

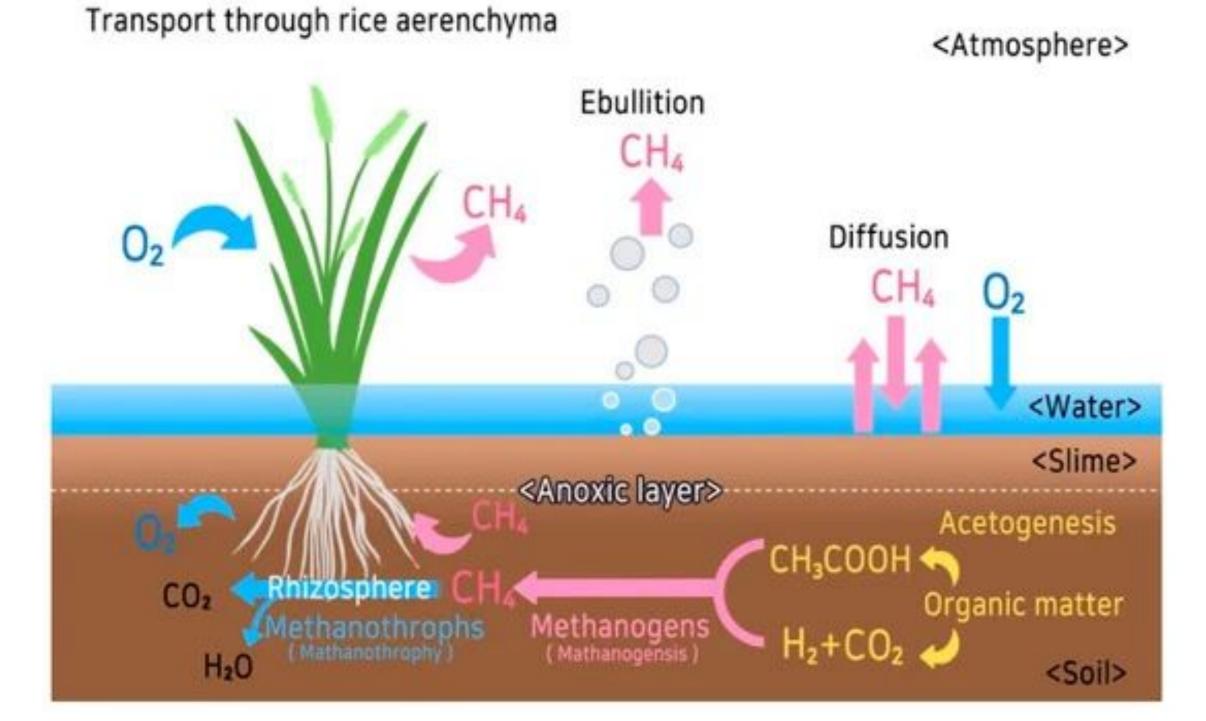
# Investigating the $\delta^{13}$ C(CH4) signature for rice stem and combined soil & water transport in a rice paddy field near Nanjing, China.

Author: Djano Persoon, University of Groningen

Supervisor: Professor Dr. Huilin Chen, Nanjing University TA: Dr. Ji Li, Nanjing University

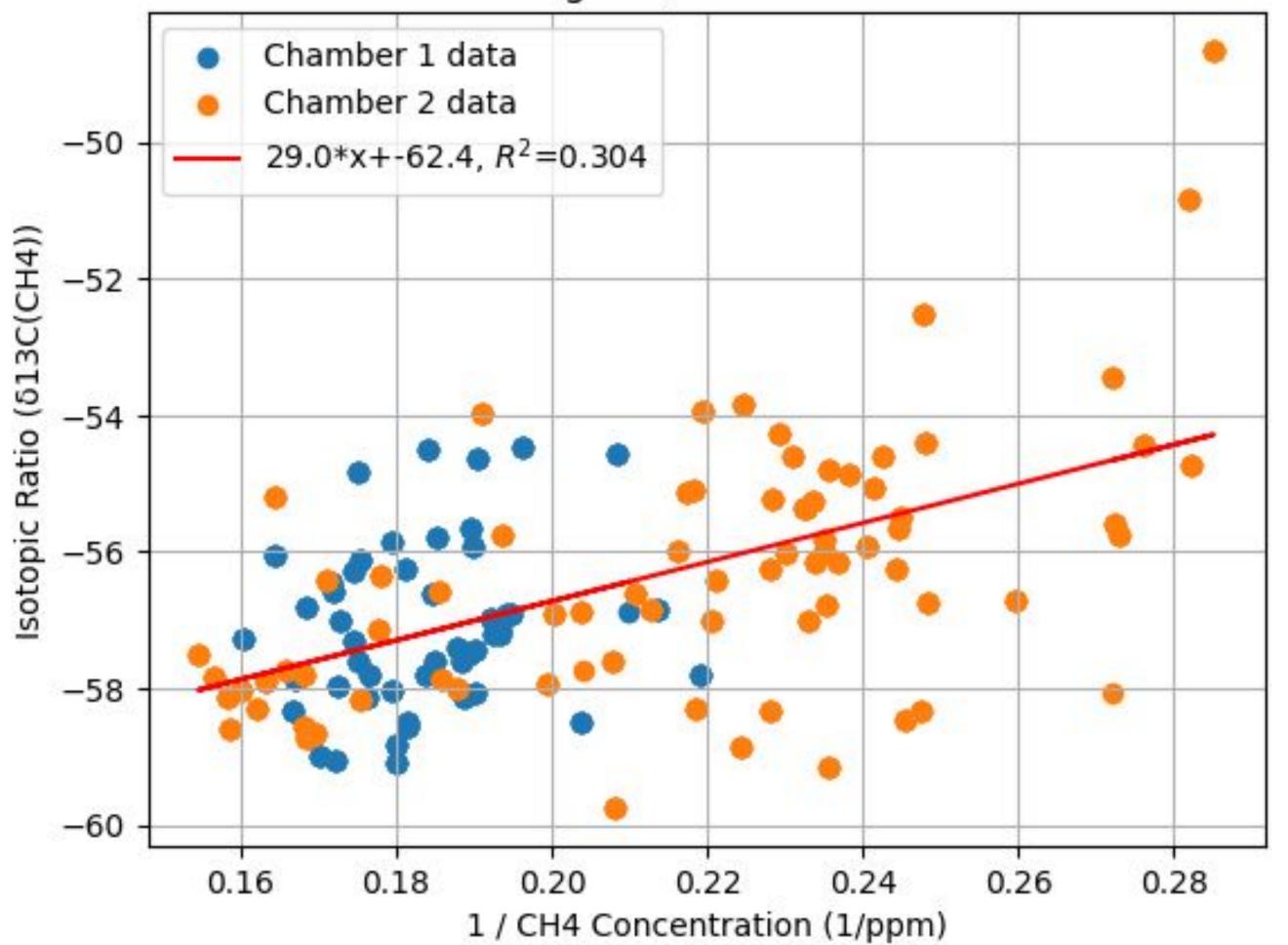
## Introduction & Background

Methane (CH<sub>4</sub>) is the second largest anthropogenic greenhouse gas, with annual emissions of 500-600 teragrams from both natural and anthropogenic sources [1]. Methane's isotopic composition varies depending on source and production process, which can be used to identify the specific process [2][3]. However, due to large temporal and spatial variability of isotopic signatures, there is still a large uncertainty when determining the global methane budget. Further research is needed to improve the understanding of methane sources and reduce the uncertainty of the global greenhouse gas budget [4].



#### **Results & Interpretation**

After data collection, Keeling plots were made in order to determine the  $\delta^{13}C(CH_{A})$ signature of the soil & water transport and the rice stem transport in the rice paddy field. When applying a linear fit to the data points, the source signature can be determined from the y-intercept.



#### Keeling Plot, Soil and water

Fig 1: Methane production and transport in a rice paddy schematically presented. Figure from Jang, et al. [5]

Approximately 80% of atmospheric methane is microbially produced in anoxic environments by methanogens, whose activity is influenced by temperature, pH, and sulfate and iron concentrations [1]. Isotopic fractionation occurs due to C-12 being biochemically more favourable than C-13. Resulting in the depletion of C-13 during methanogenesis and the enriching of C-13 during methane oxidation. [1] [3]

Water flooded rice paddies are the largest biogenic anthropogenic source of CH<sub>4</sub> with an estimated yearly emission of about 88 teragrams [1]. This investigation aims to evaluate the isotopic signature of different transport processes occurring in a rice paddy field near Nanjing, China. The research question therefore is;

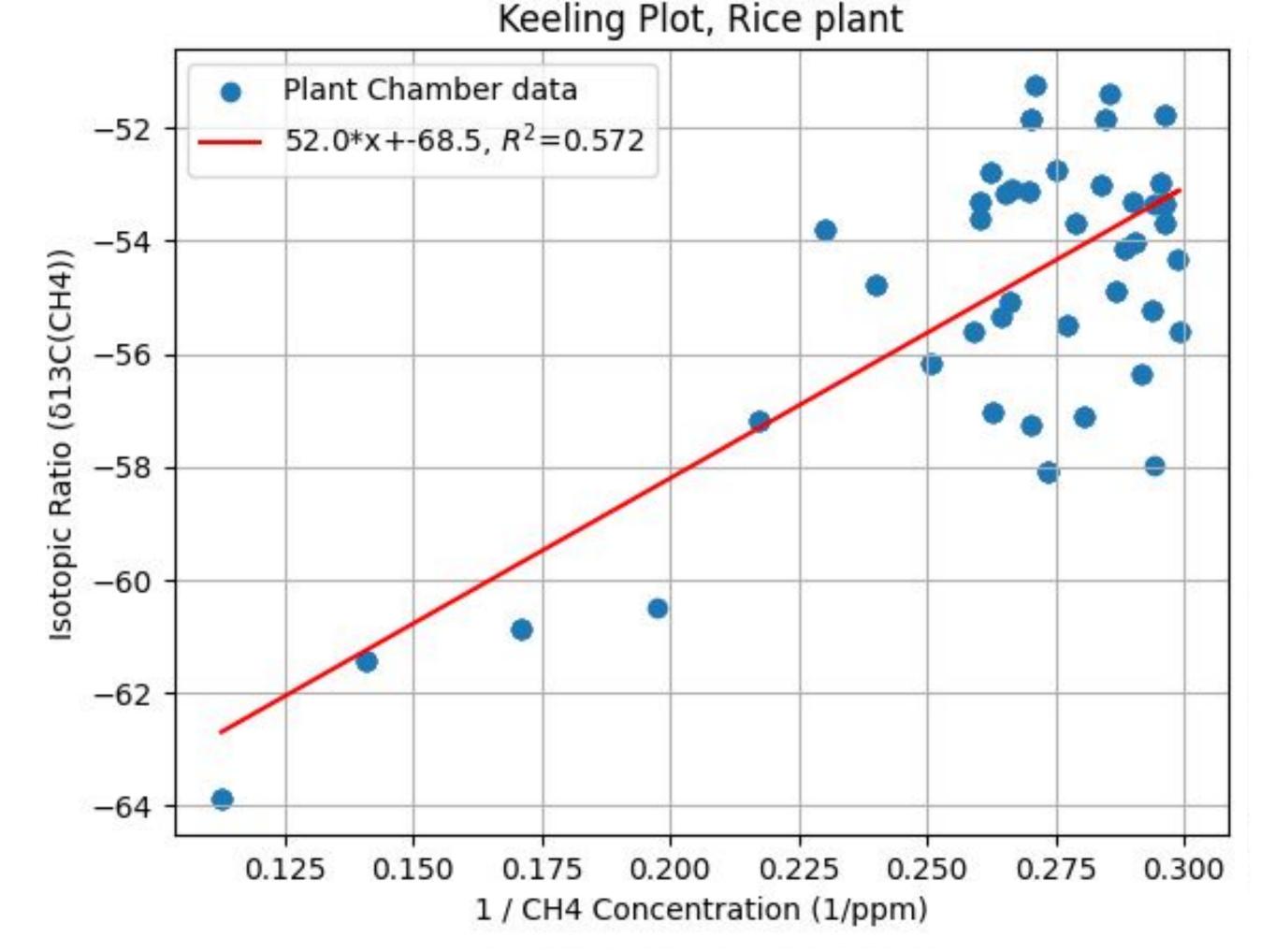
"What is the  $\delta^{13}C(CH_{A})$  signature of the transport processes in a rice paddy field near Nanjing, China?"

In order to answer this, the following research objectives had been established;

• Measure the  $\delta^{13}C(CH_{4})$  signature of methane transported through; • rice plant stems

Fig 5: Keeling plot of data corresponding to the gas transport through the soil and water. The isotopic ratio of C-13 to C-12 in methane ( $\delta^{13}C(CH_{A})$ ) has been plotted against the inverse of the total methane concentration in ppm<sup>-1</sup>.

It can be observed from Fig 5 above that the isotopic  $\delta^{13}C(CH_{A})$  signature of methane transported through soil and water in the rice paddy field is -62.4. The methane is thus C-13 depleted.



diffusion and bubbles

#### Experimental setup & Methods

The isotopic measurements were performed at the Jurong Ecological Experimental Station, Houbai State Farm, China.

Important parameters of the time and place of measurement;

- Latitude: 31°48'24.59"N
- Average soil temperature: 301.97 ± 0.03 Kelvin.
- Plant growth stage: Rice jointing stage.



Fig 2: Picture of a closed chamber device. Picture taken at the measurement site.



Fig 3: Picture of an open chamber device with a rice plant inside. Picture taken at the measurement site.

Transient chambers were used to collect gas subsamples from a closed-off captivity. Two chambers were put in a place without plants to measure methane transport through the soil and the water. Then one of the chambers was put over a rice plant with a plastic cover over the surface in order to measure the gas transport purely through the rice stem. Water vapour was removed from both the gas samples, effectively reducing the water vapour concentration to a value between 0 and 1.5%, through the use of a nation dryer before the samples entered the gas analyser.

Fig 6: Keeling plot of data corresponding to the gas transport through the rice plant stem. The isotopic ratio of C-13 to C-12 in methane ( $\delta^{13}C(CH_{A})$ ) has been plotted against the inverse of the total methane concentration in ppm<sup>-1</sup>.

It can be observed from Fig 6 above that the isotopic  $\delta^{13}C(CH_{A})$  signature of methane transported through rice plant stems in the rice paddy field is -68.5. This is more negative than the isotopic signature of transport through soil and water. Thus it seems less methane-oxidation occurs when the methane is transported through the plant than when it is transported through the soil and water, resulting in the methane being more depleted in  ${}^{13}CH_{4}$ .

#### Limitations & Future research

A few limitations should also be considered, such as;

- No acidity measurements have been performed so the pH of the soil and water were unknown.
- For each measurement method, only one day of measurements was obtained. Therefor little insights have been obtained in the temporal nature of the  $\delta^{13}C(CH_{A})$ signature.
- No insights were obtained for the differences in transport processes between soil and water.

Gas analyser used, the Picarro G2201-i [6].

- Working principle;
  - Determines isotopes from near-infrared Ο absorption spectrum.
  - Determines isotope concentration from Ο ringdown time and absorption peak height.
- Outputs;
  - $^{12}CH_{A}$  concentration. Ο
  - $^{13}CH_{4}$ , concentration. Ο
  - Water vapour concentration. Ο
  - $\delta^{13}C(CH_{4})$  signature Ο



Fig 4: Picture of the Picarro G2201-i device (box under the desktop). Picture taken at the measurement site.

Afterwards additional data correction had to be applied;

- Instrumental drift correction, using a standard gas with a know isotopic ratio.
- Water vapour correction, because of dilution of the sample.

[1] E. F. DeLong, *Prokaryotes: Prokaryotic Physiology and Biochemistry*, 4th ed. Berlin: Springer, 2012. [Online]. Available: http://public.ebookcentral.proquest.com/choice/publicfullrecord.aspx?p=3095793. [Accessed: Jul. 17, 2024].

[2] J.R. Gat, W.G. Mook, and H.A.J. Meijer, "Environmental isotopes in the hydrological cycle - principles and applications. International Hydrological Programme (IHP-V)," *Technical Documents in Hydrology*, Jan. 2000.

[3] T. Foken, Ed., Springer Handbook of Atmospheric Measurements. Cham, Switzerland: Springer Nature Switzerland AG, 2021. doi: 10.1007/978-3-030-52171-4.

[4] A. Hoheisel, C. Yeman, F. Dinger, H. Eckhardt, and M. Schmidt, "An improved method for mobile characterisation of δ 13 CH 4 source signatures and its application in Germany," Atmospheric Measurement Techniques, vol. 12, no. 2, pp. 1123-1139, Feb. 2019, doi: 10.5194/amt-12-1123-2019.

[5] E.-K. Jang, E. M. Lim, J. Kim, M.-J. Kang, G. Choi, and J. Moon, "Risk Management of Methane Reduction Clean Development" Mechanism Projects in Rice Paddy Fields," Agronomy, vol. 13, no. 6, Art. no. 1639, 2023, doi: 10.3390/agronomy13061639. [6] Picarro Inc, "G2201-i Analyzer for Isotopic CO2 / CH4 User Manual," 2020. [Online]. Available: www.picarro.com. [Accessed: Jul. 20, 2024].

For future research;

- Acidity measurements could be taken from soil and water samples, such that they can be compared with similar research at a different location but same latitude.
- Measurements could be taken for extended periods of time, while documenting weather, seasonal and plant growth stage conditions.

### Conclusions

In conclusion, for a rice paddy field located at a latitude of 31°48'24.59"N, with a soil temperature of approximately 302 Kelvin and the rice plants being in the rice jointing growth stage;

- The methane emitted by the rice paddy is depleted in  $^{13}CH_{1}$ , resulting in a negative  $\delta^{13}C(CH_{\lambda})$  signature between -62.4 and -68.5.
- Less methane-oxidation occurs when the method of methane transport is plant mediated compared to when the methane is being transported through the soil & water.

#### Acknowledgements:

I want to thank Professor Dr. Huilin Chen (NJU) for his advices, support and faith in my capabilities as a learning researcher during the period of research, but also during the process before I was admitted by Nanjing University for the GripS program.

I want to thank Dr. Ji Li (NJU) for her guidance during the research period. Whenever I had questions regarding the topic she was quickly available to answer them. She also helped out with the data correction and analysis, for I was unfamiliar with the field of research before I came to Nanjing University. Pictures of Picarro device and the chamber with the rice plant were also provided by Dr. Ji Li. Moreover she brought me along to the Jurong Ecological Experimental Station, allowing me to have glimpse of what it is like to perform isotopic data collection in the field.

I also want to thank MiaoMiao Du (NJU). Together with Dr. Ji Li she prepared and setup the experimental equipment at the Jurong Ecological Experimental Station. Together they obtained and processed the isotopic data, after which I received it for data analysis.