Results of an International Flask Inter-comparison Program (ICP) for Greenhouse Gases & Isotope measurements at a GAW site, Alert, Nunavut, Canada

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Introduction

Greenhouse gases, including CO₂, CH₄, N₂O, CO and isotopes δ¹³C, and δ¹⁸O in CO₂ have been measured globally over many decades and by many different organizations using routine flask sampling programs. In order for these data sets to be used by the scientific community, it’s important to implement mechanisms to assess systematic biases in the data amongst these various organizations. This is a challenging task due to the different types of flasks being used, various sampling systems, scale and calibration/analytical methods. For more than 20 years, WMO has set global network compatibility target goals for each greenhouse gas. Over the years, several inter-comparison programs (ICP) have been conducted to assess whether these goals are being met. In this poster, we summarize the flask comparison results (1999-2013) conducted by seven organizations at the WMO global site at Alert, Canada.

Types of Flask ICP’s

- **Same-air ICP**
  - The “host” lab at Environment Canada (EC) analyzes an aliquot of air from another laboratory’s flask sample (i.e. NOAA) in advance of forwarding them to their “home” laboratory.
  - This provides insight into analytical procedures, scale and calibration factors from these different laboratories

- **Co-located ICP**
  - The comparison of air samples collected by individual laboratories using their own dedicated sampling systems and flasks.
  - This provides insight into influences mentioned above for the same-air ICP, but also influences due to the use of different sampling systems and flask types

Sampling

<table>
<thead>
<tr>
<th>LAB</th>
<th>FLASK TYPE</th>
<th>FREQUENCY</th>
<th>SAMPLE</th>
<th>DRYING</th>
<th>HEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>2L pressurized</td>
<td>1 pr weekly</td>
<td>0°C evaporator</td>
<td>10 m</td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>1L pressurized</td>
<td>1 pr weekly</td>
<td>0°C evaporator</td>
<td>10 m</td>
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<tr>
<td>CSIRO</td>
<td>1L pressurized</td>
<td>1 pr weekly</td>
<td>0°C evaporator</td>
<td>10 m</td>
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<tr>
<td>IUP</td>
<td>2L pressurized</td>
<td>1 pr weekly</td>
<td>0°C evaporator</td>
<td>10 m</td>
<td></td>
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<tr>
<td>MPI</td>
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<td>1 pr weekly</td>
<td>0°C evaporator</td>
<td>10 m</td>
<td></td>
</tr>
</tbody>
</table>

Results

- **δ¹³C**
  - Very few laboratories are consistently able to meet the WMO target goal of ±0.01 per mil, but a few laboratories appear to show consistent offsets.
  - The variability relative to NOAA appears to get worse over time.
  - The WMO target goals are indicated as dashed lines on each figure.

- **δ¹⁸O**
  - Many laboratories are close to meeting the WMO goal of ±0.05 per mil from 2005 onwards. Prior to 2005, all laboratories show a negative bias relative to NOAA.
  - IUP shows a fairly consistent offset from 2007 onwards.

- **CO₂**
  - Most laboratories are close to meeting the WMO goal of ±0.1 ppm for both types of ICPs, although EC and LSCE have large offsets at the onset of the comparison; the offsets in the EC program impact the same-air analysis comparisons from 2005-2007.
  - In the co-located ICP, several laboratories show a small negative shift starting in 2009, with some laboratories showing results beyond the WMO target range.

- **N₂O**
  - IUP was chosen as the reference lab for the co-located ICP due to their higher measurement precision capability.
  - Most laboratories have difficulty meeting the WMO goal of ±0.1 ppb. This is primarily due to the analytical limitations of the ECD GC to attain precision levels in this range. Both comparison exercises show significant offsets and variability.

- **CH₄**
  - The flasks utilized by CSIRO and EC at Alert are not appropriate for CO due to the viton o-rings and thus, are not included. EC does have CO measurement capability, however, and was still involved in the same air analysis.
  - Some of the laboratories have difficulty consistently reaching the WMO target goal of ±2.0 ppb. Similar patterns are observed for both comparison exercises, indicating that the variability is likely due to the same sample analysis by each respective laboratory.

- **CO**
  - The flasks utilized by CSIRO and EC at Alert are not appropriate for CO due to the viton o-rings and thus, are not included. EC does have CO measurement capability, however, and was still involved in the same air analysis.