New insights into the global methane budget from measurements of atmospheric δD-CH_4

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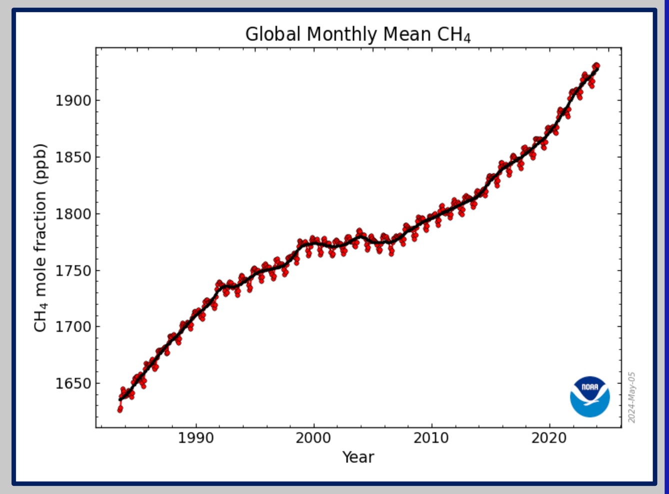
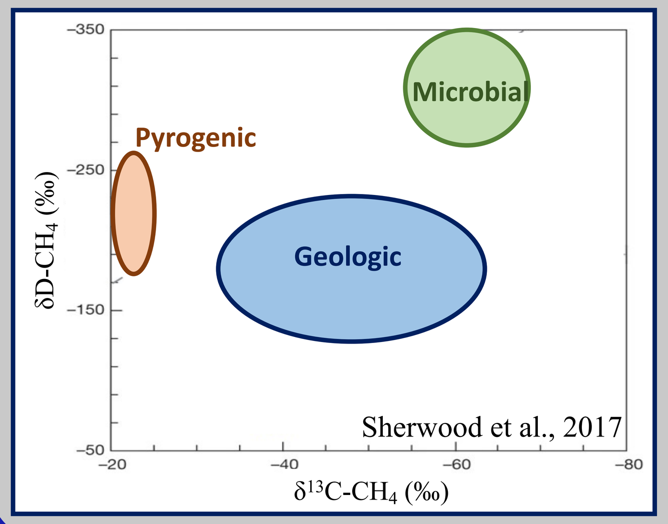
1) Introduction

- The mixing ratio of atmospheric methane (CH_4) continues to rapidly increase.
- Atmospheric δ^{13}C-CH_4 and δD-CH_4 are sensitive to isotopically distinguishable emissions and sink fractionation and can shed light on the CH_4 budget.
- Analyses of δ^{13}C-CH_4 measurements point to a microbial driver of recent CH_4 growth.



Research Question: Can measurements of δD-CH_4 improve constraints on the global CH_4 budget?



- δD-CH_4 is less sensitive to pyrogenic emissions.
- Smaller discrepancy between Cl and OH sink fractionation.
- Strong latitudinal δD-CH_4 gradient for microbial and pyrogenic emissions.

2) New δD-CH_4 datasets

1. **INSTAAR Stable Isotope Laboratory:**
   - 2005 – 2009, 14 measurement sites.
   - ~3200 measurements permits Data Extension and Integration.

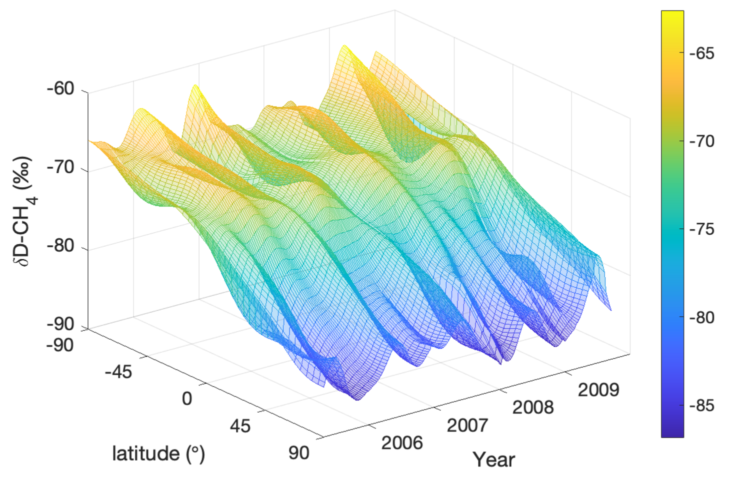


Figure 1. "Carpet diagram" of atmospheric δD-CH_4. *The result of the Data Extension and Integration analysis of for the 2005 – 2009 INSTAAR δD-CH_4 dataset are plotted as a function of time (x-axis), and latitude (z-axis). The δD-CH_4 is denoted by the color and y-axis.*

2. **Max Plank Institute for Biogeochemistry:**
   - 2011 – Present, 11 measurement sites.
   - ~3100 sample, Data Extension and Integration soon.

References

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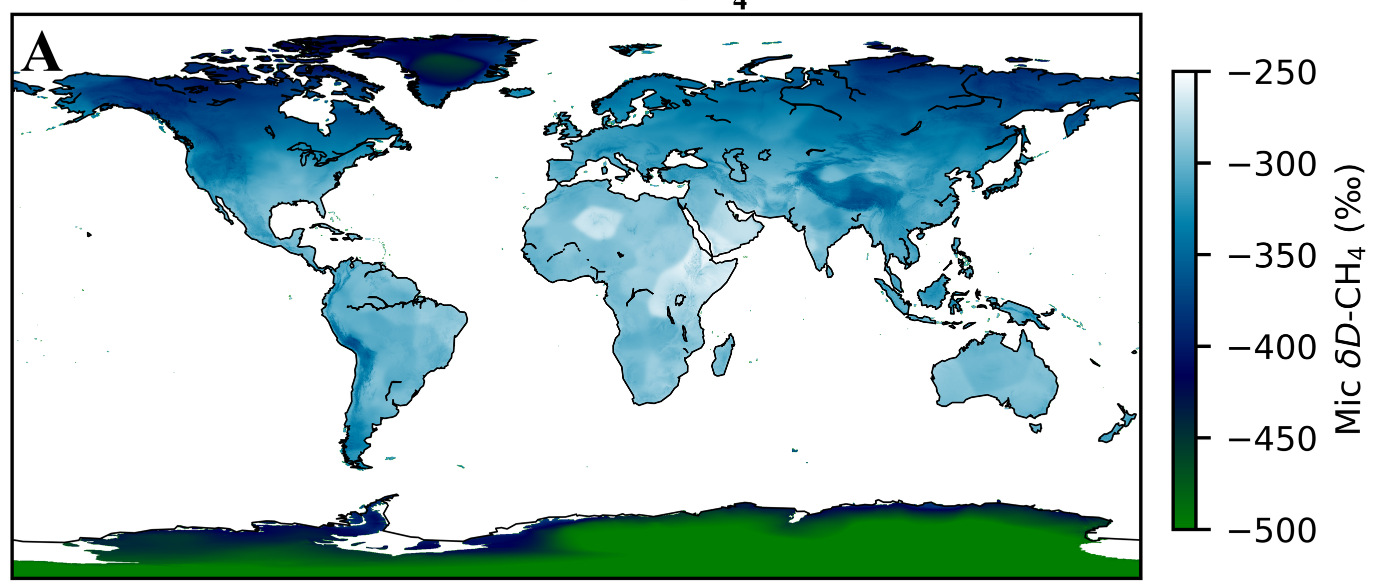
3) Box model analyses

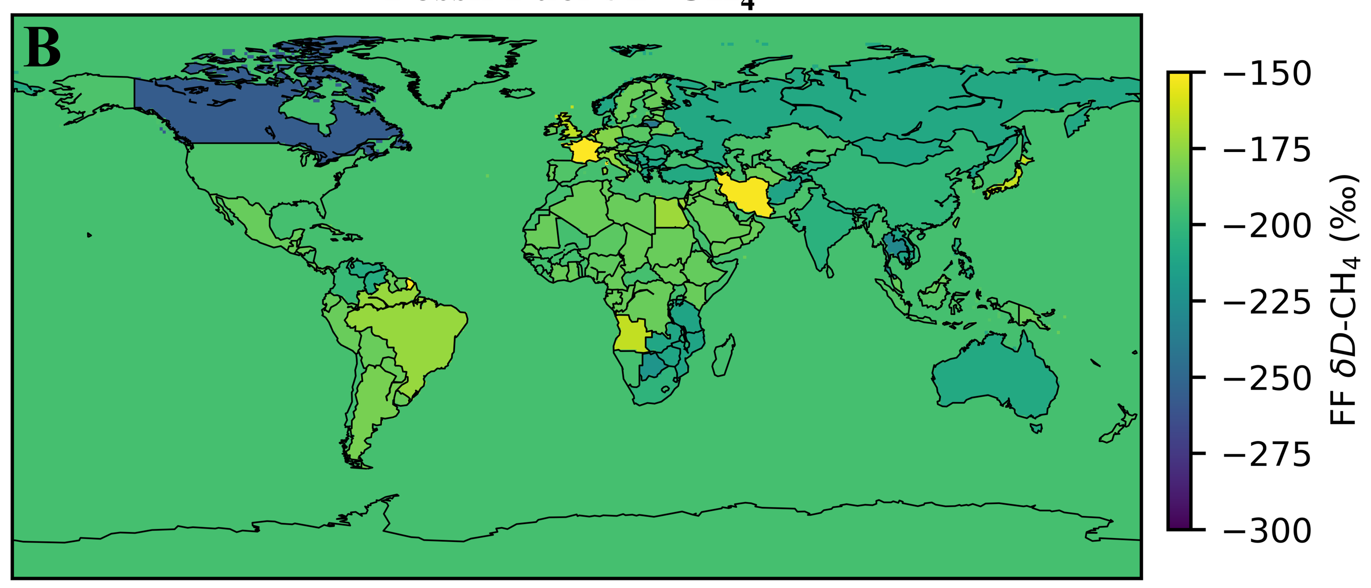
First, create 1x1° gridded source signature maps:

Microbial δD-CH_4



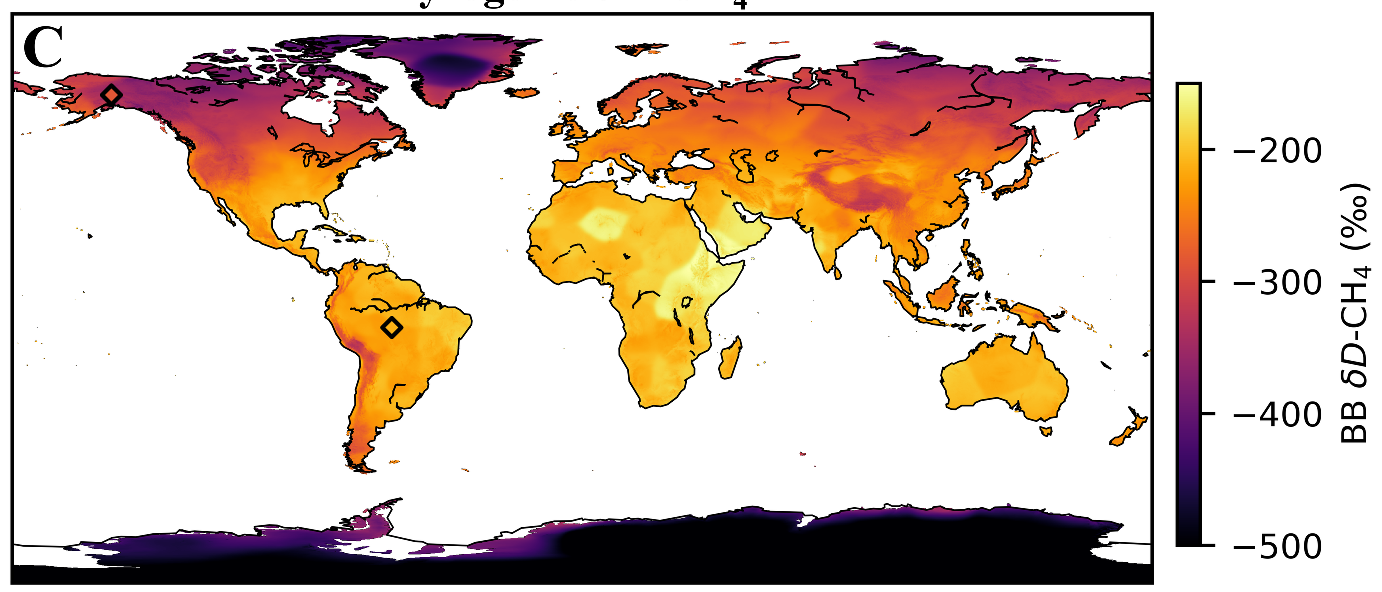
- Strong regression between microbial δD-CH_4 and δD-H_2O of local precipitation.
- Stell et al., 2021 and IsoScapes mean annual δD-H_2O of precipitation.

Fossil Fuel δD-CH_4



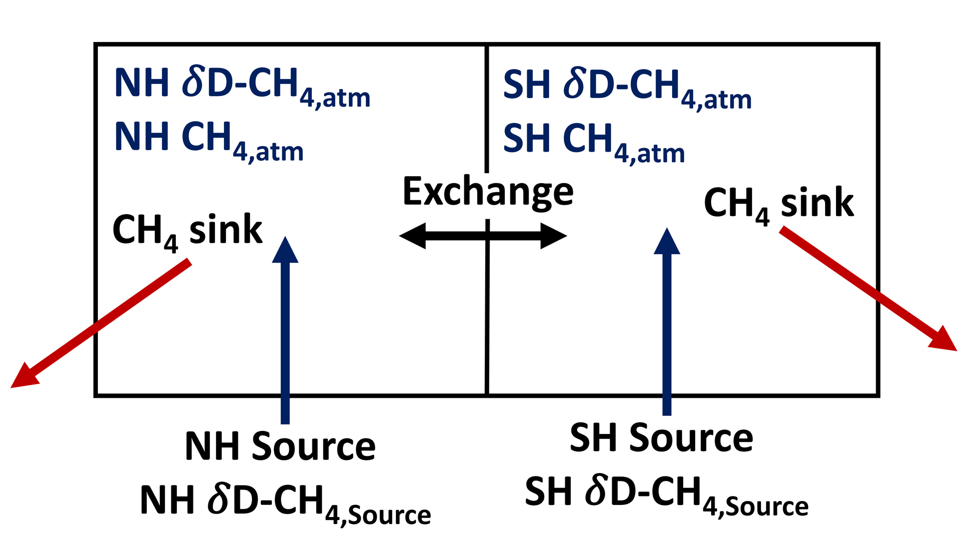
- Country-specific mean oil / natural gas and coal (ONG) δD-CH_4.
- Flux-weighted to determine average fossil fuel δD-CH_4 using EIA data.

Pyrogenic δD-CH_4



- Very limited data on pyrogenic δD-CH_4.
- Strong regression between pyrogenic δD-H_2 and local δD-H_2O (Rockmann et al., 2013).
- Regression appears to hold for δD-CH_4 (see diamonds).

Next, run two-box model with plausible emission scenarios:



- Gridded emission scenarios from CarbonTracker-CH_4 and Basu et al., 2022 (Fossil, microbial, pyrogenic).
- Calculated flux weighted hemispheric source signatures.
- Ran forward from 1997 – 2022 to calculate expected δD-CH_4.

4) Results

- Poor constraints on δD-CH_4 limit interpretation to trends over time, rather than absolute atmospheric δD-CH_4.
- Expected trends in δD-CH_4 based on Basu et al., 2022 emissions (Fig. 2A: light blue) and CarbonTracker-CH_4 emissions (Fig. 2A: green) agree with trends in the data.
- The model accurately reproduces the interhemispheric δD-CH_4 gradient and the seasonal cycle (Fig 2B).
- More data is needed to determine the true global mean annual trend from 2011 and on.

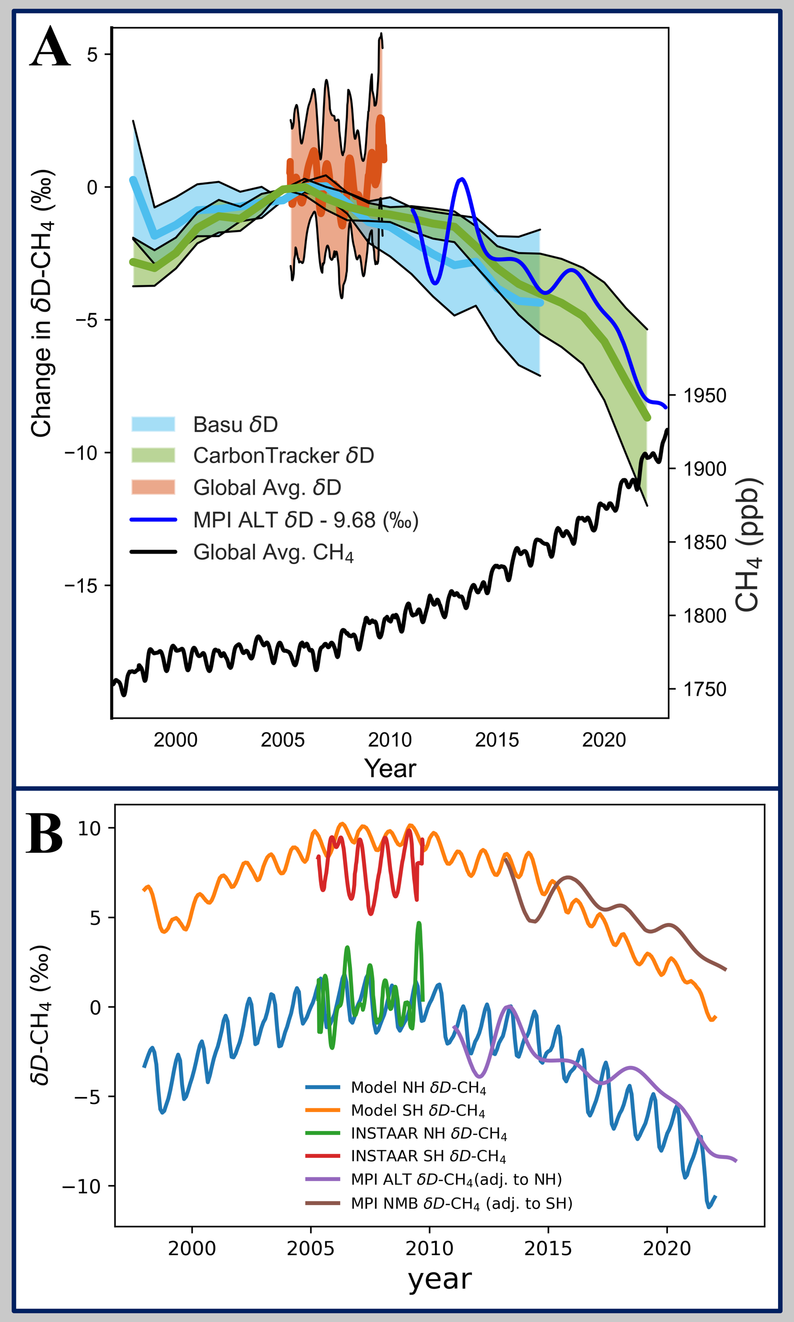


Figure 2. Results of the box model forward analysis. A) *Expected and observed trends in global mean annual* δD-CH_4. The global mean δD-CH_4 and *uncertainty from the INSTAAR dataset (Orange line and shading), the de-seasonalized MPI ALT record (Latitude = 82.45 °N), adjusted to the global mean using the average latitudinal gradient from the INSTAAR dataset (blue line). Forward box modeled global average annual mean δD-CH_4 generated using gridded emission fields from Basu et al., 2022 (blue line and shading) and the latest version of CarbonTracker CH_4 (green line and shading). Uncertainty was determined from existing uncertainties in the global mean source signature (Sherwood et al., 2017). The global mean CH_4 record is plotted in black for reference.* ***B)*** *Expected and observed trends in hemispheric mean* δD-CH_4. Forward box-modeled NH (Blue) and SH (orange) *mean* δD-CH_4 generated using the CarbonTracker CH_4 emission fields. Mean NH (green) and SH *(red)* δD-CH_4 of *the INSTAAR dataset. The de-seasonalized MPI ALT record (Latitude = 82.45 °N) and MPI NMB record (Latitude = -23.46 °S) , adjusted to the NH amd SH means, respectively, using the average latitudinal gradient from the INSTAAR dataset (purple)*

5) Key Findings

1. We present the first global dataset of δD-CH_4 and compile several datasets to create a novel time series from 2005 to 2022.
   a. Robust seasonal, latitudinal and temporal signals.
2. Box model experiments suggest that current δ^{13}C-CH_4-derived estimates of the global CH_4 budget are roughly consistent with δD-CH_4 observations.
3. Better constraints on the δD-CH_4 of emissions and fractionation during sink processes are needed to improve the use of δD-CH_4 as a tracer of the global CH_4 budget.

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