Network Observation of Greenhouse Gases and Related Tracers in China

Lingxi ZHOU, and colleagues/collaborators
CAMS, CAWAS/CMA
G.Q. ZHANG, H.H. XU, and station staffs
China GAW stations Waliguan, Shangdianzi, Lin’an and Longfengshan/CMA

15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques

7-10 September 2009, Jena, Germany
Greenhouse Gases

**the Kyoto protocol**
- CO₂
- CH₄
- N₂O
- SF₆
- HFCs: hydrofluorocarbons (C, H, F):
- PFCs: Perfluorinated Hydrocarbons (C, F)

**the Montreal protocols**
- CFCs: chlorofluorocarbons (C, Cl, F)
- HCFCs: hydrochlorofluorocarbons (C, Cl, F, H)
- Halons: (C, Br, Cl, F)
- Trichloroethane
- Carbon tetrachloride (CCl₄)
- Chloroform (CHCl₃)
- Methyl bromide (CH₃Br)
Why do we measure GHGs?

- **Long term global/regional trends by network observation**
  - Global compliance with the Kyoto and Montreal Protocols

- **Assessment of global & regional emission/absorption**
  - **Bottom-up method (conventional)**
    - Databases on production and consumption
    - Transfer functions (production-banks-emissions)
  - **Top-down method (alternative)**
    - Atmospheric observations
    - Tracer-ratio method
    - Meteorological inverse modelling
WMO/GAW Global & Regional Stations
More than 200 sites (http://www.wmo.ch)
WMO Round-robin Inter-comparison (GHGs)

4th WMO Round-robin (15 countries)
- 25+1 Labs reported CO₂
- 11+1 Labs reported CH₄
- 7+1 Labs reported CO
- 5+1 Labs reported N₂O/SF₆
- 6+1 Labs reported δ¹³C and δ¹⁸O
- 1 Lab for O₂/N₂ and 1 Lab for H₂

Lingxi ZHOU, Referee since 2002

5th WMO RR started in 2009, 41 Labs from 19 countries registered

**1st, 2nd Inter-comparison (CH₄)**

**Asia and South-West Pacific**


organized by the WMO/WCC hosted by JMA, Japan.


<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Country</th>
<th>Information</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headquarters of JMA</td>
<td>Japan</td>
<td>Measurement</td>
<td>Contact</td>
</tr>
<tr>
<td>CGAWBO, CMA</td>
<td>China</td>
<td>Measurement</td>
<td>Contact</td>
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<tr>
<td>KGAWO, KMA</td>
<td>Korea</td>
<td>Measurement</td>
<td>Contact</td>
</tr>
<tr>
<td>Headquarters of KRISS</td>
<td>Korea</td>
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<td>Contact</td>
</tr>
<tr>
<td>Headquarters of CSIRO</td>
<td>Australia</td>
<td>Measurement</td>
<td>Contact</td>
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<tr>
<td>Headquarters of NIWA</td>
<td>New Zealand</td>
<td>Measurement</td>
<td>Contact</td>
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<tr>
<td>Tohoku University</td>
<td>Japan</td>
<td>Measurement</td>
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<tr>
<td>NIES</td>
<td>Japan</td>
<td>Measurement</td>
<td>Contact</td>
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</tbody>
</table>
# WCC CH4 inter-comparison in Asia (2008-2009)

## Table 2: Results of Methane Reference Gas Intercomparison for Asia

<table>
<thead>
<tr>
<th>Laboratory and Location</th>
<th>Date of Measurement</th>
<th>Cylinder Number</th>
<th>Instrument</th>
</tr>
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<tbody>
<tr>
<td>JMA Tokyo, Japan</td>
<td>May 1, 2003</td>
<td>CPB13002</td>
<td>1664.4 1.2 10</td>
</tr>
<tr>
<td>KRISS Daejeon, RP Korea</td>
<td>Sep.-Nov., 2003</td>
<td>CPB13003</td>
<td>1848.4 1.8 10</td>
</tr>
<tr>
<td>KMA Anmyeon-do, RP Korea</td>
<td>Oct.-Nov., 2003</td>
<td>CPB13002</td>
<td>1665.1 0.2 5</td>
</tr>
<tr>
<td>CMA Mt. Weilguan, China</td>
<td>Apr. 3-5, 2009</td>
<td>CPB13003</td>
<td>1847.0 0.6 14</td>
</tr>
<tr>
<td>CMA Beijing, China</td>
<td>Apr. 13-14, 2009</td>
<td></td>
<td>1847.2 0.3 9</td>
</tr>
<tr>
<td>CMA Beijing, China</td>
<td>Apr. 14-16, 2009</td>
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<td>1846.1 1.9 10</td>
</tr>
<tr>
<td>CMA Beijing, China</td>
<td>Apr. 28-29, 2009</td>
<td></td>
<td>1847.5 0.6 10</td>
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<tr>
<td>CMA Beijing, China</td>
<td>Apr. 29, 2009</td>
<td></td>
<td>1847.3 0.1 9</td>
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<tr>
<td>CMA Beijing, China</td>
<td>Apr. 30, 2009</td>
<td></td>
<td>1847.2 1.8 12</td>
</tr>
<tr>
<td>JMA Tokyo, Japan</td>
<td>Jul. 1, 2009</td>
<td></td>
<td>1846.8 1.7 10</td>
</tr>
</tbody>
</table>

SD: Standard deviation; No: Number of measurements

Agreed very well
System + performance audits for surface $O_3$, CO, $CH_4$ were performed at WLG by the WMO/WCC hosted by EMPA, Switzerland in Sept. 2000 and Oct. 2004, respectively.
WCC (EMPA) audit in June-July 2009

Beijing Lab: 3 systems (Picarro G1301, Agilent 6890+Ametek GC, Agilent 6890 flask GC).
Mt. Waliguan: 3 systems (Picarro G1301, Agilent 6890 GC, HP5890)

Preliminary results: CH₄ by Picarro G1301, Agilent 6890+Ametek GC, Agilent 6890 flask GC consistent with the assigned values. However, CO and N₂O need further test.
Test of 6890+Amek GC by 7 CO standards from NOAA

Conclusion: Good CO response based on either Exponential fit or Polynomial fit. Considering the Residuals of the standards, exponential fit is preferred.

### Responses of Ametek (RGA) to Standards from NOAA

- **(Blue) Power (exponential) fit**
  - $y = 0.07230472x^{0.79992573}$
  - $R^2 = 0.99867461$
  - Residuals < 2.5 ppb

- **(Red) Polynomial fit of 2 order**
  - $y = -7E-09x^2 + 0.003x + 24.555$
  - $R^2 = 0.9987$
  - Residuals < 3 ppb
Test of 6890+ Ametek GC by 6 N\textsubscript{2}O standards from NOAA

Conclusion: Polynomial fit of 2 order for N\textsubscript{2}O responses and mixing ratios were perfect. Residuals less than 0.2 ppb. The system was good.

Responses of Agilent 6890 GC on 6 N\textsubscript{2}O standards from NOAA

\[ y = -2\times10^{-7}x^2 + 0.0325x - 58.744 \]

\[ R^2 = 0.999965 \]

Residuals < 0.2 ppb
Test of ‘Flask’ GC on 6 CO standards from NOAA

Conclusion: good linear fit for CO, residuals less than 2ppb.
System response is good.

Responses of ‘Flask’ GC (GC-FID/ECD) on 6 CO standards from NOAA

- Linear fit of CO responses
- $y = 409.85x - 14.484$
- $R^2 = 0.9994$
- Residuals < 2 ppb
Test of ‘Flask’ GC on 6 $\text{N}_2\text{O}$ standards from NOAA

Conclusion: The responses to standards were ok
Flask air sampling at Mt. Waliguan

Air sampling site (1991～)

$CO_2$, $CH_4$, $CO$, $H_2$, $N_2O$, $SF_6$

$^{12}C$ & $^{18}O$ of $CO_2$

$^{13}C$ of $CH_4$
Atmospheric CO₂ and CH₄

Waliguan compare to some other GAW global stations

Data other stations: WDCGG, NOAA/ESRL/GMD
Atmospheric CO₂ and CH₄

Waliguan compare to some adjacent GAW regional stations

Data other stations: WDCGG, NOAA/ESRL/GMD
Waliguan Observatory

In-situ CO$_2$, CH$_4$, CO monitoring systems on 2nd floor of the main building.

An 89m tower (20m east of the main building), to measure meteorological parameters at different levels and to obtain air samples for the in-situ CO$_2$, CH$_4$ and CO measurements.
Historical data at Mt. Waliguan (CO$_2$)

- insitu (WLG, NDIR)
- flask (WLG, analyzed by NOAA)

(WMO2007 scale)
Historical data at Mt. Waliguan (CH$_4$)

(NOAA04 scale)
GlobalView-$CO_2$, $CH_4$

Atmospheric $CO_2$ & $CH_4$ Data obtained at WLG by in-situ & discrete measurements have been used in the NOAA ESRL Cooperative Atmospheric Data Integration Project (CADIP).
# Data submit to the WDCGG

**World Data Centre for Greenhouse Gases**

## Mt. Waliguan - CMA

<table>
<thead>
<tr>
<th>Parameter (Data/Quick Plot)</th>
<th>Category</th>
<th>Period</th>
<th>Types of Data</th>
<th>Update</th>
<th>Parameters included</th>
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</thead>
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<tr>
<td>CH4 continuous</td>
<td>Air sampling observation</td>
<td>1994-01-01 - 2007-12-31</td>
<td>daily, monthly</td>
<td>2009-08-31</td>
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<tr>
<td>CO2 continuous</td>
<td>Air sampling observation</td>
<td>1994-01-01 - 2007-12-31</td>
<td>daily, monthly</td>
<td>2009-08-31</td>
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</tr>
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</table>
CO Scale Issues

• Collect calibration history info. of all cylinders.
• Discuss with Christoph and Joerg at WLG and in Beijing lab. Work out a reprocessing flow WLG history CO data (Empa 2009 WLG audit)
• Use calibrated info to calculate values link to new scale
• Use statistical method to derive a confident assigned values
• Ask for kindly help by E-mail (Jörg Klausen, QA/SAC Switzerland; Christoph Zellweger, WCC-Empa; Michele Ernst and Doug Worthy, MSC Canada……..)
• Re-process CO data using new scale CO standard numbers
## CO Calibration Scales Conversions - preliminary values

<table>
<thead>
<tr>
<th>Cylinder#</th>
<th>CA014 88</th>
<th>CA015 00</th>
<th>CA014 41</th>
<th>CA014 57</th>
<th>CA014 59</th>
<th>CA014 49</th>
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<tr>
<td>used as</td>
<td>S1</td>
<td>S2</td>
<td>S3</td>
<td>S4</td>
<td>S5</td>
<td>S6</td>
</tr>
<tr>
<td>v.m.r. assigned (ppb)(^1)</td>
<td>49.4</td>
<td>95.2</td>
<td>150.2</td>
<td>202</td>
<td>254.9</td>
<td>297.4</td>
</tr>
<tr>
<td>1997(^2)</td>
<td>58.8</td>
<td>101.1</td>
<td>153.1</td>
<td>203.2</td>
<td>255.5</td>
<td>298.3</td>
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<tr>
<td>2000(^3)</td>
<td>61.7</td>
<td>103.2</td>
<td>154.1</td>
<td>203.2</td>
<td>254.4</td>
<td>296.3</td>
</tr>
<tr>
<td>2004(^4)</td>
<td>59.0</td>
<td>103.9</td>
<td>155.7</td>
<td>205.5</td>
<td>259.1</td>
<td>298.5</td>
</tr>
<tr>
<td>2009(^5)</td>
<td></td>
<td></td>
<td>151.8</td>
<td></td>
<td>204.2</td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>59.8</td>
<td>102.7</td>
<td>153.7</td>
<td>204.0</td>
<td>256.3</td>
<td>297.7</td>
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<td>sd</td>
<td>1.6</td>
<td>1.4</td>
<td>1.6</td>
<td>1.1</td>
<td>2.5</td>
<td>1.2</td>
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<td>expander uncertainty, U</td>
<td>3.3</td>
<td>2.9</td>
<td>3.3</td>
<td>2.2</td>
<td>5.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\(^1\) MSC1997, in ppb

\(^2\) WMO2000, in ppb, by Michele, based on numbers between 1998 and 2004 of MSC

\(^3\) WMO2000, in ppb, by Empa 2000 audit, based on numbers between 2000(MSC1997) and 2004(WMO2000)

\(^4\) WMO2000, in ppb, by Joerg in R based on Empa 2004 audit

\(^5\) WMO2000, in ppb, by CAMS lab in 2009
CO Calibration Scales

Conversions (preliminary cylinder values)
CO Calibration Scales Conversions

(MSC1997-WMO2000)

\[
WMO2000 = 0.0002 \times (MSC1997)^2 + 0.9034 \times MSC1997 + 14.864
\]

\[R^2 = 1\]

\[
WMO2000 = 0.9601 \times MSC1997 + 11.168
\]

\[R^2 = 0.9998\]

“Non-linear” curve is a little better than “Linear” curve for CO calibration scales conversion from MSC1997 to WMO2000
Historical data at Mt. Waliguan (CO)

Data re-processing Not finished yet

(MSC1997 scale)
Joint AGAGE, SOGE and affiliated Networks

The Shangdianzi GAW Regional Station (Global Atmosphere Watch programme of the World Meteorological Organization) 150km northeast of urban Beijing is part of the domain of the China Meteorological Administration (CMA). It is jointly operated by the Beijing Meteorological Bureau (BMB) and the Chinese Academy of Meteorological Sciences (CAMS). The first in-situ measurement of CDDs and solvents in China has been performed by GC-ECIs at the Shangdianzi since 2005. As one of the partners of SOGE-A, Shangdianzi measurement is attached to the SOGE and linked to the AGAGE network. Furthermore, in-situ atmospheric CO2/CH4 measurements by Picarro CKDS and in-situ CH4/CO2/H2O/SF6 by GC-FID+ECID and enhanced in-situ measurements of halocarbon by the Medusa GC-MS will be implemented at the Shangdianzi in 2009.

Station Information (Shangdianzi, China)

- Latitude: 40° 39 N
- Longitude: 117° 37 E
- Time Zone: GMT+8
- Air sample intake: 301.3 m (station is 293.3 m above sea level)
- Station manager: Lingxi Zhou, hobb@bmc.bj.cn

Wind Rose (1971-2004)
Shangdianzi GAW Regional Station

SOGE-A

SDZ

Urban Beijing

>80% from clean sector
>Ca 22% from Urban Beijing sector
# Compounds currently measured at Shangdianzi

## Ozone-depleting Gases

- **CFCs**: chlorofluorocarbons (C, Cl, F): *CFC-12, CFC-11, CFC-113, CFC-115, CFC-114*
- **HCFCs**: hydrochlorofluorocarbons (C, Cl, F, H): *HCFC-22, HCFC-141b, HCFC-142b, HCFC-124*
- **Halon**: (C, Br, Cl, F): *H-1301, H-1211*
- Trichloroethane = methyl chloroform = *CH$_3$CCl$_3$*
- Carbon tetrachloride (CCl$_4$)
- Chloroform (CHCl$_3$)
- TCE (C$_2$HCl$_3$) and PCE (C$_2$Cl$_3$)
- Methyl bromide (CH$_3$Br)

## Greenhouse Gases

- **CO$_2$, CH$_4$, N$_2$O**
- **HFCs**: hydrofluorocarbons (C, H, F): *HFC-134, HFC-152a, HFC-125, HFC-23, HFC-143, HFC-227ea, HFC-161, HFC-365mfc, HFC-245fa, HFC-236fa, and many more*
- **PFCs**: Perfluorinated Hydrocarbons (C, F): *CF$_4$, C$_2$F$_6$, C$_4$F$_8$*
- **SF$_6$**

Species in red: In-situ GC-uECDs, Horiba-CO
Species in blue: Flask & in-situ G1301
Preliminary results from SDZ, China

Production and consumption of CFCs was banned on July 1st, 2007 (China National Plan)

CFC-11

Preliminary data unpublished, please do not cite.
Preliminary results from SDZ, China

Production and consumption of **Halon**s will be banned in 2010

**Halon-1301 [ ppt ]**

Preliminary data unpublished, please do not cite.

**Polluted**

**Background**
Preliminary results from SDZ, China

Production and consumption of methyl chloroform ($\text{CH}_3\text{CCl}_3$) will be banned in 2015

Preliminary data unpublished, please do not cite.
Preliminary results from SDZ, China

HCFC-142b

Preliminary data unpublished, please do not cite.
Preliminary results from SDZ, China

Preliminary data unpublished, please do not cite.
Compare with some AGAGE global sites

Preliminary data unpublished, please do not cite.

Red-Shangdianzi polluted, Black-Shangdianzi background
Blue-Mace Head polluted, Light blue -Mace Head background
Yellow-Cape Grim polluted, Pink-Cape Grim background

Courtesy AGAGE:
Mace Head / Cape Grim
Observational data
Medusa (Empa=>SOGE-A=>AGAGE) measure > 40 compounds

Beijing Lab and SDZ station

Medusa Trap making workshop
June 2008, Zurich, Switzerland
Linan GAW Regional Station

Selected ABC Observatories
Longfengshan GAW Regional Station
Atmospheric CO$_2$ from China GAW stations (flask data, 2006-)
Atmospheric CH$_4$ from China GAW stations (flask data, 2006 - )
Beijing Lab and GAW stations

Beijing Lab, Jan. 2009
Flask-GC, CO₂, CH₄, N₂O, SF₆, CO, H₂

WLG, SDZ, LA, LFS stations
In-situ CRDS, CO₂, CH₄

WLG station, Jan. 2009
In-situ GC, CH₄, CO, N₂O, SF₆
Shangdianzi station (SDZ), China -- the new home of CFADS24...

CMA/SST/Picarro group in the lab at CMA
2008年11月

Great Wall of China here
Picarro analyzer here

Shed for making gas standards
Picarro lives in this here shed

To help cut pollution, only electric bikes are allowed in urban areas of China
Picarro CH₄ & CO₂ data, Mt. Waliguan (10m, 40m, 80m agl)

Comparison of 3 levels CO₂ on Mt. Waliguan

Comparison of 3 levels CH₄ on Mt. Waliguan

Preliminary data unpublished, please do not cite.
Picarro CH₄ & CO₂ data from Jan. 1st, 2009 to present
(4 GAW stations in China)

Preliminary data unpublished, please do not cite.
Preliminary data unpublished, please do not cite.
Preliminary data unpublished, please do not cite.
CH$_4$ and CO data from May 2008 to present (in-situ GC-FID, Mt. Waliguan)

Preliminary data unpublished, please do not cite.
N$_2$O and SF$_6$ data from May 2008 to present
(in-situ GC-ECD, Mt. Waliguan)

Preliminary data unpublished, please do not cite.
Preliminary data unpublished, please do not cite.
Preliminary data unpublished, please do not cite.
On going & further implementation
International Cooperation

SIO, MIT, FMI, NILU, KMA, SNU, MSC, NOAA, CU-INSTARR, BGC, Tohoku U, NIES, JMA, CSEIRO, Bristol U, Urbino U, Empa, GAWTEC, many others ……
Beijing Lab LoFlo (CSIRO made)
Beijing Lab (CO$_2$ stable isotopes)
MAT253, Airtrap, GasBenchII

Help from MPI-BGC, MSC, INSTAAR, NIES ......
2009 funding
Picarro
GC-FID+ECD
more sites

MSC Canada
NOAA/ESRL/GMD
In-situ, CH₄/CO/N₂O/SF₆

Status:
Beijing - January 20, 2009 @ 12:11:45 PM GMT
Linan - January 20, 2009 @ 12:31:37 PM GMT
Longfengshan - January 20, 2009 @ 12:51:38 PM GMT
Shangdianzi - January 20, 2009 @ 01:11:40 PM GMT
Walquan - January 20, 2009 @ 07:32:03 AM GMT
Atmospheric $O_2/N_2$

2009 funding

Standards filled by Duane at NWR and calibrate by R. Keeling’s Lab, SIO
Cooperative China-U.S. Greenhouse Gases and Related Tracers Measurements Program


The 7 GAW stations in China and the 3D annual global carbon cycle greenhouse gases pictures showing atmospheric $^{13}\text{C}$ & $^{18}\text{O}$ in CO$_2$, CH$_4$, CO, N$_2$O, SF$_6$. Red lines indicate measurement data from Mt. Waliguan (36°17'N, 100°54'E, 3816m asl), China.
Flask, PFP, Canister

2009 funding
New sampler for 4 flask sampling: Get air through in-site sampling line

The new sampler was near finished and plan to work this month.
IPCC, Bureau of the Task Force on National Greenhouse Gas Inventories (Sept. 2008 - 2014), together with IPCC AR5

<table>
<thead>
<tr>
<th>Co-Chairs (2)</th>
</tr>
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<tbody>
<tr>
<td>Taka Hiraishi (Japan)</td>
</tr>
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<td>Thelma Krug (Brazil)</td>
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<th>Members (12)</th>
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<tr>
<td>Washington Zhakata (Zimbabwe)</td>
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<tr>
<td>Zhou Lingxi (China)</td>
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<td>Leonidas O. Girardin (Argentina)</td>
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<tr>
<td>Art Jaques (Canada)</td>
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<td>Robert Sturgiss (Australia)/</td>
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<td>Leonard J. Brown (New Zealand) *</td>
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<td>Detelina Petrova (Bulgaria)/</td>
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<td>Sadeddina Kherfan (Syrian Arab Republic) **</td>
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<td>Sergio Gonzalez Martineaux (Chile)</td>
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<td>William N. Irving (USA)</td>
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<td>Rizaldi Boer (Indonesia)</td>
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<td>Jim Penman (UK)</td>
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WMO/IAEA Meetings of Experts on CO₂ Concentration & Related Tracer Measurement Techniques

14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracers Measurement Techniques

10-13 September 2007, Helsinki, Finland
Acknowledgement

- WLG, SDZ, LA, LFS, and CAMS colleagues
- CMA, MOST, NSFC, MOP ... of China
- Environment Division, AREP, WMO
- NOAA ESRL GMD & CU-INSTAAR, USA
- MSC Canada
- BoM & CSIRO-MAR, Australia
- Empa, Switzerland and SOGE-A members
- NIES & JMA, Japan
- MPI-BGC & GAWTEC, Germany
- FMI, Finland
- GAW SAG, QA/SAC, CCL, WCC, WDC, ...

And all the people who give concern & support to China GAW