Quantifying fossil fuel CO_2 from continuous measurements of APO: a novel approach

Penelope A. Pickers[1], Andrew C. Manning[1], Corinne Le Quéré[2], Christoph Gerbig[3], Christian Rödenbeck[3], Angelina Wenger[4], Grant L. Forster[1,5], Phil A. Wilson[1], S. Thomas Barningham[1], Sander Van der Laan[1], Simon O'Doherty[4], David E. Oram[1,5] and William T. Sturges[1]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK.

[2] Tyndall Centre for Climate Change Research, School of Environmental Sciences, University of East Anglia, Norwich, UK.

[3] Max Planck Institute for Biogeochemistry, Jena, Germany.

[4] School of Chemistry, University of Bristol, Bristol, UK.

[5] National Centre for Atmospheric Science (NCAS), Natural Environment Research Council, UK.

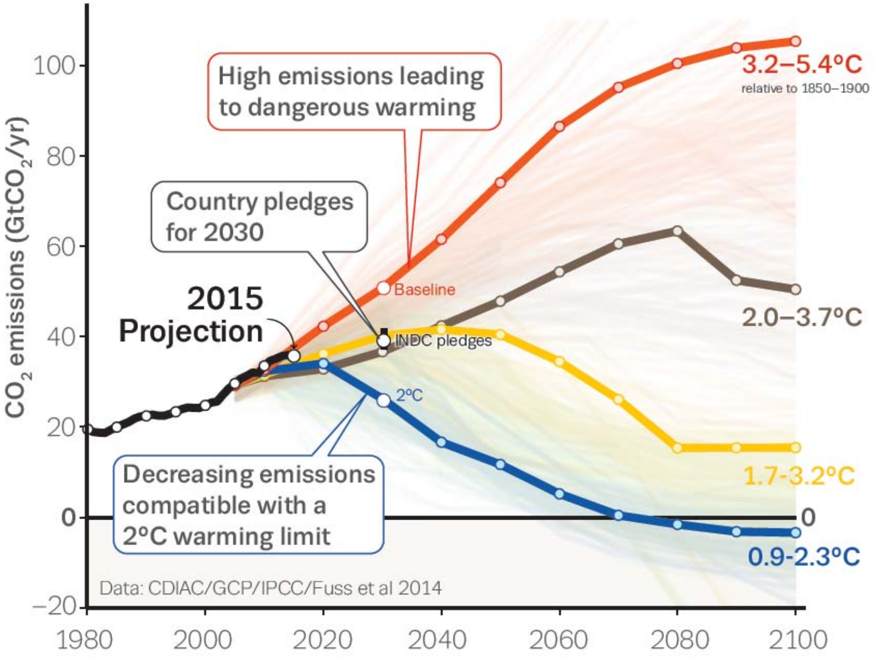
The world is going on a CO_2 diet…

- Nisbet and Weiss (2010): reducing fossil fuel emissions using ‘bottom-up’ inventory reporting is analogous to **“dieting without weighing oneself”**.

- **‘Bottom-up’** methods can be out-dated and inaccurate, with unknown uncertainty estimates.

- **‘Top-down’** methods can provide alternative option.

- For **CO_2**, however, this is complicated because **large natural fluxes** make it difficult to isolate anthropogenic emissions.

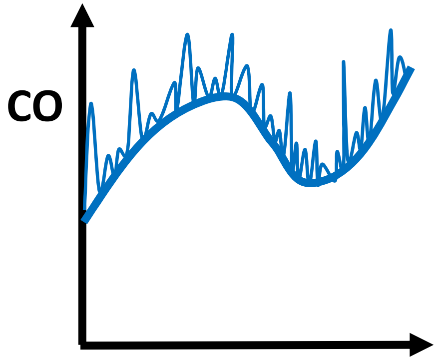


Data: CDIAC/GCP/IPCC/Fuss et al 2014

© Global Carbon Project, 2015

The CO and $^{14}CO_2$ method

$$\boldsymbol{ffCO_2(CO) = \frac{CO_{measured} - CO_{background}}{R_{CO}}}$$



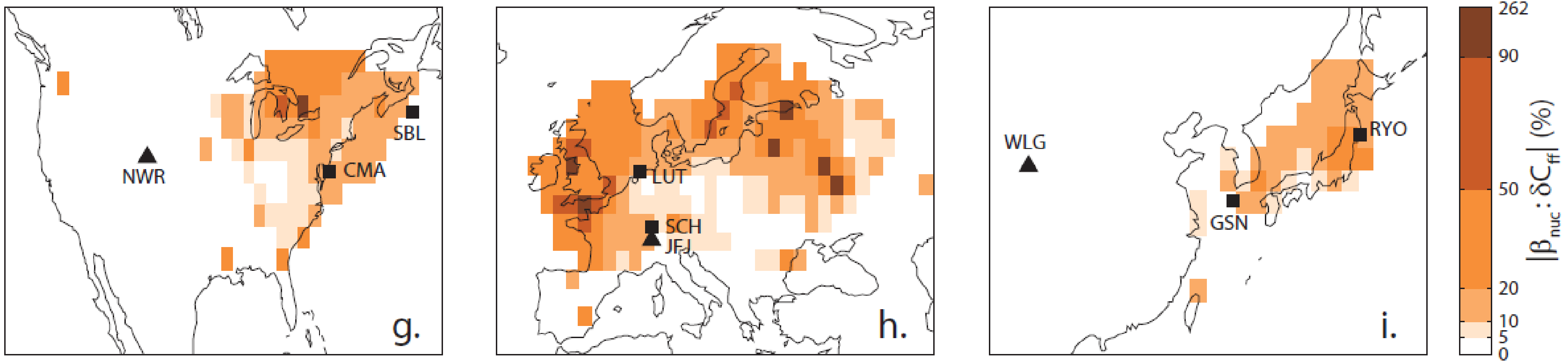
where R_{CO} is the $CO:CO_2$ ratio for fossil fuel combustion.

R_{CO} depends on **fuel type**:

	Typical range	**Maximum range**
R_{CO}	5 to 25 ppb ppm^{-1}	<2 to >100 ppb ppm^{-1}

- R_{CO} is **variable** and **not well known.**
- $ffCO_2(CO)$ is 'calibrated' using $^{14}CO_2$ data – this helps, but there are still issues:
  - E.g. CO has **natural sources and sinks** (especially in the summer).

The $^{14}CO_2$ nuclear power plant bias


Absolute ratio of nuclear bias to fossil fuel-derived CO_2

Graven and Gruber, ACP (2011)

- $^{14}CO_2$ measurements are severely affected by some types of **nuclear power plant emissions**.
  - particularly a problem in Eastern US/Canada, Western Europe and Japan.

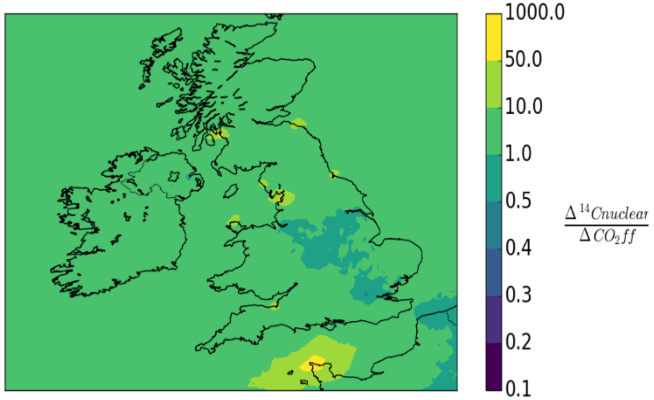


Figure from Angelina Wenger (University of Bristol)

Using Atmospheric Potential Oxygen (APO)

$$\mathbf{APO = O_2 - 1.1 \times CO_2}$$

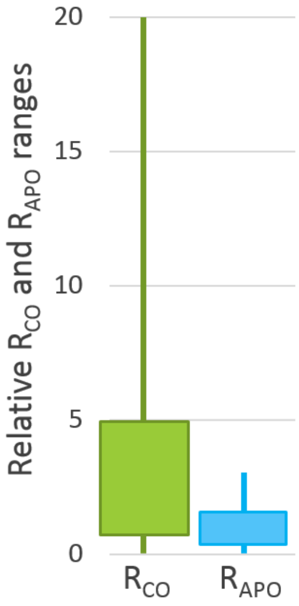
- APO is a tracer **invariant to terrestrial biosphere O_2 and CO_2 exchange**.

$$ffCO_2(APO) = \frac{APO_{measured} - APO_{background}}{R_{APO}}$$

where R_{APO} is the APO:CO_2 ratio for fossil fuel combustion.

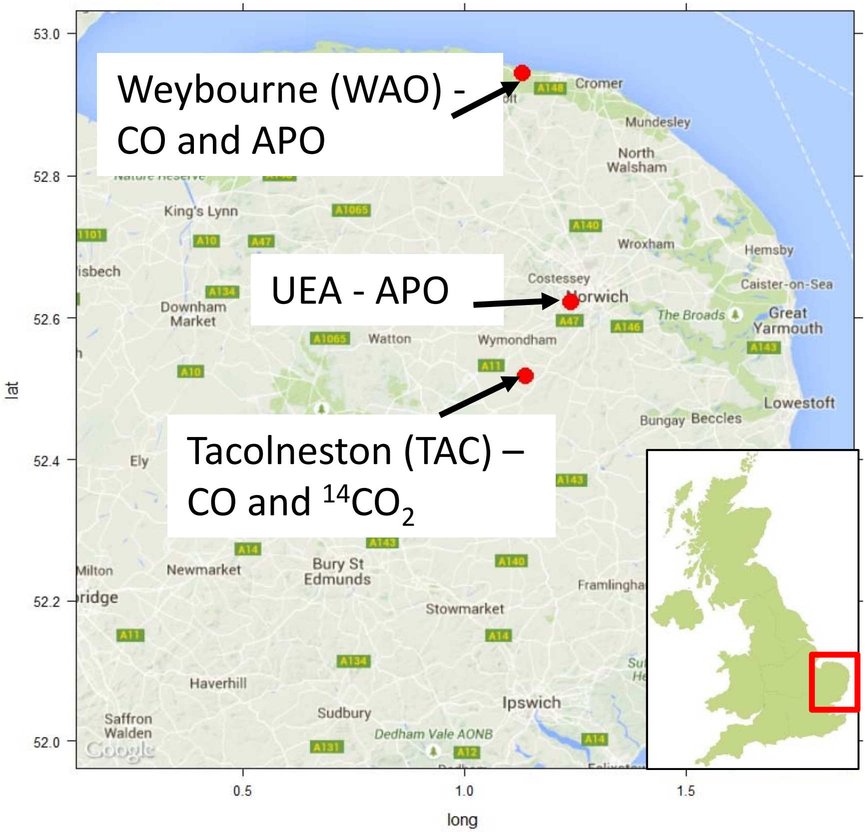
- **Main advantage over CO and $^{14}CO_2$ method**:
  - R_{APO} has a **much smaller range** than R_{CO}
  - likely to be more **precise** (and possibly more **accurate**).

	Typical range	Maximum range
R_{CO}	5 to 25 ppb ppm^{-1}	<2 to >100 ppb ppm^{-1}
R_{APO}	**0.2 to 0.5 mol mol^{-1}**	**0.1 to 0.9 mol mol^{-1}**



Example: using data from Norfolk, UK (summer 2014)

- Baselines determined using **‘Rfbaseline’ function** in R (Ruckstuhl et al. 2012).
  - Fossil fuel emission ratios:
    - **EDGAR** (**E**missions **D**atabase for **G**lobal **A**tmospheric **R**esearch – for European emissions) for R_{CO} (for 2010).
    - **COFFEE** (**CO**$_2$ release and **O**xygen uptake from **F**ossil **F**uel **E**missions **E**stimate) for R_{APO} (updated to 2014).
  - Calculated time varying R_{APO} and R_{CO} from UK Met Office **NAME** (Numerical Atmospheric Dispersion Modelling Environment) footprints.



Weybourne (WAO) - CO and APO

UEA - APO

Tacolneston (TAC) – CO and $^{14}CO_2$

ffCO_2 from $^{14}CO_2$ provided by Angelina Wenger (University of Bristol)

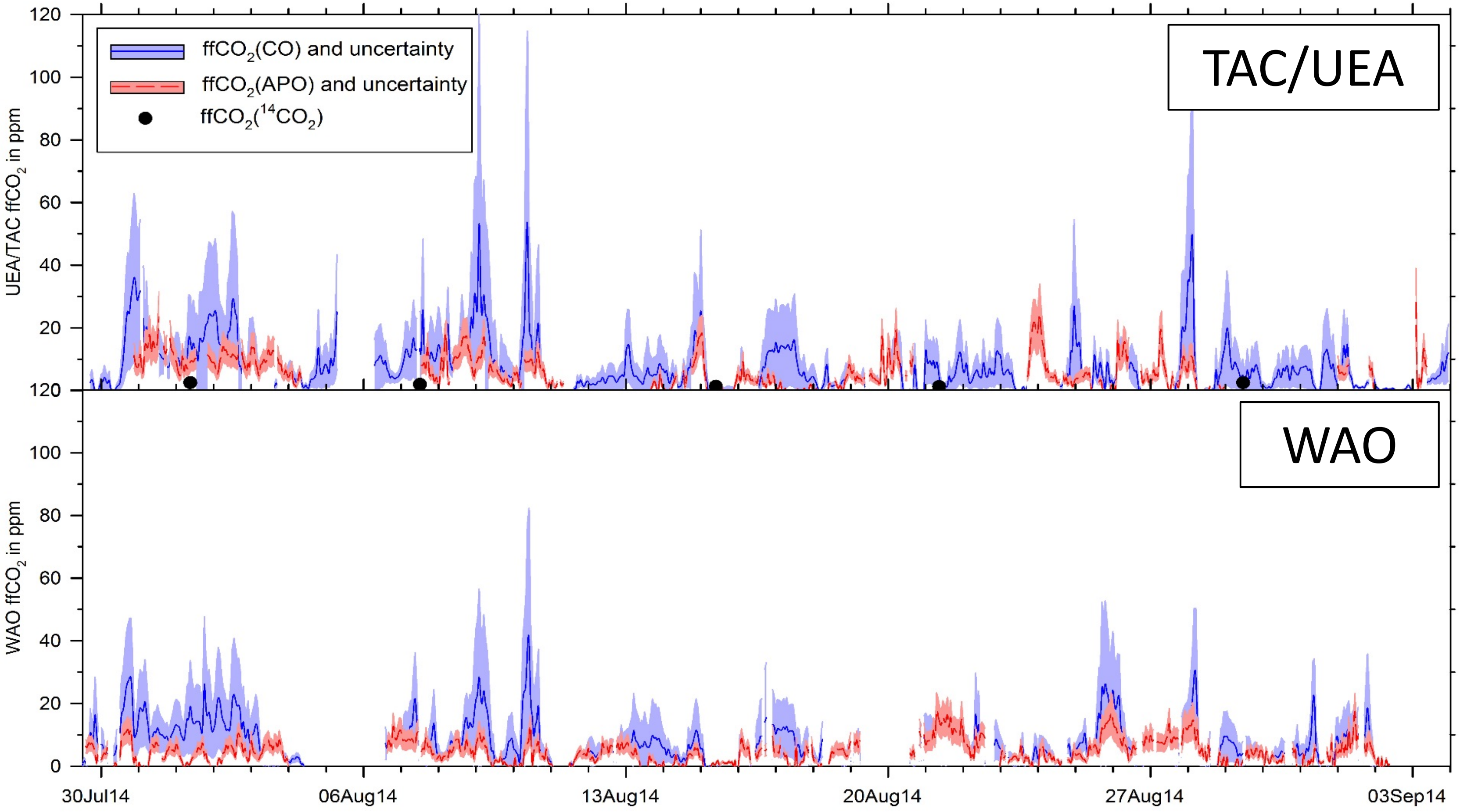
Results: uncertainty analysis

- $ffCO_2$(APO) and $ffCO_2$(CO) **uncertainties** determined by combining measurement, baseline and emission ratio uncertainties:

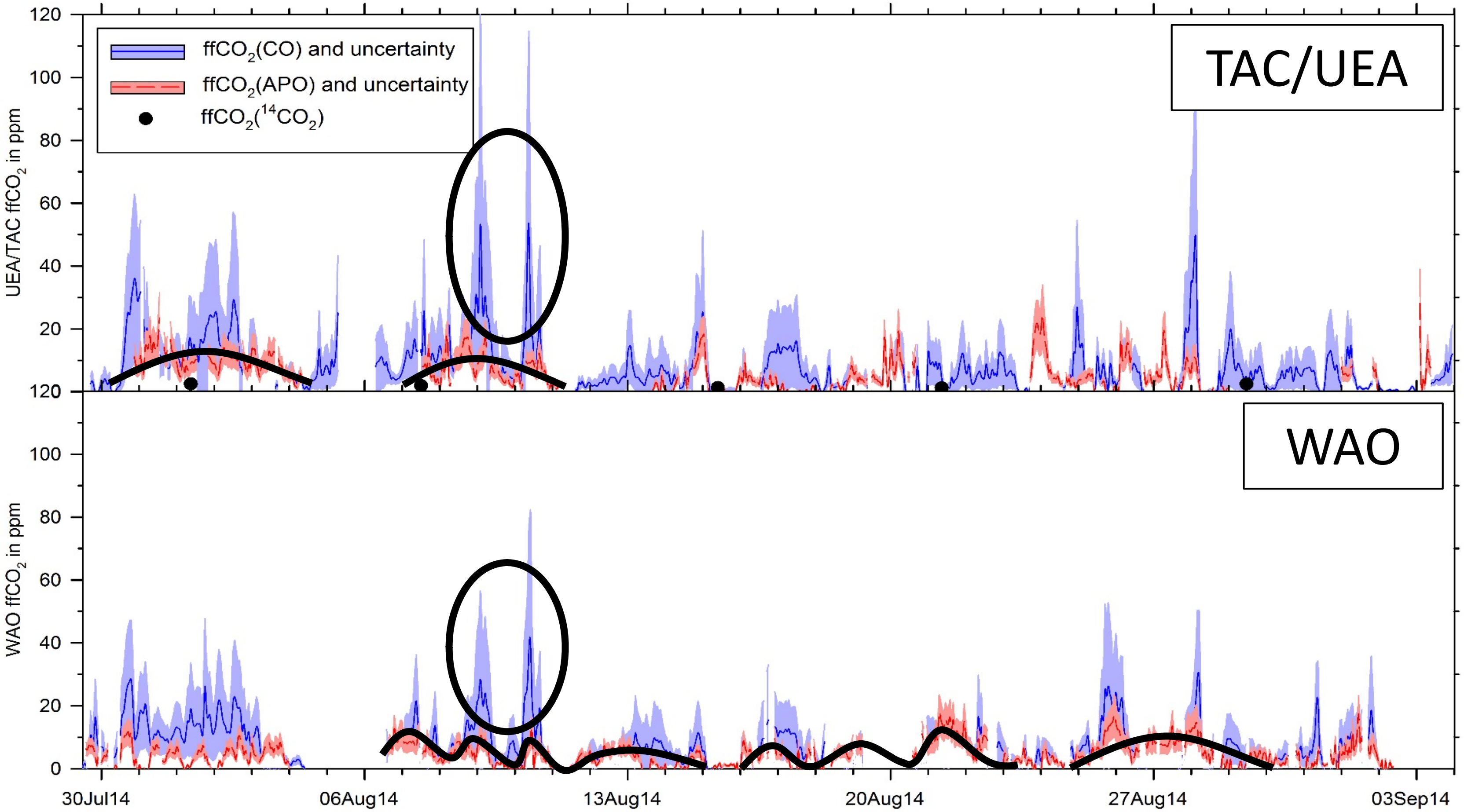
	$ffCO_2$(CO)	$ffCO_2$(APO)
Baseline uncertainty	± 18 %	± 28 %
Measurement uncertainty	± 1.3 %	± 4.1 %
Emission ratio uncertainty	± 73 %	± 22 %
Total uncertainty	**± 78%**	**± 36 %**

- APO method is significantly **more precise** than CO method.

Results: $ffCO_2$ in Norfolk



Results: $ffCO_2$ in Norfolk



Accuracy: sensitivity to different emission ratio sources

- Investigated using 4 different R_{APO} and R_{CO} sources:
  - **Time varying** ratios (as before, using EDGAR, COFFEE and NAME).
  - **Fixed** ratios (0.3 mol mol^{-1} for R_{APO} and 5 ppb ppm^{-1} for R_{CO}).
  - **$^{14}CO_2$** calibrated ratios.
  - **Measured** ratios.

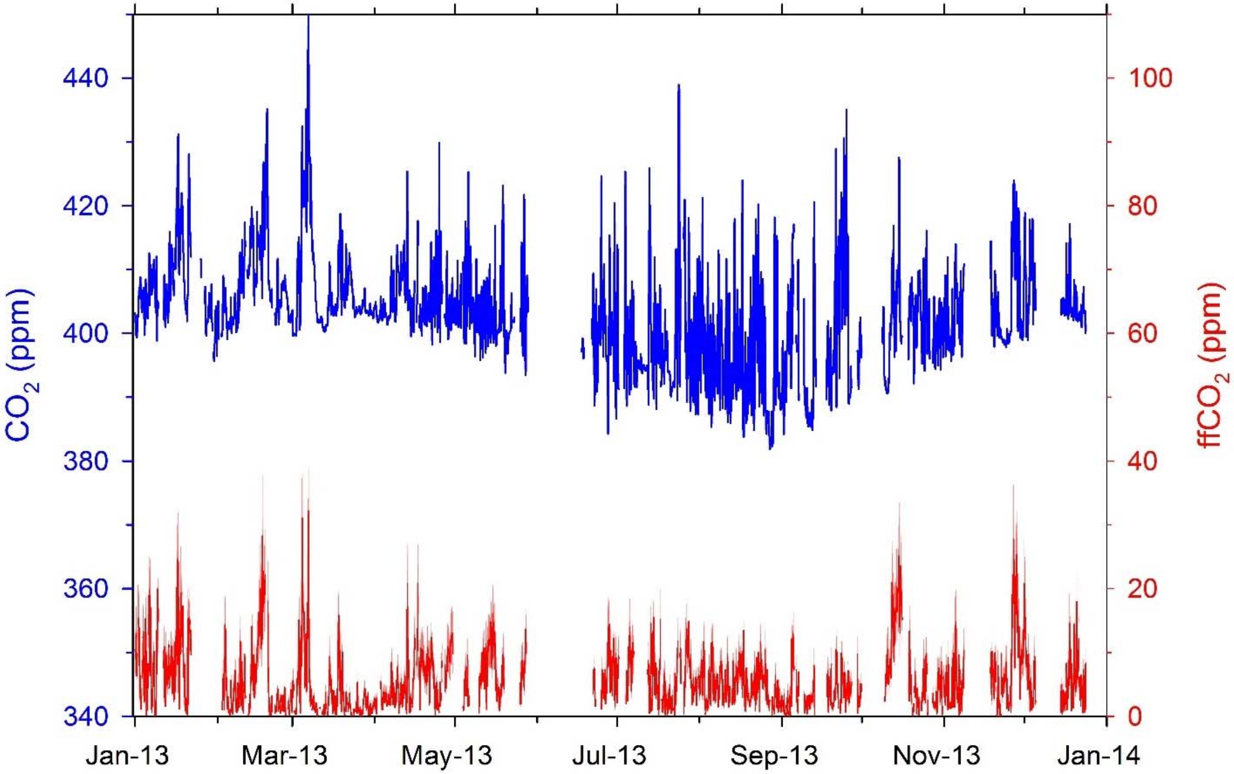
- Results: **Much smaller $ffCO_2$ range** for APO method.

CO $ffCO_2$ range	APO $ffCO_2$ range
1 to >100 ppm!	1 to 20 ppm

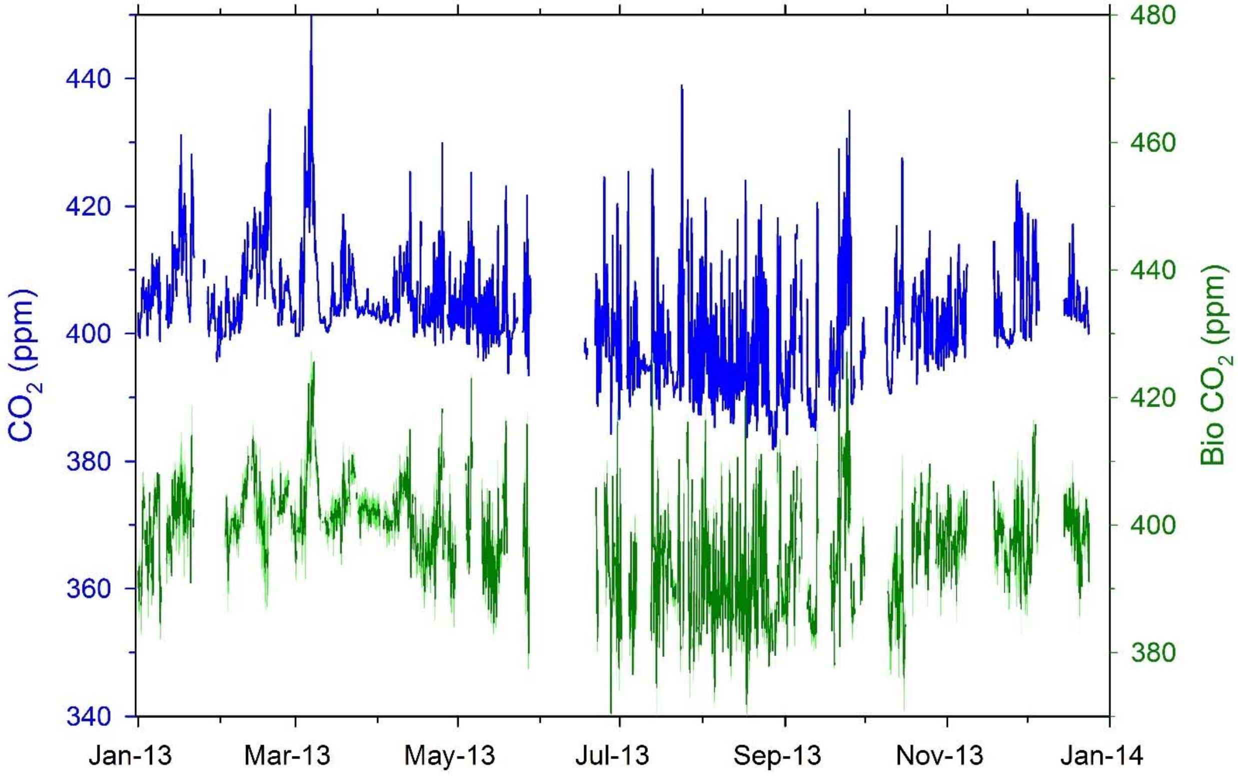
- $ffCO_2$ from $^{14}CO_2$ **still underestimated**, even though corrected for nuclear influences.
  - Had to use unrealistically high R_{CO} and R_{APO} values.

Publication	Location	Species used	Typical $ffCO_2$ range	$ffCO_2$ uncertainty
van der Laan et al. (2010)	Lutjewad, The Netherlands	$^{14}CO_2$ and CO	0 – 30 ppm	± 2.5 ppm
Lopez et al. (2013)	Paris, France	$^{14}CO_2$, CO, NOx and $^{13}CO_2$	0 – 40 ppm	Not given for most species. ± 1.0 ppm for $^{14}CO_2$
Graven et al. (2009)	California, U.S.A.	$^{14}CO_2$ and CO	0 – 10 ppm	± 1.6 – 2.9 ppm
Turnbull et al. (2006)	New England and Colorado, U.S.A.	$^{14}CO_2$, CO and SF_6	0 – 15 ppm	± 2 – 4 ppm
This work	**Norfolk, U.K.**	**CO (TAC)** **CO (WAO)** **APO (UEA)** **APO (WAO)** **$^{14}CO_2$ (TAC)**	**0 – 70 ppm** **0 – 40 ppm** **0 – 20 ppm** **0 – 15 ppm** **1.2 – 2.5 ppm**	**± 5.8 ppm** **± 4.5 ppm** **± 1.2 ppm** **± 1.1 ppm** **± 1.6 ppm**

Quantifying $ffCO_2$ throughout the year at WAO



Quantifying $ffCO_2$ throughout the year at WAO

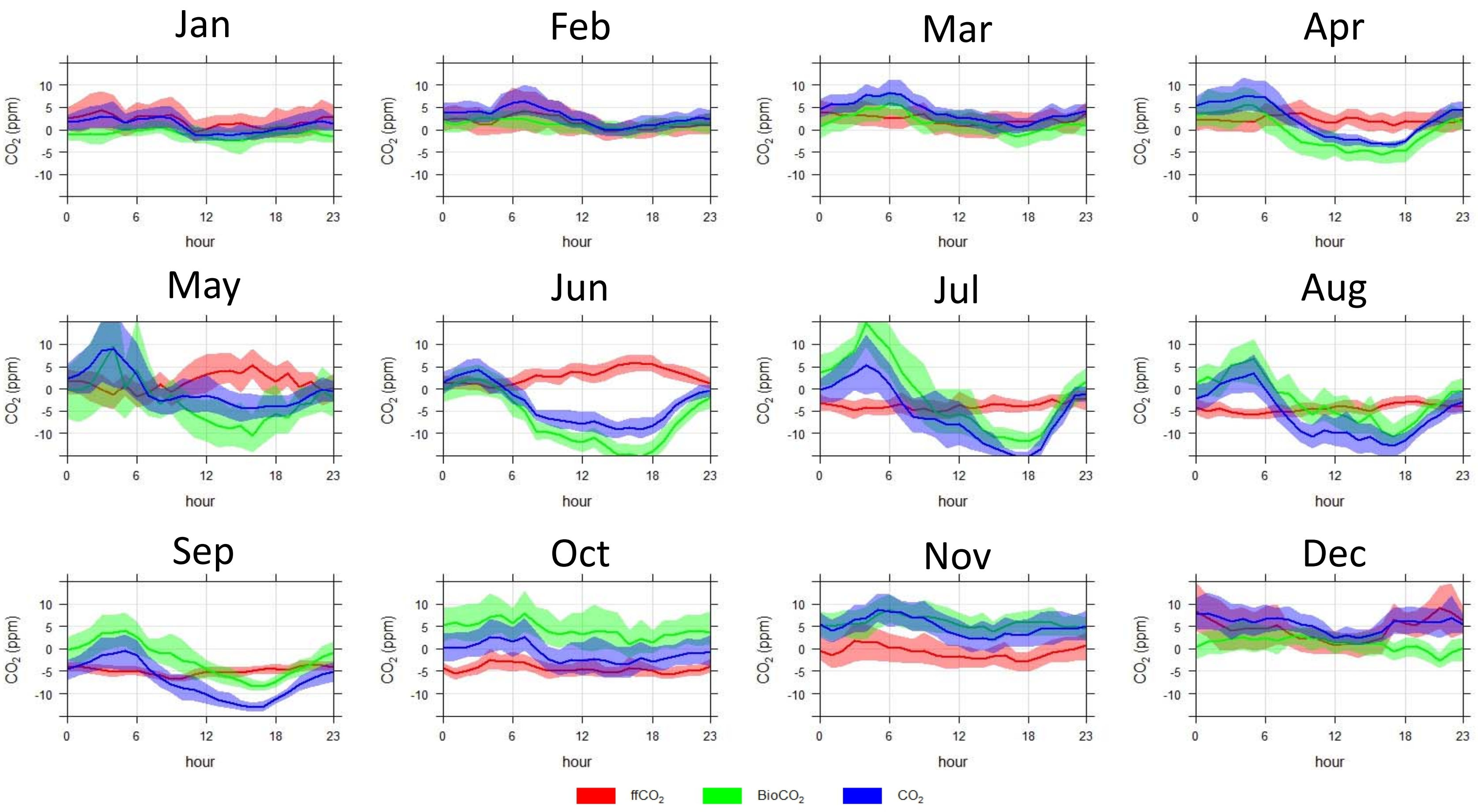


$ffCO_2$ and Bio CO_2 covariance correlation coefficient = -0.23

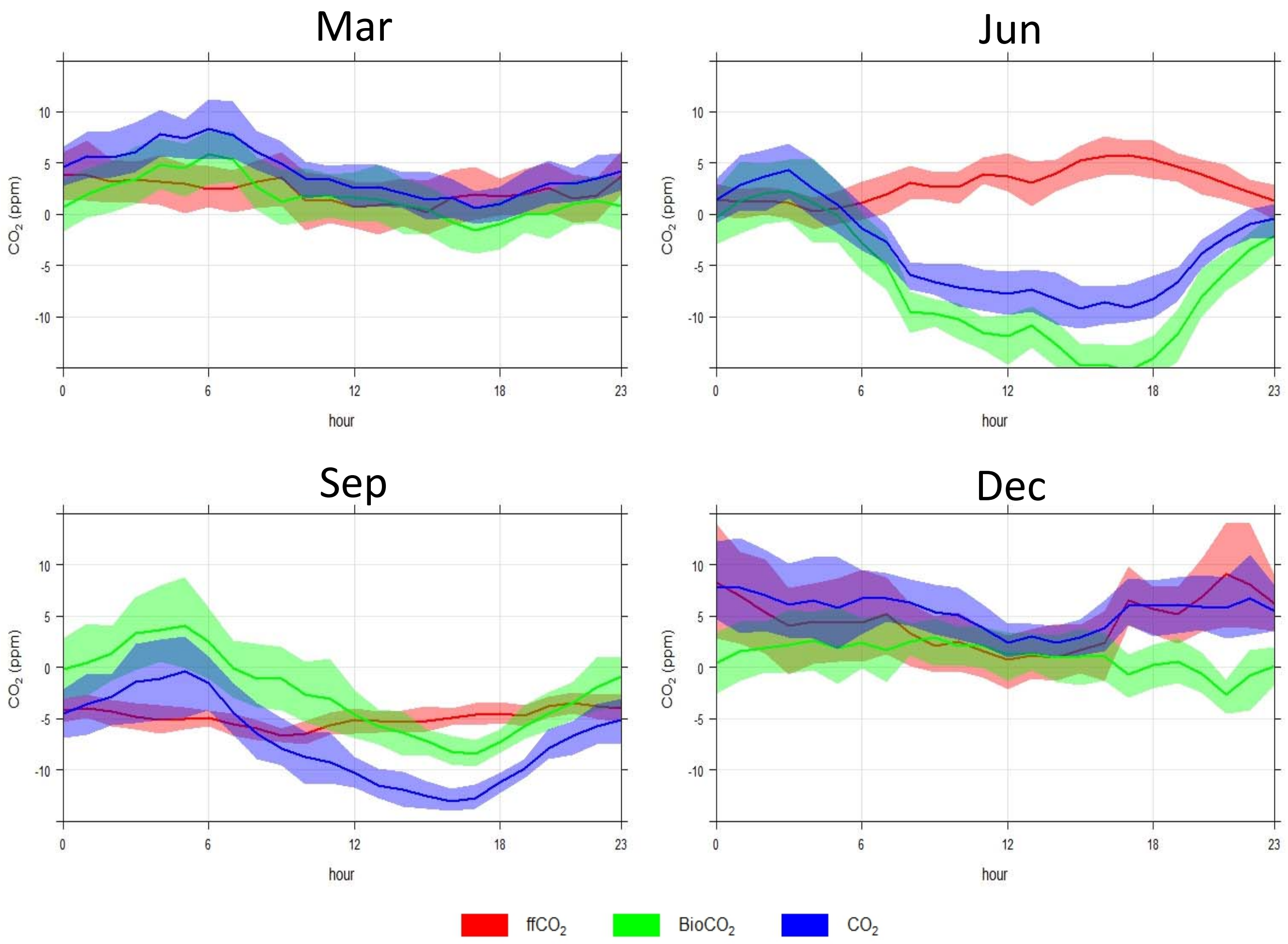
Quantifying ffCO_2 throughout the year at WAO

Monthly mean total CO_2, Bio CO_2 and ffCO_2 at WAO

Diurnal variability in $ffCO_2$ and bio CO_2 at WAO in 2012

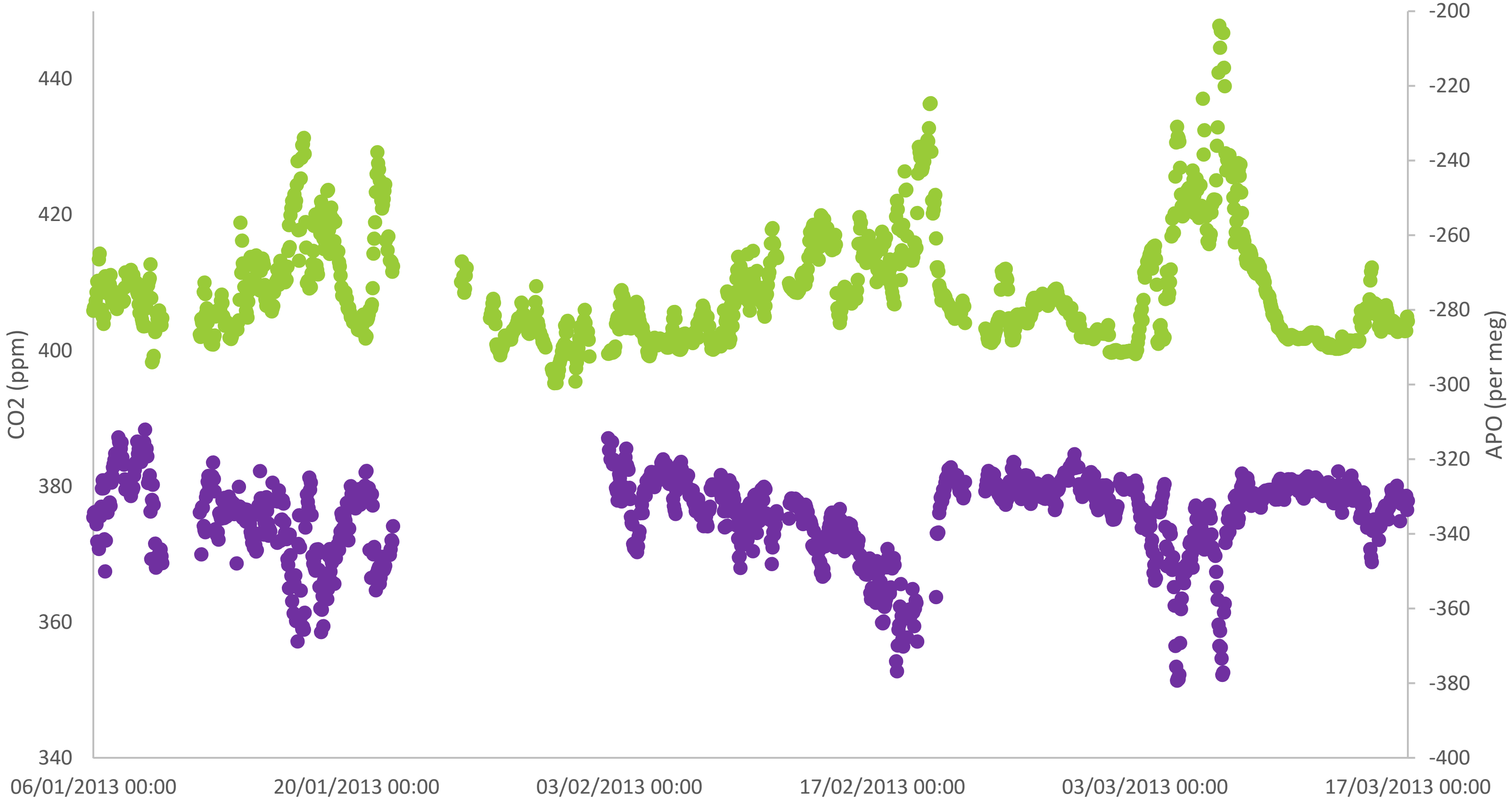


Diurnal variability in ffCO$_2$ and bio CO$_2$ at WAO in 2012

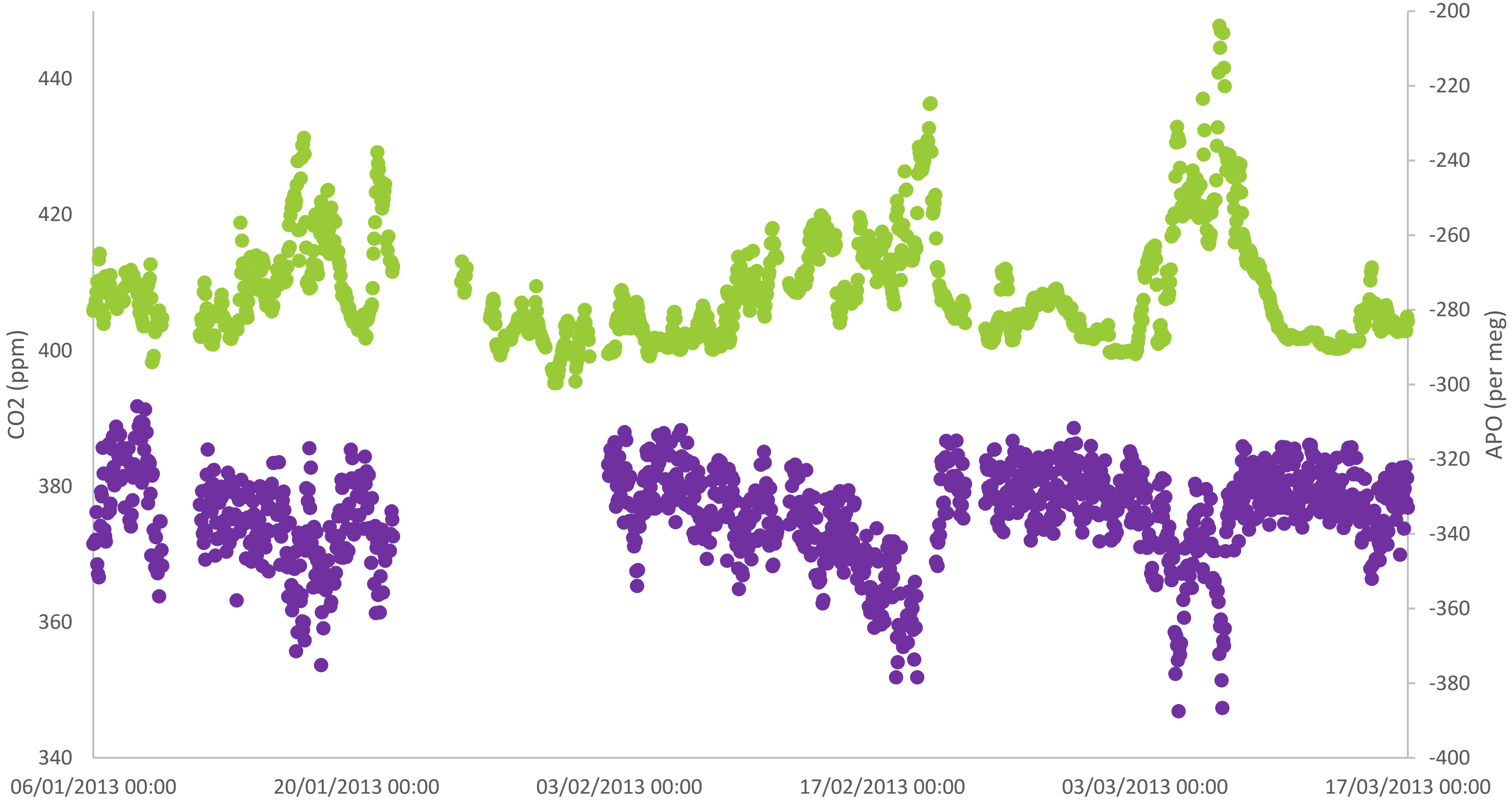


- Growing season start and end 2012: ~06 April and 22 October
- Growing season start and end 2013: ~07 April and 02 November
- UK autumn temperatures in 2012 were ~1°C below 1981-2010 average

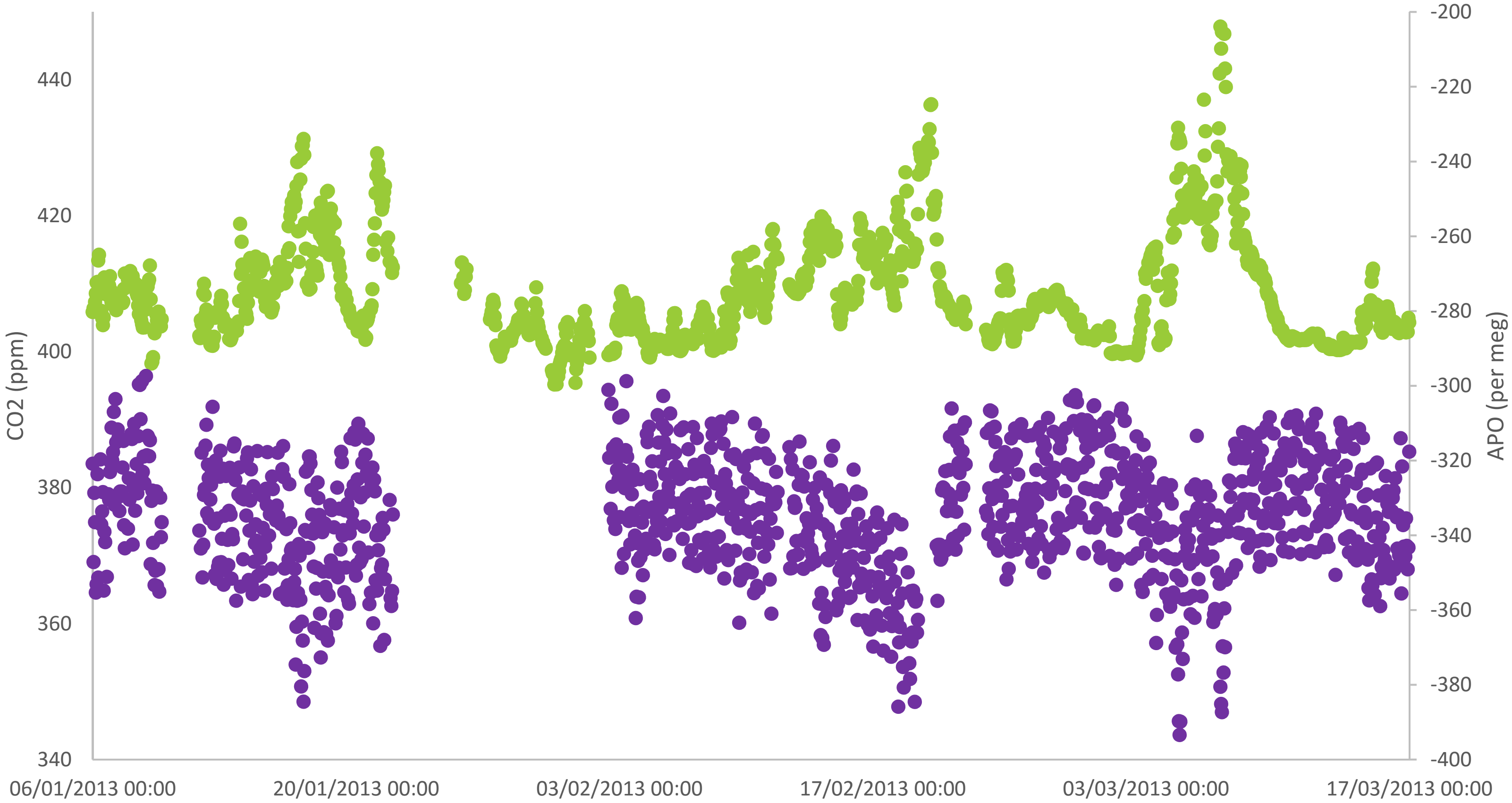
Limitation: O_2 precision



Limitation: O_2 precision

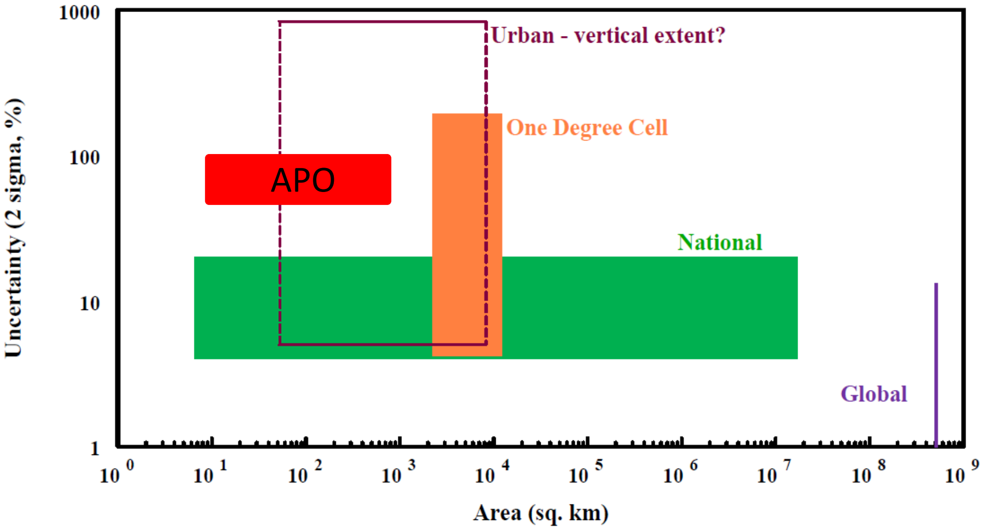


Limitation: O_2 precision



Conclusions and future outlook

- APO is a currently **under-exploited tool** for atmospheric verification of CO_2 emissions.
- We are able to use APO to separate biosphere and fossil fuel CO_2 signals **throughout the year** at WAO, UK, despite the station's rural location.
- **Next steps**:
  - Forward-modelling of inventory emissions
  - Urban APO measurements
- APO top-down method uncertainty potentially **compares favourably** with bottom-up inventory uncertainty.



Andres et al. ACPD 2016