

Earth Syst. Sci. Data Discuss., author comment AC2  
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## Reply on RC2

Malika Menoud et al.

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Author comment on "New contributions of measurements in Europe to the global inventory of the stable isotopic composition of methane" by Malika Menoud et al., Earth Syst. Sci. Data Discuss., <https://doi.org/10.5194/essd-2022-30-AC2>, 2022

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RC2: The article presents the data of methane isotopic air samples collected in Europe, their analysis, and discussions in respect to previous studies of global inventories/data. The isotopic information for various sources in methane are useful in understanding the methane budgets better. Atmospheric inverse models (top-down methods) would especially benefit from such information – not only closing the total budgets based on total methane concentration data, but also allow to separately estimate emission magnitude of different source sectors. As authors point out, the previous studies on methane isotope measurements were mainly based on samples from US. The additional data from Europe therefore increases geographical representation, and is highly valuable. The paper presents important information and data for carbon cycle community, and is worth publishing. I also appreciate the authors for making the data open access.

I have a few suggestions below to improve the presentation of the manuscript that would possibly increase the value of the paper.

- Please consider rephrasing the title. To me, updating global inventory is a by-product, and the European data collected/presented here is the most important part.

A: We have changed the title to: New contributions of measurements in Europe to the global inventory of the stable isotopic composition of methane

RC2: - Please consider focusing more on Europe. You could, for example, add information and discussion about European data from previous studies, i.e. validation and updating information on Europe. It is unclear from the current manuscript how much information/data were available in Europe previously, and what were the isotopic values. You can also add comparison of the European data to global data, i.e. discussion on geographical differences/similarities of isotopic composition. In addition, geographical bias still remains within Europe. Please comment on it – what should we still improve in Europe? Where would be critical locations, and from which sources that we should sample data from, and why?

A: A short description and outlook, specific to European emissions, has been added

(l.239-). The analysis of the European data is developed in §3.1. Our data provide new information to better constrain specifically waste (l.210-227) and fossil fuels sources (l.229-238). Further improvements are mainly through more d2H measurements, as it is stated in the conclusion.

RC2: - Please consider focusing on new information brought by newly sampled and collected data. A few suggestions/comments on this are found under Specific comments below.

A: See answers to specific comments.

RC2: - Please add temporal information about the collected data in MEMO2 and those compared (collected from previous studies). If those are from very different period, the differences in isotopic composition may indicate temporal changes in underlying processes. Please comment on such if any.

A: We specified the sampling period in the method section (l. 85). We didn't target sources that were previously measured to study temporal changes, and if investigated in the literature, these processes were not explicitly analysed in our database (l.185).

RC2: - Modern microbial section: in many cases, CH<sub>4</sub> emissions from natural sources (e.g. peatlands) are separately estimated from anthropogenic sources (e.g. waste, agriculture). It would be more helpful if you could analyse those separately. Could you separate those e.g. when comparing to previous studies (incl. Section 2.5)?

A: Modern microbial emissions are of the same formation process, and cover similar isotopic signatures. Differences between the different types of microbial emissions were mostly identified in the wetland and waste categories, and explored in more detailed in §3.2.2.

## **RC2: Specific comments**

Please check language in general. Sometimes informal structures/phrases are used. Please check the journal criteria for citations. There are a few "in review" papers that are cited several times, but the manuscript/preprint are not available. Note that those should not be included in the final version of this manuscript. Please acknowledge that some comments maybe senseless because of this, and I apologies for that. In addition, some are cited within a page, and some at the end of the manuscript. I think all should be given at the end of the manuscript.

A: We cited 3 papers that were in review. Two of them are now published, and one is accepted by the journal and will be published soon. The references have been adjusted.

RC2: P1 L2: "measurements" □ "isotopic measurements"

A: This has been revised.

RC2: P2 L44: What do you refer to by "them"?

A: This has been clarified.

RC2: L3 L60-61: "numerous CH<sub>4</sub> sources could be sampled for isotopic measurements"

I think what you sample is air, and not the sources. Please revise the sentence.

A: The sentence has been revised.

RC2: Method:

In the excel file, I see that in some locations, only <sup>13</sup>C or H isotopes are sampled/analysed (for MEMO2 data). Why both were not sampled at all locations? Could you add information about selection criteria or sort if there was such?

A: We have explained this in the beginning of §3.1 (l.193)

RC2: Section 2.1.1

- Please consider adding a table about different sampling methods, and give focus to the differences/similarities in those methods in the text. This way, you could reduce amount of details and avoid duplicates in the text.

A: The measurement methods are well explained and detailed in separate studies. It is not the purpose of this paper to compare the methods.

RC2: - Was there any location where different sampling methods were applied at the same place? What kind of differences would occur in the measured values due to the differences in sampling methods?

A: Several methods were applied sometimes during the same campaigns, and rarely at the same locations. The comparison of the methods are in this case made for the purpose of a specific study on this campaign. For the dataset, we retained the measurements made with the IRMS, either at RHUL or UU since we have worked on bringing the systems to the same scale.

RC2: P5 L116-119:

I am now confused. In the beginning of this section (2.1.2), it is written that "the mass spectrometry measurements were performed at two laboratories". However, is it so that actually four labs analysed the air samples? You have included detailed comparison and measurement precision on IRMS, but how about CRDS compared to IRMS? Was there any differences between UHEI and LSCE measurements?

A: The laboratories that perform CRDS measurements had their own calibration procedure, both described in Hoheisel et al. (2019) using cylinders that were calibrated at the Max Planck Institute in Jena. It is beyond the scope of this paper to do an inter-comparison and discuss the calibration between the different labs. We did do the round-robin inter comparisons for the MEMO2 project (<https://h2020-memo2.eu/wp-content/uploads/sites/198/2018/12/MEMO2-D2.1-Isotopic-measurements-linked-to-common-scale-final.pdf>), which showed that both the UHEI and LSCE instruments were in the correct ballpark for source measurements, and at least well-within the error bounds of each source category being isotopically characterised. It is beyond scope to include a comparison table here. We anyway report measurements from laboratories that all are on the international scale and we assume their respective calibration methods can be trusted.

RC2: P5 L133: "we did not work towards a uniform procedure"

Why? Did you allow e.g. each lab to calculate based on their choice of method? All methods being "statistically valid" does not mean that there are no differences. So I do not see why this is a valid statement to use different procedures.

A: Yes, we used the data that were provided by the different laboratories, and they use slightly different approaches. That is because we don't want the data we show here to be different than in other studies from the labs who produced it. From a broader perspective, we are comparing new data with databases that include studies that are decades old and used very different measurement methodology, and without the possibility to do laboratory inter comparison of methane isotopic scales. We acknowledge that there are differences between the methods, and this problem persists in many comparative studies. The term "statistically valid" refers to the fact that all these methods minimise errors between the data and the fit, and this can be done in slightly different ways. The resulting small differences will not affect the main message. We have explained this more clearly in the text.

RC2: P6 L139: "our objective concern only values ... of emitted CH4"

Do you mean that the forests, where samples are taken from, also emit CH4? Most of forests are net sink of CH4, but in some cases they emit CH4. Sorry for this picky comment, but I am simply interested in. Could you provide the references where those samples were taken from?

A: We included 2 source signatures from aircraft measurements above a boreal forest, reported in a 2011 study by Umezawa et. al.: Umezawa, T., Aoki, S., Kim, Y., Morimoto, S., Nakazawa, T., 2011. Carbon and hydrogen stable isotopic ratios of methane emitted from wetlands and wildfires in Alaska: Aircraft observations and bonfire experiments. *J. Geophys. Res.* 116, D15305. <https://doi.org/10.1029/2010JD015545>

RC2: P6 L141-143:

I do not see country/region in Table 1. What is the "region" in those sentences?

A: The reference was wrong. We have now included an additional table with the description of all parameters.

RC2: P8 L164: (2017-2020)

Is this the project period or actual period when data was collected? As in the earlier comments, it would be informative to state clearly the sampling period.

A: Yes, the data was collected during the years the project went on. The sampling period is now stated in section 2.1.1 (l.85).

RC2: P8 L165-167: "The first version was made accessible on October 1st 2020"

Now that it is updated, is this information needed?

A: We think it helps to understand how the data was already used in other publications before this paper.

RC2: P8 L166: "The European data was used in several publications"

This gives an impression that the data has been published already. Do you mean the first version of the data was used in those publications? If so, why did you need to update? Please also consider moving this to Introduction by add a bit more details about those studies, e.g. how and what the data (e.g. which isotopologue/country) were used, and what are the main findings. This would then show the importance of the European dataset and what new information it can bring.

A: Parts of the data have been used in previous scientific publications, and as required these days, the data used in the publications have been made available related to these publications. In this article, we present a consolidated and completed version of all measurements that were made within our project, and additional data that we found in the literature and that were previously not included in the global database. We have moved this part in the introduction (l.66) and it indeed helps to clarify our motivation and objectives.

RC2: P9 L183-187:

What were then the isotopic signature values for those coal reservoirs where natural gas of microbial origin are present? You mention "a relatively enriched  $\delta^2\text{H}$  ( $>-250$  ‰), and relatively depleted  $\delta^{13}\text{C}$  ( $<-60$  ‰)", but are those values those measured in this study or from Milkov and Etiope (2018)?

A: The median values in Silesia were  $\delta^{13}\text{C}=-49.6$  ‰ and  $\delta^2\text{H}=-180$  ‰, and for Romanian gas  $\delta^{13}\text{C}=-57.4$  ‰ and  $\delta^2\text{H}=-196$  ‰. The study from Milkov and Etiope (2018) provided ranges of isotopic values to classify the formation pathways. Isotopic signatures of  $\delta^2\text{H} > -250$  ‰ and  $\delta^{13}\text{C} < -60$  ‰ indicate microbial origin via the CO<sub>2</sub> reduction pathway. The values are discussed in comparison to western Europe later in the paragraph (p. 12, l. 231-240)

RC2: P10 L190-202:

Similar to the comment above. What is the value found in this dataset? You mention that "microbial fermentation range specified in previous reviews", but how were the waste-related source signatures compared to fermentation range measured in this study? What are the mean and range of signature values in sewage treatment plants and biogas plants? How are those values compared to those in other types of plants?

A: We have specified the values in the text (p.11-12, l. 212-218). Thank you for the suggestion, it makes our argument stronger.

RC2: P10 L207-P11 L208: "This distinction is also visible in the histograms of the European Methane Isotope Database in Fig. 5.A"

- "Fig. 5.A." □ Fig. 5(a)"

- From the figure, those from Poland and Romania have two peaks. Does this mean that within Poland and Romania, there are different types of plants, one similar to those in the UK/Netherlands and another that is microbial origin?

A: Indeed some CH<sub>4</sub> emissions in Poland and Romania are of thermogenic origin as well, with higher d<sup>13</sup>C values. However they belong to one peak, with an average around -49 per mil. The impression of seeing 2 peaks arises because the histogram bars are stacked, and the peak of western fossil fuel signatures is shown below, around -40 per mil.

RC2: P10 L208-209: "In western Europe, δ<sup>13</sup>C allows for a good separation between microbial and fossil fuel sources"

Is it true? I see a quite much overlap still.

A: Yes, the ranges of isotope signatures are well defined, and with high-precision measurements it is generally easy to distinguish microbial sources from fossil fuel based on d<sup>13</sup>C-CH<sub>4</sub> being lower and higher than in background air, respectively. Numerous studies have successfully used d<sup>13</sup>C for source attribution in Western Europe: Zazzeri et al. 2017, Xueref-Remy et al. 2020, Lowry et al. 2020, etc.

RC2: P11 L216-217: "increase in number of measurements"

I do not see from the figure how much data is increased, but only the total. Is the Figure caption or text wrong?

A: The text was wrong. We have corrected the sentence.

RC2: Section 2.5:

Much of the text seems to be more suitable as Introduction. It is unclear what is the results of this study in addition to Sherwood et al (2021). Did representativeness increased by additional data found in this study?

A: The information in this paragraph does not fit in the Introduction because it updates the previous knowledge based on the new data. We rephrased parts of the paragraph to emphasize the relevance of the new database.

RC2: Section 2.6:

There are a lot of discussion where newly sampled and collected data are compared to Sherwood et al. (2017, 2021) values. However, I feel that it is difficult to comprehend the differences from the current figures and tables. Could you consider adding figures corresponding to e.g. Fig. 4 and 5, but showing e.g. differences to the previous study? Such figures could be in the supplementary, but would be helpful for readers who does not remember all the details in Sherwood et al. (2017, 2021).

A: Thank you for the suggestion. On Figure 4, we have added maps with the increase in amount of data from each country.

RC2: P13 L255: "mainly following the fermentation pathway"

Fermentation pathway applies to agricultural sources, but not for e.g. wetlands. Please revise the sentence.

A: The isotopic signature of CH<sub>4</sub> emissions from wetlands mostly falls in the range of signatures typical of acetate fermentation, as defined in Milkov and Etiope (2018). This is the message of this sentence, and we rephrased it to make it clearer.

RC2: P13 L256: "They show a normal distribution"

Have you checked whether they really are normally distributed?

A: We rephrased the paragraph based on other comments and the normal distribution issue not mentioned anymore.

RC2: P13 L256-258:

I see quite much overlap in waste sector to, e.g. agriculture, also in MEMO2 data.

A: This is correct, we removed that statement.

RC2: P13 L271-273:

I am not sure what you wish to emphasise here. Why  $\delta^{13}\text{C-CH}_4$  from fossil fuel burning being "more variable than biomass burning" lead to "smoother" distribution?

A: We explained this more clearly in the revised version (p. 17, l. 332-334)

RC2: P13 L273-276 (and P13 L264-267):

I feel this relation and need of additional data on  $\delta^2\text{H-H}_2\text{O}$  is more suitable to be mentioned in Conclusions.

A: Our conclusions are rather general, so we think this specific statement should stay in the Results and discussion.

RC2: P14 L280: "weighted average"

What is the weight used? If it is emission weighted, did you also measure emissions at the same locations?

A: The weights we used are stated in the same sentence: "the relative emission from conventional and coal fuels production worldwide (Relative weights of 0.66 for conventional fuels (oil and natural gas) and 0.34 for coal. Emission data from Saunio et al. (2020))"

RC2: P15 L297-301:

This is more suitable to be mentioned in Conclusions.

A: This has been changed accordingly.

RC2: Conclusions: Now that the MEMO2 project has ended (if I understood correctly), is there a plan to continue activities on isotopic measurements?

A: The isotopic measurements are being continued by the labs involved, but there is no follow-up project of the same scale as MEMO2.

RC2: Figures and tables

Figure 2: The literature values seem to be illustrated by boxplot-type. Are those squares mean/median? What does the bar length illustrate? The letters presenting the types of shaded areas (e.g MF) can be bigger, and the letter "T" is better to be straight. I cannot see clearly the area "A", but is it a white space on the right side?

A: We specified what the squares and error bars represent in the legend. The letters have been made bigger and the abiotic area slightly darker.

RC2: Table 3:

- Please add/separate global to European means.
- What is "sem"?

A: - We don't think the European means are relevant here because our goal is to specifically compare the global estimates. A new table has been included in the revised version, that includes statistics for all source, for the EMID and the global database separately.

- "sem" means "standard error of the mean". We have added this in the legend.

RC2: Please consider adding A2 in the main text.

A: We have changed Table 2 (previously Table 1) to include the numbers for d2H. This provides information on the amounts of d13C compared to d2H data. We discuss these differences per categories rather than per country, so Figure A2 would not be well suited to directly illustrate the main text.

RC2: Technical comments

P2 L17: "the earth's" □ "the Earth's"

A: This has been corrected.

RC2: P5 L115: "deliverable report publically availabe" □ "deliverable report, and publically available"

A: This has been corrected.