assessments (e.g., Box 1-1 in Carpenter and Reimann et al., 2014).

Although HFCs do not absorb stratospheric UV radiation, stratospheric loss processes, such as reactions with OH and $O(^1D)$, can contribute to the loss rate of long-lived HFCs and, therefore, slightly affect their lifetimes. Photolysis at the Lyman-a wavelength (121.6 nm) can only affect lifetimes of very long-lived species (such as perfluorinated compounds) that are inert enough to reach the mesosphere (≥ 70 km) in appreciable quantities; it has a negligible effect on the lifetimes of HFCs. Recent intensive modeling efforts (SPARC, 2013) provide detailed information on model-derived total lifetimes for a number of compounds, partial lifetimes due to specific photochemical

removal processes (reactions with OH, reactions with O(^{1}D), and photolysis), and partial lifetimes associated with the atmospheric removal regions (troposphere and stratosphere). These results have been used to derive empirical correlations for estimating partial lifetimes due to stratospheric reactions of other HFCs, τ^{str}_{HFC}. The total atmospheric lifetimes, τ_{HFC}, reported in **Table 2-2** have been calculated as $(\tau_{HFC})^{-1} = (\tau^{OH}_{HFC})^{-1} + (\tau^{str}_{HFC})^{-1}$ to account for the stratospheric loss of HFCs.

Table 2-2 presents updated estimates of the lifetimes for partially fluorinated alkanes (HFCs), partially fluorinated olefins (HFCs that are also called HFOs) and perfluorinated olefins. The abundances of HFOs and perfluorinated olefins are also primarily controlled by their reactions with the hydroxyl radical. Compounds with atmospheric lifetimes shorter than ~0.5 years have been designated as very short-lived substances (VSLSs) as in previous Assessments. These compounds generally have non-uniform tropospheric distributions because their lifetimes are comparable to or shorter than the characteristic time of mixing processes in the troposphere.

The lifetime of VSLSs released into the atmosphere depends on local atmospheric conditions at the emission location and, therefore, the concept of a single global lifetime is inappropriate (e.g., Hodnebrog et al., 2013 and previous Ozone Assessment reports). Hence, the VSLS lifetimes presented in **Table 2-2** (with units of days) should not be considered as the global average atmospheric lifetime of a VSLS once emitted. Nevertheless, these estimates provide a useful scaling among such compounds and distinguish them from longer-lived HFCs that are well mixed in the troposphere. It should be noted that the local lifetimes of VSLSs tabulated in this report are ~10–20% longer than in previous Assessments primarily because they have now been calculated with the same approach that is used for longer-lived HFCs (i.e., relative to the global mean lifetime of methyl chloroform against OH oxidation), thereby avoiding arbitrary differences arising from the use of two different approaches.

For a few compounds in **Table 2-2**, experimental data on OH reactivity are not available. Lifetimes for these gases have been estimated based on either structure activity relationships or reactivity trends among similar compounds and appear in italics in **Table 2-2**.

OH reactivity for several compounds has been revised since the last Assessment based on new experimental data and/or analyses. However, these revisions do not substantially change the recommended atmospheric lifetimes. Other changes since the previous Assessment are listed below. (References related to these updates can be found in the notes to **Table 2-2**):

- HFC-72-17p, $CHF_2(CF_2)_6CF_3$, has been added.

- The lifetime of HFC-245cb is 15% shorter than estimated previously based on an analogy to HFC-143a. This revision reflects a new recommendation (Burkholder et al., 2015b), which is now based on laboratory-measured OH reactivity data.

- The estimated lifetime of HFC-272ca ($CH_3CF_2CH_3$) is based on OH reactivity calculated using the structure activity relationships. There are no experimental data.

- Lifetimes of shorter-lived HFC-152 (CH_2FCH_2F), HFC-161 (CH_3CH_2F), and HFC-281ea (CH_3CHFCH_3) are estimated to be ~18% longer than previous estimates. This revision is the result of the estimates now being made in a manner consistent with other HFCs.

- The list of fluorinated olefins has been expanded to include 7 new chemicals including stereo-isomers with different lifetimes and cyclic unsaturated fluorocarbons.

- The lifetimes of (E)-$CF_3CH{=}CHCF_3$ and (E)-$CF_3CH{=}CHCF_2CF_3$ are a factor of ~6 longer because experimental data on the OH reactivity of (E)-$CF_3CH{=}CHCF_3$ became available for the first time since the last Assessment.

- The lifetime of perfluorocyclopentene is more than an order of magnitude longer because experimental data on its reactivity toward OH became available for the first time since the last Assessment.

2.4.2 Updates on TFA Formation and Tropospheric Ozone Formation

Trifluoroacetic acid (TFA; CF_3COOH) is produced as the result of the breakdown in the atmosphere of several HCFCs and HFCs, such as HCFC-123 and HCFC-124, HFC-134a, HFC-143a, HFC-1234yf, and possibly HFC-1234ze (Burkholder et al., 2015a; Wallington et

al., 2015; Javadi et al., 2008). TFA is also produced as a breakdown product of a large number of other chemicals and is produced synthetically by the chemical industry, resulting, in many cases, in direct release to the atmosphere (Solomon et al., 2016). TFA also arises from natural processes. TFA is a stable compound that can accumulate in lakes and the ocean. As an acid or as a salt, TFA is of low to moderate toxicity to a range of organisms. The salts of TFA are inert and not of toxicological or environmental concern in the small concentrations (~200 ng L^{-1}) that are present in the ocean (UNEP, 2014a). The contribution of most sources to the total TFA budget is uncertain, although the source strength from atmospheric oxidation of HCFCs and HFCs is now better quantified.

Solomon et al. (2016) estimated TFA added to the oceans as a result of unregulated use of HCFCs and HFCs (including HFOs) up to 2050. Under an upper range scenario of global HFC use (Velders et al., 2015), it was estimated that by 2050 the total additional contribution of TFA to the oceans would be less than 7.5% of the approximately 200 ng acid equivalents L^{-1} estimated to be present at the start of the millennium (Solomon et al., 2016). With the 2016 Kigali Amendment to the Montreal Protocol, the projected use of HFCs is expected to be much lower (see **Section 3.1**) with consequently lower estimated TFA production from HFCs. Increased use of HFOs could augment TFA production and partially offset reductions in TFA production from saturated HFCs. The environmental effects of TFA, from the breakdown of HCFCs and HFCs, are therefore considered too small to be a risk to the environment over the next few decades (Solomon et al., 2016). However, potential longer-term impacts could require future evaluation due to the environmental persistence of TFA, uncertainty in future uses of HFOs, and because of uncertainties in the global budget of TFA. See **Section 6.2.6** for more information on TFA.

The atmospheric degradation of HFC-1234yf (an HFO) can also contribute tropospheric ozone and thereby contribute to reduced air quality. Luecken et al. (2010) showed that the additional tropospheric ozone from the conversion of HFC-134a to HFC-1234yf in mobile air conditioners in the USA is small compared with ambient ozone levels in cities in the USA.

2.5   POTENTIAL FUTURE CHANGES

Projections have suggested that the use and emissions of HFCs could increase substantially with the phase-out of HCFCs in developed countries by 2030 and in developing countries by 2040 (Velders et al., 2009; Gschrey et al. 2011; Rigby et al., 2014; Velders et al., 2015; UNEP, 2014c; Fang et al., 2016; Purohit and Höglund-Isaksson, 2017). Because many HFCs in use currently have high GWPs and these HFCs leak from appliances and other applications, they contribute to the radiative forcing (RF) of climate. The 2016 Kigali Amendment requires large reductions (up to 85% by 2035 or 2045 relative to a base level) for GWP-weighted HFC production and consumption for all developed and developing countries.

2.5.1   Scenarios

In this section, HFC scenarios developed elsewhere—with and without the implementation of the Kigali Amendment—are discussed, including their implications for radiative forcing of climate. Also discussed are alternatives to HFCs and factors that might be relevant for future HFC use.

2.5.1.1 HFC Scenarios Without Consideration of Controls: "Baseline" Scenarios

The Kigali Amendment of October 2016, assuming global implementation, will significantly affect the future demand for HFCs in developed and developing countries and consequently their emissions, mixing ratios, and radiative forcing of climate. The effects of the Amendment can be viewed relative to HFC baseline scenarios that were constructed in the past without including specific global control measures on HFC production or consumption. Here the results of several of these HFC baseline scenarios are compared before discussing the effects of the Kigali Amendment on future HFC emissions (**Section 2.5.1.3**). HFC-23 is not considered in these scenarios since it is not used as a replacement compound in applications that traditionally used ODSs, and it is also in a separate group in the Kigali Amendment (see **Section 2.5.1.5**).

In **Figure 2-15** the GWP-weighted emissions and corresponding radiative forcings are shown for HFCs in several of these baseline scenarios. The projected emissions in Velders et al. (2015) are an update of

Figure 2-15. HFC emissions and radiative forcing scenarios from baseline scenarios (excluding HFC-23) from Velders et al. (2009), Gschrey et al. (2011), RCPs (Meinshausen et al., 2011), UNEP (2014c), Velders et al. (2015), and Purohit and Höglund-Isaksson (2017). The Velders et al. (2009) scenarios are shown, because they were the reference scenarios in the previous (2014) Assessment. The emissions and radiative forcing shown here are based on the GWPs and radiative efficiencies in the corresponding publications, which may differ from those in **Table 2-2**; the difference in CO_2-eq emissions is less than 1%.

those of Velders et al. (2009) based on more detailed and more current information on HFC use by sector and region. The scenarios of Velders et al. (2009) are shown here because they were the reference scenarios in the previous Assessment (Harris and Wuebbles et al., 2014). The HFC emissions in Velders et al. (2015) are similar to those in UNEP (2014c); they are slightly higher than projected in other sector-specific scenarios (Gschrey et al., 2011; Purohit and Höglund-Isaksson, 2017; Höglund-Isaksson et al., 2017); and they are significantly higher than in the Representative Concentration Pathways (RCPs) scenarios (Meinshausen et al., 2011). The latter two scenarios included different assumptions for the HCFC replacement pattern and/or different growth rate projections for HFC use in applications. In these scenarios, the lifetimes of the HFCs are kept constant. Model calculations show that HFC lifetimes might change towards 2100 due to changes in temperatures and OH abundances. Most models show a decrease in lifetime

by 5–10% in 2100 relative to 2000 (SPARC, 2013). These changes depend on the future greenhouse gas abundances and are highly uncertain.

The recent sector- and region-specific HFC baseline scenarios of Velders et al. (2015) (**Figure 2-16**) assume that current uses (substances and technologies) of HFCs for specific sectors would continue without control measures and that developing countries would follow the same transitions from HCFCs to HFCs and not-in-kind alternatives as has occurred in developed countries, but at a later time. So these scenarios do not take into account the 2016 Kigali Amendment or the recent regulations of HFC use in the EU (revised F-gas regulation of the European Union; EU, 2014), USA (US EPA, 2015a) and Japan (METI, 2015). The scenarios are based on (1) robust historical HFC consumption data by sector for developed countries derived from their UNFCCC National Inventory Submissions (UNFCCC, 2014), (2) historical HFC consumption

Figure 2-16. Regional and sectoral contributions to HFC GWP-weighted emissions for the upper-range base-line scenario of Velders et al. (2015), excluding HFC-23. The percentages refer to the global average relative contributions of each sector to the total GWP-weighted emissions in 2050. In the scenario, 10 HFCs are considered. The 11 regions are Europe, USA, Japan, other OECD countries, States of the former Soviet Republics and Yugoslavia (Russia), China, India, other Asian countries, Middle and Southern Africa, Latin America, and the Middle East plus Northern Africa. The six use sectors are (1) industrial, commercial (open compressor), commercial (hermetically sealed compressor), and transport refrigeration, (2) stationary AC, (3) mobile AC, (4) domestic refrigeration, (5) foams—extruded polystyrene, polyurethane, and open cell foams, and (6) other—aerosol products, fire extinguishing systems, and solvents. The emissions shown here are based on the GWPs used in Velders et al. (2015), which differ somewhat from those in **Table 2-2**; the difference in CO_2-eq emissions is less than 1%.

data for China (Zhang and Wang, 2014) and some other developing countries, (3) historical HCFC consumption data from UNEP (2015), (4) replacements pattern of HCFCs by HFCs and not-in-kind technologies (Velders et al., 2009; 2015), (5) scenarios of gross domestic product (GDP) and population from Shared Socioeconomic Pathway (SSP) projections (O'Neill et al., 2012) as drivers for the demand for HFCs, (6) observed atmospheric abundances of HFCs from 1990 to the beginning of 2013 as constraints on the historical consumption data, and (7) leakage rates (i.e., emission factors) derived from the UNFCCC National Inventory Submissions; these are kept constant over time in the scenarios.

The largest historical HFC use and emissions are in the developed countries, primarily the USA, EU, and Japan (**Figure 2-16**). In the baseline scenario, China is projected to become the largest emitter of HFCs by 2020, and Chinese emissions are projected to reach 31% of total CO_2-eq emissions (100-yr time horizon) of all HFCs by 2050 in the upper range HFC scenario (Velders et al., 2015). In all countries or regions, the largest contributions in CO_2-eq emissions come from industrial and commercial refrigeration (range of 40–58% for the different regions by 2050), because of the large use of HFCs and relatively large leakage rates from these applications, while the second largest HFC source comes from stationary air conditioning (AC) (21–40% by 2050) (**Figure 2-16**). Historically, mobile

AC has been responsible for the largest fraction of CO_2-eq HFC emissions, but this sector is projected to account for only 10–18% of developed country emissions by 2050. In developing countries in these scenarios, mobile AC contributes only 3–12% of total CO_2-eq HFC emissions in 2050. It should be noted that this baseline scenario does not include the effects in the EU and potentially around the globe of the EU MAC directive which has recently banned the use of HFC-134a in new cars (see **Section 2.5.1.2**).

In 2050, in the scenarios of Velders et al. (2015), CO_2-eq HFC emissions (excluding HFC-23) sum to 0.8–1.0 $GtCO_2$-eq yr^{-1} for the developed countries and 3.2–4.4 $GtCO_2$-eq yr^{-1} for the developing countries, resulting in a global total of 4.0–5.3 $GtCO_2$-eq yr^{-1}. In comparison, these values are equivalent to 5–11% of the global CO_2 emissions in 2050 in the RCP6.0 and RCP8.5 scenarios. The HFC radiative forcing (RF) (excluding HFC-23) in 2050 in these scenarios is 0.22–0.25 W m^{-2}. In comparisons of projected growth, the 2015–2050 increase in HFC CO_2-eq emissions is 9–29% of that for CO_2 over the same time period in the RCP scenarios. These CO_2-eq emissions represent only the direct emissions of the HFCs. Indirect CO_2 emissions associated with the production of fossil fuel-derived energy used by the appliances or in other applications need to also be considered for the overall impact of HFCs on radiative forcing (see **Section 2.5.2.3**).

In the refrigeration and air conditioning sectors, pure HFCs or blends of HFCs are used as refrigerants. The most-used HFC refrigerants in the scenarios are HFC-134a and the blends R-404A (mix of HFC-125, HFC-134a, HFC-143a) and R-410A (mix of HFC-32 and HFC-125). Consequently, these HFCs are projected to have the largest future emissions by mass or CO_2-eq (**Figure 2-17**). See **Table 2-4** for more detail about the composition of HFC blends.

The assumptions about market saturation are important aspects for the projections of HFCs. In the scenarios of Velders et al. (2015) the demand for HFCs per capita in developing countries is limited to the demand per capita in the developed countries. These scenarios do not take into account the potentially higher future demand for stationary AC as a result of increased ambient temperatures due to climate change. They also do

Figure 2-17. Contributions of the different HFCs to global emissions (in Mt yr^{-1} and $GtCO_2$-eq yr^{-1}) in the upper range baseline scenario of Velders et al. (2015). The percentages refer to the relative contributions in 2050.
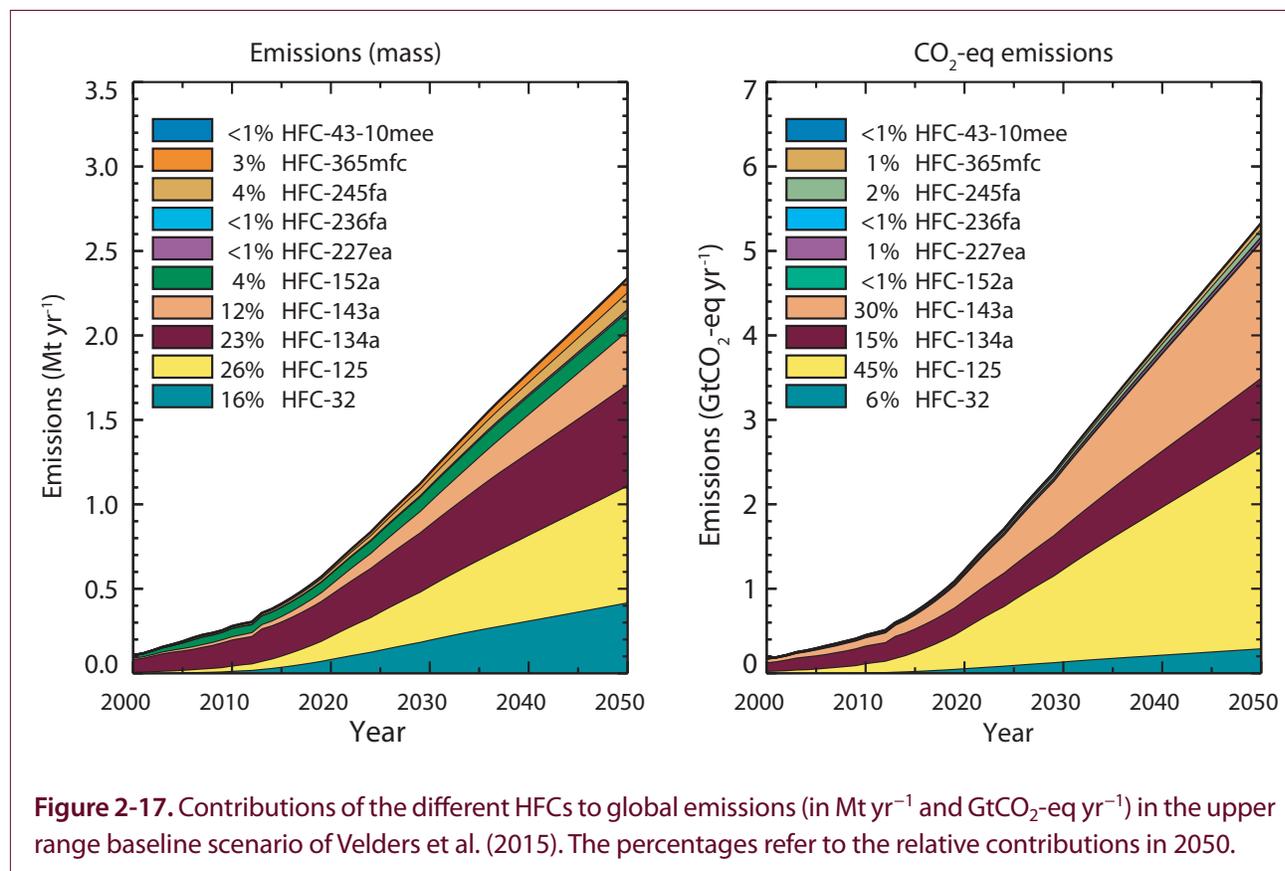
not consider the fact that many developing countries have higher ambient temperatures than the developed countries and could, therefore, have a higher demand for stationary AC and higher emissions per capita.

2.5.1.2 EFFECT OF NATIONAL AND REGIONAL HFC CONTROL MEASURES ON FUTURE PROJECTIONS

In the EU, the 2006 MAC Directive, which addresses the use of mobile air conditioning (EU, 2006), and the 2014 revised F-gas Regulation (EU, 2014) ban the use of high-GWP HFCs in certain sectors. Although there is no common definition of high- or low-GWP, in the European Union Fluorinated Greenhouse Gas Regulations, a value of 150 or higher is often referred to as high. In addition to these bans on specific HFC use, there is an HFC phasedown schedule reducing the allowable amount (GWP-weighted) of HFCs placed on the EU market starting from a cap at the 2009–2012 average in 2015 and reaching a 79% reduction by 2030 relative to that average. The USA has already implemented incentive credits for use of low-GWP refrigerants (US EPA, 2012) in support of greenhouse gas emission standards for light duty vehicles; it also removed certain high-GWP HFCs from the Significant New Alternatives Policy (SNAP) list of allowable technologies for specific sectors as of 2015 (US EPA, 2015a)[3]. Japan also adopted a regulation in 2015 to limit the use of high-GWP HFCs for specific sectors (METI, 2015).

The regulations in the EU, USA, Japan, and elsewhere likely will drive changes in sector technologies (i.e., technologies and HFC-blends that currently use high-GWP HFCs) such as refrigeration, stationary and mobile AC, and foams. Consequently, these new technologies will likely also be available for other countries, thereby increasing the climate benefits of these national regulations. With global adoption of these technologies in a revised scenario, the 2050 emissions (excluding HFC-23) in the baseline scenario of 4.0–5.3 $GtCO_2$-eq yr^{-1} are reduced to 1.5–1.9 $GtCO_2$-eq yr^{-1} following the regulations in the EU, to 1.9–2.5 $GtCO_2$-eq yr^{-1} following the regulations in

the USA, and to 2.0–2.6 $GtCO_2$-eq yr^{-1} following the regulations in Japan (**Figure 2-18**). These regulations will also lead to slower increases in radiative forcing from HFCs. The GWP-weighted emissions following the regulations are anticipated to more or less level off after 2030, at slightly more than half (reduction of 51–65%) the emissions of the baseline scenario; however, the radiative forcing continues to increase and is only reduced by 28–41% in 2050 compared to the baseline scenario because of the long atmospheric lifetimes (5–50 years) of the major high-GWP HFCs (**Figure 2-18**).

2.5.1.3 PROJECTED IMPACT OF THE KIGALI AMENDMENT

Under the Kigali Amendment there are different base level years and phasedown schedules for developed countries (non-A5 Parties) and two groups of developing countries (A5 Parties) (**Table 2-1**). Following the Amendment, the allowable GWP-weighted HFC production and consumption will have to be reduced to 15–20% of the base level by 2045–2047 for developing countries and to 15% of the base level by 2036 for developed countries.

The Kigali Amendment requires global implementation to significantly limit future radiative forcing from HFCs. The national (e.g., USA and Japan) and regional (EU) regulations (see **Section 2.5.1.3**) that are already in place will aid and accelerate developed and developing countries' efforts to meet the provisions of the Amendment. The largest effect from the Kigali Amendment, though, is expected from the reductions in HFC production and consumption in developing countries. Some reductions in HFC use might have occurred in developing countries as a result of regulations in developed countries through technology transfer, but quantifying such reductions is difficult. Instead, the Kigali Amendment ensures legally binding reductions in HFC production for the first time in both developed and developing countries. Therefore, we discuss here the reductions in emissions and radiative forcing that result from applying the phasedown of the Kigali Amendment to the global baseline scenario, acknowledging that national and regional regulations also play an important role in limiting future climate forcing from HFCs.

With compliance to the Kigali Amendment controls (**Table 2-1**) and national and regional regulations, the

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[3] In the USA, a process in the U.S. Court of Appeals is underway for SNAP rule 20, related to enabling a transition away from HFCs under Section 612 of the Clean Air Act. Implementation of the Court's direction is unclear under the EPA SNAP structure, so EPA has provided guidance stating that they will not enforce the HFC aspects of the rule while it is rewritten in compliance with the decision. (US EPA, 2018).
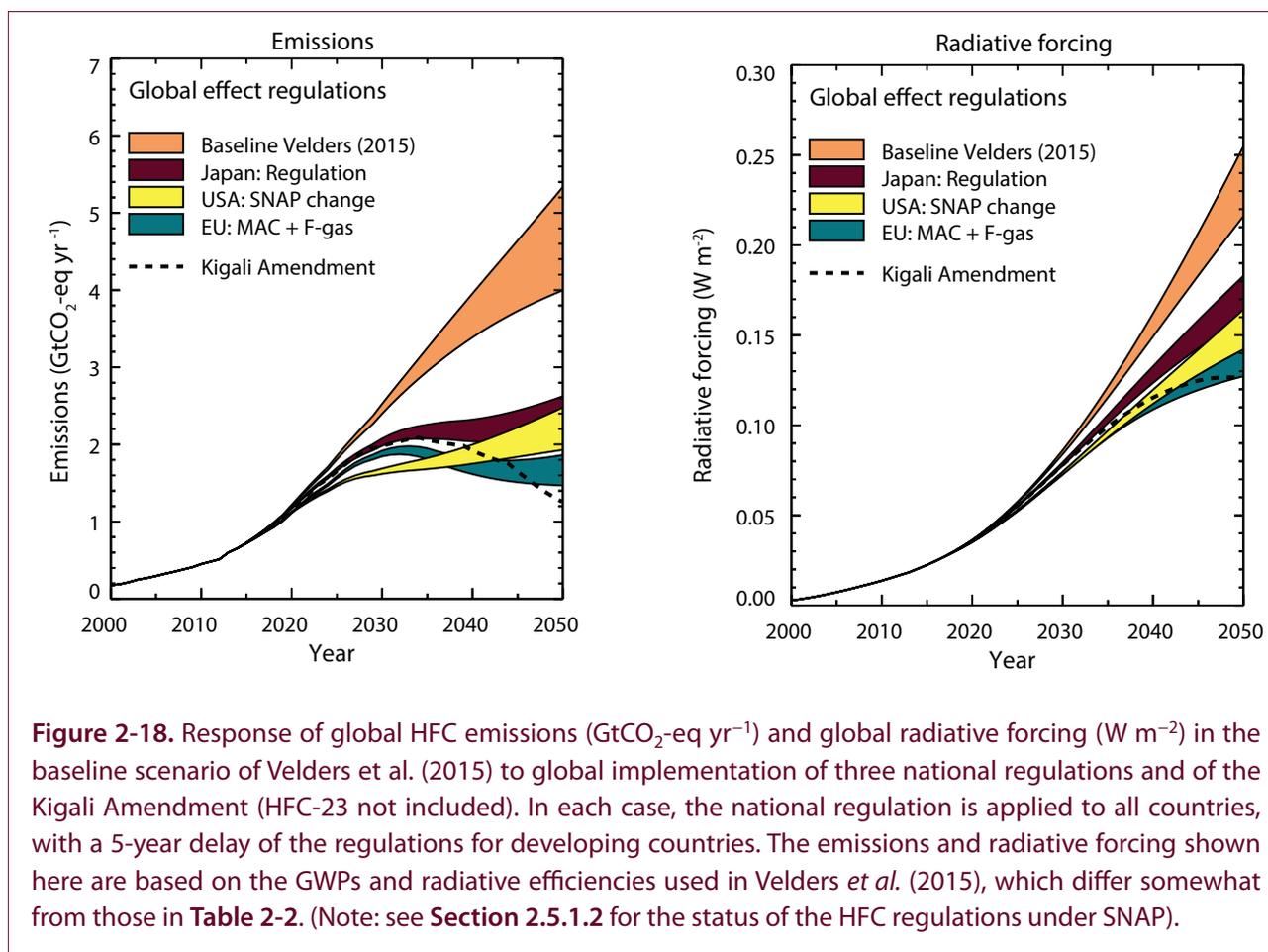
Figure 2-18. Response of global HFC emissions (GtCO$_2$-eq yr^{-1}) and global radiative forcing (W m^{-2}) in the baseline scenario of Velders et al. (2015) to global implementation of three national regulations and of the Kigali Amendment (HFC-23 not included). In each case, the national regulation is applied to all countries, with a 5-year delay of the regulations for developing countries. The emissions and radiative forcing shown here are based on the GWPs and radiative efficiencies used in Velders *et al.* (2015), which differ somewhat from those in **Table 2-2**. (Note: see **Section 2.5.1.2** for the status of the HFC regulations under SNAP).

peak in global production and consumption of HFCs is expected to occur around 2025. HFC emissions are projected to peak about a decade later (**Figures 2-18 and 2-19**; note these figures do not include HFC-23) because HFCs used as refrigerants in refrigeration and air conditioning systems are emitted gradually over a period of about a decade from the equipment during and after use (so-called banks). The total HFC bank, therefore, represents a potentially substantial source of emissions and radiative forcing even after production ceases (Velders et al., 2014). Despite this bank, adherence to controls in the Kigali Amendment results in HFC emissions from developed countries that are reduced from the baseline scenario level of 0.8–1.0 GtCO$_2$-eq yr^{-1} to 0.16 GtCO$_2$-eq yr^{-1} by 2050, and in developing countries, emissions are reduced from 3.2–4.4 GtCO$_2$-eq yr^{-1} to 1.1 GtCO$_2$-eq yr^{-1}, for a total reduction from 4.0–5.3 GtCO$_2$-eq yr^{-1} to 1.3 GtCO$_2$-eq yr^{-1}. The total reduction by 2100 is from 6.1–9.3 GtCO$_2$-eq yr^{-1} to 0.6 GtCO$_2$-eq yr^{-1}. So, the estimated benefit of the Amendment is the avoidance

of 2.8–4.1 GtCO$_2$-eq yr^{-1} emissions by 2050 and 5.6–8.7 GtCO$_2$-eq yr^{-1} by 2100. For comparison, total CH$_4$ emissions are projected to be 7.0–25 GtCO$_2$-eq yr^{-1} by 2100 in the RCP6.0 and RCP8.5 scenarios and total N$_2$O emissions 5.0–7.0 GtCO$_2$-eq yr^{-1} by 2100 (RCP emissions from Meinshausen et al., 2011; GWPs of N$_2$O and CH$_4$ from Myhre and Shindell et al., 2013).

Radiative forcing from HFCs is projected to peak around the middle of the century, or a decade after the peak in emissions, due to continued emissions from the banks and the slow breakdown of the HFCs in the atmosphere (i.e., lifetimes up to about 50 years for HFCs used as ODS substitutes). The response of the global HFC radiative forcing to the Kigali Amendment and national controls is a reduction from 0.22–0.25 W m^{-2} in the baseline scenario to 0.13 W m^{-2} by 2050, and from 0.48–0.77 W m^{-2} to 0.08 W m^{-2} by 2100. The effects of the Kigali Amendment on global emissions and RF through 2050 are similar to the effects of the different national regulations (discussed above) when implemented globally (**Figure 2-18**).

Figure 2-19. Response of HFC emissions ($GtCO_2$-eq yr^{-1}) and radiative forcing in the baseline scenario (Velders et al., 2015) for developed and developing countries to implementation of the Kigali Amendment to the Montreal Protocol (excluding HFC-23). Extending the scenarios beyond 2050 under the same assumptions gives a radiative forcing for the baseline scenario of 0.07–0.12 W m^{-2} and 0.40–0.65 W m^{-2} in 2100 for the developed and developing countries, respectively. The 2100 radiative forcing under the Kigali Amendment is 0.01 W m^{-2} and 0.06–0.07 W m^{-2} for the developed and developing countries, respectively. The emissions and radiative forcing shown here are based on the GWPs and radiative efficiencies used in Velders et al. (2015), which differ somewhat from those in **Table 2-2**.

2.5.1.4 CLIMATE IMPACTS OF HFCs

The radiative forcing from HFCs contributes to changes in atmospheric circulation, temperature, and sea level (see **Chapter 5**). Atmospheric changes in temperature and circulation arising from HFC emissions lead to a weak, indirect depletion of stratospheric ozone (Hurwitz et al. 2015). Ozone Depletion Potentials (ODPs) of the most relevant HFCs range from 0.00039 for HFC-32 to 0.03 for HFC-23 (see **Chapter 1**).

Xu et al. (2013) calculate, using a parameterized integrated carbon and radiant energy balance model, a global average surface warming by HFCs of about 0.1°C by 2050 and 0.35–0.50°C by 2100, based on the scenarios of Velders et al. (2009) (**Figure 2-20**). With a different parameterized climate model, they calculated a surface temperature change of 0.10–0.12°C for

2050 and 0.28–0.44°C for 2100 based on the scenarios of Velders et al. (2015). These scenarios differ in their assumption for the projections of the demand for HFCs past 2050 and the way potential market saturation is taken into account. To calculate the temperature response of HFCs in 2100, the emissions over the whole period from 2000 to 2100 are important. In **Figure 2-20** HFC emissions and temperature changes are shown based on the Velders et al. (2015) scenario in which the same assumptions and model are used for the period past 2050 as for 2000–2050.

With the Kigali Amendment and national and regional regulations, the future production and consumption of HFCs is strongly limited (**Table 2-1**). Under the provisions of the Amendment, the contribution of HFCs to the global average surface temperature is projected to reach a maximum around 2060, after which it slowly decreases to about 0.06°C by 2100 (**Figure**

Figure 2-20. HFC emissions and the contribution of HFCs to the global average surface warming of Earth with and without the Kigali Amendment. The scenarios without the measures are based on Xu et al. (2013) and Velders et al. (2015) which differ in their assumptions for the projections of the demand for HFCs past 2050. Also shown is a hypothetical scenario assuming that the global production of HFCs would cease in 2020. The surface temperature change based on Velders et al. (2015) is calculated using the MAGICC6 model. For comparison, the total warming from all greenhouse gases is projected to be 1.4–4.8°C by the end of the 21st century following the RCP6.0 and RCP8.5 scenarios (Collins and Knutti et al., 2013). The contribution from HFC-23 is not included here. The emissions shown here are based on the GWPs used in Velders et al. (2015), which differ somewhat from those in **Table 2-2**; the difference in CO_2-eq emissions is less than 1%.

2-20). In contrast, the surface temperature contribution from HFCs in the baseline scenario is 0.3–0.5°C in 2100 (based on Xu et al., 2013 and Velders et al., 2015). The difference in projected temperatures is relevant in the context of the 2015 UNFCCC Paris Agreement, which aims to limit the global temperature increase to well below 2°C relative to pre-industrial levels.

In **Figure 2-20**, the effects are also shown of a hypothetical scenario in which the global production of HFCs ceases in 2020. In this case, the emissions start decreasing immediately and the surface temperature contribution of the accumulated HFC emissions is projected to stay below 0.02°C for the whole 21st century. These calculated surface warmings do not include emissions from HFC-23.

Due to the thermal inertia of the ocean, the response of surface temperature and even more so sea level rise through thermal expansion is even slower than changes in radiative forcing from the controls on HFC production. After HFCs, or any other greenhouse gas, stop being emitted, the climate system is not initially in equilibrium with radiative forcing, and the ocean will continue to take up heat until equilibrium is reached (see, e.g., Zickfeld et al., 2017 and Hu et al., 2013).

Historical and projected concentrations, emissions, and contributions to climate change have been calculated for ODSs, high-GWP HFCs, and low-GWP alternatives (**Figure 2-21**), assuming full compliance with the Montreal Protocol, including the Kigali Amendment. The phase-down schedule for HFC production and consumption substantially reduces future projected global HFC emissions. Summed HFC emissions are expected to peak before 2040 and decline to less than 1 $GtCO_2$-eq yr^{-1} by 2100. This peak emission is well below summed ODS emissions at their peak
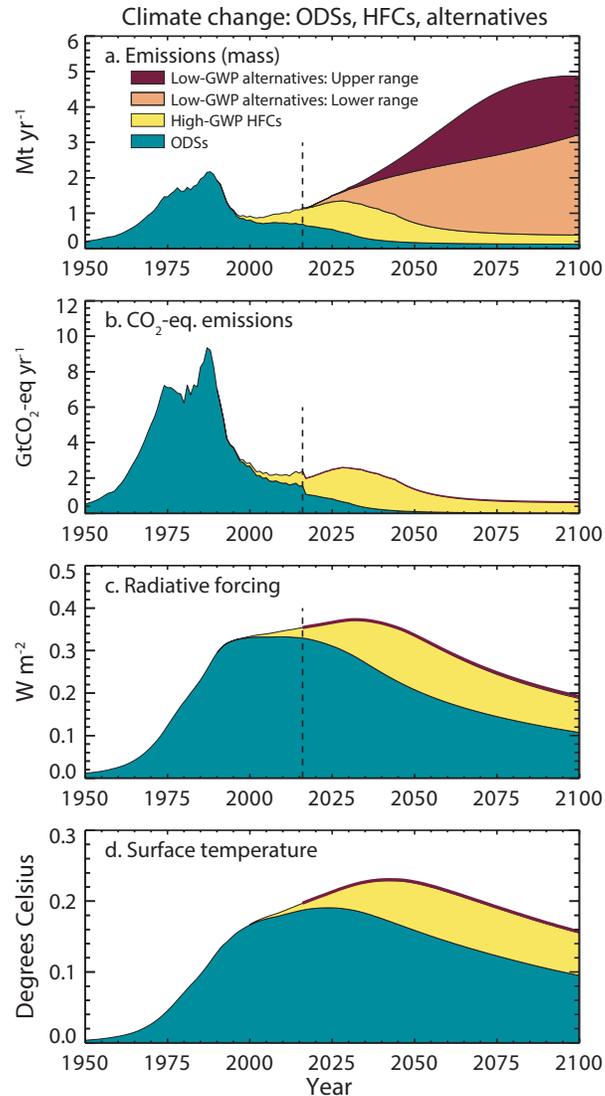
Figure 2-21. Projected contributions to climate change from ODSs, high-GWP HFCs, and low-GWP alterna-
tives assuming full compliance to the provisions of the Montreal Protocol, including the Kigali Amendment.
Shown are (a) emissions by mass, (b) CO_2-eq emissions, (c) radiative forcing, and (d) average surface tempera-
ture contributions. Only the direct GWP-weighted emissions, radiative forcing, and temperature effects of
the ODSs and HFCs are shown. The ODS data are from the baseline (A1) scenario of **Chapter 6** of this Assess-
ment. The ODS emissions from around 1980 through 2016 are derived from atmospheric observations and
after 2016 are from the scenario (distinction indicated by dashed vertical lines). The projected HFC quantities
follow the controls of the Kigali Amendment assuming full compliance (**Figure 2-20**). The projections of the
low-GWP alternatives result from imposing the controls of the Kigali Amendment to the HFC baseline sce-
nario (curve in **Figure 2-20** labeled 'without measures'; Velders et al., 2015). The difference between the HFC
baseline scenario and the Kigali Amendment scenario are assigned here to the low-GWP alternatives. These
could be chemicals with a GWP of less than 20 or alternative technologies. The low-GWP alternatives scenario
assumes that the alternatives use the same amount (by mass) per application as the HFCs they replace. The
curve with the low-GWP alternatives is based on the upper and lower range scenarios from Velders et al.
(2015) and **Figure 2-20**. The contributions of the low-GWP alternatives in panels b, c, and d are smaller than
the thickness of the green curves. Not included here are contributions from HFC-23, indirect radiative effects
from ozone depletion, and indirect effects associated with the energy used by equipment and the associated
CO_2 emissions.

in the 1980s. Only marginal increases are projected for CO_2-eq emissions of the low-GWP alternatives despite substantial projected increases in the mass of their emissions.

A more complete understanding of the climate impact of refrigerant-using equipment can be accomplished through more detailed analysis of, for example, the Life Cycle Climate Performance (LCCP), which includes direct and indirect emissions (i.e., those associated with energy use) as well as associated emissions from production and disposal (see e.g., Papasavva et al., 2010; **Section 2.5.2.3**).

2.5.1.5 HFC-23 Projection

Emissions of HFC-23 originate predominantly as a by-product of HCFC-22 production, and they have continued despite mitigation efforts. HFC-23 is a strong infrared absorber and has the longest lifetime (228 years) and highest GWP (12,690 for a 100-year time horizon; **Table 2-2**; see **Section 2.3**) of the HFCs considered in this Assessment. The amount of HFC-23 emitted depends on the amount of HCFC-22 produced, the yield of HFC-23 from the production process, and the degree to which produced HFC-23 is incinerated. Although HFC-23 is included under the phasedown schedule with other HFCs (**Table 2-1**), a separate provision is additionally included for HFC-23 in the Amendment that states: "Each country manufacturing HCFC-22 or HFCs shall ensure that starting in 2020 the emissions of HFC-23 generated in production facilities are destroyed to the extent practicable using technology approved by the Montreal Protocol" (UNEP, 2016a). Without abatement, HFC-23 emissions were projected to increase to ~20 Gg yr^{-1} by 2016 and ~24 Gg yr^{-1} by 2035 (Miller and Kuijpers, 2011). Emissions for 2016, derived from atmospheric observations, are 12.3 Gg yr^{-1}, well below the worst-case scenario, but above the best-practice scenario of ~11 Gg yr^{-1}. With implementation of the provisions of the Kigali Amendment, future HFC-23 emissions are expected to be limited significantly.

Recently, developments in chemical synthesis may have opened up the use of HFC-23 as feedstock for the production of a wide range of -CF_3 containing fluorochemicals (Grushin, 2014), which may affect future HFC-23 emissions.

2.5.2 HFC Alternatives

2.5.2.1 ALTERNATIVES: HFOS, HYDROCARBONS, CO_2, NH_3, NOT-IN-KIND ALTERNATIVES

Commercially-available alternatives with low- to medium-GWPs are available for high-GWP HFCs for many refrigeration and AC sector applications; however, more supporting work (e.g., standards development and code adoption) is needed for use of some of the lowest GWP options and fastest growing sectors, such as certain air conditioning sectors. Efforts to optimize cooling capacity and energy efficiency performance of refrigeration and air conditioning equipment containing low-GWP and zero-ODP refrigerants continue to make progress, as do standards development in all sectors.

In recent years, there has been a focus on natural refrigerants (CO_2, hydrocarbons, and ammonia), low-GWP HFCs, and HFOs alone or in blends with saturated HFCs to replace fluids with high-GWP. The use of hydrocarbons (e.g., iso-butane [R-600a] and propane [R-290]), ammonia (R-717), and carbon dioxide (R-744) continues.

European domestic refrigerator and freezer manufacturers have been required to use refrigerants with a GWP less than 150 since 2015 (EU, 2014). In the USA, domestic appliance manufacturers have created a voluntary commitment to convert away from HFC-134a use as a refrigerant (AHAM, 2016). A charge size of up to 57 g of iso-butane (R-600a) has been allowed in refrigeration and has been in commercial use for some time in self-contained refrigerated food cases and smaller domestic refrigerators (US EPA, 2011). Other options to replace HFC-134a include HFC-1234yf, HFC-152a, and non-flammable blends of HFOs and HFCs. European commercial refrigeration GWP limits are phased in gradually; limits are initially placed on HFCs with GWPs greater than 2,500, and in 2020, on HFCs with GWPs larger than 150 in applications where alternatives are available and affordable. In addition, there is a service ban on HFCs having GWPs greater than 2,500 starting in 2020 (EU, 2014). In the USA, the HFC-blend R-404A is not allowed in new equipment as of 1 January 2017 for supermarkets, as of 1 January 2018 for condensing units, and as of 1 January 2019 for self-contained systems (2020 for larger systems). High-GWP blends such as R-404A

are not allowed in new refrigerated food processing and dispensing equipment from 1 January 2021 and in new warehouse applications from 1 January 2023 (US EPA, 2015a). Canada has published draft recommendations that limit the use of fluids having GWPs above 650 starting in 2020 for stand-alone, medium temperature commercial refrigeration systems and they limit the use of fluids having GWPs above 1,500 in stand-alone low temperature commercial refrigeration (Environment and Climate Change Canada, 2017).

Low-GWP refrigerant blends of HFC/HFO/hydrochlorofluoroolefins (such as R-448A, R-449A, R-449B, R-450A, and R-513A; **Table 2-4**) have GWPs that are 50–70% lower than refrigerants they typically replace, and they are in commercial use in refrigeration equipment. The use of R-407A and R-407F (at approximately half the GWP of R-404A) continues to grow in many parts of the world. Non-halocarbon refrigerants such as CO_2 (R-744) and propane (R-290) are increasingly being used in supermarkets.

2.5.2.2 SAFETY ISSUES

Some alternatives to high-GWP HFCs (e.g., water and inert gases) pose no safety risk to handle but others do entail some risk. According to safety ratings, hydrocarbons have higher flammability than most HFCs, while ammonia and some HFOs have lower flammability, and CO_2 is non-flammable. Safety ratings also indicate higher toxicity for ammonia than for most HFCs and lower toxicity for hydrocarbons, HFC-1234yf, and CO_2 (ASHRAE, 2016). Safety issues can be resolved by changes in design of equipment, limiting the refrigerant charge sizes, and limiting potential emissions (UNEP, 2011).

2.5.2.3 ENERGY EFFICIENCY VIS-À-VIS GWP

The overall life-cycle climate impact of refrigeration and air conditioning applications that use halocarbons as refrigerants depends on many factors including, but not limited to

- the GWP of the refrigerant used,

- the loss (or recovery) of the refrigerant at the end of life of the equipment,

- the leakage rate of the refrigerant and recharge rates during service,

- the energy required to operate the coolant device,

- the number of hours that the equipment is used, and

- the carbon intensity of the electricity used to power the equipment.

Of these, for most applications, emissions due to the energy use of the equipment tend to dominate the life-cycle emissions (unless the grid is exceptionally free of carbon-emitting energy sources or the hours of use are very low). For example, Goetzler et al. (2016) estimated 73–76% of global CO_2–eq emissions from AC systems in 2010 to be indirect emissions from the energy use. Hence the energy efficiency resulting from the use of specific refrigerants is a very important consideration.

In the context of the Montreal Protocol, energy efficiency[4] has had a range of commonly accepted meanings, which include, but are not limited to the following:

1. The performance of a refrigerant relative to an HFC, HCFC, or CFC refrigerant being replaced such that it **consumes less energy to perform the same service** in the same (or similar) refrigeration or air-conditioning equipment, henceforth referred to as "refrigerant energy efficiency".

2. The performance of refrigeration or air-conditioning equipment by replacing one or more components other than the refrigerant such that it **consumes less energy to perform the same service**, henceforth referred to as "equipment energy efficiency".

There are other methods to reduce energy consumption in refrigeration, air conditioning, or other applications in which halocarbons are used, which fall under a broader consideration of "energy efficiency", such as using building insulation or maintenance to ensure optimal operation. Such methods (sometimes called "not-in-kind") are less germane to a discussion of energy efficiency in the context of the Montreal

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[4] Sometimes "energy efficiency" is also used to denote a metric or quantitative measure designed to measure the amount of energy used to perform a particular service, e.g., reduce the temperature of one ton of chilled water by 1 degree C. The less energy used to perform the same service, the more energy efficient the technology being used.

Protocol, since the influence of these approaches is generally independent of the chemical chosen as coolant.

Many studies have been conducted to evaluate both types of energy efficiency improvement mentioned above (e.g., Schultz, 2016; Abdelaziz et al., 2015). For example, in a study of refrigerant energy efficiency in air conditioners, Schultz (2016) found that some alternate low-GWP refrigerants, e.g., HFC-32 and R-452B (blend of 67% HFC-32, 7% HFC-125, and 26% HFC-1234yf, also referred to as DR-55), perform as well as or better than the HFC refrigerant R-410A (blend of 50% HFC-32 and 50% HFC-125). Meanwhile, Abdelaziz et al. (2015) found that the low-GWP refrigerant R-290 (propane) achieved a slightly higher efficiency than HCFC-22, but with a slightly lower cooling capacity under test conditions.

Equipment energy efficiency has been evaluated mainly under the aegis of market transformation programs for energy efficiency such as those run by the EU Ecodesign program (EuP, 2008) and the U.S. Department of Energy (DOE, 2017). Shah et al. (2013) found that a ~30% efficiency improvement, relative to current technologies, for air conditioners was cost-effective in many economies.

The conversion from using HFC refrigerants with high GWPs to refrigerants with lower GWPs, which will most likely result from the Kigali Amendment, provides an opportunity to consider other technological improvements that offer additional climate benefits through improvements in equipment energy efficiency.

Shah et al. (2015) found that if, in 2030, the world mini-split AC stock (i.e., the total number of installed and operational mini-split ACs[5]) transitioned from high-GWP, low-efficiency equipment to low-GWP refrigerants such as HFC-32 or propane (R-290), coupled with improved equipment that was 30% more efficient, the climate benefit over the ~10 year lifetime of the ACs would be over 25 $GtCO_2$-eq emissions. This would roughly double the CO_2-eq emission reductions in comparison with either policy (refrigerant transition or equipment energy efficiency improvement) implemented in isolation. The combined direct and indirect emissions abatement from both policies implemented together for mini-split ACs would be roughly 98 $GtCO_2$-eq emissions by 2050, as a result of the large projected growth in ACs in developing countries (**Figure 2-22**). Regions with higher hours of use or more carbon-intensive electricity grids would benefit more from energy efficiency improvement.

Based on the various alternate refrigerant testing programs listed above and the various energy efficiency market transformation studies, similar results (in % terms) may also be found for other air-conditioning and refrigeration equipment. Results are dependent on hours of use, emissions during operation or at end of life, grid carbon intensity, growth rates, and other relevant factors.

In conclusion, improvements in energy efficiency in refrigeration and air conditioning equipment during the transition to low-GWP alternative refrigerants can potentially double the climate benefits of the HFC phasedown of the Kigali Amendment. The potential magnitude of these combined benefits would contribute to achieving the targets of the UNFCCC 2015 Paris Agreement, which aims to keep global temperature rise this century well below 2°C above pre-industrial levels.

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[5]   Mini-split ACs are the most widely used type of AC system, representing roughly ~70% of sales by unit worldwide.
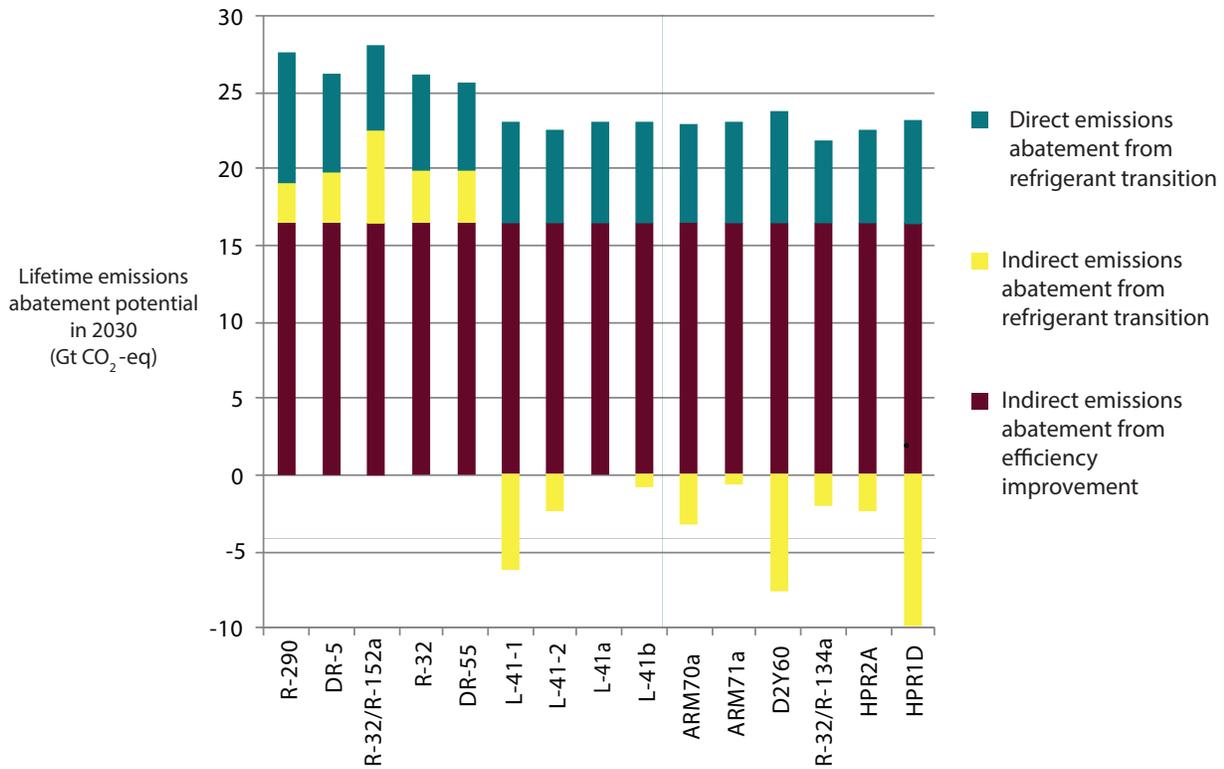
Figure 2-22. Estimated emissions abatement potential of air conditioning (AC) Stock in 2030 over 10-year AC lifetime. Positive numbers indicate CO_2 emission reductions while negative numbers indicate increases in CO_2 emissions[1]. Source: Shah et al. (2015). The purple bar indicates the "indirect" emissions abatement from the ~30% equipment efficiency improvement (compared with current technologies) while the yellow bar indicates the "indirect" emissions abatement refrigerant energy efficiency improvement (or reduction), and the blue bar indicates the direct emissions abatement due to the lower GWP of the refrigerant compared to the commonly used AC refrigerant R-410A[2]. See **Table 2-4** for the acronyms of the different refrigerants. R32/R152a is a blend of 95% HFC-32 and 5% HFC-152a. R32/R134a is a blend of 95% HFC-32 and 5% HFC-134a.

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[1] Shah et al. (2015) estimated the world AC stock (# of installed units) will grow from ~900 million units in 2015 to roughly 1.6 billion units in 2030.

[2] Indirect emissions are emissions from the electricity grid due to the energy consumption of the equipment, while direct emissions are emissions of the refrigerant from the equipment due to leakage or at the end of life.

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