MEMO^2: MEthane goes MObile – MEasurements and MOdelling

Report providing isotopic maps at grid scale from inventories and atmospheric measurements

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Deliverable D2.5

Delivery month Annex I	36		
Actual delivery month	48		
Lead participant: RHUL	Work package: 2	Nature: Report	Dissemination level: PU
Version: 01			

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 722479.

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1. Executive Summary

A report has been constructed that discusses the usefulness of understanding the spatial distribution of methane isotopic signatures. This includes maps produced from the newly created European Methane Isotopic Database (D2.2) constructed from atmospheric measurements and sampling at sources in the 2017-2020 period, and assesses how these can be used in conjunction with inventories. More than 50% of source measurements in the 2017-2020 period were from UK sources and these have been supplemented by source signatures from the 2011-2016 period to create a UK database of 300 different sources. Maps of these sources by type are presented.

Each UNFCCC SNAP category or NFR source category that is used to construct national inventories can be assigned an isotopic signature. In the UK enough measurements have been made of the dominant source categories that a characteristic signature can be assigned to each. These are Agriculture -66 ‰ (49 %), Waste -56 ‰ (37 %), Fossil Fuel -40 ‰ (10 %) and Combustion -25 ‰ (3 %). Further breakdown can be made for subdivisions of these categories and so an isotopic signature can be assigned to each 1 x 1 km square based on the proportion of each source category within each grid square.

The report presents maps constructed in this fashion for London and for England and Wales. The methodology to construct the inventory maps is outlined.

2. Introduction

2.1 Background

Methane has many anthropogenic sources, but spatially these are not equally distributed and vary between urban and rural areas. As each source has distinctive $\delta^{13}C$ and / or $\delta D(^2H)$ signatures there should be a measurable difference between the source mixes typically found for example in an urban area dominated by gas leaks and combustion sources, compared to rural areas dominated by agricultural and waste sources.

These differences have been highlighted previously by MEMO² project partners for specific study regions (e.g. Röckmann et al., 2016; Zazzeri et al., 2017) but the challenge was to gather enough high-precision source isotopic data to a) produce maps of the isotopic distribution of sources at national level, and b) have confidence in the wider representativeness of source category isotopic signatures to apply these to emission inventories to produce predictive isotopic maps.

Currently there is a far larger database of $\delta^{13}C$ data for methane (Sherwood et al., 2017), with a strong bias toward North American sources, but this has been partially redressed during this project by the analytical activities of UU and RHUL and the creation of a European Methane Isotope Database.

2.2 Scope of the deliverable

Each CH_4 emission source category has a characteristic range of isotopic signatures that in general terms are related to the temperature of CH_4 formation. Biogenic sources such as agriculture and waste, have less ^{13}C and ^2H than thermogenic sources, such as coal and gas (fossil fuels), that in turn have less ^{13}C and ^2H than pyrogenic sources, such as biomass burning and combustion. This means that each major source group can be assigned a signature for both $\delta^{13}C$ and $\delta D(^2H)$.

The European Methane Isotope Database (D2.2) for sources measured in the 2017-2020 period is subdivided by the main categories outlined above, with the biogenic category further subdivided into waste and agriculture, as these and fossil fuels are the dominant categories sampled and measured. The distribution of these sources has been mapped (Fig. 1).

More than 50 % of the $\delta^{13}C$ source measurements were from UK sources. These have been supplemented by a further 120 $\delta^{13}C$ source signatures measured in the 2011-2016 period and mapped for England and Wales. Areas that have received more intensive survey, sampling and isotopic analysis have been mapped in more detail, such as the Greater London region.

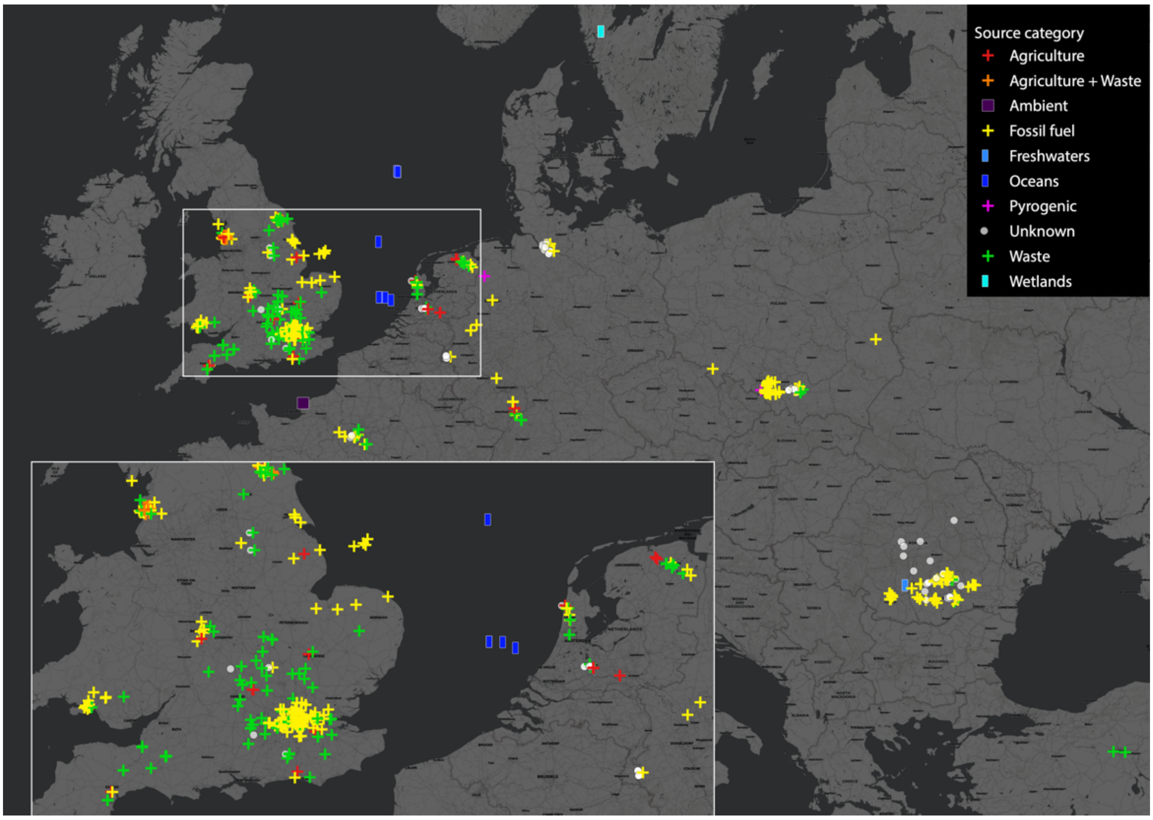

Fig. 1: Map of all locations that were sampled and characterized for $\delta^{13}C$ and/or δD, and reported in the database. The emissions were classified into 8 identified source categories.

Each UNFCCC SNAP category or NFR source category that is used to construct national inventories can be assigned an isotopic signature. In the UK enough measurements have been made of the dominant source categories that a characteristic signature can be assigned to each. Further breakdown can be made for subdivisions of these categories and so an isotopic signature can be assigned to each 1 x 1 km square based on the proportion of each source category within each grid square. This allows maps to be produced of expected isotopic signature of emissions within each grid square for comparison with the actual measured source signatures.

3. Content

The first stage of isotopic mapping converted the source distribution map above (Fig.1) into maps showing isotopic signature for both $\delta^{13}C$ and δD (Figs. 2 and 3). These highlight in both instances that there is a general isotopic enrichment in NW Europe compared to Eastern Europe. This is the result of natural gas supplies in the former being more thermogenic ($\delta^{13}C$ of North Sea source averaging -32 ‰). The natural gas in Poland and Romania is either of local source or supplied by Russia and has $\delta^{13}C$ averaging -50 ‰.

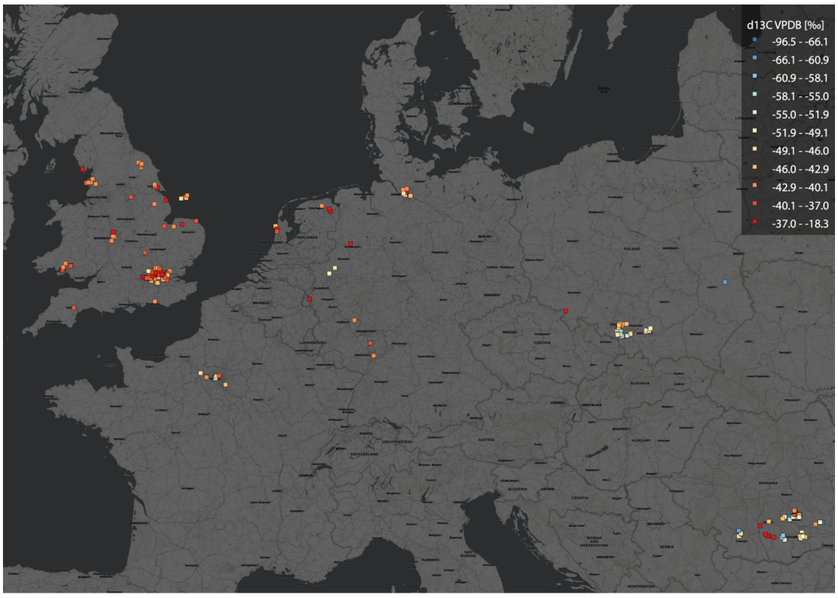

Fig. 2: $\delta^{13}C$ of European CH_4 sources with red representing most enrichment in ^{13}C (combustion and natural gas), and blue most depletion (natural wetlands and agriculture).

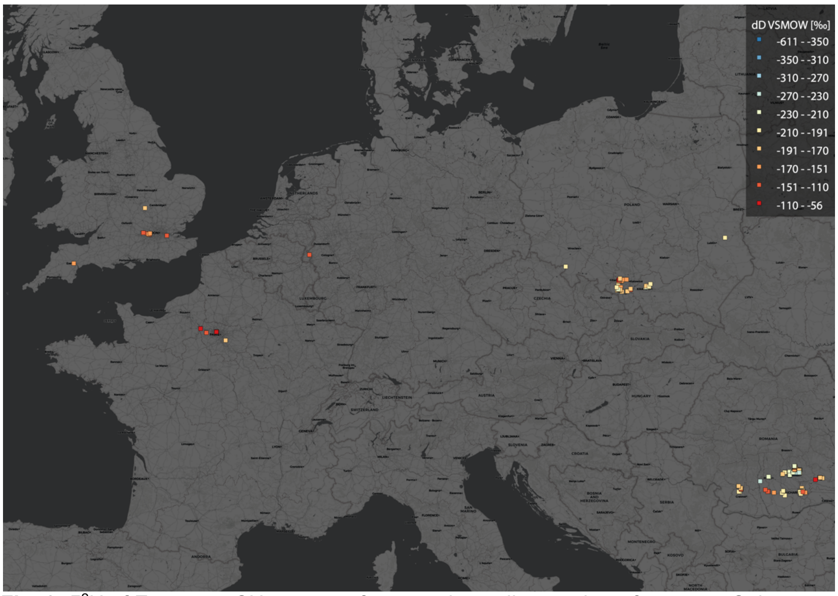

Fig. 3: δ^2H of European CH_4 sources for a much smaller number of sources. Colors as for Fig. 2 but represent ^2H enrichment. Most samples are for intensive surveys in Poland and Romania

Each source is assigned a source signature, but this depends on the category subdivision required by national inventories or UNFCCC reporting.

As these are designed to work for the whole range of atmospheric gases, they are rarely appropriate for individual gases such as CH_4. In the UK it has been possible to assign signatures to categories as in Table 1.

For some categories this required more in depth understanding, such as the proportion of coal to natural gas and the grade of coal being mined for the fossil fuel category, or the proportions of waste to eructation for cattle, sheep and pigs to assign an agricultural signature.

In simplified terms the signatures are Agriculture -66 ‰ (49 %), Waste -56 ‰ (37 %), Fossil Fuel -40 ‰ (10 %) and Combustion -25 ‰ (3 %). The averaged $\delta^{13}C$ isotopic signature for all sources in the UK for 2018 was -57.8 ‰ for 2.07 Tg of estimated emissions.

Currently this has been attempted only for $d^{13}C$ isotopic signature because there are more than 20 source measurements for each of the main NFR emission categories, but not for d^2H, as there is currently not enough data to confidently characterize the main source categories.

Inventory data for the UK can be downloaded at a variety of scales from national to local authority region to individual grid squares for the purpose of mapping emissions by total and source category. For England and Wales each 1 x 1 km grid square is assigned a $\delta^{13}C$ signature for each SNAP category (Table 1).

Table 1: Isotopic signatures assigned to NFR categories that create UK emissions time series (1970-2018) and SNAP categories used for annual emissions to the UN and mapped products

NFR / CRF Group	Source	Isotopic Signature (UK sources, ‰)	SNAP Category	Source	Isotopic Signature (UK sources, ‰)
1A1, 1A3, 1A4	Combustion	-24.5	1	Combustion - Energy	-24.5
1A2	Transport	-13.0	2	Combustion - Commercial	-24.5
1B1	Solid Fuel	-49.0	3	Combustion -Industrial	-24.5
1B2	Oil and Gas	-39.3	5	Offshore (fossil fuels)	-39.3
2	Production Processes	-25.0	7	Road Transport	-13.0
3A	Enteric Fermentation	-69.5	8	Other Transport	-13.0
3B	Animal Waste	-51.6	9	Waste	-56.1
4, 3J	Biomass Burning	-30.0	10	Agriculture	-66.5
5A	Landfill	-57.0	11	Nature (composting, AD)	-54.7
5B	Biogas / composting	-54.7			
5C	Incineration	-25.0			
5D	Wastewater Treatment	-52.6			

This signature is multiplied by the emission for that category. The same is done for each of the 11 categories. These are then added together and this total divided by the sum of the emissions for that grid square to give an expected isotopic signature. Squares with a total emission flux of less than 0.1 tonnes per year are removed from the final dataset so that small emissions do not overly influence the apparent isotopic distribution. These signatures are then mapped in QGIS to produce isotopic signature maps such as in Fig. 4. This highlights isotopic enrichment for cities because fossil fuel and combustion sources dominate over agricultural and waste sources, whereas the opposite is true in rural areas. This is then compared with maps based on actual measured isotopic signatures for the prevalent source categories (Fig. 5).

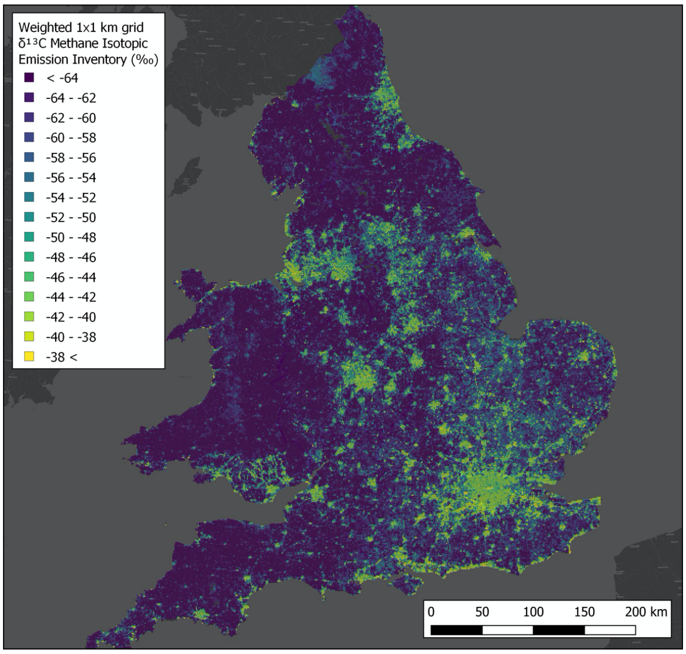

Fig. 4: Predicted isotopic distribution for England and Wales based on 1 x 1 km distribution of source emissions by category in the UK NAEI. Blue areas are dominated by ruminant agriculture emissions and pale green areas by fugitive fossil fuel emissions.

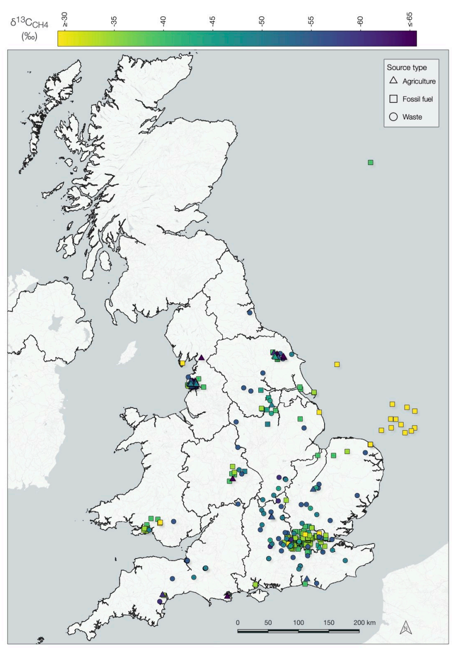

Fig. 5: Distribution of sampled and isotopically characterised CH_4 sources in England and Wales. This is biased toward SE England because of the proximity to the survey instruments and isotope laboratory.

The source maps highlight some areas where more source measurements have been made. One of these is the Greater London urban area, and so zoomed in equivalents of the figures above have been produced, confirming the dominance of fossil fuels in the inner-city region and to a lesser extent in more suburban regions (Figs. 6 and 7).

It proved difficult to gather sufficient isotopic data for sources to be able to show that the inventories are correct or not. One region of England was surveyed on 32 days over the 2017-2020 period, and sources were located only in 46 out of 208 1x1 km grid squares (Fig. 8). The proportion is much lower than these areas surveyed only once or twice, as was the case for the large city areas surveyed for the MEMO^2 project.

Inventories capture the general distribution of sources and highlight dominant fossil fuel and combustion sources in urban areas and biogenic sources in rural areas. The main discrepancy from inventory spatial distribution that is highlighted by isotopic characterisation is that gas pipelines and installations in rural areas do not form part of inventory emissions. Often these leaks go unnoticed and so are not repaired (Lowry et al., 2020), so they can be persistent and sometimes represent significant sources.

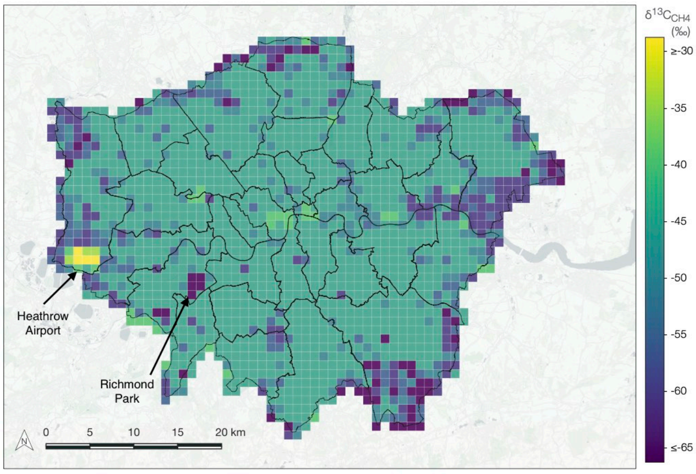

Fig. 6: Calculated isotopic signatures for Greater London grid squares. Fossil fuel signatures dominate for much of London (pale green colours) with fossil fuel and combustion signatures being dominant for Heathrow Airport (yellow).

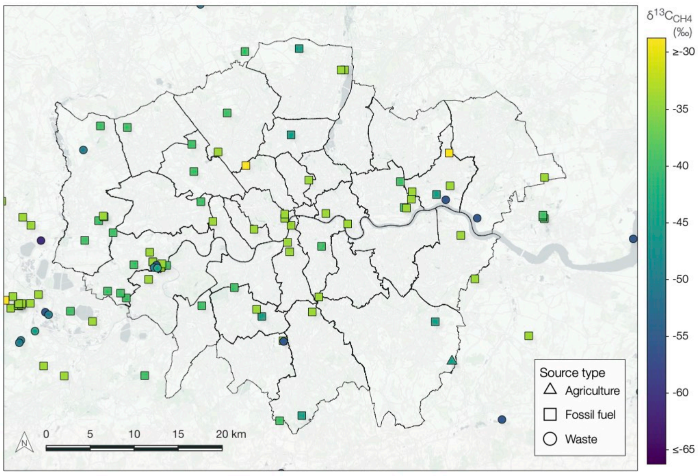

Fig. 7: Measured isotopic signatures for sources in Greater London. There is good agreement with the inventories in that fossil fuel sources dominate for much of London, but these are interspersed large waste sources, particularly waste water treatment in outer London

Methane emission plume samples were collected in Bucharest as part of the ROMEO project. This was done following the mobile surveys once the locations of the main plumes had been identified. Samples collected are very localised to specific areas of the city. These showed a wide range of isotopic signatures for both $\delta^{13}C$ and δD (Fig. 9). The latter suggested bi-modality of the data, which C2:C1 ratios later confirmed to be related to gas leak and sewage pipeline emissions that could not be distinguished using $\delta^{13}C$ alone.

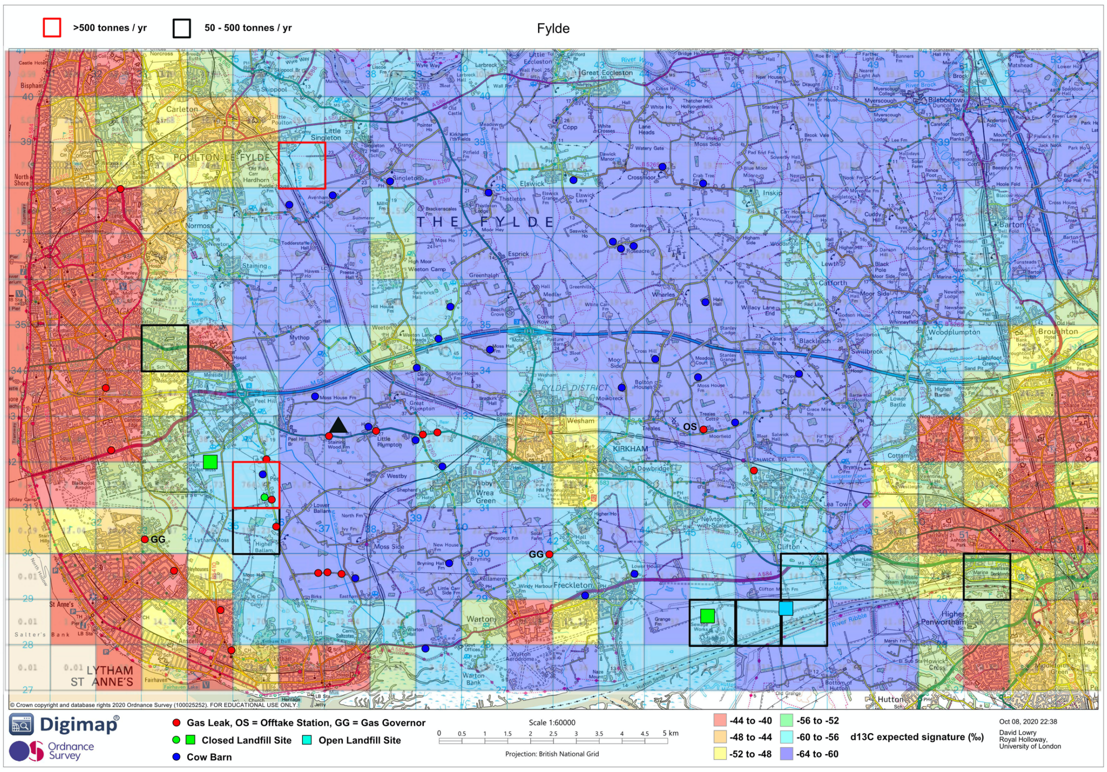

Fig.8: Measured isotopic signatures for the Fylde region of NW England are shown as colours from red (natural gas leaks to blue (cow barns). These are overlain onto the inventory isotopic signatures, that here are shown to emphasise urban areas where gas leaks are thought to dominate (red) and rural areas where agricultural emissions are thought to dominate (blue). There is good agreement except for the large number of undetected rural gas leaks that are not considered as the inventory distributes fugitive gas leaks by population density. An area of 18 x 14 km of this region was surveyed in detail on multiple occasions, but sources were identified and sampled in only 23 % of the 208 grid squares.

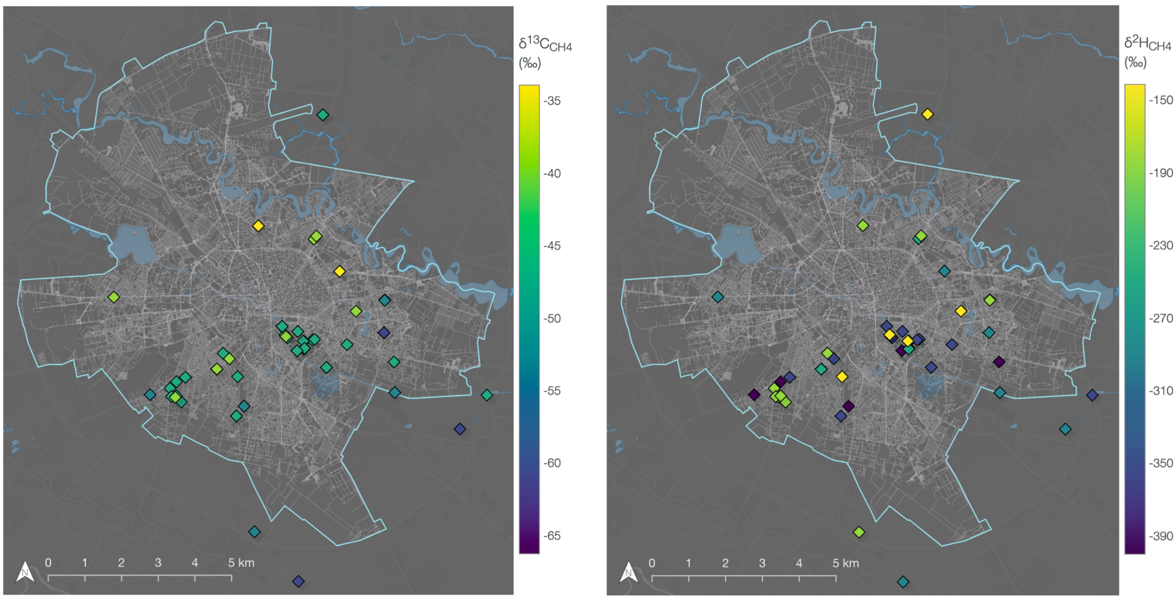

Fig. 9: Spatial distribution of $\delta^{13}C$ and $\delta^{2}H$ methane source signatures. Combined RHUL and UU $\delta^{13}C$ signatures (left), yellow colors indicate sources of ^{13}C enrichment and blue colors show ^{13}C depletion. $\delta^{2}H$ signatures (right), yellow colors are more enriched and are indicative of thermogenic sources, and purple darker shades indicate ^{2}H depletion and are more likely to be biogenic sources. Less source signature overlap for $\delta^{2}H$ is indicated by the greater color variability.

4. Conclusion and Possible Impact

A variety of maps have been produced from the MEMO^2 isotopic database (D2.2) for $\delta^{13}C$ and δD of CH_4, and the allied and extended UK $\delta^{13}C$ database. These have been used to construct distribution maps of CH_4 sources with isotopic measurements at European and national scale, but they highlight the very localised nature of measurements that are focussed around measurement labs or in the regions of the intensive MEMO^2 / COMET / UNCCAC campaigns. Isotopic measurement is not yet routine and performed by all project partners. Laser-based isotopic instruments that can be used directly in vehicles at source give data precisions that are sufficient only to separate biogenic from fossil fuel emissions for the larger plumes that are identified, but these will gain more use in conjunction with sample collection for higher-precision isotopic measurement. In areas with enough sampling (London, Bucharest), isotopic maps of city sources have been produced.

Enough measurements have been made in England and Wales over the last decade that C-isotopic signatures can be applied to the national inventory (NAEI) and produce predicted isotopic maps that assume the estimated emissions are correct. For Greater London, which has been heavily surveyed and sampled (D2.3), this has allowed comparison between real sample isotopes and predictions. These suggest that inventories for the most part can capture the general spatial distribution of sources, with the exception of rural leaks in the gas supply systems that bear no relation to the use of population density as the main distribution parameter. More than anything else the maps provide a striking visual display to highlight the variation between dominant fossil fuel and combustion methane sources in cities and agriculture and waste sources in the countryside.

5. Dissemination & Exploitation

This report will be available via the MEMO^2 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).

6. References

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