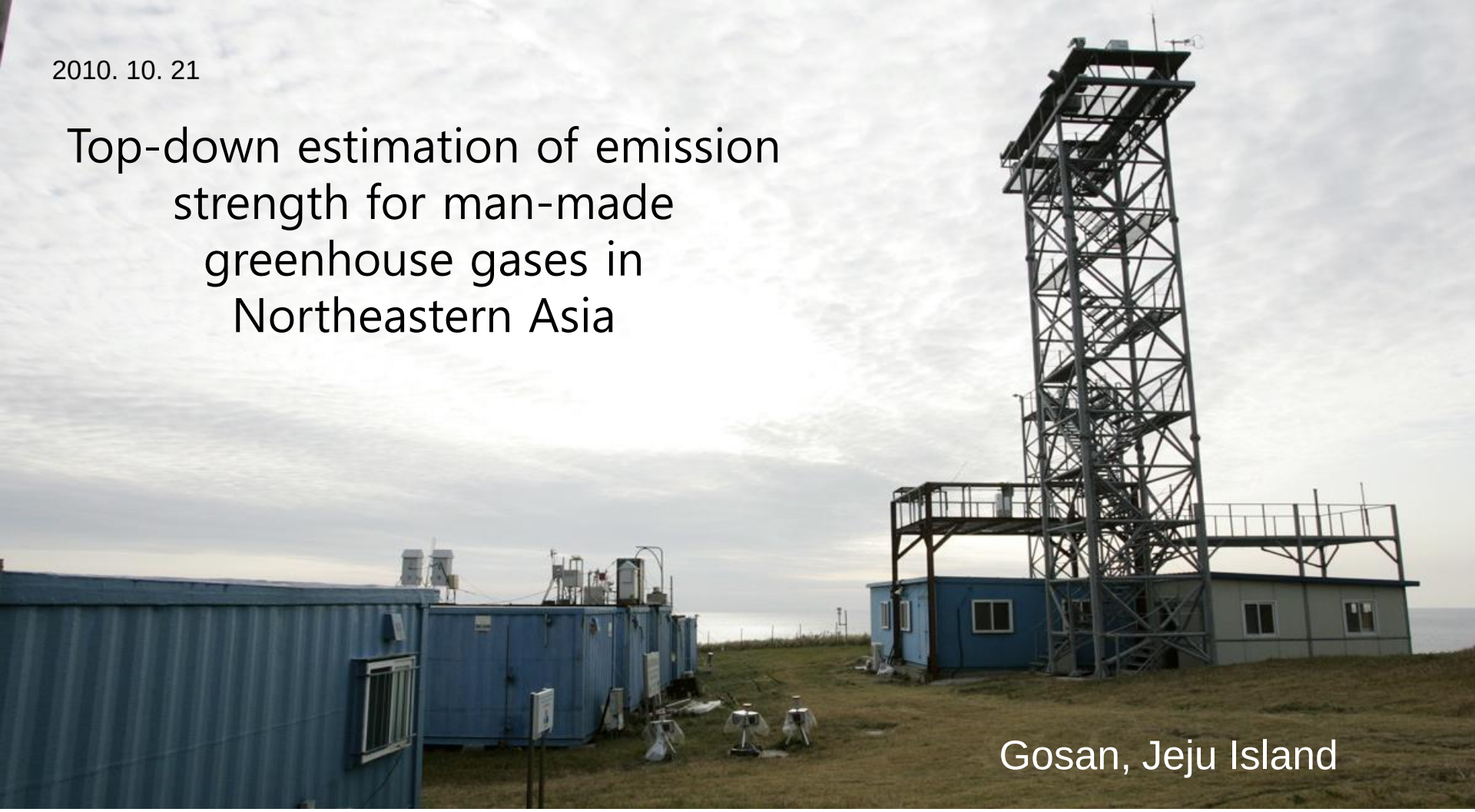
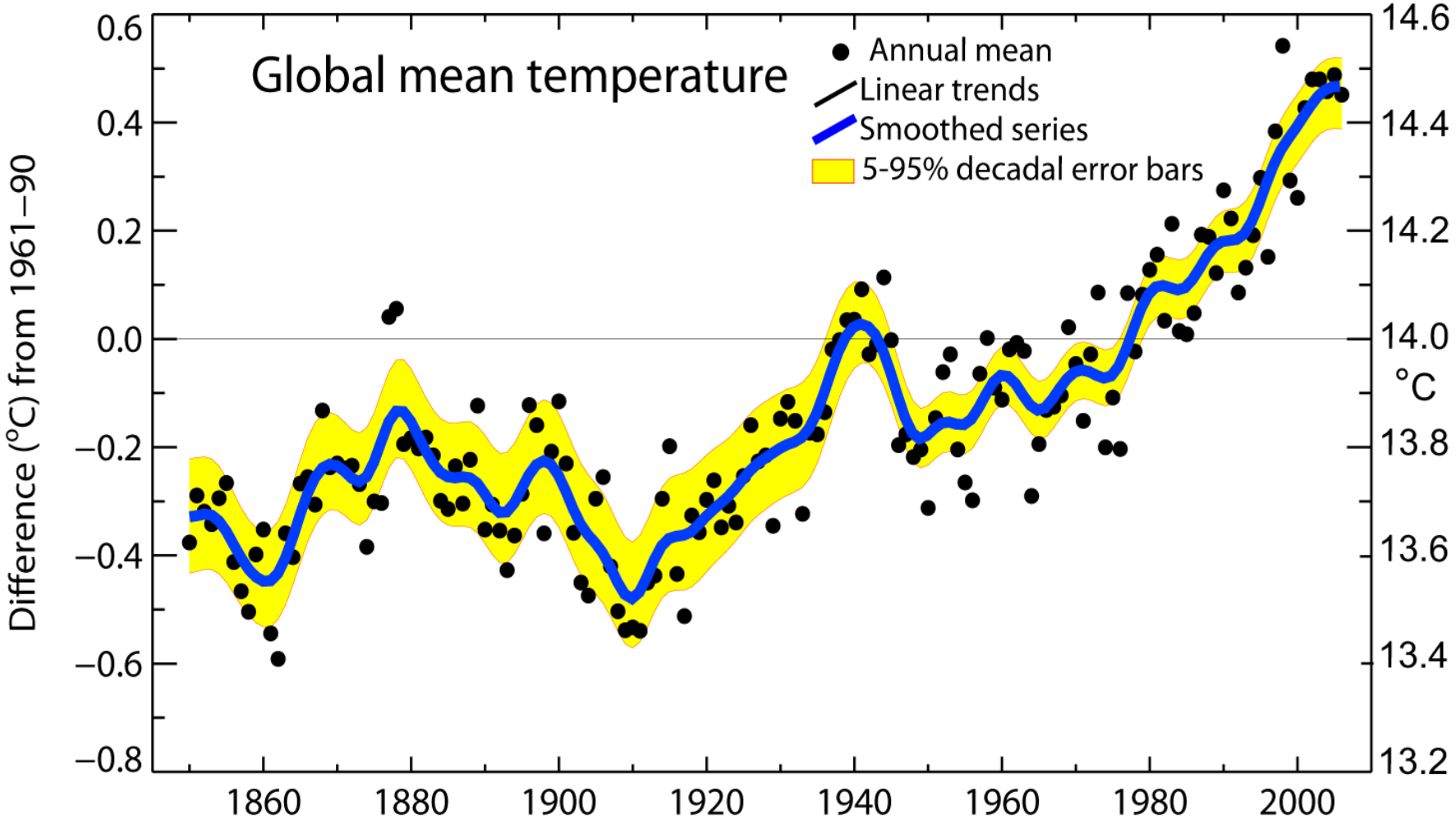
2010. 10. 21

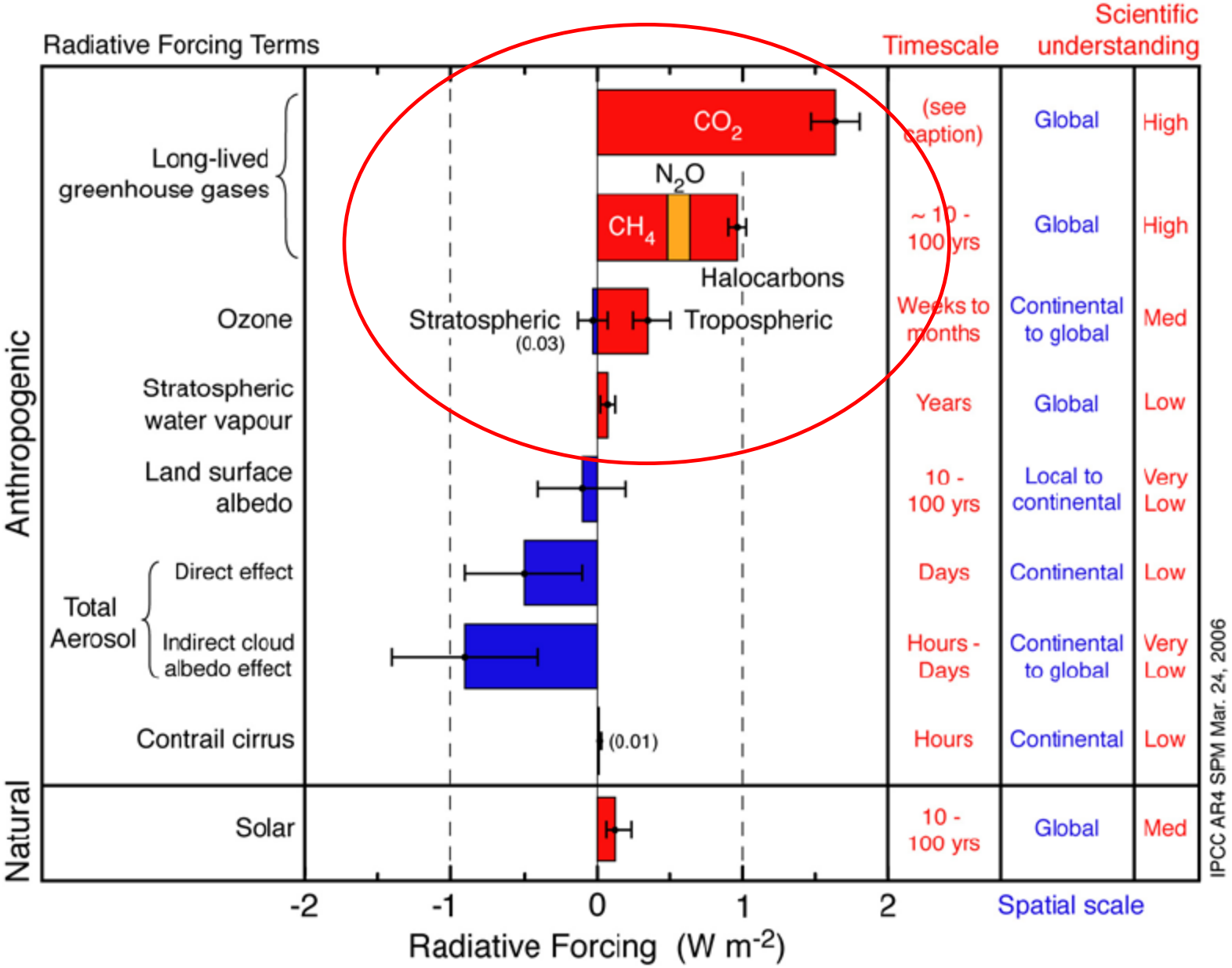
Top-down estimation of emission strength for man-made greenhouse gases in Northeastern Asia



Kyung-Ryul Kim
School of Earth & Environmental Sciences
Seoul National University

IPCC 4th Report: warming is real!




Radiative Forcing Terms
Timescale
Scientific understanding
Anthropogenic
Natural
Long-lived greenhouse gases
Ozone
Stratospheric water vapour
Land surface albedo
Total Aerosol
Direct effect
Indirect cloud albedo effect
Contrail cirrus
Solar
CO2
N2O
CH4
Halocarbons
Stratospheric
(0.03)
Tropospheric
(0.01)
(see caption)
~ 10 - 100 yrs
Weeks to months
Years
10 - 100 yrs
Days
Hours - Days
Hours
Global
Continental to global
Local to continental
Continental
Low
Med
High
Very Low
-2
-1
0
1
2
Radiative Forcing (W m-2)
Spatial scale
IPCC AR4 SPM Mar. 24, 2006

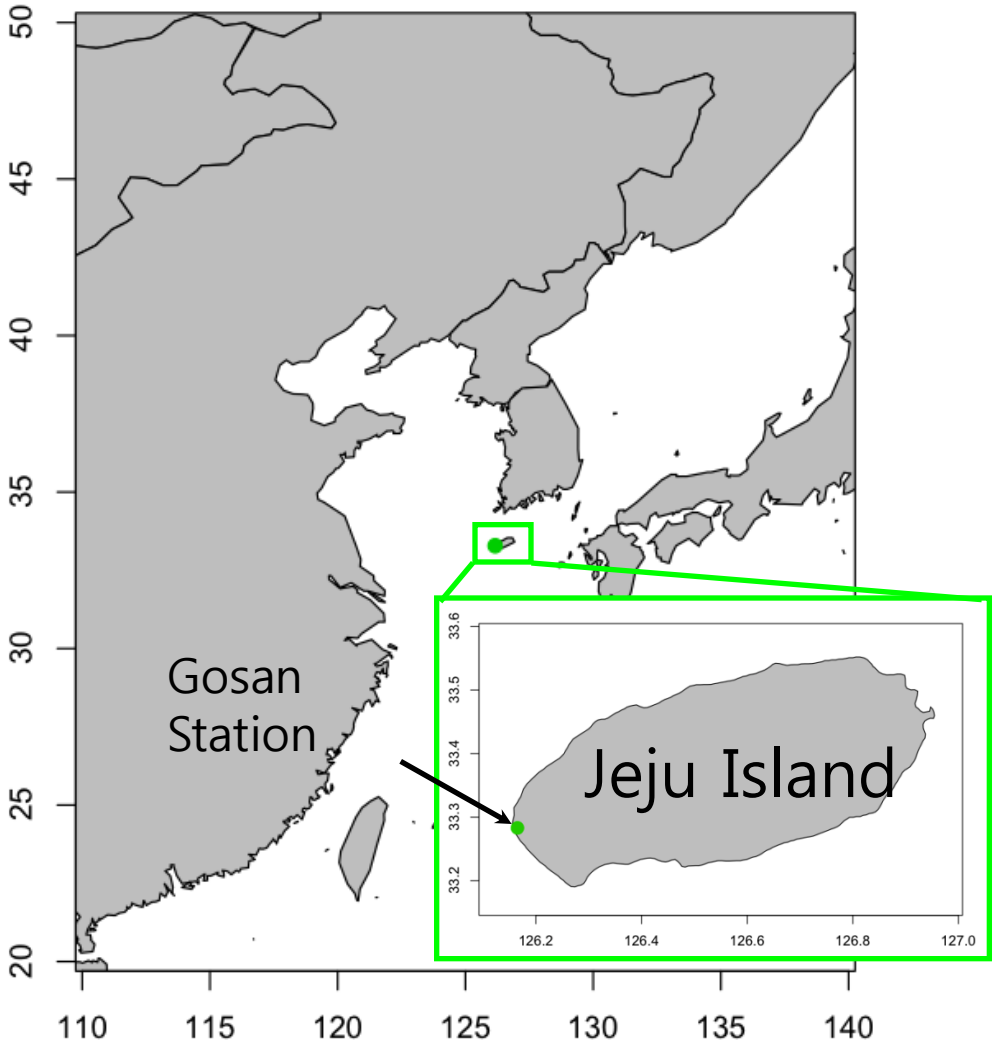
Gases involved in recent global warming

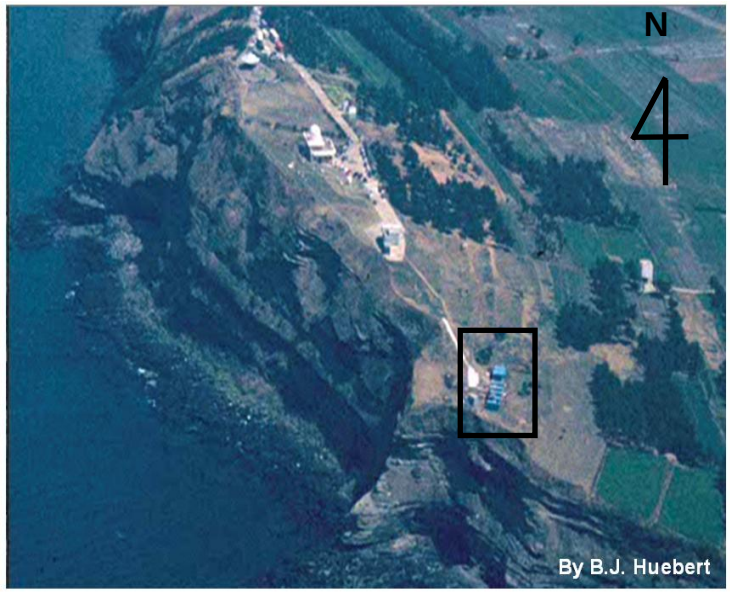
Increase in atmospheric concentrations of

1) Natural greenhouse gases
   CO_2, CH_4, N_2O,..

2) Man-made greenhouse gases
CFCs, HCFCs, HFCs, PFCs, SF_6,
halons, halogenated solvents

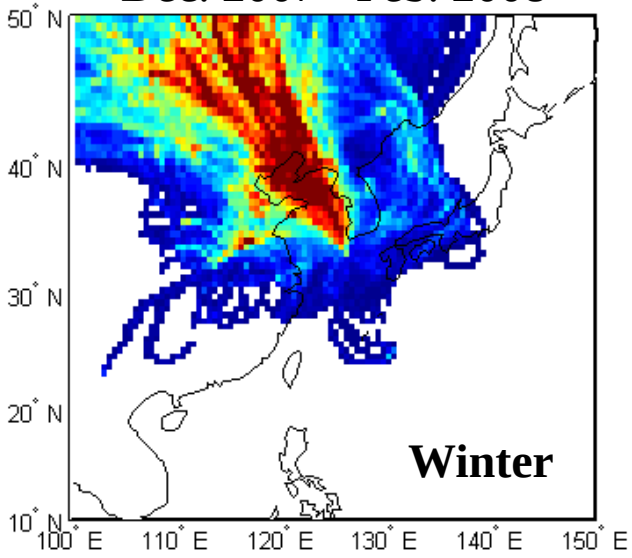
Gosan Station



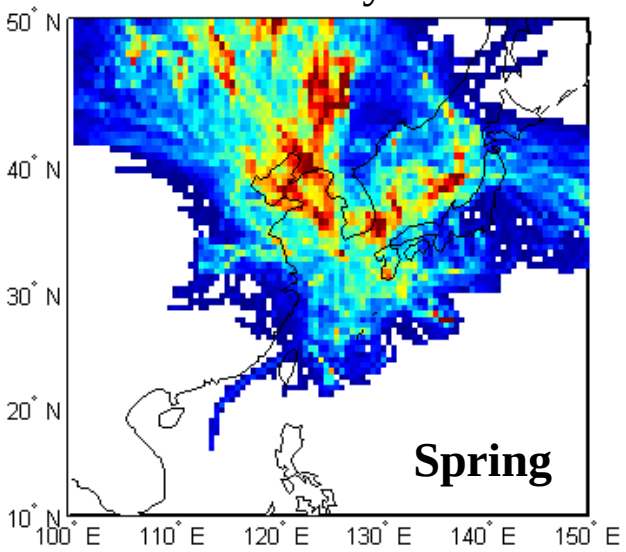


Seasonal Wind pattern at Gosan station

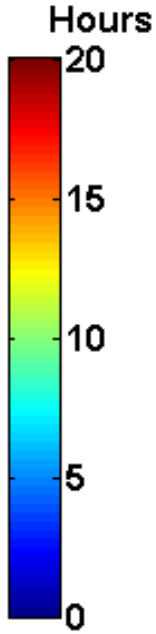
Dec. 2007 ~Feb. 2008

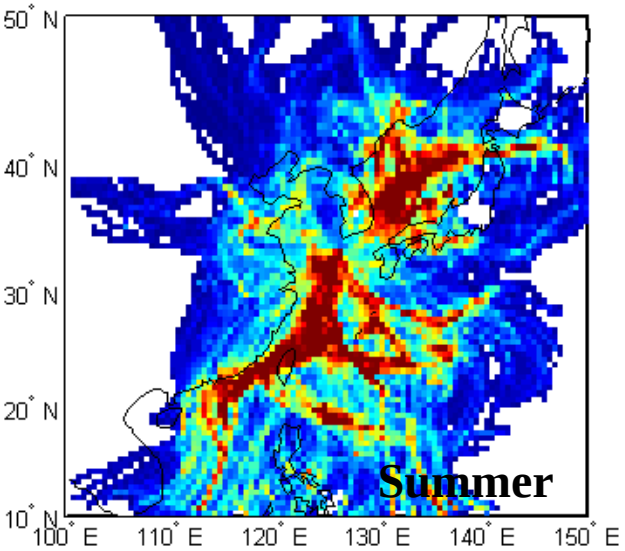


March ~May 2008

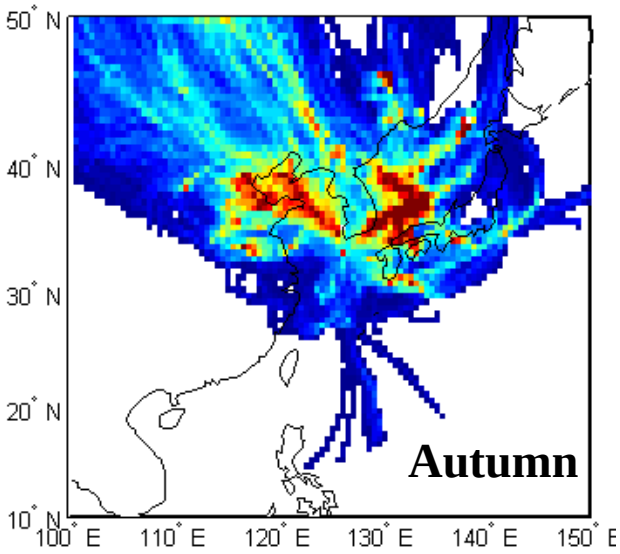


500m altitude





Jun. ~Aug. 2008



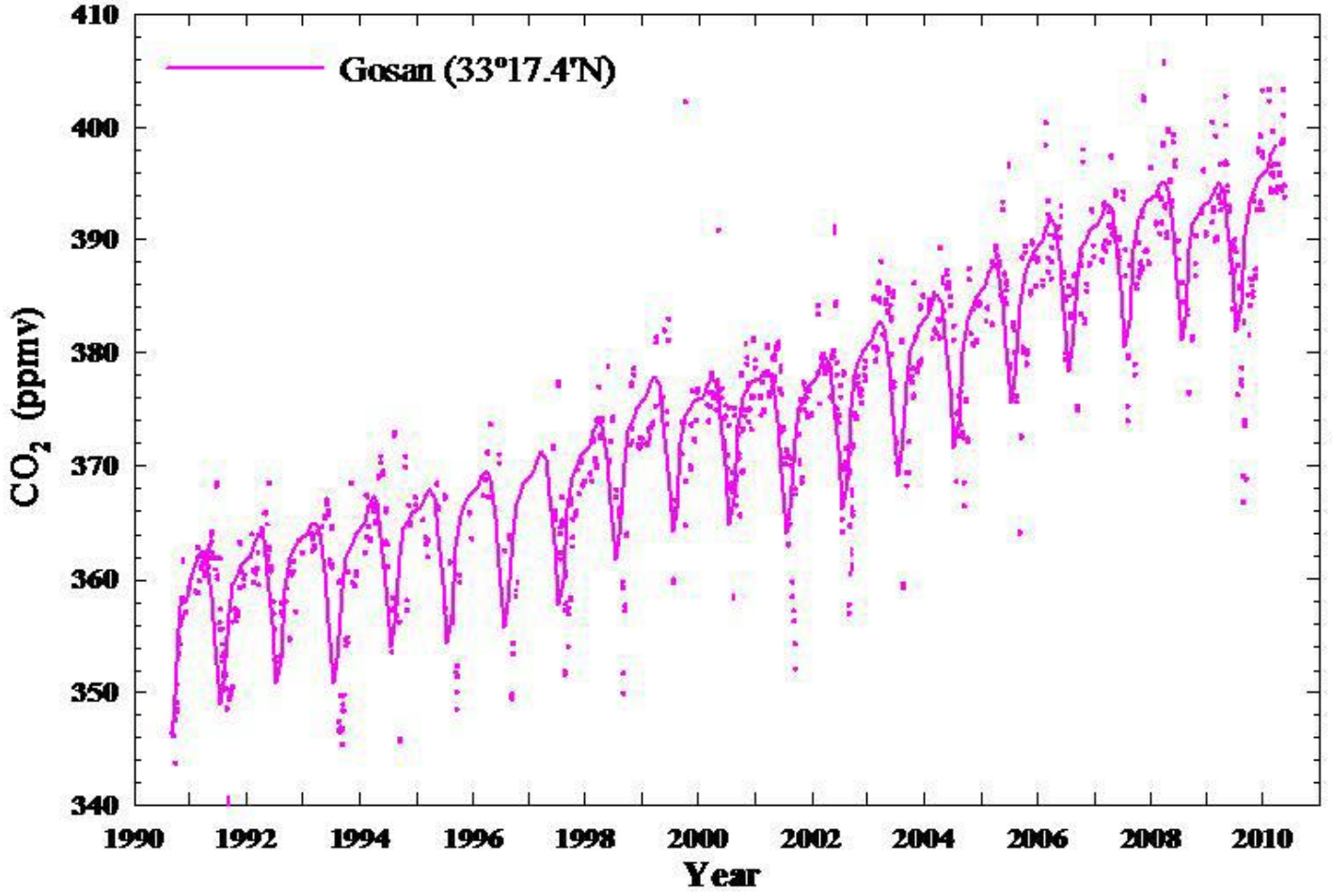
Sep. ~Nov. 2008

Gases involved in recent global warming

Increase in atmospheric concentrations of

1) Natural greenhouse gases

   CO_2, CH_4, N_2O,..


Gosan (33°17.4'N)
410
400
390
380
370
360
350
340
CO_2 (ppmv)
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
Year

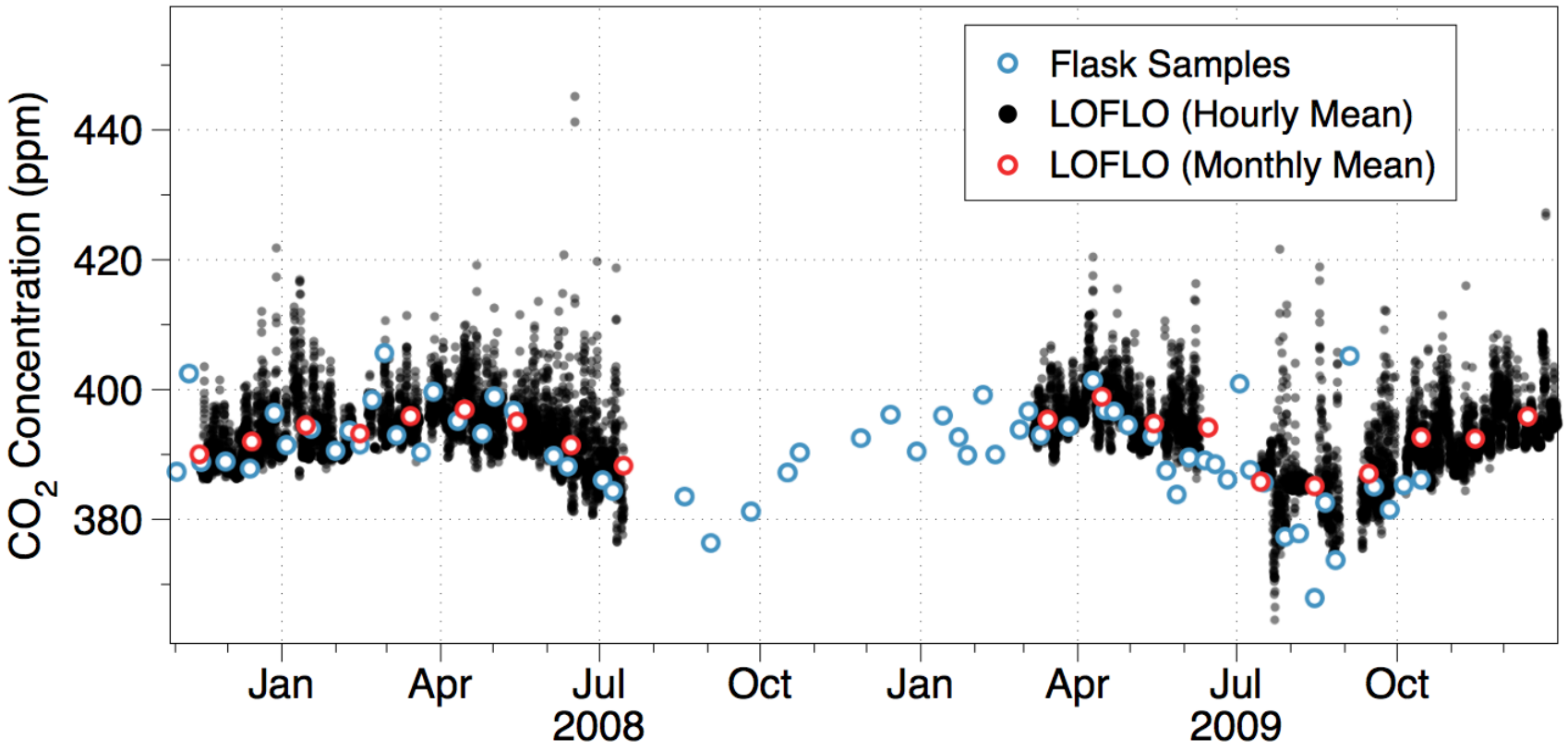
Advanced technical development-LOFLO

1. Low and stable flow rates

2. Maintenance of invariable NDIR cell pressure

   - Usage of fluistor

3. Maintenance of invariable NDIR Cell Temperature: 46℃


Flask Samples
LOFLO (Hourly Mean)
LOFLO (Monthly Mean)
CO2 Concentration (ppm)
440
420
400
380
Jan
Apr
Jul
2008
Oct
Jan
Apr
Jul
2009
Oct

Gases involved in recent global warming

Increase in atmospheric concentrations of

2) Man-made greenhouse gases
CFCs, HCFCs, HFCs, PFCs, SF_6,
halons, halogenated solvents

Man-made ultra trace greenhouse gases (Montreal protocol controlled compounds)

1. Gases **Phased out before 2000** under the Montreal Protocol and its Amendments:

   CFC-11, CFC-12, CFC-13, CFC-113, CFC-114, CFC-115, carbon tetrachloride,

   methyl chloroform, halon-1211, halon-1301, halon-2402

2. Chlorinated Hydrocarbons **Controlled** by the Montreal Protocol and its Amendments:

   HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b ….

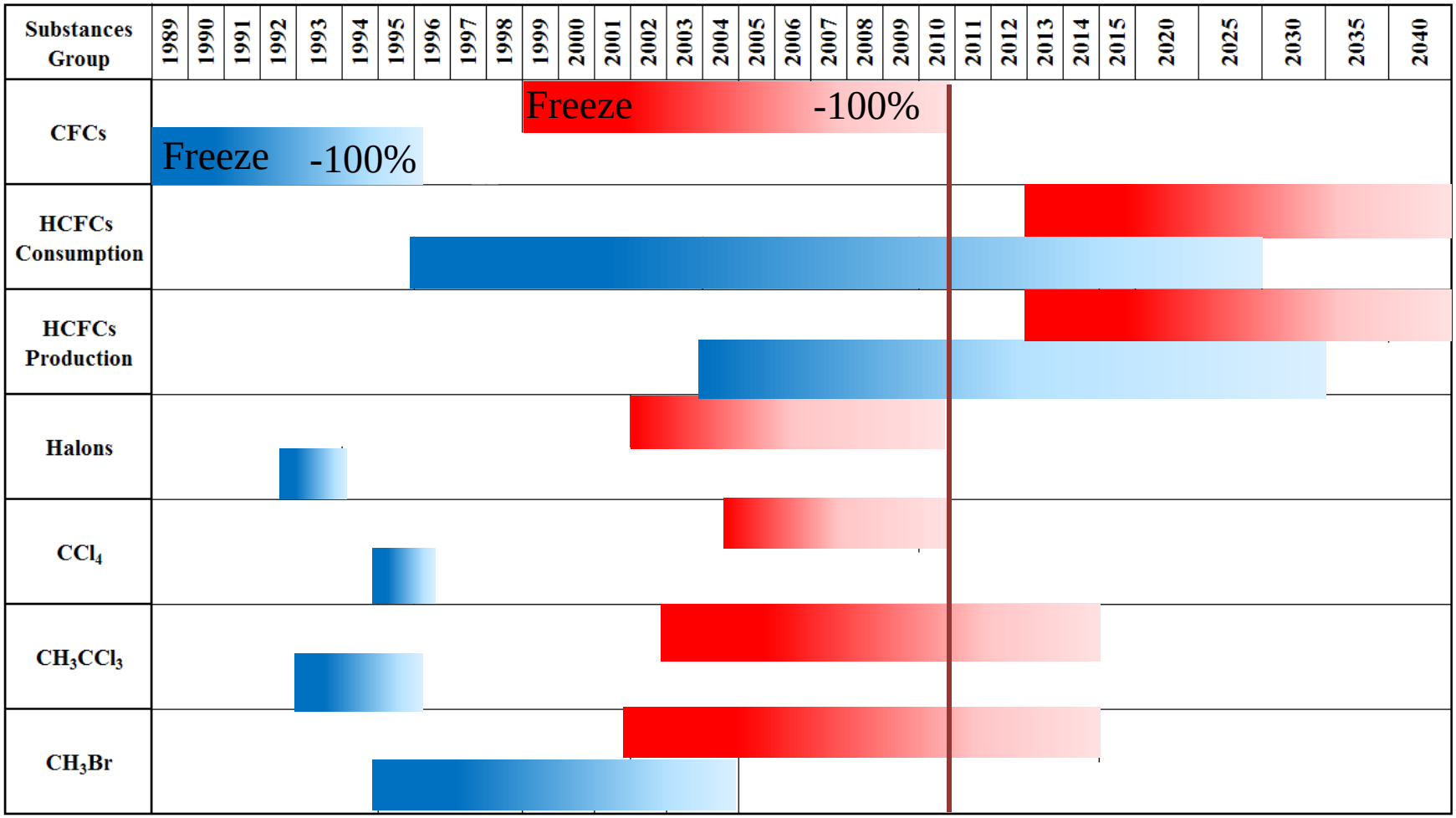
3. Anthropogenic Greenhouse Gases **Not Regulated (Proposed or in Use)**:

   HFC-23, HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152a ……

4. **Perfluorinated** Compounds:

   sulphur hexafluoride(SF_6), perfluoromethane, perfluoroethane, perfluoropropane

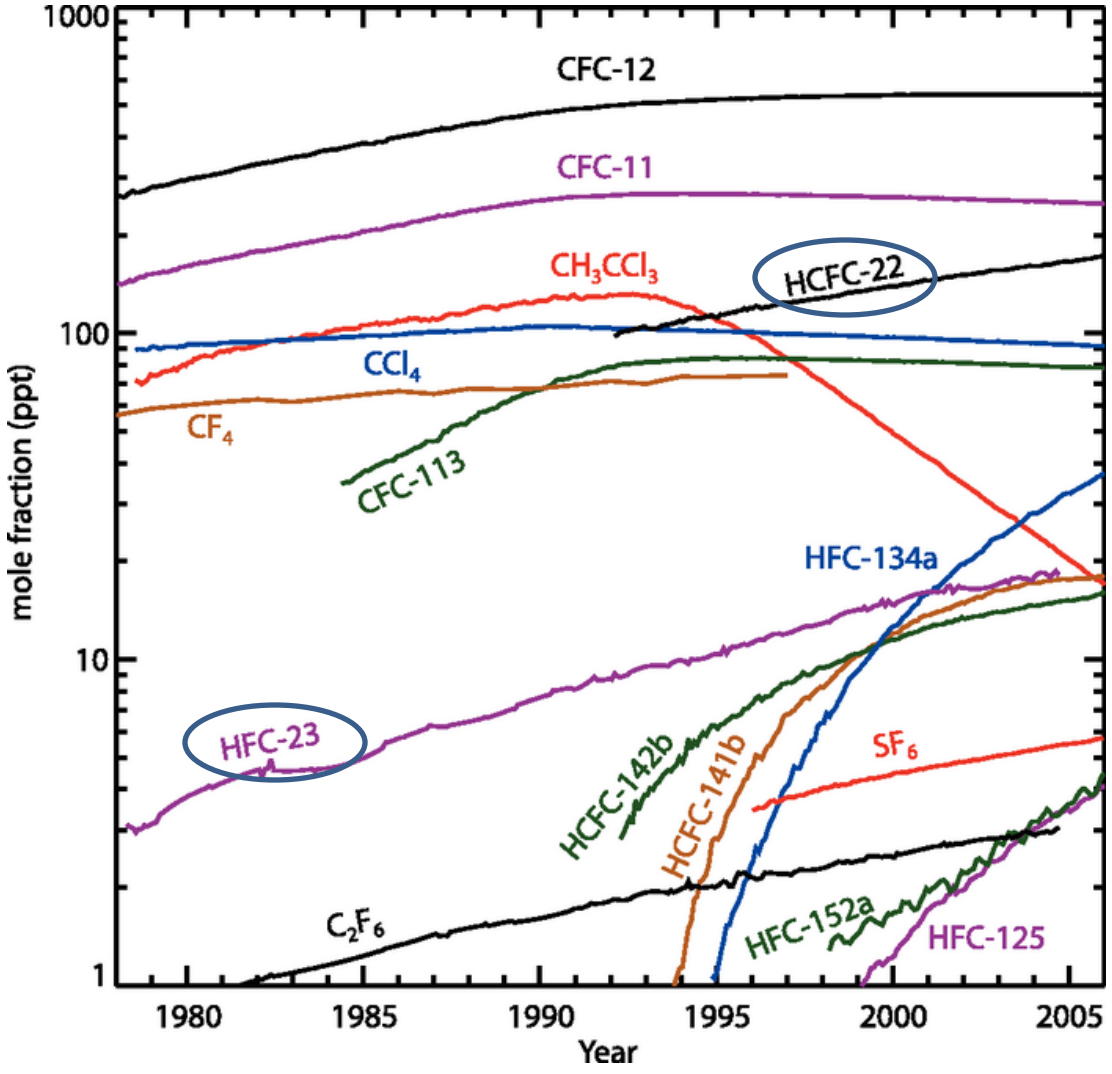
Summary of Control Measures under Montreal Protocol



Red: Developing country for MP purpose
Blue: Developed country for MP purpose

Global averaged trends of major halogenated compounds

Montreal protocol works!!

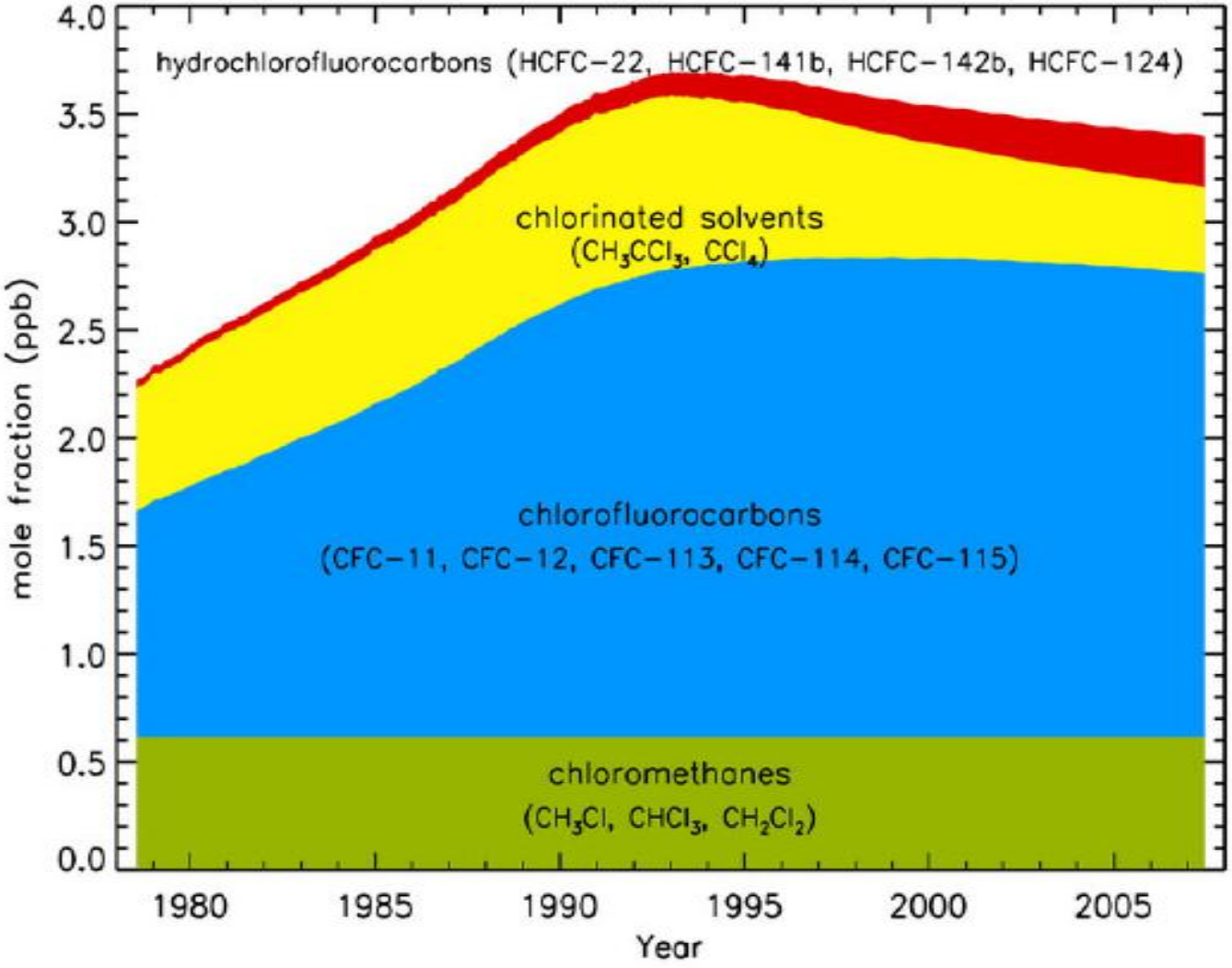


[*IPCC*, 2007]

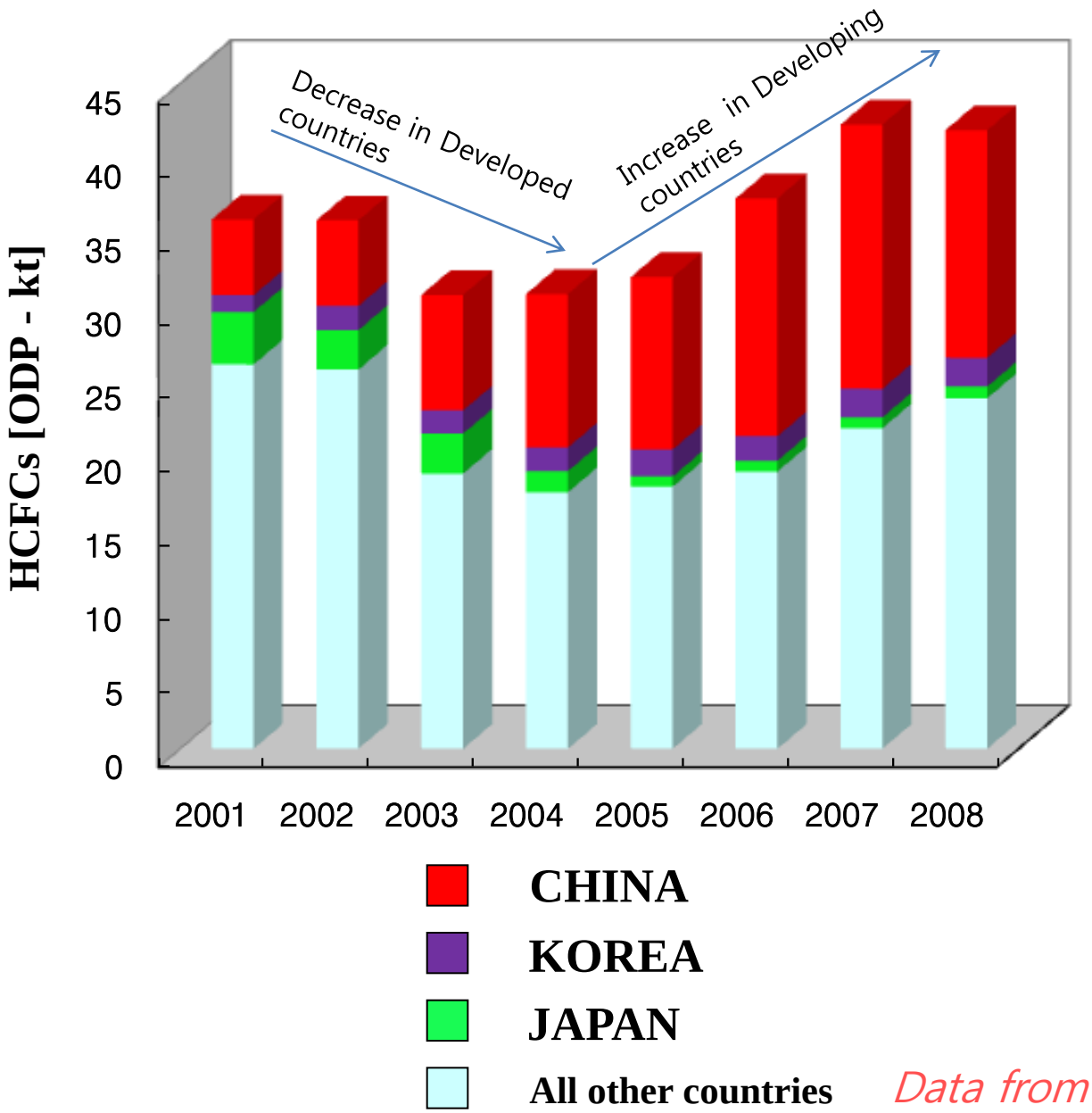
Long-lifetime species (ex. CFCs) will take much longer to disappear from the atmosphere.

Continued observation is needed to check ambient levels of the halogenated species.

Tropospheric Organic Chlorine

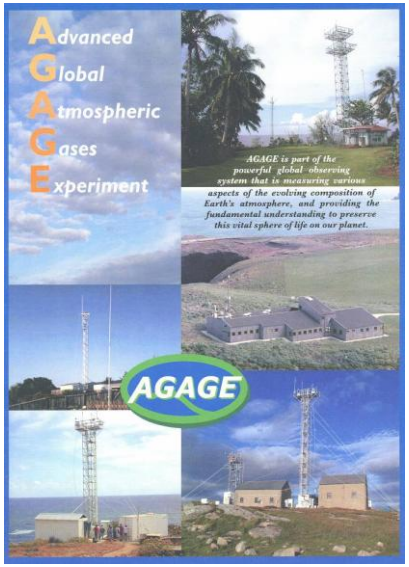


HCFCs Consumption in East Asia



Data from UNEP 2008

AGAGE Network:
(Advanced Global Atmospheric Gases Experiment)
ALE (1978) - GAGE - AGAGE



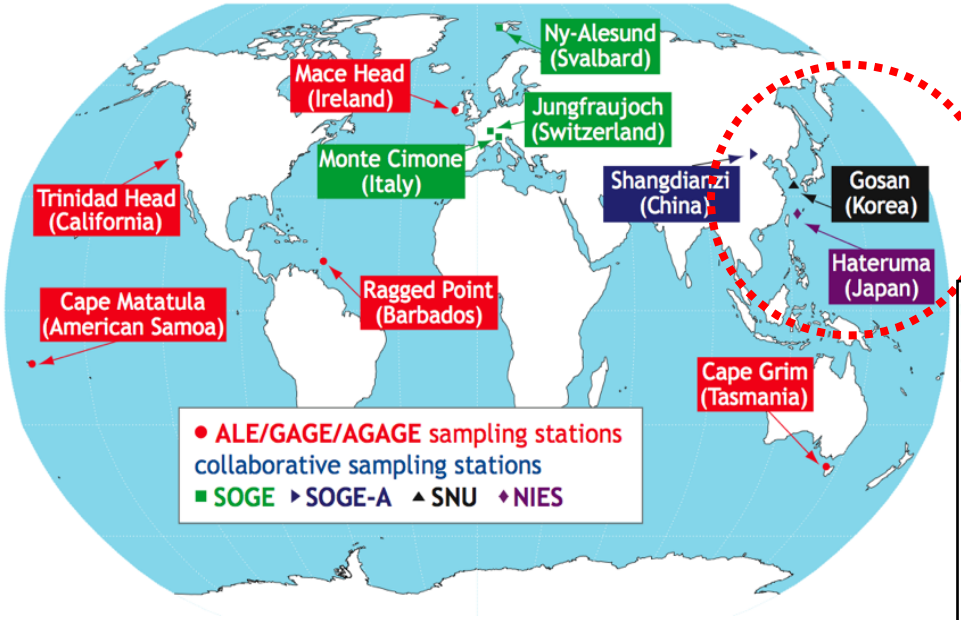
"AGAGE is distinguished by its capability to measure over the globe at high frequency

almost all of the important species in the Montreal Protocol to protect the ozone layer and

almost all of the significant non-CO_2 gases in the Kyoto Protocol to mitigate climate change." (AGAGE brochure)

AGAGE Participants:

MIT, Georgia Inst. of Tech., Scripps Inst. of Oceanography, Univ. of Bristol, CSIRO, EMPA(Swiss), NIES(Japan), NILU(Norway), Univ. of Urbino(Italy), CMA(China), Gosan, SNU(Korea)

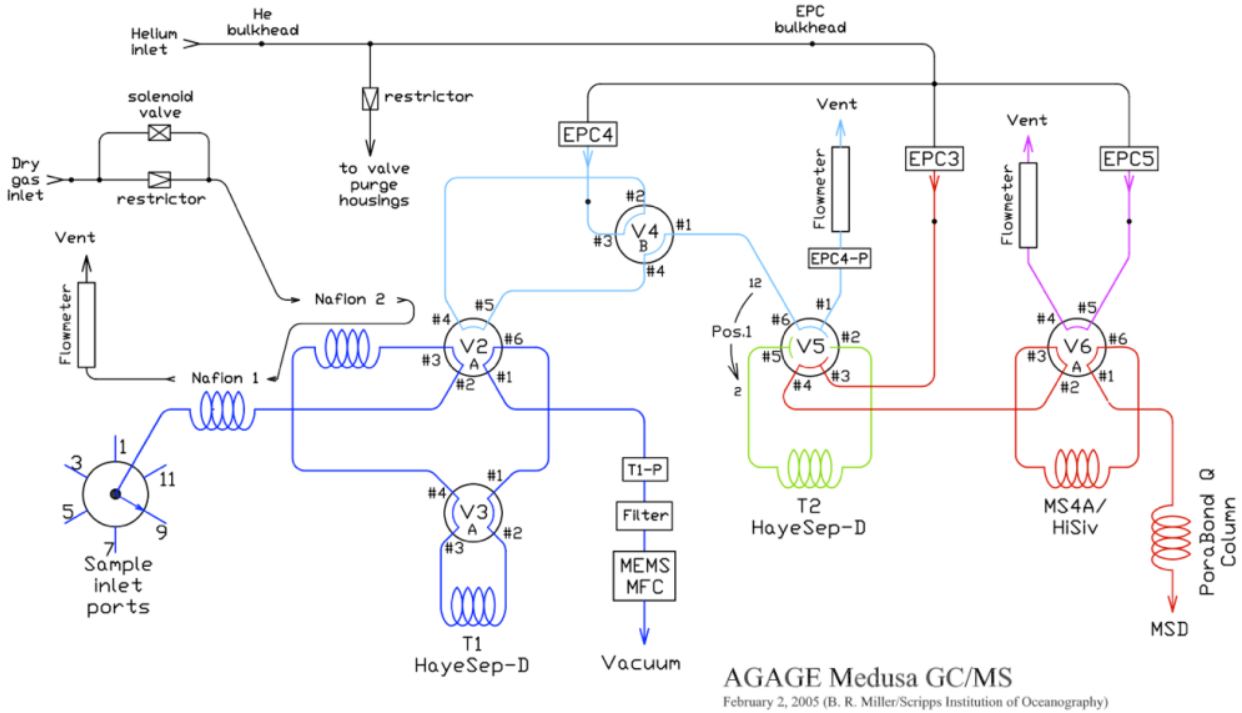


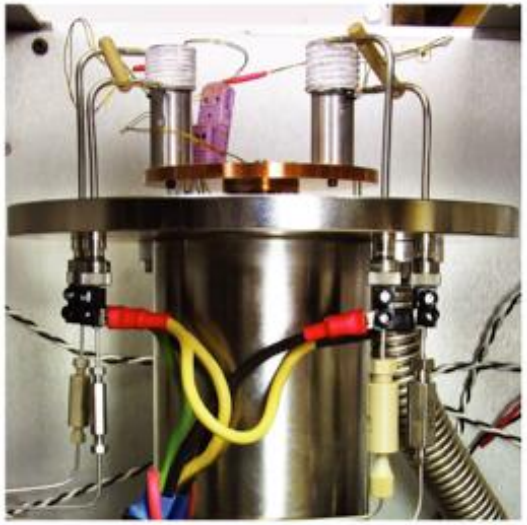
18

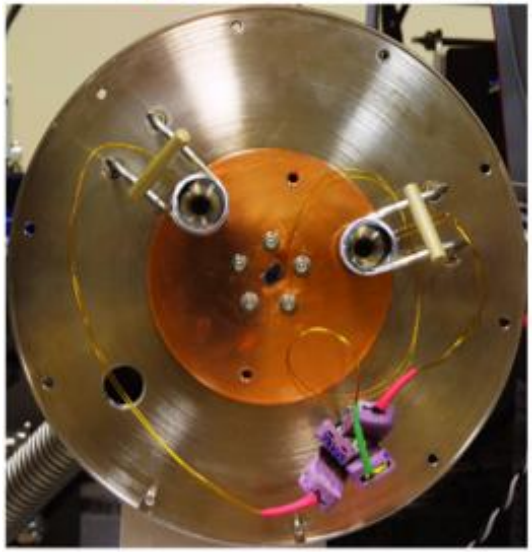
Medusa GC-MS

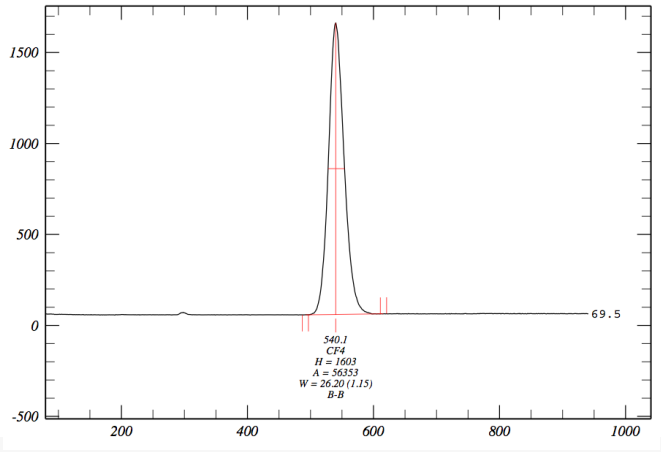
Medusa GC-MS System
- ~40 halocarbon compounds
- 2 hr intervals
- Operating since Nov. 2007

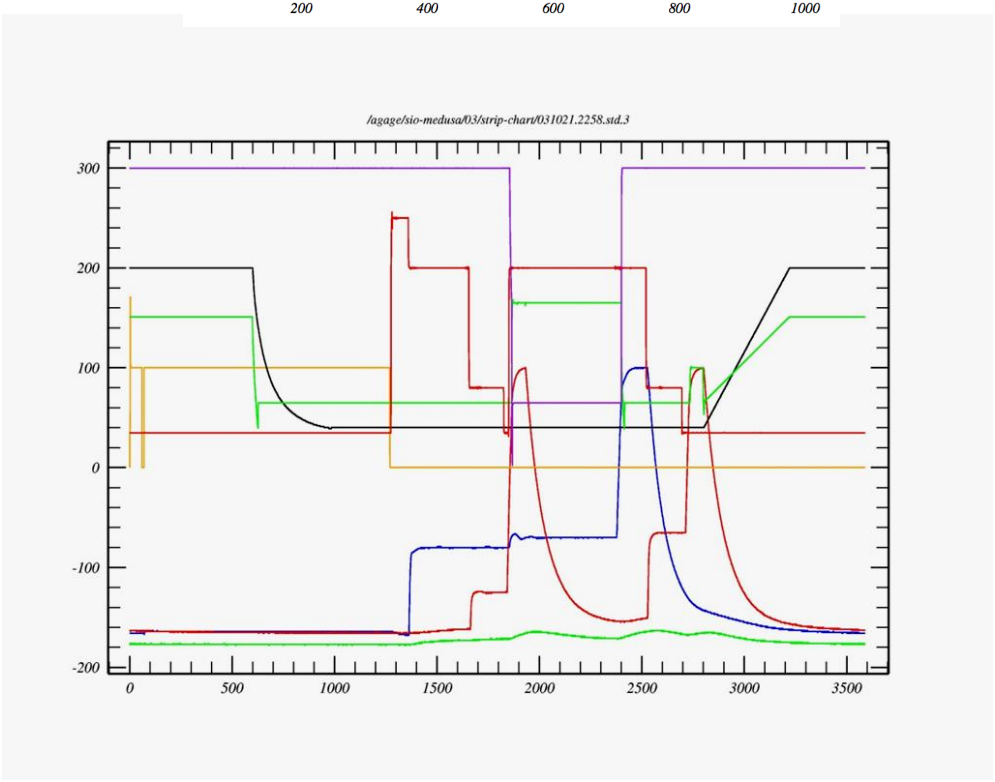
- Novel technique for cryogenic separation of compounds at -170°C without using liquid N_2
- Continuous *in situ* operations using sophisticated automation











Medusa 2 Coldhead

Compounds Measured on Medusa GC-MS

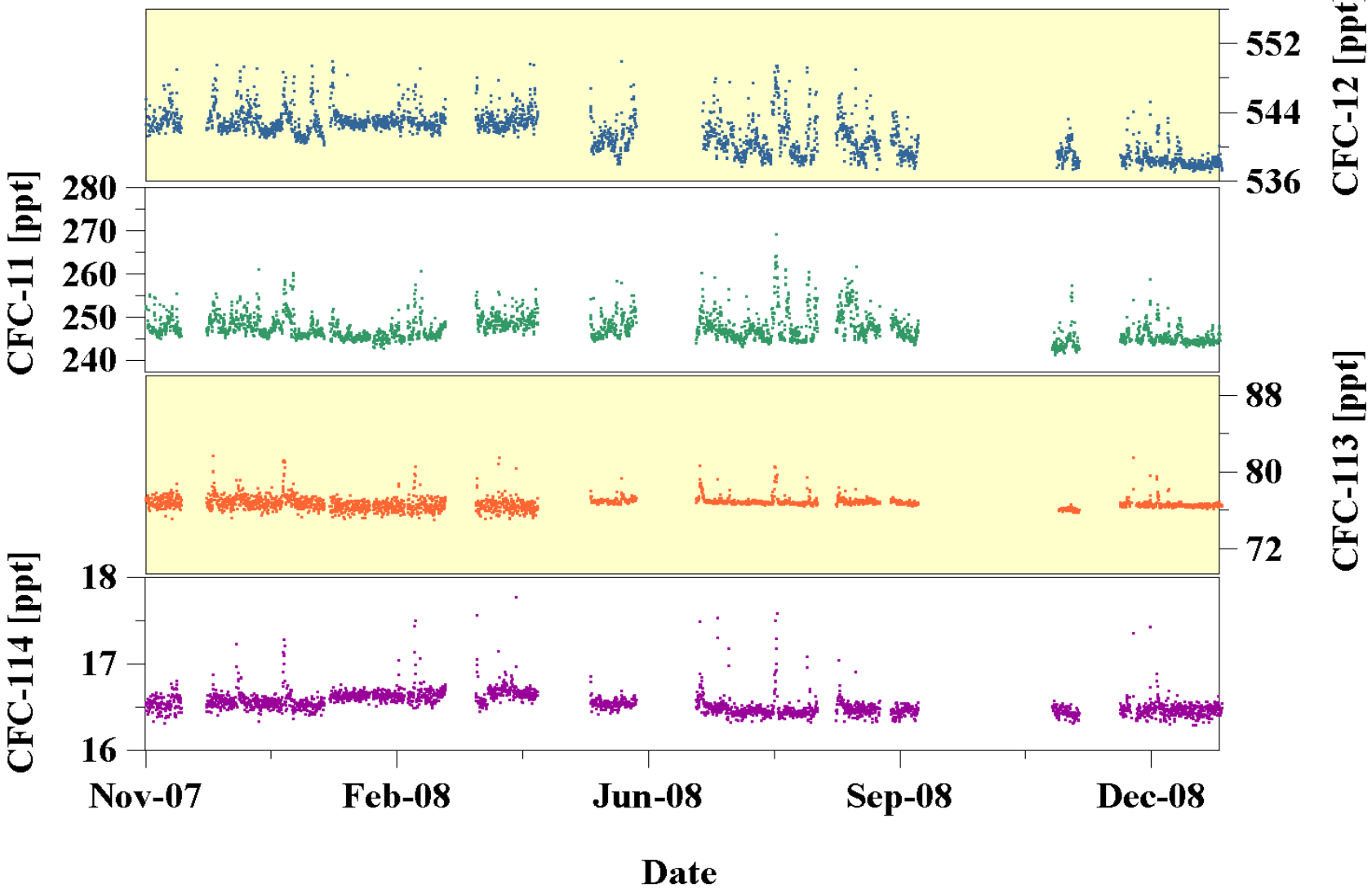
Compound	~NH (2005) (ppt)	Typical % precision
CF4	74	0.15
HFC23	25	0.7
C2F6	3.5	0.9
C3F8	0.5	3
HFC32	~1	5
SF6	5.3	0.4
SO2F2	1	1.6
HFC134a	29	0.4
HFC152a	4.2	1.2
HFC125	2.9	1
HFC143a	6.5	1.2
HFC365mfc	<1	10
HCFC22	170	0.3
HCFC141b	19	0.4
HCFC142b	15	0.6
HCFC124	1.6	2
CFC11	257	0.15
CFC12	546	0.05
CFC13	-	2
CFC113	80	0.2
CFC114	16.5	0.3
CFC115	8.4	0.8

Compound	~NH (2005) (ppt)	Typical % precision
H1301	3.1	1.5
H1211	4.5	0.5
H2402	>0.5	2
CH3Cl	570	0.2
CH3Br	10	0.5
CH3I	1	2
CH2Cl2	36	0.8
CHCl3	11	0.6
CHBr3	~3	0.6
CCl4	95	1
CH3CCl3	28	1
CHClCCl2	0.8	2.5
CCl2CCl2	5.5	0.5
C2H2	10-200	0.5
C2H4	50-500	2
C2H6	500	0.3
C6H6	10-100	0.3
C7H8	<1-10	0.6

Measurement of CFCs

Gosan Station (Jeju Island, Korea)

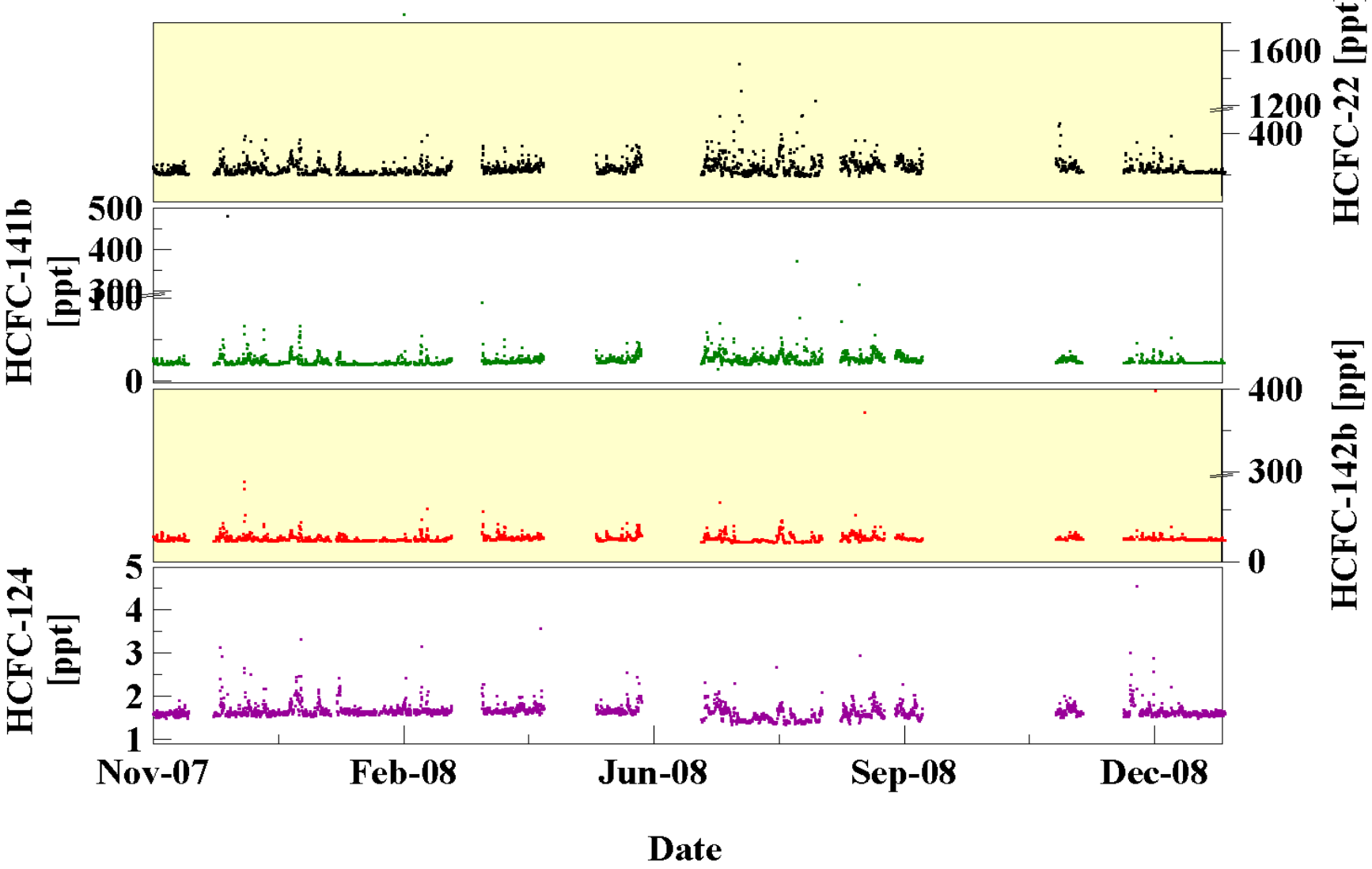
Nov. '07 ~ Jan. '09



Measurement of HCFCs

Gosan Station (Jeju Island, Korea)

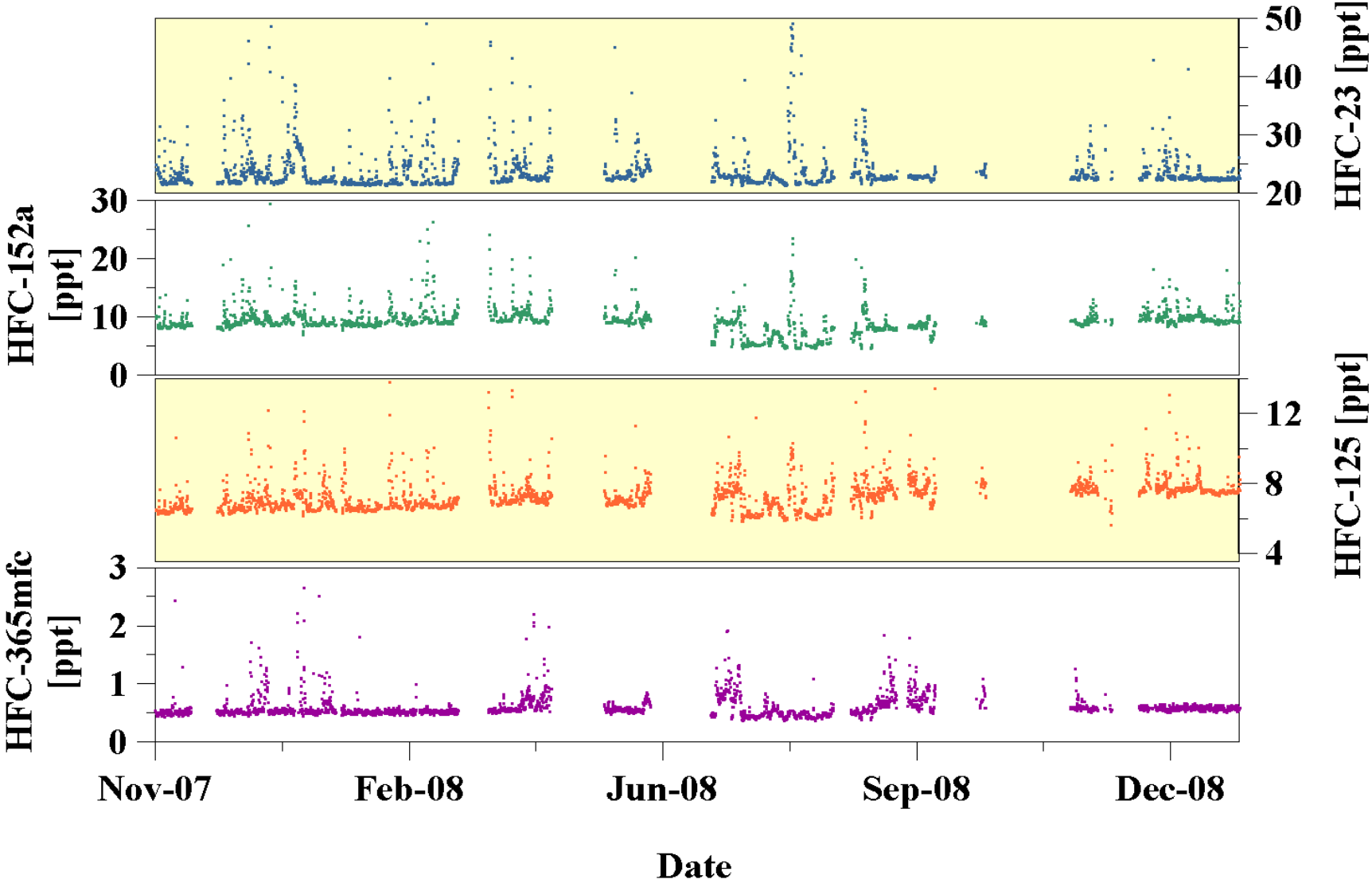
Nov. '07 ~ Jan. '09



Measurement of HFCs

Gosan Station (Jeju Island, Korea)

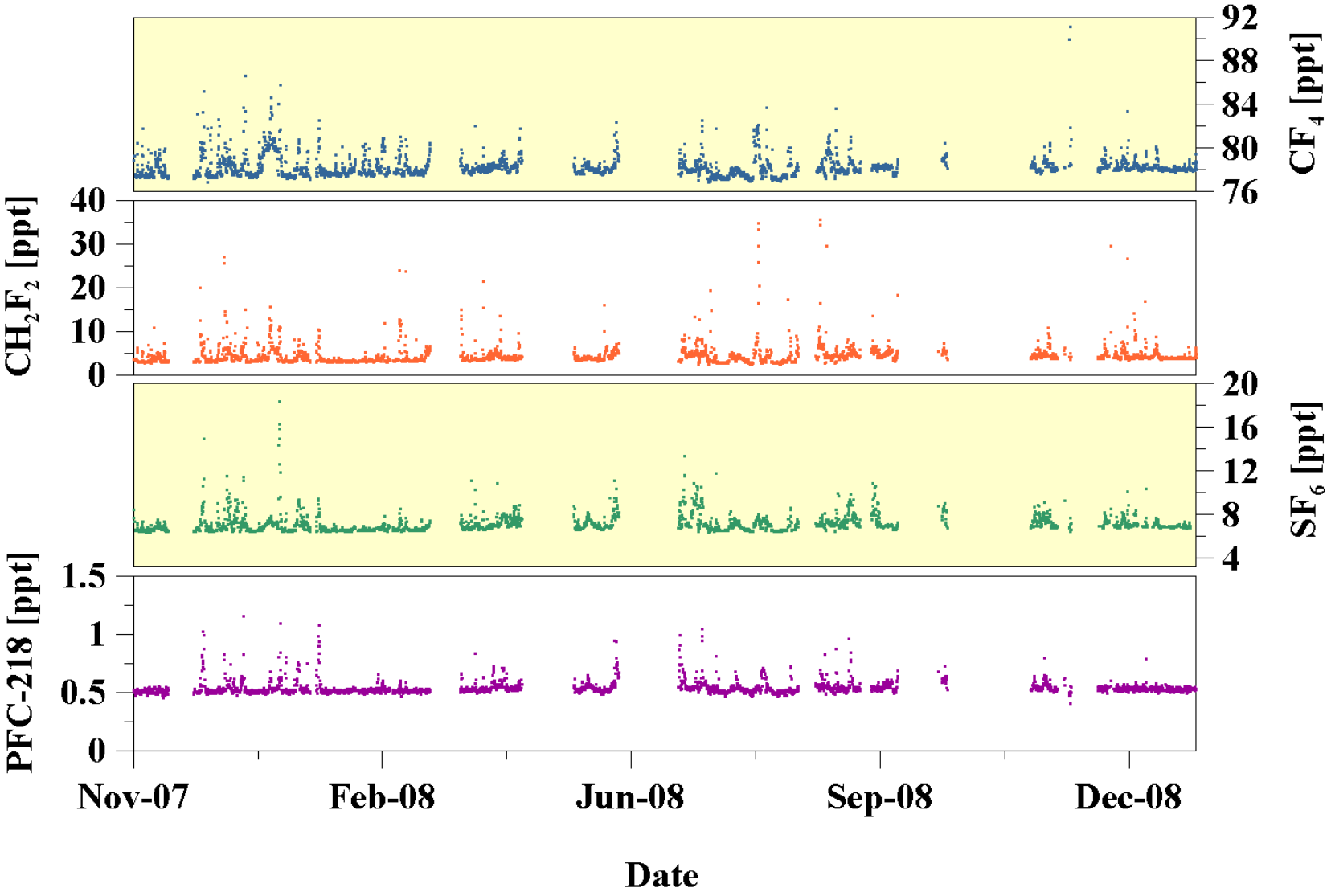
Nov. '07 ~ Jan. '09



Measurement of PFCs & SF_6

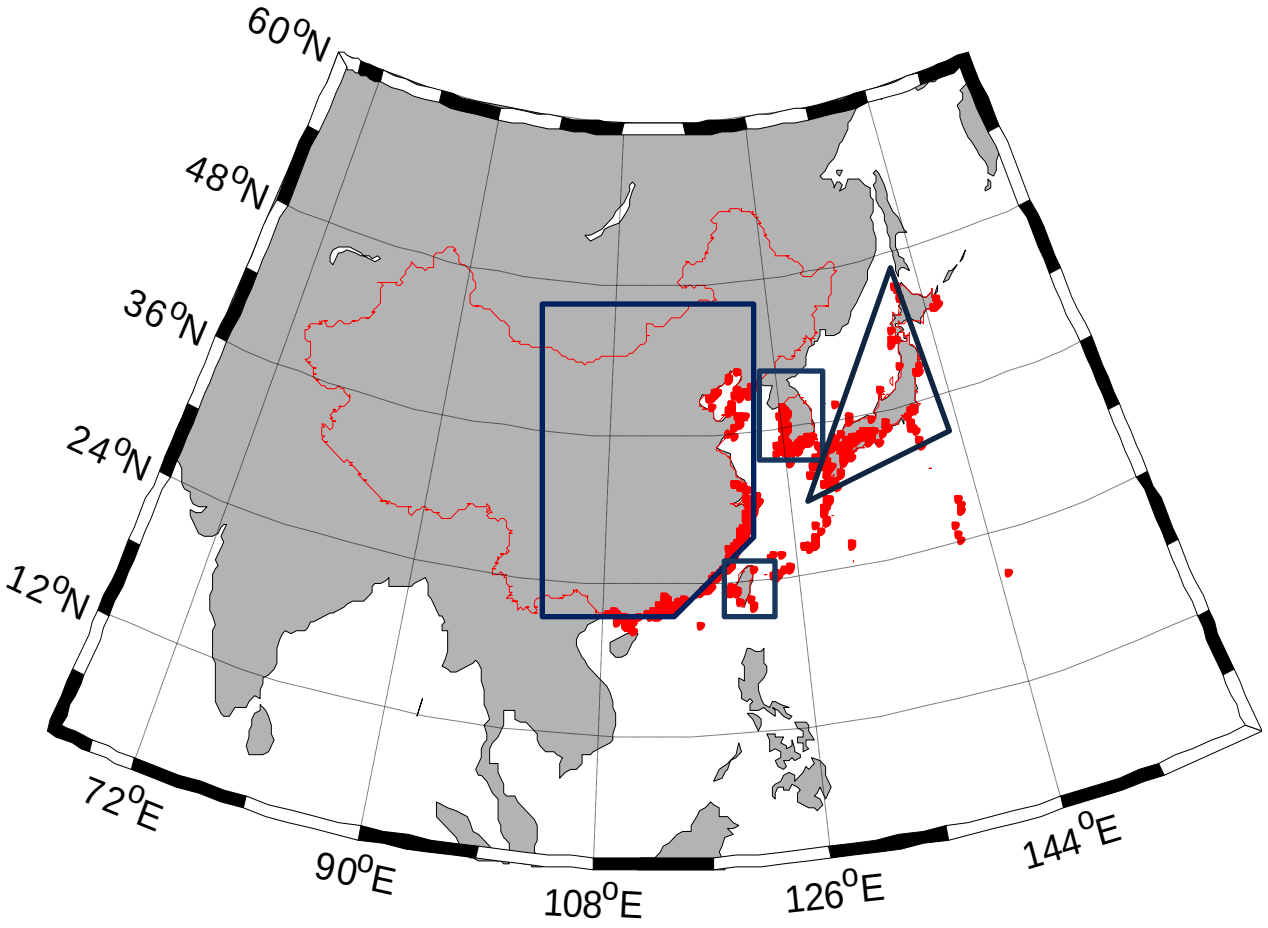
Gosan Station (Jeju Island, Korea)

Nov. '07 ~ Jan. '09

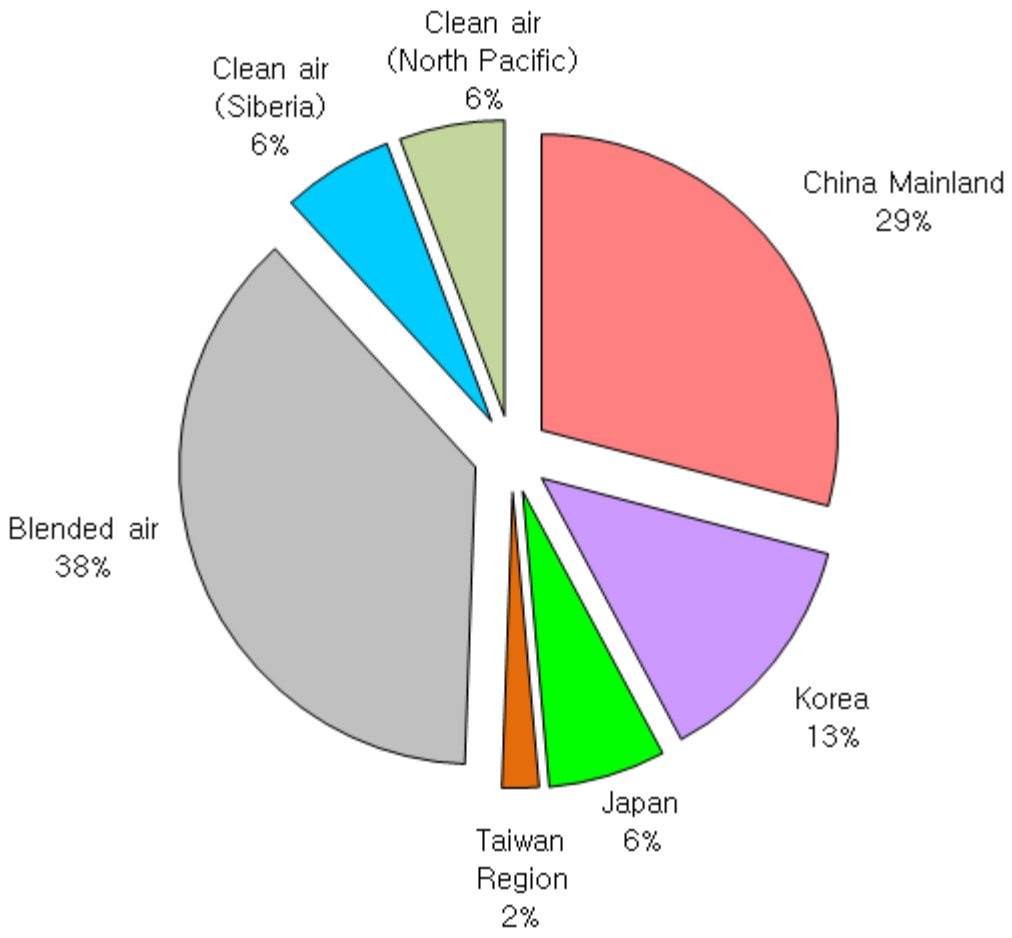


Air mass classification at Gosan

- Back-trajectory analysis-

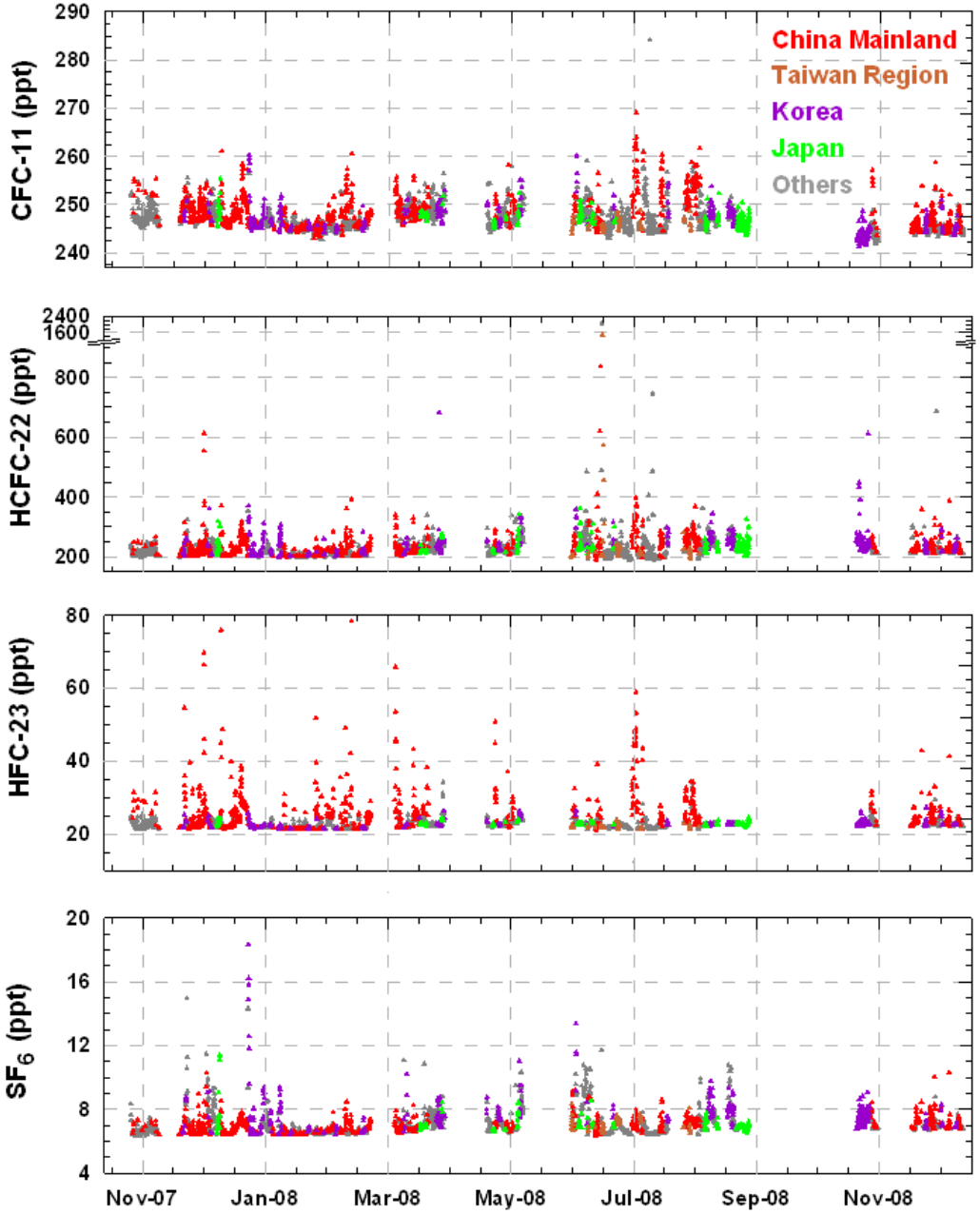


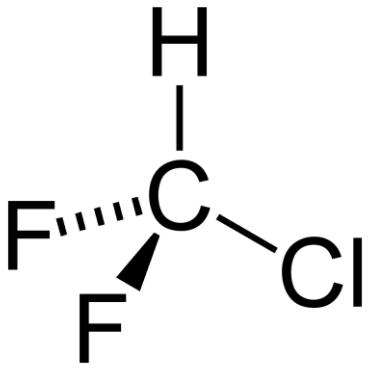
East Asian Emission source-influenced measurement data



기원에 따라 분류한 관측 자료의 분포

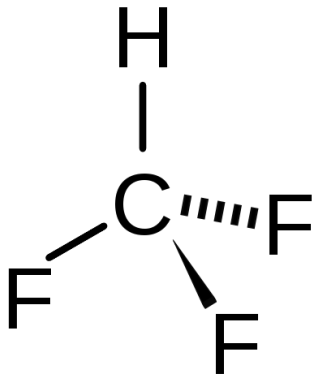
Measurement data by region





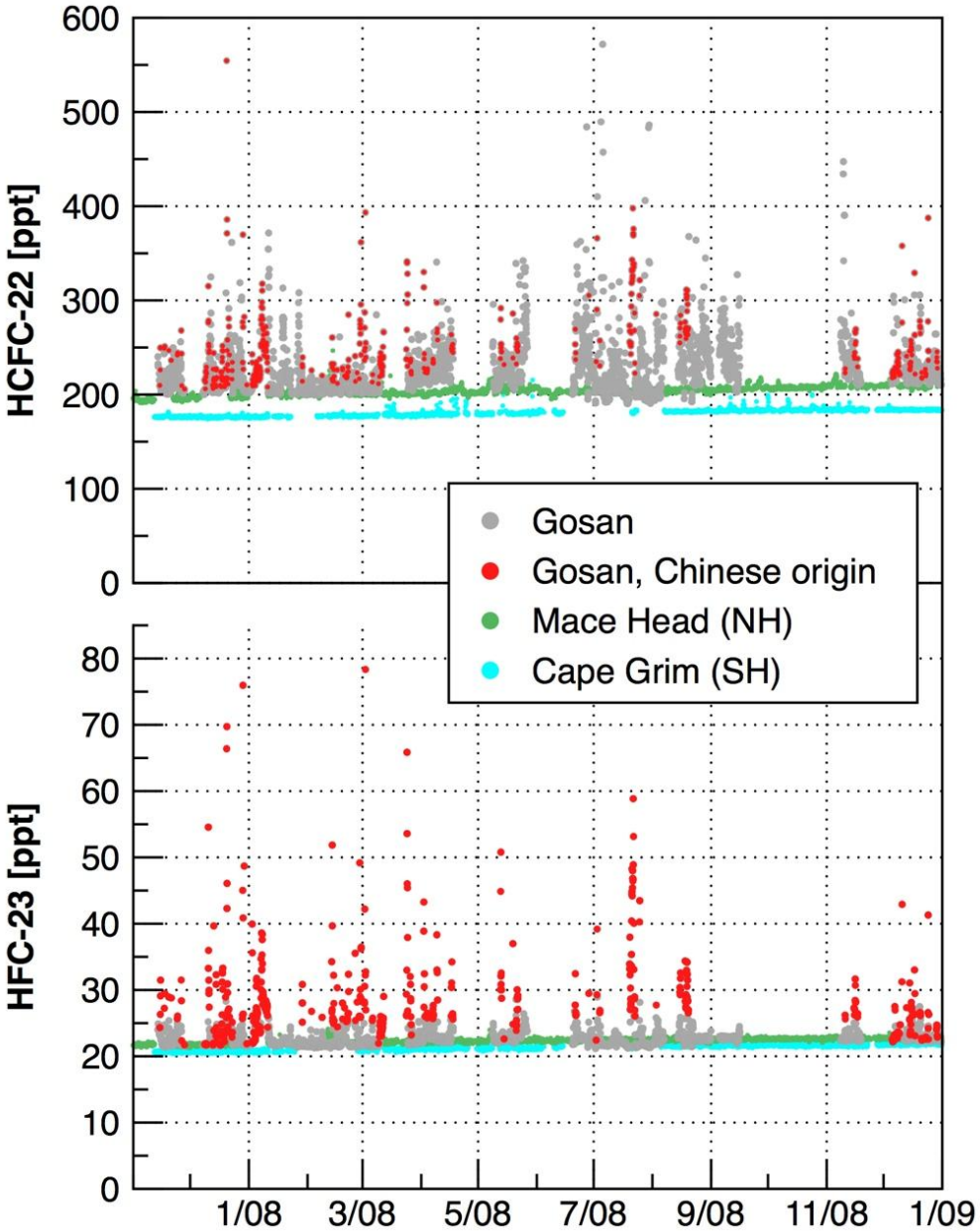
HCFC-22 (Chlorodifluoromethane)

- An important interim compound
- Major refrigerant in China and Korea



HFC-23 (Fluoroform)

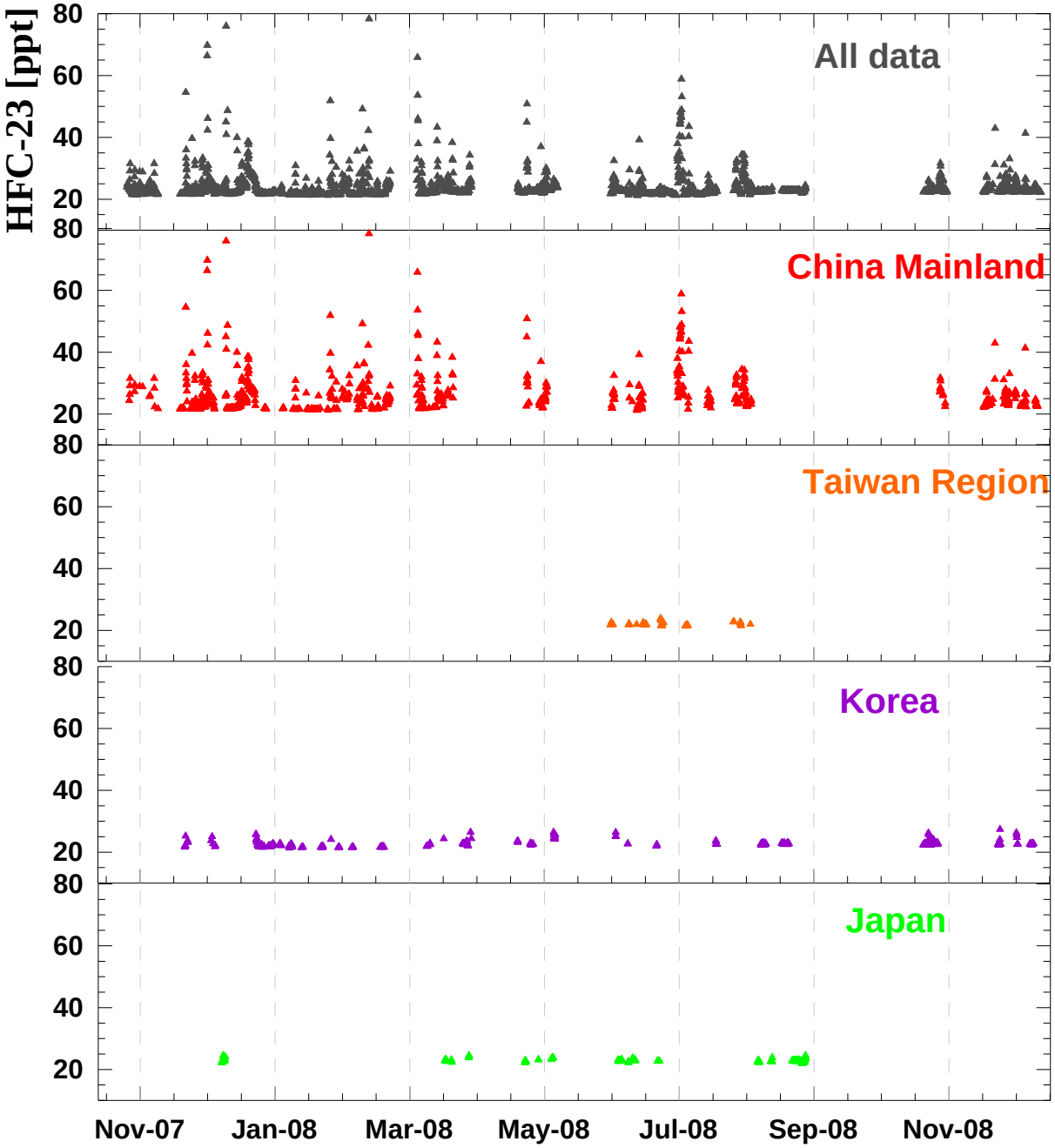
- An unwanted (due to high GWP) by-product of HCFC-22 manufacturing (1-4%)
- Under UNFCCC CDM (Clean Development Mechanism)



(Kim et al. GRL 2010)

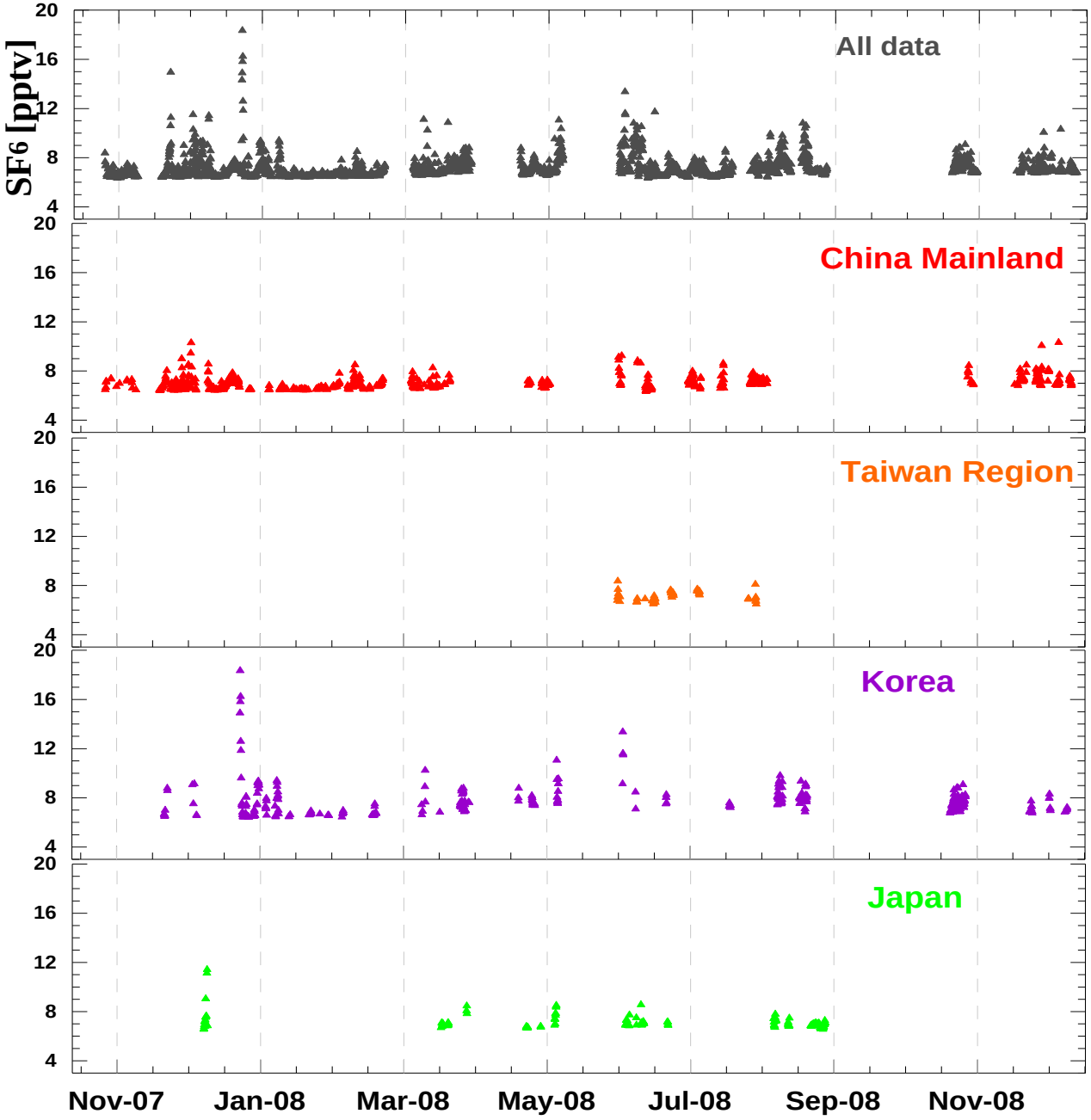
- HCFC-22 emissions come from many different source regions (Korea, Japan …)
- HFC-23 pollution events are almost all from China.

Separated time series data: example of HFC-23

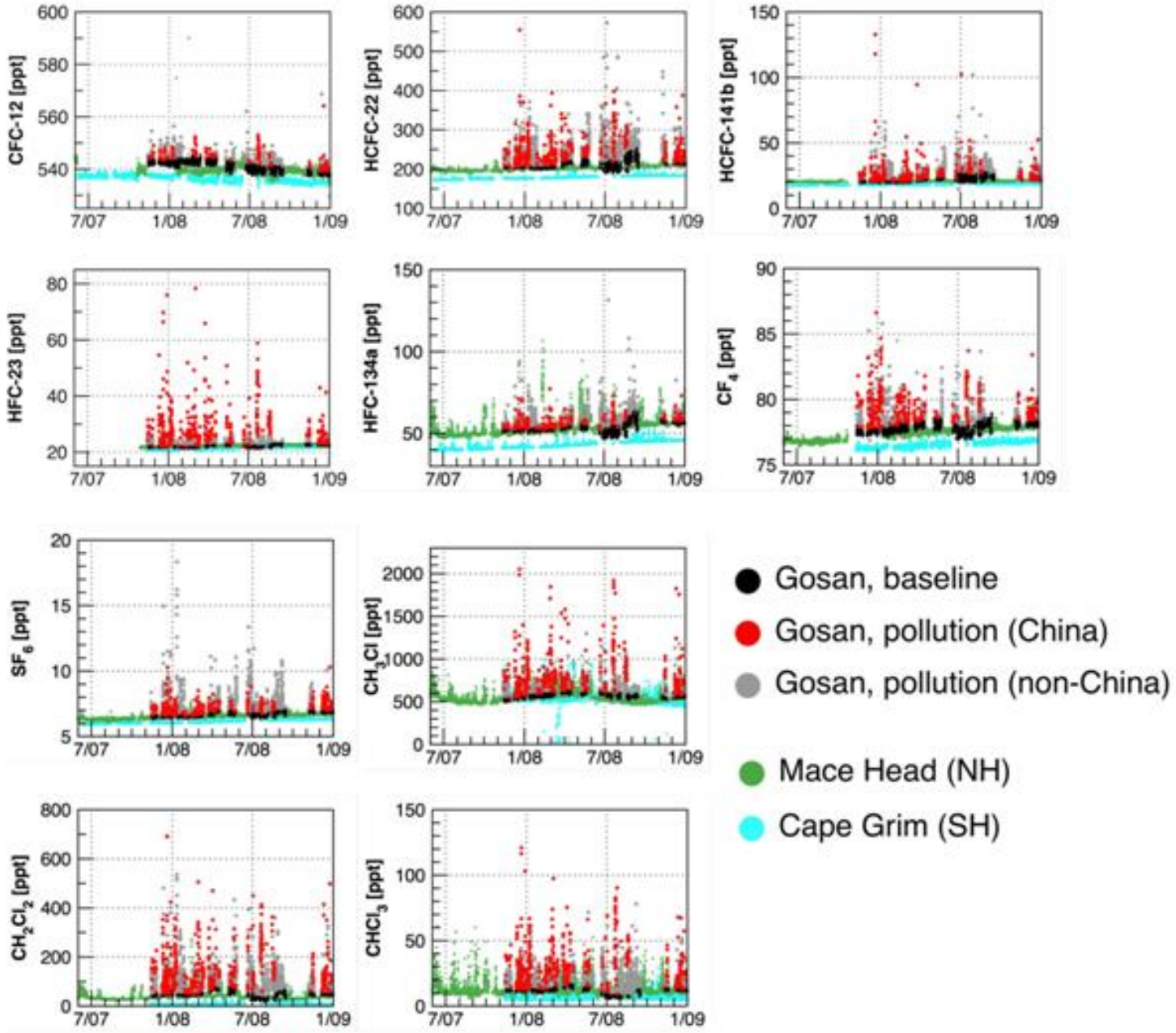


- HFC-23 pollution events are almost observed from China.
- Seasonal distribution of measurement data by region

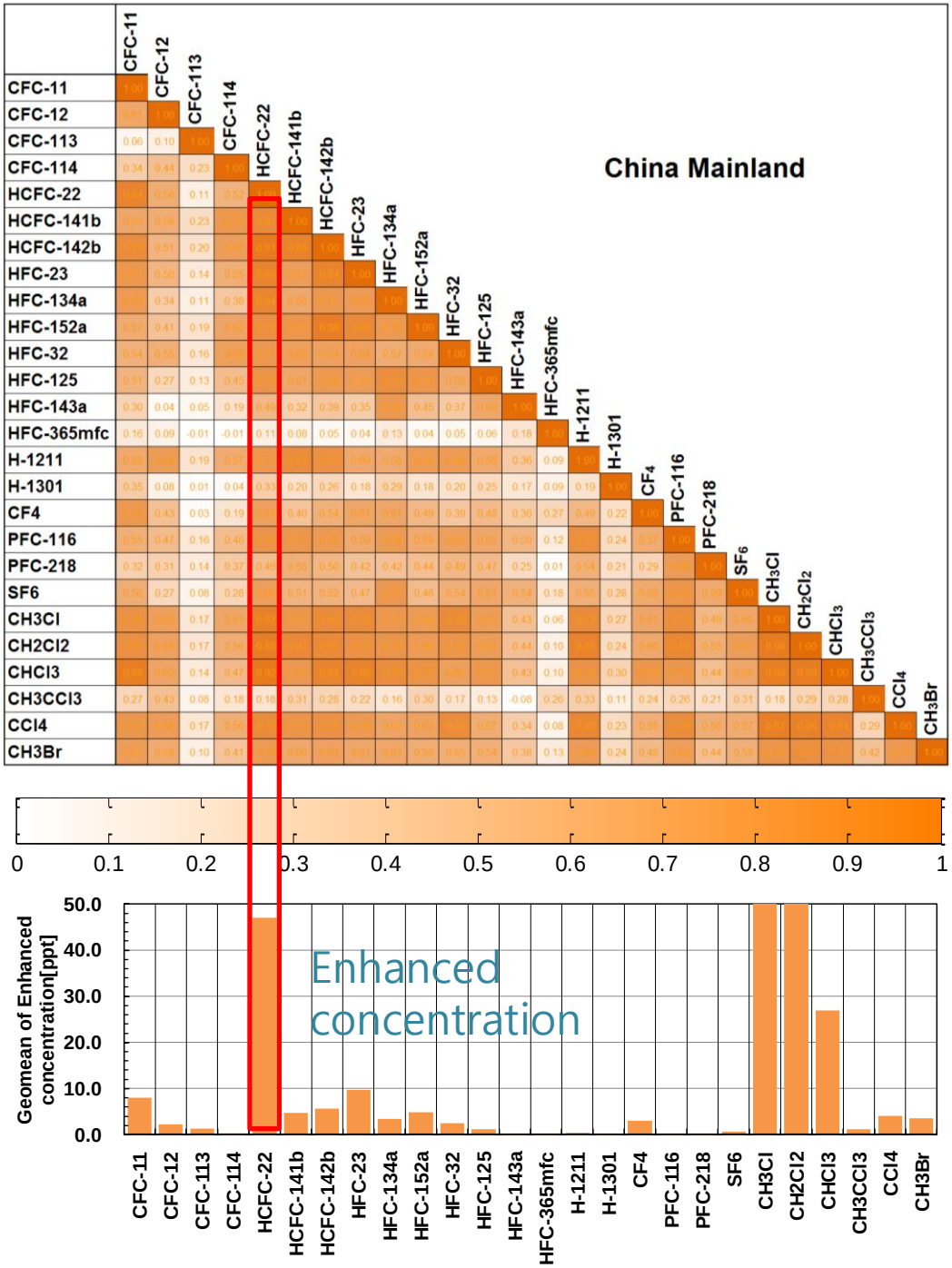
Separated time series data: example of SF_6



➢Higher SF_6 pollution events are occasionally observed from Korea.

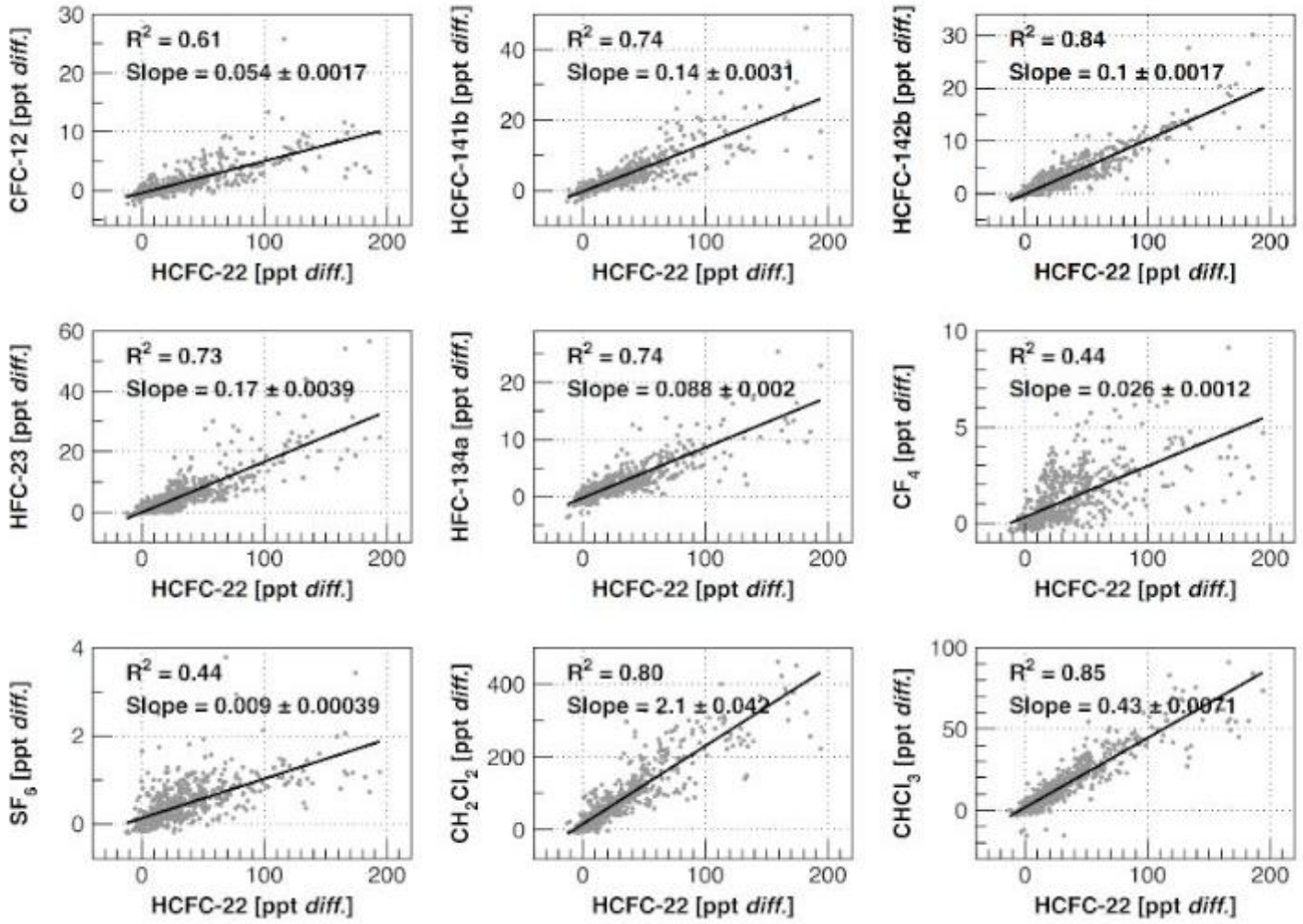

CFC-12 [ppt]
HCFC-22 [ppt]
HCFC-141b [ppt]
HFC-23 [ppt]
HFC-134a [ppt]
CF4 [ppt]
SF6 [ppt]
CH3Cl [ppt]
CH2Cl2 [ppt]
CHCl3 [ppt]
7/07
1/08
7/08
1/09
Gosan, baseline
Gosan, pollution (China)
Gosan, pollution (non-China)
Mace Head (NH)
Cape Grim (SH)

Interspecies Correlation Matrix in China during 2008



Reference compound: HCFC-22

Ratio-based emissions calculations - Chinese influence only



(Kim et al., GRL 2010)

Top-down Inverse Modeling for HCFC-22

- Backward simulations with FLEXPART
  - Lagrangian Particle Dispersion Model
  - Input data : ECMWF, 1°x1° resolution
  - 20d back trajectories in 3hr intervals

- Inversion algorithm based on FLEXPART
  - Analytical method for estimating most likely range of emissions from measurements
- *A priori* from global estimated emissions,

  reported consumption and available bottom-up reports, spread over population density

Regional HCFC-22 emissions calculated from FLEXPART

Atmos. Chem. Phys., 10, 3545–3560, 2010
www.atmos-chem-phys.net/10/3545/2010/

Atmospheric Chemistry and Physics

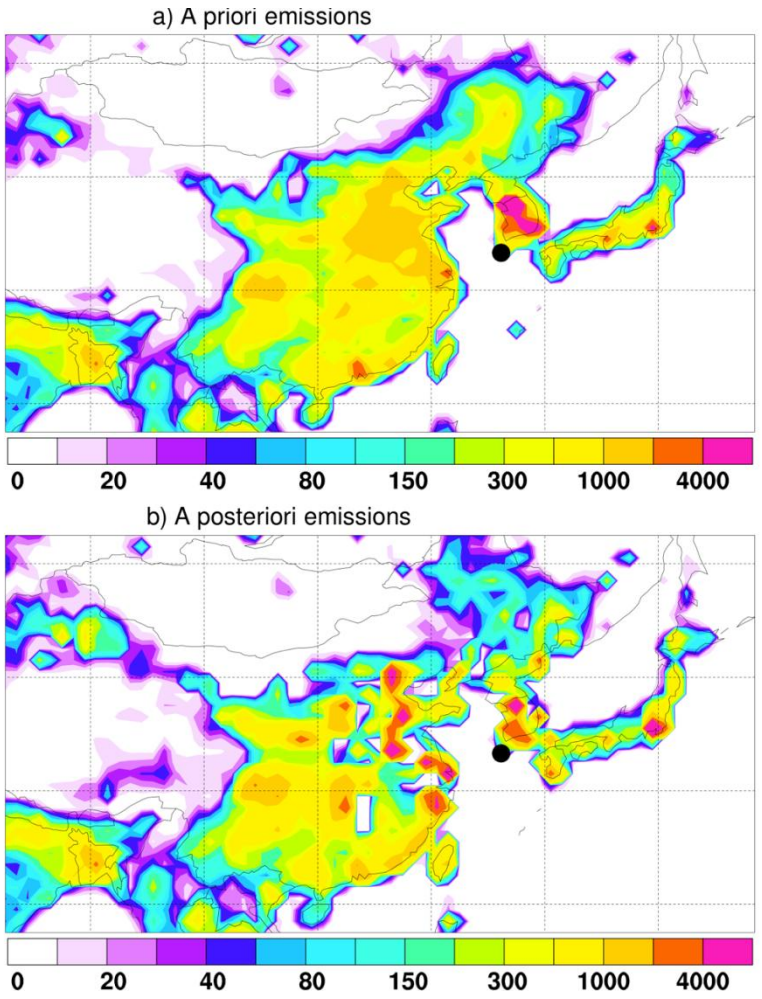
Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling

A. Stohl[1], J. Kim[2], S. Li[2], S. O'Doherty[3], J. Mühle[4], P. K. Salameh[4], T. Saito[5], M. K. Vollmer[6], D. Wan[7], R. F. Weiss[4], B. Yao[8], Y. Yokouchi[5], and L. X. Zhou[8]

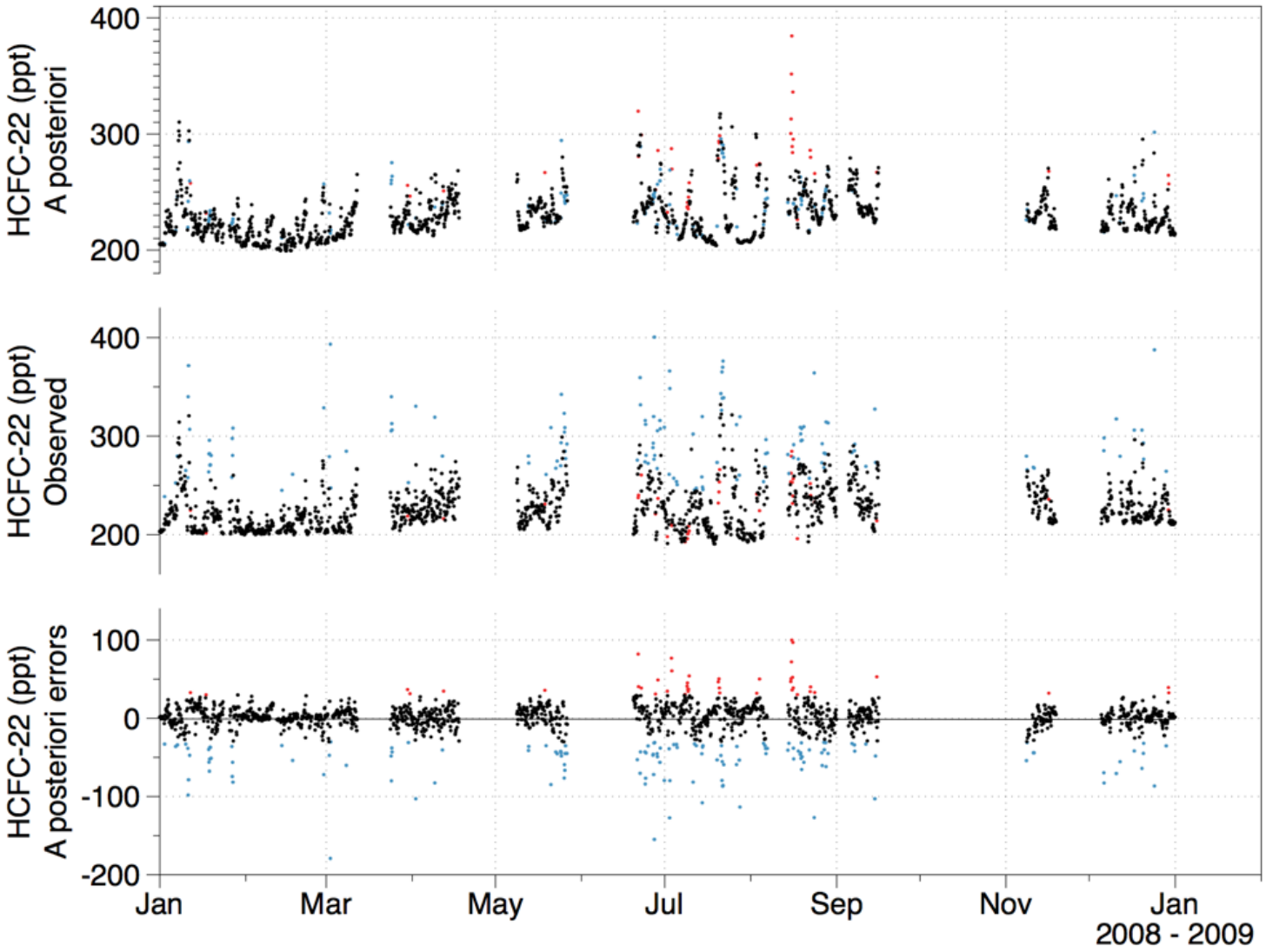
[1]Norwegian Institute for Air Research, Kjeller, Norway
[2]School of Earth and Environmental Sciences, Seoul National University, Seoul, Korea
[3]School of Chemistry, University of Bristol, Bristol, UK
[4]Scripps Institution of Oceanography, University of California, San Diego, California, USA
[5]National Institute for Environmental Studies, Tsukuba, Japan
[6]Swiss Federal Laboratories for Materials Testing and Research (Empa), Duebendorf, Switzerland
[7]State Key Joint Laboratory for Environmental Simulation and Pollution Control, Peking University, Beijing, China
[8]Centre for Atmosphere Watch and Services, Key Laboratory for Atmospheric Chemistry, Chinese Academy of Meteorological Sciences, Beijing, China

Received: 18 November 2009 – Published in Atmos. Chem. Phys. Discuss.: 1 February 2010
Revised: 3 April 2010 – Accepted: 13 April 2010 – Published: 16 April 2010

- Emission patterns can reveal dominant source regions such as factory locations, population hotspots, etc.



Comparison of Gosan concentrations modeled:
FLEXPART vs Observations



data from Stohl et al. (2010)

(units : kt/a)

Method	China						Global			$R^{2\,5}$
	Top-down				*Bottom-up*		*Top-down*	*Bottom-up*		
Data Source	**Our Study (Gosan)**		Vollmer (2009) (Shandanzi)	Yokouchi (2006) (Hateruma)	Wan (2009)	EDGARv4 (2009)[4]	Vollmer (2009)	AFEAS (2008)	EDGARv4 (2009)[4]	
	HCFC-22	**HFC-23**								
Emission Yr.	**2008**	**2008**	2007	2005	2008	2008	2007	2006	2008	
CFC-11	**13 (9.3 - 17)**	--	33 (26 - 43)	--	14.259	--	82 ± 30	--	--	0.70
CFC-12	**6.3 (4.7 - 8.5)**	--	14 (9 - 19)	--	3.869	--	79 ± 40	--	--	0.31
CFC-113	**--[1]**	--	0.8 (0.4 - 1.7)	--	0	--	--	--	--	0.01
CFC-114	**1.2 (0.84 - 1.6)[2]**	--	--	--	--	--	--	--	--	0.50
HCFC-22	**83 (64 - 109)[3]**	**71 (35 - 106)**	165 (140 - 213)	54 ± 34	79.268	--	365 ± 70	172.4	--	1.00
HCFC-141b	**16 (12 - 20)**	--	--	--	12.148	--	60 ± 10	68.1	--	0.65
HCFC-142b	**10 (7.6 - 13)**	**11 (5.5 - 16)**	12 (10 - 18)	--	--	--	41 ± 5.0	22.0	--	0.83
HFC-23	**12 (8.7 - 15)**	--	--	10 ± 4.6	--	10.6	--	--	13.8	0.72
HFC-134a	**8.6 (6.5 - 12)**	--	--	3.9 ± 2.4	--	1.03	--	138.2	165	0.70
HFC-152a	**5.7 (4.3 - 7.6)**	**6.8 (3.4 - 10)**	--	4.3 ± 2.3	--	0	--	--	28.5	0.57
HFC-32	**4.3 (3.2 - 5.9)**	--	--	--	--	0	--	--	3.6	0.50
HFC-125	**3.2 (2.4 - 4.3)**	--	--	--	--	0	--	--	30	0.54
HFC-143a	**0.6 (0.4 - 0.8)[2]**	--	--	--	--	0	--	--	31.7	0.49
HFC-365mfc	**--[1]**	--	--	--	--	0	--	--	1.9	0.01
H-1211	**1.4 (1.1 - 1.9)**	--	2.1 (1.7 - 2.5)	--	1.353	--	6.2 ± 3.0	--	--	0.51
H-1301	**0.24 (0.16 - 0.34)**	--	0.09 (0.07 - 0.11)	--	0.044	--	2.3 ± 1.1	--	--	0.11
CF_4	**2.3 (1.7 - 3.1)**	--	--	--	--	1.46	--	--	8.92	0.43
PFC-116	**0.5 (0.4 - 0.6)**	--	--	--	--	0.24	--	--	1.83	0.54
PFC-218	**0.09 (0.07 - 0.12)[2]**	--	--	--	--	0.0007	--	--	0.42	0.46
SF_6	**1.3 (1.0 - 1.8)**	--	0.80 (0.53 - 1.10)	--	--	1.64	7.5 ± 1.5	--	6.15	0.43
CH_3Cl	**264 (200 - 354)**	**239 (119 - 358)**	--	--	--	--	--	--	--	0.76
CH_2Cl_2	**175 (132 - 234)**	--	--	--	--	--	--	--	--	0.78
$CHCl_3$	**49 (37 - 66)**	**45 (22 - 67)**	86 (51 - 140)	--	--	--	--	--	--	0.84
CCl_4	**17 (13 - 23)**	--	15 (10 - 22)	--	6.764	--	53 ± 30	--	--	0.63
CH_3Br	**5.8 (4.3 - 7.9)**	--	0.24 (0.17 - 0.47)	--	--	--	--	--	--	0.48
CH_3CCl_3	**1.7 (1.2 - 2.5)[2]**	--	3.3 (3.1 - 4.0)	--	2.118	--	--	--	--	0.18

[1] Emissions of CFC-113 and HFC-365mfc were not derived from our methods, due to lack of correlation with all other species.

[2] Indirectly based on HCFC-22, using the better correlation found with HCFC-141b (for CFC-114), HFC-134a (for HFC-143a), PFC-116 (for PFC-218), CFC-12 (for CH_3CCl_3), respectively, and emissions of these alternate tracers derived through HCFC-22.

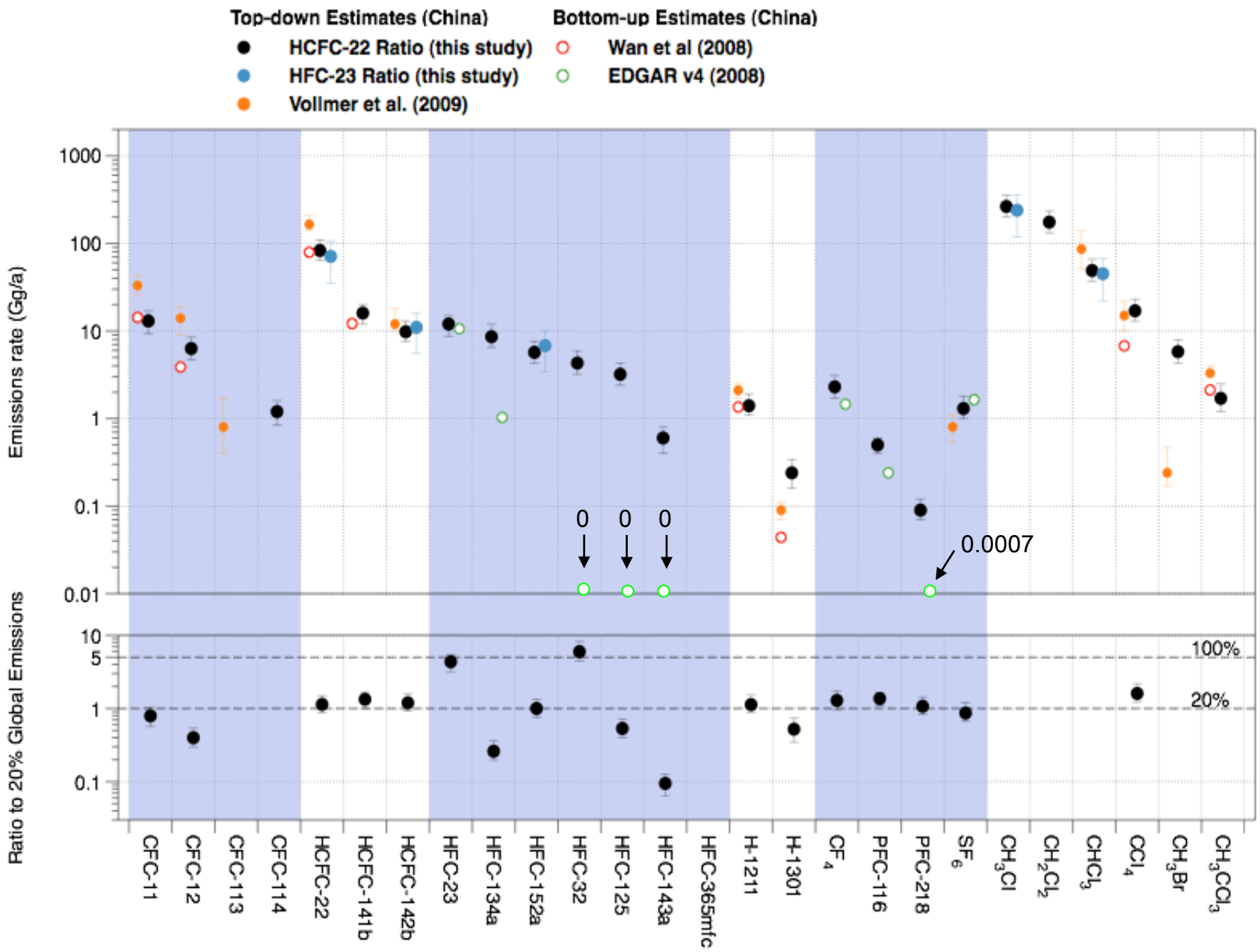
[3] Derived from inversion technique described in the methods

[4] Estimates of 2008 values from linear extrapolation of data available in EDGARv4. Data from year 2000 to 2005 were used except when the linear fit of recent years were significantly different (HFC-365mfc and SF_6, from 2002 to 2005), or longer histories were available (CF4 and PFC-116, from 1990 to 2005)

[5] Determination coefficient against HCFC-22 (or better-correlating species explained in footnote 2) derived in this study.

[5] Determination coefficient against HCFC-22 (or better-correlating species explained in footnote 2) derived in this study.

(Kim et al., GRL 2010)



(Kim et al., GRL 2010)

GEOPHYSICAL RESEARCH LETTERS, VOL. 37, L12801, doi:10.1029/2010GL043263, 2010

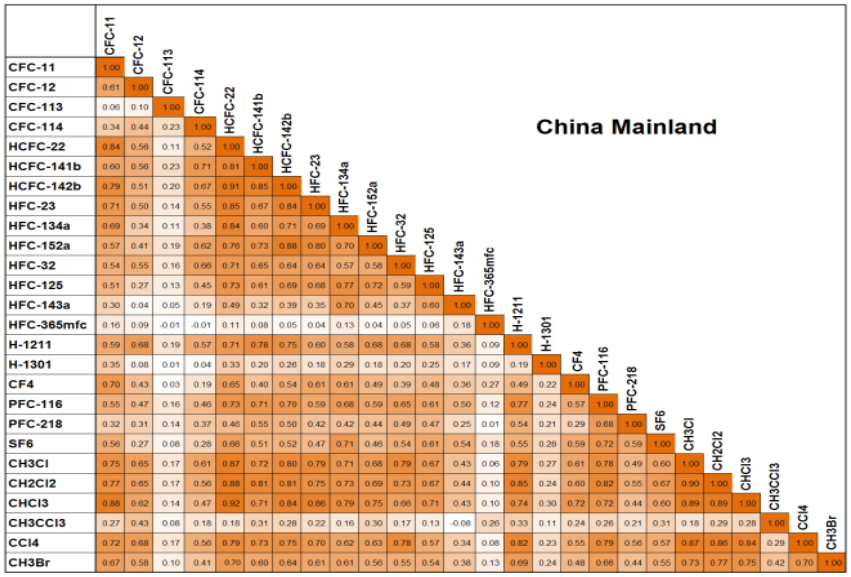
Regional atmospheric emissions determined from measurements at Jeju Island, Korea: Halogenated compounds from China

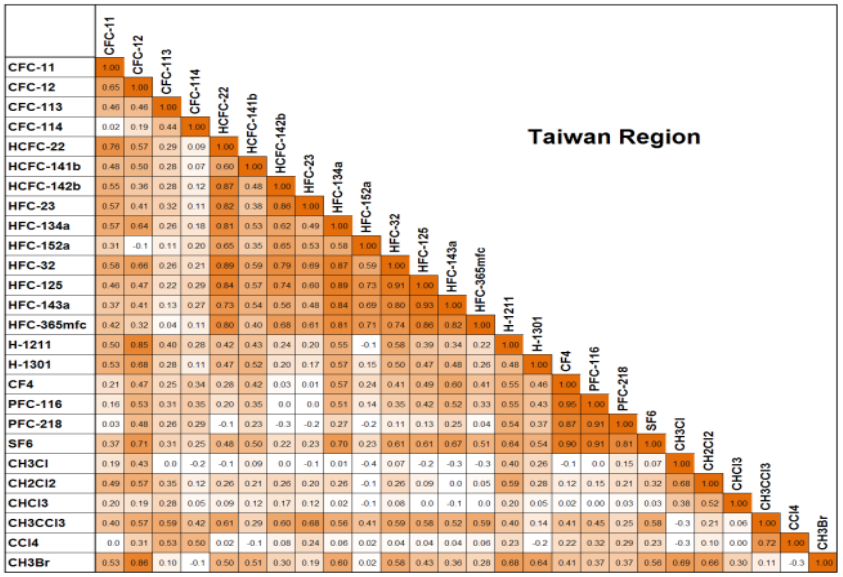
Jooil Kim,[1] Shanlan Li,[1] Kyung-Ryul Kim,[1,2] Andreas Stohl,[3] Jens Mühle,[4] Seung-Kyu Kim,[1] Mi-Kyung Park,[1,2] Dong-Jin Kang,[5] Gangwoong Lee,[6] Christina M. Harth,[4] Peter K. Salameh,[4] and Ray F. Weiss[4]

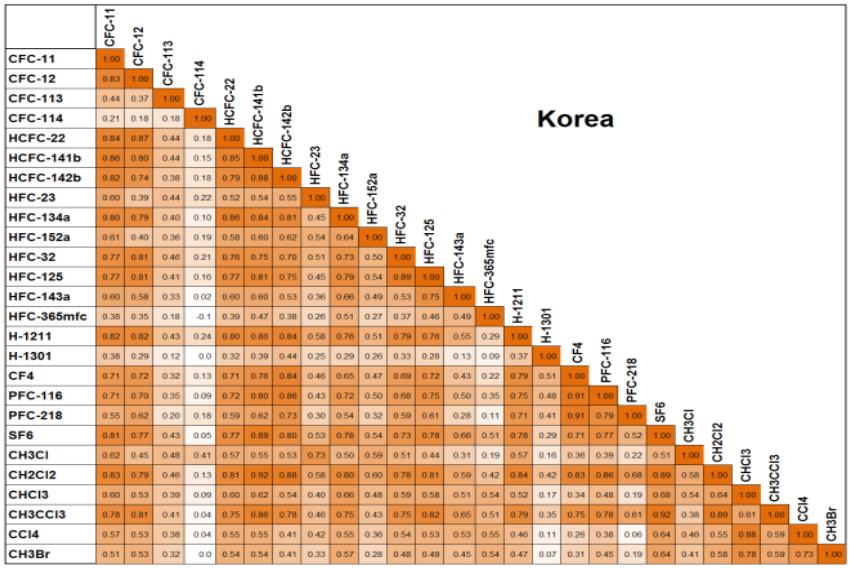
Received 16 March 2010; revised 19 April 2010; accepted 23 April 2010; published 16 June 2010.

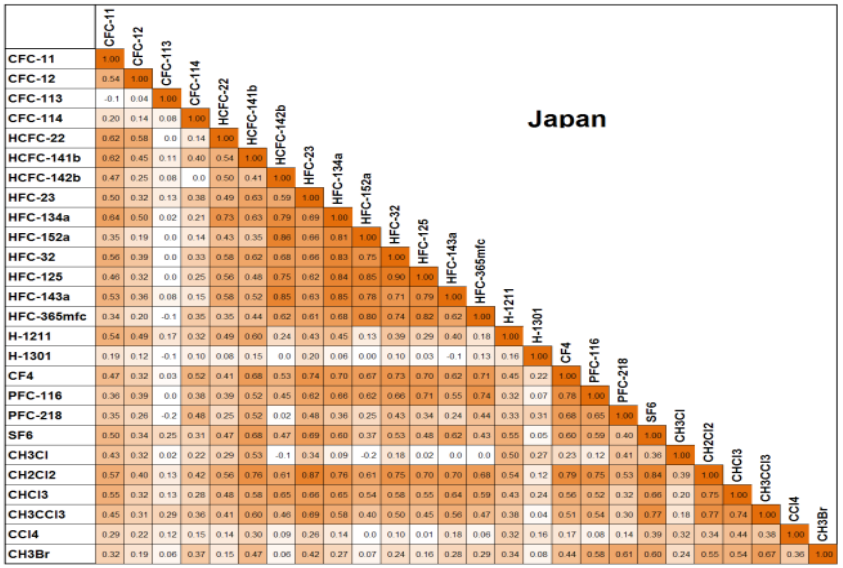
- Comprehensive overview of emissions from China presented for the first time
- Emissions of halogenated compounds from China are now equal to ~20% of global emissions in GWP and ODP.
- Current reported emissions of halogenated compounds may be underestimated
- Large emissions were found for some HFCs not known to be used in China

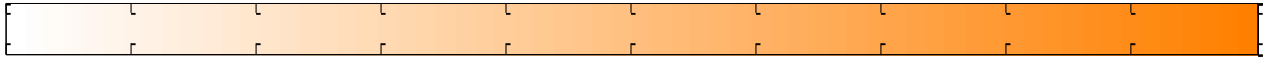
Emission source Characteristics, by Region



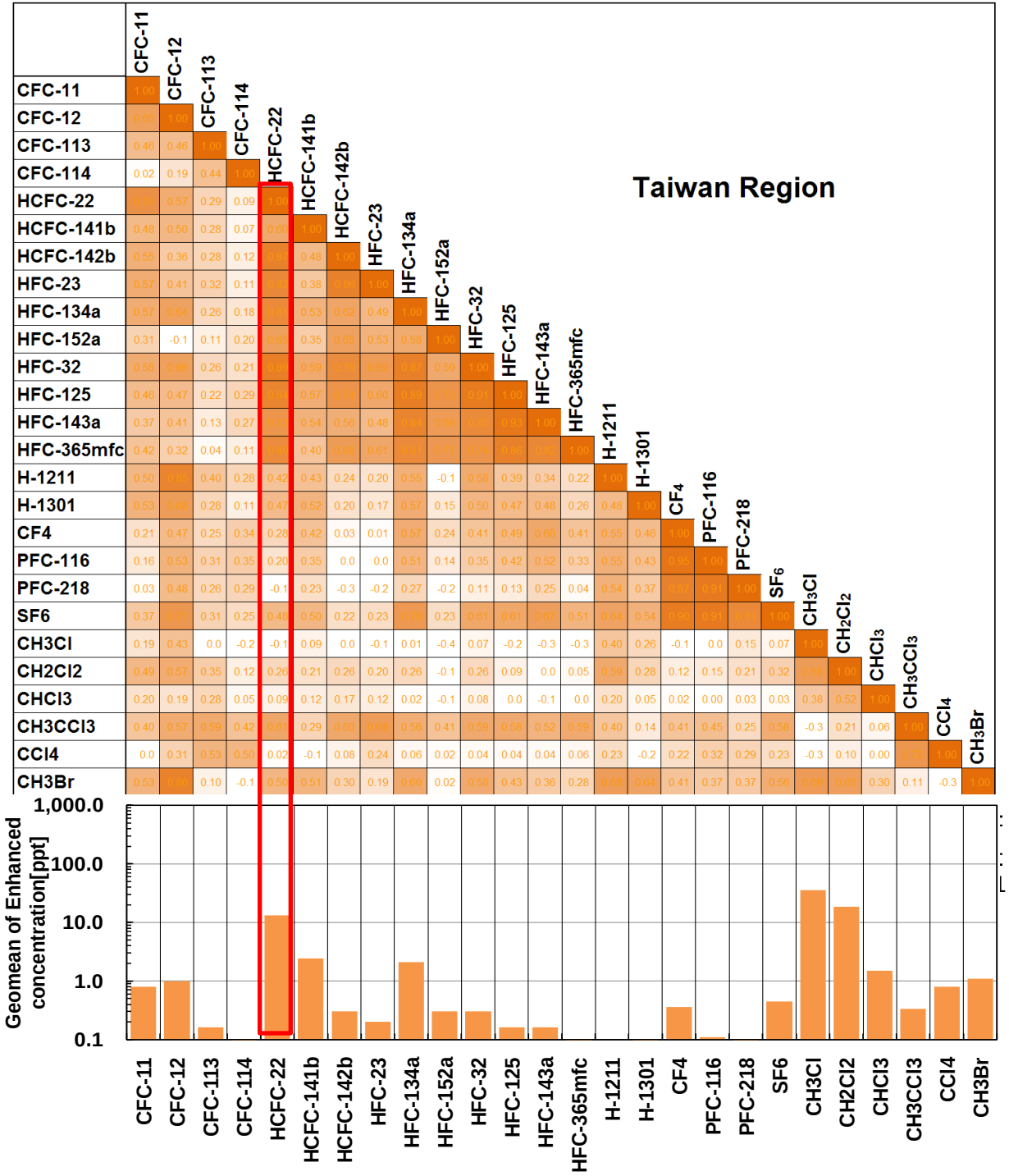






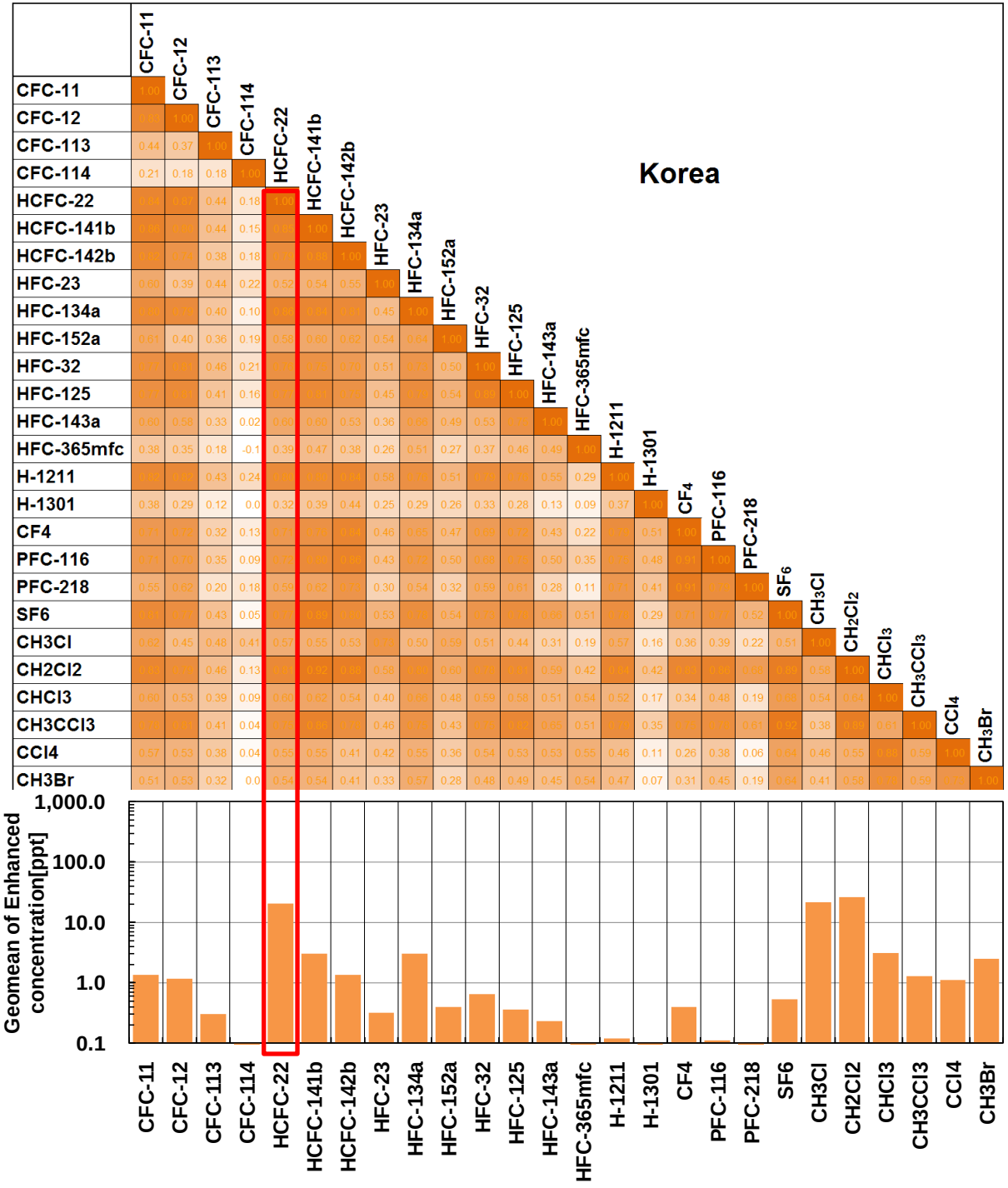


Interspecies Correlation Matrix in Taiwan Region during 2008



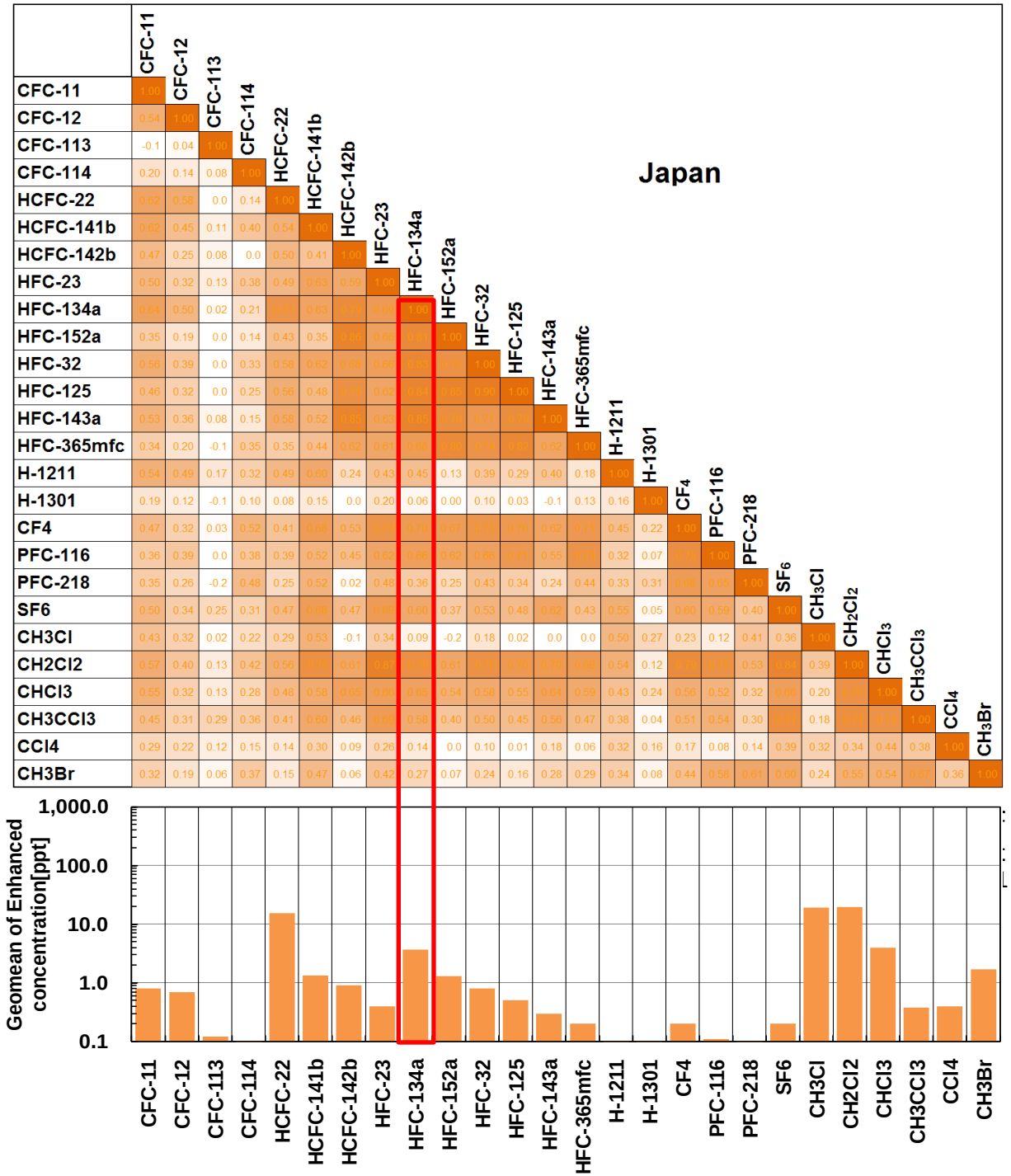
Reference compound:
HCFC-22

Interspecies Correlation Matrix in Korea during 2008



Reference compound: HCFC-22

Interspecies Correlation Matrix in Japan during 2008



Reference compound: HFC-134a

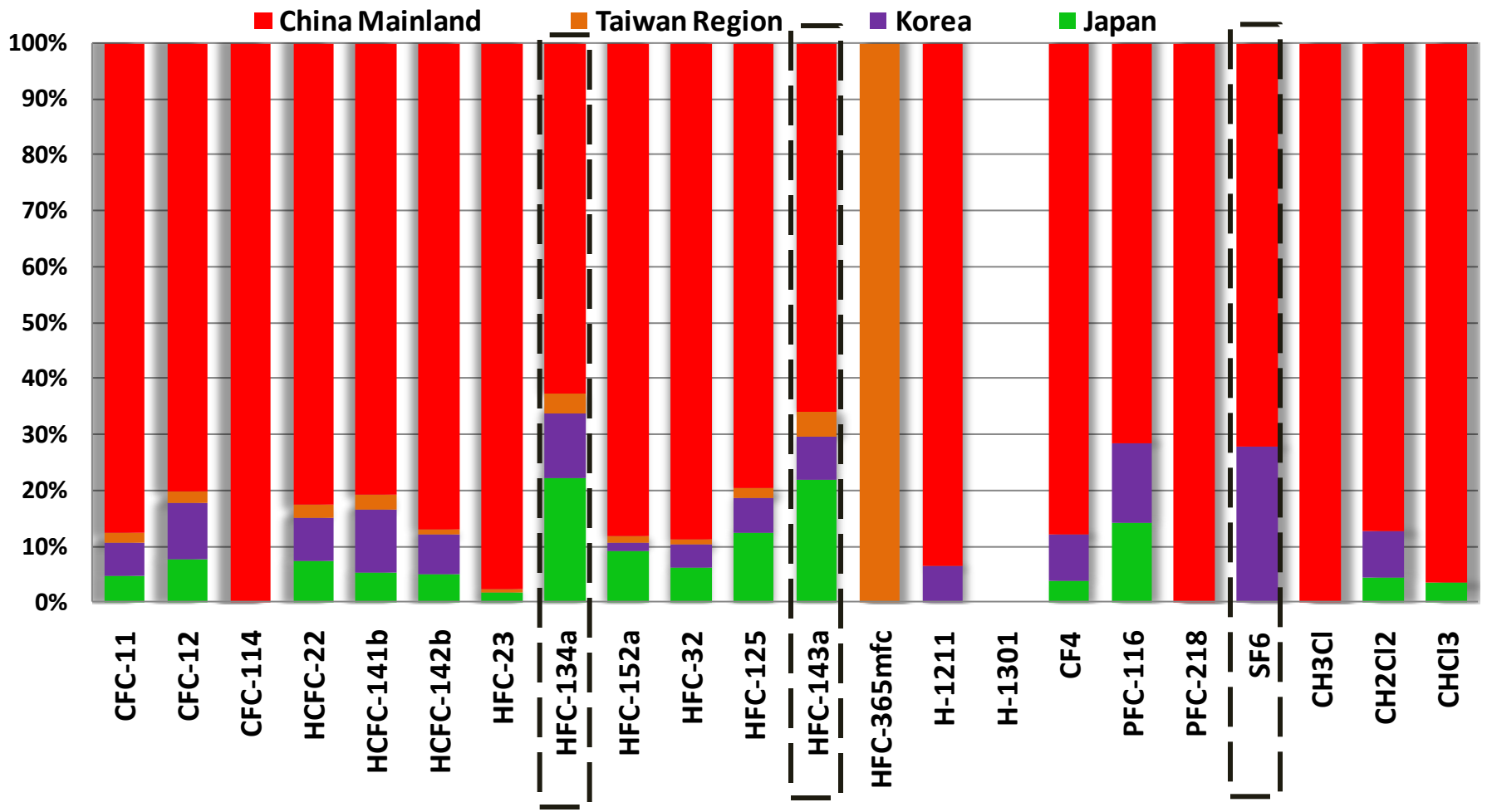
Regional emission rates in East Asian

(Units:Kt/a)

	China Mainland	Taiwan Region	Korea	Japan	Total	to Global(%)
CFC-11	13 (9.3–17)	0.27 ±0.06	0.9 ±0.2	0.7 ±0.05	14.9	18.1
CFC-12	6.3 (4.7–8.5)	0.18 ±0.04	0.8 ±0.2	0.6 ±0.04	7.9	10.0
CFC-114	1.2 (0.8–1.6)				1.2	
HCFC-22	83 (64–109)	2.2 ±0.5	7.9 ±1.5	7.5 (7–8)	100.6	27.6
HCFC-141b	15 (12–20)	0.5 ±0.11	2.1 ±0.4	1 ±0.07	18.6	31.0
HCFC-142b	10 (7.6–13)	0.12 ±0.03	0.8 ±0.1	0.6 ±0.04	11.5	28.1
HFC-23	11 (8.7–15)	0.07 ±0.02		0.2 ±0.01	11.3	81.2
HFC-134a	8.7 (6.5–12)	0.52 ±0.12	1.6 ±0.3	3.1 ±0.2	13.9	8.4
HFC-152a	5.7 (4.3–7.6)	0.08 ±0.02	0.10 ±0.02	0.6 ±0.04	6.5	22.7
HFC-32	4.3 (3.2–5.9)	0.05 ±0.01	0.20 ±0.04	0.3 ±0.02	4.9	134.7
HFC-125	3.2 (2.4–4.3)	0.07 ±0.02	0.26 ±0.05	0.5 ±0.03	4.0	13.4
HFC-143a	0.6 (0.4–0.8)	0.04 ±0.01	0.07 ±0.01	0.2 ±0.01	0.9	2.9
HFC-365mfc		0.01 ±0.003				
H-1211	1.4 (1.1–1.9)		0.1 ±0.02			
H-1301						
CF4	2.2 (1.7–3.1)		0.21 ±0.04	0.1 ±0.01		
PFC-116	0.5 (0.4–0.6)		0.1 ±0.02	0.1 ±0.01		
PFC-218	0.09 (0.07–0.12)					
SF6	1.3 (1.0–1.8)		0.5 ±0.1			
CH3Cl	265 (200–354)					
CH2Cl2	176 (132–234)		16.8 ±3.2	9.2 ±0.6		
CHCl3	49 (37–66)			1.8 ±0.1		
CH3CCl3	1.7 (1.2–2.5)	0.13 ±0.03	1.4 ±0.3	0.4 ±0.02	3.6	
CCl4	17 (13–23)					
CH3Br	5.8 (4.3–7.9)					
Per group						
CFCs	20.5	0.45	1.7	1.3	24.0	14.4
HCFCs	108	2.82	10.8	9.1	130.7	28.1
HFCs	33.5	0.84	2.2	4.9	41.5	15.5
PFCs	2.8		0.3	0.2	3.3	
Total	165	4.11	15.0	15.5	199.4	22.2

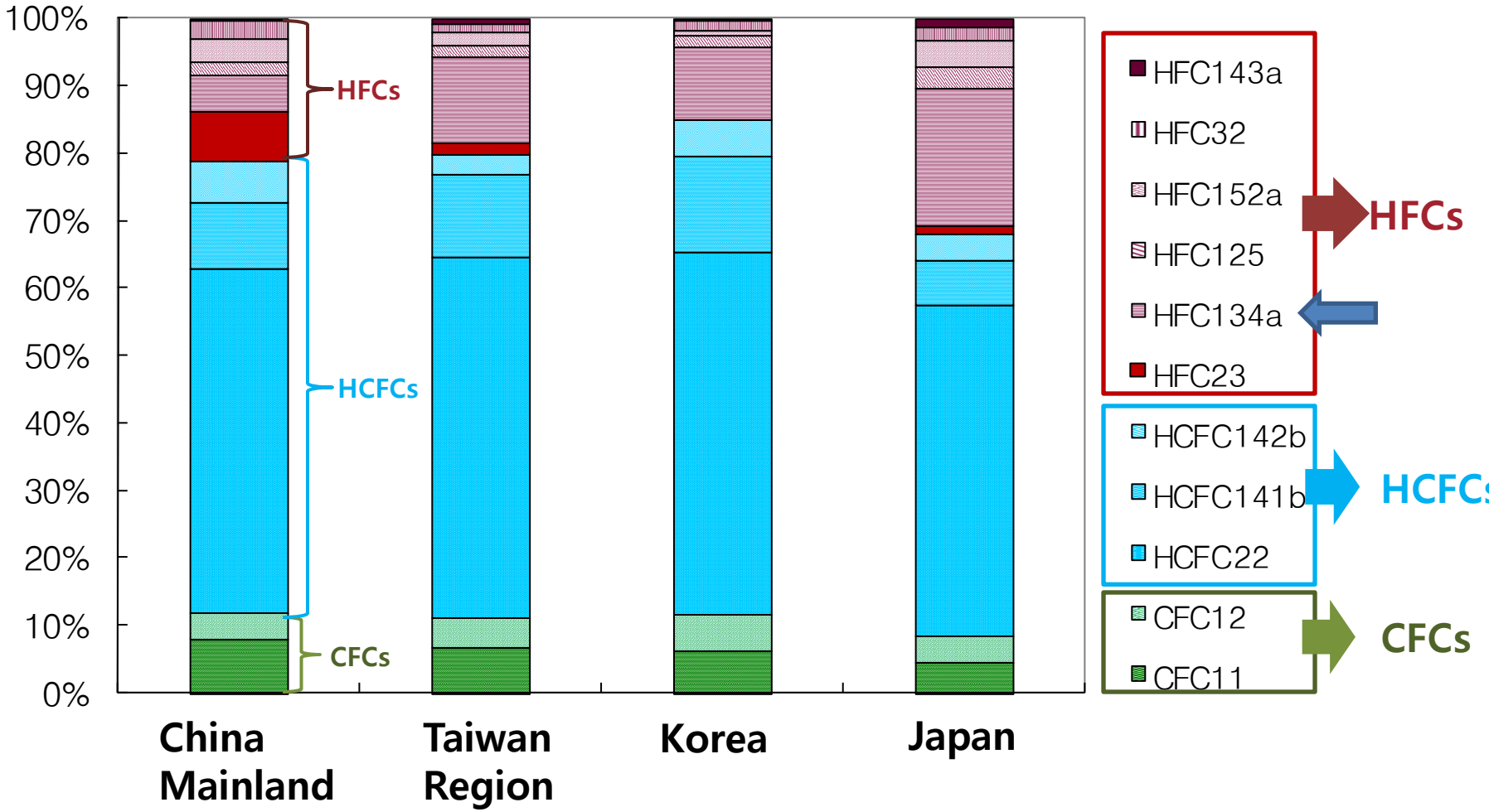
* Red: Reference tracer emission data from Stohl et al (2010)

Relative Emissions in East Asia, by Compound



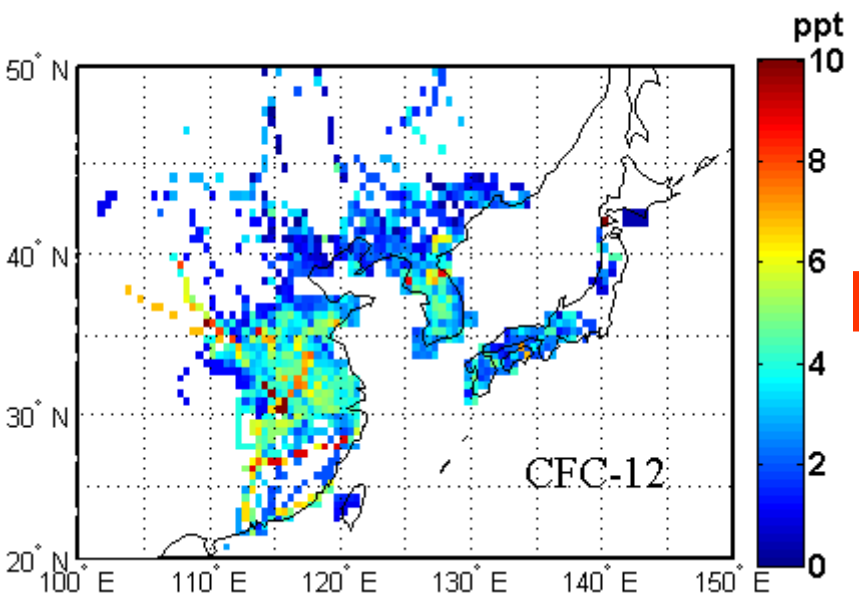
Relative Emissions in East Asia, by Region

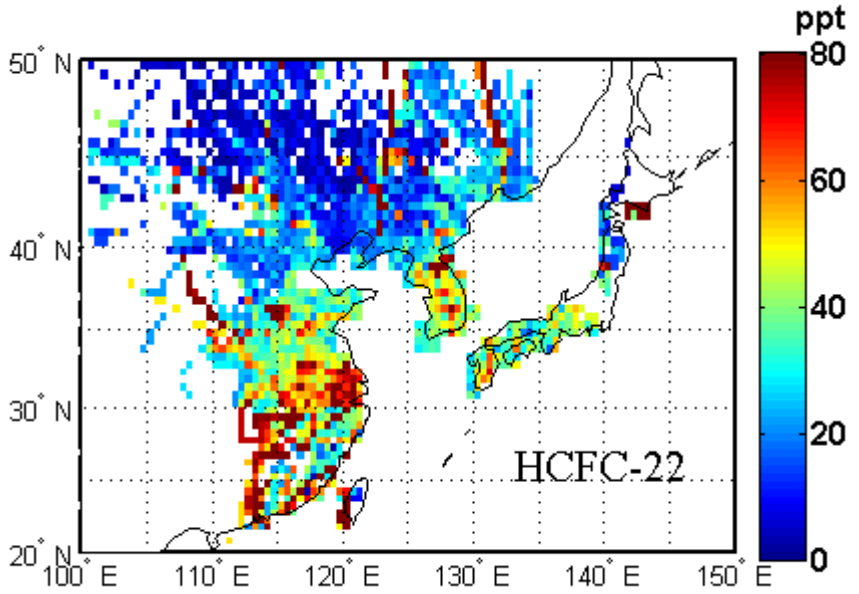
CFCs, HCFCs, and HFCs

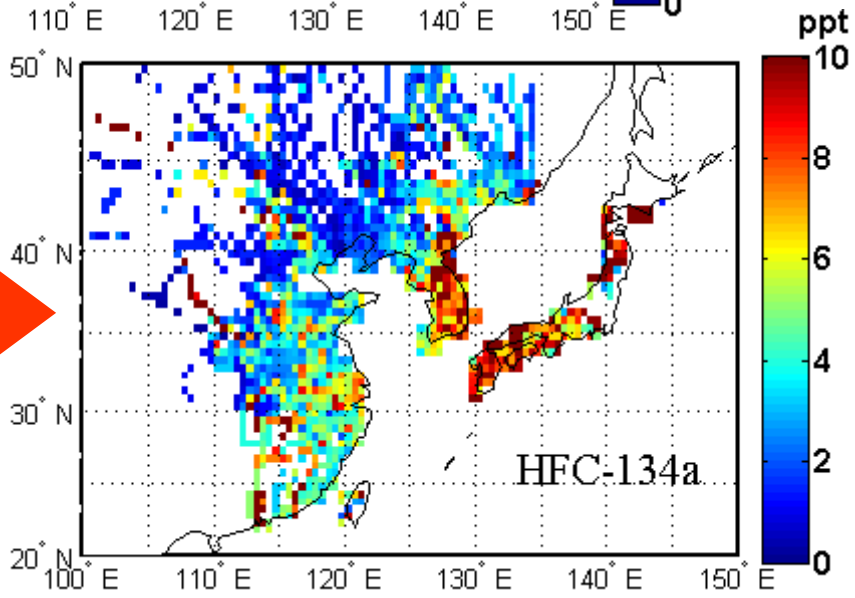


Emission Source region of Refrigeration

Nov.2007~ Nov. 2008







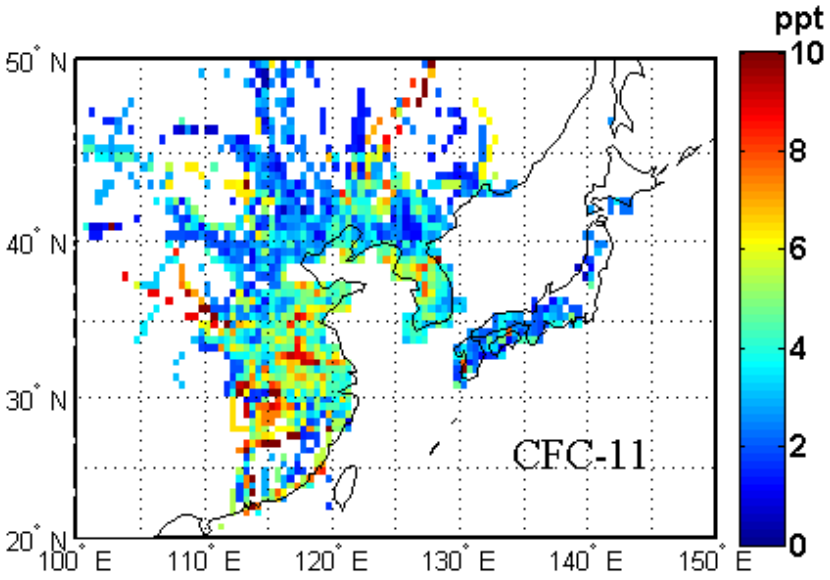
Refrigeration:

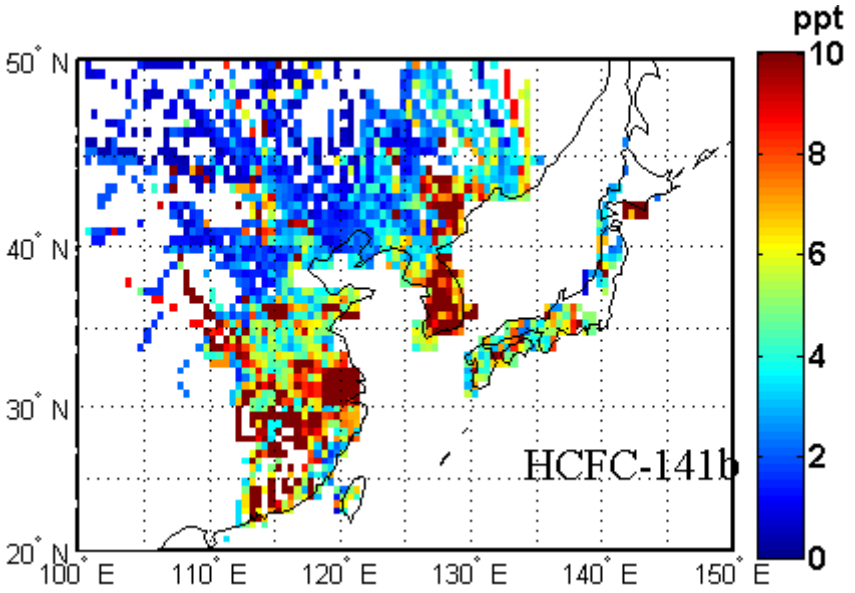
CFC-12 have been completed in Japan

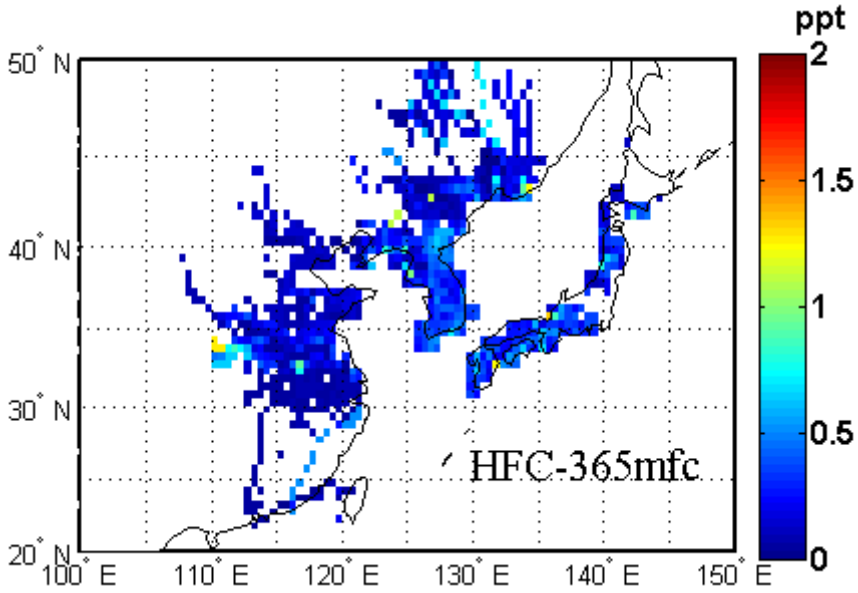
HCFC-22 are widely used in East Asia

HFC-134a are mainly used in Korea, Japan

Emission Source Region of Foam blowing







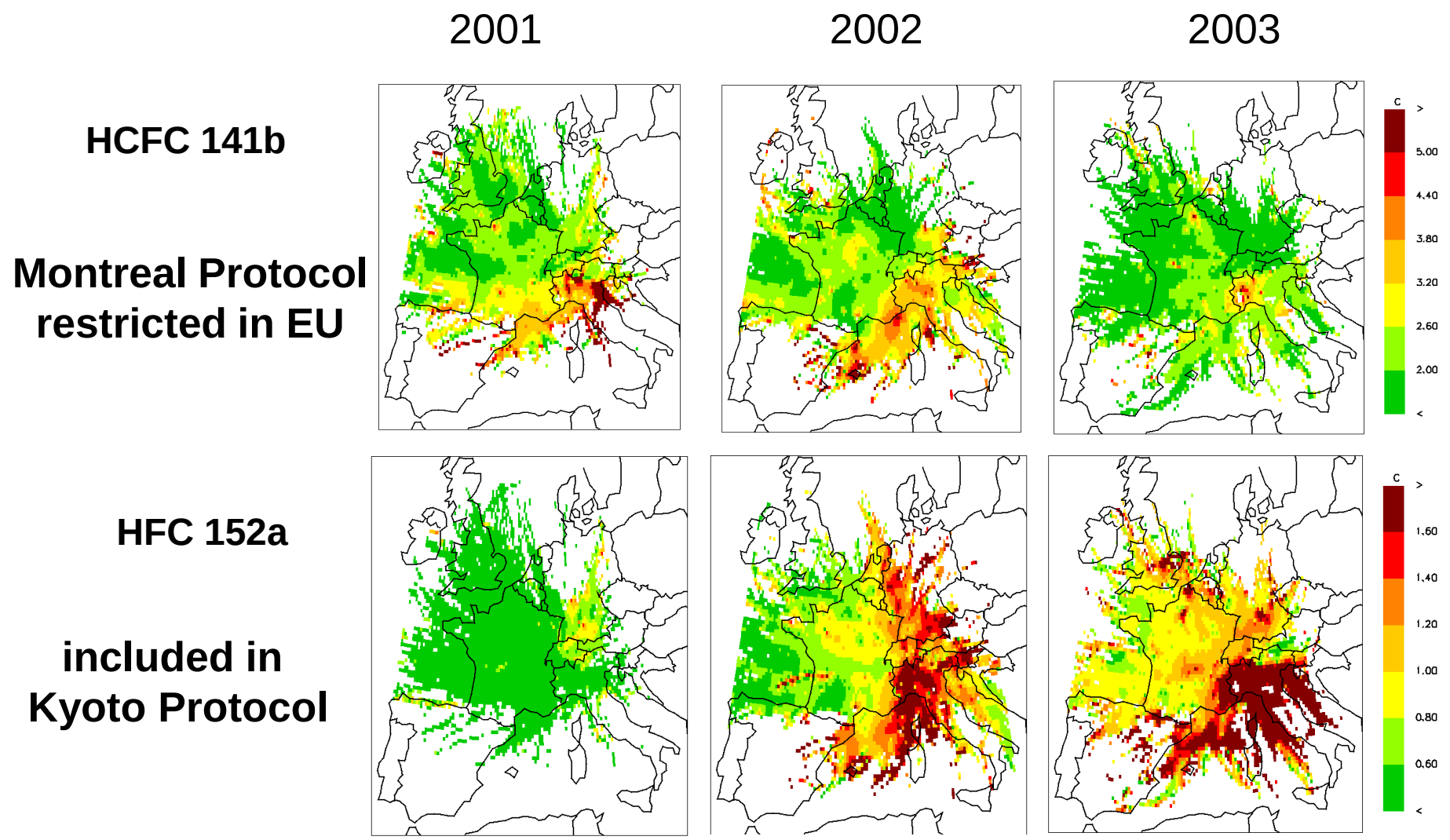
Foam blowing:

CFC-11:still used in China, Korea.

HCFC-141b: widely used in East Asia

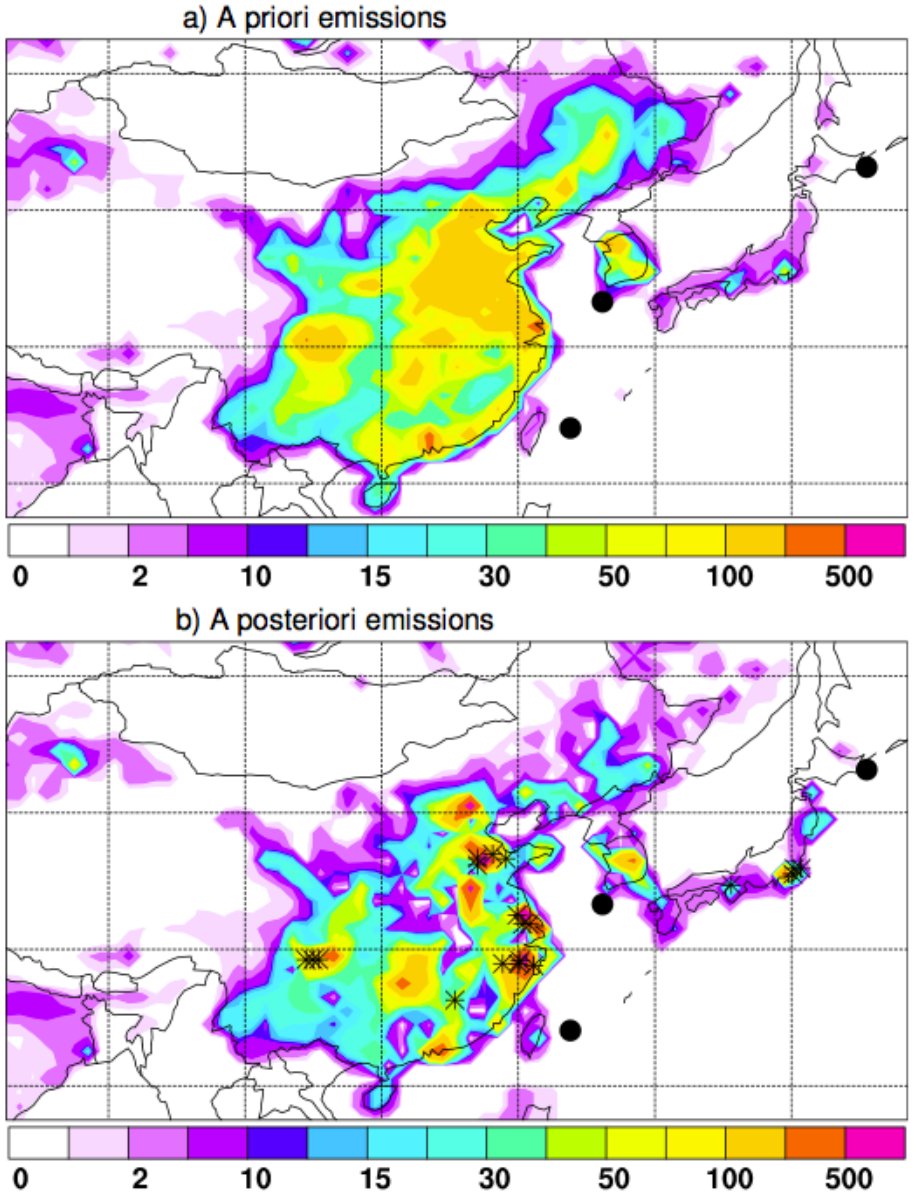
HFC-365mfc:not used in East Asia

Emission flux modeling: Jungfraujoch



HFC-23 emissions modeling:

Identification of ‘local’ sources from HCFC-22 production ?



(Stohl et al, ACP 2010)

Conclusion

Top-down estimates were performed using high-precision/high-frequency in-situ measurements at Gosan (Jeju Island, Korea) as part of AGAGE (Advanced Global Atmospheric Gases Experiment).

HCFC-22 was selected as primary tracers for deriving emissions of almost all major anthropogenic halogenated compounds in China, (Korea, Taiwan) confirming substantial Eastasian, in particular Chinese, contributions to global emissions of halogenated compounds.

Our results for Chinese emissions of some HFCs and PFCs suggest significant underestimation in current bottom-up assessments.

Top-down emission estimates should serve an important tool monitoring and diagnosing bottom-up assessment of internationally regulated compounds (even in 'local' scale?).

Thank you!

With co-workers:

Korea : Mi-kyung Park, Jooil Kim, Shanlan Li, Dong-jin Kang, Seung-kyu Kim (SNU), Kangwoong Lee(HUFS), Kyung-sik Kang (Jeju Univ.)

USA : Ray F. Weiss, Jens Muhle, Christina Harth, Peter Salameh (SIO, UC San Diego)

Norway : Andreas Stohl (NILU)

China : Lingxi Zhou, Bo Yao (CAMS, CMA), Dan Wan (Peking Univ.)

Japan : Yoko Yokouchi (NIES)