Karlsruhe Institute of Technology

GREENHOUSE GAS OBSERVATIONS AT CAPE POINT: CHALLENGES AND RESULTS

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South African Weather Service

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Overview

1. First results of Picarro G2302 [CO_2 - CO - H_2O] instrument
2. New ANSTO ^{222}Rn analyser – comparisons with former unit
3. N_2O: current analytical data quality
4. ICP results: NOAA flask sampling program
5. Latest trends for CO_2 and CH_4

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First measurements with a Picarro G2302 instrument (since July 2011) Species: CO_2 and CO

RGA 3

URAS 4

- Own sample control system – await Picarro unit
- Three whole air standards – NOAA standards on order
- Daily target analyses

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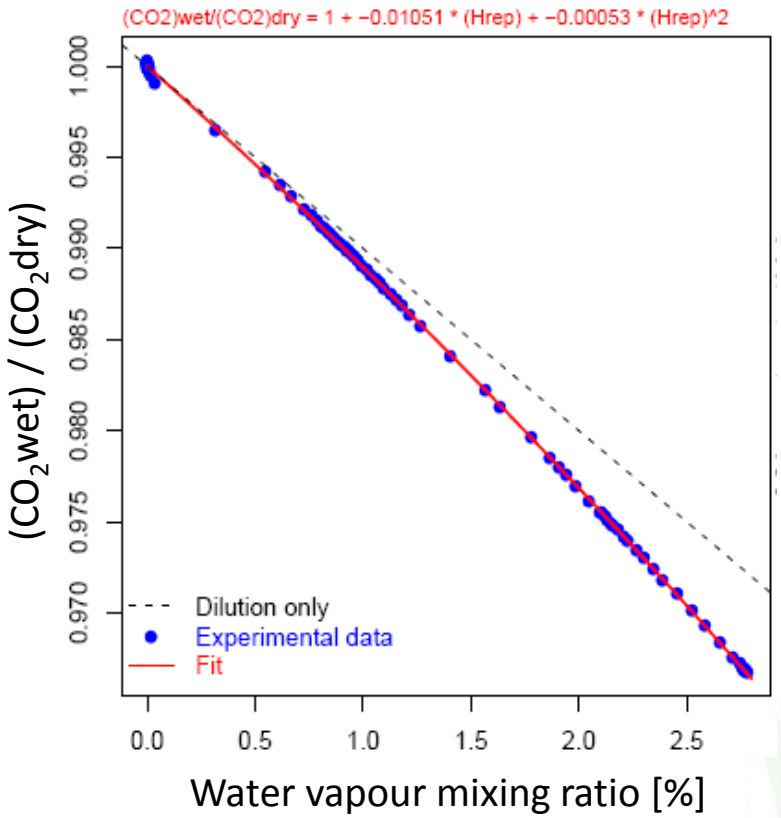
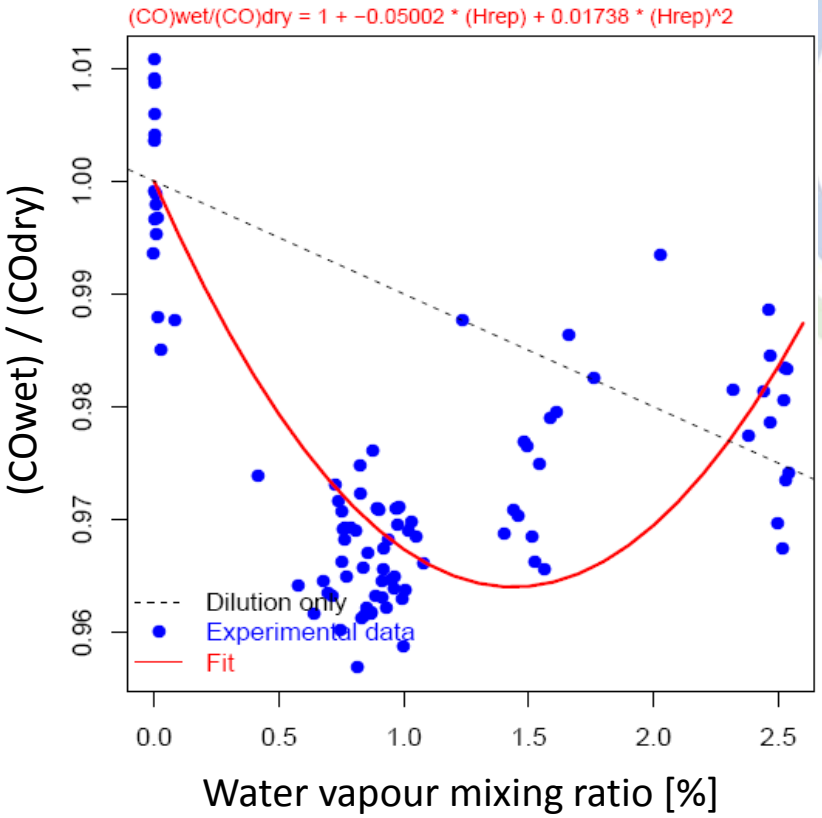
CO_2 and CO moisture tests done on Picarro (G2302): Aug 2011





- Dry air (constant flow) from cylinder with CO_2 [402.8 ppm] and CO [176 ppb] fed to Picarro via 1.5 m long Dekoron tubing with addition of 0.7 ml H_2O over 2.5 hrs.
- CO_2-dry correction meaningful, but not for CO. Unlike CO_2, CO-wet not provided by G2302, which may impede own correction.

Calculations done by courtesy of WCC-Empa, Switzerland

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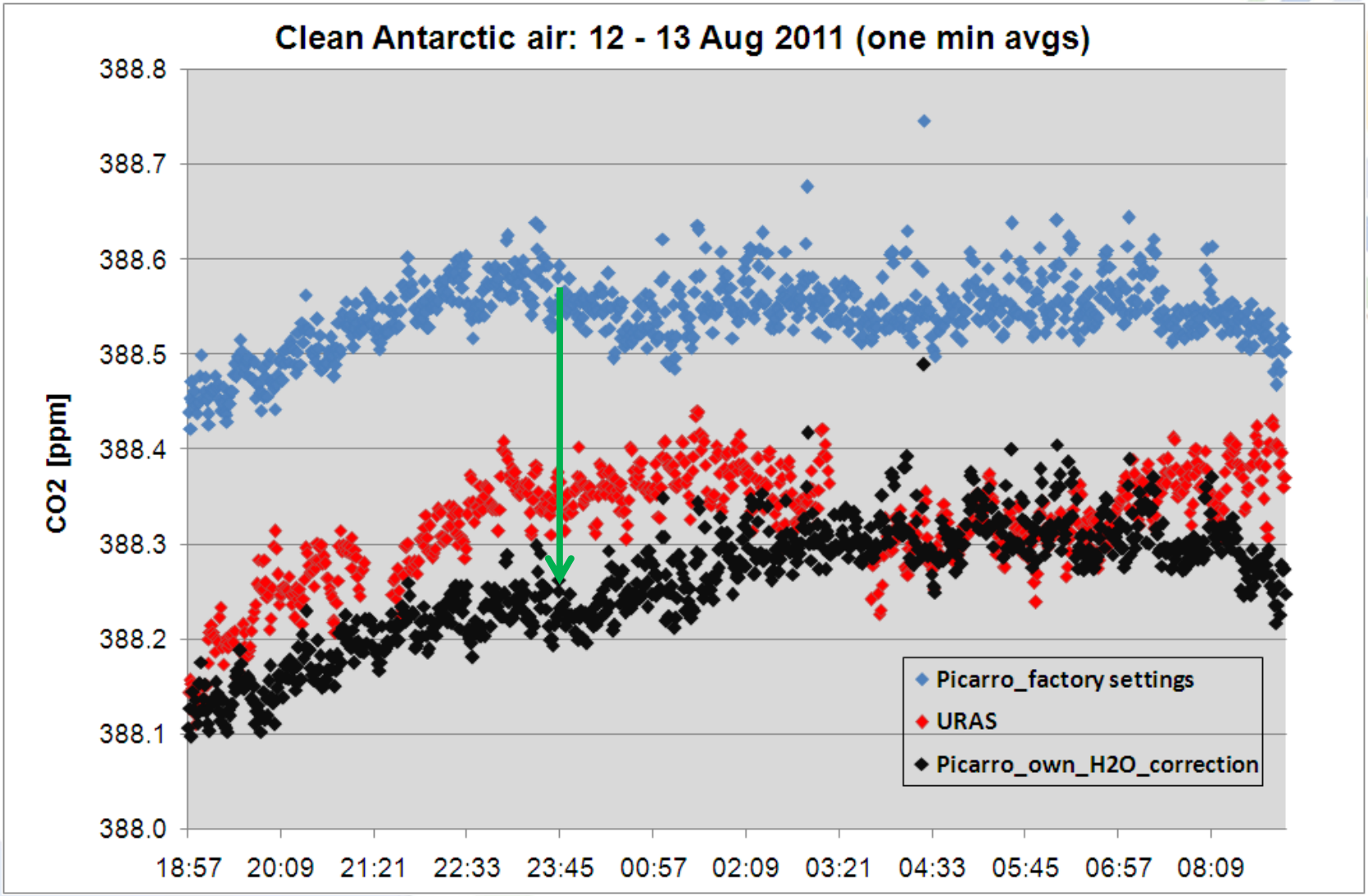
CO_2 comparison between Picarro and NDIR (URAS 4)



- Own moisture correction reduced gap between 2 data sets
- NDIR (URAS 4) > Picarro by 0.06 ppm CO_2 on average

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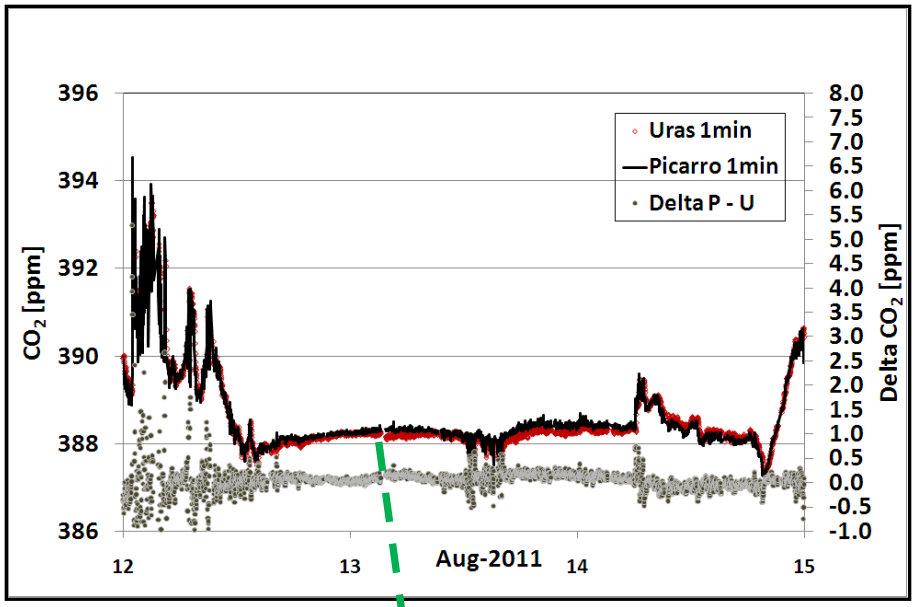
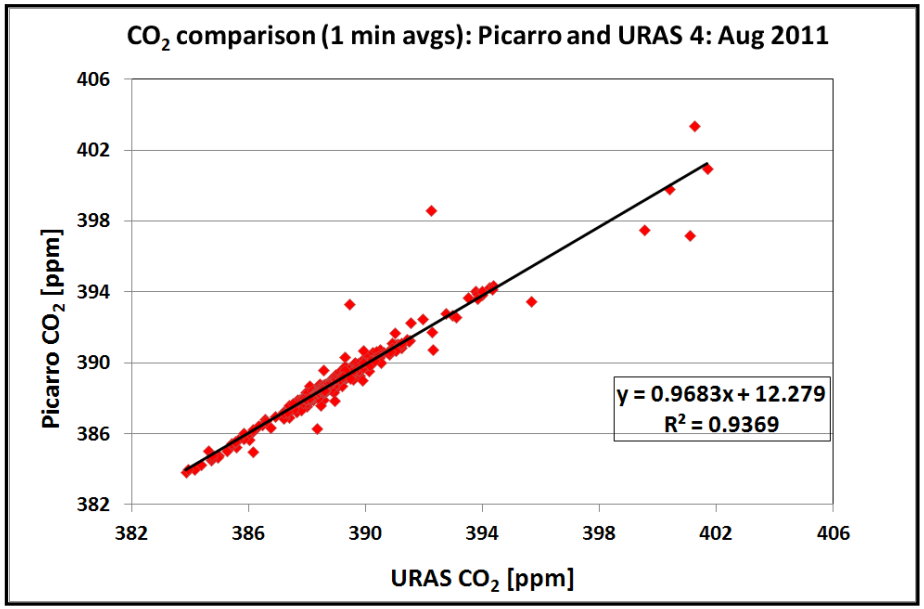
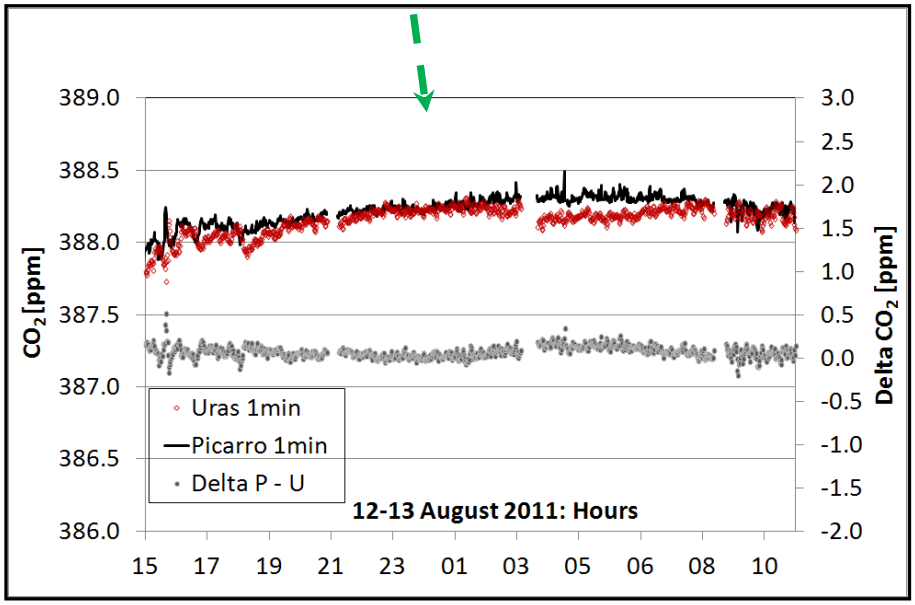
Ambient CO_2 (1 min avgs): Picarro and NDIR (URAS 4): Aug 2011





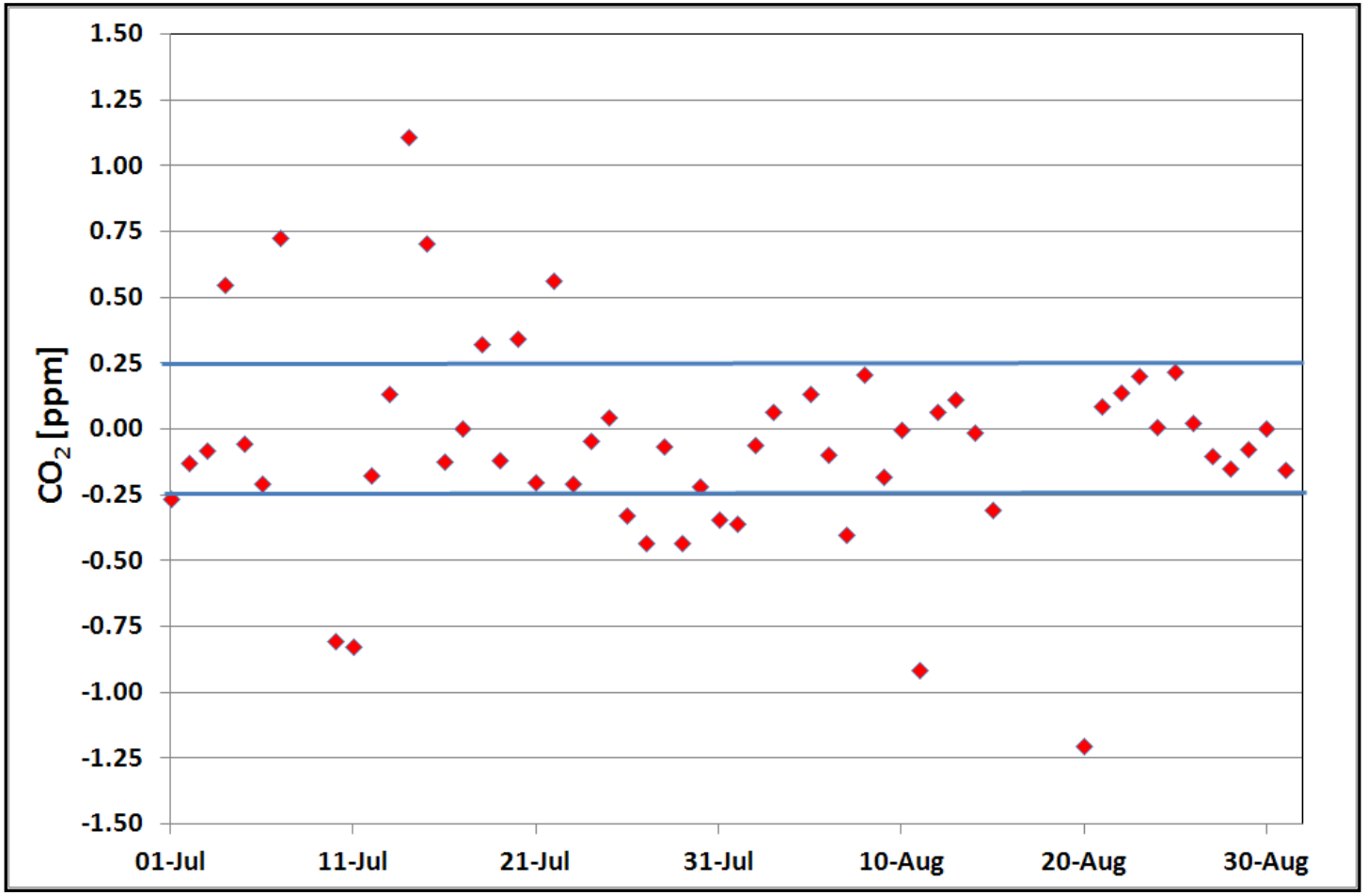


- Good agreement between two instruments under clean-air conditions

<u>1min ambient average for 12th – 13th Aug:</u>

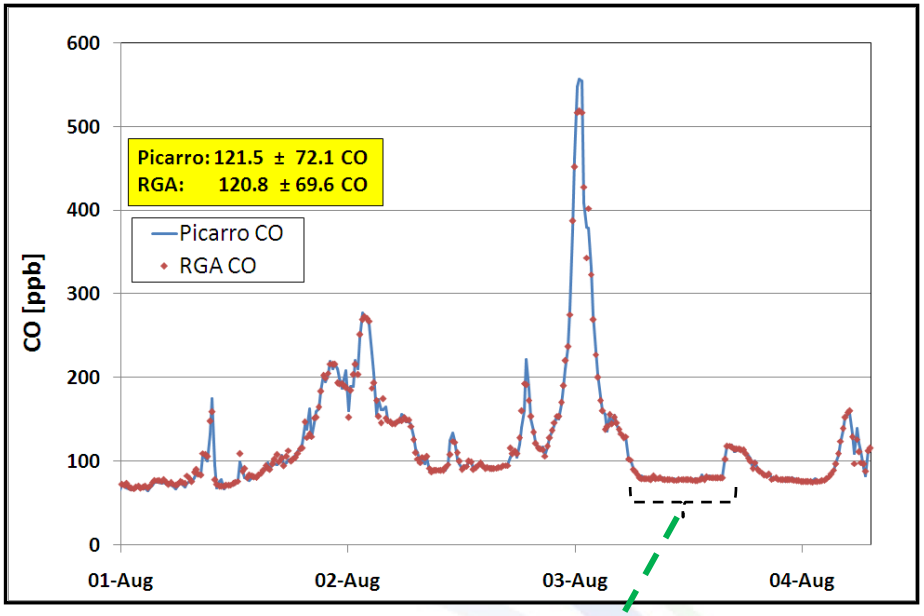
- URAS 4 (NDIR) 388.12 ± 0.14 ppm
- Picarro 388.18 ± 0.15 ppm
- Average difference (11 -15 Aug): 0.01 ± 0.32 ppm

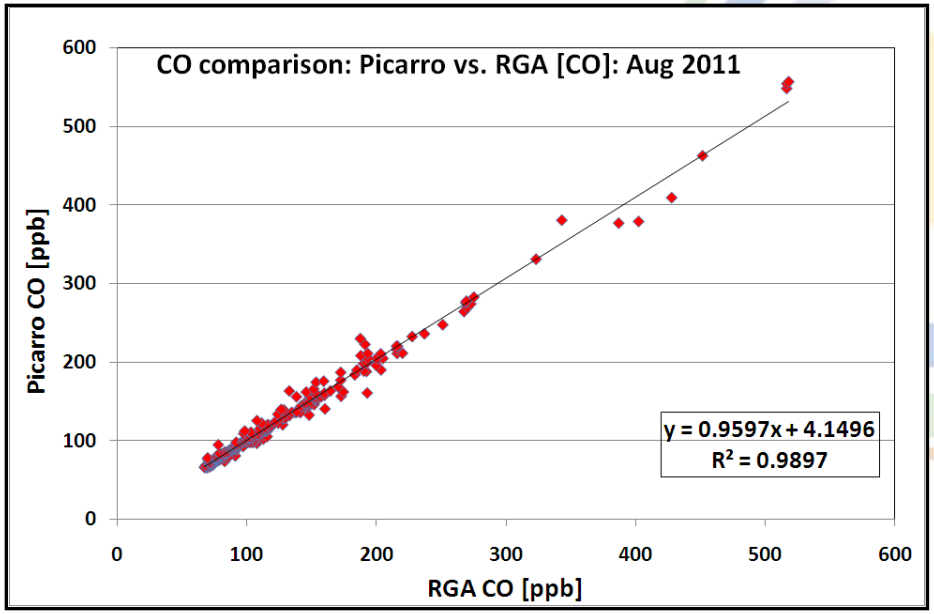
Ambient daily CO_2 averages [ppm]: Picarro minus NDIR (URAS 4)

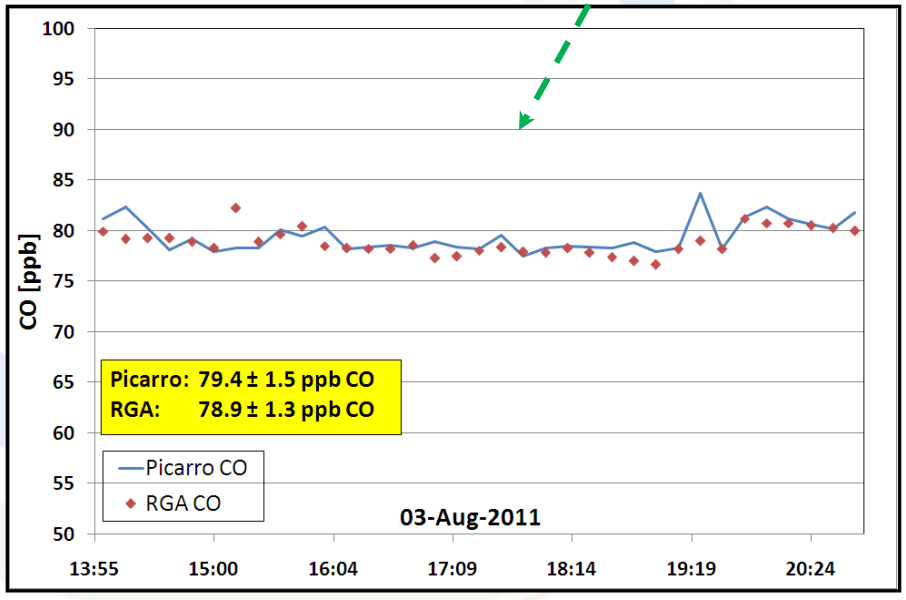


- 67 % of delta values (Picarro minus NDIR) fall within ± 0.25 ppm CO_2
- NDIR (URAS 4) > Picarro by ~0.06 ppm (± 0.39 ppm)
- Outliers perhaps due to different air inlets (air intake volumes)

CO comparison (dry air): Picarro and RGA: Aug 2011







- Good correlation between instruments under clean-air conditions
- 12min (RGA) vs. 1sec data frequency (Picarro) causes divergence at higher concentrations

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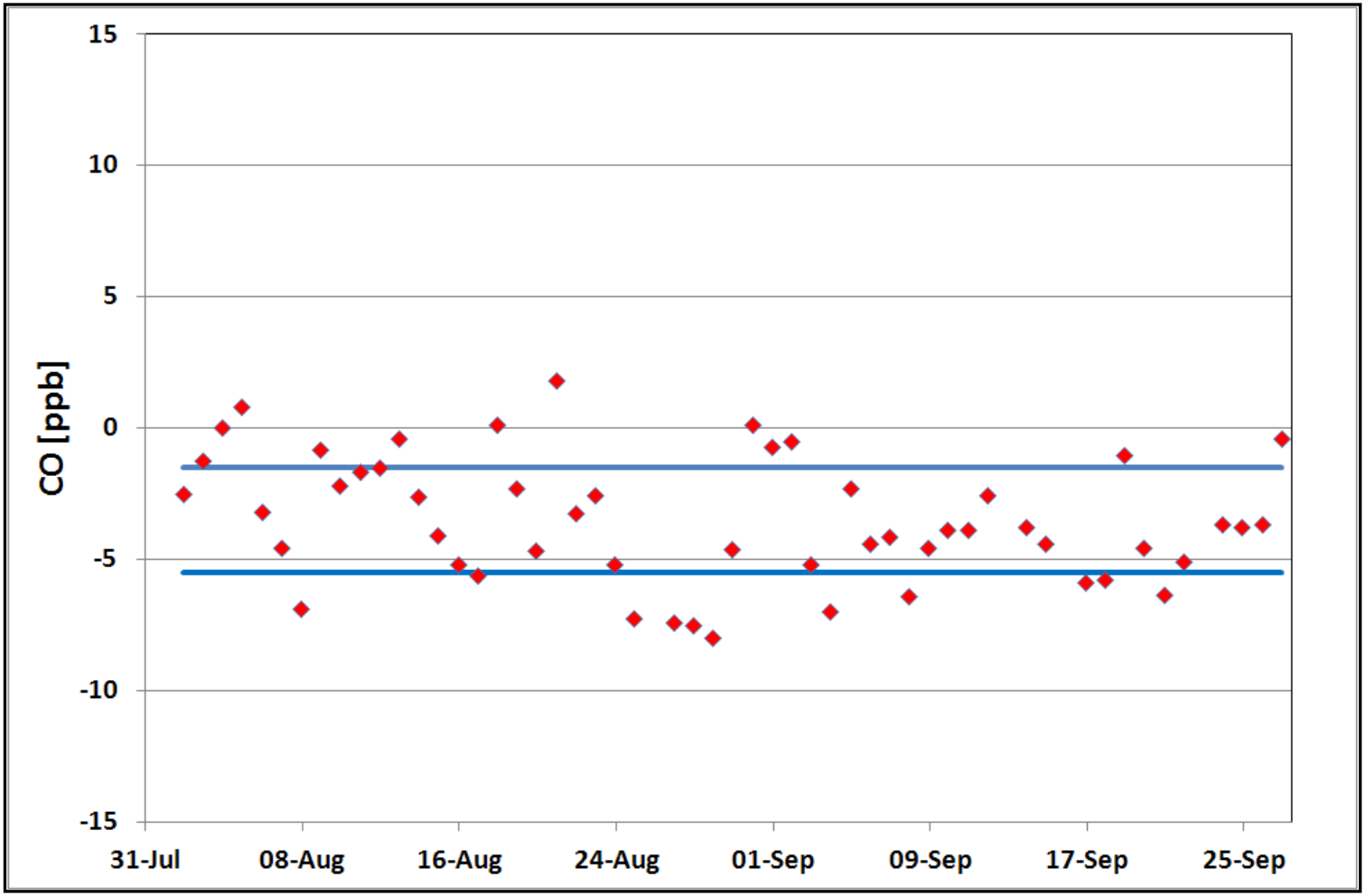
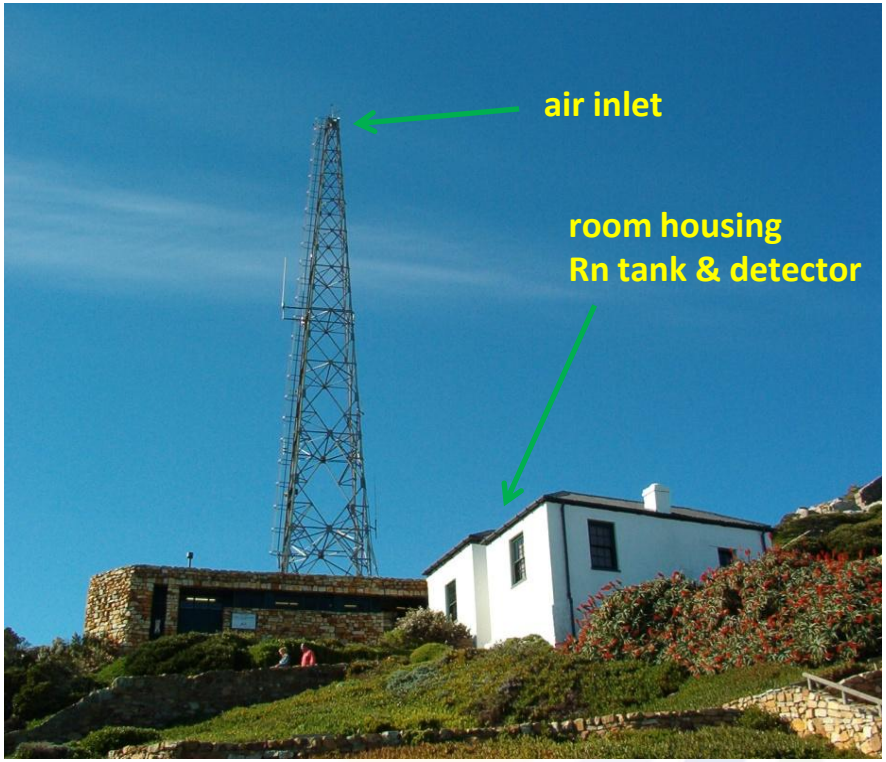
Ambient daily CO [ppb] averages (wet air): Picarro minus RGA



- 58 % of delta values (Picarro minus RGA) fall within - 1.5 and -5.5 ppb CO
- RGA > Picarro by 3.5 ppb (on average), although standards agree within 1 ppb
- Outliers perhaps due to different air inlets (drying vs. no drying) as well as inadequate moisture correction on Picarro

^{222}Rn upgrade (instrument CPT2) and comparison to former system (CPT1)



^{222}Rn detector and decay tank

Collaboration partner: ANSTO Institute for Environmental Research
Australian Nuclear Science and Technology Organization
S. WHITTLESTONE (CPT1)
W. ZAHOROWSKI & S. WERCZYNSKI (CPT2)

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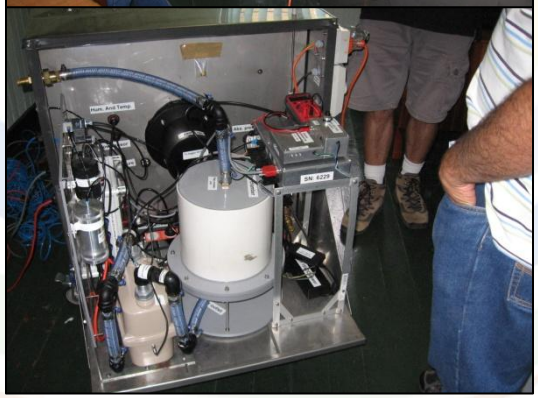
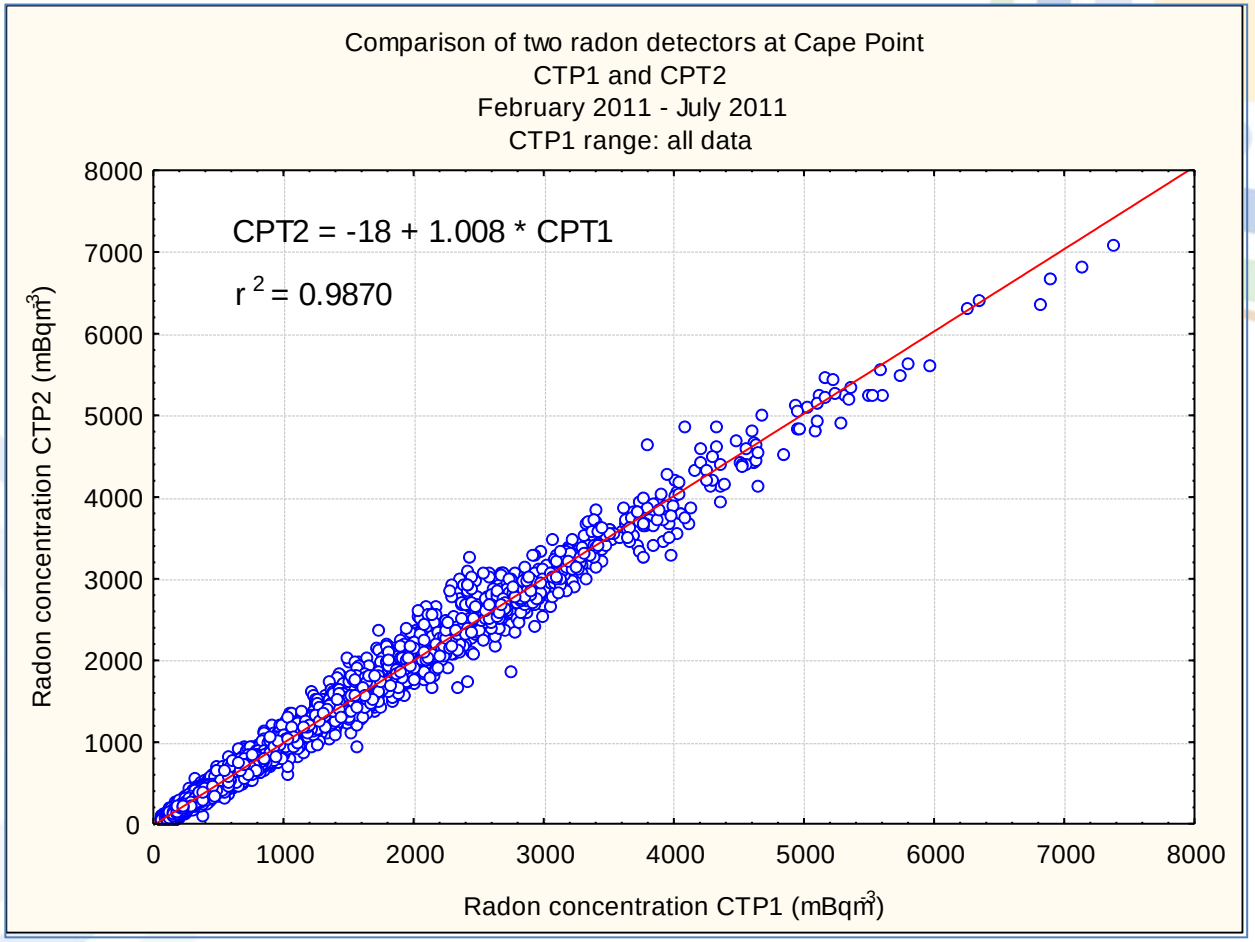
^{222}Rn upgrade and comparison to former system: CPT2 versus CPT1





Calculations by courtesy of W. Zahorowski

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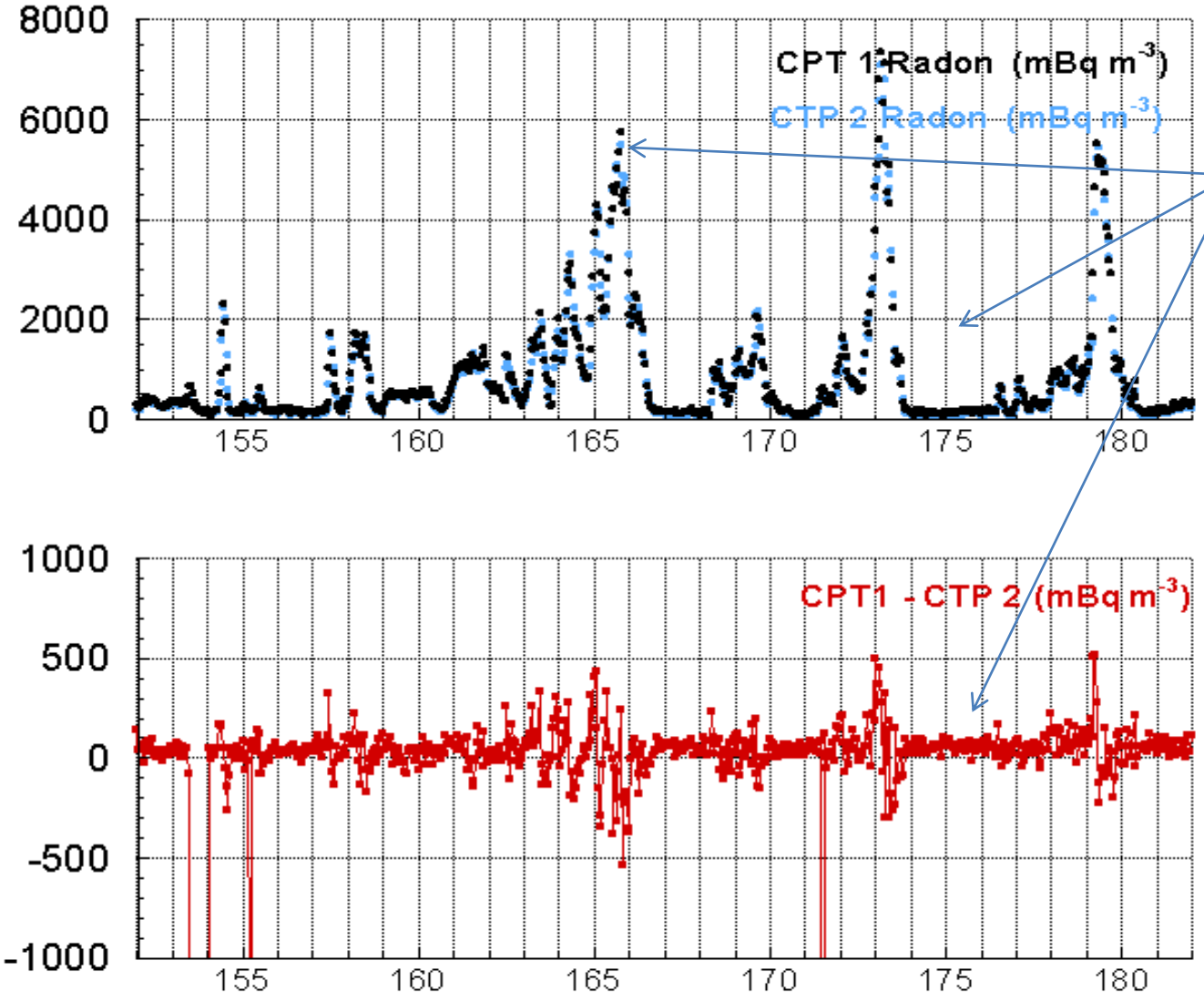
^{222}Rn upgrade and comparison to former system: Time series of 30 days



Good overall agreement

Graphs supplied by W. Zahorowski

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Correlation: CPT2 vs. CPT1 (February 2011 – July 2011)

Dataset	Sub-range	Offset (mBq^{-3})	slope	r^2
All data	full	-18	1.008	0.9870
Autumn and Winter	full	-29	1.002	0.9902
Summer only	full	-45	1.171	0.9850

CPT1 and CPT2 background estimate [mBq m^{-3}]: April – August 2011

Rn Analyser	Background	Thoron	Estimate
CPT 1	137	38	**153**
CPT2	73	22	**84**

Summary:

- Main features recorded by "old" (CPT1) and "new" (CPT2) instruments compare well, thus yielding a homogeneous time series.
- CPT2 provides better data resolution at lower ^{222}Rn levels by virtue of its lower background and greater data stability (due to lower temperature fluctuations indoors).

Data supplied by W. Zahorowski

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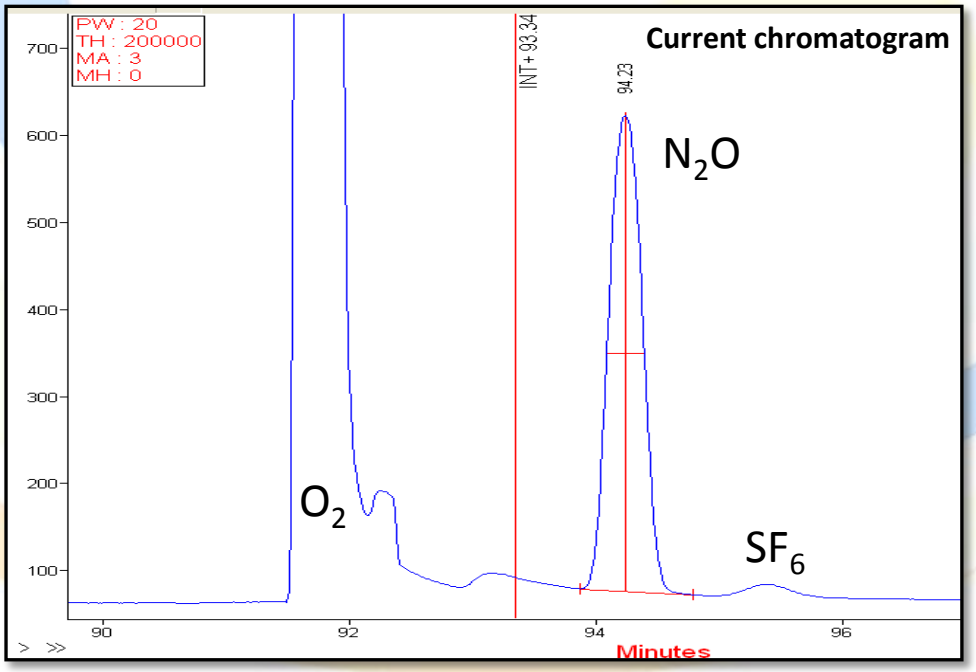
Review of Cape Point N_2O measurements

- The Agilent GC with micro-ECD posed many analytical challenges since its inception during mid-2007: sensitivity variations and data uncertainty.
- At the beginning of 2011 GC reduced to bare essentials: separate solenoids, 6-way Valco valve, carrier gas directly to column, no makeup, no back flush or O_2 removal, column length increased to 8 m.
- WCC-N_2O audit conducted under these conditions in Feb 2011: acceptable results.
- Quality of ambient measurements improved after Aug 2011



SEP 2011	Target gas [ppb]	Ambient [ppb]
Average	318.51	322.42
Std dev	0.32	0.46
RStd dev %	0.10	0.14
Count	25	109

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Current flask sampling programs: LSCE, NOAA, UEA, RHUL

LSCE since Oct 2006

UEA and RHUL since May 2011

NOAA since Feb 2010

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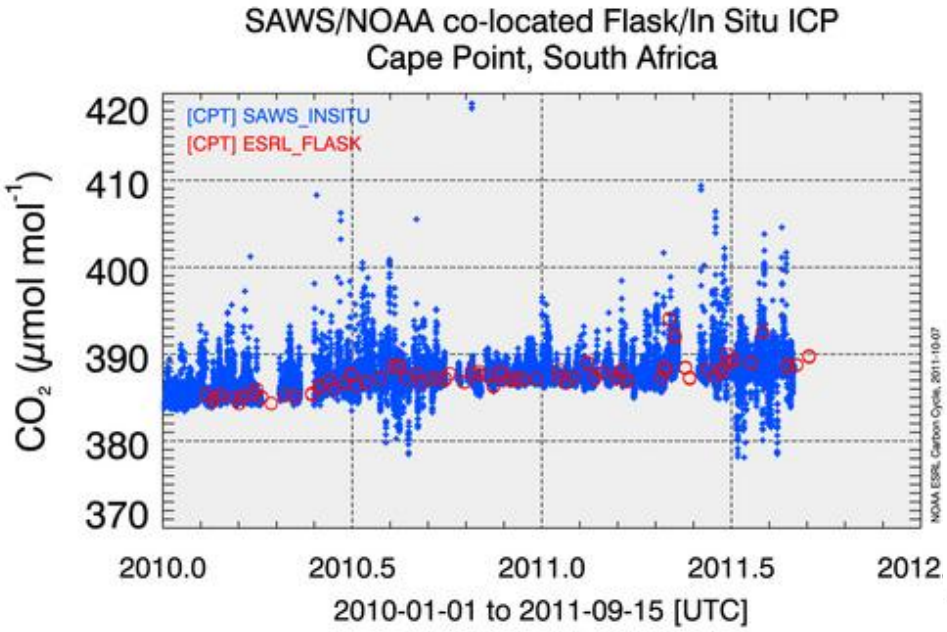
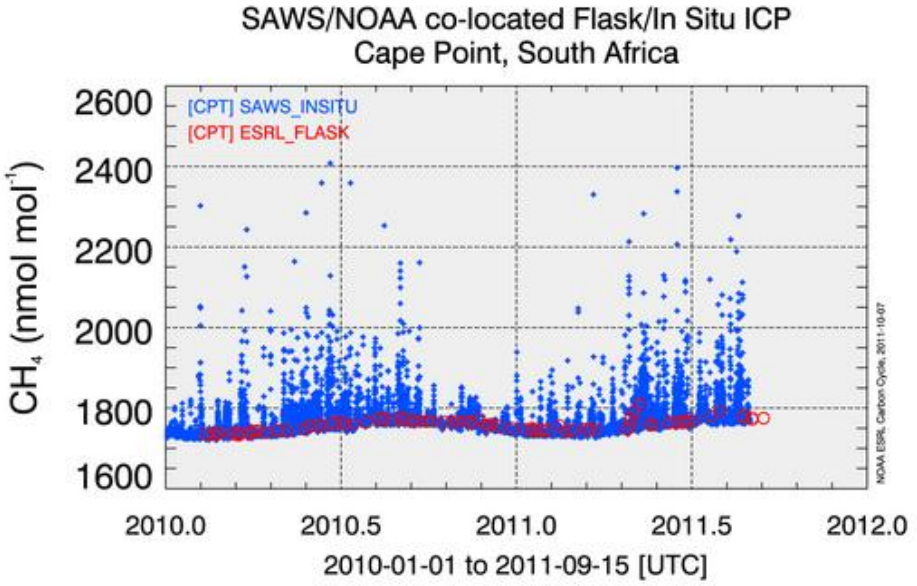
First ICP results of comparison between NOAA co-located flask sample data and Cape Point in-situ results [Feb 2010 – Aug 2011]





Blue points indicate Cape Point in-situ data; red circles NOAA-ESRL flask values.

Taken from Ken Masarie, NOAA-ESRL Flask Sampling Program, 2011

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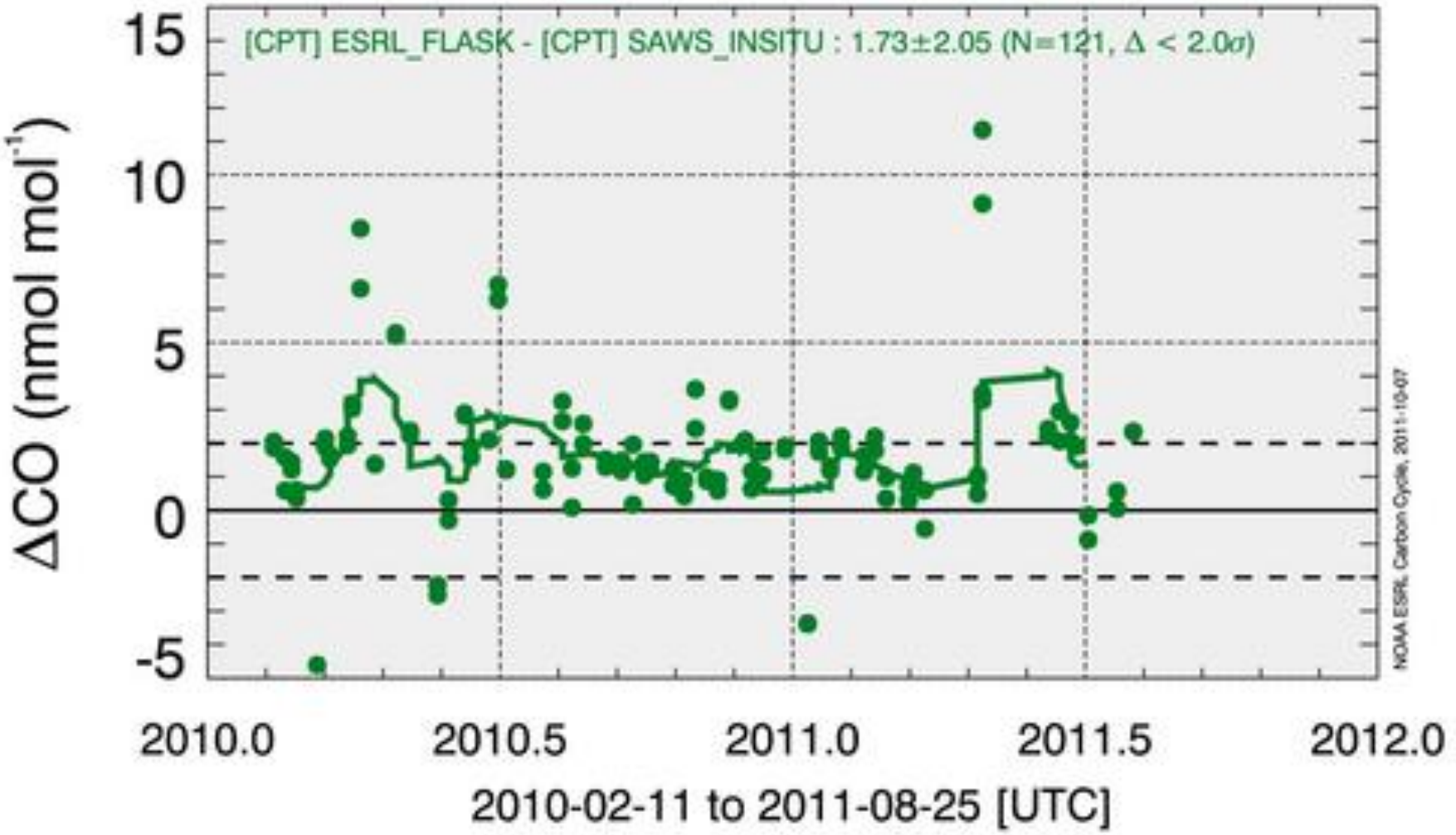
Preliminary ICP Results: NOAA-ESRL: CO



- NOAA-ESRL flask data > CPT in-situ (RGA) by about 1.7 ppb

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Taken from Ken Masarie, NOAA-ESRL Flask Sampling Program, 2011

ICP: NOAA-ESRL flask data minus CPT in-situ (February 2010 – August 2011)

Trace gas species	Mole fraction differences: within 68 % of data	Mole fraction differences: within 95 % of data
[CO]	2.19 ppb	9.14 ppb
[CH_4]	6.23 ppb	14.09 ppb
[CO_2]	0.76 ppm	1.34 ppm

Summary:

Observed differences partially explained by:

- Different sampling lines: wet vs. dry
- Difficulty in synchronizing flask sampling event with in-situ
- Flask filling during non-background conditions
- Small systematic differences in scales

Taken from Ken Masarie, NOAA-ESRL Flask Sampling Program, 2011

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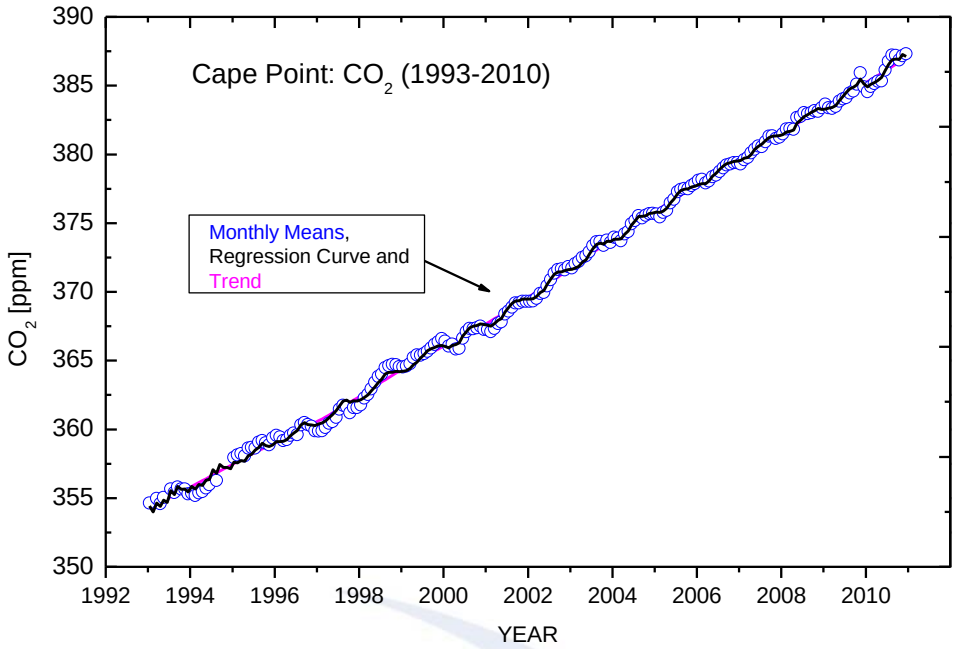
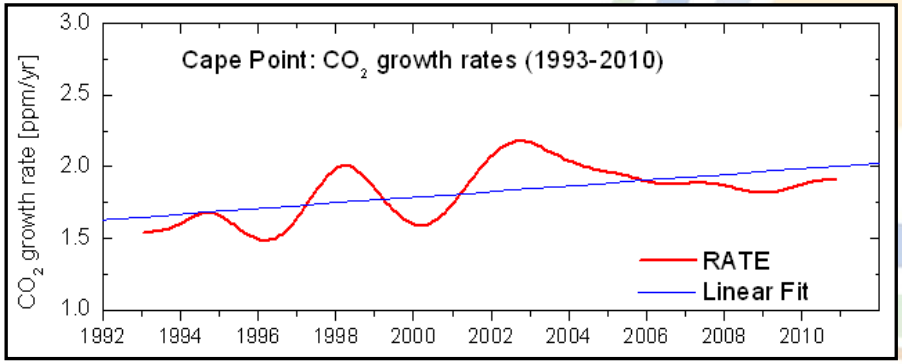
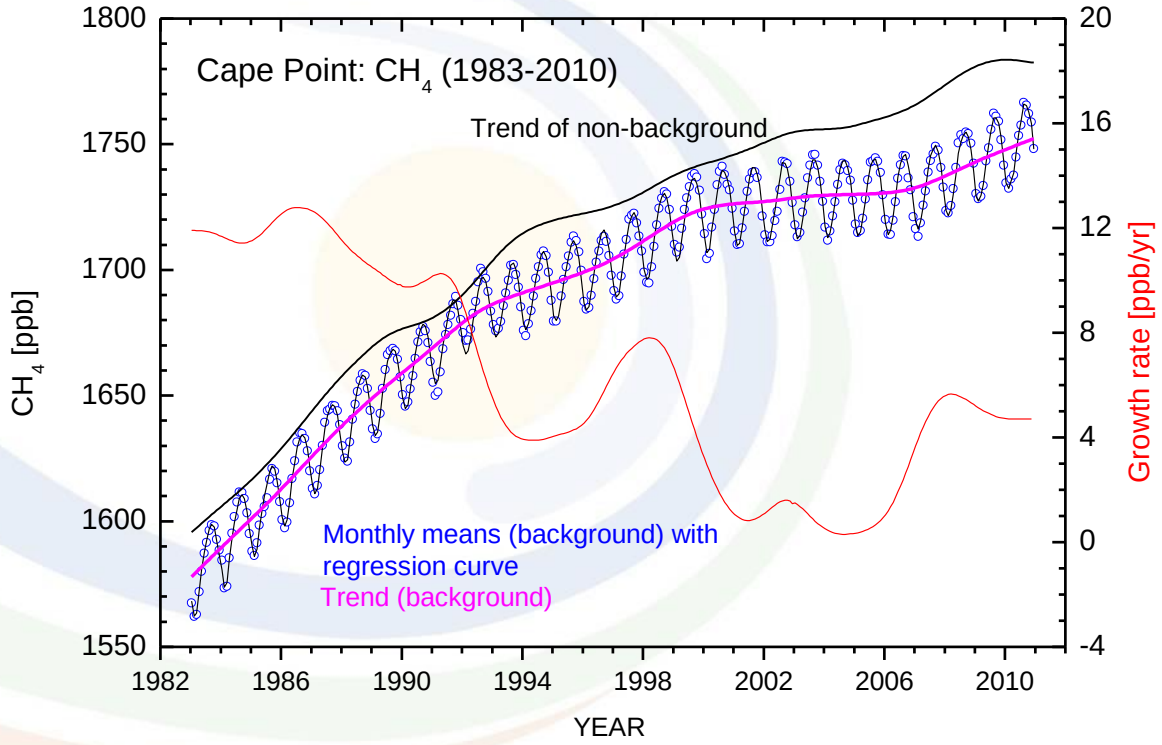
CO_2 and CH_4 growth rates under background conditions







- Trace gas growth rates in BG air (2010):

  CO_2: 1.9 ppm yr^{-1}

  CH_4: 4.1 ppb yr^{-1}

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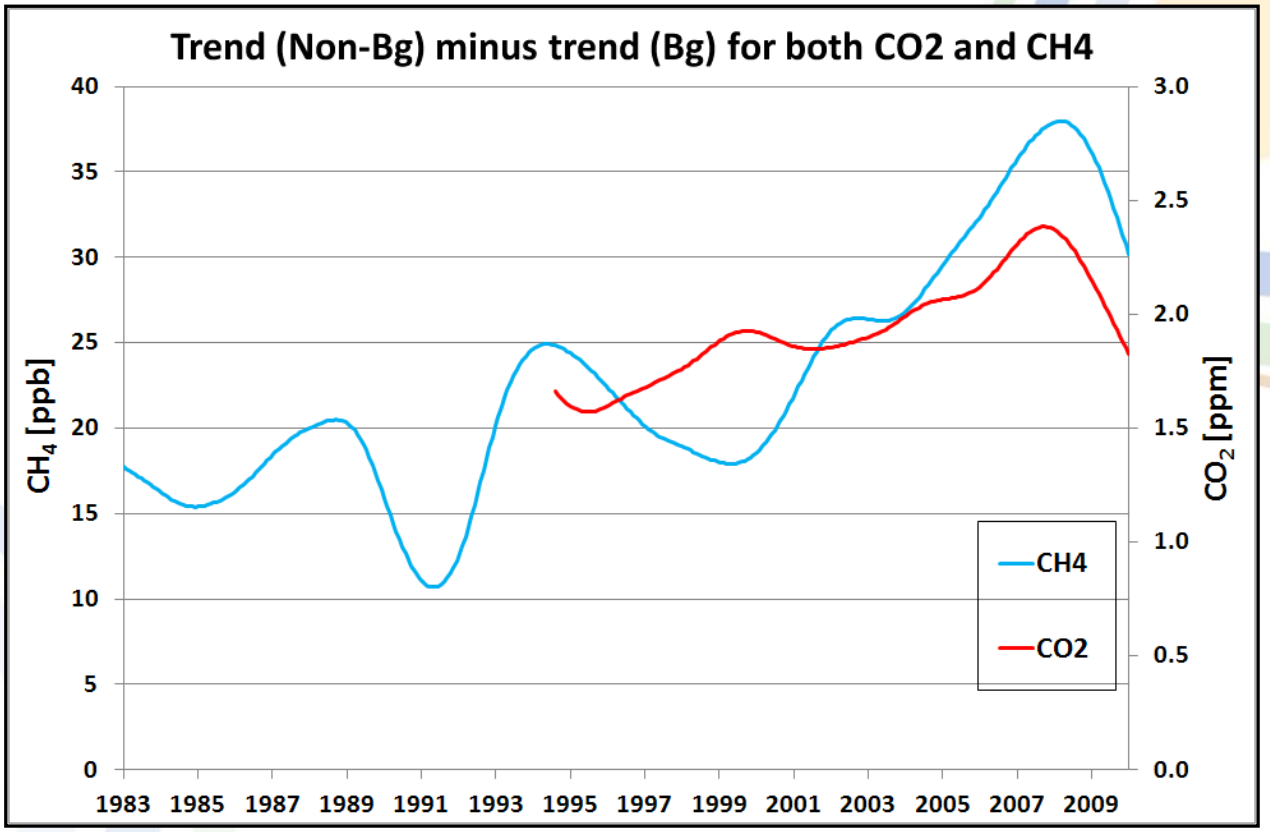
CO_2 and CH_4 growth rates in non-background air (Bg trend removed)

Suburban growth within the greater Cape Town metro-politan area over past years.



- Growth rates of the trend differences shown above (calculated from linear regression):

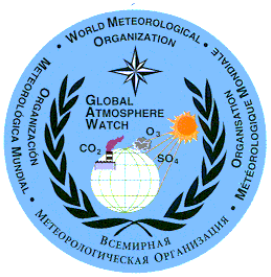
  CH_4: 0.72 ppb yr^{-1}
  CO_2: 0.04 ppm yr^{-1}

  Both rates are statistically significant
- Reason for trend decline since 2008 not known

Summary

1. Picarro CO_2 in good agreement with NDIR; CO requires fine-tuning
2. New and old ^{222}Rn analysers provide compatible results
3. N_2O data acceptable after reverting to basic analytical conditions
4. ICP: Challenges remain. Await comparisons with Picarro
5. Non-bg CO_2 and CH_4 trends related to increasing urbanization

Acknowledgements



NOAA ESRL
Global Monitoring Division

UEA University of East Anglia

LSCE
Laboratoire des Sciences du Climat & de l'Environnement

ansto

Royal Holloway University of London

CSIR ENVIRONMENTEK

Local authorities:
South African National Parks (SANP)
Portnet

KIT Karlsruhe Institute of Technology

South African Weather Service

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