

Supporting Information (SI) for

Fast Potentiometric CO₂ Sensor for High-resolution *In situ* Measurements in Fresh Water Systems

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EXPERIMENTAL SECTION

Materials and Chemicals

The following reagents were purchased in selectophore grade from Sigma-Aldrich: potassium tetrakis(4-chlorophenyl)borate (KTPCIPB), tri-n-dodecylamine(TDDA), tetrahydrofuran (THF), N,N-dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide (carbonate ionophore VII), bis(2-ethylhexyl) adipate (DOA), tridodecylmethylammonium chloride (TDMACl). Poly(vinyl-chloride) (PVC, high molecular weight), octadecyl amine (ODA), methylene chloride(CH₂Cl₂), thionyl chloride (SOCl₂), potassium hexacyanoferrate(II) trihydrate (K₄Fe(CN)₆·3H₂O), potassium hexacyanoferrate(III) (K₃Fe(CN)₆), sodium sulfide nonahydrate (Na₂S·9H₂O), zinc acetate (Zn(CH₃COO)₂), sodium carbonate (Na₂CO₃), N,N-Dimethyl-1,4-phenylenediammonium dichloride (C₈H₁₂N₂·2HCl), ammonium iron (III) sulfate (NH₄Fe(SO₄)₂·12H₂O), nitric acid (HNO₃), and hydrochloric acid (HCl), were obtained in analytical grade from Sigma-Aldrich. Biology grade 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris base) was purchased from Promega corporation, USA. Multiwall carbon nanotubes (MWCNTs) (0.5-200 μ m length and 30-50 nm diameter, M4905) were obtained from HeJi Inc. The methacrylic copolymer (MMA-DMA) was synthesized in the research group of Prof. Eric Bakker, University of Geneva, according to the protocol by Heng et al.¹ Aqueous solutions were prepared by dissolving appropriate salts or diluting standard solutions in nano-pure water with a resistance of 18.2 M Ω cm⁻¹. A double junction Ag/AgCl reference electrode (Metrohm AG, Switzerland) containing 3M KCl as an inner solution and 1M CH₃COOLi as a bridge electrolyte was used for the lab experiments.

Synthesis of f-MWCNT

MWCNTs were functionalized by following the protocol of Crespo et. al.² Briefly, 1 g of MWCNTs were refluxed for an hour at 100 °C in H₂SO₄/HNO₃ (3:1). The resultant MWCNT-COOH were then filtered through a Polycarbonate (0.10 μ m) membrane, followed by washing

with nanopure water and drying at 60°C. Further, 20 mL of thionyl chloride (SOCl₂) and 1 mL of dimethylformamide was added and the mixture was refluxed overnight, at 70°C. After the reaction, the residual solvent was removed by rotary evaporation. Finally, an excess of ODA (~1g) was added and the mixture was continuously stirred at 100°C for 96 h. After cooling to room temperature, the excess ODA was removed by sonication and several washing steps with ethanol. The resultant carbon nanotubes were then dried and stored at room temperature.

Fabrication of f-MWCNT based SC-ISE for H⁺ and CO₃²⁻

A stable dispersion of nanotubes was achieved by simply sonicating 1mg f-MWCNTs in 1 mL THF for ~10 min. For preparation of SC-ISEs 100µl of this dispersion was drop casted on a preferentially masked GC electrode surface to form a uniform layer. A new mask was prepared for each GC electrode using a simple method where, pieces of a Scotch® tape (Scotch™3M, USA) were stuck on top of each other taking care that no air is trapped to obtain a ~0.6 mm thick band. This band was punched with a punching machine for desired sized hole in order to cover the glassy carbon surface with the dispersion and mask the surrounding inert surface of the electrode body. The hydrogen ion-selective membrane cocktail was prepared by dissolving 1.95 mg TDDA, 0.58 mg KTpClPB and 97.47 mg MMA-DMA in 1 mL dichloromethane and for the carbonate ion selective membrane 8.3 mg carbonate ionophore VII, 2 mg TDMAC, 60mg PVC and 100µL DOA were dissolved in 2mL THF. The mixture was sonicated for 30 s. Then, 130 µL of the membrane cocktail was drop-cast onto the f-MWCNT layer that was previously deposited onto the glassy carbon surface.

Laboratory tests

Electrodes were conditioned before calibration by immersing carbonate selective SC-ISE in 10⁻⁴ M CO₃²⁻ for 1 day followed by 1µM solution for 1 day. For H⁺ selective electrodes in the first conditioning step was pH 3 solution for 1 day followed by a second step in pH 9 solution

for 2 days. During the lab experiments, a 16-channel EMF potentiometer (Lawson Labs Inc, USA) was used to record EMF.

Total sulfide in the samples was analyzed spectrophotometrically.³ The sampling procedure involved fixing total sulfide in the samples by adding 0.5 mL 4% zinc acetate solution to 1 mL unfiltered sample immediately after retrieving from the syringes. Sulfide standard solution (0.1M) was prepared with sodium sulfide nonahydrate in nanopure water. Standards were also treated with zinc acetate to fix total sulfide to zinc sulfide. The samples and standards were treated with an acidic solution of (~40% sulfuric acid) N,N-Dimethyl-1,4-phenylenediammonium dichloride and ammonium iron (III) sulfate to produce a blue color after 30 min incubation at room temperature. Both standard and samples were quantified for total sulfide at 665 nm.

Tris buffer preparation

10 mM Tris solution was prepared with 5 mM HCO_3^- , 150 μM NaCl in nanopure water and the pH was adjusted using sulfuric acid to 7.42, 7.98 and 8.64. The activity of CO_2 was calculated by defining the pH value, the concentration of HCO_3^- and Cl^- and the temperature as input to the speciation program PHREEQC.⁴

Sulfide sensitivity test

A sulfide sensitivity test was performed in a 100 mM Tris buffer at pH 8.2 (adjusted with H_2SO_4) with 1 mM total carbonate. The sulfide concentration was adjusted by incremental addition of a sodium sulfide solution.

Redox sensitivity test

A redox sensitivity test was performed in a 100 mM Tris buffer at pH 8.2 (adjusted with H_2SO_4) with 1 mM total carbonate for carbonate selective electrode and in an unbuffered background with 1mM H^+ for hydrogen ion selective electrode. The redox sensitivity was tested by

measuring potential in a solution with 1 mM total concentration of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ redox couple. The concentration ratios of the redox couple ranging from 1/10 to 10/1.⁵

Water layer test

Water layer tests were carried out as described in Fibbioli et al.⁶ Before the water layer test, SC-ISEs were conditioned in respective primary ion solution (10^{-4} M CO_3^{2-} in Tris buffer pH 8.2 and H^+) solution and replaced by 1mM interfering ion (Cl^- at pH 8.2 and K^+ respectively) during the course of experiment and introduced again in 1mM primary ion solution.

TABLES SI

Table S1 Selectivity coefficients as determined by previous studies for H^+ sensitive membranes by FIM⁷ and for carbonate ion by SSM² mean concentration of possible interfering ions observed in the water column of Lake Rotsee during the in situ application

Interfering ion (b)	Selectivity coefficient $K_{\text{H}^+,b}^{\text{pot}}$	Selectivity coefficient $K_{\text{CO}_3^{2-},b}^{\text{pot}}$	Mean concentration (M)
K^+	1.30×10^{-8}	-	3.90×10^{-5}
Na^+	1.10×10^{-9}	-	1.81×10^{-4}
Mg^{2+}	3.98×10^{-10}	-	1.87×10^{-4}
Ca^{2+}	4.36×10^{-9}	-	1.07×10^{-3}
Cl^-	-	1.58×10^{-7}	1.66×10^{-4}
NO_3^-	-	3.16×10^{-5}	3.00×10^{-6}

Table S2 Sensor performance respect to detection limits, long-term stability and tests for water layer and redox sensitivity.

Sensor type	Detection limit	Long term stability ^a	Water layer test	Redox sensitivity
	(M)	Drift (mV/h)		(mV/decade)
Carbonate (CO₃²⁻)	2.0 x 10 ⁻⁶	0.09	No drift	0.04
Hydrogen ion (H⁺)	1.0 x 10 ⁻⁹	0.06	No drift	0.05

^a Long term stability tests were performed in 10⁻³ M H⁺ and 10⁻⁴ M of CO₃²⁻ solution for hydrogen and carbonate sensitive SC ISE respectively.

FIGURES S1

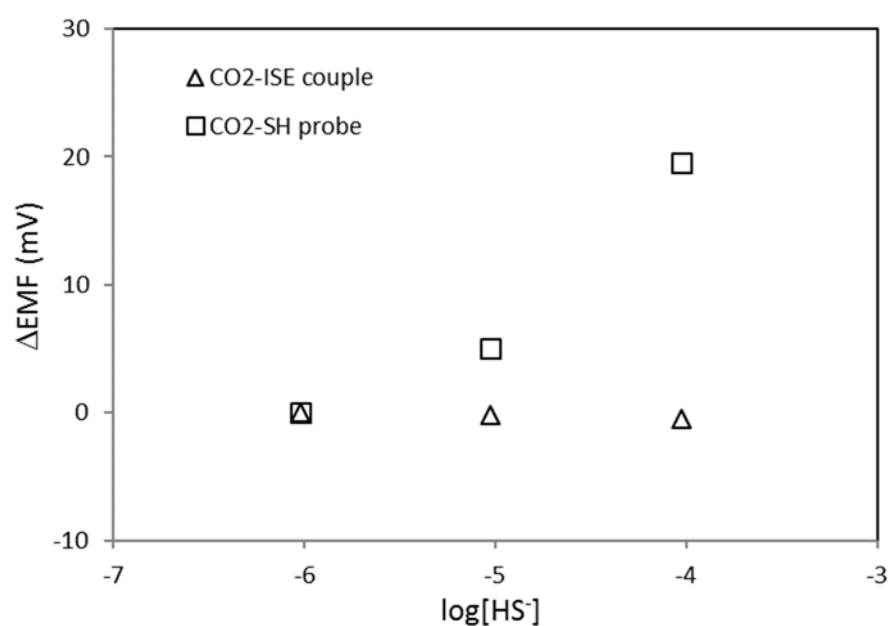


Figure S1 Sulfide insensitivity test for CO₂-ISE couple compared to a CO₂-SH probe in a buffered solution at pH 8.2

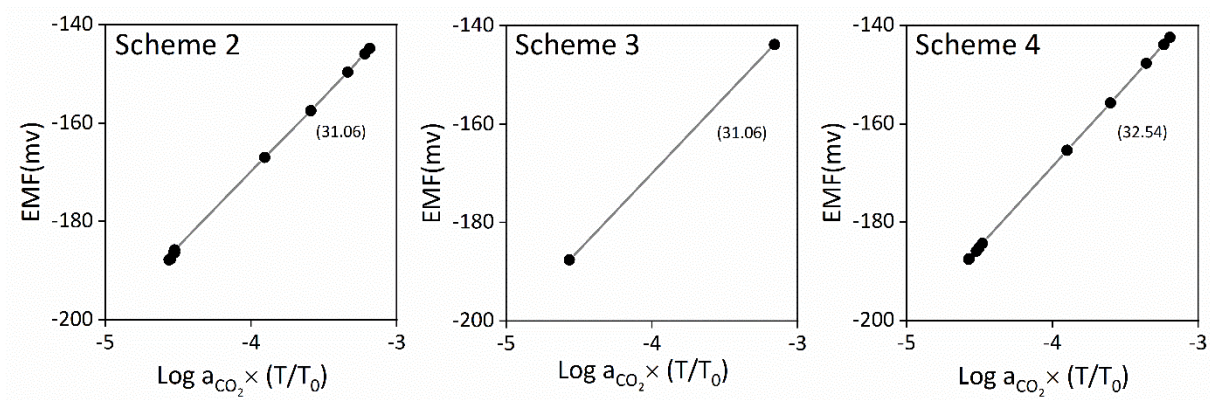


Figure S2 Schemes in optimization of *in situ* calibration where drift corrected EMF is plotted against logarithm of activity of dissolved carbon dioxide multiplied with a temperature factor to obtain values of respective temperature corrected slopes in mV/decade (in parentheses) for ISE couple 1 (Refer to Table 1b in the main text).

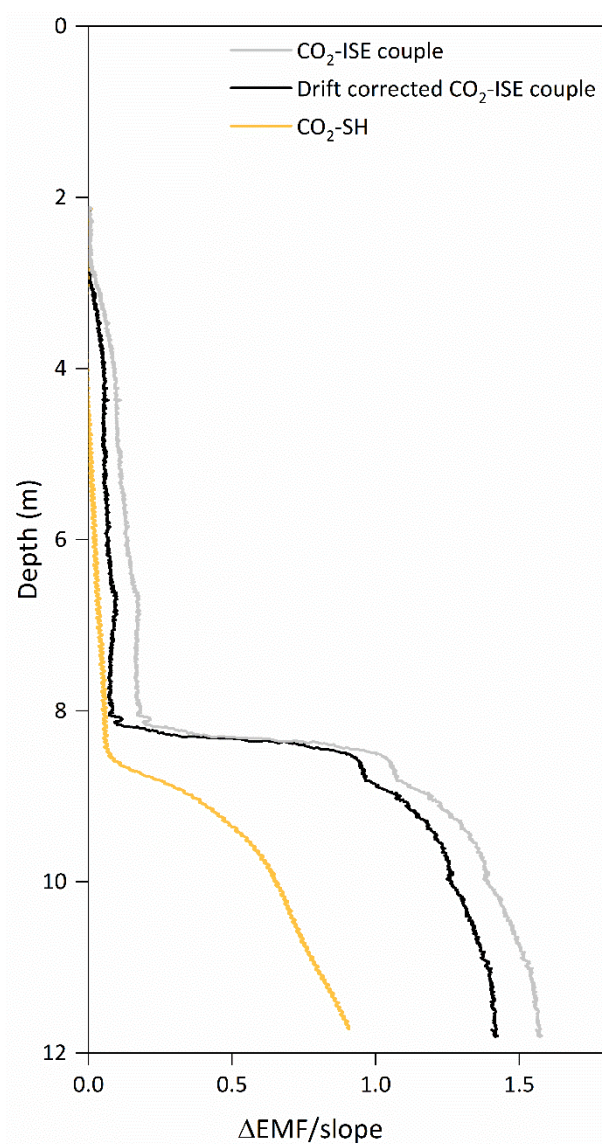


Figure S3 Depth profile of raw and drift corrected ΔEMF showing effect of drifting behavior of an ISE-couple on estimation of dissolved CO_2 concentration.

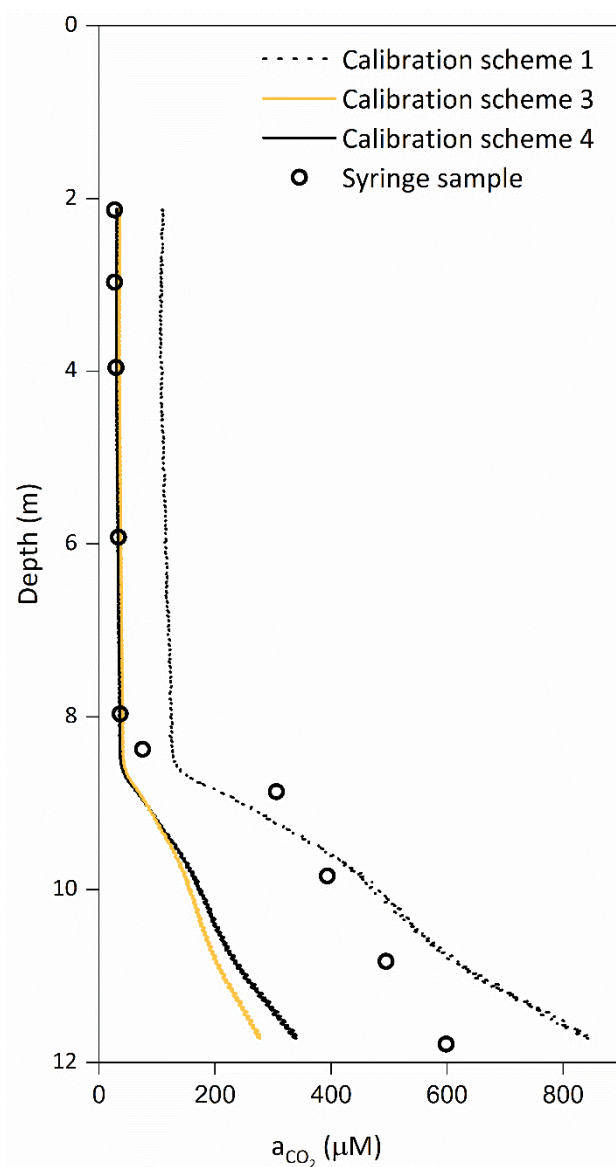


Figure S4 Depth profiles of activity of dissolved CO_2 obtained by CO_2 -SH probe calculated with different calibration parameters corresponding to the calibration schemes as described in Table 1.

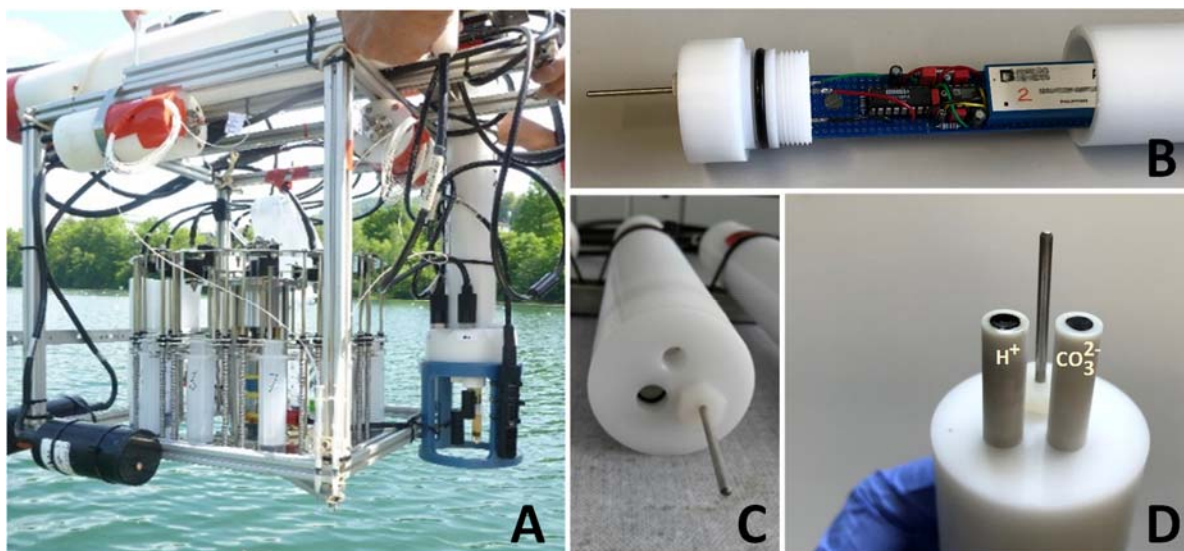


Figure S5 Profiling ion analyzer (PIA) a custom-built profiling set up that accommodates a syringe sampler, commercial sensors for physicochemical characterization of the water column (A) and waterproof amplifiers that house SC-ISEs (B, C) with SC-ISEs for hydrogen ion and carbonate installed (D) for *in situ* measurements of dissolved CO₂ in the water column.

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