

# Highlights of Analytical Chemistry in Switzerland

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## Carbon Isotopic Composition in the Water Column of Lake Rotsee Reveals Importance of Methane Oxidation in Aquatic Environments

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For estimates of global greenhouse gas emissions, the importance of lakes in carbon cycling and the emission of  $\text{CO}_2$  and  $\text{CH}_4$  has recently gained attention. Methane, an approximately 25 times stronger greenhouse gas than  $\text{CO}_2$ , is produced under anaerobic conditions in the sediments and oxidized in the water column. This oxidation is carried out by micro-organisms, whose enzymatic reactions strongly influence the carbon isotopic signal of product ( $\text{CO}_2$ ) and substrate ( $\text{CH}_4$ ), preferentially using the methane with the lighter isotope for gaining energy. The resulting isotopic fractionation can be traced by Isotope Ratio–Mass Spectrometry (IR-MS), either by measuring the enrichment of the heavy isotope in the remaining substrate or the light isotope in the product. Methane concentrations in this open system oxidation can vary from mmol/l in anoxic water layers and sediments to nmol/l in oxic waters. If concentrations are low, a sufficient amount of  $\text{CH}_4$  for the IR-MS is achieved with a Trace Gas Pre-Concentrator unit.

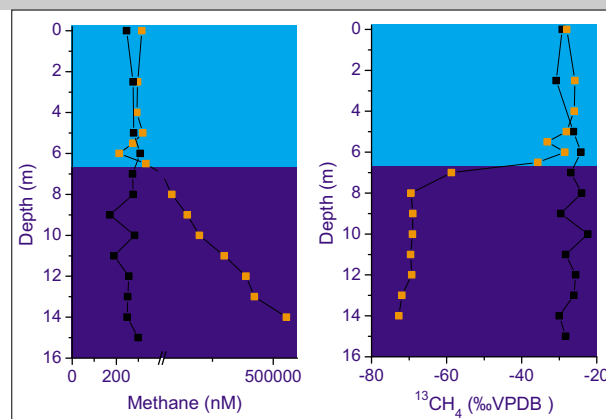
To investigate the importance of methane oxidation for the carbon cycle of small, stratified lakes we studied the Rotsee, a small wind-shielded lake close to Lucerne (famous for rowing). In general, lakes are stratified in summer with warm surface water and cold deep water. However, in winter when the surface water cools down and becomes denser the lake turns over and the water column mixes. We collected water samples from various depths of the lake and measured methane concentrations, stable isotopic composition of carbon ( $^{13}\text{C}/^{12}\text{C}$ ), oxygen concentrations, and several parameters to evaluate lake stratification (e.g. temperature, conductivity, pH). At the oxic/anoxic boundary we detected strong methane oxidation together with strong fractionation of the remaining methane, which became enriched in the heavy  $^{13}\text{C}$  isotope. Whereas isotopically light methane in the deep water and isotopically heavy methane in the surface water is the normal picture during stratification, the profile changes shortly after mixing when isotopically heavy methane (higher  $^{13}\text{C}$  content) is found in the whole water column. During stratification there was little evidence for oxidation in the oxic surface zone with only very low oxidation rates, except for times of lake mixing, when high nutrient, methane-rich and oxygenated water creates favourable conditions for very strong methane oxidation.

**Stable isotopes are a helpful tool to trace microbial processes in natural waters and were successfully used to investigate methane oxidation in a small, stratified lake.**

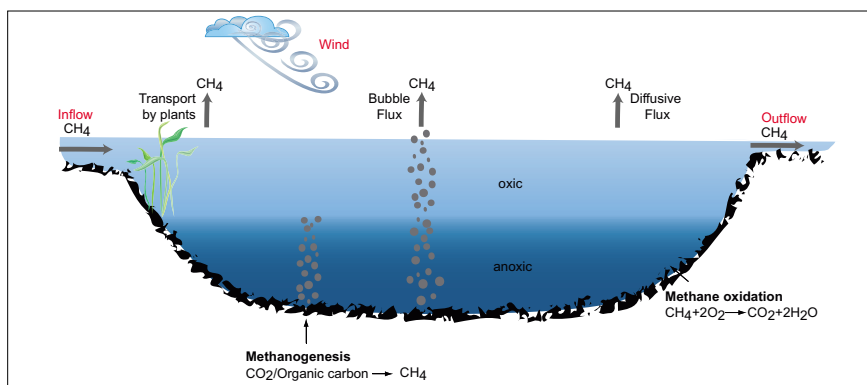
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### Reference

C. J. Schubert, F. Lucas, E. Durisch-Kaiser, R. Stierli, T. Diem, O. Scheidegger, F. Vazquez, B. Müller, *Aquatic Sciences – Research Across Boundaries* **2010**, 72, 455.



Methane concentration and isotopic composition profile of Rotsee in summer during stratification (orange dots) and in winter after the lake mixed (black dots).



Methane pathways in lakes. Depending on the specific situation, inflowing and outflowing water may contain small or larger concentrations of methane. (Artwork: Eliane Scharmin)



The Rotsee near Lucerne, prepared for a rowing regatta. (Photo: Ewi Weber)

### Can you show us your analytical highlight?

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