What happens when you measure CO$_2$ five different ways on a single aircraft: Intercomparison results from the HIPPO project

Britton Stephens, Andrew Watt, Steve Shertz (NCAR); Jonathan Bent, Ralph Keeling (SIO);
Bruce Daube, Eric Kort, Rodrigo Jiménez, Jasna Pittman, Greg Santoni, Steve Wofsy (Harvard);
Fred Moore, Ben Miller, and Colm Sweeney (NOAA)
• Pls: Harvard, NCAR, Scripps, NOAA
• Global and seasonal survey of CO$_2$, O$_2$, CH$_4$, CO, N$_2$O, H$_2$, SF$_6$, COS, CFCs, HCFCs, O$_3$, H$_2$O, CO$_2$ isotopes, Ar, black carbon, and hydrocarbons (over 80 species).
• NSF / NCAR Gulfstream V
• Five 3-week campaigns over 3 years, across Pacific between 87 N and 67 S
• Continuous profiling from surface to 10 km, and to 15 km twice per flight
• hippo.ucar.edu, www.eol.ucar.edu/hippo, hippo.ornl.gov
Five independent CO₂ measurements:

- Harvard *in situ* Quantum Cascade Laser Spectrometer (*QCLS*): high precision (0.02 ppm 1-sigma / 1-Hz)
- Harvard *in situ* OMS (Observations Middle Stratosphere): highly modified LiCor 6251, long history of balloon and aircraft work (0.1 ppm 1-sigma / 1-Hz)
- NCAR *in situ* Airborne O₂ Instrument (*AO2*): LiCor 840 sensor for O₂ dilution correction, low precision but rigorously calibrated (1.0 ppm 1-sigma / 1-Hz)
- NOAA Whole Air Sampler (*NWAS*): modified NOAA Portable Flask Packages with moderate drying, 24 flasks per flight analyzed in Boulder, CO
- NCAR/Scripps *MEDUSA* flask sampler: Active flow and pressure control with cryogenic drying, 32 flasks per flight analyzed in La Jolla, CA

*All with expected compatibility of 0.2 ppm or better*
NCAR Airborne Oxygen Instrument (AO2)

- Vacuum ultraviolet absorption technique for $O_2$
- Li-840 for $CO_2$ (dilution correction)
- Active pressure and flow control to $10^{-6}$
- 5-second 1-sigma imprecision of ± 2 per meg $O_2$ / ± 0.5 ppm $CO_2$
- HS, LS, WT, LT, and LP cylinders
The airborne measuring environment is very demanding:

- Small cylinders
- Cabin leaks
- Inlets
Things we did before HIPPO1:

- Extensive leak tests from inlet through entire system
- Wetted materials tests
- Drying system tests
- Inlet system pressure tests
- START-08 / pre-HIPPO campaign
  - AO2-QCLS-MED comparisons
  - Target tank analysis
  - Pitch maneuvers and speed runs
  - Acceleration tests
- AO2 and inlet moved to aft top from forward bottom

Routine procedures

- Breath tests
- Filter replacement
HIPPO1 Median Offsets

- AO2-MED looked good on all flights
- QCLS-OMS-NWAS looked good on research flights 1-6
- Harvard and NOAA vs. NCAR and Scripps = -0.3 ppm (but NWAS expected to be low)
- Something mysterious happened between RF06 and RF07 in Christchurch...
Positive CO$_2$ offsets positively dependent on altitude (system leak to cabin would have opposite effect):

Things we did before HIPPO2:

- HIMIL vent tubes installed
- Drying and system checks for NWAS
- More leak tests
- More materials tests
- Cylinder gas through inlet system
HIPPO2 Median Offsets

<table>
<thead>
<tr>
<th>AO2 Δ CO₂</th>
<th>OMS Δ CO₂</th>
<th>QCLS Δ CO₂</th>
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<tbody>
<tr>
<td>RF01</td>
<td>RF02</td>
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- QCLS and OMS problems fixed and QCLS-OMS-MED-NWAS looked good with one exception
- AO2 offsets larger and variable

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Evidence for both altitude (+) and time-in-flight (-) dependent AO2 CO$_2$ offsets:

Things we did before HIPPO3:

- More leak tests and more cylinder gas through inlet system tests
- Inlet system humidity and pressure tests
- Fridge trap in-line
- Replaced electro-polished SS inlet tubing
- Inlet purge system installed
HIPPO3 Median Offsets

- AO2 offsets even larger and more variable
- QCLS-MED-NWAS looks good but OMS more variable
Things we did before HIPPO4:

• More extensive leak tests
• More inlet humidity and pressure tests
• Fridge trap testing and then bypassed
• Laboratory cylinder stability tests
• Replaced all 1/8" stainless tubing with electro-polished “Sulfinert”
• More materials tests
• Replaced inlet tube

During HIPPO4:

• Pitch maneuvers
• Cabin pressure tests
• Cabin CO₂ measurement (900 ppm → 0.1% = 0.5 ppm)
HIPPO4 Median Offsets

Preliminary Data

- AO2 offsets started out good but degraded half way through mission
- QCLS-OMS looks good but QCLS and OMS appear ~ 0.2 ppm low relative to flasks
Things we did before HIPPO5:
• More extensive leak tests, including with dry ice on fittings
• Cylinder gas through inlet with dry ice on fittings
• More inlet humidity and pressure tests
• Replaced inlet tube
• Replace ferrules inside HIMIL
• Installed “ultra-torr” fitting on O₃ inlet
• Replaced inlet purge gas with sub-ambient
• 1/16” nickel dip tubes in cylinders

During HIPPO5:
• Yaw maneuvers
• Cylinder gas in inlet purge for entire profile
• HIMIL pressure measurements
• HIMIL CO₂ measurements
• HIMIL suction test
• Inlet temperature measurements
• QCLS-AO2 inlet comparison
HIPPO5 Median Offsets

Preliminary Data

- Again AO2 offsets initially improved, but then much worse than previous
- QCLS-OMS looks good
- NWAS had positive and variable offsets from in situ sensors
Things we did after HIPPO5:

- Cylinder stability tests
- Extensive leak checks on HIMIL
- Wet and dry HIMIL surface effect tests

Next steps:

- Further data analysis
- Flow modeling
- IDEAS-5 cabin leak tests
Conclusions

• Aircraft CO$_2$ measurements are challenging and require significant attention to potential sources of bias
• Recommend dedicated inlets as far outboard and forward as possible
• The only way to assess compatibility is to have multiple measurements
• QCLS looks good with a compatibility of ~ 0.2 ppm, but small altitude and time-in-flight difference offsets apparent
• Recommended CO2X product will be QCLS with some HIPPO1 flights excluded, and calibration periods gap filled by adjusted OMS
• AO2 CO$_2$ data is sufficient for O$_2$ dilution correction but we’d very much like to understand cause of offsets
• All hypotheses for AO2 offsets are both supported and unsupported by various tests, suggesting more than one cause likely and a potential role for yet unrecognized effects. . . . “back to the drawing board”
START-08 / pre-HIPPO Mean Offsets

START08 Median +/- 1-sigma Differences
AO2 Δ CO₂

QCLS Δ CO₂