Supplement of Atmos. Chem. Phys., 19, 14057–14070, 2019
https://doi.org/10.5194/acp-19-14057-2019-supplement

Supplement of

Atmospheric radiocarbon measurements to quantify CO_2 emissions in the UK from 2014 to 2015

Angelina Wenger et al.

Correspondence to: Angelina Wenger (aw12579@my.bristol.ac.uk) and Simon O'Doherty (s.odoherty@bristol.ac.uk)

Supplementary material.

Fig. S1: Comparison of TAC CO in situ observations (blue circles) on the CSIRO-98 scale with flask measurements (light green) on the WMO-2014 scale.

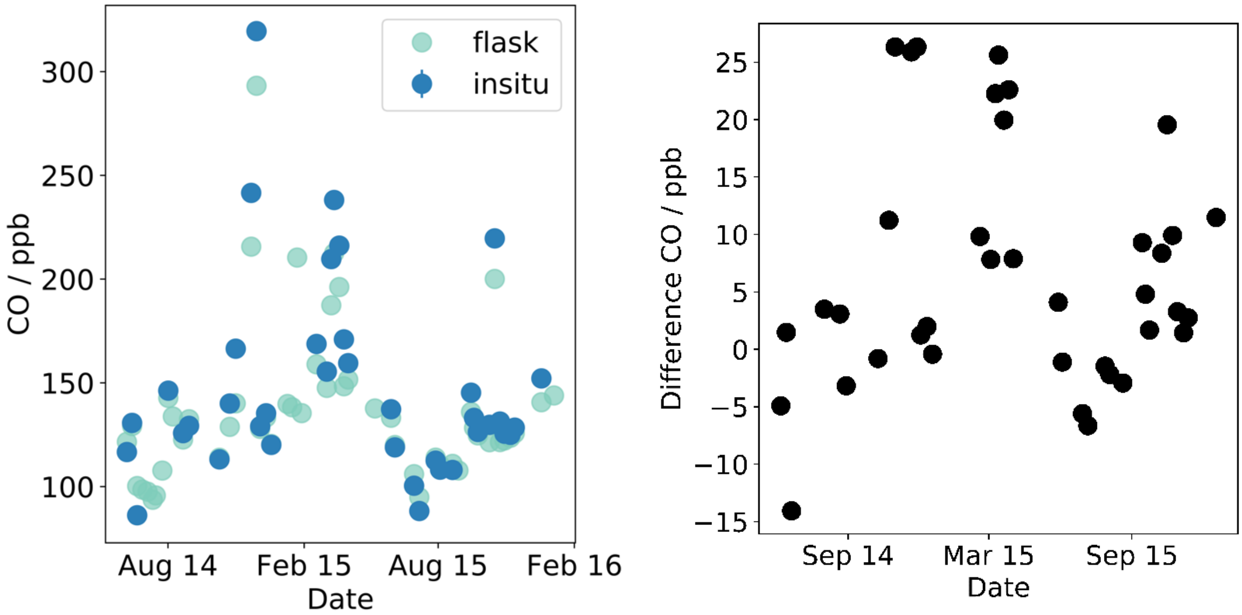
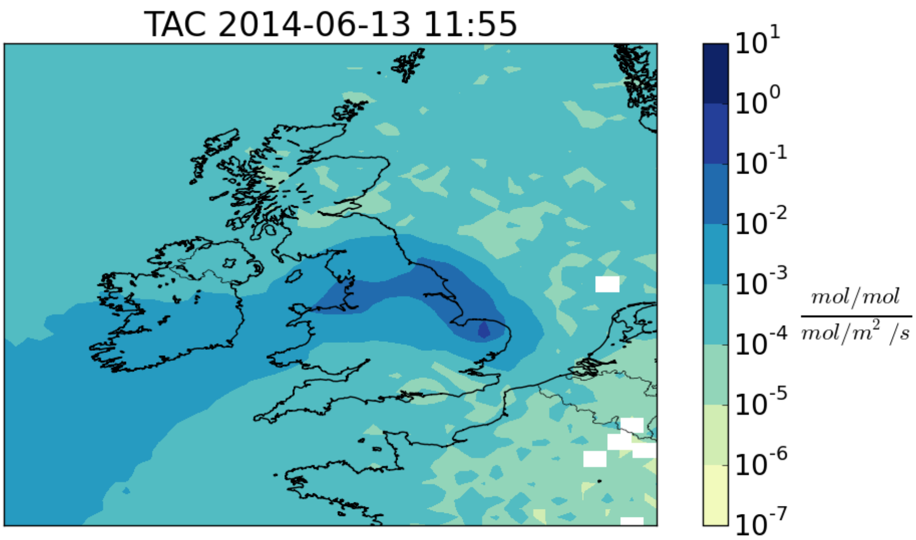


Fig. S2. Example of a back trajectory from the NAME model.



Sect. S1. Descriptions of variables and Equations used to derive Equation 2 and 3 from the Manuscript.

A_{sample}: Conventional activity of ^{14}C in a sample.

$A_{standard}$: Conventional activity of ^{14}C in the reference standard.

$\delta^{14}C$: Small delta value for ^{14}C.

$\Delta^{14}C$: Big delta value for ^{14}C.

$\delta^{13}C$: Small delta value for ^{13}C.

$^{12}C_{sample}$: Abundance of carbon 12 in sample.

$^{13}C_{sample}$: Abundance of carbon 13 in sample.

$^{14}C_{sample}$: Abundance of carbon 14 in sample.

$^{12}C_{std}$: Abundance of carbon 12 in standard.

$^{13}C_{std}$: Abundance of carbon 13 in standard.

$^{14}C_{std}$: Abundance of carbon 14 in standard.

$^{12}CO_2$: Abundance of carbon 12 CO_2.

$^{13}CO_2$: Abundance of carbon 13 CO_2.

$^{14}CO_2$: Abundance of carbon 14 CO_2.

$\delta^{13}CO_2$: Small delta value of carbon dioxide ^{13}C.

$\Delta^{14}CO_2$: big delta value of carbon dioxide ^{14}C.

CO_2: Abundance of total carbon CO_2.

$CO_{2\,bg}$: Background abundance of total carbon CO_2.

$^{12}CO_{2\,bg}$: Background abundance of carbon 12 CO_2.

$^{12}CO_{2\,i}$: Abundance of carbon 12 CO_2 caused by emissions from sector i.

$^{13}CO_{2\,bg}$: Background abundance of carbon 13 CO_2.

$^{13}CO_{2\,i}$: Abundance of carbon 12 CO_2 caused by emissions from sector i.

$^{14}CO_{2\,bg}$: Background abundance of carbon 14 CO_2.

$^{14}CO_{2\,i}$: Abundance of carbon 12 CO_2 caused by emissions from sector i.

$^{13}R_{std}$: Standard ratio $^{13}R_{std} = {}^{13}C_{std}/{}^{12}C_{std}$.

$^{14}R_{std}$: Standard ratio $^{14}R_{std} = {}^{14}C_{std}/{}^{12}C_{std}$.

$\Delta^{14}CO_{2\,i}$: Big delta value of carbon dioxide from emission source i.

$\delta^{13}CO_{2\,i}$: Small delta value of carbon dioxide from emission source i.

The calculations of $^{14}CO_2$

In Stuiver and Polach 1977 on page 361 the small and large delta values for ^{14}C are defined as:

$$\delta^{14}C = \frac{A_{Sample}}{A_{Standard}} - 1 \qquad \text{(ES.1)}$$

Where A_{Sample} is the activity per g in the sample material measured by conventional radioactive counting. An $A_{Standard}$ is the activity of the NBS oxalic acid standard. The large delta $\Delta^{14}C$ can be calculated by normalizing the small delta $\delta^{14}C$ from Equation ES.1 it to a ^{13}C signature of -25‰. This normalization assumes that the mass dependent fractionation discriminates against ^{14}C twice as much as for ^{13}C. This normalizing to a defined ^{13}C value means that the ^{14}C signature differences observed in $\Delta\,^{14}C$ is independent of any fractionation occurring due to phase changes or chemical reactions.

$$\Delta^{14}C = \delta^{14}C \quad - 2(\delta^{13}C \quad + 25) \times (1 + \frac{\delta^{14}C}{1000}) \qquad \text{(ES.2)}$$

For the samples measured in this work, accelerator mass spectrometry (AMS) was used to measure the $\Delta^{14}C$ signature of the samples. In AMS, the amount of ^{14}C vs ^{12}C molecules in a sample is measured to get the $\Delta^{14}C$ ratio rather than the radioactivity. The activity of a sample A_{Sample} is proportional to the ratio of ^{14}C atoms to the total amount of carbon atoms in the sample (Donahue 1990).

This means that Equation ES.1 can be rewritten as a ratio of ^{14}C over the sum of all carbon isotopes as in Equation ES.3.

$$\delta^{14}C = \left[\frac{{}^{14}C_{sample} / \left({}^{12}C_{sample} + {}^{13}C_{sample} + {}^{14}C_{sample}\right)}{{}^{14}C_{std} / \left({}^{12}C_{std} + {}^{13}C_{std} + {}^{14}C_{std}\right)} - 1 \right] \quad \text{(ES.3)}$$

The total carbon from S.3 can be replaced by just using ^{12}C as an approximation as given in Equation ES.4. Leaving out the ^{14}C component to the total amount of carbon in a sample does not result in significantly different results, as the ^{14}C in natural samples ^{12}C. However, dismissing the contribution of ^{13}C to the total carbon does introduce a small error and it is important to recognize that this is an approximation.

$$\delta^{14}C \approx \left[\frac{{}^{14}C_{sample} / {}^{12}C_{sample}}{{}^{14}C_{std} / {}^{12}C_{std}} - 1 \right] \quad \text{(ES.4)}$$

While the previous equations were expressed as general definitions of isotopic calculations, the following equations will specifically refer to CO_2 instead of C in an aim to clarify the definitions. Furthermore, the standard ratio $^{14}R_{std} = {}^{14}C_{std}/{}^{12}C_{std}$ will be used for the standard and the suffix sample will be omitted (e.g. $^{14}CO_2$ instead of $^{14}C_{sample}$). If we equate $\delta^{14}C$ from the in the calculation of the $\Delta^{14}C$ calculation from Equation S.2 with the approximation of the $\delta^{14}C$ value from Equation ES.4 we get Equation ES.5.

$$\Delta^{14}CO_2 = \left(\frac{\frac{{}^{14}CO_2}{{}^{12}CO_2} \times \left(1 - 2 * \frac{25 + \delta^{13}CO_2}{1000}\right)}{{}^{14}R_{std}} - 1 \right) \times 1000 \quad \text{(ES.5)}$$

We use the mass balance approach from Equation 1 in the paper to model the amount of each of the isotopes in the atmosphere. Equation ES.6-ES.8 are the mass balances for the $^{12}CO_2$, $^{13}CO_2$, $^{14}CO_2$ isotope respectively.

$$CO_2 = CO_{2\,bg} + \sum CO_{2,i} \quad \text{(1)}$$

Whereas $CO_2 = {}^{12}CO_2 + {}^{13}CO_2 + {}^{14}CO_2$

$$^{12}CO_2 = {}^{12}CO_{2bg} + \sum {}^{12}CO_{2i} \quad \text{(ES.6)}$$

$$^{13}CO_2 = {}^{13}CO_{2bg} + \sum {}^{13}CO_{2i} \quad \text{(ES.7)}$$

$$^{14}CO_2 = {}^{14}CO_{2bg} + \sum {}^{14}CO_{2i} \quad \text{(ES.8)}$$

So, for the modelling of the $\Delta^{14}CO_2$, we first have to calculate how much ^{14}C each emission sector (i) emits. For this we rearrange Equation ES.5 to solve for $^{14}CO_2$.

$$^{14}CO_2 = \frac{\left(\frac{\Delta^{14}CO_2}{1000} + 1\right) \times {}^{14}R_{std}}{1 - 2 \times \frac{25 + \delta^{13}CO_2}{1000}} \times {}^{12}CO_2 \quad \text{(ES.9)}$$

Using Equation ES.9 together with the mass balance from Equation ES.8 to calculate we can insert the resulting $^{14}CO_2$ in to the definition of the $\Delta^{14}CO_2$ from Equation ES.5 to get Equation 3 from the main text of the Manuscript.

$$\Delta^{14}CO_2 = \left(\frac{\frac{\Sigma\left(\frac{\left(\frac{\Delta^{14}CO_{2\,i}}{1000}+1\right)\times{}^{14}R_{std}}{1-2\times\frac{25+\delta^{13}CO\ _i}{1000}}\times{}^{12}CO_{2\,i} \right)}{^{12}CO_2}\times\left(1-2*\frac{25+\delta^{13}CO_2}{1000}\right)}{^{14}R_{std}} - 1 \right) \times 1000 \qquad (3)$$

The calculations of $^{13}CO_2$

The definition of the $\delta^{13}CO_2$ according to Coplen 2011 is given in Equation ES.9.

$$\delta^{13}C = \frac{^{13}C\ sample / {}^{12}C\ sample}{^{13}C\ std / {}^{12}C\ std} - 1 \qquad (ES.10)$$

The $\delta^{13}CO_2$ is commonly expressed in permil, while the definition of the delta value as given in ES.10 should not include a factor of 1000 in this work all the $\delta^{13}CO_2$ values are expressed in permil and it was decided that the factor of 1000 will be included in the Equations directly. This is done as it is a common practice in the field, and not including the factor might cause confusion in the calculations. So, for this reason a multiplication of 1000 is added to Equation ES.9 in Equation ES.10. In addition to that $^{12}C_{sample}$ will just be referred to as $^{12}CO_2$ and $^{12}C_{std}$ will be abbreviated to $^{13}R_{std}$ where as $^{13}R_{std} = {}^{13}C_{std}/{}^{12}C_{std}$. The total CO_2 from the sample was calculated using the mass balance in ES.7.

Equation ES.10 multiplies the

$$\delta^{13}CO_2 = \left(\frac{\frac{^{13}CO_2}{^{12}CO_2}}{^{13}R_{std}} - 1 \right) \times 1000 \qquad (ES.11)$$

Equation ES.11 can be rearranged to solve for the amount of $^{13}CO_2$ as given in Equation ES.12.

$$^{13}CO_2 = \left(\frac{\delta^{13}CO_2}{1000} + 1 \right) \times {}^{12}CO_2 \times {}^{13}R_{std} \qquad (ES.12)$$

This Equation ES.11 can then be combined with the Equation from the mass balance approach from ES.7 to calculate $^{13}CO_2$. When this is reintegrated in to definition of the delta value from equation ES.11 you get Equation 2 from the manuscript.

$$\delta^{13}CO_2 = \left(\frac{\frac{\Sigma\left(\left(\frac{\delta^{13}CO_{2\,i}}{1000}+1\right)\times{}^{12}CO_{2\,i}\times{}^{13}R_{std}\right)+{}^{13}CO_{2\,bg}}{^{12}CO_2}}{^{13}R_{std}} - 1 \right) \times 1000 \qquad (2)$$

Table S1: Source sectors with sources and associated isotopic $\delta^{13}C$ and $\Delta^{14}C$ signatures with the source of information.

Sector	$\delta^{13}C$ / ‰	$\Delta^{14}C$ / ‰	Comments
Combustion manufacturing EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Aviation EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Mineral processes EDGAR 2010	0 -10 to 10	-1000 -1000 to -950	(Sharp, 2007) Mostly $CaCO_3$ from limestone
Fugitive solid EDGAR 2010	-24.1 -27.1 to -21.1	-1000 -1000 to -950	(Ciais et al., 1995) Coal
Residential EDGAR 2010	-44 -49 to -39	-1000 -1000 to -950	(Andres et al., 1994) Natural gas
Solid Waste EDGAR 2010	-40 -45 to -30	150 0 to 300	(Andres et al., 1994) $\delta^{13}C$: flaring, $\Delta^{14}C$: variable depends on the mean age
Chemical processes EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Ground Transport EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Non-energy transformation EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Oil Production EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Biomass burning EDGAR 2010	-24 -29 to -19	110 110 to 120	(Sharp, 2007) $\delta^{13}C$: C3 plants -33 to -23, $\Delta^{14}C$: average biomass
Energy industry EDGAR 2010	-28.4 -38.4 to -18.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Fossil fire EDGAR 2010	-28.4 -33.4 to -23.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Shipping EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992

Metal processes EDGAR 2010	-24.1 -27.1 to -21.1	-1000 -1000 to -950	(Andres et al., 1994) Coal
Agricultural Soils EDGAR 2010	-24 -29 to -19	110 80 to 140	(Sharp, 2007) $\delta^{13}C$: C3 plants -33 to -23
Road transport EDGAR 2010	-28.4 -31.4 to -25.4	-1000 -1000 to -950	(Ciais et al., 1995) Mean fossil 1990-1992
Net ecosystem exchange NASA-CASA	-24 -27 to -21	18 15 to 21	(Sharp, 2007) Climatology
Net ocean exchange (Takahashi et al., 2002)	0 -3 to 3	50 47 to 53	(Sharp, 2007), GLODAP V2 extrapolated climatology
Hetrotrophic respiration NASA-CASA	-24 -27 to -21	110 107 to 113	NASA CASA simulations available at: https://nacp-files.nacarbon.org/nacp-kawa-01/

Fig. S3: ^{14}C signature of different carbon pools before and after the bomb-spike.

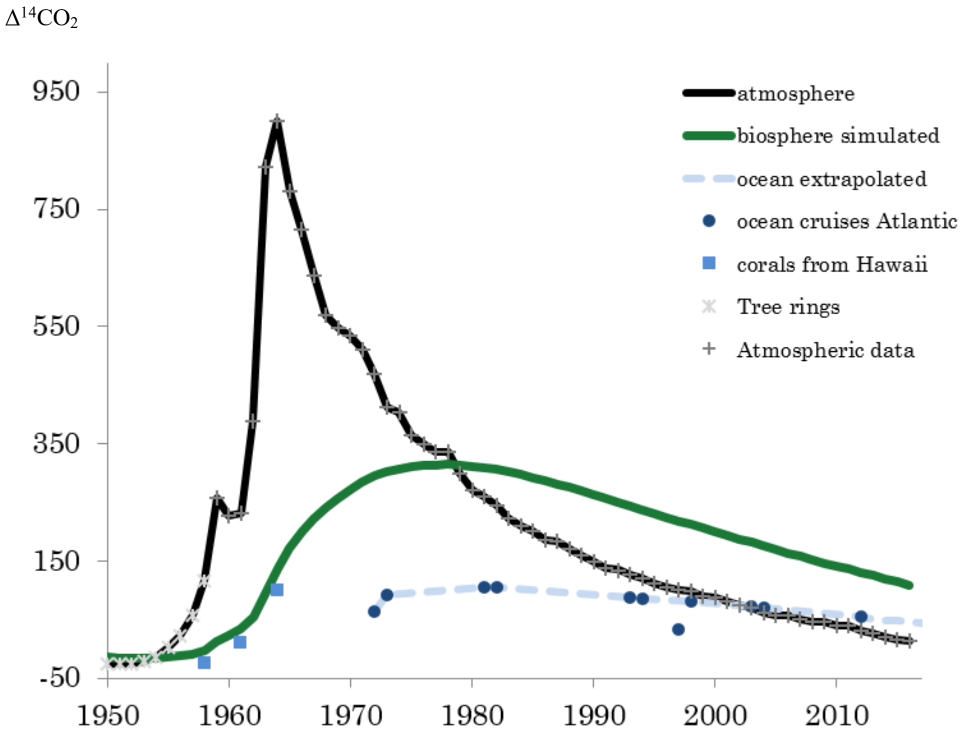


Figure S.5: Time series of $\Delta^{14}CO_2$ signature from before the bomb spike to now. The atmospheric data was compiled from northern hemisphere tree ring data (Stuiver & Quay 1981) and measurements from the University of Heidelberg (Levin & Kromer (2004),Levin et al. (2013)). The oceanic data consists of coral data from Hawaii (Druffel et al. 2001) and ocean surface measurements from the Atlantic (Glodap v2). The Biospheric value was simulated in a 1box model according to (Graven et al. 2012).

Table S2: Emissions from La Hague used for the nuclear correction for each month over the sample collection period. Monthly emissions are shown in Becquerels.

Month	Monthly emission / Bq	Month	Monthly emission / Bq	Month	Monthly emission / Bq
01/2014	0.548E+12	09/2014	1.207E+12	05/2015	1.989E+12
02/2014	2.386E+12	10/2014	1.300E+12	06/2015	1.318E+12
03/2014	2.389E+12	11/2014	2.204E+12	07/2015	2.063E+12
04/2014	2.600E+12	12/2014	1.248E+12	08/2015	2.056E+12
05/2014	2.739E+12	01/2015	0.984E+12	09/2015	1.67E+12
06/2014	2.048E+12	02/2015	1.197E+12	10/2015	6.55E+11
07/2014	1.401E+12	03/2015	1.527E+12	11/2015	1.73E+12
08/2014	1.882E+12	04/2015	2.069E+12	12/2015	2.14E+12

Fig. S4: Modelled sector specific influence on each isotope sample taken during the experiment. Sectors are details in the key and are as follows, displayed from top to bottom: road transport, agricultural soils, metal processes, shipping, fossil fire, energy industry, biomass burning, oil production, transformation non-energy, ground transport, chemical processes, solid waste, residential, fugitive soils, mineral processes, aviation and combustion manufacturing.

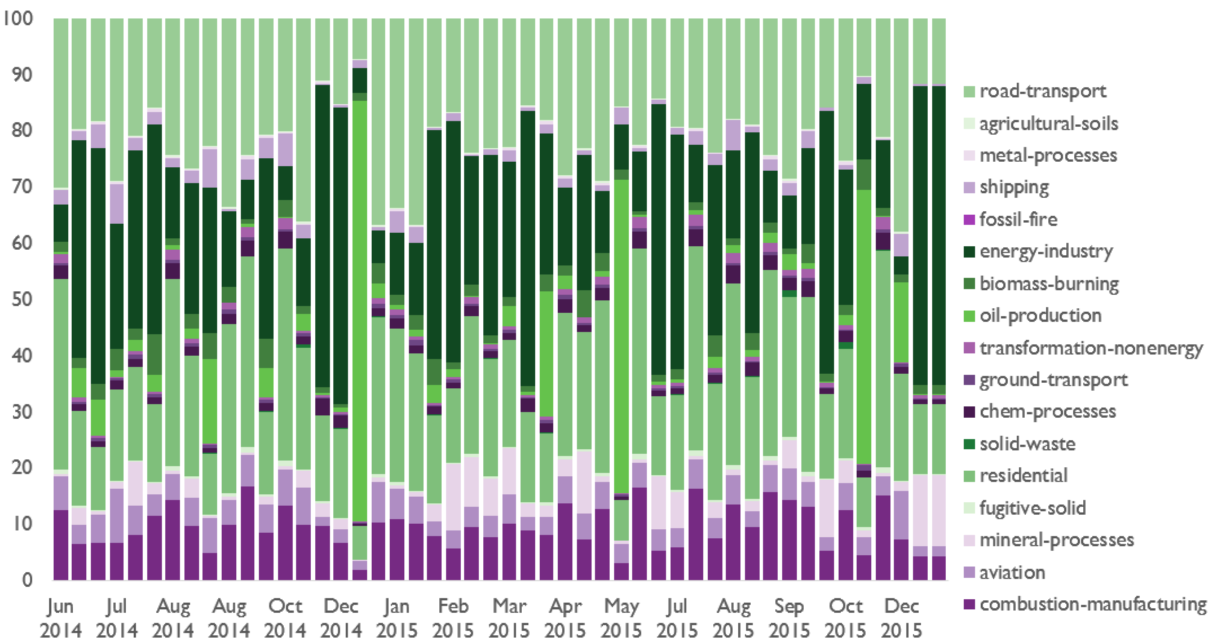


Fig. S5: CO_2 modelled (blue line) and measured (black points) at TAC using the EDGAR emissions inventory in NAME compared to CO_2 calculated using the observed daily means (24h) CO at TAC minus the MHD background CO all divided by the CO factor (4.39 for all data without the November peak derived in Table 2) (green).

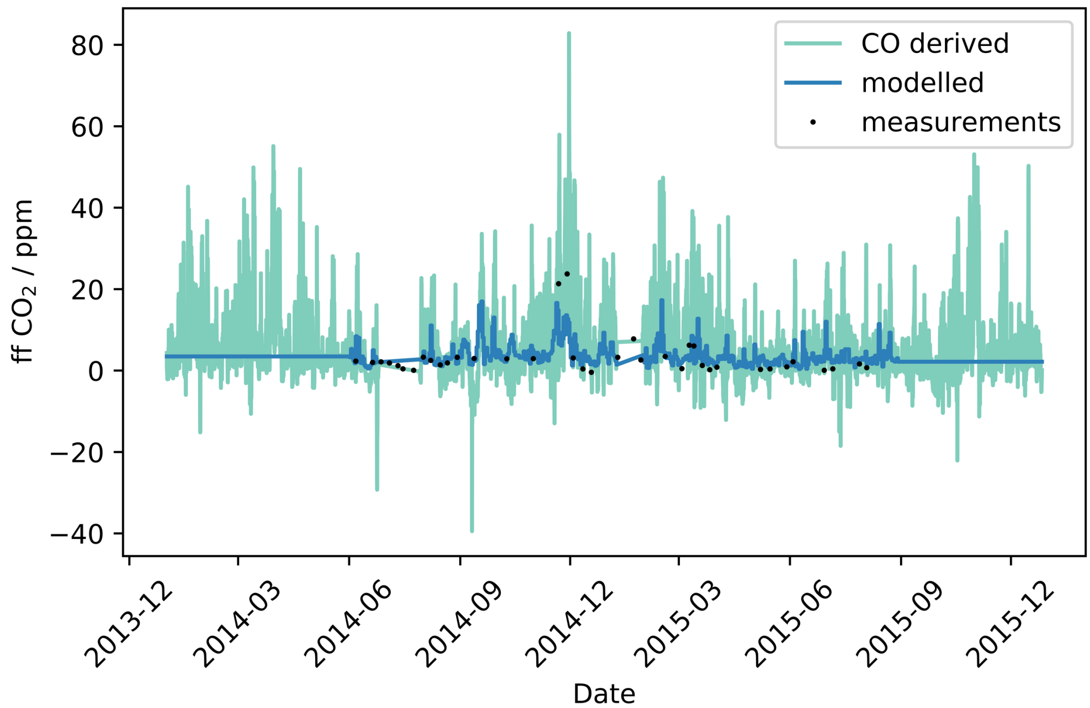


Fig S6: MHD ^{14}C background data (blue points) and the ^{14}C rolling mean values (green line) that were used as a background.

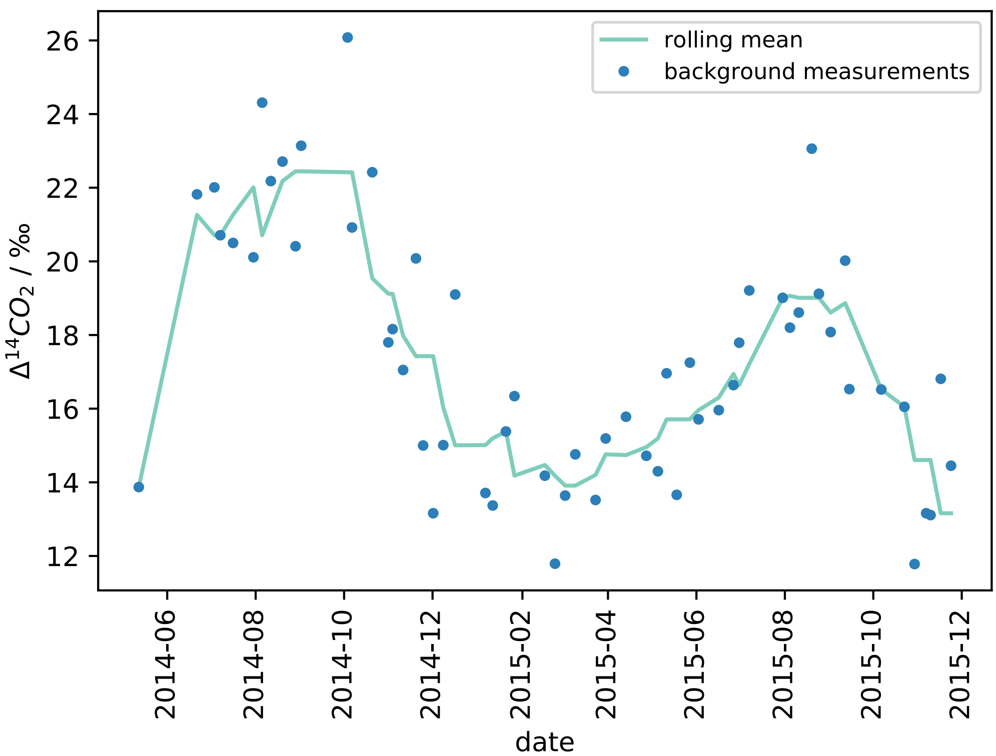


Table S3: Table showing the ^{14}C values, sampling information and corrections applied to each measurement.

Date	Time	$^{14}C_{obs}$ / ‰ TAC	Uncertainty of $^{14}C_{obs}$ / ‰	Biospheric correction (in ffCO2 equivalent / ppm)	Nuclear correction (in ffCO2 equivalent / ppm)	^{14}C Background value rolling mean MHD / ‰	$^{12}CO_2$ TAC / ppm	^{12}C Background value MHD / ppm	Resulting $ffCO_2$ / ppm
06/06/2014	10:55:00	16.64	1.80	-0.30	-0.01	21.92	397.33	401.26	2.31
13/06/2014	11:55:00	59.61	2.61	-0.44	-0.02	21.92	391.72	401.26	2.26
20/06/2014	08:35:00	16.84	2.55	-0.33	-0.02	21.92	395.18	391.67	1.55
27/06/2014	09:28:00	19.58	1.83	-0.34	-0.02	21.92	401.61	398.85	1.62
04/07/2014	08:15:00	17.43	2.64	-0.40	-0.02	21.26	400.05	394.40	0.95
11/07/2014	09:50:00	18.90	2.68	-0.47	-0.14	21.26	393.48	397.22	0.67
15/07/2014	12:53:00	20.87	2.61	-0.34	0.00	20.71	391.93	393.91	-0.64
24/07/2014	08:21:00	22.41	2.56	-0.31	-0.28	20.71	388.98	389.95	2.17
01/08/2014	09:01:00	15.52	2.53	-0.40	0.00	20.71	392.01	389.95	2.93
07/08/2014	12:06:00	16.07	2.71	-0.73	-0.15	22.18	388.65	389.10	1.30
15/08/2014	09:40:00	18.24	2.69	-0.30	-0.03	21.34	388.94	390.10	1.89
21/08/2014	08:40:00	17.88	2.51	-0.26	0.00	22.18	392.46	388.70	3.10
29/08/2014	11:20:00	14.56	1.80	-0.23	0.00	22.45	399.39	389.19	2.60
12/09/2014	11:32:00	15.87	1.80	-0.43	-0.61	22.45	403.33	388.55	2.96
09/10/2014	11:47:00	15.17	1.80	-0.17	-0.01	22.78	431.92	392.00	-1.09
23/10/2014	11:43:00	24.22	1.80	-0.30	-0.02	20.92	443.03	395.94	1.65
31/10/2014	11:42:00	15.40	2.06	-0.84	-0.01	18.16	401.89	398.80	2.01
21/11/2014	09:42:00	-31.60	1.80	-0.62	-0.33	17.42	403.55	400.36	0.16
28/11/2014	12:09:00	-35.26	1.80	-0.69	-0.49	15.01	401.79	401.04	-0.71
03/12/2014	11:23:00	9.95	1.80	-0.14	0.00	15.01	406.75	401.04	2.96
11/12/2014	12:03:00	15.33	1.80	-0.16	0.00	15.01	403.52	402.39	7.27
18/12/2014	12:23:00	16.99	1.80	-0.11	0.00	15.01	404.30	400.22	2.66

09/01/2015	09:32:00	7.39	1.80	-0.11	0.00	14.55	407.18	403.74	3.11
22/01/2015	11:52:00	-3.28	1.80	-0.32	-0.37	14.55	405.38	404.98	0.56
28/01/2015	13:52:00	7.96	1.80	-0.11	0.00	14.55	409.50	403.60	5.68
17/02/2015	15:58:00	6.42	1.80	-0.20	0.00	13.91	414.98	405.55	6.53
03/03/2015	13:06:00	12.95	2.07	-0.17	-0.01	13.91	410.18	405.24	0.97
09/03/2015	13:01:00	0.13	1.80	-0.18	0.00	13.64	404.98	404.67	0.28
13/03/2015	10:25:00	-0.35	1.98	-0.32	-0.32	13.64	406.88	415.64	0.69
20/03/2015	09:46:00	12.15	2.02	-0.42	-0.09	14.20	401.12	405.67	-0.12
26/03/2015	14:50:00	14.03	2.15	-0.11	0.00	14.20	403.52	405.67	-0.05
01/04/2015	10:46:00	13.08	2.01	-0.13	0.00	14.76	398.21	405.88	0.98
07/05/2015	13:46:00	16.56	2.03	-0.36	-0.07	14.72	396.52	405.08	2.63
15/05/2015	10:26:00	14.93	2.04	-0.16	-0.01	14.72	395.52	405.00	0.06
29/05/2015	08:50:00	13.94	2.11	-0.30	0.00	15.71	392.18	403.32	0.33
03/06/2015	13:30:00	11.06	2.02	-0.36	-0.05	15.96	393.30	404.11	0.74
29/06/2015	09:30:00	17.22	2.05	-0.38	0.00	17.22	403.45	398.68	0.58
06/07/2015	10:42:00	16.67	2.06	-0.26	0.00	17.22	399.22	398.08	2.31
28/07/2015	12:40:00	17.41	2.01	-0.30	-0.01	18.81	394.02	393.54	2.26
03/08/2015	13:52:00	17.67	2.05	-0.20	-0.01	19.01	408.36	393.09	1.55

All the MHD and TAC flask data can also be found on the NOAA data server: https://www.esrl.noaa.gov/gmd/dv/data/

References:

S.3 Equations.

Stuiver, M. and Polach, H.A., 1977. Discussion reporting of 14 C data. Radiocarbon, 19(3), pp.355-363.

Donahue, D.J., Linick, T.W. and Jull, A.T., 1990. Isotope-ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. Radiocarbon, 32(2), pp.135-142.

Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid communications in mass spectrometry, 25(17), pp.2538-2560.

S.5 Bomb spike.

Stuiver, M. and Quay, P.D., 1981. Atmospheric14C changes resulting from fossil fuel CO2 release and cosmic ray flux variability. Earth and Planetary Science Letters, 53(3), pp.349-362.

Levin, I. and Kromer, B., 2004. The tropospheric 14 CO 2 level in mid-latitudes of the Northern Hemisphere (1959–2003). Radiocarbon, 46(3), pp.1261-1272.

Levin, I., Kromer, B.E.R.N.D. and Hammer, S.A.M.U.E.L., 2013. Atmospheric Δ14CO2 trend in Western European background air from 2000 to 2012. Tellus B: Chemical and Physical Meteorology, 65(1), p.20092.

Druffel, E.R., Griffin, S., Guilderson, T.P., Kashgarian, M., Southon, J. and Schrag, D.P., 2001. Changes of subtropical North Pacific radiocarbon and correlation with climate variability. Radiocarbon, 43(1), pp.15-25.

Graven, H.D., Guilderson, T.P. and Keeling, R.F., 2012. Observations of radiocarbon in CO2 at seven global sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles. Journal of Geophysical Research: Atmospheres, 117(D2).

Olsen, A., Key, R.M., van Heuven, S., Lauvset, S.K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M. and Jutterström, S., 2016. The Global Ocean Data Analysis Project version 2 (GLODAPv2)–an internally consistent data product for the world ocean. Earth System Science Data (Online), 8(2).