

## Spatial variability of $CH_4$ and $CO_2$ production in the sediment of a small and shallow lake can be explained by organic matter quality

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Small inland waters ( $< 1 \text{ km}^2$ ) have recently been discovered as significant sources and sinks in the global carbon cycle because they cover larger areas than previously assumed and exhibit a higher metabolic activity than larger lakes. They are further expected to be particularly susceptible to changing climate conditions.

In order to explain spatial and temporal variability of the emitted greenhouse gases carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  as well as underlying controls, it is crucial to understand production processes of these gases in the anoxic sediments of those lakes.

To address this knowledge gap, we experimentally determined potential  $CO_2$  and  $CH_4$  production rates of the sediment of Windsborn crater lake, a polymictic small (1.4 ha) and shallow (max. depth 1.7 m) lake in the Eifel uplands in western Germany.

To determine the amount of  $CO_2$  and  $CH_4$  potentially being produced in the lake sediment and their controlling factors, we sampled sediment at 12 different locations in Lake Windsborn in spring 2018 and set up a four-week anaerobic incubation experiment under controlled laboratory conditions. Besides determining potential  $CO_2$  and  $CH_4$ production rates, we measured  $H_2$  and acetate concentrations, electron accepting/donating capacity (EAC/EDC<sub>org</sub>) of the particulate organic matter as well as ammonium, phosphate, chloride, sulphate, sulfide, iron (II) and iron (III) concentrations. The solid phase was analyzed for carbon (C) and nitrogen (N) contents and isotopes by Isotope-Ratio-Mass-Spectroscopy (IRMS). Organic matter quality was evaluated by Fourier-Transformed-Infrared (FTIR) spectroscopy.

We found high spatial variability of both potential  $CO_2$  and  $CH_4$  production rates in the upper 5 cm of the sediment of Lake Windsborn.  $CO_2$  production rates ranged from  $0.73 \pm 0.13 - 10.14 \pm 0.79 \ \mu mol \ g^{-1} \ d^{-1}$ ,  $CH_4$  production rates lay between  $0.62 \pm 0.16$  and  $8.21 \pm 0.51 \ \mu mol \ g^{-1} \ d^{-1}$ . Production rates decreased to less than 50 % at a sediment depth of 5 -10 cm.

C/N ratios were between 10.97 and 18.39 and showed significant negative correlations with both  $CO_2$  and  $CH_4$  production rates. Also, by FTIR spectroscopy determined peak ratios that were indicative of humic acids, lignin, aromatic compounds and esters showed negative correlations with production rates, indicating that the accumulation of recalcitrant organic material leads to lower  $CO_2$  and  $CH_4$  production.

From the change of  $H_2$  and acetate concentration levels over time, we found that the contribution of acetoclastic methanogenesis decreased during the course of the experiment while the contribution of the hydrogenotrophic pathway gained in importance. Neither EAC/EDC<sub>org</sub> nor ion concentrations showed correlations with CH<sub>4</sub> production rates, suggesting that alternative electron acceptors that could suppress methanogenesis did not play a role in explaining differences in methanogenic activity probably because the sediment was already completely in a reduced state.

Our study shows that even in sediments of small lakes there exists a significant spatial variability in potential production rates of  $CO_2$  and  $CH_4$  that can be explained by the variation of sediment organic matter quality. It has further to be verified to what extent these sediment production rates can be transferred to emission patterns.