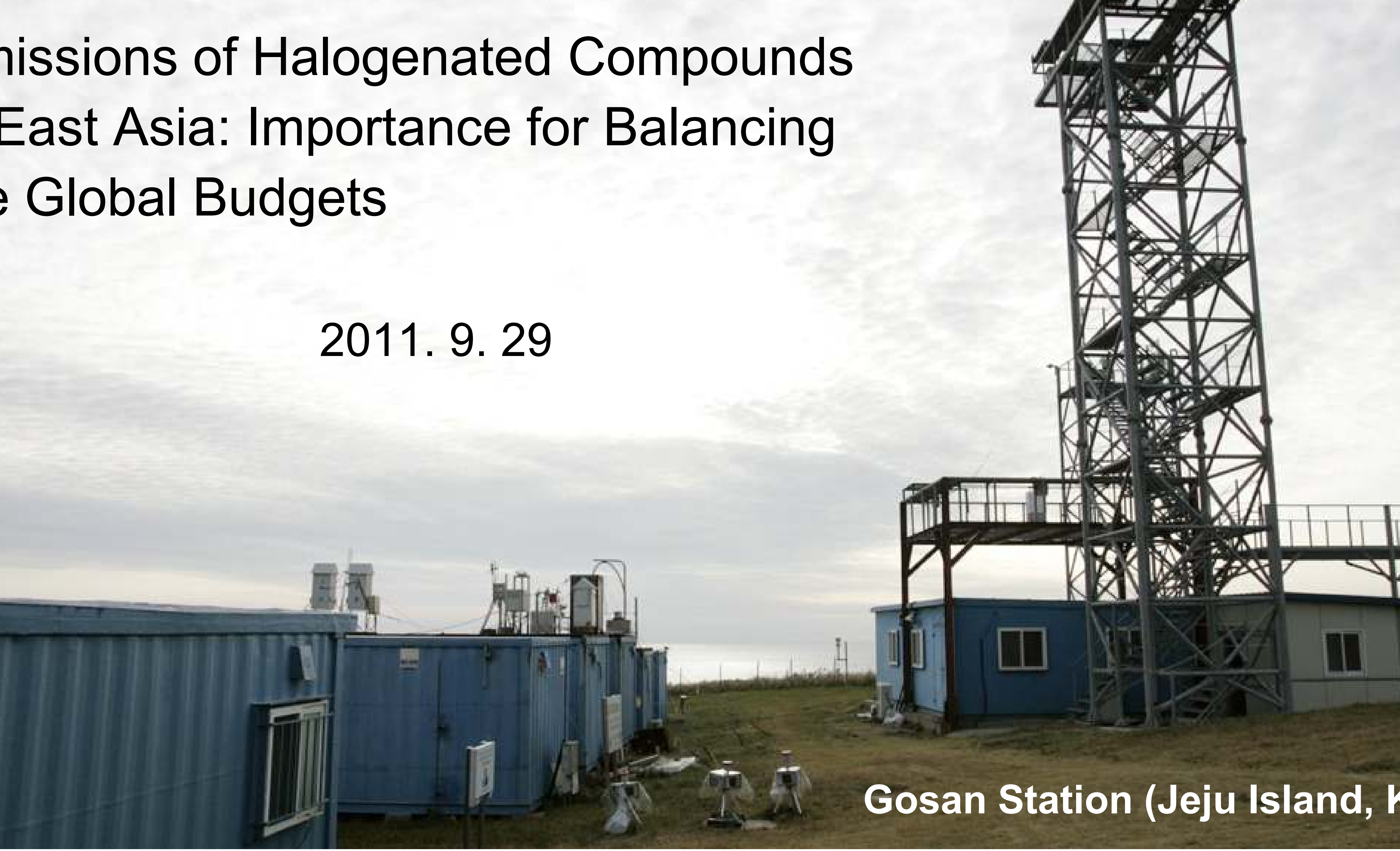
nissions of Halogenated Compounds East Asia: Importance for Balancing e Global Budgets

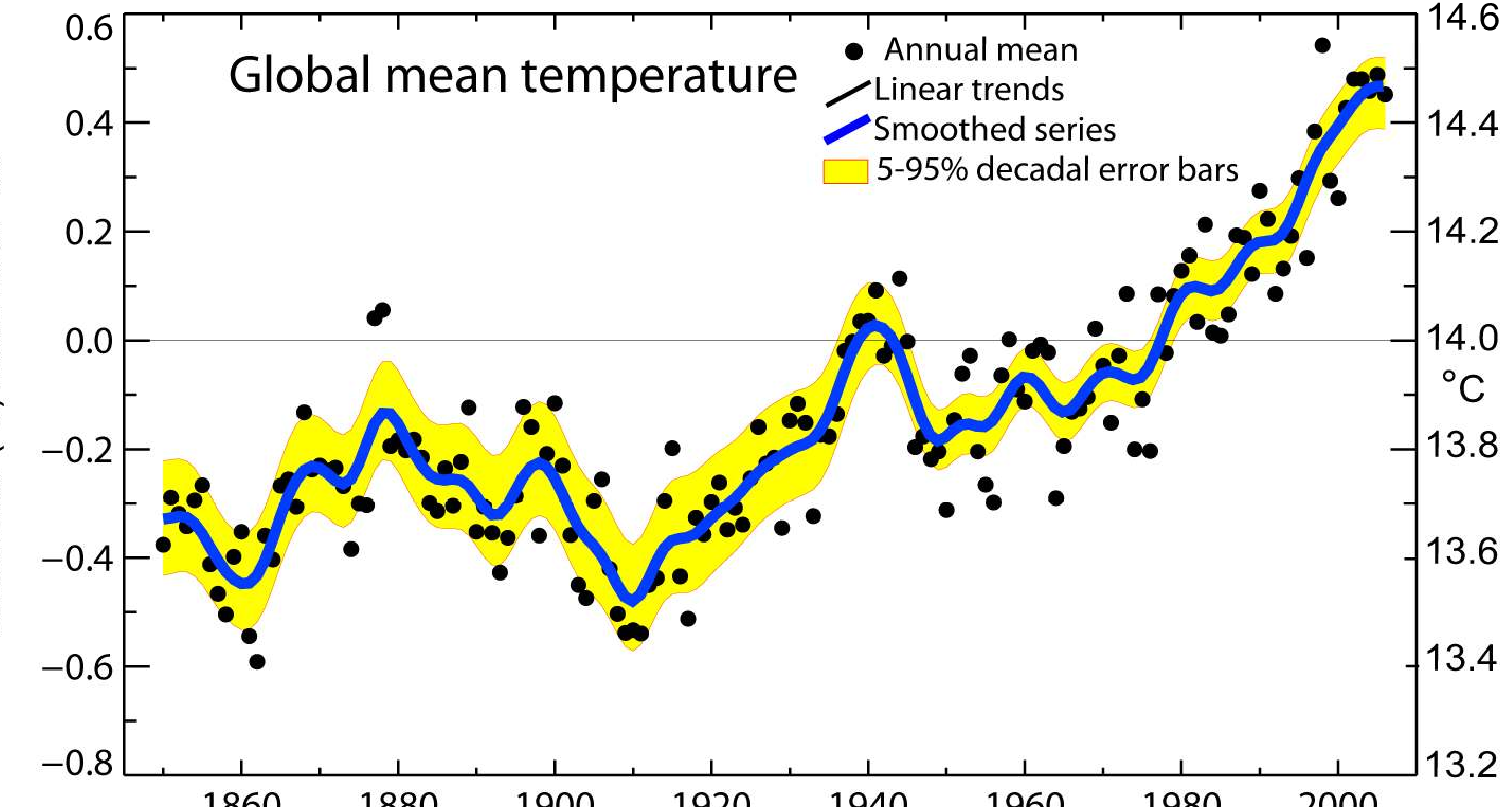
2011. 9. 29



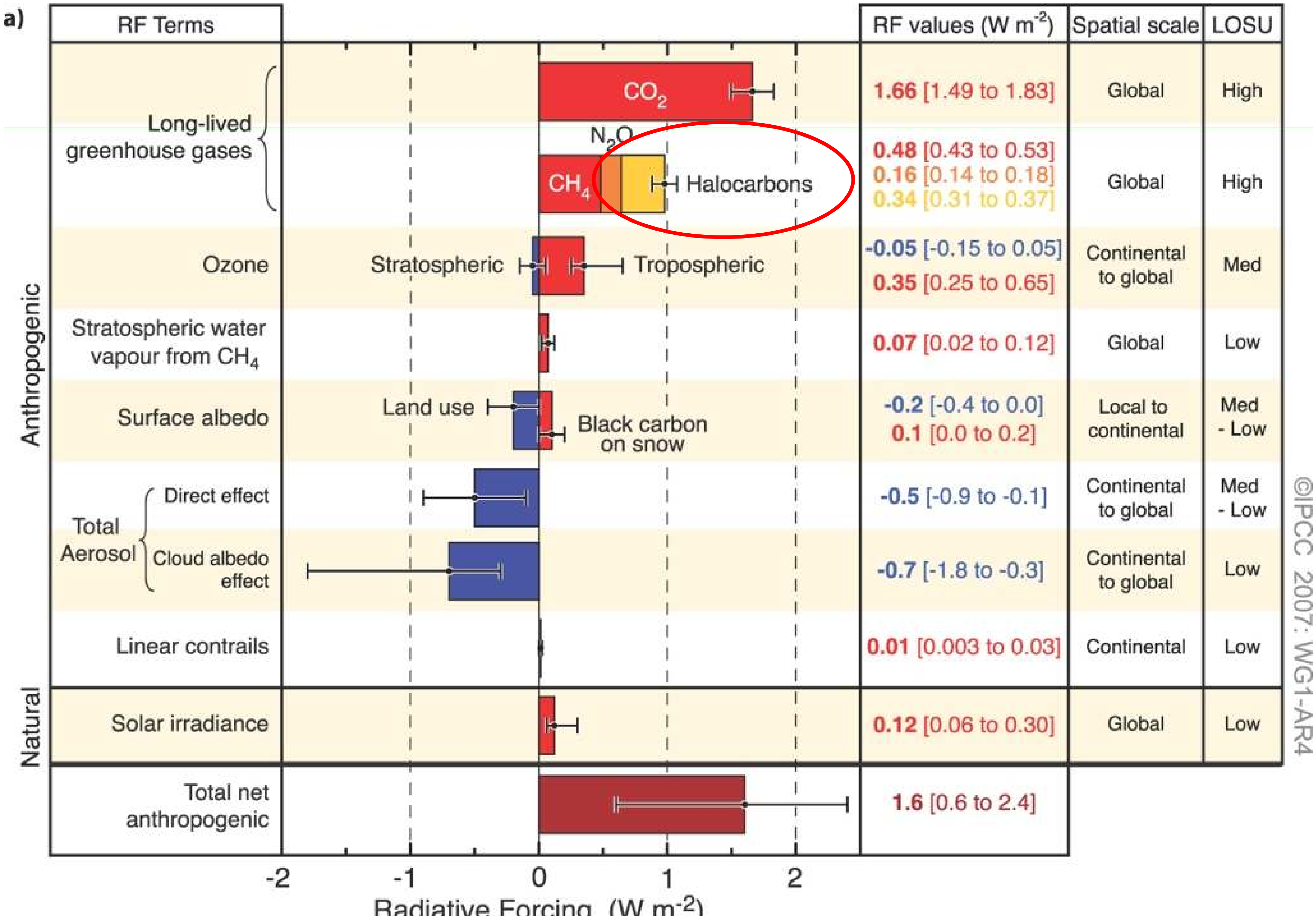
Gosan Station (Jeju Island, K

Kyung Ryul Kim
School of Earth and Environmental Sciences

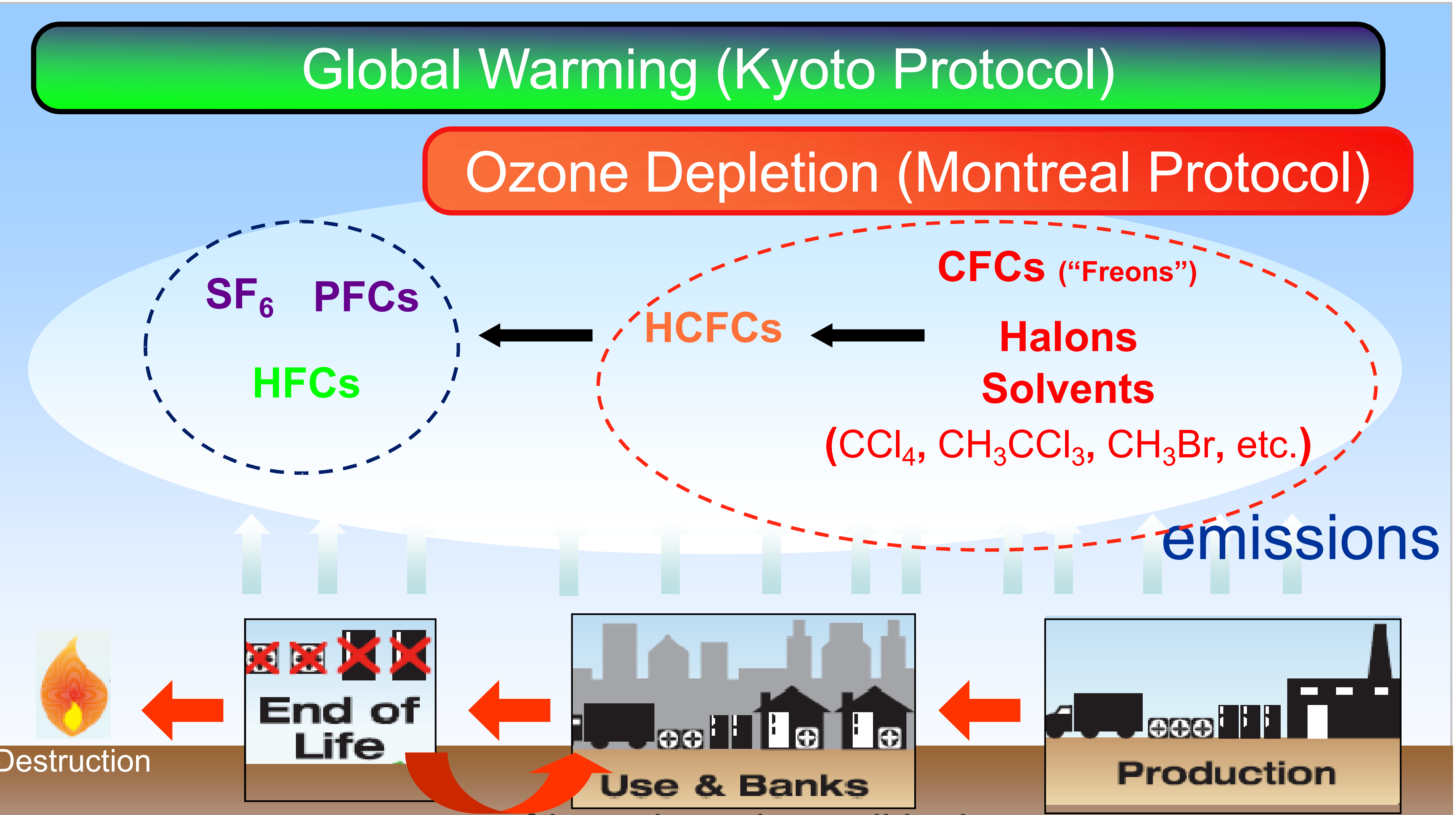
CC 4th Report: Global Warming is Real !



reenhouse Gases and Climate Change



portance of Halogenated Compounds



: refrigeration, air conditioning,
foam blowing, aerosol repellent,

an made ultra trace greenhouse gases
lontreal 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 tetrachloric

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:

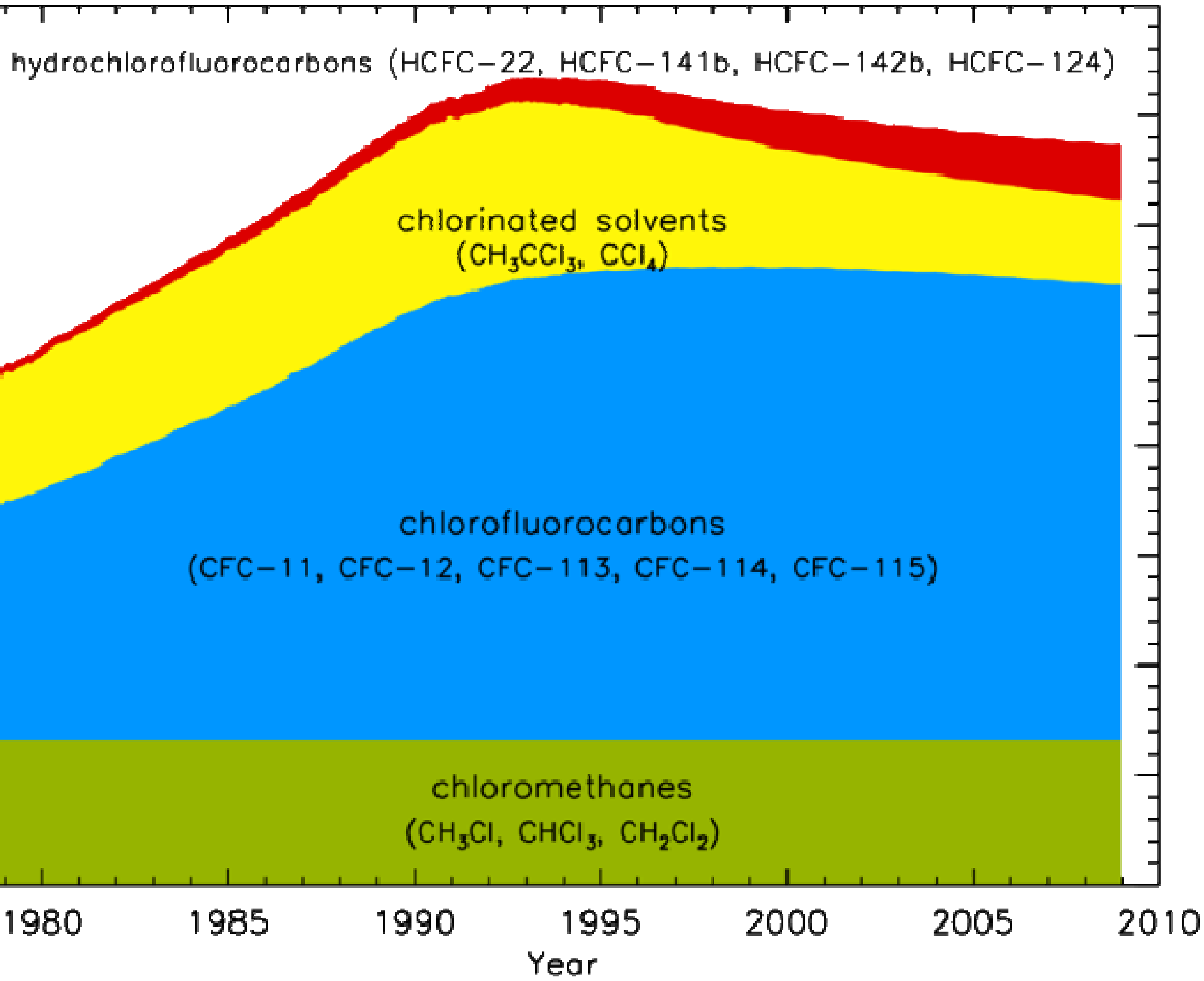
sulphur hexafluoride(SF_6), perfluoromethane, perfluoroethane, perfluoropropa

lobal Warming Threat of Halocarbons

pound egory	Compound Name	Lifetime(years)	Global Warming Potential (100yr CO_2-eq)
	Hydroflurorcarbons (HFCs)		
FCs	HFC-134a	14	1,430
	HFC-152a	1.4	124
	HFC-23	270	14,800
	HFC-32	4.9	675
	HFC-125	29	3,500
	HFC-143a	52	4,470
	Perfluroinated Compounds (PFCs)		
s, SF6	PFC-14 (CF_4)	50,000	7,390
	PFC-116 (C_2F_6)	10,000	12,200
	PFC-218 (C_3F_8)	2,600	8,830
	[illegible]	[illegible]	[illegible]

- Many AHCs are powerful greenhou gases (GHGs) regulated under th Kyoto Protocol
- Some species add almost a permane radiative burden o the atmosphere
- Previously emitted from developed countries, now increasing in

ontreal Protocol for Protecting the Ozone ayer



- Montreal Protocol has been successful in stabilizing the concentrations of ozon depleting AHCs in the atmosphere
  - Developed countrie complete phase-out
  - Developing countrie continued use of interim replacement (HCFCs)

missions of Halocarbons in East Asia

Article 5" (developing) country status under the MP (CN, KR):

- slower phase-out of CFCs, CH_3CCl_3
- dominant consumer/emitter of interim HCFCs (Montzka et al., 2009, *GR*

missions from industrial production:

- HFC-23: during HCFC-22 production (CN)
- PFCs: during primary aluminum production (CN) and semiconductor manufacture (KR, JP, TWN)

espite importance of emissions in East Asia, actual knowledge of emissio

ey Study Focus

nderstanding the emissions of halogenated compound in East Asi

- Based on accurate, high-frequency measurements encompassing all of East Asia

- Development of various methods for quantifying regional emissions

- Analyzing emission patterns, characteristics

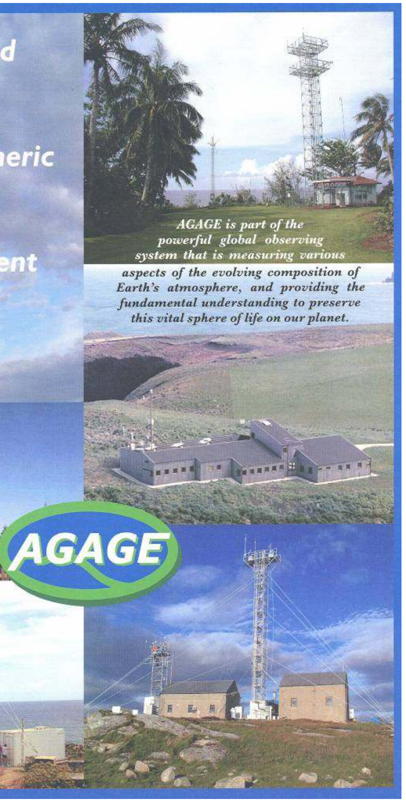
- Identifying East Asia’s role in the global budgets of halogenated compounds t 1. Measurements of GHGs at Gosan

AGE Network: (Advanced Global Atmospheric Gases

eriment) 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

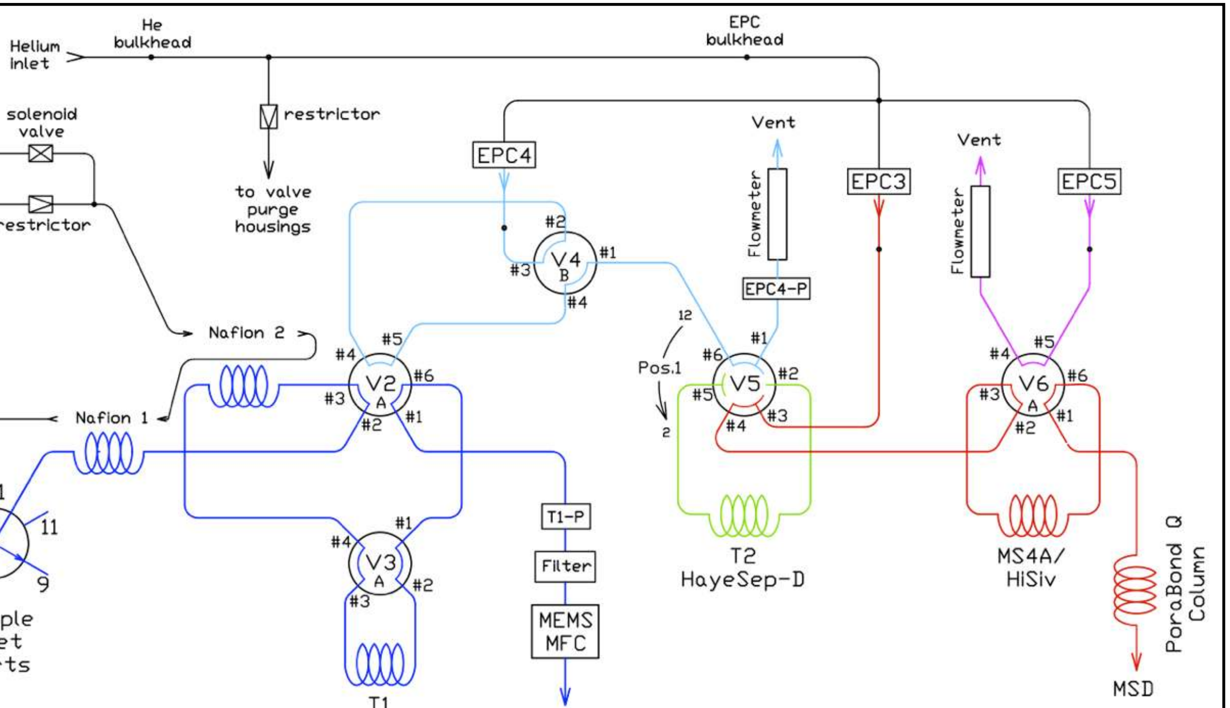
Montreal Protocol to protect the ozone layer an

almost all of the significant non-CO_2 gases in

the Kyoto Protocol to mitigate climate change."

(AGAGE brochure)

alogenated Species Measurements



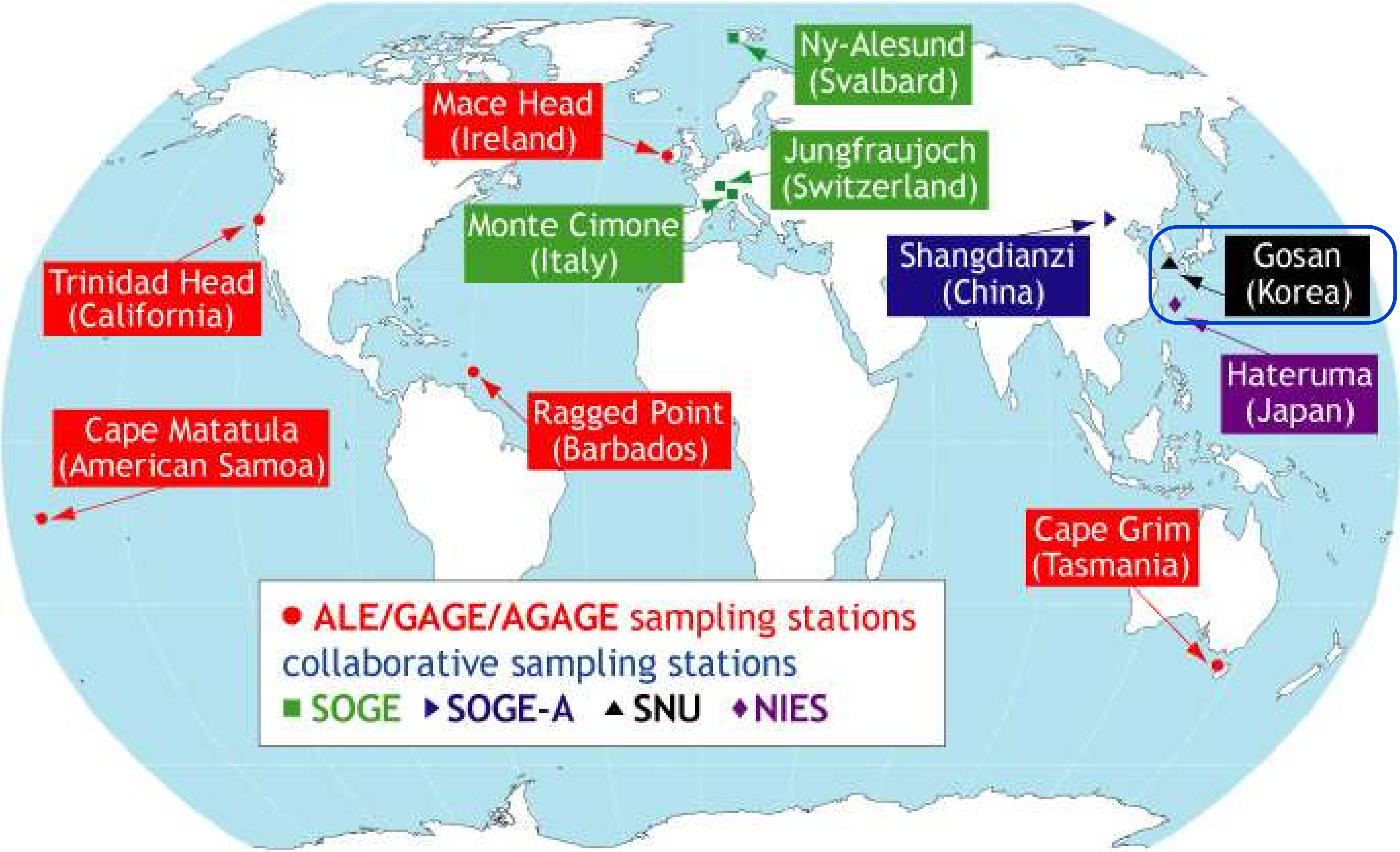
- Medusa GC-MS ('07~)
  - Developed by R. F. Weiss (SIO, UC San Diego)
  - Fully automated using custo HW/SW
  - 2L sampling, 2hr inverval
  - Cryofocusing module, combined with GC-MSD
  - Operated under the **AGAGE Network**

alogenated Species Measurements

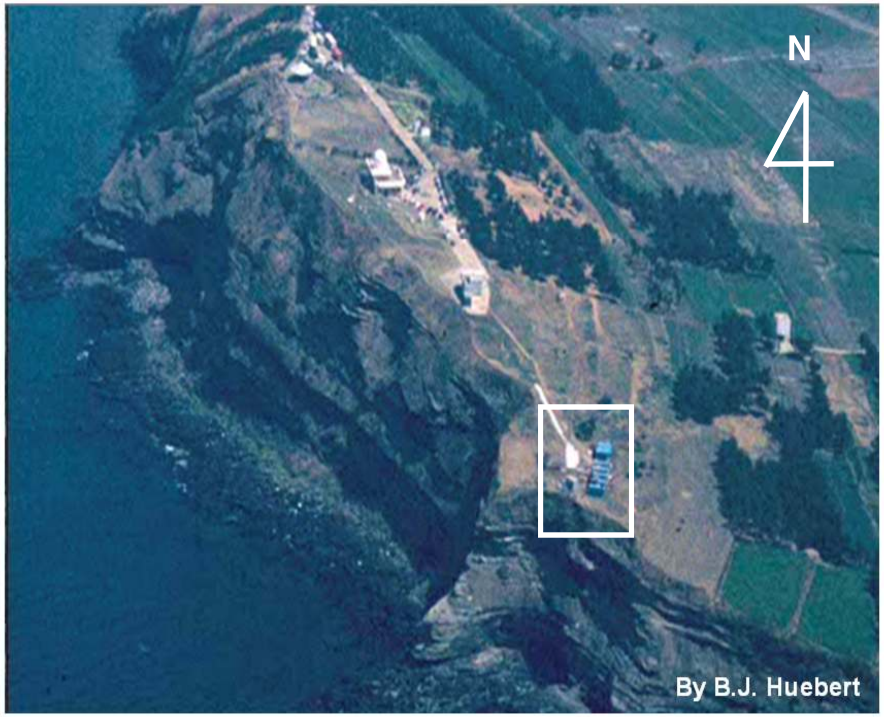
Compound	~NH (2005) (ppt)	Typical % precision
CF4	74	0.15
HFC23	25	0.7
C2F6	3.5	0.9
C3F8	0.5	3
HFC32	~1	5
SF6	5.3	0.4
SO2F2	1	1.6
HFC134a	29	0.4
HFC152a	4.2	1.2
HFC125	2.9	1
HFC143a	6.5	1.2
HFC365mfc	<1	10
HCFC22	170	0.3
HCFC141b	19	0.4
HCFC142b	15	0.6
HCFC124	1.6	2
CFC11	257	0.15
CFC12	546	0.05
CFC13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

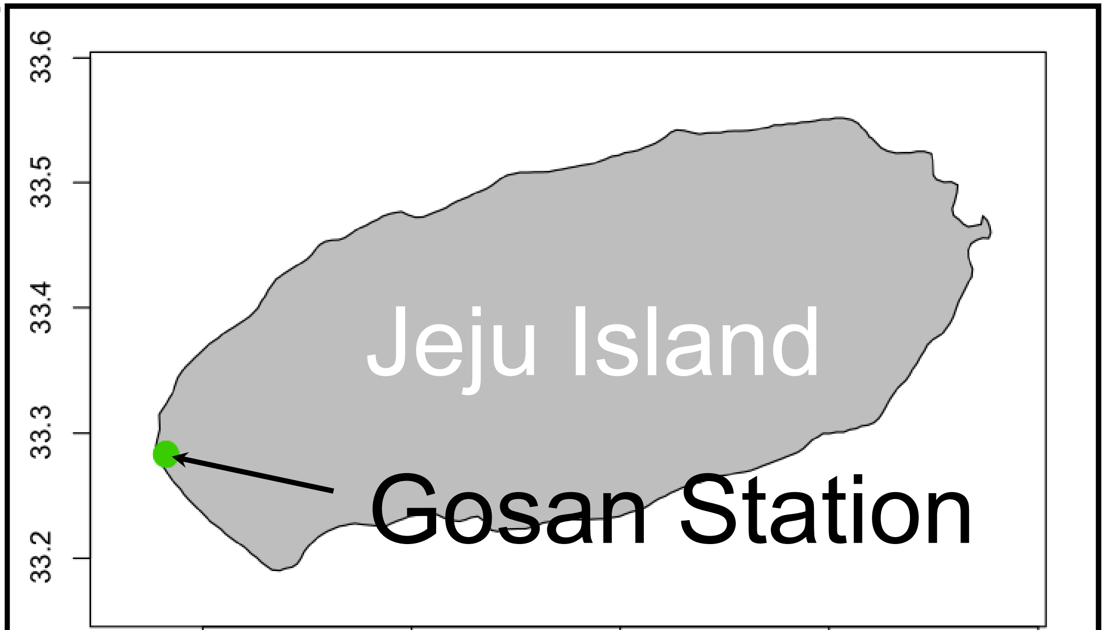
Compound	~NH (2005) (ppt)	Typical % precision
H1301	3.1	1.5
H1211	4.5	0.5
H2402	>0.5	2
CH3Cl	570	0.2
CH3Br	10	0.5
CH3I	1	2
CH2Cl2	36	0.8
CHCl3	11	0.6
CHBr3	~3	0.6
CCl4	95	1
CH3CCl3	28	1
CHClCCl2	0.8	2.5
CCl2CCl2	5.5	0.5
C2H2	10-200	0.5
C2H4	50-500	2
C2H6	500	0.3
C6H6	10-100	0.3
C7H8	<1-10	0.6

GAGE network

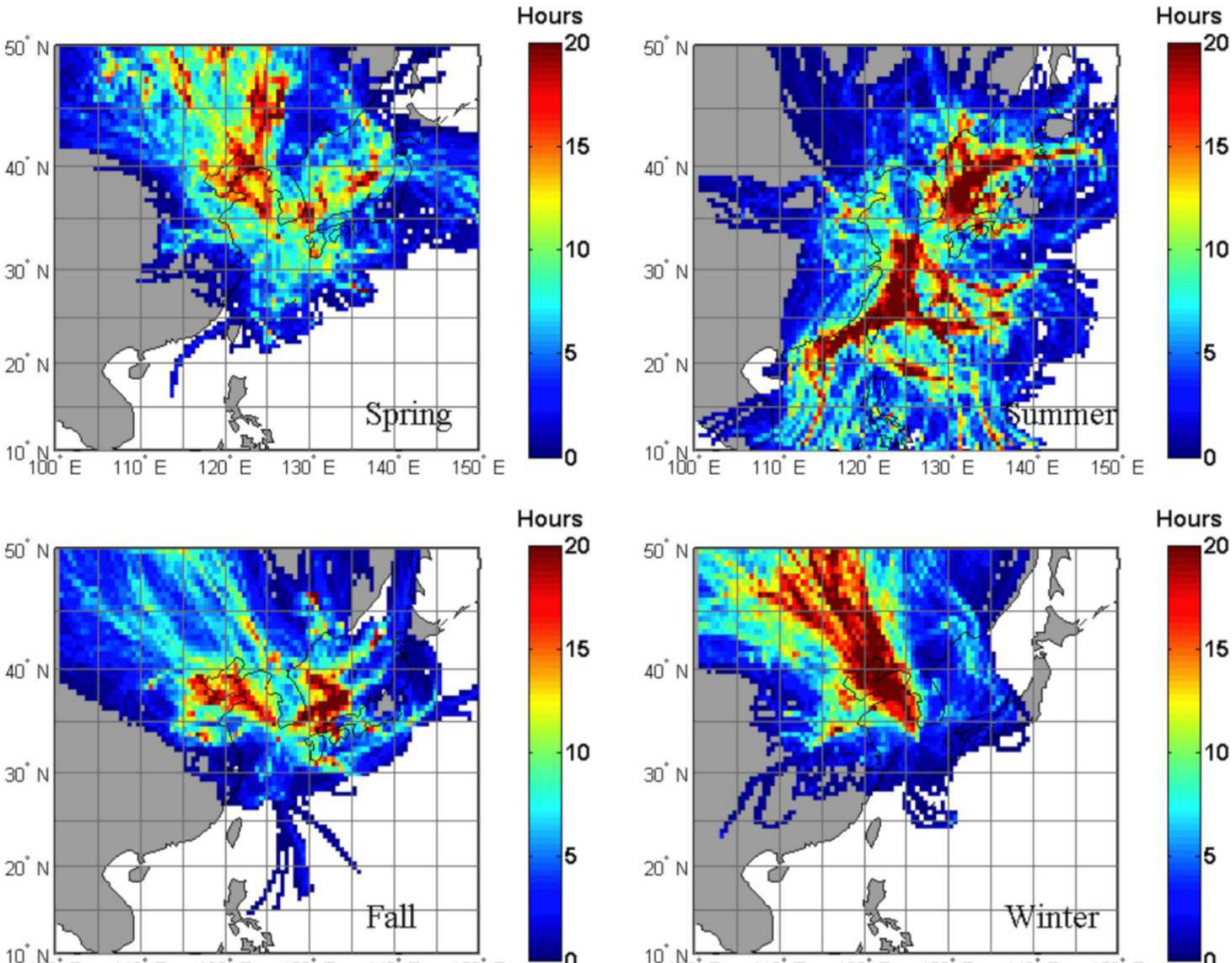


Gosan Station (Jeju Island, Korea)

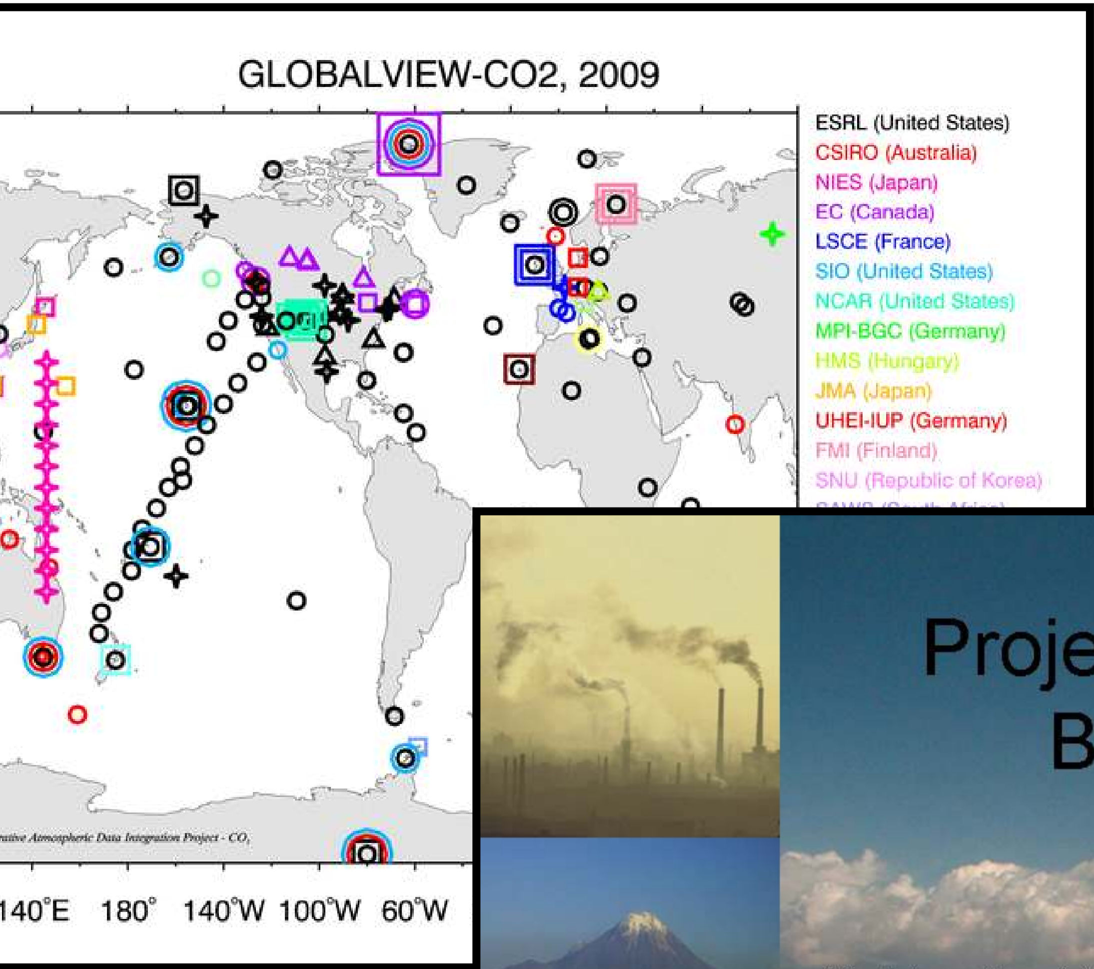


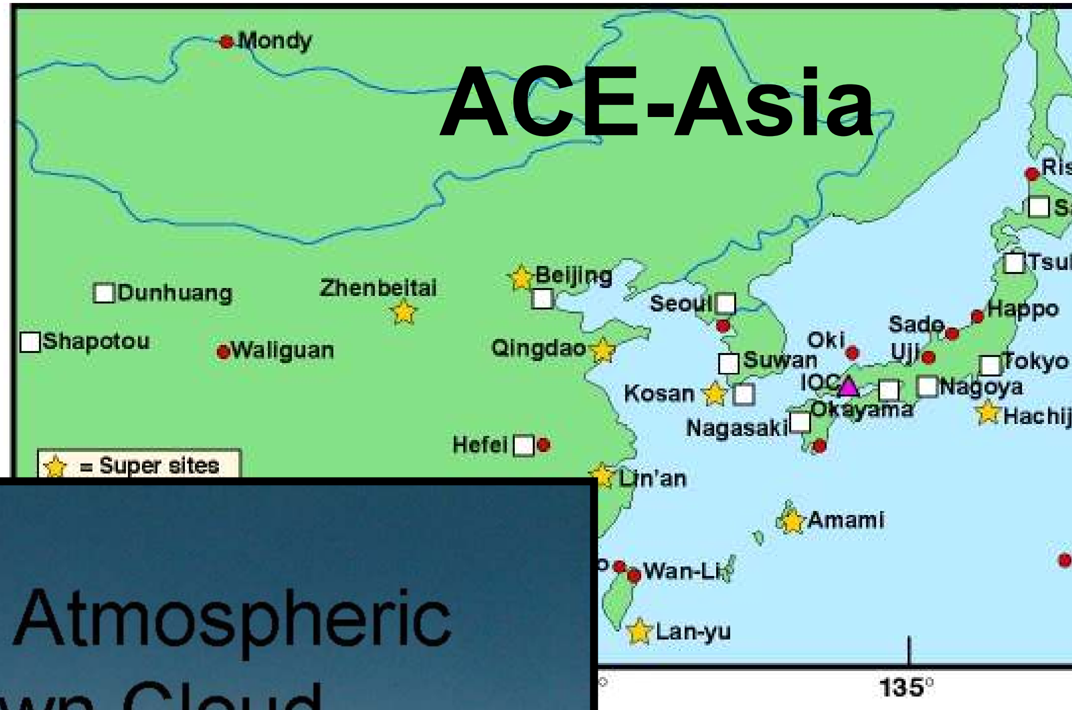


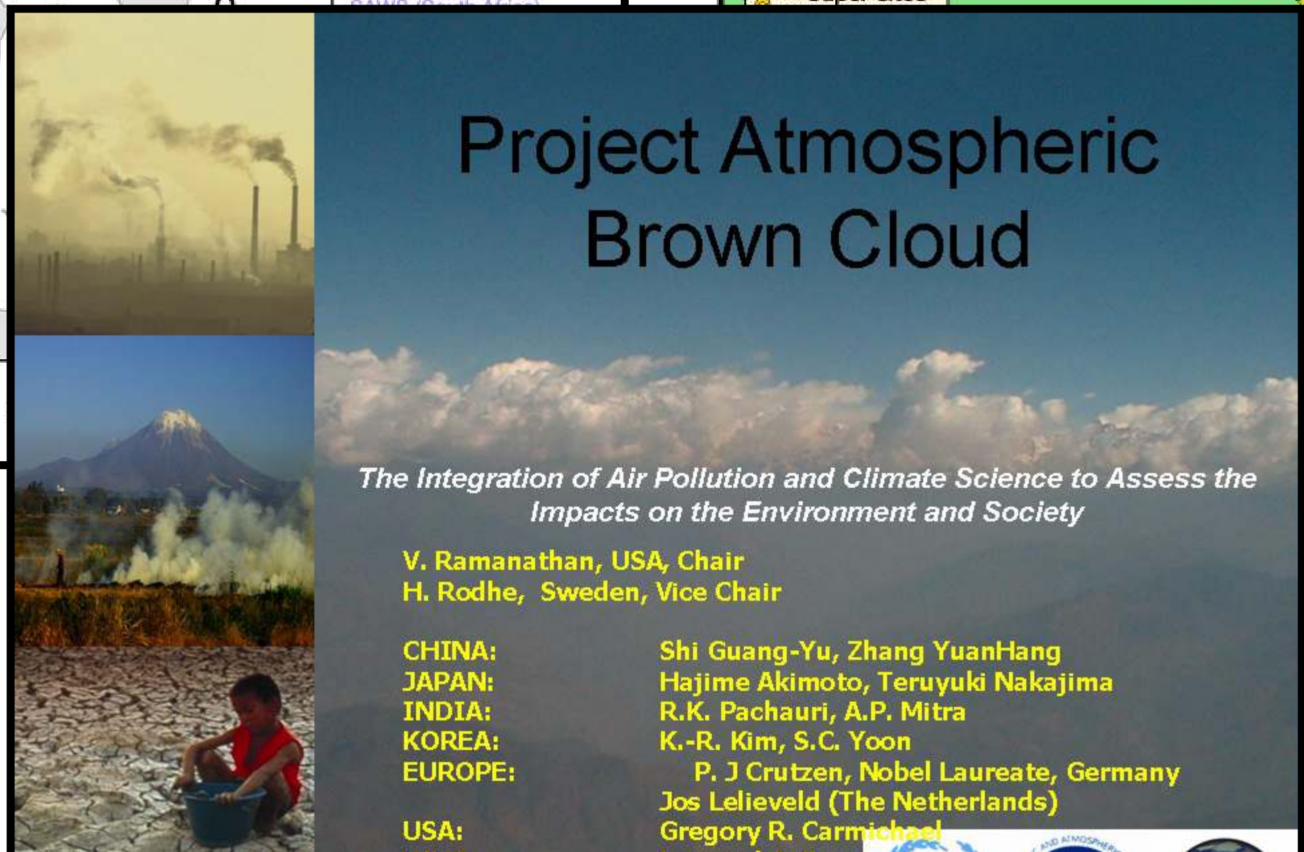
easonal Wind Patterns



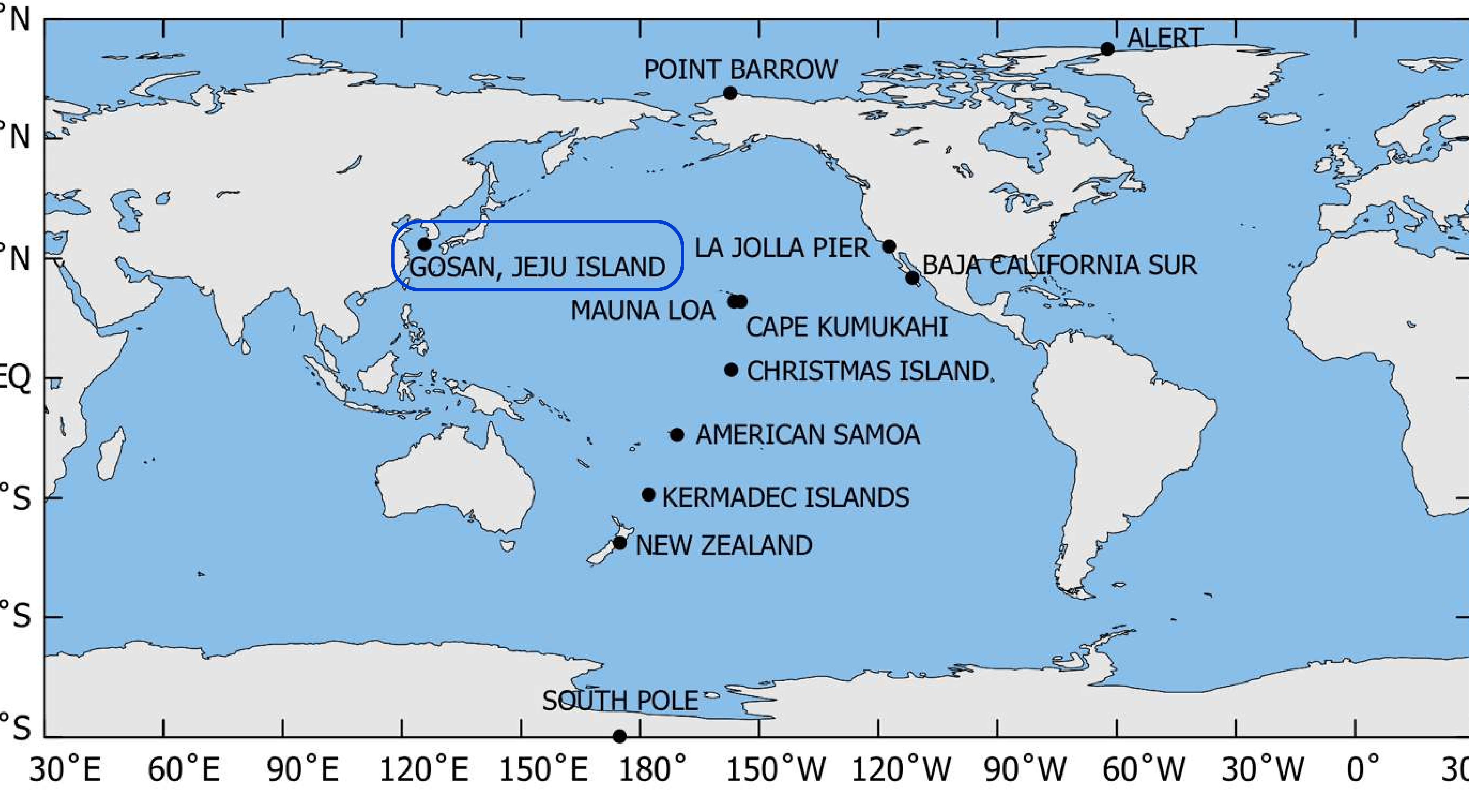
ternational Research At Gosan







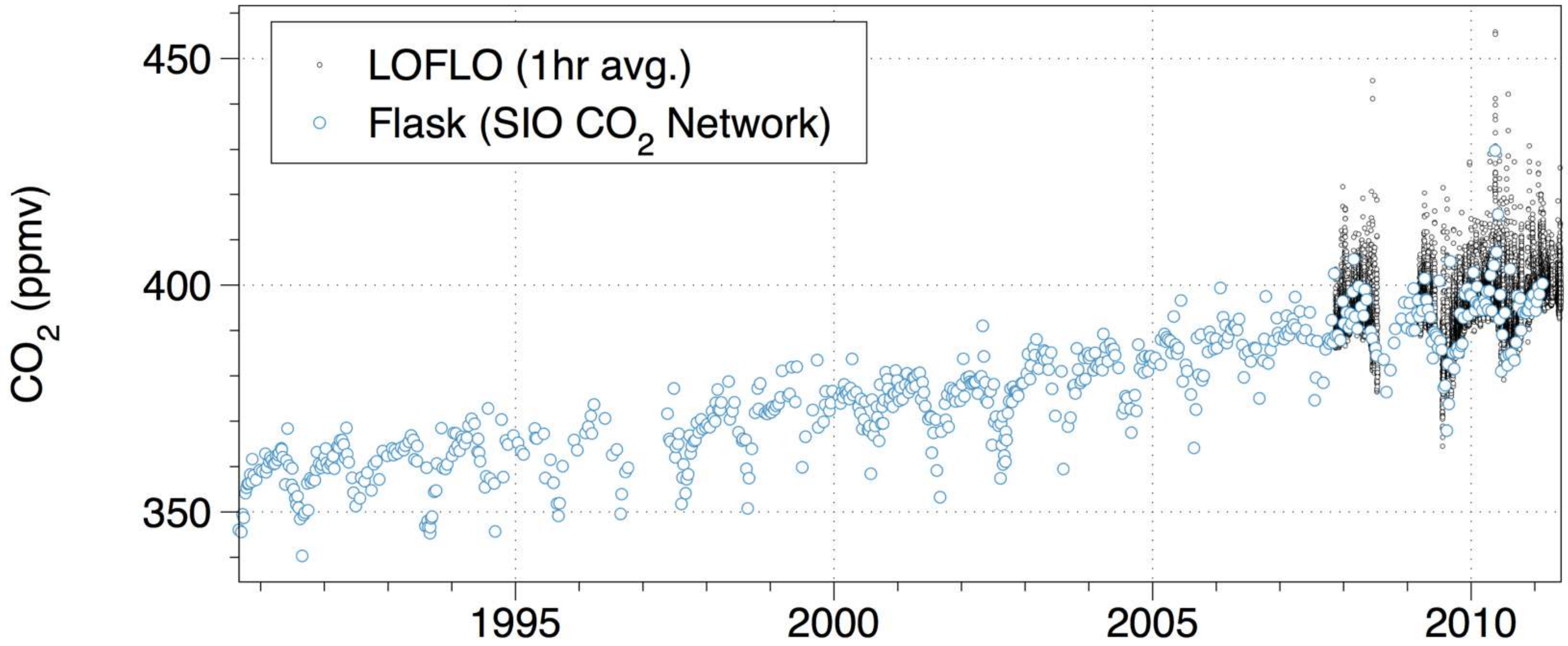
cripps CO_2 Network (Ralph Keeling)

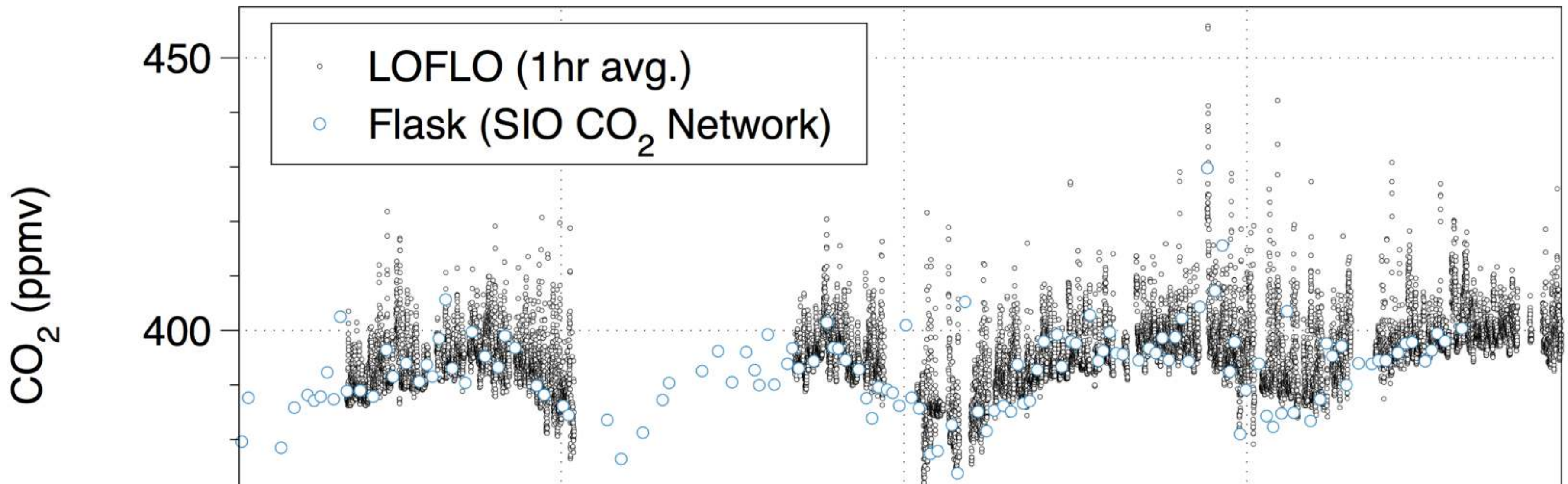


O_2 Measurements

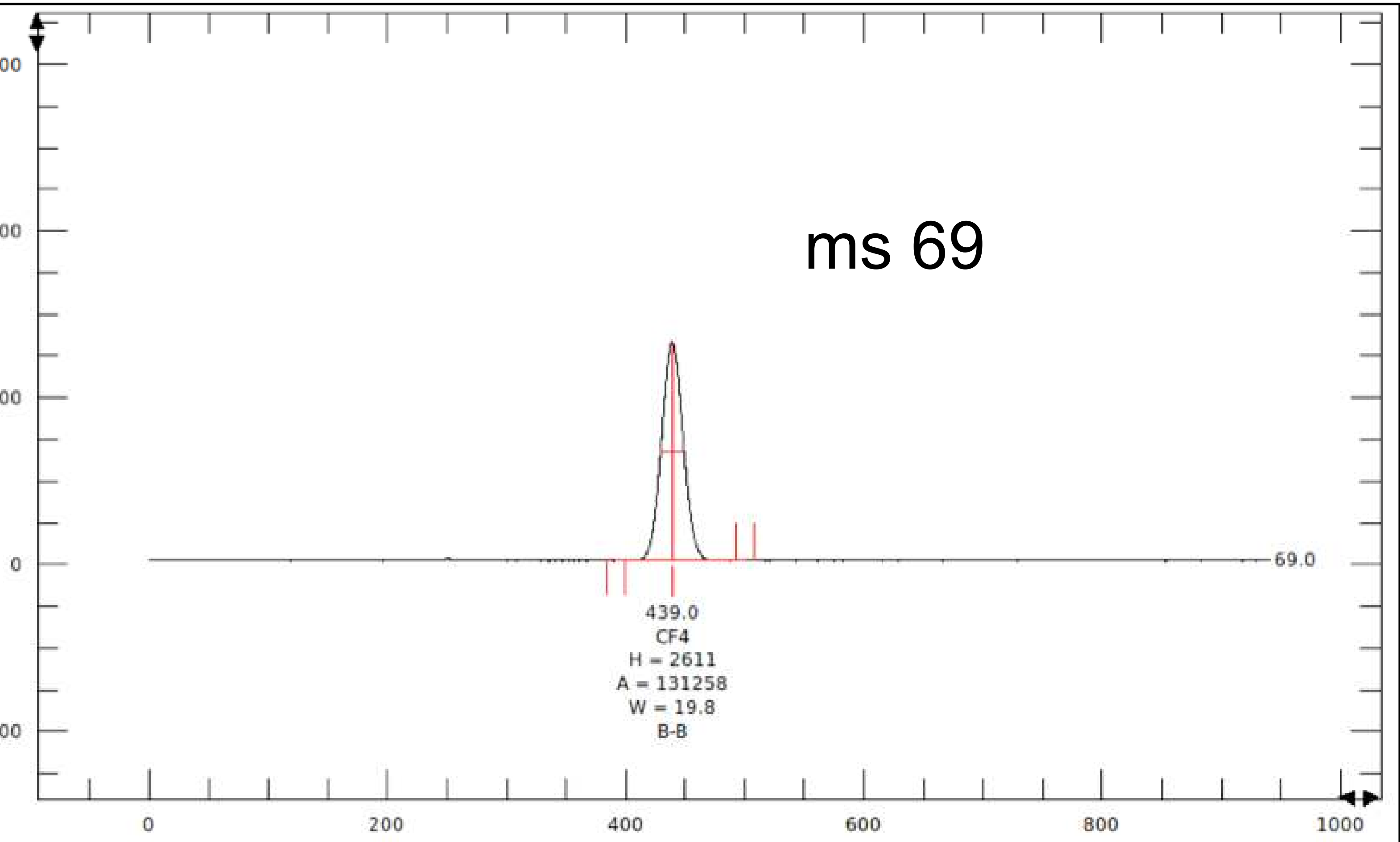
- <u>Flask Sampling ('90~)</u>
  - Sampling 1~2 times per wee
  - $^{12}C/^{13}C/^{14}C$ isotope analysis
  - **Scripps CO_2 Network**
- <u>LOFLO CO_2 Analyzer ('07 Nov.~</u>
  - 1min ~ 1hr average meas.
  - NOAA/WMO -2007x Cal. Sca

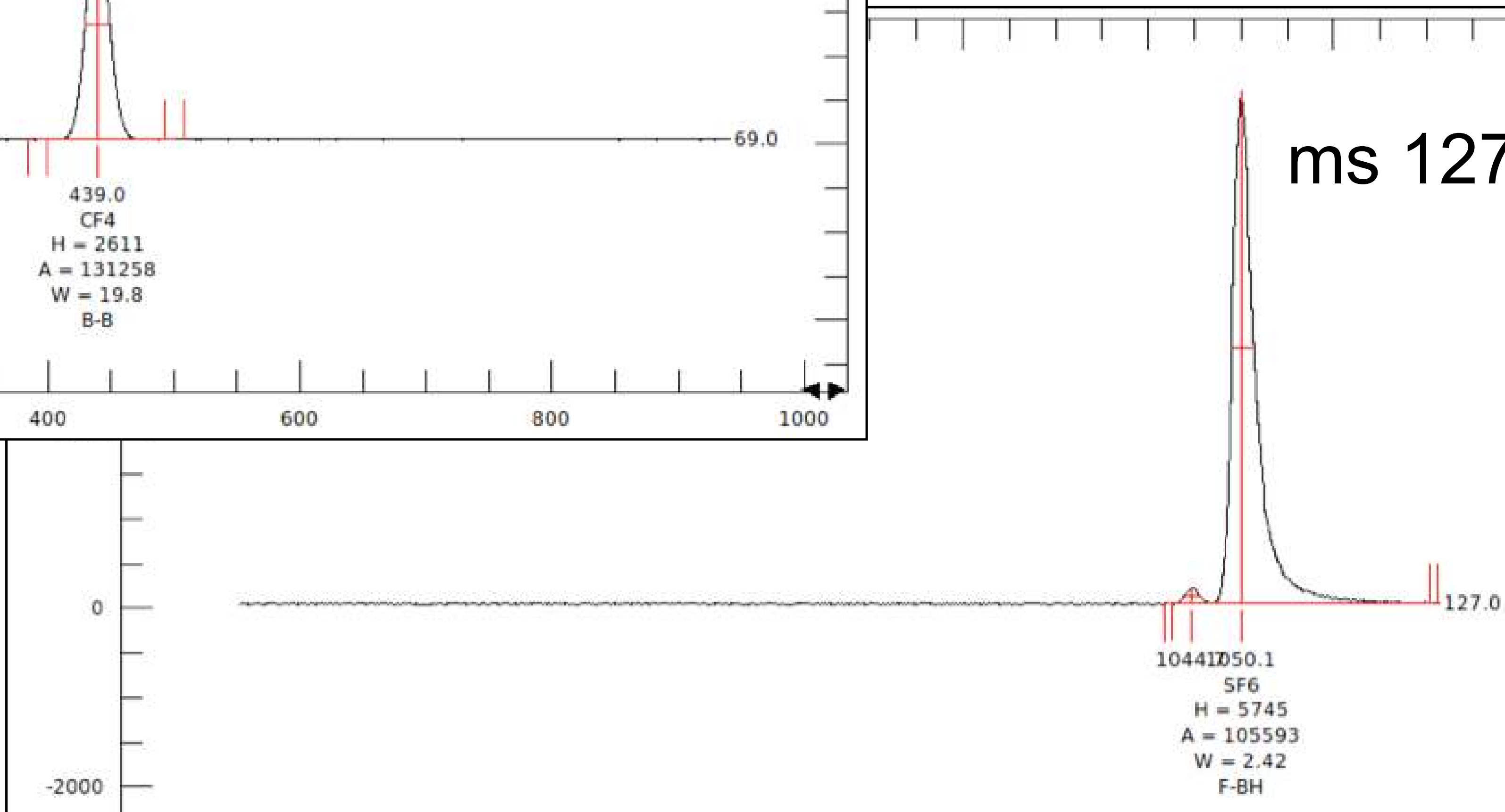
CO_2, flask and continuous measurements



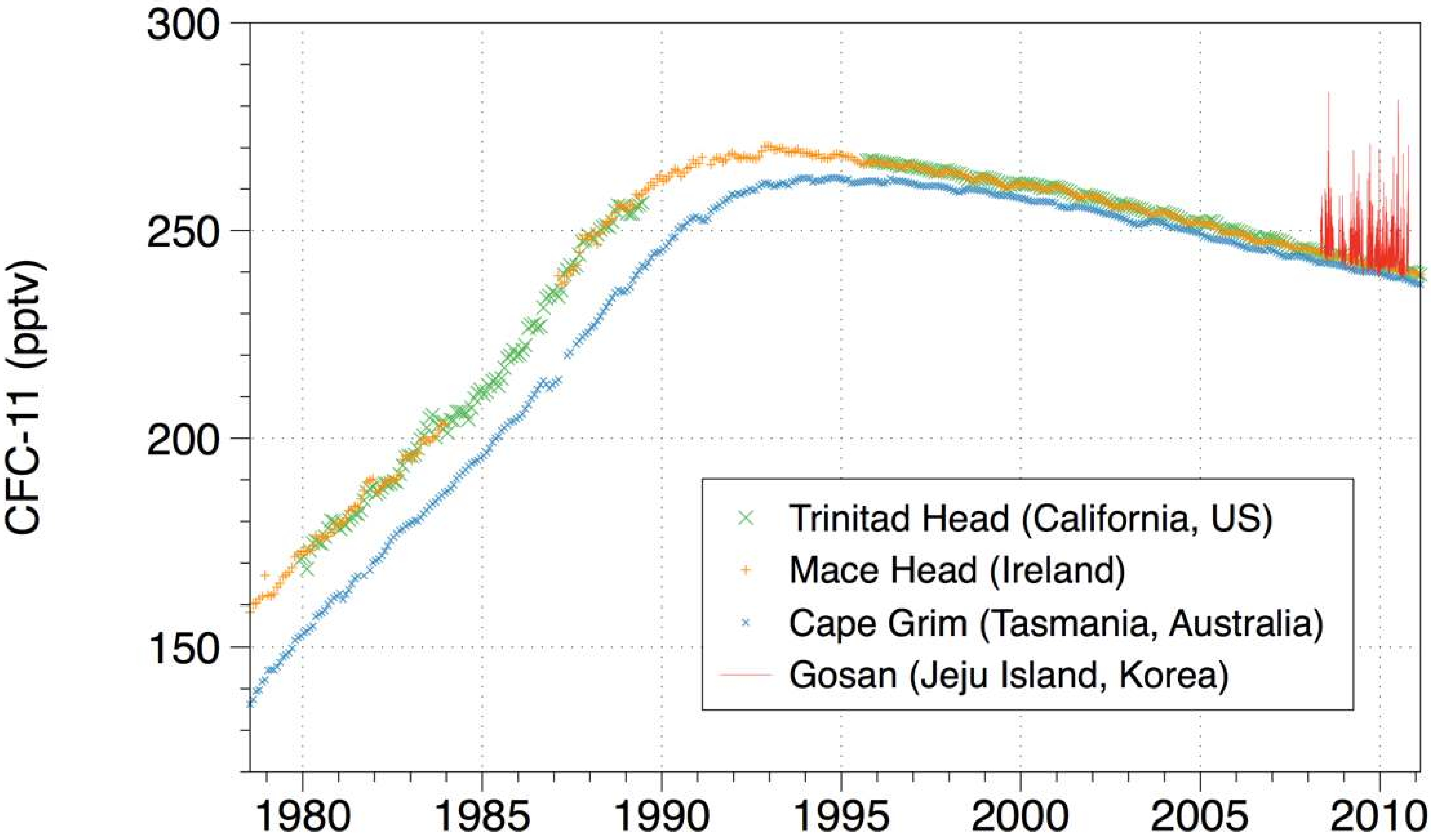


F4, SF6 Chromatograms on the Medusa GC-M

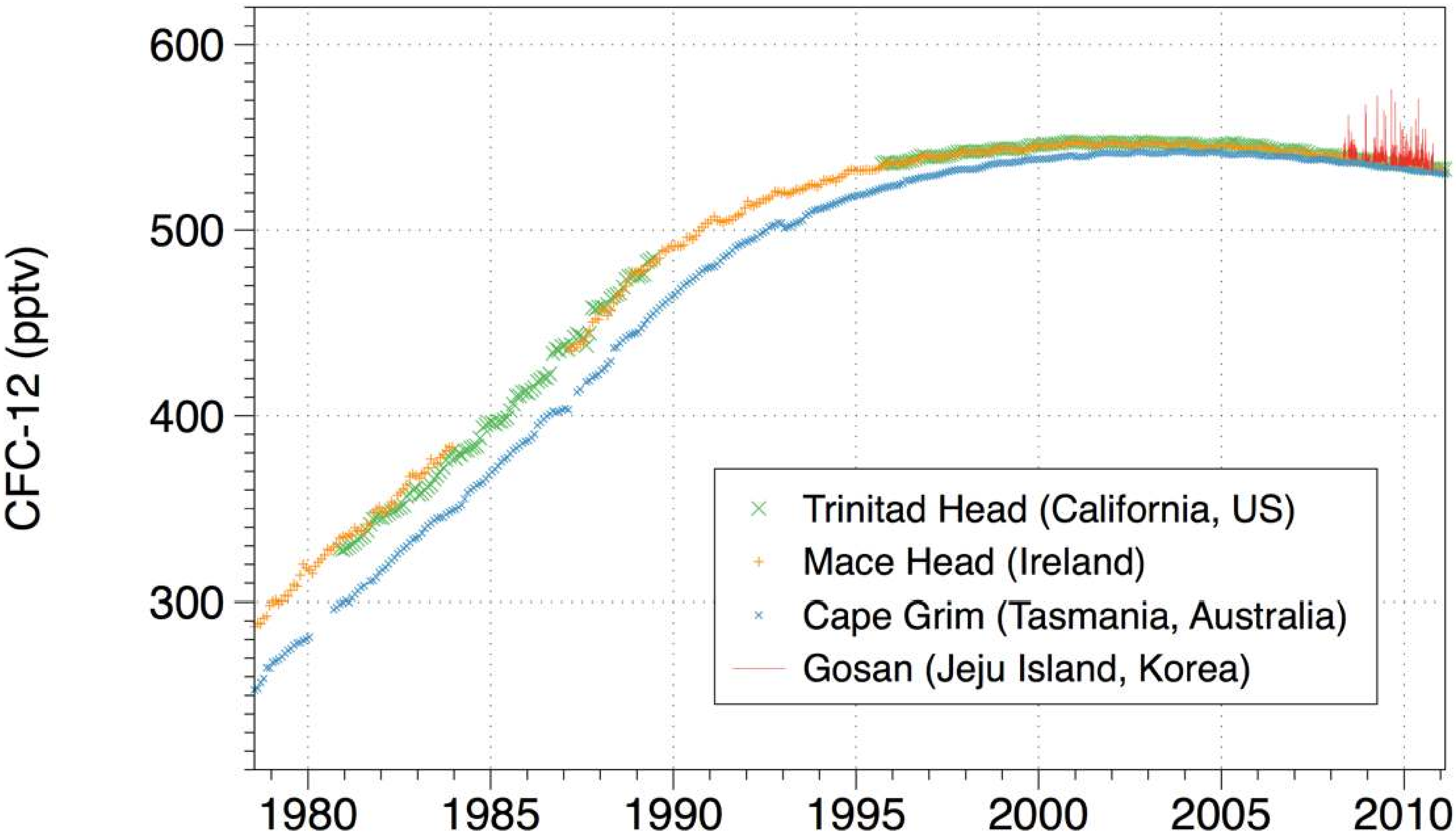




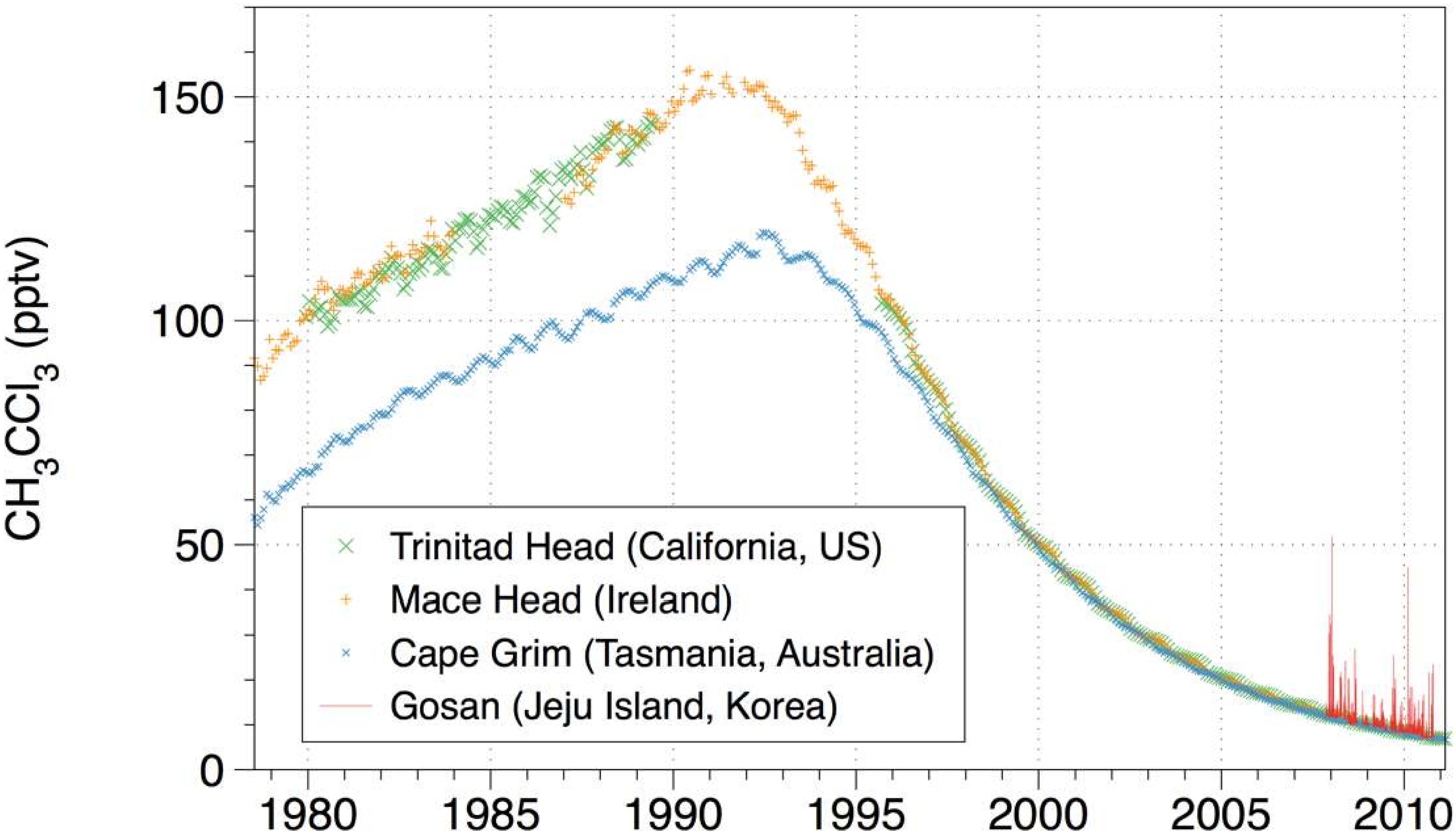
alogenated Species - CFC-11



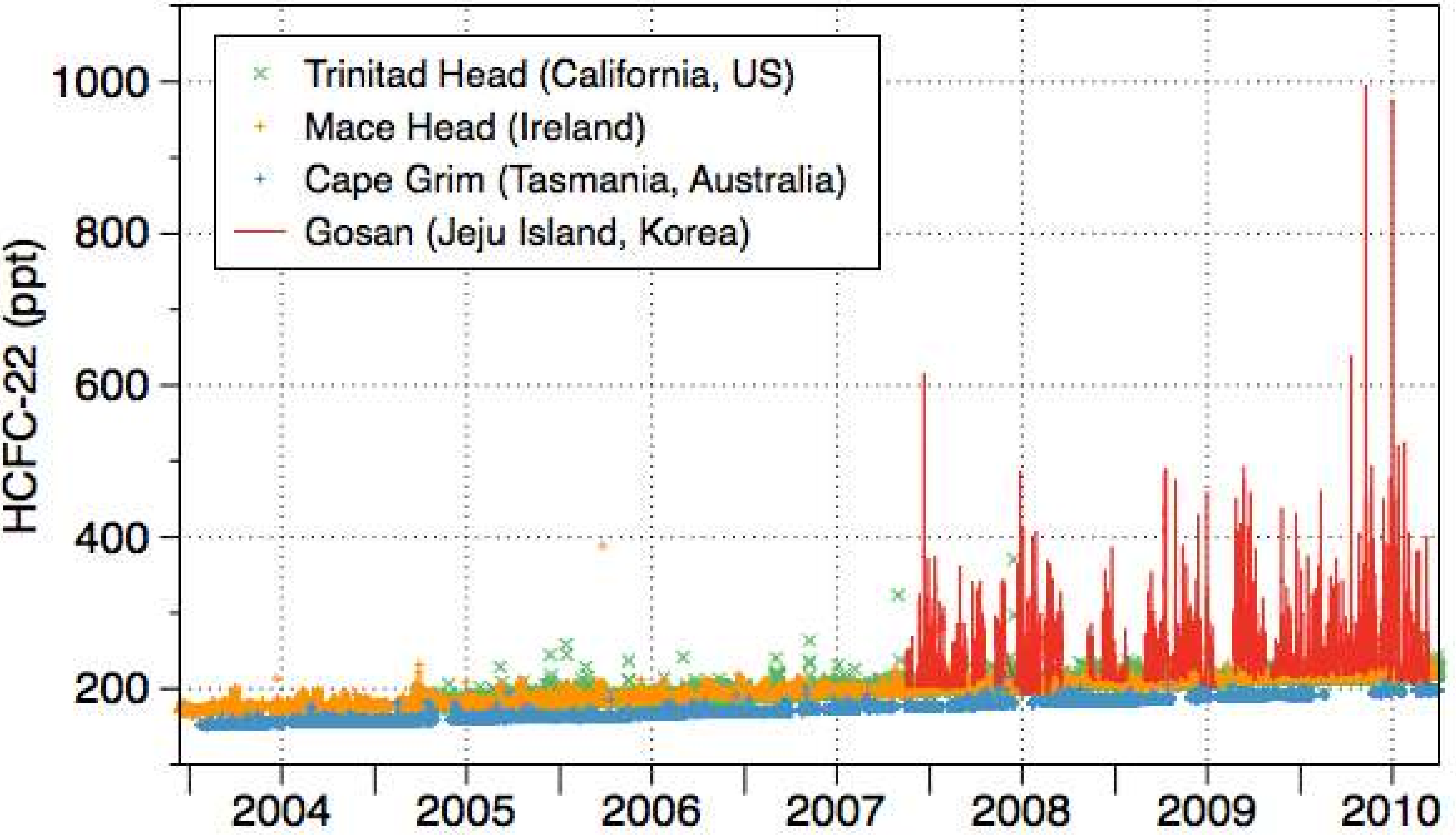
alogenated Species - CFC-12



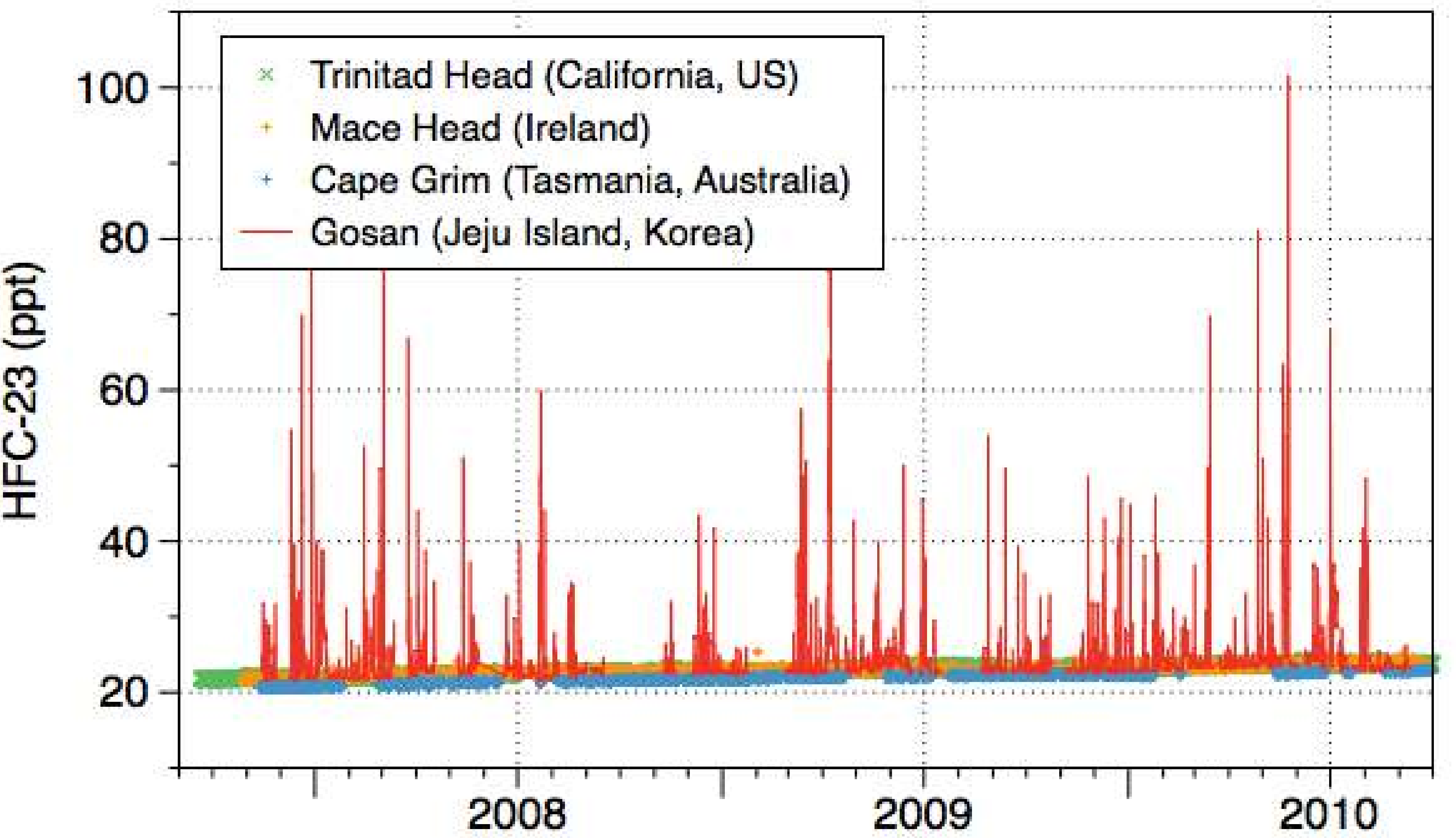
alogenated Species - CH_3CCl_3



alogenated Species - HCFC-22

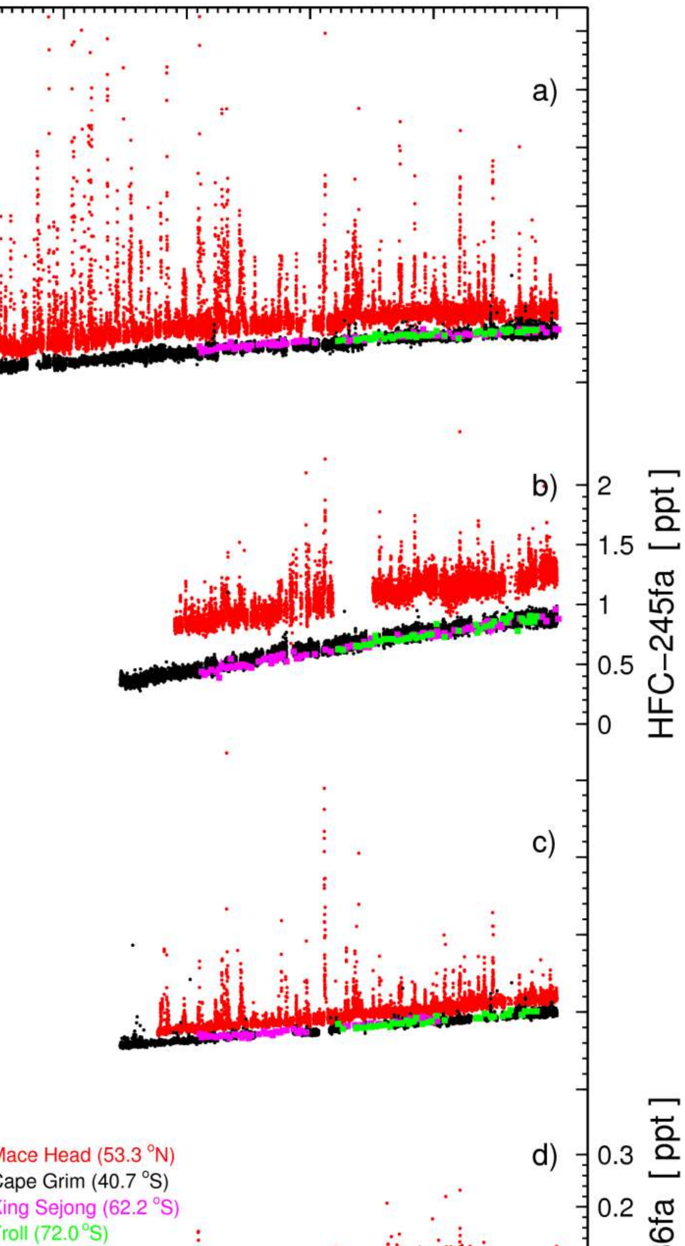


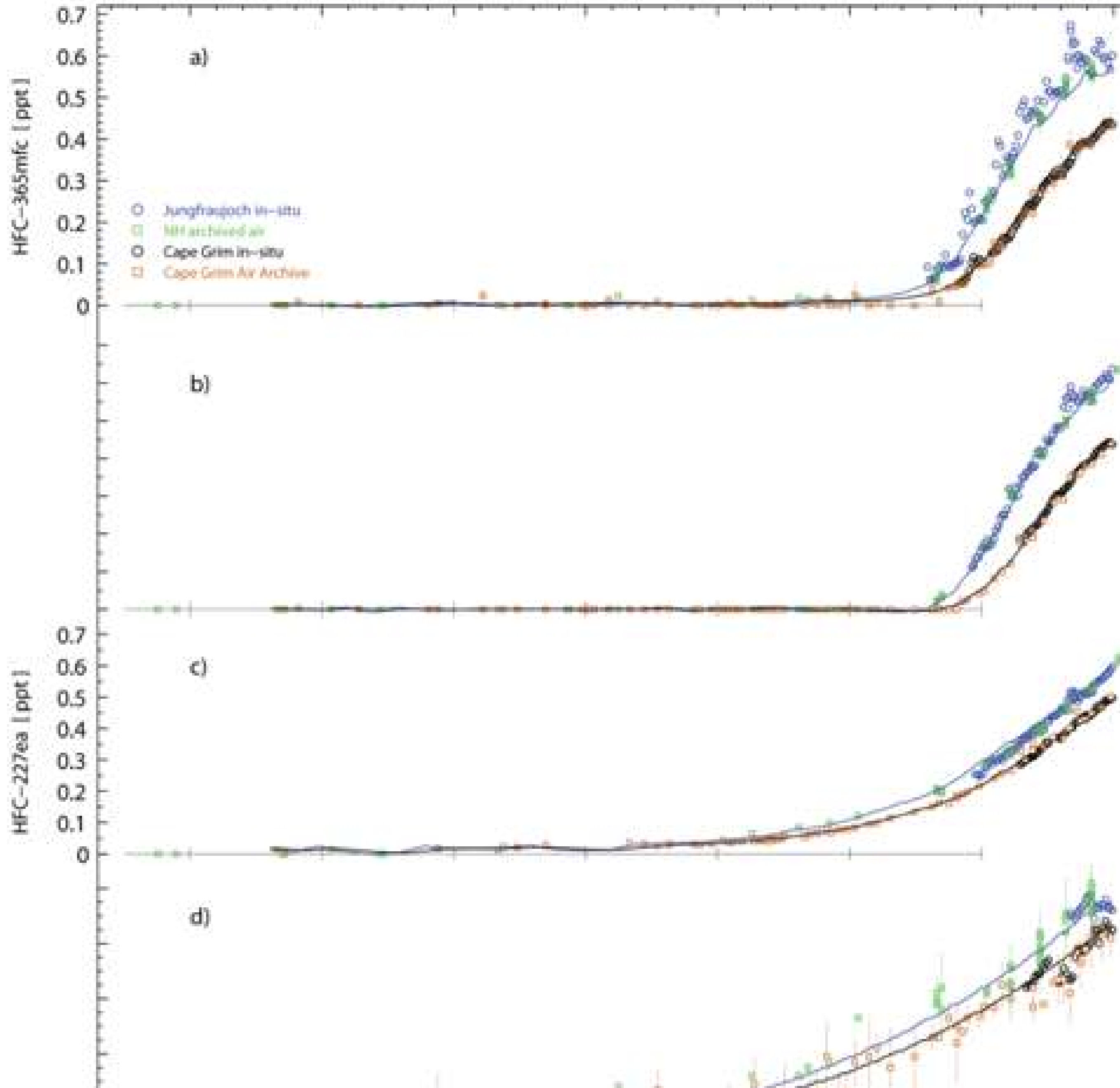
alogenated Species - HFC-23



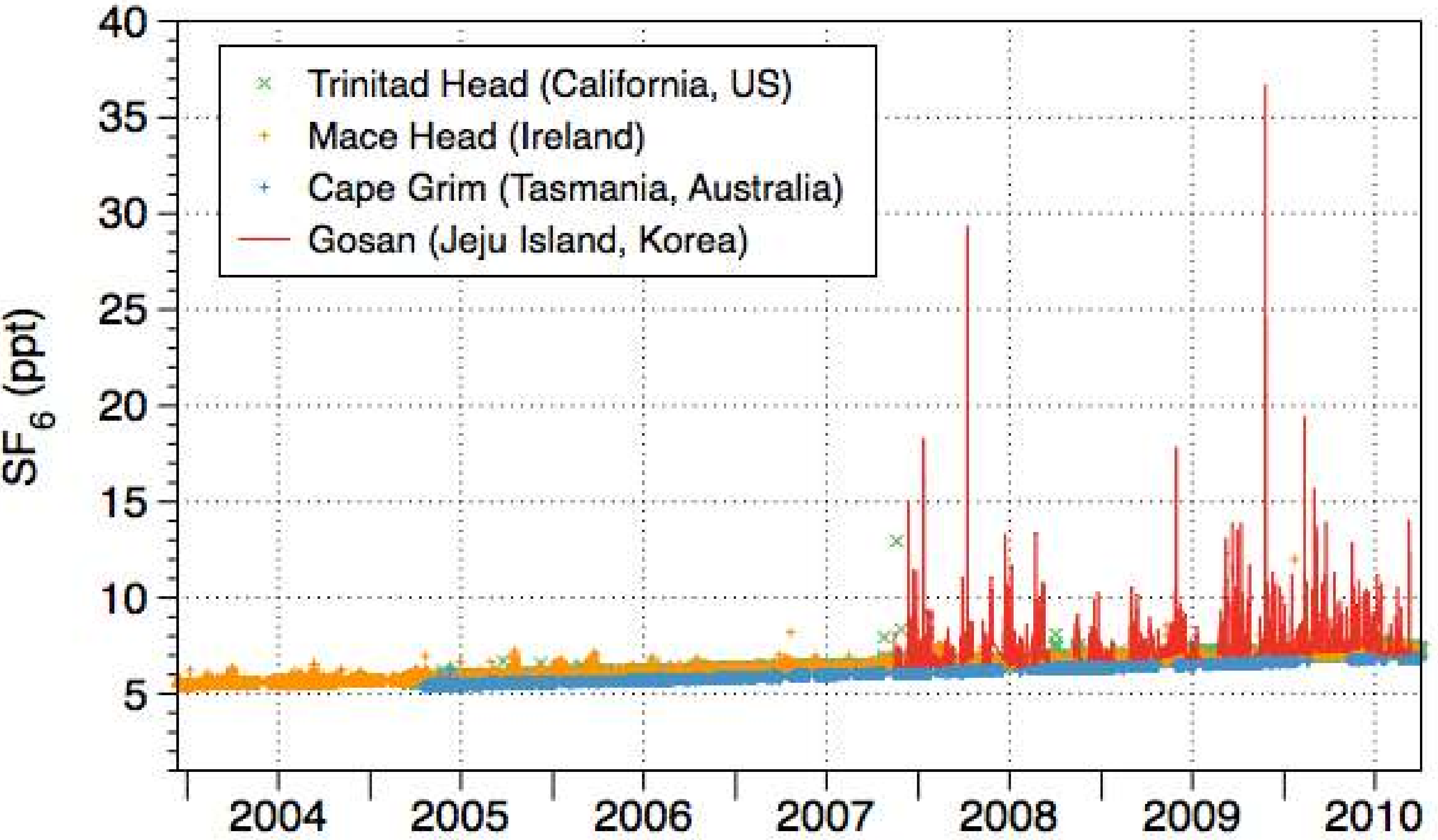
alogenated Species - HFCs

Vollmer et al., Figure 3

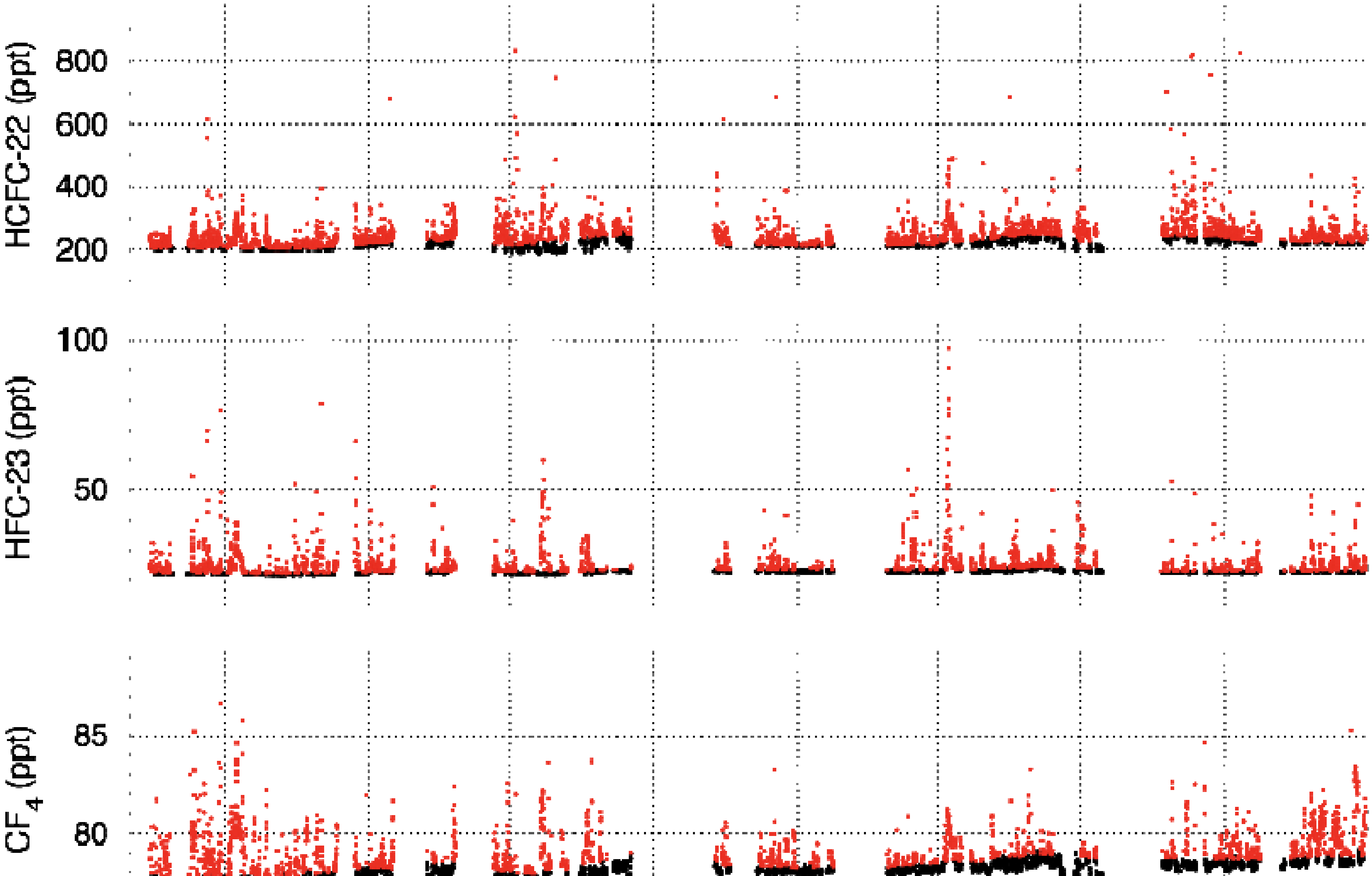




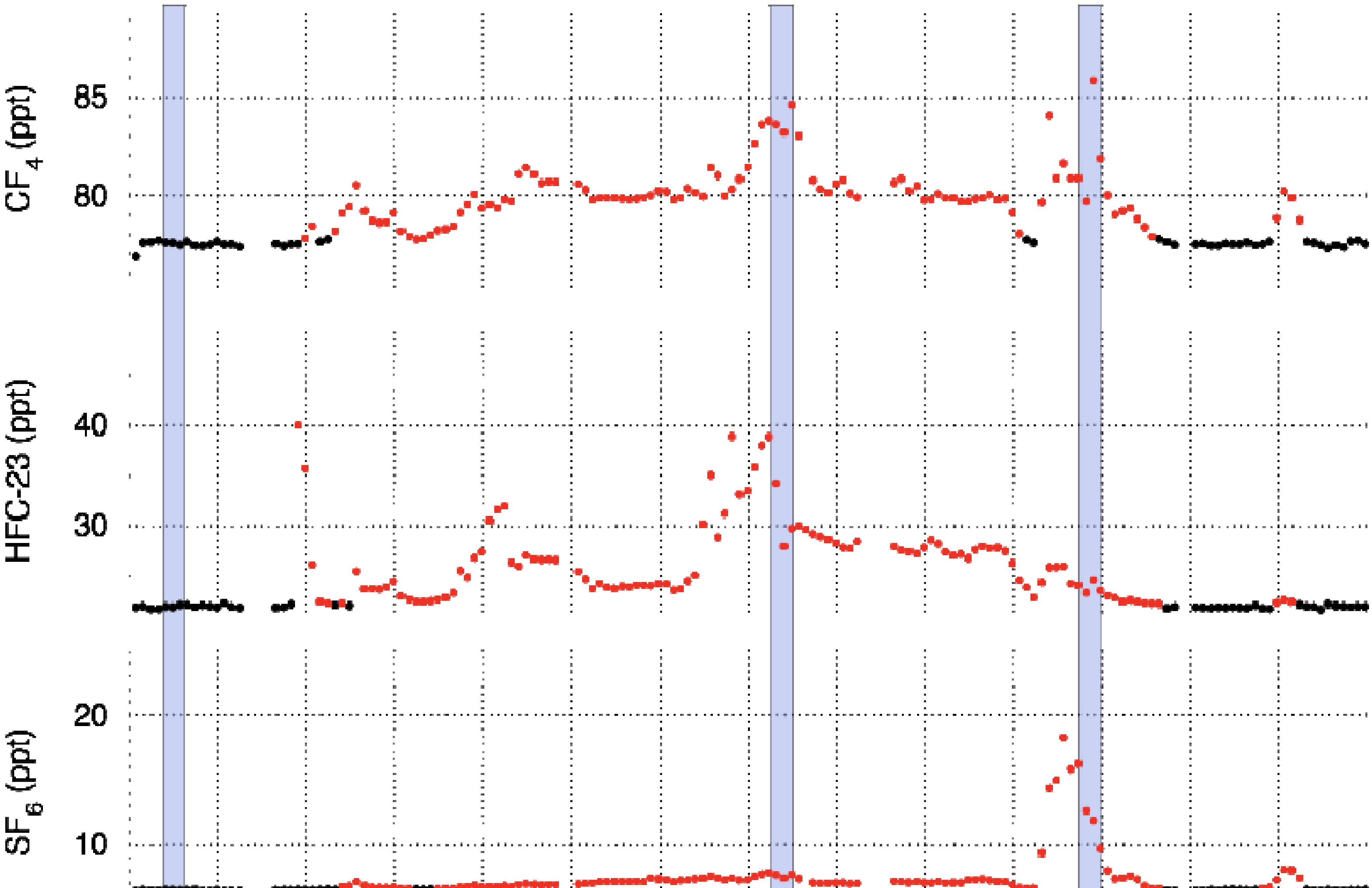
alogenated Species - SF_6



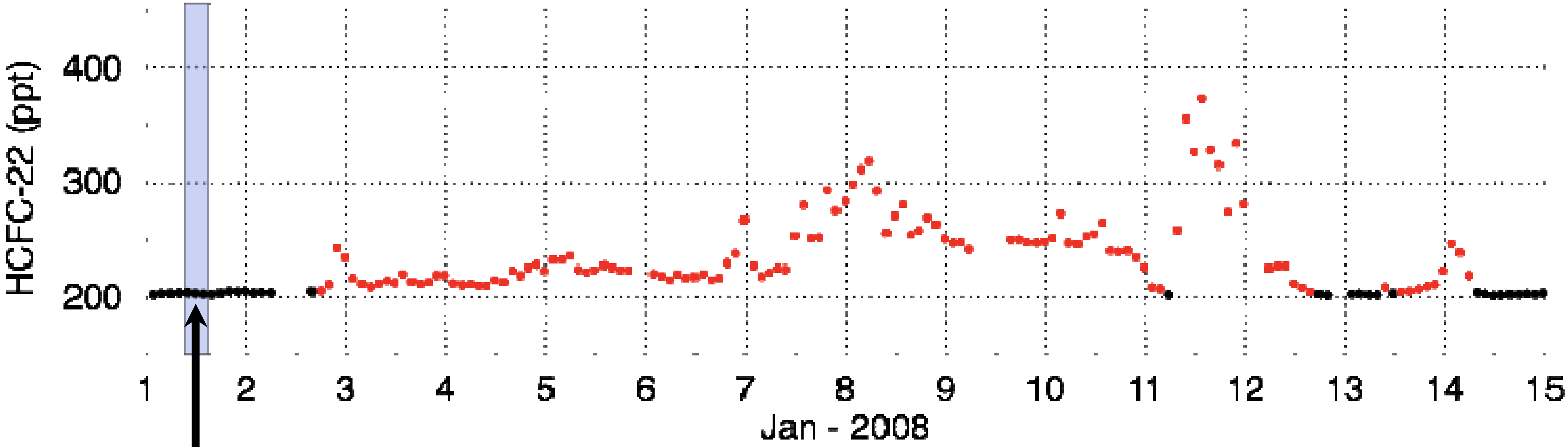
alogenated Species - Pollution Events

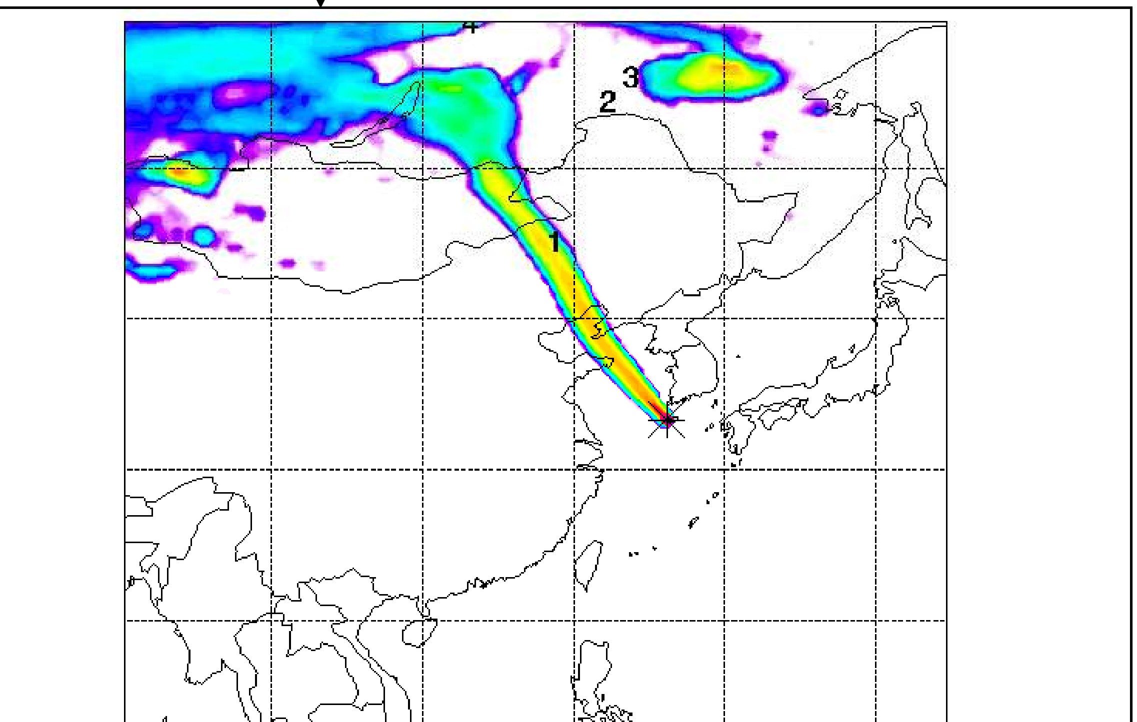


ollution and Trajectories, Jan. '08



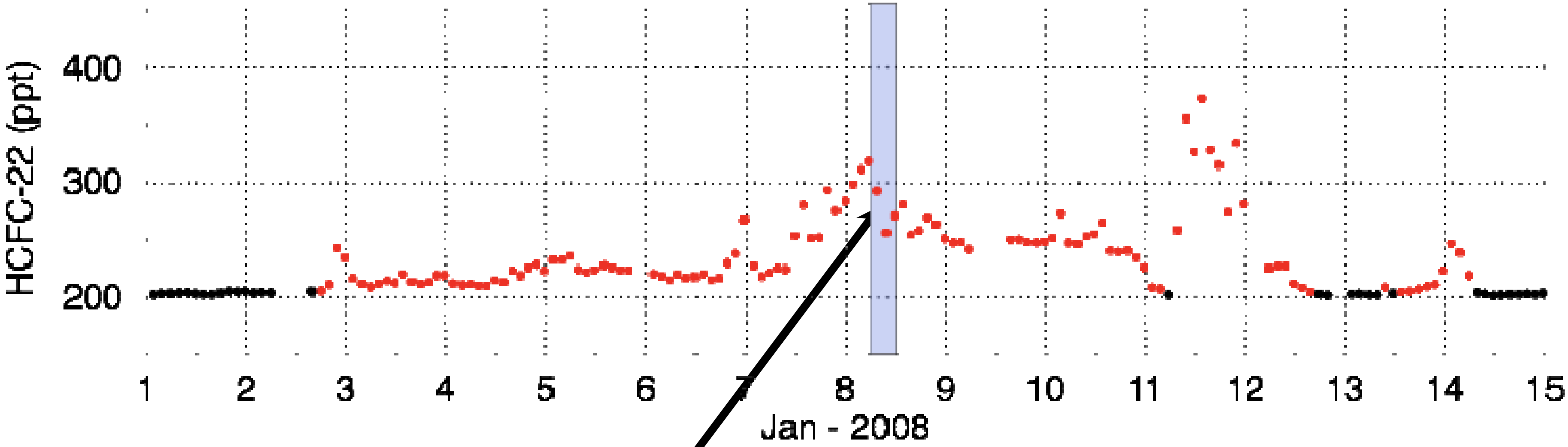
ollution and Trajectories, Jan. ‘08

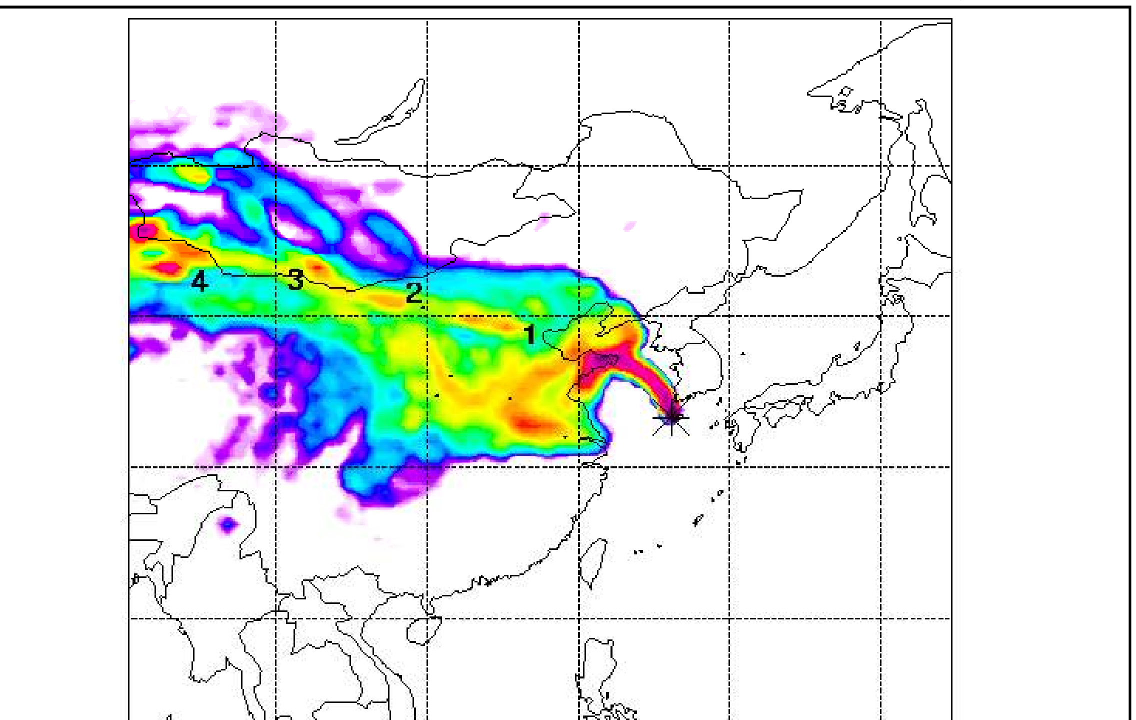




Winter background trajectories coming from northern Asia

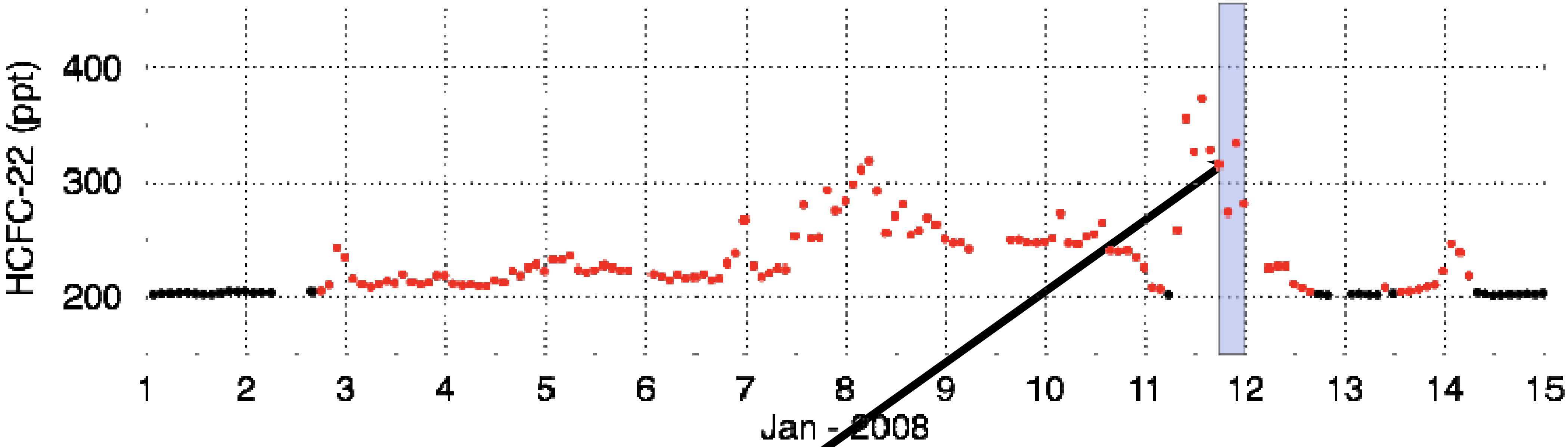
ollution and Trajectories, Jan. '08

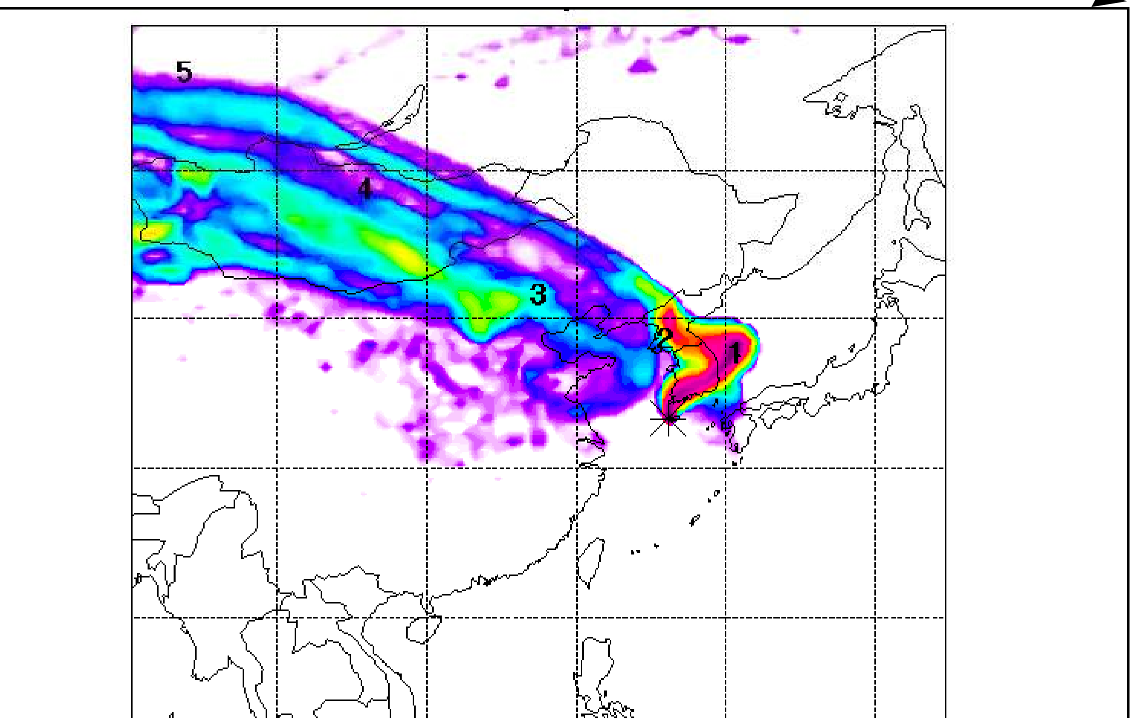




Pollution from China

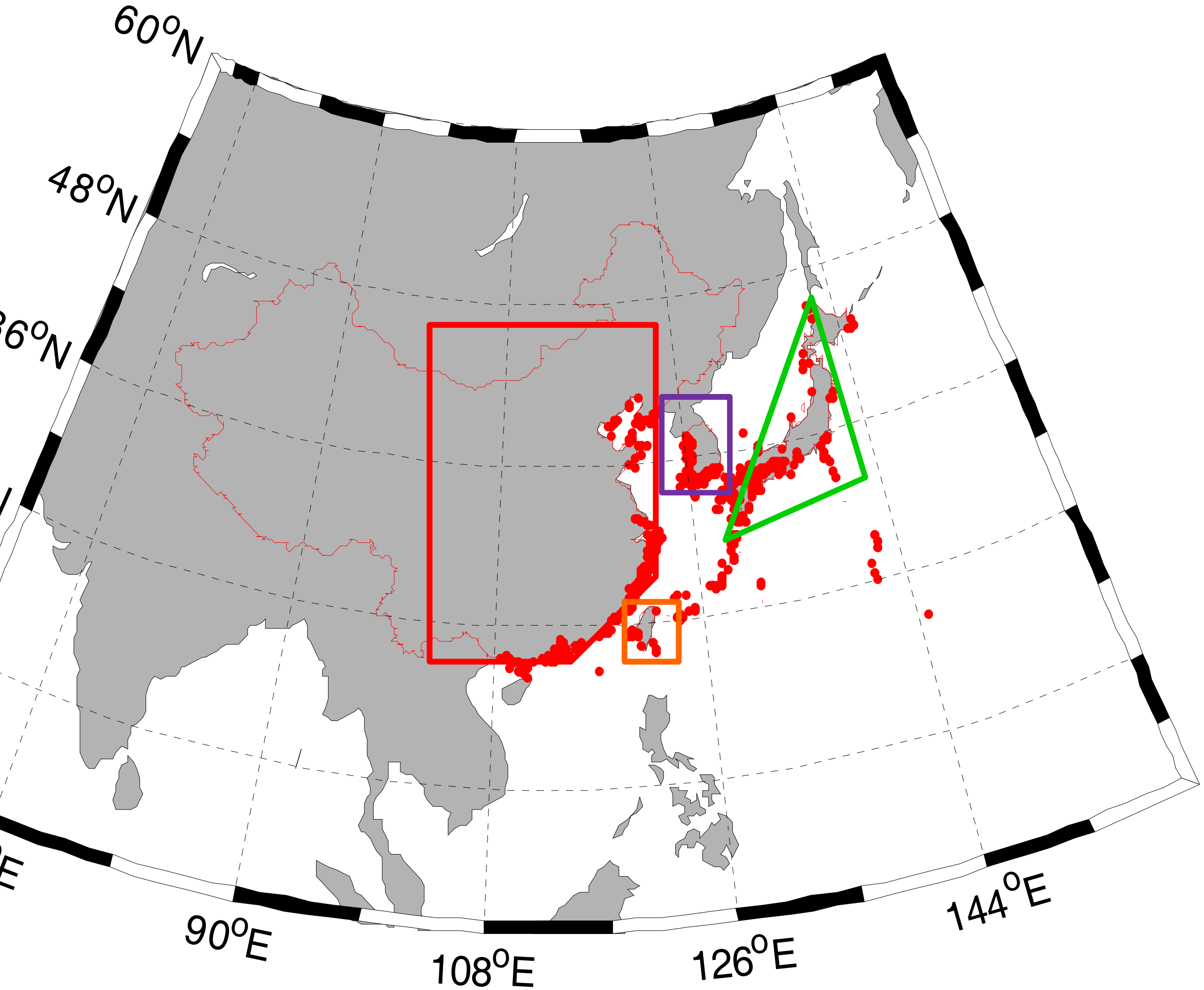
ollution and Trajectories, Jan. '08





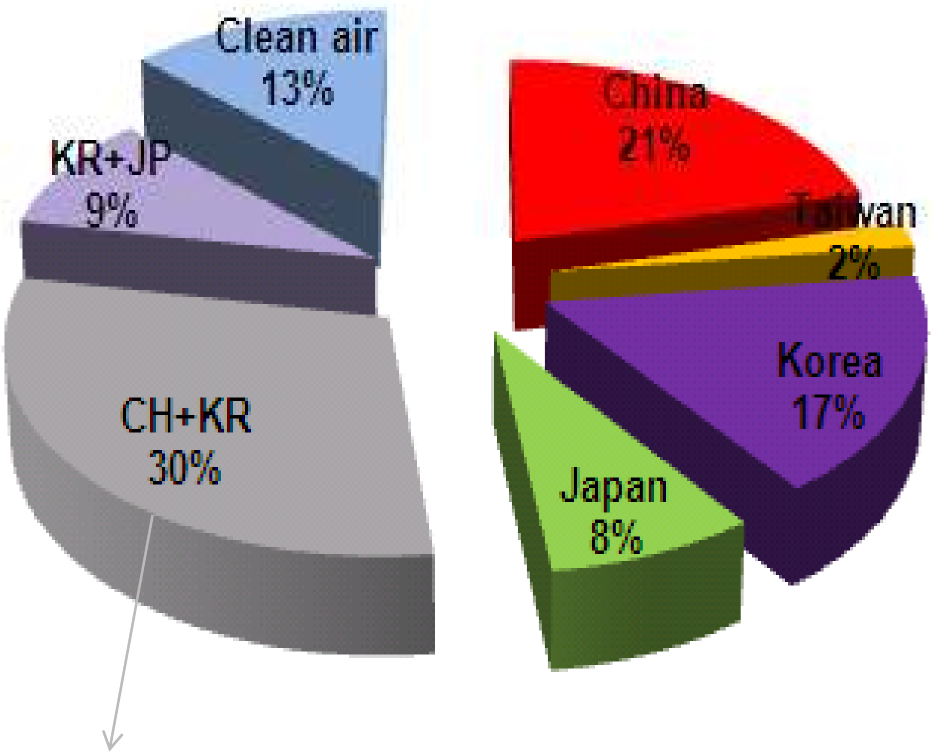
Pollution from Korea

Air masses Classification Scheme at Gosan

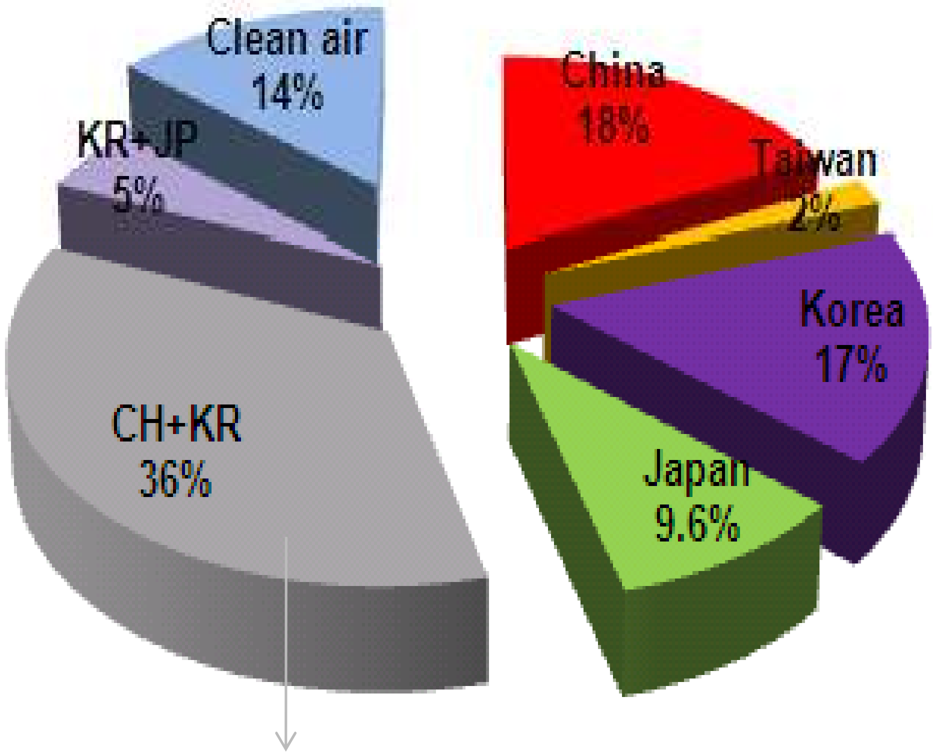


- Based on residence tim
  analysis of trajectories
  arriving at Gosan
- Air mass signatures
  with different source
  Region including
  China, Taiwan, Korea
  and Japan.
- Consider residence tim
  of back-trajectories wi
  altitudes below 2000n
- If trajectory passed throu
  two regions, the air
  mass was classified
  as blended air.

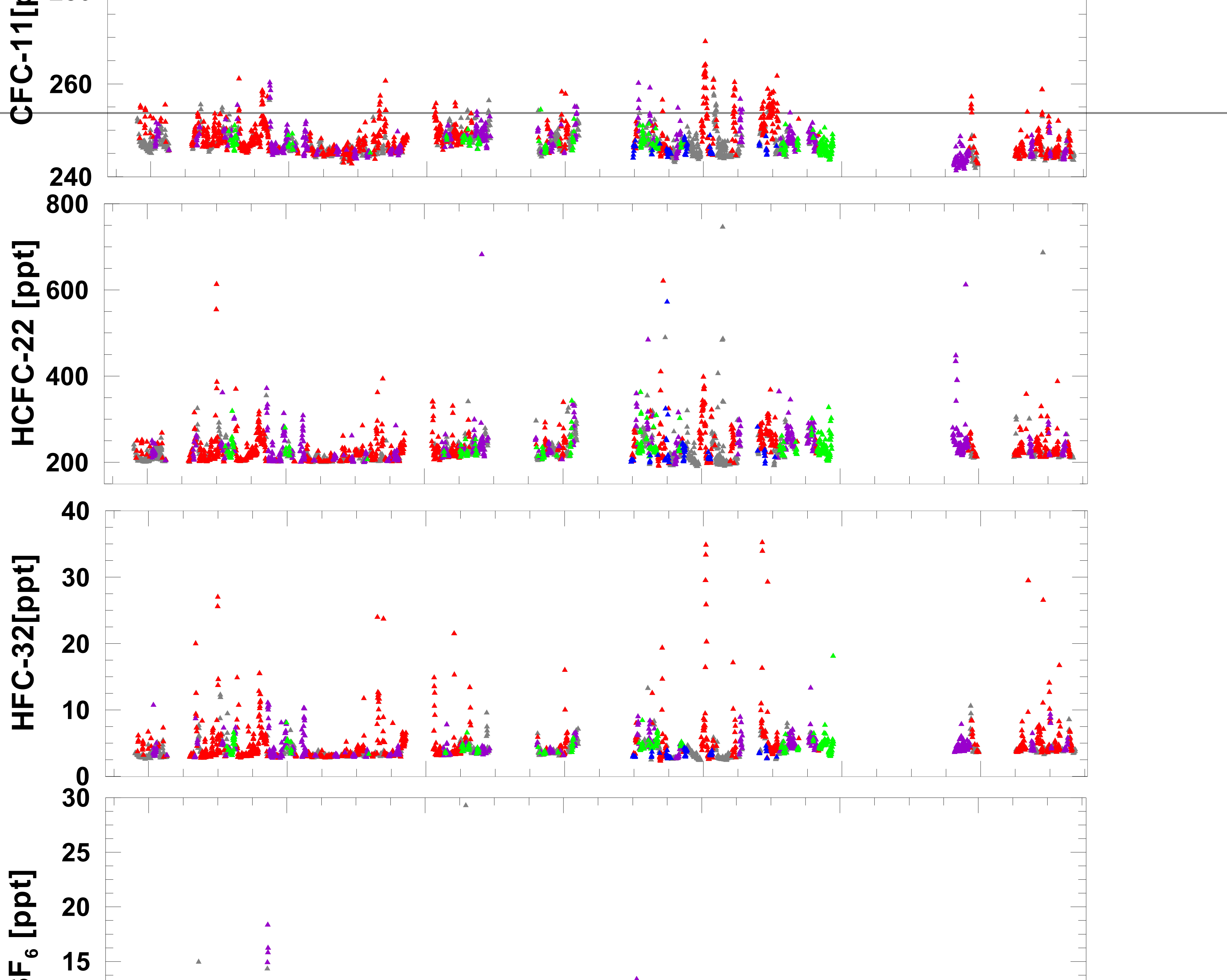
2008



2009

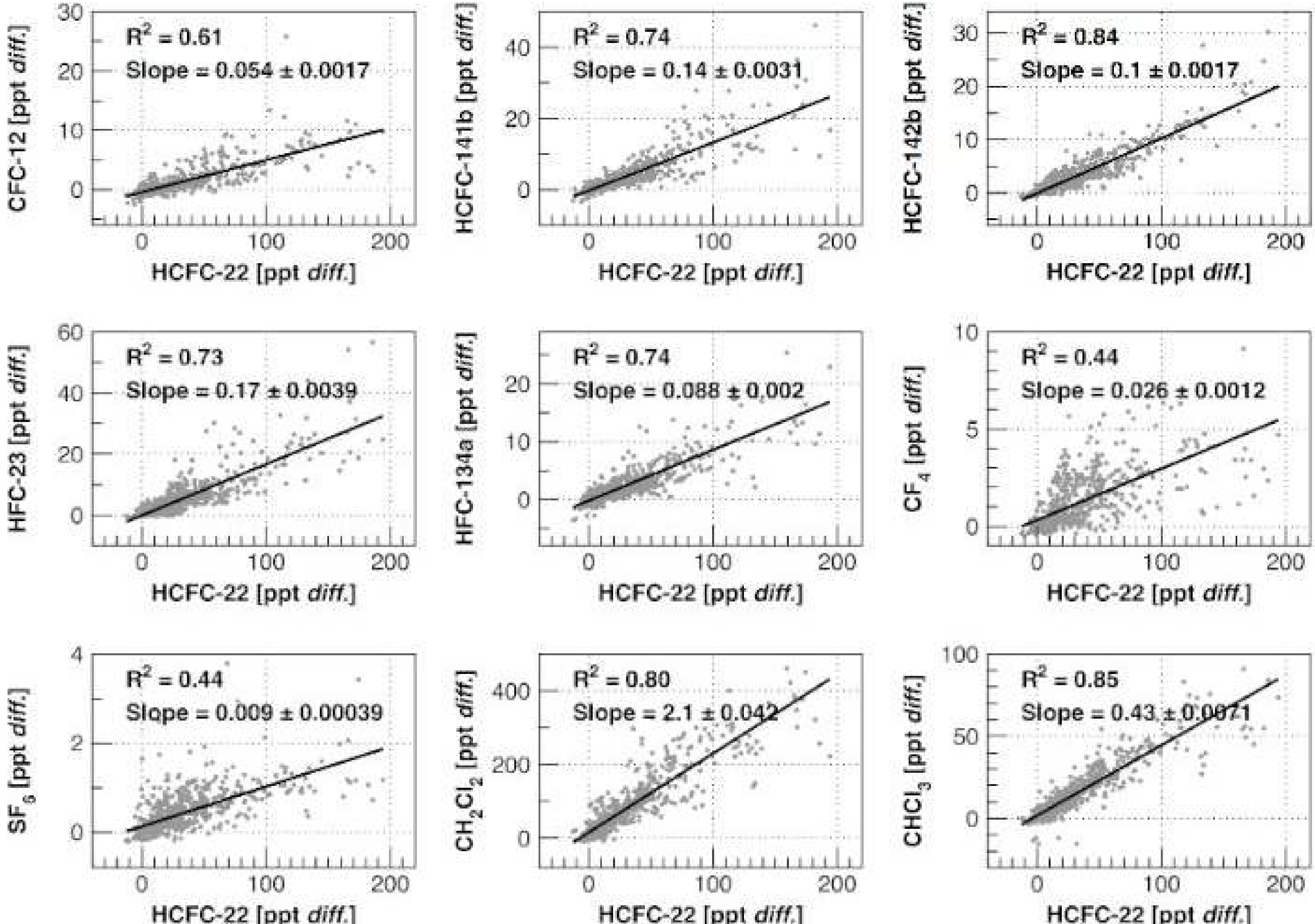


The most air masses were classified as China+Korea blended air. Residence time analysis of back-trajectories is insufficient for fully separating influence of China and Korea.


CFC-11[p
260
240
800
HCFC-22 [ppt]
600
400
200
40
HFC-32[ppt]
30
20
10
0
30
25
F6 [ppt]
20
15

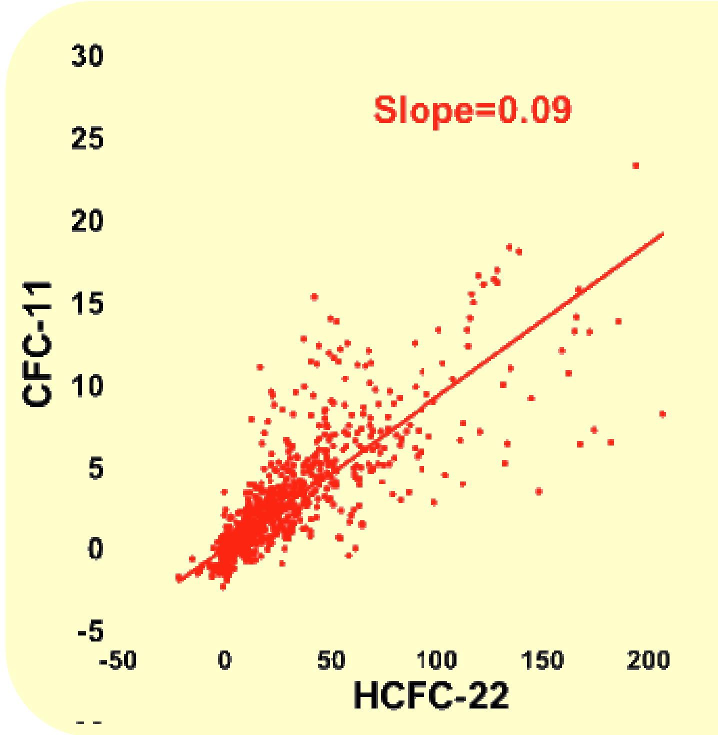
	CFC-11	CFC-12	CFC-113	CFC-114	HCFC-22	HCFC-141	HCFC-142	HFC-23	HFC-134a	HFC-152a	HFC-32	HFC-125	HFC-143a	HFC-365mf	H-1211	H-1301	CF4	PFC-116	PFC-218	SF6	CH3Cl	CH2Cl2	CHCl3	CH3CCl3	CCl4	CH3Br
CFC-11	1.00	0.61	0.06	0.34	0.84	0.60	0.79	0.71	0.69	0.57	0.54	0.51	0.30	0.16	0.59	0.35	0.70	0.55	0.32	0.56	0.75	0.77	0.88	0.27	0.72	0.67
CFC-12	0.61	1.00	0.10	0.44	0.56	0.56	0.61	0.50	0.34	0.41	0.55	0.27	0.04	0.00	0.68	0.08	0.43	0.47	0.31	0.27	0.65	0.65	0.62	0.43	0.68	0.58
CFC-113	0.06	0.10	1.00	0.23	0.11	0.23	0.20	0.14	0.11	0.19	0.16	0.13	0.05	-0.01	0.19	0.01	0.03	0.16	0.14	0.08	0.17	0.17	0.14	0.08	0.17	0.10
CFC-114	0.34	0.44	0.23	1.00	0.52	0.71	0.67	0.55	0.38	0.62	0.36	0.45	0.10	-0.01	0.57	0.04	0.10	0.46	0.37	0.28	0.61	0.56	0.47	0.18	0.56	0.41
HCFC-22	0.84	0.56	0.11	0.52	1.00	0.81	0.91	0.35	0.84	0.76	0.71	0.73	0.49	0.11	0.71	0.33	0.65	0.73	0.46	0.66	0.87	0.88	0.92	0.18	0.79	0.70
HCFC-141b	0.60	0.56	0.23	0.71	0.81	1.00	0.85	0.67	0.60	0.73	0.65	0.61	0.32	0.08	0.78	0.20	0.40	0.71	0.55	0.51	0.72	0.81	0.71	0.31	0.73	0.60
HCFC-142b	0.79	0.51	0.20	0.67	0.91	0.85	1.00	0.84	0.71	0.88	0.64	0.69	0.39	0.05	0.75	0.26	0.54	0.70	0.50	0.52	0.80	0.81	0.84	0.28	0.75	0.64
HFC-23	0.71	0.50	0.14	0.55	0.85	0.67	0.84	1.00	0.69	0.80	0.34	0.66	0.35	0.04	0.00	0.18	0.61	0.59	0.42	0.47	0.79	0.75	0.80	0.22	0.70	0.61
HFC-134a	0.69	0.34	0.11	0.38	0.84	0.60	0.71	0.39	1.00	0.70	0.57	0.77	0.70	0.13	0.58	0.29	0.61	0.68	0.42	0.71	0.71	0.73	0.79	0.16	0.62	0.61
HFC-152a	0.57	0.41	0.19	0.02	0.76	0.73	0.88	0.30	0.70	1.00	0.58	0.72	0.45	0.04	0.68	0.18	0.49	0.59	0.44	0.46	0.68	0.69	0.75	0.30	0.63	0.50
HFC-32	0.54	0.55	0.16	0.66	0.71	0.65	0.64	0.34	0.57	0.58	1.00	0.59	0.37	0.05	0.68	0.20	0.39	0.65	0.49	0.54	0.79	0.73	0.66	0.17	0.78	0.55
HFC-125	0.51	0.27	0.13	0.45	0.73	0.61	0.69	0.38	0.77	0.72	0.59	1.00	0.60	0.06	0.58	0.25	0.48	0.61	0.47	0.61	0.67	0.67	0.71	0.13	0.57	0.54
HFC-143a	0.30	0.04	0.05	0.19	0.49	0.32	0.39	0.35	0.70	0.45	0.37	0.60	1.00	0.18	0.36	0.17	0.36	0.50	0.25	0.54	0.43	0.44	0.43	-0.08	0.34	0.38
HFC-365mfc	0.16	0.09	-0.01	-0.01	0.11	0.08	0.05	0.04	0.13	0.04	0.05	0.06	0.18	1.00	0.09	0.09	0.27	0.12	0.01	0.18	0.06	0.10	0.10	0.26	0.08	0.13
H-1211	0.59	0.68	0.19	0.57	0.71	0.78	0.75	0.50	0.56	0.68	0.68	0.56	0.36	0.09	1.00	0.19	0.49	0.77	0.54	0.55	0.79	0.85	0.74	0.33	0.82	0.69
H-1301	0.35	0.08	0.01	0.04	0.33	0.20	0.26	0.18	0.29	0.18	0.20	0.25	0.17	0.09	0.19	1.00	0.22	0.24	0.21	0.28	0.27	0.24	0.30	0.11	0.23	0.24
CF4	0.70	0.43	0.03	0.19	0.65	0.40	0.54	0.31	0.61	0.49	0.39	0.48	0.36	0.27	0.49	0.22	1.00	0.57	0.29	0.59	0.61	0.60	0.72	0.24	0.55	0.48
PFC-116	0.55	0.47	0.16	0.46	0.73	0.71	0.70	0.59	0.68	0.59	0.55	0.61	0.50	0.12	0.77	0.24	0.57	1.00	0.68	0.72	0.78	0.82	0.72	0.26	0.79	0.66
PFC-218	0.32	0.31	0.14	0.37	0.46	0.55	0.50	0.42	0.42	0.44	0.49	0.47	0.25	0.01	0.54	0.21	0.29	0.68	1.00	0.59	0.49	0.55	0.44	0.21	0.56	0.44
SF6	0.55	0.27	0.08	0.28	0.66	0.51	0.52	0.47	0.71	0.46	0.54	0.61	0.54	0.18	0.55	0.28	0.59	0.72	0.59	1.00	0.60	0.67	0.60	0.31	0.57	0.55
CH3Cl	0.75	0.65	0.17	0.61	0.87	0.72	0.80	0.79	0.71	0.68	0.79	0.67	0.43	0.06	0.79	0.27	0.61	0.78	0.49	0.60	1.00	0.90	0.89	0.18	0.87	0.73
CH2Cl2	0.77	0.65	0.17	0.56	0.88	0.81	0.81	0.75	0.73	0.69	0.73	0.67	0.44	0.10	0.85	0.24	0.60	0.82	0.55	0.67	0.90	1.00	0.89	0.29	0.86	0.77
CHCl3	0.88	0.62	0.14	0.47	0.92	0.71	0.84	0.36	0.79	0.75	0.56	0.71	0.43	0.10	0.74	0.30	0.72	0.72	0.44	0.60	0.89	0.89	1.00	0.28	0.84	0.75
CH3CCl3	0.27	0.43	0.08	0.18	0.18	0.31	0.28	0.22	0.16	0.30	0.17	0.13	-0.08	0.26	0.33	0.11	0.24	0.26	0.21	0.31	0.18	0.29	0.28	1.00	0.29	0.42

Ratio-based emissions calculations



atio-based Method Details

$$E_x = E_r \times \Delta C_x/\Delta C_r \times M_x/M_r$$



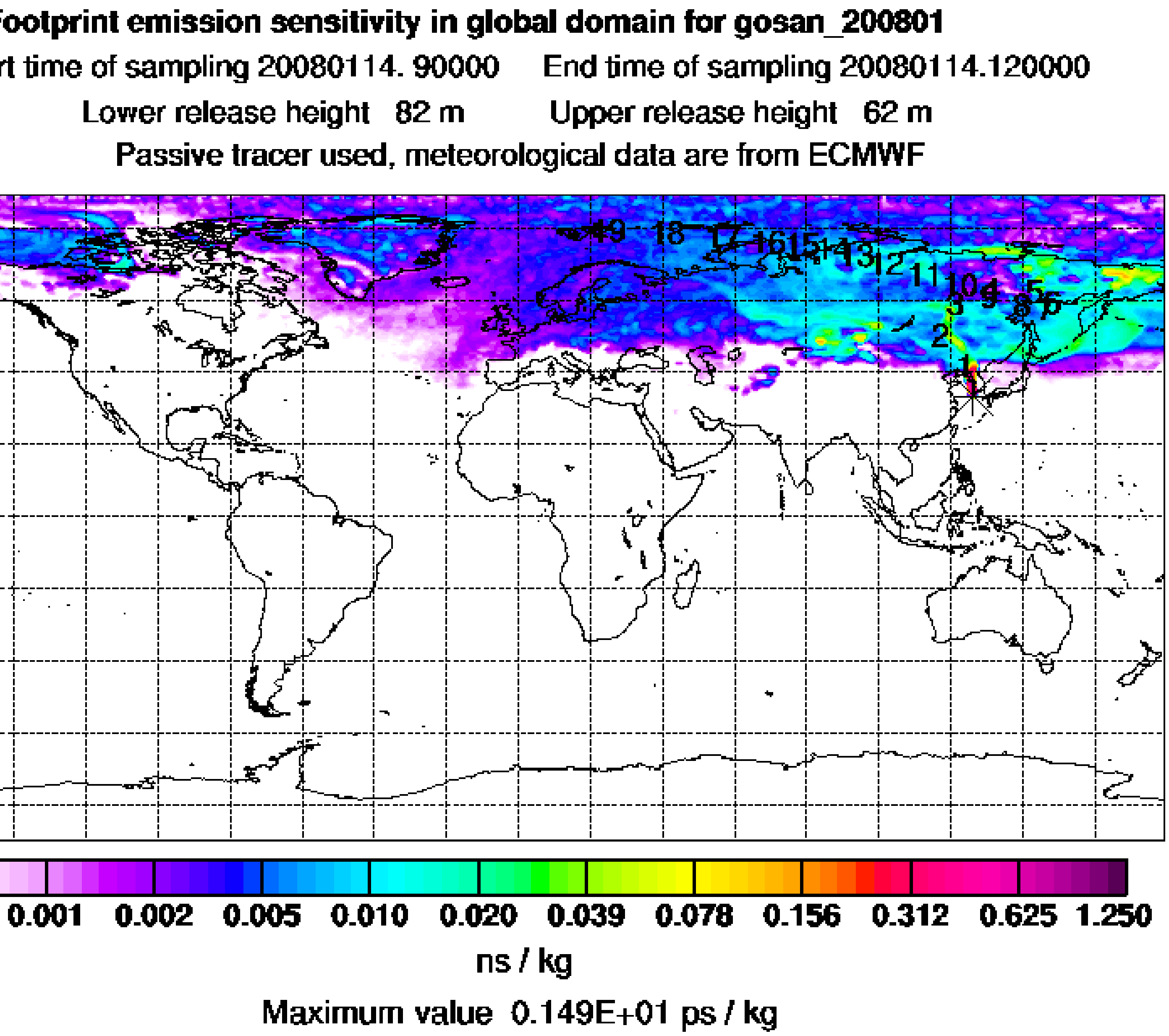
E_x : Emission of target compound.

E_r: Emission of tracer compound.

$\Delta C_x/\Delta C_r$: Relative enhancement ratio of target to

tracer compound.

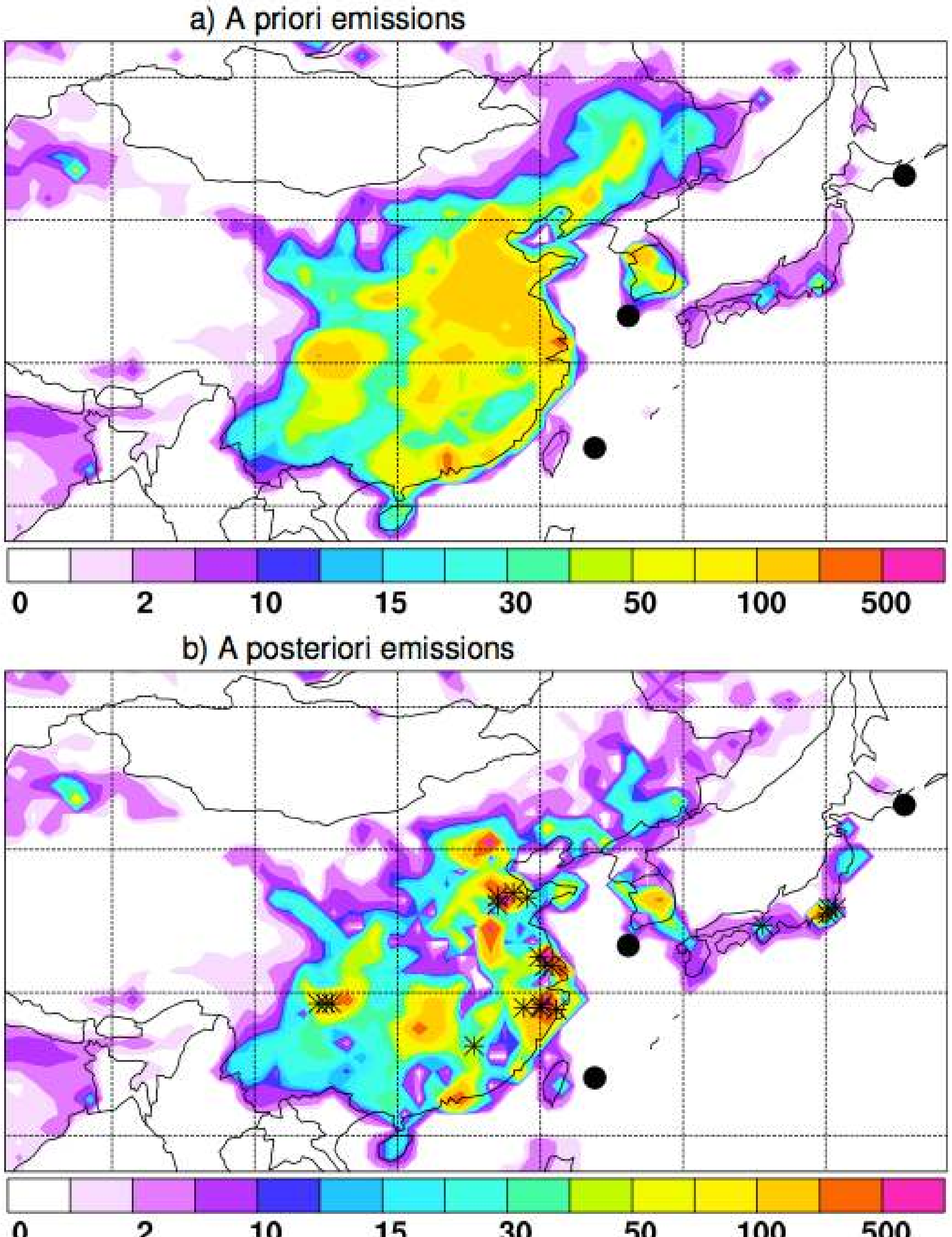
LEXPART Lagrangian particle dispersion model



eleasing and following millions of

- Open source model developed by A. Sto
(NILU, Norway)
- Meteorological data: ECMWF/GFS, 1°x1° 3~6hr
- 10d back-trajectories
- http://transport.nilu.no/flexpart

LEXPART Inversion Method



- Make first-guess of emissions (*a priori*), normally based on population density

- Statistical analysis of the *a priori* compared to measurements, deriving optimized emissions (*a posteriori*)

- Analytical method influenced by uncertainties in *a priori*

- Able to incorporate

rect Inversions of HCFCs and HFCs

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

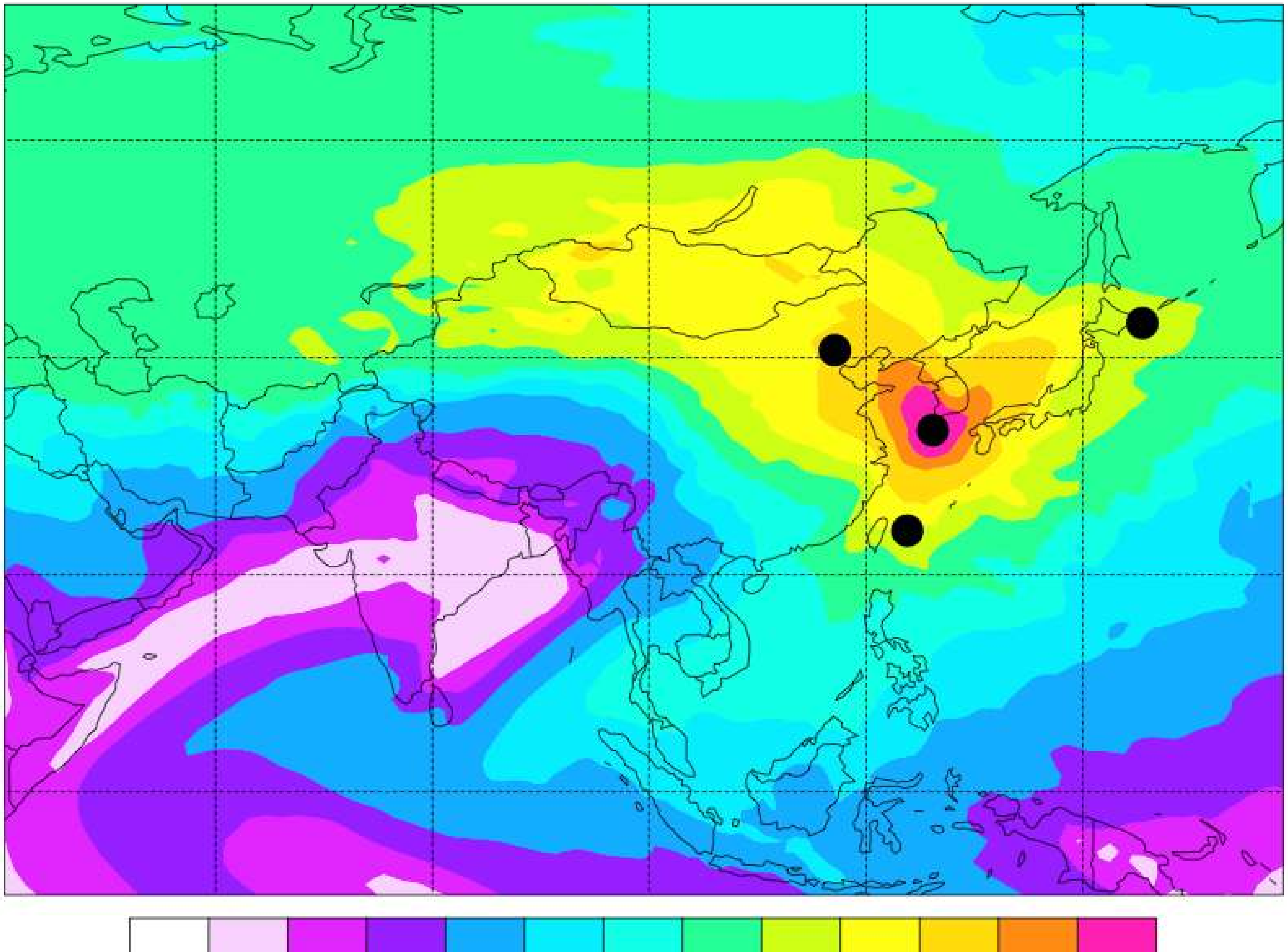
A. Stohl[1], J. Kim[2], S. Li[2], S. O'Doherty[3], J. Mühle[4], P. K. Salameh[4], T. Saito[5], M. K. Vollmer[6], D. Wan[7], R. F. Weiss[4], B. Yao[8], Y. Yokouchi[5], and L. X. Zhou[8]

[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

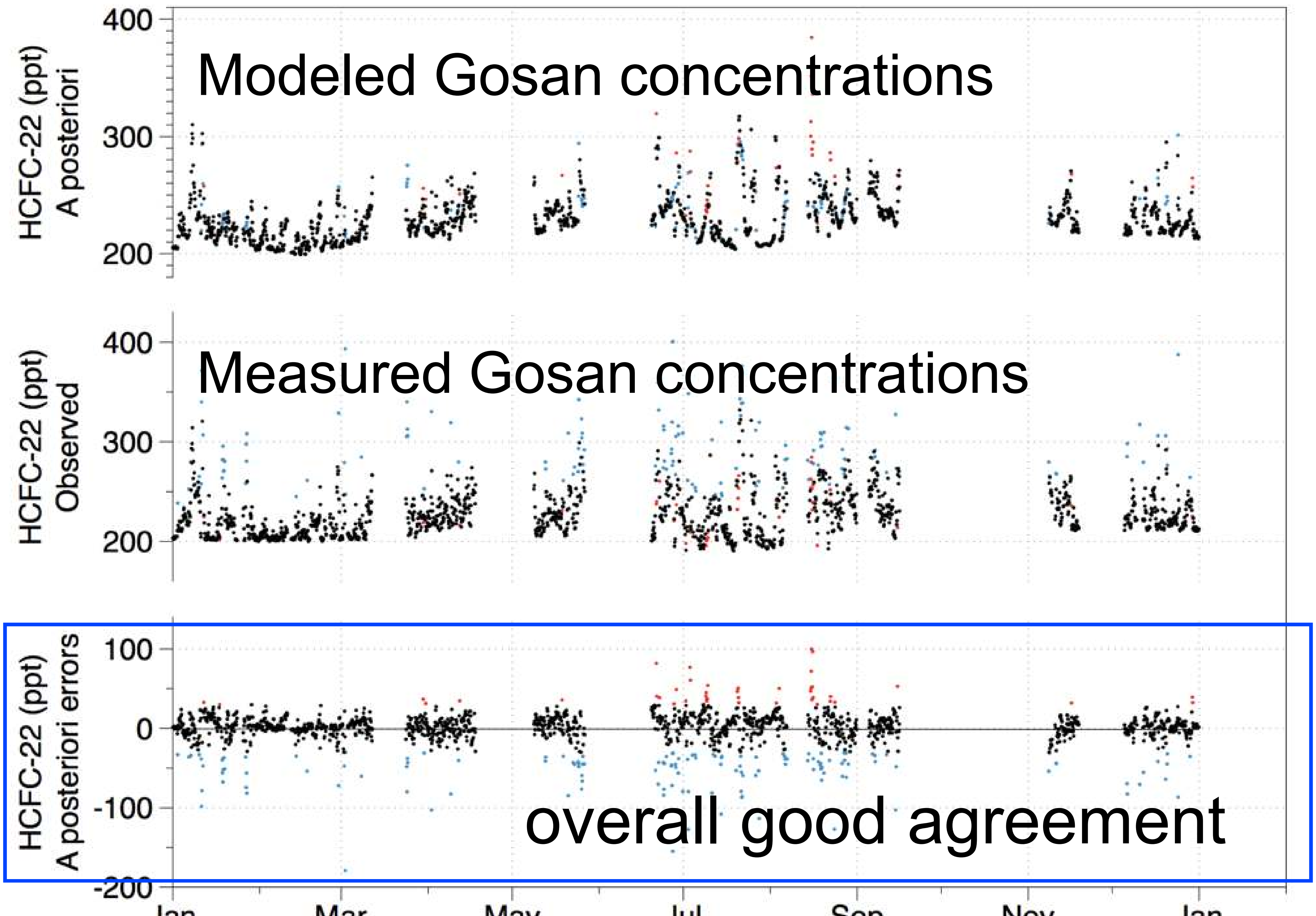
Received: 18 November 2009 – Published in Atmos. Chem. Phys. Discuss.: 1 February 2010

verage sensitivity calculated from FLEXPAR

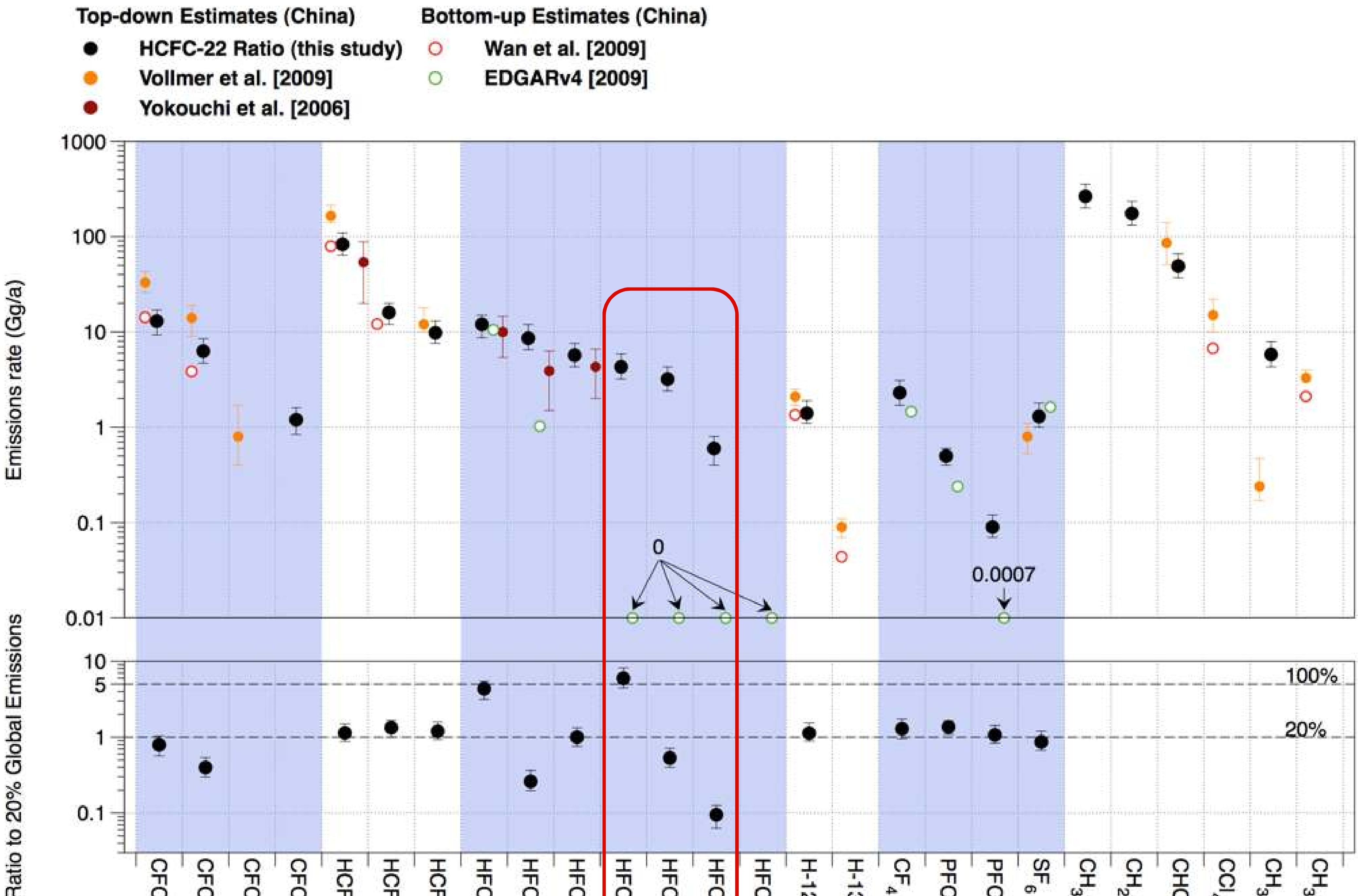
- Basis for inversion, overview of how air mass arrives at the receptor site



odel verification: HCFC-22 concentration



gure 2, Kim et al. (2010), *GRL*



missions in China: Ratio-based Method

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

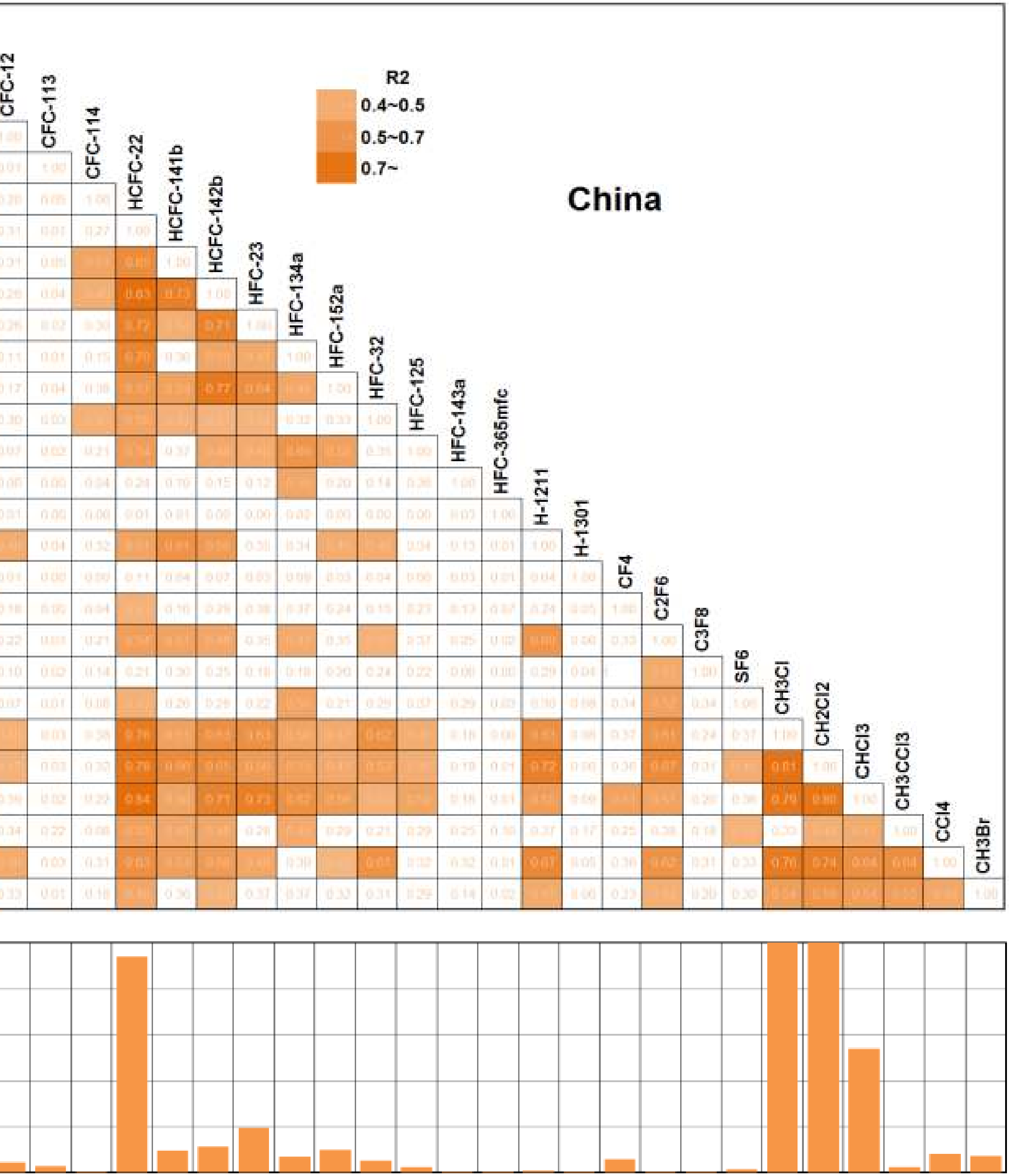
Regional atmospheric emissions determined from measurements at Jeju Island, Korea: Halogenated compounds from China

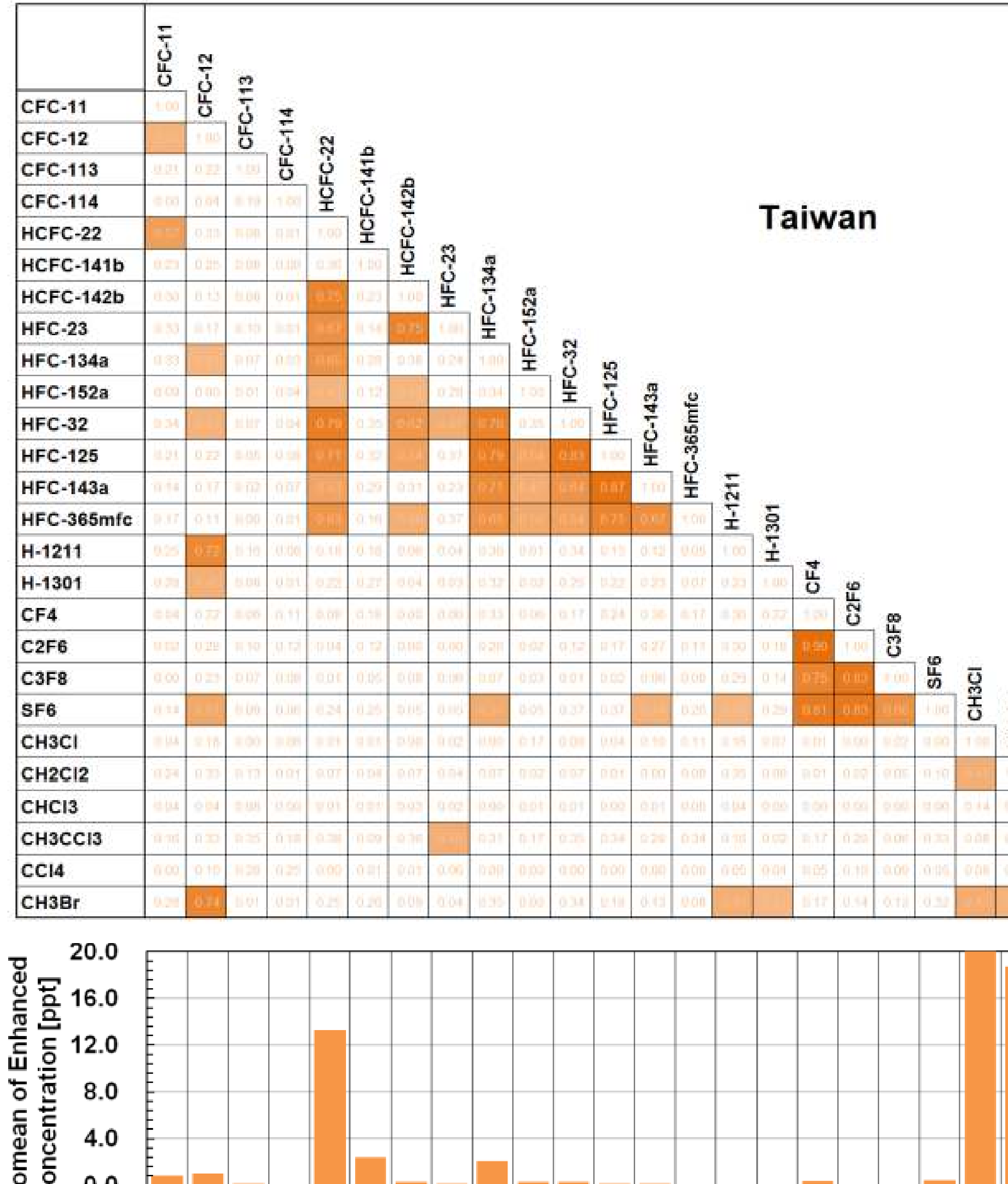
Jooil Kim,[1] Shanlan Li,[1] Kyung-Ryul Kim,[1,2] Andreas Stohl,[3] Jens Mühle,[4] Seung-Kyu Kim,[1] Mi-Kyung Park,[1,2] Dong-Jin Kang,[5] Gangwoong Lee,[6] Christina M. Harth,[4] Peter K. Salameh,[4] and Ray F. Weiss[4]

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

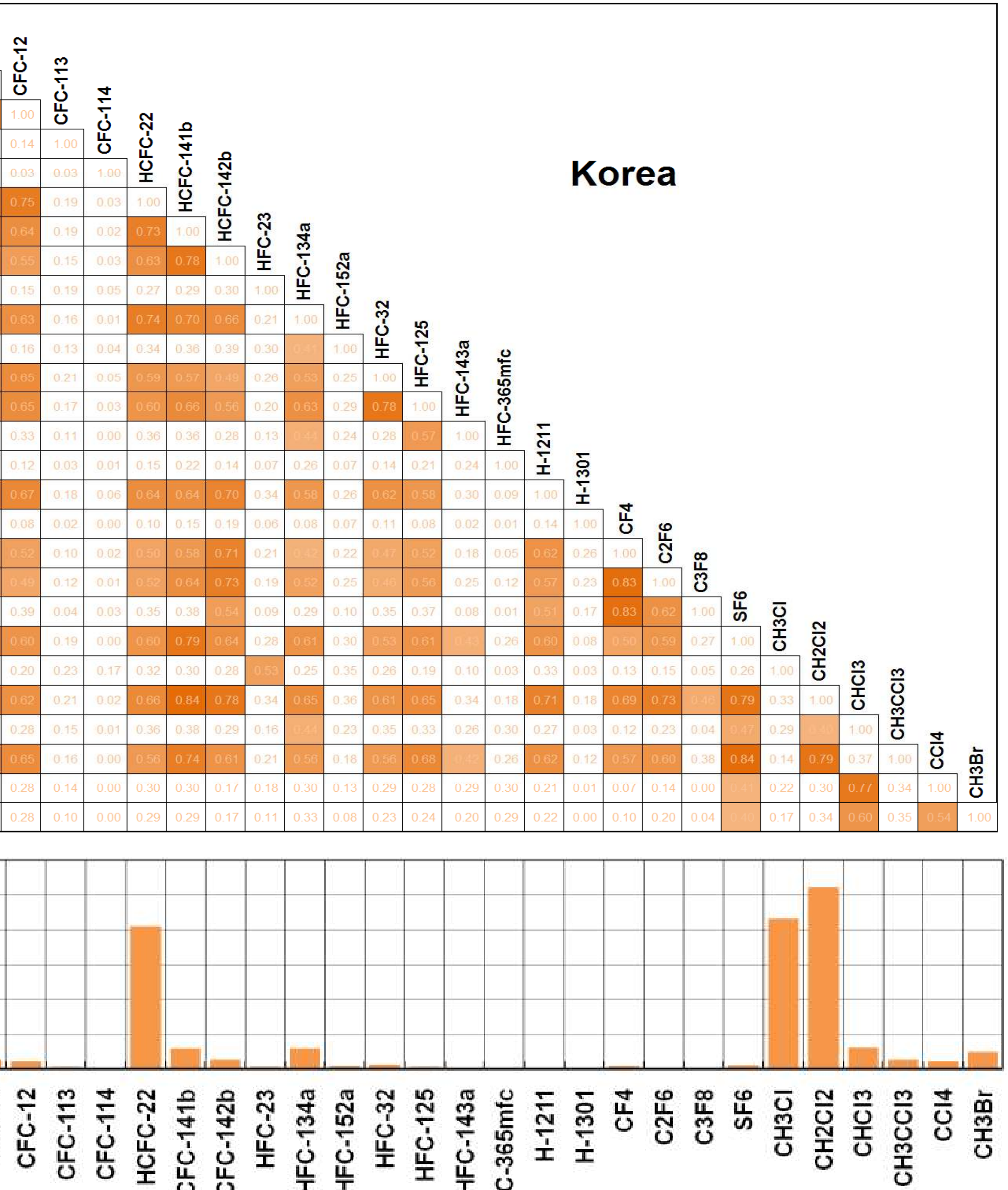
- Ratio-based technique with HCFC-22 as tracer
- Significant emissions of halogenated compounds in China, even for compounds previously expected to be small

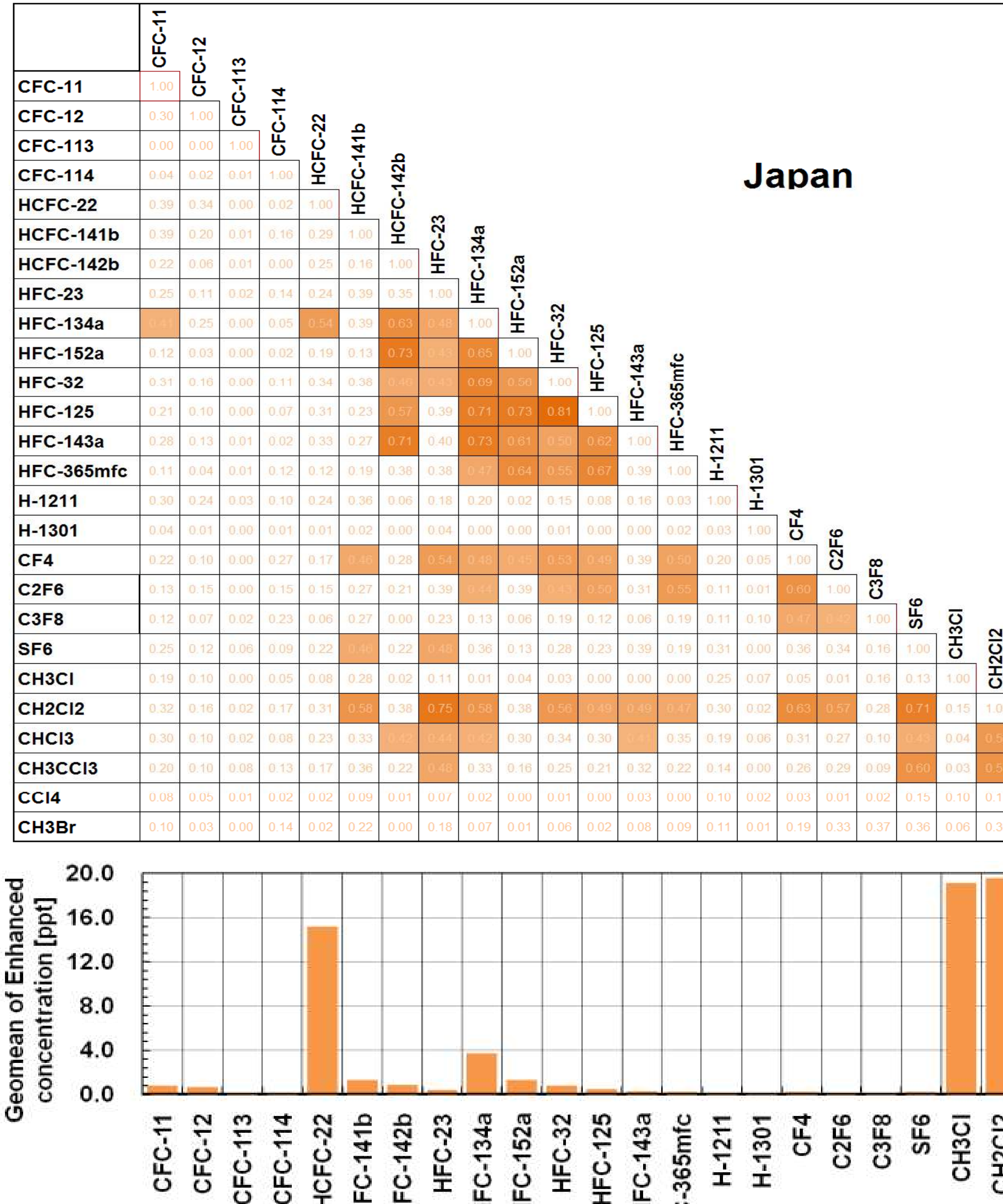
et al. (2011), *ES&T - China and Taiwan*



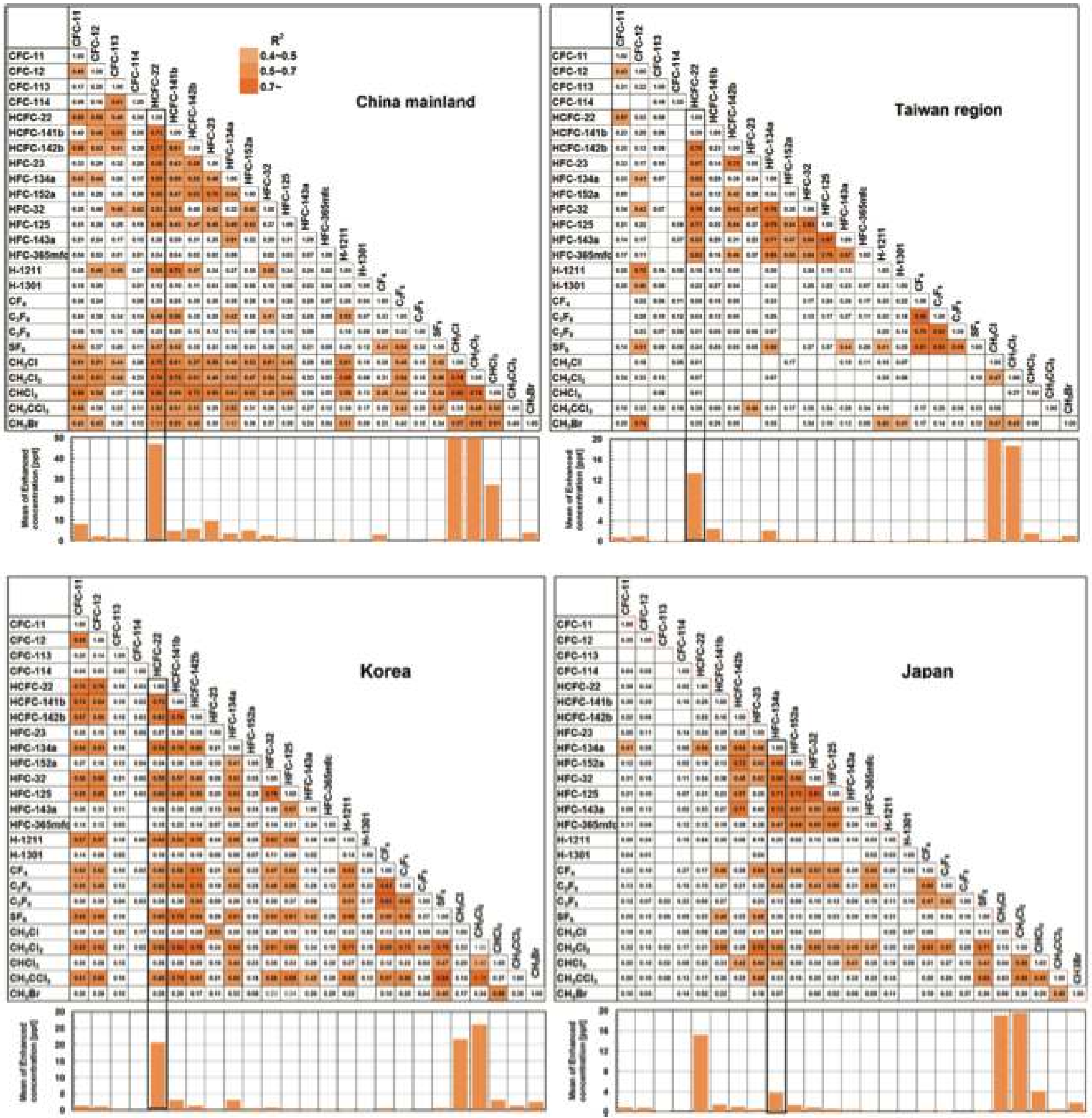


et al. (2011), *ES&T - Korea and Japan*





et al. (2011), *ES&T*



et al. (2011), *ES&T - Emissions in East Asia*

Unit: kt/a

	China	Taiwan	Korea	Japan	Total	to Global (%)
CFC-11	8.9 ±0.8	0.27 ±0.06	0.9 ±0.2	0.7 ±0.05	10.8	13.1
CFC-12	4.9 ±0.5	0.18 ±0.04	0.8 ±0.2	0.6 ±0.04	6.5	8.2
CFC-114	1.2 ±0.4				1.2	
HCFC-22	68.1 ±6.6	2.2 ±0.5	7.9 ±1.5	7.5 (7-8)	85.7	23.3
HCFC-141b	12.8 ±1.2	0.5 ±0.11	2.1 ±0.4	1 ±0.07	16.4	27.3
HCFC-142b	8.5 ±0.8	0.12 ±0.03	0.8 ±0.1	0.6 ±0.04	10.0	24.4
HFC-23	8.8 ±0.8	0.07 ±0.02	0.13 ±0.02	0.2 ±0.01	9.2	65.2
HFC-134a	7.1 ±0.7	0.52 ±0.12	1.6 ±0.3	3.1 ±0.2	12.3	7.5
HFC-152a	4.7 ±0.4	0.08 ±0.02	0.10 ±0.02	0.6 ±0.04	5.5	19.2
HFC-32	3.7 ±0.4	0.05 ±0.01	0.20 ±0.04	0.3 ±0.02	4.3	118.1
HFC-125	2.7 ±0.3	0.07 ±0.02	0.26 ±0.05	0.5 ±0.03	3.5	11.8
HFC-143a	0.5 ±0.05	0.04 ±0.01	0.07 ±0.01	0.2 ±0.01	0.8	2.6
HFC-365mfc		0.01 ±0.003			0.01	0.3
H-1211	1.1 ±0.1		0.1 ±0.02		1.2	3.8
CF_4	1.3 ±0.1		0.21 ±0.04	0.1 ±0.01	1.6	5.1
C_2F_6	0.4 ±0.04		0.1 ±0.02	0.1 ±0.01	0.6	1.9
C_3F_8	0.07 ±0.01				0.1	0.2
SF_6	0.9 ±0.1		0.5 ±0.1		1.4	18.9
CH_3Cl	201 ±19				201.0	
CH_2Cl_2	131 ±12		16.8 ±3.2	9.2 ±0.6	157.0	
$CHCl_3$	35.5 ±3.3			1.8 ±0.1	37.3	
CH_3CCl_3	1.4 ±0.3	0.13 ±0.03	1.4 ±0.3	0.4 ±0.02	3.3	
CH_3Br	3.4 ±0.3				3.4	
Per group						
CFCs	15	0.45	1.7	1.3	18.5	10.7
HCFCs	89.4	2.82	10.8	9.1	112.1	24.0

mission Patterns of Halocarbons in East Asia

Environmental Science & Technology

ARTICLE

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Emissions of Halogenated Compounds in East Asia Determined from Measurements at Jeju Island, Korea

Shanlan Li, Jooil Kim, and Kyung-Ryul Kim*

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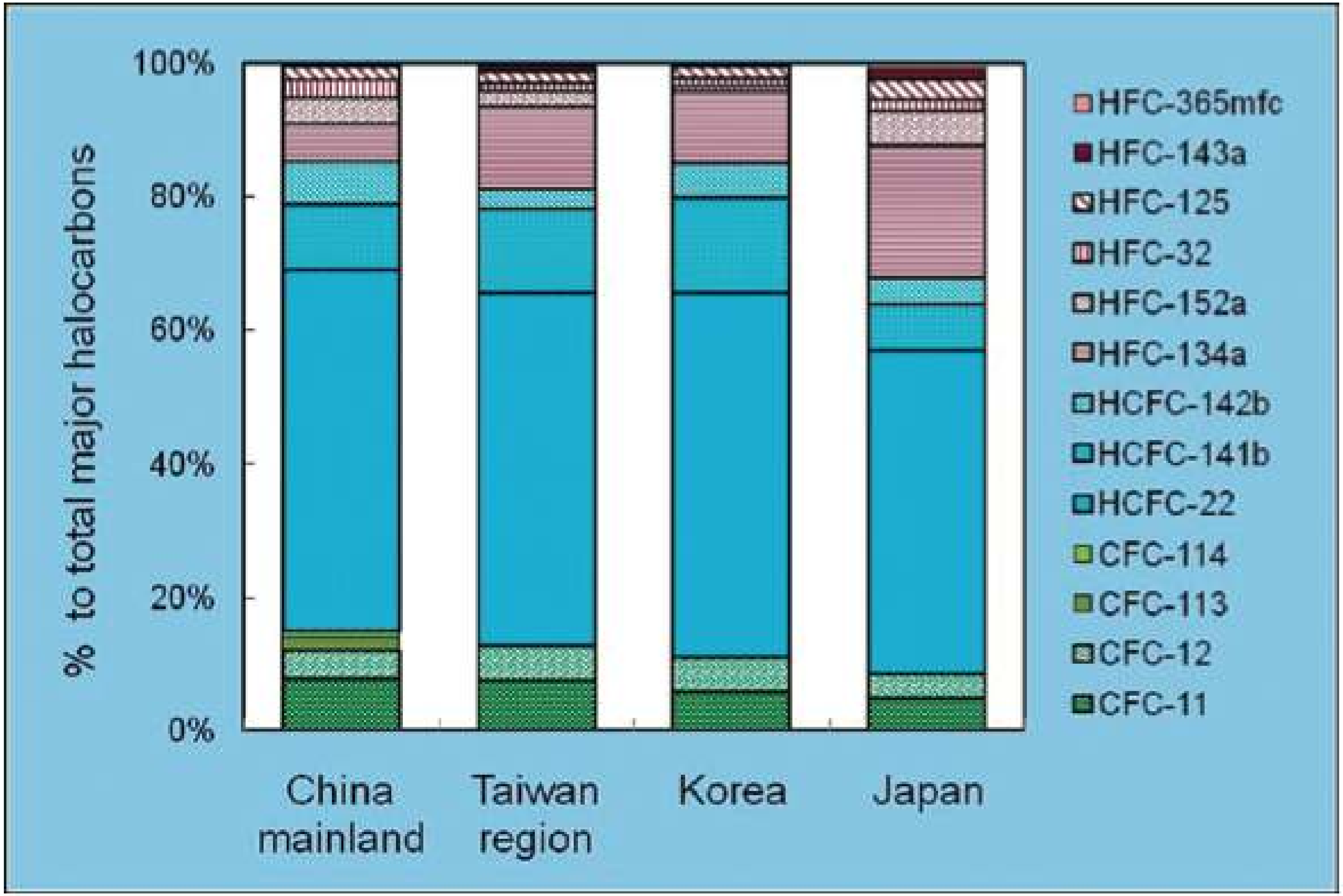
Tim Arnold, Christina M. Harth, Peter K. Salameh, and Ray F. Weiss

et al. (2011), *ES&T - Relative emissions by untry*



Fractions of each compound to total halocarbons (CFCs, HCFCs, and HFCs) emissions for 2008 in each country.

ncertainties in the FLEXPART inversions

ncertainties in the *a priori* emissions accounted for by:

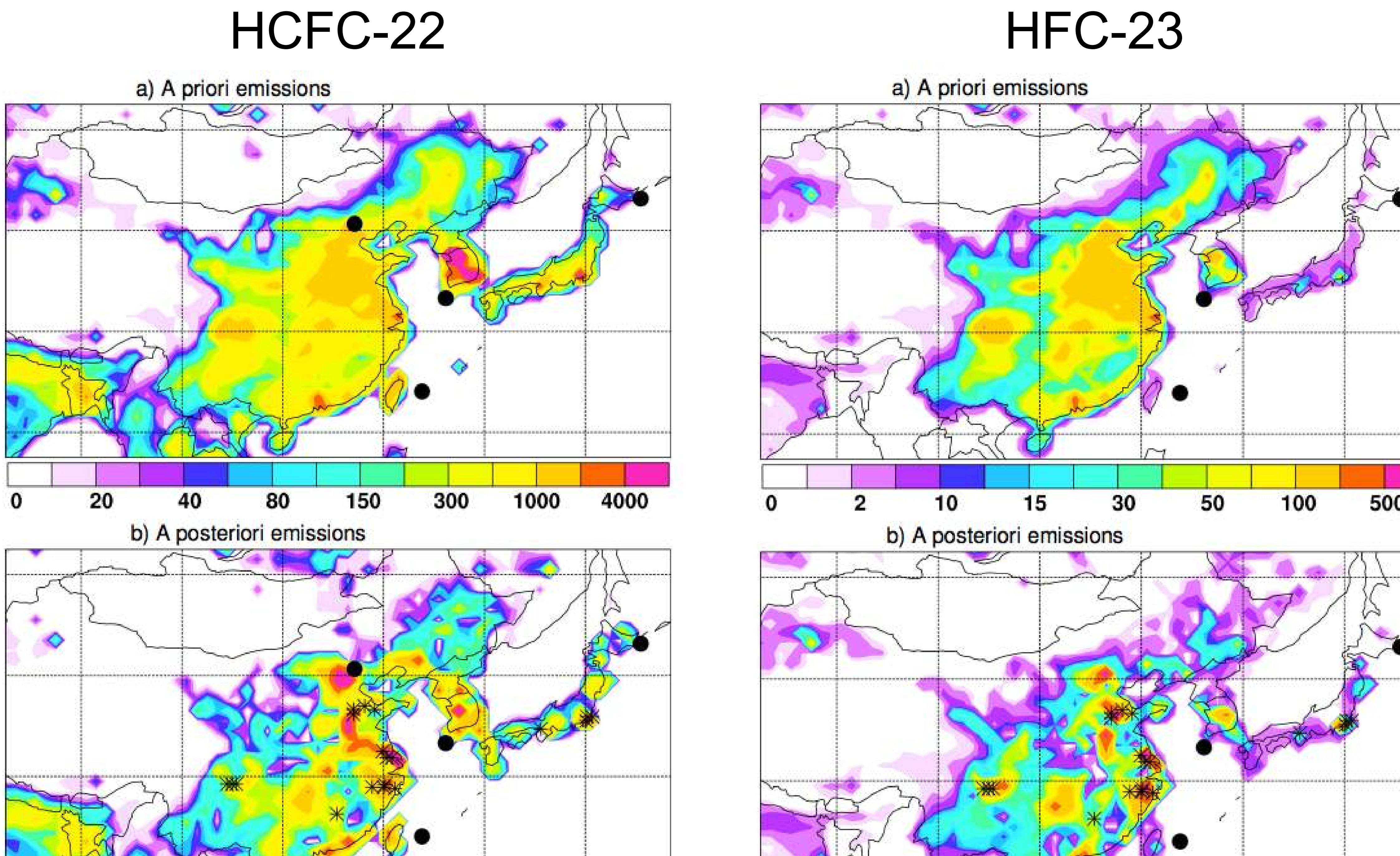
- Varying the *a priori* emissions by $\pm$50%
- Using different *a priori* distributions

ncertainties in input Met. Data

- Comparison studies between ECMWF and GFS: on-going

ncertainties can be reduced by incorporating multiple measurement sites
version

ohl et al. (2010), *ACP*



ummary and Conclusions

igh-frequency, *in situ* measurements of key GHGs for monitoring missions in East Asia at Gosan

- Halogenated compounds (CFCs, HCFCs, HFCs, PFCs, SF_6, etc), in collaboration with the AGAGE Network

Gosan measurements are very useful for monitoring GHG emissions he East Asia region

- Clear background trajectories + pollution trajectories from China, Korea, Japan and Taiwan during non-summer months
- Emissions estimated using both ratio-based and inversion modeling techniques
- East Asian emissions are significant to global budgets in halogenated compounds

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ay F. Weiss, Jens Muhle, Christina Harth, Peter Salameh (AGAGE, Scripp
stitution of Oceanography, UC San Diego)

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f Oceanography, UC San Diego)

ndreas Stohl (Norwegian Institute for Air Research)

Thank You.