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1 Historical emissions of HFC-23 (CHF₃) in China and projections
2 upon policy options by 2050

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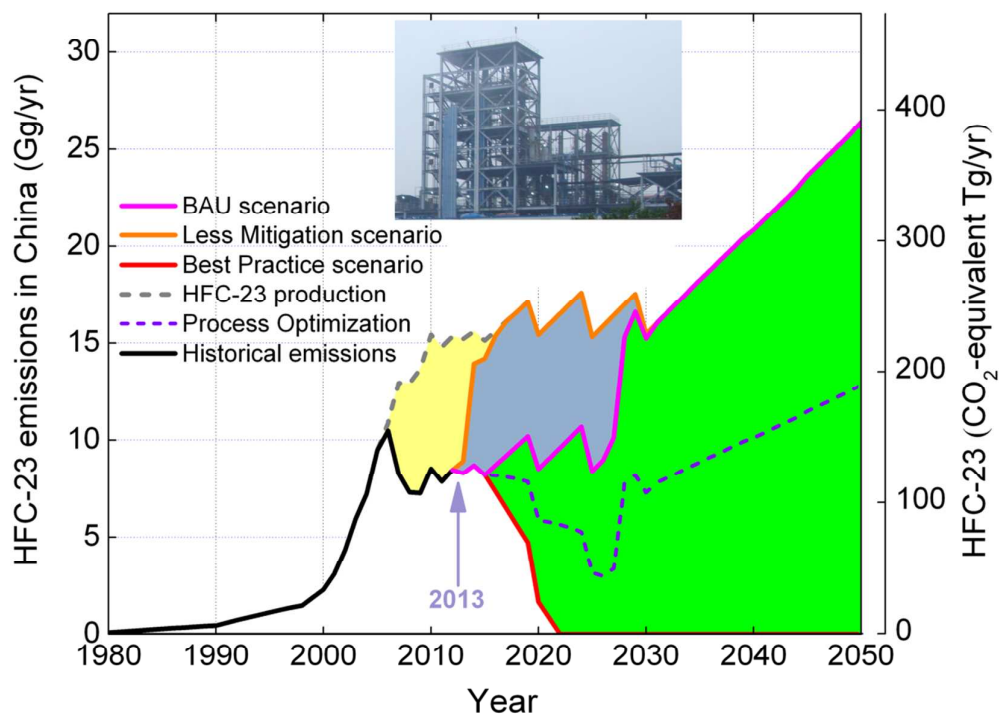
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15

16 **Abstract:**

17 Trifluoromethane (CHF_3 , HFC-23) is one of the hydrofluorocarbons (HFCs) regulated
18 under the Kyoto Protocol with a global warming potential (GWP) of 14800 (100-year).
19 China's past, present and future HFC-23 emissions are of considerable interest to
20 researchers and policymakers involved in climate change. In this study, we compiled a
21 comprehensive historical inventory (1980–2012) and a projection (2013–2050) of
22 HFC-23 production, abatements and emissions in China. Results show that HFC-23
23 production in China increased from 0.08 ± 0.05 Gg/yr in 1980 to 15.4 ± 2.1 Gg/yr
24 (228 ± 31 Tg/yr CO_2 -eq) in 2012, while actual HFC-23 emissions reached a peak of
25 10.5 ± 1.8 Gg/yr (155 ± 27 Tg/yr CO_2 -eq) in 2006, and decreased to a minimum of
26 7.3 ± 1.3 Gg/yr (108 ± 19 Tg/yr CO_2 -eq) in 2008 and 2009. Under the examined
27 business-as-usual (BAU) scenario, the cumulative emissions of HFC-23 in China over
28 the period 2013–2050 are projected to be 609 Gg (9015 Tg CO_2 -eq which
29 approximates China's 2012 CO_2 emissions). Currently, China's annual HFC-23
30 emissions are much higher than those from the developed countries, while it is
31 estimated that by year 2027, China's historic contribution to the global atmospheric
32 burden of HFC-23 will have surpassed that of the developed nations under the BAU
33 scenario.

34 Introduction

35 Trifluoromethane (CHF_3 , HFC-23) is a potent greenhouse gas (GHG) regulated
36 under the Kyoto Protocol with a global warming potential (GWP) of 14800 over a 100
37 year time horizon and an atmospheric lifetime of 270 years.¹ HFC-23 is an
38 unavoidable by-product in the production of chlorodifluoromethane (CHClF_2 ,
39 HCFC-22) which is applied widely in air conditioning, commercial refrigeration,
40 extruded polystyrene (XPS) foams (termed “dispersive production”), and also used as
41 a feedstock in Pentafluoroethane (CF_3CHF_2 , HFC-125) production² and
42 fluoropolymer manufacture³ (termed “feedstock production”). Bottom-up estimates
43 show that before 2001 developed countries dominated in HFC-23 production, while
44 thereafter developing countries took over the leading role due to a substantial increase
45 of HCFC-22 production since the 1990s. Due to the lack of market for the by-product
46 HFC-23, it has historically been directly emitted to the atmosphere from the HCFC-22
47 production facilities, and this practice continues to a significant extent today.⁴

48 In 2007, the Montreal Protocol Parties reached an agreement with an accelerated
49 phase-out schedule for production and consumption of HCFCs for dispersive
50 applications in developed and developing countries.⁵ Dispersive production of HCFCs
51 in developing countries including China, will be subject to a phase-out beginning with
52 a freeze in 2013 at the baseline level of the average of 2009 and 2010 ODP-weighted
53 production, followed by a 10% reduction with respect to that by 2015, a 35%
54 reduction by 2020, a 67.5% reduction by 2025 and a 97.5% reduction by 2030.⁶

55 However, the production of HCFC-22 for use as feedstock is unrestricted currently
56 and for the foreseeable future. Therefore, future HFC-23 production is anticipated to
57 be controlled by the increase of HCFC-22 feedstock production versus the decrease of
58 HCFC-22 dispersive production.

59 Abatement of HFC-23 emissions is an important factor contributing to the
60 difference between HFC-23 production and its actual emission. Since 2006,
61 destruction (incineration) of HFC-23 has been implemented in China under the United
62 Nations Framework Convention on Climate Change's (UNFCCC) Clean
63 Development Mechanism (CDM). There are a total of 19 CDM projects globally, with
64 11 of these located in China. Four Chinese CDM projects started in 2006, followed by
65 five starting in 2007, another starting in 2008 and a final project starting in 2009.⁷
66 When expiration of the first seven-year crediting period of CDM projects in China
67 starts in 2013, whether the abatement measures continue or not will certainly have an
68 impact on future HFC-23 emissions in China and globally.

69 HFC-23 emissions from China are suspected to have made the biggest contribution
70 to the recent annual global emissions, especially to the increase of HFC-23 emissions
71 in developing countries.⁴ Li et al. revealed the significance of HFC-23 emissions in
72 China for the period Nov-2007 to Dec-2008, which were estimated to contribute 74%
73 to global HFC-23 emissions and 95% to total East Asian HFC-23 emissions.⁸ A
74 number of other studies have estimated HFC-23 emissions from China. The earliest of
75 these used a tagged-tracer simulation in a 3D transport model and a tracer-ratio
76 technique and estimated the emission to be 10 ± 4.6 Gg/yr for the period Apr-2004 to

77 May-2005.⁹ More recent studies show a discrepancy among estimates, e.g., top-down
78 estimates 6.2 ± 0.7 Gg/yr for 2008,¹⁰ 12 (8.6–15) Gg/yr for the period Nov-2007–
79 Dec-2008,¹¹ 10 (7.2–13) Gg/yr for the period Nov-2007–Dec-2008,⁸ and a bottom-up
80 estimate 13.0 Gg/yr for 2008.¹²

81 While these recent studies do provide insight into annual emissions for specific
82 years, in order to understand the driving forces behind Chinese HFC-23 emissions,
83 there is the need for a long-term assessment of Chinese HFC-23 production,
84 abatement and emission. In this study, we first compile comprehensive inventories of
85 historical HFC-23 production, abatement and emission in China for the period 1980–
86 2012, and gain some insight into the factors governing these processes. We then
87 project these factors forward through the year 2050 to illustrate their influence on
88 future HFC-23 emissions. Finally, we quantify past, current and future contributions
89 from China, from the developing countries excluding China and from the developed
90 countries to the atmospheric abundance of HFC-23.

91 Estimating historical emissions

92 HCFC-22 production

93 Only total HCFC (not individual HCFC) production data are available from the
94 data center of United Nations Environment Programme.¹³ Even if we assume that
95 HCFC-22 makes up 100% of the total production (indeed HCFC-22 is the largest
96 contributor), we could not calculate the total HCFC-22 production values because the

97 feedstock production information is not obligatory to the public and not shown in this
98 data set. Therefore, we could not use this data set. Fortunately, information from other
99 sources for some years is available. Annual production for HCFC-22 was obtained in
100 some nation-wide production surveys,¹⁴ as well as specific information of components
101 of HCFC-22 production from 2000 onwards including domestic dispersive and
102 feedstock production and exported dispersive and feedstock production. The data
103 reveal that HCFC-22 production increased from 70 Gg/yr in 2000 to 549 Gg/yr in
104 2010. Production data for 2011 and 2012 are available from industry market websites
105 (<http://www.chinaiol.com/>). After summing up the monthly reported production,
106 annual total production was estimated to be 530 in 2011 and 543 Gg/yr in 2012.

107 Production data for the period 1980-1999 are sparse. In the late 1950s, trial
108 production of HCFC-22 started in China, and by the end of the 1970s, HCFC-22
109 production amounted to less than 2 Gg/yr. Thereafter, due to the expansion of freezers,
110 air conditioners, and fluoropolymer industrial sector, the demand for HCFC-22
111 increased rapidly. The production in the year 1990 was estimated to be 12 Gg/yr. For
112 1997, HCFC-22 total production was officially reported in the document of National
113 Program for Ozone-depleting Substances Phase-out in China to be 40 Gg/yr.¹⁵
114 HCFC-22 production in 1998 was estimated to be 44 Gg/yr.¹⁶ Production data for
115 other missing years in the 1980s and 1990s were interpolated linearly between the
116 values stated above. The total production in these two decades were really small,
117 about one fiftieth of production in 2010, therefore, errors in the values for these
118 decades will not strongly influence the total production from 1980 to 2012.

119 Co-production ratio of HFC-23/HCFC-22

120 Co-production ratio of HFC-23/HCFC-22 (mass ratio) is a crucial parameter for
121 calculating the HFC-23 production and subsequent emissions. In order to produce
122 Certified Emission Reduction (CER) credits from HFC-23 incineration, CDM plants
123 continuously monitored HFC-23 and HCFC-22 production. This information is well
124 documented in the submitted CDM project monitoring reports, which typically span
125 2–6 months of production. Co-production ratios for the period 2006–2013 are
126 available in these monitoring reports, which can be downloaded from the CDM
127 project database.⁷ For the years 2002–2004, Project Design Documents (PDD)
128 provide the more “historical” co-production ratios. Individual ratios from 264
129 monitoring reports (accessed as of 1st July 2013) and 11 PDD for 11 projects in China
130 are shown in supporting information (SI) Fig. S1, as well as values from CDM
131 HFC-23 projects in other countries (Project 0807 in Argentina was excluded due to
132 incomplete information in the monitoring reports). Independent-samples t-tests show
133 that there is no significant difference between co-production ratios in China and in
134 other countries (2-tailed).

135 The red hollow circles in Fig. S1 show the annual mean co-production ratios
136 weighted by the HCFC-22 production in each plant. Note that for estimating the
137 annual mean co-production ratio for each year, production of HFC-23 and HCFC-22
138 in some monitoring reports were divided into two parts weighted by the number of
139 days inside or outside of that year if that monitoring period crossed over two years.
140 The calculated annual mean co-production ratios reveal a slight decrease over time,

141 from 3.31% in 2002 to 2.83% in 2012. The annual relative standard deviations of the
142 co-production ratios from 11 facilities were highest in 2003 (29%) and lowest in 2012
143 (11%). Ratio data for the years 2006 and 2007 were excluded in this comparison since
144 most projects had not been launched yet in these two years. For estimating the
145 co-production ratio prior to 2002 and in 2005, 2006 and 2007, a linear extrapolation
146 of the 2002–2004 and 2008–2012 ratio data was used.

147 Based on the total HCFC-22 production from the CDM monitoring reports and the
148 estimated HCFC-22 total production from Section 0, we attribute $48 \pm 2\%$ of total
149 annual Chinese HCFC-22 production to the CDM projects during 2009–2012.

150 Considering CDM projects cover almost half of total HCFC-22 production in China,
151 we made the simple assumption that the mean co-production ratios of
152 HFC-23/HCFC-22 in these CDM projects represent the mean values from all
153 HCFC-22 production plants in China.

154 Incineration of HFC-23 from HCFC-22 production

155 Annual amounts of HFC-23 involved in CDM projects in China are shown in Fig.
156 S2. Eleven projects have produced HFC-23 emission reductions of 32 Gg eligible for
157 CER credits between 2006 and 2012 (shown as the left bar for each year in Fig. S2).
158 However, CER-eligible emission reductions are smaller than the real HFC-23
159 emission reductions, since some of the HFC-23 incinerations are not eligible for CER
160 credits (for instance, if the waste gas generation ratio or HCFC-22 production
161 exceeded the plant's historic values as documented in the Project Design Document).

162 Each project monitoring report accounted for actual HFC-23 production, incineration,
163 sales, storage and releases, and annual ‘non-release’ amounts were determined (shown
164 as the right bar for each year in Fig. S2), which appear on average to be about 20%
165 (10%–24%) higher than the annual amounts eligible for CER credits (left bars).
166 Therefore, a total of about 38 Gg HFC-23 was actually prevented from being released
167 to the atmosphere during 2006–2012 compared to the 32 Gg CER-eligible reductions.
168 Since all CDM projects in China were in operation by 2009, the annual amount
169 eligible for CER credits and “non-release” amounts have been relatively constant
170 thereafter.

171 Assembling an inventory of HFC-23 emissions

172 Annual total production of HFC-23 is calculated as the sum of annual domestic
173 HCFC-22 production for feedstock and dispersive uses and exported HCFC-22
174 production for feedstock and dispersive uses (compiled in Sect. 0), multiplied by the
175 mean annual co-production ratios of HFC-23/HCFC-22 (Sect. 0). Then Eq. 1 was
176 used for estimating emissions of HFC-23. HFC-23 may be used as feedstock in the
177 production of Halon-1301, as a fire extinguishing agent or as an etching agent in the
178 semiconductor industry. The application of HFC-23 in these industrial sectors was
179 assumed negligible, according to the assumption made for the global estimate as
180 described by Miller et al.⁴ The overall uncertainties of annual total HFC-23 emissions
181 were estimated based on uncertainties assigned to the individual components (see
182 Table S1). The assigned uncertainties for earlier time are larger than those for later

183 time, e.g., the uncertainties of HCFC-22 production during 1980–1996 and 1999 are
184 50%, while the uncertainties of HCFC-22 production during 2000 – 2010 are 5%.

$$185 \quad E = P - A - \sum C_i + \sum E_i \quad (1)$$

186 Here E is annual total emission (Gg/yr), P is annual total production (Gg/yr), A is
187 annual non-release amount (Gg/yr) by abatement measures (e.g., CDM projects), C_i
188 is consumed amount in application sector i (Gg/yr), and E_i is emission from
189 application sector i (Gg/yr). Second National Communication on Climate Change of
190 The People's Republic of China shows that emissions of HFC-23 in semiconductor
191 sector in 2005 was 0.0044 Gg/yr, which is about 1/200 of the estimated total HFC-23
192 emissions¹⁷. Thus $\sum C_i$ and $\sum E_i$ (in Eq. 1) were assigned to zero.

193 Historical emissions in China: 1980–2012

194 Historical HFC-23 emissions

195 Estimates of the annual HFC-23 production and emission in China for the period
196 1980–2012 are plotted in Fig. 1. The HFC-23 production increased from 0.08 ± 0.05
197 Gg/yr in 1980 to 15.4 ± 2.1 Gg/yr in 2012. Note that the growth rate started to
198 accelerate in the mid-1990s. For the period 1980–1990, the annual growth rate was
199 estimated to be 0.04 Gg/yr, while for the period 1990–2000, the growth rate increased
200 to 0.18 Gg/yr. After 2000, the annual growth rate was 1.1 Gg/yr. During 2000–2010,
201 all three HFC-23 production components were found to increase, including HCFC-22
202 domestic dispersive production, feedstock production and exported production.

203 Contribution from domestic dispersive production to national totals was about 60% at
204 the beginning of 2000s and declined to about 40% in 2010, while contributions from
205 domestic feedstock production increased from 25% to 35% during this period.
206 Contributions from exported production are about 25%.

207 The annual national total HFC-23 emissions were equal to the HFC-23 production
208 until 2006 when CDM projects were launched to abate HFC-23 in China. Due to the
209 emission reductions in 2006, the actual emissions of HFC-23 were 0.4 Gg/yr lower
210 than the production. In 2006, HFC-23 emissions reached a peak of $10.5 \pm 1.8 \text{ Gg/yr}$
211 and then decreased to a minimum of $7.3 \pm 1.3 \text{ Gg/yr}$ in 2008 and 2009, followed by a
212 slight increase to $8.5 \pm 2.1 \text{ Gg/yr}$ in 2012 when CDM projects abated about 45% of
213 the HFC-23 produced. Of note is that since HCFC-22 production in non-CDM plants
214 were started later than that of CDM plants, the co-production ratios of
215 HFC-23/HCFC-22 in non-CDM plants may be lower than those in CDM plants due to
216 technical improvement. This could lead to the result that the annual HFC-23
217 production and emissions in China in recent years are smaller than those estimated in
218 this study. However, information about recent co-production ratios in non-CDM
219 plants is currently very limited.

220 Comparison with other estimates

221 We compared our results with other published estimates using either bottom-up or
222 top-down approaches (Fig. 2). Using observation data from Hateruma station, a
223 tagged simulation from three-dimensional transport model and a tracer-ratio technique,

224 the HFC-23 emissions from China for May-2004 to May-2005 were estimated to $10 \pm$
225 4.6 Gg/yr.⁹ Based on observation data from three East Asian stations and inverse
226 modeling, the HFC-23 emissions in 2008 were determined to be 6.2 ± 0.7 Gg/yr.¹⁰
227 Our estimates are close to these two estimates. However, larger differences are found
228 when compared to estimates of Li et al.⁸ and Kim et al.¹¹ who used observation data at
229 the Gosan station and a tracer ratio method. It seems that the estimate in Kim et al.¹¹ is
230 identical to the global emissions which is derived from 2-D 12-box model inversions
231 of AGAGE observations.⁴ Emissions for the period May-2010 to May-2011 estimated
232 using observation data at Shangdianzi station in Yao et al.¹⁸ are significantly lower
233 than our estimates. HFC-23 is mostly emitted from point sources (HCFC-22
234 production plants), while sources of reference species carbon monoxide (CO) adopted
235 by Yao et al.¹⁸ and HCFC-22 adopted by Li et al.⁸ and Kim et al.¹¹ are widely spread.
236 Therefore, the assumption of co-location of target species and reference species in the
237 tracer-ratio method used in three studies above is not fully valid.

238 Comparisons were made with other bottom-up estimates (Fig. 2). Our estimates
239 agree well with the officially reported value of 9 Gg/yr for 2005 in Second National
240 Communication from China to UNFCCC¹⁷. EDGAR v4.2 provides a time series of
241 bottom-up estimates of HFC-23 emissions in China until 2008, which appears close to
242 our estimates within 1990–2000 but becomes higher (40% on average for the period
243 2001–2008) than our estimates thereafter. Note that the EDGAR v4.2 estimates for
244 China are even larger than the global emissions in 2007 and 2008. Our estimate
245 agrees with the estimates for 2000–2008¹⁴ and for 2000–2010¹⁹, even though there are

246 some minor differences in parameters used in these three studies. e.g. a constant
247 co-production ratio of 2.85% for all years was used by Cui et al.¹⁹ while different
248 annual mean co-production ratios were used in this study. Relatively big differences
249 occurred in 2006 and 2007 among these three bottom-up estimates. Difference
250 between HFC-23 production and emissions in 2006 is estimated as 3.5 Gg/yr in Feng
251 et al.¹⁴, larger than the other estimates, which is likely due to being unaware of the
252 difference between the designed reduction capacity and the actually achieved
253 destruction of HFC-23 in that year.

254 National and Global perspective

255 Relatively complete information of other HFC emissions is available from Li et al.⁸
256 for 2008. After comparing HFC-23 emissions estimated in this study with other HFC
257 emissions in Li et al.⁸, we found that HFC-23 emissions rank second after HFC-134a
258 in the contribution to national total HFC emissions (Fig. 3, lower left). However, in
259 terms of the 100-year GWP,¹ the contribution pattern becomes vastly different.
260 GWP-weighted HFC-23 emissions were calculated to be 108 ± 20 Tg/yr CO₂-eq in
261 2008 and emissions of other HFCs were calculated to be 29 ± 8 Tg/yr CO₂-eq. This
262 shows that HFC-23 emissions constituted $79 \pm 6\%$ of the national total
263 GWP-weighted HFC emissions, revealing a dominant role of HFC-23 in the
264 GWP-weighted HFC emissions in the year 2008 in China.

265 The contribution of HFC-23 emissions from China to the global total is also plotted
266 in Fig. 3 (top panel). Global emissions for the period 1980–2009 were derived from

267 top-down inversions in Miller et al.⁴ The calculated contributions from Chinese
268 emissions to global emissions displayed a gradual increase from $2 \pm 1\%$ in 1980 to 20
269 $\pm 6\%$ in 2000 followed by a sharp increase to $77 \pm 23\%$ in 2005. The growth rate of
270 contribution after 2000 is much higher than before 2000, which is consistent with the
271 accelerated growth rate of HFC-23 production in China after 2000.

272 Projecting emissions in China: 2013–2035

273 Policy options and emission scenarios

274 First, we defined our business-as-usual (BAU) scenario. There are four components
275 of HCFC-22 production in China. The first one is domestic dispersive production,
276 which will be subject to Montreal Protocol phase out schedule of a 10% reduction by
277 2015 compared to the baseline of the average of 2009 and 2010 production, a 35%
278 reduction by 2020, a 67.5% reduction by 2025 and a 97.5% reduction by 2030 that is
279 averaged over the next 10 years. The second one is domestic feedstock production,
280 which is extrapolated based on GDP growth of China provided by the EIA²⁰. Tests
281 show that the standardized domestic HCFC-22 feedstock production is significantly
282 correlated with the standardized GDP during the period 2000–2012 ($P < 0.05$), and that
283 the slope for this correlation is close to “1” (see Fig. S3). We also chose the GDP
284 Reference Case based on purchasing power parity out of three GDP projections
285 offered in the report, which is the same input as used in the global HFC-23 emission
286 projections by Miller and Kuijpers²¹. The relative growth rate of GDP in this case is

287 estimated to be 8.12% during 2007–2015 and will decrease afterwards to 3.49%
288 during 2030–2035. The third HCFC-22 production component is exported dispersive
289 production, which is assumed to follow the Montreal Protocol phase out schedule as
290 well since dispersive production is mainly exported to developing countries. The last
291 component is exported feedstock production, which is extrapolated based on GDP
292 growth of the whole world excluding China. EIA (2010) only provided GDP
293 projection to 2035, thus we linearly extrapolated GDP to 2050 based on values in
294 2030–2035. The average of the annual mean co-production ratio of HFC-23/HCFC-22
295 during 2008–2012 in China, 2.82%, was used for the projection calculation. In this
296 BAU scenario, it was assumed that the CDM projects in China are approved for a
297 total of three consecutive crediting periods ending between 2027 and 2030.

298 Second, we defined a Less Mitigation (LM) scenario, in which the abatement of
299 HFC-23 in CDM projects will cease after the first crediting period and no abatement
300 will exist in China thereafter. The CDM projects in China will end their first crediting
301 period during 2013–2016 after 7 years of operation. The European Commission
302 decided that the EU would cease the purchase of CER credits derived from emission
303 mitigation of HFC-23 and N₂O produced in industrial processes after May 2013,²²
304 leading to loss of the purchasers of CER credits. So Chinese CDM projects are at risk
305 of being stopped, even though all of them were registered as projects with renewable
306 crediting periods, which will lead to less mitigation of HFC-23 emissions.

307 Finally, we defined a Best Practice (BP) scenario which represents that maximum
308 effort will be made to tackle HFC-23 emissions, namely installing incineration

309 facilities in all plants. We assumed that emission reductions from the new incineration
310 facilities will start in 2016, which would be linearly increased to full reduction of
311 produced HFC-23 after 6 years' capacity construction by 2022. Miller and Kuijpers
312 (2011) have indicated that the effort of process optimization of co-production ratio of
313 HFC-23/HCFC-22 would not be an ideal solution, since only 44% of global emissions
314 projected in their reference scenario can be reduced if process optimization is adopted
315 as reduction measures. We also tested projecting emissions if implementing process
316 optimization in Chinese plants with the co-production ratio decreasing linearly from
317 2.82% in 2016 to 1.37% in 2030 which was achieved by one of the facilities in the
318 developed world.²³ Results show the emission reduction would be 31% in 2020, 52%
319 in 2030 and 51% in 2050 compared to BAU scenario (See Fig. 4 bottom panel).
320 Significant emissions remain even after implementing documented process
321 optimizations; therefore, process optimizations were not considered as the measures
322 in BP scenario.

323 Projected emissions and identifying driving forces

324 Figure 4 shows the projected HFC-23 production, abatement and emission in China
325 for the period 2013–2035 under the BAU scenario. The projected emissions show a
326 “plateau” with a growth rate of only 0.15 Gg/yr during 2008–2027, which is a result
327 of compensation of HFC-23 production increase from HCFC-22 feedstock production
328 and decrease from HCFC-22 dispersive production, either domestic or exported.
329 During this period, CDM projects were assumed to generate constant amounts of

330 HFC-23 emission abatement. Even without CDM projects, the emissions will be
331 relatively constant in the 2013–2027 period, but at a plateau which is 6.9 Gg/yr higher.
332 Since the dispersive production of HCFC-22 for domestic use or export is strictly
333 regulated by the phase out schedule of the Montreal Protocol, the total HFC-23
334 emissions (and production) are greatly dependent on the extent of increase of
335 HCFC-22 feedstock production, which means that if the actual growth rate of
336 HCFC-22 feedstock production is greater or less than the assumed growth rate in our
337 BAU scenario, the plateau will be upward or downward, respectively.

338 After a gradual annual increase of 0.15 Gg/yr during 2008–2027, there is a steep
339 increase of 1.5 Gg/yr HFC-23 emissions up to 2031. At the end of 2027, six CDM
340 projects are expected to expire after three crediting periods, followed by expirations
341 of three projects in 2028, one project in 2029 and the last one in 2030. Therefore,
342 changes in HFC-23 emissions in this stage are mostly driven by the CDM projects.
343 After 2031, the HCFC-22 feedstock production becomes the sole driving forcing to
344 the HFC-23 emissions since dispersive production reaches the minimum level
345 required by the Montreal Protocol in 2030. In 2050, the total HFC-23 emissions (and
346 production) in China will reach 26.4 Gg/yr, equal to 391 Tg/yr CO₂ emissions.

347 If the CDM projects are not renewed after the first crediting period as assumed in
348 the LM scenario and no other abatement measures take place, the steep upturn of
349 HFC-23 emissions could occur in the period 2013–2016 (Fig. 4, lower panel). On the
350 other hand, if besides CDM projects, new incineration facilities start to be installed at
351 all plants and full incineration is commenced in 2022 (BP scenario), the projected

352 HFC-23 emissions will decrease to approximately zero. By this point, the major factor
353 controlling the annual dynamics of Chinese HFC-23 emissions for the next decade
354 (2013–2022) becomes competition between closing existing abatement facilities and
355 increasing new abatement facilities.

356 Over the period 2013–2050, cumulative emissions of HFC-23 in China under BAU
357 scenario are estimated to be 609 Gg (9015 Tg CO₂-eq), which approximates the
358 China's whole-year emissions of 9864 Tg CO₂ in 2012.²⁴ Velders et al. concluded that
359 the projected global HFC emissions in 2050 could be equivalent to 9–19% of
360 projected global CO₂ emissions, but HFC-23 was not included in the emission
361 projection of the major HFCs.²⁵ Cumulative emissions of HFC-23 in China estimated
362 in this study would amount to 5.3%–8.2% the total high and low estimates of CO₂
363 equivalents from HFCs over the period 2013–2050. Compared to BAU scenario,
364 cumulative emissions of HFC-23 under LM scenario will be 97 Gg higher (1436 Tg
365 CO₂-eq), while cumulative HFC-23 emission reductions of 557 Gg (8249 Tg CO₂-eq)
366 can be achieved under BP scenario.

367 Simulating atmospheric abundance and quantifying contributions

368 Atmospheric abundance of HFC-23 was simulated using historical and projected
369 emissions and a simple 1-box model (Fig. 5). As input to the model, we used a
370 HFC-23 atmospheric lifetime of 222 years²⁶ and 5.136×10^{21} g for the mass of the
371 atmosphere²⁷. For China, historical emissions for 1980–2012 derived from the
372 bottom-up estimates and emissions for 2013–2050 derived from BAU scenario

373 projection were used in this simulation. For developing countries excluding China and
374 developed countries, emissions for 1980–2008, 2009–2035 and for 2036–2050 are
375 derived from bottom-up estimates by Miller et al.⁴, projections by Miller and
376 Kuijpers²¹ and extrapolation based on the projections, respectively.

377 Fig. 5 shows that the simulated HFC-23 atmospheric abundance for the period
378 1980–2009 driven by the estimated historical emissions agrees well with the historical
379 measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE)
380 network (the data were derived from Miller et al.⁴), which suggests that it is adequate
381 to project future atmospheric abundance using this simple model. By the year 2050,
382 the simulated atmospheric abundance of HFC-23 is 82 ppt, an increase of 233%
383 relative to its 2012 value. This yields a radiative forcing of 16 mWm^{-2} in 2050
384 assuming radiative efficiencies taken from IPCC (2007).²⁸ Accelerated growth of
385 HFC-23 atmospheric abundance during 2013–2050 was found, which is caused by the
386 sustained increase of projected HFC-23 emissions from China and other developing
387 countries. If the HFC-23 emissions in China are subject to LM scenario, the simulated
388 HFC-23 atmospheric abundance will reach 89 ppt by the year 2050, while if the
389 HFC-23 emissions in China are subject to the BP scenario, HFC-23 atmospheric
390 abundance will reach only 41 ppt (see Fig. 5). This reveals that if the measures
391 (incineration) in BP scenario are implemented in China, HFC-23 atmospheric
392 abundance in middle of 21st century could be cut to half of abundance simulated in
393 BAU scenario.

394 We also quantified contributions from China, developing countries excluding China

395 and developed countries to the atmospheric abundance (Fig. 5, lower panel), which
396 are compared with the contributions to annual global emissions giving 1980, 1995,
397 2013, 2025 and 2035 as examples (Fig. 5, upper and middle panels). Note that
398 contributions from emissions before 1980 (dash line in the plot) were attributed to
399 developed countries since almost 100% of global emissions then were from developed
400 countries revealed by Miller et al.⁴ The upper panel of Fig. 5 shows contribution of
401 Chinese annual emissions to global emissions is 2% in 1980, which increased to 68%
402 in 2013 and 76% in 2050, while the middle panel of Fig. 5 shows that the
403 accumulated contributions of emissions from China to the annual global atmospheric
404 abundance were significantly delayed compared to the annual emission contributions
405 to global emissions, e.g. accumulated Chinese emissions only contribute 32% of
406 atmospheric abundance in 2013 compared to annual Chinese emissions' contribution
407 to 68% of global emissions. In this sense, historical emissions from developed
408 countries accounted for most of atmospheric burden up to now (e.g., 61% in 2013),
409 even though now China is contributing more than 60% to current annual global
410 emissions. We estimated that in circa 2027, China will surpass the developed
411 countries with respect to the accumulated contributions to the global atmospheric
412 abundance. This delay is of course due to the long atmospheric lifetime of HFC-23.

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416 manuscript.

417 ***Supporting Information Available***

418 Uncertainties of components in assembling an inventory of HFC-23 emissions are
419 shown in Table S1. Individual co-production ratios of HFC-23/HCFC-22 in China and
420 other countries are presented in Figure S1. Annual amounts of HFC-23 involved in the
421 CDM HFC-23 emission abatement projects are provided in Figure S2. The correlation
422 between the standardized domestic HCFC-22 feedstock production and the
423 standardized GDP in China are shown in Figure S3. This information is available free
424 of charge via the Internet at <http://pubs.acs.org/>.

425 **Reference**

- 426 (1) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.;
427 Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Dorland, R. V.,
428 *Changes in Atmospheric Constituents and in Radiative Forcing*. In *Climate Change 2007: The*
429 *Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of*
430 *the Intergovernmental Panel on Climate Change*; Solomon, S.; Qin, D.; Manning, M.; Chen,
431 Z.; Marquis, Z.; Avery, K. B.; Tignor, M.; Miller, H. L., Eds.; Cambridge University Press:
432 Cambridge, United Kingdom, 2007; pp 129–234.
- 433 (2) United Nations Multilateral Fund Secretariat. *Terms of reference (TOR) for the technical audit*
434 *of HCFC production in Article 5 countries*, 2012.
435 <http://www.unmfs.org/policydoc/policy60p713.htm> (accessed October 1, 2013).
- 436 (3) McCulloch, A.; Lindley, A. A. Global emissions of HFC-23 estimated to year 2015. *Atmos.*
437 *Environ.* **2007**, *41* (7), 1560-1566.
- 438 (4) Miller, B. R.; Rigby, M.; Kuijpers, L. J. M.; Krummel, P. B.; Steele, L. P.; Leist, M.; Fraser, P.
439 J.; McCulloch, A.; Harth, C.; Salameh, P.; Mühle, J.; Weiss, R. F.; Prinn, R. G.; Wang, R. H. J.;
440 O'Doherty, S.; Grealley, B. R.; Simmonds, P. G. HFC-23 (CHF₃) emission trend response to
441 HCFC-22 (CHClF₂) production and recent HFC-23 emission abatement measures. *Atmos.*
442 *Chem. Phys.* **2010**, *10* (16), 7875-7890.
- 443 (5) United Nations Environment Programme. *Report of the 9th Meeting of the Parties to*
444 *the Montreal Protocol on Substances that Deplete the Ozone Layer. UNEP/OzL, Pro. 19/7,*
445 *Nairobi, Kenya, 2007.*

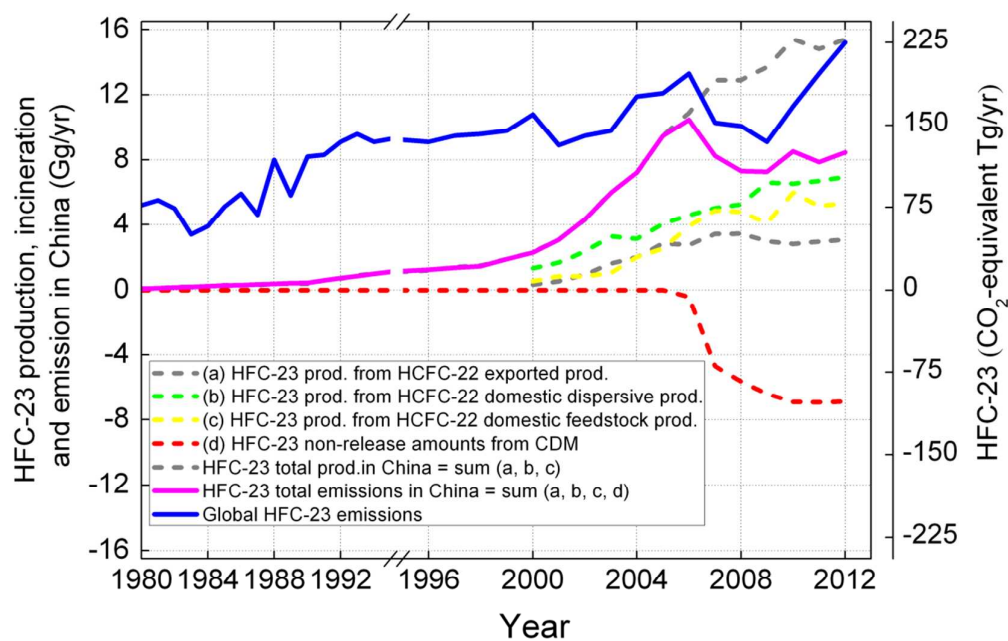
- 446 (6) United Nations Environment Programme (UNEP). *Handbook for the Montreal Protocol on*
447 *Substances That Deplete the Ozone Layer, seventh ed.*, Nairobi, Kenya, 2009.
448 http://ozone.unep.org/Publications/MP_Handbook/MP-Handbook-2009.pdf (accessed May 5,
449 2011).
- 450 (7) *United Nations Framework Convention on Climate Change: Clean Development Mechanism*
451 *(CDM)*. 2012. <http://cdm.unfccc.int/Projects/projsearch.html> (accessed December 20, 2012).
- 452 (8) Li, S.; Kim, J.; Kim, K. R.; Mühle, J.; Kim, S. K.; Park, M. K.; Stohl, A.; Kang, D. J.; Arnold,
453 T.; Harth, C. M.; Salameh, P. K.; Weiss, R. F. Emissions of Halogenated Compounds in East
454 Asia Determined from Measurements at Jeju Island, Korea. *Environ. Sci. Technol.* **2011**, *45*
455 (13), 5668-5675.
- 456 (9) Yokouchi, Y.; Taguchi, S.; Saito, T.; Tohjima, Y.; Tanimoto, H.; Mukai, H. High frequency
457 measurements of HFCs at a remote site in east Asia and their implications for Chinese
458 emissions. *Geophys. Res. Lett.* **2006**, *33* (21), L21814.
- 459 (10) Stohl, A.; Kim, J.; Li, S.; O'Doherty, S.; Mühle, J.; Salameh, P. K.; Saito, T.; Vollmer, M. K.;
460 Wan, D.; Weiss, R. F.; Yao, B.; Yokouchi, Y.; Zhou, L. X. Hydrochlorofluorocarbon and
461 hydrofluorocarbon emissions in East Asia determined by inverse modeling. *Atmos. Chem.*
462 *Phys.* **2010**, *10* (8), 3545-3560.
- 463 (11) Kim, J.; Li, S.; Kim, K. R.; Stohl, A.; Mühle, J.; Kim, S. K.; Park, M. K.; Kang, D. J.; Lee, G.;
464 Harth, C. M.; Salameh, P. K.; Weiss, R. F. Regional atmospheric emissions determined from
465 measurements at Jeju Island, Korea: Halogenated compounds from China. *Geophys. Res. Lett.*
466 **2010**, *37* (12), L12801.
- 467 (12) *Emission Database for Global Atmospheric Research (EDGAR), release version 4.2.*
468 European Commission, Joint Research Centre (JRC)/Netherlands Environmental Assessment
469 Agency (PBL): 2011. <http://edgar.jrc.ec.europa.eu> (accessed March 22, 2012).
- 470 (13) Ozone Secretariat Data Access Centre; United Nations Environment Programme (UNEP).
471 *ODS Production Reported to UNEP*, 2013.
472 http://ozone.unep.org/Data_Reporting/Data_Access/.
- 473 (14) Feng, J.; Yan, H.; Zhang, B.; Zhang, J. Prediction of HFC-23 Emission and Analysis of CDM
474 Project Impact in China. *Acta Scientiarum Naturalium Universitatis Pekinensis* **2012**, *48* (2),
475 310-316.
- 476 (15) State Environmental Protection Administration (SEPA), the People's Republic of China.
477 *National Program for Ozone-depleting Substances Phase-out in China (in Chinese)*, Beijing,
478 China, 1999.
479 <http://www.gdepb.gov.cn/wrfz/gdlxggy/ods/200808/P020080806358145713200.pdf>
480 (accessed July 19, 2011).
- 481 (16) Gas Specialization Website. *Organic Fluorine Industry Situation and Development Strategy*,
482 2013.
483 <http://www.cngspw.com/vNews/ViewNews.asp?DocID=newsY2005M09D11H16m52s04>
484 (accessed July 1, 2013).
- 485 (17) National Development and Reform Commission of China. *Second National Communication*
486 *on Climate Change of The People's Republic of China*, Beijing, China, 2012.
487 http://unfccc.int/essential_background/library/items/3599.php?rec=j&prirref=7666#beg
488 (accessed February 18, 2013).
- 489 (18) Yao, B.; Vollmer, M. K.; Zhou, L. X.; Henne, S.; Reimann, S.; Li, P. C.; Wenger, A.; Hill, M.

- 490 In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs)
491 at the Shangdianzi regional background station, China. *Atmos. Chem. Phys.* **2012**, *12* (21),
492 10181-10193.
- 493 (19) Cui, Y.; Lin, H.; Yang, L.; Zheng, W. Analysis on HFC-23 Emission Reduction Potential in
494 China's Fluorine Industry. *Advances in Climate Change Research* **2013**, *9* (2), 139-143.
- 495 (20) US Energy Information Administration. *International Energy Outlook 2010, Reference Case*
496 *Projections, Appendix A*, 2010.
497 [http://www.eia.gov/forecasts/archive/ieo10/pdf/0484\(2010\).pdf](http://www.eia.gov/forecasts/archive/ieo10/pdf/0484(2010).pdf) (accessed July 20, 2013).
- 498 (21) Miller, B. R.; Kuijpers, L. J. M. Projecting future HFC-23 emissions. *Atmos. Chem. Phys.*
499 **2011**, *11* (24), 13259-13267.
- 500 (22) EC, Emissions trading: Commission welcomes vote to ban certain industrial gas credits. In
501 European Commission: Brussels, Belgium, 2011.
- 502 (23) Duncan Rotherham. *Greenhouse Gas Emission Reduction Verification Audit for Dupont's*
503 *Louisville Works Freon®22 Plant, Final Report (ICF Consulting)* Toronto, Canada, 2004.
504 http://cdm.unfccc.int/public_inputs/inputam0001/Letter_Dupont_Annex2_03June04.pdf
505 (accessed October 1, 2013).
- 506 (24) Olivier, J. G. J.; Janssens-Maenhout, G.; Muntean, M. P.; J.H.A.W. Trends in global CO2
507 emissions - 2013 report, PBL / JRC report 83593; EUR 26098 EN; ISBN 978-94-91506-51-2,
508 October. **2013**.
- 509 (25) Velders, G. J. M.; Fahey, D. W.; Daniel, J. S.; McFarland, M.; Andersen, S. O. The large
510 contribution of projected HFC emissions to future climate forcing. *Proc. Natl. Acad. Sci.*
511 *U.S.A.* **2009**, *106* (27), 10949-10954.
- 512 (26) World Meteorological Organization (WMO). *Scientific assessment of ozone depletion: 2010.*
513 *Global Ozone Research and Monitoring Project — Report No. 52*, Geneva, Switzerland, 2011.
514 http://ozone.unep.org/Assessment_Panels/SAP/Scientific_Assessment_2010/index.shtml
515 (accessed January 1, 2012).
- 516 (27) Lide, D. R., *Handbook of Chemistry and Physics*. CRC press: Boca Raton, FL, 1996.
- 517 (28) Intergovernmental Panel on Climate Change (IPCC). *Fourth Assessment Report (AR4).*
518 *Working Group I, Chapter 2, Changes in Atmospheric Constituents and in Radiative Forcing*,
519 2007. <http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ar4-wg1-chapter2.pdf> (accessed July
520 13, 2011).

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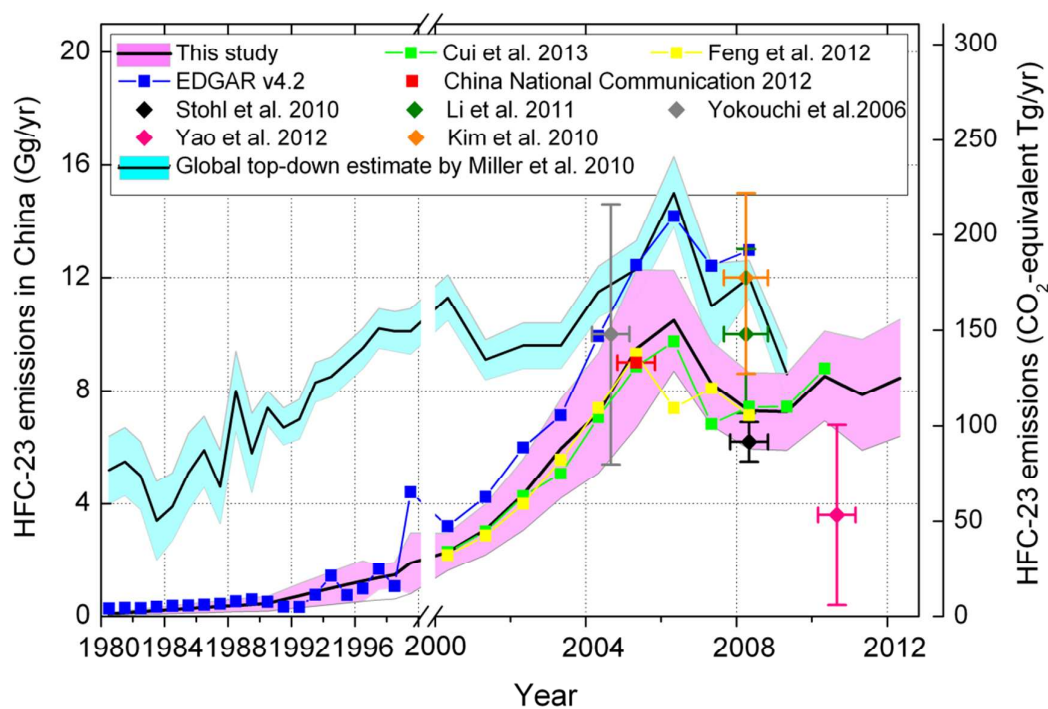
522

Figure Captions



523

524 Fig. 1. Bottom-up estimates of annual HFC-23 production and emission in China for the period
 525 1980–2012. The global HFC-23 emissions were derived from top-down estimates for 1980–1989
 526 and bottom-up estimates for 1990–2008⁴ and from projections for 2009–2012²¹. Note that the
 527 period 1980–1995 on the X-axis is compressed to show the changes during 1995–2012 more
 528 clearly.



529

530 Fig. 2. Comparison with other published estimates of HFC-23 emissions in China, as specified in the

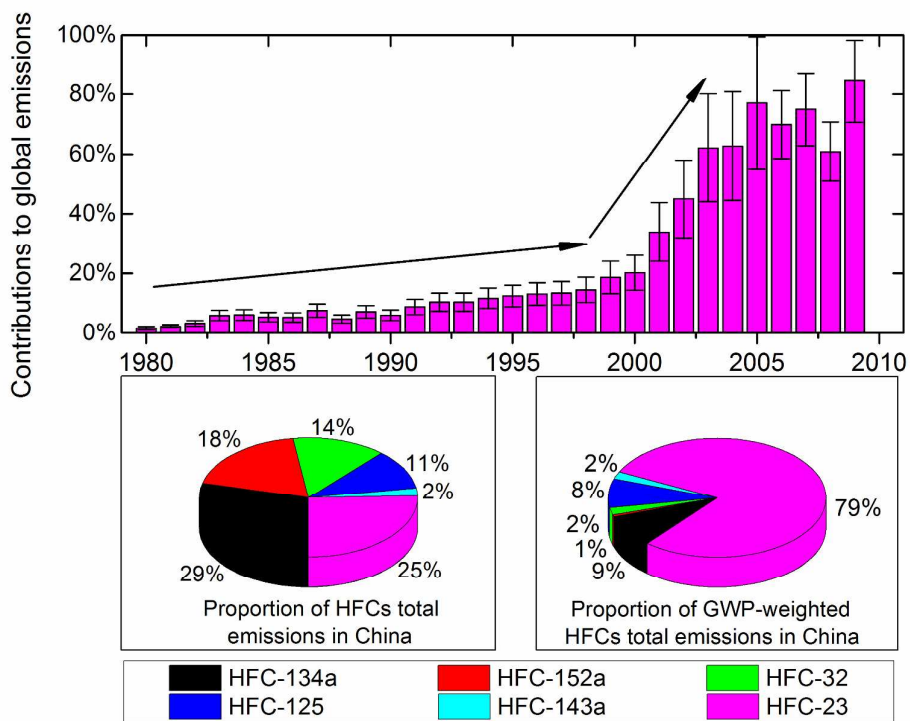
531 legend at the top. Square symbols denote bottom-up estimates and diamond symbols denote top-down

532 estimates. Note that since target time periods in most of the studies are after 2000, the period 1980–

533 2000 on X-axis is compressed to show the comparisons for 2000–2012 more clearly. X-error bar in the

534 plot represents the span of the target period in the respective study, for example 14 months of

535 Nov-2007–Dec-2008 in Li et al.⁸ while 12 months of Jan-2008–Dec-2008 in Stohl et al.¹⁰



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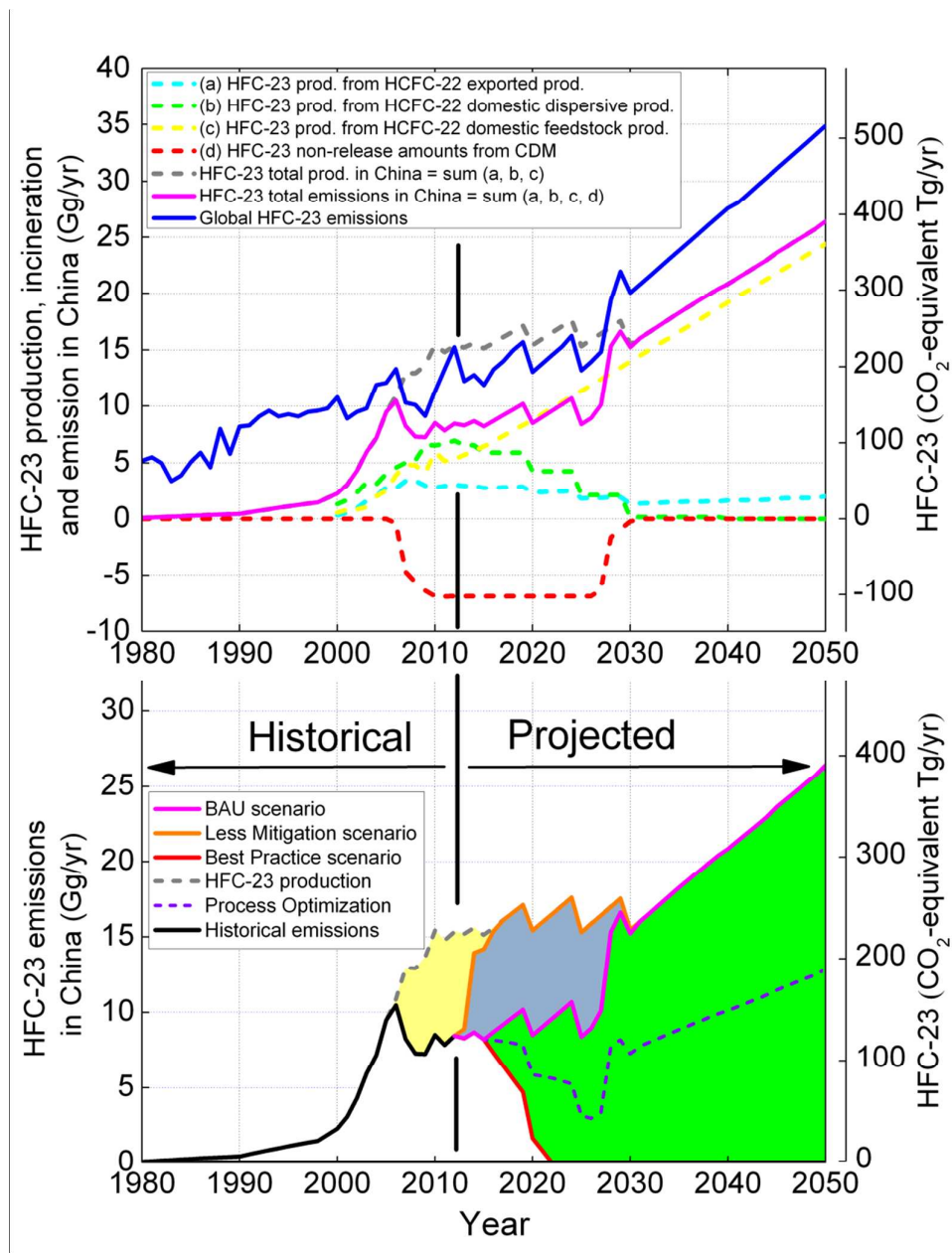
537 Fig. 3. Annual contributions of HFC-23 emissions from China to global total emissions (upper panel)

538 and proportions of HFC-23 to the total, or GWP-weighted total, HFC emissions in China in 2008.

539 Global emissions for the period 1980–2009 were derived from top-down inversions in Miller et al.⁴

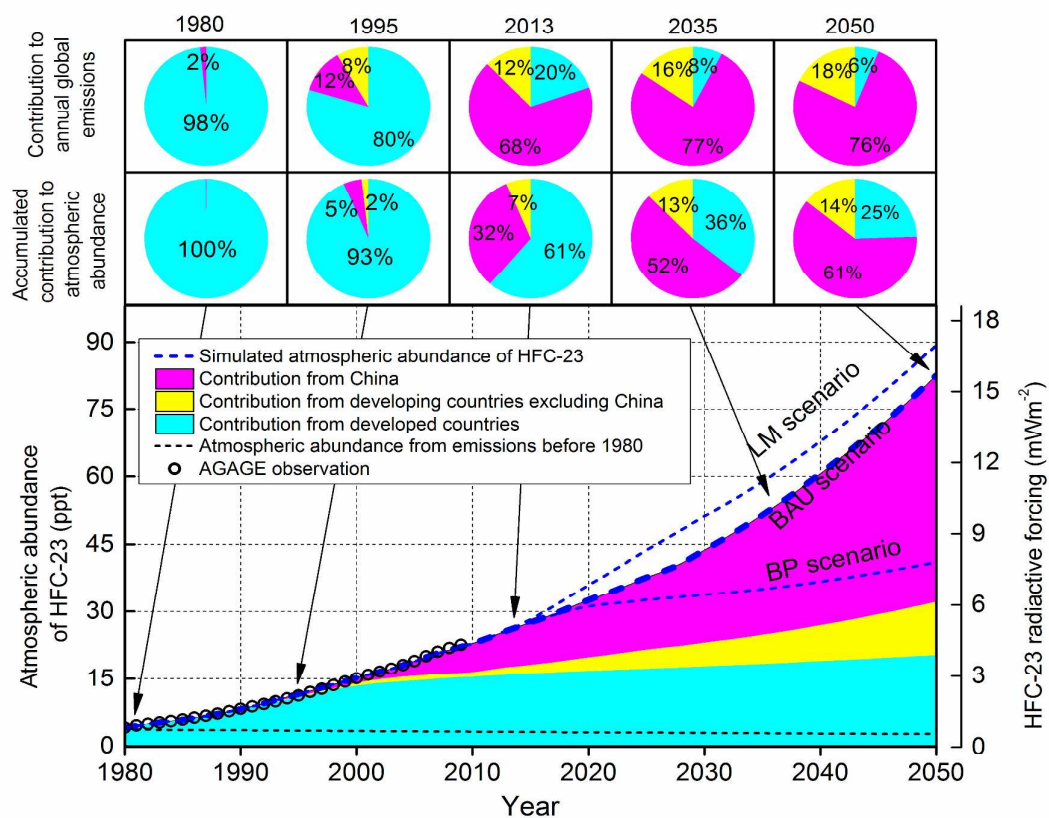
540 Emissions of HFC-23 are from this study, while emissions for other HFC emissions were derived from

541 Li et al.⁸ GWP values were taken from Forster et al.¹



542

543 Fig. 4. Projected HFC-23 production, incineration and emissions in China for the period 2013–
 544 2050 under the BAU scenario (upper panel) and projections of annual HFC-23 emissions in China
 545 under three scenarios (lower panel). The historical emissions for the period 1980–2012 are also
 546 shown for a full depiction of HFC-23 emission evolution in China. Global HFC-23 emissions for
 547 2036–2050 were linearly extrapolated based on HFC-23 emission components for the period
 548 2031–2035 in the projection by Miller and Kuijpers (2011).



549

550 Fig. 5. Simulation of HFC-23 atmospheric abundance and quantification of contributions from
 551 China, developing countries excluding China and developed countries, as well as the annual
 552 observed HFC-23 atmospheric abundance from AGAGE network. The upper panel shows
 553 contributions of emissions from these three country categories to the annual global total emissions,
 554 giving 1980, 1995, 2013, 2035 and 2050 as examples. The middle panel shows accumulated
 555 contributions of emissions from these three country categories to the global atmospheric
 556 abundance in the respective year. The lower panel shows the simulated HFC-23 atmospheric
 557 abundance (left axis) using historical and projected emissions (Chinese emissions vary under BAU,
 558 LM or BP scenarios) and a simple 1-box model, and the corresponding radiative forcing (right
 559 axis). The dashed line represents the HFC-23 atmospheric abundance caused by emissions before
 560 1980, which decreases with time.