Overview of comparisons of non-CO$_2$ trace gas measurements between AGAGE and NOAA at common sites


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Overview

This presentation will focus on comparisons between AGAGE in situ and NOAA flask or in situ data at five common sites.

Awareness in this community of non-CO$_2$ comparison activities carried out as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) program in collaboration with NOAA & other laboratories.

Outline:
- Why do comparisons?
- Participants/species/sites
- Comparison techniques/outputs
- Results
Why undertake comparisons of independent measurements?

- gives us the ability to report relationships between different calibration scales in publications or web pages;
- allows reliable integration of atmospheric data from independent laboratories and/or measurement techniques;
- becomes a powerful tool in the early identification of problems that may have gone undiagnosed for longer;
- provides a stringent quality control test of individual laboratories experimental methods and internal calibration schemes;
- enables us to compare measurements from different instruments and/or measurement techniques;
- gives you an idea of the overall uncertainty estimate on the datasets when merging data;
- WMO recommendations!
Participants in trace gas comparisons to AGAGE

AGAGE (GC-ECD/FID/MRD, GCMS) – AGAGE team, 5 sites, > 34 species

NOAA/ESRL/GMD CCGG flask (GC-FID/ECD) - Ed Dlugokencky, 5 sites, 3 species
NOAA/ESRL/GMD HATS flask (GCMS) - Steve Montzka, 4 sites, up to 27 species
NOAA/ESRL/GMD HATS flask (GC-ECD) - Jim Butler/David Nance, 4 sites, up to 8 species
NOAA/ESRL/GMD HATS CATS in situ (GC-ECD) - Geoff Dutton, 1 site (Samoa), 11 species

Uni. of Heidelberg flask (GC-ECD) – Ingeborg Levin, 1 site (Cape Grim), 1 species
CSIRO flask (GC-FID/ECD/MRD) – Steele/Langenfelds/Krummel, 1 site (Cape Grim), 4 species

NIES flask (GCMS) – Yoko Yokouchi, 1 site (Cape Grim), 12 species
UEA flask (GCMS) – David Oram, 1 site (Cape Grim), 24 species
SIO flask – Ben Miller/Martin Vollmer, 1 site (Cape Grim), 5 species – ceased
Several other flask measurement programs at Cape Grim

** A lot of data and different data formats!**
Comparisons performed approx every 6 months, results made available to all participants, copies archived and form part of the metadata.
Some species measured on multiple instruments by NOAA &/or AGAGE
NOAA species compared to AGAGE in situ records

30+ species in total:

- CH$_4$, N$_2$O, SF$_6$
- CFC-11, CFC-12, CFC-13, CFC-113, CFC-115
- HCFC-22, HCFC-141b, HCFC-142b
- HFC-23, HFC-125, HFC-134a, HFC-143a, HFC-152a
- H-1211, H-1301, H-2402
- CH$_3$CCl$_3$, CCl$_4$, CCl$_2$CCl$_2$
- CH$_3$Cl, CHCl$_3$, CH$_3$Br, CH$_2$Cl$_2$, CH$_3$I, CHBr$_3$, CH$_2$Br$_2$
- C$_6$H$_6$, OCS
Comparisons

• Controlled by input files – 24 input fields
  - Including data sources; species; smoothing/clipping parameters; begin/end times; match time window etc.
• Matching performed by taking flask sampling time and looking for nearest in situ data point within a specified time window
• Full output produces 10 panels:
  - Time series of all data; time series of matched data
  - 1:1 plot; time series of concentration difference
  - conc diff vs flask conc; conc diff vs in situ conc
  - Time series of % conc diff; % conc diff vs flask conc
  - conc diff vs matched time diff; conc diff vs abs(matched time diff)
• 3-panel ‘quick-look’ plots
• ASCII data files of matched data points produced

• Summary plots and statistics for a particular species
• Code written in IDL; needs overhaul of the code
AGAGE GC–FID in situ versus NOAA GC–FID flask: CH₄

Average diff: 0.38±1.23 ppb, 0.02±0.07 %
Av diff 2 yrs: 0.84±1.09 ppb, 0.05±0.06 %

ΔCH₄ (NOAA GC–FID–AGAGE GCMD) (ppb)

Scales: TU & NOAA–2004
AGAGE GC–ECD in situ versus NOAA GC–ECD flask: CFC–12

Average diff: $-1.53 \pm 0.47$ ppt, $-0.28 \pm 0.09\%$
Av diff 2 yrs: $-1.76 \pm 0.37$ ppt, $-0.33 \pm 0.07\%$

$\Delta$CFC–12 (NOAA ECD–AGAGE GCMD) (ppt)

<table>
<thead>
<tr>
<th>Station</th>
<th>n</th>
<th>Date</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>cgo</td>
<td>587</td>
<td>Nov 1994</td>
<td>Mar 2011</td>
</tr>
<tr>
<td>smo</td>
<td>610</td>
<td>Aug 1996</td>
<td>Mar 2011</td>
</tr>
<tr>
<td>thd</td>
<td>357</td>
<td>Mar 2002</td>
<td>Mar 2011</td>
</tr>
</tbody>
</table>

Scales: SIO–05 & NOAA–2008
AGAGE GC–ECD in situ versus NOAA GC–ECD flask: CFC–11

Average diff: 2.11±0.53 ppt, 0.84±0.20 %
Av diff 2 yrs: 0.73±0.18 ppt, 0.30±0.08 %

ΔCFC–11 (NOAA ECD–AGAGE GCMD) (ppt)

Scales: SIO–05 & NOAA–1992

cgo
n=584
Nov 1994
Mar 2011

smo
n=628
Aug 1996
Mar 2011

thd
n=355
Mar 2002
Mar 2011

mhd
n=185
Nov 1998
Mar 2011
### Results: Average differences table – CH$_4$, N$_2$O, SF$_6$

<table>
<thead>
<tr>
<th>Species Method</th>
<th>Scales</th>
<th>Av conc diff last 2 years (NOAA-AGAGE)</th>
<th>Av % diff last 2 years IHALACE (NOAA/AGAGE)</th>
<th>Comparison period; n sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ N: GC-FID A: GC-FID</td>
<td>NOAA-2004 Tohoku Uni</td>
<td>0.4±1.2 ppb 0.8±1.1 ppb</td>
<td>0.02±0.07% 0.05±0.06%</td>
<td>Aug 1993 to Apr 2011 5</td>
<td>Excellent agreement</td>
</tr>
<tr>
<td>N$_2$O N: GC-ECD A: GC-ECD</td>
<td>NOAA-2006 SIO-98</td>
<td>-0.20±0.16 ppb 0.07±0.15 ppb</td>
<td>-0.06±0.05% 0.02±0.05%</td>
<td>Aug 1993 to Apr 2011 5</td>
<td>Small trend with time</td>
</tr>
<tr>
<td>SF$_6$ N-CCGG: GC-ECD A: GC-MS</td>
<td>NOAA-2006 SIO-05</td>
<td>0.05±0.02 ppt 0.05±0.02 ppt</td>
<td>0.8±0.4% 0.8±0.4%</td>
<td>Nov 2003 to Apr 2011 5</td>
<td>Good agreement – small offset</td>
</tr>
<tr>
<td>SF$_6$ N-HATS: GC-ECD A: GC-MS</td>
<td>NOAA-2006 SIO-05</td>
<td>0.04±0.02 ppt 0.04±0.02 ppt</td>
<td>0.6±0.4% 0.5±0.3%</td>
<td>Nov 2003 to Apr 2011 4</td>
<td>Good agreement – small offset</td>
</tr>
</tbody>
</table>
## Results: Average differences table – CFCs

<table>
<thead>
<tr>
<th>Species</th>
<th>Scales</th>
<th>Av conc diff last 2 years</th>
<th>Av % diff last 2 years</th>
<th>Comparison period; n sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>NOAA-1992 SIO-95</td>
<td>2.1±0.5 ppt 0.7±0.2 ppt</td>
<td>0.8±0.2 % 0.3±0.1 % 0.6±0.2 %</td>
<td>Nov 1994 to Mar 2011 4</td>
<td>Trends down at all sites</td>
</tr>
<tr>
<td>CFC-12</td>
<td>NOAA-2008 SIO-05</td>
<td>1.5±0.5 ppt 1.8±0.4 ppt</td>
<td>-0.28±0.09 % -0.33±0.07 % -0.22±0.02 %</td>
<td>Nov 1994 to Mar 2011 4</td>
<td>Constant offset</td>
</tr>
<tr>
<td>CFC-113</td>
<td>NOAA-2003 SIO-05</td>
<td>1.5±0.2 ppt 1.1±0.2 ppt</td>
<td>1.9±0.2 % 1.5±0.2 % 2.8±0.2 %</td>
<td>Jun 1995 to Mar 2011 4</td>
<td>Offset with small trend down with time</td>
</tr>
<tr>
<td>CFC-113</td>
<td>NOAA-2003 “Montzka” SIO-05</td>
<td>0.03±0.2 ppt 0.1±0.1 ppt</td>
<td>0.04±0.3 % 0.1±0.2 % 1.1±0.3 %</td>
<td>Sep 1993 to Apr 2011 4</td>
<td>Overall good agreement</td>
</tr>
</tbody>
</table>
## Results: Average differences table – HCFCs

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>Scales</th>
<th>Av conc diff last 2 years (NOAA-AGAGE)</th>
<th>Av % diff last 2 years (\text{IHALACE} (\text{NOAA/AGAGE}))</th>
<th>Comparison period; n sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC-22</td>
<td>N: GC-MS A: GC-MS</td>
<td>NOAA-2006 SIO-05</td>
<td>-1.1±0.6 ppt -2.3±0.5 ppt</td>
<td>-0.6±0.4 % -1.1±0.2 % 0.7±0.2 %</td>
<td>Nov 2003 to Mar 2011 4</td>
<td>Step change ~2008 at all sites.</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>N: GC-MS A: GC-MS</td>
<td>NOAA-1994 SIO-05</td>
<td>-0.2±0.1 ppt -0.15±0.08 ppt</td>
<td>-1.1±0.6 % -0.8±0.4 % -1.2±0.1 %</td>
<td>Nov 2003 to Apr 2011 4</td>
<td>Small offset</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>N: GC-MS A: GC-MS</td>
<td>NOAA-1994 SIO-05</td>
<td>-0.5±0.1 ppt -0.5±0.1 ppt</td>
<td>-2.8±0.5 % -2.5±0.5 % -3.3±0.3 %</td>
<td>Nov 2003 to Apr 2011 4</td>
<td>Offset</td>
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</tbody>
</table>
### Results: Average differences table – HFCs

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>Scales</th>
<th>Av conc diff last 2 years (NOAA-AGAGE)</th>
<th>Av % diff last 2 years (NOAA/AGAGE)</th>
<th>Comparison period; n sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFC-125</td>
<td></td>
<td>NOAA UB-98</td>
<td>0.14±0.05 ppt 0.15±0.05 ppt</td>
<td>2.4±0.7 % 2.5±0.8 %</td>
<td>Jan 2007 to Apr 2009 3</td>
<td>Offset</td>
</tr>
<tr>
<td></td>
<td>N: GC-MS A: GC-MS</td>
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<tr>
<td>HFC-134a</td>
<td></td>
<td>NOAA-1995 SIO-05</td>
<td>0.0±0.2 ppt -0.1±0.2 ppt</td>
<td>0.0±0.5 % -0.2±0.3 %</td>
<td>Nov 2003 to Apr 2011 4</td>
<td>Good agreement</td>
</tr>
<tr>
<td></td>
<td>N: GC-MS A: GC-MS</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>HFC-152a</td>
<td></td>
<td>NOAA-2004 SIO-05</td>
<td>0.0±0.1 ppt 0.0±0.1 ppt</td>
<td>-0.5±2.4 % -0.3±1.4 %</td>
<td>Nov 2003 to Apr 2011 4</td>
<td>Good agreement</td>
</tr>
<tr>
<td></td>
<td>N: GC-MS A: GC-MS</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
## Results: Average differences table – Halons

<table>
<thead>
<tr>
<th>Species Method</th>
<th>Scales NOAA AGAGE</th>
<th>Av conc diff last 2 years (NOAA-AGAGE)</th>
<th>Av % diff last 2 years IHALACE (NOAA/AGAGE)</th>
<th>Comparison period; n sites</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1211 NOA-Montzka SIO-05</td>
<td>NOAA-2006 SIO-05</td>
<td>-0.23±0.02 ppt -0.24±0.02 ppt</td>
<td>-5.3±0.6 % -5.7±0.4 % -4.4±0.8 %</td>
<td>Nov 2003 to Oct 2010 4</td>
<td>Offset</td>
</tr>
<tr>
<td>H-1301 NOA-Montzka NOAA-1992-p</td>
<td>NOAA-1992-Montzka NOAA-1992-p</td>
<td>0.00±0.01 ppt 0.00±0.01 ppt</td>
<td>0.1±1.2 % 0.6±1.1 %</td>
<td>Nov 2003 to Oct 2010 4</td>
<td>Excellent agreement</td>
</tr>
<tr>
<td>H-2402 NOA-Montzka SIO-05</td>
<td>NOAA-2006 SIO-05</td>
<td>-0.12±0.04 ppt -0.13±0.04 ppt</td>
<td>-4.0±1.1 % -4.2±1.2 %</td>
<td>Mar 2004 to Feb 2008 2</td>
<td>Offset</td>
</tr>
</tbody>
</table>

**Note:**
- **N:** GC-MS
- **A:** GC-MS
- **Av % diff last 2 years IHALACE (NOAA/AGAGE)**
- **Comparison period; n sites**
- **Comments**
Conclusions and future work

• **Is this a useful exercise?** … Yes
  • Helped identify problems/issues in measurements from both networks
  • Factors used to merge datasets for modelling/inversion studies
  • Advice to people on how to convert between scales

• **Future work**
  • Rewrite code to make more modular and ‘clean-up’
  • Further automation
  • Produce HTML summary table and ‘drill-down’ links – make available on a web page
  • Ongoing activity and development
Thank You

Acknowledgements

All station personnel involved with the collection/filling of flasks and maintenance of *in situ* programs

Participants in the comparison exercise, especially the NOAA colleagues who contribute the bulk of the flask data

The AGAGE team