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Abstract: Methane stable isotope analysis, coupled with mole fraction measurement, has been used to link isotopic signature to methane emissions from landfill sites, coal mines and gas leaks in the United Kingdom. A mobile Picarro G2301 CRDS (Cavity Ring-Down Spectroscopy) analyser was installed on a vehicle, together with an anemometer and GPS receiver, to measure atmospheric methane mole fractions and their relative location while driving at speeds up to 80 kph. In targeted areas, when the methane plume was intercepted, air samples were collected in Tedlar bags, for δ^{13}C-CH4 isotopic analysis by CF-GC-IRMS (Continuous Flow Gas Chromatography-Isotopic Ratio Mass Spectroscopy). This method provides high precision isotopic values, determining δ^{13}C-CH4 to ± 0.05 per mil. The bulk signature of the methane plume into the atmosphere from the whole source area was obtained by Keeling plot analysis, and a δ^{13}C-CH4 signature, with the relative uncertainty, allocated to each methane source investigated. Both landfill and natural gas emissions in SE England have tightly constrained isotopic signatures. The averaged δ^{13}C-CH4 for landfill sites is -58 ± 3 ‰. The δ^{13}C-CH4 signature for gas leaks is also fairly constant around -36 ± 2 ‰, a value characteristic of homogenised North Sea supply. In contrast, signatures for coal mines in N. England and Wales fall in a range of -51.2 ± 0.3 ‰ to -30.9 ± 1.4 ‰, but can be tightly constrained by region. The study demonstrates that CRDS-based mobile methane measurement coupled with off-line high precision isotopic analysis of plume samples is an efficient way of characterising methane sources. It shows that isotopic measurements allow type identification, and possible location of previously unknown methane sources. In modelling studies this measurement provides an independent constraint to determine the contributions of different sources to the regional methane budget and in the verification of inventory source distribution.

Cover Letter

6/03/2015

Dear editor,

Hereby we resubmit our paper “Plume mapping and isotopic characterisation of anthropogenic methane sources” for publication in Atmospheric Environment.

We have appreciated the thoughtful comments of the two reviewers, and we have modified our manuscript to accommodate and answer the questions. In the response to reviewers we indicate point-by-point how we have accommodated their comments.

We hope you will find this revised version acceptable for publication.

With best regards, on behalf of all co-authors,

Giulia Zazzeri

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Yours sincerely,

Giulia Zazzeri, PhD student.

We thank the referees for their positive comments. We have made changes accordingly following their suggests, and we have clarified the points that were raised in the detailed comments below.

Reviewer #1:

L9: 'again' means reader already knows methane trend, I suggest to explain a bit further. Also in the introduction I'd recall the global CH4 cycle terms, and quantify the relative contribution of landfill, gas leaks and coal mines.

Thank you for the suggestion. We explained the global CH_4 trend and relative source contributions in a little more depth in the introduction.

Fig 1: what are the 5x5 big squares? seems resolution is 5 km and only in some areas it has been down-scaled?

For methane sources like landfills and sewage works the exact location within the site of the emissions are highly uncertain. Therefore, due to this inherent uncertainty, the NAEI methane emissions inventory only resolves the solid and wastewater sectors to 5x5 km, as fixing them to a 1 km^2 grid might be erroneous. However, inventory data are provided at 1km^2 resolution, and this explains why there are those big emission squares, which represent mainly landfill sites.

L110-113: why not taking natural gas from houses gas taps, instead of going to intersect a plume at far away gas storage facilities? would it work?

Measuring the isotopic signature of natural gas both from the gas tap in our geochemistry laboratory and in distant storage facilities allowed us to find an isotopic signature that was representative at a regional scale and that could be used in a regional model. Furthermore, the study is a test of how small a plume we can distinguish isotopically by Keeling plot analysis and the reason for multiple transects at further distances downwind of the source.

L153: did you always have a road perpendicular to the wind direction?

No, they were not always perpendicular as shown by the Greatness Quarry example, but the wind direction was checked before every measurement campaign and the sampling locations for the day were chosen accordingly, as we needed to be sure that the downwind area of the site was accessible. As we were not measuring fluxes we didn’t need the shape of the plume to show a Gaussian distribution.

L398: [42] is not about airborne measurements.

Thank you for spotting this. We have changed it.

Fig. 9 could use same graphics as Fig. 1, also more effective.

Thanks for the suggestion. We used the original Google Earth output in Figure 9 because it highlights the peaks in methane concentration and it shows that peaks were observed approximately at the same location by driving back and forth for few times along the same downwind transect through the emission plume.

Reviewer #2:

Minor Comments

1.- Further information on the Picarro parameters, including those related to the operating range (e.g., measuring interval and rise/fall time) should be inserted on page 6, first paragraph.

Thank you for the suggestion. We inserted more details about Picarro parameters.

2.- Section 3.1. I have several questions and recommendations:

** Why did the authors select the Mucking and Greatness Quarry landfills for presentation of the results? The reason for this choice should be added.*

Is should be pointed out here that some of the sites cannot be covered in more detail because they were measured on site and there is operator and emissions anonymity. Of the remaining sites with public access Mucking and Greatness Quarry are presented in more detail because the samples collected around those locations had the greatest concentration and isotopic range for Keeling plot analysis. Indeed, the two resulting Keeling plots show the best fitting lines and represent very good examples of source signature calculation. We added a sentence to explain that in the revised manuscript. A more detailed paper on landfill methane, including the use of isotopes in understanding methane oxidation, will follow.

** The maximum as well as range of methane concentrations measured at each landfill site should be inserted in an additional column of Table 1. Comments on the comparison results found at each landfill site should also be added in this section.*

Thanks for your indication. Concentration ranges were not included since each landfill site was surveyed following a different procedure, depending on observed meteorology, and from

different distances downwind, so as to make the range or maximum concentration recorded meaningless in relation to emissions. Methane concentrations were measured directly on site when the landfill area was accessible (but we have restricted use of the data). In other cases the methane plumes were transected by driving along roads at different distances from the emitting area. If methane emissions from a landfill site are high but are detected far away, methane concentrations recorded are only a few ppb above the background. However, thanks to high precision isotopic measurements, isotopic signatures of source plumes can be determined at near background atmospheric mole fractions. As the aim of this study is the isotopic characterisation of methane areas and not the quantification of emissions, we thought that including concentrations in the table could be misleading.

A proper comparison, including a thorough characterisation of landfill sites, will be provided in a further publication. However, following your suggestion, we have included an explanation for the variability of the results and the range of excess over background recorded by the study.

** The text and Figures presented in the paper only refer to the two above landfills mentioned. I strongly believe that, at least, a new column showing the number of samples collected at each landfill should be included in Table I.*

Thanks for the suggestion. We included a new column with the number of Tedlar bag samples collected.

3.- Section 3.2. I only found the depth of the Thoresby coal mine. Please include the depth of the Aberpergwm and Unity coal mines.

Thank you for the suggestion. Unfortunately the depth of the Aberpergwm and Unity coal mines could not be retrieved in any documentation available. We will search for that more carefully.

4.- Page 20, lines 330-333. A reference related to the average values measured in the Lab of the Earth Sciences Department should be included. The same is applicable to the comments written on page 21, lines 360-362.

The isotopic values that you mention were measured in the RHUL laboratory as part of my PhD study and both averages are the results of tests and samplings that I personally carried out for my thesis work. I still have to submit my thesis and I cannot include a reference for those values. Values from the same gas supply were published by Lowry et al. (2001), but the

isotopic signature of the gas supplied to SE England has changed significantly over the last 15 years and these are not representative of the current supply.

5.- Page 2, line 51. The reference Lowry et al. (5) written in the manuscript in not number 5 but 28 in the references presented.

Thank you for spotting this. We have changed it.

Plume mapping and isotopic characterisation of anthropogenic methane sources

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Abstract

Methane stable isotope analysis, coupled with mole fraction measurement, has been used to link isotopic signature to methane emissions from landfill sites, coal mines and gas leaks in the United Kingdom. A mobile Picarro G2301 CRDS (Cavity Ring-Down Spectroscopy) analyser was installed on a vehicle, together with an anemometer and GPS receiver, to measure atmospheric methane mole fractions and their relative location while driving at speeds up to 80 kph. In targeted areas, when the methane plume was intercepted, air samples were collected in Tedlar bags, for δ^{13}C-CH_4 isotopic analysis by CF-GC-IRMS (Continuous Flow Gas Chromatography-Isotopic Ratio Mass Spectroscopy). This method provides high precision isotopic values, determining δ^{13}C-CH_4 to ± 0.05 per mil.

The bulk signature of the methane plume into the atmosphere from the whole source area was obtained by Keeling plot analysis, and a δ^{13}C-CH_4 signature, with the relative uncertainty, allocated to each methane source investigated. Both landfill and natural gas emissions in SE England have tightly constrained isotopic signatures. The averaged δ^{13}C-CH_4 for landfill sites is -58 ± 3 ‰. The δ^{13}C-CH_4 signature for gas leaks is also fairly constant around -36 ± 2 ‰, a value characteristic of homogenised North Sea supply. In contrast, signatures for coal mines in N. England and Wales fall in a range of -51.2 ± 0.3 ‰ to -30.9 ± 1.4 ‰, but can be tightly constrained by region.

The study demonstrates that CRDS-based mobile methane measurement coupled with off-line high precision isotopic analysis of plume samples is an efficient way of characterising methane sources. It shows that isotopic measurements allow type identification, and possible location of previously unknown methane sources. In modelling studies this measurement provides an independent constraint to determine the contributions of different sources to the regional methane budget and in the verification of inventory source distribution.

1 Introduction

After a steady increase of atmospheric methane in the 1980's and a stabilisation of the global levels between 1999 and 2006, methane concentrations have risen again (Nisbet et al., 2014) with implications for related climate change (Stocker, 2013), but the source contribution to the renewed growth rate is still under debate (Kirschke et al., 2013). Globally, over 60% of total CH_4 emissions come from human activities, with 22% of emissions from the energy sector and 10% from the waste sector (Dlugokencky et al., 2011). Conurbations such as London emit methane through leaks in the natural gas network, losses from heating systems and other combustion sources, and landfill emissions, which are all highly responsive to achievable control measures. With stricter regulations for landfills and improved maintenance on the gas network, UK national inventories (Webb, 2014) suggest that methane emissions from the waste and natural gas sectors declined throughout the 1990-2012 period. Semi-rural areas around London also contribute. Agriculture is the dominant

methane-emitting sector in the UK, accounting for 44 % of total methane emissions in 2012 according to inventories. Emissions from coal mining decreased sharply with the decline of the industry after 1993 and accounted for only 3 % of all methane emissions in 2012 (Webb, 2014).

Methane inventories are compiled from statistical databases (e.g. number of cows, volume of gas used, etc. multiplied by pre-defined emission factors). This "bottom-up" approach may produce precise but highly inaccurate estimates, since databases might be incomplete and not updated, and some emission factors can be poorly established and may differ greatly among countries. Therefore, although UK national inventories suggest that methane emissions for waste, gas transmission and coal mining sectors have decreased since 1990 (Webb, 2014), the reduction trend must be verified by independent measurements. Direct atmospheric (or "top-down") verification of emission inventories has been carried out (Lowry et al., 2001).

In this study methane stable isotope analyses, coupled with mole fraction measurements, have been employed to assess proportionate contributions of the main methane sources in SE England. The source of specific methane emissions can be identified by analysing the methane isotopic composition, as different source types are characterised clearly by distinct ^{13}C signatures. Biogenic methane is ^{13}C depleted ($\delta^{13}C$ = - 50 to -70 ‰), compared to pyrogenic methane derived from incomplete combustion ($\delta^{13}C$ = - 15 to -30 ‰) and fossil methane of thermogenic origin ($\delta^{13}C \approx$ -40 ‰) (e.g. Lassey et al., 2011). Thus, the proportion of each source category within a source mix can be estimated and the actual contribution of each methane source in the atmospheric methane budget constrained. Several studies attest the value of the isotopic analysis as a tool for categorising methane sources and in verifying inventories (Levin et al., 1999; Lowry et al., 2001; Fisher et al., 2006; Townsend-Small et al., 2012). For this purpose, ^{13}C signatures of the methane sources that are listed in the UK inventories need to be defined accurately.

Isotopic data ($\delta^{13}C_{CH_4}$) are used in modelling to constrain the contributions of different methane sources in the mass balance of atmospheric methane at a global and regional scale (Quay et al., 1991; Mikaloff Fletcher et al., 2004; Bousquet et al., 2006). However, the input values vary from model to model and the errors on these values are very large at the global scale. Quay et al. (1991) report a $\delta^{13}C_{CH_4}$ range between -46 and -56 ‰ for landfills. For coal, values of -35 and -37 ‰ are suggested, whereas the isotopic signature for natural gas is thought to vary from -40 to -44 ‰ (Mikaloff Fletcher et al., 2004; Bousquet et al., 2006; Monteil et al., 2011). Errors can be narrowed down considerably when the focus is on a regional scale, as this study will prove.

This study aims to identify areas of high anthropogenic methane mole fractions in the UK and link them to specific identifiable sources, using isotopic characterisation. While there have been many previous studies of ^{13}C in methane, most are based on small scale processes and few have been on UK sources (Stahl, 1977; Deines, 1980; Chung et al., 1988; Hitchman et al., 1990; Bergamaschi et al., 1998; Levin et al., 1999; Whiticar, 1999; Lowry et al., 2001; Klevenhusen et al., 2010). Lowry at al. (2001) studied isotopic characterisation of specific methane peaks measured during diurnal air campaigns at the Royal Holloway site, on the western fringe of London, showing that peaks are derived either from natural gas leaks ($\delta^{13}C$ -33 ‰ to -35 ‰) or waste treatment emissions ($\delta^{13}C$ -51 ‰ to -53 ‰). Nevertheless, the isotopic characteristics of sources may vary

over time and season, such as for landfill sites, where the reliance on methane oxidation by topsoil and gas flaring has been largely replaced by gas extraction systems, and for natural gas because of different gas source provider countries. Therefore isotopic values need to be regularly reassessed.

Sampling campaigns were focused on the targeted sources. A mobile greenhouse gas analyser (see section 2.3) was installed on board a vehicle to allow measurement of atmospheric methane mole fractions while driving. A similar setup has been tested already by other studies to measure methane emissions at large spatial scales (Farrell et al., 2013) and to map methane leaks from a gas network (Phillips et al., 2013; Eapi et al., 2014). This work validates the use of the instrumentation for locating methane-emitting areas, as a tool to direct the sample collection for calculating the bulk isotopic signature of the methane released into the atmosphere.

2 Methods

The isotopic composition of methane sources from a 100 m to km-scale spatial area, such as landfills and open-cut coal mines, needs to be evaluated by assessing integrated emissions from the whole source site. Measurements of methane mole fractions downwind and upwind of the site enable a qualitative estimate of the source in terms of its importance in the atmospheric methane budget. Once the location has been identified as a source of methane emissions, the methane isotopic analysis of air samples collected downwind across the source plume allows assignment of a specific $\delta^{13}C$ signature to the source in question.

Each source investigation required a dedicated sampling campaign. By utilising the mobile gas analyser, various potential source sites were investigated on the same day, driving on public roads around the target area and collecting samples whenever relatively high mole fractions were measured. The mobile gas analyser was also used to detect the locations of gas leaks in a similar way to Phillips et al. (2013). Methane plumes and spikes are easily measured, and the subsequent isotopic analysis of the air sampled reveals the origin of these ‘unexpected’ methane peaks of local origin.

2.1 Identification of methane sources

The National Atmospheric Emission Inventory (NAEI) website (http://naei.defra.gov.uk/) makes available total methane emissions per km^2 per year and is updated annually with some time delay. Emissions for 2009 for the London region and surrounding boroughs have been mapped using the ArcGIS software. The resulting emission map (Figure 1), where each square represents one km^2, offers a picture of the methane emissions distribution in the London area and was used to focus measurement campaigns. Red squares represent high emission areas. These are sited mainly outside and on the margins of the London conurbation, whereas central London emissions are uniformly in the range of 50-100 tonnes / km^2 / yr. Hotspots were located and identified as first targets for the measurement campaigns from the map. Their exploration allows the consistency of the emissions data to be verified and has uncovered many discrepancies.

Figure 1

2.2 Sampling Locations

The 2013 and 2014 monitoring campaigns aimed to characterise isotopically the most important UK anthropogenic methane sources in terms of tonnes of methane emitted, with a focus on London conurbation and SE England. Landfills, coal mines and natural gas are the three source categories that have been assessed in this study (Figure 2). All downwind plumes measured at these sources were at sub-regulatory levels.

Figure 2

The landfill sites studied are all located within 70 km of London, whereas the evaluation of the coal mining isotopic signature required an extension of the survey beyond the London area, to include South Yorkshire, Nottinghamshire, Warwickshire and South Wales. A more detailed study of the isotopic signatures from UK coal mines is in preparation. The isotopic signature of natural gas supplied to SE England has been identified by sampling methane plumes downwind of the British Gas gas storage facility in Staines and downwind of Bacton, on the Norfolk coast, where pipelines bring all southern and much northern North Sea Norwegian gas onshore, as well as gas from the interconnector pipeline to Belgium.

2.3 Methodology and Material

2.3.1 Picarro Mobile System

The greenhouse gas monitoring system utilised in the monitoring campaigns consists of a mobile Picarro G2301 CRDS (Cavity Ring-Down Spectroscopy) analyser, which provides a new measurement of carbon dioxide (CO_2) and methane (CH_4) mole fractions in ppm and water vapour in % every 5 seconds, with a rise and fall time between high and low concentrations that is 90% accurate in less than 3 seconds. The mobile module (A0941) consists of a pump, control systems for a Climatronics sonic anemometer and a Hemisphere GPS receiver. Two air inlets, plus the GPS and sonic anemometer are attached to a mast above the roof of the vehicle at 2.2 m above the ground. Three fully charged 12 V, 110 Ah lead-acid batteries allow the instrument to run for up to 9 hours. The airline is ¼" outer diameter and 1.83 m length Nylon tube with the inlet end blocked and a series of 2mm diameter holes drilled into the first 30 cm to allow ingress of air (air inlet 1 on Figure 3) (Picarro, 2012). This is pumped to the mobile module through a 2 µm Swagelok filter, where the flow splits allowing approximately 300 cc/min to flow through the Picarro, and the rest of the air to vent. This greatly reduces the lag time between air entering the inlet and the measurement allowing successful surveying of small plumes at a vehicle speed of up to 50 km/hr, and large plumes at up to 80 km/hr on first pass. The second air inlet is another ¼" O.D. Nylon tube (air inlet 2 in Figure 3a) connected to a battery operated diaphragm pump (KNF Neuberger) used to collect plume and background air samples for later isotopic analysis in the RHUL (Royal Holloway University of London) laboratory. The pump fills a 5L Tedlar air sample bag in 30 seconds.

Figure 3

The system is controlled by a laptop, so that continuous measurement of CO_2 and CH_4 mole fractions can be observed by the passenger during travel. Communication between the laptop and

the Picarro mobile is by WiFi connection to a 3G or 4G system. Both CH_4 and CO_2 mole fractions can be displayed in real time on Google Earth, allowing the gas plumes to be geospatially visualised on site. The time delay between the instantaneous GPS location and the display of Picarro mole fractions has been calculated as approximately 7 seconds by measuring the time lag of the CO_2 peak arrival after blowing into the inlet tube.

The Picarro 2301 instrument was calibrated in the RHUL greenhouse gas laboratory before each survey against two National Oceanic and Atmospheric Administration (NOAA) calibrated air samples, with a resulting precision for CH_4 better than ±0.3 ppb at mole fractions ranging from 1840 and 1975 ppb and accuracies of better than ±1 ppb. A target gas has been analysed using the Picarro instrument while driving in order to test the stability of measurement during motion, with a precision of 0.3 ppb (1 σ) over 2 minutes of analysis.

The sites of interest were studied by driving downwind and visualising the mole fractions on Google Earth in real time. At some points plumes could be bisected perpendicular to the wind direction, allowing the Gaussian shape to be mapped. Changes in wind direction and speed affect the plume dispersion; methane peaks might also change position and intensity from one pass to the next downwind of the same methane source. However, the current study is not aimed at calculating fluxes or accurately pinning down the location of small gas leaks, but at proportioning source inputs via the isotopic signatures of the sources. A strict accuracy of source position is also not required for large spatial sources such as landfills and open-cut coal mines where methane plumes can be easily transected.

Once the methane plume was identified, 5L Tedlar bags were filled as close to the plume centre as possible and at the edges of the plume. When the road traffic conditions allowed, air bags were collected along the plume transect by stopping the vehicle whenever above-background methane mole fractions were observed. When sampling was on a major road and the vehicle could not be stopped, and when the methane mole fraction was not steady during the sampling at a given point (due to a high variability of the wind direction or obstructions between the source and the road), samples were collected while driving, at a speed of 48 km/hr (30 mph), giving an integrated sample over a distance of up to 400 m.

Figure 4

Figure 4 demonstrates an example view of data as seen on Google Earth during sampling. The mole fraction data were re-plotted during post-analysis using ArcGIS software, utilising satellite images of the sites as base maps to give a clearer spatial representation of the data.

2.3.2 Sample Analysis

The CH_4 mole fraction data representation along the route provided information on the actual plume extent, whereas the methane source characteristics were investigated by the isotopic analysis of the samples collected. CH_4 mole fractions of the air samples in Tedlar bags were measured independently in the laboratory with a Picarro G1301 CRDS analyser. Each sample was analysed for 3 minutes, with an average precision of ±0.5 ppb. The carbon isotopic ratio ($\delta^{13}C$) was measured in triplicate to high precision (+/- 0.05 ‰) by continuous flow gas chromatography isotope ratio

mass spectrometry (CF GC-IRMS) (Fisher et al., 2006). This ratio is expressed in δ notation from the following equation:

$$\delta=(R_A/R_{std}-1)\times 1000 \quad \textbf{(Eq 1)}$$

where R_A denotes the isotopic ratio in CO_2 derived by combustion of the methane sample ($^{13}C/^{12}C$) and R_{std} is the corresponding ratio in the CO_2 reference gas which is calibrated to the V-PDB scale for $\delta^{13}C$ using international standards. The isotopic ratio is expressed as per mil (‰).

2.3.3 Keeling Plot approach

The signature of each methane source (or mixture of sources in an urban conurbation) was characterised using the Keeling plot method (Keeling, 1958). According to this approach, $\delta^{13}C$ values must be plotted against the inverse of mole fraction data to calculate the isotopic signature of the methane source responsible for the excess over background. Following the Keeling plot procedure, one isotopic signature (with calculated error to allow for some variability of source methane production pathways) was assigned to every methane source explored.

Keeling Plot and the regression analysis

The atmospheric mixing ratio (mole fraction) of a gas ($\mathbf{c_a}$) in the lower boundary layer results from the combination of the background atmospheric mole fraction ($\mathbf{c_b}$) and the mole fraction of the gas added by the source ($\mathbf{c_s}$) (Pataki et al., 2003):

$$\boldsymbol{c_a = c_b + c_s} \quad \textbf{(Eq 2)}$$

By assuming the conservation of mass, the $\delta^{13}C$ signature of the source input to atmosphere can be calculated as follows:

$$\delta^{13}C_a = \boldsymbol{c_b}\,(\delta^{13}C_b - \delta^{13}C_s)\cdot 1/\boldsymbol{c_a} + \delta^{13}C_s \quad \textbf{(Eq 3)}$$

$\delta^{13}C_a$ and $1/\mathbf{c_a}$ values are respectively the y and the x values of a best-fit line, whose intercept (at $1/\mathbf{c_a} = 0$) is the isotopic value at which the methane mole fraction tends to infinity. This is interpreted as the isotope signature of the methane source responsible for the excess over background.

A linear regression of data must be performed in order to compute the line slope and intercept. However, the estimate of the line parameters might be biased if an ordinary least squared (OLS) method is applied (as in many spreadsheets), which assumes errors are confined to the dependent variable (Leng et al., 2007). For our sources, both variables are measured with errors and another regression model must be implemented. Moreover, our measurements are affected by heteroscedasticity, where the error of a variable changes across the range of values of a second variable that predicts it (Berry and Feldman, 1985). Errors may increase as the value of the independent variable ($1/[CH_4]$) is decreasing, as higher mole fractions are measured with higher standard deviations. Although there are several fitting models that allow for errors in the independent variable (Sokal and Rohlf, 1995), e.g. orthogonal distance regression and geometric mean regression (recommended by Pataki (2003)), few models accommodate for heteroscedastic

measurement errors. If a typical OLS approach, intended to minimize $\sum e_i^2$, is applied in case of heteroscedasticity, the calculation of the regression line would give greater emphasis to the extreme values (with greater errors), which are conversely less precise and, hence, contain less information.

Akritas et al. (1996) introduced the BCES estimators procedure (for Bivariate Correlated Errors and intrinsic Scatter). This statistical procedure, designed to overcome the heteroscedasticity case, accounts for correlated errors between the two variables and allows for the magnitude of measurement errors to be dependent on the measurements. These features make the BCES approach well suited for computing the slope and the intercept of the Keeling plot. Therefore the BCES regression program, available to download (http://www.astro.wisc.edu/~mab/archive/stats/stats.html), has been used to find the Keeling plot intercept with the relative uncertainty, and so the $\delta^{13}C$ value of the methane source. This technique results in a much more robust calculation of source signature but will only give very tightly constrained ‰ errors when the precision of both mole fraction and isotopic measurements are very high and the $\delta^{13}C$ of the source signature is homogenous across the plume (i.e. single source).

3 Results

3.1 Landfill sites

The widest plumes and highest recorded mole fractions of methane were from landfill sites, both still active and recently closed, as suggested by the UK national inventories. The excess methane over background recorded off site ranged from 0.1 ppm to 15 ppm.

Table 1

Isotopic signatures observed for all the landfill studied (Table 1) span a range from -60.2 ± 1.4 to -55.2 ± 0.6 ‰, with an averaged value of -58.0 ± 3 (2SD) ‰. Wapsey's Wood was surveyed twice, in July and April, and the identified isotopic signature was consistent. The isotopic variability among sites depends upon several parameters such as waste composition, temperature and the level of methane oxidation performed by methanotrophic bacteria in the top-soil cover (Liptay et al., 1998).

The two landfill sites presented herein, Mucking and Greatness Quarry, were carefully surveyed thanks to the accessibility of public roads downwind of the sites, obtaining a wide range of mole fraction values for Keeling plot analysis.

Although it was closed in 2012, Mucking landfill (Figure 5a) is still emitting a large amount of methane: the maximum mole fraction recorded in the measured part of the plume was approximately 17 ppm. With wind from the SSW it was possible to intersect the plume on 4 transects at different distances from the NNE side of the landfill and 11 samples were collected, covering a wide range of mole fractions, ideal for precise Keeling plot analysis.

The intercept of the Keeling plot based on all the samples collected in the vicinity of the landfill is -56.1 ± 0.5‰ (2SD) (Figure 6a).

Greatness Quarry (Figure 5b) is an active landfill site to the north of the town of Sevenoaks, which was surveyed on the 24th of October 2013. A methane plume was intercepted along the NW

side of the landfill and 8 samples were collected for isotopic analysis. An averaged isotopic signature for the plume of -57.4 ± 0.5 ‰ (2SD) resulted from Keeling plot analysis of samples (Figure 6b).

Figure 5

Figure 6

These two landfill sites, taken as representative examples of UK landfills, show a similar isotopic signature, although Mucking landfill was closed in 2012, while the Greatness Quarry is still active.

3.2 Coal Mines

Table 2

Thoresby colliery in Nottinghamshire is one of the deep mines investigated for this study. It is one of the UK's largest coal mines but scheduled for closure in 2015. Mining is currently taking place at about 650 m underground. Although methane is drained off for 2.8 MWe electrical power generation (Holloway et al., 2005), mole fraction levels up to 4.6 ppm were observed in the downwind plume. As Figure 7a shows, the methane plume was transected three times and 9 samples were collected. The resulting Keeling plot intercept is -51.2 ± 0.3 ‰ (2SD).

Aberpergwm and Unity deep coal mines in Wales (Figure 7b), which closed in December 2012 and in October 2013 respectively, were investigated on 17th October 2013. Mole fraction peaks of 6 ppm were observed downwind of both deep mines. The Keeling plots based on the samples collected near these deep mines give an isotopic source signature of -33.3 ± 1.8 ‰ for Aberpergwm and -30.9 ± 1.4 ‰ for the Unity colliery, both highly ^{13}C-enriched relative to Thoresby colliery (Figure 8).

Figure 7

Figure 8

The coal exploited in Thoresby colliery, as in all deep English coal mines, is bituminous coal (Hill, 2001), whereas collieries in the north-west coalfield area of Wales exploit pure anthracite (Alderton et al., 2004). The characterisation of methane released from different coal types suggests a link between enrichment in the ^{13}C content of methane emitted to atmosphere with progression of coal rank as previously alluded to by Chung and Sackett (1979). This hypothesis will be tested by further study of coalfield composition for comparison with plumes sampled at other UK coal mines.

3.3 Natural Gas signature

Table 3

Staines and Bacton (Figure 2 for the location) have been chosen as sampling sites for assessing the isotopic signature of natural gas. A 1.2 km path was surveyed on the south (downwind side) of the Staines storage facility and 16 samples were collected for isotopic analysis with mole fractions ranging from 1.98 to 3.85 ppm. The Keeling plot for the whole transect (Figure 11a) shows a constant origin for the methane of -36.3 ± 0.3 ‰ that is consistent with a dominantly thermogenic North Sea gas source (Lowry et al., 2001). It suggests that there are other leaks in the gas

distribution system along with the storage tank ("gasometer") that is located in the middle of the transect (Figure 9).

Figure 9

Mole fractions up to 24 ppm were recorded in the plume downwind of Bacton and 19 air samples were collected for isotopic analysis. An isotopic signature of -35.7 ± 1.2 ‰ was observed (Figure 11b), which is consistent with the isotopic value that has been ascribed to Staines gas works.

Figure 10

Figure 11

The intercept values of -36.3 ± 0.3 ‰ and -35.7 ± 1.2 ‰ are both in good agreement with the averaged value of -37.3 ± 0.9 ‰ (2SD) obtained by collecting monthly samples of natural gas in the geochemistry lab of the Earth Sciences Department at RHUL and measuring their isotopic signatures.

4 Discussion and Conclusions

This study focuses on the isotopic characterisation of methane emission plumes from major UK anthropogenic methane sources. Landfill sites, coal mines and gas leaks have been surveyed and sampled using a mobile system based around the Picarro G2301 instrument. A $\delta^{13}C$ signature has been allocated to each methane source that has been investigated by the isotopic analysis of samples collected at each site. The $\delta^{13}C$ signatures for landfill sites span a range between -60.2 ± 1.4 ‰ (2SD) and - 55.2 ± 0.6 ‰ (2SD), whereas signatures for coal mines fall within a range of -51.2 ± 0.3 ‰ (2SD) to -30.9 ± 1.4 ‰ (2SD). The ^{13}C signature for gas leaks is found to be fairly constant around -36 ± 2 ‰ (2SD).

Detailed exploration of an area the size of a landfill or open-cut coal mine in its entire extent, measuring gas mole fractions, fluxes and isotopic signatures in order to estimate its contribution in terms of methane emissions, requires time consuming and labour-intensive procedures (e.g. flux chamber technique). Several previous studies have investigated isotopic signatures of methane emissions from landfills using flux chambers to capture methane fluxes from the soil and collect air samples (Liptay et al., 1998; Chanton and Liptay, 2000). In order to ensure a representative area is covered, many chambers need to be arranged across the site, often highlighting the large spatial variability of the ^{13}C signature measured. Isotopic signatures of landfill emissions from covered areas have been shown to differ from uncapped active tipping areas, due to the oxidation mediated by methanotrophic bacteria in the cover soil (Bergamaschi et al., 1998). Bergamaschi et al. (1998) obtained values highly enriched (-45.9 ± 8 ‰) in covered areas relative to those observed in uncovered areas (-55.1 ± 5.2 ‰).

When the methane plume downwind of a landfill is intercepted and analysed, the overall signature of the methane released into the atmosphere from the whole site can be estimated, which is the number needed at a minimum of regional level for atmospheric inversion models. The isotopic signatures of methane emissions from SE England landfills do not show great variability and a value of -58 ‰ could be safely used as model input for the whole of UK CH_4 emissions from

active or recently closed landfills. Emissions from old landfills that predate gas extraction will likely account for a small proportion of emissions that are more enriched in $\delta^{13}C$ toward -50 ‰. As methane emissions from landfills can isotopically change over time, following enhanced landfill management schemes (e.g. gas extraction), systematic measurements of ^{13}C signatures of methane emissions need to be carried out in order to provide up-to-date and more representative values.

The isotopic range for coal is found to be relatively wide, compared to those assigned to landfill and natural gas emissions. Many factors are involved and might explain the variety of isotopic values measured, such as the depth of coal seams and coal rank. Preliminary results suggest a ^{13}C enrichment of methane with progression of rank, which needs to be confirmed with further sampling campaigns with the Picarro mobile system around other UK coal mines.

The $\delta^{13}C$ range for the natural gas source has been constrained to a value of -36 ‰, which represents the isotopic signature of the natural gas supplied to the whole of SE England. Natural gas samples from Holland and Italy were analysed at RHUL, giving values of -29.5 ± 0.09 ‰ (2SD) and -46.7 ± 0.09 ‰ (2SD) respectively. In the NW European Atlas report (Lokhorst, 1997), carbon isotope ratios between -33 and -36 ‰ for the Carboniferous reservoir gas in the North Sea and between -30 and -24 ‰ for the Rotliegend strata in the southern North Sea are indicated. The natural gas supply from western Siberia has been measured near source, and in St. Petersburg by the RHUL group and in Heidelberg by Levin et al. (1999) and is characterised by an isotopic signature of approximately -50 ‰. The isotopic value of the natural gas supply to SW London has changed little in recent years, being close to -34‰ over the 1998-99 period (Lowry et al., 2001) and close to -36‰ since at least 2002, and the new data show that this figure can be applied to emissions from a much larger region of England.

By using the Picarro mobile system, the survey of methane sources can be focused on a specific region or country, obtaining more precise isotopic values to be used in regional models. Furthermore, the isotopic precision of +/- 0.05 ‰ achieved by CF GC-IRMS on collected samples is significantly better than current laser-based isotopic measurement systems, such as the CRDS analyser, which is within 1 ‰ for $\delta^{13}C$ of CH_4 (Phillips et al., 2013) operating under similar conditions of mobile measurement. This means that precise isotopic signatures of source plumes can be determined at near background atmospheric mole fractions (50 ppb excess CH_4 for a 20 ‰ difference between source and background air isotopic signatures, 100 ppb for 10 ‰ difference, 200 ppb for 5 ‰).

In areas with multiple sources, such as urban conurbations, where leaks in the natural gas supply pipes can occur near landfill sites and sewage works, high precision isotopic measurements allow different potential sources to be carefully distinguished. Due to the mixed nature of methane sources and their temporal variability, the evaluation of methane fluxes in urban environments involves numerous observations and measurement techniques, including the eddy covariance method (Gioli et al., 2012), techniques based on a mass balance approach (Zimnoch et al., 2010) and airborne measurements allowing a large surface footprint (O'shea et al., 2014). The estimated methane fluxes are then linked to methane sources using inventory data. The high uncertainty

affecting inventories is therefore propagated to the source partitioning, whereas isotopic measurements provide an independent constraint on source proportions.

To conclude, the Picarro mobile methane measurement system, coupled with the isotope analysis of sampled methane emissions by high precision CF GC-IRMS, is an efficient way of locating and precisely identifying methane emissions by source, since it enables a large spatial coverage and rapid location of downwind plumes in the survey of methane source areas. The instantaneous display of methane mole fractions during the survey allows the methane plume extent to be directly visualized and sample collection to be carefully directed. The technique can be further applied to detect small leaks from gas pipelines and fugitive emissions from alternative methane sources. Therefore this system can be widely employed and has the potential to help in the reduction of methane emissions in a cost effective manner.

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List of captions

Figure 1 London Region emission map derived from 1 km^2 methane emission data for 2009 from the NAEI website . Red squares represent high emission areas. These are sited mainly outside and on the margins of the London conurbation, whereas central London emissions are uniformly in the range of 50-100 tonnes / km^2 / yr.

Figure 2 Map of the sites surveyed for this study. White diamonds represent the landfill sites studied. Black diamonds indicate Bacton, on the Norfolk coast, and the gas storage facility in Staines, on the west side of London region. White pentagons represent coal mines.

Figure 3 a) Schematic set up of the RHUL Picarro mobile measurement system and all the physical connections b) Picarro Mobile c) vehicle used in the sampling campaigns.

Figure 4 Google Earth view of methane plumes detected around Mucking landfill location on 14th October 2013. The maximum mole fractions are labelled for each source plume measured.

Figure 5 ArcGIS plot of methane mole fractions in ppm recorded on 14th October 2013 around Mucking landfill site (a) and on 24th October 2013 around Greatness Quarry landfill site (b). The grid coordinates are displayed in the British National Coordinate System. The red arrow represents the wind direction.

Figure 6 Keeling plot based on the samples collected around Mucking landfill site (a) and around Greatness Quarry landfill site (b). Error bars are not shown as they are smaller than displayed symbols.

Figure 7 ArcGIS plot of methane mole fractions in ppm recorded on 22nd November 2013 around Thoresby Colliery (a) and on 17th October 2013 around Aberpergwm and Unity deep mines in Wales (b). The grid coordinates are displayed in the British National Coordinate System. The red arrow represents the wind direction. Stars represent the coal mine locations.

Figure 8 Keeling plots based on samples collected downwind of two deep mines in Wales (Aberpergwm and Unity coal mines) on 17th October 2013 and the Thoresby Colliery on 22nd November 2013. Error bars are not shown as they are smaller than displayed symbols.

Figure 9 Sample locations (yellow markers) and mole fraction peaks measured downwind of gas works in Staines (3 km ENE of RHUL) on 11th April 2014. 16 samples were collected for isotopic analysis, with mole fractions ranging from 1.98 to 3.85 ppm.

Figure 10 ArcGIS plot of methane mole fractions in ppm recorded on 30th of April 2014 around Bacton gas terminals. The grid coordinates are displayed in the British National Coordinate System. The red arrow represents the wind direction.

Figure 11 Keeling plot based on samples collected downwind of gas works in Staines on 11th April 2014 (a) and downwind of gas terminals in Bacton on 30th April 2014 (b). Error bars are not shown as they are smaller than displayed symbols.

Table 1 Landfill surveyed with the calculated δ^{13}C signature. Errors are calculated as 2 standard deviations. An averaged value of -58.0 ± 3 (2SD) ‰ was calculated.

Table 2 Collieries discussed in the text and δ^{13}C signatures of methane plumes sampled. Errors in the ^{13}C signature are calculated as 2 standard deviations.

Table 3 Gas installations discussed in the text and δ^{13}C signatures of methane plumes sampled. Errors in the ^{13}C signature are calculated as 2 standard deviations.

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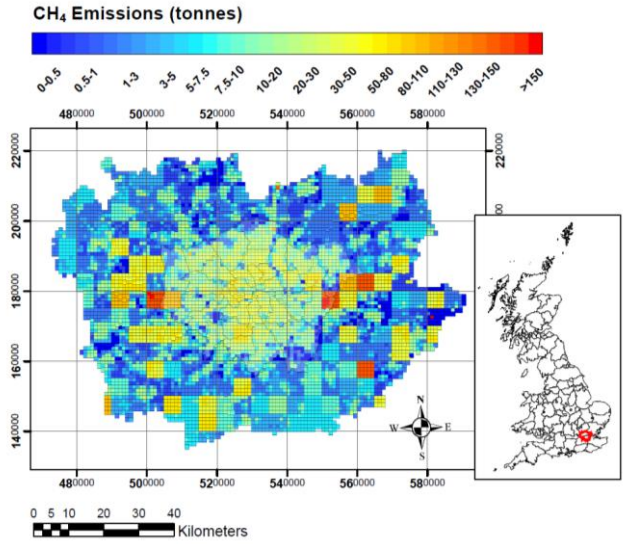

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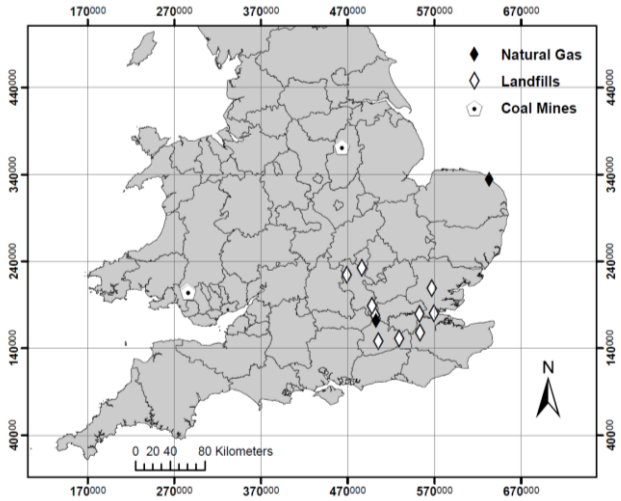


Figure 2

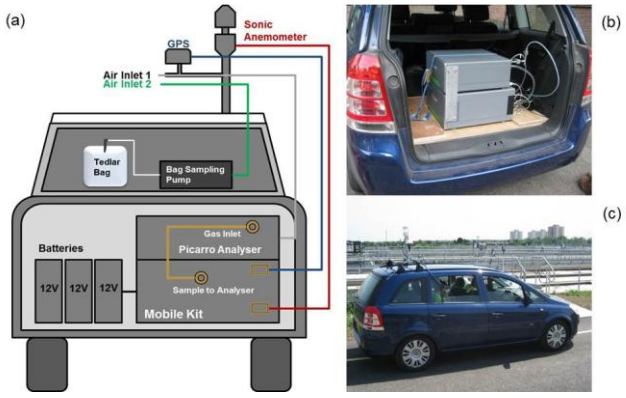


Figure 3

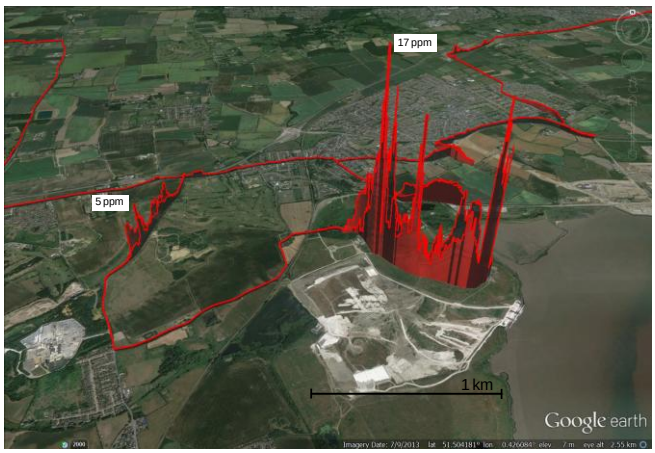
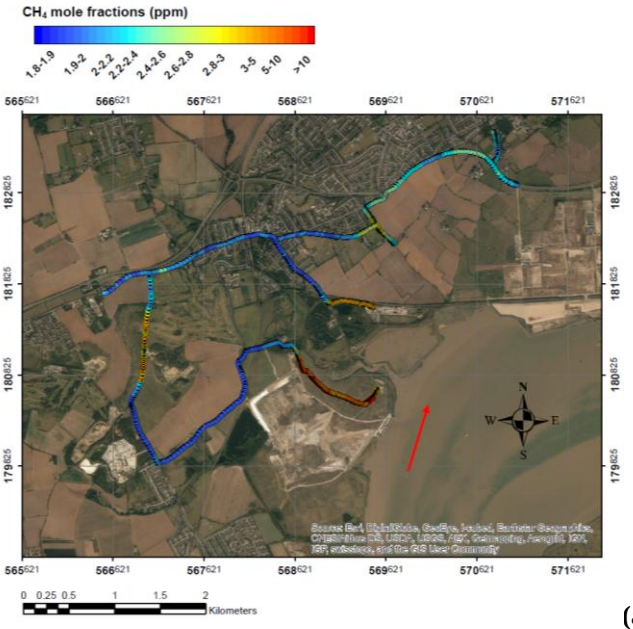
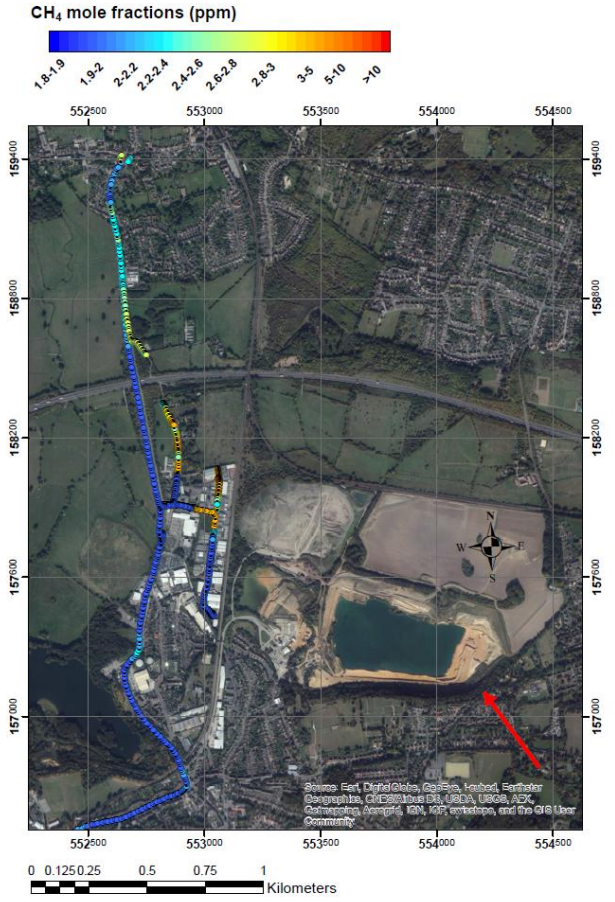


Figure 4



553 **(a)**



(b)

Figure 5

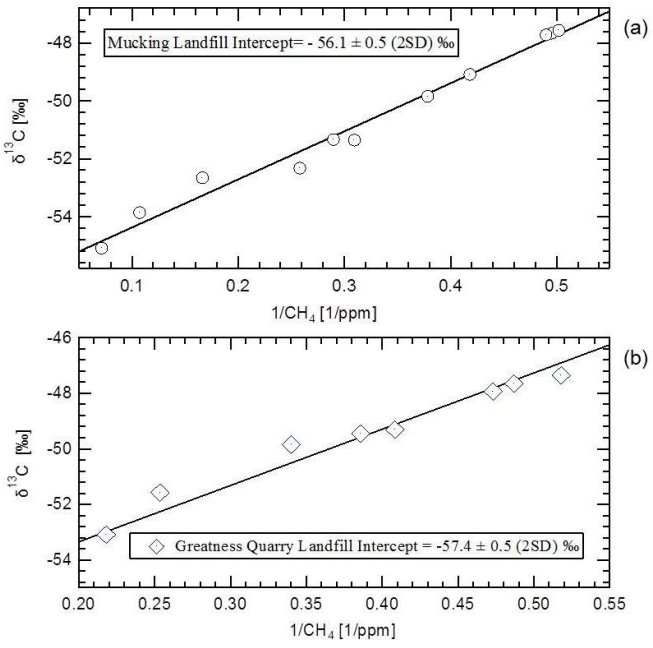
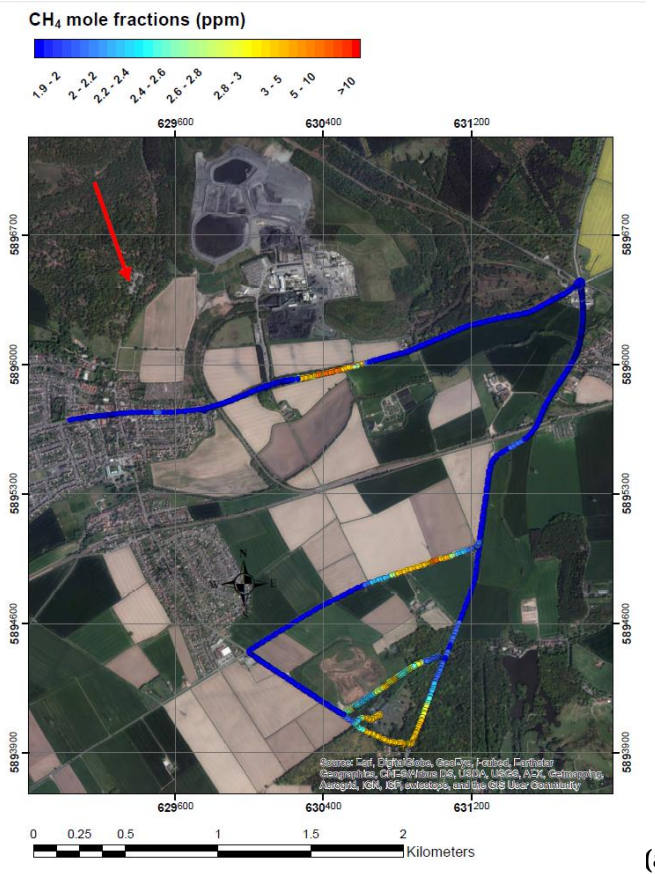
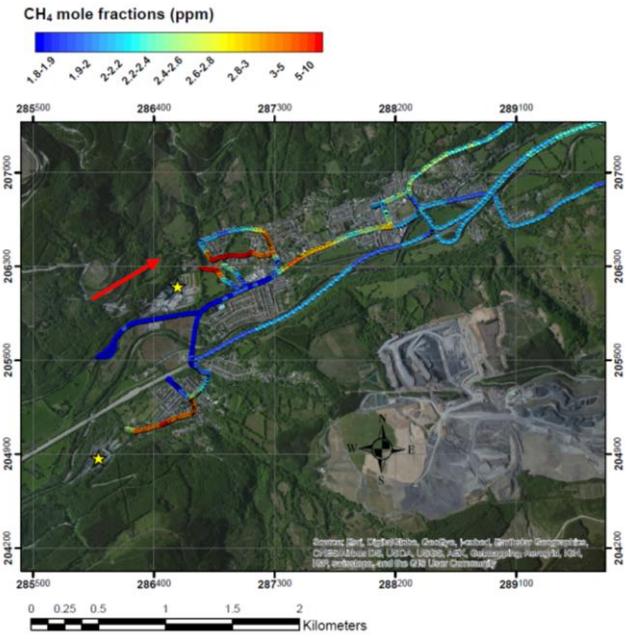


Figure 6


CH4 mole fractions (ppm)
1.9 - 2
2 - 2.2
2.2 - 2.4
2.4 - 2.6
2.6 - 2.8
2.8 - 3
3 - 5
5 - 10
>10
629600
630400
631200
589700
589600
589300
589400
589900
0
0.25
0.5
1
1.5
2
Kilometers

(a)


CH4 mole fractions (ppm)
1.8-1.9
1.9-2
2-2.2
2.2-2.4
2.4-2.6
2.6-2.8
2.8-3
3-5
5-10
285500
286400
287300
288200
289100
207000
206300
205600
204900
204200
0
0.25
0.5
1
1.5
2
Kilometers

(b)

Figure 7

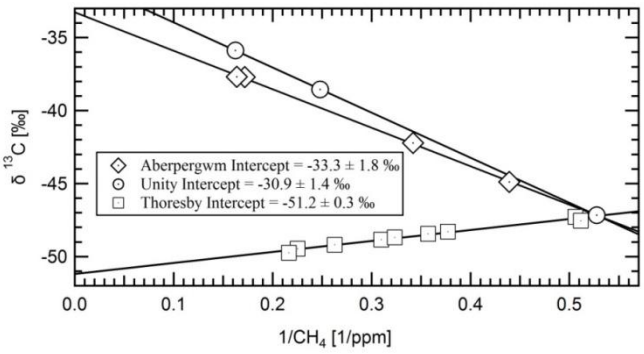


Figure 8

Figure 9

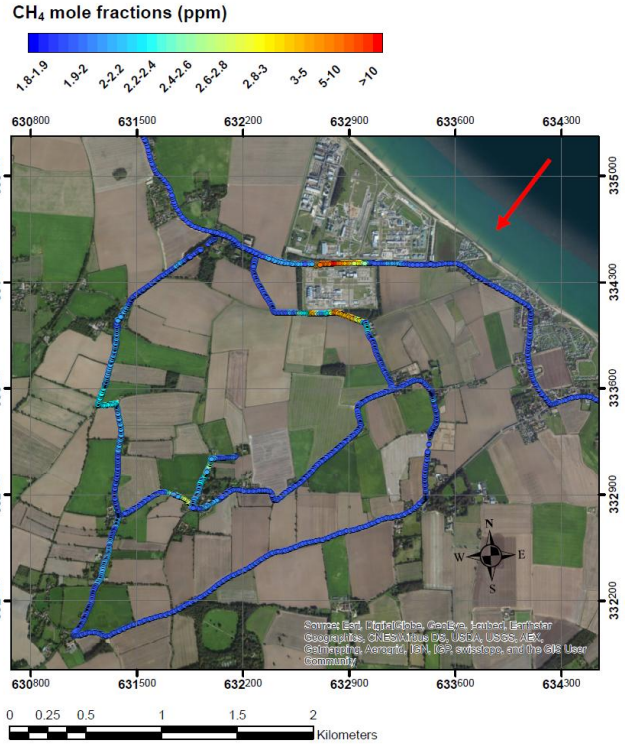


Figure 10

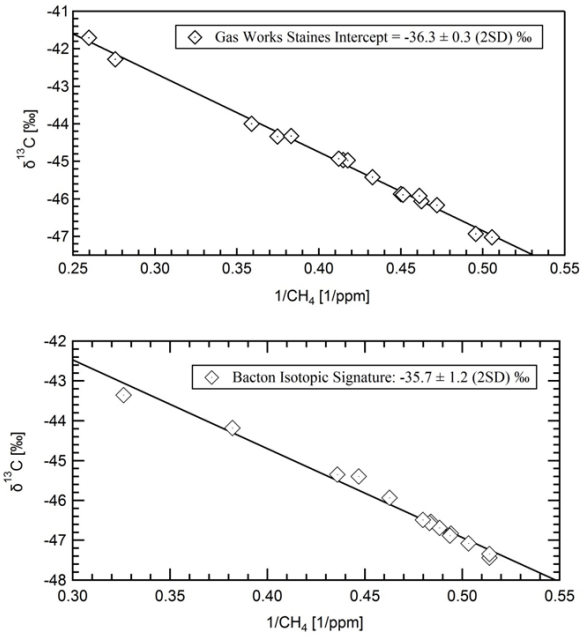


Figure 11

Landfill	*Current Status*	*Sampling Date*	*Number of samples collected*	*$\delta^{13}C$ Signature (‰)*
Albury	Active	Oct-13	4	-59.7 ± 1.1
Bletchley	Active	Mar-13	26	-58.8 ± 0.5
Calvert	Active	Mar-13	28	-58.5 ± 0.6
Colnbrook	Closed (2012)	Jul-13	6	-60.2 ± 1.4
Greatness Quarry	Active	Oct-13	8	-57.4 ± 0.5
Mucking	Closed (2011)	Oct-13	11	-56.1 ± 0.5
Redhill	Active	Oct-13	5	-59.6 ± 0.7
Roxwell	Active	Oct-13	5	-55.2 ± 0.6
Wapsey's Wood	Active	Jul-13	5	-57.6 ± 0.7
		Apr-14	6	-57.3 ± 1.6

554 **Table 1**

Colliery	*Current Status*	*Sampling Date*	*Number of samples collected*	*$\delta^{13}C$ signature (‰)*
Thoresby	Active	11/2013	9	-51.2 ± 0.3
Aberpergwm	Closed (2012)	10/2013	4	-33.3 ± 1.8
Unity	Closed (2008)	10/2013	3	-30.9 ± 1.4

555 **Table 2**

Gas Installation	*Current Status*	*Sampling Date*	*Number of samples collected*	*$\delta^{13}C$ signature (‰)*
Staines	Closed (2014)	04/2014	16	-36.3 ± 0.3
Bacton	Active	04/2014	14	-35.7 ± 1.2

556 **Table 3**

***Highlights (for review)**

- CH_4 source plumes were located by a mobile Picarro analyser
- CH_4 plumes from landfill sites, coal mines and gas leaks were sampled
- High precision isotopic analysis of air samples collected was carried out
- CH_4 isotopic signatures were allocated to CH_4 sources in UK
- The method provides an independent constraint to determine CH_4 sources contribution