Recent increases in global HFC-23 emissions

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[1] Firn-air and ambient air measurements of CHF_3 (HFC-23) from three excursions to Antarctica between 2001 and 2009 are used to construct a consistent Southern Hemisphere (SH) atmospheric history. The results show atmospheric mixing ratios of HFC-23 continuing to increase through 2008. Mean global emissions derived from this data for 2006–2008 are 13.5 ± 2 Gg/yr (200 ± 30 × 10^{12} gCO_2-equivalent/yr, or $MtCO_2$-eq./yr), ∼50% higher than the 8.7 ± 1 Gg/yr (130 ± 15 $MtCO_2$-eq./yr) derived for the 1990s. HFC-23 emissions arise primarily from over-fluorination of chloroform during HCFC-22 production. The recent global emission increases are attributed to rapidly increasing HCFC-22 production in developing countries since reported HFC-23 emissions from developed countries decreased over this period. The emissions inferred here for developing countries during 2006–2008 averaged 11 ± 2 Gg/yr HFC-23 (160 ± 30 $MtCO_2$-eq./yr) and are larger than the ∼6 Gg/yr of HFC-23 destroyed in United Nations Framework Convention on Climate Change Clean Development Mechanism projects during 2007 and 2008.
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1. Introduction

[2] Trifluoromethane (HFC-23) has an atmospheric lifetime of 270 yr, a 100-yr global warming potential (GWP) of 14,800 [*Forster et al.*, 2007], and is an unavoidable by-product of chlorodifluoromethane (HCFC-22) production. Climate concerns have prompted efforts to reduce HFC-23 emissions by optimizing conditions during production of HCFC-22 and by destroying HFC-23 before it escapes to the atmosphere. Through voluntary and regulatory efforts in developed (Annex 1) countries [e.g., *Environmental Protection Agency*, 2009; *Ministry of the Environment*, 2009] and projects funded through the United Nations Clean Development Mechanism (CDM) in developing (non-Annex 1) countries, significant amounts of HFC-23 emissions have been avoided. Annual reported HFC-23 emissions from Annex 1 countries totaled 2.8 Gg/yr (42 $MtCO_2$-eq./yr) in 2007, down from 6 – 8 Gg/yr during the 1990s [*United Nations Framework Convention on Climate Change* (*UNFCCC*), 2009]. Emissions from non-Annex 1 countries are not reported to the United Nations Framework Convention on Climate change (UNFCCC). Approved CDM projects in non-Annex 1 countries generated Certified Emission Reductions (CERs) of 5.7 and 6.5 Gg of HFC-23 (84 and 97 $MtCO_2$-eq.), in 2007 and 2008, respectively [*UNFCCC*, 2009]. These CDM projects had a value during 2007 and 2008 of nearly US$1 billion annually (at US$13 per ton CO_2-eq.), which is substantially higher than the estimated industry cost of this HFC-23 emission abatement alone [*Wara*, 2007].

[3] The importance of understanding the influence of HFC-23 emission abatement efforts has increased with rapid growth in recent production of HCFC-22 in developing countries for both dispersive and feedstock uses [*United Nations Environment Programme* (*UNEP*), 2009]. Atmosphere-based estimates of HFC-23 emissions are relevant to ongoing discussions under the UNFCCC and its Kyoto Protocol regarding renewing existing CDM projects and approving additional projects for HCFC-22 facilities that are not currently eligible to participate in this program. In this paper global HFC-23 emissions are estimated from measurements of HFC-23 in ambient air and air from the perennial snowpack (firn) during three separate excursions to Antarctica between 2001 and 2009. The analysis of air trapped in firn provides a robust record of atmospheric trace-gas changes during the past 50–100 years [*Bender et al.*, 1994; *Battle et al.*, 1996; *Butler et al.*, 1999].

2. Experiment

2.1. Firn-Air Sampling

[4] Established techniques (*Bender et al.*, 1994; *Battle et al.*, 1996; *Butler et al.*, 1999) were used to extract air samples from the Antarctic firn (10–120 m below surface) at South Pole in January of 2001 (89.98°S; 2800 m above sea level) (SPO'01); at the West Antarctic Ice Sheet Divide in late December of 2005 (79.46°S; 112.13°W; 1759 masl) (WAIS-D); and at South Pole in December 2008–January 2009 (89.98 °S; 2835 masl) (SPO'08-09). This same equipment was used to collect ambient air samples above the firn during each of these excursions. Firn-air and ambient air samples collected in 2001 and 2005 were stored in stainless-steel electropolished canisters ranging in size from 3–30L prior to analysis in 2007 or 2008. In 2001, a surface sample was similarly filled and stored in a 30L acculife-treated aluminum tank. Samples from two independent holes drilled during SPO'08-09 were stored in 3L electropolished stainless-steel and 2L glass flasks and were analyzed during spring and summer of 2009. Results from both holes in 2008-2009 are considered together here.

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Table 1. Reduced χ^2 Between the HFC-23 Versus HCFC-22 Relationship Measured in Firn-Air and That Which Was Modeled Using Different HFC-23 Trial Atmospheric Histories and the Known HCFC-22 History[a]

History	Reduced χ^{2b} Firn Sampling Missions			HFC-23 Emissions Record Used to Derive Atmospheric Histories[c]
	SPO'01	WAIS-D	SPO'08-09	
		Preliminary Trial History		
C	**0.7**	**0.7**	**1.3**	see text and Text S1
		Additional Trial Histories Different From C Only After 1995		
E1[d]		10		1996-2008: M&L Business as usual
E2[d]		9		1996–2008: M&L Best available practice
F1[e]	**0.8**	**1.0**	**0.8**	1996–2008: P_{22}(UNEPa)[b] 2.8%
F2[e]	**0.8**	**0.8**	**1.5**	1996–2008: P_{22}(UNEPa)[b] 3.0%
F3[e]	0.6	2.1	2.6	1996–2008: P_{22}(UNEPa)[b] 3.2%
G	**0.8**	**0.8**	**1.4**	1996–2008: P_{22}(M&L)[b] 2.0%
H		0.6	2.3	1996–2008: E_{23} to give linear mixing ratio increase to 18.1 ppt in December 2005; constant emission thereafter
K1		1.0	5.1	1996–2008: $P_{22}(UNEP_{A5\ total})$[b] 2.4% + $P_{22}(UNEP_{(nonA5\ total)})$[b] 1.7%)
K2	**0.6**	**0.9**	**1.4**	same as K1, minus CDMs in 2003–2008

[a]Histories giving the lowest cumulative reduced χ^2 are denoted with bold text and are shown with red lines in Figures 1 and 2a. Additional trial atmospheric histories (total of 20) were derived but gave poor fits (see Text S1). E_{23} = HFC-23 emission. P_{22} = HCFC-22 reported production.

[b]Reduced χ^2 values for SPO'01 were calculated with all firn data, but for WAIS-D and at SPO'08-09 with samples only from the mid-to-upper firn (see text). For the eight degrees of freedom associated with the nine samples used to assess histories at both WAIS-D and SPO'08-09 (HCFC-22 > 90 ppt), $P < 0.1$ for $\chi^2 \geq 1.67$ ($P < 0.05$ for $\chi^2 \geq 1.938$). For SPO'01 (degrees of freedom = 10), $P < 0.1$ for $\chi^2 > 1.6$ [*Bevington and Robinson*, 2003].

[c]Atmospheric HFC-23 histories were derived by incorporating the indicated emission record into box models simulating the global atmosphere.

[d]M&L = *McCulloch and Lindley* [2007]—these emissions are very similar to those in *IPCC* [2005] as they were both derived from updates to *Oram et al.*'s [1998] atmospheric record.

[e]UNEPa = UNEP HCFC-22 production amounts for dispersive uses only. Fractions of 2.8, 3.0, and 3.2% of UNEPa production correspond approximately to 1.8, 1.9, and 2.0% of total UNEP HCFC-22 production. UNEP($P_{22,\ A5\ total}$) and UNEP($P_{22,\ nA5\ total}$) correspond to total HCFC-22 production reported for all uses by developing (A5) and developed (nonA5) countries, respectively (terms used as defined in the Montreal Protocol) (see Text S1).

2.2. Firn-Air Analysis

[5] Flask air was analyzed using gas chromatography with mass spectrometry and sample cryo-trapping techniques [*Montzka et al.*, 1993]. Separation was performed on a 30-m Gas-Pro column. Both HFC-23 and HCFC-22 were detected with the CHF_2^+ ion (m/z = 51) eluting at different times. Calibration is based upon static HFC-23 standards at 8.53 and 25.12 ppt that were prepared with gravimetric techniques. Calibration for HCFC-22 has been discussed previously [*Montzka et al.*, 1993]. Consistency in HFC-23 calibration was checked by periodic analyses of 4 archived air tanks. Results from these analyses showed no significant secular trend in HFC-23 mixing ratios (0.1 ± 0.1 ppt/yr) during 2007–2009. Based on repeat analyses of ambient air and differences between simultaneously filled flasks, the uncertainty on HFC-23 measurements is estimated to be 0.3 ppt.

2.3. Firn Modeling

[6] Diffusive air movement within firn was simulated with two different firn models: the Bowdoin model for SPO'01 and WAIS-D [*Mischler et al.*, 2009], and the UCI model for SPO'08-09 [*Aydin et al.*, 2004]. These models allow the consistency between a given trace-gas atmospheric history and firn-air measurements to be tested. The modeled diffusivity *vs.* depth relationships for each of the field studies were empirically determined by optimizing the agreement between modeled and measured CO_2 depth profiles and the known Antarctic atmospheric CO_2 history [*Etheridge et al.*, 1996; *Conway et al.*, 2004].

[7] An initial atmospheric history for HFC-23 from the 1940s to 2009 (history C) was derived from consideration of multiple inputs: during 1943 to 1995 with an atmospheric box model [*Montzka et al.*, 2009] in which HFC-23 emissions were derived as a constant percentage of past HCFC-22 production (Alternative Fluorocarbons Environmental Acceptability Study, data tables, 2009, available at http://www.afeas.org) and scaled to fit published measurements of HFC-23 from 40°S during the early 1990s [*Oram et al.*, 1998]; during 1996–2006 with firn-model-based dating of HFC-23 and HCFC-22 firn data using the "effective age technique" [*Trudinger et al.*, 2002]; and with ambient measurements made during the firn-air collections in Jan. 2001, Dec. 2005, and Dec. 2008–Jan. 2009 and constant emissions during 2006–2008.

[8] Nineteen additional trial mixing ratio histories were considered for HFC-23 (Table 1 and Text S1 of the auxiliary material).[1] Most differed from C only in years after 1995 and were derived with an atmospheric box model incorporating HFC-23 emissions as different and variable fractions of reported HCFC-22 production (F, G, and K histories). A constant emissions scenario was also tested (history H) as were emissions histories derived from updated Cape Grim observations [*McCulloch and Lindley*, 2007; *Intergovernmental Panel on Climate Change* (*IPCC*), 2005] (E histories). Histories were also derived from constant HFC-23 emission to HCFC-22 production (E_{23}/P_{22}) fractions to match observed atmospheric HFC-23 mixing ratios at certain dates and as modifications to good-fitting histories, but these trial histories gave poor fits to firn-air results (J and L histories in Text S1).

[1]Auxiliary materials are available in the HTML. doi:10.1029/2009GL041195.

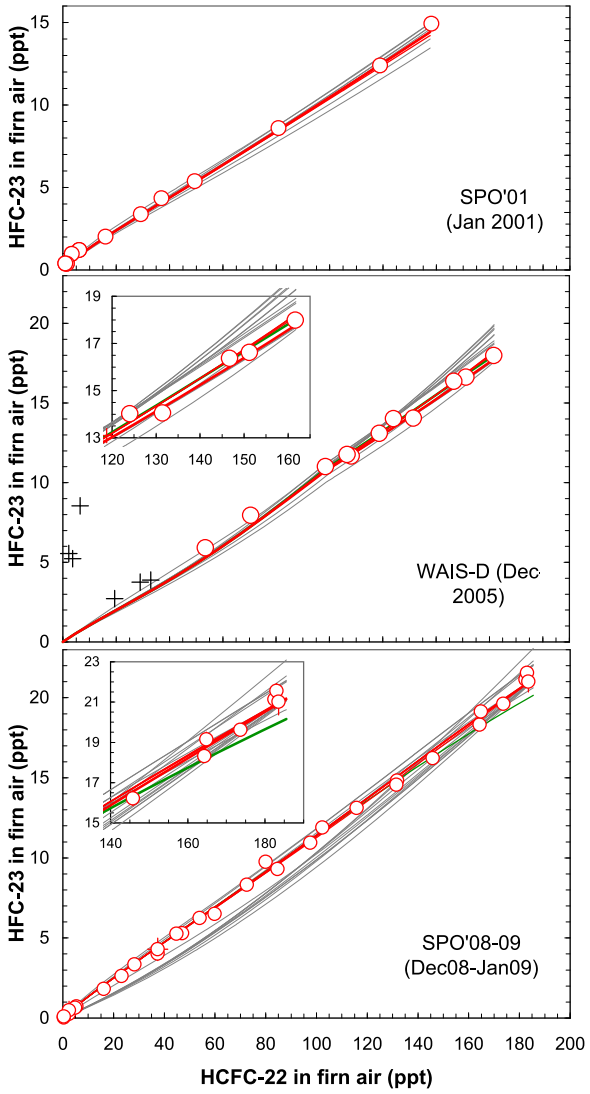

Figure 1. Modeled and measured firn-air mixing ratios of HFC-23 vs. HCFC-22 from three different firn samplings. Multiple trial histories were derived (lines) and incorporated into the firn models to assess their consistency to firn-air measurements (points) (see Table 1 and Text S1 for history descriptions). Best-fitting histories (C, F1, F2, G, K2) are shown as red lines; others are shown in gray, except history H (green line). Results from WAIS-D showing substantial pump contamination are indicated as plus symbols. Insets are expanded views of results from the upper firn. Uppermost points are ambient air samples filled through firn-sampling apparati.

[9] The well known atmospheric history of HCFC-22, derived from ongoing and archived surface flask measurements [*Montzka et al.*, 1993; 2009; *Miller et al.*, 1998] (see Text S1), provides the basis here for deriving accurate HFC-23 histories from firn air. The consistency between trial HFC-23 histories and firn-air data was objectively assessed by calculating reduced χ^2 between the modeled and measured HFC-23 *vs.* HCFC-22 relationship in firn air (Table 1). Reduced χ^2 is calculated as $\sum[(\text{model}-\text{observed})^2/\text{error}^2]/(\text{degrees of freedom})$; a χ^2 of 1.0 indicates that residuals and uncertainties are similar. The HFC-23 *vs.* HCFC-22 relationship was used to assess trial HFC-23 histories in order to minimize the influence of errors in the firn diffusivity *vs.* depth parameterization [*Battle et al.*, 1996]. The accuracy of these models was validated using firn-air measurements of other compounds having well known atmospheric histories (HCFC-22, CFC-12, HFC-134a, and CH_3CCl_3). Consistent results were obtained for all these gases despite their very different histories (see Text S1). Similar conclusions regarding which HFC-23 trial histories are most consistent with the firn data are reached when trial histories are evaluated with the SH atmospheric history and firn data for CO_2.

3. Results and Discussion

[10] Results from all three Antarctic firn-air samplings show tight correlations between HFC-23 and HCFC-22 mixing ratios that are nearly linear, suggesting similar relative atmospheric changes for these trace gases in the past (Figure 1). This observation is consistent with emissions of HFC-23 arising primarily from HCFC-22 production at a fairly constant yield. Yields of 1.5 to 4% (by mass) of HFC-23 are typical during the production of HCFC-22, depending upon how well this process is optimized [*McCulloch and Lindley*, 2007].

[11] Firn air diffusion models provide a means to compare trial atmospheric histories with firn-air observations. A rough estimate of 20th-century changes in HFC-23 mixing ratios was initially provided with history C. This history, when modeled with the Bowdoin and UCI models, yields an expected firn profile that is highly consistent with the entire measured firn profile from SPO'01 and SPO'08-09 (χ^2 = 0.7 for SPO'01 and 0.8 for SPO'08-09). This history is also reasonably consistent with *Oram et al.*'s [1998] results. Contamination of the deepest samples collected at WAIS-D by the KNF pump prevented an assessment of the older part of history C with the WAIS-D data (see Text S1).

[12] To improve our understanding of atmospheric HFC-23 changes since the mid-1990s, a set of trial histories was derived as modifications of history C in years after 1995. These histories were also assessed with the reduced χ^2 metric but only against firn samples in the mid-to-upper firn profile having HCFC-22 mixing ratios >90 ppt (>68 m depth at WAIS-D and >62 m depth at SPO'08-09) (Table 1). HCFC-22 mixing ratios of >90 ppt are representative of high-latitude SH sites since the early 1990s [*Montzka et al.*, 1993; *Miller et al.*, 1998]. Calculated in this way, the reduced χ^2 metric reflects model-data agreement for the past two decades.

[13] Among these trial atmospheric histories, only a few provided a good fit ($P < 0.1$ for reduced $\chi^2 > 1.67$) to results from WAIS-D and SPO'08-09 in the mid-to-upper firn (Table 1 and Figure 1). All of these best-fit histories suggest an increase in the growth rate of HFC-23 in the atmosphere after 2005. Trial history H was derived as a linear increase to match ambient mixing ratios in 2001 and at the end of 2005. This history provides a good fit to the WAIS-D firn profile collected in December 2005 (χ^2 = 0.6), but, when extrapolated to January 2009, underestimates the surface mixing ratio measured during SPO'08-09 in three different flasks by ~1 ppt (Figure 1). History H also gives a poor fit to the SPO'08-09 firn results (χ^2 = 2.3; Table 1), providing

further evidence that the atmospheric growth rate of HFC-23 increased in recent years.

[14] The range of trial atmospheric histories considered here leads to a wide range of past global HFC-23 emissions (Figure 2a). The atmospheric histories giving the lowest χ^2 all suggest fairly constant emissions from 1990 to 2003 and increased emissions thereafter. A best estimate HFC-23 emissions record was derived from the mean of the five best-fitting SH atmospheric histories and indicates global HFC-23 emissions of 8.7 ± 1 Gg/yr during the 1990s and 13.5 ± 2 Gg/yr (200 $MtCO_2$-eq./yr) during 2006–2008 (Figure 2b). By comparison, HCFC-22 emissions during 2006-2008 averaged 610 $MtCO_2$-eq./yr [*Montzka et al.*, 2009]. The best estimate HFC-23 emissions history is consistent with one derived from all 20 trial histories after weighting annual emissions by the sum of $1/\chi^2$ from WAIS-D and SPO'08-09. It is also consistent with the mean emissions implied by measured HFC-23 changes in ambient air since 2001 (Figure 2b; see also Text S1). When considered with global HCFC-22 production data (including feedstocks), these results suggest a global mean E_{23}/P_{22} fraction of 1.7% by mass for 2003–2008, which is slightly less than observed in the 1990s (Figure 2c) [*Oram et al.*, 1998; *McCulloch and Lindley*, 2007].

[15] HFC-23 emissions from Annex 1 countries reported to the UNFCCC indicate a substantial decline beginning in 1998 as a result of voluntary and regulatory efforts (Figure 2b) [*UNFCCC*, 2009] (see Table 2 of Text S1). The decline in Annex 1 emissions stems from reduced HCFC-22 production and a decrease in the E_{23}/P_{22} fraction from approximately 2% in the 1990s to 0.9% during 2003–2007 (Figure 2c). Reported reductions in Annex 1 HFC-23 emissions and in the E_{23}/P_{22} fraction cannot be directly verfied with our atmospheric data because during this same period HFC-23 emissions were changing as HCFC-22 production was increasing rapidly in non-Annex 1 countries (Figure 2d).

[16] The difference between global emissions derived here and those reported to the UNFCCC from Annex 1 countries provides an estimate of HFC-23 emissions from non-Annex 1 countries, which are not reported to the UNFCCC (Figure 2b). This analysis suggests steady increases in HFC-23 emissions from non-Annex 1 countries at the same time their HCFC-22 production was increasing on average by ~50 Gg/yr (from 2000 to 2007) (Figures 2b and 2d). Mean HFC-23 emissions from non-Annex 1 countries are estimated to have been 11 ± 2 Gg/y during 2006–2008. A mean E_{23}/P_{22} of 2.4 ± 0.3% is derived for this same period using total non-Annex 1 HCFC-22 production (Figure 2c).

[17] UNFCCC data show that 5.7 and 6.5 Gg of HFC-23 (84-97 $MtCO_2$-eq.) were destroyed in 2007 and 2008, respectively, through the execution of CDM projects approved by the UNFCCC (Figure 2d; see Table 2 of Text S1). This represents the destruction of HFC-23 emissions from 43–48% of the HCFC-22 produced in non-Annex 1

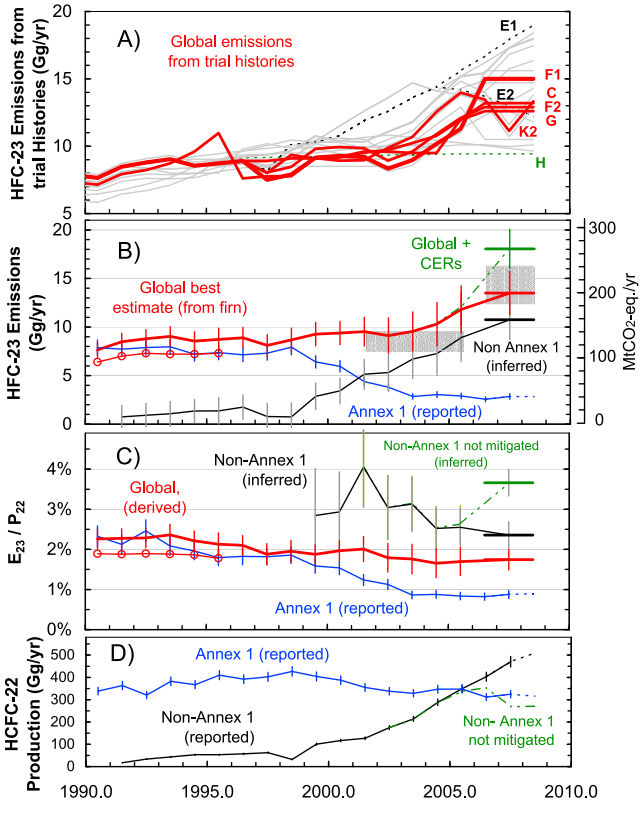

Figure 2. (a and b) HFC-23 emissions, (c) the HFC-23 emission to HCFC-22 production ratio (E_{23}/P_{22}), and (d) HCFC-22 production including chemical feedstock uses. Results are shown for the globe (red lines), for Annex 1 countries (blue lines) and for non-Annex 1 countries (black lines). Figure 2b includes a global best-estimate HFC-23 emissions history calculated from the mean of the best-fit trial histories in Figure 2a (bold red lines; other histories shown as different colors). Global emissions derived from surface measurements alone are indicated as shaded gray regions (Figure 2b, see Text S1). HFC-23 emissions from non-Annex 1 countries are calculated from the difference between the best-estimate global emissions and HFC-23 emissions reported by Annex 1 countries [*UNFCCC*, 2009] (Figure 2b). E_{23}/P_{22} values are derived from emissions in Figure 2b and HCFC-22 production data including unrestricted amounts for feedstocks, which accounted for 37% of global production in 2007 [*UNEP*, 2009]. Adding CDM-related CER quantities to the best-estimate global HFC-23 emissions shows the world avoided by CDM projects (green dot-dot-dashed lines (Figure 2b; see Table 2 in Text S1). The green dot-dot-dashed line in Figure 2c is calculated from total non-Annex 1 HFC-23 emissions divided by non-Annex 1 HCFC production not covered by CDMs. Firn and ambient air results yield only a single average for 2006–2008 emissions and quantities derived from these emissions. Global quantities estimated elsewhere are also shown (red circles and lines [*Oram et al.*, 1998] (Figures 2b and 2c). Production and Annex 1 emission data for 2008 are projections (dashed lines in Figures 2b–2d). Uncertainties on firn-derived global emissions represent the spread of best-fit trial histories plus a modeling uncertainty of 10%. Uncertainties of ± 5% are applied to production data and ±10% on reported Annex 1 HFC-23 emissions (see Text S1). Though a 100-yr GWP of 14800 is used here to convert HFC-23 emissions to CO_2-eq. emissions [*Forster et al.*, 2007], the *UNFCCC* [2009] uses a GWP of 11700. Annual values are plotted at mid-year.

countries during these years. In the world avoided defined by the absence of HFC-23 destruction by CDM projects, global emissions of HFC-23 would have doubled from ~9 Gg/yr to ~18 Gg/yr during the past decade as HCFC-22 production increased in non-Annex 1 countries (Figure 2b).

[18] Our results indicate that 11 ± 2 Gg/yr of HFC-23 (160 ± 30 $MtCO_2$-eq./yr) was emitted during 2006–2008 from non-Annex 1 countries. These emissions are associated with HCFC-22 production not covered by CDM projects and have an inferred E_{23}/P_{22} ratio of 3.7 ± 0.3% (Figure 2c; Table 2 of Text S1). This ratio is slightly higher, on average, than inferred for non-Annex 1 countries in most other years and is substantially larger than reported by Annex 1 countries. There are uncertainties in this ratio related to the precise timing of the inferred global emission changes and the extrapolation to 2008 of the Annex 1 reported emission and HCFC-22 production magnitudes. However, these uncertainties do not appreciably affect our derived 2006–2008 emission and E_{23}/P_{22} estimates because these estimates represent averages over a 3-year period. The rather high yield ratio inferred for non-Annex 1 HCFC-22 production not currently covered by CDM projects explains why the global E_{23}/P_{22} fraction did not decrease between 2003 and 2008, even though HFC-23 emissions associated with ~30% of total global HCFC-22 production were abated by CDM projects during 2007–2008 (Figures 2c and 2d).

[19] In summary, the new atmospheric and firn air observations presented here indicate a substantial increase in global HFC-23 mixing ratios and emissions during the early 2000s. These increases are derived for a period when Annex 1 countries reported decreasing emissions to the UNFCCC, indicating that HFC-23 emissions from non-Annex 1 countries increased as they produced more HCFC-22. Although CDM projects destroyed a large fraction of HFC-23 emissions from non-Annex 1 countries during 2007–2008, both HCFC-22 production data and the non-Annex 1 HFC-23 emissions inferred here suggest that a substantial amount of HCFC-22 production and associated HFC-23 emission continued unabated during these years.

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References

Aydin, M., E. S. Saltzman, W. J. De Bruyn, S. A. Montzka, J. H. Butler, and M. Battle (2004), Atmospheric variability of methyl chloride during the last 300 years from an Antarctic ice core and firn air, *Geophys. Res. Lett.*, *31*, L02109, doi:10.1029/2003GL018750.

Battle, M., et al. (1996), Atmospheric gas concentrations over the past century measured in air from firn at the South Pole, *Nature*, *383*, 231–235, doi:10.1038/383231a0.

Bender, M. L., T. Sowers, J.-M. Barnola, and J. Chappellaz (1994), Changes in the O_2/N_2 ratio of the atmosphere during recent decades reflected in the composition of air in the firn at Vostok Station, Antarctica, *Geophys. Res. Lett.*, *21*, 189–192, doi:10.1029/93GL03548.

Bevington, P. R., and D. K. Robinson (2003), *Data Reduction and Error Analysis for the Physical Sciences*, 3rd ed., McGraw Hill, New York.

Butler, J. H., et al. (1999), A twentieth century record of atmospheric halocarbons in polar firn air, *Nature*, *399*, 749–755, doi:10.1038/21586.

Conway, T. J., et al. (2004), Carbon cycle greenhouse gases, *Clim. Monit. Diagn. Lab. Summary Rep. 27 2002–2003*, edited by R. Schnell, D. A.-M. Buggle, and R. Rosson, chap. 2, pp. 32–57, NOAA, Boulder, Colo.

Environmental Protection Agency (2009), Inventory of U.S. greenhouse gas emissions and sinks: 1990-2007, *Rep. EPA 430-R-09-004*, Environ. Prot. Agency, Washington, D. C.

Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, and J.-M. Barnola (1996), Natural and anthropogenic changes in atmospheric CO_2 over the last 1000 years from air in Antarctic ice and firn, *J. Geophys. Res.*, *101*, 4115–4128, doi:10.1029/95JD03410.

Forster, P., et al. (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon et al., pp. 129–234, Cambridge Univ. Press, Cambridge, U. K.

Intergovernmental Panel on Climate Change (IPCC) (2005), *Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons*, edited by B. Metz, et al., Cambridge Univ. Press, Cambridge, U. K.

McCulloch, A., and A. A. Lindley (2007), Global emissions of HFC-23 estimated to year 2015, *Atmos. Environ.*, *41*, 1560–1566, doi:10.1016/j.atmosenv.2006.02.021.

Miller, B. R., J. Huang, R. F. Weiss, R. G. Prinn, and P. J. Fraser (1998), Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, *J. Geophys. Res.*, *103*, 13,237–13,248, doi:10.1029/98JD00771.

Ministry of the Environment (2009), National greenhouse gas inventory report of Japan, Minist. of the Environ., Tsukuba, Japan.

Mischler, J. A., et al. (2009), Carbon and hydrogen isotopic composition of methane over the last 1000 Years, *Global Biogeochem. Cycles*, *23*, GB4024, doi:10.1029/2009GB003460.

Montzka, S. A., R. C. Myers, J. H. Butler, J. W. Elkins, and S. O. Cummings (1993), Global tropospheric distribution and calibration scale of HCFC-22, *Geophys. Res. Lett.*, *20*, 703–706, doi:10.1029/93GL00753.

Montzka, S. A., B. D. Hall, and J. W. Elkins (2009), Accelerated increases observed for hydrochlorofluorocarbons since 2004 in the global atmosphere, *Geophys. Res. Lett.*, *36*, L03804, doi:10.1029/2008GL036475.

Oram, D. E., W. T. Sturges, A. S. Penkett, A. McCulloch, and P. J. Fraser (1998), Growth of fluoroform (CHF_3, HFC-23) in the background atmosphere, *Geophys. Res. Lett.*, *25*, 35–38, doi:10.1029/97GL03483.

Trudinger, C. M., D. M. Etheridge, P. J. Rayner, I. G. Enting, G. A. Sturrock, and R. L. Langenfelds (2002), Reconstructing atmospheric histories from measurements of air composition in firn, *J. Geophys. Res.*, *107*(D24), 4780, doi:10.1029/2002JD002545.

United Nations Environment Programme (UNEP) (2009), HCFC Production Data, http://ozone.unep.org/Data_Reporting/Data_Access/, U. N. Eviron. Programme, Nairobi.

United Nations Framework Convention on Climate Change (UNFCCC) (2009), Greenhouse Gas Emissions Data, http://unfccc.int/ghg_data/ghg_data_unfccc/items/4146.php, U. N. Framework Conv. on Clim. Change, Bonn, Germany.

Wara, M. (2007), Is the global carbon market working?, *Nature*, 445, 595–596, doi:10.1038/445595a.

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Supplemental information to the manuscript by Montzka *et al*., Recent increases in global HFC-23 emissions.

1) Deriving global emissions from SH atmospheric records and a description of additional trial histories:

Global HFC-23 emissions histories were calculated using simple box models (Montzka *et al*., 2009) for trial SH atmospheric histories. A comparison between global emissions derived for HFC-23 with these box models and those derived with 2-D models (Oram *et al*., 1998) suggests rather small differences (~7%).

Supplement Table 1: Trial histories giving poorer fits and not included in Table 1 of the published paper. Reduced χ^2 between the HFC-23 *vs.* HCFC-22 relationship measured in firn-air and that which was modeled using different HFC-23 trial atmospheric histories and the known HCFC-22 history..

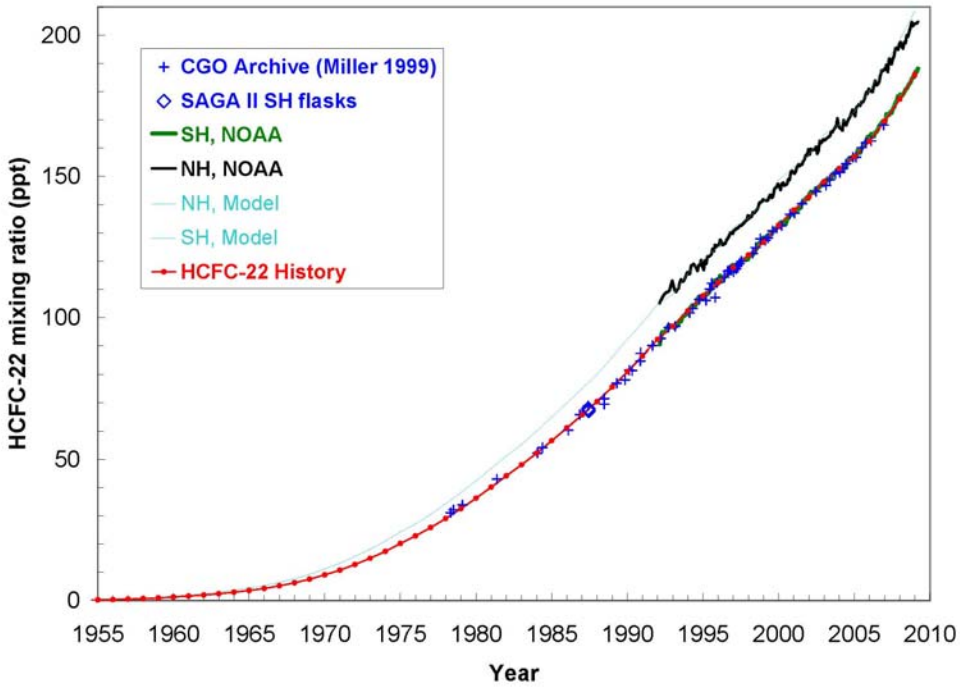
History	*Reduced χ^{2*}*			*HFC-23 emissions record used to derive atmospheric histories* [#]
	Firn sampling missions			
	SPO'01	*WAIS-D*	*SPO'08-09*	
Additional trial histories different from C only after 1995:				
D1	na	13	na	After 1996: IPCC/TEAP (2005) BAU
D2	na	12	na	After 1996: IPCC/TEAP (2005) BAP
Modifications to history F1, which shows good consistency with firn results:				
L1	na	1.1	12	smoothed F1 emissions (~const from '94-'02)
L2	na	1.3	12	F1 but slightly less in '98-03 and higher after
L3	na	0.7	8	'93-'02 const, then linear increase to 14.3 in '09
L4	na	5	5	linear increase until '02; decreasing after
Based on HFC-23 emissions derived from different E_{23}/P_{22} fractions:				
J4	0.5	6	16	E_{23}/P_{22} const at 2.17% to match Jan'96=11 ppt
J5	0.5	6	9	J4 with CERs subtracted (2003 onward)
J6	3	8	21	E/P const at 1.98% to match Jan'09=21.2 ppt
J7	1.1	2.0	12	E/P const at 2.06% with CDMs, match Jan'09

___

na = not analyzed
const = constant

2) HCFC-22 history in the southern hemisphere

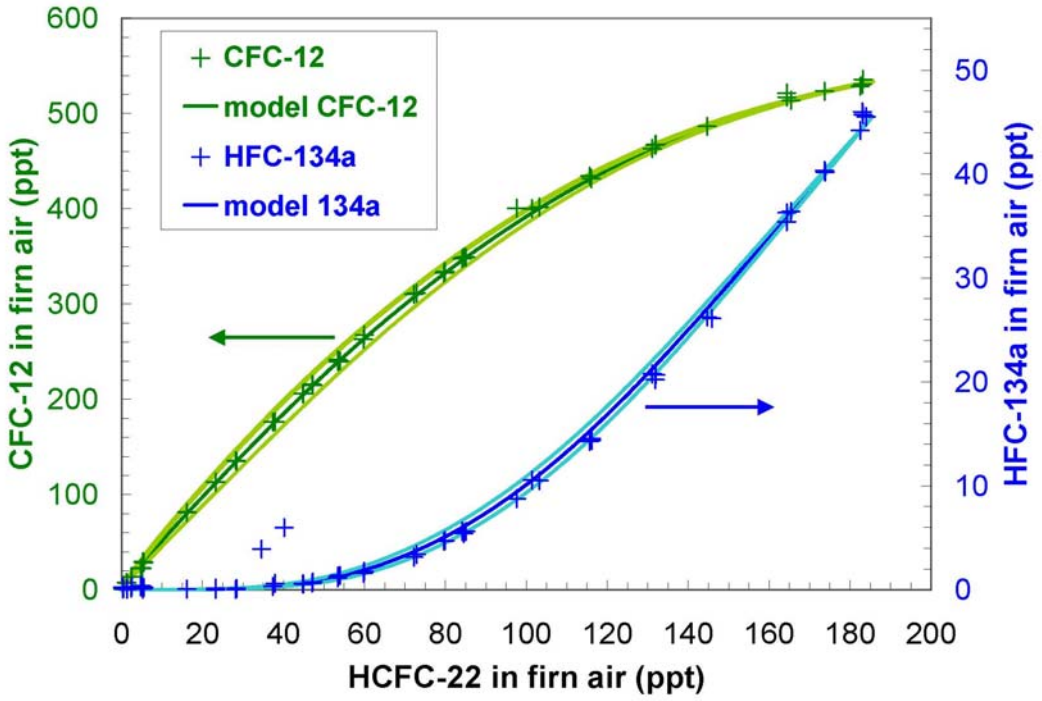
The atmospheric record of HCFC-22 in the southern hemisphere is based on measurements of archived air since 1978 and regularly collected samples since 1992 (see Supplement Figure 1). The high degree of consistency (agreement typically within 2 ppt) between these HCFC-22 atmospheric histories derived with different techniques by independent laboratories suggests that atmospheric changes in HCFC-22 since the late 1980s are accurately known.

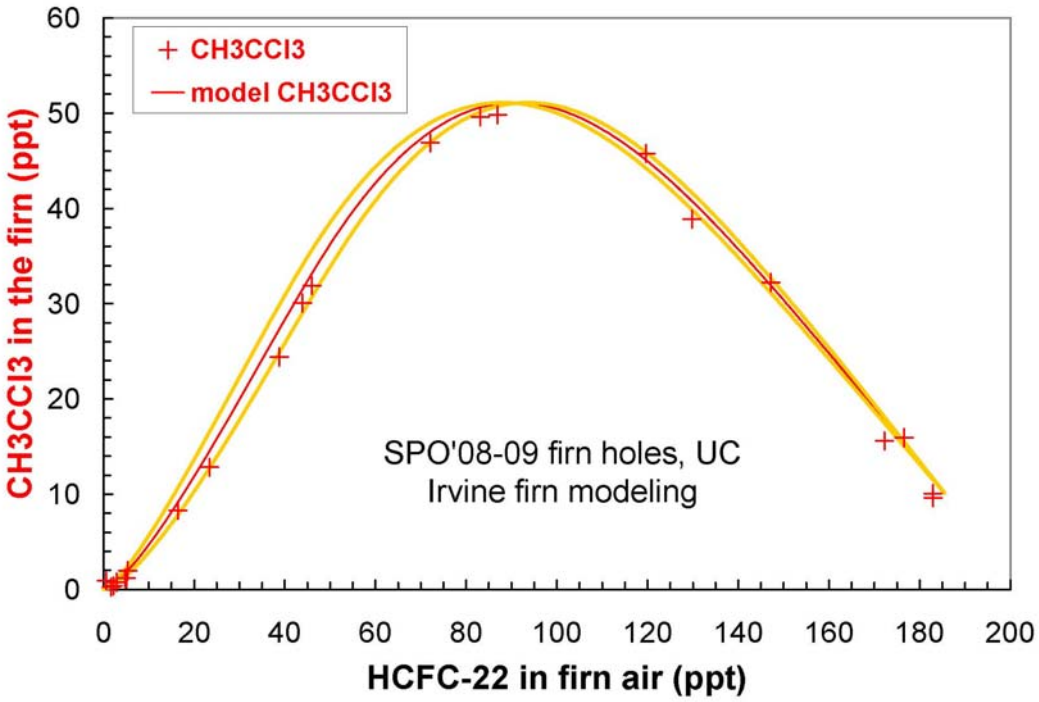


Supplement Figure 1. Secular changes in the southern hemisphere (SH) abundance of HCFC-22 (red points and line). This history is based upon Cape Grim archive air samples (blue plus symbols) (Miller *et al*., 1998) and samples collected and analyzed regularly since 1992 (green line for SH and black line for Northern Hemisphere) (Montzka *et al*., 1993 updated at ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/). Mixing ratios before 1978 were derived with a constant 0.95 scaling of AFEAS emissions in a simple 2-box model. Two flasks filled at 22°S and 29°S during the 1987 SAGA II cruise were analyzed in 1992 (Montzka *et al*., 1993) and in 2009 (diamonds) and show good consistency with this history.

3) Validation of firn modeling relative to HCFC-22 and other trace gases with well known southern hemispheric histories.

Good consistency was observed between modeled and measured firn results for CFC-12, HFC-134a and CH_3CCl_3 when their known histories were incorporated into the different firn models and compared to results for HCFC-22 given its past atmospheric changes (**see Supplement Figures 1 and 2**). Molecular diffusivities used in firn models are calculated (Wilke and Lee, 1955) and uncertainties on them are poorly quantified. Good consistency is noted in these validation tests only when HCFC-22 diffusivities were within ±5% of the calculated value, suggesting that larger errors in these diffusivities are unlikely.





Supplement Figure 2: Observed *vs*. modeled trace-gas relationships between CFC-12, HFC-134a, CH_3CCl_3, and HCFC-22 in firn air collected during the SPO'08-09 firn sampling and modeled with the UC Irvine firn model. Data have been corrected for gravitational effects based upon ^{15}N of N_2 data (Bender *et al*., 1994). Models were run with a range of ±5% on the molecular diffusivity of HCFC-22 calculated with the method of Wilke and Lee (1955). Good consistency was also observed with the Bowdoin firn model applied to the WAIS-D results. Known southern hemisphere histories were derived from observational data alone for HFC-134a and for other species from a combination of box-model mixing ratios incorporating industry emissions scaled to match observations, and, in the latter years (generally after 1977), measured mixing ratios (Montzka *et al.*, 1996; 1999; 2000; Prinn *et al*., 2000).

4) Contamination of WAIS-D deep-hole HFC-23 data

HFC-23 mixing ratios in WAIS-D flasks sampled deep in the firn and for which flushing flows were reduced (flow < 5 lpm) appear substantially elevated relative to measured amounts of other gases (*e.g.*, HCFC-22) and were not considered further (see Figure 1b in manuscript). Flasks were filled at WAIS-D with 2 pumps in series, a Metal Bellows Corp (MB-158) pump followed by a Viton®-diaphragm pump (KNF Neuberger model #N05SVI). When operated against large pressure gradients at reduced flows, sampling pumps containing Viton® parts can produce HFC-23 (Miller *et al*., 2008). HFC-23 contamination is minimized when pressure gradients are reduced. Contamination was eliminated during the SPO'08-09 sampling by using only the Metal Bellows Corp (MB-158) pump to fill flasks. The cleanliness of this pump is demonstrated by the near zero mixing ratios of HFC-23 that were measured in the deepest samples of SPO'08-08 where flows are reduced and pressure gradients are largest (see paper, **Figure 1**). Contamination in samples collected during WAIS-D at shallower depths and at the surface was likely insignificant given that a consistent history can be derived from all three firn missions after these deep samples are excluded from the record.

5) Inferring recent emissions from changes measured in ambient air.

Mixing ratios of HFC-23 and a suite of other trace gases were determined from ambient air samples collected over Antarctica during these three firn-air collection efforts. Measured mixing ratios for HFC-23 were 14.9±0.2 in Jan. 2001, 18.1±0.3 in Dec. 2005, and 21.1±0.24 ppt in Dec08-Jan09. Results for other gases (e.g., HFC-134a, HCFC-22, CFC-12, HFC-125, HFC-143a) from these particular ambient air samples were in excellent agreement (within 1%) with annual mean mixing ratios measured at remote sites (South Pole, 90°S, and Cape Grim, 40°S) in the NOAA cooperative global air-sampling network. This strongly suggests that the measured HFC-23 mixing ratios similarly provide a good estimate of its annual mean mixing ratio in the SH. These measured HFC-23 increases in the SH imply a mean global emission rate of 8.4±1 from 2001 through 2005 and 14±2 Gg/yr from 2006 through 2008 when considered with our atmospheric box model. Uncertainties here were derived from the magnitude of measurement uncertainties (±0.3 ppt for HFC-23, see text)). Potential errors related to atmospheric model uncertainties (e.g., vertical distributions of HFC-23 and atmospheric exchange times) are encompassed by these stated ranges.

6) Supplement Table 2. Used and derived quantities related to HFC-23 emissions, HFC-23 emission abatements, and HCFC-22 production.

	HCFC-22 Prod. From McCulloch and Lindley (2007) or UNEP.		HCFC-22	HCFC-22	HCFC-22	HCFC-22	HCFC-22 Prod. associated with CDM projects abating HFC-23 emissions	HFC-23		HFC-23	HFC-23		HFC-23
			UNEP Prod.	UNEP Prod.	UNEP Prod.			Emiss. Firn derived		Emiss.	Emiss. Derived here		Certified Emiss. Reductions from CDM projects
			Reported	Augmented [d]	Reported	Mis-match [e]	Reported [g]		error est.	Reported	Non-Annex 1	error est	Reported non-Annex 1
	Global		nA5	nA5	A5	Global		Global		Annex 1			
Year	(Gg)		(Gg)	(Gg)	(Gg)	%	(Gg)	(Gg)	(Gg)	(Gg)	(Gg)	(Gg)	(Gg)
1990	339	a	58	339	7	-2		7.6	0.8	7.9	f		
1991	373	a	131	364	17	-2		8.5	0.9	7.7	f		
1992	385	a	223	320	33	8		8.8	0.9	7.9	f		
1993	382	a	283	382	43	-11		9.0	1.0	8.0	f		
1994	387	a	305	367	53	-9		8.5	1.0	7.2	f		
1995	410	b	357	410	53	-13		8.7	1.2	7.4	f		
1996	424	b	367	392	57	-6		8.9	1.0	7.1	f		
1997	431	b	369	403	63	-8		8.1	1.1	7.3	f		
1998	444	b	412	427	32	-3		8.7	1.2	7.9	f		
1999	495	b	394	404	101	-2		9.3	1.2	6.4	2.9	1.2	
2000	477	b	360	387	117	-6		9.4	1.2	6.0	3.4	1.2	
2001	475	b	348	355	127	-1		9.5	1.5	4.4	5.1	1.5	
2002	509	b	335	338	175	-1	0	9.1	1.8	3.8	5.3	1.8	0
2003	543	b	329	329	214	0	1	9.5	2.0	2.8	6.7	2.0	0.04
2004	623	b	335	347	288	-2	2	10.3	2.2	3.0	7.3	2.2	0.1
2005	697	b	348	348	349	0	11	11.8	2.4	2.9	8.9	2.4	0.3
2006	709	b	306	312	403	-1	50	13.5	1.7	2.6	10.9	1.7	1.4
2007	795	b	325	325	470	0	201	13.5	2.2	2.8	10.7	2.2	5.7
2008	826 [c]		316 [c]	316 [c]	510 [c]		239	13.5	2.1	2.8 [c]	10.7	2.1	6.5
source			b	b	b		g	*This work*		h	*This work*		l

Notes:

To calculate CO_2-equivalent emissions as defined by the UNFCCC, multiply HFC-23 emissions by a 100-yr GWP of 11700 (IPCC, 2001; UNFCCC, 2009). CO_2-eq. emissions quoted in the published paper were calculated with the updated 100-yr GWP of 14800 (Forster *et al*., 2007). Uncertainties on global emissions inferred from firn data are derived from the spread of trial histories showing good fits (see text) plus a modeling uncertainty of 10%. These same uncertainties are propagated to non-Annex 1 emissions. Gg denotes 1×10^9 grams.

a) Global HCFC-22 production from McCulloch and Lindley (2007).

b) UNEP (2009) data: Global HCFC-22 production reported to the WMO Ozone Secretariat for all uses including dispersive and feedstock applications (G. Mutisya, personal communication, 2009) from Parties to the Montreal Protocol operating under Article 5 of that Protocol (A5 or 'developing' countries—taken to be equivalent to non-Annex 1 parties to the UNFCCC) and Parties not operating under Article 5 of that Protocol (nA5—taken to be equivalent to Annex 1 parties to the UNFCCC). A ±5% error in the developed and developing HCFC-22 production data is assumed when calculating uncertainties in associated E_{23}/P_{22}.

c) Projected for 2008 based on early year data.

d) Apparent gaps in data reported to UNEP for feedstock and dispersive uses in developed countries (nA5) were filled by interpolation on a country-by-country basis with estimated HCFC-22 production amounts. These augmented amounts averaged to be 0.4% from 2001-2007, 5.6% from 1996-2000, and 32% from 1991-1994 of annual totals.

e) Mismatch (% of global reported in column a) between reported global totals and the sum of production in A5 (non-Annex 1) and augmented production in non-A5 (Annex 1) countries.

f) Not estimated in years before 1999 when the difference between firn-derived global emission and reported Annex 1 emissions were small relative to uncertainties.

g) Calculated from UNFCCC (2009) reported HFC-23 Certified Emission Reductions divided by the yield ratio of HFC-23 to HCFC-22 production documented by project during the certification period .

h) Emissions of HFC-23 reported by Annex 1 countries (Australia, Canada, EC, Japan, Russia and the US) are from UNFCCC (2009) under "Total GHG emissions" and "Actual Emissions" for HFC-23. These numbers were augmented additionally with amounts compiled in the UK. HFC-23 emissions for Japan during 1990-1995 were estimated from total HCFC-22 production amounts and the average E_{23}/P_{22} calculated for Japan during 1995-2003 of 2.3±0.5%. An uncertainty on Annex 1 total HFC-23 emissions of ±10% is used here based on uncertainties quoted in Annex 1 greenhouse gas reports.

i) Compiled from files at the UNFCCC's CDM web site pages (http://cdm.unfccc.int/index.html).

7) Supplement Table 3: Molecular diffusivities used in firn modeling*.

	Bowdoin model SPO'01 and WAIS-D	UCI model SPO'08-09
Absolute diffusivity (cm^2/s):		
CO_2	0.1479	0.144
Diffusivity relative to CO_2:		
HCFC-22	0.6775	0.675
HFC-23	0.8283	0.808
CFC-12	0.610	0.56
HFC-134a	0.646	0.613
CH_3CCl_3	0.46	0.46

* Slightly different diffusivities were used in the different models in this study and reflect the uncertainties associated with deriving these values with various methods.

8) Supplemental Information references:

Bender, M. L., T. Sowers, J.-M. Barnola, and J. Chappellaz (1994), Changes in the O2/N2 ratio of the atmosphere during recent decades reflected in the composition of air in the firn at Vostok Station, Antarctica, *Geophys. Res. Lett*., 21, 189–192.

Forster, P., *et al.*, 2007: Changes in Atmospheric Constituents and in Radiative Forcing. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., *et al*. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC, 2001: *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* [Houghton, J.T., et al. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 881 pp.

IPCC/TEAP, Special report on safeguarding the ozone layer and the global climate system: Issues related to hydrofluorocarbons and perfluorocarbons, Geneva, 2005**.**

McCulloch, A. and A.A. Lindley, Global emissions of HFC-23 estimated to year 2015, *Atmos. Environ., 41*, 1560, 2007.

Miller, B.R., J. Huang, R.F. Weiss, R.G. Prinn, and P.J. Fraser, Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, *J. Geophy. Res., 103*, D11, 13237, 1998.

Miller, B.R., Weiss, R.F., Salameh, P.K., Tanhua, T., Greally, B.R., Mühle, J. and Simmonds, P.G., Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons and Sulfur Compounds, *Analytical Chemistry, 80*, 1536-1545, 2008.

Montzka, S.A., R.C. Myers, J.H. Butler, J.W. Elkins, and S.O. Cummings, Global tropospheric distribution and calibration scale of HCFC-22, *Geophys Res. Lett*., *20*, 703-706, 1993.

Montzka, S.A., R.C. Myers, J.H. Butler, J.W. Elkins, L. Lock, A. Clarke, and A.H. Goldstein, Observations of HFC-134a in the remote troposphere, *Geophys Res. Lett.*, *23*, 169-172, 1996.

Montzka, S.A., J.H. Butler, J.W. Elkins, T.M. Thompson, A.D. Clarke, and L.T. Lock, Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, *398*, 690-694, 1999

Montzka, S.A., C.M. Spivakovsky, J.H. Butler, J.W. Elkins, L.T. Lock, and D.J. Mondeel, New observational constraints for atmospheric hydroxyl on global and hemispheric scales, *Science*, *288*, 500-503, 2000.

Montzka, S.A., B.D. Hall, J.W. Elkins, Accelerated increases observed for hydrofluorocarbons since 2004 in the global atmosphere, *Geophys. Res. Lett.*, *36*, L03804, doi:10.1029/2008GL036475, 2009.

Prinn, R. G., *et al*. (2001), A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, *105*, D14, 17751, 2000.

UNEP (2009) HCFC Production Data reported at http://ozone.unep.org/Data_Reporting/Data_Access/, 2009.

UNFCCC (2009), Greenhouse Gas Emissions Data reported at: http://unfccc.int/ghg_data/ghg_data_unfccc/items/4146.php, 2009.

Wilke, C.R. & Lee, C.Y. *Industrial and Engineering Chemistry 47*, 1253-1257 (1955).

Recent increases in global HFC-23 emissions

Published by Stephen A. Montzka, Lambert Kuijpers, Mark O. Battle, Murat Aydin, Kristal Verhulst, Eric S. Saltzman, and David W. Fahey

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Global atmospheric concentrations and emissions of HFC-23 have continued to increase despite efforts in both developed and developing countries to reduce emissions of this potent greenhouse gas during the past decade.

• **Observations:** Recent HFC-23 emissions were derived from gas measurements made in ambient air and in the Antarctic snowpack (firn) three times between 2001 and 2009.

Background: HFC-23
Hydrofluorocarbon-23 (HFC-23) emissions arise primarily from over-fluorination of chloroform during HCFC-22 production.

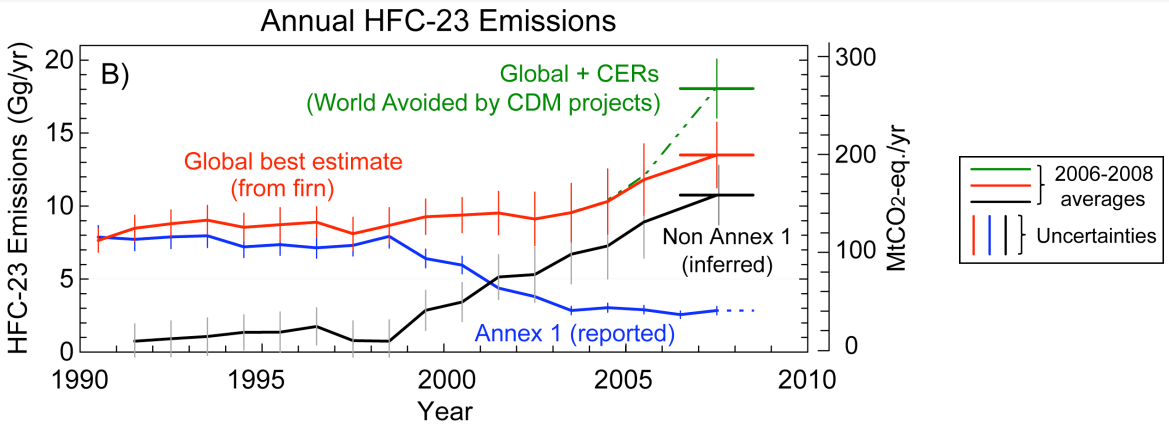


Figure lines

Global annual HFC-23 emissions derived from atmospheric and firn air observations.

Global HFC-23 emissions have increased by 55% :
• 2006-2008 average: 13.5 ± 2 Gg/yr or 200 ± 30 Mt CO2-eq.
• 1990-2000 average: 8.7 ± 1 Gg/yr or 129 ± 15 Mt CO2-eq.

Background:
HFC-23 has a 100-yr global warming potential (GWP) of 14,800 (or 11,700 for UNFCCC CDM purposes).

1Gg HFC-23 = 14.8 Mt CO2-eq
1Gg HCFC-22 = 1.8 Mt CO2-eq

Developed country (Annex 1) annual HFC-23 emissions reported to UNFCCC.

• HFC-23 emissions have decreased in developed countries from 6 - 8 Gg/yr in the late 1990s to 2.8 Gg/yr in 2007.

Developing country (non-Annex 1) annual HFC-23 emissions. They are inferred here as the difference between derived global emissions and reported Annex-1 emissions. Non-Annex-1 HFC-23 emissions are generally not reported to the UNFCCC.

• HFC-23 emissions have increased steadily in developing countries from 1 - 3 Gg/yr in the 1990s to 11 ± 2 Gg/yr in 2006-2008 as a result of rapidly increasing HCFC-22 production.

World Avoided by CDM projects: Global annual HFC-23 emissions from atmospheric observations + HFC-23 amounts destroyed by Certified Emission Reductions (CERs) under the UNFCCC Clean Development Mechanism (CDM).

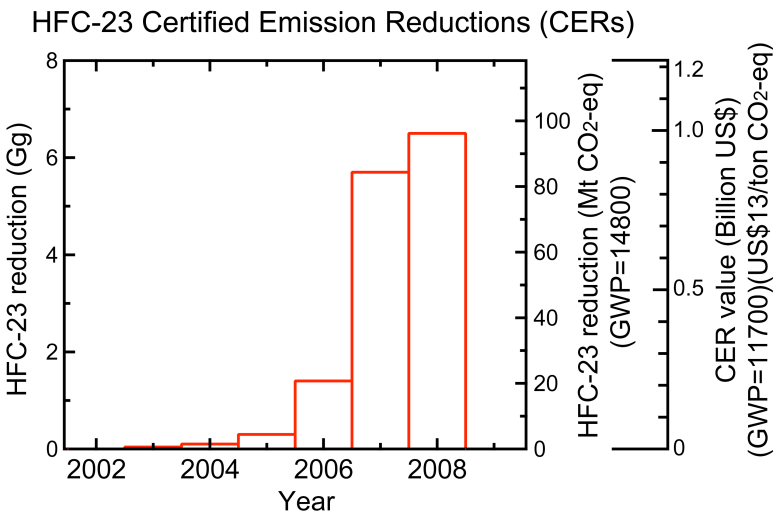
• Without CERs, HFC-23 global emissions would have doubled from approximately 9 to 18 Gg/yr between 2000-2002 and 2006-2008.

• Substantial amounts of HCFC-22 were produced but not covered by existing CDM projects (~57%) in 2007 and the HFC-23 associated with this production appears to be emitted to the atmosphere.

• HFC-23 CERs through 2008 total 14 Gg which corresponds to 208 Mt CO_2-eq. of emission reduction.

• HFC-23 CO_2-eq. emissions in recent years have been about 1/3 as large as HCFC-22 CO_2-eq. emissions because of the large GWP of HFC-23 and despite the low yield in HCFC-22 production.

• The total value of CERs between 2003 and 2008 is 2.1 Billion US$ assuming a HFC-23 GWP of 11700 and a US$13/ton CO_2-eq market value. (Wara, 2007)



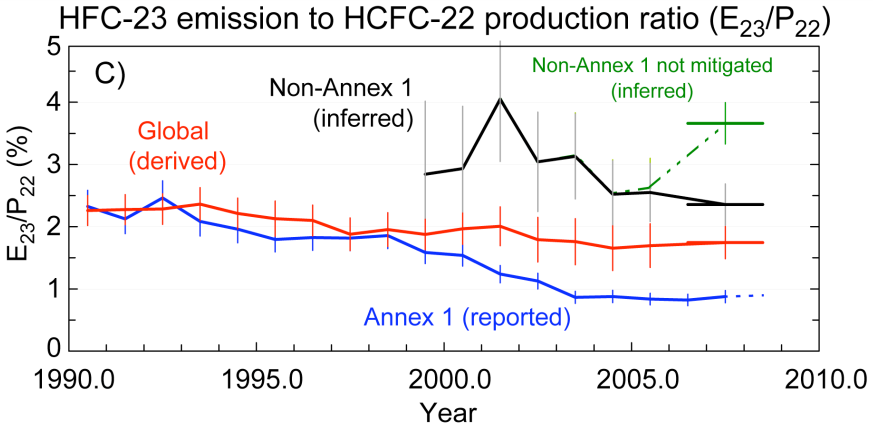


Figure lines

Annual ratio of global HFC-23 emissions to global HCFC-22 production (E_{23}/P_{22})

• Global HFC-23 emissions as a percentage of total HCFC production have decreased since the mid 1990's to an average value of 1.7% in 2006-2008.

Developed country (Annex 1) annual E_{23}/P_{22} ratios from values reported to UNFCCC and UNEP.

• E_{23}/P_{22} values have steadily decreased in developed countries from approximately 2% in the 1990s to 0.9% during 2003-2007.

Developing country (non-Annex 1) annual E_{23}/P_{22} ratios from inferred HFC-23 emissions and reported HCFC-22 production.

• E_{23}/P_{22} values have decreased in developing countries since the early 2000's to reach 2.4 ± 0.3% for 2006-2008.

Developing country (non-Annex 1) annual E_{23}/P_{22} ratios from inferred HFC-23 emissions and HCFC-22 production not associated with CDM projects.

• E_{23}/P_{22} values in HCFC-22 production not associated with CDM projects are high (3.7 ± 0.3%) compared to values in the past obtained in either non-Annex-1 or Annex-1 countries.

Background:
Under the Montreal Protocol HCFC-22 production and consumption for non-feedstock uses will end in developed/ developing countries in 2020/2030. The Montreal Protocol does not restrict feedstock production of HCFC-22.

Annual Total HCFC-22 Production

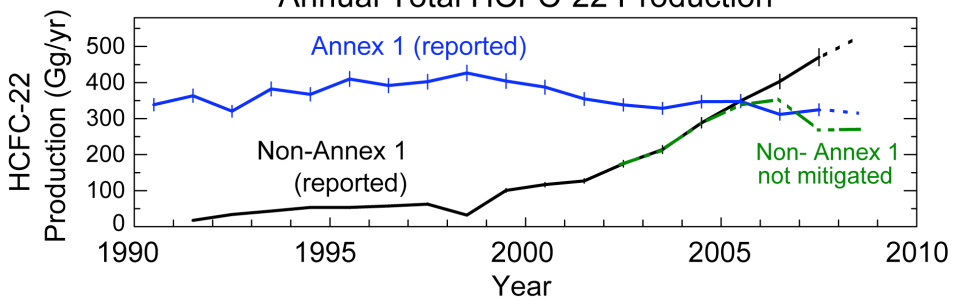


Figure lines

Developed country (Annex 1) annual HCFC-22 production as reported to UNEP.

• Developed country annual HCFC-22 production has decreased in the last decade.

Developing country (non-Annex 1) annual HCFC-22 production as reported to UNEP.

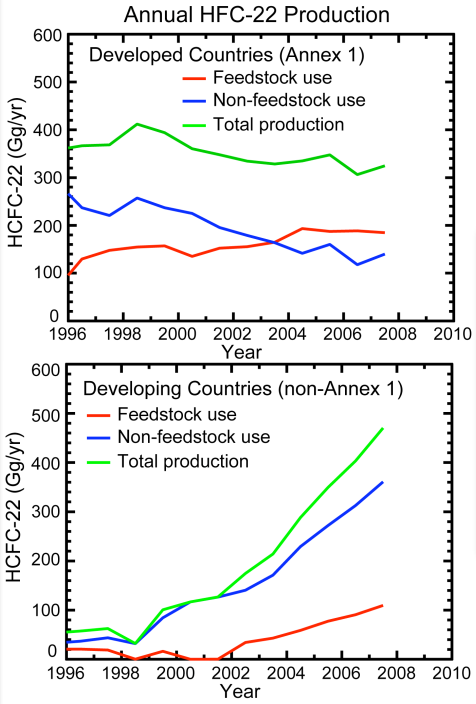
• Developing country annual HCFC-22 production has increased with a substantial growth rate in the last decade.

Developing country (non-Annex 1) annual HCFC-22 production not associated with CDM projects.

• A large fraction (57%) of developing country HCFC-22 production was not included in CDM projects in 2007 and hence is associated with unmitigated HFC-23 production.

* Total HCFC-22 production = feedstock (fluoropolymers) + non-feedstock (emissive uses, *e.g.*, air conditioning and refrigeration).

Annual HCFC-22 Feedstock and Non-feedstock Production **



** Data reported to the United Nations Environment Programme (UNEP). Data for years before 1996 are incomplete for feedstock and non-feedstock uses.

In the Montreal Protocol HCFC-22 feedstock production is not controlled. Thus, when the HCFC-22 phaseout is complete in 2020/2030, HFC-23 will potentially still be emitted from continuing HCFC-22 feedstock production.

Figure lines

Total annual HCFC-22 production from feedstock and non-feedstock (emissive) uses.

Annual HCFC-22 production for feedstock use.

• Production for feedstock use of HCFC-22 since the mid 1990s has increased in both Annex-1 and non-Annex-1 countries and currently has a large growth rate in non-Annex-1 countries.

Annual HCFC-22 production for non-feedstock uses.

• Production for non-feedstock use has fallen steadily in developed countries in the last decade while it has increased strongly (25%/yr) in developing countries since 2002.

• Production of HCFC-22 for feedstock use worldwide accounted for 37% (over a third) of total HCFC-22 production in 2007 and has been increasing at ~5% per year in recent years.

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