

Constraining methane formation/removal pathways with stable isotopes in different aquatic environments throughout the summer season in the Kolyma Region, North-East Siberia

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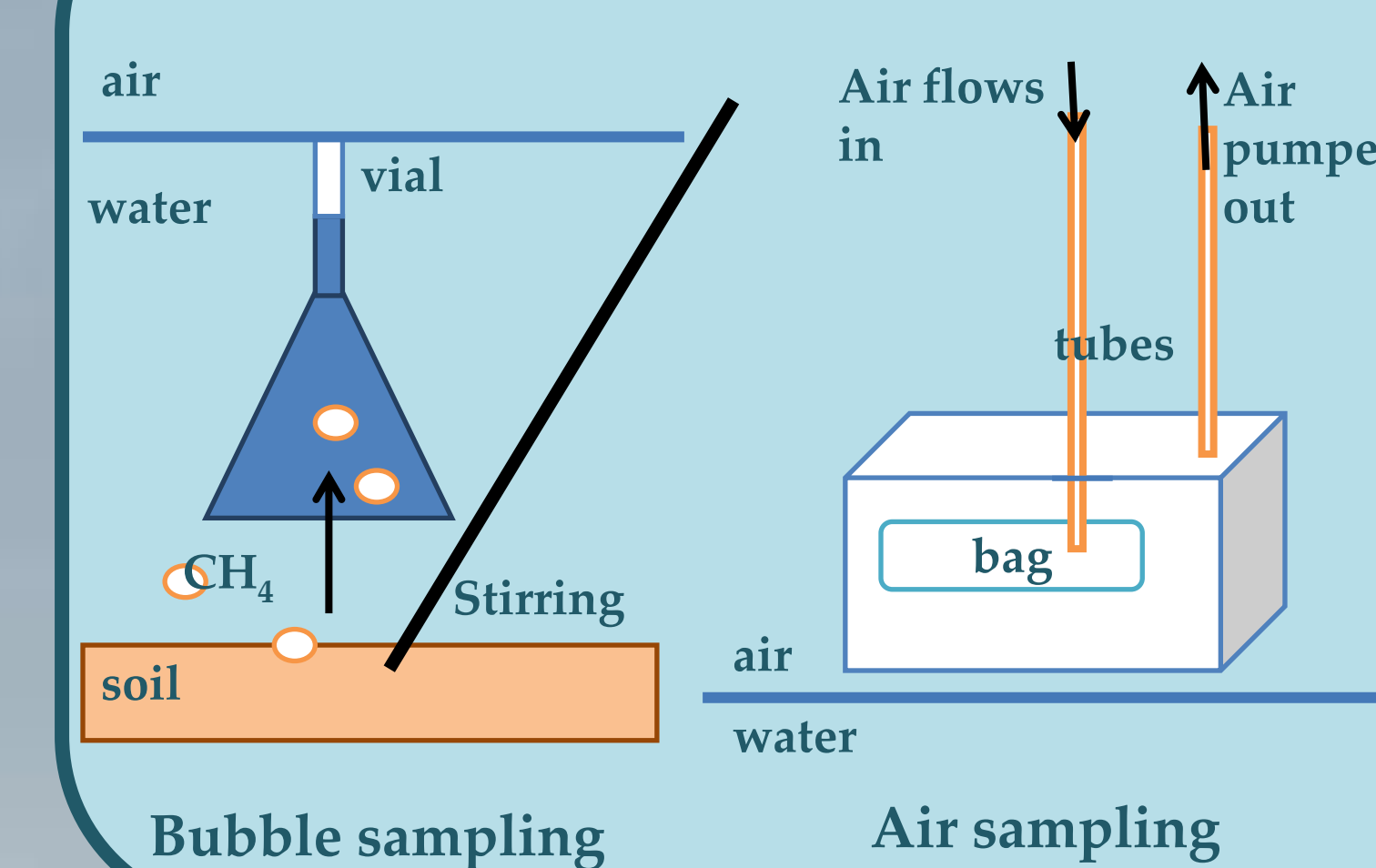
Relevance

The methane flux from arctic wetlands to the atmosphere will likely increase in the future in response to climate change. Analyzing the hydrogen isotope composition of methane ($\delta D(CH_4)$) allows a better understanding of its formation and removal in different types of environment. Moreover, the seasonal changes and type of underlying permafrost also affect the $\delta D(CH_4)$. The $\delta D(CH_4)$ in different type of environments can be used to better constrain atmospheric models.

Research questions

- Is there a difference in $\delta D(CH_4)$ between samples taken at Yedoma (Pleistocene-aged) permafrost and floodplain (Holocene-aged) locations, and between different aquatic environments during the summer season?
- What is the source signature of methane reaching the atmosphere in the Kolyma region?

Sampling and method

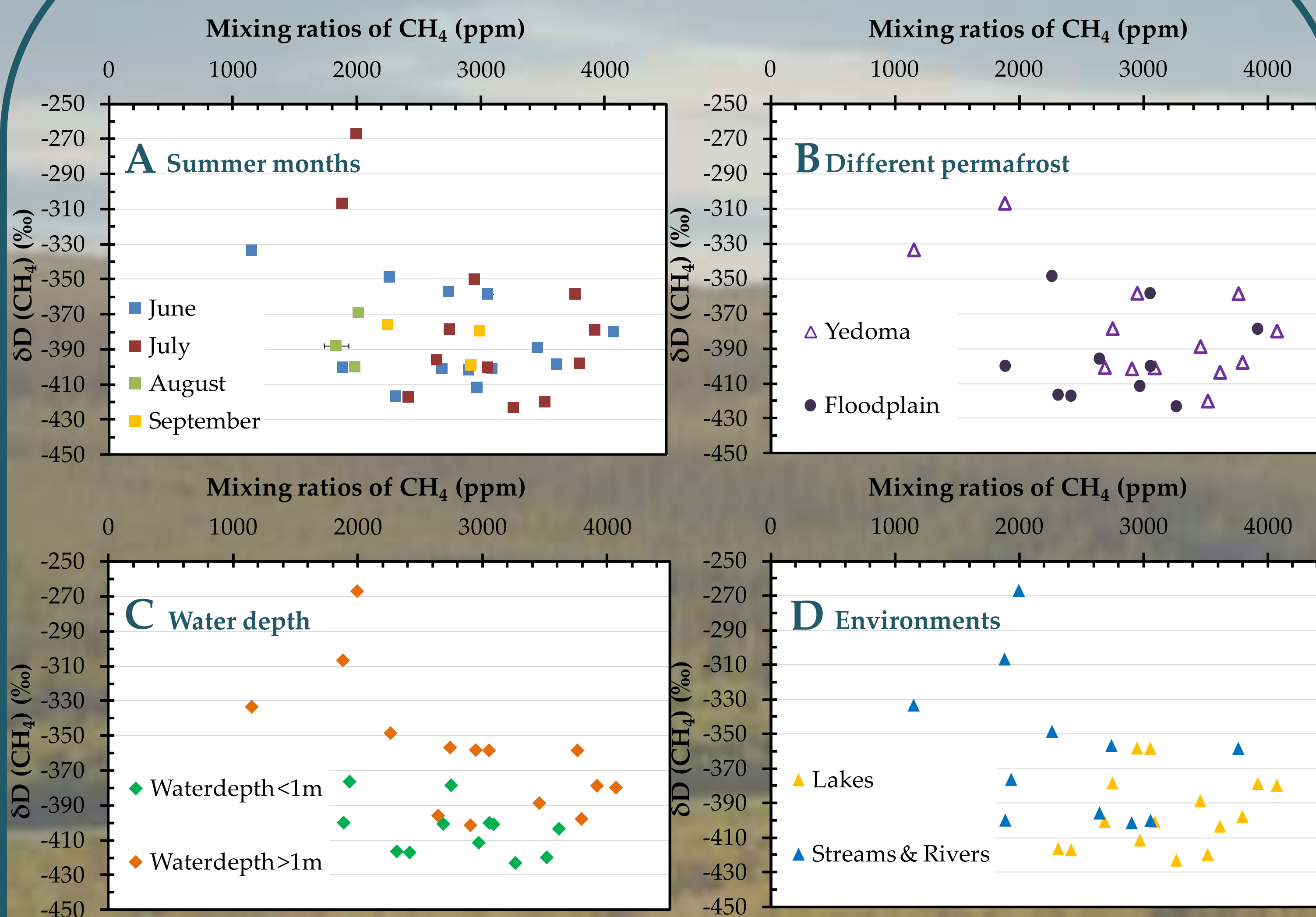


Bubble sampling: Below the water column, the surface of the sediment was stirred until bubbles were released. Bubbles were caught by a funnel.

Air sampling: Samples were taken at the same location as the bubbles. A Tedlar airbag was placed in a box (evacuated afterwards). Via a tube the bag was connected to the outer air. Due to the low pressure in the box caused by evacuation, atmospheric air flew into the airbag.

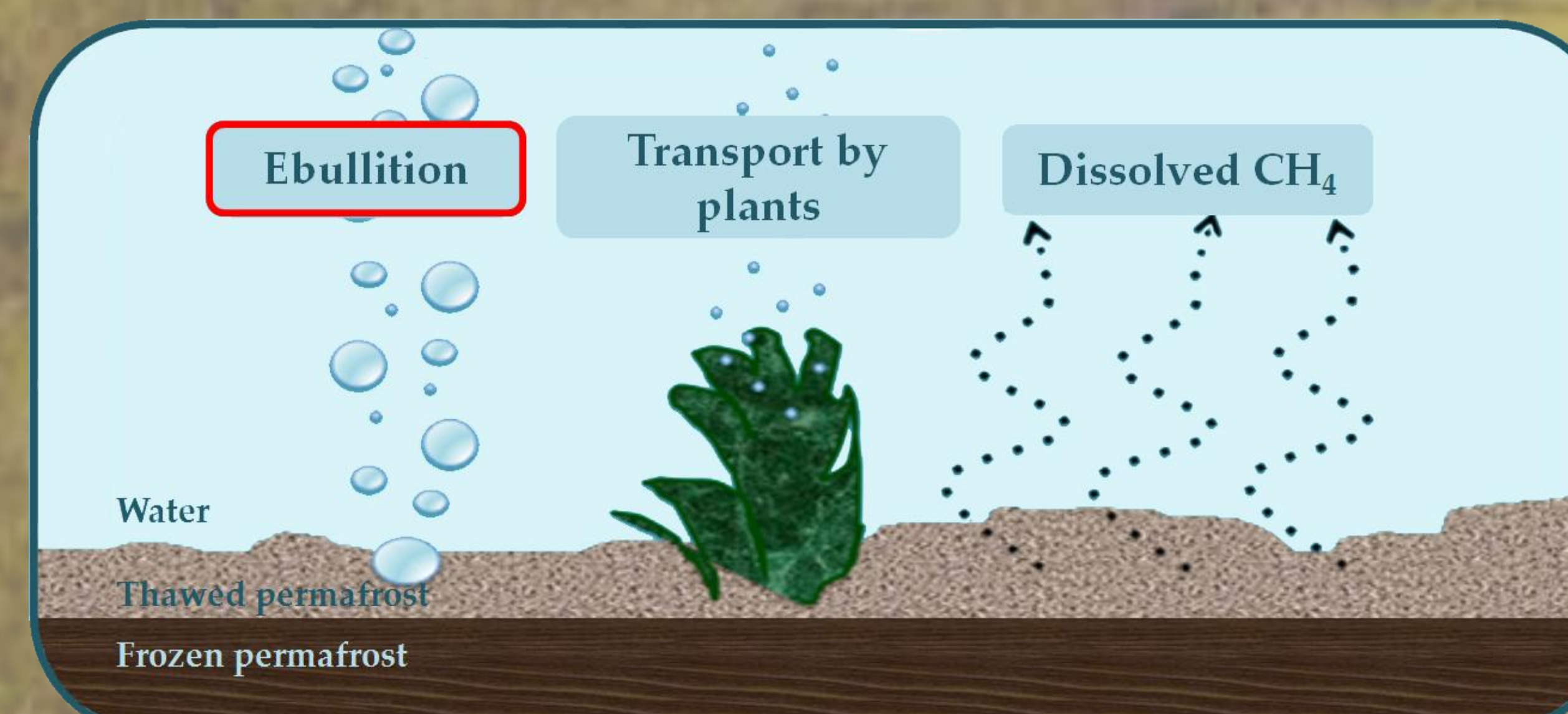
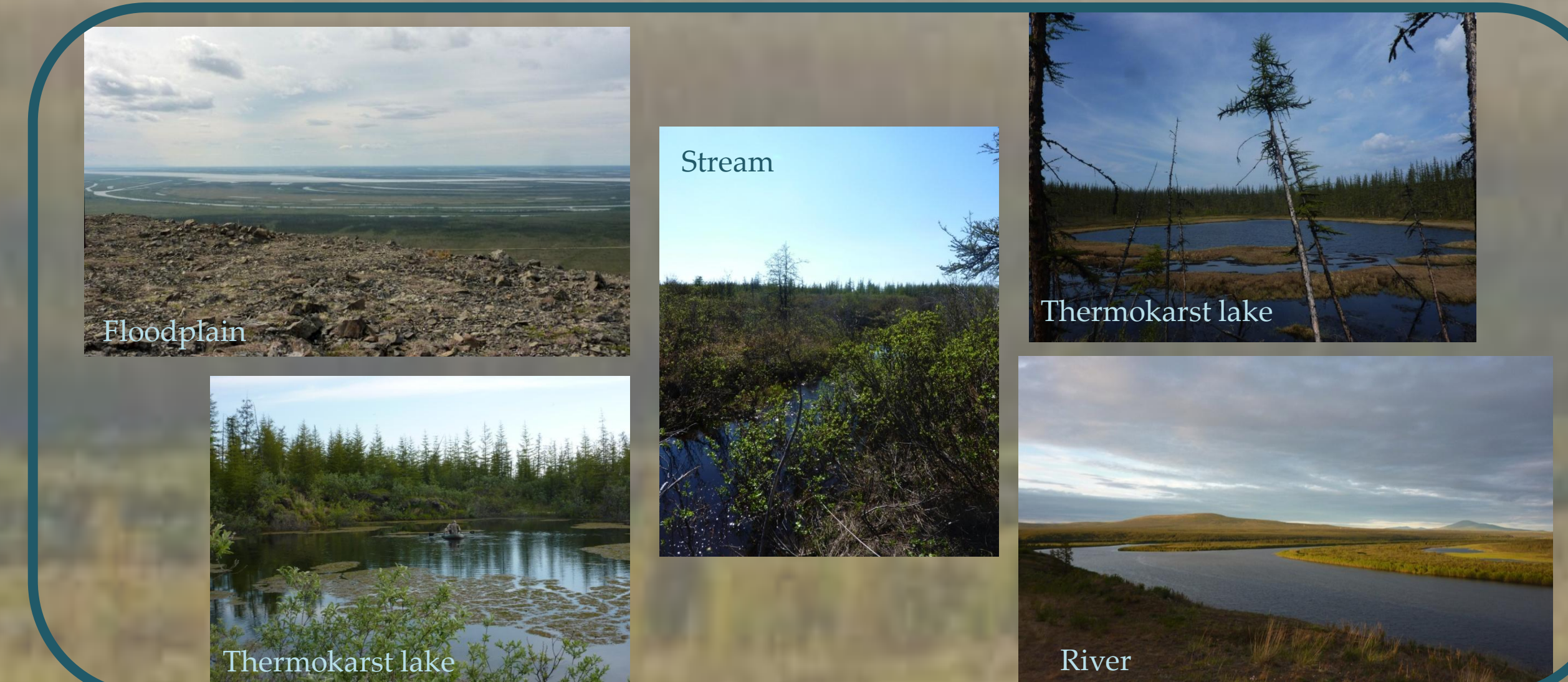
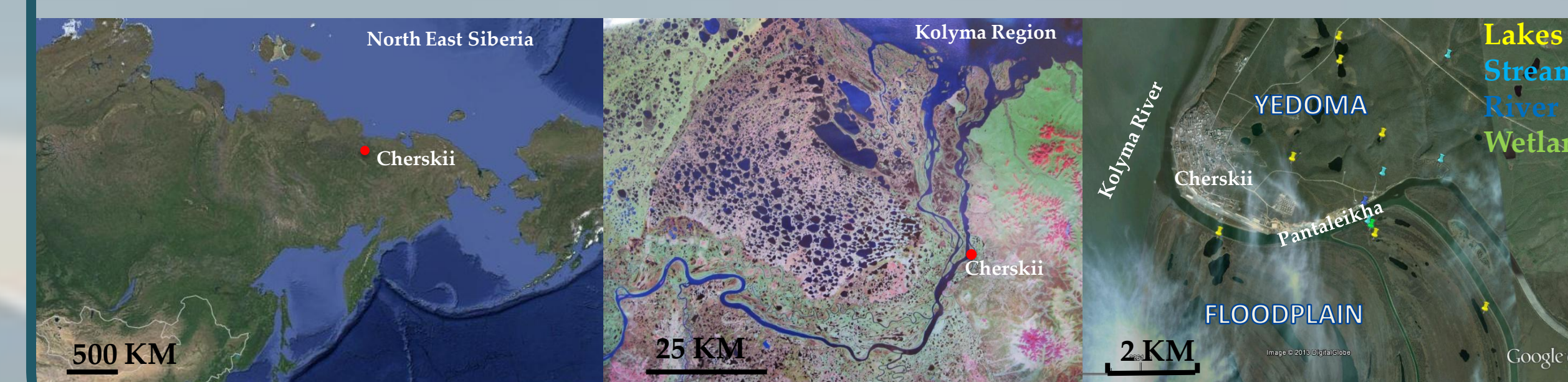
Measurements: All samples were measured for $\delta D(CH_4)$ by a Continuous Flow - Isotopic Ratio Mass Spectrometer.

Ebullition samples

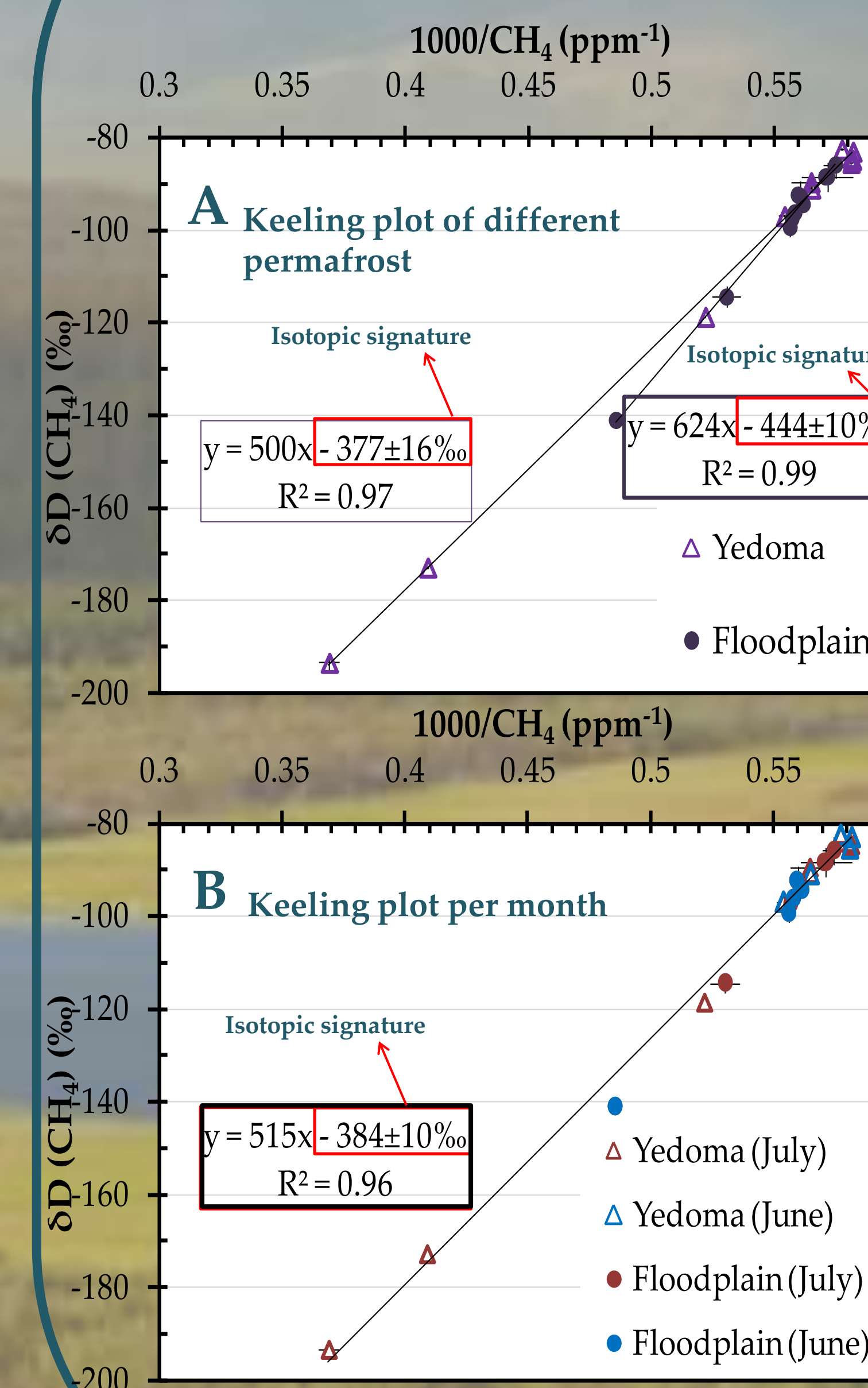


- The monthly averages (\pm stdev) for $\delta D(CH_4)$ for June, July, August, September 2013 are: $-384 \pm 26\text{‰}$, $-375 \pm 46\text{‰}$, $-385 \pm 22\text{‰}$ and $-385 \pm 13\text{‰}$, respectively, typical for acetoclastic methane. Mixing ratios are $2084 \pm 737\text{ppm}$, $2857 \pm 725\text{ppm}$, $1944 \pm 97\text{ppm}$ and $2721 \pm 410\text{ppm}$, respectively, showing that the amount of methane in ebullition is widespread.
- The Pleistocene-age Yedoma permafrost shows no clear difference in $\delta D(CH_4)$. For Yedoma: avg $\delta D(CH_4) -378 \pm 32\text{‰}$ and Holocene-age floodplain samples avg. $-395 \pm 25\text{‰}$. in the same range as Walter et al. (2007).
- Samples taken at locations with a total water column depth $<1\text{m}$ are more depleted in D (avg. $\delta D(CH_4) -402 \pm 14\text{‰}$) than samples taken where water depth is deeper than $>1\text{m}$ (avg. $\delta D(CH_4) -359 \pm 38\text{‰}$). Due to short travel time of the bubbles, oxidation differences in the water column are unlikely, we instead reason that at deeper sites (1) there is additional CO_2 reduction and/or (2) (anaerobic) oxidation in the sediment.
- Streams and rivers show higher methane mixing ratios (avg. $2289 \pm 661\text{ppm}$) and are slightly more enriched in D (avg. $\delta D(CH_4) -364 \pm 40\text{‰}$) than lake samples (avg. $3120 \pm 551\text{ppm}$ and avg. $\delta D(CH_4) -394 \pm 21\text{‰}$). Streams and rivers are generally more oxygenated, therefore higher oxidation levels are likely responsible for the enrichment of D and lower mixing ratios compared to lakes.

Location 68°N, 161°E



Atmospheric samples



The Keeling plot approach allows us to calculate the source signature of CH_4 added into a background reservoir. The intersection of the linear fit with the y-axis represents the isotopic signature of the added source.

A. The $\delta D(CH_4)$ signature of the Yedoma ($-377 \pm 16\text{‰}$) is more enriched than the samples from the floodplain ($-444 \pm 10\text{‰}$) and is in the range measured by Walter et al. (2007). Potential reasons for this enrichment could be (1) the influence of biomass/waste burning as on average the Yedoma sites are closer to town, or (2) a contribution of CO_2 reduction in the Yedoma. We will investigate this further with $\delta^{13}C(CH_4)$ analysis.

A. The difference in mixing ratio is likely due to the sampling technique in which the height of sampling varies, thus no clear seasonal variations are observed. The average methane source signature for the Kolyma region is $-384 \pm 10\text{‰}$. For the isotopes, the different months do not show significant source differences: June $\delta D(CH_4)$ is $-386 \pm 5\text{‰}$ and July $-394 \pm 5\text{‰}$.

Conclusion

- Acetate fermentation is the main formation pathway of CH_4 in the Kolyma region. Yedoma (Pleistocene-aged) permafrost is slightly more enriched in D (ebullition: $-378 \pm 32\text{‰}$, air: $-377 \pm 16\text{‰}$) compared to Holocene-aged floodplain samples (ebullition: $-395 \pm 25\text{‰}$, air: $-444 \pm 10\text{‰}$). The Yedoma results are in the same range of values as similar studies. Rivers and Streams and lakes with deeper water depth show more oxidized CH_4 , decreasing the flux of CH_4 from wetland to atmosphere. During the summer season there are no significant changes in $\delta D(CH_4)$.
- The source signature for deuterium of methane in the Kolyma region is $-384 \pm 10\text{‰}$ as calculated in the Keeling plot.