

Comparison of instruments for atmospheric CO₂ observations at Baring Head, New Zealand

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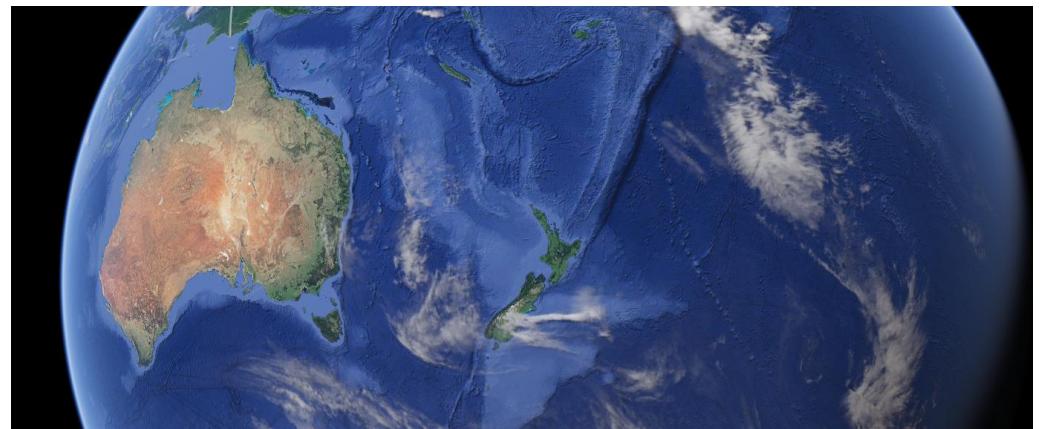


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Background

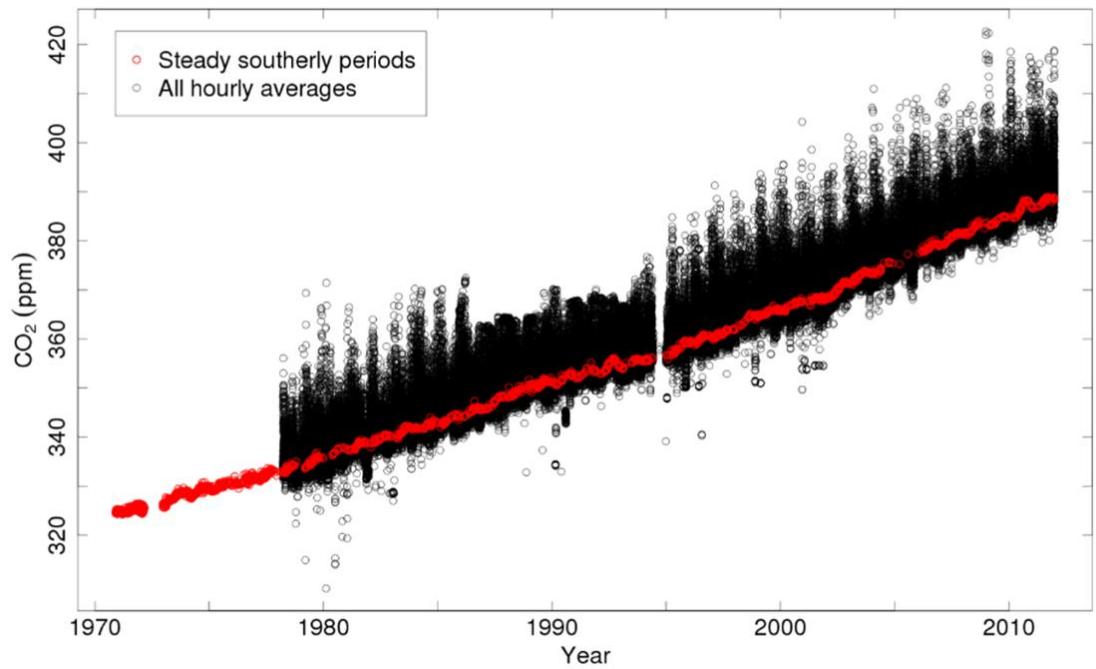
Time-series of CO₂ observations

- Observations started 1972
- Three Non-dispersive infra-red analysers
 - URAS-1, 1972–1977
 - URAS-2T, 1976–1987
 - Siemens Ultramat 3, 1986–present



Upgrade required as the Siemens is aging and with technological advances.

- Picarro cavity ring down spectrometer
 - Has linear response compared with non-linear Siemens
 - Wider concentration range
 - Uses less gas
 - More stable
 - Measures CO₂, CH₄ and H₂O



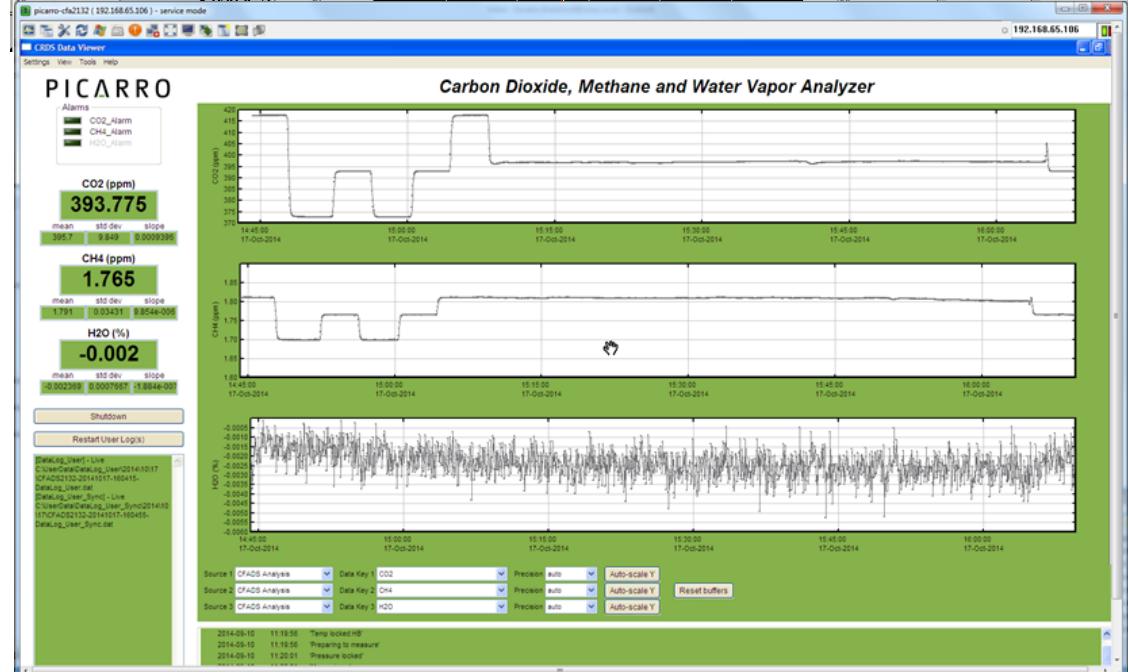
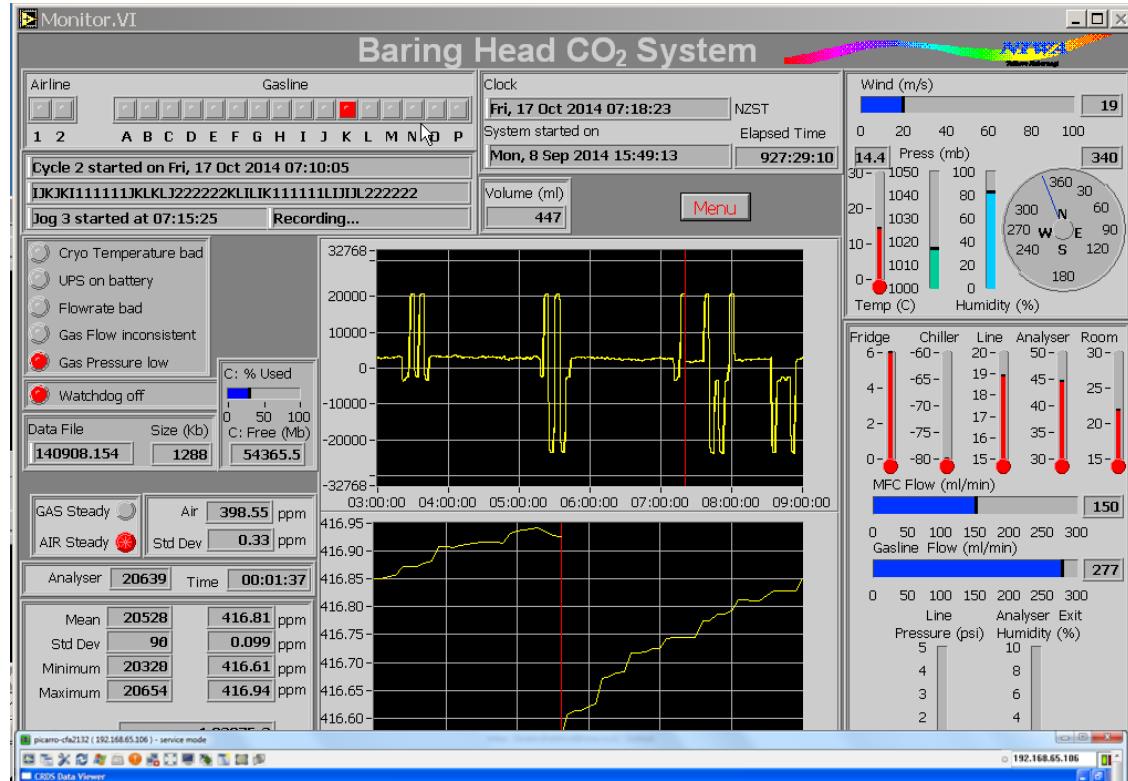
Instrument features

Siemens-Ultramat 3

- samples at 1 Hz
- 64,000 bits over a range of 60ppm
- Larger cells ~ 100 ml
- Single pass cell
- Sensitive to water
- Coarse temperature control
- Only “sees” $^{12}\text{CO}_2$

Picarro -G 2301

- samples at ~ 0.3 Hz
- “ppm” output, 4 decimal places to obtain the required sensitivity
- Small cell size
- Long path length 20km
- Measures water and is sensitive to it
- Fine temperature control
- Only “sees” $^{12}\text{CO}_2$



Comparing instruments

Requirements

We need to compare the two instruments using:

The same calibration gases

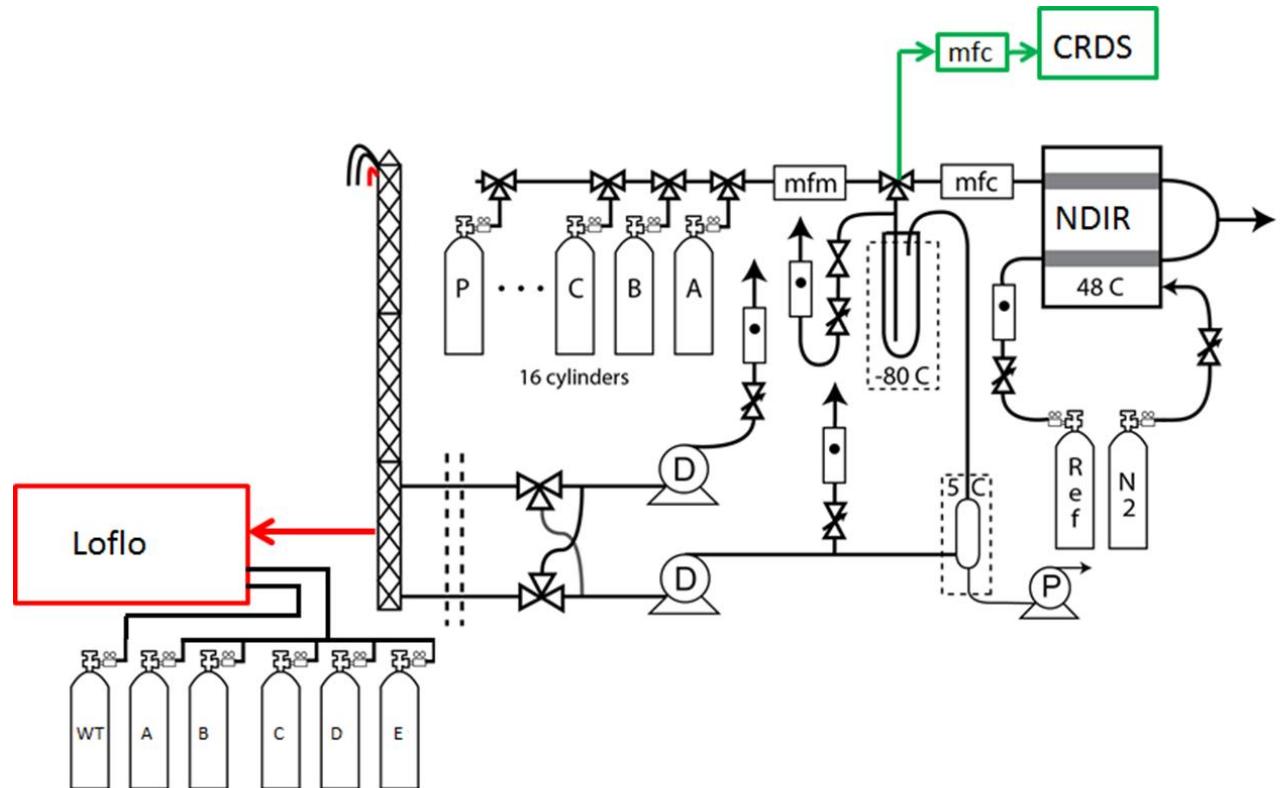
- 8 CCL gases
- 4 Working tanks
- Up to 4 unknowns

The same:

- Air, 2 airlines in common
- Plumbing
- Cryogenic drying to avoid H₂O issues

We connect Siemens (NDIR) and Picarro (CRDS) in parallel directly before the instruments

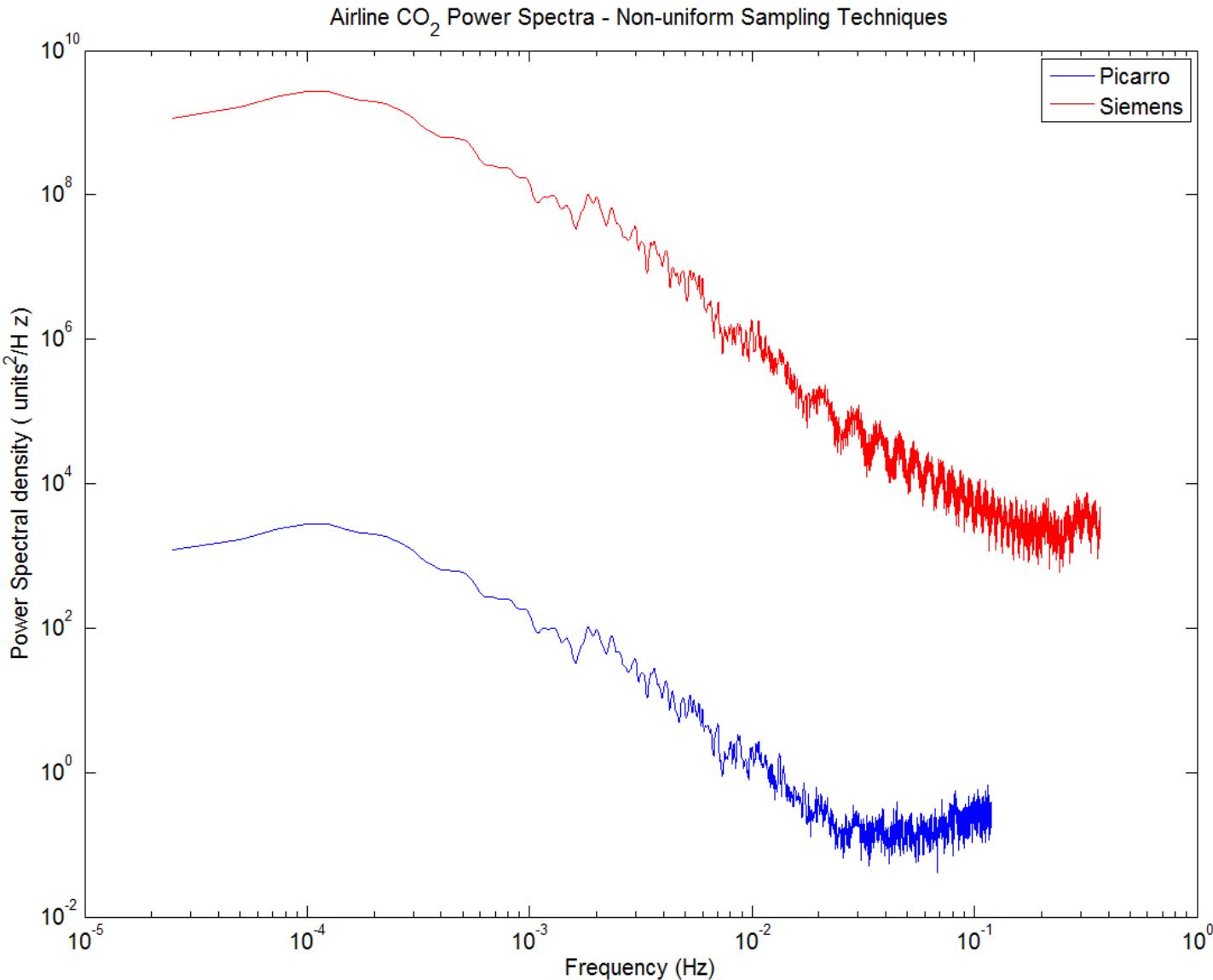
- Siemens to be master, Picarro the slave
- The same processing code



Instrument response

Power spectrum of one day of Air

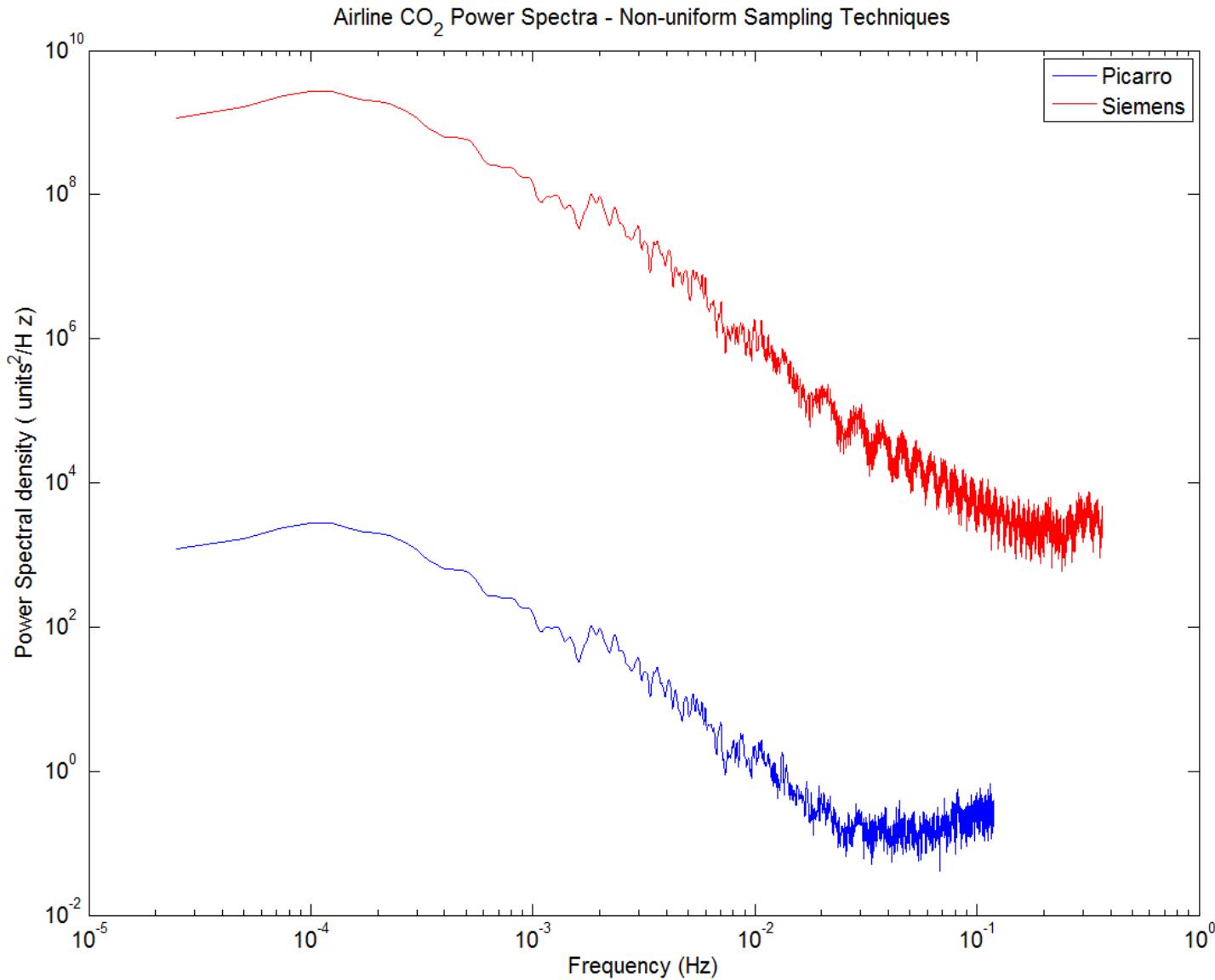
- Instruments have a different sampling rates
- non-uniform for Picarro
- Breaks in record for calibrations
- resolved through using non-uniform analysis techniques
- Siemens uses 64,000 bits, while Picarro uses “ppm” range



Instrument response

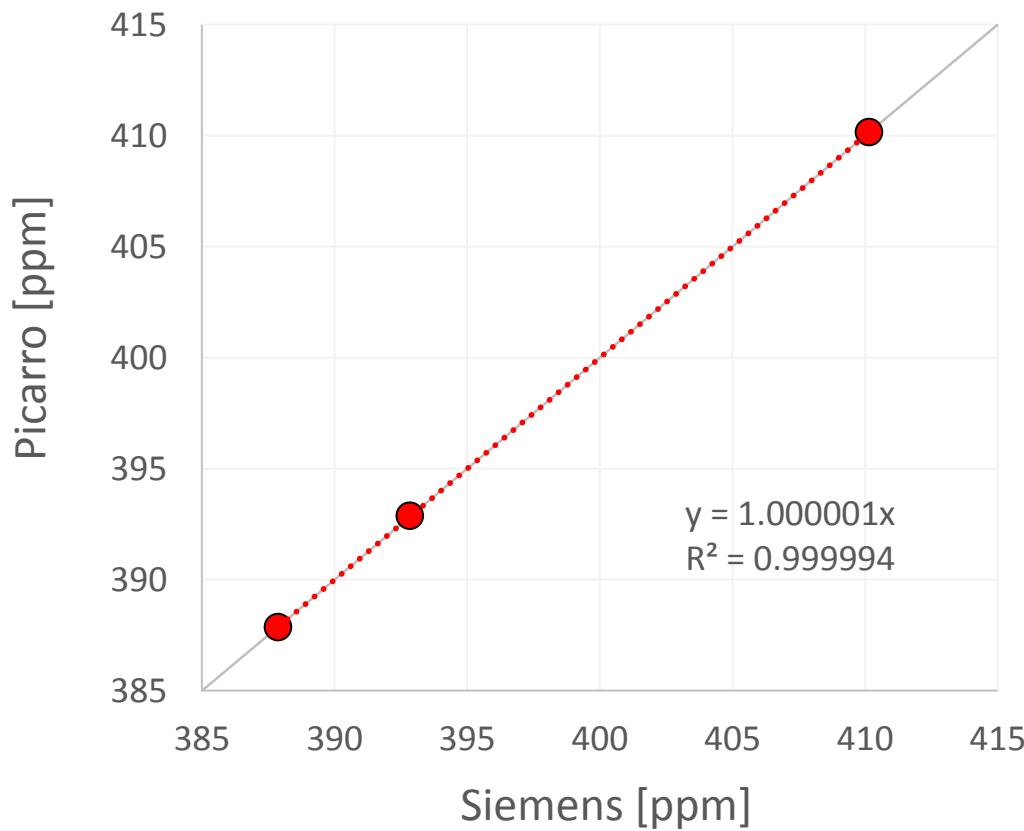
Power Spectrum interpretation

- What it tells us
- NDIR oscillations a
- High degree of similarity in form
- Where spectra agree at lower frequencies these are dominated by real air variations
- Where they differ at higher frequencies this is due to instrumental differences
- Higher frequency oscillations on Siemens data, 10–100 secs. Potential pressure/flow controller effects?



Calibration gas

CCL tanks: Picarro vs. Siemens



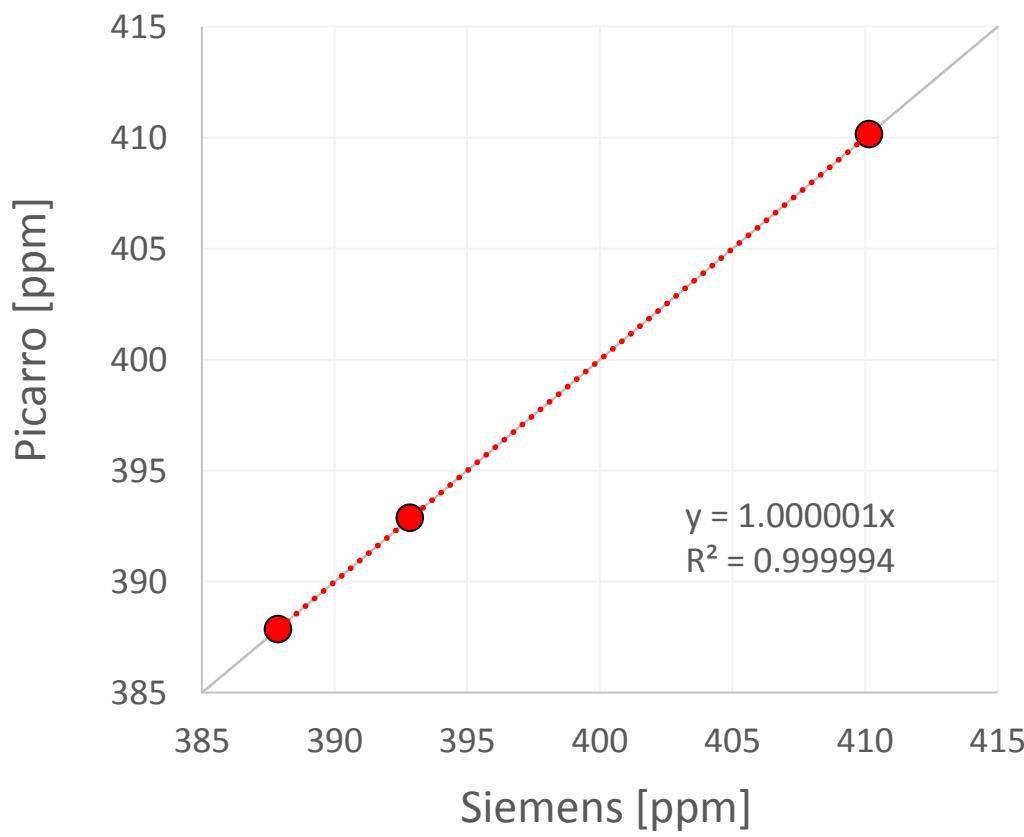
CCL tank comparison

Good agreement...

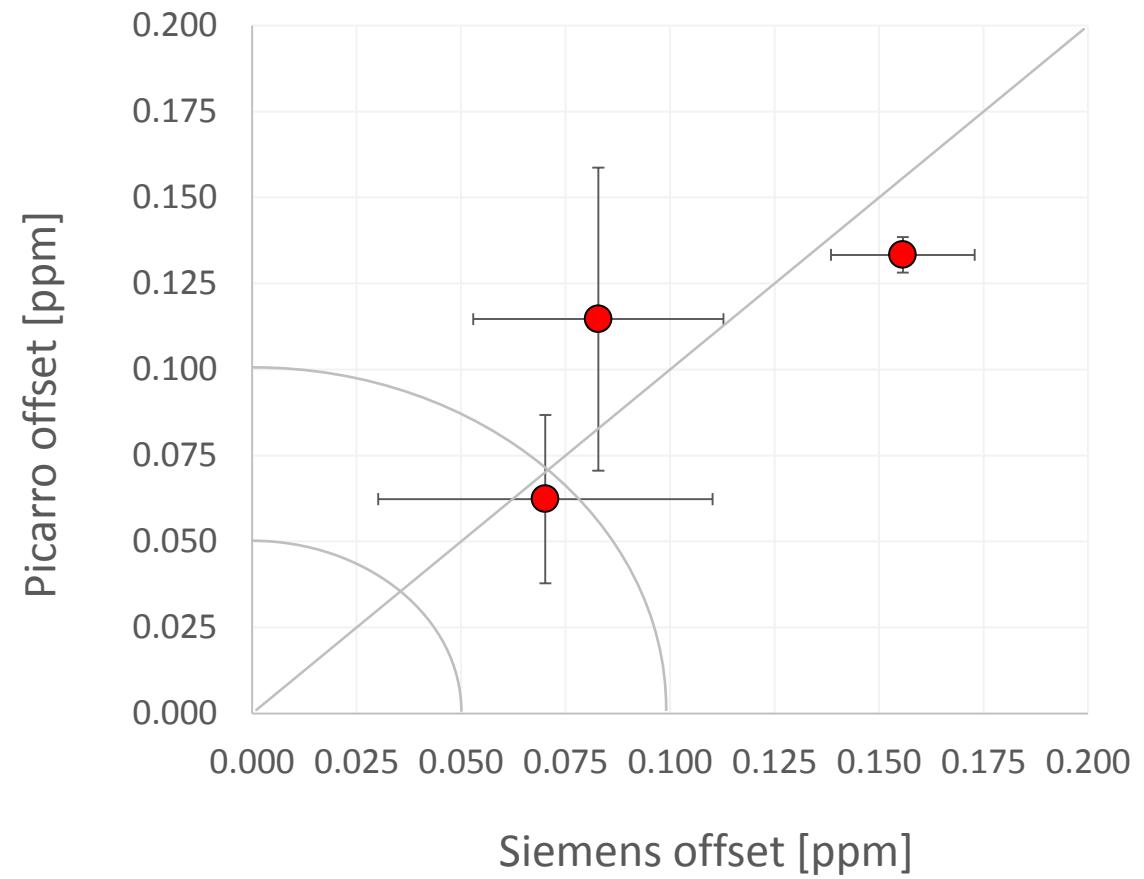
...at first glance

Calibration gas

CCL tanks: Picarro vs. Siemens

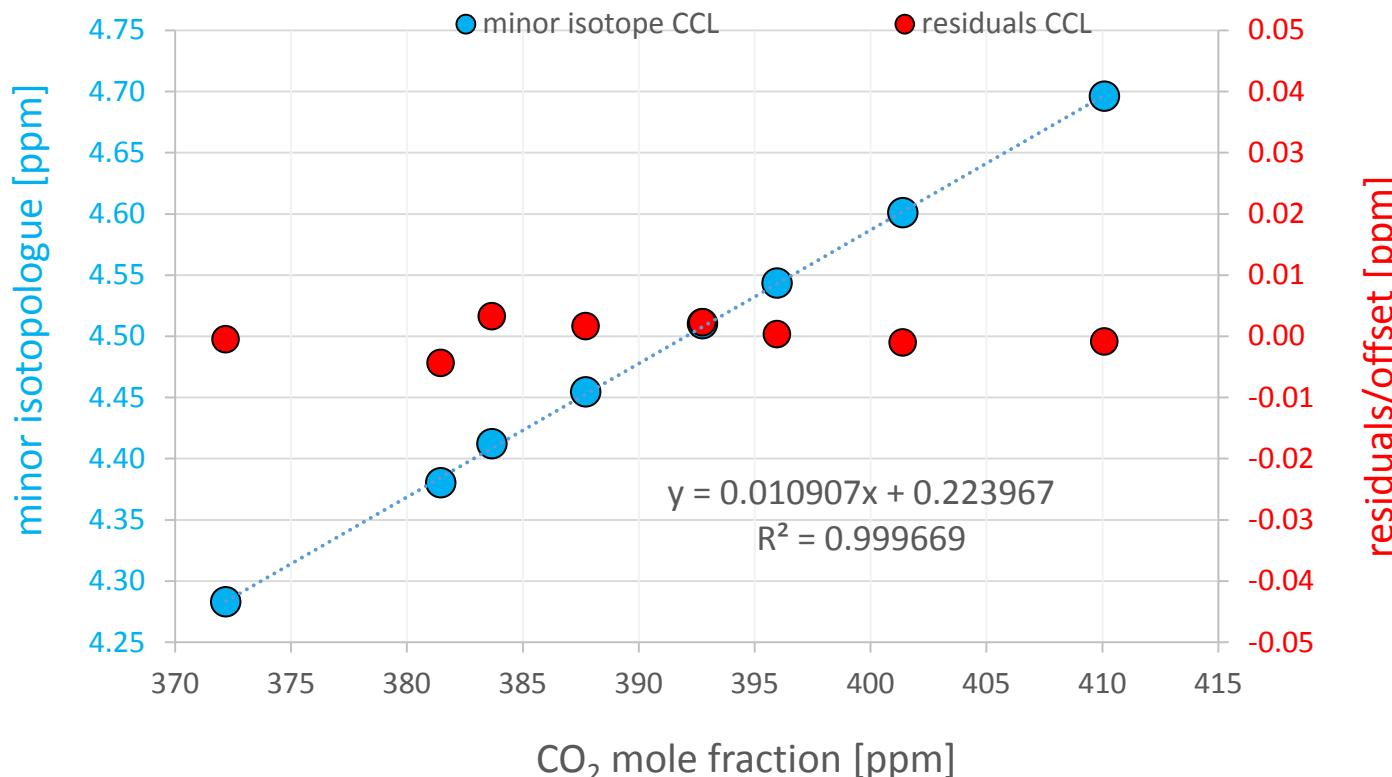


Offset to CCL, Picarro over Siemens



Isotope effects

CCL tanks: Isotope effect over CO₂



CCL calibration tank suite

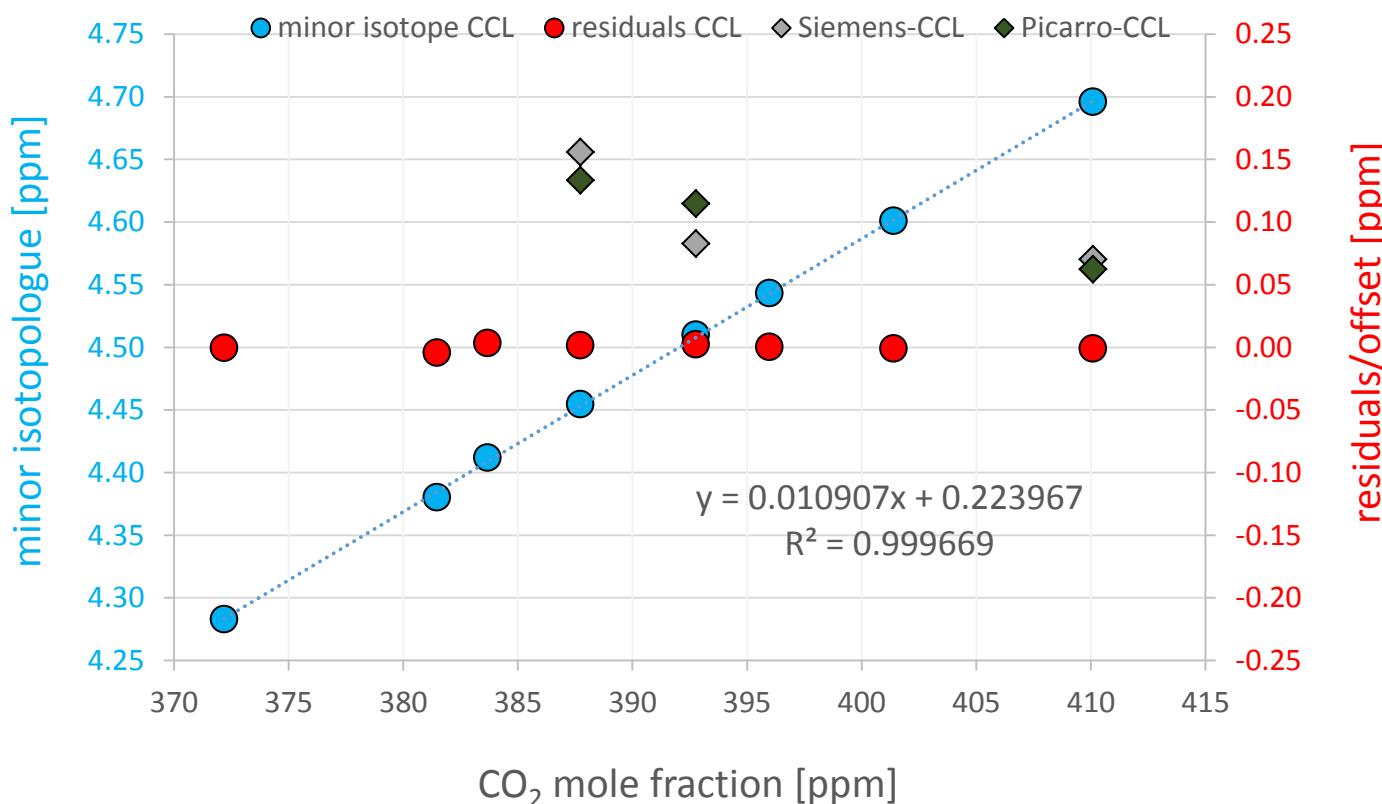
- ¹³C range → 1.5‰
- ¹⁸O range → 7‰
- Isotope effect
→ <0.01 ppm (0.05 ppm)

Effects

- For ¹³C we need a 10 ‰ change to exceed 0.05 ppm compatibility goal (0.05 ppm, Southern Hemisphere)
 - For ¹⁸O we need 30 %
- Calibration gases are prepared with isotopic composition similar to air

Isotope effects

CCL tanks: Isotope effect over CO₂

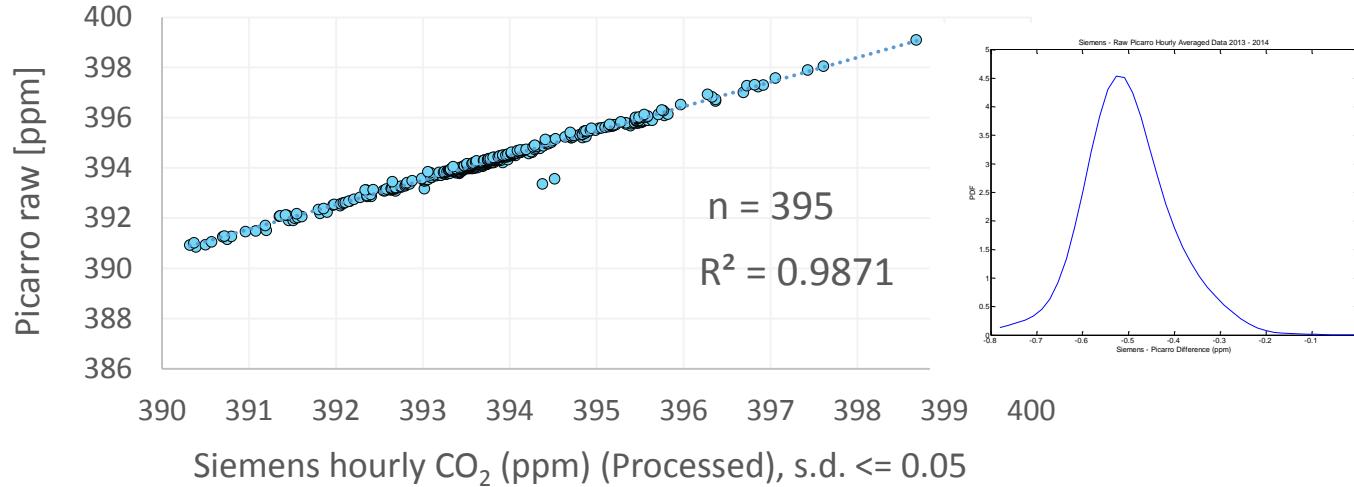


CCL tank suite

Differences to CCL values greater than can be explained through isotope effects.

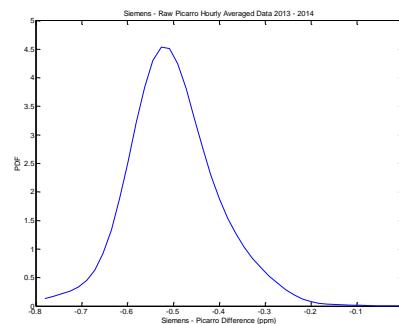
Air

Picarro versus Siemens, air



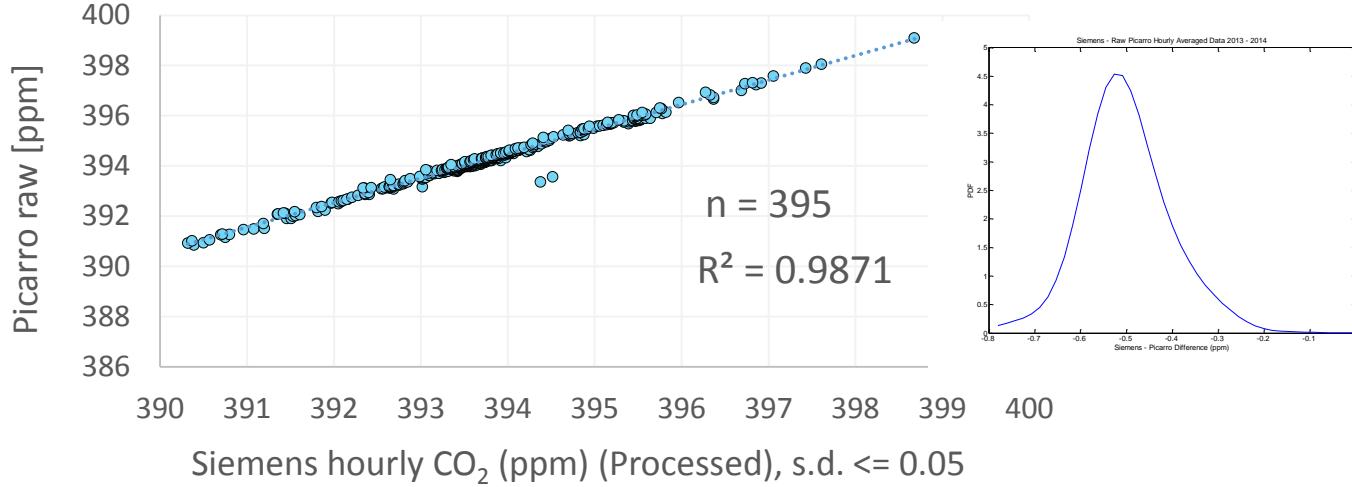
BHD air observations

- Raw Picarro data relates well with processed Siemens data
- Gaussian distribution about a mean

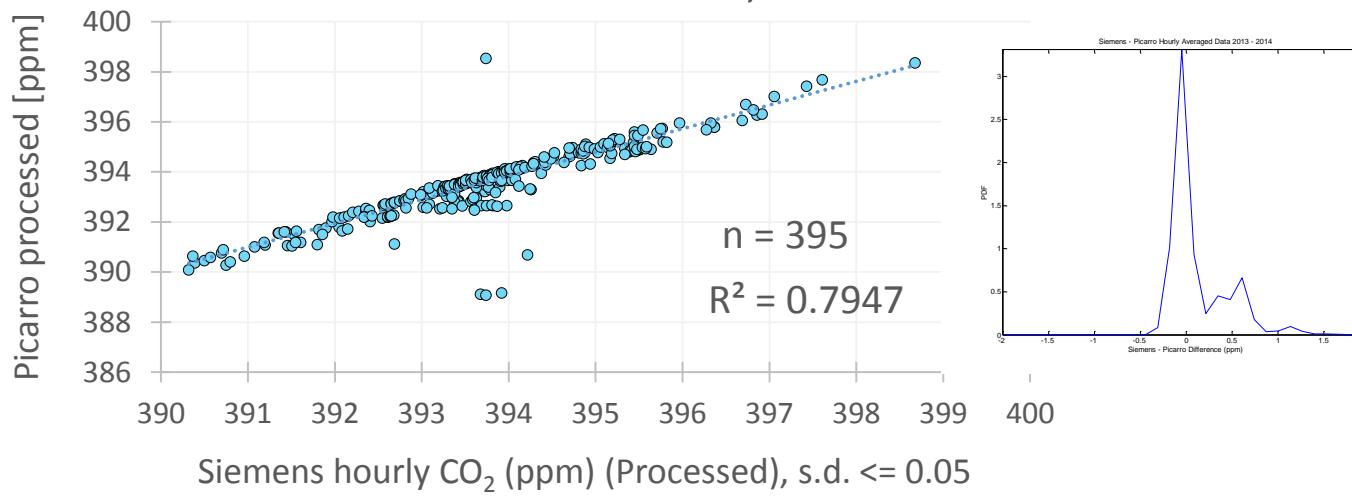


Air

Picarro versus Siemens, air



Picarro versus Siemens, air



BHD air observations

- Linear version of historic processing code is producing a bi-modal distribution to air data
- Manual processing does not do this

Summary

- Two instruments seeing the same air and calibration gases respond slightly differently
- Aim to measure a single cylinder of air for 24 hours on both instruments to observe Power Spectrum in unchanging systems.
- The historic NDIR processing methods need to be altered to provide Picarro data that is referenced properly to the suite of calibration gases used.
- Isotope effects are not a factor in ensuring a compatible data set.
- Aim to transition to Picarro as the master instrument and Siemens as the slave, as we move to the Picarro as the primary instrument.