

MEMO²: MEthane goes MObile – MEasurements and MOdelling

Isotopic measurements linked to common scale

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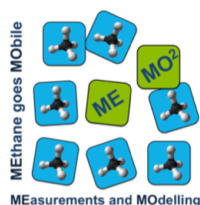
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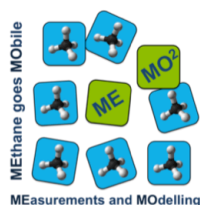


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1. Executive Summary

Isotopic characterization and mapping of methane sources requires that all laboratories measuring the isotopes of methane be on the same scale across the range of values commonly encountered in emissions from European sources. To achieve this goal five 22-litre cylinders were filled to 2 bars with natural gas at 2 and 10 ppm CH₄, landfill gas at 2 and 10 ppm CH₄ and ambient background air at 2 ppm CH₄. These were each measured 4 times on 3 different days at RHUL and then sent to UU for measurement. Values at 3 points on the $\delta^{13}\text{C}$ isotopic scale were compared. Both laboratories obtained results for all 5 cylinders that were in analytical error of each other so that the results obtained within the MEMO² project can be confidently interpreted, and directly compared with other results obtained globally.

2. Introduction

2.1 Background

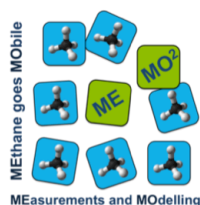
The isotopes of each element of each atmospheric species need to be measured to a common scale. For methane the most commonly utilized ratio is that of carbon 13 to carbon 12, because this allows the discrimination of methane produced by biogenic (e.g. cows), thermogenic (e.g. natural gas) and pyrogenic (combustion) sources. This can be measured on emissions directly from source where the methane % is very high, such as a gas supply (95%) or a landfill gas (50%), but for the MEMO² studies many of the sources are unknown and sometimes sampled at many hundreds of metres downwind of the point of emission. This means that measured methane varies from the ambient global background (around 1.9 ppm CH₄) to about 10 ppm CH₄. International standards are not available for CH₄ in air at these concentrations and it requires that one of the laboratories that can measure methane to high precision will prepare such gases for circulation between and measurement by laboratories who participate in the round-robin inter-comparison events.

2.2 Scope of the deliverable

As part of the MEMO² project the two participating laboratories at UU and RHUL that can measure the carbon isotopes of methane to high precision (better than 0.1 ‰) by isotope-ratio mass spectrometry must inter-compare their results and develop a common scale of measurement. This means that all methane plume samples collected and analyzed by both groups and those supplied by other groups in the project can be provided to the project database and subsequently used to characterize individual sources and source categories, to create isotopic maps and be used by modellers to understand how methane sources and their distribution are changing. It is essential that this common scale is developed early enough in the project so that isotopic data can be harmonized prior to interpretation.

3. Content

RHUL and UU have been measuring the isotopes of methane by IRMS for many years, but as the MEMO² project developed from the writing stage to the kick-off meeting, the expansion of use of newly-developed cavity ring-down laser spectroscopy (CRDS) techniques for measurement of the $^{13}\text{C}/^{12}\text{C}$ ratio of methane (referred to hereafter as $\delta^{13}\text{C}$), meant that 3 of the partner groups making mobile methane measurements had acquired these new instruments. The technique allows field measurements of isotopes to a much lower precision than by IRMS, but gives near instantaneous measurements rather than later laboratory analyses. Without direct access to high-precision isotopic measurement it was soon apparent that any gases prepared for inter-comparison between RHUL and UU for this deliverable should also be suitable for subsequent analysis by the CRDS instruments. Given that the CRDS instruments have inherently poor precision at the 2 ppm ambient background levels of CH₄, but with an improvement of an order of magnitude at 10 ppm CH₄ (from ± 4 ‰ to ± 0.4 ‰), the preparation of inter-calibration tanks was tailored with the aim of bringing these instruments onto the common isotopic scale.



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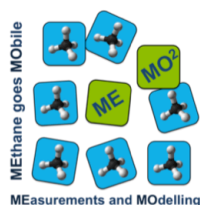
Pure samples of CH₄ from European methane sources can have $\delta^{13}\text{C}$ signatures from -70 ‰ (cow breath, peat wetlands) to -30 ‰ (gas supply, forest fires), but in plumes downwind of source, where emissions have mixed with ambient air, the values are rarely so extreme. The first gas chosen for dilution to make up the inter-comparison tanks was the gas supply from the RHUL geochemistry laboratory, which has been measured many times over the last 2 decades and recently with values of $\delta^{13}\text{C}$ in the -38 to -36 ‰ range. This contains more than 90% CH₄, with 4-6% C₂H₆. The second gas selected was collected from the gas engines at the Heathfield landfill site, Devon (Viridor UK). This contained approximately 20% CH₄ with much of the remainder being CO₂. Active UK landfills have been widely analysed by the RHUL group with $\delta^{13}\text{C}$ values of -58 ± 3 ‰. The third gas was ambient air collected from 2m above the roof of the RHUL Earth Sciences building and expected to contain close to 2 ppm CH₄ with an isotopic signature around -48 ‰. These three samples would provide calibration over at least 20 ‰ of range around the atmospheric background value, sufficient for accurate extrapolation to the rarely encountered extremes of the 40 ‰ range. For better inter-comparison with the CRDS instruments the decision was made to create 2 and 10 ppm CH₄ dilutions for both the natural gas and landfill gas samples.

RHUL has a large number of electro-polished and internally cleaned 22-litre stainless steel flasks of gas flow through design (see Figure). Five of these were selected and evacuated to 2×10^{-3} bar. For landfill and natural gases the flasks were injected using an SGE syringe with 2 μl and 10 μl , then diluted with zero air until the cylinders contained at least 40 litres of air (1.8 bars, 26 psig) to achieve concentrations close to 2 and 10 ppm respectively. This low pressure is below the dangerous goods exemption of 2 bars, allowing the flasks to be circulated around the laboratories without excessive dangerous goods surcharges. Given the difficulties of extracting such small quantities through the septum of the air bag and transferring to the 22-litre flasks without some contamination with ambient air, it was expected that there would be some isotopic difference between the 2 and 10 ppm dilutions from the same source, but the D2.1 tests only require that there is a significant range of values at both 2 and 10 ppm concentration, and measurements between labs will be compared for each flask individually. The flasks were shipped to UU on 2 October 2018.

Below is a table of results that shows the internally corrected data for both laboratories for each flask on each day it was measured, and the final value agreed by both groups for each flask.



Fig. 1: One of the stainless steel flasks sent to UU for inter-comparison measurement



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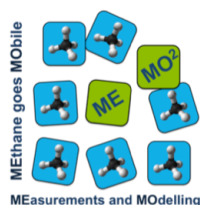
Table 1: Results of the inter-comparison between IRMS systems at RHUL and UU of 5 flasks. Air = Ambient RHUL air, Gas = RHUL natural gas supply, LF = Heathfield landfill gas. Date is the date of analysis by the laboratories. (D) indicates that the 10 ppm samples have been diluted to a lower concentration with zero air (oxygen and nitrogen mix) prior to analysis. Samples were measured 4 consecutive times on at least 3 days at RHUL, and measured 6 consecutive times on 1 day at UU, both at full concentration and diluted.

Sample ID	RHUL Date	RHUL (‰)	RHUL (SD)	UU Date	UU (‰)	UU (SD)	Agreed value (‰)
Air 2 ppm	20/9/18	-48.08	0.08				
Air 2 ppm	21/9/18	-48.07	0.02				
Air 2 ppm	25/9/18	-48.05	0.04				
Average		-48.07	0.01	5/10/18	-48.09	0.03	-48.1
Gas 2 ppm	27/7/18	-39.65	0.01				
Gas 2 ppm	28/7/18	-39.67	0.04				
Gas 2 ppm	29/7/18	-39.61	0.04				
Average		-39.64	0.02	5/10/18	-39.61	0.07	-39.6
Gas 10 ppm	23/7/18	-38.22	0.05				
Gas 10 ppm	26/7/18	-38.21	0.04				
Gas 10 ppm	31/7/18	-38.22	0.05				
Gas 10 ppm	31/8/18	-38.20	0.02				
Average		-38.21 (D)	0.01	5/10/18	-38.14	0.07	-38.2
				5/10/18	-38.17 (D)	0.09	
LF 2 ppm	27/7/18	-59.68	0.00				
LF 2 ppm	28/7/18	-59.79	0.02				
LF 2 ppm	31/7/18	-59.71	0.09				
Average		-59.73	0.05	5/10/18	-59.80	0.10	-59.8
LF 10 ppm	31/7/18	-60.89	0.02				
LF 10 ppm	28/8/18	-60.94	0.02				
LF 10 ppm	29/8/18	-60.99	0.06				
LF 10 ppm	30/8/18	-60.90	0.03				
Average		-60.93 (D)	0.04	5/10/18	-61.02	0.09	-60.9
				5/10/18	-60.91 (D)	0.05	

Once the data was agreed and correction factors derived this was applied to unknown samples from measurement campaigns that were analysed in both RHUL and UU laboratories as part of Milestone 7 work.

4. Conclusion and possible impact

An agreed common scale has been defined by UU and RHUL for C-isotopic measurement of CH₄, and a correction factor derived so that all samples analysed so far on the MEMO² project can be retrospectively corrected to this scale, and likewise going forward for all new analyses on the project. The inter-comparison cylinders will now be sent to UHEI and then subsequently to the other MEMO² groups with CRDS instruments so that all methods of isotopic measurement used within the project can be reported to a common scale. This will have a major impact on the project going forward as it will allow groups to create isotopic maps, assess inventories and model changing methane sources with a higher degree of confidence.



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5. Dissemination & Exploitation

This report will be available via the MEMO² website to all project partners, and once the CRDS partners have measured the cylinders we will consider how to circulate a more expansive document to the wider methane isotopic community.

6. References

Levin, I., Veidt, C., Vaughn, B. H., Brailsford, G., Bromley, T., Heinz, R., Lowe, D., Miller, J. B., Poss, C., and White, J. W.C. (2012) No inter-hemispheric $\delta^{13}\text{C}_{\text{CH}_4}$ trend observed, *Nature*, 486, E3–E4, <https://doi.org/10.1038/nature11175>.

Umezawa, T. & 29 others (2018), Interlaboratory comparison of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements of atmospheric CH_4 for combined use of data sets from different laboratories. *Atmos. Meas. Tech.*, 11, 1207–1231, <https://doi.org/10.5194/amt-11-1207-2018>.

7. History of the document

7.1 Document history

Version 1.0	Author(s)	Date	Changes
	David Lowry	19/10/18	5/11/18
	Thomas Rockmann		
	Rebecca Fisher		
	Malika Menoud		
	Julianne Fernandez		

7.2 Internal review history

Internal Reviewer	Date	Comments