

# **Use of bi-potentiostat as a simple and accurate electrochemical approach for the determination of orthophosphate in seawater**

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**Supplementary information**

The screenshot shows the 'Electrochemical Injection Analyzer' GUI. It features a table for configuring 10 ports, each with time, move-to, pump state, and speed settings. A 'Run' button is green and a 'Stop' button is red. A status bar at the bottom shows the pump status. A clock icon is also present.

Port	Time (seconds)	Move to	Pump state_1	Pump speed_1 [%]	Pump state_2	Pump speed_2 [%]	Repeat number	measure?
Port 1 (Blank)	0	Port 1	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 2 (Standard 1)	0	Port 2	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 3 (Standard 2)	0	Port 3	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 4 (Standard 3)	0	Port 4	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 5 (Sample)	0	Port 5	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 6 (deactivated)	0	Port 6	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 7 (MiliQ)	0	Port 7	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 8 (H2SO4)	0	Port 8	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 9 (deactivated)	0	Port 9	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>
Port 10 (wash)	0	Port 10	OFF	0	Pump OFF	0	Pump 0	<input type="checkbox"/>

Number of cycles: 1

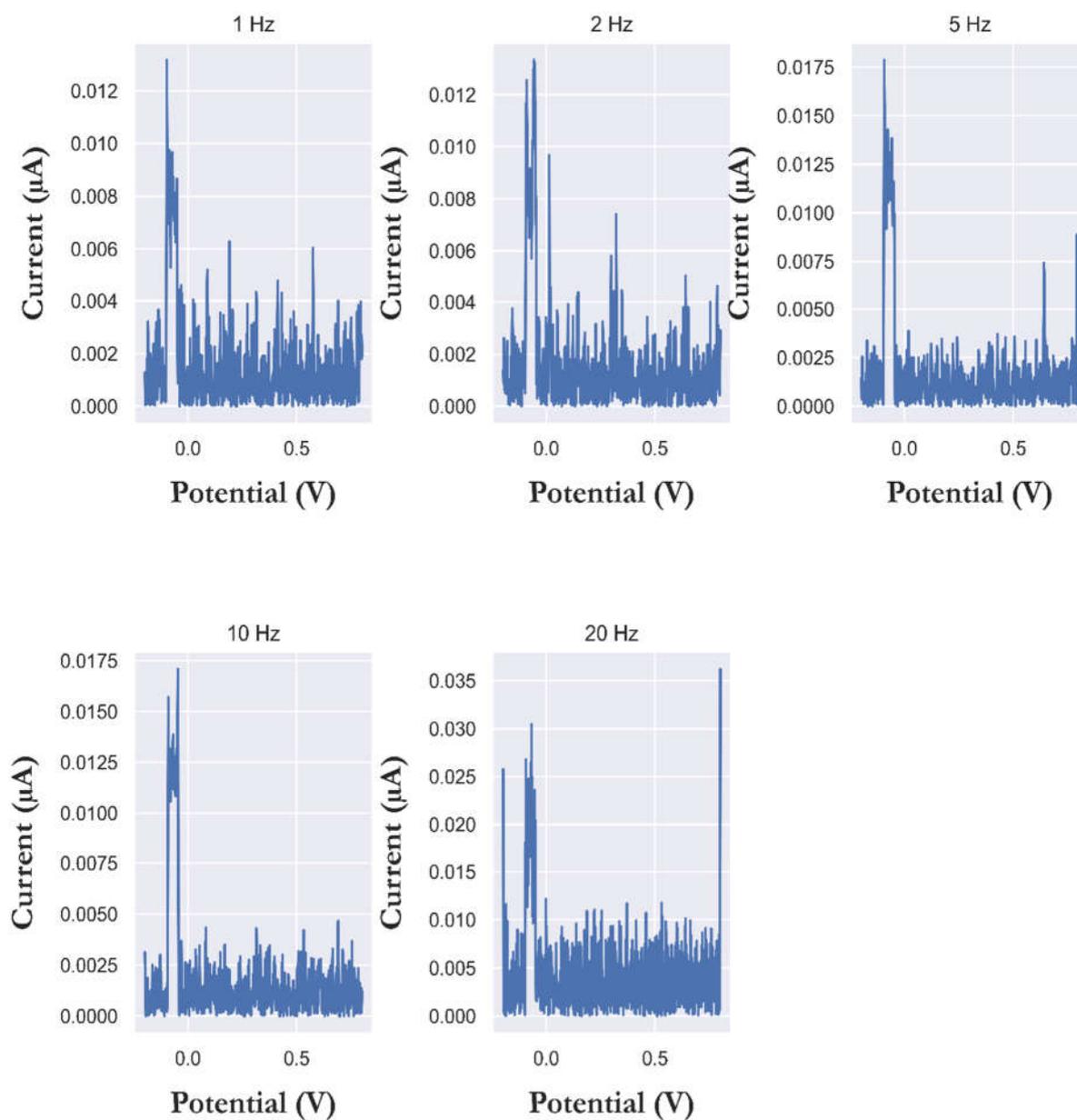
Run (green button), Stop (red button)

Status: 17

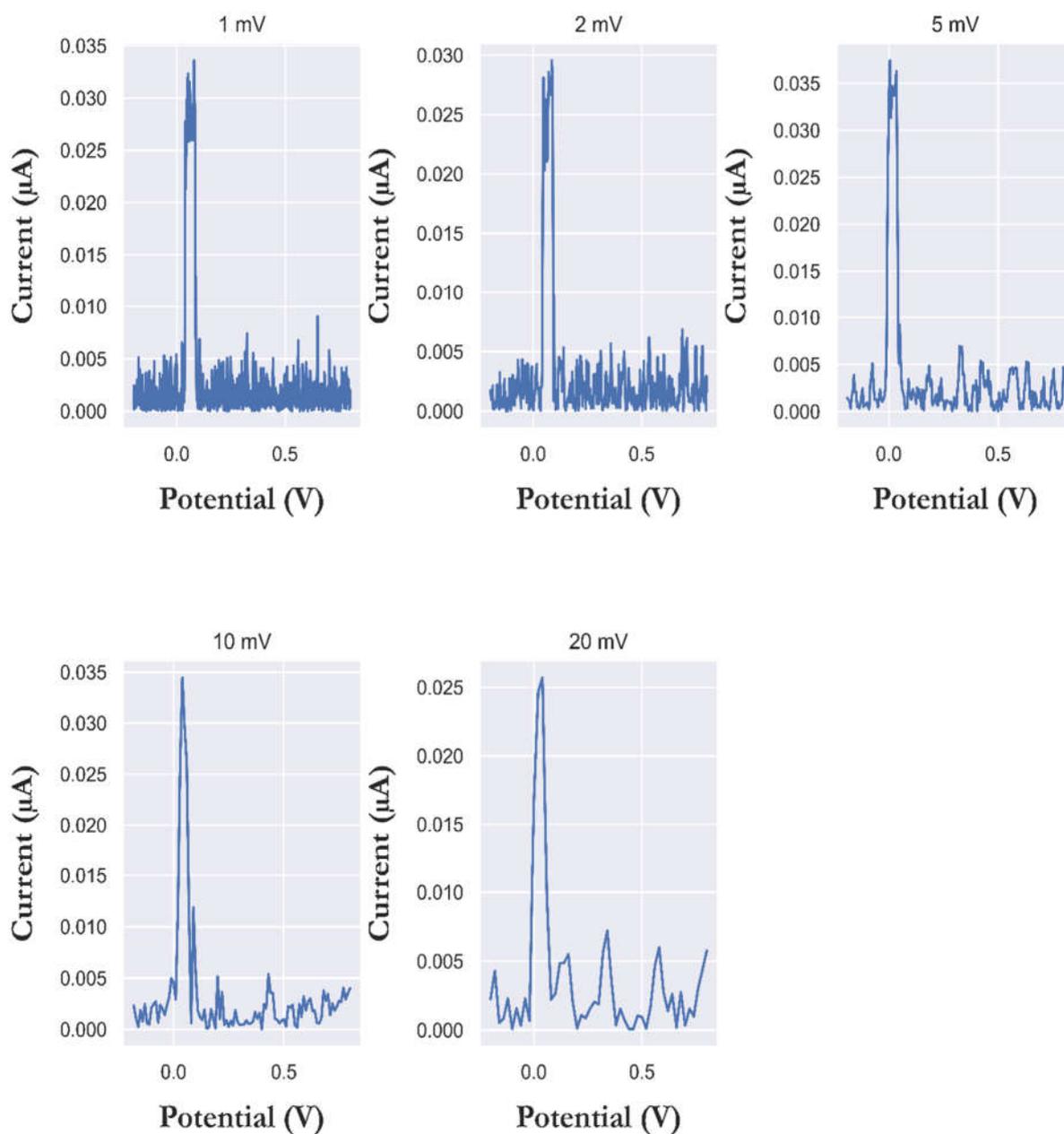
17 Status bar showing the status of the pump

- 1 OptionMenu button to select COM port for switching valve
- 2 Labels for Switching valve Ports
- 3 Entry widgets for the time to stay at the port
- 4 Button to manual switch between ports
- 5 OptionMenu button to select COM port for the peristaltic pump
- 6 OptionMenu button to select the 1<sup>st</sup> state for the peristaltic pump (CW, CC, Off)
- 7 Entry widgets for the time to set the speed (0-100 %) for the 1<sup>st</sup> state assigned for the pump
- 8 Button to manual set the 1<sup>st</sup> state of the pump
- 9 OptionMenu button to select the 1<sup>st</sup> state for the peristaltic pump (CW, CC, Off)
- 10 Entry widgets for the time to set the speed (0-100 %) for the 2<sup>nd</sup> state assigned for the pump
- 11 Button to manual set the 2<sup>nd</sup> state of the pump
- 12 Entry widgets to assign how many times each step can be repeated
- 13 Check button to perform the measurement
- 14 Picture showing at which the port, the switching valve is in
- 15 Entry widgets to assign how many times we want to repeat the full loop
- 16 Start button to start the loop stop button to abort the loop

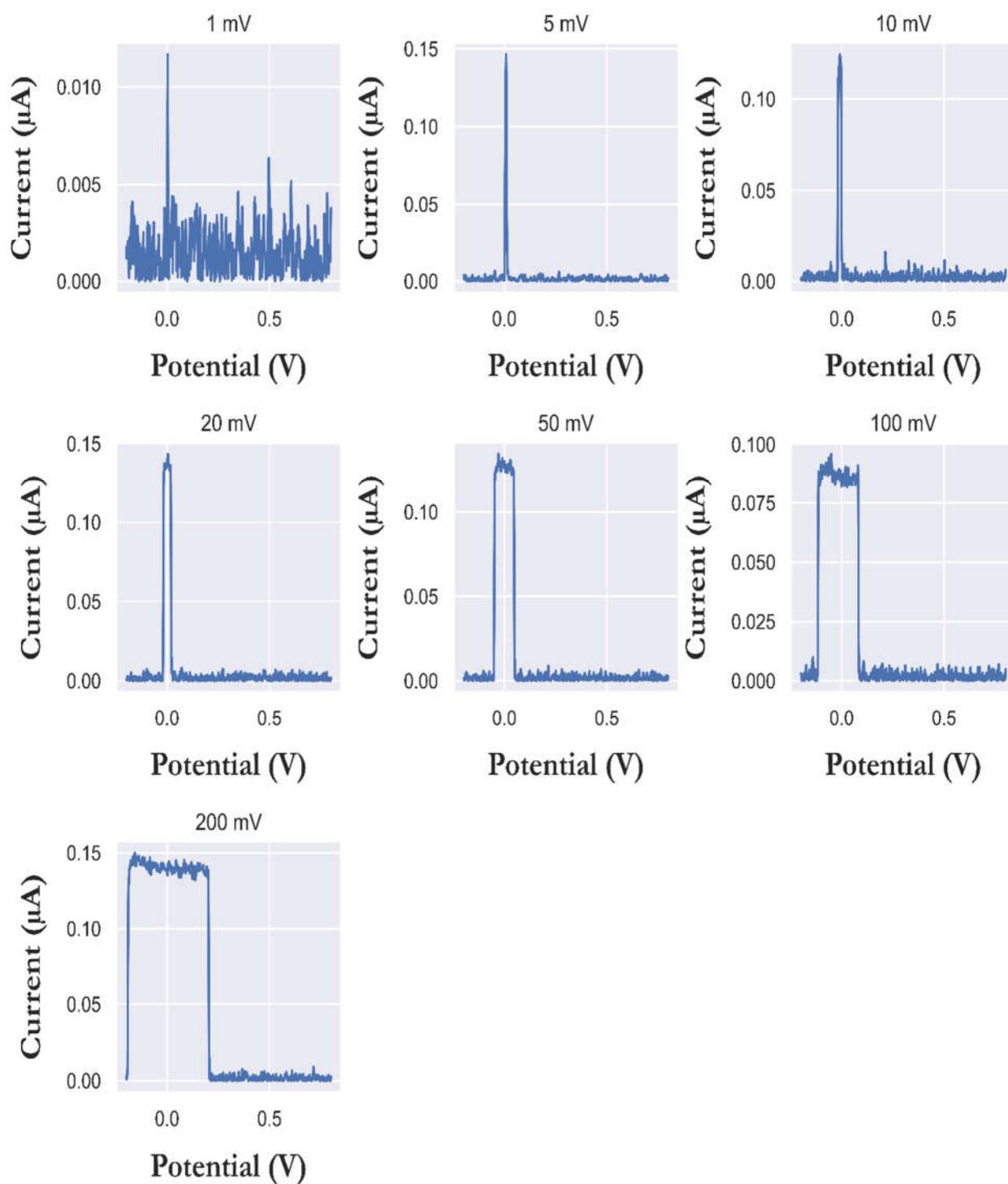
**Figure S1** graphical user interface (GUI) of the ‘Electrochemical FIA.exe’ to program switching valve, peristaltic pump, and synchronization with the Metrohm  $\mu$ Stat 400 Bi-potentiostat..



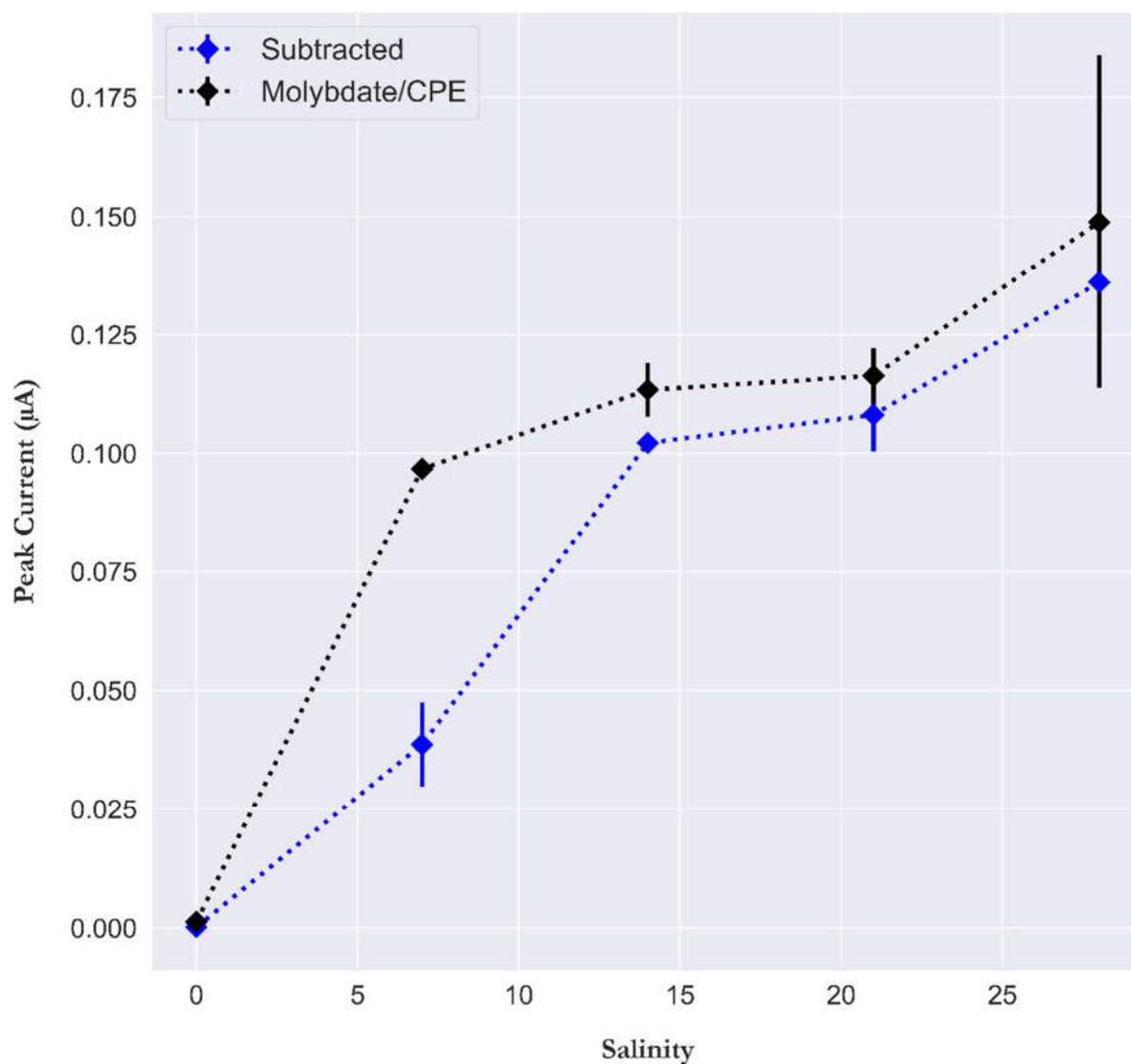
**Figure S2** Square wave voltammograms of  $0.5 \mu\text{M PO}_4^{3-}$  in  $30 \text{ g/L NaCl}$  ( $\text{pH } 0.8$ ) (corrected voltammogram) at a step potential of  $1 \text{ mV}$ , square wave amplitude  $25 \text{ mV}$  at frequencies  $1 \text{ Hz}$ ,  $2 \text{ Hz}$ ,  $5 \text{ Hz}$ ,  $10 \text{ Hz}$  and  $20 \text{ Hz}$ .



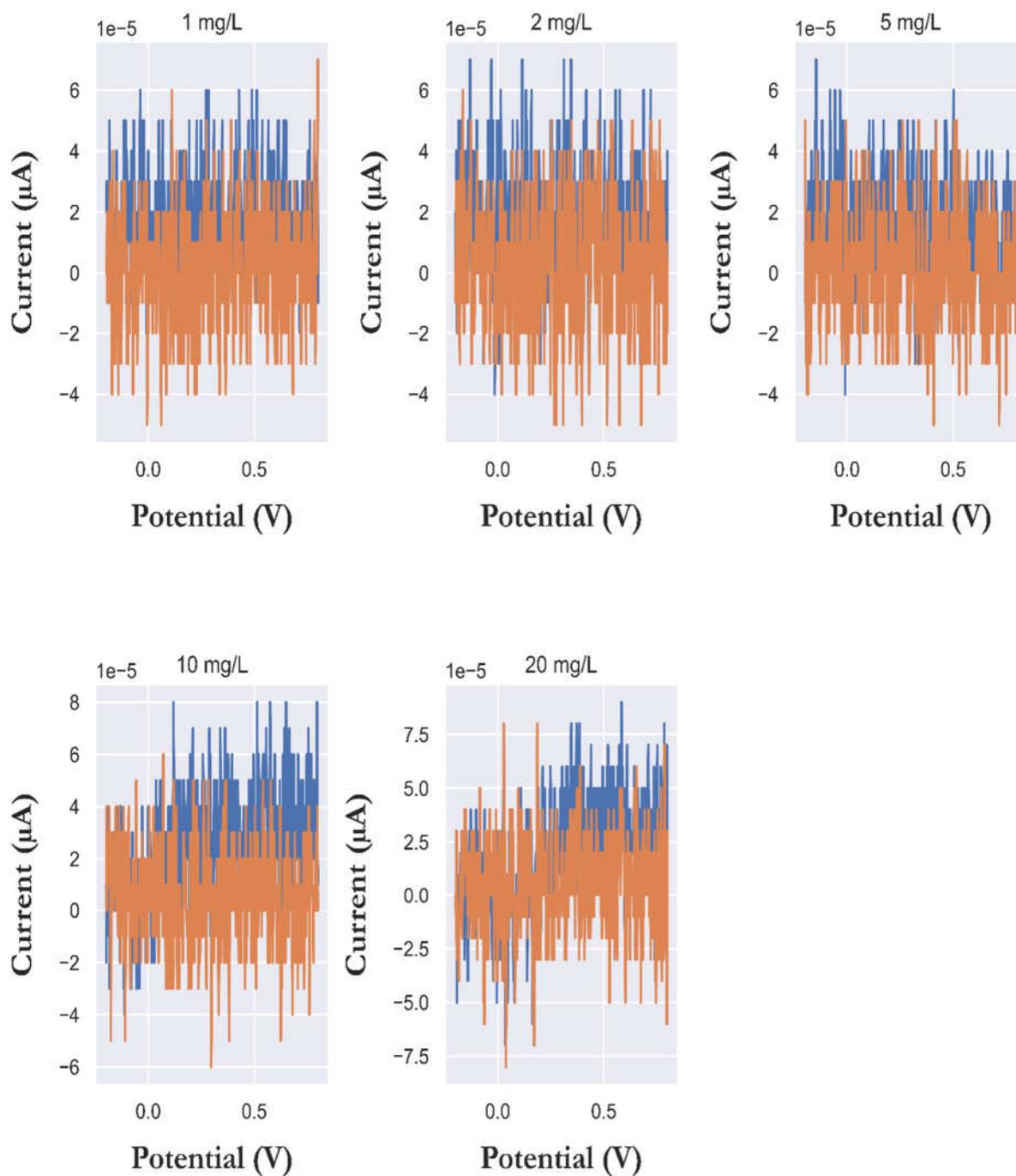
**Figure S3** Square wave voltammograms of  $0.5 \mu\text{M PO}_4^{3-}$  in  $30 \text{ g/L NaCl}$  ( $\text{pH } 0.8$ ) (corrected voltammogram) at a frequency of  $10 \text{ Hz}$ , amplitude  $25 \text{ mV}$  at a step potential of  $1 \text{ mV}$ ,  $2 \text{ mV}$ ,  $5 \text{ mV}$ ,  $10 \text{ mV}$  and  $20 \text{ mV}$ .



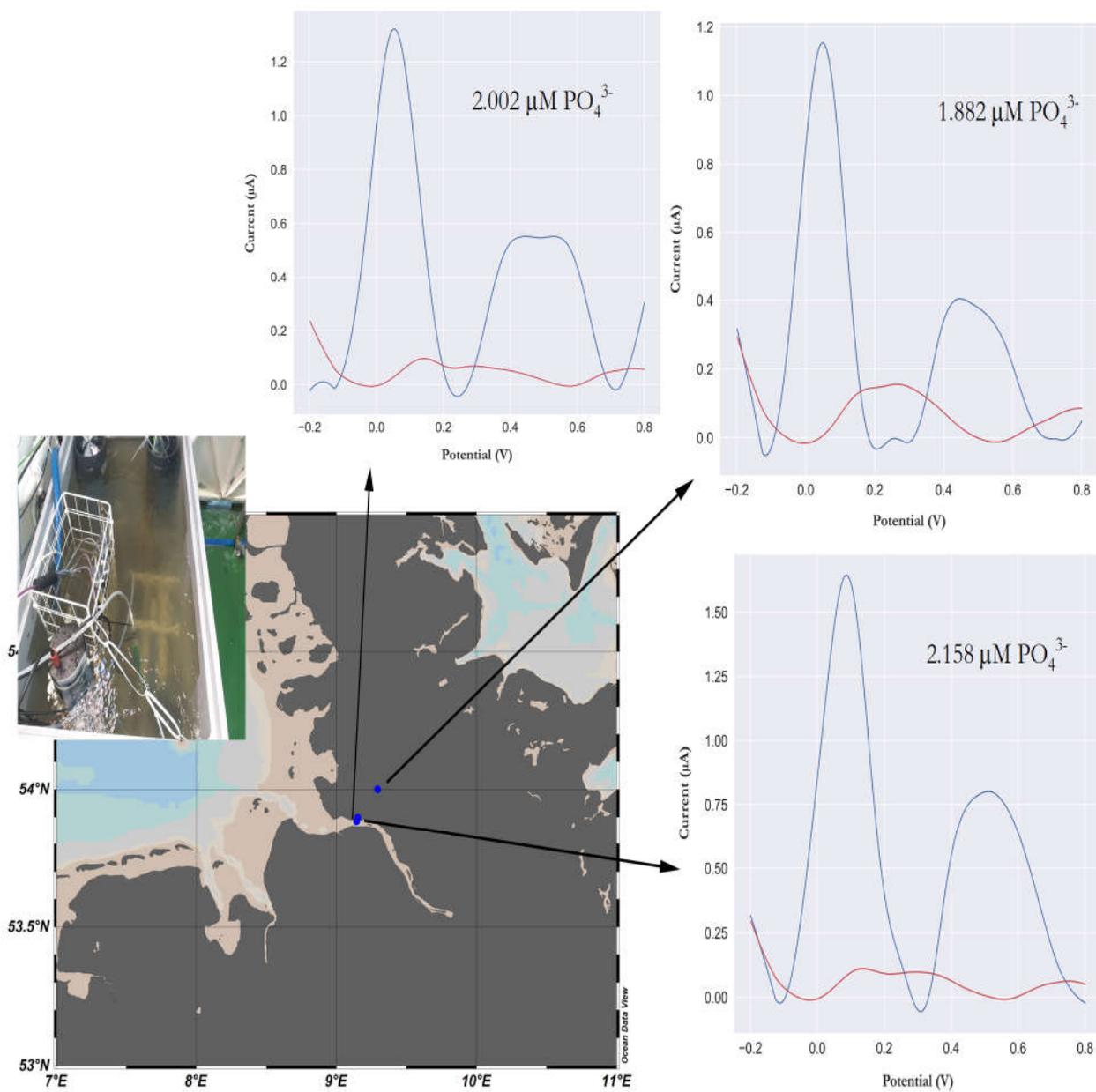
**Figure S4** Square wave voltammograms of  $0.5 \mu\text{M PO}_4^{3-}$  in  $30 \text{ g/L NaCl}$  ( $\text{pH } 0.8$ ) (corrected voltammogram) at a step potential of  $1 \text{ mV}$  and a frequency of  $10 \text{ Hz}$  at square wave amplitudes of  $1 \text{ mV}$ ,  $5 \text{ mV}$ ,  $10 \text{ mV}$ ,  $20 \text{ mV}$ ,  $50 \text{ mV}$ ,  $100 \text{ mV}$  and  $200 \text{ mV}$ .



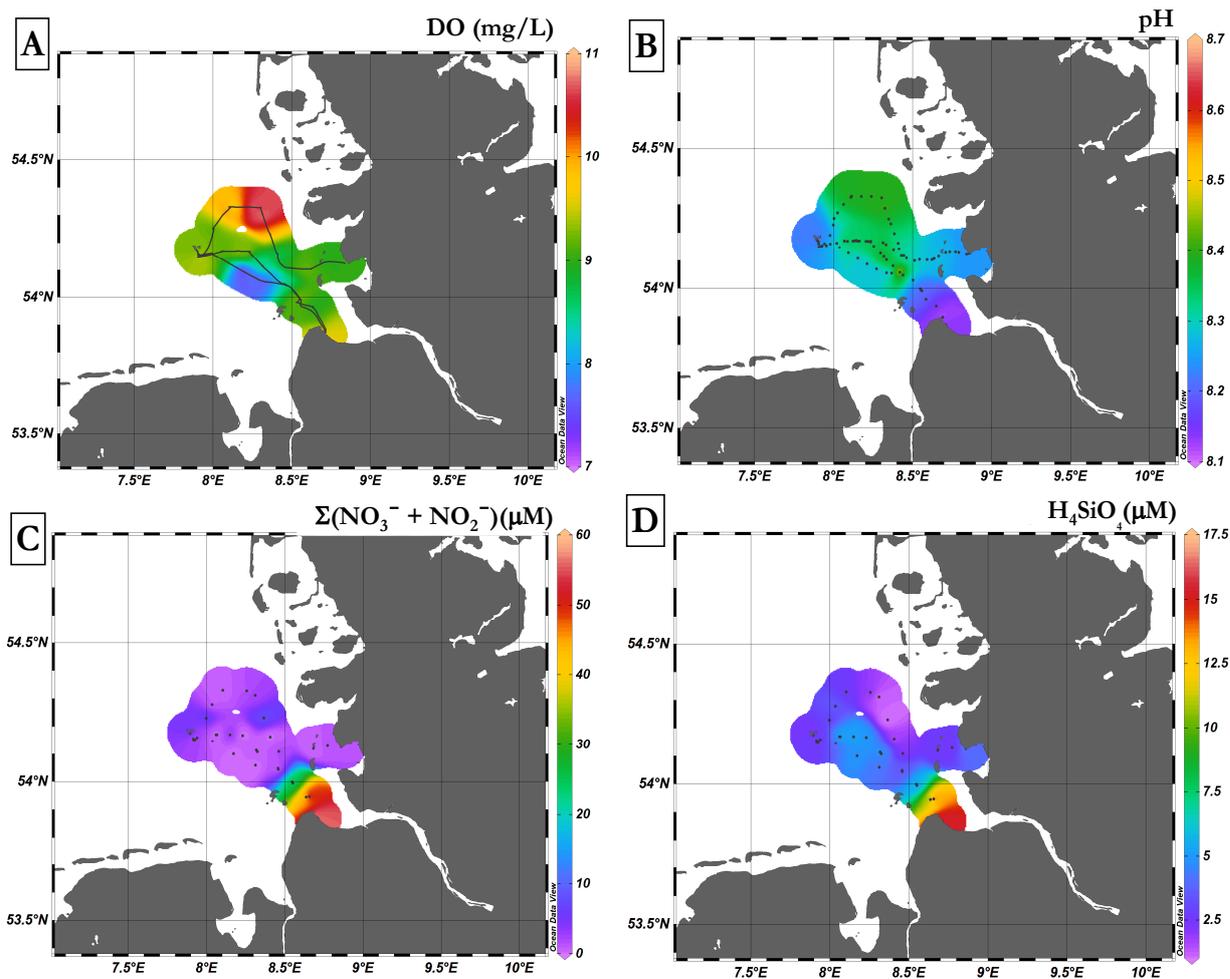
**Figure S5** Effect of the variation of the salinity (0, 7, 14, 21 and 28) on the peak current of 1  $\mu\text{M}$   $\text{PO}_4^{3-}$  (pH 0.8) where the peak current of molybdate/CPE is shown as black circles and the peak current of corrected voltammogram is shown as blue circles. Error bar ( $n = 5$ ).



**Figure S6** Square wave voltammograms of  $1 \mu\text{M PO}_4^{3-}$  (30 g/L NaCl) pH 0.8 on molybdate/CPE (blue line) and CPE (orange line) in the presence of 1, 2, 5, 10, and 20 mg/L HA. Step potential 2 mV, frequency 10 Hz and amplitude of square wave 100 mV.



**Figure S7** Location of three *on-site* data points taken at the Kiel Canal with square wave voltammograms at molybdate/CPE (blue line) and CPE (red line). The left inset shows the turbidity of the water entering the tank.



**Figure S8** Overviews of (A) the distribution of surface dissolved oxygen (DO) in mg/L obtained from EXO sonde sensor, (B) distribution of pH obtained from sunburst SAMipH and corrected for CTD salinity and temperature, (C) distribution of  $\Sigma(\text{NO}_3^- + \text{NO}_2^-)$  in  $\mu\text{M}$  (bottom left panel) and (D) distribution of  $\text{H}_4\text{SiO}_4$  in  $\mu\text{M}$  for the discrete samples collected from underway water supply and analyzed via QuAAtro air-segmented analyser.