HFCs in the Atmosphere: Concentrations, Emissions and Impacts

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ABSTRACT

Concentrations of hydrofluorocarbons (HFCs) have increased in the global background atmosphere in recent years. By 2011 global mean HFC concentrations ranged from ≤ 1 parts per trillion for HFC-227ea to 65 ppt for HFC-134a. Although HFCs in the atmosphere do not deplete ozone, they are greenhouse gases (GHGs) that exert a warming influence on Earth's climate. Total direct heating supplied by all HFCs in 2011 was 0.019 W m^{-2}*, which is ≤ 1% of the heating supplied by fossil-fuel-derived carbon dioxide (1.8 W m*$^{-2}$*) or anthropogenic methane (0.5 W m*$^{-2}$*) in the atmosphere. This warming influence, known also as radiative forcing, is currently small for HFCs because their concentrations are more than 6 orders of magnitude smaller than* CO_2*. A comprehensive assessment of climate impacts of different GHGs, however, also accounts for their influence on climate integrated over time following their release to the atmosphere. This is important particularly for GHGs because some remain in the atmosphere for only days, while others have lifetimes longer than a century. The Global Warming Potential (GWP) provides a measure of the time-integrated radiative forcing arising from an emission of a GHG relative to that from an equivalent emission (by mass) of carbon dioxide. Most HFCs emitted to the atmosphere today have 100-year GWPs ranging from 100 to 14000, which are many times larger than* CO_2 *(GWP = 1). Large increases in use and emission of high-GWP HFCs projected in the future imply a similarly large increase in radiative forcing from HFCs. Such an increase would offset much of the climate gains supplied by the Montreal Protocol in phasing out chlorofluorocarbons. The climate impact of future HFC use, however, would be minimized if the mix of HFCs (or other chemicals) adopted as substitutes had substantially lower GWPs than those in use today.*

WHY HFCS ARE IN THE ATMOSPHERE

Hydrofluorocarbons (HFCs) are present in today's atmosphere primarily as a result of society's efforts to reduce consumption and use of ozone depleting substances (ODSs). Since HFCs do not deplete stratospheric ozone and are effective refrigerants, air conditioning and foam-blowing agents, aerosol propellants, and solvents, they have received wide use as ODS substitutes in these applications.

The fully revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer set schedules for phasing out industrial production for dispersive uses of ODSs such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, methyl bromide, and some long-lived chlorinated solvents. The success of this Protocol has been substantial. Global-scale production and emission of the most potent ODSs (CFCs, halons, methyl bromide and long-lived chlorinated solvents) are now a small fraction of what they were in the mid-1980s; atmospheric concentrations of nearly all potent ODSs have peaked and are now declining (Figure 1) (Montzka and Reimann *et al.*, 2011). In contrast, atmospheric concentrations of HCFCs, which are less potent ODSs, continue to increase in the background atmosphere. Production and emission of HCFCs continues at substantial levels because these chemicals are used as temporary substitutes for the more potent ODSs (Figure 1). Production and

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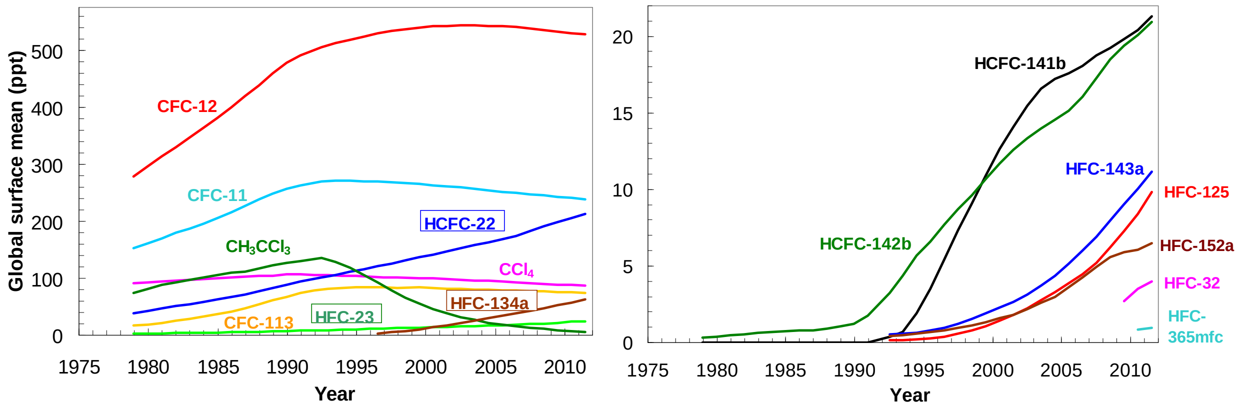

Figure 1. Annual global mean atmospheric concentrations (expressed as mixing ratios or mole fractions; units are parts per trillion or ppt) of ozone depleting gases and their long-lived substitutes derived from measurements in the remote atmosphere. Two panels are presented to show with detail atmospheric changes for trace gases at higher (left panel) and lower (right panel) concentrations. These observational records are from the Global Monitoring Division of NOAA's Earth System Research Laboratory and the Advanced Global Atmospheric Gases Experiment or AGAGE (Prinn et al., 2000) (compiled in the most recent WMO Scientific Assessment of Ozone Depletion; Montzka and Reimann et al., 2011; updated data are from NOAA, see: ftp://ftp.cmdl.noaa.gov/hats/).

consumption of HCFCs in developed countries is now decreasing, while that in developing countries has increased rapidly in recent years and is capped only after 2012 (UNEP, 2012).

The threat to the ozone layer from ODSs has been declining for over a decade as a result of the Montreal Protocol. The summed concentration of ozone-depleting chlorine and bromine has decreased by up to 10% from its peak in different regions of the stratosphere (Montzka and Reimann *et al.*, 2011). Despite this success, it will still be 2050 to 2080 before the summed concentration of all ozone-depleting halogen declines back to 1980 levels (approximately pre-ozone-hole levels). This is primarily because only a few percent of CFCs and halons are photochemically destroyed each year by natural processes; these chemicals have "lifetimes" of 20-100 years in the global atmosphere and their concentrations decrease only slowly even when emissions are negligible.

Because CFCs are strong GHGs, the success of the Montreal Protocol has also provided a substantial benefit to climate (Velders *et al.*, 2007). In the absence of this Protocol, emissions of CFCs would have been much larger and concentrations of these gases would have been significantly higher for decades and centuries thereafter (Newman *et al.*, 2009). As of 2010, the emission reduction brought about by the Montreal Protocol is equivalent to reducing CO_2 emissions by about 10 Gt yr^{-1}, which is about five times the annual emission reduction target of the Kyoto Protocol for 2008-2012 (Velders *et al.*, 2007).

HFCs were produced in large quantities as non-ozone-depleting substitutes for CFCs, HCFCs, and other ODSs beginning in the early 1990s. Atmospheric concentrations have increased relatively rapidly since that time, although as of 2011, the global HFC concentration of any individual HFCs was still < 100 ppt (Figure 1). Although HFCs do not deplete ozone, they do have some environmental impacts that could be of concern if concentrations were to increase without control in the future. HFCs oxidize in the atmosphere to produce TFA, a toxic chemical that accumulates in biological tissues. Given current projections of increased use of HFCs, however, HFCs are not likely to contribute substantially to the background amount of TFA relative to other existing TFA sources (Montzka and Reimann *et al.*, 2011).

Of greater concern is that some HFCs, particularly those receiving much use today, are strong GHGs. Projections of uncontrolled HFC use in "business as usual" scenarios show large increases in production and emissions of HFCs by 2050, primarily as a result of developing countries becoming fully industrialized (Velders *et al.*, 2009; UBA, 2009). This future production is not controlled by the Kyoto Protocol, as target dates for this

Protocol are now expiring and it did not cover all countries. If emissions of the strong GHG HFCs in use today increase as projected, the climate benefit that had been achieved by the Montreal Protocol (as annual emissions) would be largely erased. As a result, alternatives with smaller climate impacts are being considered, such as HFCs with shorter lifetimes, or not-in-kind solutions.

MEASURING HFCS IN THE ATMOSPHERE

Assessing the global environmental impact of a trace gas starts with characterizing the concentration of that trace gas in the global atmosphere. For chemicals with lifetimes longer than about 0.5 yr, a measurement made at a site far removed from sources can be representative of a broad region of the global atmosphere. As a result, the global background mean concentration of a trace gas can be fairly accurately derived from measurements at only a few sites.

When measurements are made at more than one site, they more accurately characterize the global mean concentration and also supply information about the location of sources (Montzka *et al.*, 2009). For example, when CFCs, HCFCs, and HFC are emitted in large quantities relative to losses, higher concentrations are measured in the remote northern hemisphere (NH) than in the southern hemisphere (SH), and concentrations in the SH lag those in the NH by at least 1 year (Figure 2). These observations are consistent with human activities being the primary source of these chemicals to the atmosphere, given that most humans live in the NH. As emissions become small (already observed for CFCs), hemispheric concentration differences diminish. Furthermore, concentrations in the SH lag those observed in the NH because the largest substantial barrier to meridional mixing in the lower atmosphere is near the equator (the inter-tropical convergence zone), so it typically takes much longer for an HFC molecule to be transported from North America to South America than from North America to central Asia, for example. As a result of these considerations, current sampling networks for characterizing global

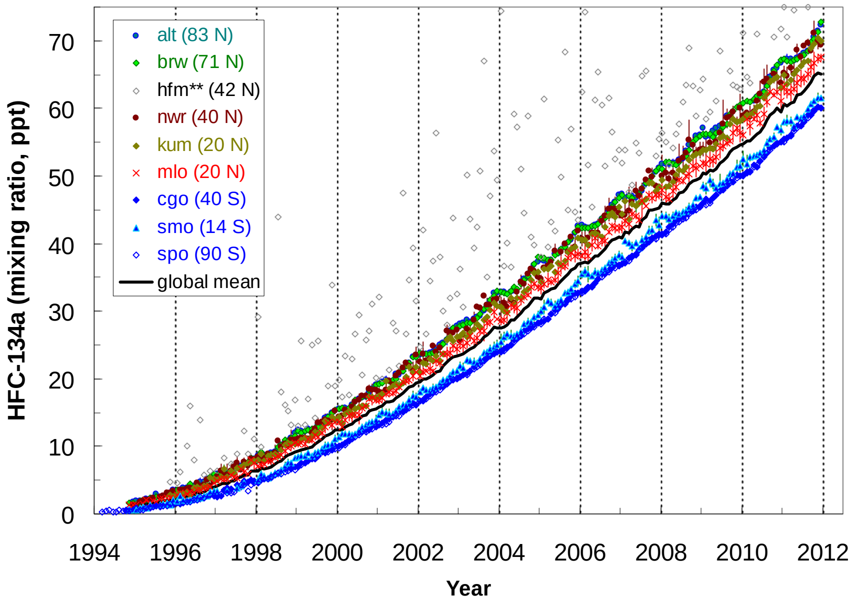

*Figure 2. Past atmospheric changes for HFC-134a. Points represent monthly mean concentrations determined from NOAA flasks sampled approximately weekly at 8 remote stations in both hemispheres and one non-remote site in the north-eastern U.S.A. (hfm**). Error bars are shown for remote sites only and represent 1 standard deviation of all measurements during that month (error bars are often smaller than points). The black line represents the global surface mean concentration. Station latitudes are indicated in the legend. Data are an update of Montzka et al. (1996) and are available at: ftp://ftp.cmdl.noaa.gov/hats/hfcs/hfc134a_GCMS_flask.txt.*

atmospheric concentrations of long-lived gases include measurements at remote sites in both the NH and SH, and fewer sites at similar latitudes.

Trends in global atmospheric concentrations of long-lived trace gases are routinely derived from ongoing measurements at Earth's surface. Measurements from periodic aircraft campaigns have demonstrated that long-lived trace gases such as CFC, HCFCs, and HFCs are fairly rapidly mixed vertically within the lower atmosphere so that measurements made at the surface at a few remote locations provide an accurate representation of concentrations and their time-dependent changes throughout the entire lower atmosphere (Wofsy *et al.*, 2011). Surface measurements also allow an accurate picture of compositional changes in the stratosphere, once time lags for mixing are considered (Schauffler *et al.*, 2003). As a result, surface-based measurements allow one to evaluate adverse environmental impacts arising from the presence of trace gases in other regions of the atmosphere such as stratospheric ozone depletion and climate change.

Atmospheric measurements of CFCs, HCFCs, and HFC are typically made with well-established chromatographic techniques with instruments deployed at remote sites that regularly and automatically collect and analyze samples multiple times per day (Elkins *et al.*, 1993; Prinn *et al.*, 2000), or with flasks collected weekly that are subsequently shipped to and analyzed in a central laboratory (Montzka *et al.*, 1996). Measurements made with chromatographic techniques can be highly precise and accurate. Repeatability for replicate measurements is typically <1% for trace gases at concentrations above a few parts per trillion. Differences in results reported by the two main independent laboratories making global measurements of these gases are typically < 5%, and most differences can be traced to the preparation of calibration standards as opposed to instrumental artifacts.

OBSERVED CHANGES IN ATMOSPHERIC HFC CONCENTRATIONS

Measurements of HFCs currently in use by society and produced by industry show increasing atmospheric concentrations throughout the global atmosphere (Figure 1). The observations show higher atmospheric concentrations and larger spatial and temporal concentration variations at NH surface sites, consistent with most emissions emanating from the NH as a result of use by humans in a variety of applications (Figure 2). Even higher variability is observed at sites near large populations (*i.e.*, non-remote locations such as hfm in Figure 2). NOAA measurements at a number of continental sites in the U.S. during the past few years, for example, show concentrations of HFC-134a in individual samples that are up to 6 times higher than observed at remote sites.

Measurements of HFCs from independent sampling networks provide a consistent picture of global mean concentrations and yearly increases for HFCs measured by both networks (Montzka and Reimann *et al.*, 2011). The most abundant HFC in the atmosphere currently is HFC-134a, followed by HFC-23. Other HFCs are present at lower concentrations, and most are increasing relatively rapidly at the present time. HCFC-22 is the only HCFC present at higher concentrations than HFC-134a in the global background atmosphere currently, and the concentration of the three major CFCs are still higher than any HFC (Figure 1).

Natural emissions of HFCs are thought to be extremely small or non-existent. Some trace-gas measurement networks existed in the late 1980s when HFCs were first produced. As a result, atmospheric records for some HFCs start concurrently with the first release of these industrially produced chemicals into the atmosphere. Concentrations of these particular HFCs increase from near zero (< 1 parts-per-trillion) in the measurement record, suggesting that any natural sources of these gases are insignificant (Figure 2). For HFCs for which ongoing measurements began years after initial production, societal use and emission, atmospheric concentrations during these initial years are derived from the collection and analysis of archived canister air samples (Fraser *et al.*, 1999 and Miller *et al.*, 2010) and the extraction and analysis of air trapped in the snowpack above glaciers in Antarctica and Greenland (Butler *et al.*, 1999; Montzka *et al.*, 2010). Both methods provide a reliable way to derive atmospheric composition of many stable gases. The negligible concentrations measured in the oldest air samples demonstrate that HFCs, CFCs and HCFCs are present in the atmosphere entirely as a result of industrial production and use by humans.

GREENHOUSE GASES THAT INFLUENCE CLIMATE

Many different trace gases, water vapor, clouds, and aerosols interact with light energy across the electromagnetic spectrum (from high energy ultraviolet to lower-energy infrared wavelengths) and affect the balance of heat in Earth's climate system. The main contributors to Earth's greenhouse are currently water vapor, carbon dioxide (CO_2), clouds, aerosols, methane (CH_4), ozone, nitrous oxide (N_2O), and halocarbons (Schmidt *et al.*, 2010). The GHGs, for example, absorb infrared radiation emitted from Earth's surface and allow less of that emitted heat to escape to space. This additional absorption adds heat to Earth's climate system. Water vapor and clouds provide much of the atmospheric greenhouse heating in today's atmosphere but are "highly active components of the climate system that respond rapidly to changes in temperature and air pressure by evaporating, condensing, and precipitating" (Lacis *et al.*, 2010). Water vapor and clouds are different from other GHGs in that they respond to the physical atmospheric conditions set by other chemicals. As a result, water vapor and clouds supply important feedbacks to climate conditions set by GHGs and other processes (e.g., orbital variations), rather than being the primary drivers of climate change.

The primary drivers of recent climate change are the non-condensing GHGs including CO_2, CH_4, ozone, N_2O, and halocarbons, and aerosols. Of these chemicals, many are emitted to the atmosphere from both natural processes and human activities. Emissions from both sources affect the balance of heat in the climate system. In quantifying the human contribution to present-day climate change, only trace-gas concentration changes since the beginning of the industrial revolution (1750) are considered. Atmospheric concentrations of trace gases in 1750 are fairly well known based on measurements of air extracted from glacial ice bubbles (Etheridge *et al.*, 1996; Etheridge *et al.*, 1998).

Radiative efficiencies and direct radiative forcing

The instantaneous contribution of GHGs to climate change is typically evaluated with the metric of radiative forcing (Forster and Ramaswamy *et al.*, 2007). Radiative forcing (units of W m^{-2}) refers explicitly to the climate forcing or heating influence arising from the change in the atmospheric concentration of a trace gas between 1750 and the present day. The direct radiative forcing of a trace gas is determined by the trace gas concentration and how efficiently it absorbs infrared (longwave) radiation emanating from Earth's surface (*i.e.*, its radiative efficiency expressed in W m^{-2} ppb^{-1}). For trace gases at very low concentrations (*e.g.*, HFCs, CFCs, and HCFCs), direct radiative forcing is linearly proportional to atmospheric concentration. For trace-gases at higher concentrations (*i.e.*, CO_2, CH_4, N_2O), however, radiative forcing is non-linearly related to atmospheric concentration. Radiative efficiencies for HFCs in use today range between 0.02 and 0.4 W m^{-2} ppb^{-1}, which is orders of magnitude larger than the current radiative efficiencies of CO_2 (0.000014 W m^{-2} ppb^{-1}), CH_4 (0.00037 W m^{-2} ppb^{-1}), and N_2O (0.00303 W m^{-2} ppb^{-1}) (Forster and Ramaswamy *et al.*, 2007). In other words, HFCs are potent GHGs; the additional heat trapped from an added HFC molecule is orders of magnitude larger that the additional heat trapped by an added molecule of CO_2. Interestingly, the radiative efficiencies of HFCs in use today are comparable to those of previously used CFCs and currently used HCFCs (0.14–0.32 W m^{-2} ppb^{-1}) .

Although most HFCs in use today are potent GHGs on a per-molecule basis, their summed contribution to climate forcing currently is less than 1% of that from all long-lived GHGs. The radiative forcing from HFCs in 2011 totaled about 0.019 W m^{-2} (Figure 3). HFC-134a accounts for most radiative forcing from HFCs (0.0096 W m^{-2}), followed by HFC-23 (0.0045 W m^{-2}), and other HFCs. In comparison, the radiative forcing contributed by all long-lived GHGs was 2.8 W m^{-2} in 2011 (http://www.esrl.noaa.gov/gmd/aggi/) (Figure 3). In other words, the total direct heating influence from HFCs was 0.6% of the direct heating supplied from all long-lived, non-

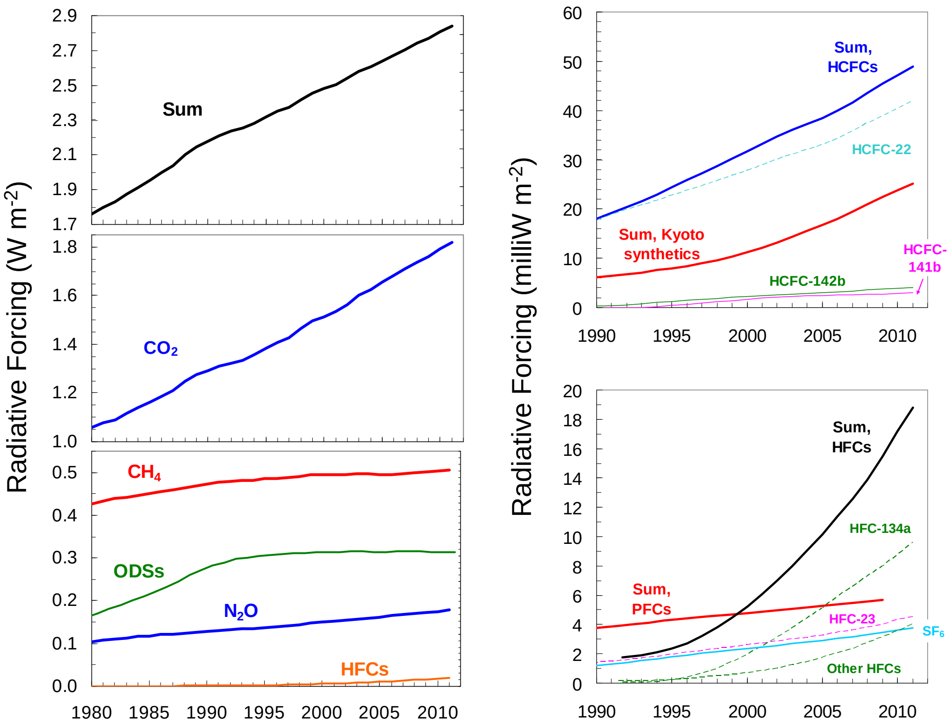

Figure 3. *Direct radiative forcing from long-lived greenhouse gases. These forcings are calculated from global annual surface mean mixing ratios and published radiative efficiencies (Daniel and Velders et al., 2011; Forster and Ramaswamy et al., 2007). Left-hand panels show the contributions from all the substantial, long-lived GHGs or groups of gases; right-hand panels show subsets of lesser contributors (note the 1000-fold change in y-scale). The "ODSs" grouping includes CFCs, HCFCs, and chlorinated solvents, the "Sum, Kyoto synthetics" includes all synthetic gases in the Kyoto Protocol (HFCs, PFCs, and SF_6); and "other HFCs" includes HFC-143a, HFC-125, and HFC-152a. Data are from NOAA and AGAGE compiled in Montzka and Reimann et al. (2011); updated data are from NOAA; PFC data are from Mühle et al. (2010).*

condensing GHGs in 2011 (when only anthropogenic contributions are included).

It is useful to put the direct heating influence supplied by long-lived GHGs in perspective. Approximately 240 W m^{-2} of incoming solar energy is absorbed by Earth's surface and atmosphere (Hansen *et al*., 2007). The 2.8 W m^{-2} supplied by human-caused increases in long-lived GHGs in 2011 is about 1.2% of this absorption and is quite large compared to the peak-to-peak solar variability across solar cycles (~0.1%) or the long-term increase in radiative forcing (~0.1 W m^{-2}) from changes in total solar irradiance since the 17th-century (Forster and Ramaswamy *et al*., 2007). Put in another context, the heat added from long-lived GHGs is equivalent to the heat from about 14 trillion 100-W light bulbs distributed evenly across Earth's surface, operating continuously. This corresponds to a 100-W light bulb positioned on every 6×6 m (or 20×20 ft) grid covering Earth's entire surface.

Total direct radiative forcing from all long-lived gases has increased over the past 2 decades at a fairly constant annual rate (Figure 3). The atmospheric increase in CO_2 accounts for most of this radiative forcing increase. HFCs account for a small portion of the overall increase. Over the past 5 years, for example, increases in HFCs have accounted for about 4% of the increase in total radiative forcing from all long-lived GHGs.

At NOAA, global mean concentrations of long-lived GHGs are measured with a global sampling network on a continuous basis. The results provide a rich source of ongoing information about atmospheric composition and how it is changing. One metric derived from these data is the NOAA Annual Greenhouse Gas Index (AGGI), which is a measure of the radiative forcing supplied by these gases relative to the forcing supplied in 1990, the baseline year for the Kyoto Protocol (Hofmann *et al*., 2006; http://www.esrl.noaa.gov/gmd/aggi/). The AGGI in

2011 was 1.30, indicating that in 2011 the radiative forcing arising from anthropogenic activities has increased by 30% since 1990.

Global Warming Potentials: Estimating the time-integrated climate impact of a trace-gas emission

Direct radiative forcing is an estimate of the instantaneous heating influence supplied by a trace gas at a given atmospheric concentration. This metric does not capture the full climate impact of a trace gas emission, however, because different GHGs persist in the atmosphere from weeks to centuries. To compare time-integrated climate impacts of GHG emissions, the global warming potential (GWP) is often used. The GWP is a measure of the radiative forcing from a trace gas emission, integrated over a specific time period and expressed relative to the climate influence of an equivalent mass emission of CO_2 (Forster and Ramaswamy *et al.*, 2007; Daniel and Velders *et al.*, 2011; Montzka *et al.*, 20011a). The GWP derived for a 100 year period is often used to compare the integrated climate impacts of different trace gas emissions. Multiplying a trace-gas emission amount by its respective 100-yr GWP allows a 'CO_2-equivalent' (CO_2-eq) emission to be calculated.

Emissions derived from inventory accountings or global atmospheric observations (see Box at end of paper) can be converted to CO_2-eq emissions. The resulting values allow an assessment of the relative contributions of the current emissions of different GHGs to future climate change (Figure 4). At 33.5 Gt yr^{-1} in 2010, CO_2

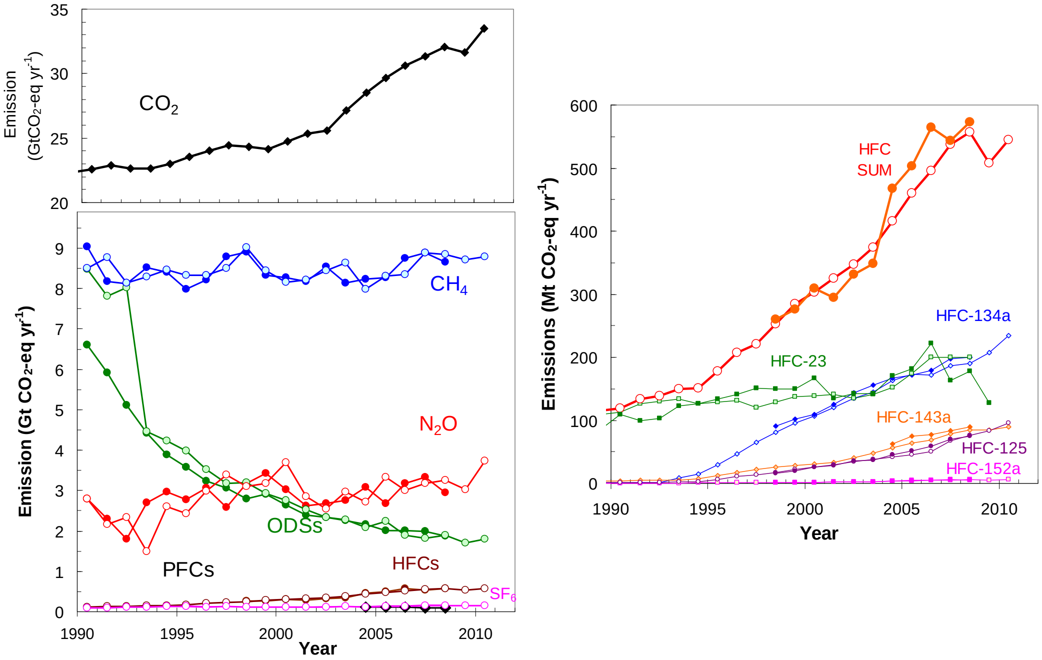

Figure 4. *CO_2-equivalent emissions of greenhouse gases. Carbon dioxide emissions are derived from inventories of fuel use and cement production (additional amounts from land-use change of about 3 $GtCO_2$ in recent years are not shown) (source: http://cdiac.ornl.gov/ftp/ndp030/global.1751_2008.ems and http://cdiac.ornl.gov/trends/emis/prelim_2009_2010_estimates.html). Emissions of non-CO_2 gases were derived from measured global concentrations (Figure 3) and estimates of annual losses (see Box). CO_2-equivalent emissions are derived by multiplying emissions by 100-year Global Warming Potentials (100-year GWPs from Daniel and Velders et al., 2011). Different colors represent different chemicals or chemical classes, and the multiple lines given for a single chemical or chemical class represent emissions derived from independent global sampling networks (NOAA; and AGAGE—see Prinn et al., 2000; data compiled in Montzka and Reimann et al., 2011). Right-hand panel shows CO_2-equivalent emissions of individual HFCs and their sum derived similarly (note 1000-fold expanded scale). Contributions from individual HFCs that are less than about 10 Mt CO_2-eq yr^{-1} in 2011 are not shown.*

emissions are larger than the sum of all non-CO_2 GHG emissions by a factor of about 2. HFCs emissions in 2010 amounted to 0.6 Gt CO_2-eq yr^{-1}, or slightly more than 1 percent of total greenhouse gas emissions during that year. CO_2-eq emissions of ODSs have decreased by about 10 Gt CO_2-eq yr^{-1} owing to the Montreal Protocol but were still 1.8 Gt CO_2-eq yr^{-1} in 2010 (Figure 4). At the present time the increases in annual HFC emissions have only slightly offset the reduction in annual ODS emissions brought about by the Montreal Protocol.

Although halocarbons such as CFCs, HCFCs, and HFCs have fairly similar radiative efficiencies, their GWPs span more than two orders of magnitude because they have a range of lifetimes (Figure 5). Differences in lifetime stem from differences in chemical reactivity: Chemicals with longer lifetimes have correspondingly larger GWPs because they contribute to radiative forcing for longer periods after emission and because the accumulated atmospheric concentration following emission is higher than for a short-lived gas. For example, although the radiative efficiencies for HFC-23 and HFC-152a are different only by a factor of about 2 (0.19 for HFC-23 and 0.09 for HFC-152a), their 100-yr GWPs are different by a factor of 100 (14,200 for HFC-23 *vs.* 133 for HFC-152a) (Daniel and Velders, 2011). In other words, an emission of HFC-23 has a much larger integrated impact on climate than does an equal emission of HFC-152a.

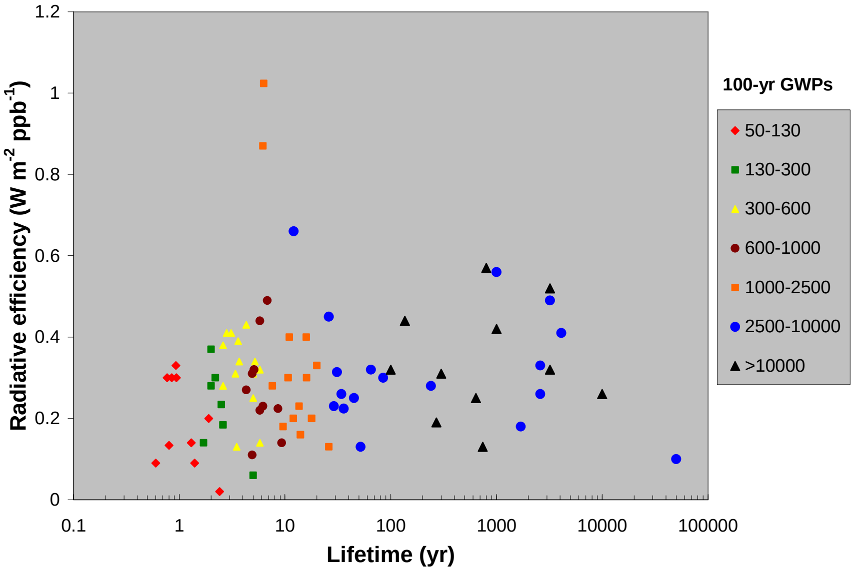

Figure 5. The radiative efficiency for halocarbons with a range of lifetimes and their respective 100-yr GWPs. Each point represents a different halocarbon (for a list of halocarbons included here, see Table 5-A2 in Daniel and Velders et al., 2011). Halocarbons with shorter lifetimes generally have smaller time-integrated impacts on climate and, hence, smaller 100-yr GWPs.

Different values are derived for the GWP of any individual trace gas depending on the time period over which climate impacts of a pulse emission are integrated. This is because the time-evolution in concentration and radiative forcing after an emission of a trace gas is typically much different than it is for CO_2 (see Box). Carbon dioxide is unique among trace gases because it is not removed from the atmosphere by processes that can be characterized by a single timescale (or lifetime). Despite this, it takes about 100 years for 63% (or 1-1/e, see Box) of a pulse emission of CO_2 to be removed from the atmosphere (and much longer for remaining amounts to be removed). Hence, the integrated radiative influence of a chemical with a lifetime < 100 yr over a short time horizon (*e.g.*, 20 years) relative to CO_2 is much larger than when that time-integration period is 100 or 500 years.

Over longer time horizons, the GWP is smaller for a short-lived gas because it becomes completely removed from the atmosphere and, hence, its radiative forcing contribution approaches zero while CO_2, as the reference, persists in the atmosphere for centuries. Accordingly, short-lived chemicals have 20-yr GWPs that are substantially larger than their 100-yr or 500-yr GWPs. The opposite is generally true for chemicals with lifetimes longer than about 200 years. For these chemicals, their 20-yr GWPs are smaller than their 500-yr GWP because 500 years after emission a larger fraction of the non-CO_2 gas remains in the atmosphere compared to CO_2.

Finally GWPs reported in the scientific literature have changed over time as our scientific understanding improves. GWPs in the late 1990s and early 2000s (*e.g.*, those that appeared in Ramaswamy *et al.*, 2001) were adopted by the United Nations Framework Convention on Climate Change as the official values to use for calculating CO_2-equivalent emissions going forward. With each scientific assessment report of ozone depletion or climate, updates to these initial values are derived from improved scientific understanding (Forster and Ramaswamy *et al.*, 2007; Daniel and Velders *et al.*, 2011). As a result, a range of GWP values for individual gases can be found in the literature.

POTENTIAL FUTURES

By the different measures discussed above it is clear that the climate influence of HFCs emitted to date is relatively small in comparison to other GHGs, particularly CO_2, and will remain so in the immediate future. Yet there is concern about this influence increasing substantially on longer terms (Figure 6). This concern arises

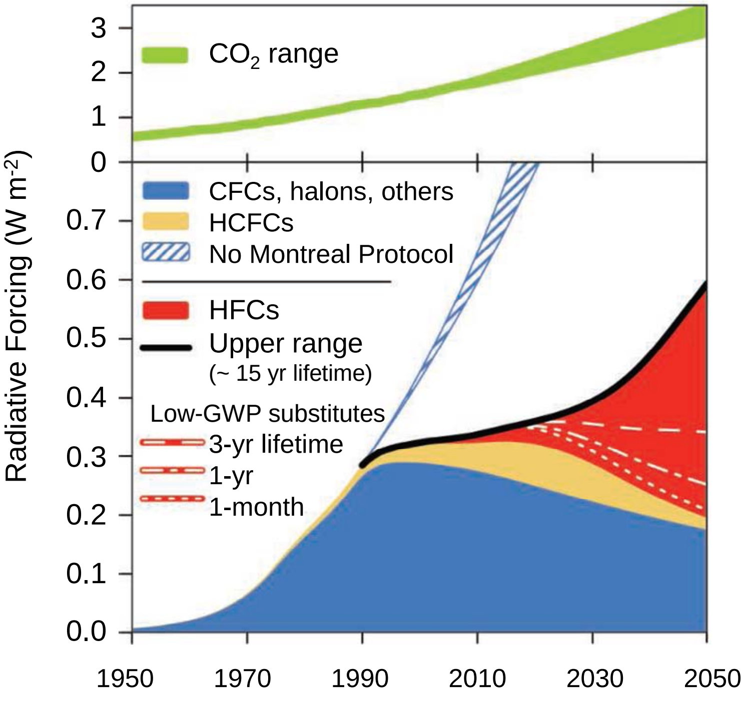

Figure 6. Projected future radiative forcings for a single HFC emissions scenario in which the mix of HFCs used in the future have range of lifetimes (and, therefore, GWPs): 15 years, 3, years, 1 year, and 1 month (adapted from Velders et al., 2012). For reference, the current mix of HFCs has an average lifetime of ~15 years and a 100-yr GWP of 1630. The average 100-yr GWP of HFCs associated with the scenario with an average HFC lifetime of 1-month is 11. The future radiative forcing arising from increased HFC emissions depends substantially on the average lifetime (and GWP) of the HFCs chosen for use by society. Also shown are the anticipated increases in radiative forcing from CO_2 in the future (upper panel, note different scale; green shaded area), and the radiative forcing that might have resulted if the Montreal Protocol had not been adopted (blue hatched range).

primarily from the potentially large increase in production and emissions of high-GWP HFCs that could occur by mid-century in the absence of global controls (Velders *et al.*, 2009; UBA, 2009). Although emissions from developed countries likely account for most of the HFCs present in today's atmosphere, most of the projected increases in production and emissions of HFCs stem from developing countries as they phase out CFCs and HCFCs and further industrialize. Demand for CFCs and HCFCs in developing countries has increased rapidly since 1998 (~8% yr^{-1} through 2007) and is likely to continue increasing in the future (Velders *et al.*, 2009; UBA, 2009). Projections suggest that a large fraction of future demand in these countries will be met with HFCs, given that CFC production is phased out and production of HCFCs will be capped in 2013 and subsequently phased out gradually.

In the absence of controls on high-GWP HFCs, this increased demand is projected to cause substantial increases in future radiative forcing from HFCs (Velders *et al.*, 2009; UBA, 2009) (Figure 6). The actual climate impact arising from substantial future increases in HFC emissions, however, is not pre-determined. Instead, it depends on the magnitude of emissions over time and the GWPs of HFCs and other alternatives predominantly used globally. For example, if the mix of HFCs used during the next several decades has an average 100-year GWP similar to the HFCs in use today (*i.e.,* 1370-4180 for HFC-134a, -125, and -143a), total radiative forcing from HFCs is expected to increase to between 7 and 16% of that from CO_2 in 2050 (compared to 0.6% in 2011) (Figure 6). In such a scenario, projected CO_2-eq emissions of HFCs increase to between 3 and 8 GtCO_2-eq by 2050 (Velders *et al.*, 2009; UBA, 2009). If, however, the mix of substitute chemicals had a substantially smaller average GWP, the increase in radiative forcing would be much less, *even for the same total mass of emissions* (Figure 6). Both non-HFC and HFC alternatives with smaller climate impacts per mass emission are being developed by industry and are beginning to receive use as substitutes for the long-lived, high-GWP HFCs.

CONCLUSION

HFCs are reliably measured in the remote atmosphere by independent sampling networks even at current concentrations (< 100 ppt). Observations show increasing concentrations of HFCs owing to industry production and societal use in multiple applications in place of CFCs and HCFCs that are being phased out by the Montreal Protocol. Direct climate forcing caused by HFCs in the atmosphere today (0.019 W m^{-2}) is currently less than 1% of that caused by other long-lived GHGs. When considered on a CO_2-eq basis, 2011 emissions of all HFCs amount to 0.6 Gt CO_2-eq, or about 1% of summed CO_2-eq emissions from all long-lived GHGs in that year. Concern over continued use of the current mix of HFCs stems from the possibility that their climate impacts become substantial in the coming decades. HFC emissions and contributions to climate change are projected to increase substantially in response to increased demand especially in developing countries. The projected climate influences are dramatically reduced if the HFCs and other alternatives used in the future have substantially lower average GWPs than the mix of HFCs in widespread use today.

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BOX: Deriving emissions from atmospheric data and trace-gas lifetimes.

Measurements of long-lived halocarbons in the atmosphere can be used to derive information about their emission magnitudes on multiple spatial scales. If we consider the entire atmosphere as a single box, mass balance considerations can be used to derive global emission magnitudes of a long-lived trace gas from atmospheric measurements at remote locations and an understanding of the rate at which the trace gas is destroyed in the atmosphere:

The rate of change of the atmospheric mass of a trace gas is derived from emissions minus losses as:

$$dG/dt = E - kG \quad (1)$$

where G is the global burden (mass) derived from globally distributed measurements in remote locations, E is the magnitude of emissions (mass yr^{-1}), and k is the first-order rate constant for loss (yr^{-1}) of the chemical from all loss processes. The inverse of k has units of time and is known as the trace gas ***lifetime***, which represents the timescale over which 63% (or 1-1/e) of the trace gas is removed from the atmosphere by all loss processes. For example, a gas with a 5-yr lifetime is destroyed at the rate of 18% yr^{-1} (*i.e.*, 18% = 1-1/exp(1/5)). For atmospheric gases such as CFCs, HCFCs, and HFCs, this timescale for removal is first-order, *i.e.*, it does not depend on the magnitude of emission or time since emission. Among long-lived GHGs, only CO_2 has a timescale for removal that is not first-order. Instead, CO_2 becomes removed from the atmosphere on multiple timescales that depend on the time elapsed since emission (Forster and Ramaswamy *et al.*, 2007, and Archer and Brovkin, 2008).

In general, trace gas lifetimes are not directly observable; however, if global emissions are known accurately enough or if they have become insignificant, one can use Eq. (1) to estimate a trace gas lifetime directly from measured global atmospheric concentrations and trends (Prinn *et al.*, 2000; Montzka *et al.*, 2011b). Conversely, lifetimes can be estimated from multiple sources of information, such as laboratory measurements of primary chemical reactions and physical processes, including rate constants for reactions that destroy the trace gas and photolysis rates. A quantitative understanding of oxidant concentrations and of the light flux capable of photolytically decomposing a trace gas throughout the global atmosphere over all seasons is also required. For most HFCs, the primary mechanism for atmospheric removal is reaction with the hydroxyl radical (OH). For example, for HFC-134a the reaction:

$$CH_2F\text{-}CF_3 + {\cdot}OH \rightarrow {\cdot}CHF_2\text{-}CF_3 + HOH \quad (2)$$

occurs in the atmosphere and the radical produced (${\cdot}CHF_2\text{-}CF_3$) generally reacts with oxygen to form polar molecules that are fairly rapidly scavenged by liquid aerosols and removed from the atmosphere. Based on the laboratory-measured rate of reaction (2) and our understanding of global OH concentrations, the lifetime of HFC-134a is approximately 13 years (Montzka and Reimann *et al.*, 2011).

Lifetime estimates provide information about loss rates, and global emission magnitudes can be derived for long-lived trace gases from eq (1) with global atmospheric observations that define the global burden (G) and its change over time. Emissions are often derived with a simple 1-box approach (e.g., eq. (1)), but are also obtained with more sophisticated inverse models that attempt to derive more accurate emission magnitudes by extrapolating the available information (measured global mean surface concentration, the temperature-dependent loss rate constant, hydroxyl radical concentrations) to a time-varying, 3-dimensional field. For HCFCs and other gases with lifetimes and growth rates similar to those of most HFCs, the simplistic 1-box approach provides a fairly robust emission estimate (Montzka and Reimann *et al.*, 2011).

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