MEMO^2: MEthane goes MObile – MEasurements and MOdelling

Publications on the use of isotopes for CH_4 source attribution in urban / industrial regions

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1. Executive Summary

Methane has many anthropogenic sources and in rural areas it is often easy to identify the source of an emission plume as a farm or a landfill site. In urban areas and industrial complexes there may be multiple sources within the same 1 x 1 km grid square. Many of these may not be obviously visible, such as leaks from gas or wastewater pipes. Additionally, emission plumes from these may merge to form single larger plumes, particularly under atmospheric inversion conditions.

Deliverable 2.3 focused on urban emissions and in conjunction with UN CCAC (United nations Climate and Clean Air Coalition) projects has facilitated detailed city surveys in many of the partner countries. These included London, Birmingham and Swansea in the UK, Utrecht in Holland, Hamburg and Heidelberg in Germany, Paris in France, and through the UN CCAC ROMEO project, Bucharest in Romania.

These surveys were performed as part of WP1, but when major source emission plumes were encountered the air was sampled for subsequent isotopic analysis at the laboratories of IMAU, Utrecht and RHUL, Egham. Newly available isotopic CRDS (laser-based) instruments were used in the mobile campaigns in Paris and Heidelberg, and in addition samples were collected for laboratory analysis to calibrate the CRDS measurements.

These isotopic measurements are an integral part of publications about the city surveys. A paper on Utrecht and Hamburg is already published, one on Paris has been reviewed, one on Krakow is submitted, one on Bucharest will be submitted soon, and others on London and Heidelberg are in preparation. Surveys in Hamburg, London, Paris and Utrecht suggest that 60-90% of the fugitive methane emissions are from leaking natural gas infrastructure, with the remainder from waste sources. The Bucharest survey suggests that up to 60% of the emissions could come from wastewater pipelines, with the remainder from gas infrastructure.

2. Introduction

2.1 Background

Methane has many anthropogenic sources and in rural areas it is often easy to identify the source of an emission plume as a farm or a landfill site. In urban and industrial complexes there may be multiple sources in small areas. Many of these may not be obviously visible, such as leaks from gas or wastewater pipes. Additionally, emission plumes from these may merge to form single larger plumes, particularly under atmospheric inversion conditions. Isotopes provide a good way to distinguish between different sources of methane. In some environments the ratio of $^{13}C/^{12}C$ ($\delta^{13}C$) provides the best discrimination, in others it is the $^{2}H/^{1}H$ (δD) ratio. Where possible measurement of both of these ratios on each sample is carried out.

2.2 Scope of the deliverable

As part of the MEMO² project the two participating laboratories at UU and RHUL can measure the carbon isotopes of methane ($\delta^{13}C$) to high precision (better than ±0.1 ‰) by isotope-ratio mass spectrometry. UU measures (δD) also, to precision of better than ±2 ‰). RHUL is currently setting up a procedure to measure δD and has preliminary data for a small number of UK sources. Student secondments at UU resulted in selected δD measurements for most of the city campaigns. All methane plumes that were sampled and analyzed by both groups and those supplied by other groups in the project were provided to the project database (D2.2) and subsequently used to characterize individual sources and source categories. The data has been evaluated for many European cities and forms part of many papers, some already published or in press and others in the process of being written.

3. Content

This task has been significantly aided by additional funding from UN CCAC to study fossil fuel infrastructure emissions in cities, and using ethane and isotopic proxies can distinguish fossil fuel and combustion sources from biogenic sources during mobile surveys. Isotopic measurements to back-up mobile methane mapping have been completed for the following cities: Hamburg (ESR10, aided by ESR8 and ESR9; Fig. 1), Bucharest (ESR9 and ESR10 aided by ESR8; Figs. 2, 3), London (Figs. 4, 5), Birmingham and Swansea (ESR9 aided by ESR7), Paris (ESR5 and aided by ESR9; Fig. 7), Heidelberg (ESR1) and Katowice (ESR3), with additional work in the Groningen and Alkmaar regions of NL. Continuous isotopic measurements for Krakow were made for 6 months (ESR8) and these contribute additionally to D2.4. The Deliverable 2.3, originally scheduled for Month 36, was delayed partly by the additional requirement of the ROMEO project to conduct surveys in Romania, and latterly by Covid-19 lockdown restrictions impacting on final surveys and subsequent data processing.

The first of these studies has now been published. Maazallahi et al. (2020) used $\delta^{13}C$ and δD source signatures in combination with C_2:C_1 ratios (ethane:methane), for plumes encountered and measured during mobile surveys of Hamburg, to distinguish dominant gas leaks from combustion sources and biogenic sources such as wastewater treatment, landfill and farms. Biogenic sources are generally depleted in carbon 13 and deuterium, and have very low C_2:C_1 ratios compared to thermogenic (fossil) and pyrogenic (combustion) sources.

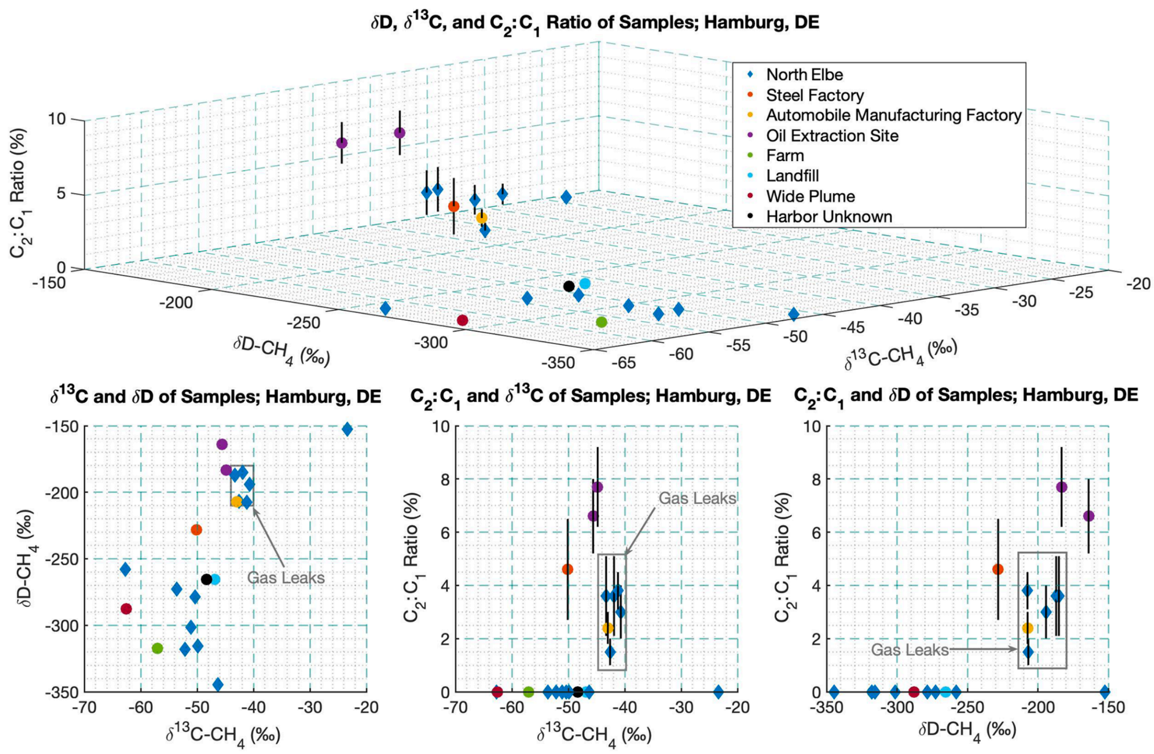

Fig. 1: Results from the attribution measurements in Hamburg: C_2 : C_1 ratios and isotopic signatures ($\delta^{13}C$ and δD) of collected air samples; measurement uncertainty in $\delta^{13}C$ is 0.05 ‰ – 0.1 ‰ and in δD 2 ‰ – 5 ‰ (Maazallahi et al., 2020).

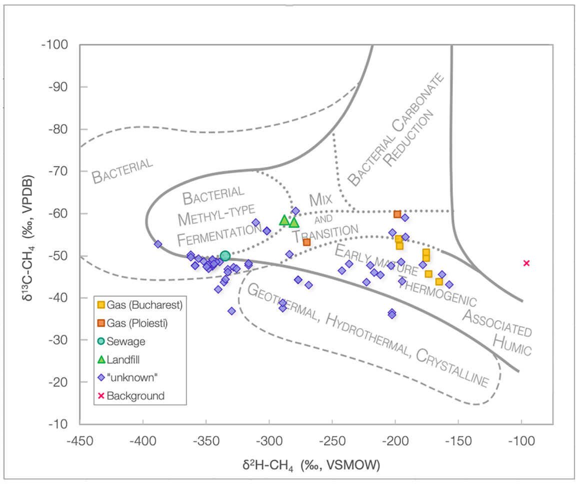

Fig: 2: Isotopic source signatures of CH_4 enhancements in Romanian cities. Comparison between 11 known and 55 unknown (purple diamond) source signatures. Known $\delta^{13}C$ source signature ranges: gas -59.7 to -43.7 ‰ (yellow & orange, n=5), landfill -58.5 to 57.8 ‰ (green triangle, n=2), and wastewater is -49.9 ‰ (circle). Known $\delta^{2}H$ source signature ranges: gas -270.1 to -165.9 ‰, landfill -288.1 to -280.3 ‰, and wastewater is -335.0 ‰. Points overlay bacterial and thermogenic classifications from Whiticar (1990).

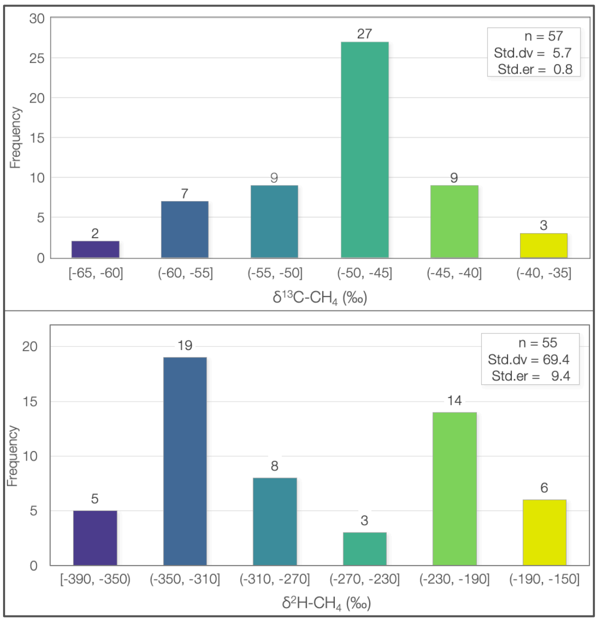

Fig. 3: Romanian city source signature population distribution ($\delta^{13}C$ and $\delta^{2}H$-CH_4). There is a normal distribution of $\delta^{13}C$ signatures (top) ranging from -64.8 to -36.5 ‰. $\delta^{2}H$ source signatures (bottom) show a bimodal distribution ranging from -388.1 to -157.3 ‰.

The same proxies to separate source categories are being used in Bucharest and London. In Bucharest the $\delta^{13}C$ signatures were not able to separate plumes from the gas distribution network from those coming from the wastewater pipe ventilation, but δD and C_2:C_1 ratios are able to distinguish between them, and give very close agreement when considering the proportion of these two dominant source categories for the city. These suggest between 56 and 59% biogenic (wastewater sources) and 37 to 44% thermogenic (fossil fuel) sources.

The sources of the United Kingdom can be distinguished using $\delta^{13}C$ because the natural gas supply is significantly enriched in ^{13}C compared to biogenic sources. This will be confirmed with ongoing C_2:C_1 ratio analysis. During 30 days of London surveys a total of 72 plumes were sampled for isotopic analysis (Fig. 4).

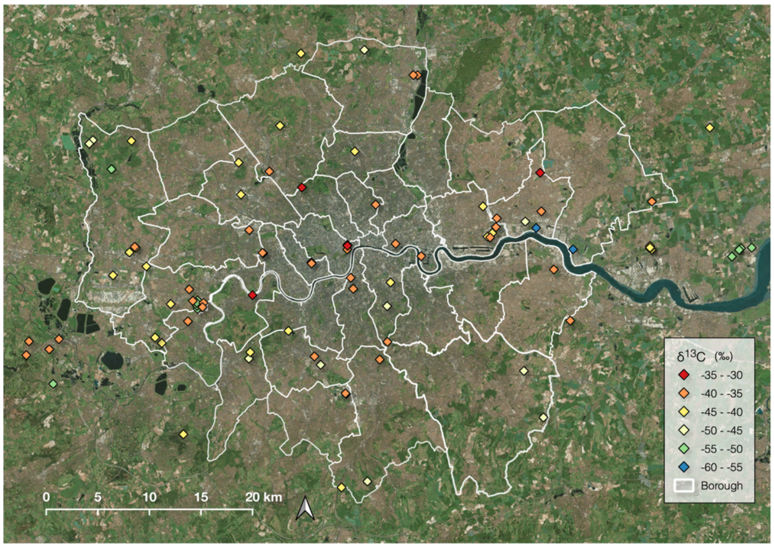

Fig. 4: Map of the calculated $\delta^{13}C$ isotopic signatures for Greater London. The red, orange and yellow points represent fugitive emissions from the gas distribution system. The generally more peripheral green symbols are waste sources.

Of these 75% were considered to be leaks from natural gas pipelines and other gas infrastructure based on δ^{13}C signatures of -39.5 ± 2.5 ‰ and recorded ethane peaks. The other 25% were biogenic plumes from landfill sites (-60 to -54‰) and wastewater / manure sites (-56 to -49‰) in the peripheral regions of the city (Fig. 5).

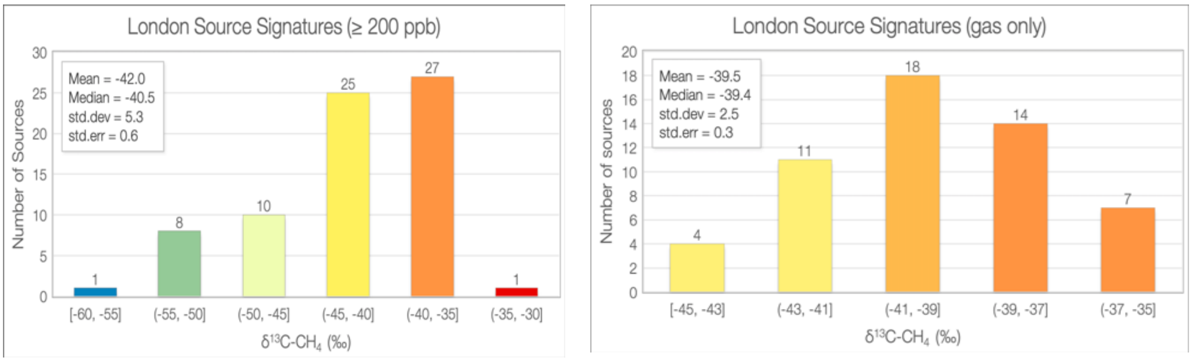

Fig. 5: Histograms of the calculated isotopic signatures for Greater London. The red, orange and yellow points represent fugitive emissions from the gas distribution system. The generally more peripheral green symbols are waste sources. The right-hand histogram selects just the gas leaks with a mean δ^{13}C signature of -40 ‰. For improved precision of the source calculation only plume samples with >200 ppb excess CH_4 over background are used.

Continuous mmeasurements of CH_4 mole fraction, δ^{13}C and δD in CH_4 in ambient air were performed over 6 months in 2018 and 2019 in the Polish city of Krakow. Isotopic source signatures of local sources were obtained from mobile campaigns around the urban area and in the coal mining region of Silesia, west of the city. They were compared with the signatures from each peak in the time series (Fig. 6).

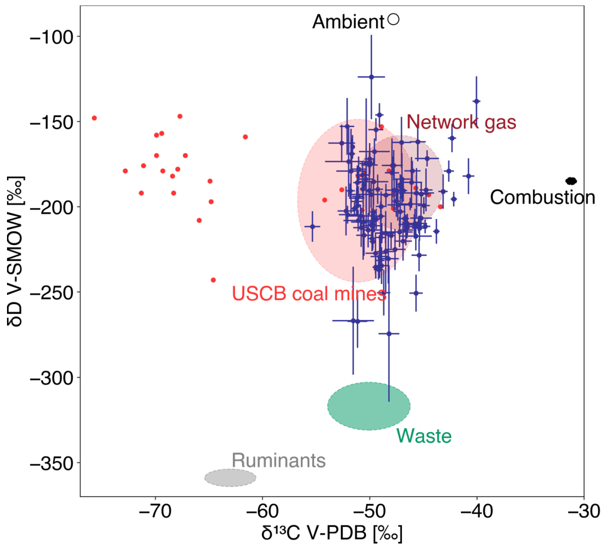

Fig. 6: Dual isotope plots of the resulting source signatures from the CH_4 peaks identified in the time series. Dark blue: source signatures with their associated 1σ uncertainties. Coloured areas: ranges of source signatures obtained from the collected samples. Red dots: source signatures of USCB coal gas derived from the literature. The combustion source signature is from coal waste burning samples reported in Menoud et al., 2020.

The use of δD was crucial to distinguish the fossil fuel emissions because, like Bucharest, their relatively depleted δ^{13}C values overlap with the ones of microbial sources. The peak source signatures suggest fossil fuel related emissions as a major source, with δ^{13}C between -55.3 and -39.4 ‰ V-PDB, and δD between -285 and -124 ‰ V-SMOW (Fig. 6). They confirm the influence of Silesian coal mines when the wind is from the west, and of natural gas leaks from the network as a local source advected by low wind speed. The comparison with modelled time series allowed identification of the use of fuel in residential heating and energy production as a greater contributor of local urban emissions than waste sources.

The MEMO² project has also facilitated the calibration and quality control assessment of new Picarro CRDS isotopic analysers that use lasers rather than IRMS. While IRMS data is more precise and so allows source characterisation with far greater accuracy, there are methods being developed to reduce these differences, so that in field, corrected δ^{13}C measurements of a quality that will distinguish combustion, fossil fuel and biogenic sources, can be obtained in less than 30 minutes. These instruments have been used in the Paris city surveys and calibrated with co-located bag sampling for IRMS analysis (Defratyka et al., under review).

This has been used to characterise gas compressor stations (Fig. 7), using AirCore to trap air when crossing a plume and then replay air through the instrument to get a more precise isotopic measurement. Similar techniques have been developed in Germany (Hoheisel et al., 2019) and used for Heidelberg surveys.

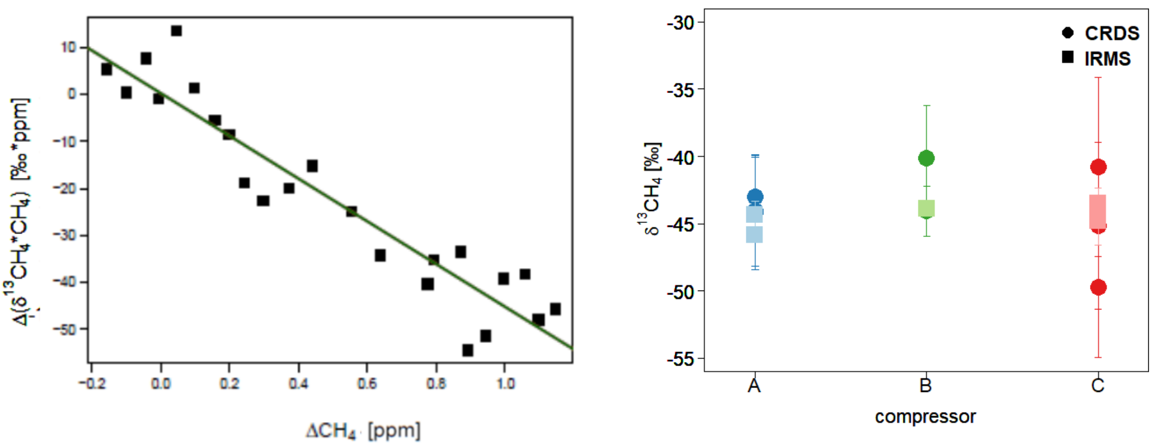

Fig. 7: Left: Example of a Miller-Tans plot for an AirCore sample taken from compressor A, identifying the source δ^{13}C signature as -45.5 ±3.6 ‰. Right: δ^{13}C comparison between CRDS and IRMS measurement techniques for 3 gas compressors in the Ile-de-France around Paris, surveyed between January 2019 and March 2020.

The paper for Hamburg (Maazallahi et al., 2020) has been published (see Section 6). The paper for Paris has been reviewed (Defratyka et al., 2021). The paper for Krakow is submitted (Menoud et al., submitted). The second draft of the Bucharest paper is out for author comment (Fernandez et al., in prep) and the London paper is partly written ahead of the final C2:C1 ratio analysis component (Fernandez et al., in prep). Other papers published by the MEMO² participating groups, during the MEMO² project period, that contain isotopic signatures of methane in urban areas of Europe, are Zazzeri et al. (2017; London), Hoheisel et al. (2019; Heidelberg) and Xueref-Remy et al. (2020; Paris). A review of urban isotopic signatures in Europe will follow the current crop of papers.

4. Conclusion and possible impact

Mobile surveys of cities alone cannot provide the source attribution that is necessary for comparison with published emissions inventories for these cities. Many of the earlier mobile surveys, mostly for cities in the USA, made the presumption that these were from gas leaks if the plumes were <160m wide, plus the main biogenic sources, such as landfill sites and wastewater treatment plants were large visible infrastructure. Measurement of source characterization proxies such as δ^{13}C and δD signatures and C_2:C_1 ratios are showing that while gas leaks may be dominant, they are far from being the only source of urban emissions, even for smaller plume widths.

Surveys in Hamburg, London and Paris suggest that 60-80% of the fugitive methane emissions are from leaking natural gas infrastructure, with the remainder from waste sources. The Bucharest survey suggests that up to 60% of the emissions could come from wastewater pipelines, with the remainder from gas infrastructure. Use of such proxies can assist in reporting of significant fugitive emission peaks to the appropriate operator. Furthermore, an understanding of urban and industrial source isotopic signatures compared to rural signatures will aid in the understanding of spatial distribution of emissions in comparison to National Inventory distribution, assisting in targeted source experiments ahead of inventory refinement.

5. Dissemination & Exploitation

This report will be available via the MEMO² website to all project partners. The component isotopic dataset contains all of the measurements made on samples collected in urban and industrial areas, and can be used to geographically sort and select data. This has been submitted to the ICOS database and is published online (Menoud et al., 2020).

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