THE USE OF MOBILE MEASUREMENTS TO TRACK REGIONAL SOURCES OF METHANE EMISSIONS IN UK

Giulia Zazzeri[1], D. Lowry[1], R. E. Fisher[1], A. Al-Shalan[1], J. L. France[2], M. E. Lanoisellé[1], E. G. Nisbet[1]

[1] Royal Holloway, University of London

[2] University of East Anglia

The importance of knowing sources

CH_4 sources are **isotopically distinct:**

- **Biogenic Sources**:

^{13}C depleted ($\delta^{13}C_{CH_4}$<- 50 ‰)

- **Pyrogenic and thermogenic Sources**:

^{13}C enriched ($\delta^{13}C_{CH_4}$ > - 50 ‰)

- **Background** isotopic value: $\delta^{13}C_{CH_4}$ **- 47 ‰**

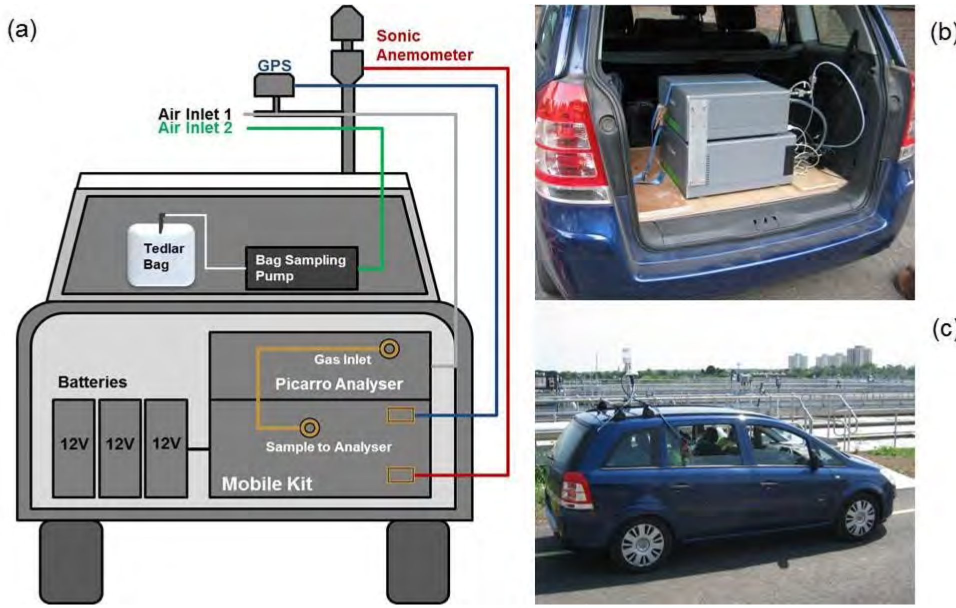
Typical isotopic signatures have been revised after sampling campaigns around the source sites

UK Methane Sources	Emission Kt (2012)	Typical $\delta^{13}C_{CH4}$ (‰)
Waste disposal and Landfills	884	-58*
Enteric Fermentation (cows)	745	-66*
Agriculture (Manure Management)	316	-58
Gas Transmission and distribution	189	-36*
Wastewater handling	78	-53*
Coal Mining	76	-51 to -30*
Combustion (Industrial and Domestic)	43	-25
Road transport	3	-11*
Biomass Burning	3	-28
UK Total	**2337**	**-57.2**

Table 1 ^{13}C signatures of UK methane sources, based on measured values (Lowry et al., 2001; Fisher, 2007) and literature review. * indicates values which have been revised by this study. Emission inventories are provided without errors. Errors of measured isotopic values are within ± 3 ‰, except coal. Emission values from NAEI (National Atmospheric Emission Inventories) website.

Material and Methodology

- The GGLES mobile greenhouse gas monitoring system includes:
    - a mobile Picarro G2301 Cavity Ring-Down Spectrometer equipped with a battery power supply;
    - Climatronics sonic anemometer;
    - Hemisphere GPS receiver ;
    - an air inlet.
- Both CH_4 and CO_2 concentrations columns are displayed on Google Earth in real time
- Sampling upwind and downwind of sources through emission plumes



Google Earth view of CH_4 mole fractions around the RHUL campus

Material and Methodology

- CH_4 and CO_2 were measured in our lab with a Picarro G1301 Cavity Ring-Down Spectrometer
- Calibration against NOAA Standards
- The carbon isotopic ratio was measured in ‰ to high precision (**+/- 0.05 ‰**) by GC-IRMS (Fisher et al., 2006)

Picarro G1301 CRDS
(Cavity Ring-Down Spectroscopy)

Trace Gas CF-GC-IRMS
(Gas Chromatography – Isotopic ratio Mass Spectrometry)

The Keeling Plot approach

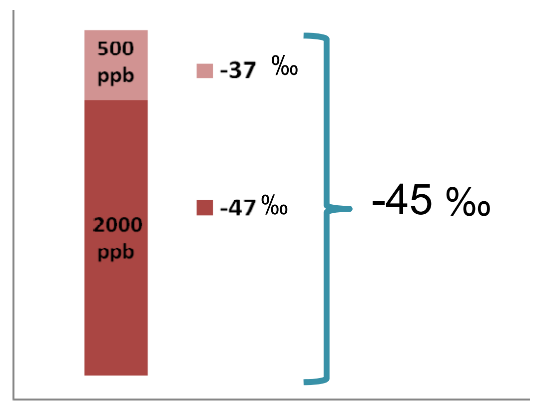
$c_a = c_b + c_s$

c_a = atmospheric methane concentration

c_b = background concentration

c_s = additional concentration component produced by the source

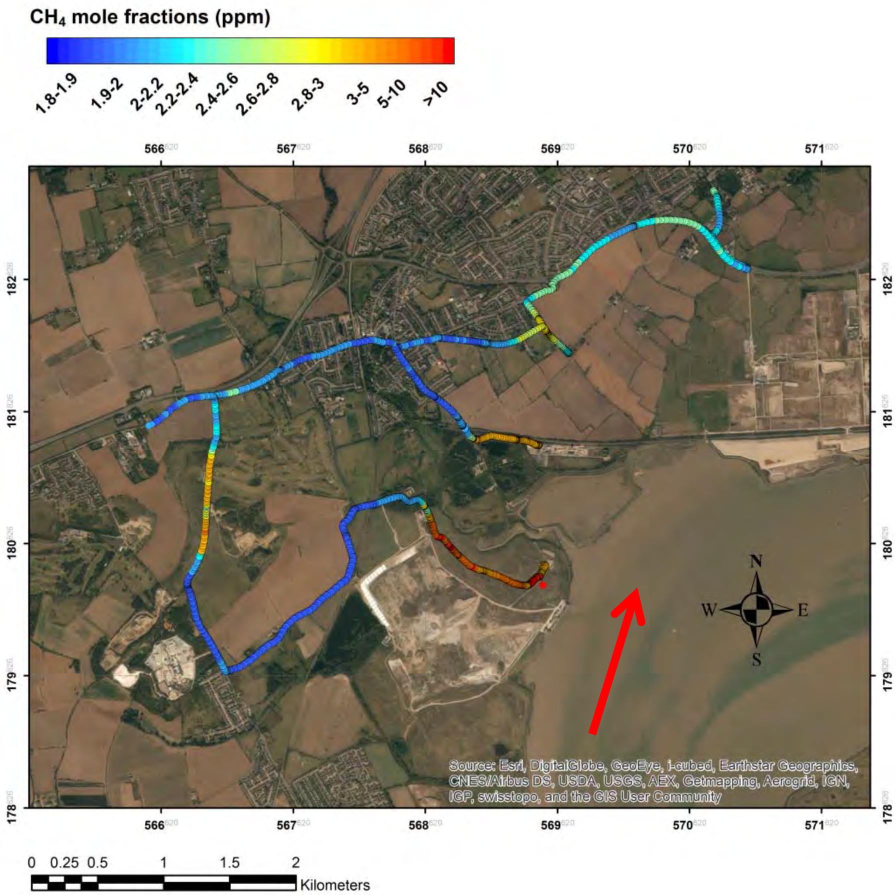
$\delta^{13} C_a c_a = \delta^{13} C_b c_b + \delta^{13} C_s c_s$

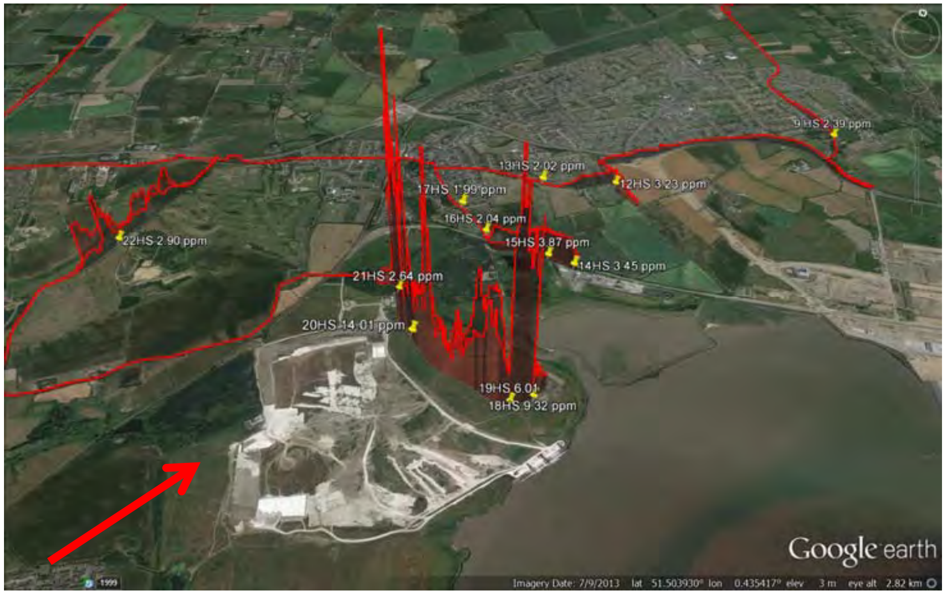


$$\boldsymbol{\delta^{13} C_a = c_b(\delta^{13} C_b - \delta^{13} C_s)*1/c_a + \delta^{13} C_s}$$

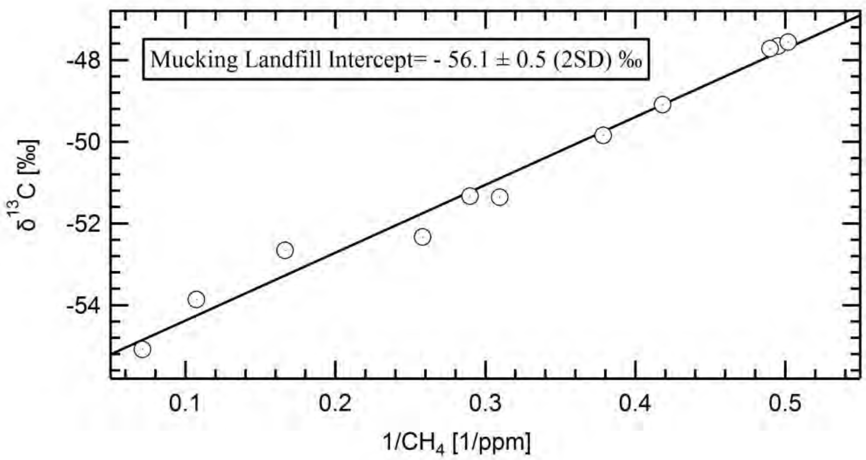
UK Landfill Isotopic Signature

Methane mole fractions plot on Google Earth



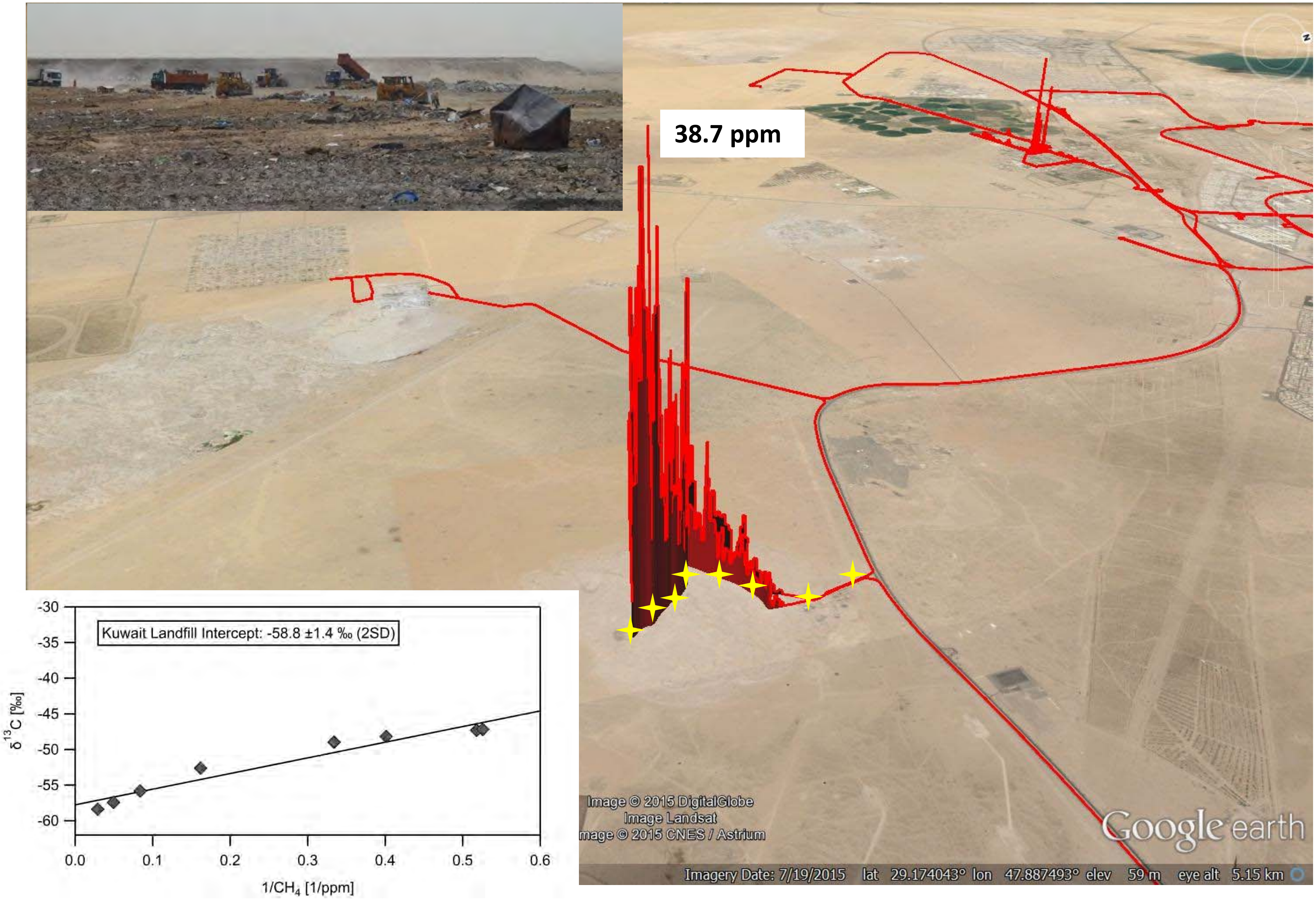


Methane mole fractions plot with GIS Software



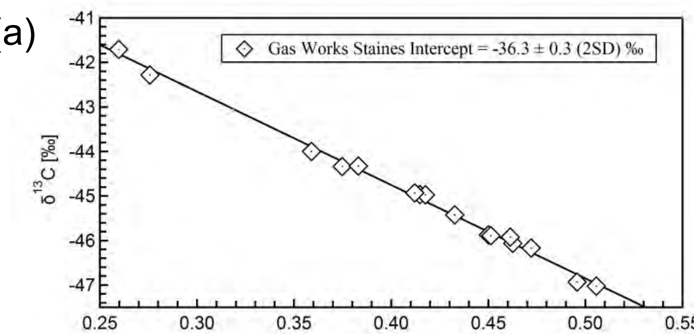
Keeling Plot based on samples collected down-wind Mucking Landfill site

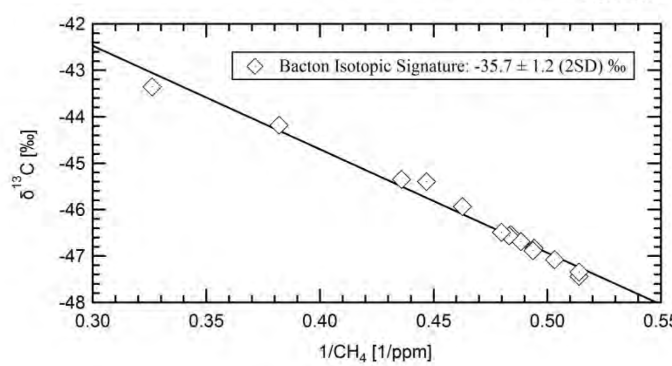
Kuwait Landfill Isotopic Signature



UK Natural Gas Isotopic Signature

(a)

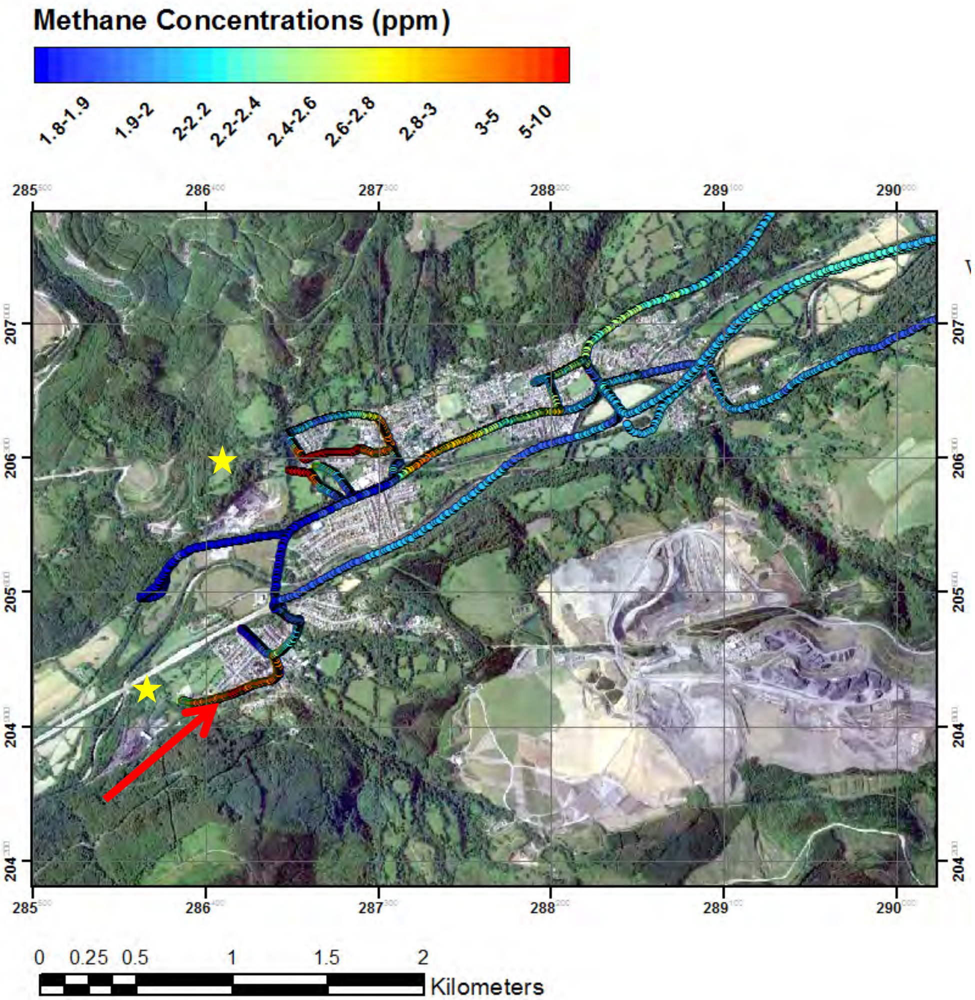




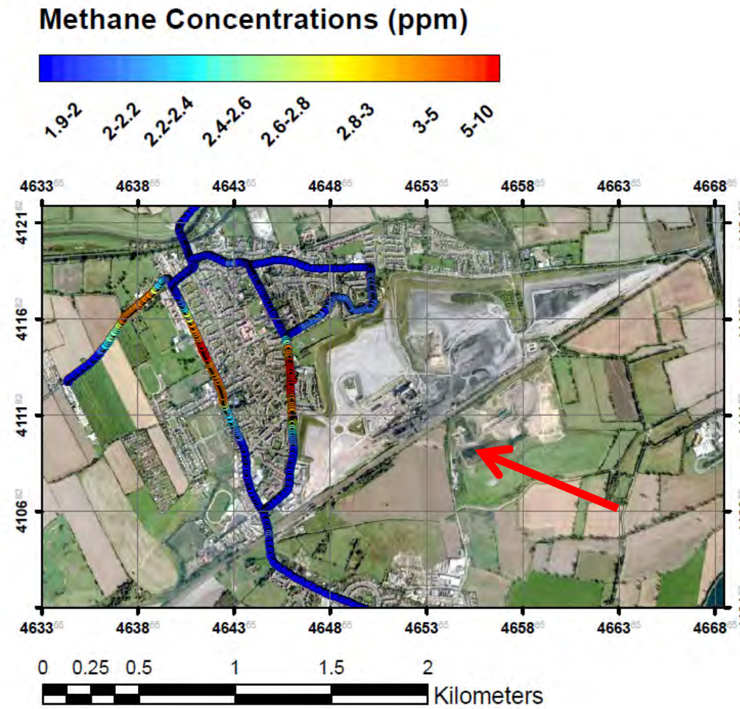
(b)

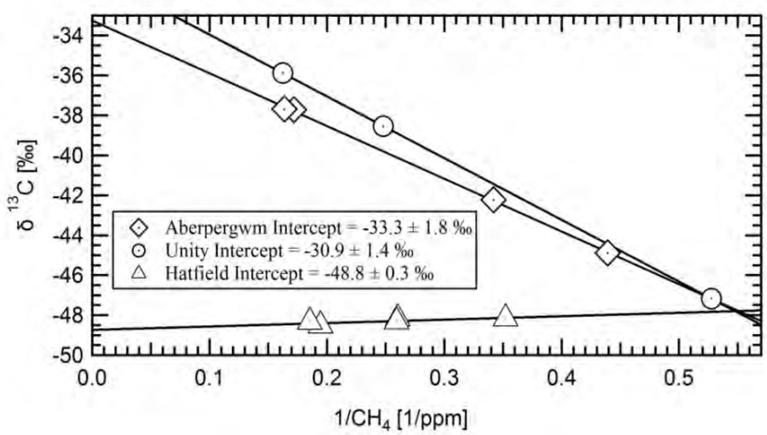
Keeling Plot based on samples collected downwind of gas works in Staines (a) and of gas terminals in Bacton (b)

UK Coal Mines signature

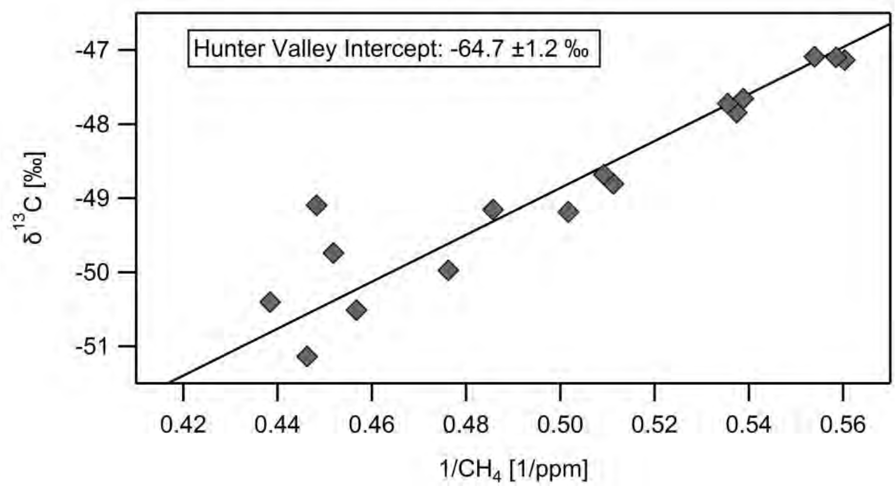


ArcGIS plot of Aberpergwm and Unity deep coal mines in Wales





Australian Coal Mines signature



Methane from open-cast mines in Sydney Basin is mostly of biogenic origin.

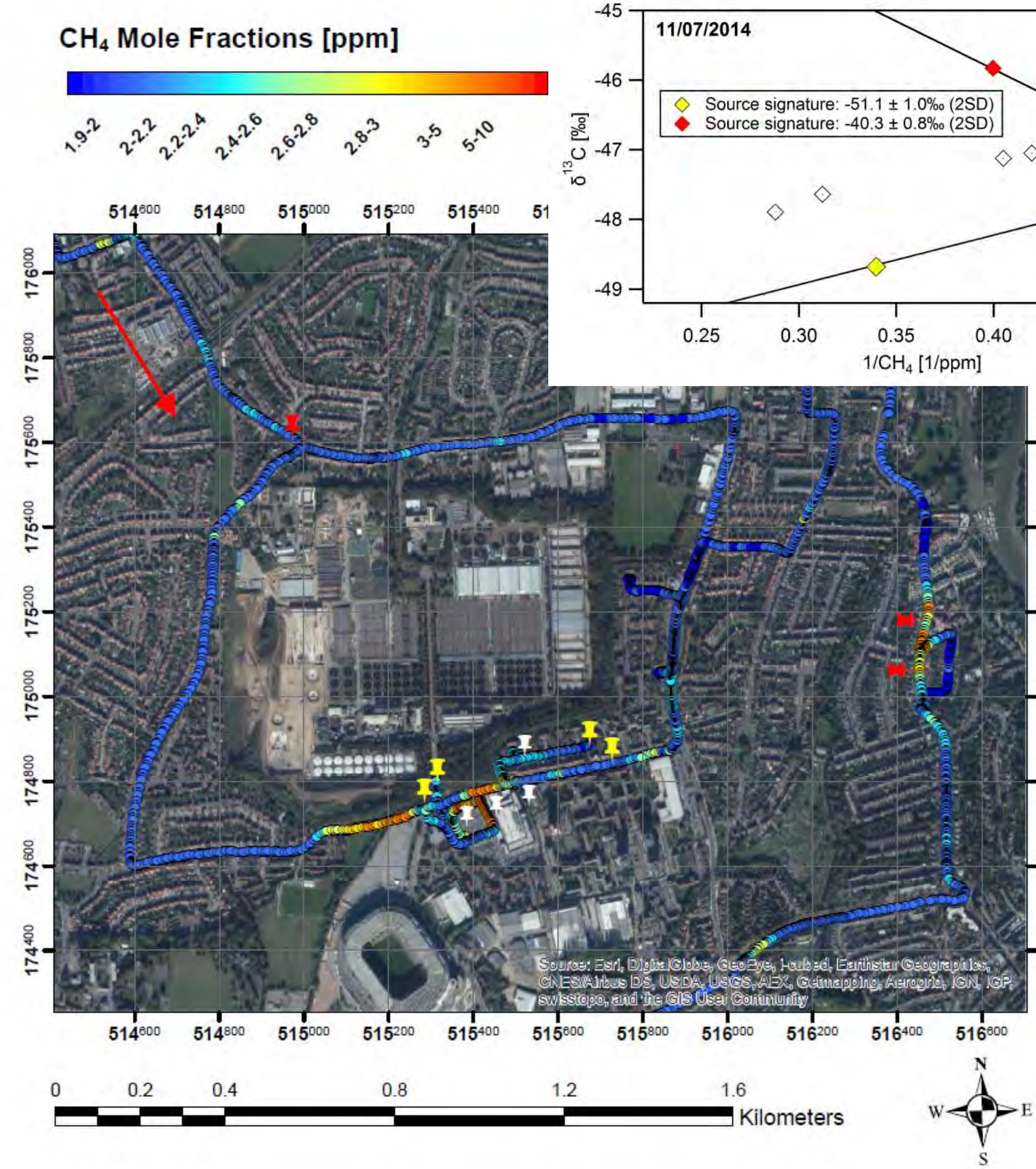
Two stages process can be suggested:

- Progression in coal rank (-50 ‰ for bitumen and -30 ‰ for anthracite)
- 10 ‰ meteoric water depletion (-40 ‰ for Welsh anthracite opencast and -60 ‰ for Australian bituminous opencast).

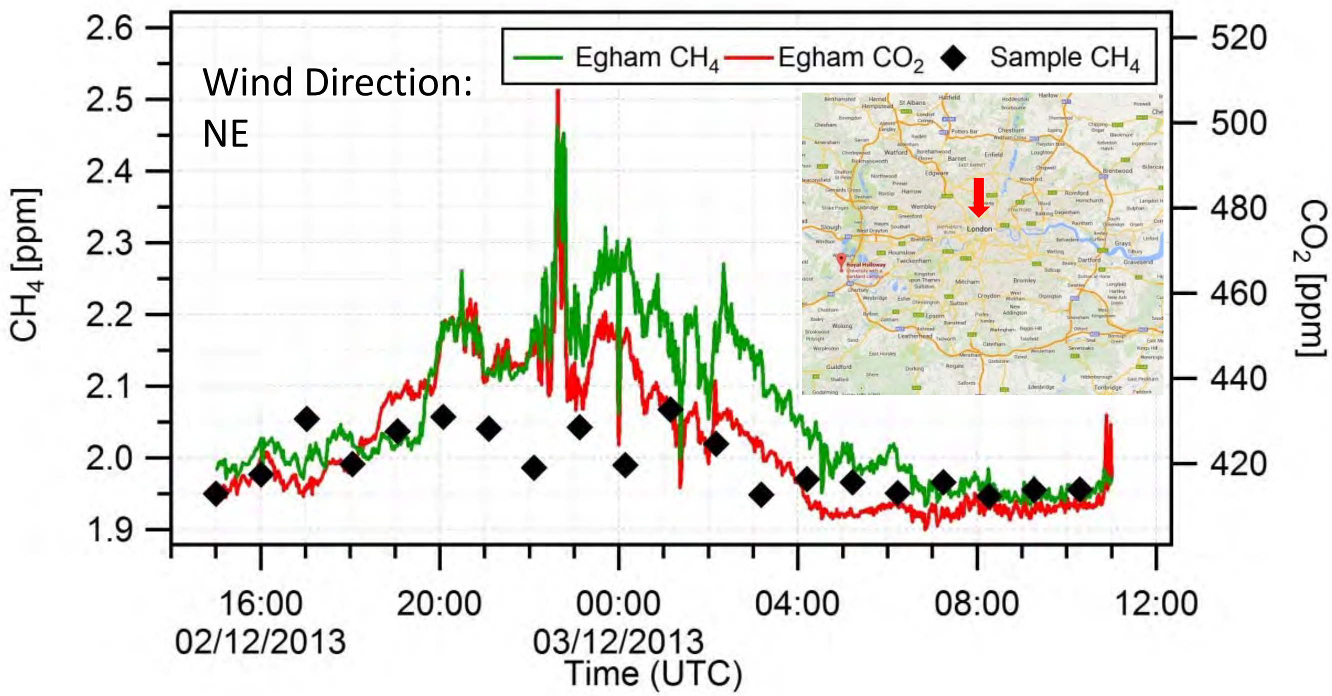
UK Sewage Works Isotopic Signature: a complicated case

3 sources:

- **biological treatment**
- **biogas releases from the anaerobic digesters**
- **releases of uncombusted biogas from the power station**



Source mix in central London
Diurnal Studies



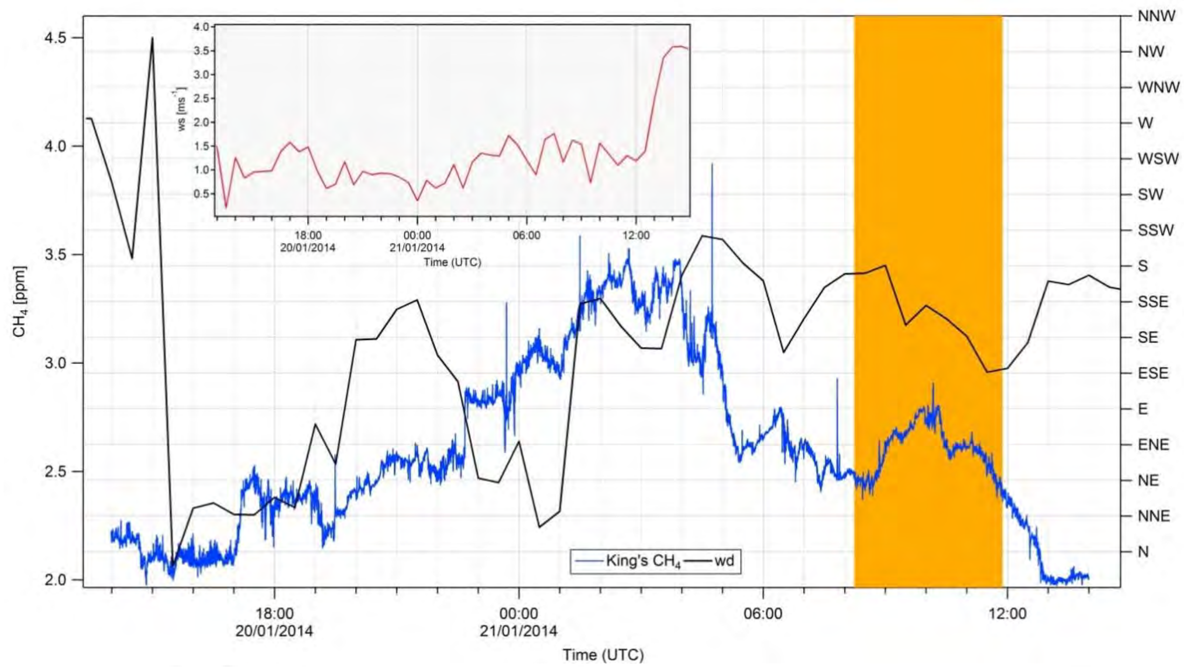
Source mix in central London

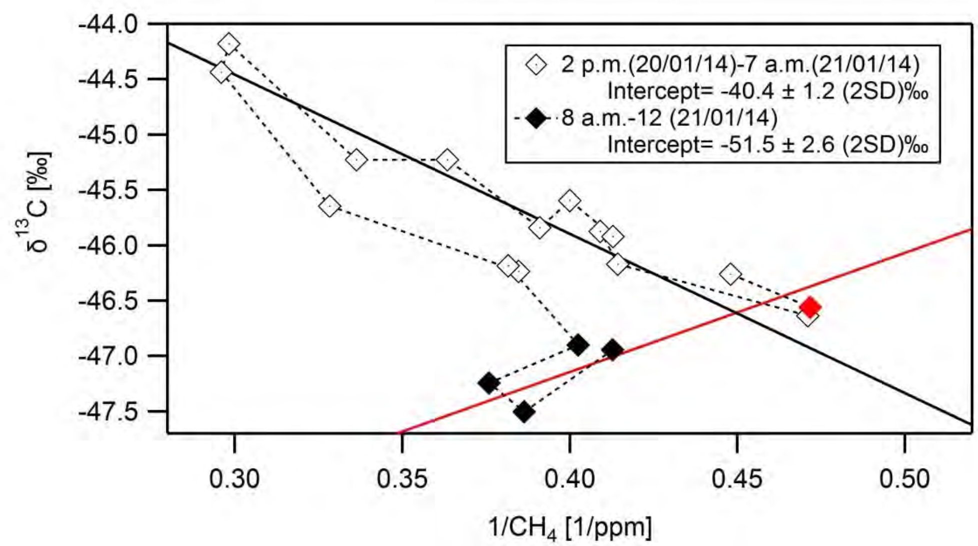
Diurnal Studies

20-21/01/14

- A ^{13}C enriched signature of -40‰ for air sampled between 2 p.m. and 7 a.m. revealed a mainly fossil CH_4 contribution to CH_4 emissions

- The morning build-up is characterised by a $\delta^{13}C$ signature related to a biogenic source: this is a *recurrent pattern*

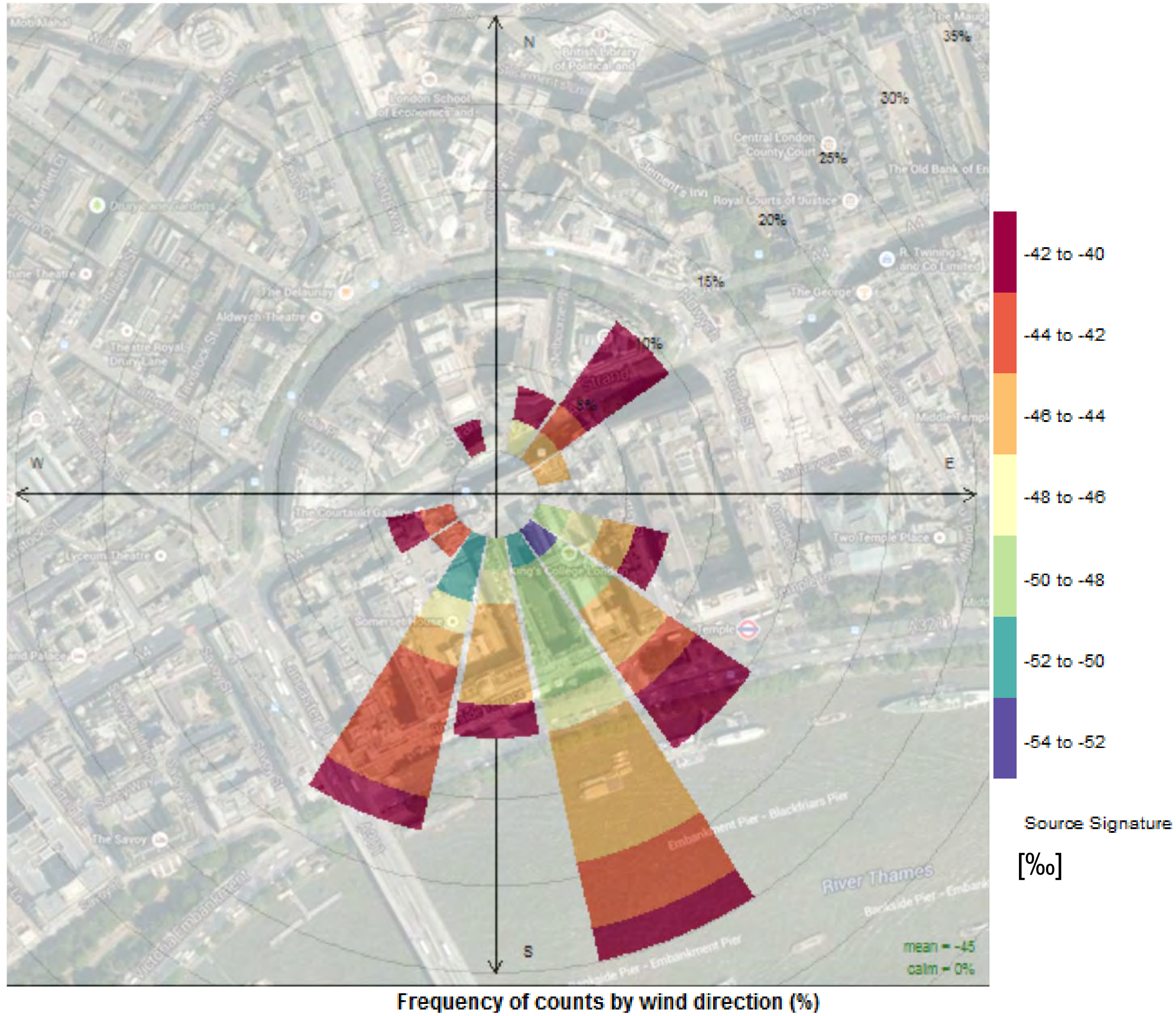




Source mix in central London

Diurnal Studies

- Source Signature Rose based on samples with concentrations 10% over background
- Lighter isotopic source signatures from the SE Sector
- Methane emissions from the Thames River?

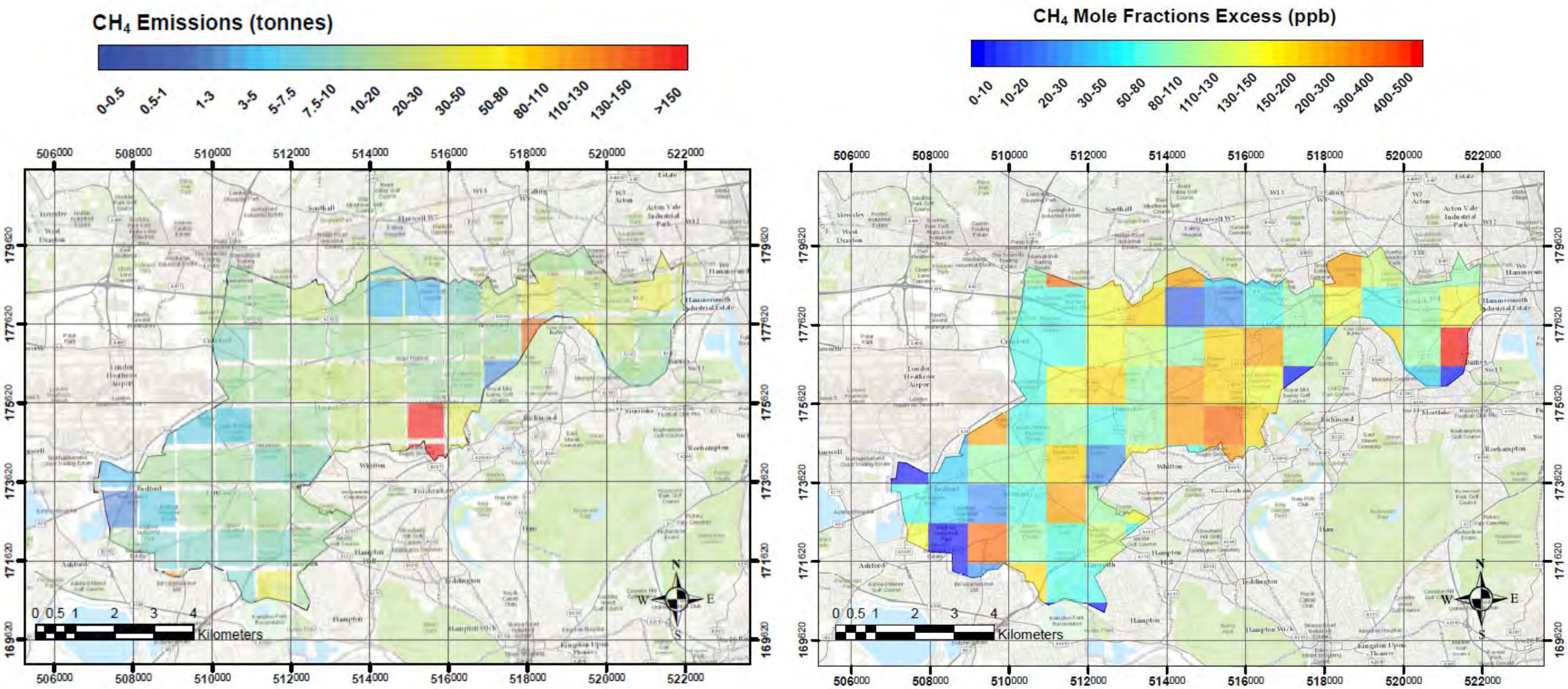


UK $\delta^{13}C$-CH_4 signatures revised

Methane Source	$\delta^{13}C$-CH_4 signatures
Natural Gas	-36 ± 2 (2SD) ‰
Anthracite coal mines	-30 ± 3 (2SD) ‰
Bituminous coal mines	-51 ± 3 (2SD) ‰
Welsh opencast mines	-41± 1 (2SD) ‰
Sewage works: anaerobic digesters	-51 ± 1 (2SD) ‰
Sewage works: secondary treatment	-59 ± 1 (2SD) ‰
Sewage works: power station	-48 ± 1 (2SD) ‰
Landfill sites	-58 ± 3 (2SD) ‰
Enteric fermentation	-66 ± 3 (2SD) ‰

Final source isotopic signatures revised in this study (Zazzeri et al., 2015)

Verification of local methane sources



Inventories Hotspots: Mogden Sewage Works and old landfill sites

Mobile Measurements: high mole fractions downwind of Mogden and gas leaks

The inclusion of gas leaks in inventories would change the emissions figure

Key Notes

- By driving with the Picarro Mobile Instrument , methane plumes can be identified and transected . The subsequent isotopic analysis of bag samples allows the isotopic signature of methane sources to be defined.

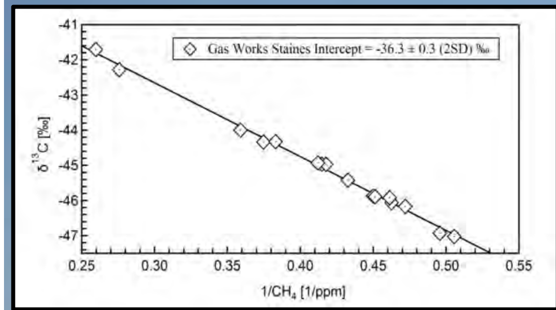
- The survey of methane sources can focus on a specific region, obtaining more precise isotopic values to be used in regional models.

- In areas with multiple sources different source inputs can be distinguished, such as sewage works and urban areas.

- Location of hotspots and source apportioning suggested by inventories can be verified.

ARADAY GIVING HIS CARD TO FATHER THAMES

And we hope the Dirty Fellow will consult the learned Professor.



Giulia.Zazzeri.2011@live.rhul.ac.uk

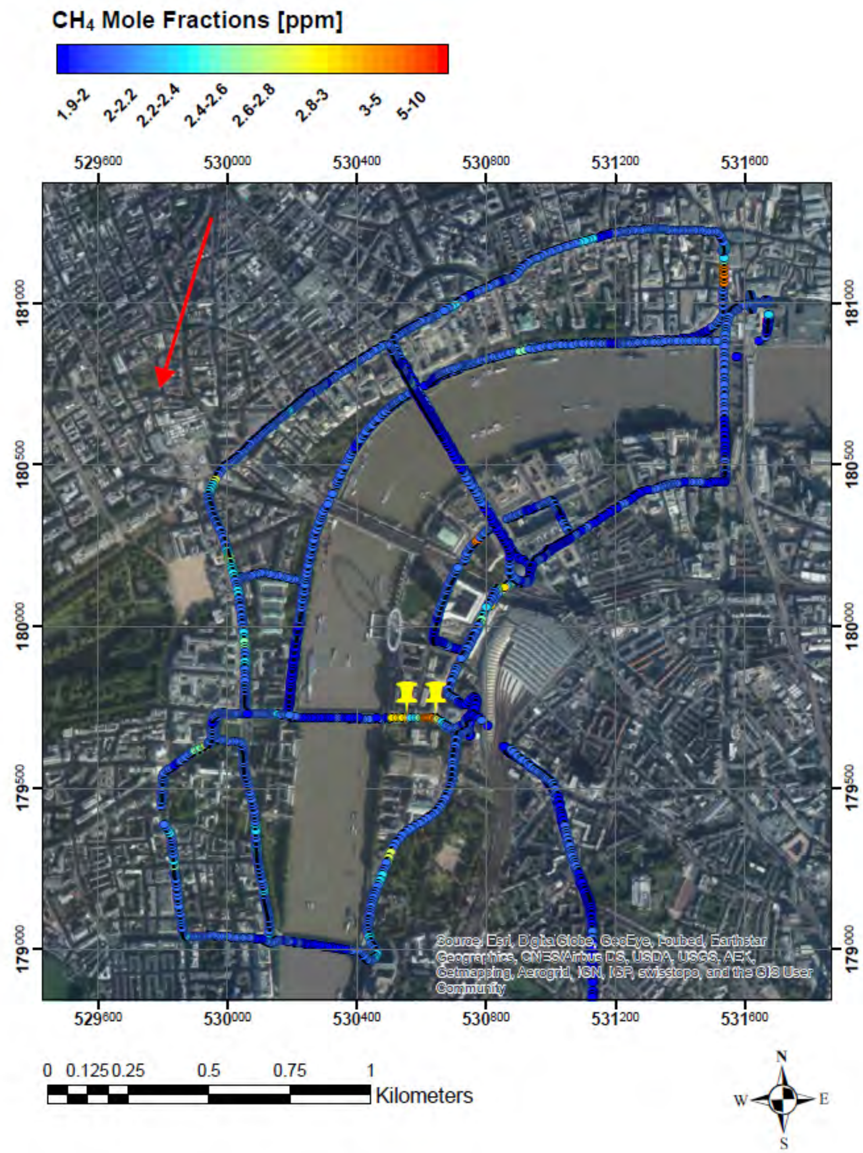
References:

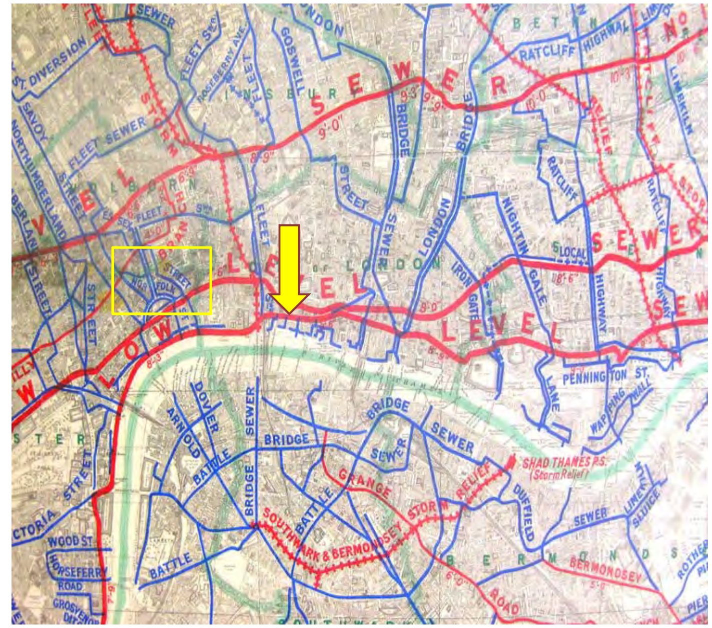
Zazzeri, G., Lowry, D., Fisher, R.E., France, J.L., Lanoisellé, M. and Nisbet, E.G. (2015) Plume mapping and isotopic characterisation of anthropogenic methane sources, Atmos. Environ., 110,151-162.

Royal Holloway mucking out

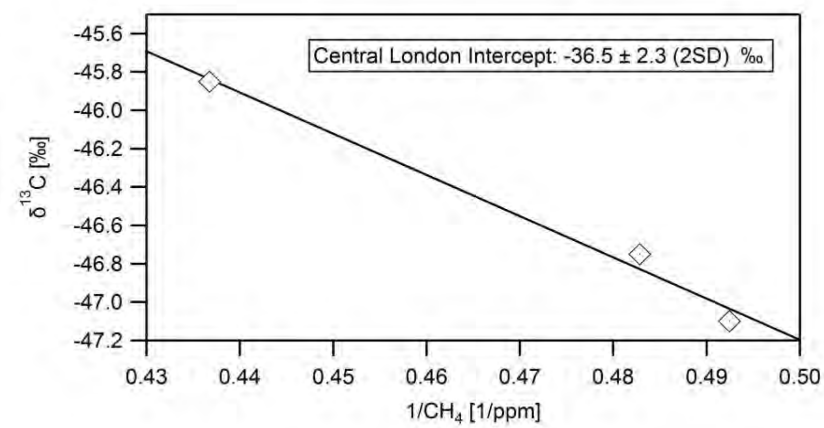
Source mix in central London

Biological source



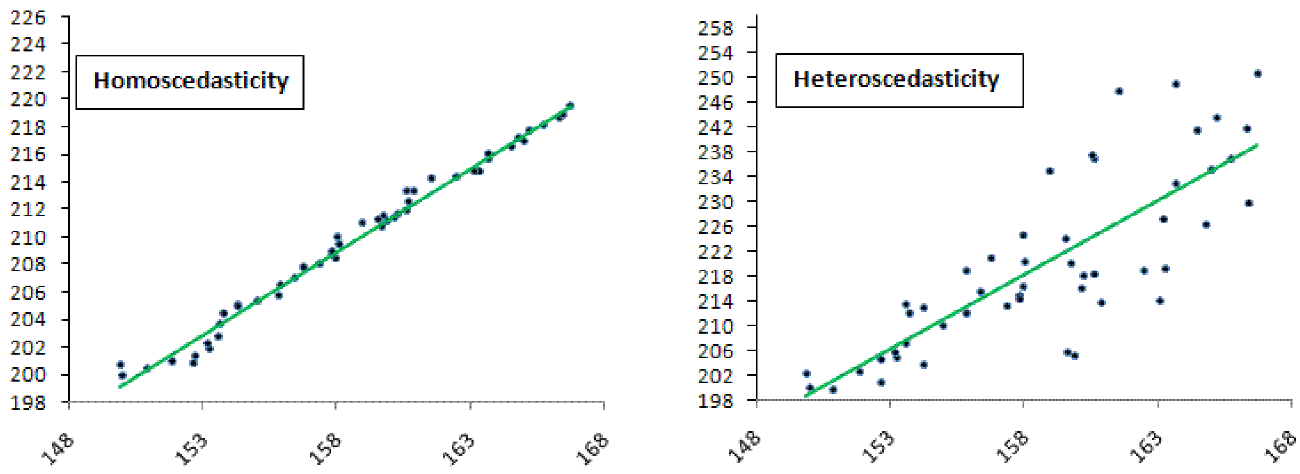


Sewer Network of City of London (planned by Joseph Bazalgette) and Bankside map (1950s)
Blue: main sewers
Red: intercepting ones which the main sewers connect to
Red crossed: storm relief drains (buried rivers which flow straight to the rivers)



Error calculation

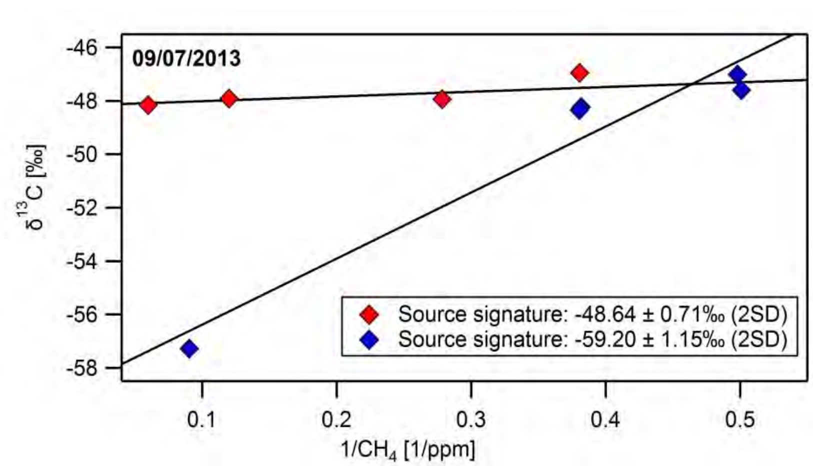
- No Ordinary Least Squared (OLS) method is applied, which assumes errors are confined to the dependant variable
- Both variables are measured with errors and are affected by heteroscedasticity (the error of one variable changes across the range of a second variable that predicts it)



- BCES (Bivariate Correlated Errors and intrinsic Scatter) estimator (Akritas et al., 1996) that accounts for correlated errors between the two variable. It is a well suited approach for computing the slope and the intercept of the Keeling Plot

Sewage Works Isotopic Signature: a complicated case

Fermentative processes: -65 to -50 ‰ (Whiticar et al., 1986)



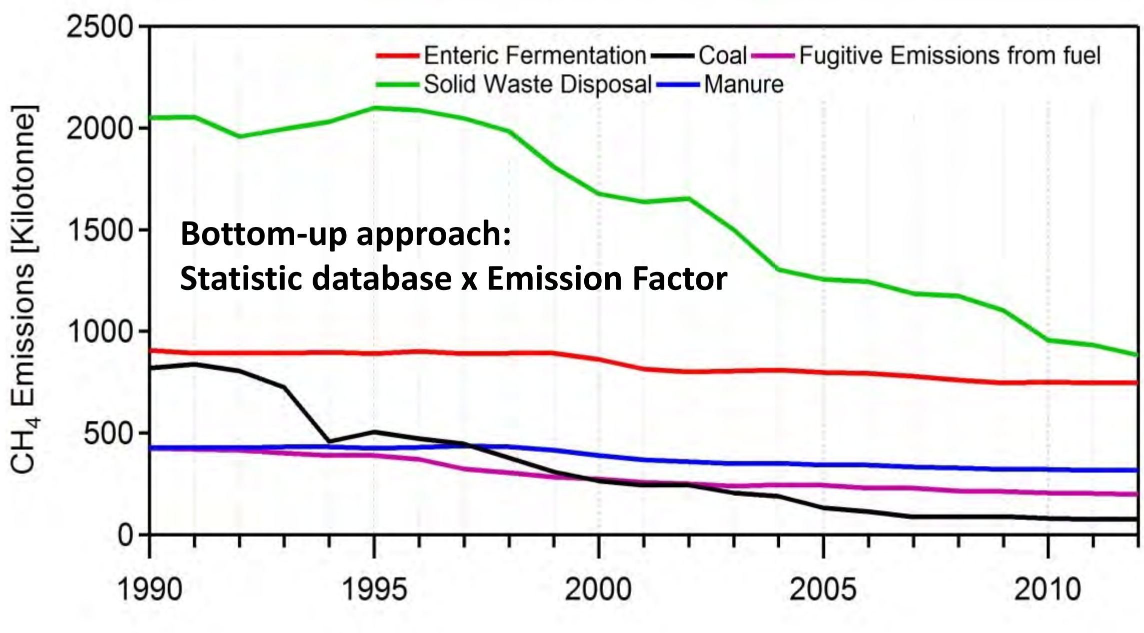
The importance of knowing methane sources

- Second most important greenhouse gas in terms of its contribution to global warming potential
- Compared to CO_2 short life time (~ 9 years) in the atmosphere
- Inventories are affected by high uncertainty

"Cutting emissions without verification is like dieting without weighing yourself"

(R. Weiss)

Gas Species	Contribution	Residence Time
CO_2	61 %	120-150 yrs
CH_4	15%	9-10 yrs
CFCs	11 %	60-120 yrs
N_2O	4 %	170 yrs



UK Methane Inventories 1990-2012 (UK National Atmospheric Emissions Inventories website)