

Robust Solid-Contact Ion Selective Electrodes for High-Resolution *In Situ* Measurements in Fresh Water Systems

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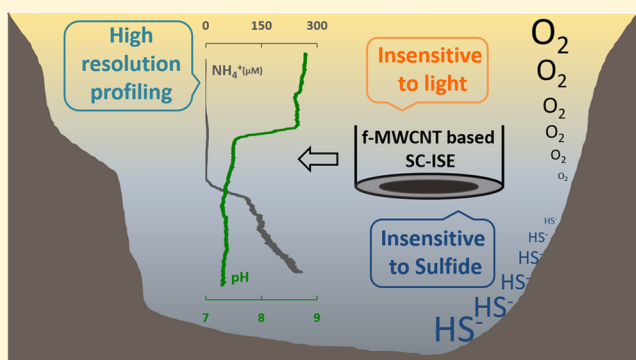
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S Supporting Information

ABSTRACT: Biogeochemical processes are often confined to very narrow zones in aquatic systems. Therefore, highly resolved *in situ* measurements are required to study these processes. Potentiometric solid-contact ion selective electrodes (SC-ISEs) are promising tools for such measurements. SC-ISEs show good performance in analyses under controlled experimental conditions. Very few sensor designs, however, can sustain the challenges of natural water matrices and external environmental conditions during *in situ* applications. We fabricated ammonium and pH selective SC-ISEs with functionalized multiwalled carbon nanotubes (f-MWCNT) as a solid contact. Their functionality was tested in the laboratory and applied *in situ* for vertical profiling in a eutrophic lake.

Sensors were insensitive to strong redox changes, high sulfide concentrations, and bright daylight conditions during the application in the lake. In addition, sensors are easily fabricated and exhibit short response times (<10 s). The proposed design of SC-ISEs based on f-MWCNTs is quite suitable for high-resolution *in situ* profiling of ionic species in fresh water lakes.



INTRODUCTION

Tracking dynamic biogeochemical processes taking place on a very narrow spatial scale requires high-resolution *in situ* measurements. For example, to study processes occurring at very steep oxic–anoxic interfaces in lakes with low mixing¹ or to investigate the patchiness of phytoplankton communities depending on small-scale chemical gradients in the water pocket surrounding the biomass,² *in situ* measurements with a spatial resolution in the range of <10 cm are needed. One promising approach for high-resolution profiling in lakes relies on integrating suitable solid-contact ion selective electrodes (SC-ISEs) with an *in situ* profiling setup.³ SC-ISEs are emerging tools in modern potentiometric analysis offering down to nanomolar detection limits,⁴ stable signals, and fast response times in the range of seconds.⁵ SC-ISEs comprise three components: a transducer, an ion selective membrane (ISM), and an electrical conductor. The ISM facilitates the formation of analyte-dependent phase boundary potential; a transducer mediates ion-to-electron conversion, and an electrical conductor further transfers this electron in the electrical circuit established for potentiometric measurements.⁶ SC-ISEs are promising for *in situ* profiling application as they offer inherent

advantages like an all solid-state pressure proof design and a flexible fabrication procedure with the possibility of utilizing a variety of materials to suit the needs of complex and challenging environmental matrices and conditions.⁷

The choice of the right design of SC-ISEs is important for the analysis of natural waters. Two designs for obtaining *in situ* high-resolution profiles in a eutrophic lake were recently explored.³ The double-layer (DL) design using the conducting polymer poly(3-octylthiophene) (POT) as a transducer forming a layer between a glassy carbon electrode (GCE) and an ISM proved to be superior to a single-layer (SL) design based on multiwalled carbon nanotubes (MWCNTs) as a transducer forming a single composite layer together with an ISM matrix on a GCE. The SL design was prone to sulfide interference. Apparently, the suspension of the MWCNTs in the ISM matrix allowed the reaction of sulfide with MWCNTs. In the DL design, the transducer layer (POT) was shielded by

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the layer of the ISM that kept reactive solutes such as dissolved sulfides from diffusing across the membrane. The potential stability delivered by POT is attributed to the POT–POT^{ox} redox couple at the GCE–POT interface and its lipophilic nature that prevents water-layer formation.⁴ Although POT proved to be insensitive to changing redox and pH conditions in the laboratory as well as in eutrophic lake systems, its performance is strongly limited by its sensitivity to light.^{3,4,8}

Thus, an alternative transducing material compatible with the environmental matrices and conditions is needed for *in situ* applications in natural waters. Carbon-based nanomaterial is an attractive choice over conducting polymers as its functioning is not affected by varying light conditions.⁸ Furthermore, as the transducing property is based on the capacitive mechanism,⁹ they are equally suitable for anions and cations.^{5,8} Despite these advantages, deposition of a homogeneous layer of MWCNTs remains a challenge, as they form an unstable dispersion in most solvents.¹⁰ Recently, a simple fabrication process of SC-ISEs based on lipophilization of MWCNTs was demonstrated by Crespo et al.⁸

Following this approach, we integrate functionalized multi-wall carbon nanotubes (f-MWCNT) as a solid-contact base layer on a GCE with a methacrylic copolymer-based cation selective membrane on top to form a DL design in this study. We demonstrate the suitability of this sensor design for *in situ* measurements for ammonium (NH₄⁺) and pH (H⁺) in a eutrophic lake. We compare this design with the DL POT-based design.³ The levels of both cations selected for this study vary greatly throughout the lake water column, with steep gradients at the redoxcline. NH₄⁺ is the most reduced member in the N cycle with energetically favored assimilation during primary production. It is released by mineralization of organic matter sinking through the water column and consumed via nitrification and primary production.^{11,12} Therefore, changes in the NH₄⁺ concentration are indicative of these processes. The high reaction rates of these processes, especially in eutrophic systems, result in narrow reaction hot spots and steep gradients, which can be observed only with high-resolution measurements. The activity of H⁺ determines the species distribution, e.g., in the inorganic C cycle. It also provides clues about the vertical zonation of redox reactions because pH is strongly influenced by various biologically mediated mineralization processes.¹³

MATERIALS AND METHODS

Sensor Design. Two types of transducing materials were used to fabricate SC-ISEs in a DL design. For one type, we used f-MWCNTs and POT. MWCNTs were oxidized to produce carboxylic acid groups followed by amide formation with octadecylamine to yield f-MWCNTs. Separate SC-ISEs for ammonium and pH were fabricated by depositing first a uniform transducer layer on a polished GCE (Supporting Information). Then, a methacrylic copolymer (MMA-DMA)-based, ion selective membrane matrix was drop-cast on top of the transducer layer. The ISM cocktail solution for ammonium (NH₄⁺) was prepared following the protocol of Athavale et al.³ and for pH (H⁺) by adapting the recipe of Crespo et al.¹⁴ The sensor quality was assessed by Nernstian response, redox and pH sensitivity, long-term stability, and water-layer formation (Supporting Information). Redox sensitivity was determined with the help of the [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ couple that creates the redox conditions relevant to those expected at the chemocline without reacting at or within the membrane.¹⁵

Field Site. Lake Rotsee, a eutrophic lake with a surface area of 0.48 km², an average depth of 9 m, and a maximal depth of 16 m, in Central Switzerland was chosen as the study site. It stratifies from spring until late autumn with a strong chemocline located between 8 and 11 m. Because of its eutrophic nature, steep redox and nutrient gradients are observed across the oxycline during the stratification period.¹⁶ The biogeochemical conditions in Lake Rotsee during the summer are ideal for testing chemical sensors as the lake offers a water column with various redox conditions and successive water layers characterized by diverse dissolved as well as particulate organics and inorganics.

In Situ Profiling. To assess the *in situ* performance of f-MWCNT-based SC-ISEs, they were deployed in eutrophic and dimictic Lake Rotsee during summer stratification. *In situ* profiles were recorded during the stratification period in July 2015 at night to compare the performance of POT- and f-MWCNT-based NH₄⁺ SC-ISEs. The second field study in September 2015 involved *in situ* profiling with f-MWCNT-based NH₄⁺ and H⁺ selective SC-ISEs to explore two cations with the same design under daylight conditions. The potentiometric sensing system was a part of a custom-built profiling ion analyzer (PIA) (see the Supporting Information and Figure S6). Syringe samples were taken simultaneously during the profile recording at different depth intervals. The pH was recorded on board by a hand-held pH meter for each syringe sample. Concentrations of ammonium in the oxic epilimnion and total sulfide were determined by spectrophotometric analysis following the procedures of Parsons et al.¹⁷ and Cline et al.¹⁸ (Supporting Information), respectively, and concentrations of ammonium in the hypolimnion were determined by ion chromatography (IC). Concentrations of K⁺, Ca²⁺, Mg²⁺, and Na⁺ in the water column were also measured by IC (Table S2).

In Situ Calibration. *In situ* calibration was performed following the procedure of Athavale et al.³ to correct raw electromotive force (EMF) values for cation interference and drift. Syringe sampling with ongoing profile recording ensured an optimal calibration of the EMF response versus concentration by excluding spatiotemporal misalignment between measurements. The values for drift correction d (millivolts per second), intercept E^0 (millivolts), and slope S (millivolts per decade) were determined by fitting $\log(c_a + c_b K_{a,b}^{\text{pot}})$ determined from syringe sample analyses to eq 1 using least-squares optimization:

$$\log(c_a + c_b K_{a,b}^{\text{pot}}) = (\text{EMF} - dt - E^0)/S \quad (1)$$

where EMF is expressed in millivolts, t is the time passed since the start of profiling (seconds), c_a is the concentration of the ion of interest (moles per liter), and c_b is the concentration of an interfering ion (moles per liter). The concentration of K⁺ throughout the water column was almost constant. High-resolution profiles for $c_{\text{NH}_4^+}$ were calculated by subtracting the depth average of $c_{\text{K}^+} K_{\text{NH}_4^+, \text{K}^+}^{\text{pot}}$ to correct for K⁺ interference. No correction was applied for other ions as the interference by all relevant ions was found to be negligible (Table S2). Because of the high selectivity of the H⁺ SC-ISEs (Table S2), no correction was necessary for the SC-ISE-based pH measurements.

RESULTS AND DISCUSSION

Quality tests were performed in the laboratory for the Nernstian response of SC-ISEs, their redox sensitivity, and

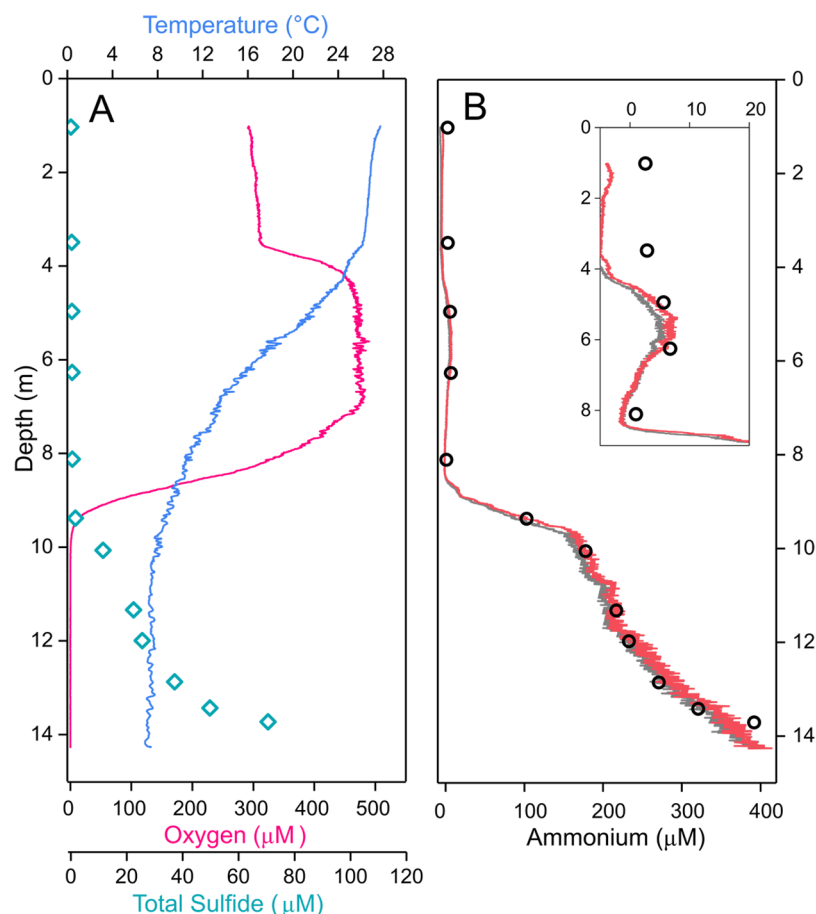


Figure 1. *In situ* profiles of dissolved oxygen, temperature, and total sulfide in July 2015 obtained simultaneously with the SC-ISE measurements in Lake Rotsee (A) and recorded by SC-ISEs to compare the performance of POT-based (red) and f-MWCNT-based (gray) ammonium sensors under dark conditions, where black circles represent ammonium concentrations in syringe samples taken simultaneously during the *in situ* profiling (B).

water-layer formation before the *in situ* application. The insets in Figure S1 show time traces of the EMF for NH_4^+ and H^+ with a change in concentration in nanopure water. All SC-ISEs show a Nernstian response, with slopes of 59.84 ± 1.7 mV/decade for NH_4^+ ($\log c_{\text{NH}_4^+} = -6$ to -3) and 55.6 ± 0.45 mV/decade for H^+ ($\log c_{\text{H}^+} = -9$ to -6) selective electrodes (Figure S1). The response time ($t_{95\%}$) was estimated to be <10 s for both sensors as determined following IUPAC conventions.¹⁹ The redox sensitivity test and water-layer tests did not show any significant changes in the EMF (Figures S2 and S3 and Table S3).

Lake Rotsee physicochemical conditions typical for summer stratification were encountered (Figures 1A and 2A). In July, the oxygen maximum was observed between 4 and 7 m, while in September, it was at around 7 m with a steep gradient going down from 500 to 0 μM within <0.75 m. The maximal temperature gradient shifted from 4 m in July to 7 m in September. The ammonium concentration in syringe samples analyzed in the laboratory was found to be close to 0–8.5 μM until 8 m, except for a small increase in July of 6.77 μM at a depth of 6.25 m followed a sharp increase from ~ 200 μM between 8 and 10 m going to 400 μM near 14 m in the anoxic region. On-board measurements of pH show a strong gradient of 0.85 units within 0.5 m starting at 6.9 m in September (Figure 2B). The maximal total sulfide concentration was ~ 70 μM in July and ~ 110 μM during the September campaign (Figures 1A and 2A).

The *in situ* calibration confirmed a Nernstian response for all sensor types throughout the water column (Table S1). High-resolution *in situ* profiles for ammonium and pH were obtained after applying the calibration parameters to the continuous EMF profile (Figures 1B and 2B). The response of POT- and f-MWCNT-based ammonium selective SC-ISEs during the July study is shown in Figure 1B when surface PAR values were <5 $\mu\text{E m}^{-2} \text{ s}^{-1}$ during the night profiling. The response of ammonium SC-ISE to small gradients in the epilimnion between 4 and 8 m (inset, Figure 1B) is confirmed by the trend of ammonium concentrations in syringe samples. In the anoxic region from 8 to 10 m, both POT and f-MWCNT based sensors resolve the steep gradient of ammonium. Sensors mark the exact start of the ammonium increase at 8.3 m. Sensor drift was generally low for all profile recordings, which may also be due to the low DOC concentration (maximal value of ~ 0.3 mM encountered) because the interaction of DOC with the ISM is a possible source of drift.²⁰

Figure 2B shows *in situ* profiles obtained in ≥ 400 $\mu\text{E m}^{-2} \text{ s}^{-1}$ daylight with SC-ISEs based on f-MWCNTs for pH and NH_4^+ in September. Both pH and NH_4^+ profiles follow the trend of syringe samples very well, suggesting that there is indeed no influence of light on the electrode signal. A sharp decrease in pH values from 8.7 to 7.5 at the oxycline occurs along with small gradients in the epilimnion and hypolimnion between the syringe sampling points.

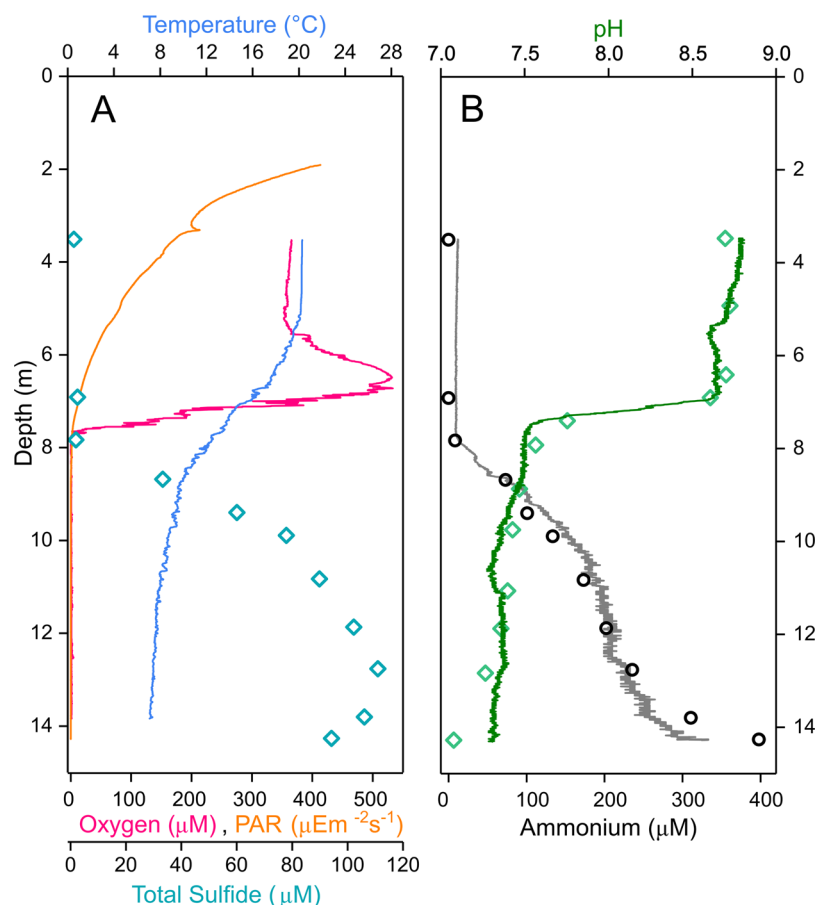


Figure 2. *In situ* profiles of dissolved oxygen concentration, temperature, and total sulfide in September 2015 obtained simultaneously with the SC-ISE measurements in Lake Rotsee (A) and recorded by SC-ISEs to extend the application to pH (green) measurements in addition to ammonium (gray) with f-MWCNT-based SC-ISEs in intense daylight, where black circles represent ammonium concentrations and green diamonds represent pH measurements in syringe samples taken simultaneously during the *in situ* profiling (B).

Our new protocol for the construction of SC-ISEs based on f-MWCNTs as a transducer and MMA-DMA-based sensing membranes facilitated the construction process significantly and provided electrodes, which are well suited for *in situ* measurements in challenging natural environments. Because dispersions of MWCNTs are typically unstable in most solvents, obtaining homogeneous dispersions and a uniform solid-contact layer on a GCE without the use of any surfactant is difficult.²¹ Even traces of any additive, e.g., a surfactant, can favor water-layer formation, which ultimately affects the stability of the signal.⁸ Using the modification protocol of Crespo et al.,⁸ this issue was resolved. MWCNTs were functionalized by octadecylamine molecules, and a homogeneous, stable dispersion of f-MWCNTs was obtained with a polar aprotic organic solvent, tetrahydrofuran (THF), upon slight sonication. A uniformly deposited layer of a controlled thickness over a GCE was formed by simply drop-casting the obtained dispersion of f-MWCNTs in THF. Avoiding the use of any water-soluble surfactants in the process and making MWCNTs highly lipophilic by introducing octadecylamine molecules on their surface reduced the possibility of formation of any water layer.²² Consequently, no soluble or reactive components like O₂ and sulfide can interact with the transducer surface, which resulted in the observed stable responses over a long period of time during the water-layer test and negligible redox sensitivity in the laboratory (Figure S3). In addition, all sensors showed a sensitivity close to the theoretically expected

value of 59.6 mV per 10-fold concentration change in the laboratory (Figure S1) as well as in the field (Table S1 and Figure S4), and this excellent agreement confirms the successful production and deployment of the sensors.

In the field test in eutrophic Lake Rotsee, the f-MWCNT-based SC-ISEs showed no sensitivity to light, redox changes, or high sulfide concentrations. An oxic epilimnion with an oxygen concentration maximum that indicates the zone of primary production and a very narrow (50–150 cm) oxic–anoxic interface with steep gradients in NH₄⁺ concentration and pH and an anoxic hypolimnion rich in dissolved sulfide were observed during both deployments (Figures 1A and 2A). The sulfidic conditions in bottom waters make the *in situ* application of SC-ISEs more challenging because sulfide interferes by interacting with the transducing mechanism of the solid contact as found in our previous studies.³ The *in situ* profiles (Figures 1B and 2B) obtained by SC-ISEs show stable responses under both dark and daylight conditions. They follow the concentration profiles of syringe samples determined in the laboratory. This demonstrates the functionality of the f-MWCNT-based double-layer design of SC-ISEs, which, unlike POT-based ISEs, is independent of light conditions during measurements in the field. Also, at increasing sulfide concentrations (≤100 μM) with depth, POT-based as well as f-MWCNT-based SC-ISEs with a DL design did not show the strong drift in the *in situ* profiles caused by sulfide interference as experienced before for SL SC-ISEs based on MWCNTs.³

This insensitivity to sulfide can be attributed to various building blocks of the proposed DL design. Mainly, MMA-DMA provides an efficient shield for the f-MWCNT layer because of its low diffusivity.^{23–25} Additionally, lipophilic functional groups on f-MWCNTs (CNT-COOH, 20% functionalization)⁸ preclude the possibility of formation of a water layer between the transducer and membrane surface, which can be a potential path for interaction of reactive solutes on the transducer surface.

As the product of the interfering ion concentration and the corresponding selectivity coefficient ($c_b K_{ab}^{\text{pot}}$) determines the limit of detection (LOD) of the ISEs,²⁶ it limits the application of ISEs in natural waters. Potassium that interferes most strongly with ammonium determination, with relatively low and uniform concentrations of ~ 50 – $80 \mu\text{M}$ and a selectivity coefficient of 0.145^3 , sets the LOD to ~ 6 – $11 \mu\text{M}$ in the water column (Table S2). Still, f-MWCNT-based as well as POT-based SC-ISEs for ammonium revealed also features like small-scale concentration changes close to the LOD ($6.77 \mu\text{M}$ at 6.25 m) (inset, Figure 1B). Because the potentiometric response of SC-ISEs in EMF is calibrated against $\log c$ by linear regression (Figure S4), uncertainties in absolute concentration²⁷ and therefore their errors increase with their value (Figure S5). The characteristic response time of a few seconds of the SC-ISEs is a prerequisite for the high spatial resolution obtained in pH profiles with a profiling speed of 5 mm/s only the over $\sim 50 \text{ cm}$ thick redox boundary from 6.9 to 7.4 m in the September study (Figure 2B). This is a significant advantage of the new H^+ sensor design as it facilitates continuous *in situ* profiling at an acceptable speed. This is an improvement to the glass-type pH electrodes, which have a higher stabilization time when a precision of $>0.1 \text{ pH unit}$ is needed,²⁸ resulting in time lags and peak flattening of the actual pH profiles.

In summary, we were able to overcome the challenges for *in situ* profiling in complex lake systems by developing a robust design of SC-ISEs, which can cope with the conditions encountered at many field sites using a light-insensitive transducer and a membrane with a low diffusion coefficient. The ease of fabrication along with the robust analytical performance of f-MWCNT-based SC-ISEs for ammonium and pH represents a significant step toward more reliable high-resolution profiling in fresh water systems.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00130.

Experimental section with electrode fabrication, laboratory calibration (Figure S1), water-layer test (Figure S2), redox sensitivity test (Figure S3), uncertainty analysis (Figure S4), absolute error analysis (Figure S5), *in situ* profiling setup (Figure S6), *in situ* calibration parameters (Table S1), selectivity coefficients for ion selective membranes and mean concentrations of relevant ions in the lake water column (Table S2), and properties of SC-ISEs (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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