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HCFC-22 emissions at global and regional scales between 1995 and 2010: Trends and variability

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[1] HCFC-22 (CHClF₂, chlorodifluoromethane) is an ozone-depleting substance, the consumption of which is controlled under the Montreal Protocol. Within a Bayesian inversion framework, we use measurements of HCFC-22 atmospheric concentrations to constrain estimates of HCFC-22 emissions, at the grid point $3.75^\circ \times 2.5^\circ$ and 8 day resolution, from January 1995 to December 2010. Starting from a new gridded bottom-up inventory which is then optimized, our method shows continuously rising global emissions, from 182 ± 11 Gg in 1995 to the maximum of 410 ± 9 Gg in 2009. This is mainly due to an increase of emissions in developing regions, particularly in Eastern Asia, and occurs despite the current phase-out in developed countries. The high temporal resolution of our inversion (8 day) allows to reveal some of the emission seasonality, the global posterior sources ranging from 25 Gg/month in November to 42 Gg/month in July, for example, in 2010.

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1. Introduction

[2] Chlorodifluoromethane (CHClF₂), commonly called HCFC-22, is a gas of purely anthropogenic origin. Used as a refrigerant in the air-conditioning and refrigeration industry, as a component in foam blowing and as a chemical feedstock in the manufacture of synthetic polymers, HCFC-22 is the most abundant of the hydrochlorofluorocarbons measured in the atmosphere [O'Doherty *et al.*, 2004; Montzka *et al.*, 2009; Saikawa *et al.*, 2012]. Mainly removed from the atmosphere by its reaction with hydroxyl radicals (OH), it has a lifetime of about 11.9 years [Montzka *et al.*, 2011; Saikawa *et al.*, 2012]. There exist two other sinks for HCFC-22: an oceanic sink and one from a reaction with chlorine (Cl). They are limited to only a few percent of that due to OH [Cox *et al.*, 1995; Miller *et al.*, 1998]. The mean surface HCFC-22 concentration is still rising, from 110 ppt in 1995 to 188–192 ppt in 2008 [Montzka *et al.*, 2011; Saikawa *et al.*, 2012].

[3] HCFC-22 is an important topic for research in atmospheric sciences both as a greenhouse gas and as an ozone-depleting substance. Its global warming potential reaches 1790 over the 100 yr time horizon, according to the World Meteorological Organization. Since 1996, HCFC-22 has been an interim replacement gas for more potent ozone-depleting substances such as chlorofluorocarbons (CFCs). However, it is itself ranked among the Class-1 controlled substances in Annex C of the Montreal Protocol on Substances that Deplete the Ozone Layer (hereafter referred to as the Montreal Protocol). In this context, aggregated global production and sales of individual HCFCs (including HCFC-22) are listed by the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) until 2007. Parties to the Montreal Protocol are also required to submit their annual consumption (referred to as production plus imports minus exports) to the United Nations Environment Programme (UNEP). At their 19th meeting in 2007, parties to the Montreal Protocol agreed on an accelerated phase-out of HCFCs [U.N. Environment Programme, 2007], covering only the dispersive application (not the feedstock in fluoropolymer manufacture). In developed countries, the phase-out shall have been largely completed by 2020 when the consumption shall have been reduced by 99.5% compared with the CFC and HCFC consumption in 1989 (–35% in 2004; –75% in 2010; –90% in 2015). In developing countries (parties operating under Article 5 of the Montreal Protocol), consumption of HCFC-22 for emissive uses shall be largely phased out by 2030. In 2030, the consumption shall be reduced by 97.5% compared with the average level in 2009 and 2010 (freeze in 2013; –10% in 2015; –35% in 2020; –67.5% in 2025).

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Table 1. HCFC-22 Measurements Site Information

Station	Code	Latitude	Longitude	Altitude (m.a.s.l)	Network	Type	Data Period Used
Alert, Canada	ALT	82.50	−62.30	210	NOAA	flask	12/1994 to 03/2011
Pt. Barrow, AK, USA	BRW	71.30	−156.60	11	NOAA	flask	12/1994 to 03/2011
Cape Grim, Tasmania	CGO	−40.68	144.68	104	AGAGE	continuous	01/1998 to 03/2011
Cape Grim, Tasmania	CGO	−40.68	144.68	21	NOAA	flask	12/1994 to 03/2011
Cape Ochi-ishi, Japan	COI	43.15	145.50	96	NIES	continuous	08/2006 to 12/2010
Hateruma, Japan	HAT	24.05	123.80	46.5	NIES	continuous	05/2004 to 12/2010
Harvard Forest, USA	HFM	42.90	−72.30	340	NOAA	flask	11/1995 to 03/2011
Jungfraujoch, Switzerland	JFJ	46.54	7.98	3580	AGAGE	continuous	01/2000 to 03/2011
Cape Kumakahi, HI, USA	KUM	19.52	−154.82	3	NOAA	flask	11/1995 to 03/2011
Park Falls, WI, USA	LEF	45.92	−90.27	868	NOAA	flask	10/1996 to 03/2011
Lampedusa, Italy	LMP	35.52	12.63	45	ENEA	flask	12/2003 to 12/2008
Mace Head, Ireland	MHD	53.33	−9.90	25	AGAGE	continuous	12/1994 to 03/2011
Mace Head, Ireland	MHD	53.33	−9.90	8	NOAA	flask	10/1998 to 03/2011
Mauna Loa, USA	MLO	19.54	−155.58	3397	NOAA	flask	12/1994 to 03/2011
Niwot Ridge, CO, USA	NWR	40.03	−105.54	3021	NOAA	flask	12/1994 to 03/2011
Palmer Station, Antarctica	PSA	−64.92	−64.00	10	NOAA	flask	12/1997 to 03/2011
Ragged Point, Barbados	RPB	13.17	−59.43	42	AGAGE	continuous	05/2005 to 03/2011
Cape Matatula, Samoa	SMO	−14.24	−170.57	77	AGAGE	continuous	05/2006 to 03/2011
Cape Matatula, Samoa	SMO	−14.24	−170.57	42	NOAA	flask	12/1994 to 03/2011
South Pole, USA	SPO	−89.98	−24.80	2810	NOAA	flask	12/1994 to 03/2011
Summit, Greenland	SUM	72.58	−38.48	3238	NOAA	flask	06/2004 to 03/2011
Tierra del Fuego, Argentina	TDF	−54.87	−68.48	20	NOAA	flask	05/2004 to 05/2010
Trinidad Head, CA, USA	THD	41.05	−124.15	120	NOAA	flask	03/2002 to 03/2011
Trinidad Head, CA, USA	THD	41.05	−124.15	140	AGAGE	continuous	03/2005 to 03/2011
Ny-Alesund, Norway	ZEP	78.90	11.88	474	AGAGE	continuous	01/2001 to 03/2011

[4] However, emissions are more relevant than consumption data to estimate the HCFC-22 loading to the atmosphere, and there is a growing interest in better estimating global and regional emissions of this species. *McCulloch et al.* [2003] estimated global annual emissions for the years 1943–2000, a study that has been updated and lengthened up to 2015 by *McCulloch* [2005], based on the UNEP statistics. *McCulloch et al.* [2003] also built gridded emission estimates for the specific year 1990. *Stohl et al.* [2009] created and inferred their own gridded HCFC-22 emissions, using an inverse procedure and a Lagrangian transport model. *Stohl et al.* [2010] inferred HCFC-22 emissions from four East Asian countries and the Taiwan region. *Saikawa et al.* [2012] also built gridded prior emissions for the years 1995–2009 and optimized the HCFC-22 annual emissions at global (for years 1995–2009) and regional (for years 2005–2009) scales. These authors found that global HCFC-22 emissions have a positive trend from 1995 to 2009 [*Saikawa et al.*, 2012], with an important contribution of China [*Stohl et al.*, 2009, 2010; *Saikawa et al.*, 2012]. Nevertheless, they estimated regional fluxes for relatively large predefined regions, inducing aggregation errors [*Kaminski et al.*, 2001], and for relatively short periods (years 2005–2009 for *Saikawa et al.* [2012], years 2005–2006 for *Stohl et al.* [2009], and year 2008 for *Stohl et al.* [2010]).

[5] For the present study, we develop an atmospheric inversion system with high spatial and temporal resolutions: the quantification of the HCFC-22 fluxes is attempted at the grid-cell resolution of our global chemistry-transport model ($3.75^\circ \times 2.5^\circ$) and at an 8 day resolution. The HCFC-22 fluxes are inferred over the long period of 16 years (1995–2010), with a simultaneous optimization of OH concentrations for four latitudinal bands. The components of the inversion system are described in section 2. Section 3 provides the global and regional trend and variability of HCFC-22 emissions over the period 1995–2010.

2. Methodology

[6] Our approach consists in optimizing the sources and sinks of a trace gas within a Bayesian framework. It requires atmospheric measurements $\mathbf{y}$, prior estimates of the source and sink space-time distributions $\mathbf{x}_b$, and a chemistry-transport model H , given their respective uncertainties represented by their error covariance matrix $\mathbf{R}$ and $\mathbf{B}$. The optimal solution (in a statistical sense), which is called *posterior* in the following, is found by the iterative minimization of the Bayesian cost function J defined as follows:

$$J(\mathbf{x}) = (\mathbf{x} - \mathbf{x}_b)^T \mathbf{B}^{-1} (\mathbf{x} - \mathbf{x}_b) + (H(\mathbf{x}) - \mathbf{y})^T \mathbf{R}^{-1} (H(\mathbf{x}) - \mathbf{y}) \quad (1)$$

where $\mathbf{x}$ is the state vector that contains the variables to be optimized by the inversion:

[7] 1. HCFC-22 surface emissions at an 8 day and at a $3.75^\circ \times 2.5^\circ$ (longitude, latitude) resolution.

[8] 2. HCFC-22 column initial conditions at a $3.75^\circ \times 2.5^\circ$ resolution.

[9] 3. Four factors to scale the OH atmospheric concentrations at an 8 day resolution, for four latitude bands (90°S – 30°S , 30°S – 0°S , 0°S – 30°N , 30°N – 90°N).

[10] The operator H is the global 3-D Chemistry Transport Model (CTM) LMDz-SACS that couples an offline version of the atmospheric general circulation model LMDz [*Hourdin et al.*, 2006] with the atmospheric chemistry module SACS (Simplified Atmospheric Chemistry System) [*Pison et al.*, 2009]. For this study, SACS has been adapted to represent the interaction between OH and HCFC-22. The most important sink for HCFC-22 in the troposphere is its reaction with OH: $\text{CHClF}_2 + \text{OH} \rightarrow \text{CF}_2\text{Cl} \cdot + \text{H}_2\text{O}$. SACS uses the reaction rate $k = 1.05 \times 10^{12} \exp\left(\frac{1600}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$, as recommended by *Sander et al.* [2011]. Its other sinks are neglected in SACS. The OH prior distribution is obtained from a previous simulation of the full atmospheric chemistry

Figure 1. Locations of the stations measuring HCFC-22 dry air mole fraction.

model LMDz-INCA (Intéractions Chimie et Aérosols [Hauglustaine *et al.*, 2004]).

[11] The observations in *y* gather HCFC-22 dry air mole fractions measured at 29 stations (Table 1) for the 1995–2010 period, available on the World Data Centre for Greenhouse Gases site (<http://ds.data.jma.go.jp/gmd/wdogg/>, accessed 15 November 2012). We use instantaneous values, named “event” in the database, from flask (from the National Oceanic and Atmospheric Administration, Earth System Research Laboratory (NOAA/ESRL) [Montzka *et al.*, 1993] and from the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) [Artuso *et al.*, 2010] networks) and from continuous measurements (from the Advanced Global Atmospheric Gases Experiment (AGAGE) [O’Doherty *et al.*, 2004; Saikawa *et al.*, 2012] and from the National Institute for Environmental Studies (NIES) [Yokouchi *et al.*, 2006] networks). The monitoring stations are mainly located in the Northern Hemisphere and particularly around North America (Figure 1). The yearly numbers of measurements used in the inversion are displayed in Figure 2. The number of measurements remains small until 1998 (148 in 1995, 181 in 1996, 210 in 1997, and 1351 in 1998), but it has risen continuously since 1998: from a few thousands between 1998 and 2003 to more than 25,000 in 2007 onwards.

[12] The diagonal *R* matrix representing observation errors is filled with variances which combine representation errors (e.g., the mismatch between the observation and model resolutions), errors of the observation operator (including transport and chemical-scheme errors in LMDZ-SACS), and measurement errors including instrumental precision for HCFC-22 measurements of approximately 0.4–1% and the errors involved in the calibration scale of approximately 1% [Saikawa *et al.*, 2012]. Differences between networks (calibrations uncertainties, intercalibration factors) are small considering other causes of uncertainties such as representation or model errors. The errors on the observation operator and the representation error are difficult to estimate precisely. The synoptic variability reported in the NOAA and ENEA files is taken as a proxy for observation uncertainty, which includes transport model error. Such

information is not given in the AGAGE and NIES files, and a value of 3 ppt has been assigned to the observation error standard deviation.

[13] In the absence of established gridded inventories of the HCFC-22 emissions, we follow the methodology of Stohl *et al.* [2009] to build our gridded prior information in *x_p*: we combine (1) the global annual emission estimates of McCulloch [2005], including their forecast for years 2002 to 2010; (2) the country totals for the annual consumption of HCFCs (i.e., not only HCFC-22) from 1995 to 2010, available from the United Nations Environment Programme (UNEP 2011, Data Access Centre, available at: http://ozone.unep.org/new_site/en/ozone_data_tools_access.php) and (3) a population distribution over the globe for year 1995, available from the Distributed Active Archive Center for Biogeochemical Dynamics (ORNL DAAC, <http://daac.ornl.gov/projects.shtml>). Given the $3.75^\circ \times 2.5^\circ$ resolution of our grid, we exploit the UNEP country totals after aggregation at subcontinental scales (14 continental regions). The relative contribution of each region to the global consump-

Figure 2. Number of measurements per year, for the globe (in yellow) and for the Northern Hemisphere (in blue), from 1995 to 2010.

Figure 3. Prior HCFC-22 emissions for (left) 1995 and (right) 2010 prepared for this study, at the grid resolution, in Gg/yr.

tion is calculated and is taken as the relative contribution of each region to the global emissions. The regional emissions are then distributed proportionally to the population, at the $3.75^\circ \times 2.5^\circ$ pixel resolution. They are left constant within each year. For some countries, the HCFC consumption in 2010 is missing in the UNEP inventory (UNEP, 2011). Therefore, our prior emissions for 2010 are assumed to be equal to our prior emissions for 2009. Figure 3 shows the resulting gridded maps of the prior HCFC-22 emissions and displays the evolution of the HCFC-22 emissions in the world from 1995 to 2010, after the Montreal Protocol:

emissions increase in developing countries and decrease in developed countries.

[14] We represent the uncertainty of this prior inventory of our prior OH field and of our initial conditions in the covariance matrix $\mathbf{B}$ (see equation (1)). The grid point standard deviations for the HCFC-22 emissions (i.e., the diagonal terms of $\mathbf{B}$) are set at a relatively large value, 60%, because of the large and uncertain interannual variability of the regional HCFC-22 emissions in recent years. For the initial conditions, errors are set to 10% for HCFC-22. The errors assigned to the scale factor of OH are set at 10%,

Figure 4. Simulated prior (green) and posterior (blue) compared to the observed HCFC-22 concentrations (red), from 1995 to 2010 at stations Alert (ALT), Cape Kumukahi (KUM), American Samoa (SMO), and Cape Grim (CGO). See Figure 1 for the station locations.

Table 2. Global HCFC-22 Emissions and Their Uncertainties for Years 1995 to 2010 Before the Inversion and After the Inversion, in Gg/yr

	Prior	Posterior		Prior	Posterior
1995	173 ± 14	182 ± 11	2003	278 ± 19	279 ± 8
1996	187 ± 14	198 ± 11	2004	302 ± 19	289 ± 8
1997	187 ± 14	199 ± 11	2005	324 ± 26	320 ± 9
1998	195 ± 14	212 ± 11	2006	350 ± 26	338 ± 9
1999	210 ± 14	227 ± 11	2007	369 ± 26	371 ± 9
2000	229 ± 19	256 ± 8	2008	415 ± 26	375 ± 9
2001	241 ± 19	266 ± 8	2009	416 ± 26	410 ± 9
2002	264 ± 19	270 ± 8	2010	416 ± 26	386 ± 9

which is consistent with the differences between estimates of the OH concentrations from several studies [Prinn *et al.*, 2001; Krol and Lelieveld, 2003; Bousquet *et al.*, 2005]. Assuming that the approach used to build the prior inventory leads to errors that are coherent at large space-time scales, spatial correlations are represented by an e-folding length of 500 km over land (1000 km over sea), without any correlation between land and ocean, and we prescribe a temporal correlation e-folding length of 8 weeks. These prior error statistics lead the HCFC-22 prior error emissions (displayed in Figure 9a) as an example for the year 2007 and to annual HCFC-22 budgets of 173 ± 14 Gg/yr in 1995 and of 416 ± 26 Gg/yr in 2010. Here and in the following, the numbers behind the plus-minus signs refer to one-sigma standard deviations.

[15] The cost function J and the norm of its gradient are minimized with the quasi-Newton minimization algorithm M1QN3 [Gilbert and Lemaréchal, 1989]. After 17 iterations corresponding to 4 weeks of sustained parallel computing (on eight Intel Xeon 64 bit CPUs), the norm of the gradient is reduced by 99.9%. The uncertainty on the posterior emissions is calculated with the Monte Carlo approach of Chevallier *et al.* [2007]. As a trade-off between computing resources and exhaustivity, we only estimate the posterior

one-sigma uncertainty for the years 1997, 2002, and 2007. In the following, these values are used to characterize the 5 year periods 1995–1999, 2000–2004, and 2005–2010, respectively. Conservatively, we also applied these uncertainties to multiyear averages, even though these values are probably overestimated.

3. Results

3.1. Prior and Posterior Fit at Stations

[16] Figure 4 shows the simulated prior (in green), the simulated posterior (in blue), and the measured (in red) HCFC-22 concentrations, from 1995 to 2010, at stations Alert (ALT), Cape Kumukahi (KUM), American Samoa (SMO), and Cape Grim (CGO), representative of the four latitude bands chosen for the OH constraint. Observed concentrations have increased continuously since 1995, from 120 ppt in 1995 to more than 220 ppt in 2010 in the Northern Hemisphere (from 105 ppt in 1995 to 200 ppt in 2010 in the Southern Hemisphere). The mean observed growth rate of about +5.5 ppt/yr for the 1995–2005 period (similar to the rate of 6 ppt/yr measured by O'Doherty *et al.* [2004] at stations MHD and CGO) has slightly increased in both hemispheres after 2006, with about +7.9 ppt/yr for the 2006–2010 period (similar to the averaged annual growth rate of 8.0 ± 0.5 ppt/yr deduced by Montzka *et al.* [2011] during 2007–2008). This also accords with the increasing growth rate beginning since 2006 seen by Saikawa *et al.* [2012].

[17] Compared to the observed concentrations, an underestimation by about 5% is seen during the period 1995–2005 in the prior-modeled concentrations (growth rate of about +4.3 ppt/yr). Slight overestimations are seen after 2008 (growth rate of about 9 ppt/yr). After optimization, the model does not succeed in capturing the magnitude of HCFC-22 observations for the stations CGO and SMO from 1995 to 1998. This mainly results from very low number of HCFC-22 observations in the Southern Hemisphere

Figure 5. Partition into six regions.

Figure 6. Monthly prior (in blue) and posterior (in yellow) HCFC-22 emissions for the globe (top) and for Eastern Asia (bottom) from 1995 to 2010. Error bars denote the posterior one-sigma uncertainty in the monthly emissions estimates.

during these years. Nevertheless, the posterior simulation is in excellent agreement with the HCFC-22 observations from 1998 to 2010.

3.2. Global Budget of HCFC-22 Emissions

[18] Figure 6 (top) displays the global monthly prior and posterior HCFC-22 emissions from 1995 to 2010. Prior and posterior emissions consistently represent a rise of the emissions from 1995 to 2010 (also seen in Table 2). The global posterior emissions are reduced by a maximum of 10% compared to prior values, indicating the good quality of the forecast made by McCulloch [2005] used here as prior.

[19] Posterior HCFC-22 emissions range from 182 ± 11 Gg/yr in 1995 (starting from a prior of 173 ± 14 Gg/yr, see Table 2) to the maximum of 410 ± 9 Gg/yr in 2009 (starting from a prior of 415 ± 26 Gg/yr). Our posterior global budget is in a reasonable agreement with other recent

Figure 7. Monthly prior (in blue) and posterior (in yellow) HCFC-22 emissions for the USA (top) and for Western Europe (bottom), from 1995 to 2010. Error bars denote the posterior one-sigma uncertainty in the monthly emissions estimates.

Figure 8. Monthly prior (in blue) and posterior (in yellow) HCFC-22 emissions for the regions Middle East (top) and South American Temperate (bottom), from 1995 to 2010. Error bars denote the posterior one-sigma uncertainty in the monthly emissions estimates.

studies: over the period 2005–2009, we find a posterior global budget of 363 ± 9 Gg/yr (starting from a prior of 382 ± 26 Gg/yr), which is 13% higher than the optimized magnitudes obtained by Saikawa *et al.* [2012] with 314.6 ± 79 Gg/yr. Over the period 2005–2006, our posterior budget of 329 ± 9 Gg/yr (starting from a prior of 337 ± 26 Gg/yr) is also in a fair agreement with the 333 Gg/yr of Stohl *et al.* [2009]. Our posterior budget of 371 ± 9 Gg/yr in 2007 (starting from a prior of 369 ± 26 Gg/yr) is only 1% higher than the optimized magnitudes obtained by Vollmer *et al.* [2009] (365 Gg/yr).

3.3. Regional Budget

[20] We investigate the regional variations of HCFC-22 emissions by aggregating the grid point estimates over the

Table 3. Regional HCFC-22 Emissions and Their Uncertainties for the Years 1997, 2002, and 2007, in Gg/yr^a

		Prior	Posterior	Error Reduction
USA	1997	70 ± 9	75 ± 8	10
	2002	112 ± 12	110 ± 8	37
	2007	60 ± 6	71 ± 6	4
Western Europe	1997	50 ± 6	55 ± 6	3
	2002	26 ± 3	26 ± 3	5
	2007	10 ± 1	11 ± 1	2
Eurasian Boreal	1997	0.5 ± 0.1	0.5 ± 0.1	-
	2002	7 ± 1	2 ± 7	2
	2007	10 ± 1	9 ± 1	11
Eastern Asia	1997	42 ± 4	46 ± 4	10
	2002	77 ± 8	84 ± 6	24
	2007	190 ± 20	176 ± 5	75
South Am Temp	1997	5 ± 0.5	5 ± 0.5	-
	2002	10 ± 1	10 ± 1	1
	2007	23 ± 3	25 ± 3	6
Middle East	1997	2 ± 0.3	2 ± 0.3	-
	2002	6 ± 1	6 ± 1	1
	2007	17 ± 2	19 ± 2	3

^aThe regional error reduction is indicated in %.

Figure 9. (a) Prior errors on HCFC-22 emissions at the grid-cell resolution for year 2007, in Gg/yr. (b) Uncertainty reduction obtained by the inversion at the grid-cell resolution for the year 2007, in %.

six main source regions of Figure 5 (three for developed countries: USA, Western Europe, and Russia; three for developing countries: Eastern Asia, Middle East, and South American Temperate). Our 2005–2006 average estimate for the US emissions (80 ± 7 Gg/yr, starting from a prior of 69 ± 8 Gg/yr) is, for example, in excellent agreement with the estimates of *Stohl et al.* [2009] and *Saikawa et al.* [2012], with 80 Gg and 77 ± 20 Gg/yr, respectively. We find a significant increase in HCFC-22 emissions from 1995 to 2010 in South American Temperate, Middle East, and in Eastern Asia, particularly in China. The large increase of emissions in the developing regions is not surprising considering the rise in HCFC-22 consumption for this period (UNEP, 2011). These three regions contributed 70% of the global emissions in 2010. Eastern Asia itself contributes 45% of these global emissions. The importance of Eastern Asia, and particularly

of China, as a HCFC-22 source has been highlighted by *Yokouchi et al.* [2006], *Vollmer et al.* [2009], *Stohl et al.* [2009], and *Saikawa et al.* [2012]. Our posterior Chinese emissions (128 ± 18 Gg/yr) are 22% lower than the 165 Gg/yr of *Vollmer et al.* [2009] in 2007 (starting from a prior of 149 ± 24 Gg/yr). On the contrary, for the year 2008, our posterior Chinese emissions of 111 ± 18 Gg/yr (starting from a prior of 152 ± 24 Gg/yr) are 69% higher than the estimates of *Stohl et al.* [2010] (65 Gg/yr ± 7).

3.4. Seasonality

[21] The 8 day resolution of the inversion allows creating seasonal variations in the global posterior emissions (compared to the prior annual estimates, Figure 6, top). A seasonal cycle is seen after 2004, probably because of the increase of measurements (from about 5000 observations

Figure 10. (a) Regional HCFC-22 emissions calculated for year 2007. The red bar represents the prior production and each symbol a posterior production for the reference inversion (in green) and the five sensitivity cases (in black). Case A: stations removed; case B: error on the prior HCFC-22 emissions set to 40%; case C: error on the prior HCFC-22 emissions set to 80%; case D: observations error set to 6 ppb; case E: temporal correlation length set to 4 months. (b) Differences of the posterior HCFC-22 emissions between the sensitivity tests and the reference inversion (in % relative to the reference). Error bars show the one-sigma uncertainty associated with the posterior reference (calculated using the Monte Carlo approach).

per year in 2003 to more than 15,000 observations per year in 2005, as seen in Figure 2). The posterior sources range from 25 Gg/month in November to 42 Gg/month in July, for example, in 2010. It is interesting to see that few regions

drive these seasonal variations: Eastern Asia (Figure 6, bottom, the Asian posterior sources ranging from 10 Gg/month in winter to 26 Gg/month in boreal summer in 2010) and, to a lesser extent, the USA (Figure 7, top) and the Middle East (Figure 8, bottom).

[22] To our knowledge, such a seasonal cycle has not been referenced yet in the literature. This may be explained by higher needs in refrigeration and air-conditioning during the warmest months of the year, correlated with the maintenance activity of the cooling systems (S. Barrault, personal communication, 2012), during which extra leak of HCFC-22 may occur. Also, these regions are probably responsible for a more extensive use of such systems than other parts of the world. However, artifacts such as misrepresentation of the stratosphere-troposphere exchange in LMDz or a misallocation of the seasonal OH sink cannot be ruled out, and further work would be needed to better understand these seasonal variations.

3.5. Performance of the Inversion

3.5.1. Uncertainty Reduction

[23] The uncertainty reductions reached by the inversion for the years 1997, 2002, and 2007 are synthesized in Table 3 for regional and global aggregations. The uncertainty reduction at the grid scale resolution is also shown in Figure 9b for year 2007. The uncertainty reduction is defined as $(1 - \sigma_a/\sigma_b) \times 100$, with σ_b the prior error standard deviation and σ_a the theoretical posterior error standard deviation. In 1997, the global error reduction reaches 21%. However, due to fewer observations (210 in that year), the inversion does not reduce the uncertainties on HCFC-22 emissions at regional scale, except over the USA (uncertainty reduction of 10%), where most measurement stations are located. Note that these constraints also bring information over the region Eastern Asia (uncertainty reduction of 10%), even though there is no station in this region until 2004.

[24] The progressive extension of the surface network (see Figure 2) increases the number of observational constraints in the inversion over time. Combined with the increased emissions in the atmosphere, this leads to larger uncertainty reductions on HCFC-22 emissions since 2002 both at global (65% in 2007) and at regional scales (Table 3). Nevertheless, the uncertainty reduction remains small for less constrained and/or emitting regions (i.e., for regions Middle East and South American Temperate, see Figure 9b).

3.5.2. Sensitivity Tests

[25] In this section, we discuss the robustness of our system through five sensitivity tests (cases A to E) with respect to different prior settings:

Table 4. HCFC-22 Targets of the Montreal Protocol for Developed Countries^a

	Emission Baseline	2004			2010			2015
		Objective	Prior	Posterior	Objective	Prior	Posterior	Objective
USA	122	79	57 ± 15	59 ± 9	31	32 ± 8	35 ± 8	12
EU	47	31	15 ± 4	15 ± 4	12	10 ± 2	10 ± 2	5
Russia	48	31	7 ± 1	7 ± 1	12	11 ± 2	9 ± 2	5

^aThe emission baseline is calculated with the same methodology as for the prior emissions construction in section 2 but for year 1989. The 2004 (−35%), 2010 (−75%), and 2015 (−90%) objectives compared to the baseline are calculated. They are compared to the regional prior and posterior emissions inferred in this study for years 2004 and 2010. Units are Gg/yr.

Table 5. HCFC-22 Consumption Baseline and Objectives That the Developing Regions Have to Reach According to the Montreal Protocol^a

	2009–2010 Average		Objectives Based on Emission Baseline			
	Prior	Posterior = Emissions Baseline	Freeze in 2013	–10% in 2015	–35% in 2020	–67.5% in 2025
Eastern Asia (including China, India, Thailand)	215 ± 27	185 ± 7	185	166	120	60
China	180 ± 24	148 ± 6	148	146	96	48
Middle East	31 ± 3	33 ± 3	33	30	21	11
Temperate South America	30 ± 3	31 ± 3	31	28	21	10

^aExpressed in terms of emissions, as we assumed that HCFC-22 emissions mirror consumption with a potential delay. The emission baseline is defined here as the average of the 2009 and 2010 posterior emissions. Prior is for the average of the 2009 and 2010 prior emissions. Units are Gg/yr.

[26] 1. In case A, the European station Lampedusa, Italy (LMP) and the Asiatic stations Hateruma, Japan (HAT) and Ochi-ishi, Japan (COI) have been removed.

[27] 2. In case B, the HCFC-22 prior emissions grid point error is reduced to 40% instead of 60%.

[28] 3. In case C, the HCFC-22 prior emissions grid point error is increased to 80% instead of 60%.

[29] 4. In case D, the observation error (i.e., the model–observation error) is set to 6 ppt instead of 3 ppt.

[30] 5. In case E, the temporal e-folding correlation length of prior error HCFC-22 emissions is set to 4 weeks instead of 8 weeks.

[31] The HCFC-22 emissions for the whole year 2007, for each case, are given for the six regions of interest in Figure 10a. These posterior regional results are further compared with the reference inversion in terms of anomalies in Figure 10b. The regional estimates of HCFC-22 emissions obtained by the different sensitivity tests are in a good agreement, even though some differences can be seen at the regional scale (i.e., from –0.15% to 3% for Western Europe). The range of the inverted fluxes is well within the one-sigma posterior uncertainty for all regions except for the region Eastern Asia, where the scatter of the sensitivity tests is large (e.g., range of 53 Gg). However, it is limited to 15%, in this region emitting more than 180 Gg/yr.

[32] For the other regions, the largest range is observed in case A, when the European station Lampedusa, Italy (LMP) and the Asiatic stations Hateruma, Japan (HAT) and Ochi-ishi, Japan (COI) have been removed. This highlights the importance of observational constraints in the region Eastern Asia. Finally, it is worth noting that the difference between the regional inverted emissions in cases B and C relative to the reference inversion is small, indicating that the inversion is not very sensitive to the prior errors statistics at the scales of interest here.

3.6. Targets and Objectives of the Montreal Protocol

[33] The Montreal Protocol objectives are based on consumption statistics. For the developed regions, the phase-out imposed a reduction of 35% of their consumptions by 2004 and a reduction of 75% by 2010 compared to the CFC and HCFC consumptions of 1989. The phase-out has not been activated in developing countries yet, but the consumption shall have been reduced by 97.5% in 2030 compared to the average level in 2009 and 2010.

[34] An independent way to verify that these objectives are reached is to assess the effective release of HCFC-22

into the atmosphere. HCFC-22 emissions mirror consumption with a potential delay. Consequently, in the following paragraphs, we use our optimized emissions as a proxy (i) to determine whether the objectives have been reached for the developed regions and (ii) to provide a baseline for the developing regions.

[35] In developed regions, the emissions indeed started to decrease since the early 2000s: since 2000 for the EU and since 2002 for the US, as seen in Figure 7. According to the UNEP consumption statistics (UNEP, 2011), USA and Europe have reached their 2004 and 2010 reduction targets. Our inversion confirms this success (with a one-sigma range of 24–42 Gg/yr and of 8–12 Gg/yr, respectively, for the US and Europe in 2010, see Table 4). The Russian emissions have increased from 2000 to 2010 but stay in the range authorized by the Montreal Protocol.

[36] Our atmospheric inversion suggests that the baselines for each of the regions Middle East, South American Temperate, and Eastern Asia are 33 ± 3 , 31 ± 3 , and 185 ± 7 Gg/yr (including 148 ± 6 for China), respectively (see Table 5).

4. Conclusion

[37] This study aims at estimating HCFC-22 emissions for 16 years, between 1995 and 2010 at a $3.75^\circ \times 2.5^\circ$ and 8 day resolution, using an inversion system, a new gridded bottom-up inventory, and the HCFC-22 dry air mole fraction measurements from the NOAA, AGAGE, ENEA, and NIES networks.

[38] Our variational inversion framework allows high-resolution estimates (grid point and 8 day), and its benefits can be seen here, revealing seasonal variations of the emissions in Eastern Asia and to a lesser extent in the US and in Middle East. Such variations are not represented in the prior annual-based inventory but are expected from the seasonality of the activity of cooling systems, including their maintenance. However, with sparse observing stations, results have not been presented at spatial resolutions smaller than subcontinents. Monitoring HCFC-22 mole fractions in the large regions South America and Russia is needed to get finer estimates in the future.

[39] Except for the region Eastern Asia, the inversion generates small increments from the prior HCFC-22 estimates, indicating that our consumption-based inventory provides a reasonable prior information. Because of the increase of emissions in developing countries, and particularly in Eastern Asia, since year 2000, global emissions have

reached the unprecedented level of 410 ± 9 Gg/yr in 2009, 56% higher than the budget of 182 ± 11 Gg/yr in 1995. As a consequence, the Asian upcoming phase-out will be critical to decline HCFC-22 global concentrations.

[40] Finally, the inverse modeling approach offers an attractive solution for an independent evaluation of the reduction plans of emissions. Developed regions (USA, Western Europe, and Russia) appear to have reached both their 2004 and 2010 targets. The 2009–2010 baseline emissions for the developing regions South America, Middle East, and Eastern Asia are 31 ± 3 , 33 ± 3 , and 185 ± 7 Gg/yr, respectively. Our study suggests the possibility for future amendments of the Montreal Protocol to consider emissions rather than consumption statistics.

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References

- Artuso, F., P. Chamard, S. Chiavarini, A. di Sarra, D. Meloni, S. Piacentino, and D. M. Sferlazzo (2010), Tropospheric halocarbons and nitrous oxide monitored at a remote site in the Mediterranean, *Atmos. Environ.*, **44**(38), 4944–4953.
- Bousquet, P., D. Hauglustaine, P. Peylin, C. Carouge, and P. Ciais (2005), Two decades of OH variability as inferred by an inversion of atmospheric transport and chemistry of methyl chloroform, *Atmos. Chem. Phys.*, **5**, 2635–2656, doi:10.5194/ACP-5-2635-2005.
- Chevallier, F., F.-M. Breon, and P. Rayner (2007), The contribution of the Orbiting Carbon Observatory to the estimation of CO₂ sources and sinks: Theoretical study in a variational data assimilation framework, *J. Geophys. Res.*, **112**, D09307, doi:10.1029/2006JD007375.
- Cox, R. A., R. Atkinson, G. K. Mootgat, A. R. Ravishankara, and H. W. Sidebottom (1995), Atmospheric degradation of halocarbon substitutes, in *Scientific Assessment of Ozone Depletion: 1994*, vol. 37, edited by Albritton, D. L., R. T. Watson, and P. J. Aucamp, pp. 12.1–12.23, World Meteorol. Organ., Geneva.
- Gilbert, J., and C. Lemaréchal (1989), Some numerical experiments with variable-storage quasi-Newton algorithms, *Math. Program.*, **45**, 407–435.
- Hauglustaine, D. A., F. Hourdin, L. Jourdain, M.-A. Filiberti, S. Walters, J.-F. Lamarque, and E. Holland (2004), Interactive chemistry in the Laboratoire de Meteorologie Dynamique general circulation model: Description and background tropospheric chemistry evaluation, *J. Geophys. Res.*, **109**, D04314, doi:10.1029/2003JD003957.
- Hourdin, F., I. Musat, S. Bony, P. Braconnot, and F. Codron (2006), The LMDZ4 general circulation model: Climate performance and sensitivity to parametrized physics with emphasis on tropical convection, *Clim. Dyn.*, **27**, 787–813, doi:10.1007/S00382-006-0158-0.
- Kaminski, T., P. J. Rayner, M. Heimann, and I. G. Enting (2001), On aggregation errors in atmospheric transport inversions, *J. Geophys. Res.*, **106**, 4703–4715.
- Krol, M., and J. Lelieveld (2003), Can the variability in tropospheric OH be deduced from measurements of 1,1,1-trichloroethane (methyl chloroform)? *J. Geophys. Res.*, **108**(D3), 4125, doi:10.1029/2002JD002423.
- McCulloch, A., P. M. Midgley, and P. Ashford (2003), Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere, *Atmos. Environ.*, **37**, 889–902, doi:10.1016/S1352-2310(02)00975-5.
- McCulloch, A. (2005), Determination of comparative HCFC and HFC emission profiles for the foam and refrigeration sectors until 2015, Part 3: Total emissions and global atmospheric concentrations, *Report*, U.S. Environ. Prot. Agency, Washington, D. C. [Available at: http://www.epa.gov/ozone/snap/emissions/downloads/FoamEmissionProfiles_Part3.pdf].
- 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**(D11), 13,237–13,248, doi:10.1029/98JD00771.
- 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**(8), 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.
- Montzka, S. A., et al. (2011), Ozone-depleting substances (ODSs) and related chemicals, in *Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project Report No. 52*, World Meteorol. Organ., Geneva, Switzerland, Chapter 1, 41–150.
- O'Doherty, S., et al. (2004), Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons 141b, 142b and 22 from AGAGE observations at Cape Grim, Tasmania and Mace Head, Ireland, *J. Geophys. Res.*, **109**, D06310, doi:10.1029/2003JD004277.
- Pison, I., P. Bousquet, F. Chevallier, S. Szopa, and D. Hauglustaine (2009), Multi-species inversion of CH₄, CO and H₂ emissions from surface measurements, *Atmos. Chem. Phys.*, **9**, 5281–5297.
- Prinn, R. G. et al. (2001), Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, *Science*, **292**, 1882–1888.
- Sander, S. P., et al. (2011), Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10 - 6, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov>.
- Saikawa, E., et al. (2012), Global and regional estimates for HCFC-22, *Atmos. Chem. Phys.*, **12**, 10,033–10,050, doi:10.5194/ACP-12-10033-2012.
- Stohl, A., et al. (2009), An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, *Atmos. Chem. Phys.*, **9**, 1597–1620.
- Stohl, A., et al. (2010), Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling, *Atmos. Chem. Phys.*, **10**, 3545–3560.
- Vollmer, M. K., et al. (2009), Emissions of ozone-depleting halocarbons from China, *Geophys. Res. Lett.*, **36**, L15823, doi:10.1029/2009GL038659.
- U.N. Environment Programme, (2007), Report of the 19th Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer, *Technical Report*, Montreal, Canada.
- Yokouchi, Y., S. Taguchi, T. Saito, Y. Tohjima, H. Tanimoto, and H. Mukai (2006), High-frequency measurements of HFCs at a remote site in east Asia and their implications for Chinese emissions, *Geophys. Res. Lett.*, **33**, L21814, doi:10.1029/2006GL026403.