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

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

15-17 May 2012
NOAA/ESRL 40th Global Monitoring Annual Conference
Boulder, CO, UAS
Montreal protocol
- CFCs
- Halons
- CH₃CCl₃
- CCl₄
- CH₃Cl
- CH₃Br
- HCFCs

Kyoto protocol
- CO₂
- CH₄
- N₂O
- HFCs
- PFCs
- SF₆

Halogenated Greenhouse Gases
Halogenated Greenhouse Gases measurements in China

Barletta et al, 2006

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

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

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

Qin, 2007; 孙学至等, 2010
Shangdianzi Station

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

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, CO₂/CH₄/CO/N₂O/SF₆/isotope
- NDIR: Since March 2007, CO
- CRDS: Since Januray 2009, CO₂/CH₄/CO
- GC-FID/ECD: Since January 2010, CH₄/CO/N₂O/SF₆
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

}
In-situ CFCs/ HCFCs/ Halons measurement since 2006
Sampling | Separation | Detection
---|---|---
Sample loops | packed columns | SF6
| | | CFC-12
| | | CFC-11
| | | CFC-113
| | | CHCl_3
| | | CH_3CCl_3
| | | CCl_4
| | | CH_2HCl_3
| | | C_2Cl_4
| | | H-1301
| | | HCFC-22
| | | HCFC-142b
| | | CH_3Br
| | | H-1211

capillary columns

2 m Poraplot Q 30 m | capillary columns | ECD 1

trap

500 ml room temp

2 ml

10 ml

Mol Sieve 5A 350 cm 90 °C

30 cm Silicone SP-2100 3 m

45 °C → 85 °C temp ramping

ECD 2

O_2 Doping
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

# 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**
  - CH₃CCl₃, CCl₄, CH₃Br, CH₃Cl

## 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**
  - CF₄, C₂F₆, CF₃CF₂CF₃
  - C₄F₁₀, c-C₄F₈, CF₃CF₃
- **SF₆**

Compounds in blue are those that can be measured by both systems. In black are only measured by Medusa-GC/MS.
Join AGAGE and Affiliated Networks

- Mace Head (Ireland)
- Ny-Alesund (Svalbard)
- Jungfraujoch (Switzerland)
- Shangdianzi (China)
- Gosan (Korea)
- Hateruma (Japan)
- Cape Grim (Tasmania)
- Trinidad Head (California)
- Cape Matatula (American Samoa)
- Ragged Point (Barbados)

**ALE/GAGE/AGAGE** sampling stations
**collaborative sampling stations**

- SOGE ▶ CMA ▲ SNU ♦ NIES
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

CAMS laboratory instrument

quaternary standard

tertiary standard

Shangdianzi instrument

tertiary standard

quaternary standard

air compressor at Shangdianzi

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

Mixing ratio

Chromatogram

Scientific research

data flag

distinguish background and pollution data
Longest record of SF₆, CFCs and HCFCs and Cl-solvents in-situ measurement in China

July 1ˢᵗ, 2007

Consumption freeze on Jan. 1ˢᵗ, 2013
base level: 2009-2010
First in-situ HFCs/ PFCs measurement in China


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


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

**Impact of local surface horizontal winds**

**Seasonal cycles**

**Emission estimate**
Medusa-GC/MS and GC-ECD make comparison for one year (May 2010 to May 2011)
• Time resolution of air: GC-ECD 80 min  
  Medusa-GC/MS 120 min
• Scale: SIO or UB or EMPA scale (AGAGE)
• Precisions:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>CFC-11</th>
<th>CFC-12</th>
<th>CFC-113</th>
<th>HCFC-22</th>
<th>HCFC-142b</th>
<th>H-1211</th>
<th>H-1301</th>
<th>CH₃Br</th>
<th>CCl₄</th>
<th>CH₂CCl₃</th>
<th>CHCl₃</th>
<th>SF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-ECD</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.3%</td>
<td>2%</td>
<td>1%</td>
<td>1%</td>
<td>2%</td>
<td>3%</td>
<td>0.2%</td>
<td>1%</td>
<td>3%</td>
<td>1%</td>
</tr>
<tr>
<td>Medusa-GC/MS</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.3%</td>
<td>2%</td>
<td>0.3%</td>
<td>1%</td>
<td>2%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>0.2%</td>
<td>1%</td>
</tr>
</tbody>
</table>
**SF6-comparison between standards**

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

<table>
<thead>
<tr>
<th>Systems</th>
<th>C-133</th>
<th>C-135</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>Mean /ppt</td>
</tr>
<tr>
<td>GC-ECD</td>
<td>16</td>
<td>7.14</td>
</tr>
<tr>
<td>GC-MS</td>
<td>11</td>
<td>7.15</td>
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</tbody>
</table>

### Different Scales

<table>
<thead>
<tr>
<th>Scale</th>
<th>CA07473</th>
<th>CA07483</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIO-05 /ppt</td>
<td>5.03±0.03</td>
<td>9.87±0.12</td>
</tr>
<tr>
<td>NOAA /ppt</td>
<td>5.12±0.02</td>
<td>10.01±0.04</td>
</tr>
</tbody>
</table>
SF6-comparision between two in-situ measurements
Differences between average mixing ratios of the two systems in the same time window

GC-ECD: 80 min
Medusa/GC-MS: 120 min

4 hr

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
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 CCl₄, GC-MS shows better or equal precisions compared to GC-ECDs.

SF₆ measured at both systems in the time window of 4 hrs are compared, there is no significant difference between two systems.

Conclusion
Acknowledgement

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