

Supporting information

1 Measurement of water physiochemical properties

Water pH, temperature, conductivity, and DO were measured *in-situ* at the time of manual water sample collection. Water pH was measured using an ISFET pH Tester (n = 99, accuracy: ± 0.1 pH) and a PD 450 Handheld Meter (n = 35, accuracy: ± 0.01 pH), respectively. Water temperature and specific conductivity were measured using an EcoSense® EC300 Instrument accurate to ± 0.2 °C and $\pm 1\%$ respectively. The DO concentration, [DO], was measured using a YSI Pro20 DO meter accurate to $\pm 2\%$. To measure alkalinity, water samples were filtered by GF/F filter paper (Whatman, glass microfiber, $0.7 \mu\text{m}$) in a vacuumed system to remove particulate material. Then alkalinity was measured by acidifying samples with $0.01 \text{ M H}_2\text{SO}_4$ to pH 3.9 using a Mettler Toledo G20 Compact Titrator.

2 Testing Equilibration Duration

After a 50 mL headspace was created, the samples for dissolved CH_4 and CO_2^* were equilibrated for 24 hours in the cold room (6 °C) with light excluded. Time series incubation experiments were conducted to test time required for stable equilibration and if 24-hour incubation would result in significant changes to the carbon pools. Results showed that headspace [CO_2^*] and $\delta^{13}\text{C-CO}_2$ were stable after 2-hours and showed no change over the subsequent 22-hour incubation period. Headspace [CH_4] and $\delta^{13}\text{C-CH}_4$ equilibrated slightly slower (6-hours) and also showed no significant change after this time. These tests indicate that CH_4 was not significantly influenced by oxidation after initial equilibration and CO_2 was not influenced by the related biochemical process,

e.g., respiration. Taking into consideration of the error produced by standard sample analytical procedures, there is no evidence incubation duration had an effect on our data.

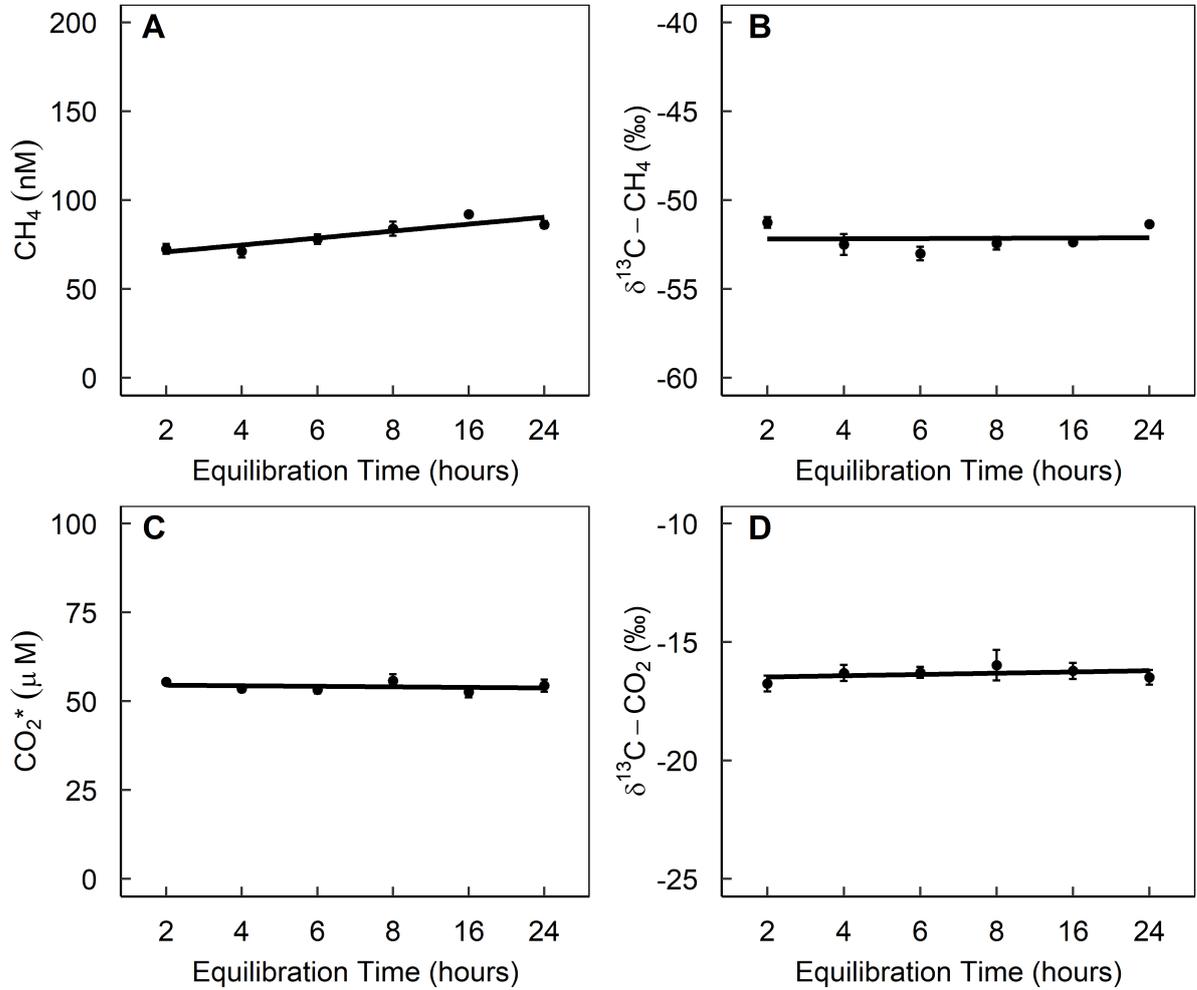


Figure S1. Standard results showing the variation of [CH₄], δ¹³C-CH₄, [CO₂*], and δ¹³C-CO₂ with equilibration time.

3 Flux calculation

The gas transfer velocity of CH₄ (k_{CH_4}) is related to k_{CO_2} by

$$k_{CH_4}/k_{CO_2} = \left(\frac{Sc_{CH_4}}{Sc_{CO_2}} \right)^{-n} \quad (S1)$$

where n is the Schmidt number exponent which varies from 0.5 to 1 based on the process of gas transfer and 0.67 is commonly used for moderately turbulent

conditions (Striegl, Dornblaser, McDonald, Rover, & Stets, 2012). k_{CO_2} is the gas transfer velocity of CO_2 and can be calculated by

$$F_{CO_2} = k_{CO_2} \cdot ([CO_2]_{water} - [CO_2]_{air}) \quad (S2)$$

Sc is the Schmidt numbers of CH_4 and CO_2 adjusted by in situ water temperature ($^{\circ}C$) (Wang et al., 2017).

$$Sc_{CH_4} = 1897.8 - 114.28 \cdot T + 3.2902 \cdot T^2 - 0.039061 \cdot T^3 \quad (S3)$$

$$Sc_{CO_2} = 1911.1 - 118.11 \cdot T + 3.4527 \cdot T^2 - 0.04132 \cdot T^3 \quad (S4)$$

4 Temporal variation of water physiochemical properties and CO₂ efflux

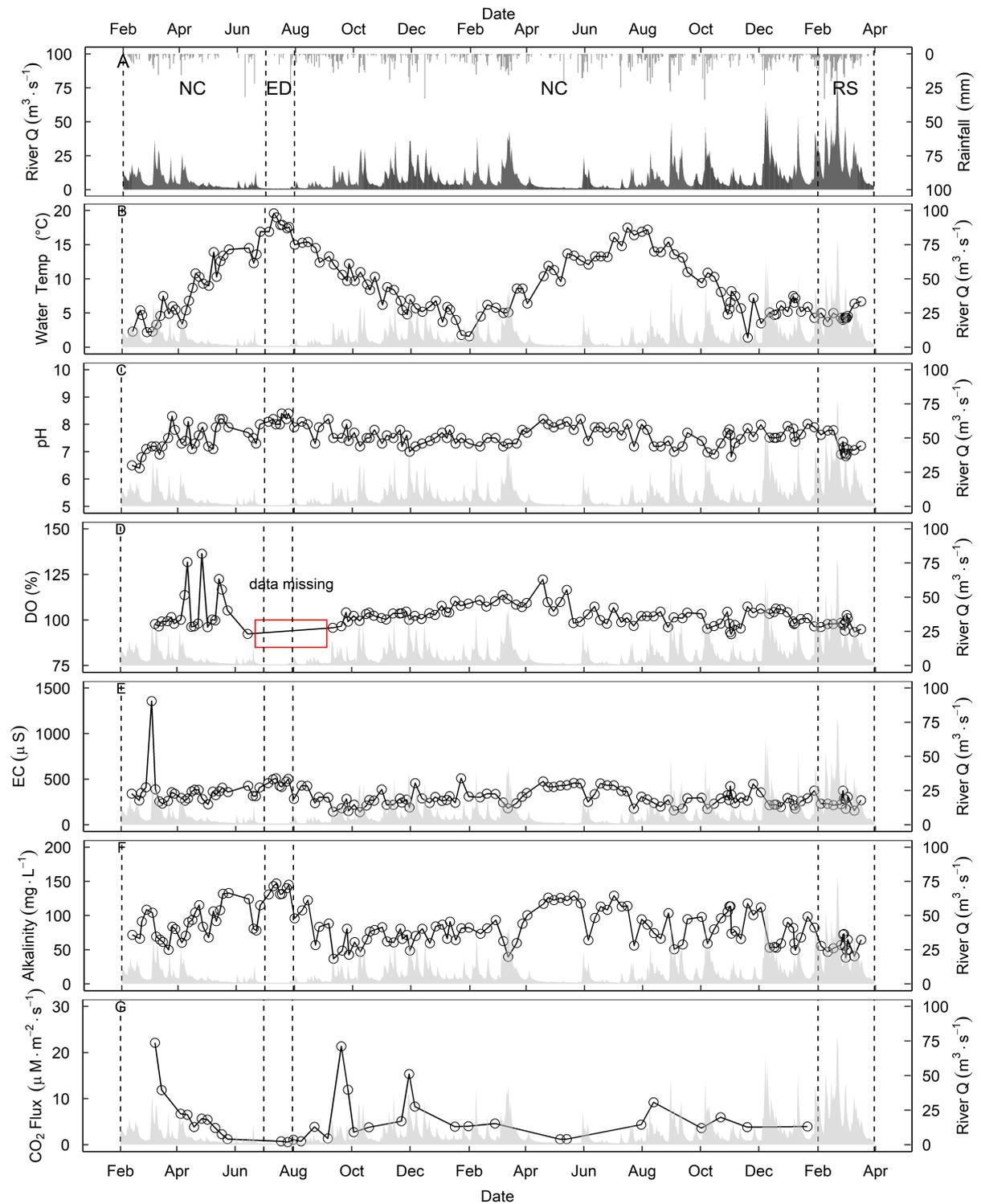


Figure S2. Temporal variation of water properties and in-situ CO₂ flux during the 2-year sampling period

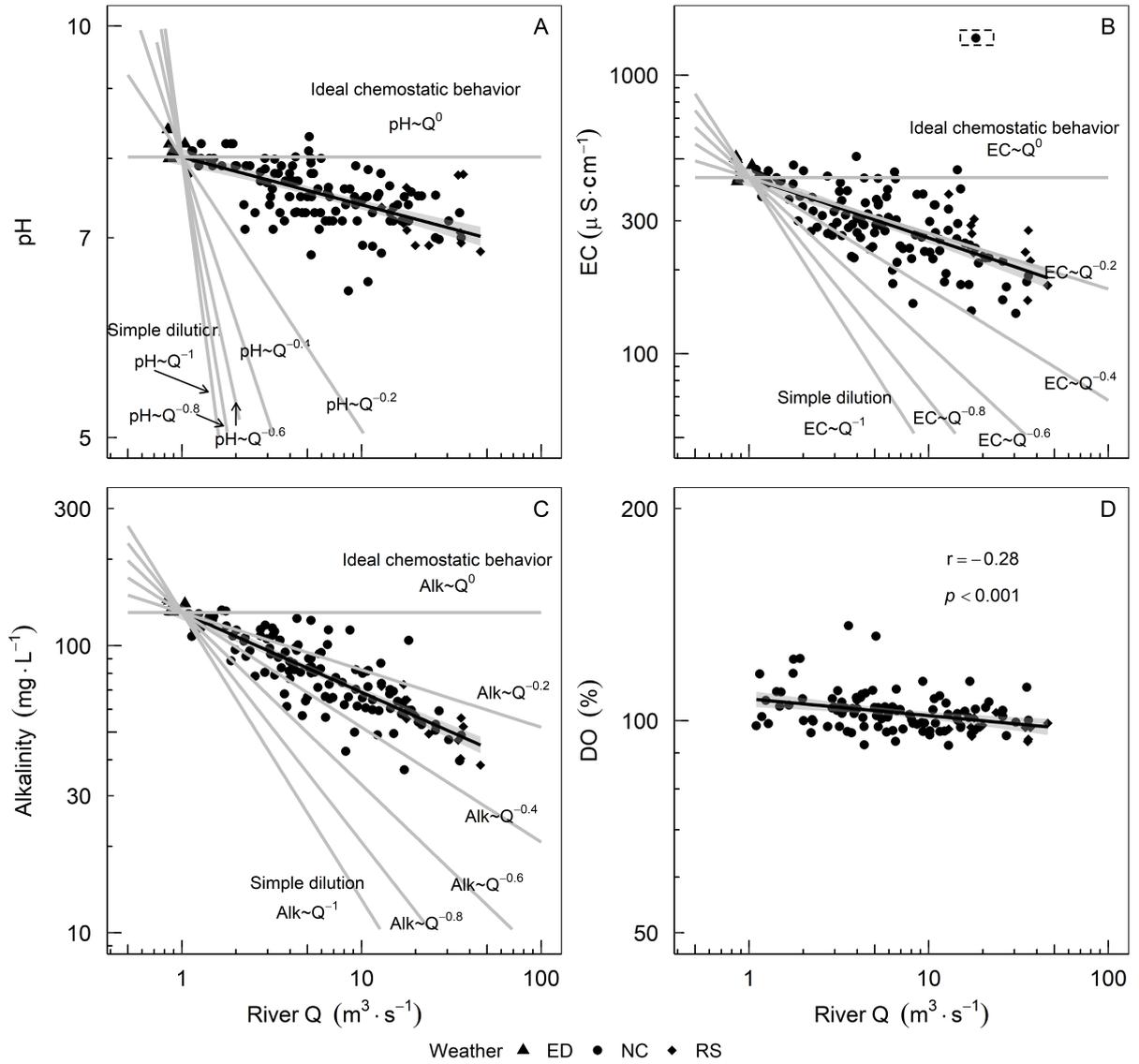


Figure S3. Correlations between water properties (pH, specific EC, alkalinity, and DO) with the river discharge. One outlier of EC resulted from the used of deicers is labelled by the dashed rectangle in B.

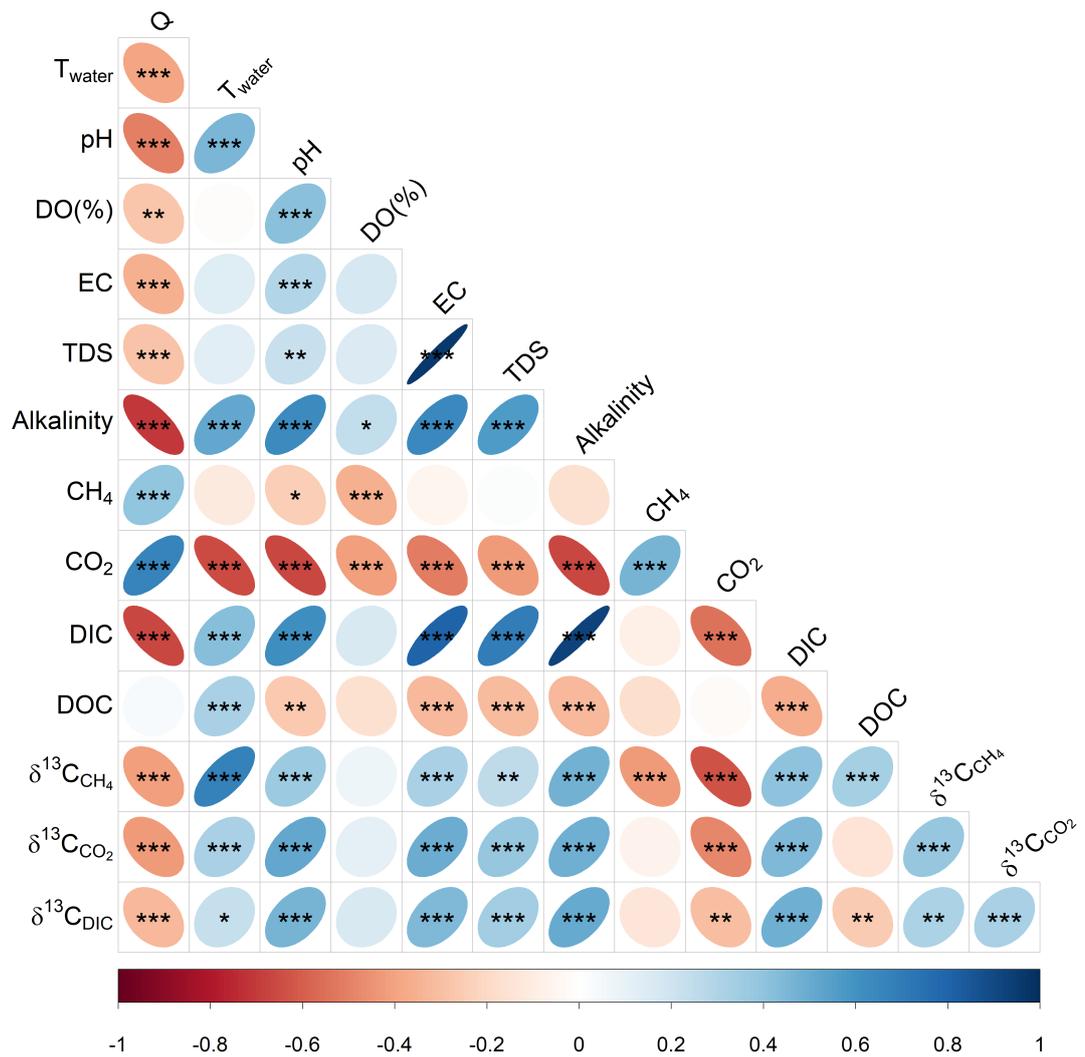


Figure S4. Correlations between dissolved C concentration and / or $\delta^{13}\text{C}$ and water physiochemical properties (* indicates $p < 0.05$, ** indicates $p < 0.01$, and *** indicates $p < 0.001$).

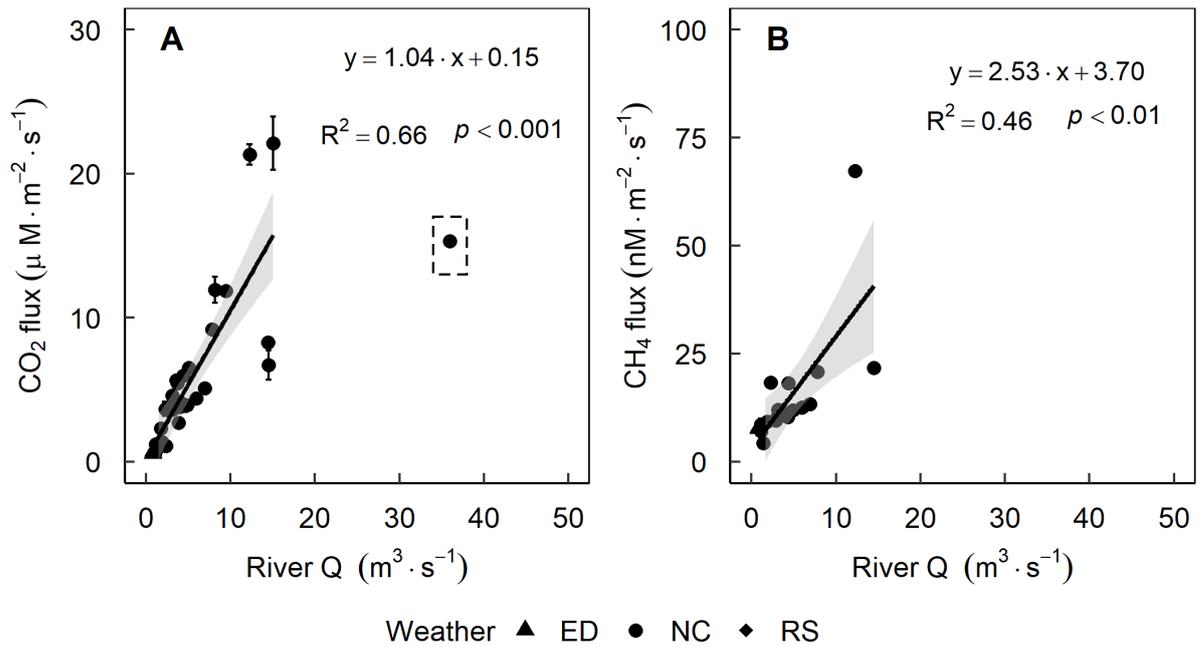


Figure S5. Correlations between *in-situ* CO₂ flux / calculated CH₄ flux and river discharge. There was one low CO₂ flux in high discharge (in the dashed rectangle). The high discharge in that sampling day increased the river level, the position where we usually measured CO₂ flux was too far away from the riverbank to connect the floating chamber and LiCor, so the sampling site had to move to a site closer to the riverbank, where the river level was shallower, and the discharge was smaller than site 1. The distance between site 1 and site 2 was less than 10 m. This particular result was excluded when doing the regression analysis.

5 Stable Isotope Calibration Standards

Two batches of stable isotope calibration standard gases (ALPHAGAZ, Air Liquide) had been used during the study period (Table S1). Batch 1 was applied from February 2018 to October 2019 and Batch 2 was used subsequently.

Table S1. The concentration and $\delta^{13}\text{C}$ value of CH_4 and CO_2 in the stable isotope calibration standard.

		Batch 1		Batch 2	
		CH_4	CO_2	CH_4	CO_2
Standard.1	Concentration (ppm)	2	400	1.77	399
	$\delta^{13}\text{C}$ (‰)	-68.6	-32.5	-49.4	-8.5
Standard.2	Concentration (ppm)	103	1200	10.00	1000
	$\delta^{13}\text{C}$ (‰)	-32.0	-15.2	-68.6	-20.1
Standard.3	Concentration (ppm)	1500	2000	/	/
	$\delta^{13}\text{C}$ (‰)	-69.0	+0.2	/	/

References

- Striegl, R. G., Dornblaser, M. M., McDonald, C. P., Rover, J. R., & Stets, E. G. (2012). Carbon dioxide and methane emissions from the Yukon River system. *Global Biogeochemical Cycles*, 26(4). doi:10.1029/2012GB004306
- Wang, X., He, Y., Yuan, X., Chen, H., Peng, C., Yue, J., . . . Liu, S. (2017). Greenhouse gases concentrations and fluxes from subtropical small reservoirs in relation with watershed urbanization. *Atmospheric Environment*, 154, 225-235. doi:<https://doi.org/10.1016/j.atmosenv.2017.01.047>