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

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Met Office

NERC SCIENCE OF THE ENVIRONMENT

InGOS Integrated non-CO_2 Greenhouse gas Observing System

DEPARTMENT OF ENERGY & CLIMATE CHANGE

UEA University of East Anglia School of Environmental Sciences *Carbon Related Atmospheric Measurement Lab*

University of BRISTOL

National Centre for Atmospheric Science NATURAL ENVIRONMENT RESEARCH COUNCIL

Outline

Introduction

Motivation – why use APO as well/instead of CO?

How? –fossil fuel CO_2 ($ffCO_2$) quantification method

Results – from Weybourne, UEA/Tacolneston

Conclusions/Next steps…

Introduction

Separating land biosphere and fossil fuel derived atmospheric CO_2 contributions will facilitate **more accurate emissions verification and CO_2 inversions.**

Current 'top-down' $ffCO_2$ approach:

- High frequency CO measurements combined with low frequency $\Delta^{14}C$ measurements to determine the $ffCO_2$ component of atmospheric CO_2 time series (e.g. van der Laan et al. 2010, Graven et al. 2009, Turnbull et al. 2006)
- But applying $\Delta^{14}C$ method in the UK is problematic, owing to the influence from nuclear power stations.

Motivation for using APO vs. CO measurements

CO as tracer for $ffCO_2$:

- Dependent on $CO:CO_2$ fossil fuel emission ratios.
  - highly variable spatially and temporally; not well known.
- Biased by photochemical processes in summer and cannot differentiate fossil fuel from biomass burning/biofuel use.
  - do not affect APO method.

APO as a tracer for $ffCO_2$:

- $APO:CO_2$ fossil fuel emission ratios less variable than $CO:CO_2$ ff emission ratios.
- Invariant to biomass burning and biofuels.
  - Biofuel use predicted to become more widespread in the future.
- Also affected by ocean-atmosphere exchange.
  - Oceanic influence is relatively easy to identify and thus can be removed.

Using APO **and** CO as tracers for $ffCO_2$:

- Might provide more accurate quantification of $ffCO_2$.
- Might mitigate biases associated with any one particular species.

Previous fossil fuel quantification studies

Reference	Location	Species used	$ffCO_2$ range	$ffCO_2$ uncertainty
van der Laan et al. 2010	Lutjewad/The Netherlands	$\Delta^{14}C$ and CO	0 – 30 ppm	± 2.5 ppm
Lopez et al. 2013	Paris/France	$\Delta^{14}C$, CO, NOx and $^{13}CO_2$	0 – 40 ppm	Not given for most species. ± 1 ppm for $\Delta^{14}C$
Graven et al. 2009	California/ USA	$\Delta^{14}C$ and CO	0 – 10 ppm	± 1.6 – 2.9 ppm
Turnbull et al. 2006	New England and Colorado/ USA	$\Delta^{14}C$, CO and SF_6	0 – 15 ppm	± 2 – 4 ppm

APO $ffCO_2$ quantification method

$$ffCO_2(APO) = \frac{APO_{meas} - APObg}{R_{APO}}$$

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

R_{APO} depends on **<u>fuel type</u>**:

- values range from 0.1 to 0.9.

- APO_{bg} determined using **<u>'Rfbaseline' function</u>** in R (Ruckstuhl et al. 2012):
  - Statistical method based on robust local regression.
  - applies asymmetrical weighting to residuals.

APO $ffCO_2$ quantification method

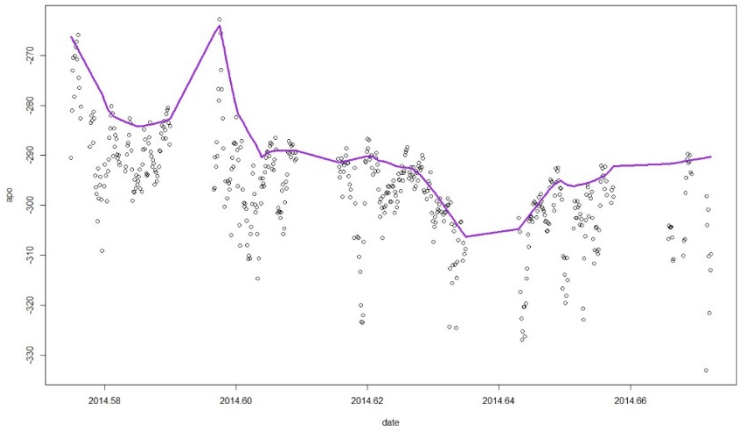
$$ffCO_2(CO) = \frac{CO_{meas} - CO_{bg}}{R_{CO}}$$

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

R_{CO} depends on **<u>fuel type</u>**:

- values typically range from 5 – 25 but can be much higher/lower

- APO_{bg} determined using **<u>'Rfbaseline' function</u>** in R (Ruckstuhl et al. 2012):
  - Statistical method based on robust local regression.
  - applies asymmetrical weighting to residuals.



R_{APO} and R_{CO} from inventories and NAME

COFFEE (**C**O_2 release and **O**xygen uptake from **F**ossil **F**uel **E**missions **E**stimate) dataset used to calculate APO:CO_2 fossil fuel emissions ratios:

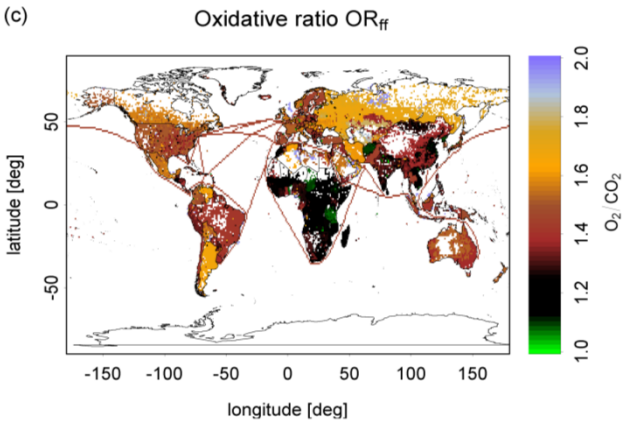
- gridded global O_2:CO_2 ratios (available for 2008, but update is in progress).

Made gridded CO:CO_2 ff ratios from **EDGAR** (**E**missions **D**atabase for **G**lobal **A**tmospheric **R**esearch – for European emissions)

Combine **COFFEE** derived gridded APO:CO_2 ff ratios and EDGAR derived CO:CO_2 ff ratios with UK Met Office **NAME** (Numerical Atmospheric Dispersion Modelling Environment) footprints to determine temporally varying R_{APO} and R_{CO}.

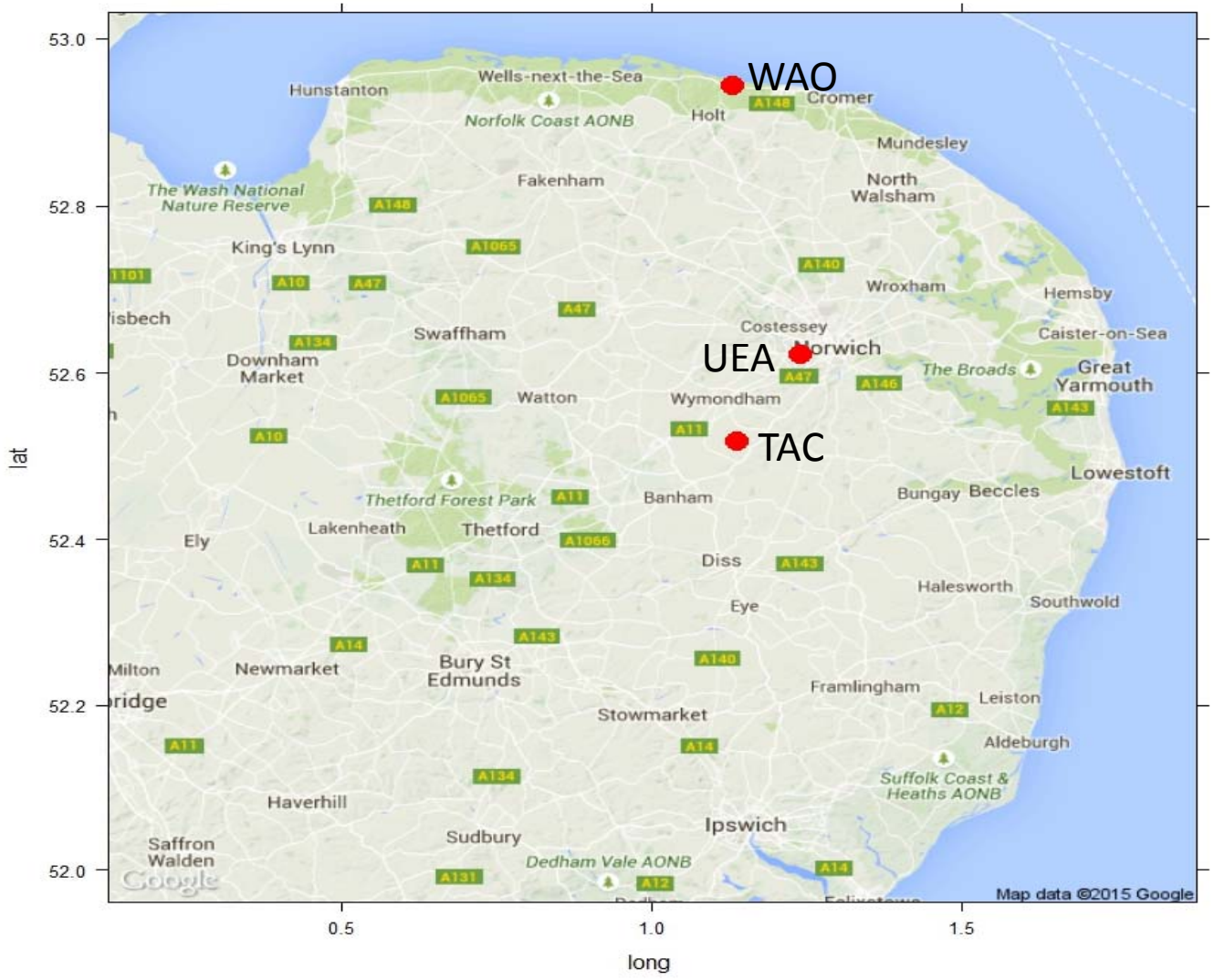
Extras:

- **Reduce oceanic influence** on ffCO_2(APO):
  - filtering out periods that contain APO variation with no corresponding CO_2 variation.
- **Check for atmospheric boundary layer diurnal variability influence** on both APO and CO data.



From Steinbach et al. 2011

Data: Weybourne Observatory (WAO), Tacolneston tall tower (TAC) and UEA – **August 2014**



Advantages and disadvantages: WAO vs ENV/TAC

UEA/TAC:

- **Advantage**: less ocean influence on APO.
- **Disadvantage**: O_2, CO_2 and CO measurements are not co-located.

WAO:

- **Advantage**: co-located O_2, CO_2 and CO measurements.
- **Disadvantage**: more potential for ocean influence on APO.

$ffCO_2$ from $\Delta^{14}C$ data provided by Angelina Wenger (Bristol):

- ~ weekly flask measurements from Tacolneston
- ~40% of data are affected by nuclear power plant influences.

Quantifying uncertainties: measurement uncertainty

CO_2 hourly measurement uncertainty (u_{CO2}):

- ± 0.47 ppm for UEA and ± 1.01 ppm for WAO.

O_2 hourly measurement uncertainty (u_{O2}):

- ± 3.48 per meg for UEA and ± 6.80 per meg for WAO.

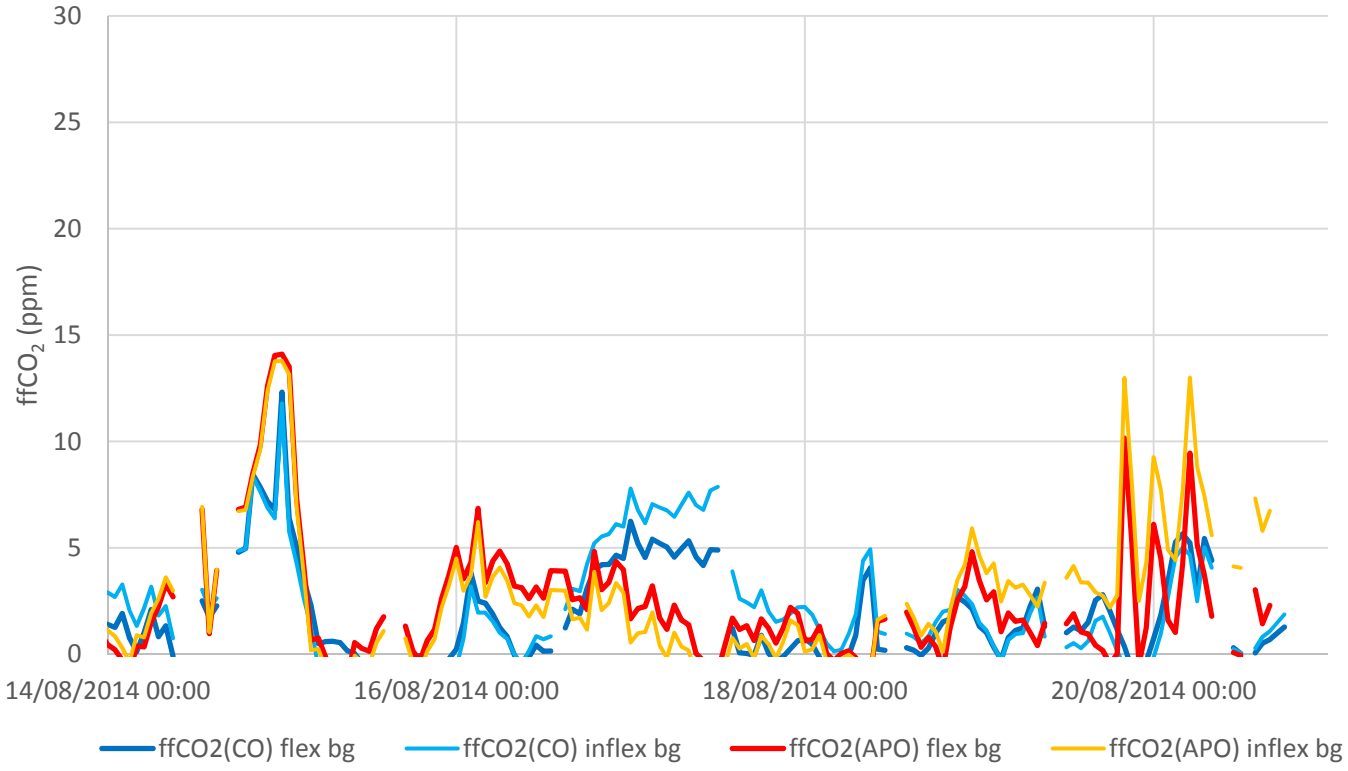
CO hourly measurement uncertainty (u_{CO}):

- **± 5.54 ppb for TAC and ± 1.58 ppb for WAO.**

APO uncertainty (u_{APO}), calculated by quadrature sum of uncertainties:

- $APO \pm u_{APO} = O_2 \pm u_{O2} - (1.1 \pm u_{\alpha B} / 0.2095)(350 - CO_2 \pm u_{CO2})$
- Where $u_{\alpha B}$ represents the uncertainty associated with the assumed ratio of O_2:CO_2 biosphere exchange (I used $u_{\alpha B} = \pm 0.05$).
- **Gives mean value of ± 13.8 per meg for UEA and ± 12.35 per meg for WAO.**

Quantifying uncertainties: baseline uncertainty



Data are from ENV/TAC. Assume **20% error in CO_{bg}** and **APO_{bg}**

Quantifying uncertainties: ff emission ratio uncertainty

Calculated by dividing the emission ratio for each time stamp by the 1σ standard deviation of all the ratios in the footprint.

CO:CO_2 ff uncertainty (u_{RCO}):

- ~75 %

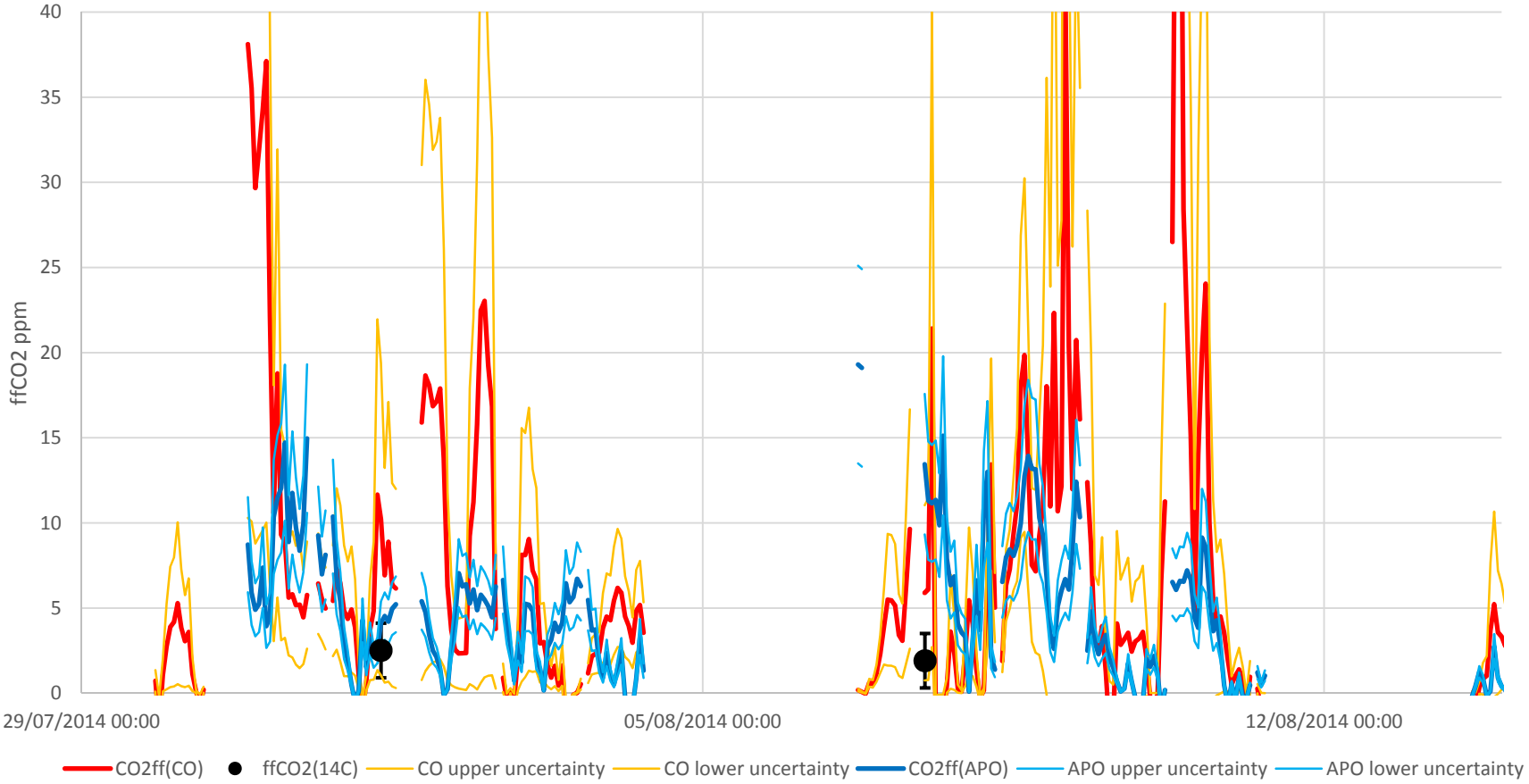
APO:CO_2 ff uncertainty (u_{RAPO}):

- ~21 %

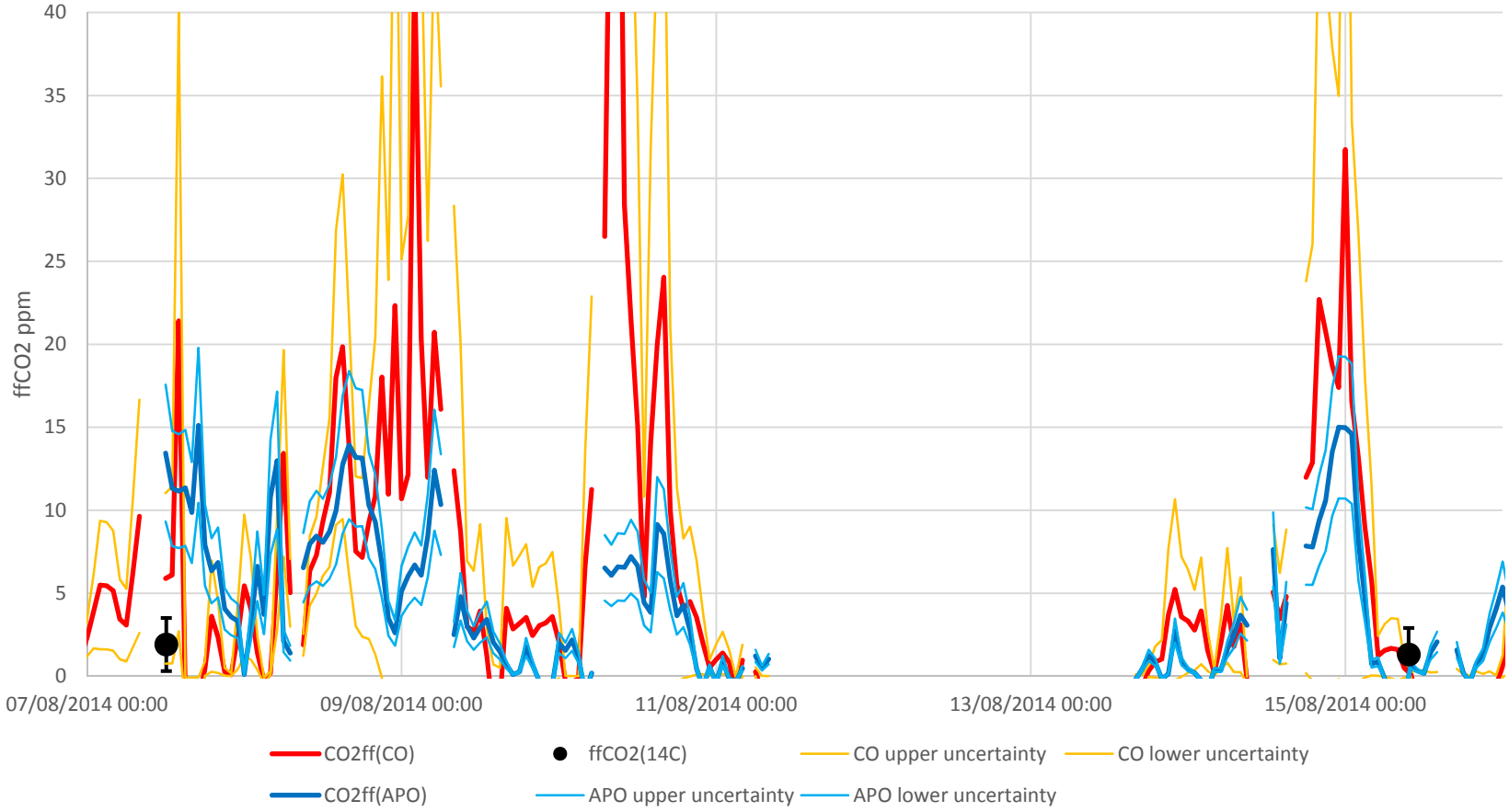
APO:CO_2 emission ratio uncertainty is much less than CO:CO_2 emission ratio uncertainty.

$$\boldsymbol{ffCO_2(APO) \pm u_{ff(APO)} = \frac{(APOm_{eas} \pm uAP_O) - (APObg \pm ubg)}{R_{APO} \pm u_{RAPO}}}$$

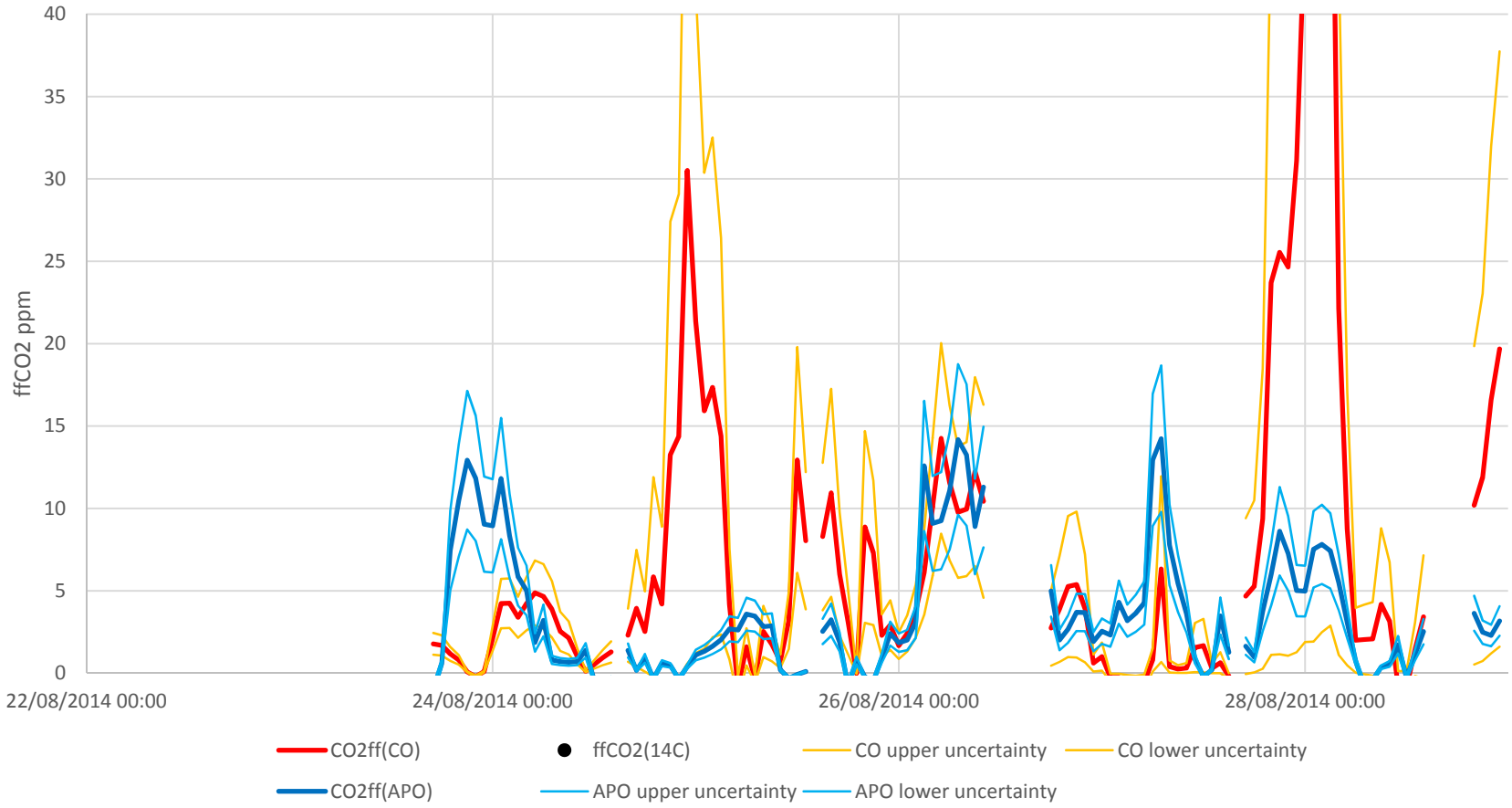
Results: UEA/TAC



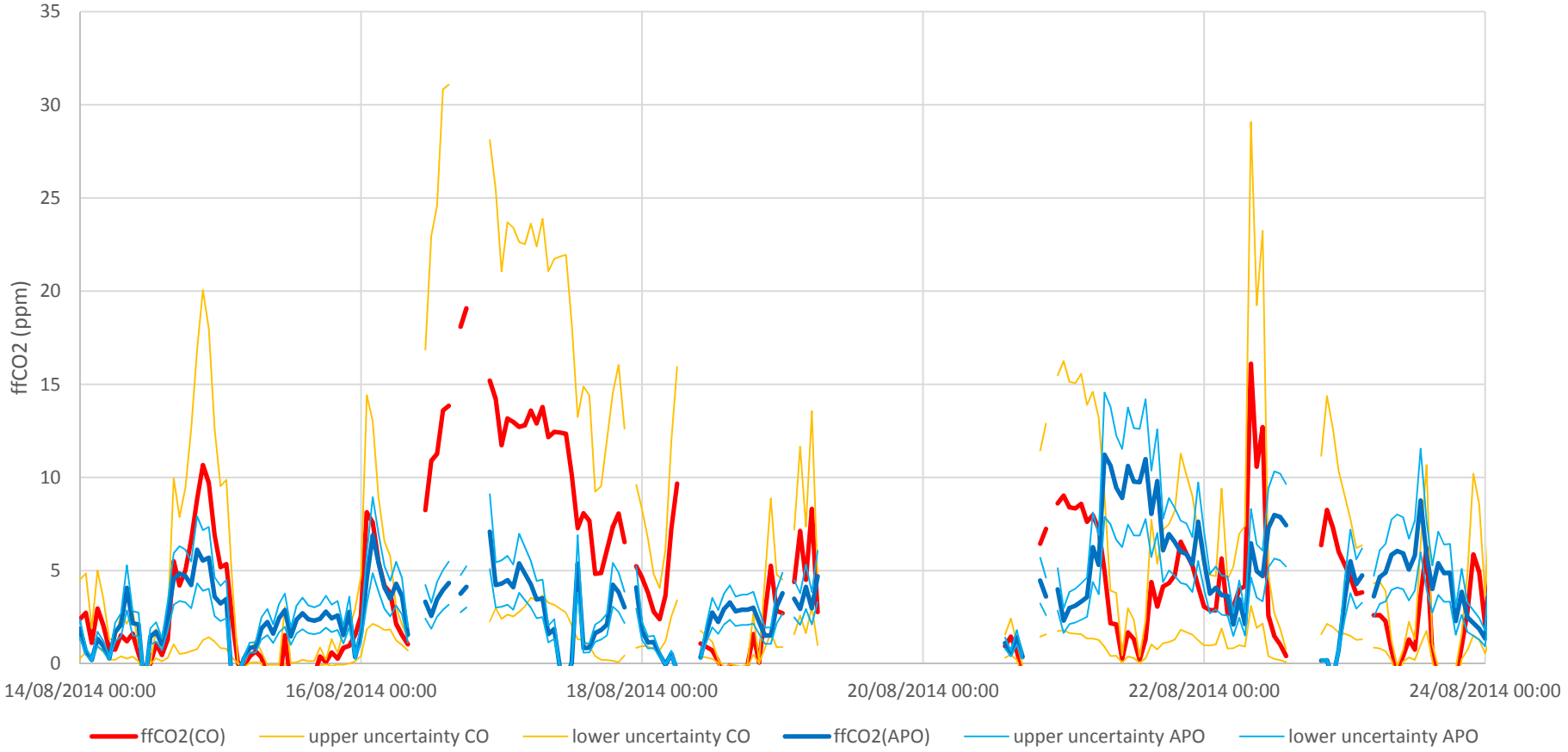
Results: UEA/TAC



Results: UEA/TAC



Results: WAO

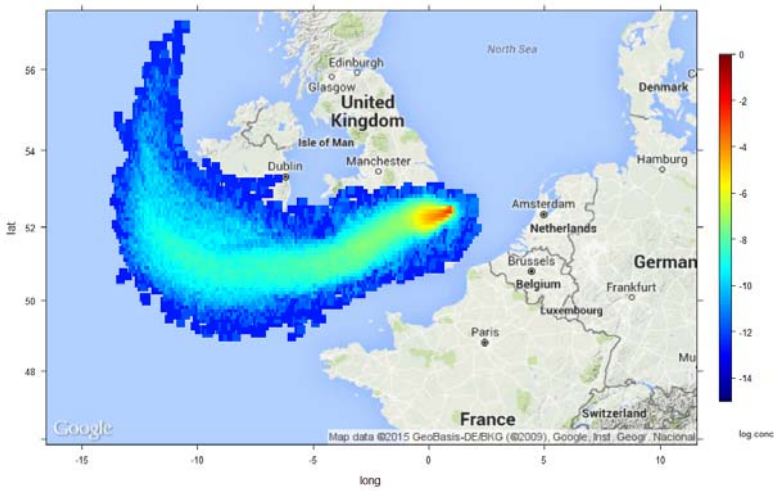

35
30
25
20
15
10
5
0
ffCO2 (ppm)
14/08/2014 00:00
16/08/2014 00:00
18/08/2014 00:00
20/08/2014 00:00
22/08/2014 00:00
24/08/2014 00:00
ffCO2(CO)
upper uncertainty CO
lower uncertainty CO
ffCO2(APO)
upper uncertainty APO
lower uncertainty APO

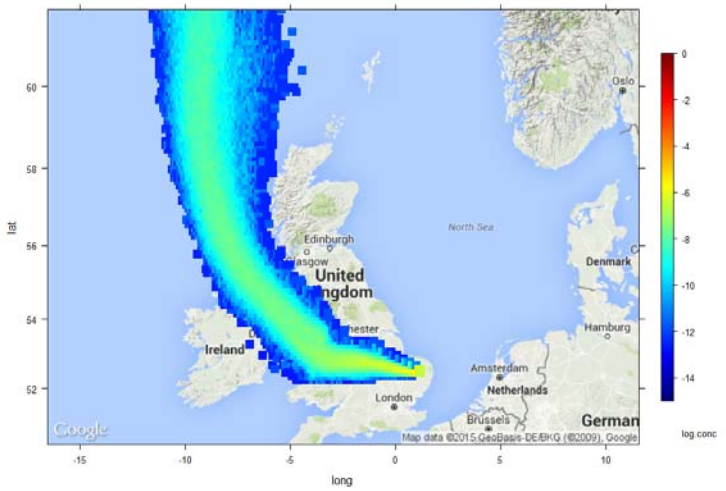
$^{14}CO_2$ as a constraint on CO and APO methods

Date/time	$ffCO_2$ ($^{14}CO_2$ method) in ppm	$ffCO_2$ (CO method) in ppm	$ffCO_2$ (APO method) in ppm
01/08/2014 09:01	2.51 ± 1.6	10.21 ± 9.2	4.13 ± 1.3
07/08/2014 12:06	1.91 ± 1.6	5.90 ± 5.1	13.44 ± 4.1
15/08/2014 09:40	1.30 ± 1.6	0.11 ± 0.1	0.67 ± 0.2
21/08/2014 08:40	1.19 ± 1.6	-	-
29/08/2014 11:20	2.51 ± 1.6	-	-

Periods of disparity between CO and APO methods

- See similar signals but not same magnitude – largely due to differences in emission ratios.
- UEA/TAC measurements are not co-located.
- CO has relatively short life-time in summer.





CO vs. APO vs. $14CO_2$

WAO:

	Mean ff CO_2 (ppm)	St dev ff CO_2 (ppm)	Mean uncertainty (ppm)	Mean uncertainty (%)
CO	5.59	6.12	4.52	75.8
APO	3.71	2.62	1.14	29.9

UEA/TAC:

	Mean ff CO_2 (ppm)	St dev ff CO_2 (ppm)	Mean uncertainty (ppm)	Mean uncertainty (%)
CO	6.35	8.99	5.78	81.4
APO	3.98	4.00	1.24	30.0
$14CO_2$	2.02	0.66	1.60	87.9

Reference	Location	Species used	$ffCO_2$ 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 ppm for $^{14}CO_2$
Graven et al. 2009	California/USA	$^{14}CO_2$ and CO	0 – 10 ppm	± 1.6 – 2.9 ppm
Turnbull et al. 2006	New England and Colorado/USA	$^{14}CO_2$, CO and SF_6	0 – 15 ppm	± 2 – 4 ppm
This work	**Norfolk/UK**	**CO** **APO** **$^{14}CO_2$**	**0 – 70 ppm (TAC)** **0 – 40 ppm (WAO)** **0 – 15 ppm (UEA)** **0 – 13 ppm (WAO)** **1.2 – 2.5 ppm (TAC)**	**± 5.78 (TAC)** **± 4.52 (WAO)** **± 1.24 (UEA)** **± 1.14 (WAO)** **± 1.60 (TAC)**

Conclusions and next steps

- CO and APO methods show similar variability at each site most of the time, but not always.
- CO method likely over-estimates $ffCO_2$.
- $^{14}CO_2$ method likely under-estimates total $ffCO_2$ due to 'clean air sampling'.
- About 40% of the $^{14}CO_2$ data are severely affected by nuclear power plant influences.
- Uncertainty using APO method is much smaller than using CO method.
- Periods when both methods show strong agreement gives very high confidence.

- more investigation of **baseline uncertainty.**
- Use NAME to **identify $ffCO_2$ sources**, e.g. Norwich, London, Birmingham, Europe, and also differentiate between fuel types using COFFEE.
- Masters' student Ben Evans will do similar analysis using continuous MHD data.