Identifying bulk regional methane isotopic signatures using long-term records from UK sites

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Long term records are vital for understanding the way in which our environment is changing.
A significant rise in atmospheric methane began in 2007 and has accelerated thereafter, particularly since 2014. This trend was observed globally and was coupled with a sustained isotopic shift to more negative $\delta^{13}C_{CH4}$ values. Currently, there is no consensus as to why these observations have occurred. However, long-term methane isotopic measurements can provide information about changes in the source mix of this important greenhouse gas. Here, long-term records of both CH_4 mole fraction and $\delta^{13}C_{CH4}$ from 5 sites across the UK are presented, showing an increase in CH_4 and a shift to more negative values of $\delta^{13}C_{CH4}$ from 2007, similar to those recorded globally, but at the regional-local scale.

Methods

Collection and measurement methods

- Air samples are collected approximately weekly from 5 UK sites. The air samples are collected in flasks in Egham and in Flexfoil bags at the other sites.
- The samples are analysed at the department of Earth Sciences, Royal Holloway, University of London (RHUL).
- CH_4 mole fraction is analysed by a Picarro cavity ring-down analyser, to the WMO X2004A scale.
- Stable carbon isotope ratio measurements were carried out using CF-GC-IRMS (Continuous Flow Gas Chromatography-Isotope Ratio Mass Spectrometry). Technique outlined in Fisher et al. (2006).
- Reproducibility is 0.05 ‰ or better for most $\delta^{13}C_{CH4}$ measurements.

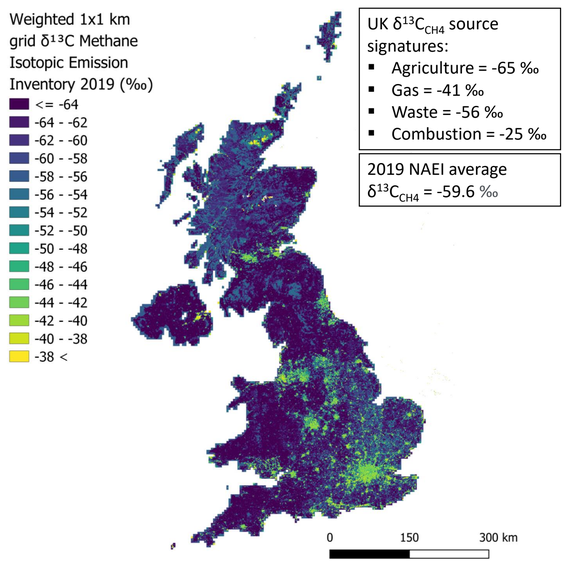
Barra (BAR)

Weybourne Atmospheric Observatory (WAO) – University of East Anglia

Egham (EGH) – Royal Holloway, University of London

Western Channel Observatory (WCO) – Plymouth Marine Lab

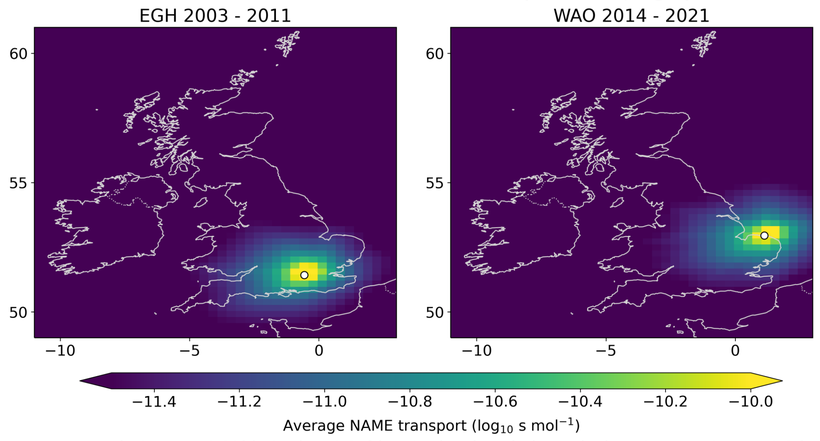
Expected UK source signatures from the National Atmospheric Emissions Inventory



- Using mapped emission data from the National Atmospheric Emissions Inventory (NAEI) and expected signatures for the main source categories based on Royal Holloway mobile measurements, weighted methane isotope values were calculated for each grid cell.
- From this calculation, the inventory suggests that emissions from urban areas should be isotopically heavier in $\delta^{13}C_{CH4}$. The expected $\delta^{13}C_{CH4}$ signature for total methane emissions from the UK, according to the 2019 NAEI data, is -59.6 per mil.

Numerical Atmospheric-dispersion Modelling

The Met Office's Numerical Atmospheric-dispersion Modelling Environment (NAME) was used to calculate the sensitivity of measurements, taken at RHUL and WAO, to the surrounding emissions field. This is done by releasing and tracking simulated particles backwards in time and establishing where they intercept the surface layer. Footprints, which refer to the sensitivity of each observation to the emissions, of the measurement can be plotted (Rigby et al. 2011).

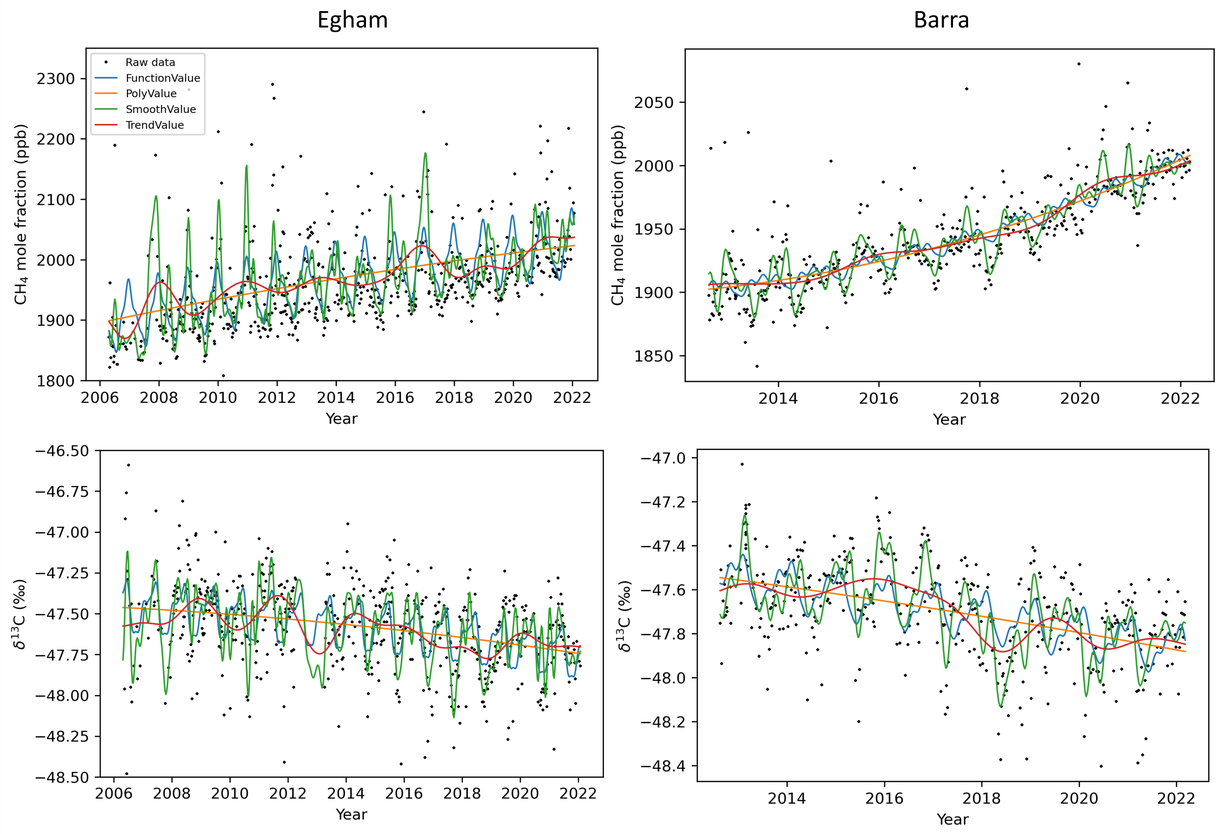


For this analysis, the NAME output resolution was 0.23° latitude × 0.35° longitude. The whole study domain was 10.7 to 79.3 °N, −97.9 to 39.7 °E. NAME was run with a UK meteorological product for the UK, at a spatial resolution of 1.5km and temporal resolution of 1 hour. The UK Met Office's Unified Model was used to provide meteorology for the rest of the domain at temporal resolution of 3 hours.

Results

Time series

The time series for both CH_4 mole fraction and $\delta^{13}C_{CH4}$ for Egham (left) and Barra (right), with fits from the NOAA GGCCRV programme applied (Thoning et al. 1989). Nisbet et al. (2016) reported that the globally averaged mole fraction of methane increased after 2006, coupled with a shift to more depleted $\delta^{13}C_{CH4}$ values. This phenomenon is evident in all UK sites where RHUL has collected long-term samples.

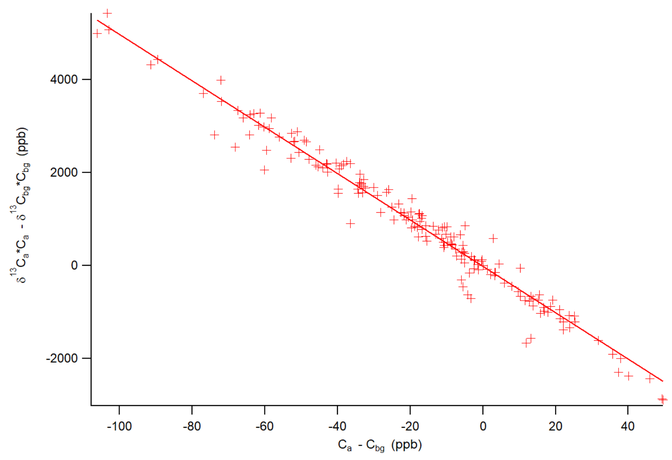


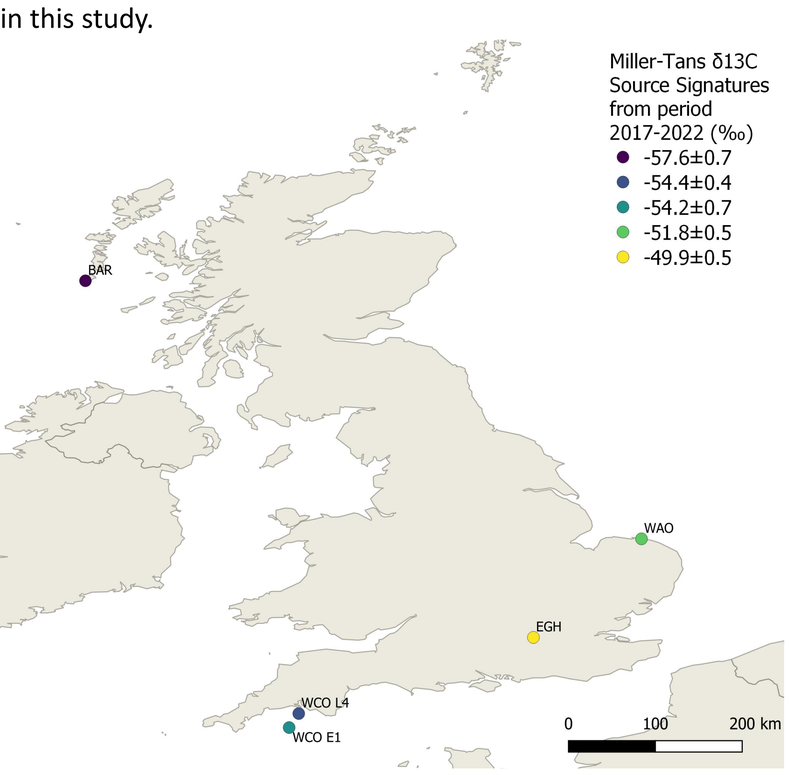
Miller-Tans analysis

- A method for isotopic discrimination from atmospheric measurements of CO_2 and $\delta^{13}C$ was outlined by Miller and Tans (2003). In this study the method is applied to CH_4.
- Miller-Tans plots (right) allow for the explicit specification of background values.
- The source signature is found from the slope of the regression line which represents a flux weighted average of the sources, according to the equation,

$$\delta_{obs}C_{obs} - \delta_{bg}C_{bg} = \delta_s\,(C_{obs} - C_{bg})$$

- The smooth curve fit from the NOAA CCGCRV curve fitting program are used as background values in this study.





Conclusion

- At all sites, there has been an increase in CH_4, which in most cases has been coupled with a decline in $\delta^{13}C$.
- Using the Miller Tans method, it is possible to calculate bulk regional source signatures.
- Miller-Tans analysis shows that there is a distinction between the sources of rural and urban emissions, which agrees with the NAEI.
- The isotopic signatures calculated using the Miller-Tans technique are heavier than expected based on the NAEI emissions. From these initial results it seems that there is a bigger proportion thermogenic/pyrogenic emissions compared to the NAEI inventory.

Next steps:

- Divide data in order to do a sector analysis to look at different source regions.
- RHUL have recently installed an automatic sampler at Heathfield Tall tower site.
- Compare the specific area that the NAME footprints cover to the NAEI.

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