

High spatial resolution measurements in lake sediments with PVC based liquid membrane ion-selective electrodes

Abstract—Ion-selective liquid membrane electrodes for Ca^{2+} , CO_3^{2-} , NH_4^+ , NO_3^- , NO_2^- , and pH have been miniaturized and their characteristics evaluated in view of their application in sediment pore water of lakes. PVC membranes were prepared in polyethylene pipette tips with an end diameter of 0.6 mm. This is a simple method to produce inexpensive disposable ion-selective electrodes for various applications. Detection limits were 1 μM for Ca^{2+} , CO_3^{2-} , NH_4^+ , and NO_3^- , and 10 μM for NO_2^- . The pH sensor was linear in the pH range of 4–11. Selectivities for Ca^{2+} , CO_3^{2-} , and pH are high enough for the application in seawater. The sensors for NH_4^+ , NO_3^- , and NO_2^- in their low concentration range experience interferences from K^+ , SO_4^{2-} , and HCO_3^- , respectively, in lake pore water. Reproducibility in pure solutions is between ± 0.2 and ± 0.6 mV. The applicability of the miniaturized sensors are demonstrated in measurements of concentration gradients across the sediment–water interface in sediment cores of several lakes.

Measurements with high spatial resolution are an analytical prerequisite in order to characterize and model early diagenetic processes at the sediment–water interface and to calculate fluxes of nutrients and electron acceptors through the boundary layer. Ion-selective electrodes (ISEs) have some unique features that make them specially suited for in situ measurements in oceans and lakes. Measurements with ISEs do not require sampling or sample treatment. Electrodes are miniaturizable and allow continuous measurements with high resolution in time or space. Artifacts produced by outgassing of CO_2 , contamination with oxygen, and other factors are avoided for in situ measurements. Oceanographers have thus far applied microelectrodes for in situ measurements of oxygen and pH microprofiles to determine diffusive fluxes between bottom water and sediment pore water in the deep ocean with submersible profiling instruments (Reimers et al. 1986; Reimers 1987; Archer et al. 1989a,b; Gundersen and Jørgensen 1990, 1991; Gundersen et al. 1992; Glud et al. 1994). Besides pH and O_2 sensors, a variety of new electrodes have been applied in natural systems, in shallow sediments, or on sediment cores in the laboratory. This includes sensors for CO_2 (Cai and Reimers 1993; Lefèvre et al. 1993; De Grandpre, 1993), NO_3^- (Sweerts and de Beer 1989; Jensen et al. 1993; Larsen et al. 1996), NO_2^- (de Beer et al. 1997), N_2O (Revsbech et al. 1988; Glud et al. 1995), NH_4^+ (de Beer et al. 1991), H_2S (Ramsing et al. 1993; Eckert and Frevert 1984; Visscher et al. 1991), CH_4 (Damgaard and Revsbech 1997), and voltammetric electrodes for the determination of dissolved Fe, Mn, O_2 , and S(-II) (Brendel and Luther 1994; Luther et al. 1996). Optodes were developed for measurements of oxygen (Klimant et al. 1995; Rosenzweig and Kopelman 1995) and CO_2 (Müller and Hauser 1996a).

The high concentration of the background electrolyte of

seawater, however, limits the application of ISEs because, except for oxygen and pH, the selectivities of ISEs are too low for this application, and nutrient concentrations in ocean sediments are at the detection limit of these electrodes. Freshwater lakes, however, have far lower concentrations of background electrolytes, and nutrient concentrations are often much higher due to eutrophication.

A profiling instrument for in situ measurements of concentration gradients on the bottom of lakes on a 100- μm scale (Wehrli et al. 1994; Müller et al. 1997) is under development, and liquid membrane electrodes for pH, NO_3^- , NO_2^- , NH_4^+ , Ca^{2+} , and CO_3^{2-} , as well as solid state electrodes for S^{2-} , and conventional amperometric oxygen electrodes will be applied. Pressure dependence of this kind of miniaturized liquid membrane ISEs were tested up to 30 bar and was found to be $\sim 10 \mu\text{V bar}^{-1}$ (Müller and Hauser 1996b). Temperature dependence was ~ 0.23 mV per $^\circ\text{C}$, and was therefore close to the value of 0.198 mV per $^\circ\text{C}$ demanded by the Nernst equation.

Ion-selective microelectrodes made with glass capillaries (Ammann 1986) are difficult to handle under high pressures and pressure changes, are fragile to use in sediments, and quite delicate toward influences of electrostatic fields owing to their high membrane resistance. We use polyvinyl chloride (PVC)-based membranes to minimize these problems and miniaturize the electrode body in such a way that the electrode is still stable enough to be applied in a sediment on the lake bottom. It is always a tradeoff between small size (allowing high resolution) and physical robustness and better stability of the potential.

In this note we report on the evaluation, construction, and application of ion-selective liquid membrane electrodes for pH, Ca^{2+} , CO_3^{2-} , NH_4^+ , NO_3^- , and NO_2^- in sediment cores, and discuss their potential for porewater studies in freshwater lakes and in ocean water.

Ion-selective ligands for a variety of ions are published in the literature (e.g. Ammann 1986) and are commercially available (Fluka Chemie AG, Buchs, Switzerland). The recommended membrane composition proved optimal in most cases.

The H^+ ionophore we use is 1.8 mg tridodecylamine (Fluka 95292), together with 117.9 mg bis(1-butylpentyl)decane-1,10-diyl diglutarate (ETH469, Fluka 30585) as membrane solvent, 1.8 mg potassium tetrakis(4-chlorophenyl)borate (Fluka 60591), and 59.4 mg high-molecular-weight PVC (Fluka 81392) dissolved in 2 ml of tetrahydrofuran (THF). The inner filling solution consists of 1 M citric acid, 2.73 M NaOH, and 0.01 M NaCl (Anker et al. 1983).

Ca^{2+} ionophore is 1.8 mg *N,N,N',N'*-tetracyclohexyl-3-oxapentanediamide (ETH129, Fluka 21193), with 118.1 mg 2-nitrophenyloctylether (*o*-NPOE, Fluka 73732), 1.1 mg potassium tetrakis(4-chlorophenyl)borate, and 59 mg PVC dis-

solved in 2 ml of THF. Inner filling solution is 0.01 M CaCl_2 (Schefer et al. 1986).

Methyltridodecylammonium nitrate (10.8 mg) (MTDDA- NO_3 , Fluka 91664) was used as ion exchange ligand for NO_3^- , together with 117 mg 2-nitrophenyloctylether (*o*-NPOE) and 52.2 mg PVC. The inner filling solution is 0.01 M NaCl and 0.01 M NaNO_3 (Wegmann et al. 1984).

Nitrite, NO_2^- , was determined with 1.8 mg aquocyanocobalt(III)-hepta(2-phenylethyl)cobyrinate perchlorate (Fluka 72590), 117.9 mg *o*-NPOE, 0.2 mg potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (K(TFPB), Fluka 60588; Nishida et al. 1984), and 59.4 mg PVC. The electrolyte was 0.01 M NaNO_2 and 0.01 M NaCl (Stephanek et al. 1986; Schaller et al. 1994).

The antibiotic nonactin (1.8 mg) (Fluka 9877) was used for NH_4^+ -selective membranes in 120.2 mg of bis(1-butylpentyl)adipate (BBPA) (Fluka 2150) and 58 mg of PVC. NH_4Cl (0.01 M) was used as filling solution (Thanei-Wyss et al. 1983).

The trifluoroacetophenone derivative *N,N*-dioctyl-4-trifluoroacetylbenzamide (ETH 6019, Fluka 21853) was applied for the carbonate (CO_3^{2-})-selective membrane. The membrane solution consisted of 6.5 mg ligand and 3.7 mg of methyltridodecylammonium chloride (MTDDA-Cl, Fluka 91661) in 101 mg dioctylsebacate (DOS, Fluka 84818) and 75.8 mg PVC dissolved in 2 ml THF. The inner filling solution is 0.1 M NaH_2PO_4 , 0.1 M Na_2HPO_4 and 0.01 M NaCl (Behringer et al. 1990; Keller-Lehman 1990).

Polyethylene microcapillary tips with an outer tip diameter of 0.6 mm and inner diameter of 0.3 mm (microcapillary round tips, code B, Fluka) were rinsed with THF and dipped in the membrane solution. About 1 μl of the solution was drawn up by capillary force, and the tips were placed in a rack inside an evaporation chamber and covered with a glass plate. After 30 min the tip was again dipped into the membrane solution, and evaporation was allowed during the night. The inner filling solution was added and the tip was equilibrated with this solution for at least 2 h. A silver wire (0.5 mm in diameter, chlorinated by plating for 40 min in 0.1 M HCl at 0.4 mA cm^{-2}), was used as internal reference. The reference electrode was a commercially available Ag/AgCl double junction cell from Metrohm (Buchs, Switzerland). For a few experiments a self-made miniaturized solid-state Ag/AgCl electrode of 1-mm diameter was applied (Müller and Hauser 1996b). Electrode signals were transformed with an impedance converter and recorded with the MacLab 4e system (ADInstruments).

Calibration curves were determined in pure solutions of the corresponding sodium or chloride salts at 20°C without stirring or ionic strength adjustment. The potential value was taken when the drift was $<0.1 \text{ mV min}^{-1}$. For the highly diluted solutions, the sample was discarded and renewed three times before the actual measurements. Total equilibration for these nonbuffered, highly diluted solutions could take up to 5 min. Activities were calculated with the extended Debye-Hückel approximation (Meier 1982). Detection limits were determined from calibration curves at the intercept of the two asymptotes—from the zone of maximum sensitivity and the zone of insensitivity (Fig. 1). The pH sensor was tested by a titration of a solution of 10 mM

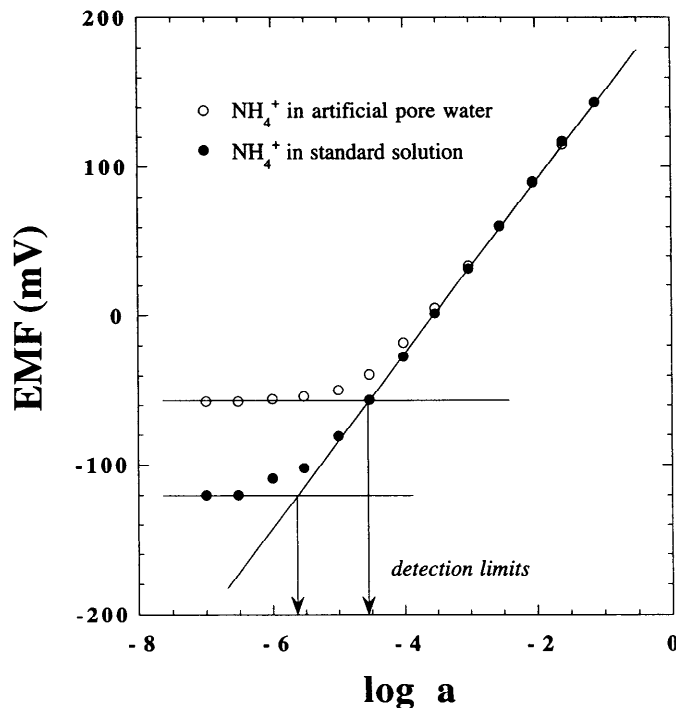


Fig. 1. Titration curves from ion-selective NH_4^+ minielectrode in pure solutions and with artificial pore water as bulk electrolyte.

NaOH , 130 mM NaCl, and 10 mM Tris (Tris-hydroxymethylaminometane) with 0.12 M HNO_3 and compared with a conventional pH glass electrode. Detection limits for the various electrodes in pure solutions are 10^{-6} M for Ca^{2+} , NH_4^+ , NO_3^- , and CO_3^{2-} , and 10^{-5} M for NO_2^- (Table 1). The pH ISE showed linear behavior in the pH range 4–11 with near Nernstian slope.

Selectivities were determined with the “separate solution method”: The potential of an electrode is measured in a solution of the measuring ion i , producing E_i , and in a solution of the interfering ion j , in the same concentration, yielding E_j . According to the Nicolsky–Eisenmann equation (Amman 1986), the selectivity coefficient K_{ij}^{pot} is calculated as

$$\log K_{ij}^{\text{pot}} = (E_j - E_i) \frac{z_i F}{2.3 RT} + \log \frac{a_i}{a_j^{(z_i/z_j)}}, \quad (1)$$

where i and j are the measuring and interfering ions, z_i and z_j the charges of the ions i and j , a_i and a_j activities, F the Faraday constant ($96,490 \text{ C mol}^{-1}$), R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T the temperature in Kelvin. Experimental selectivities and corresponding values from the literature for all major ions occurring in lake pore water are shown in table 2. Experimental values from the minielectrodes compare very well with literature data. A notable exception is the low selectivity of our NO_2^- electrode against HCO_3^- .

Generally, the application of the sensors is limited by either the detection limit or the selectivity. We compared experimental detection limits in an artificial pore water with detection limits calculated with selectivity coefficients (50% interference). The test solution consisted of 0.5 mM CaCO_3 , 0.35 mM NaCl, 0.15 mM KHSO_4 , 0.1 mM K_2HPO_4 , 1 mM

Table 1. Detection limits for electrodes in pure solutions, in artificial porewater (*see text*), and slopes of calibration curves. With the assumption of an interfering ion to give the same potential as the measuring ion, theoretical measuring limits were calculated with experimental selectivity coefficients.

Analyte	Detection limit in pure solutions	Slope (mV/decade)	Exp. detection limit in artificial pore water*	Slope (mV/decade)	Detection limit calculated for artificial porewater†	Interfering ion
Ca ²⁺	10 ⁻⁶	30.7	5 × 10 ⁻⁶	30.5	<10 ⁻⁶	—
NH ₄ ⁺	10 ⁻⁶	59.2	2 × 10 ⁻⁵	57.1	4.8 × 10 ⁻⁵	K ⁺
NO ₃ ⁻	10 ⁻⁶	-57.9	4 × 10 ⁻⁴	-60.7	2 × 10 ⁻⁵	SO ₄ ²⁻
NO ₂ ⁻	10 ⁻⁵	-50.5	4 × 10 ⁻⁵	-44.3	4.3 × 10 ⁻⁵	HCO ₃ ⁻
CO ₃ ²⁻	10 ⁻⁶	-39.2	10 ⁻⁶	-37.7	<10 ⁻⁶	—
H ⁺	10 ⁻¹¹ –10 ⁻⁴	57.4	—	—	—	—

* Composition (*see text*).

† For the method of calculation, *see text*.

(NH₄)₂CO₃, 0.5 mM MgCl₂, and 50 µl 1M HCl per 100 ml to adjust a pH of 8. Actually, these concentrations are very high and represent a worst case scenario. Examples of titration curves for NH₄⁺ in pure solutions and in artificial pore water are shown in Fig. 1. Data for experimental and calculated detection limits are shown in Table 1. Experimental and theoretical detection limits correspond quite well. The calculated values show that the measurements of Ca²⁺ and CO₃²⁻ remain undisturbed by all interfering ions considered, which is verified by the experiment. For the concentrations chosen for the interfering ions, the application of the NH₄⁺ electrode is limited by K⁺ to 2 × 10⁻⁵ M, the NO₃⁻ electrode by SO₄²⁻ to 4 × 10⁻⁴ M, and the NO₂⁻ electrode by HCO₃⁻ to 4 × 10⁻⁵ M.

Corresponding experiments in artificial seawater also can be compared with concentrations calculated from selectivity coefficients (Table 3): Ca²⁺ can be determined down to 10⁻⁴ M (limited by Na⁺), NH₄⁺ to 10⁻³ M (limited by K⁺), and NO₃⁻ to 10⁻² M (limited by Cl⁻). Artificial seawater was prepared with 28 g NaCl, 7 g MgSO₄·7H₂O, 5 g MgCl₂·6H₂O, 2.4 g CaCl₂·6H₂O, and 0.2 g NaHCO₃ and made up to 1 liter with bi-distilled H₂O. Detection limits in artificial pore water and seawater were calculated for the assumption of equal contributions of measuring and interfering ion to the potential.

The response times of the sensors (the time the electrode needs to reach a stable potential) were determined by measuring alternately two standard solutions of 10⁻³ M and 10⁻⁴ M. Reproducibility was checked by five alternate measurements, and long-term stability was investigated following the potential for 1 h. All electrodes showed response times of <1 min. Standard deviations of repeated measurements were between ±0.2 and ±0.6 mV. The potentials remained constant (±0.05 mV) during the time the signal was observed.

Electrodes should be stored cool to avoid bacterial growth. The NO₂⁻ sensor lost its activity after ~10 d. The NO₂⁻ membrane solution, however, was found to be stable since newly prepared electrodes functioned faultlessly. Some electrodes prepared with membrane solutions older than 2 months show decreased sensitivities, and thus new membrane solutions were prepared each month.

Only three liquid membrane electrodes (NH₄⁺, NO₃⁻, and NO₂⁻) were used so far by other authors to measure concentration gradients in environmental biofilms. The NH₄⁺ non-actin microelectrode used for measurements in cores of lake sediments by de Beer (de Beer et al. 1991; de Beer and van den Heuvel 1988) was a glass microcapillary with a 1-µm tip diameter. It produced reduced sensitivity, longer response time (τ_{90%} = 1 min), and lower selectivities for K⁺, Na⁺, and Ca²⁺ than did the minielectrode used here. The different se-

Table 2. Experimental selectivity coefficients for minielectrodes as determined by the separate solution method. Literature values are collected from Ammann et al. 1987 (Ca²⁺), Thanei-Wyss et al. 1983 (NH₄⁺), Wegmann et al. 1984 (NO₃⁻), Schaller et al. 1994 (NO₂⁻), and Keller-Lehmann 1990 (CO₃²⁻).

Interfering cation	Selectivity coeff.				Interfering anion	Selectivity coefficient					
	Ca ²⁺ electrode		NH ₄ ⁺ electrode			NO ₃ ⁻ electrode		NO ₂ ⁻ electrode		CO ₃ ²⁻ electrode	
	Exp.	Litt.*	Exp.	Litt.†		Exp.	Litt.‡	Exp.	Litt.§	Exp.	Litt.¶
Ca ²⁺	—	—	-3.5	-5.2	NO ₃ ⁻	—	—	-3.6	-3.4	-1.9	-2.1
NH ₄ ⁺	-4.5	-3.6	—	—	NO ₂ ⁻	-1.2	—	—	—	-2.9	—
K ⁺	-2.5	-3.9	-0.9	-0.9	HCO ₃ ⁻	-2.6	-2.2	-1.5	-3.3	—	—
Na ⁺	-3.2	-3.6	-3.8	-3.0	Cl ⁻	-1.8	—	-3.5	-3.7	-5.3	-4.8
Mg ²⁺	-4.9	-4.9	-3.4	-5.1	SO ₄ ²⁻	-2.8	-2.3	-3.7	-4.1	-5.1	-4.4
H ⁺	-3.4	-2.5	-3.2	-3.7	HPO ₄ ²⁻	-2.9	-2.4	-3.9	—	-5.9	—

* Ammann et al. 1987 (Ca²⁺). † Thanei-Wyss et al. 1983 (NH₄⁺). ‡ Wegmann et al. 1984 (NO₃⁻). § Schaller et al. 1994 (NO₂⁻). ¶ Keller-Lehmann 1990 (CO₃²⁻).

Table 3. Detection limits of ion-selective minielectrodes in artificial seawater.

Analyte	Exp. detection limit in artificial seawater	Detection limit calculated for artificial seawater	Interfering ion
Ca ²⁺	10 ⁻⁴	1.6 × 10 ⁻⁴	Na ⁺
NH ₄ ⁺	7 × 10 ⁻³	1.4 × 10 ⁻³	K ⁺
NO ₃ ⁻	10 ⁻²	1.4 × 10 ⁻²	Cl ⁻

* Composition (see text).

lectivities may be caused by the different membrane solvent used by these authors. The signal of the microelectrode showed strong disturbances during penetration of sandy sediment due to collisions of the electrode tip with sand grains, and profiles were recorded during the retraction of the electrode.

NO₃⁻ microelectrodes with 1-μm tips were used by de Beer and Sweerts (1989) and by Sweerts and de Beer (1989) to measure penetration depths and calculate fluxes of NO₃⁻ in sediment cores. Jensen et al. (1993) described the manufacture of a glass microelectrode with a coaxial shielding that was totally protected from disturbances due to electrostatic fields and its application in sediment cores. Selectivities and detection limits of these microelectrodes were similar to our NO₃⁻ PVC minielectrode. A new amperometric NO₃⁻ biosensor developed by Larsen et al. (1996) could overcome the insufficient selectivities of the liquid membrane ISE. The sensor carries immobilized denitrifying bacteria on a capillary wall in front of a N₂O microsensor. However, because acetylene is needed to inhibit total denitrification, the sensor is not applicable to our purpose in its present state.

The carrier and membrane solvent of a recently published NO₂⁻ electrode by de Beer et al. (1997) is identical to the NO₂⁻ sensor presented in this paper. They presented measurements in biofilms with a glass microcapillary sensor using a gelled PVC membrane and a hydrophilic coating for tip protection. This resulted in more sturdy sensors, higher signal stability, and lower detection limit. The selectivities for Cl⁻, NO₃⁻, and HCO₃⁻ of the sensor of de Beer et al. are about a factor of 10 better than those for our minielectrode. Detection limit too was better by a factor of 10.

To demonstrate the applicability of the sensors at the sediment–water interface, sediment cores were sampled with a gravity corer in polyethylene tubes of 7-cm diameter from Lake Baldeg, Lake Rotsee, and Lake Lucerne. Lake Baldeg is a highly eutrophic lake situated in the Swiss midland that has been artificially aerated since 1982. Cores were taken from the deepest point at 65 m. Lake Rotsee is a shallow eutrophic lake (14 m in depth) where free sulfide is detectable in the water column during the stagnation period. Lake Lucerne is an oligotrophic prealpine lake; cores were taken from the littoral zone just off Kastanienbaum at 17-m depth. The sediment cores were transferred to our institute and either cooled with ice or transferred and measured in a climatized chamber at 5°C. Ion-selective minielectrodes for pH, Ca²⁺, NH₄⁺, NO₃⁻, and (or) CO₃²⁻ were fixed to a small horizontal plate with plastic fittings. The distance between sensors was ~1 cm. A commercial amperometric 737-GC Clark-style oxygen microelectrode with a guard cathode (Diamond General) was used to measure oxygen profiles. The

sensor array was moved stepwise with a micromanipulator (Newport Instr.). Measurements were performed within a few hours after the core was taken. Calibration solutions and electrodes were conditioned to ~5°C. The measurements were started after a few minutes equilibration time of the electrodes in the overlying water. The profiles were measured in steps of 0.25 to 0.5 mm. One-half to 1 min of equilibration time was needed when large concentration changes occurred. The sensors were calibrated with three solutions before and after the sediment profile. Slopes and intercepts of the calibration curves provided a good control on the performance and reliability of the electrodes. Interferences by other ions can be corrected mathematically over a limited concentration range applying a rearranged form of the extended Nicolsky–Eisenmann equation:

$$a_i = 10^{(E_i - E_0)/s} - \sum_j K_{ij}^{\text{pot}}(a_j)^{z_i/z_j} \quad (2)$$

E_0 and s are the reference potential and Nernstian slope of the calibration curve of the parameter in question, and all other expressions are as defined in Eq. 1.

This is the first study that presents concentration profiles of Ca²⁺ and CO₃²⁻ in lake sediments with ion-selective electrodes. Advantages are the simple and inexpensive preparation of the sensors, as well as their physical robustness compared to electrodes with glass bodies. Also, using PVC membranes in miniaturized sensors renders them less susceptible to mechanical effects of pressure differences and disturbances due to grains in the sediment compared to true microelectrodes with liquid-carrier membranes. Signal stability is better due to the much larger electrode surface.

Figure 2A presents measurements of pH, Ca²⁺, and NH₄⁺ from a core from lake Rotsee. At low concentrations of NH₄⁺, interference of K⁺ is observed. This can be corrected for in that K⁺ behaves conservatively across the sediment–water interface, so its concentration can be determined, and the selectivity coefficient is known. The determination of Ca²⁺ is delicate since the range of concentration change is only a factor of 0.5. Because the sensitivity for this electrode is only 28 mV per decade, the total change in potential across the concentration gradient will be only 5 mV. Fig. 2B shows profiles for O₂, NO₃⁻, and NH₄⁺ in a sediment of Lake Lucerne. NH₄⁺ is liberated in the deeper sediment owing to mineralization of organic material. The measurement is not corrected for the K⁺ interference, and therefore the signal for NH₄⁺ does not approach zero concentration in the water above the sediment. O₂ disappears in a thin zone of a few millimeters just at the sediment–water interface. After O₂ is depleted, NO₃⁻ is consumed quite rapidly. The detection limit for NO₃⁻ is lower than estimated from the experiments in artificial pore water (Table 1) by a factor of 20 due to the very low concentrations of interfering ions, especially SO₄²⁻ and H₂PO₄⁻, in the sediment of the oligotrophic Lake Lucerne. Fig. 2C depicts the determination of CO₃²⁻ and pH in a littoral sediment from Lake Lucerne. The concentration is calculated for HCO₃⁻ with the simultaneous measurements of pH and CO₃²⁻. The measurement of CO₃²⁻ is difficult since this parameter is susceptible to outgassing of CO₂ when the core is brought to the surface, and the concentration of CO₃²⁻ is at the lower detection limit of the electrode. However, no interference of any other ions is observed.

Concentration gradients at the sediment–water interface are susceptible to disturbances caused by the sampling of the

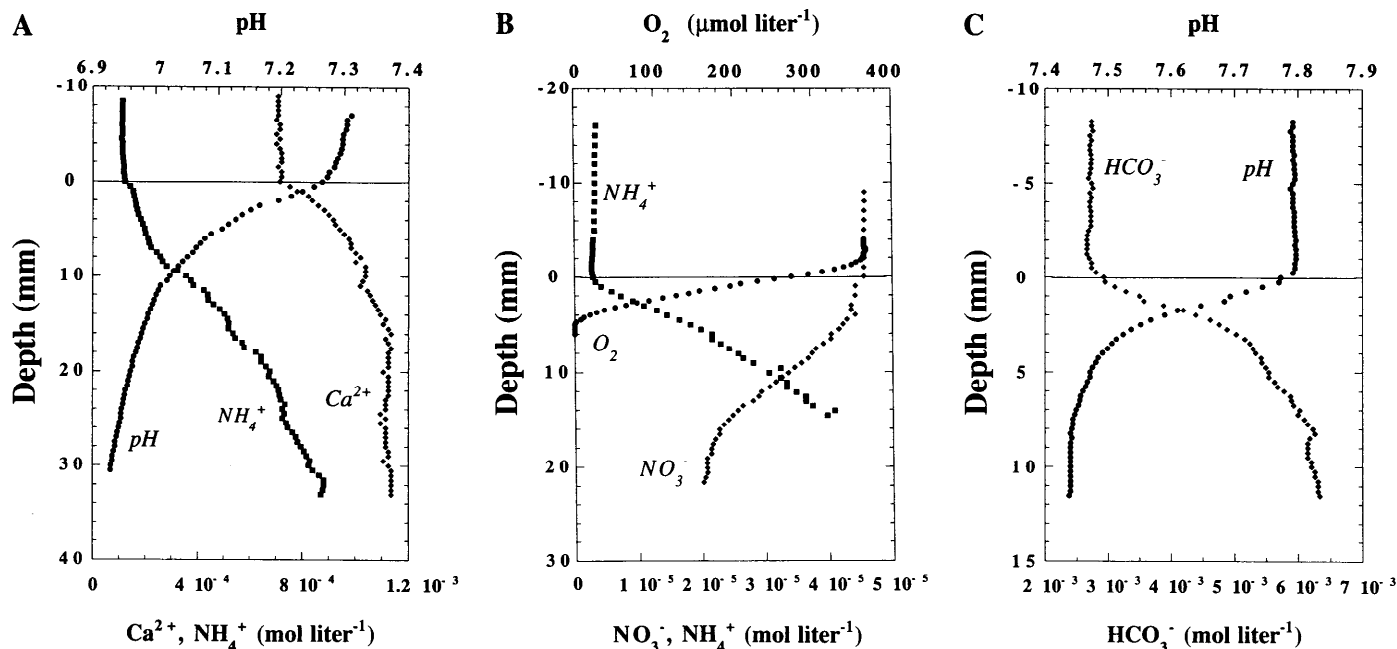


Fig. 2. Concentration profiles at the sediment–water interface for (A) pH, Ca²⁺, and NH₄⁺ on a core from Lake Rotsee (14-m depth), (B) O₂, NH₄⁺, and NO₃⁻ on a core from Lake Lucerne (20-m depth), and (C) pH and HCO₃⁻ (as calculated from pH and CO₃²⁻ measurements) in a sediment from Lake Lucerne (17-m depth).

cores, transport, and temperature changes. It is important to take special care with the handling of cores. Some measurements were performed directly at the lakeshore only minutes after coring. Comparison with measurements in the laboratory a few hours later showed good consistency.

We conclude that PVC-based ion-selective minielectrodes provide a simple, fast, and inexpensive way of producing disposable sensors of constant quality. Experimental specifications show that Ca²⁺, CO₃²⁻, and pH can be detected in artificial lake pore water without interference from other major ions. Their reproducibilities are in the range of ± 0.2 to ± 0.6 mV. Detection limits of NH₄⁺, NO₃⁻, and NO₂⁻ electrodes may be affected when concentrations of interfering ions are high. Usually, detection of NH₄⁺ is limited by interference of K⁺, and of NO₃⁻ by SO₄²⁻ in the deeper sediment. These findings were confirmed with measurements in sediment cores of various lakes. In seawater, high concentrations of K⁺, Na⁺, and Cl⁻ (0.01, 0.47, and 0.55 M, respectively; Stumm and Morgan 1996) increase the detection limits as calculated with our experimental selectivity coefficients. Detection limits due to these interfering ions are 1.6×10^{-4} M Ca²⁺, 1.4×10^{-3} M NH₄⁺, 1.4×10^{-2} M NO₃⁻, 1.6×10^{-4} M NO₂⁻, and 1.7×10^{-6} M CO₃²⁻, respectively. Sensors for Ca²⁺, CO₃²⁻, and pH can potentially be applied for seawater concentration ranges without restrictions by interferences.

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