

MEMO²: MEthane goes MObile – MEasurements and MOdelling

Improved isotopic source signatures of local and regional CH₄ emissions

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Deliverable D2.2

Delivery month Annex I 36

Actual delivery month 40

Lead participant: UU 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 Skłodowska-Curie grant agreement No 722479.



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1. Executive Summary

From November 2017 to March 2020, atmospheric samples were taken close to CH₄ emission locations by different beneficiaries of the MEMO² project. They were measured at Utrecht University (UU) and Royal Holloway University of London (RHUL) labs, where high precision measurements are performed with Isotope Ratio Mass Spectrometry (IRMS) systems. Some CH₄ sources were also characterized using a Cavity Ring Down Spectrometry instrument. This method was used at the Heidelberg University (UHEI), AGH University of Science and Technology and Université de Versailles Saint-Quentin-en-Yvelines (UVSQ).

A total of 817 CH₄ sources in 8 different countries were characterized. The source signatures ($\delta^{13}\text{C}$ and partially δD) obtained were combined into a common database that is now openly available.

Previous inventories gathered the data on isotopic measurements of CH₄ emissions made until today (Bréas et al. 2001, Sherwood et al. 2017, Milkov and Etiope 2018). However, they do not represent a wide geographical spread of the sources. The work by Milkov and Etiope 2018 illustrates the large heterogeneity in the isotopic composition of CH₄ released from fossil fuel reservoirs. It emphasized the challenge in the isotopic characterization work, and demonstrated the use of additional measurements such as other hydrocarbons, as well as the need for additional measurements in more remote locations.

Our results, because of their sub-continental scale, represent this isotopic heterogeneity. They show that on a regional scale, isotopic analysis remains a precious tool for source characterization. On a global scale, the inclusion of isotopes in global transport models is a key to understand the variations in CH₄ atmospheric mole fractions of the last decades. Our results also bring a substantial addition to the existing isotopic signature database. They are a significant step forward to assess accurately the contributions from different CH₄ sources to the global budget.

2. Introduction

2.1 Background

Methane production pathways can be classified into three main categories:

- biogenic: through the metabolism of methanogens, by either fermentation of methyl-organics or carbonate reduction.
- thermogenic: through decomposition of organic molecules in sediments under elevated temperature and pressure.
- pyrogenic: from the incomplete combustion of organic matter.

These different pathways influence the ratio of stable isotopes of methane (Levin et al. 1993, Quay et al. 1999, Whiticar 1999). The measurements of both $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ ratios in CH₄ have been widely used to constrain changes in the CH₄ budget (among others: Monteil et al. 2011, Sapart et al. 2012, Schwietzke et al. 2016, Worden et al. 2017). Atmospheric models use fixed CH₄ isotopic signatures for each source categories they consider, based on previous measurements. These isotopic signatures are expressed as the relative difference in $^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$ ratios compared to a reference material: Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (SMOW), respectively. The values are reported in per mill (‰), and expressed as $\delta^{13}\text{C}$ and δD .

New measurements from a wide range of sources allow determination of the spatial and temporal heterogeneity of the signatures between the source categories, as well as within each source category. Performing high precision isotopic measurements of methane in air samples is technically challenging due to the low concentration, therefore very few studies were made before the 90's. Since then, the number of measurements has increased considerably, and data have been collected in isotope



inventories. Several inventories have been made; the most recent by Sherwood et al. 2017, followed by Milkov and Etiope 2018, focusing on fossil fuel emissions.

Despite their use in global models, these databases have some weaknesses:

- Unbalanced geographical coverage (> 1/3 of all reported signatures are from the United States)
- The extensive reporting of geological emissions, in comparison with other sources
- The wide ranges of values from each source category are poorly understood

2.2 Scope of the deliverable

Field surveys were carried out regularly by MEMO² consortium partners, targeting different methane sources and in several European countries. With this network, we've collected samples for isotopic analysis, aiming at a better characterization of the CH₄ source categories in Europe.

In this report, we present the results of the campaigns from November 2017 to March 2020. The samples were taken during individual ESR campaigns and 2 collective campaigns of a larger scale: CoMet and ROMEO. The samples were measured either using isotopic ratio mass spectrometry at UU or RHUL labs, or using cavity ring-down spectrometry at UHEI, AGH or UVSQ. All results were combined into a common database.

3. Content

3.1 Sampling procedure

Samples were collected during mobile surveys, often also aiming at the detection and quantification of the emissions. Several vehicles could be used, from bicycles to aircraft. A cavity ring down spectrometer (CRDS) in the vehicles provided real-time values of CH₄ mixing ratio to identify emission plumes from sources. The samples that were to be measured in the lab were collected in either Flexfoil bags, Tedlar bags, glass flasks or stainless-steel canisters. Direct isotopic measurements were also performed using isotopic CRDS instruments.

The campaigns were made in 8 different countries.

Table 1 shows the distribution of the surveys and results per country. Fig. 1 shows the locations that were characterized, and the different source categories. Many are in the UK and the Netherlands due to the proximity with the measurement labs. However, 2 intensive campaigns were organized involving several MEMO² beneficiaries, one in June 2018 in Poland (CoMet), and another one in October 2019 in Romania (ROMEO). They contributed significantly to extending the geographical range of the dataset.

Table 1: Survey days and results per country

Country	Number of survey days	Number of characterized sources
United Kingdom	70	303
Romania	24	196
Poland	23	98
The Netherlands	26	71
Germany	33	78
France	17	47
Sweden	2	21
Turkey	1	2
TOTAL	196	816

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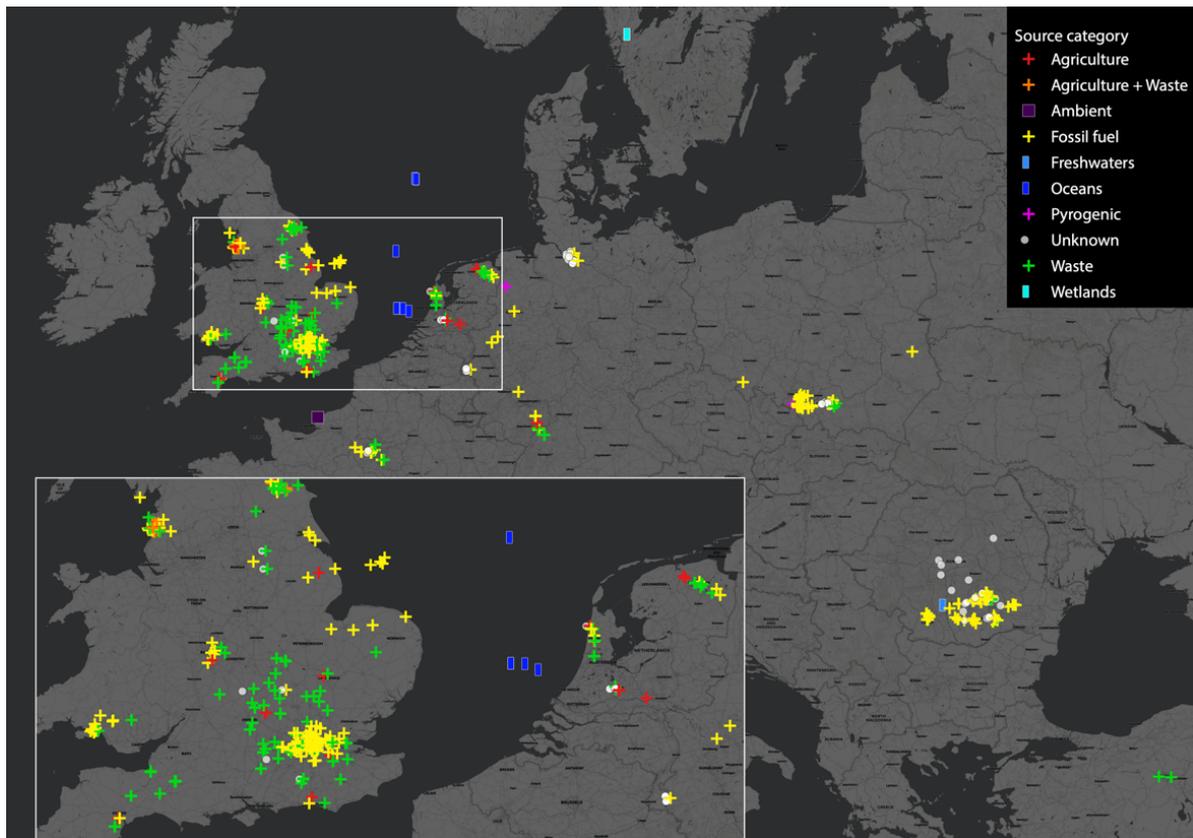


Fig. 1: Map of all locations that were sampled and characterized for $\delta^{13}\text{C}$ and/or δD , and reported in the database. When identified, the emissions were classified into 8 source categories.

3.2 Measurements

The mass spectrometry measurements were performed at two labs: the IMAU (Institute for Marine and Atmospheric research Utrecht) at Utrecht University, and at the Department of Earth Sciences at the Royal Holloway University of London (RHUL).

Both measurement systems are using a CF-IRMS (continuous flow isotopic ratio mass spectrometry) system to measure $\delta^{13}\text{C}$, and also δD at IMAU. The system at IMAU is described by Röckmann et al. (2016) and the one at RHUL by Fisher et al. (2006). The reproducibility both groups can achieve is of 0.05 ‰ for $\delta^{13}\text{C}\text{-CH}_4$. At IMAU, δD measurements have a reproducibility better than 2 ‰.

Isotopic CRDS measurements were made at Heidelberg University (UHEI), AGH University of Science and Technology (Krakow), and at the Université de Versailles Saint-Quentin-en-Yvelines (UVSQ). They were performed with the Picarro G2201-i Isotopic Analyzer (Picarro Inc., Santa Clara, CA). They concern 80 sources out of a total of 798 characterized sources for $\delta^{13}\text{C}\text{-CH}_4$ isotopologues.

The reported values are source signatures per sample location. They were mainly calculated from the sample measurements using the Keeling plot or Miller-Tans methods (Keeling 1961, Miller and Tans 2003). Both are mass balance approaches that allow derivation of the isotopic signature of a source based on isotopic measurements of plume samples that are a mix of source emissions and ambient air. The equations are shown in the appendix.

3.3 Results

The results are combined into a single spreadsheet, available on the ICOS repository, where all the MEMO² data is also stored. It is therefore accessible to all the beneficiaries. It is also now openly available at <https://doi.org/10.5281/zenodo.3975543>.

Fig. 2 gives an overview of the sources that have both $\delta^{13}\text{C}$ and δD signatures available, together with literature data. The fossil fuel signatures partly overlap with the thermogenic range, but also spread towards lower $\delta^{13}\text{C}$. This indicates emissions of microbial origin CH₄ in the sampled reservoirs. The large spread of signatures from the waste category does not exactly correspond to the microbial fermentation values. The $\delta^{13}\text{C}$ appears to be higher in many cases. In the locations we sampled, the use of δD measurements is particularly valuable as it allows to separate microbial fermentation and fossil fuel sources better than with $\delta^{13}\text{C}$ only.

The signatures of “Unknown” sources are compared with data for known sources in the same area, to identify their origin.

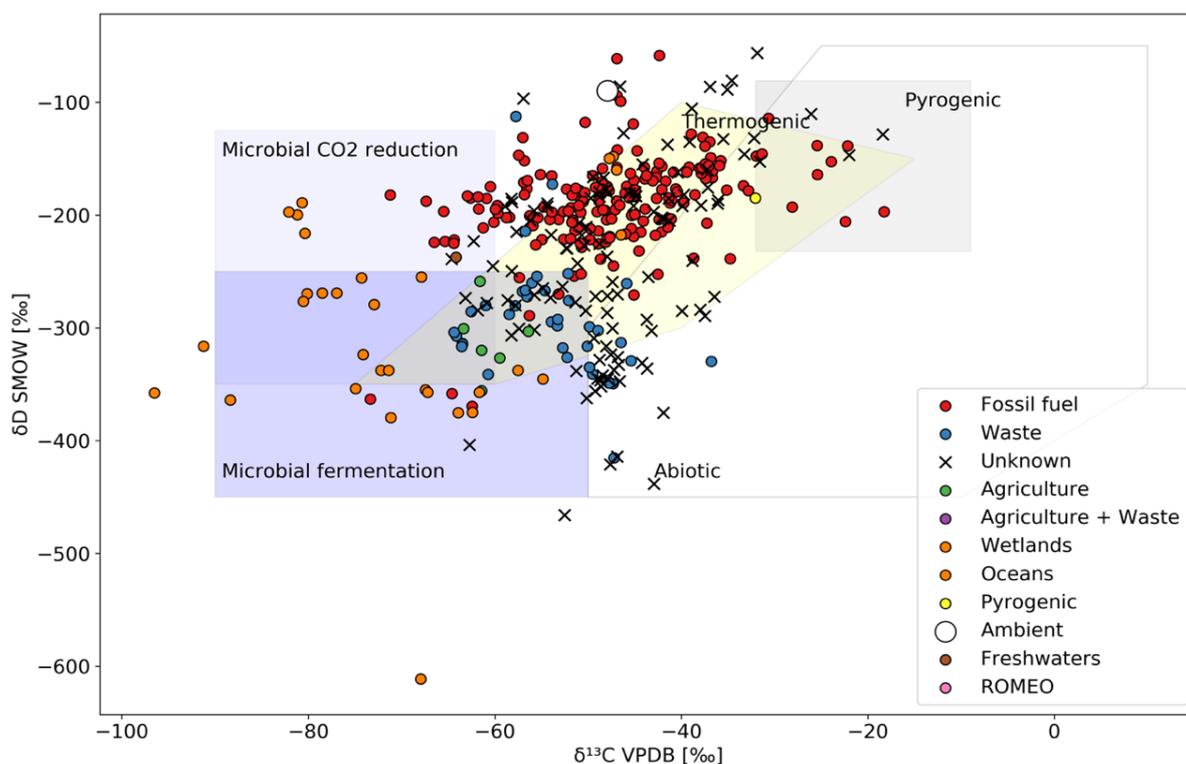


Fig. 2: $\delta^{13}\text{C}$ vs δD cross plot of the sources characterized during the MEMO² project. The sources are classified by emission category. The coloured background boxes represent the range of values from previous studies, according to Milkov and Etiope (2018) and Sherwood et al. (2017)

δD is measured only at IMAU, so the locations that were only analyzed by RHUL do not report these values. In our database, δD signatures are available for 399 locations out of 736. The histogram in Fig. 3(a) represents all the $\delta^{13}\text{C}$ values that we report in the database. The distinction between fossil fuel and biogenic sources is not obvious, especially from waste sources. Fig. 4 highlights distinguishing power of δD measurements in this matter. Fig. 3(b) shows the example $\delta^{13}\text{C}$ data for the UK only, where the largest number of sources were characterized. In this case, a 1-variable isotopic analysis remains sufficient to distinguish fossil fuel from biogenic emissions of anthropogenic origin.

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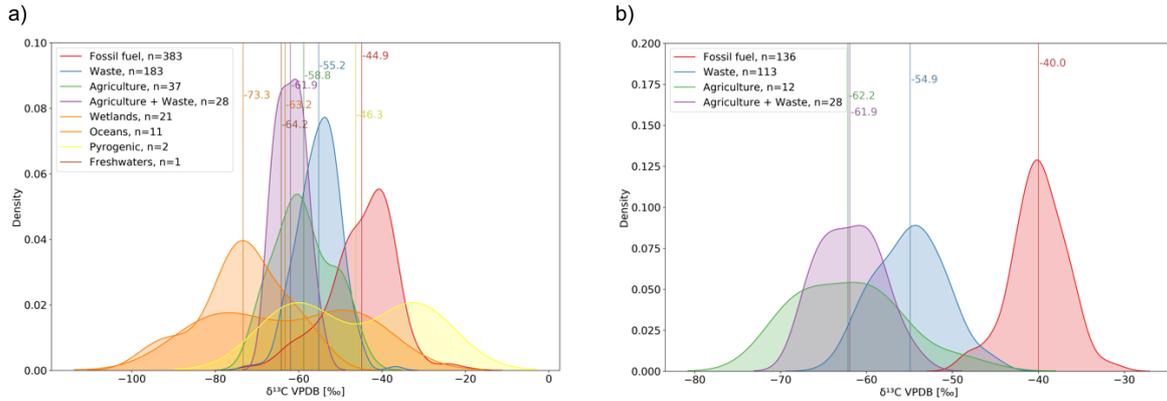


Fig. 3: Histograms of the $\delta^{13}\text{C}$ signatures of all identified CH₄ sources (a) and only from the UK (b).

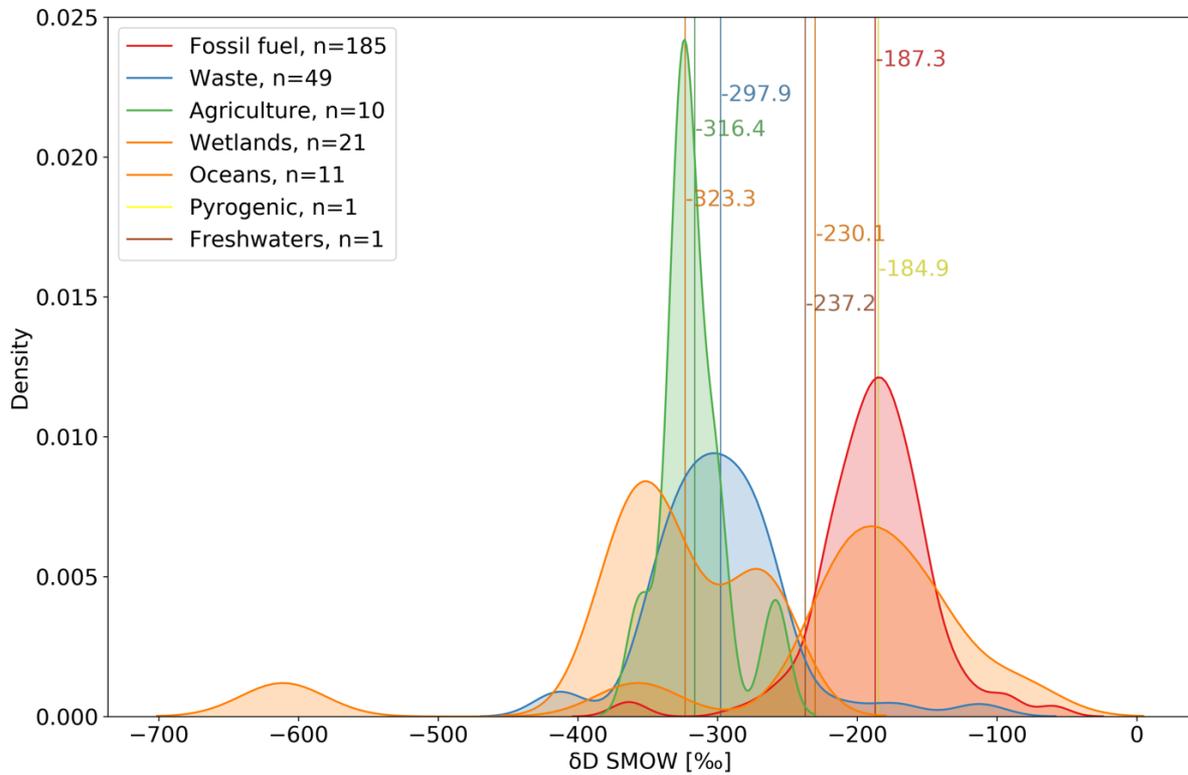


Fig. 4: Histogram of the δD signatures of all identified CH₄ sources

The maps in appendix show the $\delta^{13}\text{C}$ and δD source signature values from anthropogenic activities, fossil fuel extraction and microbial fermentation (i.e. waste and agriculture, mostly from livestock) respectively in Fig. A1 and Fig. A2. These are also the sources that we sampled the most. We can see that the $\delta^{13}\text{C}$ signatures we obtained from fossil fuel extraction in Poland and Romania are clearly different from what is found in western Europe. This reflects the complexity of CH₄ formation processes and the need of direct measurements in the study location for a better analysis of CH₄ source contributions at different scales.



4. Conclusion and possible impact

The isotopic characterization of methane sources in Europe that we performed so far within the MEMO² project is now gathered into an openly available database. The results represent a substantial new contribution to the existing isotope datasets. We have visited all types of sources in Europe, and also locations that were never measured before, despite their significant contributions to the European total emissions. For example, the work we did in Romania or in Poland represents a great improvement in the understanding of European CH₄ emissions, especially from fossil fuel. Future studies on source attribution of methane emissions in Europe using isotopic measurements will benefit from our results.

The maps in the appendix (Fig. A1 and A2) demonstrate that the analysis of isotopic data must be location-specific. The $\delta^{13}\text{C}$ gradient in the CH₄ from fossil fuel extraction across Europe is clearly visible. On the other hand, the isotopic composition of microbial sources of anthropogenic origin is rather stable. The signatures assigned to the fossil fuel extraction category in atmospheric models therefore need to be adjusted depending on the geographical domain. These considerations will improve the modelling of isotopes on a sub-continental to global scale, and contribute to reduce the uncertainties in the CH₄ budget. Finally, our findings illustrate the need of measurements in new, and more remote regions.

5. Dissemination & Exploitation

The database containing the MEMO² isotope measurements is openly available at <https://doi.org/10.5281/zenodo.4062356>.

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7. History of the document

Version	Author(s)	Date	Changes
1.0	Malika Menoud	07/08/2020	First draft
2.0	Malika Menoud	17/09/2020	First round comments + CRDS data
3.0	Malika Menoud	01/10/2020	Text, font size of figures
3.0	Sylvia	08.10.2020	Min. formatting, submitting

8. Appendix

8.1 Calculation of the source isotopic signatures

The Keeling plot method uses the linear relation between the isotopic values in the samples and the inverse of CH₄ mole fractions (Keeling 1961). The source signature (δ_s) will be the y-intercept of the regression line such as the following equation applies:

$$\delta_m = \frac{c_{bg}}{c_m} (\delta_{bg} - \delta_s) + \delta_s$$

where δ_m , δ_{bg} and δ_s are the measured, background and source isotopic signatures, respectively. c_m and c_{bg} are the CH₄ mole fractions in the sample and background, respectively. In this approach, it is assumed that the background $\chi(\text{CH}_4)$ and isotopic signature are constant.

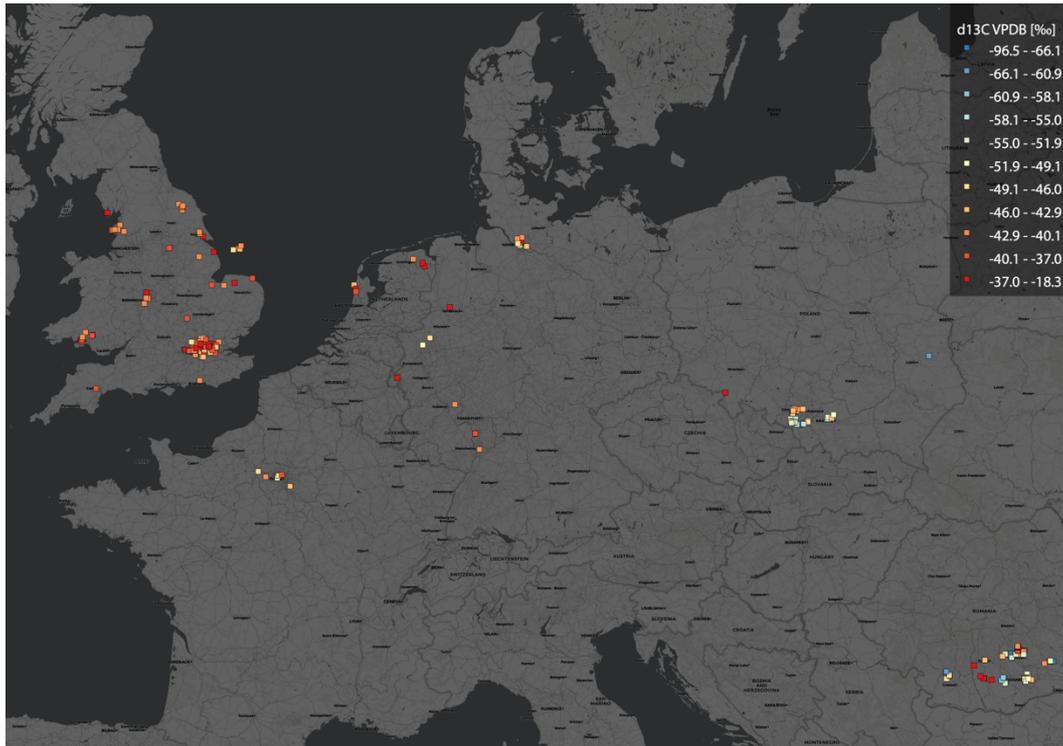
The Miller-Tans method is based on this formula (Miller and Tans 2003):

$$\delta_m c_m = \delta_s c_m - c_{bg} (\delta_{bg} - \delta_s)$$

where δ_m , δ_{bg} and δ_s are the measured, background and source isotopic signatures, respectively. c_m and c_{bg} are the CH₄ mole fractions in the sample and background, respectively.

8.2 Mapping isotopic signatures

a)



b)

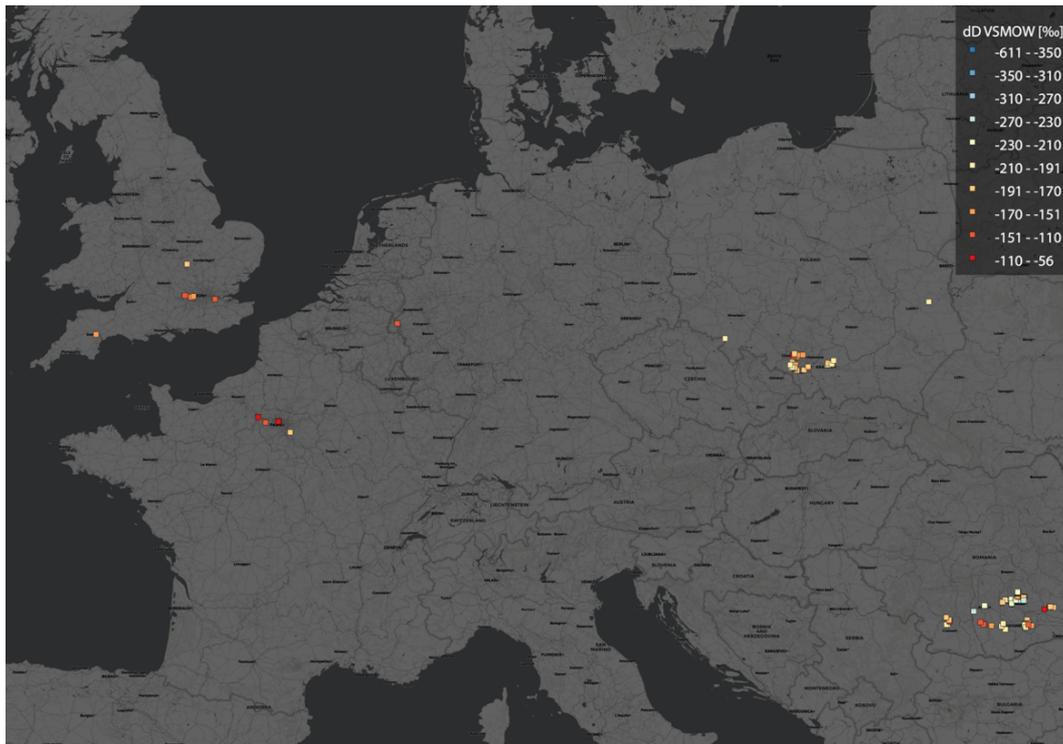
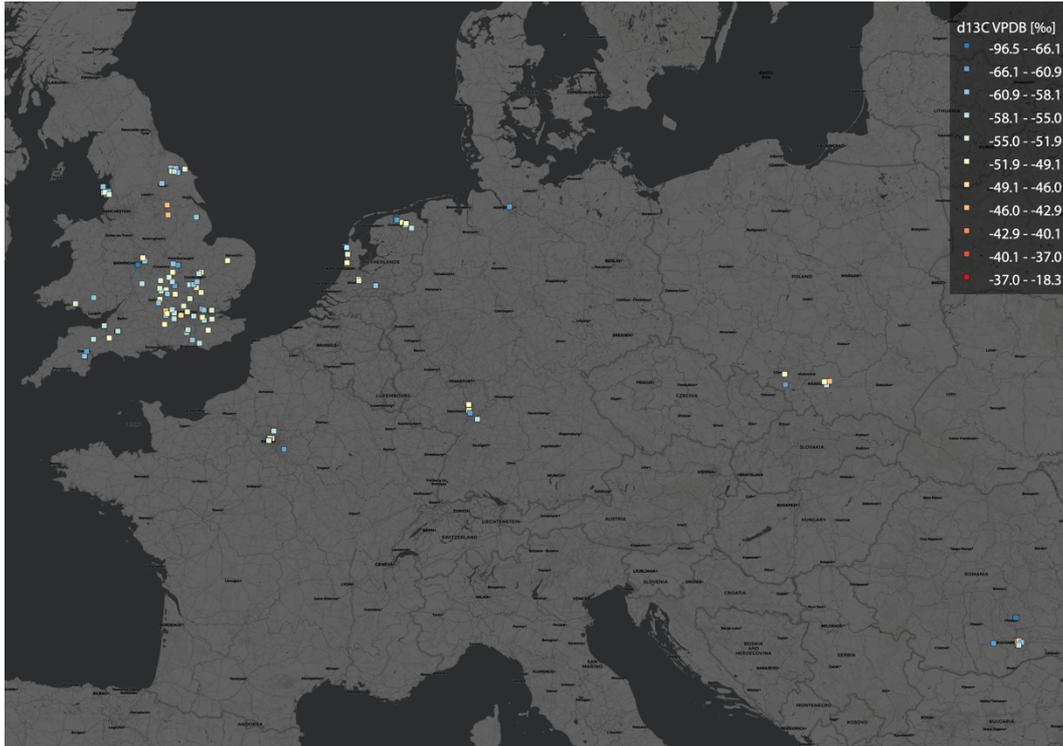


Fig. A1: Maps of $\delta^{13}\text{C}$ (above) and δD (below) source isotopic signatures of all the sites in the fossil fuel extraction category.

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a)



b)

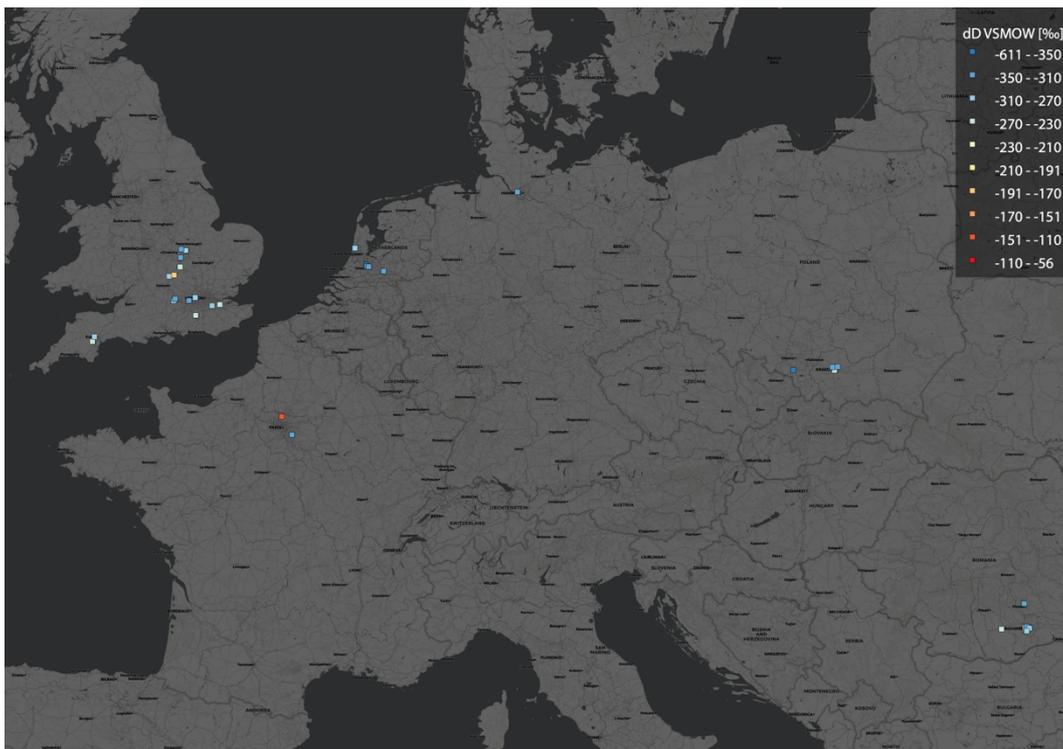


Fig. A2: Maps of $\delta^{13}\text{C}$ (above) and δD (below) isotopic signatures from anthropogenic emissions of microbial fermentation origin. This means waste management and agriculture, here being mostly cattle farming.