



Recent increases in global HFC-23 emissions

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[1] Firn-air and ambient air measurements of CHF₃ (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 ($200 \pm 30 \times 10^{12}$ gCO₂-equivalent/yr, or MtCO₂-eq./yr), ~50% higher than the 8.7 ± 1 Gg/yr (130 ± 15 MtCO₂-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 MtCO₂-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. **Citation:** Montzka, S. A., L. Kuijpers, M. O. Battle, M. Aydin, K. R. Verhulst, E. S. Saltzman, and D. W. Fahey (2010), Recent increases in global HFC-23 emissions, *Geophys. Res. Lett.*, 37, L02808, doi:10.1029/2009GL041195.

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 MtCO₂-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 MtCO₂-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 CO₂-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 aculife-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 Firm-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	
C	0.7	0.7	1.3	see text and Text S1
<i>Preliminary Trial History</i>				
<i>Additional Trial Histories Different From C Only After 1995</i>				
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

^aHistories 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). E₂₃ = HFC-23 emission. P₂₂ = HCFC-22 reported production.

^bReduced 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].

^cAtmospheric HFC-23 histories were derived by incorporating the indicated emission record into box models simulating the global atmosphere.

^dM&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.

^eUNEPa = 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, nonA5 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 CO₂ depth profiles and the known Antarctic atmospheric CO₂ 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 (E₂₃/P₂₂) 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).

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

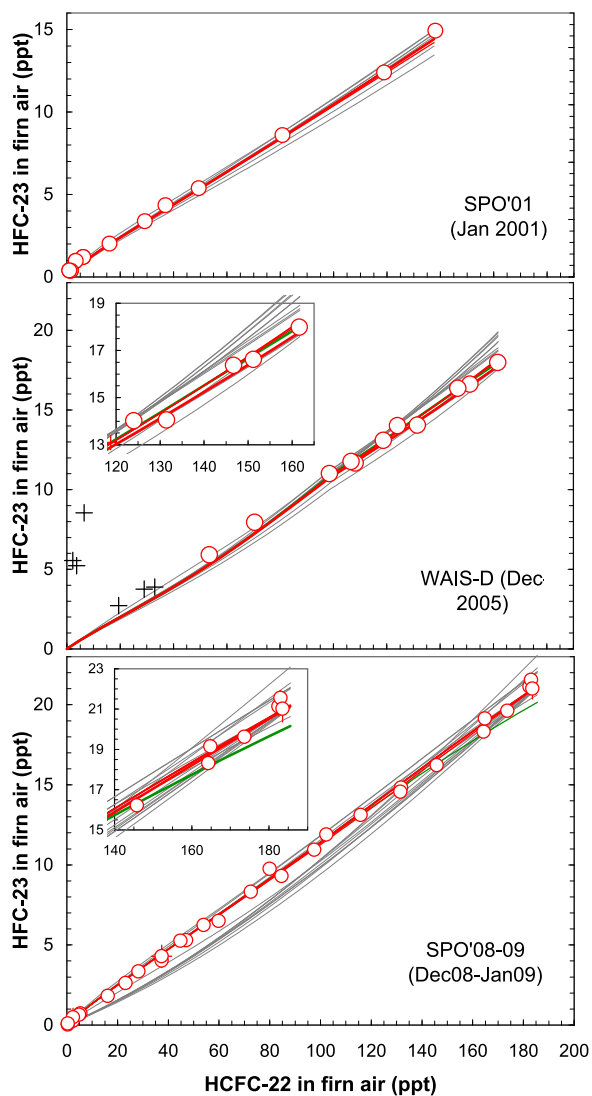


Figure 1. Modeled and measured firm-air mixing ratios of HFC-23 vs. HCFC-22 from three different firm samplings. Multiple trial histories were derived (lines) and incorporated into the firm models to assess their consistency to firm-air measurements (points) (see Table 1 and Text S1 for history descriptions). 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 firm. Uppermost points are ambient air samples filled through firm-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 firm air. The consistency between trial HFC-23 histories and firm-air data was objectively assessed by calculating reduced χ^2 between the modeled and measured HFC-23 vs. HCFC-22 relationship in firm 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 firm diffusivity vs. depth parameterization [Battle *et al.*, 1996]. The accuracy of these models was validated using firm-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 firm data are reached when trial histories are evaluated with the SH atmospheric history and firm data for CO_2 .

3. Results and Discussion

[10] Results from all three Antarctic firm-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] Firm air diffusion models provide a means to compare trial atmospheric histories with firm-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 firm profile that is highly consistent with the entire measured firm profile from SPO'01 and SPO'08-09 ($\chi^2 = 0.7$ 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 firm samples in the mid-to-upper firm 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 firm (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 firm profile collected in December 2005 ($\chi^2 = 0.6$), 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 firm results ($\chi^2 = 2.3$; 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 MtCO₂-eq./yr) during 2006–2008 (Figure 2b). By comparison, HCFC-22 emissions during 2006–2008 averaged 610 MtCO₂-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 WAISD 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 verified 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 $2.4 \pm 0.3\%$ 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 MtCO₂-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

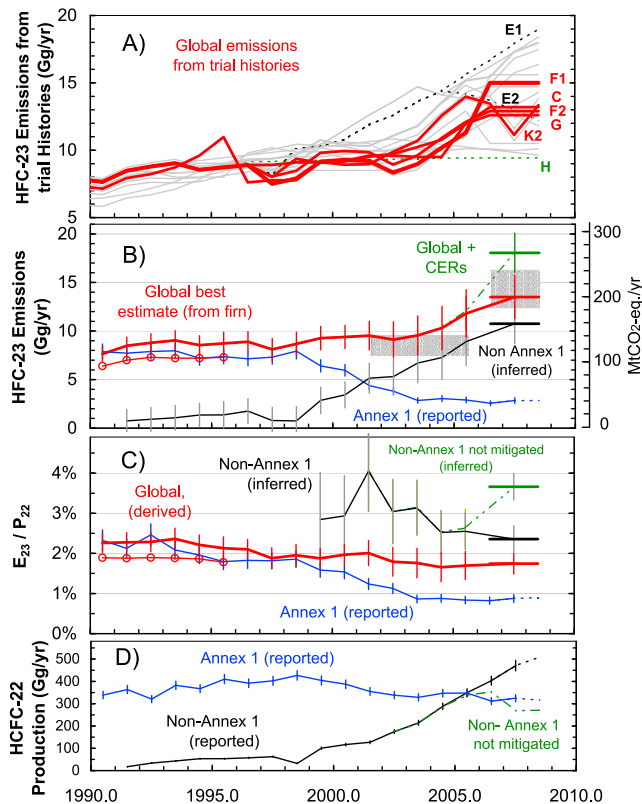


Figure 2. (a and b) HFC-23 emissions, (c) the HFC-23 emission to HCFC-22 production ratio (E_{23}/P_{22}), and (d) HCFC-22 production including chemical feedstock uses. Results are shown for the globe (red lines), for Annex 1 countries (blue lines) and for non-Annex 1 countries (black lines). Figure 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-dotted lines (Figure 2b; see Table 2 in Text S1). The green dot-dotted 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. Firm 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 firm-derived global emissions represent the spread of best-fit trial histories plus a modeling uncertainty of 10%. Uncertainties of $\pm 5\%$ are applied to production data and $\pm 10\%$ 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 CO₂-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 MtCO₂-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 $3.7 \pm 0.3\%$ (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 $\sim 30\%$ 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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