



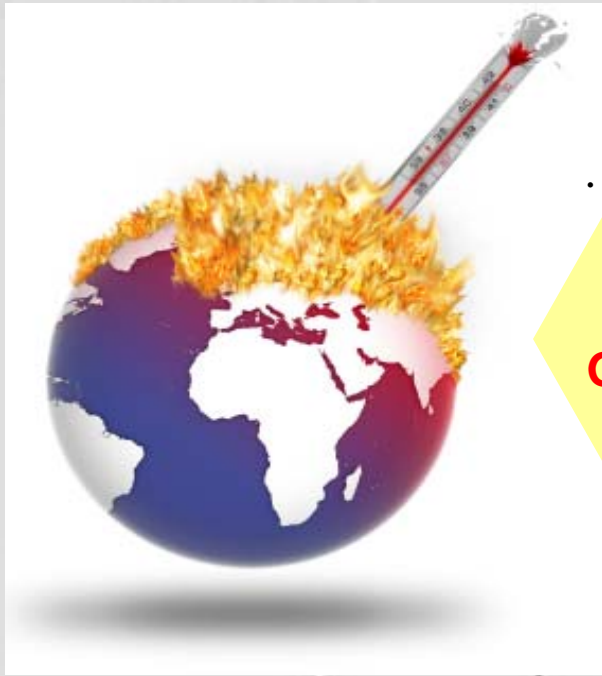
Materials Science & Technology

# Co-located halogenated greenhouse gases measurements by GC-ECDs and Medusa-GC/MS at the Shangdianzi GAW regional station, China

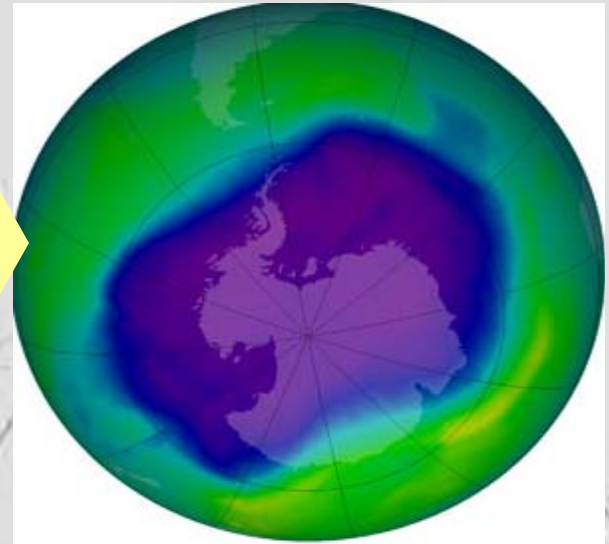
*Bo Yao<sup>1</sup>, Lingxi Zhou<sup>1</sup>, Martin K. Vollmer<sup>2</sup>,  
Fang Zhang<sup>1</sup>, Peichang Li<sup>1</sup>, Lifeng Guo<sup>3</sup>*

**CAMS, CMA, China;  
EMPA, Switzerland;  
HIMS, CMA, China;**

*15-17 May 2012  
NOAA/ESRL 40<sup>th</sup> Global Monitoring Annual Conference  
Boulder, CO, UAS*



## Halogenated Greenhouse Gases



### Kyoto protocol

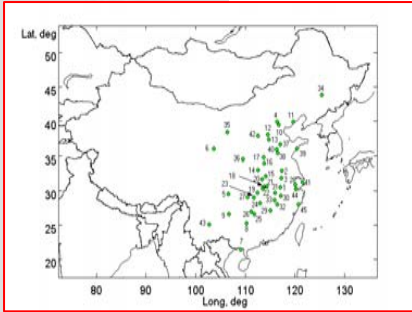
- $\text{CO}_2$
- $\text{CH}_4$
- $\text{N}_2\text{O}$
- **HFCs**
- **PFCs**
- **$\text{SF}_6$**

### Montreal protocol

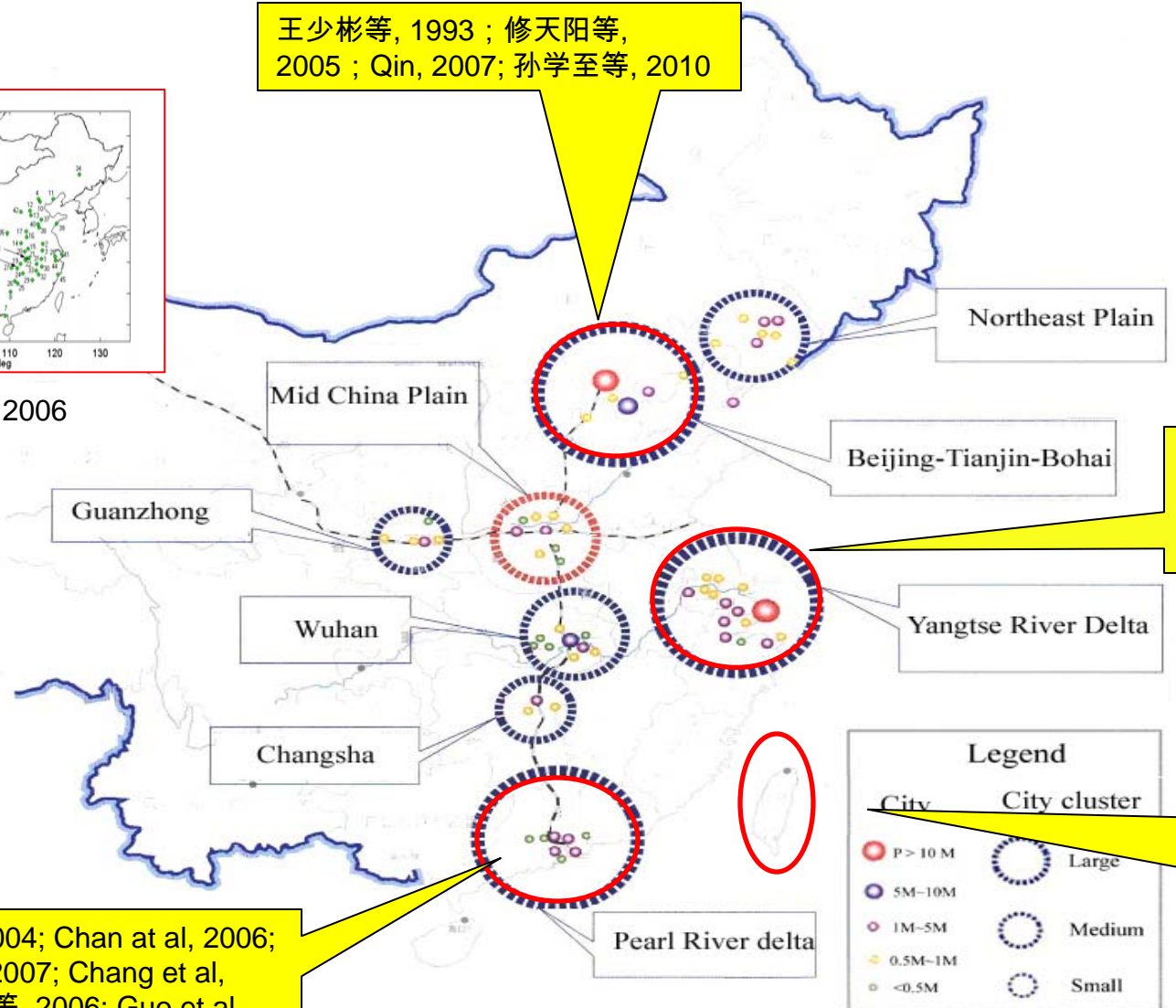
- **CFCs**
- **Halons**
- **$\text{CH}_3\text{CCl}_3$**
- **$\text{CCl}_4$**
- **$\text{CH}_3\text{Cl}$**
- **$\text{CH}_3\text{Br}$**
- **HCFCs**

# Halogenated Greenhouse Gases measurements in China

王少彬等, 1993 ; 修天阳等, 2005 ; Qin, 2007; 孙学至等, 2010



Barletta et al, 2006



陈立民等, 1999; 吴力波等, 2000; 孙皓林等, 2001 ; 杨越等, 2001 ; Wu et al, 2001

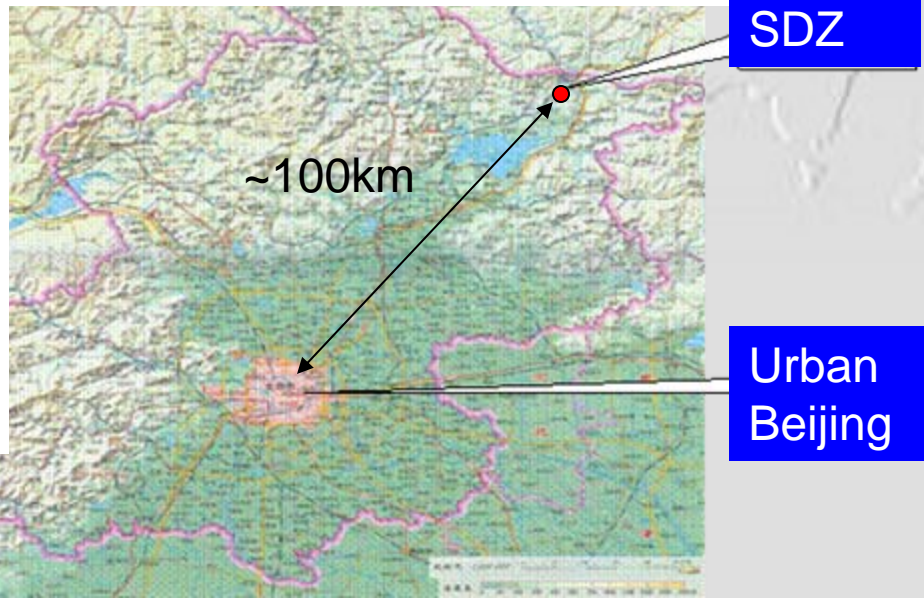
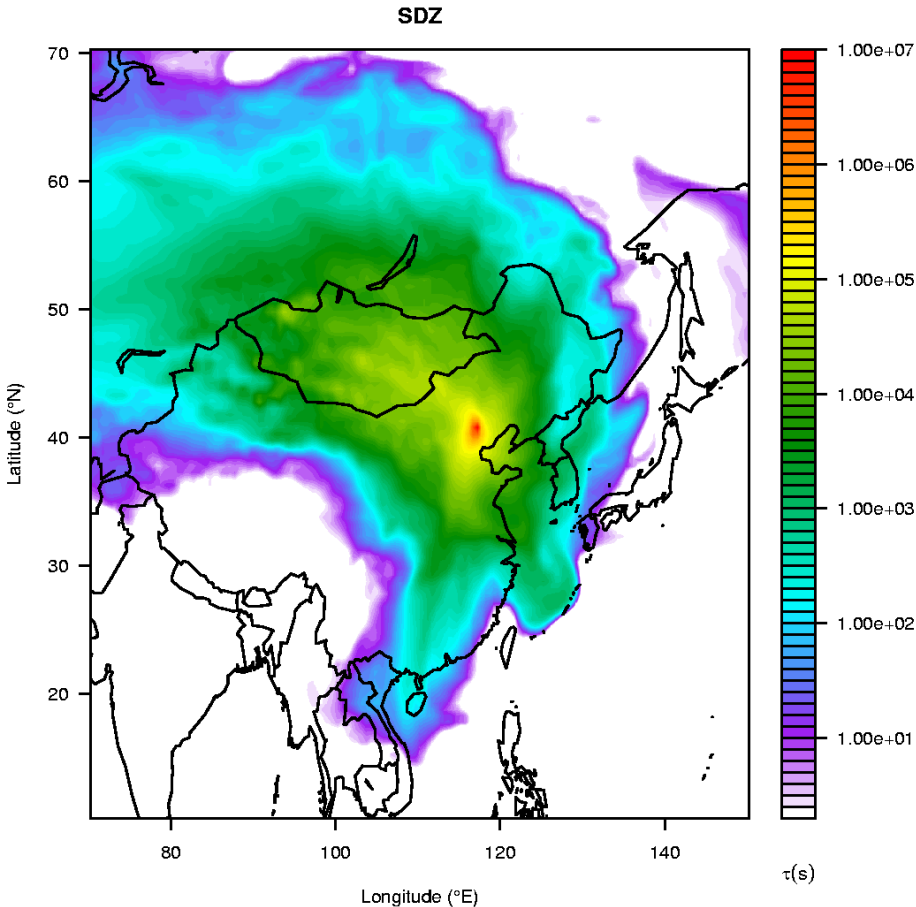
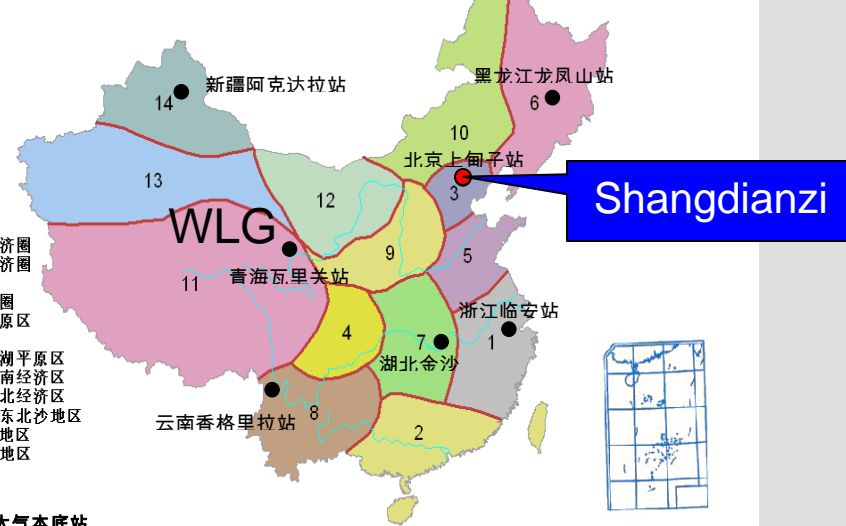
Wang et al, 1998; Chang et al, 2001; Chang et al, 2007 ; Lee et al., 2007 ; Lee et al., 2008

Guo et al, 2004; Chan et al, 2006; Chan et al, 2007; Chang et al, 2008 ; 张芳等, 2006; Guo et al. 2009; Shao et al, 2011

# Shangdianzi Station

40°39'N, 117°07'E, 291.3 m asl  
 WMO/GAW regional station  
 CMA background station

中国气象局大气本底站网  
 Black points are background station run by CMA



Nov 2006 - Oct 2007  
 5 day trajectories  
 Calculations done by S. Henne, Empa



## Halogenated greenhouse gases :

- **GC-ECDs:** Since October 2006
- **Medusa-GC/MS:** Since May 2010
- **Canister Sampling:** Since September 2010

## Carbon cycle greenhouse gases

- **Flask Sampling:** Since July, 2007, CO<sub>2</sub>/CH<sub>4</sub>/CO/N<sub>2</sub>O/SF<sub>6</sub>/isotope
- **NDIR:** Since March 2007, CO
- **CRDS:** Since January 2009, CO<sub>2</sub>/CH<sub>4</sub>/CO
- **GC-FID/ECD:** Since January 2010, CH<sub>4</sub>/CO/N<sub>2</sub>O/SF<sub>6</sub>



EU Sixth Framework Programme (FP6)

Priority 1.1.6.3

**GLOBAL CHANGE AND ECOSYSTEMS**

**Specific Support Action (SSA)**

- Project acronym: **SOGE-A**
- Project full title: **System for Observation of halogenated Greenhouse gases in Europe and Asia**
- Contract no.: **GOCE-CT-2003-505419**
- Period of contract: **01/06/2004 - 31/05/2007**

Participants:

CAMS

Empa

NILU

U. Bristol

U. Urbino

} SOGE



# In-situ CFCs/HCFCs/Halons measurement since 2006



Inlet



2007/03/26

## Sampling

## Separation

## Detection

Sample loops

packed columns

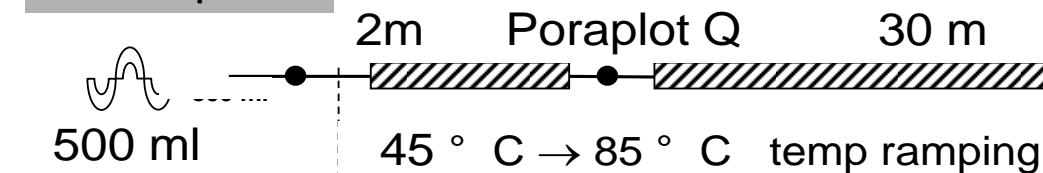


ECD 1

SF<sub>6</sub>  
CFC-12  
CFC-11  
CFC-113  
CHCl<sub>3</sub>  
CH<sub>2</sub>CCl<sub>3</sub>  
CCl<sub>4</sub>  
C<sub>2</sub>HCl<sub>3</sub>  
C<sub>2</sub>Cl<sub>4</sub>

trap

capillary columns



ECD 2

O<sub>2</sub> Doping

H-1301  
HCFC-22  
HCFC-142b  
CH<sub>3</sub>Br  
H-1211



# Medusa-GC/MS assemble at EMPA and install at SDZ station in May 2010

June 2008, Empa



July 2009, Empa

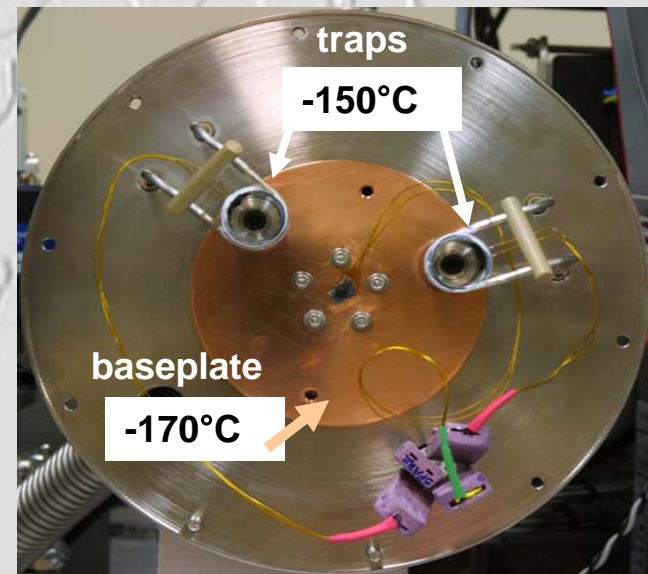


May 2010, Shangdianzi



# Medusa-GC/MS

## The new generation of instrument for Halogenated Greenhouse Gases measurement



Miller, B. et al.2008. Medusa: a sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds. Anal. Chem. 80 (5), 1536–1545.

# Halogenated Greenhouse Gases Measured

## Montreal Protocol

- **CFCs: Fluorochlorocarbons**

*CFC-11*   *CFC-12*,   *CFC-13*  
*CFC-113*   *CFC-114*   *CFC-115*

- **HCFCs: Hydrofluorochlorocarbons**

*HCFC-141b*   *HCFC-124*   *HCFC-22*  
*HCFC-142b*

- **Halones: (containing bromo)**

*H-1301*   *H-1211*   *H-2402*

- **Halogenated Solvents**

*CH<sub>3</sub>CCl<sub>3</sub>*   *CCl<sub>4</sub>*   *CH<sub>3</sub>Br*  
*CH<sub>3</sub>Cl*

**Other Solvents:**

*CH<sub>3</sub>I*   *CHCl<sub>3</sub>*   *CH<sub>2</sub>Cl<sub>2</sub>*   *CCl<sub>2</sub>CHCl*  
*CCl<sub>2</sub>CCl<sub>2</sub>* .....

## Kyoto Protocol

- **HFCs: Hydrofluorocarbons**

*HFC-32*   *HFC-23*  
*HFC-125*   *HFC-134a*  
*HFC-143a*   *HFC-152a*  
*HFC-227ea*   *HFC-245fa*  
*HFC-143a*   *HFC-236fa*  
*HFC-365mfc*

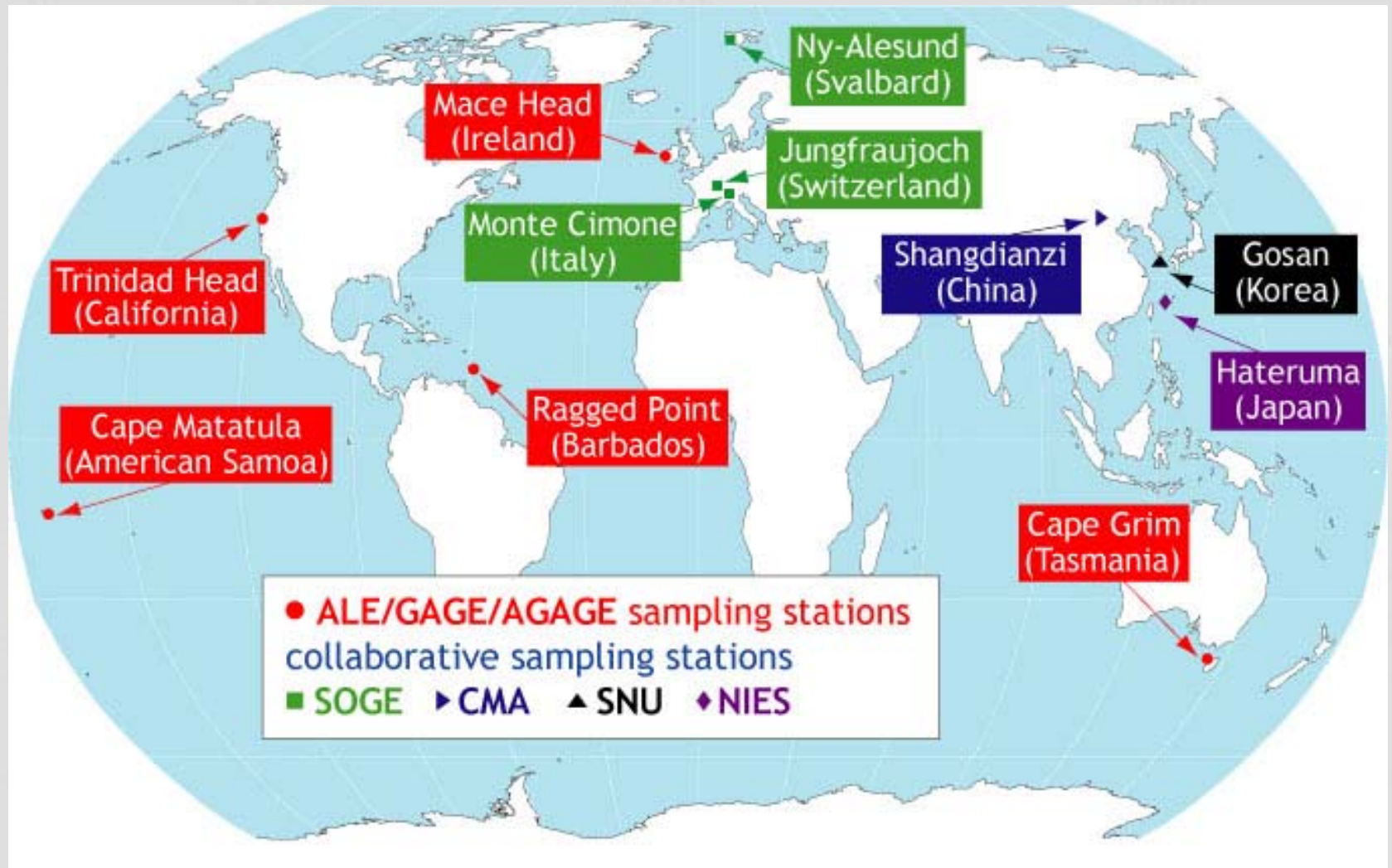
- **PFCs: Perfluorocarbons**

*CF<sub>4</sub>*   *C<sub>2</sub>F<sub>6</sub>*   *CF<sub>3</sub>CF<sub>2</sub>CF<sub>3</sub>*  
*C<sub>4</sub>F<sub>10</sub>*   *c-C<sub>4</sub>F<sub>8</sub>*   *CF<sub>3</sub>CF<sub>3</sub>*

- **SF<sub>6</sub>**

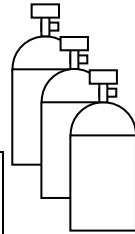
Compounds in blue are those  
can measured by both systems,  
In black are only measured by  
Medusa-GC/MS

# Join AGAGE and Affiliated Networks

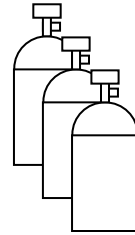


# Standard preparation and transfer

**AGAGE**  
Primary Calibration  
Scale  
Schripps Institution  
of Oceanography  
(SIO)



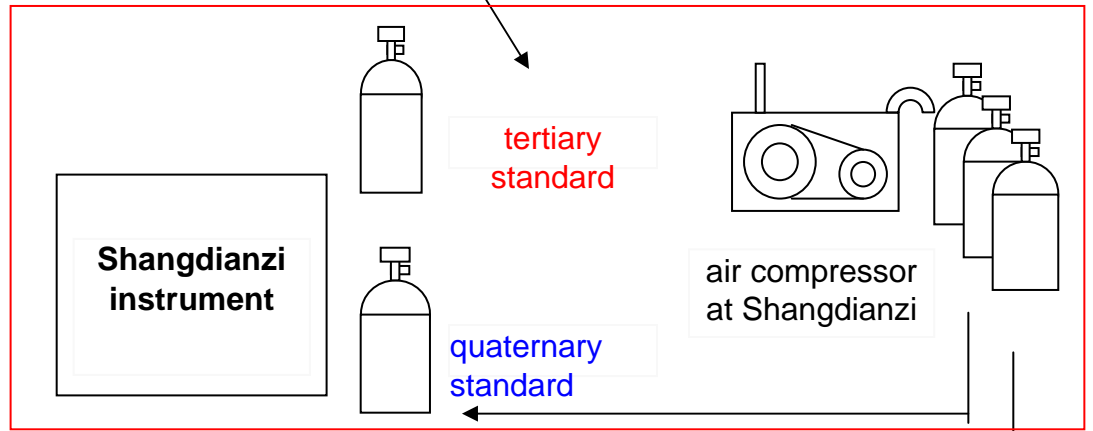
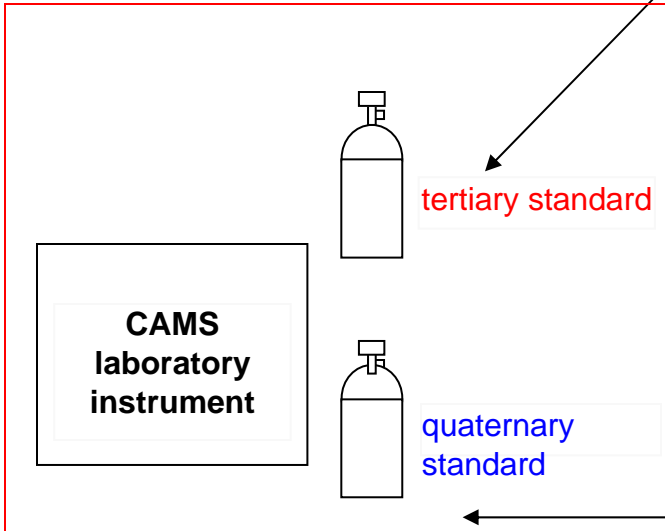
Primary/secondary  
standards



Transfers from SIO  
(Tertiary Standards)

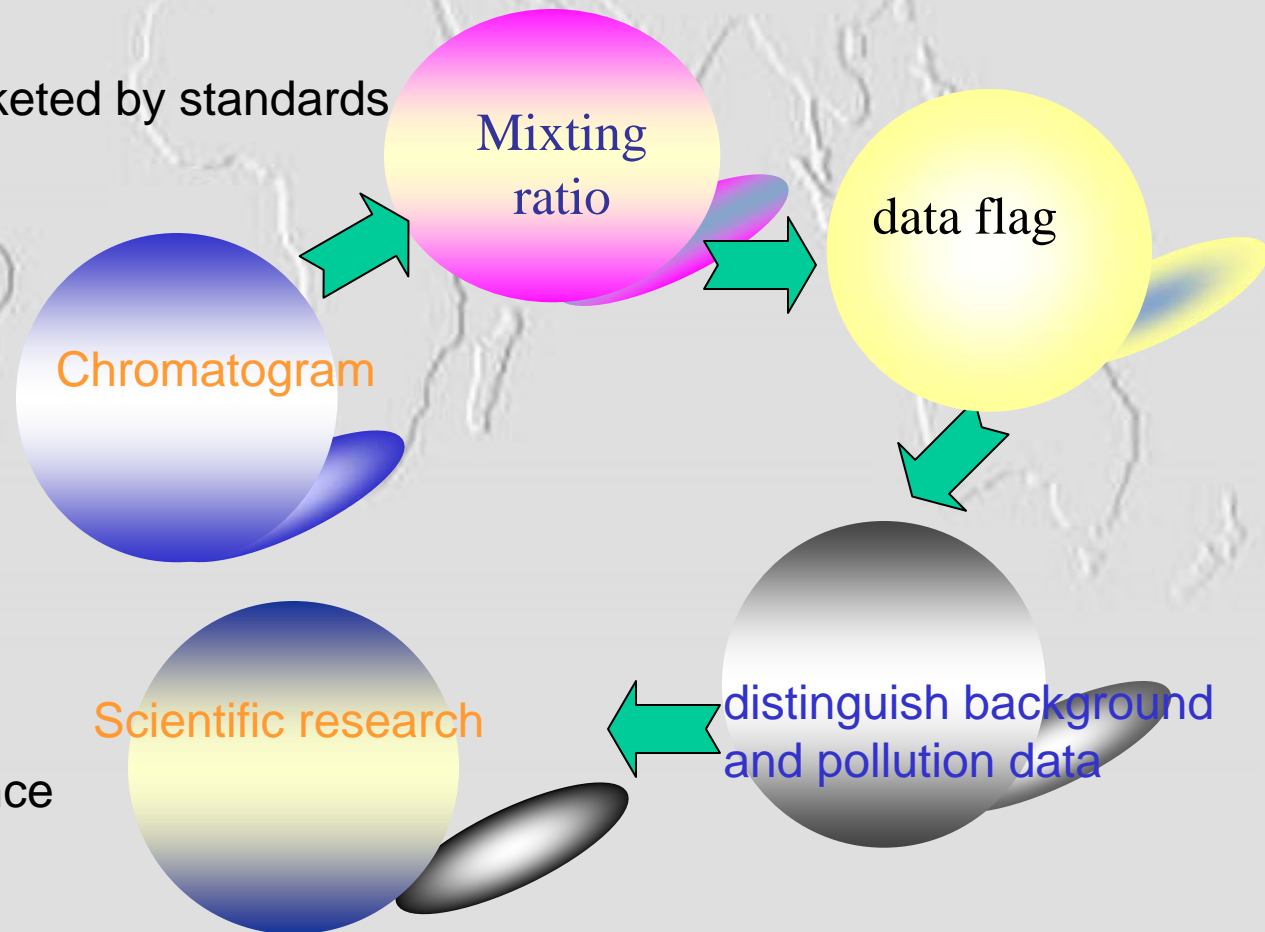


Install in May 2010



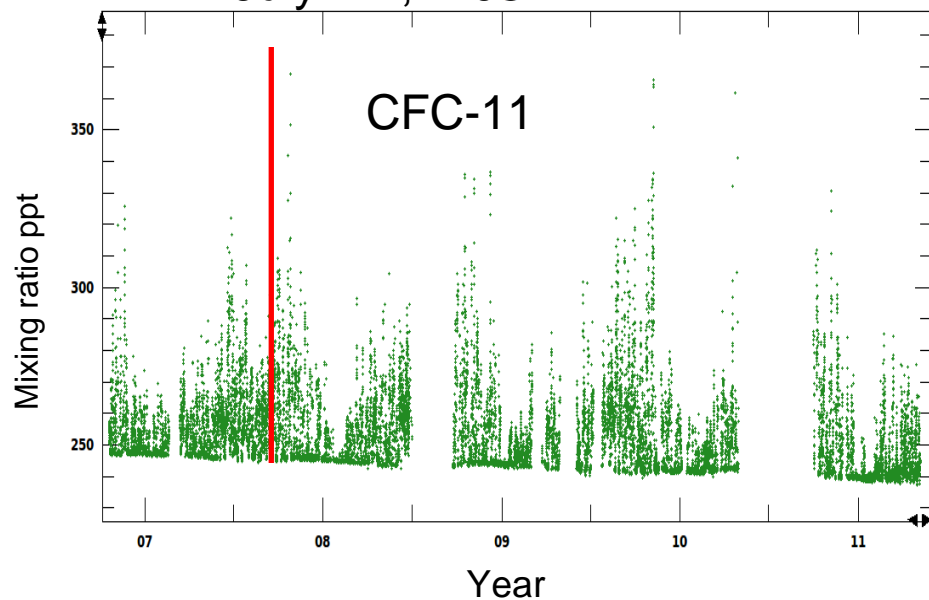
# QA/QC procedure and data process

- ✓ Air measurement is bracketed by standards
- ✓ Weekly target runs
- ✓ Weekly blank runs
- ✓ Weekly lab-air runs
- ✓ Non-linear test
- ✓ Daily system check
- ✓ Yearly system maintenance

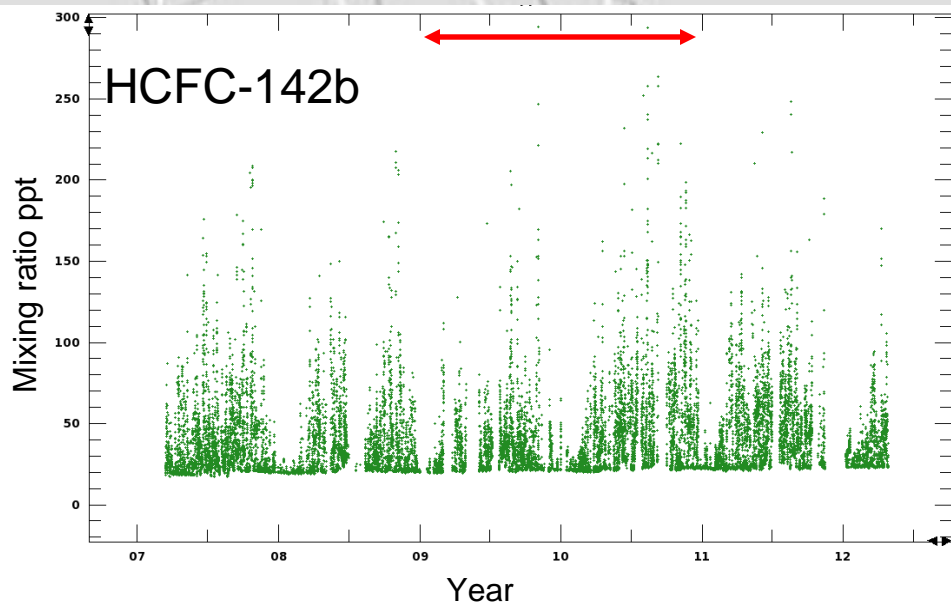


# Longest record of SF<sub>6</sub>, CFCs and HCFCs and Cl-solvents in-situ measurement in China

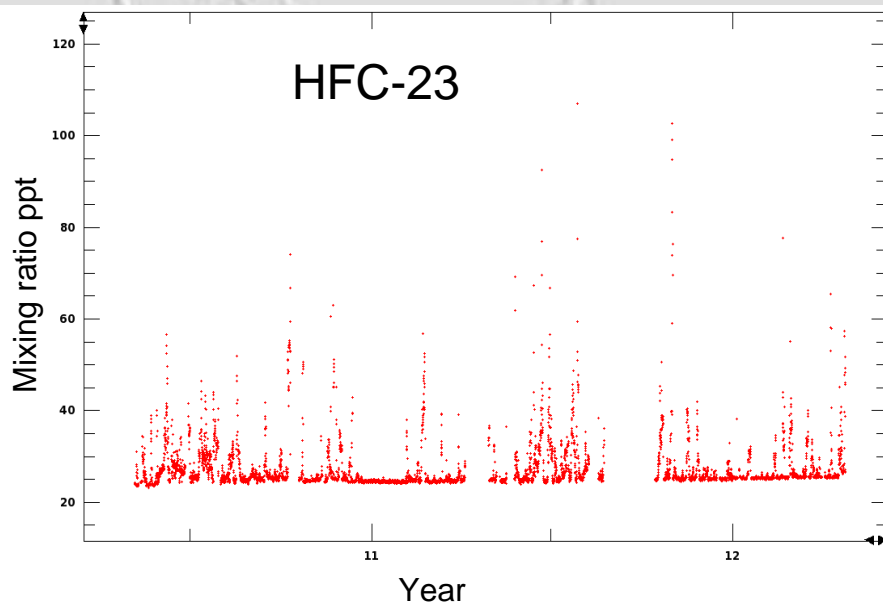
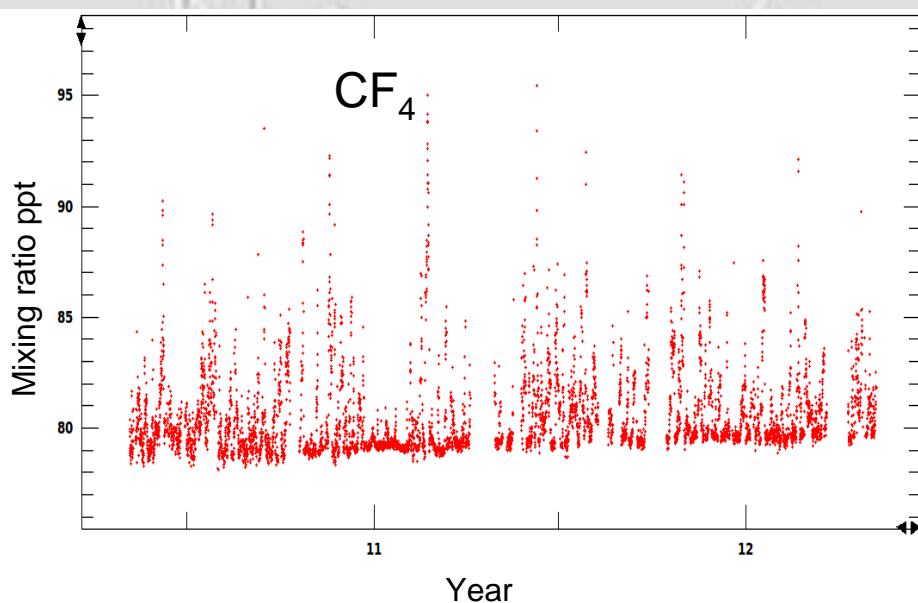
July 1<sup>st</sup>, 2007



Consumption freeze on Jan. 1<sup>st</sup>, 2013  
base level: 2009-2010

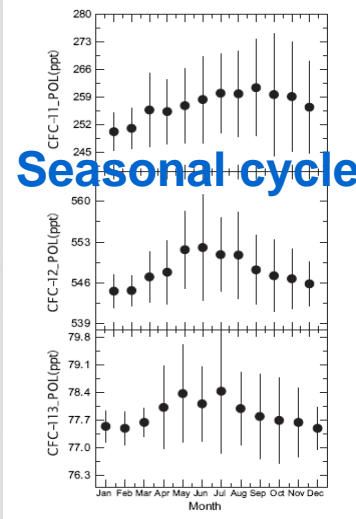


# First in-situ HFCs/PFCs measurement in China



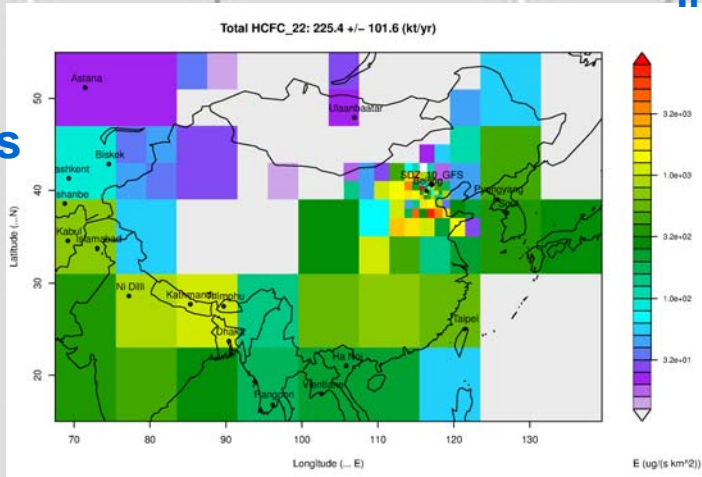


- ✓ Vollmer M. K., Zhou L. X., Gready B. R. et al. Emissions of ozone-depleting halocarbons from China, *Geophys. Res. Lett.*, 36, L15823, doi:10.1029/2009GL038659, 2009
- ✓ Zhang F, Zhou L. X., Yao B et al. Analysis of 3-year observations of CFC-11, CFC-12 and CFC-113 from a semi-rural site in China. *Atmos. Environ.*, Atmospheric Environment 44 :4454-4462, 2010,
- ✓ Stohl A., Kim J., Li S. et al. Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling. *Atmos. Chem. Phys.*, 10, 3545–3560, 2010
- ✓ Zhang F, Zhou L. X., Yao B et al. In-situ measurement of CFC-11 at Shangdianzi GAW regional station. *Science in China*, series D, 54 (2): 293-304, doi: 10.1007/s11430-010-4118-5, 2011
- ✓ An X., Zhou L.X., Yao B. et al, Analysis on Source Features of Halogenated Greenhouse Gases at Shangdianzi Regional Atmospheric Background Station. *Atmos. Environ.*, accepted
- ✓ An X., Henne S., Yao B. et al. Estimating Chinese Emissions of Major Halocarbons by Atmospheric Observations and Inverse Modeling, *Science in China*, accepted
- ✓ Yao B., Vollmer M. K., Zhou L. X. et al., In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) at the Shangdianzi regional background station, China. *Atmos. Chem. Phys. Discuss.*, 12, 11151-11173, 2012



Seasonal cycles

Fig. 5. Seasonal variations of pollution events for CFC-11, CFC-12 and CFC-113.



Emission estimate

Impact of local surface horizontal winds

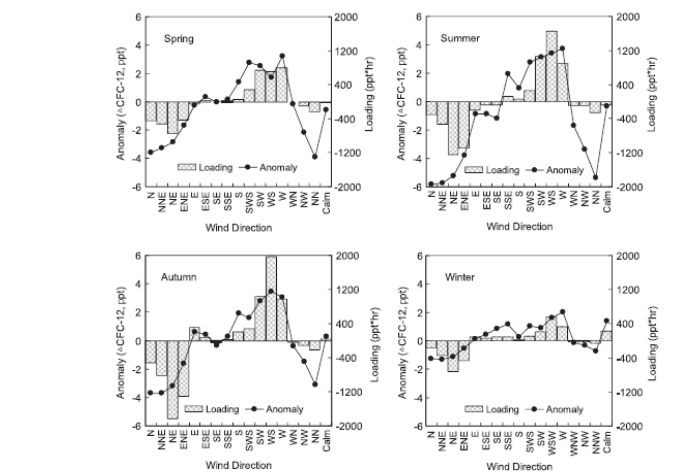


Fig. 7. 3-years statistical anomalies (CFC-11 mean mixing ratios for each wind sector minus its seasonal means) and loadings (anomalies multiplied by wind frequencies) for different wind sectors in spring, summer, autumn and winter at SDZ from November 2006 to October 2009.

Medusa-GC/MS and GC-ECD  
make comparison for one year  
(May 2010 to May 2011)



# Comparison

- Time resolution of air: GC-ECD 80 min  
Medusa-GC/MS 120 min
- Scale: SIO or UB or EMPA scale (AGAGE)
- Precisions:

Compounds	CFC-11	CFC-12	CFC-113	HCFC-22	HCFC-142b	H-1211	H-1301	CH <sub>3</sub> Br	CCl <sub>4</sub>	CH <sub>3</sub> CCl <sub>3</sub>	CHCl <sub>3</sub>	SF <sub>6</sub>
GC-ECD	0.2%	0.2%	0.3%	2%	1%	1%	2%	3%	0.2%	1%	3%	1%
Medusa-GC/MS	0.2%	0.2%	0.3%	2%	0.3%	1%	2%	1%	1%	1%	0.2%	1%

# SF6-comparion between standards

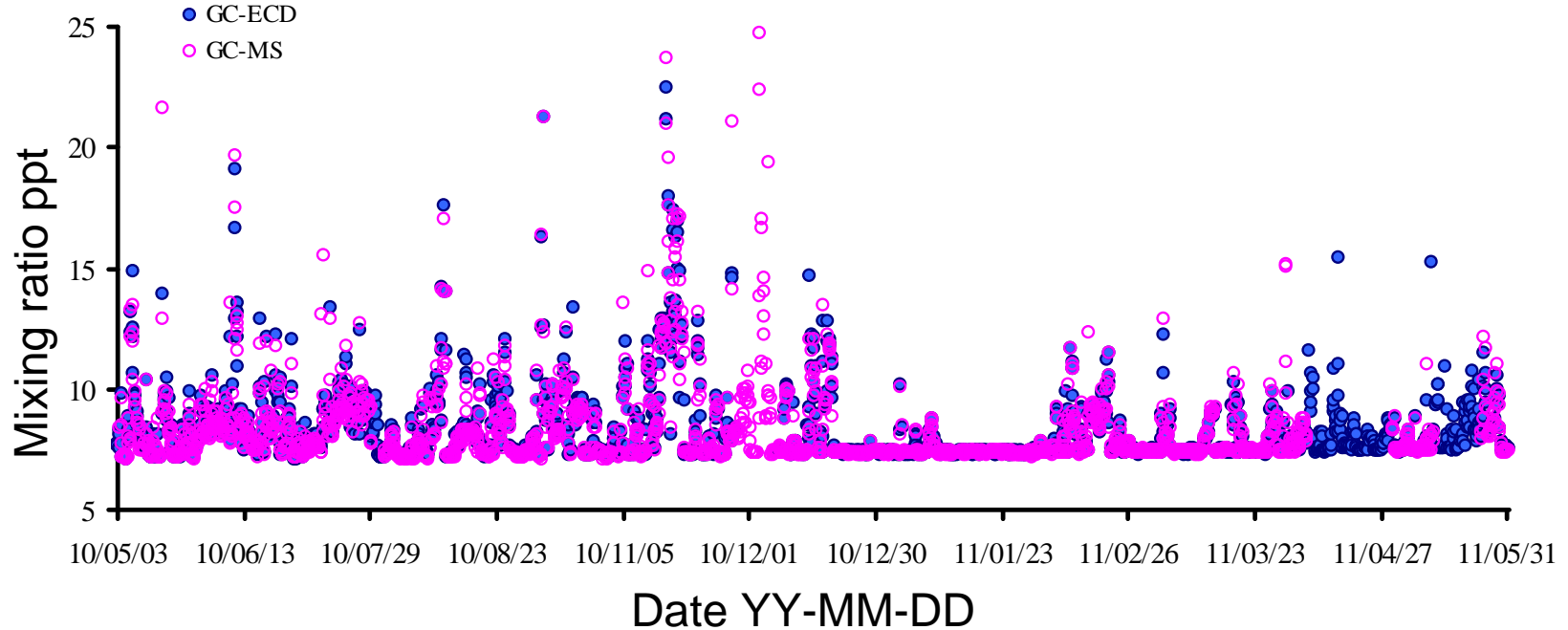
## Same Scale (SIO-2005), different instruments

Systems	C-133			C-135		
	No.	Mean /ppt	Stdev /ppt	No.	Mean /ppt	Stdev /ppt
GC-ECD	16	7.14	0.04	19	7.11	0.04
GC-MS	11	7.15	0.05	9	7.13	0.05

## Different Scales

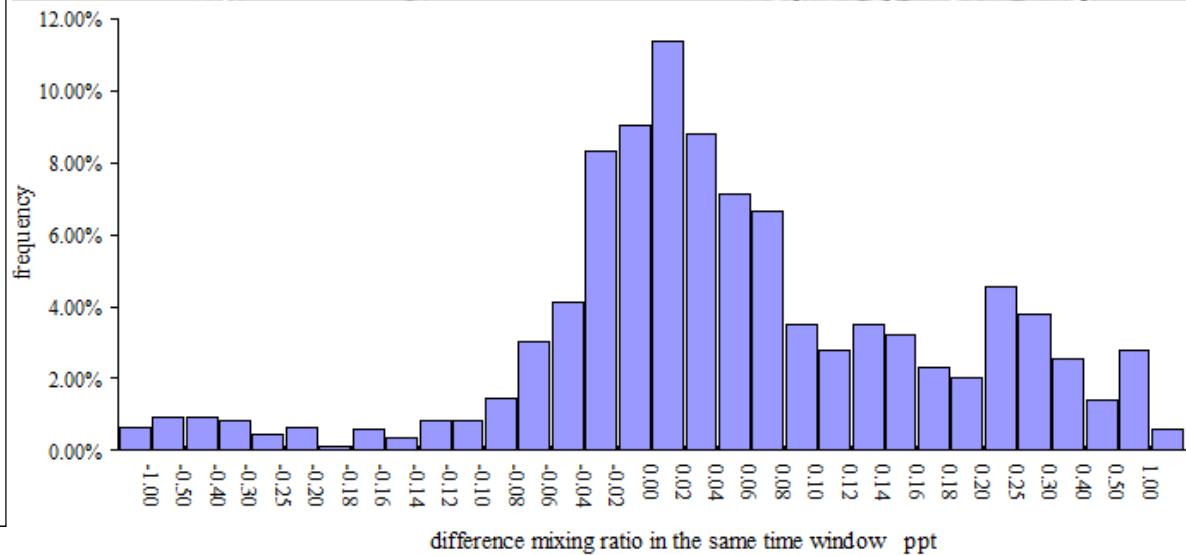
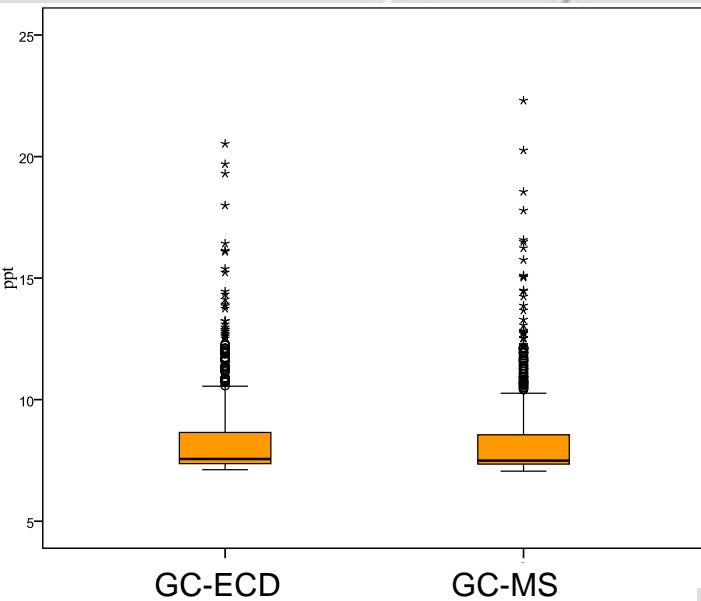
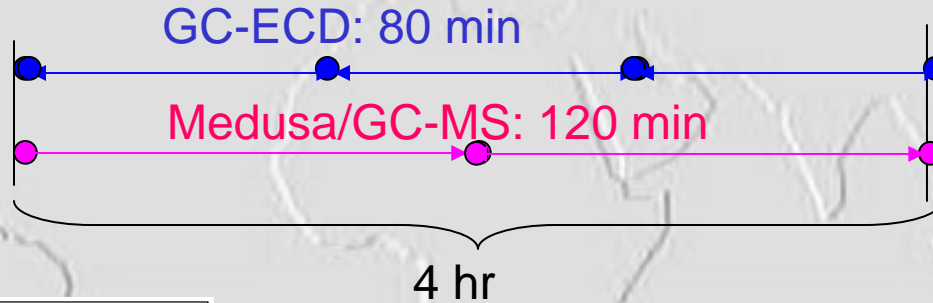
Scale	CA07473	CA07483
SIO-05 /ppt	5.03±0.03	9.87±0.12
NOAA /ppt	5.12±0.02	10.01±0.04

# SF6-comparion between two in-situ measurements



# Differences between average mixing ratios of the two systems in the same time windows

N=1082, 49.4%



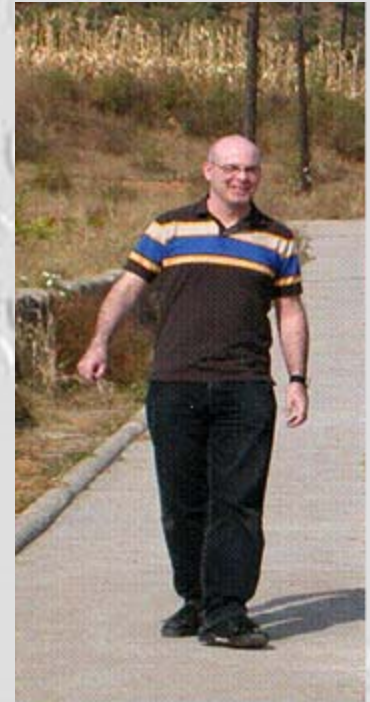
Difference (average, 10,25,50,75,90 percentile) between two systems are within precision  
No significant difference between the results of two systems

# Conclusion

- ✓ In-situ halogenated greenhouse gases measurements were conducted at Shangdianzi station by GC-ECDs since October 2006, and by Medusa-GC/MS since May 2010. Both measurements are linked to AGAGE scales.
- ✓ The precision of common species were compared. Except for  $\text{CCl}_4$ , GC-MS shows better or equal precisions compared to GC-ECDs.
- ✓  $\text{SF}_6$  measured at both systems in the time window of 4 hrs are compared, there is no significant difference between two systems.

# Acknowledgement

Brian Greally (1969-2010), worked for the University of Bristol, has significantly contributed to GC-ECDs.



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