Author Responses (AR) to Referee Comments (RC) and resulting revisions of manuscript egusphere-2026-411: "Distinct dual-isotopic signatures of major methane sources in South Asia" by Peng Yao, Katja Belec, Henry Holmstrand, Josh Balacky, Abdus Salam, Krishnakant Budhavant, Mohanan Remani Manoj, Khaled Shaifullah Joy, Md. Alamin Hossain, Atinderpal Singh, Anil Patel, Neeraj Rastogi, Chinmay Mallik, Kirpa Ram, Gyanesh Kumar Singh and Örjan Gustafsson.

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We sincerely thank the editor and both reviewers for thoroughly reviewing and giving constructive feedback that is helping to clarify the significance and importance of this manuscript during revision. All reviewer comments are included below in *italic font* each followed by our detailed author responses, in normal font.

Anonymous Referee #1: [*https://doi.org/10.5194/egusphere-2026-411-RC1]*

This article provides very valuable data for understanding global methane emissions. The measurements concern both carbon 13 and deuterium isotopes in methane from several anthropogenic sources in South Asia. There were almost no data of this kind available in the literature before, therefore I recommend publishing this study. However, I think the methodology and interpretation needs to be severely revised first.

Response: We appreciate the recognition that this study fills an important gap and the overall strong support. We have addressed the detailed review comments below, which have contributed to further improve the manuscript.

General comments:

- *You don't mention background samples in the methods, though Miller-Tans was chosen over Keeling, without background-related justification. In the Keeling plots of the supplementary material, we see the lowest concentrated samples are always >2 ppm… even more in the case of ruminants; which means the hypothesis of the stability of background conditions, which is inherent to the Keeling plot approach[1], isn't fulfilled. Your data shows background samples taken at least for ruminants and biomass burning (labeled "blank"?), why aren't they appearing on the Keeling plots?*

Response: We understand your concerns regarding the treatment of **background** in the **application of Keeling and Miller-Tans plots**. To address this point, we have revised the manuscript to add clarifications and discussion in both the main text and the Supporting Information.

(1) We would like to emphasize that the CH_4 concentrations in our source samples are very high, and therefore largely insensitive to background influence. Both Keeling and Miller-Tans approaches are fundamentally based on isotopic mass balance:

$$\delta_{obs} = \frac{c_{bg} \times \delta_{bg} + c_{source} \times \delta_{source}}{c_{bg} + c_{source}} \qquad (S1)$$

When the source concentration is much higher than the background:

$$c_{source} \gg c_{bg} \tag{S2}$$

Eq. (S1) simplifies to:

$$\delta_{obs} \approx \delta_{source} \tag{S3}$$

This implies that when source concentrations are sufficiently high, the observed isotopic composition approaches that of the source. Therefore, high-concentration data points alone can provide a good approximation of the source isotopic signature, even without applying Keeling or Miller-Tans analyses.

(2) Why stable background conditions are often emphasized in Keeling and Miller-Tans analysis? In practice, background conditions are never strictly constant, raising the question of how much variability is acceptable. Our answer is that it depends on the relative magnitude of source and background signals. To clarify this, we briefly revisit the mathematical structure of the Keeling approach.

In the Keeling formulation, background terms are embedded in the slope:

$$\delta_{obs} = c_{bg} \times \left(\delta_{bg} - \delta_{source}\right) \times \frac{1}{c_{obs}} + \delta_{source} \tag{S4}$$

As a result, variability in background leads to variations in the slope, which can distort the linear relationship (e.g., rotation or fan-shaped distributions in the data).

In contrast, the Miller-Tans formulation places the background contribution in the intercept:

$$\delta_{obs} \cdot c_{obs} = \delta_{source} \times c_{obs} + c_{bg} \cdot \left(\delta_{bg} - \delta_{source}\right) \tag{S5}$$

This means that the slope (i.e., the isotopic source signature) is less directly affected by background variability, while background fluctuations primarily influence the intercept, potentially increasing scatter without fundamentally altering the slope.

Nevertheless, both approaches reflect the combined influence of source and background variability. The key point is that the relative importance of background depends on the magnitude of source-driven variability. When source signals (variation of c_{source}) are much stronger than background signal (variations of c_{bg}), the derived Keeling intercepts and Miller-Tans slopes remain dominated by the source signal (c_{obs} variation dominated by c_{source}), even if background variability is present. This is consistent with the case of $c_{source} \gg c_{bg}$ (Eq. S2).

Conversely, when source-induced variations are comparable to background variability, even small background fluctuations may bias the inferred source signature. This situation may occur when source signals are weak or when observations are far away from the source but close to background conditions. For example, in some atmospheric observations over rice paddies, CH_4 concentrations are close to background levels, such that background variability, although small in absolute terms, can still influence Keeling-derived source signatures.

(3) In our dataset, atmospheric background conditions are represented in the Keeling plots shown in the Supporting Information Figs. S1–S2, where low-concentration data points (around ~2 ppm) are included for ruminant and biomass burning samples, although their influence is negligible due to the dominance of high-concentration samples ($c_{source} \gg c_{bg}$). For aqueous samples (rice paddies and wastewater), background methane is expected to be very low (effectively negligible), and the observed concentrations span several orders of magnitude, further confirming the dominance of source signals over background variability.

We have added the above clarifications to the Supporting Information (Section S2) to improve transparency and facilitate interpretation (Main text Page 12, Line 252–264). We agree that this is an important methodological consideration.

“Keeling and Miller-Tans plots are two formulations of the isotopic mass balance (Eq. 4), differing primarily in their treatment of background contributions. The Keeling approach (Eq. 2) derives the source signature from the intercept but is sensitive to background variability through its effect on the slope, which can distort linearity. In contrast, the Miller-Tans formulation (Eq. 3) derives the source signature from the slope, with background variability mainly affecting the intercept and increasing scatter while largely preserving linearity. As both methods rely on linear regression, increased scatter is generally less detrimental than distortion of linearity, making the Miller-Tans approach more robust in practical applications. Both approaches are most reliable when source-driven variability dominates over background variability. In our case, some high-concentration observations approach the condition $c_{source} \gg c_{bg}$ (Eq. 5), leading to $\delta_{obs} \approx \delta_{source}$ (Eq. 6), such that the influence of atmospheric background variability becomes negligible. Further discussion of background effects is provided in the Supporting Information Section S2.” (Page 12, Line 252–264)

- *I also notice the source signatures are derived from samples taken at different sites, with potentially specific environments. How different the isotopic signatures per source would be if there were average of individual signatures calculated per site?*

Response: For some individual sites, the number of samples is not sufficient to apply Keeling or Miller-Tans analyses. Therefore, we performed a combined analysis using all available data. As discussed above, a subset of our samples exhibits very high methane concentrations, for which the isotopic composition can directly serve as a good approximation of the isotopic source signature. Therefore, we calculated weighted average isotopic values, which better represent the integrated characteristics across different sites and environments.

- *not sure if this would help, but the link between δ^2H of precipitations and into CH_4 from biomass burning was studied before[2]. Your study only looks at the link with microbial CH_4.*

Response: Thank you, this is a very interesting point. We have now added this relevant reference (δ^2H in H_2 from biomass burning) and included a brief discussion in the revised manuscript (Main text Page 26, Line 567–571). However, current constraints on the isotopic signature of methane from biomass burning remain limited at the global scale. In particular, the available data of methane δ^2H are still insufficient to robustly assess potential relationships with precipitation δ^2H across different regions and environmental conditions, so we cannot move further but only raise a potential hypothesis. Therefore, in this study, we focus on the link with microbial methane, for which observational constraints are relatively better established. Revised text:

“In addition, previous studies have shown that the δ^2H of H_2 produced from biomass burning exhibits a latitudinal dependence (Röckmann et al., 2010). By analogy, the δ^2H of CH_4 from biomass burning may also be influenced by the isotopic composition of surface water and precipitation. However, as shown in Fig. 2E (Supplementary Data S2), the currently available global dataset is too limited to resolve such variability.” (Main text Page 26, Line 567–571)

Specific comments:

l. 57: "methane emitters" -> "methane emitting region"

Response: Revised as suggested.

l. *92: please rephrase to avoid too many pronouns.*

Response: Revised to "A global review of methane isotopic values was further conducted to compare with South Asian sources". (Page 5, Line 94–95)

l. 103-104 & 106: can you provide more details on the "clean air" you've used? What is the composition and/or manufacturer?

Response: Revised to "The flasks were pre-conditioned with clean air (Strandmøllen, 20.9% oxygen, and 79.180% nitrogen, $C_nH_m \leq 3$ ppm, $CO_2 \leq 1$ ppm, $CO \leq 1$ ppm, $H_2O \leq 3$ ppm) to eliminate contaminants." (Page 5, Line 105–107)

l. 123: Can you specify how deep the samples were taken (it is written "mid-depth") ? I am concerned by how representative of CH_4 emissions the dissolved CH_4 is. Do you have any information on the isotopic effect (fractionation) of transport processes (through plant-mediated transport or oxidation in the water column)? If not, I would say the distance to the surface is an important parameter to take into account.

Response: We have added additional details on the sampling procedure in the revised manuscript. The samples were collected at approximately 20 cm depth, although the exact depth varied depending on the flooding conditions in individual paddy fields. Sampling at this depth is expected to capture dissolved CH_4 that integrates multiple processes occurring within the water column, including plant-mediated transport and potential oxidation. At the same time, it minimizes direct influence from air-water exchange at the surface, as well as from additional complexities associated with the underlying soil. We have clarified this information in the manuscript:

"Samples were then collected by submerging the vials to mid-depth (approximately 20 cm depth, the exact depth varied depending on the flooding conditions in individual paddy fields) for 20 seconds until bubbling ceased, followed by an additional five-second hold." (Page 6, Line 125–128)

l. 167: "mesh size ##" ?

Response: Thank you for catching this, where ## should have been replaced by mesh size number. This has now been corrected to "mesh size 60–80".

l. 190 to 196: The Miller-Tans and Keeling approaches are based on assumptions. I would appreciate a more detailed analysis of which assumptions are valid in your case, and resulting arguments for choosing one approach or another.

Response: We agree and have now provided a quite detailed discussion above and in the revised manuscript. Here, we briefly repeat and summarize the key points. The primary difference between the two approaches lies in their treatment of background contributions: in the Miller-Tans formulation, the background term is incorporated into the intercept, whereas in the Keeling approach it affects the slope, making the latter more sensitive to background variability and potential distortion of linearity. As a result, the Miller-Tans method is generally less sensitive to background fluctuations. For our dataset, characterized by high methane concentrations, both approaches yield consistent results. Under these conditions, source-driven variability clearly dominates over background variability, such that the assumptions underlying both methods are well satisfied. Indeed, high-concentration samples alone provide a close approximation of the source isotopic signature.

l. 236 to 240: Your assumptions here need to be supported by references, to provide more evidences and precisions. For example: "more sensitive" (to which parameter?); "wide range of conditions" (what type of conditions? explain with clear variables or parameters).

Response: We have revised the comparison between the Keeling and Miller-Tans methods by starting from the fundamental equations, clarifying their differences and the conditions under which they are applicable to our dataset:

"Keeling and Miller-Tans plots are two formulations of the isotopic mass balance (Eq. 4), differing primarily in their treatment of background contributions. The Keeling approach (Eq. 2) derives the source signature from the intercept but is sensitive to background variability through its effect on the slope, which can distort linearity. In contrast, the Miller-Tans formulation (Eq. 3) derives the source signature from the slope, with background variability mainly affecting the intercept and increasing scatter while largely preserving linearity. As both methods rely on linear regression, increased scatter is generally less detrimental than distortion of linearity, making the Miller-Tans approach more robust in practical applications. Both approaches are most reliable when source-driven variability dominates over background variability. In our case, some high-concentration observations approach the condition $c_{source} \gg c_{bg}$ (Eq. 5), leading to $\delta_{obs} \approx \delta_{source}$ (Eq. 6), such that the influence of atmospheric background variability becomes negligible. Further discussion of background effects is provided in Supporting Information Section S2." (Main text Page 12, Line 252–264)

l. 240: "primarily" -> "only"

Response: Revised as suggested.

l. 246 and 250: the effect of C3/C4 types of vegetation on the CH_4 isotopic composition is well known; please provide references to support what you observed.

Response: We have added references that report and discuss the isotopic source signatures of C3 and C4 biomass burning as follows:

"There appeared to be a significant $\delta^{13}C$ difference between methane emissions from C3 and C4 biomass combustion globally (Vernooij et al., 2022; Nisbet et al., 2022), presumably driven by the differing $\delta^{13}C$ content of the feedstocks (Yao et al., 2022)." (Page 13, Line 269–271)

l. 261: refer to Table 1, since the calculation to understand it are explained here.

Response: We have added a reference to Table 1 at the appropriate location in the revised manuscript:

"Using the isotopic values measured for C3 combustion in South Asia, the global mean for C4 combustion, and the regional C3/C4 ratio, we derived a C3/C4-weighted $\delta^{13}C$ value of –29.5±2.0‰ for South Asia (Table 1)." (Page 13, Line 286–288)

l. 271: "In tropical regions, …" this sentence is true on the global scale, not specifically for tropical regions. Your C3 $\delta^{13}C$ data is in agreement with global, within the uncertainties. It provides evidence *of the type of plant being the main driver of CH_4 isotopic composition variations, in the case of biomass burning.*

Response: We agree that this statement applies at the global scale rather than being specific to tropical regions and have revised to:

"The relative proportions of C3 and C4 biomass remain a key determinant of isotopic signatures globally, while geographic variations have a minor influence." (Page 14, Line 298–300)

l. 300-301: Variations in δ^2H of CH_4 is in a way influenced by diet, as it reflects the hydrogen isotopic signature in water. This sentence is strange because the causality isn't very clear; what is it from the global mean value that suggests the δ^2H of CH_4 isn't influenced by diet? By diet, if you only mean C3 or C4 plants, please clarify.

Response: Thank you for pointing this out. We agree that the original sentence was ambiguous and could be misleading. We have revised the text accordingly. The δ^2H signature of CH_4 is primarily influenced by the isotopic composition of environmental water, which varies systematically with latitude and climate, rather than directly by diet (e.g., C_3 vs. C_4 plants). In this context, our intention was to convey that the hydrogen isotopic signature ultimately reflects the water ingested by the animals, which is controlled by environmental conditions. We have clarified this point in the revised manuscript to avoid confusion:

"The δ^2H signature of methane is expected to be primarily derived from surface water, and thus may exhibit regional variability. The global mean δ^2H value (–311±46‰) likely reflects this variability, which may arise from differences in the isotopic composition of environmental water as well as variations in rumination processes." (Page 15, Line 327–330)

l. 302-311: You write the adjusted δ^{13}C in methane (–63.3±1.1‰) compares well with the global value (–67.0±3.0‰), but C3-fed ruminant data for S Asia (-68.7±0.5‰) is written to be more depleted while being closer to the global value. It isn't consistent.

Response: Our previous description may have been ambiguous. These values correspond to the δ^{13}C signatures of C3 diet ruminants and the C3/C4-weighted mean, respectively. We have revised the manuscript to clarify this distinction:

"Methane emissions from C3-fed ruminants in South Asia (–68.7±0.5‰, Fig. 3A) were more depleted in δ^{13}C than the global mean of C3-fed ruminants (–67.0±3.0‰, Fig. 3D)." (Page 15, Line 331–332)

"Using the isotopic values measured for C3 diet ruminants in South Asia, the global mean for C4 diet ruminants, and the regional C3/C4 ratio, we derived a C3/C4-weighted δ^{13}C value of –63.3±1.1‰ for South Asia, which is comparable to the global C3/C4-weighted mean (–63.8±2.4‰)." (Page 16, Line 336–339)

l. 331: you state that ruminant δ^2H in South Asia deviates from the global mean, but it doesn't fall out of the range of uncertainty. Hydrogen isotopes can present large variations, with certainly more complex drivers linked to the H_2O cycle. Your result are within these variation window.

Response: We agree that the ruminant δ^2H values in South Asia still fall within the overall global range, but they are consistently offset from the global mean. This systematic deviation suggests a regional signal rather than random variability. We have clarified this point in the revised manuscript to better reflect both aspects:

"Ruminant methane showed similar $\delta^{13}C$ source signatures globally but displayed distinct $\delta^{2}H$ values in South Asia that deviate from the global mean (still within the uncertainty)." (Page 17, Line 359–360)

l. 338: The linearity of the Keeling plot is recognized as being poor, but the causes aren't discussed. Anyway, these plots can't be interpreted because are not scientifically valid (see general comment on Keeling plots)

Response: We agree that the linearity of the Keeling plot for the rice paddy samples is not ideal, and we have clarified this point in the revised manuscript and Supporting Information. We interpret the reduced linearity as reflecting the complexity of methane production and processing in rice paddies. In particular, multi methane sources and partial oxidation within the water column can generate isotopically distinct methane at different concentrations, effectively resulting in multiple coexisting source signatures. Under such conditions, both Keeling and Miller-Tans approaches tend to be influenced by the highest-concentration (least oxidized) endmember. However, because the Keeling formulation incorporates background contributions into the slope, the presence of multiple source-like components can act analogously to variable background, leading to reduced linearity. In contrast, in the Miller-Tans formulation, background contributions are incorporated into the intercept. When concentration differences span several orders of magnitude, the slope remains largely controlled by the dominant source signal, even in the presence of multiple components. For this reason, we primarily rely on the Miller-Tans approach for the rice paddy samples and have added a discussion in the manuscript to explain the limitations of the Keeling method in this context.

We have added more description in the revised manuscript (Main text Page 17, Line 367–386; Supporting Information Section S3) for the details.

"In contrast, the Keeling plots showed reduced linearity and more enriched $\delta^{13}C$ and $\delta^{2}H$ values (Supplementary Fig. S3), reflecting the complexity of methane production and processing in rice paddies (Supplementary Section S3.2). The sample concentration range spanned several orders of magnitude and some high-concentration samples satisfied the condition $c_{source} \gg c_{bg}$ (Eq. 5), yielding $\delta_{obs} \approx \delta_{source}$ (Eq. 6), and their isotopic values still exhibited noticeable variability, indicating the coexistence of multiple methane sources and/or the influence of in situ oxidation within the water column. Both Keeling and Miller-Tans methods are fundamentally designed for single-source perturbations; in multi-source systems, they tend to be biased toward the highest-concentration source (Monte Carlo mixing simulation in Supplementary Section S3.1), while weaker sources are suppressed or even negligible when concentration differences are large. In the Keeling method, background contributions are incorporated into the slope (Eq. 2). Under multi-source conditions, lower-concentration methane sources do not represent true background, but their influence becomes effectively indistinguishable from background variability within the Keeling framework. As a result, the combined variability of background and lower-concentration sources became significant in rice paddy samples, leading to deviations from linearity and reduced robustness. In contrast, the Miller-Tans formulation incorporates background into the intercept (Eq. 3); when concentration differences spanned several orders of magnitude for rice paddy methane, the slope was primarily controlled by the highest-concentration source, resulting in a more stable and interpretable relationship." (Page 17, Line 367–386)

l. 350-351: This hypothesis explains more depleted values obtained with Miller-Tans, what are the reasons for other methods to give higher values from the same samples?

Response: In our rice paddies dataset, the Miller-Tans δ^{13}C value (–53.8 ± 0.8‰) is relatively enriched compared to previous studies, whereas the δ^{2}H value (–311 ± 6‰) is consistent with the literature. The agreement in δ^{2}H suggests that oxidation is unlikely to be the primary driver of the observed differences, as oxidation would be expected to affect both isotopes simultaneously. Both the Keeling and Miller-Tans approaches tend to be weighted toward the highest-concentration source, meaning that the Miller-Tans result primarily reflects the isotopic signature of the dominant, minimally oxidized methane source. In contrast, simple averages and concentration-weighted means integrate contributions from a broader mixture of sources and therefore more strongly reflect the influence of partially oxidized methane. In rice paddies, plant-mediated transport is the dominant emission pathway, transferring methane from subsurface anoxic layers and thus generally preserving a relatively unoxidized isotopic signature. However, due to mixing within the water column and the presence of oxic microenvironments near roots, partially oxidized methane can also be entrained and transported through plant aerenchyma. Therefore, concentration-weighted averages are not without significance; rather, they provide a complementary perspective by capturing the integrated effect of both primary emissions and oxidation processes. We have revised the description for better understanding.

"A significant linear relationship between δ^{13}C and δ^{2}H (Fig. 4C) further supports the presence of methane oxidation, consistent with isotopic enrichment associated with methanotrophic activity (Schaefer and Whiticar, 2008). In rice paddies, only 1–2% of methane is emitted via diffusion through floodwater, whereas ~90% is transported via plant-mediated pathways (aerenchyma) and 8–9% through ebullition (Cicerone and Shetter, 1981; Schütz et al., 1989; Smartt et al., 2016). Plant-mediated transport primarily transfers methane from subsurface anoxic layers and is therefore generally less affected by oxidation. However, due to mixing and circulation within the water column and the presence of oxic zones near roots, partially oxidized methane may also be entrained and transported through plant aerenchyma. Ebullition is also less affected by oxidation, while the diffusion pathway is more susceptible to isotopic enrichment through oxidation.

Previous studies have primarily relied on atmospheric sampling, whereas this study focuses on aquatic measurements, raising questions of representativeness. Key challenges include the presence of multiple sources, oxidation processes, and multiple transport pathways. These issues are discussed in detail in Supplementary Sections S3.3–S3.4. Briefly, both atmospheric and aquatic sampling may be subject to representativeness biases, as the Keeling and Miller-Tans methods are dominated by the highest-concentration source (Supplementary Section S3.1), while contributions from lower-concentration sources may be indistinguishable from background variability within the fitting framework. Nevertheless, the Miller-Tans estimates are considered to best represent the isotopic signature of the dominant, minimally oxidized methane source and are therefore adopted as the most consistent metric across sampling approaches." (Page 18, Line 390–410)

l. 384-387: Indeed, the sensitivity to this source is very high. Not only it is important to apply region-specific signatures, but also to reduce the uncertainties by doing more measurements ? (Which is what your study started to do!)

Response: Yes, agree – thank you for seeing this importance. We revised the sentence to:

"applying region-specific isotopic source signatures and reducing the uncertainties is essential for accurately constraining methane emissions in South Asia." (Page 20, Line 445–446)

l. 395-396: Can you explain what you provide the values of the "concentration gradient", and the reasons why it can be linked to minimal oxidation? Generally for the water sources, were all the samples taken at mid-depth, and what does this imply in term of oxidation?

Response: Thank you for this question. The interpretation is based on the known direction of isotopic fractionation during methane oxidation. This can be inferred from the distribution of data points in the dual-isotope space (Fig. 5C), where oxidation would produce a characteristic co-enrichment trend in both isotopes. In our wastewater dataset, such a trend is not clearly observed, suggesting that oxidation is limited.

All water samples were collected at mid-depth. Under these conditions, the differences between rice paddies and wastewater systems are mainly related to microbial processes. Rice paddies typically host active methanotrophic communities that can oxidize methane, whereas wastewater systems often undergo substantial anaerobic treatment prior to sampling, favoring methanogenic conditions. As a result, methane oxidation is expected to be less pronounced in the wastewater samples. We have clarified these points in the revised manuscript:

"Methane oxidation would be expected to produce a characteristic co-enrichment trend in both isotopes. However, no clear relationship between δ^{13}C and δ^{2}H was observed for methane in wastewater (Fig. 5C). This lack of a systematic isotopic trend suggested minimal oxidation, indicating that degradation processes prior to release were limited for wastewater methane." (Page 21, Line 453–457)

l. 408: "dispersed and irregular patterns", or wider range of values?

Response: Yes, this is a clearer and more precise description. We have revised the sentence to:

"Other sources, such as composting, biogas fermentation and other organic waste decomposition (Lu et al., 2021; Bakkaloglu et al., 2022), exhibited wider range of values." (Page 21, Line 467–468)

l. 422-429: there can be variation up to 10 ‰ in the waste methane δ^{13}C, this is quite large. Also, we know wastewater CH_4 is more enriched than from landfills, but you don't have landfill data in your study. I think your wastewater results could be representative, as you claim on l. 224, but not for landfills. Please rephrase.

Response: We agree that these data are for wastewater and not for landfills. We have scrutinized and revised the text so that this should not be misunderstood:

"However, our global review showed only minor distinctions among various waste sources, suggesting that the isotopic signatures we measured in South Asia should be representative for wastewater in the region. Further exploring other waste sources and various factors may improve our understanding of methane emissions from the waste sector." (Page 22, Line 483–487)

l. 451-453: Please explain in which way the "general oxidation level" is reflected here. These more enriched signatures show that some oxidation occurred, but if you write "level", is it that you can quantify it?

Response: We cannot quantify the oxidation fraction, but the isotopic fractionation direction is known. When comparing with the Miller-Tans results, the isotopic values are more enriched, which means oxidation happened. The manuscript text has been slightly revised to more clearly articulate this:

"More enriched production-weighted concentration-weighted means (δ^{13}C=–41.7±7.5‰ and δ^{2}H=–236±45‰) reflected the influence of oxidation." (Page 23, Line 513–514) *l. 454: “these fractionation patterns”. Do you refer to oxidation or diffusion here? Perhaps using “process” rather than “pattern” is more suitable?*

Response: Yes, oxidation process is more suitable here. Manuscript text revised accordingly (Page 23, Line 515).

l. 471: “similar” to what?

Response: The surface water and microbial sources are similar in regional patterns of δ^2H. We have revised the sentence to clarify this:

“Global microbial methane δ^2H exhibited a moderate or weak correlation with surface water δ^2H (Fig. 7; R^2=0.549 for ruminants, 0.363 for rice paddies and wetlands, 0.217 for waste), reflecting similar regional patterns among surface water and microbial sources.” (Page 24, Line 530–533)

l. 470-471: can you provide values or representation of this correlation? It isn’t very clear on the maps.

Response: We added the R^2 for the δ^2H of three different microbial groups with the surface water, i.e., R^2=0.549 for ruminants, 0.363 for rice paddies and wetlands, 0.217 for waste (Page 24, Line 530–533).

l. 472: “Hydrogen atoms in surface water likely served as a source for microbial methane, contributing to the observed spatial similarities in isotopic signatures.”. Please refer

Response: We have added relevant references to support this statement, including early foundational studies that describe the origin of hydrogen atoms in microbial methane and their relationship with environmental water:

“Hydrogen atoms in surface water likely served as a source for microbial methane (Whiticar et al., 1986; Whiticar, 1999), contributing to the observed spatial similarities in isotopic signatures.” (Page 24, Line 534–536)

l. 494: “resulting in fewer studies focusing on δ^2H”. The lack of study on hydrogen isotopes isn’t because of one or “Some studies”, it’s mostly because of the technical challenges in the measurements. Also, other studies point at the additional constrains hydrogen gives.

Response: We agree that the limited number of studies on δ^2H is primarily due to technical challenges associated with its measurement. We have revised the text accordingly and added recent studies highlighting that δ^2H can provide additional constraints on methane source attribution:

“Compared to the extensive observations and studies of δ^{13}C (Nisbet et al., 2023), measurements and constraints based on δ^2H remain much more limited, largely due to technical challenges associated with its analysis. However, a growing body of recent studies suggests that δ^2H can provide valuable additional constraints on methane sources (Dasgupta et al., 2025; Riddell-Young et al., 2025).” (Page 25, Line 556–560)

l. 513: “Conversely, methane from rice paddies and wastewater displayed more enriched δ^{13}C values than global means.”. For wastewater, please compare with the mean for wastewater as well.

Response: We agree that a comparison between South Asian wastewater emissions and global wastewater-specific values is more appropriate. The sentence has been revised accordingly:

"Conversely, methane from rice paddies displayed more enriched $\delta^{13}C$ values than global means, and wastewater methane was more enriched in $\delta^{13}C$ relative to global waste means (Fig. 8A) and also global wastewater means (Fig. 5; Table 4)." (Page 26, Line 581–584)

l. 545: "and… and…". Please rephrase.

Response: We have rephrased the sentence to:

"In South Asia, reported emissions varied substantially in both magnitude and source composition, from 37±3.7 Tg C yr^{-1} in the 2000s (Patra et al., 2013) to 50.3 Tg C yr^{-1} in more recent estimates(Ito et al., 2023), with further estimates of 52 Tg C yr^{-1} from top-down approaches (n=6) and 58 Tg C yr^{-1} from bottom-up approaches (n=27) (Saunois et al., 2025)." (Page 28, Line 612–617)

l. 546: you mention seasonality. But does it affect all the sources, and why? Why not including this consideration in your analysis for the sources that are concerned?

Response: We discussed that seasonality can affect the strength of different methane sources, although the magnitude and mechanisms of this influence may vary among sources. In this study, seasonal variability is mentioned primarily for discussion purposes, rather than being explicitly incorporated into the determination of isotopic source signatures.

Our aim is to highlight that continuous atmospheric methane isotope observations, when combined with source-specific isotopic signatures, have the potential to provide additional constraints on temporal variations in source strength. Such seasonal details are often difficult to resolve using concentration measurements alone or through conventional bottom-up and top-down approaches. Explicitly incorporating seasonal variations in source isotopic signatures would introduce substantial additional complexity and uncertainty, potentially making the system underconstrained and more difficult to interpret robustly. We revised the content to avoid misunderstanding:

"Atmospheric methane in South Asia exhibited pronounced seasonal variations in both mixing ratios and isotopic composition (Rao et al., 2008; Tiwari et al., 2020; Metya et al., 2022; Guha et al., 2018), reflecting a combination of changes in source activity, transport, and atmospheric processing that are difficult to capture using conventional models. Given these limitations, regional isotopic source signatures, together with dual-isotope top-down approaches, offer an independent and valuable framework for improving constraints on regional methane budgets." (Page 28, Line 617–623)

l. 550: … if the underlying factors of variations are well-understood.

Response: We have revised the sentences to avoid misunderstanding:

"Given these limitations, regional isotopic source signatures, together with 619 dual-isotope top-down approaches, offer an independent and valuable framework for improving 620 constraints on regional methane budgets." (Page 28, Line 621–623)

l. 570: remove "potential"

Response: Removed.

Figure 1: I think adding the countries boundary lines would improve the figure.

Response: We initially included country boundary lines in the figure. However, after discussion among co-authors, we chose to remove them because some borders in the region are subject to dispute. To avoid potential geopolitical sensitivities and keep the focus on the scientific content, we present the figure without national boundaries.

Figure 2:

- *"isotopic characteristics" isn't the right phrasing; rather use "isotopic source signatures" or "isotopic composition"*
- *(D) and (E): I suggest to add a comparison with averages of this study.*

Response: We have revised "isotopic characteristics" to "isotopic source signatures" throughout Figures 2–5, which is indeed a more accurate description.

Regarding panels D and E of Figure 2, we have already provided a detailed comparison of South Asian and global values in Table 1. The South Asian values are displayed in Figure 2A–2B, while Figure 2D–2E show global statistics, which are clearly distinguished from the regional data. Including South Asian values in Figure 2D–2E would overly complicate the figure and could make it harder for readers to interpret. This separation was chosen to maintain clarity and avoid potential confusion. Furthermore, comparisons between South Asian and global values are presented again in Figure 8 and Table 5, ensuring that the regional-to-global context is fully emphasized without adding unnecessary complexity to Figure 2.

Table 1: Please explain in the legend that you've used the global values for C4 to derive the mean for South Asia.

Response: We added one sentence accordingly.

"The global δ^{13}C value for C4 biomass burning was applied in computing the weighted mean for the South Asian WM δ^{13}C of C3/C4." (Page 33, Line 670–671)

Figure 3, (D) and (E): I suggest to add a comparison with averages of this study.

Response: We appreciate the suggestion, but a detailed comparison of South Asian and global values is provided in Table 2. Figure 3A–B shows the South Asian values, while Figure 3D–E present global statistics, distinguished from the regional data. Including South Asian values in Figure 3D–E would overly complicate the figure and reduce readability. This separation maintains clarity, and regional-to-global comparisons are further emphasized in Figure 8 and Table 5, avoiding unnecessary figure complexity in Figure 3.

Figure 6: can you indicate the region boundaries for the averages we see on the figure?

Response: Some country borders in this region are subject to political dispute. To avoid potential geopolitical sensitivities and maintain focus on the scientific analysis, we will not display explicit political boundaries.

Figure S4: why 2 different color scales for the same variables? Also, the concentration units are in ppm on the x-axis, but should be L/nmol, considering the color scale and that there were water samples.

Response: We have now standardized the color scales across all three panels and corrected the x-axis labels with the proper units (L nmol^{-1}).

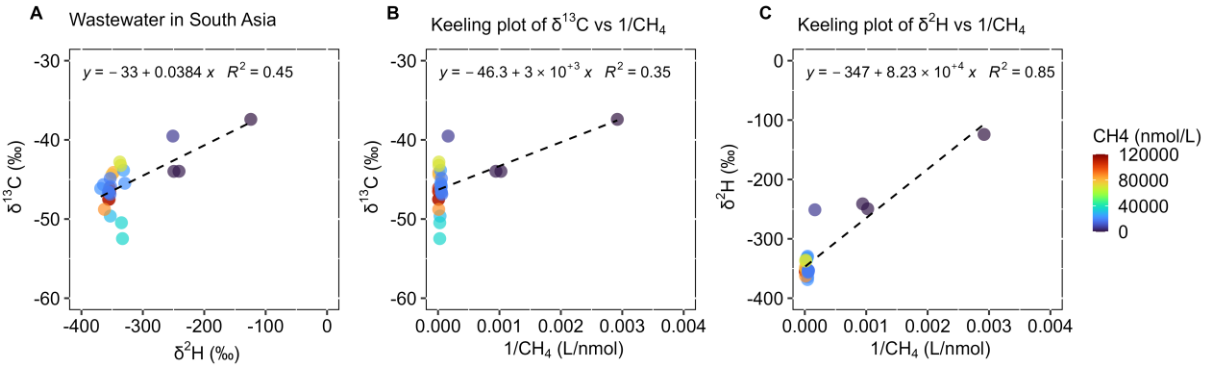

Fig. S4. Mixing ratios and isotopic characteristics of CH_4 from wastewater in South Asia. (A) Synchronous variations in $\delta^{13}C$ and δ^2H of CH_4. **(B)** Keeling plot for $\delta^{13}C$. **(C)** Keeling plot for δ^2H.

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Author Responses (AR) to Referee Comments (RC) and resulting revisions of manuscript egusphere-2026-411: "Distinct dual-isotopic signatures of major methane sources in South Asia" by Peng Yao, Katja Belec, Henry Holmstrand, Josh Balacky, Abdus Salam, Krishnakant Budhavant, Mohanan Remani Manoj, Khaled Shaifullah Joy, Md. Alamin Hossain, Atinderpal Singh, Anil Patel, Neeraj Rastogi, Chinmay Mallik, Kirpa Ram, Gyanesh Kumar Singh and Örjan Gustafsson.

Reference: https://doi.org/10.5194/egusphere-2026-411

We sincerely thank the editor and both reviewers for thoroughly reviewing and giving constructive feedback that is helping to clarify the significance and importance of this manuscript during revision. All reviewer comments are included below in *italic font* each followed by our detailed author responses, in normal font.

Anonymous Referee #2: [*https://doi.org/10.5194/egusphere-2026-411-RC2]*

Yao et a.: Distinct dual isotope signatures of major methane sources in South Asia.

GENERAL COMMENTS

This is a very welcome paper that provides important new isotopic source signature information which will greatly help those using isotopes to model the global methane budget. The paper should be published, but after some revision.

In global and regional budgets of atmospheric methane, source attribution is often a difficult task, as many areas have co-located emissions from different sources (e.g. coal mines, cattle herds, wetlands). To split the source inputs, isotopic discrimination is very powerful. But there are very few isotopic measurements from South Asia, even though this is a major methane-emitting region. Thus this paper is important – it presents a large number of new measurements in a region that is an important contributor to the global budget.

I have a number of queries. Many of these are small. Larger questions, however, do arise. They concern: 1. the use of Miller-Tans plots, and 2. the ricefield 'signatures': do they represent methane actually emitted into the air?

Response: Thank you very much for your valuable comments and suggestions. We provide a consolidated response below to address the two main issues.

1. The application of Keeling and Miller-Tans plots

We understand your concerns regarding the treatment of **background** in the **application of Keeling and Miller-Tans plots**. To address this point, we have revised the manuscript to add clarifications and discussion in both the main text and the Supporting Information.

(1) We would like to emphasize that the CH_4 concentrations in our source samples are very high, and therefore largely insensitive to background influence. Both Keeling and Miller-Tans approaches are fundamentally based on isotopic mass balance:

$$\delta_{obs} = \frac{c_{bg} \times \delta_{bg} + c_{source} \times \delta_{source}}{c_{bg} + c_{source}} \tag{S1}$$

When the source concentration is much higher than the background:

$$c_{source} \gg c_{bg} \tag{S2}$$

Eq. (S1) simplifies to:

$$\delta_{obs} \approx \delta_{source} \tag{S3}$$

This implies that when source concentrations are sufficiently high, the observed isotopic composition approaches that of the source. Therefore, high-concentration data points alone can provide a good approximation of the source isotopic signature, even without applying Keeling or Miller-Tans analyses.

(2) Why stable background conditions are often emphasized in Keeling and Miller-Tans analysis? In practice, background conditions are never strictly constant, raising the question of how much variability is acceptable. Our answer is that it depends on the relative magnitude of source and background signals. To clarify this, we briefly revisit the mathematical structure of the Keeling approach.

In the Keeling formulation, background terms are embedded in the slope:

$$\delta_{obs} = c_{bg} \times \left(\delta_{bg} - \delta_{source}\right) \times \frac{1}{c_{obs}} + \delta_{source} \tag{S4}$$

As a result, variability in background leads to variations in the slope, which can distort the linear relationship (e.g., rotation or fan-shaped distributions in the data).

In contrast, the Miller-Tans formulation places the background contribution in the intercept:

$$\delta_{obs} \cdot c_{obs} = \delta_{source} \times c_{obs} + c_{bg} \cdot \left(\delta_{bg} - \delta_{source}\right) \tag{S5}$$

This means that the slope (i.e., the isotopic source signature) is less directly affected by background variability, while background fluctuations primarily influence the intercept, potentially increasing scatter without fundamentally altering the slope.

Nevertheless, both approaches reflect the combined influence of source and background variability. The key point is that the relative importance of background depends on the magnitude of source-driven variability. When source signals (variation of c_{source}) are much stronger than background signal (variations of c_{bg}), the derived Keeling intercepts and Miller-Tans slopes remain dominated by the source signal (c_{obs} variation dominated by c_{source}), even if background variability is present. This is consistent with the case of $c_{source} \gg c_{bg}$ (Eq. S2).

Conversely, when source-induced variations are comparable to background variability, even small background fluctuations may bias the inferred source signature. This situation may occur when source signals are weak or when observations are far away from the source but close to background conditions. For example, in some atmospheric observations over rice paddies, CH_4 concentrations are close to background levels, such that background variability, although small in absolute terms, can still influence Keeling-derived source signatures.

(3) In our dataset, atmospheric background conditions are represented in the Keeling plots shown in the Supporting Information Figs. S1–S2, where low-concentration data points (around ~2 ppm) are included for ruminant and biomass burning samples, although their influence is negligible due to the dominance of high-concentration samples ($c_{source} \gg c_{bg}$). For aqueous samples (rice paddies and wastewater), background methane is expected to be very low (effectively negligible), and the observed concentrations span several orders of magnitude, further confirming the dominance of source signals over background variability.

We have added the above clarifications to the Supporting Information (Section S2) to improve transparency and facilitate interpretation (Main text Page 12, Line 252–264). We agree that this is an important methodological consideration and have thus revised the ms text as follows:

"Keeling and Miller-Tans plots are two formulations of the isotopic mass balance (Eq. 4), differing primarily in their treatment of background contributions. The Keeling approach (Eq. 2) derives the source signature from the intercept but is sensitive to background variability through its effect on the slope, which can distort linearity. In contrast, the Miller-Tans formulation (Eq. 3) derives the source signature from the slope, with background variability mainly affecting the intercept and increasing scatter while largely preserving linearity. As both methods rely on linear regression, increased scatter is generally less detrimental than distortion of linearity, making the Miller-Tans approach more robust in practical applications. Both approaches are most reliable when source-driven variability dominates over background variability. In our case, some high-concentration observations approach the condition $c_{source} \gg c_{bg}$ (Eq. 5), leading to $\delta_{obs} \approx \delta_{source}$ (Eq. 6), such that the influence of atmospheric background variability becomes negligible. Further discussion of background effects is provided in Supporting Information Section S2." (Page 12, Line 252–264)

2. Isotopic signatures of rice paddy methane

We thank the reviewer for raising the question regarding the validity of our observations for **rice paddy methane**, which indeed warrants detailed discussion.

(1) Interpretation of Keeling and Miller-Tans analyses in multi-source systems

An important issue to clarify is what Keeling and Miller-Tans analyses represent in a multi-source system. Both methods were originally developed for a single source perturbing a relatively stable background, with the aim of deriving the isotopic signature of that source. In multi-source systems, however, the situation becomes more complex.

To illustrate this, we have added a mixing simulation in the Supplementary Information (Section S3). We want to show that, in a multi-source system, both Keeling and Miller-Tans analyses tend to be dominated by the source with the highest concentration. This can be understood intuitively: when one source is much stronger than the others, the system effectively reduces to the case discussed above (i.e., $c_{source} \gg c_{bg}$), and the weaker sources behave similarly to background variability and are largely neglected. Between this limiting case and situations where multiple sources are of comparable magnitude, the interpretation becomes more nuanced.

(2) Implications for atmospheric observations over rice paddies

Based on the above, the validity of using atmospheric measurements to characterize rice paddy methane depends on several factors.

First, surrounding emission sources (e.g., biomass burning, ruminants, or domestic waste) may interfere with the signal, unless rice paddy emissions are significantly stronger than other potential sources.

Second, methane emitted from rice paddies may originate from different pathways. For example, plant-mediated transport can carry methane from subsurface water to the atmosphere. In addition to relatively unoxidized methane, it is possible that the plant-mediated methane emissions also include the oxidized methane with convection and diffusion in water column. When these different components are mixed in the atmosphere, Keeling and Miller-Tans analyses will tend to reflect the dominant (highest-concentration) emission component, while weaker components may be underrepresented.

Third, when rice paddy methane emissions are weak, the resulting atmospheric perturbation may be small or close to ambient methane levels. In such cases, source-induced variability is comparable to background variability, and both Keeling and Miller-Tans approaches may become unreliable, with inferred source signatures strongly influenced by background fluctuations. This may explain why some studies report isotopic values close to atmospheric background.

Overall, these considerations suggest that atmospheric sampling over rice paddies can be subject to uncertainties depending on the relative strength of emissions and the complexity of surrounding sources.

(3) Advantages of aqueous sampling in this study

Our water-based sampling approach provides a complementary perspective.

First, the high-concentration methane measured in water samples can directly constrain the isotopic signature of the source. Under conditions where $c_{source} \gg c_{bg}$, even without applying Keeling or Miller-Tans analyses, high-concentration samples already indicate the source signature. In our case, these methods are used to derive a representative isotopic value for the dominant, high-concentration methane source, which primarily reflects relatively unoxidized methane.

Second, we also report weighted isotopic values to account for the complexity of methane production and transport in rice paddies. Plant-mediated transport may carry both unoxidized and partially oxidized methane, and methane concentrations in the water column are spatially heterogeneous, with additional effects from mixing and diffusion. Therefore, the weighted values are intended as a reference that integrates these processes.

Third, the final values adopted in this study are based on Keeling and Miller-Tans analyses, which are conceptually consistent with atmospheric approaches, but are here applied under conditions where source signals are dominant and better constrained.

We have added the above clarifications to the Supporting Information (Section S3) to improve transparency and facilitate interpretation (Main text Page 17–19, Line 367–386, Line 390–410). We agree that this is an important methodological consideration.

"In contrast, the Keeling plots showed reduced linearity and more enriched $\delta^{13}C$ and $\delta^{2}H$ values (Supplementary Fig. S3), reflecting the complexity of methane production and processing in rice paddies (Supplementary Section S3.2). The sample concentration range spanned several orders of magnitude and some high-concentration samples satisfied the condition $c_{source} \gg c_{bg}$ (Eq. 5), yielding $\delta_{obs} \approx \delta_{source}$ (Eq. 6), and their isotopic values still exhibited noticeable variability, indicating the coexistence of multiple methane sources and/or the influence of in situ oxidation within the water column. Both Keeling and Miller-Tans methods are fundamentally designed for single-source perturbations; in multi-source systems, they tend to be biased toward the highest-concentration source (Monte Carlo mixing simulation in Supplementary Section S3.1), while weaker sources are suppressed or even negligible when concentration differences are large. In the Keeling method, background contributions are incorporated into the slope (Eq. 2). Under multi-source conditions, lower-concentration methane sources do not represent true background, but their influence becomes effectively indistinguishable from background variability within the Keeling framework. As a result, the combined variability of background and lower-concentration sources became significant in rice paddy samples, leading to deviations from linearity and reduced robustness. In contrast, the Miller-Tans formulation incorporates background into the intercept (Eq. 3); when concentration differences spanned several orders of magnitude for rice paddy methane, the slope was primarily controlled by the highest-concentration source, resulting in a more stable and interpretable relationship." (Page 17, Line 367–386)

"A significant linear relationship between $\delta^{13}C$ and $\delta^{2}H$ (Fig. 4C) further supports the presence of methane oxidation, consistent with isotopic enrichment associated with methanotrophic activity (Schaefer and Whiticar, 2008). In rice paddies, only 1–2% of methane is emitted via diffusion through floodwater, whereas ~90% is transported via plant-mediated pathways (aerenchyma) and 8–9% through ebullition (Cicerone and Shetter, 1981; Schütz et al., 1989; Smartt et al., 2016). Plant-mediated transport primarily transfers methane from subsurface anoxic layers and is therefore generally less affected by oxidation. However, due to mixing and circulation within the water column and the presence of oxic zones near roots, partially oxidized methane may also be entrained and transported through plant aerenchyma. Ebullition is also less affected by oxidation, while the diffusion pathway is more susceptible to isotopic enrichment through oxidation.

Previous studies have primarily relied on atmospheric sampling, whereas this study focuses on aquatic measurements, raising questions of representativeness. Key challenges include the presence of multiple sources, oxidation processes, and multiple transport pathways. These issues are discussed in detail in Supplementary Sections S3.3–S3.4. Briefly, both atmospheric and aquatic sampling may be subject to representativeness biases, as the Keeling and Miller-Tans methods are dominated by the highest-concentration source (Supplementary Section S3.1), while contributions from lower-concentration sources may be indistinguishable from background variability within the fitting framework. Nevertheless, the Miller-Tans estimates are considered to best represent the isotopic signature of the dominant, minimally oxidized methane source and are therefore adopted as the most consistent metric across sampling approaches.” (Page 18, Line 390–410)

SPECIFIC POINTS

Line 31 “more depleted” and “more enriched” – compared to what? C4??

Response: It is compared to global mean isotopic values. We have revised the sentence accordingly:

“Methane from C3 biomass burning is more depleted in δ^{13}C (–30.9±2.2‰) but more enriched in δ^{2}H (–201±18‰) relative to global means, while ruminant methane (C3) is strongly depleted in both δ^{13}C (–68.7±0.5‰) and δ^{2}H (–343±6‰).” (Page 2, Line 30–33)

L52 maybe mention Ciais et al, 2026 Science 391: eadx8262, and Nisbet & Manning 2026. Science 391: 556-557

Response: We agree that these are important and timely studies. We have added citations to these recent works to reflect the latest developments in the field:

“Despite its significance, the drivers of recent methane increases remain uncertain (Nisbet et al., 2023; Schaeffer et al., 2025), recent studies are beginning to address these gaps (Ciais et al., 2026; Nisbet and Manning, 2026), highlighting the need for precise monitoring and effective mitigation strategies.” (Page 3, Line 52–55)

L57 – fastest-growing emitter? – can this be backed up with a reference? – African sources are also growing fast.

Response: We agree that the original phrasing may be misleading. We have revised the text accordingly to provide a more accurate and balanced description:

“South Asia is one of the largest and fastest-growing methane emitting regions, with contributions believed to be primarily from anthropogenic sources (Stavert et al., 2022).” (Page 3, Line 59–61)

L59 biomass burning – perhaps cite a newer reference: note also that biomass burning includes crop fires and landfill fires as well as 'quasi natural' grass and forest fires/

Response: We have added more recent reviews to better reflect the broad range of biomass burning sources, including both natural and anthropogenic processes. The sentence has been revised accordingly to clarify this point:

"The region experiences extensive both natural and anthropogenic biomass burning (Kirschke et al., 2013; Saunois et al., 2025), hosts the world's largest ruminant population (Ganesan et al., 2017), is a major rice producer (Singh et al., 2021) and has substantial waste emissions from the dense population (Chakraborty et al., 2011)." (Page 3, Line 61–64)

L66 – combustion sources …ARE believed. Also maybe split natural microbial sources and agricultural microbial sources (see Nisbet et al. 2025. Phil Trans Royal Soc. 481(2309).

Response: We have revised the wording accordingly. We also clarified the distinction between natural and agricultural sources within biomass burning and included the suggested reference to support this classification:

"Combustion sources of methane is dominated by natural and agricultural biomass burning emissions but also include coal combustion, traffic emissions and other combustion processes (Saunois et al., 2025; Nisbet et al., 2025)." (Page 3, Line 68–70)

L70 maybe briefly mention 'and geological sources', though I suspect the Saunois et al budget over states them.

Response: We agree that including geological sources improves the precision of the description. The sentence has been revised accordingly:

"Thermogenic methane originates from fugitive emissions during fossil fuel extraction, transport and processing, as well as geological sources (Sherwood et al., 2017; Menoud et al., 2022)." (Page 3, Line 70–72)

L84 – 'nearly completely lacking. Indeed – the powerful reason this paper needs to be published. Incidentally for South East Asia see Woolley Maisch et al. Identification of Sources of Methane in Ho Chi Minh City, Vietnam. ACS ES&T Air (2025), and Brownlow et al Glob Biogeo Cycl 31 (2017): 1408-1419.

Response: Thank you for the recommended papers. We cited the paper (Brownlow et al., 2017) to support this statement. (Page 4, Line 87).

L97-111 – this methodology is impressive. See also parallel study by Woolley Maisch et al. Characterising methane emissions from dairy farm sources using mobile and dual-isotope measurements in Jersey, Channel Islands." Atmospheric Environment: X (2025): 100384.

Response: Thank you for highlighting this interesting study. We have now cited the new paper in the revised manuscript (Page 22, Line 480).

L118. Ricefields. Here I have a major concern. The text describes careful and meticulous sampling of water in the paddy field. But the topic of the paper is the atmospheric source signature – in other words, the measurement target here is the isotopic ratio of the methane that is actually emitted into the air, NOT the methane that is present in the water body. Later on (line 375) the text explains that ~30-90% of methane is emitted by plant-mediated transport and thus may avoid the passage through oxygenated (i.e. methanotroph-rich) near surface water. In other words, methane that gets to the air via rice stalks is likely to be much lighter than the methane that escapes from the top of the water column, which is the residual methane after strong and isotopically selective oxidation.

Response: We have addressed this point in detail above and provide a brief clarification here. Both Keeling and Miller-Tans approaches applied to atmospheric and aquatic samples essentially constrain the same dominant source, namely the highest-concentration, minimally oxidized methane emitted from rice paddies. Keeling and Miller-Tans methods were originally developed for systems influenced by a single source perturbation. In multi-source environments, high-concentration sources (i.e., data points farthest from the background) tend to dominate the linear regression, particularly when their concentrations differ from the background by orders of magnitude. In contrast, lower-concentration sources have relatively little or even negligible impact on the linear regression. Therefore, both aquatic and atmospheric sampling approaches can yield meaningful source signatures, but they are subject to similar biases toward dominant, high-concentration sources. We have added more details and revised the discussion in Main text (Page 17–19, Line 367–386, Line 390–409) and Supporting Information (Section S3).

L147 – equilibration – how long?

Response: 2 hours. We have added the equilibration time accordingly (Page 7, Line 151).

L149 – standards – specify the origin of the standards in Supp Info. Are they based on WMO X(ch4) from NOAA?

Response: We have added the origin information of methane isotopic standards accordingly:

"Three methane standards with multiple concentrations (1.6 ppm ± 2%, Air liquid; 80.3 ppm ± 2.0 ppm, Linde; 250 ppm ± 0.5%, Strandmøllen; 95% confidence) in synthetic air were used for calibration. (Page 7, Line 153–155)

L194 – the Miller Tans approach needs background information. The choice of background for each specific plot needs to be carefully established. There are various approaches to the problem but the way background was established wasn't obvious to me in the main text, nor in the supplemental information.

Response: We have addressed this question above, where we clarify our approach to background evaluation. Additional descriptions and discussion of the background have been incorporated into the main text (Page 12, Line 252–264) and in Supporting Information (Section S2).

L209 and also L222 – a new paper, now in ACP discussions, may be of interest. Tapin, Emeline, et al. A global dataset of δ 13 C-CH 4 source signatures and associated uncertainties (1998–2022), with a sensitivity analysis to support isotopic inversions. Earth System Science Data Discussions 2026: 1-55

Response: Thank you for this interesting paper. We have cited this paper (Page 29, Line 638).

L237 – Miller Tans depends on background choice and that's not discussed here. That's an important judgement call and needs to be properly discussed in the text. Note – this is a major point and should be addressed properly before the paper is accepted.

Response: We addressed these background question all together above. Additional descriptions and discussion of the background have been incorporated into the main text (Page 12, Line 252–264) and in Supporting Information (Section S2).

L250 – in part the hydrogen comes from the biomass and in part from the water. As water varies strongly with meteorological source latitude, this needs to be dicussed. See for example: Liu, Jingfeng, et al. Variations in stable hydrogen and oxygen isotopes in atmospheric water vapor in the marine boundary layer across a wide latitude range. Journal of Environmental Sciences 26.11 (2014): 2266-2276.

Also: Zakharov, Vyacheslav I., et al. "Latitudinal distribution of the deuterium to hydrogen ratio in the atmospheric water vapor retrieved from IMG/ADEOS data." Geophysical Research Letters 31.12 (2004).

NOTE – Later comment – I have now seen L653-656. Maybe put some of that in the main text.

Response: Thank you for these insightful references. We agree that the hydrogen isotopic composition of methane may be influenced by environmental water, which exhibits strong latitudinal variability, and this is an important aspect to consider. However, the currently available isotopic constraints for methane from biomass burning remain limited. As a result, the existing dataset is not sufficient to robustly assess whether such latitudinal variations are reflected in the δ^2H signature of biomass burning methane. As shown in Fig. 2E, the available values exhibit relatively limited overall variability, making it difficult to draw firm conclusions regarding latitudinal or regional dependence at present. This is an important topic, and it would benefit from additional measurements in future studies to better resolve potential spatial patterns.

We have added a statement noting that these signatures may be influenced by surface water; however, the extent of this influence remains uncertain, as available data are still very limited:

"Some studies have shown that δ^2H in surface water exhibits spatial (latitudinal) variability (Zakharov et al., 2004; IAEA/WMO, 2023), which would logically also influence biomass burning signatures. However, available δ^2H source signatures for methane remain limited, preventing further differentiation at present." (Page 13, Line 276–279)

L257 – 90:10 ratio. I'm a bit surprised at this number – note L297 gives global 70:30. Is it seasonal? I don't know India but I thought the autumn harvest Kharif season had C4 maize crop burning while the spring harvest Rabi was C3 wheat.

L279 – biomass burning – see comment above L257.

Response: This isotopic source apportionment reflects winter conditions in South Asia, and some seasonal variability can be expected. For example, differences in crop types and associated biomass burning (e.g., C_3 vs. C_4) between seasons may influence the relative contributions. A more detailed assessment of seasonal variations would be valuable and could be explored in future work. At present, however, this represents our best estimate based on the available observations. We have added the season "in winter" to the sentence:

"Based on our previous isotopic source apportionment of elemental carbon (EC) in South Asian atmospheric aerosols, C3 and C4 biomass combustion accounted for 90% and 10% of EC in winter, respectively (Dasari et al., 2020)." (Page 13, Line 282–285)

L300 note comment on L250 – d2H in water is latitude dependent.

Response: We understand your point regarding the latitude dependency, but as indicated in Fig.2E, we cannot find any latitude dependency with the limited existing isotopic signatures. This may be explored over these regional scales in the future in new studies.

L302-303 these two ‰ numbers are the same - easily in error of each other.

Response: Yes, these two numbers are close. We revised the sentence to avoid potential confusion:

"Methane emissions from C3-fed ruminants in South Asia (–68.7±0.5‰, Fig. 3A) were more depleted in δ^{13}C than the global mean of C3-fed ruminants (–67.0±3.0‰, Fig. 3D)." (Page 13, Line 331–332)

L312 – 32‰ number – that has a large uncertainty.

Response: We acknowledge that this value has a relatively large uncertainty. Although there is some overlap with the global isotopic range, the deviation remains notable and can still influence isotopic source apportionment.

L315 – maybe cite the EDGAR7-based Figure 5 in Nisbet et al 2025 on agricultural emissions. Phil Trans Royal Soc. 481(2309).

Response: Thank you for the suitable reference. We have revised accordingly:

"Recent studies have indicated that biogenic methane emissions have increased in the tropics, with considerable emissions from agricultural activities such as ruminant livestock farming and rice cultivation (Schaefer et al., 2016; Nisbet et al., 2025)." (Page 16, Line 343–345)

L326 – mention also manure emissions. These are important when cattle are intensively farmed and the manure is held in anoxic conditions. Maybe that's not a major factor in India where cattle roam extensively. Also mention wild ruminants, like small deer.

Response: We have revised the text to include wild ruminants (e.g., deer). Manure-related emissions are considered within the waste category in our framework and are therefore not treated separately under ruminant emissions:

"While cattle are a major source, other domesticated species, including buffalo, sheep, and goats, as well as wild ruminants such as deer, also contribute substantially to methane emissions." (Page 16, Line 355–357)

L342 – -45.3 ‰ value. Here is my other major point that needs to be cleared up before publication. For global budget studies the source signature that matters is the signature of the methane actually emitted into the air above the rice field, NOT the signature of the methane in the water. A lot of the methane that reaches the air comes from mud up the plant stems, and may escape the methanotrophy trap. The methane in the water is subject to methanotrophy, that selectively targets the 12C and hence the residual methane in water is enriched in 13C. Thus ambient water likely diffuses methane that is a bit heavier that the methane up the plant stems. Large bubbles quickly coming direct from the mud may contain lighter methane, but small bubbles are attacked my methanotrophs as they rise up. To get back to my main point, the methane source signature that matters for methane budget calculations is the methane that actually gets into the atmosphere above the rice paddy and is then carried away by the wind to join the regional and global burden. In other words, this needs to be sampled in the air, maybe at about 2m above the water and well above the plant stems.

Response: We greatly appreciate your extensive sampling experience and your substantial contributions to this field. Your points prompted us to carefully reconsider the fundamental differences between atmospheric and aquatic sampling. As a result, we have substantially rewritten this section to clarify these distinctions. Detailed discussion of the differences between aquatic and atmospheric sampling, and their implications for source signatures, has been addressed together above and in revised manuscript (Page 17–19, Line 367–386, Line 390–410) and Supporting Information (Section S3).

L348 and 350, also L365, 368 - My impression (I may have misunderstood the supplementary database) is that the results here are from measurements in water, not air. Thus there needs to be a methanotrophy correction applied.....the bulk of what enters the air via plants is likely to be much lighter than -45%, which is ‰ value of the residual methane in the water. That's much more enriched than I'd expect for the actual bulk ricefield input to ambient air.

I think this section needs a bit of rewriting…

The authors may wish to look at Table 2 in France et al. 2022. In particular, note the results from Yi O rice paddies in Hong Kong.

δ13C methane source signatures from tropical wetland and rice field emissions. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 380, no. 2215.

See also Brownlow, R., et al. 2017. Isotopic ratios of tropical methane emissions by atmospheric measurement. Global Biogeochemical Cycles, 31(9), pp.1408-1419.

Response: Thank you for the recommended papers, which we have now cited and added discussions (Page 17–19, Line 367–386, Line 390–410). For the question on aquatic and atmospheric sampling, we addressed this above. In addition, this section has been rewritten a lot (Section 3.3) together with more details in the Supporting Information (Section S2 and S3).

L416/421 – see discussion of waste and landfills in Nisbet, E. G., et al. Methane mitigation: methods to reduce emissions, on the path to the Paris agreement. Rev Geophys 58.1 (2020): e2019RG000675.

Response: Thank you for the important review paper. We have cited the paper to support our discussions (Page 22, Line 481).

L435, L476, L 489 – remember the latitude impact on water for d2H.

Response: Yes. We have revised the sentences accordingly:

"In tropical regions, microbial methane δ^2H values were more depleted than global mean values, potentially indicating unique microbial, environmental processes, and/or different surface water δ^2H that require further investigation." (Page 25, Line 538–540)

L444, also 450-457. – Miller tans on rice – see earlier comments.

Response: We addressed this question above and it is addressed in the revised manuscript (Page 17–19, Line 367–386, Line 390–410) and Supporting Information (Section S3).

L461 – what does 'per capita' mean here? Averaged over the total human population of South Asia??? Or cattle heads? I'm lost! Explain the calculation.

Response: "Per capita" here refers to the human population. We assume that per-person waste emissions are approximately similar across the population in South Asia. The isotopic signature of waste emissions is then weighted by population to estimate the overall contribution from human waste. We have revised the sentence to:

"assuming similar per capita methane production across South Asia" (Page 24, Line 522)

L494 – "supposed"…"weaker" - did Nisbet et al 2023 really say this? I skimmed the text and didn't find any such remark. But maybe I looked too quickly..

Response: We have reviewed the discussion and revised the relevant text to ensure accurate representation of Nisbet et al. (2023) and avoid any potentially misleading statements:

"Compared to the extensive observations and studies of δ^{13}C (Nisbet et al., 2023), measurements and constraints based on δ^2H remain much more limited, largely due to technical challenges associated with its analysis. However, a growing body of recent studies suggests that δ^2H can provide valuable additional constraints on methane sources (Dasgupta et al., 2025; Riddell-Young et al., 2025)." (Page 25, Line 556–560)

L528 note the isotopic fractionation is extremely locally specific. Over the Inter Tropical Convergence in the moist mid-troposphere at a few thousand metres in the air of the brightly lit tropics, methane's lifetime is very short indeed and the fractionation huge. Over the North Pole in dark winter the lifetime is very long. So applying this bul global number of 6-7‰ is not valid for a snapshot data point over India. I think lines 522-534 need rewriting.

Response: We appreciate the reviewer's point regarding the spatial and temporal variability of isotopic fractionation. While atmospheric oxidation is indeed spatially heterogeneous (e.g., stronger OH-driven oxidation in the tropics and weaker activity at higher latitudes), atmospheric methane isotopic composition reflects a steady-state balance between sources and sinks. In the tropics, although the sinks are stronger and tend to enrich the remaining methane isotopically, this effect is counterbalanced by intense source emissions that continuously supply isotopically depleted methane. As a result, the atmospheric methane pool is renewed, and the net isotopic composition does not deviate substantially from the combined source signature. In other words, sink-driven enrichment is largely offset by source-driven depletion, helping to maintain relatively stable background isotopic values in tropical regions.

Most box models simplify global isotopic fractionation using fixed values. Considerable global methane sources (a study suggested 64% from tropics (Jackson et al., 2020)) and sinks are located in the tropics, where the fractionation values used in the leading studies are broadly consistent with the commonly adopted global value of ~6–7‰. We acknowledge that such simplifications inevitably introduce some uncertainty, but they represent a necessary balance between model complexity and interpretability.

L542. 'severalfold' – what does this mean?? – there are big discepancies but in most categories not as big as many multiples.

Response: We agree that "severalfold" was inaccurate, as most categories do not differ by multiple times, only a few shows larger deviations. We have revised the wording to "substantially" to better reflect the magnitude of the discrepancies:

Bottom-up inventories showed large discrepancies, with estimates differing substantially (Stavert et al., 2022). (Page 28, Line 612–617)

L555 – 'enriched' – see earlier points: of course the methane in water is enriched relative to methane that actually reaches air – the methane in water is the left-behind.

Response: The observed enrichment may not be caused by methane oxidation; rather, it reflects a regional characteristic of South Asia. Specifically, only δ^{13}C values are more enriched, but δ^{2}H in this region is comparable to the global average. If oxidation were the main cause of enrichment, both δ^{13}C and δ^{2}H would change simultaneously, as isotopic fractionation affects both isotopes in the same direction. As discussed above, the use of Keeling and Miller-Tans analyses effectively accounts for the influence of water-column oxidation, reaching the isotopic signatures of the highest-concentration unoxidized methane.

L574 – cite Riddell-Young, Ben, et al. Microbial driver of 2006–2023 CH4 growth indicated by trends in atmospheric δD–CH4 and δ13C–CH4. Proceedings of the National Academy of Sciences 122.50 (2025): e2516543122.

Response: We have now cited Riddell-Young et al. (2025) (Page 29, Line 647), which is a highly relevant and insightful study. At the time of our submission, this article was not yet published.

L587 – caption needs more explanation, especially for Miller Tans.

Response: We addressed this problem above. Detailed explanations have been added to the Supporting Information Section S2 and S3.

CONCLUSION

This is a very valuable study, that should be published, but needs significant revision before publication.

Response: Thank you very much for your constructive comments and suggestions. Many of the points you raised are highly insightful, and some highlight aspects we had not previously considered. We and the ms have benefited greatly from your feedback.