21GRD04 - isoMet

D3: Report on the methods for creation of a database of isotopic sources in CH_4 for use in atmospheric transport modelling exercises

Organisation name of the lead participant for the deliverable: UVSQ

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Deliverable Cover Sheet

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1. GOAL

Using input from A1.3.4, A2.1.1-A2.1.5, A3.1.1 and A3.1.4, UVSQ with support from Empa, UU, UofG, UoB, RHUL and NPL will draft a report on the methods for creation of a database for European δ13C(CH4) and δ2H(CH4) source signatures.

Once agreed by the consortium, the coordinator on behalf of UVSQ, Empa, UU, UofG, UoB, RHUL and NPL will submit the report to EURAMET as D3: ‘Report on the methods for creation of a database of isotopic sources in CH 4 for use in atmospheric transport modelling exercises’.

2. INTRODUCTION

Atmospheric observations provide a reality check on the true efficacy of climate change mitigation policy. Methane is a potent greenhouse gas (GHG) with multiple complex sources, and stable isotope ratios provide a fingerprint needed to verify emissions by source type. This project seeks to improve 1) ambient air monitoring capabilities; 2) the quality of source signature information; and 3) the modelling information necessary to direct the measurement strategy and make top-down emissions estimates.

The aim of WP2 is first to develop a sustainable metrological infrastructure for a dataset for $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$-source measurements in Europe, and second, to evaluate the potential for source apportionment of rare doubly substituted $^{13}CH_3D$ and $^{12}CH_2D_2$ isotopologues analysis in selected campaigns.

Currently there are significant gaps in the characterisation of CH_4 isotope source signatures, both from a methodological and standardisation point of view and in terms of data gaps. A dataset for $\delta^{13}C(CH_4)$ and $\delta^{2}H(CH_4)$ will include source signatures traceable to the VPDB and VSMOW/SLAP scales with relevance for calculating emissions from categories meaningful at an integrated European scale. Results from WP3 will inform this WP of the major knowledge gaps that can be targeted for source signature measurements. Uncertainties of 0.2 ‰ for $\delta^{13}C(CH_4)$ and 2 ‰ for $\delta^{2}H(CH_4)$ will be targeted on individual source measurements (specific location and time), enabling uptake by the atmospheric modelling community.

Within Task 2.1, the internal format of a database for European CH_4 isotope source data will be established, published data recorded, their uncertainty assessed, and relevant underrepresented emission sectors, regions and time periods identified.

3. CREATION OF THE DATABASE

3.1 INPUT FROM THE PROJECT ACTIVITIES

Within Isomet work package 2, a literature review was done on the different sources of methane in Europe to highlight the major sources and their isotopic signatures. This review concluded that the largest sources of methane emissions in Europe are agriculture, waste, and fossil fuel. Their isotopic signatures will vary depending on their creation pathways and may vary between countries depending on fossil fuel supply chains, waste practices and animal feed types.

3.2 DESIGN OF THE DATABASE FORMAT

We used as the basis the format from Sherwood et al., reused in Menoud et al. (see Table 1)

That is to say:

CONTINENT	COUNTRY	STATE_REGION	GROUP_TYPE	GROUP	CATEGORY	SUB-CATEGORY	SNAP	LONG	LAT	d13C_CH4_MEAN	d13C_CH4_ERR	d13C_CH4_N	d2H_CH4_MEAN	d2H_CH4_ERR	d2H_CH4_N	TYPE_UNCERTAINTY	COMMENTS	REFERENCE

Table 1: List of parameters used in Menoud et al.

Then using input from work package 3 activity, and discussion within the consortium, we came up with additional categories to allow the best traceability.

The full list of columns is listed below:
CONTINENT;COUNTRY;STATE_REGION;**LOCATION**;LAT;LONG;**COORDINATES_FROM_PRIMARY_SOURCE**;GROUP_TYPE;GROUP;CATEGORY;SUB-CATEGORY;**SOURCE_SPECIFIC_INFORMATION;RESERVOIR_SAMPLE_DEPTH;RESERVOIR_DEPTH_UNIT**;SNAP;**IPCC;**d13C_CH4;d13C_CH4_UNCERTAINTY;d**13C_CH4_UNCERTAINTY_DESCRIPTION**;d13C_CH4_N;d2H_CH4;d2H_CH4_UNCERTAINTY;**d2H_CH4_UNCERTAINTY_DESCRIPTION**;d2H_CH4_N;**D18;D18_UNCERTAINTY;D18_UNCERTAINTY_DESCRIPTION;D18_N;D13CH3D;D13CH3D_UNCERTAINTY;D13CH3D_UNCERTAINTY_DESCRIPTION;D13CH3D_N;D12CH2D2;D12CH2D2_UNCERTAINTY;D12CH2D2_UNCERTAINTY_DESCRIPTION;D12CH2D2_N;COLLECTION_START_TIME;COLLECTION_END_TIME;ANALYSIS_DATE;INSTRUMENT_TYPE;SAMPLE_TYPE;SAMPLING_METHOD;FITTING_METHOD;MEASUREMENT_LABORATORY**;COMMENTS;**DATA_PROVIDER;DATA_PROVIDER_CONTACT**;DOI_REFERENCE;**DOI_DATA_SOURCE**

The categories in red are to be chosen from a list while the other categories would be free text.

For older data without all available categories, the unknown will be filled with NA. For the new input, all fields will be mandatory.

The SNAP categories can be found here:
https://en.eustat.eus/documentos/elem_13173/definicion.html

SNAP Code	SNAP Description
01	Combustion in the production and transformation of energy
02	Non-industrial combustion plants
03	Industrial combustion plants
04	Industrial processes without combustion
05	Extraction and distribution of fossil fuels and geothermal energy
06	Use of solvents and other products
07	Road Transport
08	Other mobile sources and machinery
09	Waste treatment and disposal
10	Agriculture
11	Other sources and sinks (nature)

Table 2: SNAP categories

The categories and sub-categories are from Sherwood et al.:

Modern microbial data are from rice paddies, ruminants (C3- and C4-plant eating cattle, sheep, goats, and their manure), termites, waste (landfills manure, biogas (AD), composting, wastewater treatment), and wetlands (bogs and/or peat, deltas, estuaries, floodplains, lagoons, lakes, marshes, ponds, rivers, swamps and tundra). Biomass burning data are from brush, forests and/or woodlands, grasses, and pastures.

4. POPULATION OF THE DATABASE

The database was populated first with data from Menoud et al. Database. If additional information for these entries were known, they were added as well.

Then new data from the United Kingdom and data from the clumped isotopes using Defratyka et al. Clumped isotopes database were added as well.

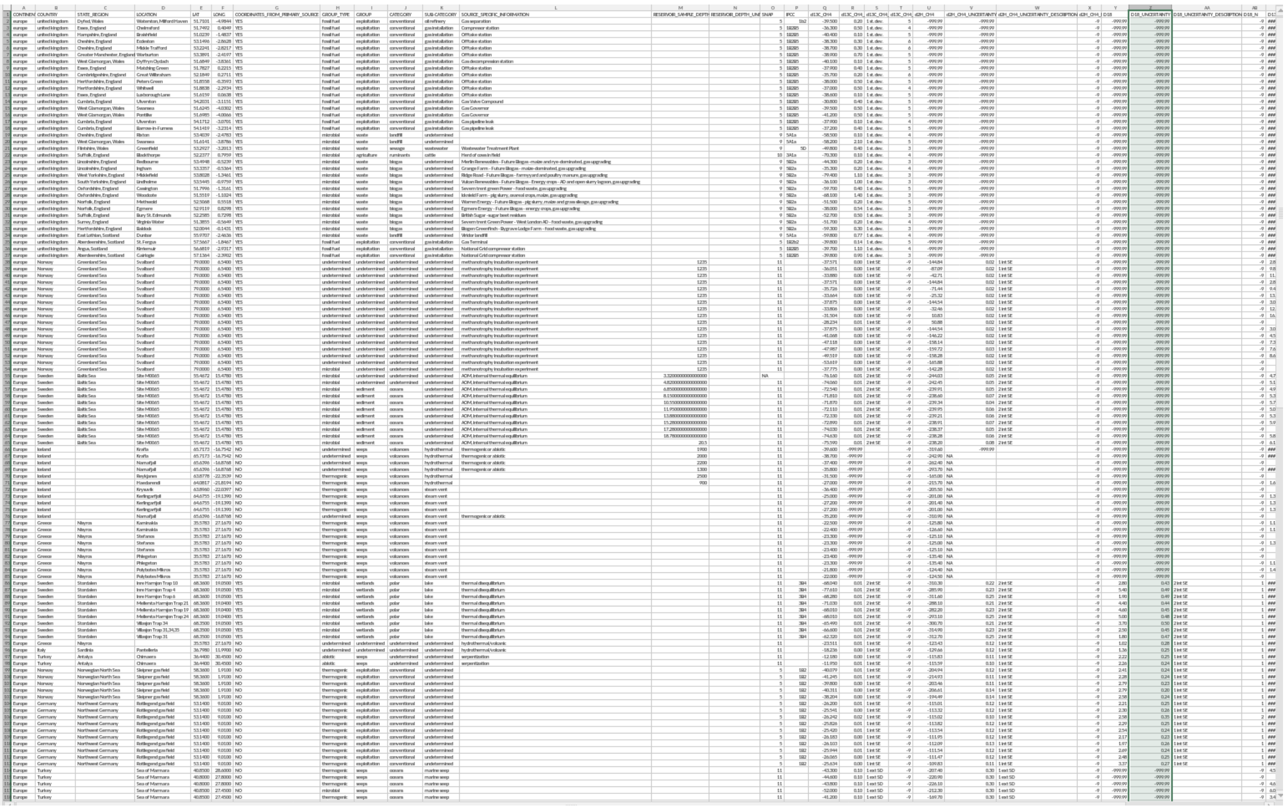


Figure 1: Snapshot of the database

5. ANALYSE OF THE DATABASE

Within work package activity A2.1.4, an analysis of the first data in the database was conducted. Menoud *et al.* (2022) compiled the CH_4 isotopic source signatures ($\delta^{13}C$-CH_4, δD-CH_4) from the MEMO2 project with the latest version of the Sherwood *et al.* (2017); Sherwood *et al.* (2021) global database. The study also searched the literature for more measured CH_4 source signatures to add to the dataset. At present, the number of measurements made in fossil fuel reservoirs and compiled in the database by Sherwood *et al.* (2021) is comparatively larger than from studies of other CH_4 emission sources, e.g. microbial or pyrogenic. In addition, the number of measurements is not evenly spread geographically: significantly more measurements were made in North American and European countries, Australia, Brazil, and Japan. Measurements of δD-CH_4 are more scarcely spread than $\delta^{13}C$-CH_4, and no data exists even from several European countries, e.g. Switzerland, Slovenia, Hungary and Finland. The analysis of the new Isomet database mostly based on Menoud database shows that the first five European countries where measurements are done are the UK, Romania (following the ROMEO campaign), Germany, Poland and France. 60% are from fossil fuel sources and 39% from biogenic sources. Time periods are not available for most of the historical data.

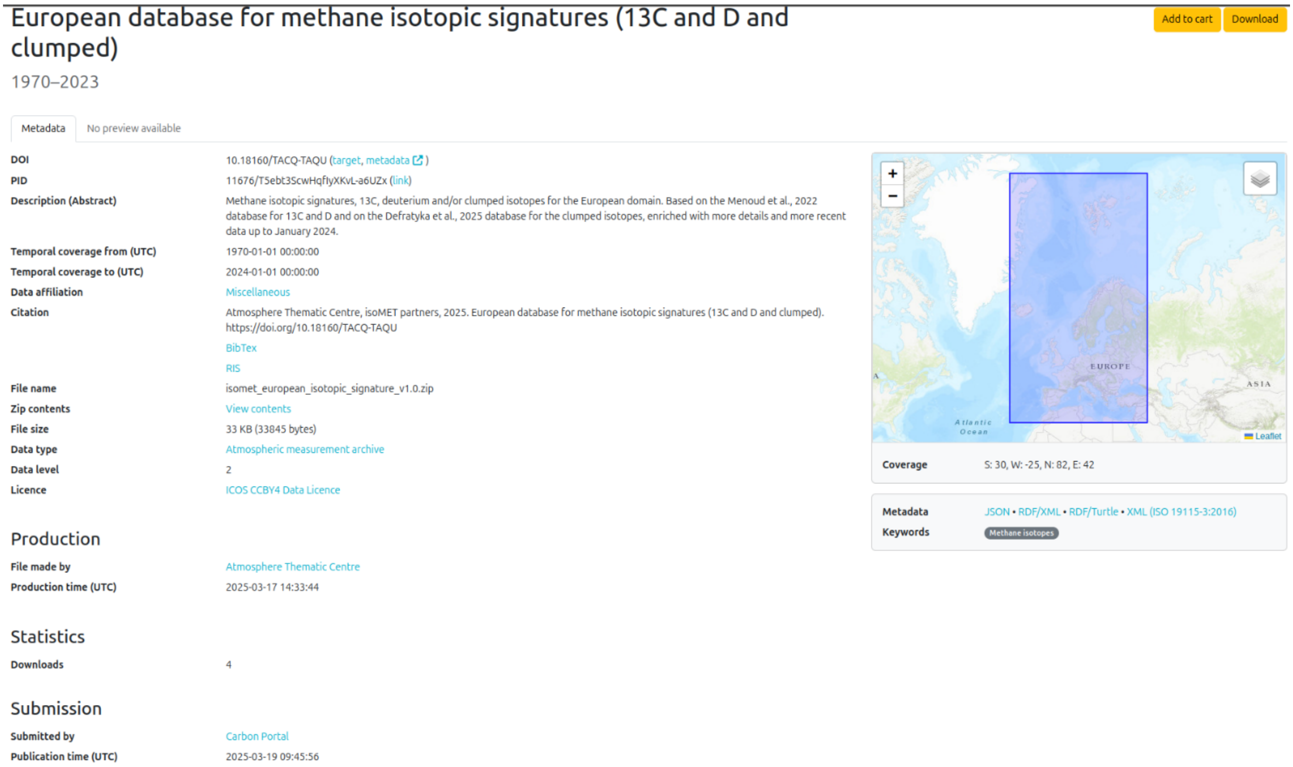
Wang *et al.* (2023) assembled a first clumped CH_4 database to predict the steady-state atmospheric methane clumped isotope composition. Within the isoMET project Sara Defratyka will compile a much more comprehensive review of $\Delta^{12}CH_2D_2$, $\Delta^{13}CH_3D$ data, based on articles published until spring 2024. The current working document contains more than 1100 entries, based on almost 80 scientific articles, focused both on studies from field samples and laboratory experiments. In short, clumped isotopes of CH_4 ($\Delta^{12}CH_2D_2$, $\Delta^{13}CH_3D$) aside conventional isotopic (i.e., $\delta^{13}C$ and δD) and molecular (C1, C2, C3, etc.) composition of hydrocarbons have been primarily used as tracers of the origin of natural gas and post-genetic physical and biologic processes (e.g. Kim *et al.*, 2023). Source studies have shown that the clumped isotopes of CH_4 often reflect formation temperatures, with exceptions from kinetically controlled processes (Gruen *et al.*, 2018) or mixtures of gases with different origins.

As measurements of clumped isotopes of methane have been started few years, previous measurements of clumped methane isotopologues from different sources have been spatially and temporally limited. Remarkably, most of existing studies were made by geochemistry community, with a main focus on deep reservoirs samples. Therefore, clumped isotopes of methane from sectors with significant emission to the atmosphere are poorly characterized. For example, only two samples were collected from ruminants and three from rice paddies, while no samples were collected from waste sector. Regarding natural methane emissions, few studies were focused on measurements of clumped isotopes of methane from lakes (Douglas *et al. 2016*; Lalk *et al. 2024*). However, in most cases, sample size (≤3) is insufficient to differentiate lake source signatures. Additionally, for clumped isotopes of methane, field samples are even more spatially limited than for $\delta^{13}C$-CH_4 and δD-CH_4, coming mostly from the US and China. Thus, more sampling from the main methane emission sectors from different locations over the globe, collected over different seasons would be required to spatially and temporally resolved clumped isotopologue source signatures, similar to existing studies for $\delta^{13}C$-CH_4 and δD-CH_4.

First direct measurements of $^{13}CH_3D$ and $^{12}CH_2D_2$ in the atmosphere, however, point to a different atmospheric methane composition as previously assigned (Haghnegahdar *et al.*, 2023; Sivan *et al.*, 2024). Differences are attributed to a microbial flux with less clumping (greater deficits relative to stochastic), which emphasizes our currently limited know-how on source signatures and their spatial and temporal variation. Also, more direct measurements of clumped isotopes in the atmosphere, especially from background stations, conducted during different seasons are crucial to find explanation of observed discrepancy between modelled (Haghnegahdar *et al. 2017*; Chung and Arnold *2021*) and observed (Haghnegahdar *et al. 2023*; Sivan *et al. 2024*) $^{13}CH_3D$ and $^{12}CH_2D_2$ in the atmosphere.

6. PUBLICATION OF THE DATABASE

The first version of the database has been published on the ICOS Carbon Portal on the landing page https://meta.icos-cp.eu/objects/T5ebt3ScwHqfIyXKvL-a6UZx and the DOI: https://doi.org/10.18160/TACQ-TAQU.



European database for methane isotopic signatures (13C and D and clumped)

1970–2023

DOI	10.18160/TACQ-TAQU (target, metadata)
PID	11676/T5ebt3ScwHqflyXKvL-a6UZx (link)
Description (Abstract)	Methane isotopic signatures, 13C, deuterium and/or clumped isotopes for the European domain. Based on the Menoud et al., 2022 database for 13C and D and on the Defratyka et al., 2025 database for the clumped isotopes, enriched with more details and more recent data up to January 2024.
Temporal coverage from (UTC)	1970-01-01 00:00:00
Temporal coverage to (UTC)	2024-01-01 00:00:00
Data affiliation	Miscellaneous
Citation	Atmosphere Thematic Centre, isoMET partners, 2025. European database for methane isotopic signatures (13C and D and clumped). https://doi.org/10.18160/TACQ-TAQU BibTex RIS
File name	isomet_european_isotopic_signature_v1.0.zip
Zip contents	View contents
File size	33 KB (33845 bytes)
Data type	Atmospheric measurement archive
Data level	2
Licence	ICOS CCBY4 Data Licence

Coverage	S: 30, W: -25, N: 82, E: 42
Metadata	JSON • RDF/XML • RDF/Turtle • XML (ISO 19115-3:2016)
Keywords	Methane isotopes

Production

File made by	Atmosphere Thematic Centre
Production time (UTC)	2025-03-17 14:33:44

Statistics

Downloads	4

Submission

Submitted by	Carbon Portal
Publication time (UTC)	2025-03-19 09:45:56

Figure 2: Snapshot of the database landing page

7. CONCLUSION

Measurements of ambient isotopic composition and source isotopic signatures of CH_4 allowed the modelling communities to assess the contributions of different source categories as well as the sink strengths. The conventional isotopic information has been used for source attribution, e.g. Thanwerdas *et al.* (2024). The clumped isotopologues, especially the $^{12}CH_2D_2$, were identified by Chung and Arnold (2021) as a useful tracer that can constrain the sink strength. However, the current disagreements between the model and measurement indicate our gap in the knowledge in atmospheric CH_4 fluxes.

The improvements in modelling of atmospheric isotopic composition can be achieved by the following. Firstly, an easy-to-use source signature database that lists spatial-sectoral information with data entries from which temporal variations can be inferred, i.e. interannual-seasonal regular measurements of sources. This would allow for the best prescription of source signatures for the models, as it is common to use a priori source signature that lacks spatio-temporal variation. Secondly, better spatial coverage of measurements of isotopic compositions, especially ^2H, is desired.

In terms of modelling of $^{13}CH_3D$ and $^{12}CH_2D_2$ in the atmosphere, improved database, especially from the main emission sectors, is required. Similar to $\delta^{13}C$-CH_4 and δD-CH_4 studies, sampling strategy should be more focused on unrepresented microbial sources and on understanding spatio-temporal variability of clumped isotopes of individual emission sectors.

Also, better understanding of methane sinks in the atmosphere is crucial to obtain realistic results from modelling clumped isotopes. Currently, there is insufficient understanding of isotopic fractionation effects during reactions with main sinks of methane in the atmosphere (OH and chlorine) (Whitehill *et al. 2017*), what also can affect modelling results and observed disrepency between measurement and models (Haghnegahdar *et al. 2023*; Sivan *et al. 2024*).

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