High precision F-gas measurement and application in estimate Chinese F-gas emission

Bo Yao, Liying Yi, Haibo Yu, Xuekun Fang, Lingxi Zhou, Jianxin Hu

IPCC TFI expert meeting, Geneva, Switzerland

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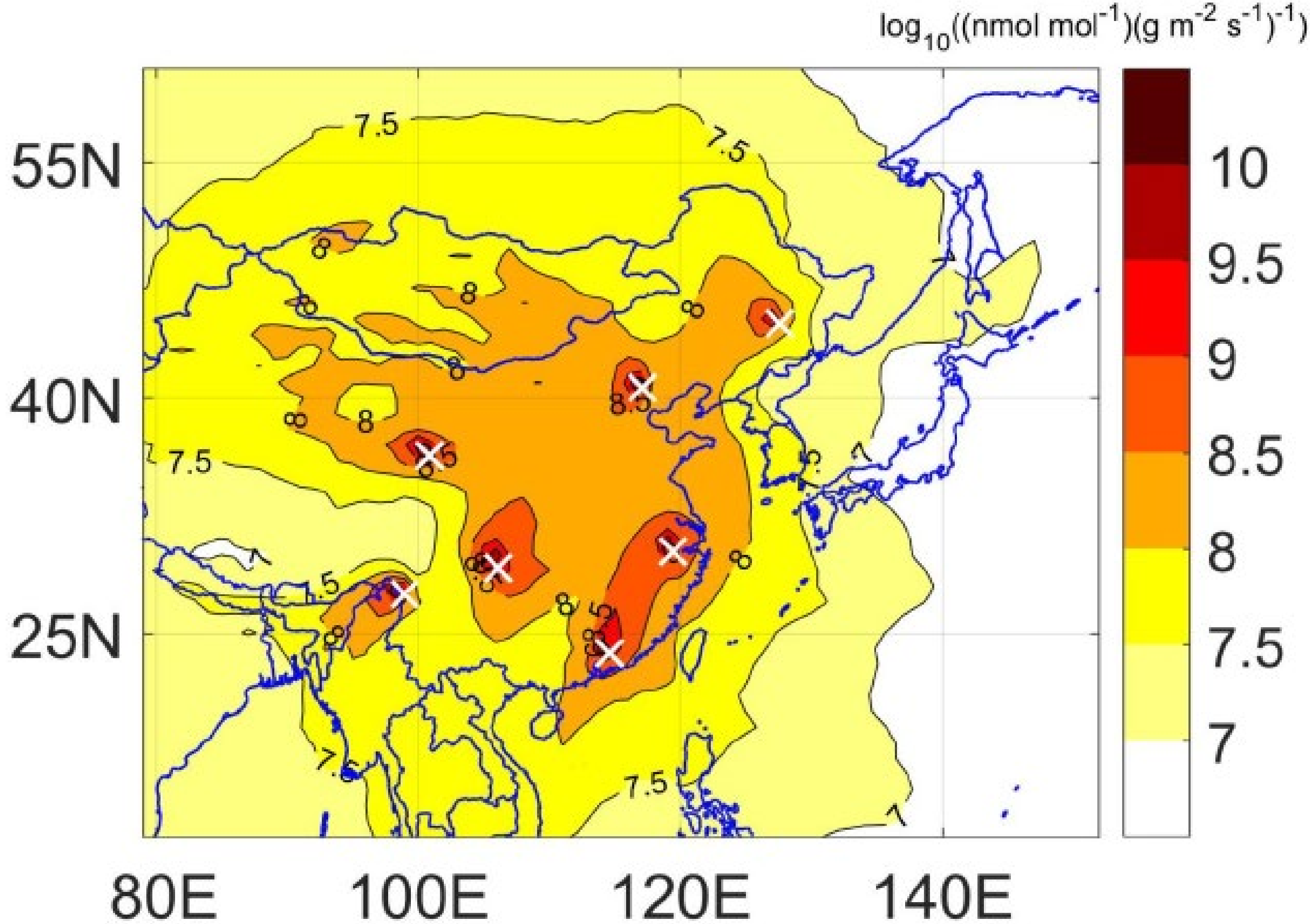
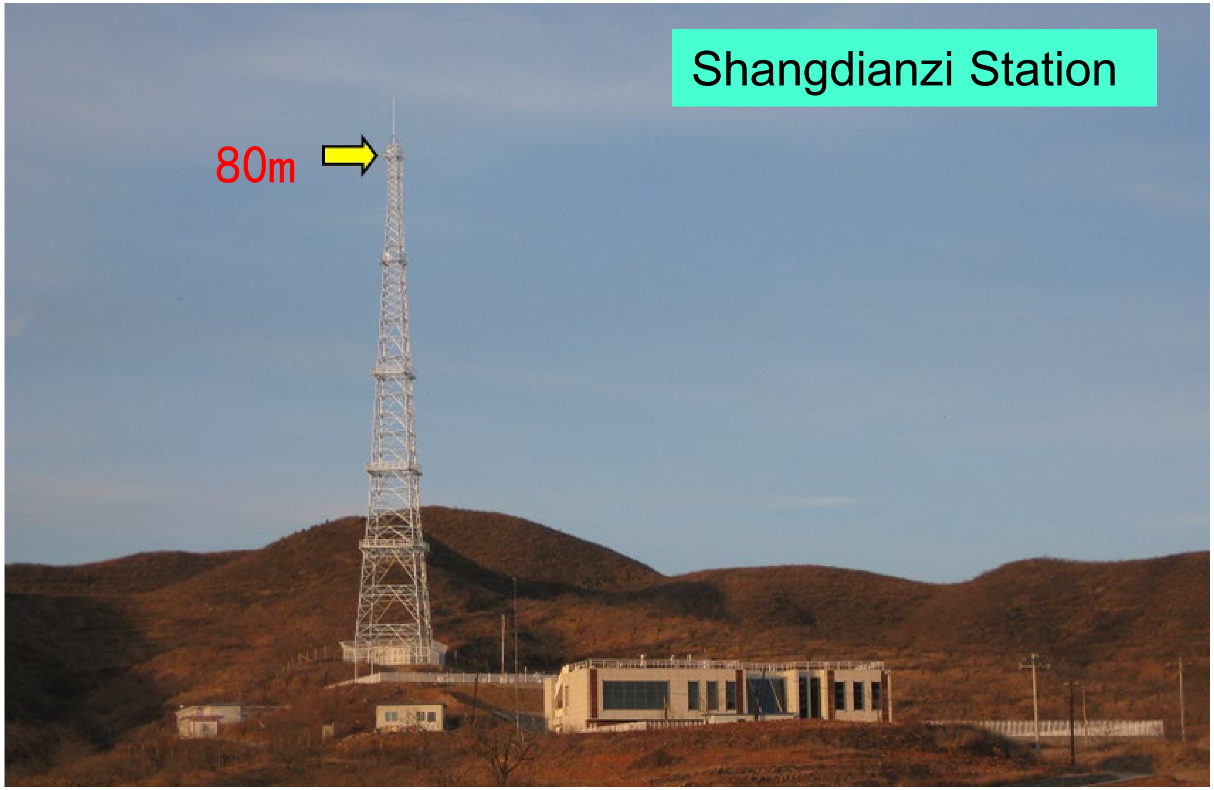
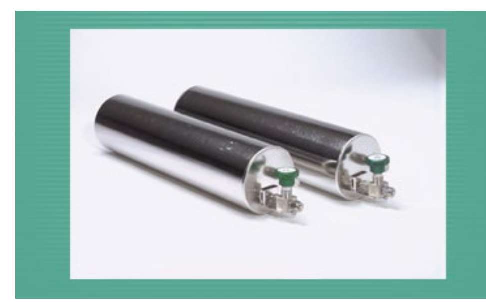
Flask and in situ measurements of ODSs and HFCs （CMA）

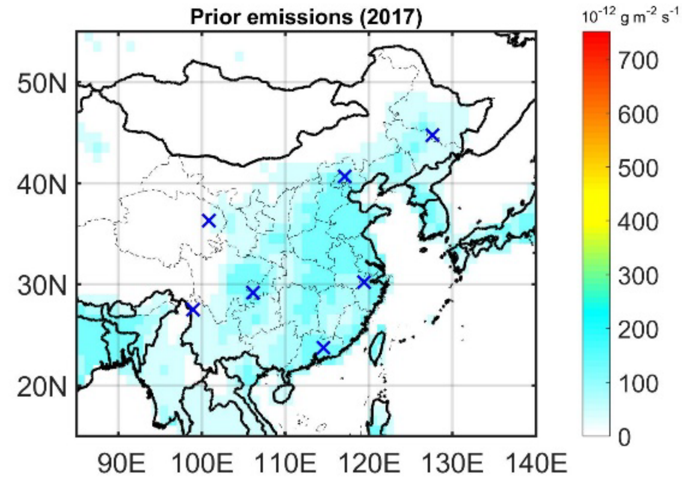






Medusa-GC/MS, technique developed by AGAGE

Prior emission field (1*1)
(constant over 2011-2017)
Roughly populated distributed



Simulating mole fractions

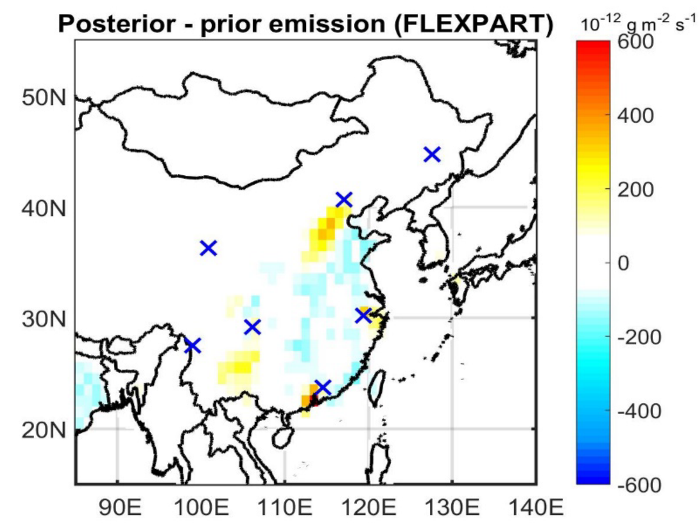
3-hourly emission sensitivity map

FLEXPART

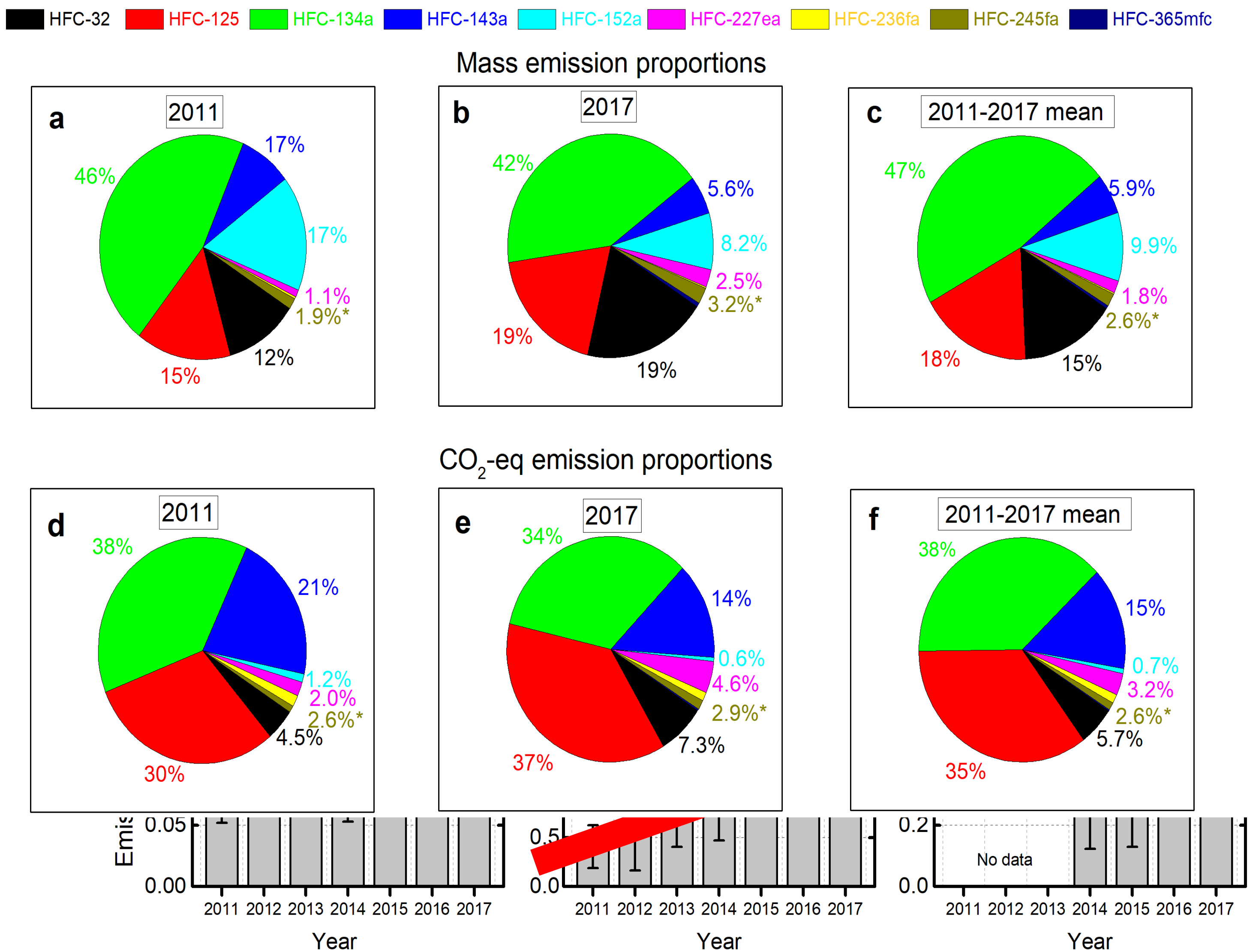
Observation data

Bayesian inversion

Posterior emission field
1*1

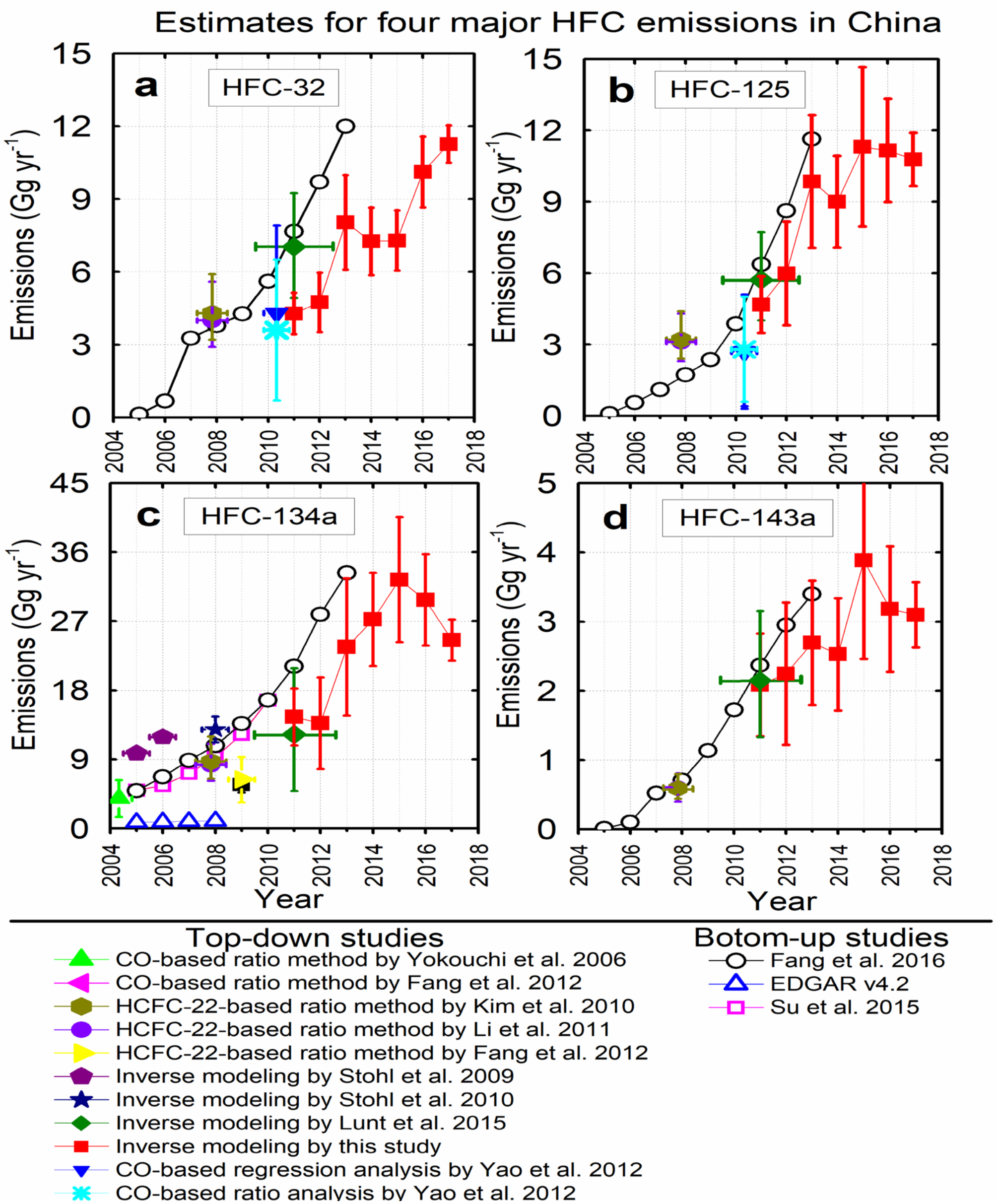


Changes of Chinese HFC emissions by inverse modeling



Yao & Fang et al. EST Letters, 2019

Comparison with bottom-up inventory



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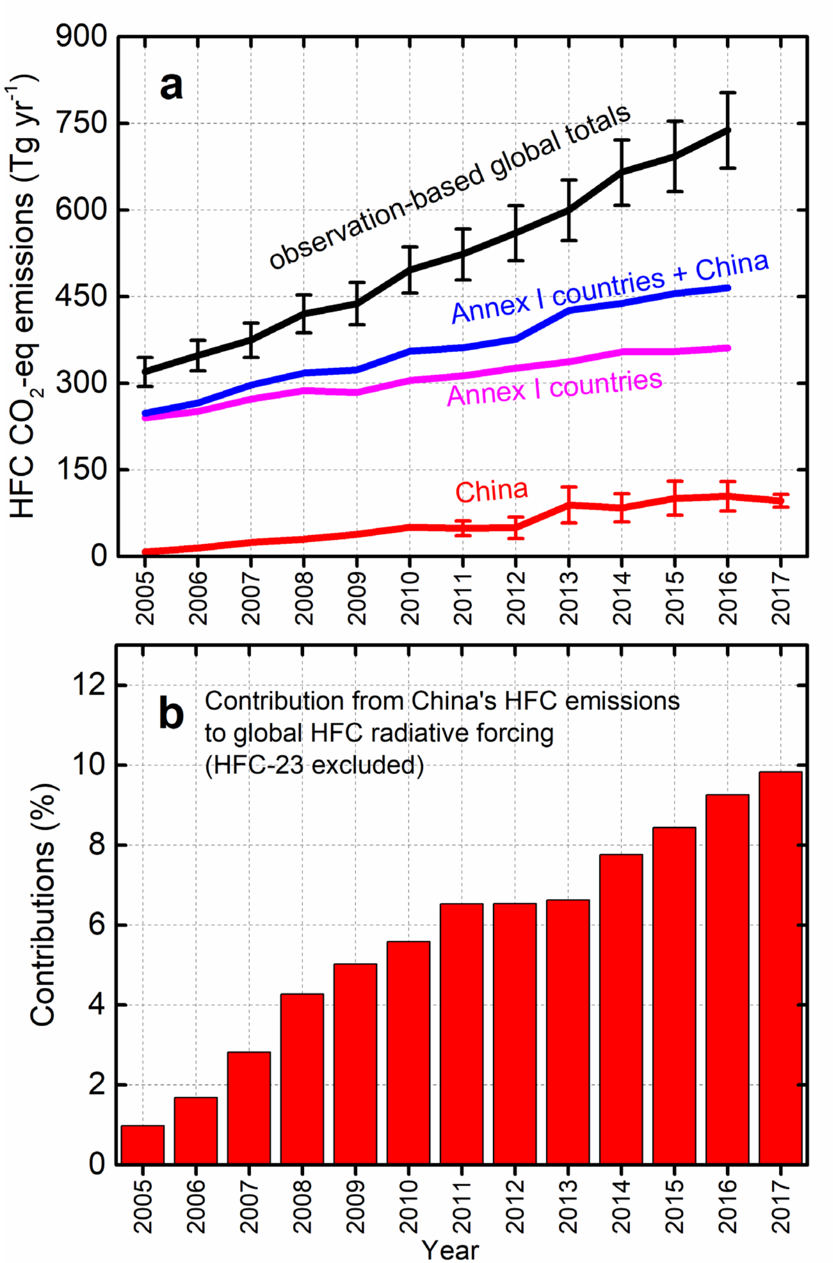
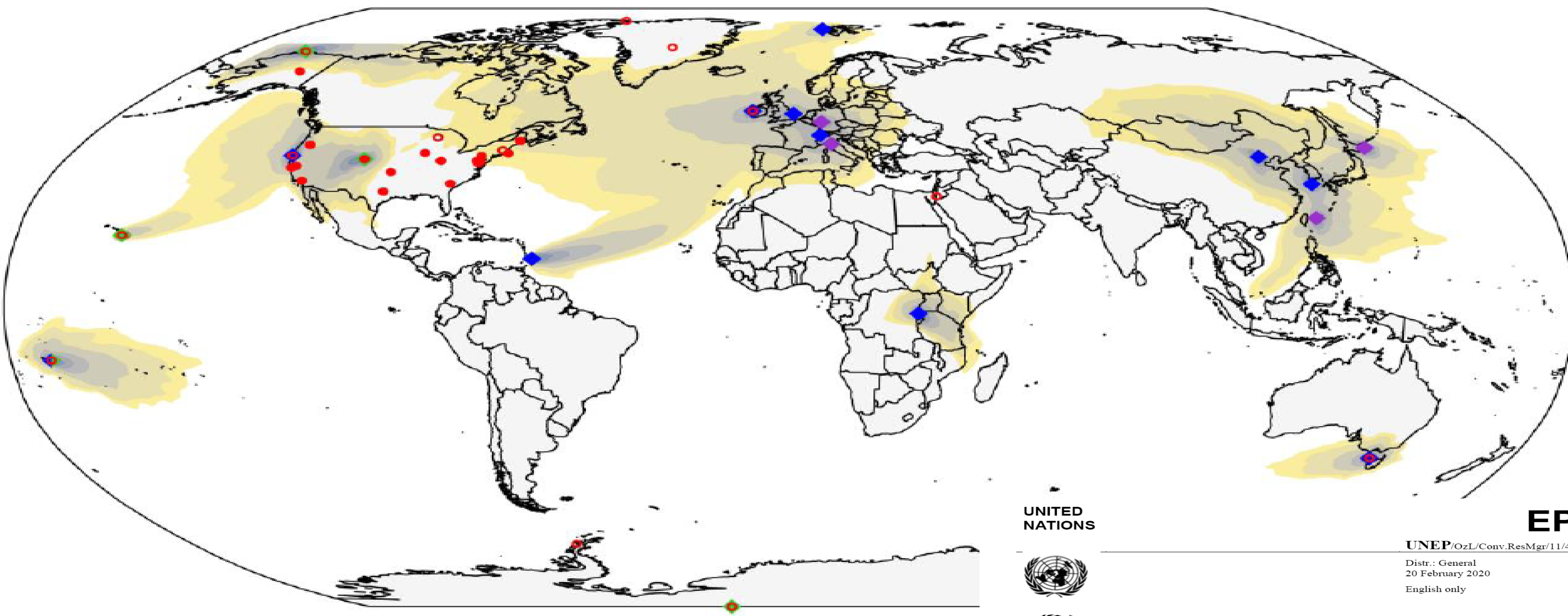


For 2005−2016, emission gap (~ 270 Tg CO_2-eq in 2016) between the summed emissions from Annex I countries and China and the global total HFC CO_2-eq emissions increased over 2005−2016, which suggests substantial increases in HFC use and emissions in developing countries (not obligated to report emissions to the UNFCCC) other than China.

Yao & Fang et al. EST Letters, 2019

More stations to fill the emission gap of controlled ODS and F-gas



Footprint of AGAGE and NOAA stations

UNITED
NATIONS

EP

UNEP/OzL/Conv.ResMgr/11/4

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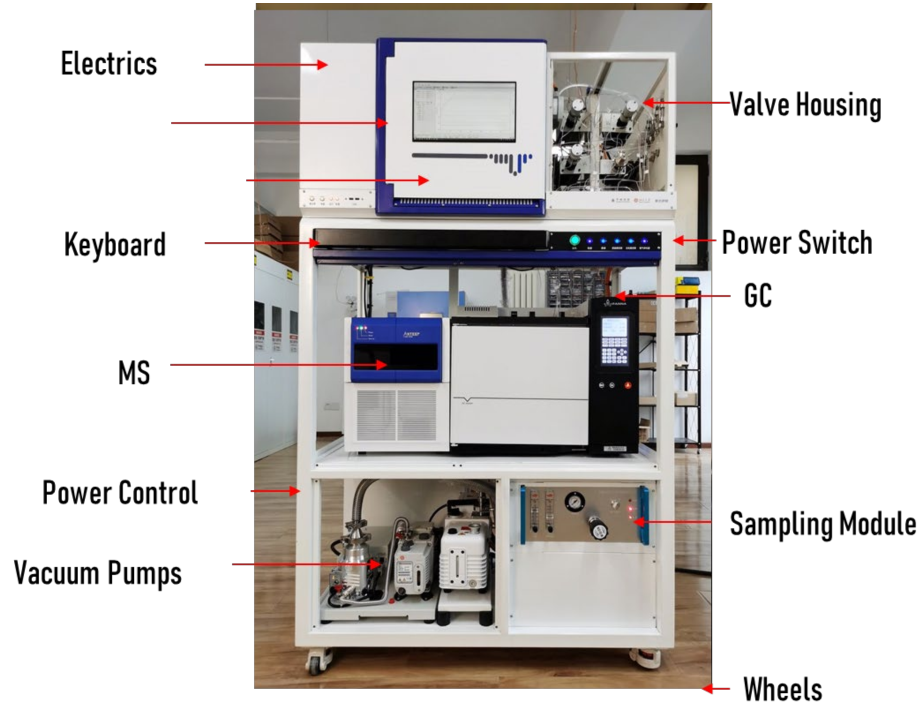
United Nations
Environment
Programme

Ozone Research Managers of the Parties to the Vienna Convention for the Protection of the Ozone Layer
Eleventh meeting
Geneva, 1–3 April 2020

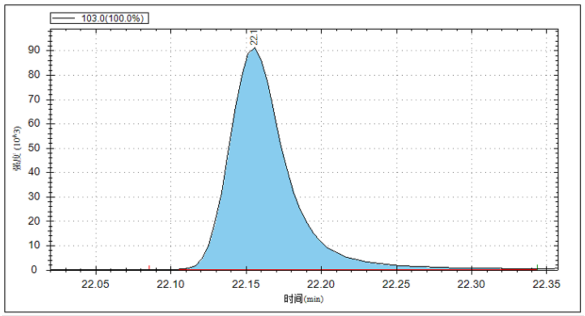
Identification of gaps in the global coverage of atmospheric monitoring of controlled substances and options to enhance such monitoring

ODS5-PRO: System composition

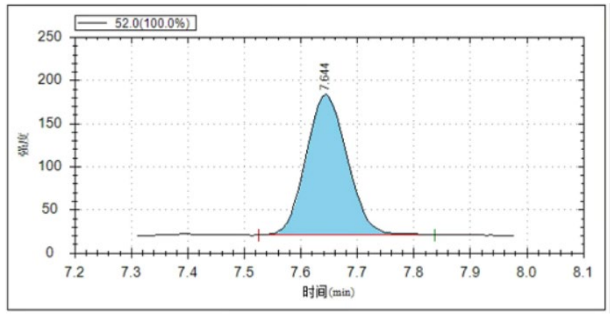
- Design
  - All parts in one frame.
  - Separated compartments for electrics, traps and cooling, and valves.
  - Built-in cryocooler.
  - Built-in trap heater.
  - Built-in control PC.
  - Automatic power control.
  - Wheels for moving.



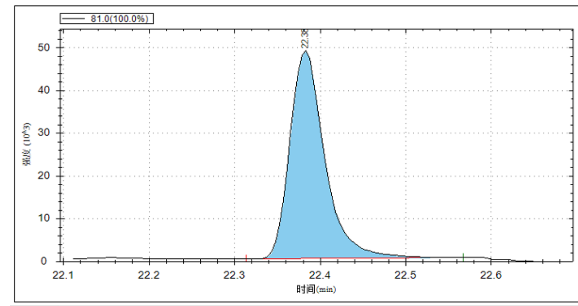
Chromatograph of ambient air sample



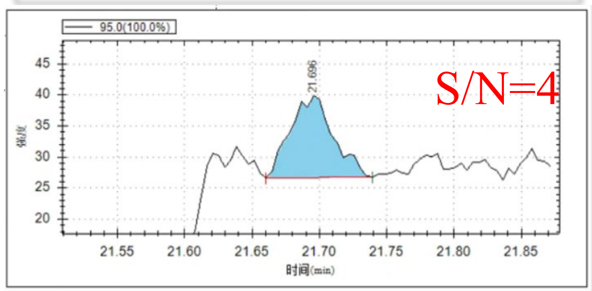
CFC-11 226.9ppt



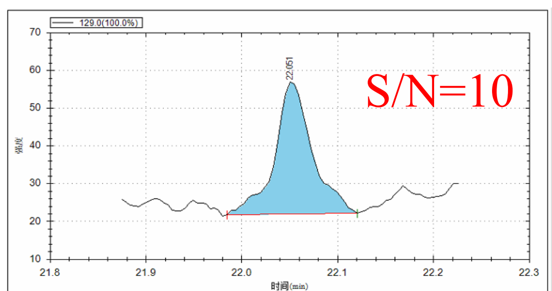
NF_3 3.8 ppt



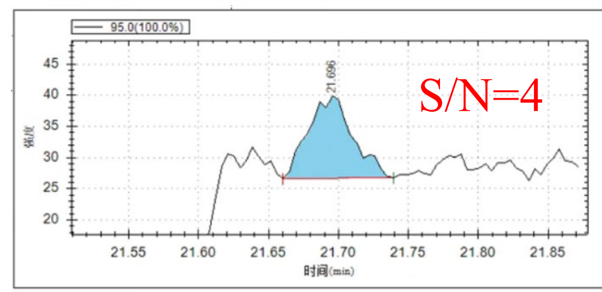
HCFC-141b 28.4ppt



HFO-1233zeE 43ppq

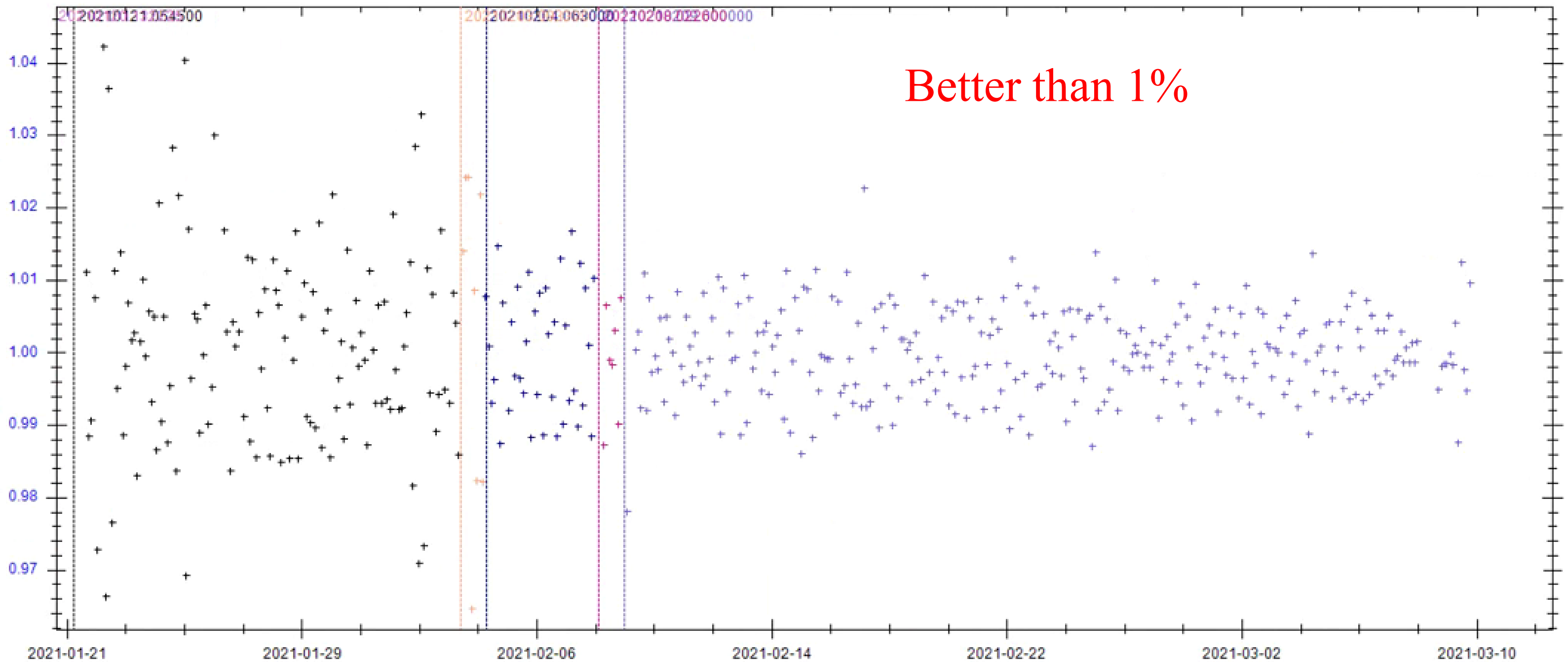


H-1202 50ppq



HFO-1233zeE 43ppq

CCl4



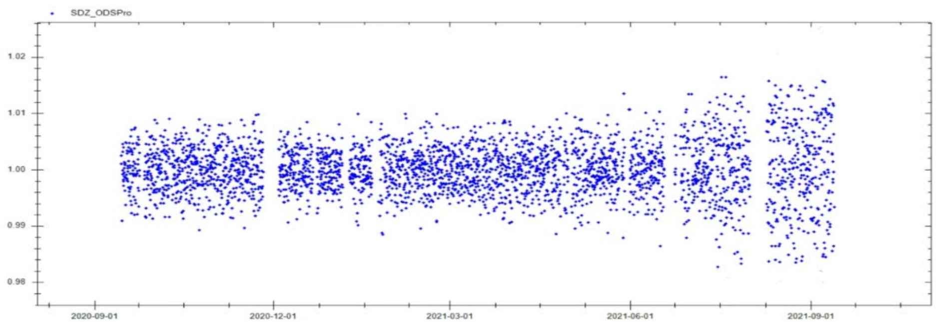
20210121054500
20210204063000
20210208222600000
Better than 1%
1.04
1.03
1.02
1.01
1.00
0.99
0.98
0.97
2021-01-21
2021-01-29
2021-02-06
2021-02-14
2021-02-22
2021-03-02
2021-03-10

Precisions of major species

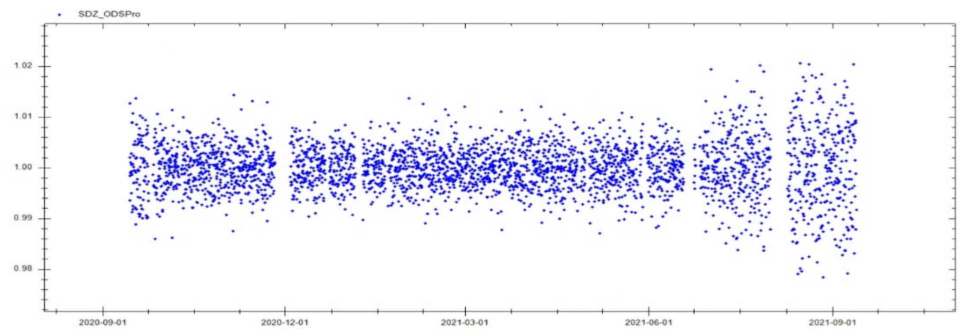
No.	Species	ODS-Pro	SDZ Medusa	Mixing ratio	No.	Species	ODS-Pro	SDZ Medusa	Mixing ratio	No.	Species	ODS-Pro	SDZ Medusa	Mixing ratio
1	PFC-116	1.6%	3.0%	5.27	19	CFC-12	**0.4%**	**0.2%**	503.1	37	H-1211	1.8%	2.0%	3.34
2	PFC-218	4.0%	6.0%	0.71	20	CFC-13	5.1%	1.5%	3.37	38	H-1301	2.9%	3.0%	3.42
3	PFC-318	2.4%	2.0%	2.52	21	CFC-112	3.7%	10.0%	0.56	39	H-2402	2.7%	3.0%	0.40
4	C_6F_{14}	5.7%	5.0%	0.32	22	CFC-113	**0.4%**	**0.5%**	70.1	40	CH_3CCl_3	4.6%	3.0%	1.55
5	SF_6	0.8%	1.0%	10.5	23	CFC-114	0.7%	0.5%	16.3	41	CH_3Cl	0.4%	0.8%	563.9
6	SO_2F_2	2.6%	3.0%	2.68	24	CFC-115	1.8%	1.5%	8.79	42	CH_2Cl_2	1.5%	1.0%	86.1
7	HFC-23	**0.5%**	**1.0%**	75.6	25	CFC-1113		5.0%		43	$CHCl_3$	0.5%	3.0%	24.7
8	HFC-32	**1.9%**	**2.0%**	31.9	26	HCFC-21		3.0%	~ 0.5	44	CCl_4	**0.8%**	**2.0%**	77.2
9	HFC-125	**0.8%**	**2.0%**	35.8	27	HCFC-22	**0.9%**	**0.5%**	272.1	45	CH_3Br	1.2%	0.8%	6.99
10	HFC-134a	**0.6%**	**0.5%**	121.1	28	HCFC-123		10.0%		46	CH_2Br_2	1.3%	1.5%	1.04
11	HFC-143a	**1.3%**	**2.0%**	26.9	29	HCFC-124	4.9%	3.0%	1.08	47	$CHBr_3$	1.7%	2.0%	0.76
12	HFC-152a	**1.9%**	**2.0%**	12.6	30	HCFC-132b	5.2%	5.0%	0.20	48	CH_3I	3.8%	2.0%	0.12
13	HFC-227ea	2.8%	3.0%	6.3	31	HCFC-133a	6.2%	4.0%	0.52	49	COS	0.5%	0.5%	595.8
14	HFC-236fa	9.0%	6.0%	0.27	32	HCFC-141b	**0.6%**	**0.8%**	28.4	50	HCFO-1233zdE	18%	10.0%	0.17
15	HFC-245fa	3.8%	3.0%	3.64	33	HCFC-142b	**0.7%**	**0.5%**	25.5	51	HFO-1234yf		10.0%	0.51
16	HFC-365mfc	4.1%	3.0%	1.33	34	HFC-161		3.0%	~ 0.1	52	HFO-1234zeE	15%	15.0%	0.10
17	HFC-4310mee	13%	8.0%	0.31	35	HCFC-31		10.0%		53	PCE	0.6%	1.5%	6.49
18	CFC-11	**0.4%**	**0.3%**	226.9	36	H-1202		15.0%	~ 0.06	54	TCE	7.7%	5.0%	0.75

Test at Shangdianzi for 14 months (2020.9-2021.11)

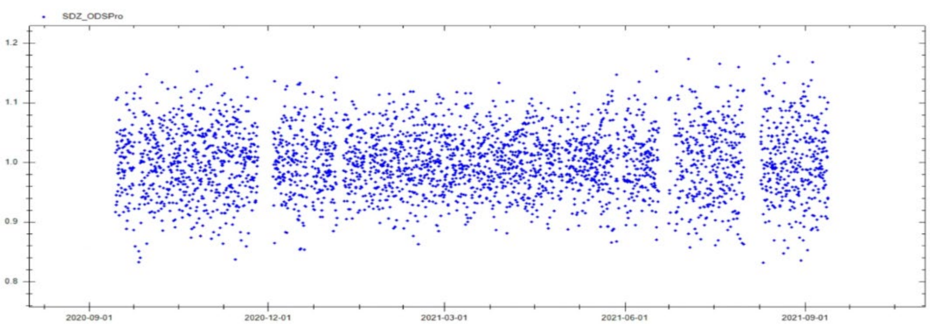
CFC-11



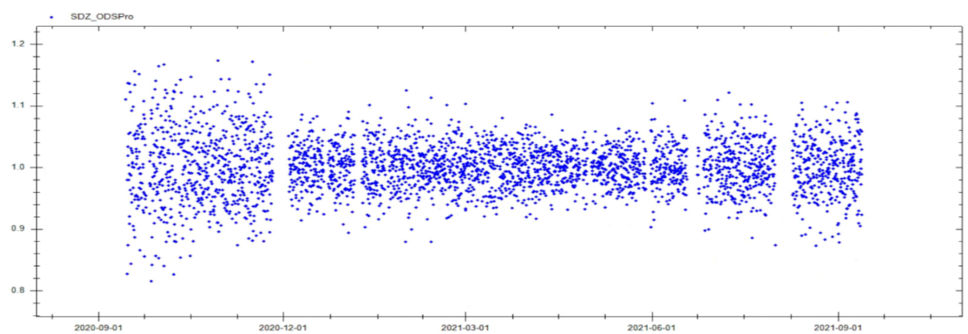
CFC-12



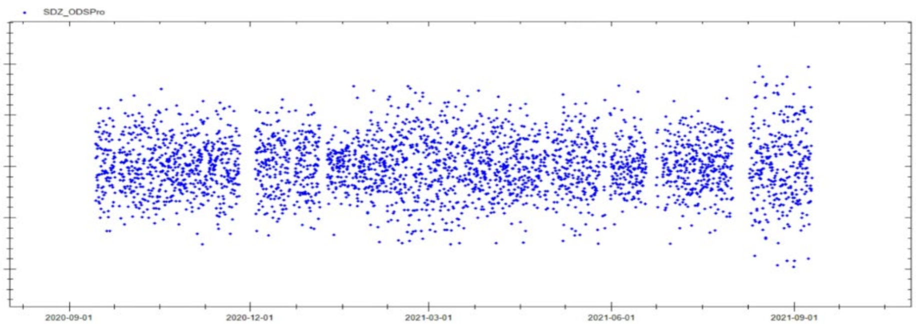
CFC-13



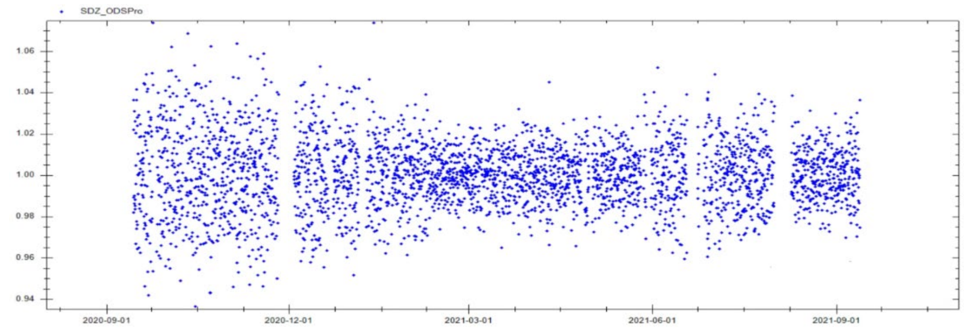
CFC-112



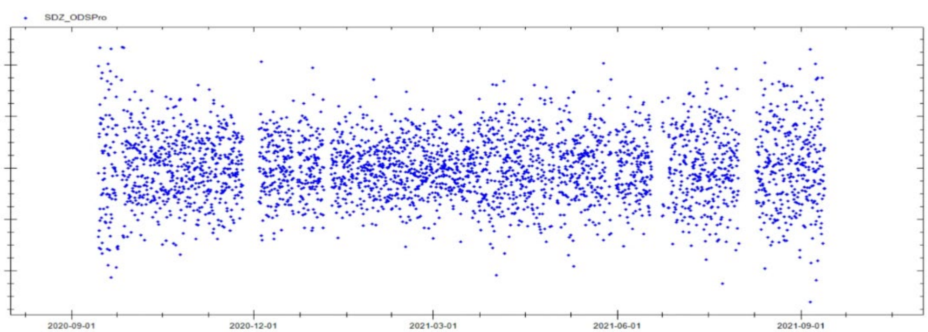
HFC-23



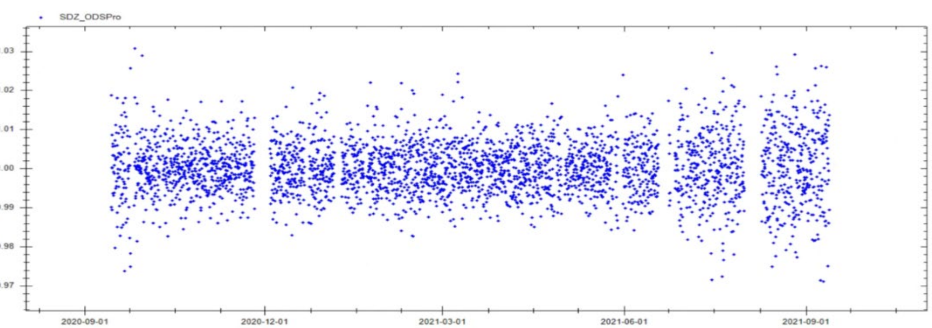
HFC-32



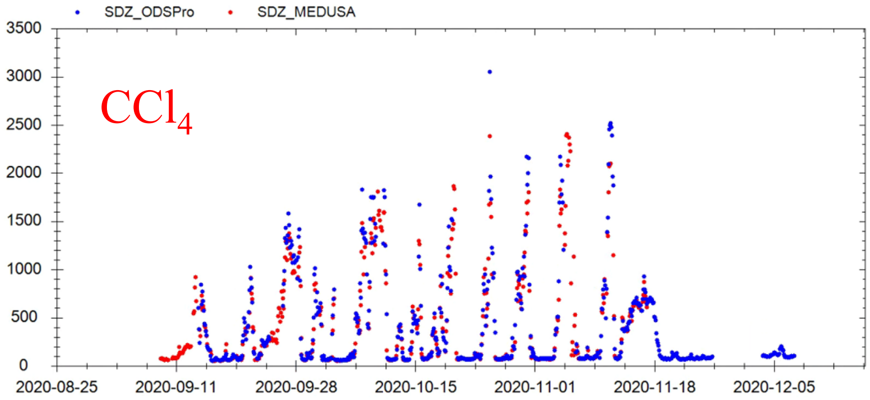
HFC-125

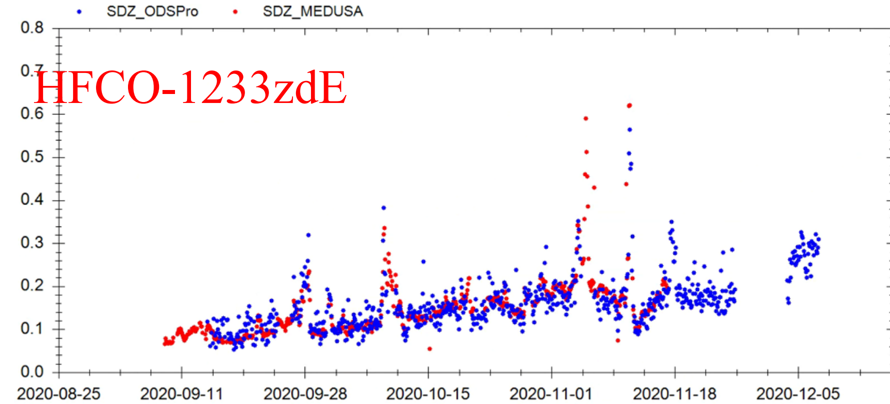


HFC-134a



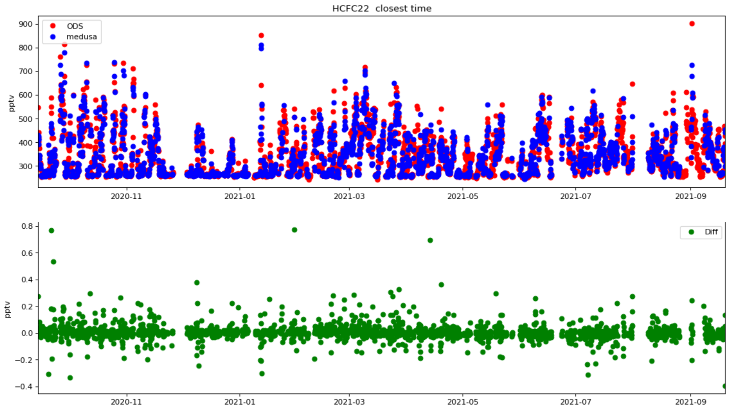
Comparison between ODS5-Pro and Medusa



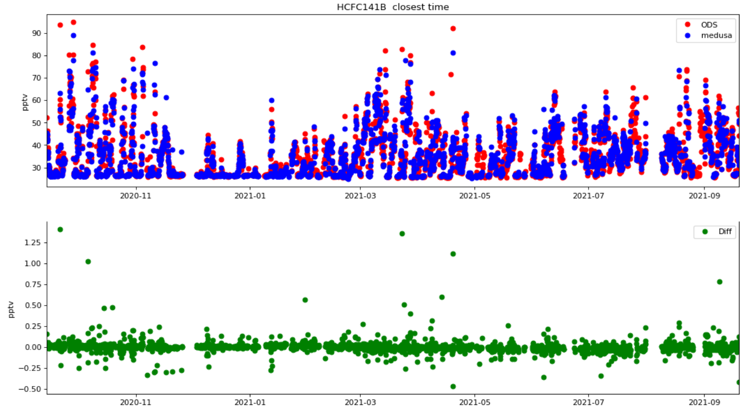


Comparison between ODS5-Pro and Medusa

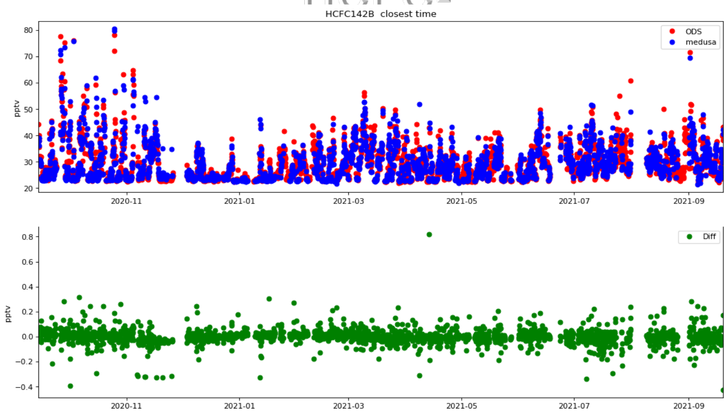
HCFC-22



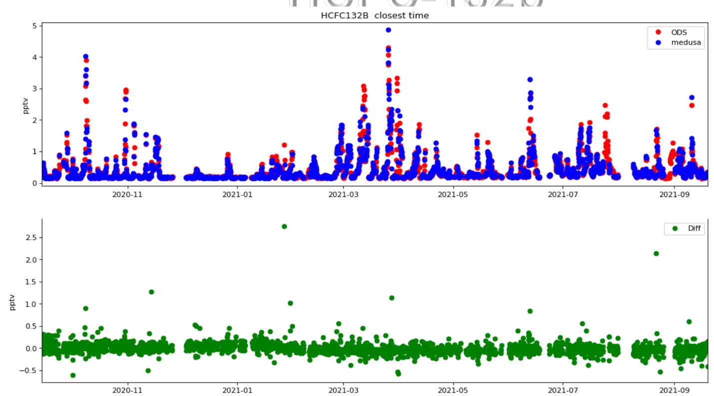
HCFC-141b



HCFC-



HCFC-132b

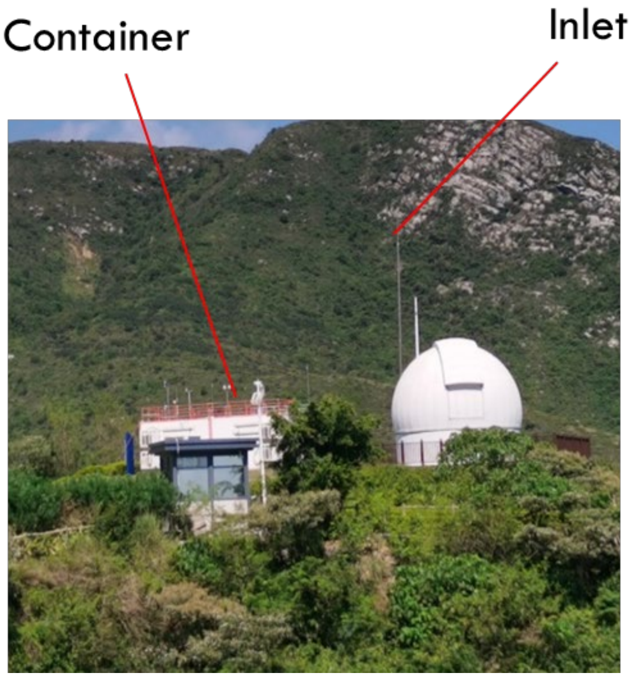


Comparison between ODS5-Pro and Medusa

Differences for 4 hours time interval	10 percentage	median	90 percentage
	0.01%-5.01%	0.02%-6.49%	0.23%-11.7%

Substance	Precision	10 %			median			90 %		
		ODS5-pro	Medusa GC-MS	Diff	ODS5-pro	Medusa GC-MS	Diff	ODS5-pro	Medusa GC-MS	Diff
NF_3	1.98%	2.58	2.63	-1.95%	2.90	3.09	-6.17%	5.54	6.01	-7.73%
CF_4	0.39%	87.4	87.3	0.10%	89.1	88.7	0.53%	93.1	92.3	0.91%
SF_6	0.61%	10.4	10.6	-1.35%	11.3	11.4	-0.92%	13.9	14.3	-2.57%
PFC-318	1.72%	1.91	1.91	0.39%	2.04	2.02	0.88%	2.77	2.81	-1.68%
CFC-11	0.41%	229.1	229.1	-0.02%	245.7	245.7	-0.02%	285.3	289.4	-1.44%
CFC-12	0.41%	496.8	497.2	-0.08%	499.9	499.2	0.14%	503.3	501.4	0.38%
CFC-13	4.74%	3.10	3.27	-5.01%	3.30	3.34	-1.09%	3.51	3.42	2.68%
CFC-113	0.38%	68.4	67.9	0.68%	69.3	68.9	0.59%	71.1	70.4	1.00%
CFC-114	0.68%	16.0	16.0	-0.13%	16.3	16.3	-0.12%	16.8	16.6	1.33%
CFC-115	1.56%	8.60	8.71	-1.23%	8.79	8.82	-0.36%	9.13	9.19	-0.62%
HCFC-22	0.71%	260.0	259.6	0.15%	312.1	314.3	-0.68%	469.5	471.1	-0.33%
HCFC-141b	0.99%	26.2	26.2	-0.01%	31.5	32.0	-1.65%	47.9	48.9	-2.08%
HCFC-142b	0.81%	23.2	23.0	0.59%	27.4	27.5	-0.26%	37.6	37.7	-0.46%
HFC-23	0.51%	34.7	34.8	-0.34%	36.0	36.0	0.19%	42.7	43.4	-1.50%
HFC-32	1.20%	31.1	31.8	-2.25%	42.8	45.8	-6.49%	71.8	81.3	-11.7%
HFC-125	1.26%	37.9	37.9	0.02%	42.7	43.5	-1.68%	56.7	57.2	-0.88%
HFC-134a	0.55%	124.0	125.0	-0.77%	136.8	140.2	-2.40%	168.5	173.1	-2.69%
HFC-143a	1.13%	27.8	27.9	-0.12%	29.4	29.5	-0.47%	33.2	33.1	0.23%
HFC-152a	1.63%	10.5	10.3	1.81%	12.4	12.3	0.86%	18.0	17.7	1.57%
H-1211	2.04%	3.12	3.17	-1.31%	3.25	3.25	-0.09%	3.60	3.58	0.59%
H-1301	3.59%	3.25	3.30	-1.37%	3.40	3.44	-1.28%	3.64	3.70	-1.73%
H-2402	3.78%	0.37	0.39	-4.33%	0.40	0.39	0.51%	0.42	0.41	4.72%
CH_3CCl_3	3.31%	1.25	1.26	-0.81%	1.38	1.36	0.90%	1.51	1.45	4.05%
CH_3Cl	0.51%	524.1	525.6	-0.29%	649.5	652.9	-0.52%	1059.9	1053.5	0.61%
CH_2Cl_2	0.77%	76.8	76.2	0.77%	228.8	227.2	0.71%	860.3	825.6	4.19%
$CHCl_3$	0.48%	13.7	13.9	-1.86%	31.6	32.8	-3.42%	98.7	95.0	3.98%
CCl_4	0.67%	75.4	74.3	1.56%	78.7	77.2	1.95%	89.4	83.8	6.76%
CH_3Br	1.35%	6.94	6.71	3.55%	8.18	8.32	-1.66%	12.6	12.4	0.98%

Commercialization and Application



ODS5-Pro at Shenzhen Station

ODS5-Pro with automatic flask analysis module

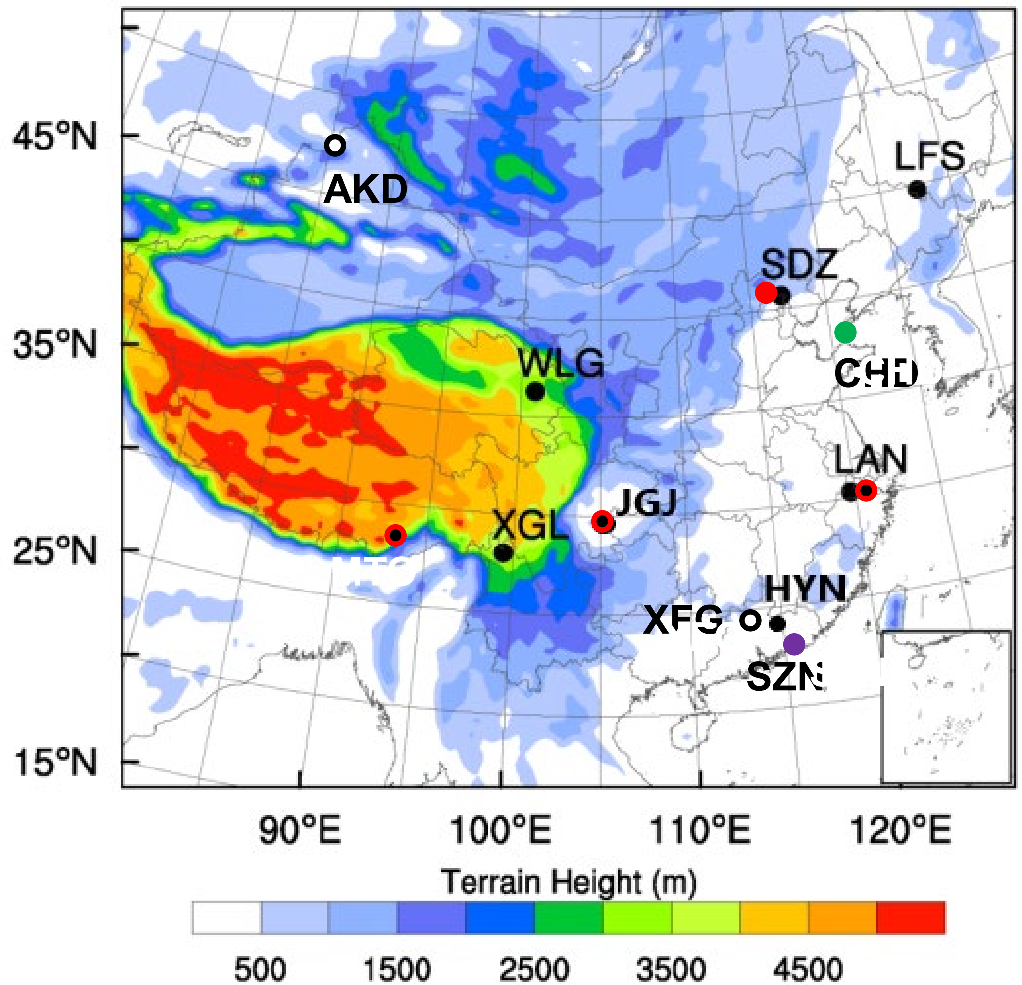
Commercialization and Application

8 units in operation now

1. Joint lab of Fudan University and Huanaco Inc: system development, flask analysis for daily sampling sites, calibration
2. State Key Laboratory for Environmental Pollution and Control @Peking University: system development and sample analysis
3. State Key Laboratory for Organic Geochemistry@ Chinese Academy of Sciences: flask analysis & urban in-situ measurement
4. Changdao Station, Shangdong Province (MEE background station) : In-situ measurement
5. Shenzhen Station, Guangdong Province (SUST): In-situ measurement
6. Central Lab at China Environmental Monitoring Center: flask analysis from MEE urban sites
7. Central Lab at National Environmental Analysis and Testing Center: flask analysis from MEE background stations
8. Shenzhen Environmental Monitoring Center: flask analysis

ODS and F-gas measurements in China in 2022

- ● **In-situ by CMA**
- ● **In-situ by MEE**
- ● **In-situ by SUST**
- ○ **Weekly sampling by CMA**
- ⊙ **Daily sampling or campaign by universities**



- ✓ There are five sampling sites by MEE
- ✓ some potential sites planned by provinicial government, not marked
- ✓ In-situ measurement at SDZ and weekly samples are conducted by Medusa-GC/MS
- ✓ Other measurements are conducted by ODS-pro

Emission Estimate (2020/10-2021/09)

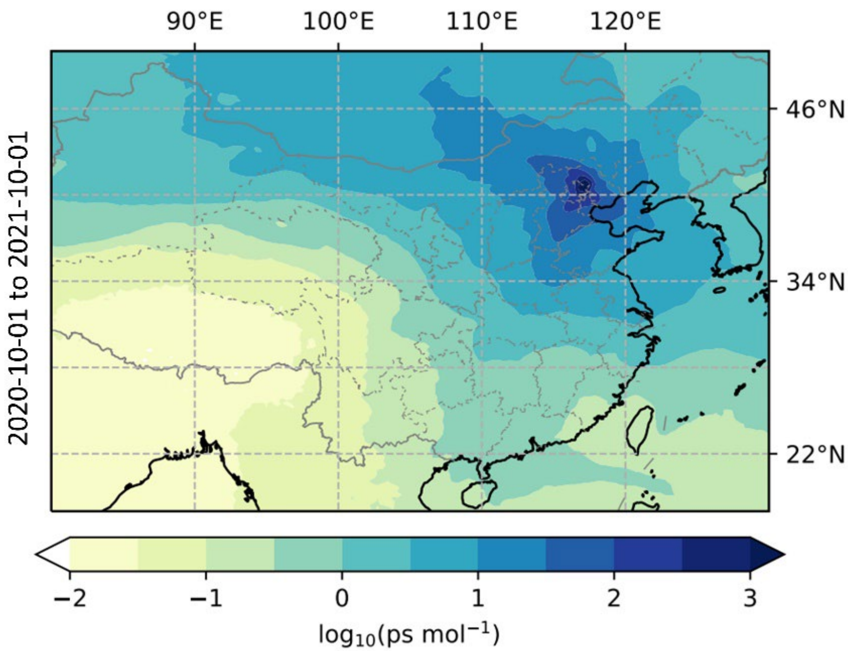
Interspecies correlation method (a ratio method)

- The atmospheric enhancement ratios between halogenated gases and a tracer can quantify the ratios in their emission strengths when introducing their molecular weights
- The method requires the tracer to have a well quantified emission and the same emission source as halogenated gases
- The lifetimes of compounds should be much greater than their transport time and there is no chemical reactivity during the transportation
- Both CO and HCFC-22 were used as the tracer in this study for comparison
- The enhanced concentration data was observed by ODS5-pro at SDZ station during 2020/10-2021/09

$$E_X = E_{tracer} \times (\Delta X / \Delta tracer) \times (M_X / M_{tracer})$$

Average sensitivity of the observations at SDZ station to emissions of halogenated gases (2020/10-2021/09)

- Greatly affected by the emissions from the North China Plain, including provinces of Beijing, Tianjin, Hebei, Shanxi, Inner Mongolia, Liaoning, Shandong and Henan with high population densities.
- An additional uncertainty of ± 10 % was added when calculating the emissions from the whole area of China.

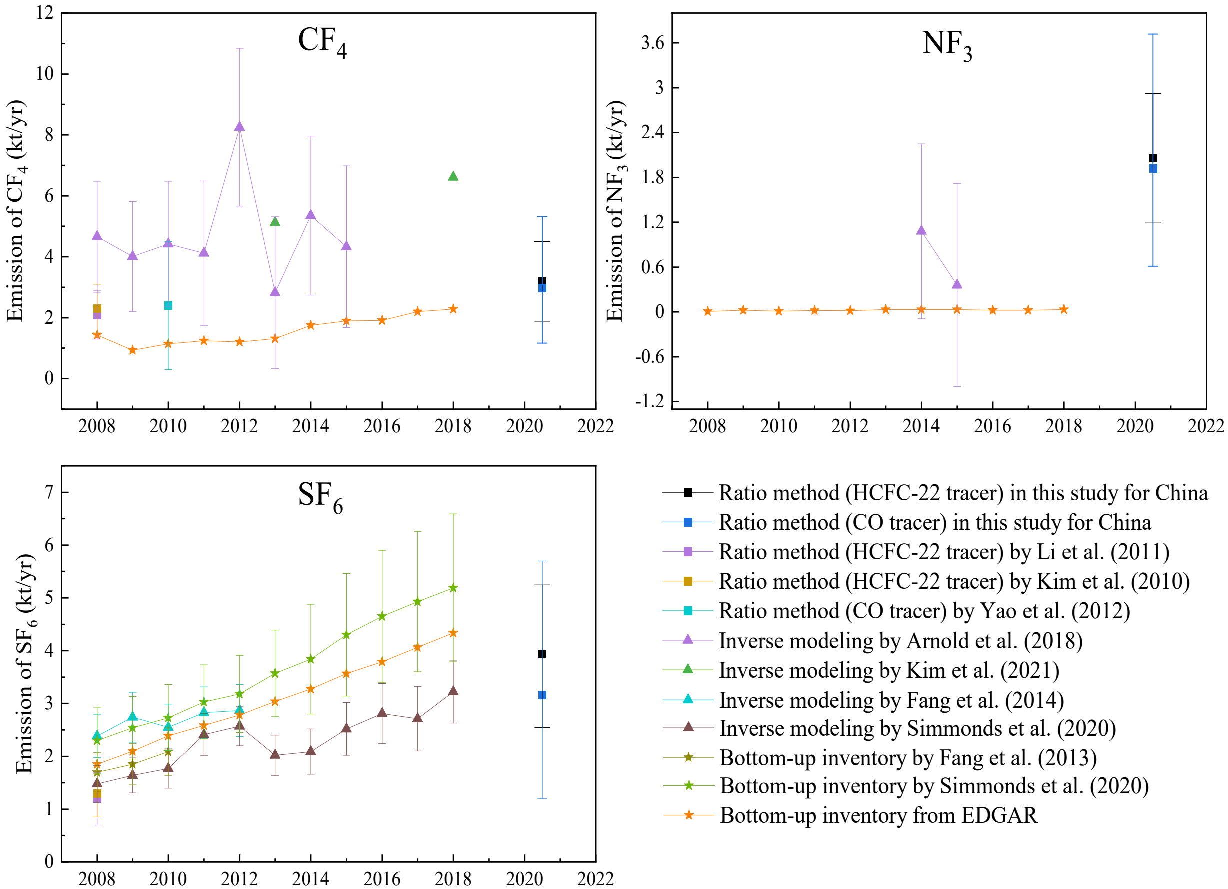


The emissions of F-gases and HCFCs from the North China Plain and all China in 2020-2021 (kt yr^{-1})

Substances	the North China Plain		China	
	Tracer HCFC-22	Tracer CO	Tracer HCFC-22	Tracer CO
CF_4	1.09 (0.79 – 1.42)	0.99 (0.41 – 1.79)	3.19 (1.86 – 4.51)	2.98(1.17 – 5.32)
NF_3	0.70 (0.51 – 0.92)	0.64 (0.23 – 1.26)	2.06 (1.19 – 2.92)	1.92 (0.61 – 3.72)
SF_6	1.34 (1.06– 1.65)	1.05 (0.43 – 1.92)	3.94 (2.54 – 5.25)	3.16 (1.20 – 5.70)
HCFC-22	57.8 (52.2 – 63.4)	46.5 (20.8 – 79.9)	169.8 (144.1-186.6)	140.2 (60.1 – 238.5)
HCFC-141b	8.18 (6.95 – 9.50)	5.54 (2.32 – 9.94)	24.0 (16.8 – 30.4)	16.7 (6.60 – 29.6)
HCFC-142b	4.05 (3.40 – 4.75)	2.37 (0.94 – 4.40)	11.9 (8.20 – 15.2)	7.15 (2.63 – 13.1)
HFC-23	2.33 (1.63– 3.14)	1.88 (0.72 – 3.55)	6.85 (3.81 – 9.93)	5.67 (2.00 – 10.5)
HFC-32	5.80 (4.81 – 6.89)	4.63 (2.06 – 8.01)	17.1 (11.6 – 22.0)	14.0 (5.95 – 23.9)
HFC-125	5.99 (4.92 – 7.16)	4.52 (1.93 – 8.02)	17.6 (11.8 – 22.9)	13.7 (5.53 – 23.9)
HFC-134a	12.5 (10.0 – 15.2)	7.10 (2.34 – 14.4)	36.6 (24.0 – 48.4)	21.4 (6.19 – 42.7)
HFC-143a	0.99 (0.77 – 1.24)	0.70 (0.29 – 1.27)	2.91 (1.84 – 3.94)	2.11 (0.82 – 3.78)
HFC-152a	1.48 (1.09 – 1.91)	1.08 (0.40 – 2.06)	4.34 (2.58 – 6.08)	3.25 (1.11 – 6.10)

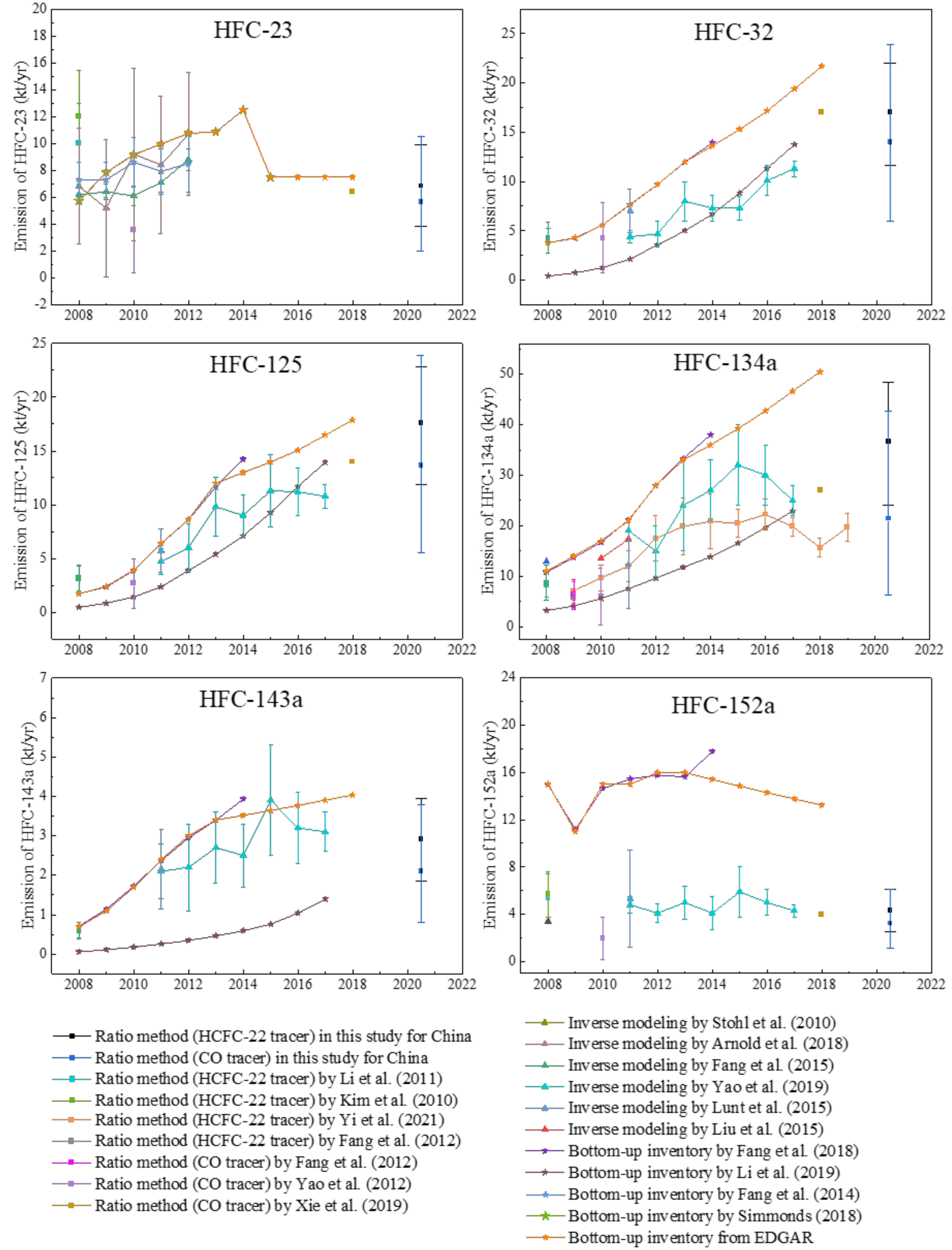
Emissions of perfluorinated gases (2020-2021)

- NF_3 emissions from China reached 2.06 (1.19 - 2.92) kt yr^{-1}, more than twice the emissions from China six years ago ,having exceeded the global emission of 1.9 kt yr^{-1} in 2016.
- SF_6 emissions from China continuously grew and reached 3.94 (2.54 - 5.25) kt yr^{-1}, consistent with the growth rate estimated by the inverse modeling.



Emissions of HFCs (2020-2021)

- Emissions of HFC-32 and HFC-125 were close to 1:1, consistent with the growth rates of the inverse modeling results
- An expected increase was found for HFC-134a
- HFC-143a and HFC-152a had fluctuated emissions over the years
- HFC-23 still has emissions of (3.81 - 9.93) kt yr^{-1} in China.



Thank you!

yaobo@fudan.edu.cn