

In situ measurements in lake sediments with chemical sensors

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Intense mineralization processes take place at the sediment-water interface of lakes within a narrow zone of a few mm to cm magnitude. Material fluxes across this interface contribute substantially to the nutrient budgets of lakes. Inventive sampling devices such as benthic flux chambers and dialysis plates have been built and applied to investigate the system, yet each suffers from specific disadvantages. The use of chemical sensors avoids sampling artefacts and allows *in situ* measurements with high spatial resolution due to miniaturization and continuous recording. Chemical analysis is thus accomplished with minimum disturbance of the system investigated (Müller *et al.*, 1997). To position ion-selective electrodes at the lake bottom and to collect data a special submersible device was built which is presented in a parallel contribution at this conference (Dinkel *et al.*, 1998). The Lander for Ion-Selective Analysis (LISA) is now applied to investigate seasonal changes of fluxes of nutrients, electron acceptors, and bottom currents in lakes.

Methods

Potentiometric ion-selective electrodes with liquid membranes (Ammann, 1986) were miniaturized to a convenient geometry: membranes were cast in polyethylene tips of 8 cm length and 0.6 mm tip diameter. Pressure compensation with the filling solution was assured by a rubber balloon. We used a specially developed solid state reference electrode with excellent stability against pressure changes (Müller and Hauser, 1996). Sensor membranes for pH, NO_3^- , NH_4^+ , Ca^{2+} , CO_3^{2-} , and commercially available O_2 microelectrodes (MasCom, Bremen, D) were applied. First experiments were performed in Lake Alpnach, a mesotrophic lake in Central Switzerland which receives its water from a 391 km² calcareous catchment area. The hydraulic residence time is 90 days. The lake was slightly eutrophic in the 70s and recovered to a mesotrophic state in the last decade. Its sediments, however, are still rich in organic carbon and annual sedimentary deposition can be up to 1 cm. Measurements were

performed at the deepest location at 35 m depth. Two sensors of a kind were used in parallel. Step size was variable, each step taking 0.5–1 min for the process of advancing the electrodes, pausing for equilibration, and recording.

Results and discussion

Figure 1 presents concentration profiles *in situ* at the sediment water interface of Lake Alpnach. In all profiles one recognizes the zone of benthic boundary mixing in bottom waters (Gloor *et al.*, 1994). The O_2 profile is extremely steep, O_2 is used up within 2.5 mm. Detailed analysis of this profile reveals a diffusive boundary layer just above the sediment with a typical magnitude of 0.1 to 0.2 mm. The flux of O_2 across the interface as calculated by Fick's first law is $15.1 \text{ mmol m}^{-2} \text{ d}^{-1}$. pH shows a steep increase just below the interface and decreases a few mm further down in the sediment. This shape develops towards the end of the stagnation period. It can be attributed to intense alkalinity generation by denitrification, sulphate reduction, and release of Fe^{2+} and Mn^{2+} . The pH sensor is reliable and no interference from other ions was observed. Ammonium is below detection limit in the bottom water and K^+ interferes at concentrations $<10 \mu\text{M}$. In the sediment, however, NH_4^+ is easily detectable and increases due to mineralization of settled detritus. In contact with oxygen nitrification occurs. The largest flux is observed in the zone of intense mineralization 0.5–1 cm below the sediment surface. The concentrations of NO_3^- are close to the detection limit of the sensor. Concentration above the sediment agrees with chemical analysis. In the zone of mineralization, however, concentrations of interfering ions such as HCO_3^- and H_2PO_4^- increase dramatically and the selectivity of the sensor is too low. Signals from the NO_3^- sensor cannot be interpreted quantitatively. Changes in the concentrations of Ca^{2+} are delicate to measure since the changes in potential are very small and the sensitivity of this sensor is only 30 mV per decade. Hence, accuracy is unsatisfactory even though no interfering ions are present. The sensor

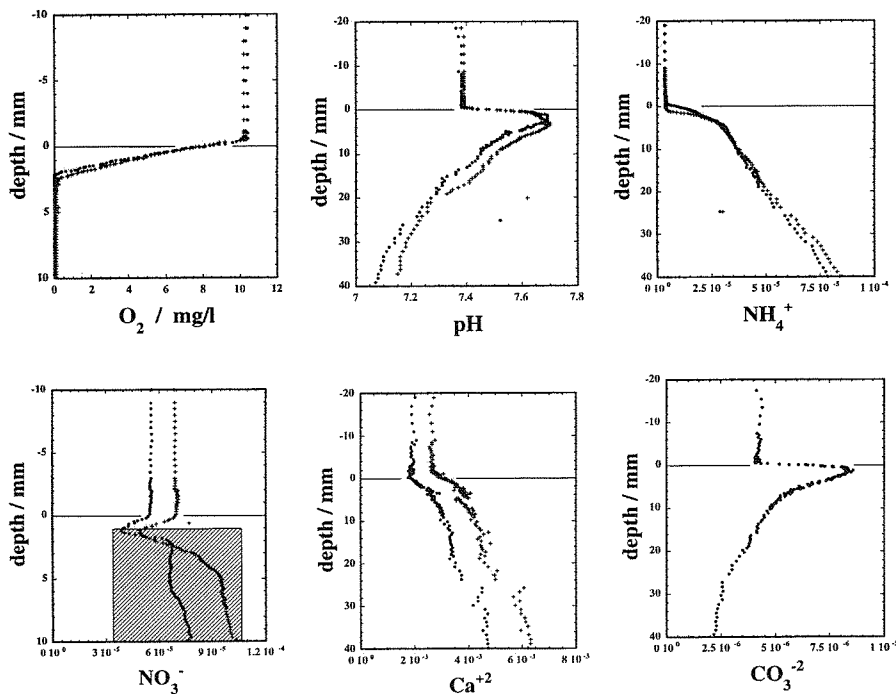


FIG. 1. Concentration profiles of O_2 , pH, NH_4^+ , NO_3^- , Ca^{2+} , and CO_3^{2-} at the sediment-water interface at the deepest point in Lake Alpnach, 35 m, (21.10.97).

for CO_3^{2-} is useful together with the profile for pH to calculate HCO_3^- and thus the amount of alkalinity produced by mineralization of organic material. One has to consider, however, that the sensitivity of this sensor too is only 30 mV/dec which makes it more susceptible to deviations from true values. Similar to Ca^{2+} , it can be normalized with the help of chemical analysis of the overlying water which is sampled after profiling. Most parameters were measured with two electrodes positioned 1 cm apart and comparison of the two profiles reveals different shapes and gradients of the profiles. At present it is not clear whether this indicates heterogeneity of the sediment or measurement artefacts. However, lake sediments can be rather fluffy consisting of flake-like structures. The sediment surface is not well defined and patchiness can be observed even with the video endoscope mounted to the LISA system.

Conclusion

Miniaturized ion-selective electrodes proved capable to measure and resolve concentration gradients of O_2 ,

pH, NO_3^- , NH_4^+ , Ca^{2+} , and CO_3^{2-} at the sediment-water interface *in situ* on the lake bottom. The use of the NO_3^- electrode is limited because of HCO_3^- and probably $H_2PO_4^-$ interference in the main mineralization zone just below the sediment-water interface. Accuracy of the Ca^{2+} and CO_3^{2-} measurements is limited due to the low sensitivity of these sensors. In a next step the sensor measurements will be directly compared with high-resolution sampling by dialysis plates.

References

- Ammann, D. (1986) *Ion-selective microelectrodes*. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo.
- Dinkel, Ch., Müller, B. and Wehrli, B. (1998) *this issue*.
- Gloor, M., Wüest, A. and Münnich, M. (1994) *Hydrobiologia*, **284**, 59–68.
- Müller, B. and Hauser P.C. (1996) *Anal. Chim. Acta*, **320**, 69–75.
- Müller, B., Wehrli, B., Power, M. and van der Meer, J.R. (1997) *Chimia*, **51**, 878–83.