Global inventory of the stable isotopic composition of methane surface emissions, augmented by new measurements in Europe

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Abstract. Recent climate change mitigation strategies rely on the reduction of methane (CH_4) emissions. $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ measurements can be used to distinguish sources and thus to understand the CH_4 budget better. The CH_4 emission estimates by models are sensitive to the isotopic signatures assigned to each source category, so it is important to provide representative estimates of the different CH_4 source isotopic signatures worldwide.

5   We present new measurements of isotope signatures of various, mainly anthropogenic, CH_4 sources in Europe, which represent a substantial contribution to the global dataset of source isotopic measurements from the literature, especially for $\delta^2H_{CH_4}$. They improve the definition of $\delta^{13}C_{CH_4}$ from waste sources, and demonstrate the use of $\delta^2H_{CH_4}$ for fossil fuel source attribution. Results from previous studies were combined in a common database that we updated with our new measurements, as well as with additional literature. We found that microbial sources are generally well characterised. The large variability in fossil fuels

10   isotopic compositions requires particular care in the choice of weighting criteria for the calculation of a representative global value. The global dataset could be further improved by measurements from African, South American and Asian countries, as well as more measurements from pyrogenic sources.

The final version of the European methane isotope database coupled with a global inventory of fossil and non-fossil $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ source signature measurements, is available at: https://doi.org/10.24416/UU01-4PO56T (Menoud et al., 2021a).

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1 Introduction

The current change of the earth's climate is mainly caused by the emissions of greenhouse gases from anthropogenic activities (IPCC, 2013; IPCC 2021, 2021a). Methane (CH_4) is a strong greenhouse gas, with a global warming potential 32 times that of CO_2 over 100 years (Etminan et al., 2016). The increase in CH_4 concentration has contributed to an average warming of

20 0.5ºC in 2010-2019 compared to 1850-1900, which is slightly smaller than the contribution of CO_2 (IPCC 2021, 2021b). The global CH_4 mole fraction ($\chi(CH_4)$) in the atmosphere has drastically increased since 1984, when direct regular measurements started, changing from 1645 ppb to 1850 ppb in 2017 (Nisbet et al., 2019). Compared to pre-industrial times (before 1750), the global $\chi(CH_4)$ has increased by 160%, from 720 to 1850 ppb (IPCC 2021, 2021a).

In the past 30 years, we have not observed a steady growth of atmospheric CH_4 mole fraction. Instead the increase in $\chi(CH_4)$

25 levelled-off between 2000 and 2007, and has been increasing again since then, from 2014 at the highest rate since the 1980's (Nisbet et al., 2019). This renewed increase presents a significant threat to reaching the goals of the Paris agreement, and mitigation policies are now also targeting CH_4 emissions (Shindell et al., 2017; Mayfield et al., 2017; Nisbet et al., 2020). Efficient strategies require good knowledge of the different kinds of CH_4 sources, their location and relative contributions. While emission estimates are reported at a country-level using statistical indicators, atmospheric inversions, based on observations,

30 can be used to verify the inventories (Houweling et al., 2000; Zavala-Araiza et al., 2015; Henne et al., 2016; Maasakkers et al., 2019). But the results from two approaches, respectively called bottom-up and top-down, are not fully compatible, reflecting a lack in our understanding of the CH_4 cycle (Etiope and Schwietzke, 2019; Saunois et al., 2020; Stavert et al., 2021).

Measurements of CH_4 isotopologues provide additional constraints on the relative contribution of the various source categories, because CH_4 isotopic composition depends on the formation processes (Schoell, 1980; Whiticar, 1999; Quay et al.,

35 1999). Time series of ambient CH_4 isotopic ratios are already used to derive emission scenarios in global models (Bousquet et al., 2006; Schaefer et al., 2016; Turner et al., 2017; Thompson et al., 2018; Fujita et al., 2020; Lan et al., 2021), and at the regional scale (Röckmann et al., 2016; Stieger et al., 2019; Menoud et al., 2020, 2021b; Varga et al., 2021). In addition, isotope measurements have proven to be very successful for source attribution in cities (Phillips et al., 2013; Zazzeri et al., 2017; Maazallahi et al., 2020; Xueref-Remy et al., 2020; Defratyka et al., 2021; Fernandez et al., in review), and larger regions

40 (Tarasova et al., 2006; Fisher et al., 2011; Beck et al., 2012; Warwick et al., 2016; Fisher et al., 2017; Lu et al., 2021). The uncertainties in the resulting emission rates of the different source categories depend on our knowledge of the different isotopic source signatures, and understanding of their variability (Rigby et al., 2012; Schwietzke et al., 2016; Szénási, 2020).

Direct measurements of the isotopic signature of CH_4 sources allow us to characterise them well, and a lot of data is avail-

45 able in the literature. Several review articles on CH_4 isotopic source signatures were previously published (Rice and Claypool, 1981; Cicerone and Oremland, 1988; Bréas et al., 2001). The most recent one presented by Sherwood et al. (2017), and recently updated in Sherwood et al. (2021), gathered values from 13 489 locations (10 778 fossil fuel, 2711 non-fossil) from 347 published references. The 2017 study focused on (fugitive) fossil fuel sources, and allowed to re-evaluate the global $\delta^{13}C_{CH_4}$ value assigned to this emission category towards more depleted values (Schwietzke et al., 2016). A disadvantage of this database

50 is that it is rather US-centered, and that the dataset is strongest for fossil fuel sources, but less robust for non-fossil sources. Therefore the database can be completed by more studies, especially concerning non-fossil sources.

The MEMO[2] project (MEthane goes MObile - MEasurements and MOdeling) was a H2020 MSCA European Training Network[1] with the goal to use innovative mobile measurement and modelling tools to improve the quantification of CH_4

55 emissions in Europe (Walter et al., 2019). An important component of MEMO[2] was the isotopic characterisation of CH_4 sources. Two laboratories involved in MEMO[2], at Utrecht University, The Netherlands, and at the Royal Holloway University of London, UK, carried out a large number of high-precision measurements with isotope ratio mass spectrometry (IRMS). Another method, using cavity ring-down spectroscopy (CRDS) was developed for the mobile measurements of ambient CH_4 isotopic composition. Several research groups were involved in field work with mobile measurements that targeted specific

60 sources or environments in several European countries. Using this network, numerous CH_4 sources could be sampled for isotopic measurements. The resulting isotopic source signatures were gathered in a publicly available database: The European Methane Isotope Database.

This article presents the data collected within MEMO[2], and the implications for the global understanding of CH_4 source isotopic composition. To place the new data in context, we analyse it together with an updated version of the Sherwood et al.

65 (2017, 2021) global database of measured CH_4 source signatures.

2 Methods

2.1 Measurements within the MEMO[2] project

2.1.1 Sampling

The data was collected by the research teams of 8 universities and research institutes: Utrecht University (UU), the Royal

70 Holloway University of London (RHUL), the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Heidelberg University (UHEI), AGH University of Science and Technology (AGH), Lund University (LU), the University of Groningen (UG), and the Netherlands Organisation for Applied Scientific Research (TNO). They participated in several campaigns in the Netherlands, the United Kingdom, France, Germany, Poland, Sweden, Romania and Turkey. Several other teams collaborated in two intensive campaigns: the CoMet[2] campaign in the Upper Silsian Coal Basin (USCB) in Poland (Fiehn et al., 2020;

75 Gałkowski et al., 2021), and the ROMEO campaign in Romania[3] (Röckmann, 2020).

Different sampling methods were used:

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[1]Marie Skłodowska-Curie actions, Horizon 2020 Innovative Training Networks founded under the grant agreement No 722479: https://cordis.europa.eu/project/id/722479

[2]Carbon dioxide and Methane mission, May-June 2018

[3]ROmanian Methane Emissions from Oil & gas, October 2019

- Mobile sampling on a road vehicle, using a fast analyser (0.1 to 10 Hz) on-board to detect CH_4 enhancements (G2301, G2201-i, and G4302, Picarro Inc., USA; MGGA-918 and UGGA, Los Gatos Research, ABB, USA; LI-7810 Trace Gas analyser, LI-COR, USA; Dual Laser Trace Gas Monitor, Aerodyne Research, USA). The samples were taken using a small electric pump connected to an inlet outside of the vehicle. The sample receptacles were bags of 1 to 3 L (Supel™-Inert Multi-Layer Foil bags, Sigma-Aldrich Co. LLC, USA; Tedlar or FlexFoil sample bags, SKC Inc., USA). Surveys were made around known sources of CH_4, where we sampled the elevated mole fractions as well as background CH_4 on the same day. If it was not practical to approach a source with the vehicle during mobile surveys, samples were taken on foot.

- Mobile sampling onboard of an aircraft, during the ROMEO campaign. A CRDS instrument (G4302, Picarro Inc., USA) was installed in the aircraft, and samples were taken from the outflow of the instrument into bags of 2 L (Supel™-Inert Multi-Layer Foil bags, Sigma-Aldrich Co. LLC, USA) when an increase in CH_4 mole fractions was observed. The method is described in detail in Menoud et al. (in review).

- Mobile sampling on foot, without analyser. The samples were taken at regularly spread locations around a known CH_4 source, to make sure we collected air with CH_4 from the emission plume and background. In this case, the sample receptacles were bags of 2 to 3 L (Supel™-Inert Multi-Layer Foil bags, Sigma-Aldrich Co. LLC, USA; Tedlar sample bags, SKC Inc., USA), filled with a portable hand pump.

- Soil chambers on wetlands in north Sweden and coal waste disposal areas in Poland. In wetlands, we installed transparent Plexiglas chambers on top of stainless steel collars that were pushed 20 cm into the peat. Samples from the chambers were taken during closure times, when $\chi(CH_4)$ increased, generally after 10 to 25 min. The soil chambers in Poland were made of plastic buckets covered with aluminum foil that were pushed about 5 cm in the ground and left for 30 min. In both cases, air was pumped into 2L sample bags (Supel™-Inert Multi-Layer Foil, Sigma-Aldrich Co. LLC, USA) for further analysis in the lab.

- From an unmanned aerial vehicle (UAV), carrying an AirCore (coiled tubing) system to collect air samples (Andersen et al., 2018). The air samples were continuously pulled into the AirCore while flying transects across the plume of a CH_4 emission source, and were transferred to a 0.5 or 1 L bag sample after landing (Supel™-Inert Multi-Layer Foil, Sigma-Aldrich Co. LLC, USA) for further analysis in the laboratory.

Some photos taken in the field illustrate the different sampling procedures that were used, and are available in Fig. A1 of the supplementary material.

2.1.2 Measurements of isotopic composition

The mass spectrometry measurements were performed at two laboratories: the IMAU (Institute for Marine and Atmospheric research Utrecht) at UU, and at the Department of Earth Sciences at RHUL. Both laboratories use a CF-IRMS (continuous flow isotopic ratio mass spectrometry) system to measure $\delta^{13}C$, and also δ^2H at IMAU. The system at IMAU was described

110 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 to 0.1 ‰ for $\delta^{13}C_{CH_4}$. At IMAU, δ^2H measurements have a reproducibility lower than 2 ‰. For consistency of the results, the two laboratories measured a set of 5 cylinders that contained air with CH_4 of different isotopic composition. The resulting differences in $\delta^{13}C_{CH_4}$ for each cylinder ranged beetween 0.02 and 0.04 ‰. They were within the analytical error reported by the two laboratories, so that the isotopic results obtained within the MEMO^2 project are consistent across the laboratories. The

115 inter-comparison exercise is presented in detail in a MEMO^2 deliverable report publically availabe [4].

The UHEI and LSCE groups performed isotopic measurements using CRDS instruments (G2201-i, Picarro inc., USA). Their methods were described in Hoheisel et al. (2019) and Defratyka et al. (2021).

In the database, the method of isotopic measurements is specified by the "Measurement type" parameter, as either 'IRMS' or 'CRDS'. The laboratory where the measurements were performed is specified in the column "Measurement lab".

2.1.3 Calculation of isotopic signatures

120 The measurement results of $\delta^{13}C$ and δ^2H of CH_4 are for ambient air, and not the sources themselves. There are different methods to derive the isotopic source signatures from the sampled CH_4 enhancement signatures; the Keeling plot and Miller-Tans methods are commonly used mass balance approaches. The Keeling plot method is based on the assumption that the background is stable during the sampling period (Keeling, 1961; Pataki et al., 2003). The Miller-Tans method is also applicable

125 when the condition of a stable background is not fulfilled (Miller and Tans, 2003). Because background samples were taken on each survey day and in the same region, the condition of stable background was usually fulfilled. Defratyka (2021) showed that in this case, both methods lead to similar results within their uncertainty.

Both methods involve a linear regression model to fit the observed data. Different models were used: ordinary least squares (OLS) minimising the difference in the y-axis coordinate, bivariate correlated errors and intrinsic scatter (BCES) (Akritas and

130 Bershady, 1996), and ordinary distance regression (ODR) (Boggs and Rogers, 1990). Zobitz et al. (2006) compared different regression methods when applied in Keeling plots. The ODR can induce a bias towards lower values in the case the data points cover a relatively small range on the x-axis, so the OLS and BCES methods were usually prefered.

All the mass balance and regression methods are statistically valid. Therefore we did not work towards a uniform procedure, but the different approaches are specified for each entry of the database by the parameters "Mass balance approach" and

135 "Regression method".

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[4]Lowry, D., Röckmann, T., Fisher, R., Menoud, M., Fernandez, J., 2018. Isotopic measurements linked to common scale (Deliverable No. 2.1), WP2. MEMO^2: MEthane goes MObile – MEasurements and MOdelling, Available at: https://h2020-memo2.eu/wp-content/uploads/sites/198/2018/12/MEMO2-D2.1-Isotopic-measurements-linked-to-common-scale-final.pdf.

2.2 Update of the global database

2.2.1 Structure of the database

We used the same parameters as in the database of Sherwood et al. (2017, 2021) for non-fossil data. That is because our objectives concern only values for δ^{13}C and δ^2H of emitted CH_4, and do not include measurements of other gases or isotope signatures that Sherwood et al. (2017) reported in the fossil fuel database. The variables of interest are listed in Table 1 and include the site description (country, region, group, category and sub-category) and the δ^{13}C and δ^2H of CH_4. We grouped the sources reported in the European Methane Isotope Database by region and sub-category in order to integrate it in the literature database. We kept the categories and sub-categories as defined in Sherwood et al. (2017, 2021), but when the new entries from MEMO[2] measurements and published literature required it, we added additional source categories or sub-categories. The categories are grouped into the three main CH_4 formation pathways: modern microbial, pyrogenic, and fossil fuels. The "modern microbial" CH_4 is formed by microorganisms in surface ecosystems or in animals through enteric fermentation, and are refered simply as "microbial" throughout the paper. Microbial CH_4 formations in the subsurface related to petroleum systems belongs to the "fossil fuels" category. Compared to Sherwood et al. (2017, 2021), we extended the biomass burning type to include emissions from all combustion sources, such as traffic or industry (Table 1).

Table 1. Number of data entries ($\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$) per source category in the updated CH_4 isotopic signature database.

				Sherwood et al. (2017)	Additional literature	MEMO[2]
microbial	agriculture	ruminants	C3/C4	313	57	41
		rice paddies	flooded, flooded seasonally	499	15	
		piggery			20	
	waste	landfill		186	115	76
		sewage	wastewater, manhole	4	33	147
		biogas	manure, C4/C3	30	23	47
		manure	cattle		9	22
		compost				4
		abattoir	cattle		27	
	wetlands	temperate	marsh, bog, swamp, lake, estuary, pond, delta, fen, lagoon, reeds, flooded forest, wet prairie, river, mangrove	385	158	12
		tropical	floodplain, lake, swamp, marsh, river, riverine reeds, mixed	199	94	
		polar (incl. boreal)	bog, marsh, swamp, tundra, lake, estuary, fen, wet tundra, (thaw) permafrost, mire	557	72	30
	other	forest	boreal forest		2	
		termites		30	7	
fossil fuels	exploitation	conventional	gas leak, gas installation, oil field, mixed, natural gas, oil refinery	8669	112	600
		coal	active coal mine, inactive coal mine, coal seam gas	2904	184	111
		shale		737		
	seeps	oceans	marine seep			8
		coal seam gas			70	
		volcanoes			8	
pyrogenic	biomass burning	grass, pasture, brush, woodland, wood, forest, crop	C3/C4	113	2	
	fossil fuel burning	conventional	car, traffic, residential heating		71	5

2.2.2 Reported variables

The analytical parameters reported in the database are $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$, which are defined as:

$$\delta X = (\frac{R_{sample}}{R_{standard}} - 1)$$

with $R = \frac{^{13}C}{^{12}C}$ for $X = ^{13}C$ or $R = \frac{^2H}{^1H}$ for $X = ^2H$

The unit is in per mille (‰), and values are relative to the international standard materials Vienna Pee Dee Belemnite (VPDB) for $\delta^{13}C$, and Vienna Standard Mean Ocean Water (VSMOW) for δ^2H.

2.2.3 Literature data

We found additional data in the literature to complete the referred data listed in Sherwood et al. (2021). Because we aim at reflecting the actual CH_4 surface emissions to the atmosphere, we excluded studies that reported results from laboratory experiments, and of CH_4 dissolved in water (i.e. in oceans, wetlands and inland waters). We note that the search for data was biased because of the use of English language. The references we added concern published peer-reviewed articles and to a lesser extent thesis and conference papers. The studies were performed from 1982 to 2021 in various laboratories in the world. We did not perform additional data quality assessment.

2.3 Results and discussion

The data on isotopic source signatures from the measurement campaigns carried out within the MEMO[2] project (2017-2020) were compiled into one database: The European Methane Isotope Database. The first version was made accesssible[5] on October 1st 2020, and described in a publicly available report[6]. The European data was used in several publications over the past 2 years by Menoud et al. (2020, 2021b, in review); Maazallahi et al. (2020); Defratyka et al. (2021); Bakkaloglu et al. (2021, in review); Fernandez et al. (in review). The final version of the global database, including the MEMO[2] measurements and the additional literature are available at: https://doi.org/10.24416/UU01-4PO56T.

2.4 The European Methane Isotope Database

The isotopic signatures obtained within the MEMO[2] project concern 734 locations over 8 countries, with δ^2H source signatures being measured at 54 % of the sites (Table 2). Figure 1 shows the geographical distribution of the sampled sites in the different countries, according to the type of source. The number of sources we sampled does not necessarily represent the emission magnitudes.

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[5]Menoud, M., Röckmann, T., Fernandez, J., Bakkaloglu, S., Lowry, D., Korben, P., Schmidt, M., Stanisavljevic, M., Necki, J., Defratyka, S., Kwok, C.Y., 2020. mamenoud/MEMO2_isotopes: v8.1 complete. Zenodo.

[6]Menoud, M., Röckmann, T., Lowry, D., Fernandez, J., 2020. Improved isotopic source signatures of local and regional CH_4 emissions (Deliverable No. 2.2), WP2. MEMO[2]: MEthane goes MObile – MEasurements and MOdelling, Available at: https://h2020-memo2.eu/wp-content/uploads/sites/198/2021/03/MEMO2-D2.2-v3-final.pdf.

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Table 2. Number of locations where CH_4 isotopic source signatures were derived from sample measurements.

	$\delta^{13}C_{CH_4}$	$\delta^2H_{CH_4}$
The Netherlands	50	27
United Kingdom	240	54
Poland	98	73
Germany	73	23
France	46	23
Sweden	21	21
Romania	184	174
Turkey	2	0
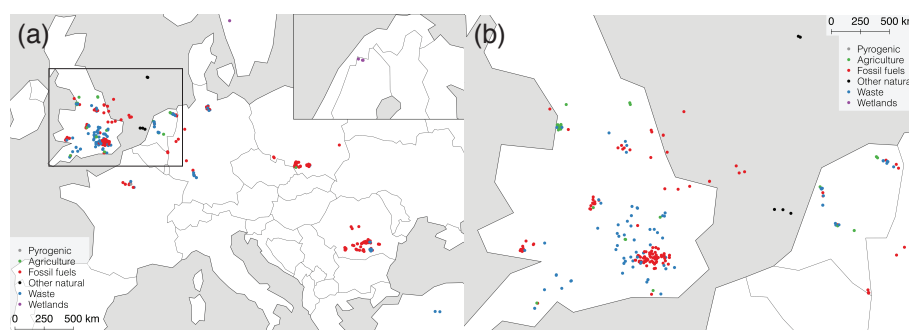
Figure 1. Geographical distribution of isotopic signature measurements ($\delta^{13}C$ and/or δ^2H of CH_4) carried out within the MEMO[2] project (2017 to 2020), depending on the type of source. **(a)** All locations. **(b)** Only in the UK, Netherlands and Germany.

175   During mobile surveys, we mostly targeted anthropogenic emissions from the exploitation and use of fossil fuels and waste processing facilities (Fig. 1). These are the most obvious anthropogenic CH_4 sources in densely populated regions, and we acknowledge a deliberate sampling bias towards urbanised areas. No biomass burning emissions were characterised during the MEMO[2] project. The European Methane Isotope Database partially address the geographical bias pointed out by Sherwood et al. (2017): it particularly includes a large number of measurements made in Romania, where almost no data was available

180   before.

We characterised 376 locations by both $\delta^{13}C$ and δ^2H values, and we compared the results to ranges reported in the literature in Fig. 2. The fossil fuel sources partly overlap with the range of thermogenic CH_4, but also spread towards lower $\delta^{13}C$ or higher δ^2H. This is due to the presence of natural gas of microbial origin in the coal reservoirs of Silesia, in Poland (Kotarba, 2001;

185   Kotarba and Pluta, 2009; Menoud et al., 2021b), as well as in Romania (Baciu et al., 2018; Fernandez et al., in review; Menoud et al., in review). We concluded that this microbial CH_4 originates from the CO_2 reduction pathway, because of a relatively enriched δ^2H (>-250 ‰), and relatively depleted $\delta^{13}C$ (<-60 ‰) (Milkov and Etiope, 2018). The δ^2H measurements were

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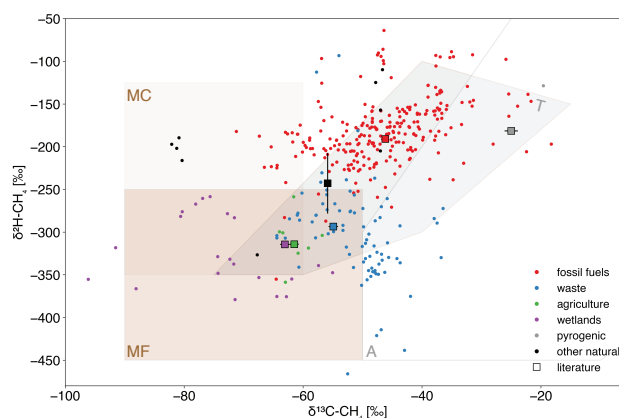
Figure 2. Dual isotope plot presenting the new European Methane Isotope Database (circles); the literature data for the same source categories, taken from Sherwood et al. (2017, 2021) and completed with additional publications (squares); and shaded areas represent the different methanogenesis pathways from Milkov and Etiope (2018): MF = microbial fermentation, MC = microbial CO_2 reduction, T = thermogenic, A = abiotic.

in these cases particularly useful to distinguish fossil fuels from microbial sources (Menoud et al., 2021b; Fernandez et al., in review; Menoud et al., in review).

The waste-related source signatures are generally more enriched in $\delta^{13}C$ than the typical microbial fermentation range specified in previous reviews. The most enriched values concern sewage treatment plants and biogas plants. Changes in waste management practices towards less disposal and more biogas production can likely explain the higher $\delta^{13}C$ values found in recent studies (Bakkaloglu et al., 2021). A new study also reported surprisingly enriched $\delta^{13}C_{CH_4}$ (and δ^2H) around a wastewater treatment plant in Australia: $\delta^{13}C$ = -47.6 $\pm$ 2 ‰ (Lu et al., 2021). The $\delta^{13}C$ of CH_4 emitted from sewage treatment plants depends on process parameters: oxic conditions lead to more enriched signatures than anaerobic treatment (Toyoda et al., 2011). Regarding biogas facilities, Bakkaloglu et al. (in review) emphasised the link between the type of substrate and the emitted CH_4 isotopic signatures: facilities that operate with C4 plant substrates emit CH_4 with higher $\delta^{13}C$ values in comparison with C3 plant substrates. Another driver for more or less enriched $\delta^{13}C_{CH_4}$ emissions from waste sources is isotopic fractionation when CH_4 reacts or diffuses. Diffusion and oxidation in the soil layers when CH_4 migrates from the deeper layers are secondary processes that cause isotopic fractionation (Bergamaschi et al., 1998; De Visscher, 2004; Conrad, 2005; Gebert and Streese-Kleeberg, 2017; Obersky et al., 2018; Bakkaloglu et al., 2021), which increases the range of possible isotopic signatures of the emitted CH_4.

The maps in Fig. 3 emphasise the similarities between $\delta^{13}C$ source signatures from modern microbial and fossil fuel sources in Poland and Romania. The average $\delta^{13}C_{CH_4}$ of fugitive emissions from coal, oil and gas extraction sites in Poland and Romania was -48.5 $\pm$ 0.6 ‰ (n=235), compared to -38.9 $\pm$ 0.3 ‰ (n=154) from gas leaks in only the UK and the Netherlands (and -40.4 $\pm$ 0.3 ‰ (n=217) including France and Germany). This distinction is also visible in the histograms of the European

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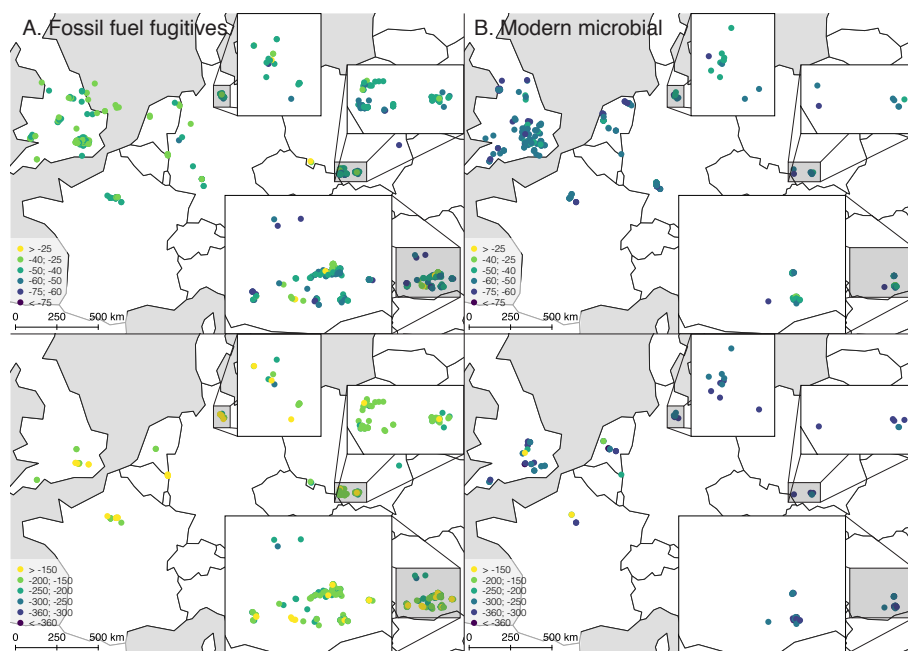
Figure 3. Measured δ^{13}C (top) and δ^2H (bottom) in CH$_4$ from European anthropogenic sources sampled within MEMO^2. **A.** CH$_4$ fugitive emissions from the exploitation of fossil fuels (gas leaks, oil and gas extraction and processing sites). **B.** CH$_4$ emissions from modern microbial fermentation sources (ruminants, landfills, sewage treatment plants and biogas plants).

Methane Isotope Database in Fig. 5.A. In western Europe, δ^{13}C allows for a good separation between microbial and fossil fuel sources, which is well-established in the literature (Levin et al., 1993; Lowry et al., 2001; Röckmann et al., 2016; Zazzeri et al., 2017; Lowry et al., 2020). Yet we show that we can't use only δ^{13}C data to distinguish microbial and fossil fuel CH$_4$ from all European regions. Fortunately, the δ^2H$_{CH_4}$ source signatures allow for a clear distinction between fossil fuel and modern microbial emissions of anthropogenic origin (Fig. 3 and 5.A).

2.5 Global data overview and representativeness

The extended global database including all literature data and the aggregated MEMO^2 data consists of 13313 and 4337 measurements of δ^{13}C and δ^2H, respectively, from 64 countries. The map in Fig. 4 shows the partitioning of the data per country, and Table 1 the number of records per CH$_4$ source. The maps in Fig. A2 of the supplementary material illustrate the increase in number of measurements of each isotopologue.

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 (Table 1), and the amount of measurements is not evenly spread geographically: significantly more measurements were made in North American and European countries, Australia, Brazil and Japan. In Russia and China, there were relatively more measurements as well, but only for fossil fuel sources. Despite including the first few measurements reported from Africa and the middle-east (France et al., 2021; Al-Shalan et al.,
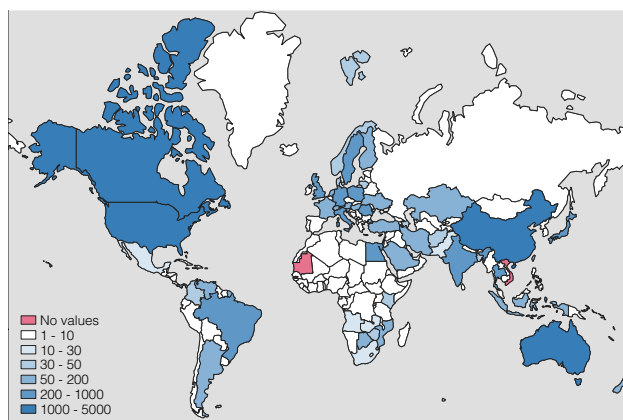
Figure 4. Number of isotopic signature measurements (δ^{13}C and δ^2H of CH$_4$) carried out in different countries worldwide and reported in the present database.

2022), the data distribution remains unbalanced. Nevertheless, specific isotope signatures dependencies can be further analysed for the different source categories:

Fossil fuels Fugitive emissions from fossil fuel reservoirs are highly variable not only on a large scale, but also from one basin
to another, or even within the same basin (Sherwood et al., 2017; Milkov and Etiope, 2018; Lan et al., 2021). Therefore,
CH$_4$ isotopic composition from one basin can't be simply upscaled to a country scale. Any new isotopic measurement
from a production basin with large fugitive CH$_4$ emissions brings relevant information.

Sherwood et al. (2017) pointed out the lack of data for a list of conventional oil and gas and coal production countries,
in Africa, the middle-east, central and southern Asia, and South America. Previous estimates of global CH$_4$ isotopic
signatures from the exploitation of fossil fuels weighted the source signatures from one basin by its fuel production
(Schwietzke et al., 2016). Recent work suggest that fuel production is not a reliable proxy to estimate CH$_4$ fugitive
emissions (Zavala-Araiza et al., 2015; Alvarez et al., 2018; Rutherford et al., 2021; Chen et al., 2021; Maazallahi et al.,
2021). Thus, the most relevant sampling locations would be ideally related to estimated emission rates from top-down
measurements, instead of production or bottom-up emission estimates. Unfortunately, these data are lacking in many
cases. Recently, particularly large CH$_4$ emissions were detected in central Asia (Varon et al., 2019), or measured in
Mexico (Zavala-Araiza et al., 2021).

Modern microbial The isotopic signatures of CH$_4$ from modern microbial sources (mainly wetlands, ruminants, waste degra-
dation, rice paddies, termites) are largely dependent on environmental parameters such as the type of substrate and other
ecosystem conditions. Figures A3 and A4 show that our new data confirm the trends previously observed: the δ^{13}C
sensitivity to C3 or C4 plants in ruminant diet (Rust, 1981; Levin et al., 1993; Klevenhusen et al., 2010; Brownlow et al.,
2017), to wetland latitudes (δ^{13}C depletion in polar regions because of less oxidation and the absence of C4 plants)
(Fisher et al., 2017; Brownlow et al., 2017; Ganesan et al., 2018), and the δ^2H dependency on δ^2H$_{H_2O}$ of precipitation,

and ultimately on the latitude (established for freshwater emissions) (Waldron et al., 1999; Chanton et al., 2006; Douglas

245   et al., 2021; Stell et al., 2021). Based on the correlation with the plant metabolism (C3 or C4), $\delta^{13}C_{CH_4}$ from wetlands could be mapped on a global scale (Ganesan et al., 2018). Douglas et al. (2021) also suggested a spatial extrapolation of wetland $\delta^2H_{CH_4}$ using $\delta^2H_{H_2O}$ data, which can be interesting for under-sampled locations, such as the southern hemisphere. However, a certain variability will always remain because of the influence of other parameters such as the dominant methanogenic pathway (acetate fermentation or CO_2 reduction) (Waldron et al., 1998; De Visscher, 2004;

250   Conrad, 2005; McCalley et al., 2014; Inglett et al., 2015; Chan et al., 2019; Douglas et al., 2021), or the composition of the substrate in organic matter for $\delta^{13}C$ Conrad et al. (2011); Ganesan et al. (2018).

2.6 Global data distribution

The global distribution of CH_4 isotopic signatures in the complete extended database is shown in Fig. 5. The values were grouped in categories that correspond to the largest reported emissions (Saunois et al., 2020). The categories agriculture, waste,

255   wetlands, and partly other natural are all of modern microbial origin, mainly following the fermentation pathway (Milkov and Etiope, 2018). They show a normal distribution, and an overlap between the categories, except for the waste sources that are more enriched in ^{13}C. This difference is particularly visible in the MEMO[2] data, and from a relatively large number of sites from waste related sources. As mentioned in section 2.4, additional parameters control the isotopic signature of the emitted CH_4, such as the type of substrate, the presence of oxygen, or secondary (e.g. oxidation) processes. We recommend to sepa-

260   rate the waste category from the other microbial sources to minimise the uncertainty in the assigned isotopic signature. The fractionation factors derived for CH_4 microbial oxidation are larger for δ^2H (Coleman et al., 1981; Bergamaschi et al., 1998; Chanton et al., 2006), but we don't clearly see an influence of these additional parameters on the $\delta^2H_{CH_4}$ signatures of our dataset. Indeed, the range of δ^2H signatures for waste is the same for as agriculture and wetlands (Fig. 5), but these are based on few measurements compared to $\delta^{13}C$ (42 % of all measured waste sources reported δ^2H signatures). The relation between

265    $\delta^2H_{CH_4}$ from wetlands and the $\delta^2H_{H_2O}$ from precipitation has been established (Waldron et al., 1999; Chanton et al., 2006; Douglas et al., 2021). But, further δ^2H measurements are required to better define the isotopic dependancies to secondary processes.

In Sherwood et al. (2017, 2021), the pyrogenic category only contained biomass burning data, and the binary distribution clearly illustrates the difference between C3 and C4 plants in terms of $\delta^{13}C_{CH_4}$ signatures. The additional biomass burning

270   data we added from published literature confirms the dependency of $\delta^{13}C_{CH_4}$ on the plant metabolism. We also added pyrogenic data of fossil fuel burning from both our measurements and the literature. The resulting distribution of the $\delta^{13}C$ data is therefore smoother than in Sherwood et al. (2017) (Fig. 5), because $\delta^{13}C_{CH_4}$ from fossil fuel burning is more variable than from biomass burning, and does not show a clear distinction between C3/C4 plant metabolisms. $\delta^2H_{CH_4}$ isotopic signatures from pyrogenic sources cover a wide range of values, and overlap with the ones of fossil fuels. Data on $\delta^2H_{H_2O}$ could help to

275   parametrise the biomass burning $\delta^2H_{CH_4}$ in more detail (Vigano et al., 2010), similar to the above mentioned relation between $\delta^2H_{CH_4}$ and $\delta^2H_{H_2O}$ (Waldron et al., 1999; Chanton et al., 2006; Röckmann et al., 2010; Douglas et al., 2021).

Table 3. CH$_4$ isotopic source signatures assigned to the fossil fuel related emissions in global scale models

| Reference	δ^{13}C VPDB [‰]	δ^{2}H VSMOW [‰]
Gupta et al. (1996); Tyler et al. (2007)	-38 / -37[1]	-175
Rigby et al. (2012)	-40[2]	-175
Monteil et al. (2011)	-40 / -35[1]	
Rice et al. (2016)	-41.7	-175
Schaefer et al. (2016)	-37	
Schwietzke et al. (2016)	-44	
Fujita et al. (2020)	-45.2	-209
This database, mean ± sem	-44.5 ± 0.5 / -50.7 ± 1.3[1]	-183 ± 3 / -210 ± 5[1]

[1] for natural gas/coal; [2] also in Lassey et al. (2000); Houweling et al. (2000); Bousquet et al. (2006); Thompson et al. (2018)

Fugitive CH$_4$ emissions from fossil fuels cover a wide range of isotopic signatures: δ^{13}C from -72.5 to -18.3 ‰ and δ^{2}H from -349 to 14.0 ‰. The average δ^{13}C of all fugitive CH$_4$ emissions from the exploitation of fossil fuels in the European

280 Methane Isotope Database was -44.6 ± 0.4 ‰ (n=452), and the weighted average was -46.6 ± 1.8 ‰ according to the relative emission from conventional and coal fuels production worldwide[7]. Our averages are lower than δ^{13}C values used in global models, and than the mean of the global database (Table 3). But the value of -44 ± 0.7 ‰ suggested by Schwietzke et al. (2016), based on the database from Sherwood et al. (2017) scaled with the fossil fuel production in the different regions, is relatively close to our average. The mean values we calculated in Table 3 (bottom row) do not necesseraly represent the global

285 isotopic signature of fossil fuel emissions, because this should be weighted by the magnitude of emissions in the different basins. However, our averages are an indication of the general δ^{13}C signatures from all measurements until now. Because of the high heterogeneity of the δ^{13}C of CH$_4$ from fossil fuel related activities, and the temporal variations in the production from the different regions (Stavert et al., 2021; US Energy Information Administration, 2021; Lan et al., 2021), it is important to keep a relatively large uncertainty when estimating in the global signature of fossil fuel emissions.

290 In section 2.4, we have shown the use of δ^{13}C$_{\text{CH}_4}$ to distinguish fossil fuel emissions in western Europe, and the need for δ^{2}H$_{\text{CH}_4}$ measurements in central and eastern Europe. In the global database, most fossil fuels records (83.5%) have δ^{2}H$_{\text{CH}_4}$ values >-250 ‰. The few values of δ^{2}H <-300 ‰, indicating microbial fermentation as gas origin, were found in some coal formations in the United States and Canada. Figure 5 still allows us to generally conclude that δ^{2}H measurements are more reliable to distinguish fossil fuel vs. biogenic CH$_4$ sources at the global scale than δ^{13}C only, which further emphasises the

295 need for more δ^{2}H$_{\text{CH}_4}$ measurements.

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[7]Relative weights of 0.66 for conventional fuels (oil and natural gas) and 0.34 for coal. Emission data from Saunois et al. (2020)
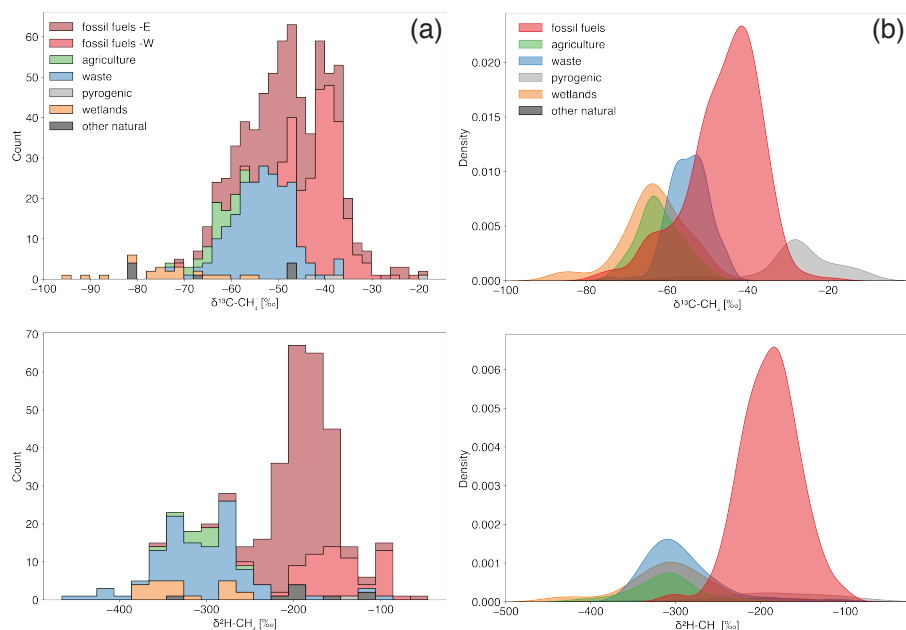
Figure 5. Distribution of $\delta^{13}C$ (top) and δ^2H (bottom) in CH_4 for different source categories. **(a)** The European Methane Isotope Database (absolute numbers). "fossil fuels -E" shows fossil fuels data from Poland and Romania, and "fossil fuels -W" from the UK, the Netherlands, Germany, and France. **(b)** the global literature database, including the new European data (normalised probability density).

The updated database is beneficial for deriving a representative concept of the isotopic composition of CH_4 sources, but it is important to note that applying appropriate weighting arithmetic is essential. Users need to define the dominant CH_4 sources impacting an area, as well as the relative source type emission rates. Emission inventories provide such estimates, but top-down

300   approaches are essential to identify potential biases and evaluate the bottom-up approaches (Alvarez et al., 2018; Etiope and Schwietzke, 2019; Rutherford et al., 2021; Stavert et al., 2021).

3 Conclusions

This study presents an updated dataset of isotopic source signatures of CH_4 from recent atmospheric measurements, while including additional data from published literature which were not previously included. The new data is a contribution from

305 the European Methane Isotope Database, that results from the sampling activities performed within the MEMO² project. It represents a substantial contribution to the global dataset for fugitive fossil fuels and waste sources, mainly sampled in urban areas.

We have highlighted two main improvements in our understanding of the CH_4 isotopic composition: (i) A more robust range of values for modern microbial sources, and a better characterisation of the $\delta^{13}C$ enrichment in CH_4 from waste sources. (ii)

310 Fossil fuel related sources could have more depleted values than previous estimates used in global models. In this respect, our data confirm the analysis made by Schwietzke et al. (2016).

Finally, the new European data contain comparatively more δ^2H measurements. In the case of fossil fuel emissions, the use of $\delta^2H_{CH_4}$ is of particular interest. In general, utilizing both $\delta^{13}C$ and δ^2H for CH_4 improves our ability to clearly separate fossil fuel and microbial sources, compared to $\delta^{13}C$ alone. The use of δ^2H as additional constraint could help to answer open

315 questions regarding the CH_4 global budget. To better understand the drivers of δ^2H variability (except for δ^2H of precipitation), more measurements are required, especially of pyrogenic and waste sources.

The present dataset can be used for CH_4 source attribution, and also to derive global signatures for the different types of emissions. Appropriate use of the database requires the analysis of specific parameters in relation to source type and the region

320 of interest. A future improvement of this database would be to include more measurements on the African, Asian and South American continents, where experimental studies are lacking. Because of its potential for source characterisation, new studies should also focus on $\delta^2H_{CH_4}$ measurements.

4 Data availability

The database is made freely available to the scientific community in the belief that it provides the most complete picture of the

325 stable isotopic composition of CH_4 sources. The free availability of these data does not constitute permission for publication of the data. For research projects, if the data used are essential to the work to be published, or if the conclusion or results largely depend on the data, co-authorship should be considered. Full contact details and information on how to cite the data are given in the accompanying database. The database is currently stored in a publically available repository: https://doi.org/10.24416/UU01-4PO56T (Menoud et al., 2021a).

Earth System
Science
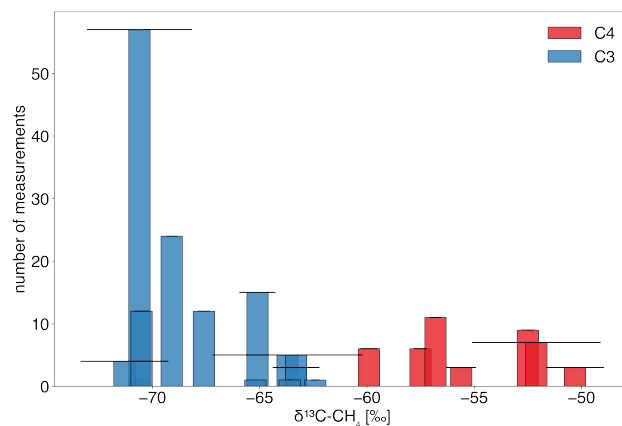Data

Open Access

Discussions

330 **Appendix A: Supplementary material**

Figure A1. Photos of the laboratory setup used for isotopic measurements during the MEMO[2] project and of the sample collection during field surveys. (a) IRMS system setup used at GGRL RHUL, for $\delta^{13}C_{CH_4}$ measurements. (b) IRMS system setup used by the UU team, here deployed at Krakow, for $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ measurements. (c) Mobile measurement setup used by the Heidelberg University (UHEI) team, using cavity ring-down spectrometry (CRDS) isotope analyser and an air-core, as described in Hoheisel et al. (2019). *Photo: Piotr Korbeń* (d) Sample collection directly from an emission source on foot: a manhole in the city of Bucharest, Romania. CH$_4$ mole fractions were measured using a portable CRDS analyser. *Photo: Octavian* (e) Mobile measurements and sampling on-board of a car. Air was pumped from the top of the car and continuously measured with a CRDS analyser, and bag samples were taken when CH$_4$ enhancement were detected by the instrument. (f) Soil chamber placed on a coal waste disposal area in Poland. Samples were collected from the chamber several hours after it was placed. CH$_4$ mole fractions in the chamber were measured using a portable integrated cavity output spectroscopy (ICOS) instrument. *Photo: Mila Stanisavljević* (g) Full sample bag before analysis, collected on a landfill in Devon, UK.
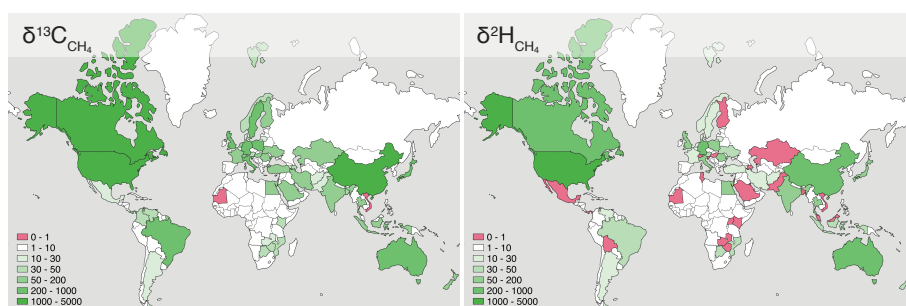
Figure A2. Number of isotopic signature measurements reported in the present database, including the previous database of Sherwood et al. (2017, 2021), additional literature we found, and the European Methane Isotope Database, for $\delta^{13}C$ (left) and δ^2H (right) of CH_4 separately.

Figure A3. Measured $\delta^{13}C_{CH_4}$ signatures from ruminants in the literature[1] and MEMO[2] database according to the feed: a majority of C3 plants (red) or C4 plants (blue).

[1] Al-Shalan et al. (2022); Brownlow et al. (2017); Klevenhusen et al. (2009, 2010); Levin et al. (1993); Lu et al. (2021); Rust (1981); Townsend-Small et al. (2012); Wahlen et al. (1989)
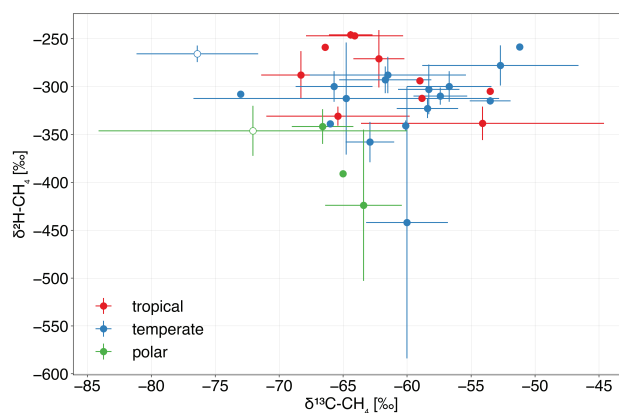
Figure A4. Measured $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ signatures from wetlands sites as reported in the literature[2] (solid circled) and MEMO$_2$ (open circles) database, color coded by the latitude zones.

[2] Beck et al. (2012); Burke and Sackett (1986); Day et al. (2015); Happell et al. (1994); Kuhlmann et al. (1998); Lansdown (1992); Levin et al. (1993); Martens et al. (1992); Nakagawa et al. (2002); Smith et al. (2000); Sugimoto and Fujita (2006); Umezawa et al. (2011); Wahlen et al. (1989); Wassmann et al. (1992); Woltemate et al. (1984)

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Competing interests. The authors declare that they have no conflict of interest.

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