Comparing atmospheric CO_2 measurements from two instruments at Baring Head, New Zealand

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Introduction

- Measurements of atmospheric CO_2 began at Baring Head (41.41° S, 174.87° E) in 1972 (Table 1).

Instrument	Method	Years in operation
URAS-1	Non-dispersive infrared analyser	1972-1977
URAS-2T	Non-dispersive infrared analyser	1976-1987
Siemens Ultramat 3	Non-dispersive infrared analyser	1986-2016
Picarro G2302	Cavity ring down spectrometer	2011-present

Table 1: Summary of CO_2 instrumentation used at Baring Head

- The Siemens and Picarro ran in parallel from 2011 to 2016 using the same calibration gases, the same two airlines, plumbing, cryogenic cooling (Figure 1), and the same processing code.

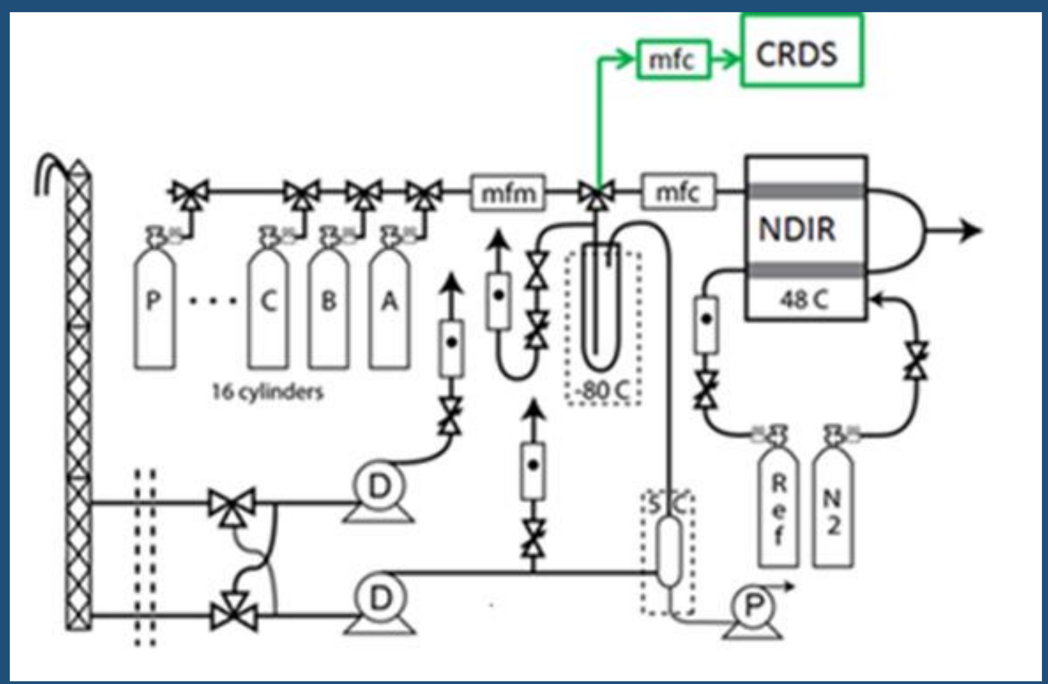

Figure 1: Baring Head CO_2 measurement system (2011-2016), with Siemens (NDIR) and Picarro (CRDS). Air is drawn from a 10m mast and cryogenically dried before sample and reference gases are measured by the two instruments operating in parallel. The Siemens is operating as the Master instrument and the Picarro as the Slave.

- The Picarro has some advantages over the Siemens (Table 2): it measures over a wider concentration range, uses less gas, is more stable, is more linear, and also measures CH_4 and H_2O.

Siemens-Ultramat 3	Picarro-G2301
Samples at 1 Hz	Samples at ~ 0.3 Hz
64,000 bits over a range of 60ppm	"ppm" output, 4 decimal places to obtain the comparable sensitivity
Non-linear response	Linear response
Single pass cell	Long path length (20 km)
Sensitive to water	Measures water and is sensitive to it
Coarse temperature control	Fine temperature control
Only "sees" $^{12}CO_2$	Only "sees" $^{12}CO_2$
Does not measure CH_4	Measures CH_4

Table 2: Comparison of main features of Siemens Ultramat 3 and Picarro G2301

Steady Period Air Comparison

- During steady period events the air arriving at Baring Head has very low CO_2 variability, making these events ideal for comparing the final processed air values from each instrument.
- A steady interval occurs when the standard deviation of measured values from a single inlet line over a six-hour interval is 0.1 ppm or less. Multiples of these overlapping "intervals" of steady data are then combined to form steady "periods", such that CO_2 can slowly vary within a several day steady period as long as 6-hourly subintervals still satisfy the variability criteria.
- Between 2014 and 2016 the Siemens measured 116 steady periods, and the Picarro measured 137, which demonstrates the greater stability of the Picarro. These steady periods varied in length from 6 hours to 3 days. The Picarro steady periods tend to be longer than the Siemens steady periods. Figure 2 shows the CO_2 mole fractions for these steady periods. Some of the differences between the Siemens and Picarro values can be due to real differences in CO_2, as the actual time periods for the steady period do not necessarily exactly coincide.
- Figure 2 also includes the same–air ICP flask data measured on gas chromatographs at NIWA and NOAA. There is a consistent difference of about 1.1 ppm between the NIWA and NOAA ICP flask values for samples from March 2016 onwards; NIWA is currently re-assessing the CO_2 GC working tank values versus the new CCL transfer gasesfor this period.

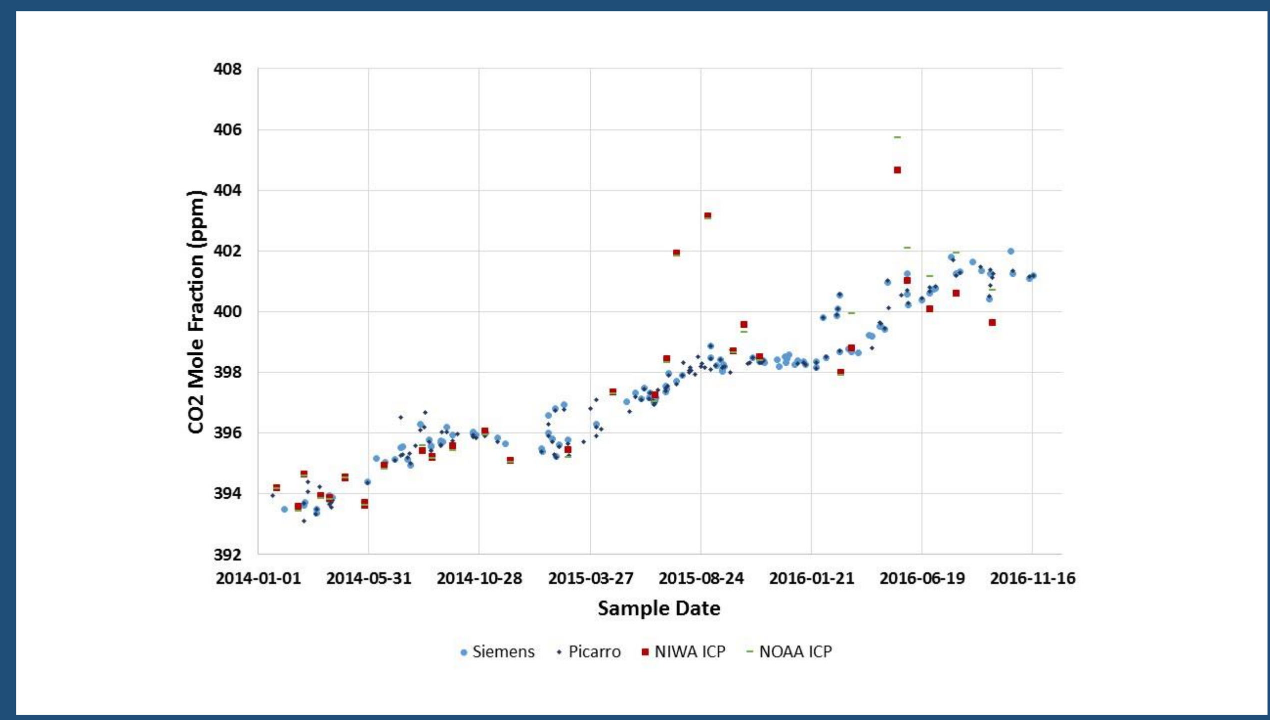

Figure 2: CO_2 mole fractions for all the steady interval periods in 2014-2016, and the same-air ICP flask data .

- Figure 3 shows the agreement between the Siemens and the Picarro steady period data, when the values were calculated over exactly the same time periods. There are 82 steady interval periods in Figure 3. The average difference between the two instruments is 0.045 ppm, and the standard deviation of the differences is 0.097 ppm.

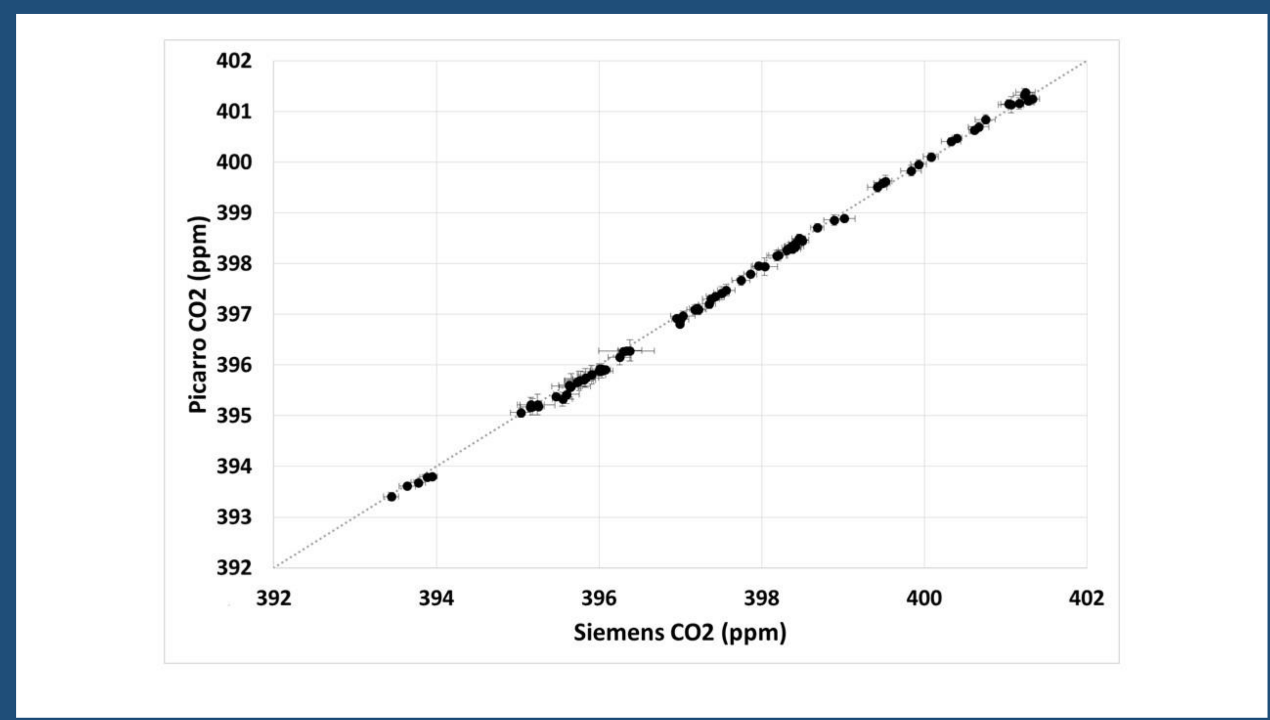

Figure 3: Siemens and Picarro measured CO_2 values, calculated over exactly the same time periods, for steady period air in 2014-2016.

Central Calibration Laboratory (CCL) Tank Comparison

- Eight CCL calibration gases are used in the measuring system as long-term transfer standards to provide a link to the WMO mole fraction scale.
- The offsets between the Picarro average measured value and the assigned value for each CCL tank lies in the range 0.02 to 0.07 ppm (Figure 4), which is very close to the GAW compatibility goal of 0.05 ppm for southern hemisphere stations.
- The Siemens offsets for six of the CCL tanks (with concentrations between 381 and 401 ppm) range from 0.02 to 0.07 ppm, but the values for the 372 ppm and 410 ppm tanks are well outside this range (Figure 4).

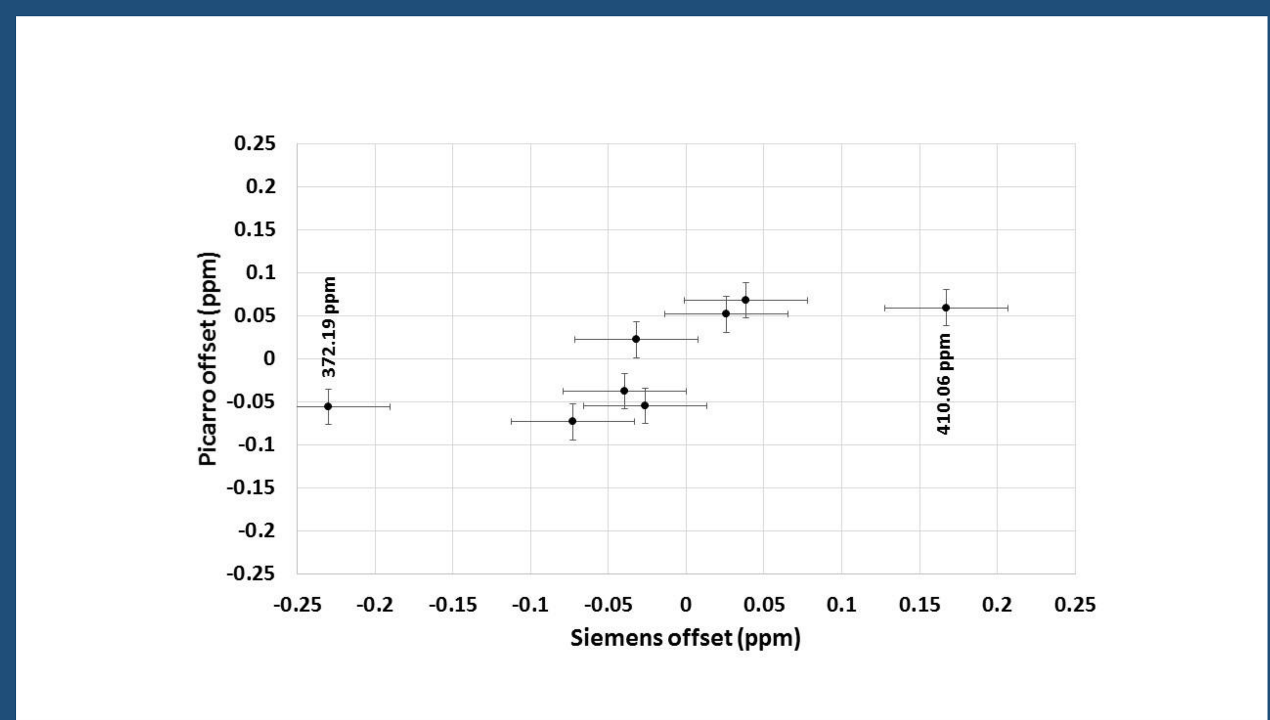

Figure 4: Offsets between the average measured values for the CCL tanks and the CCL assigned value. The error bars are the standard deviations.

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