

## Determination of carbon dioxide dynamics in lakes

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**Abstract.** The carbon dioxide concentration is an important parameter for characterizing the trophic state of freshwater lakes and represents a biological production indicator. For long-term measurements of CO<sub>2</sub> concentrations in different depths of a lake an electrochemical CO<sub>2</sub> sensor has been used in a special flow-through system, which also contains sensors for measuring other parameters. Furthermore, the CO<sub>2</sub> concentrations were calculated with the thermodynamic computer program Phreeqc. The comparison of the measured and calculated values on one hand showed good correlation, but also pointed out that the *in situ* CO<sub>2</sub> measurement with a sensor is more favourable or even necessary in certain cases.

### 1 Outline of the problem

The CO<sub>2</sub> concentration in freshwater lakes is mainly determined by the organic primary production (phytoplankton algae) and the decomposition of organic substances. In contrast to the epilimnic oxygen production and the hypolimnic oxygen consumption, the hypolimnic accumulation of CO<sub>2</sub> represents a biological production indicator and is an important parameter for characterizing the trophic state of freshwater lakes (Cole, 1994).

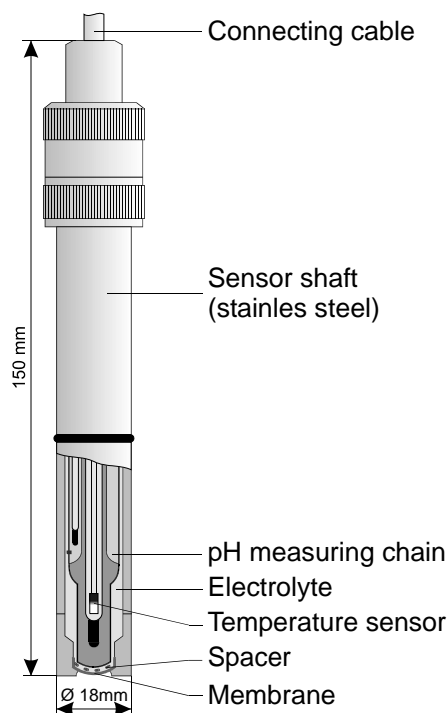
The aim of this work was to investigate the process of autochthonous calcite precipitation and the coprecipitation of phosphorus in a eutrophied hardwater gravel pit lake (Lake Willersinnweiher, Ludwigshafen/Rhine). Since the aqueous carbonate system is strongly dependent on the CO<sub>2</sub> conditions, the studies were focused on precisely recording the CO<sub>2</sub> dynamics. *In situ* measurement of CO<sub>2</sub> concentrations were performed in a special flow-through system with a newly developed electrochemical CO<sub>2</sub> sensor. For comparison the CO<sub>2</sub> concentrations were calculated with the thermodynamic computer program Phreeqc.

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### 2 Experimental

Lake water is continuously pumped from different depths with a submersible pump and a hose. An oxygen sensor was attached directly to the submersible pump to measure the O<sub>2</sub> saturation *in situ*. The hose ends in the water- and gas proof flow-through system in a boat, where different parameters (temperature, pH value, electrical conductivity, CO<sub>2</sub>, chlorophyll-*a*, SAK 254, H<sub>2</sub>S) are continuously measured by sensors and flow-through photometers. Dissolved CH<sub>4</sub> (by headspace gas chromatography), Ca, P and Ca particles were determined from water samples in a laboratory. The pressure in the flow-through system was controlled by means of valves to prevent any possible emissions of gases present in the water. The water runs through a hose behind the flow system back into the lake. From this hose water samples are taken. This system assured the measurement and capturing of mostly undisturbed water samples.

For the *in situ* measurement of dissolved free CO<sub>2</sub> an electrochemical carbon dioxide sensor as shown in Fig. 1 was used. This sensor, which had been developed at the Meinsberg Kurt-Schwabe Research Institute, works according to a potentiometric principle: CO<sub>2</sub> from the lake water permeates through the polymer membrane into the sensor system and causes there a defined and reproducible pH shift of the sensor electrolyte, which is measured by means of a pH glass electrode. A battery operated instrument with integrated micro-computer and data logger was used for monitoring the sensor voltage signal, which is proportional to the logarithm of CO<sub>2</sub> concentration in the water. After careful calibrating the sensor yields reliable measuring values down to about 0.5 mg/l CO<sub>2</sub> with a sensitivity of approx. 54 mV/dec. at 10°C. In laboratory tests the measuring accuracy of 1 mg/l ±4% and the temperature coefficient <1%/K had been determined. The long-term drift of the sensor signal is <1 mg/l within a measuring period of 1 month without intermediate calibration. The sensor response time depends strongly on temperature; at 10°C it amounts to  $T_{90} < 8$  min.



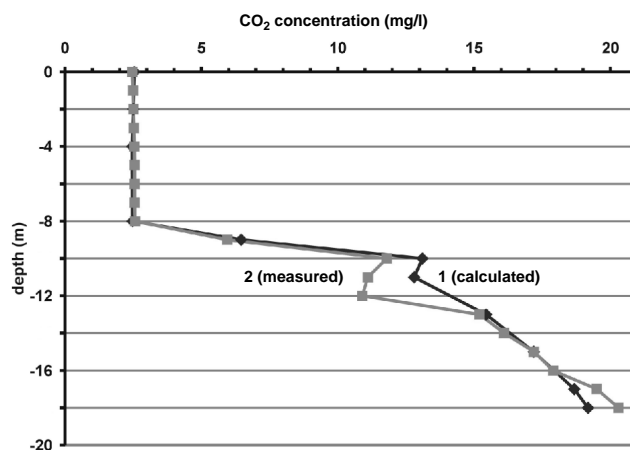
**Fig. 1.** Construction and dimensions of the electrochemical carbon dioxide sensor (Meinsberg Kurt-Schwabe Institute).

### 3 Results and discussion

During summer stratification the  $\text{CO}_2$  concentrations are low in the epilimnion due to the assimilation by phytoplankton algae, rise sharply in the metalimnion and reach maximum values in the anoxic hypolimnion by the degradation of organic substance in the sediment. After lake overturn in December 2000  $\text{CO}_2$  concentrations of 6.1 mg/l were measured throughout the entire depth. Until the end of January 2001 the  $\text{CO}_2$  concentrations fell down only caused by equilibrium exchange with the atmosphere. Subsequently the  $\text{CO}_2$  concentrations fell below the equilibrium concentration with the atmosphere from about 0.8 mg/l in February 2001 caused by the phytoplankton assimilation.

$\text{CO}_2$  equilibrium between lake water and atmosphere is conditioned by the aqueous carbonate system and superimposed by the phytoplankton assimilation. The emission of 4 t  $\text{CO}_2$  to the atmosphere was calculated in the period from 20 December 2000 to 29 January 2001. This resulted in a continuous rise of pH values and caused a significant quantitative non biogenically calcite precipitation with high coprecipitating rates of phosphorous (Schmid, 2002).

$\text{CO}_2$  concentrations were measured with the sensor as well as calculated with the thermodynamic computer program Phreeqc. Generally the comparison of measured and calculated  $\text{CO}_2$  values shows a good correlation. The deviations, which are obvious in Fig. 2 between 9 and 13 m of depth during the stagnation of the lake in the metalimnion, are caused by dissolution and precipitation processes of calcite



**Fig. 2.** Comparison of calculated and measured  $\text{CO}_2$  concentrations during the stagnation period (October 2000).

and the oxidation of  $\text{CH}_4$  (Schmid et al., 2002). In this region of depth methanotrophic bacteria oxidize all the dissolved methane to  $\text{CO}_2$ . The formation of  $\text{CO}_2$  through methane oxidation is confirmed by the small peaks of  $\text{CO}_2$  concentrations in Fig. 2. This  $\text{CO}_2$  is the reason for considerably lower pH values.

Given the high concentrations of chlorophyll-*a* in 10 m of depth, a lowering of  $\text{CO}_2$  concentrations, together with higher pH values due to phytoplankton assimilation, may be expected. But two processes overlap one another:  $\text{CO}_2$  is generated through methane oxidation and decreased through the high concentration of phytoplankton. Particularly noteworthy are the high Ca particle concentrations exactly in these depths, which are evidence of autochthonous calcite precipitation. Sediment traps provided further proof for this process. Based on the high chlorophyll-*a* concentrations, the calcite precipitation is most likely biogenically induced, even though the pH brings the saturation indices of calcite to below 0 (SI calcite  $-0.12$  in 10 m of depth) and calcite precipitation should be impossible. After lake overturn data show the release of  $\text{CO}_2$  to the atmosphere, resulting in decreased  $\text{CO}_2$  concentrations in the upper 4 m of the water column. In greater water depths the calculated values increase with depth because the presence of acid buffering substances (Calcite, sulfide). This results in wrong  $\text{CO}_2$  calculations.

During the mixing period in springtime the generally low  $\text{CO}_2$  values show a good correlation. But above 10 m, where  $\text{CO}_2$  concentrations are below atmospheric  $\text{CO}_2$  equilibrium concentrations due to the assimilation by phytoplankton, the results of the sensor reflect the dissolution of atmospheric  $\text{CO}_2$  in the lake water to balance the  $\text{CO}_2$  equilibrium water/atmosphere. This represents a general error source for calculated  $\text{CO}_2$  concentrations in lake water, since these calculations assume a balanced aqueous carbonate system, which is not the case in those dynamic lake water systems.

#### 4 Conclusions

A flow-through measuring system and sampling equipment was used successfully for the investigation and capturing of mostly undisturbed water samples from the lake Willersinnweiher with high resolution of depth (up to 10 cm). The measurement results show that the CO<sub>2</sub> dynamic is strongly determined by organic processes and the interactions between numerous physical, biological and chemical influencing parameters.

The comparison of the measured CO<sub>2</sub> concentrations with calculated values on one hand showed a strong correlation, but also gave evidence that the *in situ* measurement of CO<sub>2</sub> with a sensor is preferable or even necessary in many cases, because errors in the CO<sub>2</sub> calculation can be caused by the inaccuracy of the titrimetric determination of alkalinity or at measurements in disturbed water samples (Sellers et al., 1995).

The electrochemical carbon dioxide sensor proved to be very suitable for continuous use. It makes possible *in situ* measurements, shows outstanding long-term stability, is easy to handle, very accurate and scarcely influenced by disturbing ions or substances. Furthermore, by directly measuring CO<sub>2</sub> concentrations with the sensor immediately underneath and above the water surface the gas exchange between the

water and the surrounding atmosphere can be studied.

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