USA Emissions estimates of CH₃CHF₂, CH₂FCF₃, CH₃CF₃ and CH₂F₂ based on in situ observations at Mace Head

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Abstract

We investigate the low level, surface-to-surface transport of five hydrofluorocarbons (HFC-152a, -134a, -143a, -125 and -32) from North America to the Advanced Global Atmospheric Gases Experiment (AGAGE) observing station at Mace Head, Ireland during 2005-2012. Using the UK Meteorological Office Numerical Atmospheric dispersion Modelling Environment (NAME) we select air masses, which are dominated by direct transport from the North American continent to Mace Head, thereby eliminating any significant influence from local or other regional sources. To estimate emissions of individual HFCs we use the interspecies correlation method with HFC-125 as the reference compound. We then compare these derived North American emissions with those reported to UNFCCC. Our results indicate an under-reporting of HFC-152a emissions by the USA to the UNFCCC, with an annual average difference of 24 Gg (9-36 Gg). For HFC-134a our estimated emissions indicate an over-reporting of USA reported emissions by 24 Gg (21-28 Gg). For HFC-143a USA reported emissions are lower than our estimates by 1.8 Gg (1-3.5 Gg); whereas for HFC-32 there is close agreement, within the uncertainties, between the USA emissions reported to UNFCCC and our emissions estimates. Combining our USA emissions estimates for HFC-152a, HFC-134a, HFC-143a and HFC-32 with the UNFCCC estimate for

HFC-125 could contribute potentially 201 ± 36 Tg-CO₂ eq yr⁻¹ to atmospheric radiative forcing in 2011-2012. This compares with UNFCCC of 146 Tg-CO₂ eq yr⁻¹ for the same five HFCs.

1. Introduction

Intercontinental scale transport of man-made pollutants first became evident over 50 years ago following the atmospheric testing of nuclear weapons (Junge, 1963). Since then, intercontinental transport has been invoked to explain the increase in carbon dioxide at Mauna Loa, Hawaii (Keeling et al., 1989), the transport of Saharan dust to the Caribbean from Africa (Savoie et al., 1989), particulate sulphate to the Arctic (Rahn and Heidam, 1981), the influence of Asian emissions on the sulphur budget for the west coast of North America (Andreae et al., 1988) and the North American emissions on ozone and carbon monoxide (CO) levels over Europe (Parrish et al., 1992). Intercontinental transport is now well recognised as an atmospheric phenomenon and its mechanisms are becoming more clearly identified (HTAP, 2007).

In a previous study, the long-range intercontinental transport of chlorofluorocarbons CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂) from sources in North America to the Mace Head observatory on the Atlantic Ocean coastline of Ireland has been investigated using NAME a Lagrangian atmospheric dispersion model (Ryall et al., 1998). We return to this same issue here, taking advantage of technical improvements in the overall sensitivity of our detection system for halocarbons (Miller et al., 2008) and the many improvements and enhancements made to the NAME model. The Mace Head observations of a wide range of trace gases have been used to work back to the European regional emissions of these trace gases that are required to support them using the NAME model (Manning et al., 2003; O'Doherty et al., 2004; Greally et al., 2007; Manning et al., 2011).

HFCs are the principal replacement compounds for both CFCs and hydrochlorofluorocarbons (HCFCs). However, with high global warming potentials (GWP) and relatively long atmospheric lifetimes they are included in the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC). Their main uses are in mobile and stationary air-conditioning systems, foam blowing and aerosol sprays. Reported emissions estimates of HFCs are obtained from methods based on production and consumption/usage data (“bottom-up”) with large uncertainties within industry and government reporting, and where local activity data are combined with associated emission factors and aggregated to form the national inventory. Nisbet and Weiss (2010) have questioned the validity of these inventories, suggesting that they be verified by direct atmospheric measurements. This alternative approach estimates emissions using actual atmospheric measurements (“top-down”) by inverse modelling methods from aircraft or observatory measurements.

In this study we use high frequency HFC measurements recorded at the AGAGE station, Mace Head, coupled with the NAME dispersion model, to estimate USA emissions of HFCs-152a, 134a, 143a and 32 using the interspecies correlation method with HFC-125 as the reference tracer. Table 1 lists the GWPs, lifetimes, and reported growth rates of the five HFCs investigated in this study. Increasing and unregulated emissions of HFCs are potentially significant contributors to global radiative forcing (Velders et al., 2009, 2012; Rigby et al., 2014).

HFC-125 (C_2HF_5) is mainly used as a component of refrigerant blends for commercial refrigeration applications with a minor use in fire-fighting equipment. It was selected as the reference compound, as its emissions are most likely to be co-located with emissions of other HFCs (due to its use in refrigerant blends) and there is a comprehensive record of US national emissions in the UNFCCC database (described in section 2.3). This database is, as a whole,

consistent with measured global concentrations of HFC-125 (O'Doherty et al., 2009). Other investigators have used carbon monoxide (CO), (Millet et al, 2009; and Barletta et al, 2011), carbon dioxide ($^{14}\text{CO}_2$), (Miller et al., 2012), or HCFC-22 (CHClF_2), (Yokouchi et al, 2006) as reference compounds.

HFC-134a is used as a single compound in both mobile and stationary refrigerant systems, refrigerant blends, foam blowing agent, fire suppressant and propellant in metered-dose inhalers and aerosols. HFC-152a is used predominately in foam-blowing and aerosol spray applications with some minor use in refrigerant blends (Ashford et al., 2004), with the USA believed to be the largest emitter of HFC-152a. The remaining two HFCs 143a and 32 are mainly used in various refrigerant blends listed in Table 2. HFC-143a is primarily a component of refrigerant blends R404A and R507A, while HFC-32 is a component of blends R410A, R407A and R407C.

Global top-down HFC emissions estimates have been reported in a number of publications (O'Doherty et al., 2004, 2009; Grealley et al., 2007 and Rigby et al., 2014). There are also some limited studies of regional-scale emissions (Grealley et al., 2007; Maione et al., 2008; O'Doherty et al., 2009; Vollmer et al., 2009; Stohl et al., 2009, 2010 and Kim et al., 2010). Recently, O'Doherty et al., (2014) have published a comprehensive report on global emissions of HFC-143a and HFC-32.

2. Experimental Methods

2.1. Instrumentation and calibration

HFCs mixing ratios are measured in 2L air samples using the “Medusa” automated custom-built cryogenic pre-concentration system with gas chromatographic (Agilent 6890, GC)- mass selective detection (Agilent 5973, MS). The Medusa instrument, described in detail in Miller et al., (2008), was installed in October 2004 at Mace Head, Ireland (53° N,

10° W); one of the primary stations in the AGAGE network of globally-distributed stations (Prinn et al., 2000). Ambient measurements are bracketed by an on-site calibration standard to give 2-hourly calibrated measurements. All measurements are reported (as dry mol fractions in pmol mol^{-1}) relative to the Scripps Institution of Oceanography or University of Bristol scales (SIO-05 for HFC-152a and HFC-134a; SIO-07 for HFC-32 and HFC-143a; UB-98 for HFC-125). The uncertainty of the calibration scales is 1.5% for HFC-134a, 3% for HFCs-32, -152a, -143a and 5% for HFC-125. Additional details of the measurement and calibration procedures are available in (Miller et al., 2008; O'Doherty et al., 2009 and Mülhe et al., 2010).

2.2. NAME model attribution of USA transport events.

Backward simulations of the NAME model (Jones et al., 2007; Manning et al., 2011) are used to estimate the recent (30-day) history of the air reaching Mace Head in each 2-hr period. Baseline concentrations are defined as those that have not been influenced by significant emissions within the previous 30d of travel on route to Mace Head, i.e., those that are well mixed and are representative of the mid-latitude Northern Hemisphere background concentrations. By removing the time-varying baseline concentrations from the raw measurement data, a time series of excursions from the baseline, for each observed gas has been generated, averaged over each 2-hour period. As part of the baseline calculation the uncertainty (5th and 95th percentile range) in the baseline estimate is determined and details of this methodology are reported in (Manning et al., 2011). The enhancements above baselines are driven by emissions on regional scales that have yet to be fully mixed on the hemisphere scale. In this analysis we select enhancements that are above the upper bound (the upper bound is defined as the 95th percentile value) of the estimated baseline to ensure that emissions from the USA are well-defined. Using NAME air history maps, the contribution of each air parcel from a number of regions was estimated. We select only those transport events where the model attributes >95% to the USA with little or no contribution

from other source regions (e.g. Europe) and with little local influence; as these could significantly impact the ratio of the two gases used in the interspecies correlation method. Identified USA transport events pass predominately over the eastern part of the USA. It is reasonable to expect that our study will be heavily influenced and therefore possibly biased by emissions which have been emitted on the eastern part of the USA, as this is the region of the USA most regularly “seen” at Mace Head.

2.3. Interspecies correlation method

The interspecies correlation method states if the emission of one species (E_r , t/y) from an area is known, then the emission rates of all other compounds (E_x , t/y) in the same dataset can be calculated from the pollution enhancement (ΔC) by using the following equation, (Yokouchi et al., 2006).

$$E_x = E_r \frac{(M_x \Delta C_x)}{(M_r \Delta C_r)} \dots \dots \dots (1)$$

Where M_x and M_r are the molecular weights of species x and reference compound r, respectively and ΔC_x and ΔC_r are expressed in ppt.

During each transport event from the USA we calculate emission estimates for HFC-152a, HFC-134a, HFC-143a and HFC-32 using HFC-125 as the reference compound. This method is based on the assumption that the compounds have co-located emission sources which certainly will be the case for refrigerant blends. Although not strictly co-located, HFC emissions from other sources will have similar industrial and domestic uses and emissions from mobile air conditioners, dominated by HFC-134a, will be distributed across the continent. In practice these more diverse sources will combine as a well-mixed regional source during the several days of transport. Furthermore, given their long atmospheric lifetimes relative to the transport time of several days to cross the North Atlantic Ocean, we assume there are no significant losses during transport. We also reject air masses which may have undergone significant dilution with upper tropospheric air as estimated by NAME.

Here we use the ratio of the measured mixing ratio enhancements of the two species (HFC_x:HFC-125) above their estimated baselines, together with the NAME selected trajectories of surface-to-surface transport from North America to Mace Head. Where there are a significant number of robust measurements in a particular event we obtain a tracer correlation ratio from the slope of the XY-scatterplot between HFC_x and the reference HFC-125.

2.4. National (UNFCCC) estimates of HFC emissions

The data were abstracted from submissions by the US Government to the UNFCCC (Rio Convention) and were reported in Table 2(II) s1 in the Common Reporting Format (CRF), available on the UNFCCC website (unfccc.int). The values were taken from the 2014 database and cover years 1990 to 2012. Values of emissions (HFCs 23, 32, 125, 134a, 143a and 236fa) are calculated specifically for the individual substances in the U.S. However, HFCs 152a, 227eas, 245ca and 43-10mee are shown in the database as “commercially confidential” and their emissions constitute the aggregated “unspecified” emissions reported. These unspecified annual emissions were divided between HFCs 152a, 227eas, 245ca and 43-10mee, assuming the same ratio as their reported global emissions. Thus the emissions of HFCs 32, 125, 134a and 143a discussed here are as reported in the U.S. database, while the emissions of HFC-152a have been calculated with the assumption that U.S. use patterns are similar to global use. This will increase the uncertainty of the estimate for HFC-152a. Values are reported in the UNFCCC database in metric tonnes to two places of decimals. The emissions are not measured but estimated and this level of accuracy (to within 10 kilograms) is completely spurious. Given the method of estimation and the U.S. Government’s own estimates of uncertainties, a more reasonable but still optimistic uncertainty would be 5%, or a range of 3000 tonnes in the case of recent USA emissions of HFC-134a.

3. Results and Discussion

Figures 1-4 are four representative examples (January 2006, March 2007, August 2008 and December 2011) of surface-to-surface transport events from the USA to Mace Head with the corresponding NAME model trajectories shown in Figure 5. Each individual HFC shows a substantial enhancement in the mixing ratio over the estimated mean baseline. The peak amplitudes of the enhancements range from about 5-12% above the baseline for HFC-125 and 6-15% for HFC-32, HFC-134a and HFC-143a. HFC-152a has notably the largest enhancements in excess of the baseline (50-95%), implying that the dominant emissions of HFC-152a are from the USA.

Figure 6 provides a more detailed illustration of the high temporal correlation ($R^2=0.98$) between HFC-152a and HFC-125 during the January 16th, 2006 transport event. Also shown are the upper bounds (dashed line) of the estimated baseline uncertainty. For all measurements we specifically calculate enhancements above this high estimated baseline to obtain an enhancement ratio of $\text{HFC}_x:\text{HFC-125}$. These volume ratios are converted into mass ratios by multiplying by the respective molecular weights and then by the annual USA HFC-125 UNFCCC emission estimate to obtain individual HFC_x emissions. As noted above we assume an uncertainty in the UNFCCC HFC-125 reported emissions of $\pm 5\%$.

There is a high degree of variability in the actual number of surface-to-surface transport events in any one year between the USA and Mace Head. For example, there were only 5 events in 2009 and 7 events in 2010. This compares with 10 events in 2011 and 13 events in 2012. Furthermore, individual transport events may be sustained for many hours between the two locations, although generally not longer than about 30 hours. In this type of event the HFCs are highly correlated. Conversely, some events may be only of short duration, providing just a few measurements, or in a few cases just a single measurement, which is inadequate for a reliable analysis. Interestingly, we observe that HFC-143a and HFC-32 are

not detectable above the upper bound of the estimated baseline in some events compared with HFC-152a, -134a and -125 which routinely have significant enhancements above the upper bound of the estimated baseline in almost all USA transport events.

For the purposes of this study, we provide our most accurate annual estimates of USA emissions where the tracer correlation ratio has a coefficient of determination $R^2 > 0.5$. For those cases where the transport event is sustained for only a few hours we are restricted to using the mean value of the tracer ratio calculated from the corresponding small number of measurements. Recognising these values will have less statistical significance we still include them with the most accurate estimates to provide an overall emission estimate for all data. Table 3 summarises these results with annual USA emission estimates from 2005-2012, including uncertainties reported as ± 1 -sigma (standard deviation) of the annual mean. For the most accurate data ($R^2 > 0.5$) we have good estimates for HFC-152a and HFC-134a, and even including all of the data, emissions estimates generally agree within the uncertainties. For HFC-143a there is insufficient highly correlated data in 2005 and 2006 to provide the most accurate emission estimates. HFC-32 only has sufficient data with a high correlation ($R^2 > 0.5$) in 2006, 2011 and 2012.

Figure 7 plots the most accurate annual USA emission estimates for HFC-152a, including 1-sigma uncertainties, compared with the UNFCCC estimates and also with previous published estimates. Only in 2005 and 2012 is there agreement, within the uncertainties, between the two estimates. Most notable is the apparent under-reporting of HFC-152a emissions by the USA to the UNFCCC with an annual average (2006-2012) difference of about 24 Gg (9-36 Gg) compared with this study. Our results in 2008 are in close agreement with Barletta et al., (2011), (31.3 ± 5.9 Gg versus 32 ± 4 Gg). Barletta et al., (2011) used carbon monoxide (CO) as the reference gas, and therefore to more directly compare our results we include our 2008 data also referenced to USA National 2008 CO

emissions of 7226 Gg, obtained from the US Environment Protection Agency (<http://www.epa.gov/ttnchie1/net/2011.inventory.html>). Our HFC-152a emission estimate for 2008, using comparable CO measurements at Mace Head as the reference gas is $33 \text{ Gg} \pm 6 \text{ Gg}$; again in close agreement with Barletta et al., (2011), unfortunately there are no reported uncertainties for the USA CO emission data. Miller et al., (2012) also provide HFC-152a emissions estimates averaged from 2004-2009 of 25 Gg (range 11-50Gg), which is very close to our average annual estimate (2005-2009) of 26 Gg (12-39 Gg). HFC-152a emission estimates for 2005 and 2006 reported by Stohl et al., (2009) are close to the UNFCCC estimates in those years, Millet et al., (2009) report an average emission for 2004-2006 of 7.6 Gg, which is also in reasonable agreement with the 2005 USA UNFCCC estimate and the estimate from this study, given the uncertainties.

Figure 8 charts our most accurate annual USA emission estimates for HFC-134a compared with the UNFCCC estimates. From 2005-2009 our estimates are lower than those reported to the UNFCCC by an annual average of about 24 Gg (21-28 Gg). From 2010-2012 the HFC-134a emission estimates begin to merge and agree within the uncertainties. Our 2008 emission estimates using HFC-125 ($44.6 \pm 9.5 \text{ Gg}$) and CO ($46 \pm 8 \text{ Gg}$), as the reference gases, are in excellent agreement with the results ($43 \pm 6 \text{ Gg}$) published by Barletta et al., (2011). HFC-134a emissions reported by Manning and Weiss (2006) for the western USA using the NAME model are also in reasonable agreement with our estimate (43 Gg versus 37.8 Gg). Miller et al., (2012) also provide HFC-134a emissions estimates averaged from 2004-2009 of 46 Gg (range 10-86 Gg), which is in close agreement with our average annual estimate (2005-2009) of 41 Gg (38-48 Gg). Previously published HFC-134a emissions by Stohl et al., (2009) and Millet et al., (2009) are slightly lower than our estimates which potentially implies over-reporting of HFC-134a emissions by the USA to the UNFCCC from 2005-2009.

Barletta et al., (2011) also adjusted their annual emission rates to allow for seasonal variability. In this 8-year study we record USA emissions in almost every month. In Figures 9 and 10 we examine the monthly average HFC emissions to determine if there is an indication of variations in seasonal emissions. Both HFC-152a and HFC-134a have statistically significant seasonal variations in emissions with a summertime maximum in the case of 134a, presumably due to higher ambient temperatures and possibly an increase in automobile usage with a concomitant increase in emissions from mobile air conditioners. The summertime minimum for HFC-152a is surprising, as it would not be expected that emissions from foam blowing, aerosols and the other sources of HFC-152a would have any seasonality. Yokouchi et al., (2006) also noted that HFC emissions were lower in summer than in other seasons associated with oceanic air masses transported from the south. This would not explain the lower summertime emissions observed in this study.

Turning now to HFC-143a, Figure 11 plots our most accurate emission estimates from 2007-2012 compared with the USA UNFCCC reported emissions. For 2005-2006, where data are not so well correlated, we include all data. In general, the USA reported emissions to the UNFCCC are lower relative to our estimates, with an annual average difference of about 1.8 Gg (0.95-3.5 Gg). Miller et al., (2012) also provide HFC-143a emissions estimates averaged from 2004-2009 of 5.2 Gg (range 3.6-11.3Gg), compared to our average annual estimate (2005-2009) of 4.3 Gg (3.2-5.0 Gg) which agree within the uncertainties.

For HFC-32, Figure 12 compares our emission estimate with those reported to the UNFCCC. As noted previously HFC-32 is only highly correlated in 2006, 2011 and 2012, therefore we include all data to obtain as many observations as possible. Surprisingly, in spite of the less accurate data we observe close agreement, within the uncertainties, between the two emission estimates with the exception of 2010. Our estimate for 2010 appears to be anomalously high by 1.9 Gg relative to the UNFCCC estimate. The tracer correlation ratio

HFC-32:HFC-125 is consistently larger throughout 2010 compared to all the other years, so it cannot be attributed simply to a particular transport event with an unusually high emission of HFC-32 or unusually low emission of HFC-125.

O'Doherty et al., (2013) have published global emission estimates for HFC-32 which shows a major increase in emissions beginning in 2010. They also show an acceleration of the annual growth rate of HFC-32 in 2010-2011, which slows again in 2012-2013. Emissions depend on many factors and although this may not fully explain our 2010 HFC-32 emission estimate it does suggest that there were significant changes in the emissions during this period. There appears to be a slowdown in the emissions of the primary HFCs, particularly in 2009, which is consistent with the slower economic activity during the 2008-2009 recessions. Furthermore, the drive to employ refrigerants with lower GWP will favour the use of HFC-32 in blends with HFC-125, at the expense of HFC-143a, consistent with the patterns shown in Figures 11 and 12. Assuming that our USA HFC -152a and HFC-134a emissions estimates, which are in very good agreement with other recently published emissions (Millet et al., 2009; Barletta et al., 2011; Miller et al., 2012), are correct then their joint mean USA contribution to atmospheric radiative forcing during 2011 would be equivalent to 95 ± 12 Tg- $\text{CO}_2\text{eq yr}^{-1}$. Including our mean 2011-2012 HFC-143a and HFC-32 emissions estimates and the USA UNFCCC HFC-125 reported emissions shows that the USA could potentially contribute 201 ± 36 Tg- $\text{CO}_2\text{eq yr}^{-1}$ to the global total for these five HFCs. This compares with UNFCCC of 146 Tg- $\text{CO}_2\text{eq yr}^{-1}$.

4. Conclusions.

Comparing our emissions estimates with those reported by the USA to the UNFCCC indicates an under-reporting of HFC-152a emissions by about 24 Gg (9-36 Gg). This exactly matches the apparent over-reporting of HFC-134a emissions 24 Gg (21-28 Gg) during 2005-2009, although after 2009 emission estimates agree within the uncertainties. We estimate that

HFC-143a is under-reported by about 1.8 Gg (0.95-3.5 Gg). This suggests incomplete reporting of these compounds and or biases in the accounting methodology. HFC-32 is not so highly correlated with HFC-125 during the USA transport events as the other three tracers; nevertheless we find that our emissions estimates and UNFCCC estimates agree within the uncertainties, except for 2010 when we estimate a difference of about 1.9 Gg. We note that the 2010 increase in USA emissions is consistent with recent global emission estimates for HFC-32. In addition we speculate that the trend towards lower GWP refrigerants would favour HFC-32 blends, with its lower GWP, relative to HFC-143a blends. We also noted a statistically significant summertime maximum in HFC-134a emissions and a summertime minimum in HFC-152a emissions.

Because the UNFCCC HFC-125 emissions are likely to have similar uncertainty to the other reported HFCs, we also estimated HFC-152 and HFC-134a emissions using 2008 Mace Head CO data as the reference tracer and the 2008 USA national CO emissions and found excellent agreement with recently published USA emission estimates for HFC-152a and HFC-143a providing some confidence in our methodology. Overall we find that the five principal HFCs during 2011-2012 could contribute approximately 201 Tg-CO₂ eq yr⁻¹ to radiative forcing compared with the UNFCCC of about 146 Tg-CO₂ eq yr⁻¹ for the same five HFCs.

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522 Table 1. GWPs, lifetimes, and reported growth rates of the five HFCs.

HFC	Formula	GWP*	Lifetime (years)	Growth rate (ppt yr ⁻¹)
125	C ₂ HF ₅	3170	29	0.9 (2007-2008), (O'Doherty et al., 2009)
134a	CH ₂ FCF ₃	1300	9.6	4.6 (2007-2008) WMO ¹
152a	C ₂ H ₄ F ₂	138	1.4	0.6 WMO ¹
143a	C ₂ H ₃ F ₃	4800	47	1.4 ± 0.04 in 2011, (O'Doherty et al., 2014)
32	CH ₂ F ₂	677	5.2	1.1 ± 0.04 in 2011, (O'Doherty et al., 2014)

523 *100-year time horizon, (Myhre et al., 2013). ¹ Scientific Assessment of Ozone depletion:
524 2010. WMO Global Ozone Research and Monitoring Project-Report No. 52. Switzerland.

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526 Table 2. The five most important refrigerant blends and the percentage contribution of each
527 HFC to the blend.

REFRIGERANT	125	32	134a	143a
	%	%	%	%
410A	50	50		
407C	25	23	52	
407A	40	20	40	
404A	44		4	52
507A	50			50

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533 Table 3. Summary of USA Emission estimates (2005-2012)

Year	152a ($R^2 > 0.5$) Gg $\pm$ 1 sigma	N	152a (All data) Gg $\pm$ 1 sigma	N	134a ($R^2 > 0.5$) Gg $\pm$ 1 sigma	N	134a (All data) Gg $\pm$ 1 sigma	N
2005	12.1 $\pm$ 2.9	10	12.7 $\pm$ 2.7	33	38.7 $\pm$ 5.9	11	34.0 $\pm$ 8.6	33
2006	21.5 $\pm$ 4.1	28	21.7 $\pm$ 3.5	38	37.8 $\pm$ 6.4	25	38.1 $\pm$ 7.6	32
2007	29.1 $\pm$ 5.5	48	29.4 $\pm$ 5.5	55	37.5 $\pm$ 8.7	52	37.8 $\pm$ 8.5	55
2008	31.3 $\pm$ 5.9	21	30.3 $\pm$ 7.0	42	44.6 $\pm$ 9.5	19	42.1 $\pm$ 10.8	47
2009	39.4 $\pm$ 4.3	12	33.5 $\pm$ 9.1	20	48.1 $\pm$ 7.4	12	41.0 $\pm$ 11.0	23
2010	43.6 $\pm$ 14.8	12	41.6 $\pm$ 14.6	14	62.0 $\pm$ 16.9	7	56.8 $\pm$ 13.8	18
2011	46.3 $\pm$ 6.1	17	48.7 $\pm$ 12.9	40	66.8 $\pm$ 15.3	7	60.1 $\pm$ 12.8	40
2012	51.5 $\pm$ 16.0	58	53.2 $\pm$ 16.5	78	69.6 $\pm$ 18.4	51	68.0 $\pm$ 17.7	78

Year	143a ($R^2 > 0.5$) Gg $\pm$ 1 sigma	N	143a (All data) Gg $\pm$ 1 sigma	N	32 ($R^2 > 0.5$) Gg $\pm$ 1 sigma	N	32 (All data) Gg $\pm$ 1 sigma	N
2005			3.2 $\pm$ 1.0	24			0.6 $\pm$ 0.2	13
2006			3.8 $\pm$ 0.9	23	0.8 $\pm$ 0.4	10	1.1 $\pm$ 0.3	17
2007	4.5 $\pm$ 0.9	11	4.8 $\pm$ 1.0	43			1.6 $\pm$ 0.7	29
2008	5.0 $\pm$ 1.1	27	4.9 $\pm$ 1.1	37			2.0 $\pm$ 0.9	31
2009	5.0 $\pm$ 1.0	5	4.8 $\pm$ 0.9	7			2.2 $\pm$ 0.6	15
2010	5.3 $\pm$ 1.8	5	7.1 $\pm$ 2.5	15			5.7 $\pm$ 1.5	13
2011	6.6 $\pm$ 1.5	6	7.4 $\pm$ 1.4	21	5.6 $\pm$ 1.1	8	5.5 $\pm$ 1.3	26
2012	8.5 $\pm$ 1.9	18	8.2 $\pm$ 2.9	32	5.5 $\pm$ 1.9	6	6.5 $\pm$ 2.2	54

535 Notes: ($R^2 > 0.5$). Coefficient of determination from the regression slopes of HFC-152a,
536 HFC-134a, HFC-143a and HFC-32 versus HFC-125. (All data). Includes all measurements
537 attributed to USA transport. N = Number of data points. (1 sigma = standard deviation of the
538 annual mean).

543 Figures 1-4. Examples of direct transport events from the USA to Mace Head, showing the
 544 close temporal correlation of the enhancements in mixing ratios (ppt) of the five HFCs. The
 545 coefficient of determination R^2 for each HFC relative to HFC-125 are also included in each
 546 figure.

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Figure 5. NAME air histories during transport events shown in Figures 1-4.

18-21Z
16/01/2006

06-09Z
14/03/2007

12-15Z
27/08/2008

18-21Z
19/12/2011

Figure 6. Detailed temporal correlation between HFC-152a and HFC-125, showing mean baseline (solid line) and upper bound of baseline uncertainty (=high baseline, dashed line) and XY scatterplot (insert).

Figure 7. HFC-152a Annual USA emissions estimates. This study and other published estimates compared to UNFCCC.

Figure 8. HFC-134a Annual USA emissions estimates. This study and other published estimates compared to UNFCCC.

Figure 9. Seasonal variability of the average monthly emissions of HFC-152a.

Note: A seasonal cycle of the form: $a + b \cdot \sin(\pi t + \theta)$ was fitted through the data using a non-linear regression programme (NLREG, Sherrod, 1997) where t is the time since 1st January and θ is the phase angle.

Figure 10. Seasonal variability of the average monthly emissions of HFC-134a.

Note: A seasonal cycle of the form: $a + b \cdot \sin(\pi t + \theta)$ was fitted through the data using a non-linear regression programme (NLREG, Sherrod, 1997) where t is the time since 1st January and θ is the phase angle.

Figure 11. HFC-143a Annual USA emission estimates compared to UNFCCC.

Note: For 2005 and 2006 all data are plotted.

636 Figure 12. HFC-32 Annual emission estimates compared to UNFCCC.

637 Note: For 2005, 2006 and 2011 $R^2 > 0.5$. For other years all data are plotted.

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HFCs-152a, -134a,-143a,-32 USA emissions estimated by the tracer correlation method

HFC-152a average (2005-2012) USA emission estimates are 34.3 ± 7.5 Gg yr⁻¹ (12-53 Gg)

Average annual 152a USA emissions reported to UNFCCC are 24 Gg lower than this study

HFC-134a average (2005-2012) USA emission estimates are 50.6 ± 11.1 Gg yr⁻¹ (38-70 Gg)

Average annual 134a USA emissions reported to UNFCCC are 24 Gg higher than this study