In-situ ammonium profiling using solid contact ion selective electrodes in eutrophic lakes

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ABSTRACT

A promising profiling setup for *in-situ* measurements in lakes with potentiometric solid-contact ion-selective electrodes (SC-ISE) and a data processing method for sensor calibration and drift correction are presented. The profiling setup consists of a logging system, which is equipped with a syringe sampler and sensors for the measurement of standard parameters including temperature, conductivity, oxygen and photosynthetically active radiation (PAR). The setup was expanded with SC-ISEs in galvanically separated amplifiers. The potential for high resolution profiling is investigated by deploying the setup in the eutrophic Lake Rotsee (Luzern, Switzerland) using two different designs of ammonium sensing SC-ISEs. Ammonium was chosen as a target analyte since it is the most common reduced inorganic nitrogen species

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involved in various pathways of the nitrogen cycle and is therefore indicative of numerous biogeochemical processes that occur in lakes such as denitrification and primary production. One of the designs, which uses a composite carbon-nanotube-PVC based membrane, suffered from sulfide poisoning in the deeper, sulfidic regions of the lake. In contrast, electrodes containing a plasticizer free methacrylate copolymer based sensing layer on top of a conducting polymer layer as a transducer did not show this poisoning effect. The syringe samples drawn during continuous profiling were utilized to calibrate the electrode response. Reaction hotspots and steep gradients of ammonium concentrations were identified on-site by monitoring the electrode potential online. Upon conversion to high-resolution concentration profiles, fine scale features between the calibration points were displayed, which would have been missed by conventional limnological sampling and subsequent laboratory analyses. Thus, the presented setup with SC-ISEs tuned to analytes of interest can facilitate the study of biogeochemical processes going on at the centimeter scale.

INTRODUCTION

In-situ measurements are becoming increasingly important for the study of lake ecosystems as numerous biogeochemical processes in the water column are confined to very narrow zones and can be highly dynamic in time and heterogeneous in space,¹⁻³ resulting in steep gradients of nutrients and redox conditions. The investigation of these processes requires monitoring at high temporal and spatial resolution, which cannot be obtained by discrete sampling and subsequent laboratory analysis. New insights into these biogeochemical dynamics and their intensity can only be gained by high resolution *in-situ* measurements, which eliminate biases resulting from preservation and storage of samples, as well as from changing environmental conditions. In addition, *in-situ* profiling helps define boundaries of different layers such as the oxic-anoxic interface.⁴ These boundaries can be extremely narrow in lakes (less than 1 meter) and are thus not accessible by classical water sampling techniques, since samplers typically integrate over ~50 cm due to their dimensions. Modern sensor techniques are promising tools to overcome the shortcomings of classical analytical approaches. Existing automated platforms or buoys on lakes are usually equipped with sensors for physical parameters like temperature, conductivity, photosynthetically active radiation (PAR) and fluorescence based sensors for chlorophyll

61 measurements.⁵⁻⁷ *In-situ* sensor applications for lake-water profiling are rarely reported for the
62 parameters beyond the standard set of oxygen, pH, and sulfide.⁵ Reliable sensors for other
63 parameters like nutrient species are lacking.

64 Ion-selective electrodes (ISEs) have not been widely used for profiling dissolved chemical
65 species like NO_3^- , NH_4^+ , NO_2^- or trace metals in lakes. This can be attributed to the presence of
66 these chemical species in surface waters at concentrations close to the detection limits reported
67 for the commercially available electrodes and the presence of interfering ions which cause
68 additional complications for the measurement. Therefore the quantification of the
69 aforementioned chemical species poses challenges in terms of electrode performance and signal
70 stability. Most commercially available ISEs are based on an inner filling design,⁸ which suffer
71 from changes in pressure with depth and thus are not suitable for *in-situ* profiling deep in lakes.
72 In addition, very low detection limits are difficult to reach with an inner filling design due to
73 transmembrane ionic flux from the inner electrolyte to the sample.⁹ During the last decade,
74 significant achievements in potentiometric sensing have been reported that could widen the
75 application of ISEs in freshwater studies, most notably improved selectivity and low detection
76 limits that can reach nanomolar concentrations for some analytes.¹⁰⁻¹² The introduction of the
77 solid-contact (SC) design makes ISEs more robust and insensitive to high pressures and also
78 allows storage in dry conditions.¹³⁻¹⁵ Thus, SC-ISEs, which were mainly used under controlled
79 laboratory conditions until now have evolved into promising tools both for limnologists and
80 managers of lakes and river basins to carry out *in-situ* measurements in the water column at high
81 temporal and spatial resolution. The current lack of systematic studies and protocols for the *in-*
82 *situ* application of SC-ISEs and hence lack of commercialization, has motivated the presented
83 work.

84 In this manuscript, we aim to present a profiling system for *in-situ* measurements in lakes and
85 investigate its applicability for two designs of ammonium selective solid contact ISEs and also
86 illustrate advantages and limitations of the individual designs. The system was validated in the
87 stratified eutrophic Lake Rotsee (Luzern, Switzerland) with a steep oxycline. NH_4^+ is one of the
88 dominant forms of dissolved nitrogen in fresh water systems generated by heterotrophic bacteria
89 as the primary nitrogenous end product of decomposition of proteins and other N-organic
90 compounds. As it is photosynthetically assimilated, stored, transformed and excreted by aquatic
91 organisms, turnover rates for NH_4^+ -N are rapid in water and thus NH_4^+ concentrations are

indicative of zones of high biogeochemical activity.¹⁶ Since concentrations are commonly low, NH_4^+ contents of water samples can change quickly and markedly. Storage of samples can cause unavoidable changes after classical sampling. Thus *in-situ* chemical profiling of ammonium at the centimeter scale can shed more light on biogeochemical drivers and factors governing the growth of algal blooms, which is important for the management of a number of ecosystem services linked to water quality and eutrophication.¹⁷

We employed two different sensor designs for *in-situ* profiling: a single layer design based on a single composite polyvinyl chloride (PVC) membrane impregnated with carbon nanotubes (CNTs) as a transducer and a double layer design made up of a plasticizer-free methyl methacrylate-decyl methacrylate copolymer (MMA-DMA) sensing layer on top of a conducting polymer poly(3-octylthiophene-2-5-diyl) (POT) layer as a solid contact. Both designs were adapted for NH_4^+ analysis following previous reports.^{12,18}

EXPERIMENTAL SECTION

The single layer design electrode was fabricated following Zhu et al.¹⁸ and the double layer design by adapting the basic protocol of Chumbimuni-Torres et al.¹² and modifying the membrane composition to yield a NH_4^+ selective SC-ISE. A detailed description of electrode preparation, reagents, and laboratory tests can be found in the supporting information (SI).

Profiling Ion Analyzer

The sensing system for the ISE measurements was integrated into a custom built Profiling Ion Analyzer (PIA; see Kirf et al.⁴ for details). For *in-situ* deployment, the SC-ISEs were connected to a waterproof galvanically isolated potentiometric sensing system in order to preclude cross-talk between the measuring units. For stability and noise rejection, an instrumentation amplifier (BURR-BROWN, INA116, Texas Instruments, USA) with ultra-low input bias current (3 fA) and a high common-mode rejection (84 dB) was used. The EMF for each indicator electrode (mini glassy carbon electrode, Metrohm AG, Switzerland) was measured against a separate solid-state reference electrode (MRX11 NT-sensors S.L., Spain) by using a Platinum wire as common solution ground (INA116 datasheet, BURR-BROWN).¹⁹ All data was recorded by a Z-Brain data logger (Schmid Engineering Systems AG, Switzerland). In addition to the ISE system, PIA was equipped with additional sensors to characterize the water column, specifically a

photosynthetically active radiation (PAR) sensor (193SA spherical sensor, LI-COR, USA), a CTD probe for measuring conductivity, temperature and depth (XR-420, RBR Ltd., Canada) and needle type optodes for measuring dissolved oxygen concentrations (PreSens - Precision Sensing GmbH, Germany). A syringe sampler was integrated into the PIA system that allowed retrieval of 12 syringe water samples at different depths with a volume of 60 mL along with simultaneous recording of EMF by ISE and all other integrated measurements.

Field site

Lake Rotsee is a small lake in Canton Luzern (Switzerland) with a surface area 0.48 km², mean depth of 9 m and a maximum depth of 16 m. Stratification of the lake starts in spring and continues until late autumn. During the stratification period the chemocline develops at 8-11 m depth and anoxic conditions are established within the first month of stratification in the hypolimnion.²⁰ Lake Rotsee was chosen as a study site due to its steep solute and redox gradients across the oxycline, permitting evaluation of the ability of SC-ISEs to detect changes in NH₄⁺ concentration and their performance under conditions as they typically occur in temperate lakes.

Profile recording

In-situ profiles were recorded during the stratification period in August 2013 (first study) and July 2014 (second study). In the first study the single layer CNT-PVC composite based SC-ISEs were deployed (abbreviated here as SL-CNT) and during the second campaign the double layer design based on MMA-DMA layer on top of a POT layer was tested in the field (abbreviated here as DL-POT). PIA was deployed with an electric winch that allowed maintenance of a very low constant profiling speed (5 mm/s). The data was recorded in time steps of 0.5 seconds. Ammonium-sensing SC-ISEs were deployed along with a syringe sampler and samples were taken simultaneously during the profile recording at different depth intervals to calibrate the SC-ISE response *in-situ*. Employing a syringe sampler instead of a conventional sampler avoided possible smearing of gradients and peaks in the water column due to its high spatial resolution of approximately 7.5 cm compared to classical water samplers with a spatial resolution of about 50 cm.

Lab analyses of syringe samples

Total sulfide and ammonium was determined by spectrophotometric analysis following Cline et al.²¹ and Parsons et al.,²² respectively (Figure 2). Concentrations of K⁺, Ca²⁺, Mg²⁺ and Na⁺ were determined using ion-chromatography (SI Table S-1).

RESULTS AND DISCUSSION

Choice of sensor design

The focus of this manuscript is the *in-situ* application of two types of NH_4^+ SC-ISEs integrated with PIA in a eutrophic lake with steep NH_4^+ and redox gradients. We were inclined to adapt POT-based sensors for NH_4^+ because of their quality with respect to their detection limit ($\sim 0.22 \mu\text{M}$, this study), lack of drift in long term potential monitoring under lab conditions, excellent stability over changing redox and pH conditions, lack of drift in water layer tests and encouraging reports^{23,24} on the design and materials. The employed membrane matrix (MMA-DMA) has a diffusion coefficient ~ 1000 times lower than PVC, which is the conventional material for membrane matrices.²⁵ The lower diffusion coefficient translates into lower detection limits. Clear advantages of the transducer (POT) are the ease of deposition of due to its solubility in organic solvents, the ability to achieve lower detection limits by facilitating small ion-fluxes between ion selective membrane and solid contact layer, the excellent properties as an ion to electron transducer and its commercial availability in a reduced and semiconducting form.²⁶ Since light sensitivity can limit the use of POT-based ISEs under field conditions,²⁷ we chose to test the single layer design with carbon nanotube (CNTs) as ion to electron transducer which served as an alternative electrode design. Previous studies claimed that CNTs are not sensitive to light,^{28,29} changes in pH and redox potential.^{18,30,31} The ease of application of the membrane solution with dispersed CNTs as transducer on a glassy carbon substrate was the major reason to employ composite membrane design for CNT based SC-ISEs. Also the commercial availability of all membrane components directed us to test the field applicability of this single layer design.

Quality checks on electrode response, redox, pH sensitivity, and water layer formation were performed prior to the *in-situ* measurements (Table 1 and SI). These tests revealed almost no drifts in potential during the water layer test (Figure S-2). Also pH and redox sensitivity tests did not reveal any significant changes in potential for the double layer design (Table 1 and SI Figure S-3 and S-4) and only slight changes in redox sensitivity for the single layer design (Table 1 and SI Figure S-3). The detection limit for DL-POT SC-ISEs was $\sim 2.2 \times 10^{-7} \text{ M}$ and for SL-CNT SC-ISEs was $\sim 2.6 \times 10^{-7} \text{ M}$, showing linear responses within the range $\log c_{\text{NH}_4^+} = -6$ and -3 (Table 1

and SI Figure S-1). The response time ($t_{95\%}$) was calculated according to IUPAC conventions and was found to be less than 10 s after changing the activity of the test solution.

Physico-chemical conditions in the Lake Rotsee

Temperature, oxygen and sulfide profiles show the typical behavior frequently encountered in eutrophic lakes during the stratification period and were similar during both campaigns (Figure 1 and 2). During the first campaign the thermocline was observed at a depth from 4.5 - 6.5 m with a drop in temperature from 24 °C to 14 °C, while in the second study the thermocline extended between a depth of 5.0 - 9.0 m and the temperature dropped from 20 °C to 11 °C in this zone. A 2 m thick oxycline started below the thermocline at 8.0 m, where the O₂ concentration dropped from 650 µM to a sub-micromolar level in the first study and from 480 µM to a sub-micromolar level at about 10 m depth during the second study (Figure 1A, 1B). Below 10 m, sulfide was detected and its concentration increased with depth. A maximum concentration of 140 µM during the first study and 147 µM in the second field study was detected at 14 m depth (Figure 2A, 2B). The NH₄⁺ concentration measured by spectrophotometry increased from 3.0 µM at 2.0 m depth to 280 µM at the lake bottom in the first study and from 2.0 µM at 2.0 m depth to 219 µM at 14 m in the second study. The K⁺ concentration was relatively constant throughout the water column. During the first study it ranged from 33 - 45 µM, while in the second study it was observed to be 41 - 52 µM (Figure 2A, 2B, SI Table S-1).

In-situ calibration of ISEs

The baseline EMF value (E^0) for a SC-ISE is not absolute but depends on many factors such as the conditioning state of the sensing membrane, the matrix in which measurements are performed, leaching of membrane components etc.^{32,33} Thus to have control on varying E^0 and drift experienced in the field, which is inherent with ISE applications, frequent calibration is needed for each profile to estimate reliable concentration profiles from electrode response. High resolution sampling during profile recording ensured an optimal calibration of EMF response against ammonium concentration values by excluding spatiotemporal misalignment between measurements. The syringe samples were also analyzed for other ions, which might interfere with ammonium analysis by the proposed SC-ISEs (e.g. K⁺, Na⁺, Mg²⁺, Ca²⁺). Since the concentrations of major dissolved ions and thus also ionic strength are relatively constant within the lake water column (Figure 2A and B, Table S-1) and NH₄⁺ is not involved in many complexation reactions, we considered NH₄⁺ concentrations and not activities. During both

campaigns, we tested two electrodes in parallel. The *in-situ* calibration curve, where the EMF values at respective depth points were plotted against $\log c_{\text{NH}_4^+}$ values obtained from spectrophotometric analysis showed a sub-Nernstian response ranging from 44.7-50.8 mV/decade (Figure 3A, Table 2) for all four electrodes. The existence of sub-Nernstian response indicated the presence of interferences.^{34,35} Therefore, we developed a data processing and correction scheme by critically examining the concentrations of all possible interfering ions present in individual syringe samples and the EMF value at the corresponding water depths (SI Table 1). The main quality criteria of the data correction was how closely the corrected EMF- $\log c_{\text{NH}_4^+}$ displayed the Nernstian slope. In the anoxic part of the lake SL-CNT1 and SL-CNT2 were found to undergo sulfide poisoning (discussed in detail in the section *sulfide sensitivity*) so EMF values at lower depths were not considered for the *in-situ* calibration. Also at first two depth points the EMF values displayed by DL-POT1 and DL-POT2 were lower than the trend for reasons not known to us and were therefore not considered for the calibration.

Cation interference and drift correction

A potential explanation for the sub-Nernstian response is interference from other cations, especially in the upper part of the water column, since the concentration of NH_4^+ at a depth above 5 m was observed to be very low ($<5 \mu\text{M}$). The selectivity coefficient $K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}}$ for the PVC membrane with ammonium ionophore, nonactin, is 0.130.³⁶ For the MMA-DMA membrane $K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}} = 0.145 \pm 0.01$, which was experimentally determined by the fixed interference method³⁴ and found to be similar to the value reported by Muller et al..³⁶ The high selectivity coefficient for potassium and its concentration ($\sim 38 \mu\text{M}$ and $\sim 46 \mu\text{M}$ for the first and the second study, respectively), (Figure 2, SI Table 1) suggest that it is the most interfering ion and can introduce a concentration error of 5-7 μM to the measurements. For all other possible interfering ions, i.e. Ca^{2+} , Na^+ and Mg^{2+} , the respective selectivity coefficients and concentrations in the water column were low enough to discard the possibility of substantial effect on the measurements (SI Table 1).³⁶ Plotting EMF values against $\log (c_{\text{NH}_4^+} + c_{\text{K}^+} \times K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}})$ resulted in super-Nernstian slopes for all ISEs ranging from 67.96-75.69 mV/decade (Table 2). Very low ammonium concentrations (1-10 μM) in the epilimnion caused the increase in the slope after consideration of the interference factor ($c_{\text{K}^+} \times K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}}$) (Figure 3A and 3B).

To address this super-Nernstian response, we determined an additional value for drift correction d [mV/s], a new intercept E^0 [mV] and a new slope S [mV/decade].

The expression

$$\log (c_{\text{NH}_4^+} + c_{\text{K}^+} \times K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}}) = (\text{EMF} - (d \times t) - E^0) / S \quad (\text{Eq. 1}),$$

where, EMF is expressed in [mV] and t is the time passed since the start of profiling [s], was fitted to the observed $\log (c_{\text{NH}_4^+} + c_{\text{K}^+} \times K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}})$ by minimizing the least squares difference.

This correction resulted in close to Nernstian responses, which suggests that the super-Nernstian slopes observed before fitting Eq. 1 were mainly caused by electrode drift in the ISEs (Figure 3C). The drifts were relatively similar for both designs of electrodes (Table 2).

The long-term stability experiment and the water layer test in the laboratory could not account for the drift witnessed during the field deployment (Table 1). A long-term potential drift due to light dependence of the DL-POT design can be ruled out since the SL-CNT sensors show similar drift values. The electrode drift observed in the field applications can be due to the interaction of the membrane surface with dissolved organics and the leaching of membrane components due to continuous exposure of the sensor surface to lake water, which might alter the membrane surface of the electrode.^{32,37} A parallel drift¹³ with slow and unidirectional changes in E^0 was observed. The drift correction obtained by minimizing the least square difference resulted in a single drift value which allowed rectifying the high resolution EMF profiles for the presented *in-situ* application (Table 2).

In the next step the corrected calibration parameters were applied to the continuous EMF profiles. As the potassium concentration throughout the water column was observed as almost constant, high resolution profiles for $c_{\text{NH}_4^+}$ were calculated by subtracting the depth average of $(c_{\text{K}^+} \times K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}})$ in order to correct for the K^+ interference. The correction factors were 5.03 μM and 6.78 μM respectively for the first and the second field study. The average error between SC-ISE derived concentration values in the high resolution profile and spectrophotometrically determined values from syringe samples at corresponding depths was calculated. It was found to be 1.45 μM , 2.70 μM for SL-CNT1 and SL-CNT2, respectively, down to 10 m depth and 6.90 μM , 8.04 μM for DL-POT1 and DL-POT2, respectively, to 13 m depth.

In the epilimnion above 5 m depth, NH_4^+ concentrations were $<5 \mu\text{M}$, meaning that K^+ had a major contribution to the EMF signal and ammonium concentrations were practically below the

limit of detection for the presented SC-ISEs from 2 to 5 m. From 5 to 10 m depth it was possible to identify small scale features like peaks and gradient changes in the range (insets in Figure 5A and B). Below 11 m in the hypolimnion the SL-CNT ISEs suffered from a disturbance indicated by a strong decrease of the electrode signal in spite of increasing NH_4^+ concentrations. This was also reflected in the concentration profiles delivered by SL-CNT ISEs (Figure 5A) while the DL-POT ISEs displayed increases in EMF with increasing ammonium concentrations in the hypolimnion and revealed high resolution concentration profiles which followed the concentration trend after application of the calibration protocol (Figure 5B).

Light-sensitivity

While POT-based sensors were reported to be light sensitive under strong irradiation,²⁷ none of the profiles recorded with the DL-POT type sensors revealed any light disturbance. This suggests that this type of sensor is suitable for field measurements under moderate light conditions as they are encountered during cloud cover. Light intensities measured by a PAR sensor (LI-190, LICOR, USA), had a maximum at $\sim 200 \mu\text{Em}^{-2}\text{s}^{-1}$ (Figure 1B) owing to diffused light conditions during the second field study.

Sulfide sensitivity

In the first study, we observed a strong discrepancy between the NH_4^+ concentration estimated by spectrophotometry and by SL-CNT1 and SL-CNT2 starting at $\sim 11\text{m}$. This is due to strong decrease in EMF values in spite of increasing NH_4^+ concentrations. At 14 m depth the NH_4^+ concentration was about $280 \mu\text{M}$, but estimates from SL-CNT1 and SL-CNT2 were as low as $40 \mu\text{M}$, due to a decrease of EMF of about 50 mV. This severe discrepancy in the hypolimnion could neither be attributed to the linear consistent electrode drift nor be explained only by a possible redox sensitivity (Table 1, SI Figure S-3). The decrease in EMF of SL-CNTs coincided with the appearance of sulfides (Figures 2A and 5A). The possibility of the solid state reference electrodes being sensitive towards increasing sulfide concentrations in the hypolimnion was discarded by performing a sulfide sensitivity check (data not shown) in which EMF values were recorded against a double junction Ag/AgCl reference electrode under increasing sulfide concentrations up to $300 \mu\text{M}$ of total sulfide ($0.0014 \text{ mV}/\mu\text{M}$).

In order to assess the possible influence of sulfides, a sulfide sensitivity test for SL-CNT SC-ISEs was performed. EMF of SC-ISE was recorded in N_2 flushed 10^{-4} M NH_4Cl solution buffered at pH 7-8. Na_2S solution was added to raise the sulfide concentration stepwise by 100

μM . Before sulfide addition a drift of -0.001 mVs^{-1} was observed, which was similar to the initial drifts recorded in the lake (Table 2). After the addition of Na_2S , the drift increased significantly. On average, the drift increased by -0.008 mVs^{-1} after each addition step (Figure 4), while no instantaneous change in potential was observed. The electrode drift in the sulfidic zone at the lake bottom was even higher (-0.015 to -0.035 mVs^{-1}). Profiling data also revealed that at only about $20 \mu\text{M}$ sulfide concentration, the induced drift masked the electrode response to NH_4^+ concentration (Figure 5A). The laboratory test as well as the change of the EMF recorded in the sulfidic zone suggests that sulfides react continuously with the sensor membrane instead of causing an instantaneous change in the membrane potential. In contrast, high-resolution concentration profiles obtained by DL-POT ISEs agreed well with the ammonium concentrations at sampling points from around 2 m down to 13 m where the total sulfide concentration was around $75 \mu\text{M}$ (Figure 2B and 5B). The sulfide sensitivity test for the DL-POT sensors revealed almost no change in EMF values with successive increments of Na_2S solution till $200 \mu\text{M}$ of total sulfide concentration. The average drift was observed to be 0.0003 mVs^{-1} . The drift values plotted against the increasing sulfide concentration, clearly show that the drift for the double layer design is negligible and is constant under increasing sulfide concentrations while that for the single layer design changes (Figure 4). While high resolution profiles obtained by both designs follow the trend of ammonium concentrations in discrete samples throughout the oxic zone of the lake (insets Figure 5), the DL-POT design also delivered concentration profiles in sulfidic-anoxic region (Figure 5B). Although the SL-CNT design was observed to be sensitive in sulfidic regions, it is possible to obtain high resolution profiles with this type of sensor in anoxic but not sulfidic zones in lakes. This implies that the DL-POT type SC-ISEs are suitable for the *in-situ* application even in sulfidic environments in the lake water column. The active involvement of the single layered membrane with dispersed CNTs in sulfide sensitivity could be addressed in future by adapting a double layer design as described in recent studies.^{30,38,39}

New insights gained by high resolution NH_4^+ profiling

High-resolution NH_4^+ profiles in combination with dissolved oxygen measurements can shed light on the zonation of primary production and mineralization of organic matter in the water column. The results from the field campaign in August 2014 with the DL-POT SC-ISEs (Figure 1B and 5B) show increase in NH_4^+ concentration at the oxic-anoxic interface at approximately 10 m which is typical for lakes with an anoxic hypolimnion (Figure 5B).²⁰ But the peak in NH_4^+

concentration between 6-8 m is quite surprising. It is interesting to note that this peak in NH_4^+ concentration is situated exactly at the oxygen minimum (7 m) (inset Figure 5B), observed between two oxygen maxima at 6 m and 8 m (Figure 1B). Two oxygen peaks in the profile suggest existence of two groups of photosynthesizing organisms with different requirements of light and nutrient supply. A likely explanation for the NH_4^+ peak is the mineralization of organic substrate sinking from the upper zone of intense primary production at 6 m. The released NH_4^+ in turn is consumed in both zones with intense phototrophy, while a part is likely oxidized to NO_3^- . Features like these are normally missed when field campaigns rely only on the conventional water sampling or could be mistaken for artifacts since, peaks show up as only one data point. With *in-situ* profiling using SC-ISEs we were able to resolve the whole peak instead of only obtaining a single, coincidental data point (inset Figure 5B), adding credibility to the observations.

CONCLUSION

In-situ profiling measurements at high spatial and temporal resolution are becoming increasingly important for limnologists to study specific regions of intensive biogeochemical activity (reaction hotspots) within a temporally dynamic and spatially heterogeneous aquatic environment. The presented profiling setup in combination with ammonium selective SC-ISEs is a first step in this direction. Issues like reactive solutes, interferences from other ions and unexpected signal drift during the actual deployment in lake water posed challenges on sensor design and data processing. In our study, the sulfide poisoning was tackled by choosing a double layer design with a plasticizer free polymeric sensing membrane. The interference and drift encountered were compensated for by empirical corrections. An *in-situ* calibration protocol based on parallel sampling during profiling followed by quantitative analysis via standard laboratory procedures was developed. On following such a protocol, the obtained high resolution concentration profiles not only agreed with the concentration values in discrete samples but also revealed fine-scale features in between sampling points. Although the derived *in-situ* calibration protocol was found suitable for the reported application, further studies should test the general applicability of the presented calibration and data correction scheme. In addition, the profiling system could be equipped with a facility to allow *in-situ* calibration and drift monitoring.

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TABLES

Table 1. Comparison of two designs with respect to detection limits, long term stability and tests for water layer, pH sensitivity and redox sensitivity.

Sensor design	Detection limit	Long term stability ^a	Water layer test ^a	pH sensitivity test ^b	Redox sensitivity ^a
	(M)	Drift (mV/h)		(mV/decade)	(mV/decade)
SL-CNT	2.6×10^{-7}	<1	No drift	No drift ¹⁸	3.4
DL-POT	2.2×10^{-7}	3.6	No drift	0.07	0.6

^a was carried out in 10^{-3} M NH_4^+ solution

^b was carried out in 10^{-4} M NH_4^+ solution

Table 2. Values of drift correction, optimized slopes and intercept determined by the *in-situ* calibration.

SC-ISE	Drift	Slope	Intercept
	(mV/s)	(mV/decade)	(mV)
<i>Without Correction</i>			
SL-CNT1	-	50.89	294.33
SL-CNT2	-	44.67	212.22
DL-POT1	-	50.59	411.34
DL-POT2	-	50.74	439.11
<i>Correction for the K^+ interference</i>			
SL-CNT1	-	75.69	400.17
SL-CNT2	-	67.53	310.32
DL-POT1	-	67.98	477.77
DL-POT2	-	67.96	504.79
<i>Drift correction by minimizing square difference</i>			
SL-CNT1	0.011	57.82	269.41
SL-CNT2	0.004	63.54	276.02
DL-POT1	0.012	61.04	431.71
DL-POT2	0.005	60.14	466.80

FIGURES

Figure 1. Profiles of dissolved oxygen concentration, temperature and photosynthetically active radiation (PAR) in Lake Rotsee in the first (August 2013) (A) and the second (July 2014) (B) field study.

Figure 2. Concentration profiles of ammonium, potassium and sulfide in the first (A) and the second (B) field study determined in discrete syringe samples.

Figure 3. Concentrations of NH_4^+ measured spectrophotometrically vs. EMF (A), concentration values obtained on potassium interference inclusion vs. EMF (B), concentration values obtained on potassium interference inclusion vs. drift corrected EMF (C), values in brackets are the slopes of linear regression.

Figure 4. Sulfide sensitivity test in 0.1 mM NH_4Cl buffered at pH 7-8 under nitrogen, for both designs of SC-ISEs.

Figure 5. Profiles of NH_4^+ concentrations in Lake Rotsee recorded by SC-ISEs for the first (A) and the second (B) field study and NH_4^+ concentrations in discrete syringe samples by spectrophotometry. Insets show the same dataset at the low concentration range.

“For Table of Contents Only”

1 **Supporting information for**
2 **In-situ ammonium profiling using solid contact ion**
3 **selective electrodes in eutrophic lakes**
4

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17 # Equal contribution

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29 EXPERIMENTAL SECTION

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31 *Chemicals*

32 Nonactin (ammonium ionophore I), sodium tetrakis [3,5-bis(trifluoromethyl) phenyl]borate
33 (NaTFPB), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) and
34 tetrahydrofuran (THF) were purchased in selectophore grade from Sigma-Aldrich.
35 dioctylsebacate (DOS), high molecular weight poly(vinyl chloride) (PVC), block polymer
36 PEO-PPO-PEO (Pluronic F-127), conducting polymer Poly(3-octylthiophene-2-5-diyl),
37 chloroform, methylene chloride, NaCl, NaOH, NH₄Cl, K₄Fe(CN)₆·3H₂O, K₄Fe(CN)₆, Na₂S
38 and HNO₃ were purchased from Sigma-Aldrich. Multiwall carbon nanotubes (MWCNTs)
39 with purity > 95%, outside diameter < 8 nm, inside diameter 2-5 nm, length 0.5-2.0 μm were
40 purchased from NanoAmor Inc., MMA-DMA copolymer was obtained from the research
41 group of Prof. Eric Bakker, University of Geneva, and was synthesized according to the
42 protocol by Heng et al.¹

43 Aqueous solutions were prepared by dissolving appropriate salts or diluting standard
44 solutions in Nanopure deionised water with a resistance of 18.2 MΩ cm⁻¹. All standard and
45 conditioning solutions with a concentration of 1 mM or less were freshly made prior the use.

46 *Indicator and reference electrodes*

47 A mini glassy carbon electrode (Metrohm AG, Switzerland) was used as an indicator
48 electrode both in the lab and in the field. A double junction Ag/AgCl reference electrode
49 (Metrohm AG, Switzerland) containing 3M KCl as an inner solution and 1M CH₃COOLi as
50 a bridge electrolyte was used for the lab experiments. Solid-state miniaturized reference
51 electrodes RE MRX11 (NT Sensors, Spain) were used for in-situ measurements. The proper
52 functioning of these electrodes was also tested in the laboratory.

53 *Preparation of SL-CNT type SC-ISE*

54 ISEs with PVC based membranes were prepared following Zhu et al.² 0.5 wt% of MWCNTs
55 and 5 wt% of block polymer Pluronic 127 were dispersed in 1ml THF under the sonication
56 for at least 3 h. Then 1 wt% of ionophore, 5 mmol/kg NaTFPB, PVC and plasticizer DOS in
57 ratio 1:2 (by weight) were dissolved in 1 mL THF containing a dispersion of MWCNTs and
58 Pluronic 127 in order to give a 100 mg of the total mass of membrane cocktail. About 70 μL
59 of membrane cocktail were applied by drop casting on the top of the indicator electrode. A 2
60 mm high fringe constructed using a PVC tube was used to prevent the membrane cocktail
61 from flowing from the electrode tip. Prepared ISEs were left to dry overnight at room

62 temperature. Before calibration ISEs were conditioned for 24 hours in 1 μ M NH_4Cl followed
63 by 48 hours in 1 nM NH_4Cl .

64 *Preparation of DL-POT type SC-ISE*

65 For preparation of MMA-DMA-POT based SC-ISE the basic protocol by Chumbimuni-
66 Torres et al.³ was adapted. The membrane was prepared by dissolving a total of 200 mg of
67 components in 1.5 mL of methylene chloride: ammonium ionophore (I) (15 mmol kg^{-1}),
68 NaTFPB (5 mmol kg^{-1}), ETH 500 (10 mmol kg^{-1}) and MMA-DMA. The membrane cocktail
69 was degassed by sonication for 10 min. Glassy carbon electrodes were cleaned and washed
70 with methylene chloride. The indicator electrode was introduced in the PVC tube at ~ 1 mm
71 depth and 0.25 mM POT solution in chloroform was applied by drop-casting 10 μL , repeated
72 three times. The film was left to dry for an hour and then 80 μL of membrane cocktail
73 solution was applied on top of the POT layer and was allowed to dry overnight. Electrodes
74 were conditioned before calibration by immersing them in 1 mM NH_4Cl for 1 day followed
75 by conditioning in 1 nM NH_4Cl for 2 days.

76 *Laboratory tests*

77 During the lab experiments, a 16-channel EMF potentiometer (Lawson Labs Inc, USA) was
78 used to record EMF. Water layer test was carried out as described in Fibbioli et al.⁴. Before
79 the water layer test, SC-ISEs were conditioned in 1 mM NH_4Cl solution.

80 The redox sensitivity was tested by measuring potential in a solution with 1 mM total
81 concentration of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ redox couple. The concentration ratios of the red-
82 ox couple were changed from 1:10 to 10:1.

83 The sulfide sensitivity test was carried out by monitoring EMF of SC-ISE on increasing
84 concentrations of sulfide by addition of Na_2S 0.01 M in 0.1 mM NH_4Cl solution till 200 μM
85 of the total sulfide concentration by maintaining lake water pH (pH ~ 7 -8) under nitrogen.

86 The pH sensitivity test was performed for the DL-POT SC-ISEs in 0.1 mM NH_4Cl by
87 adjusting pH with 0.01 M NaOH .

88

89 RESULTS

90

91 *Laboratory tests*

92 SL-CNT electrodes exhibited detection limits $\sim 2.6 \times 10^{-7}$ M with linear response
93 57.2 ± 1.1 mV/decade while detection limits for double layer design were $\sim 2.2 \times 10^{-7}$ M with
94 linear response 58.2 ± 0.2 within the range $\log c_{\text{NH}_4^+} = -6$ and -3 (Figure S-1). In order to

95 assess the performance of the setup for *in-situ* measurements, the electrodes were first
96 calibrated in the laboratory by measuring changes of the potential of ion selective electrodes
97 against the solid-state reference electrodes and the EMF was recorded with amplifiers
98 integrated in PIA. Both the designs exhibited Nernstian response on the PIA setup. DL-POT
99 electrodes exhibited offset of ~20 mV during calibration, which is acceptable for similarly
100 built SC-ISEs^{5,6}, can arise due to slight differences in fabrication and conditioning process.

101 *Water layer test*

102 Signal stability of electrodes is an essential prerequisite for their practical application in
103 environmental monitoring in order to get reliable measurement data over longer time
104 periods. The test was performed to check for the formation of water layer in between solid
105 contact and membrane which leads to drifts. If there is no undesirable water layer between
106 the ion-selective membrane and transducer or conductor, electrodes do not exhibit positive
107 potential drift after the replacement of the solution containing primary ions with one
108 containing interfering ions. Both designs described in this manuscript didn't show any
109 significant changes in a potential indicating that there is no formation of undesirable water
110 layer (Figure S-2).

111 *Redox sensitivity test*

112 In temperate lakes thermal stratification of water column can develop in late summer and
113 continue till late autumn. In the hypolimnion of nutrient rich lakes, dissolved oxygen is
114 consumed in the mineralization processes of organic substances and along with the oxygen
115 gradient also a redox gradient develops. Concentrations of reduced compounds can increase
116 when the content of dissolved O₂ is less than 3.12 µM⁷. In order to evaluate the suitability of
117 the fabricated electrodes to work across a chemocline, redox sensitivity tests were
118 performed. SL-CNT SC-ISEs exhibited a potential change of -3.4±0.2 mV/decade. In
119 contrast, Zhu et al¹. didn't observe any changes in potential when switching ratios of the
120 redox couple [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ from 3:7 to 7:3. The MMA-DMA-POT based
121 electrodes exhibited potential change of 0.7±0.2 mV/decade (Figure S-3).

122 *Sulfide sensitivity test*

123 Sulfides may appear in the anoxic zone of eutrophic lakes with maximal concentrations near
124 sediment water interface. The maximum concentration of sulfides was found to be ~150 µM
125 during both field studies. The sulfide test for SL-CNT electrodes was performed by addition
126 of 0.01 M Na₂S solution to a 10⁻⁴ M NH₄Cl solution till final Na₂S concentration was 200
127 µM and by recording EMF of the SC-ISEs over time under nitrogen. We calculated drift in

128 the EMF over time for each design and plotted the drift values against the increasing sulfide
 129 concentration (Figure 5). Each addition at lake water pH (7-8) showed continuous decrease
 130 in the EMF over time for SL-CNT SC-ISEs. While the double layer electrodes exhibited
 131 negligible change in EMF (0.0003mV sec^{-1}) on increasing sulfide concentration.

132 *pH sensitivity test*

133 The pH sensitivity test was performed for double layered DL-POT based SC-ISE to check
 134 for the stable EMF over the range of pH encountered in lake water. The pH sensitivity test
 135 did not show any significant changes in EMF values over pH 5.5-8.5 (Figure S-4). As
 136 reported by Zhu et al.² SL-CNT based electrode show no pH sensitivity.

137

138 **Figures for SI**

139

140 **Figure S-1** Calibration (A) SL-CNT1 and SL-CNT2, (B) DL-POT1 and DL-POT2

Figure S-2 Water layer test (A) SL-CNT1 and SL-CNT2, (B) DL-POT1 and DL-POT2

Figure S-3 Redox sensitivity test. Values in brackets are slopes of the linear regressions.

Figure S-4 pH response of DL-POT based SC-ISE

Table for SI

Table S-1 Selectivity coefficients for Nonactin based ammonium sensing membranes by SSM⁸⁻¹⁰ and mean concentration of possible interfering ions observed during two field studies

Interfering Cation (b)	Selectivity coefficient $K_{NH_4^+, K^+}^{pot}$	Mean concentration (M)	
		First study	Second study
K^+	0.13	3.87×10^{-5}	4.65×10^{-5}
Na^+	1.26×10^{-3}	1.5×10^{-3}	1.2×10^{-3}
Mg^{2+}	3.16×10^{-6}	2.0×10^{-4}	2.2×10^{-4}
Ca^{2+}	1.58×10^{-5}	3.05×10^{-4}	2.5×10^{-4}

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