

Supplementary Material

# Improvement of *on-site* sensor for simultaneous determination of phosphate, silicic acid, nitrate and nitrite in seawater

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**Table S1.** Detailed Procedure for measurements during the analyzer deployment with the number of ports as mentioned in Figure 2.

		Step	Port open	Linear movement <sup>a</sup>		Operation & Description		
		1	a	3	4500 (r <sup>b</sup> )	Draw up the cleaning solution into the syringe and all detectors, and set the light intensity for blank measurement.		
			b	8	4500 (i <sup>c</sup> )			
			c	3	4500 (r)			
			d	15	4500 (i)			
			e	3	4500 (r)			
			f	16	4500 (i)			
		2	4	4500 (i)	Initialize the syringe motor and detector, align the switching valve and ensure that the syringe plunger is fully retracted.			
PO <sub>4</sub> <sup>3-</sup> Calibration	Blank	3	a	7	4500 (r)	2x flushing	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with deionized water	
			b	8	4500 (i)			
		4	a	7	2700 (r)		Draw up the blank and set the light intensity for the reference ( $I^R, V^R$ )	
			b	4	1350 (i)			
			c	8	1350 (i)			
		5	a	8	720 (r)		Withdraw the blank from the flow cell and add R1 (Molybdate mixed reagent) and R2 (Ascorbic Acid)	
			b	9	180 (r)			
			c	10	180 (r)			
		6	a	8	450 (i)	4x mixing	Mixing the reagent with the blank and inject the reaction mixture inside the detector and waiting for 3 minutes for color development and set the light intensity for the measurement ( $V, I$ )	
					450 (r)			
			b	4	180 (i)			
			c	8	900 (i)			
	Standar d 1, 2, 3	7	a	7	4500 (r)	2x flushing	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with deionized water	
			b	8	4500 (i)			
		8	a	13(14, 2) <sup>d</sup>	4500 (r)			

			b	8	4500 (i)	2x flushing	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with STD1 (STD2, STD3)
		9	a	13(14, 2)	2700 (r)		Draw up STD1(STD2, STD3) and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	1350 (i)		
			c	8	1350 (i)		
		10	a	8	720 (r)		Withdraw STD1 from the flow cell and add R1 and R2
			b	9	180 (r)		
			c	10	180 (r)		
		11	a	8	450 (i)	4x mixing	Mixing the reagent with STD1 and inject the reaction mixture inside the detector and waiting for 3 minutes for color development and set the light intensity for the measurement ( $V, I$ )
					450 (r)		
			b	4	180 (i)		
			c	8	900 (i)		
		washing		12	a	3	4500 (r)
b	8				4500 (i)		
c	3				4500 (r)		
d	15				4500 (i)		
e	3				4500 (r)		
f	16				4500 (i)		
Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) Calibration	Blank	13		4	4500 (i)		Initialize the syringe motor and detector, align the switching valve and ensure that the syringe plunger is fully retracted.
		14	a	7	4500 (r)	2x flushing	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with deionized water
			b	8	4500 (i)		
		15	a	7	4500 (r)	2x flushing	Washing the syringe and the Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) detector with deionized water
			b	16	4500 (i)		
		16	a	7	2700 (r)		Draw up the blank and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	700 (i)		
			c	16	2000 (i)		
		17	a	16	1440 (r)		Withdraw the blank from the flow cell and add mixed reagent (Griess reagent + VCl <sub>3</sub> )
			b	5	360 (r)		
		18		16	450 (i)	4x mixing	Mixing the blank with the reagent
					450 (r)		
		19		8	1800 (i)		Waiting 30 minutes into PO <sub>4</sub> <sup>3-</sup> detector to allow NO <sub>3</sub> <sup>-</sup> reduction during incubation with VCl <sub>3</sub> reagent at maximum temperature (~ 50 °C).
		20	a	8	1800 (r)		Withdraw the reaction mixture from the PO <sub>4</sub> <sup>3-</sup> detector, waiting 2 min. inside the syringe housing to cool the mixture and open the Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) detector, inject the mixture and set light intensity for the measurement ( $V, I$ )
			b	4	225 (i)		
			c	16	1575(i)		

	Standard 1, 2, 3	21	a	7	4500 (r)	2x	flushing	Washing the syringe and the $\text{PO}_4^{3-}$ detector with deionized water
			b	8	4500 (i)			
		22	a	7	4500 (r)	2x	flushing	Washing the syringe and the $\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ detector with deionized water
			b	16	4500 (i)			
		23	a	13(14, 2)	4500 (r)	2x	flushing	Washing the syringe and the $\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ detector with STD1 (STD2, STD3)
			b	16	4500 (i)			
		24	a	13(14, 2)	2700 (r)			Draw up STD1 (STD2, STD3) and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	700 (i)			
			c	16	2000 (i)			
		25	a	16	1440 (r)			Withdraw STD1 (STD2, STD3) from the flow cell and add mixed reagent (Griess reagent + $\text{VCl}_3$ )
			b	5	360 (r)			
		26		16	450 (i)	4x	mixing	Mixing STD1 (STD2, STD3) with the reagent
					450 (r)			
		27		8	1800 (i)			Waiting 30 minutes into $\text{PO}_4^{3-}$ detector to allow $\text{NO}_3^-$ reduction during incubation with $\text{VCl}_3$ reagent at maximum temperature ( $\sim 50^\circ\text{C}$ ).
		28	a	8	1800 (r)			Withdraw the reaction mixture from the $\text{PO}_4^{3-}$ detector, waiting 2 min. inside the syringe housing to cool the mixture and open the $\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ detector and inject the mixture and set light intensity for the measurement ( $V, I$ )
			b	4	225 (i)			
			c	16	1575(i)			
washing		29	a	3	4500 (r)			Draw up the cleaning solution into the syringe and all detectors, and set the light intensity for blank measurement.
			b	8	4500 (i)			
			c	3	4500 (r)			
			d	15	4500 (i)			
			e	3	4500 (r)			
			f	16	4500 (i)			
$\text{H}_4\text{SiO}_4$ Calibration		30		4	4500 (i)			Initialize the syringe motor and detector, align the switching valve and ensure that the syringe plunger is fully retracted.
	Blank	31	a	7	4500 (r)	2x	flushing	Washing the syringe and the $\text{H}_4\text{SiO}_4$ detector with deionized water
			b	15	4500 (i)			
		32	a	7	2700 (r)			Draw up the blank and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	1350 (i)			
			c	15	1350 (i)			
		33	a	15	225 (r)			Withdraw the blank from the flow cell and add R1(molybdc acid)
			b	11	225 (r)			
		34		15	300 (i)	4x	mixing	Mixing the blank and R1 and waiting 3 min for complexation
					300 (r)			
	35	a	12	225 (r)				

			b	10	225 (r)		Add R2 (Oxalic acid) and R3 (Ascorbic Acid) to the reaction mixture
		36		15	450 (i)	4x	Mixing the blank and the reagents
					450 (r)	mixing	
		37	a	4	225 (i)		Inject the reaction mixture into the H <sub>4</sub> SiO <sub>4</sub> detector and set the light intensity for measurement ( $V$ , $I$ )
	b		15	675 (i)			
	Standard 1, 2, 3	38	a	7	4500 (r)	2x	Washing the syringe and the H <sub>4</sub> SiO <sub>4</sub> detector with deionized water
			b	15	4500 (i)	flushing	
		39	a	13(14, 2)	4500 (r)	2x	Washing the syringe and the H <sub>4</sub> SiO <sub>4</sub> detector with STD1 (STD2, STD3)
			b	15	4500 (i)	flushing	
		40	a	13(14, 2)	2700 (r)		Draw up STD1 (STD2, STD3) and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	1350 (i)		
			c	15	1350 (i)		
		41	a	15	225 (r)		Withdraw STD1 (STD2, STD3) from the flow cell add R1(molybdcic acid)
			b	11	225 (r)		
		42	15		300 (i)	4x	Mixing STD1 (STD2, STD3) and R1 and waiting 3 min for complexation
					300 (r)	mixing	
		43	a	12	225 (r)		Add R2 (Oxalic acid) and R3 (Ascorbic Acid) to the reaction mixture
			b	10	225 (r)		
		44	15		450 (i)	4x	Mixing STD1 (STD2, STD3) and the reagents
					450 (r)	mixing	
		45	a	4	225 (i)		Inject the reaction mixture into the H <sub>4</sub> SiO <sub>4</sub> detector and set the light intensity for measurement ( $V$ , $I$ )
	b		15	675 (i)			
washing	46	a	3	4500 (r)		Draw up the cleaning solution into the syringe and all detectors, and set the light intensity for blank measurement.	
		b	8	4500 (i)			
		c	3	4500 (r)			
		d	15	4500 (i)			
		e	3	4500 (r)			
		f	16	4500 (i)			
CRM	PO <sub>4</sub> <sup>3-</sup> determination	47		4	4500 (i)		Initialize the syringe motor and detector, align the switching valve and ensure that the syringe plunger is fully retracted.
		48	a	7	4500 (r)	2x	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with deionized water
			b	8	4500 (i)	flushing	
		49		6	4500 (r)	2x	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with CRM
				8	4500 (i)	flushing	
		50	a	6	2700 (r)		Draw up CRM and set the light intensity for the reference ( $I^R, V^R$ )
			b	4	1350 (i)		
			c	8	1350 (i)		
		51	a	8	720 (r)		Withdraw CRM from the flow cell and add R1 (Molybdate mixed reagent) and R2 (Ascorbic Acid)
			b	9	180 (r)		

$\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ determination		c	10	180 (r)		Mixing the reagent with CRM and inject the reaction mixture inside the detector and waiting for 3 minutes for color development and set the light intensity for the measurement ( $V$ , $I$ )
	52	8	450 (i)	4x		
			450 (r)	mixing		
		4	180 (i)			
	8	900 (i)				
	53	a	7	4500 (r)	2x	Washing the syringe and the $\text{PO}_4^{3-}$ detector with deionized water
		b	8	4500 (i)	flushing	
	54	a	6	4500 (r)	2x	Washing the syringe and the $\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ detector with CRM
		b	16	4500 (i)	flushing	
	55	a	6	2700 (r)		Draw up CRM and set the light intensity for the reference ( $I^R, V^R$ )
		b	4	700 (i)		
		c	16	2000 (i)		
	56	a	16	1440 (r)		Withdraw CRM from the flow cell and add mixed reagent (Griess reagent + $\text{VCl}_3$ )
		b	5	360 (r)		
	57	16	450 (i)	4x	Mixing CRM with the reagent	
			450 (r)	mixing		
	58	8	1800 (i)		Waiting 30 minutes into $\text{PO}_4^{3-}$ detector to allow $\text{NO}_3^-$ reduction during incubation with $\text{VCl}_3$ reagent at maximum temperature ( $\sim 50^\circ\text{C}$ ).	
	59	a	8	1800 (r)		Withdraw the reaction mixture from the $\text{PO}_4^{3-}$ detector, waiting 2 min. inside the syringe housing to cool the mixture and open the $\Sigma (\text{NO}_3^- + \text{NO}_2^-)$ detector and inject the mixture and set light intensity for the measurement ( $V$ , $I$ )
		b	4	225 (i)		
c		16	1575 (i)			
$\text{H}_4\text{SiO}_4$ determination	60	a	7	4500 (r)	2x	Washing the syringe and the $\text{H}_4\text{SiO}_4$ detector with deionized water
		b	15	4500 (i)	flushing	
	61	a	6	4500 (r)	2x	Washing the syringe and the $\text{H}_4\text{SiO}_4$ detector with CRM
		b	15	4500 (i)	flushing	
	62	a	6	2700 (r)		Draw up CRM and set the light intensity for the reference ( $I^R, V^R$ )
		b	4	1350 (i)		
		c	15	1350 (i)		
	64	a	15	225 (r)		Withdraw CRM from the flow cell and add R1(molybdic acid)
		b	11	225 (r)		
	65	15	300 (i)	4x mixing	Mixing CRM and R1 then waiting 3 min for complexation	
300 (r)						
66	a	12	225 (r)		Add R2 (Oxalic acid) and R3 (Ascorbic Acid) to the reaction mixture	
	b	10	225 (r)			
67	15	450 (i)	4x	Mixing CRM and the reagents		
		450 (r)	mixing			
68	a	4	225 (i)			

			b	15	675 (i)		Inject the reaction mixture into the H <sub>4</sub> SiO <sub>4</sub> detector and set the light intensity for measurement ( <i>V</i> , <i>I</i> )	
washing	69	a	3	4500 (r)		Draw up the cleaning solution into the syringe and all detectors, and set the light intensity for blank measurement.		
		b	8	4500 (i)				
		c	3	4500 (r)				
		d	15	4500 (i)				
		e	3	4500 (r)				
		f	16	4500 (i)				
Sea water	PO <sub>4</sub> <sup>3-</sup> determination	70	4	4500 (i)		Initialize the syringe motor and detector, align the switching valve and ensure that the syringe plunger is fully retracted.		
		71	a	1	4500 (r)	6x flushing	Washing the syringe and the PO <sub>4</sub> <sup>3-</sup> detector with seawater	
			b	8	4500 (i)			
		72	a	1	2700 (r)		Draw up seawater and set the light intensity for the reference ( <i>I</i> <sup><i>R</i></sup> , <i>V</i> <sup><i>R</i></sup> )	
			b	4	1350 (i)			
			c	8	1350 (i)			
		73	a	8	720 (r)		Withdraw seawater from the flow cell and add R1 (Molybdate mixed reagent) and R2 (Ascorbic Acid)	
			b	9	180 (r)			
			c	10	180 (r)			
		74	a	8	450 (i)	4x mixing	Mixing the reagent with seawater and inject the reaction mixture inside the detector and waiting for 3 minutes for color development and set the light intensity for the measurement ( <i>V</i> , <i>I</i> )	
					450 (r)			
			b	4	180 (i)			
		c	8	900 (i)				
	Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) determination	75	a	1	4500 (r)	6x flushing	Washing the syringe and the Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) detector with seawater	
			b	16	4500 (i)			
		76	a	1	2700 (r)		Draw up seawater and set the light intensity for the reference ( <i>I</i> <sup><i>R</i></sup> , <i>V</i> <sup><i>R</i></sup> )	
			b	4	700 (i)			
				16	2000 (i)			
		77	a	16	1440 (r)		Withdraw seawater from the flow cell and add mixed reagent (Griess reagent + VCl <sub>3</sub> )	
			b	5	360 (r)			
		78	16	450 (i)	4x mixing	Mixing seawater with the reagent		
				450 (r)				
		79	8	1800 (i)		Waiting 30 minutes into PO <sub>4</sub> <sup>3-</sup> detector to allow NO <sub>3</sub> <sup>-</sup> reduction during incubation with VCl <sub>3</sub> reagent at maximum temperature (~ 50 °C).		
		80	a	8	1800 (r)		Withdraw the reaction mixture from the PO <sub>4</sub> <sup>3-</sup> detector, waiting 2 min. inside the syringe housing to cool the mixture and open the Σ (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> ) detector and inject the mixture and set light intensity for the measurement ( <i>V</i> , <i>I</i> )	
			b	4	225 (i)			
			c	16	1575 (i)			

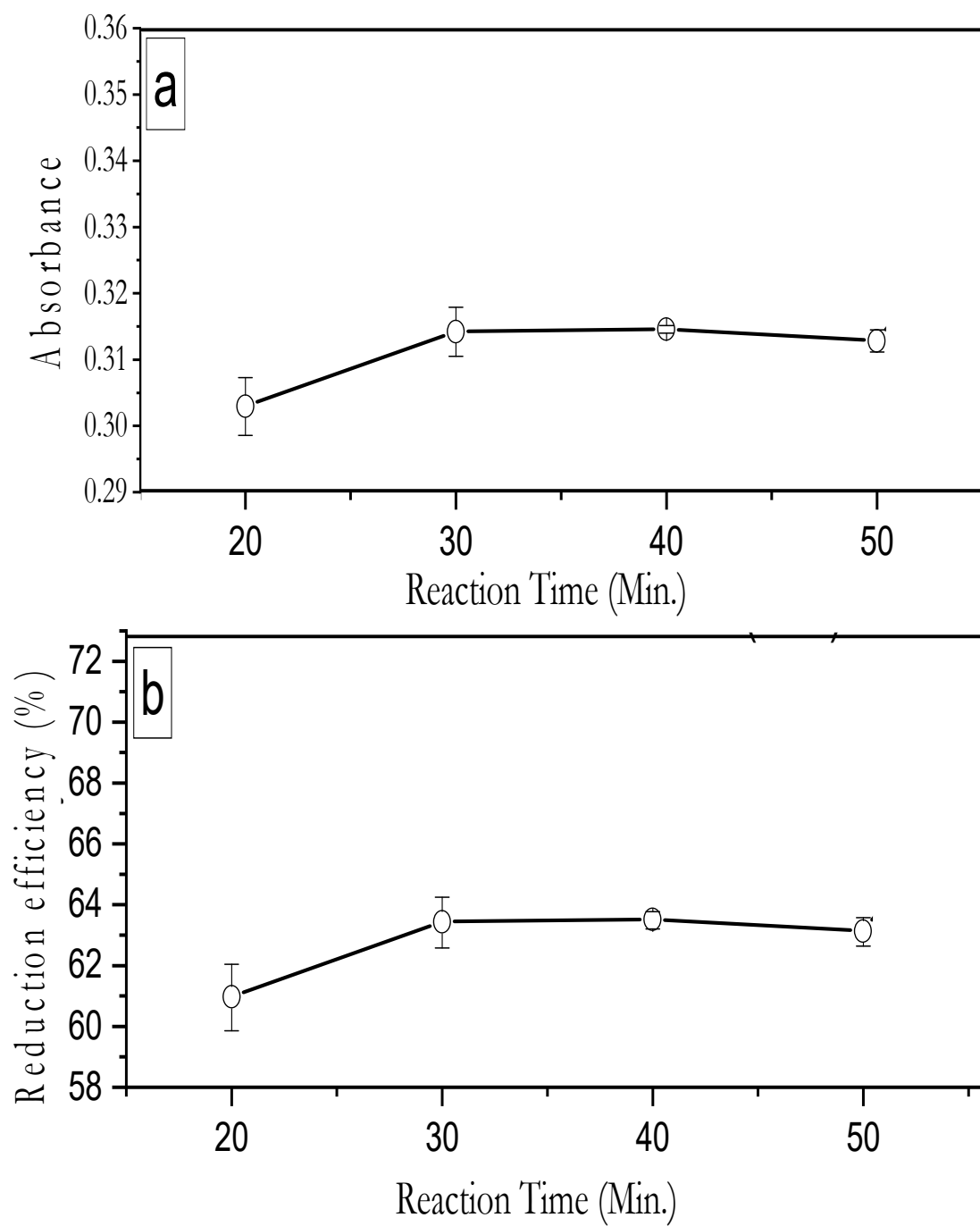
10 x (measurement loop)

H <sub>4</sub> SiO <sub>4</sub> determination	81	a	1	4500 (r)	6x flushing	Washing the syringe and the H <sub>4</sub> SiO <sub>4</sub> detector with seawater
		b	15	4500 (i)		
	82	a	1	2700 (r)		Draw up seawater and set the light intensity for the reference ( $I^R, V^R$ )
		b	4	1350 (i)		
		c	15	1350 (i)		
	83	a	15	225 (r)		Withdraw seawater from the flow cell and add R1(molybdcic acid)
		b	11	225 (r)		
	84		15	300 (i)	4x mixing	Mixing seawater and R1 then waiting 3 min for complexation
				300 (r)		
	85	a	12	225 (r)		Add R2 (Oxalic acid) and R3 (Ascorbic Acid) to the reaction mixture
		b	10	225 (r)		
	86		15	450 (i)	4x mixing	Mixing seawater and the reagents
				450 (r)		
	87	a	4	225 (i)		Inject the reaction mixture into the H <sub>4</sub> SiO <sub>4</sub> detector and set the light intensity for measurement ( $V, I$ )
		b	15	675 (i)		

<sup>a</sup> maximum movement of the syringe is 4500 (~2.2 ml)

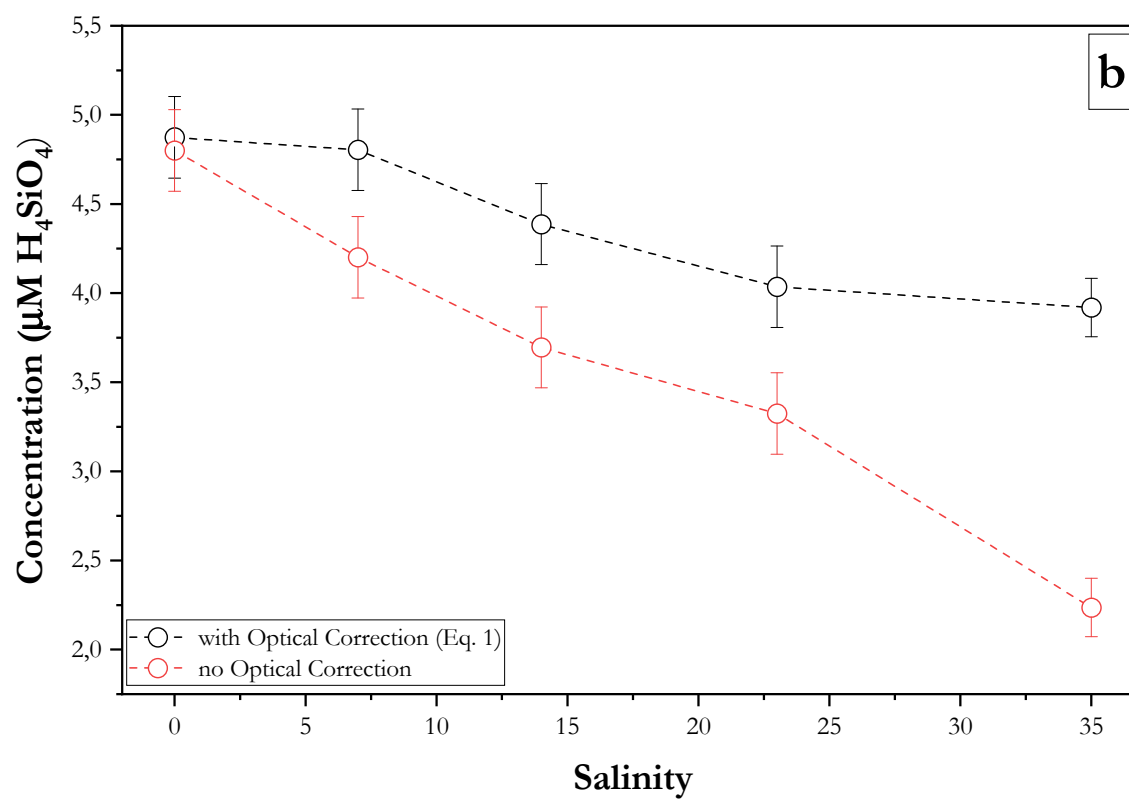
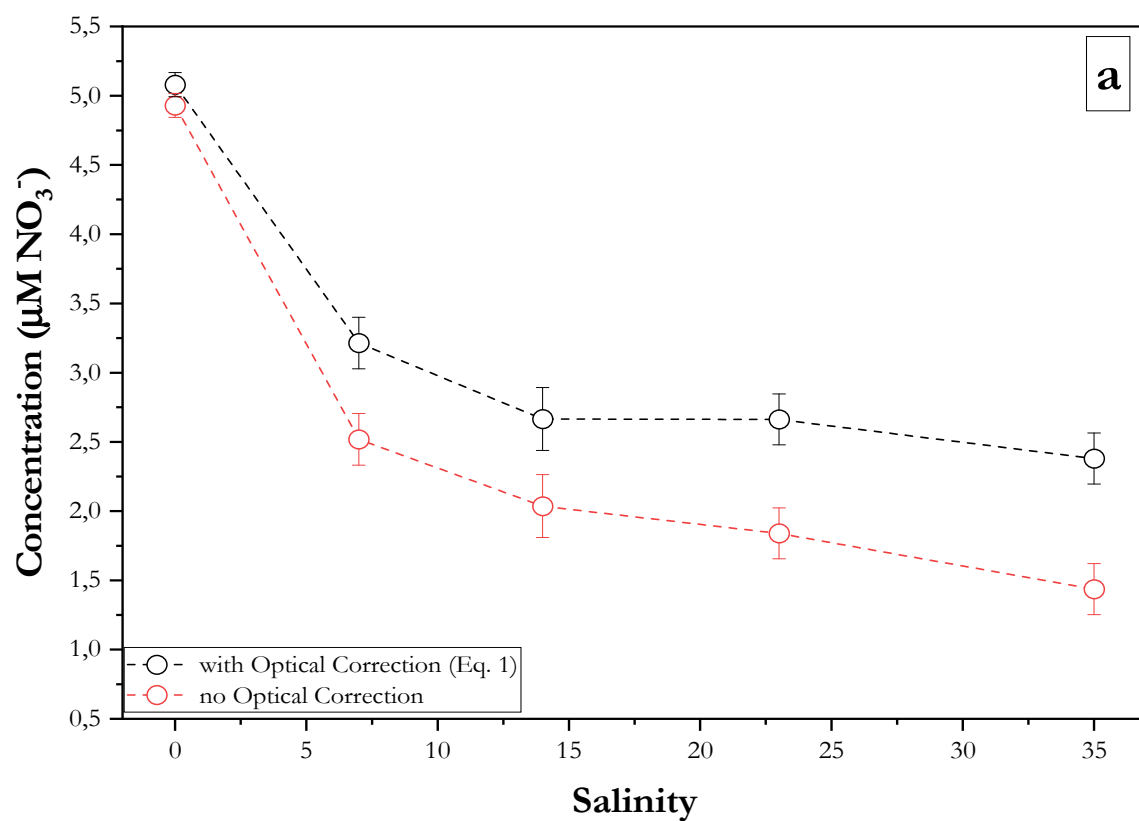
<sup>b</sup> r: retract; <sup>c</sup> i: inject

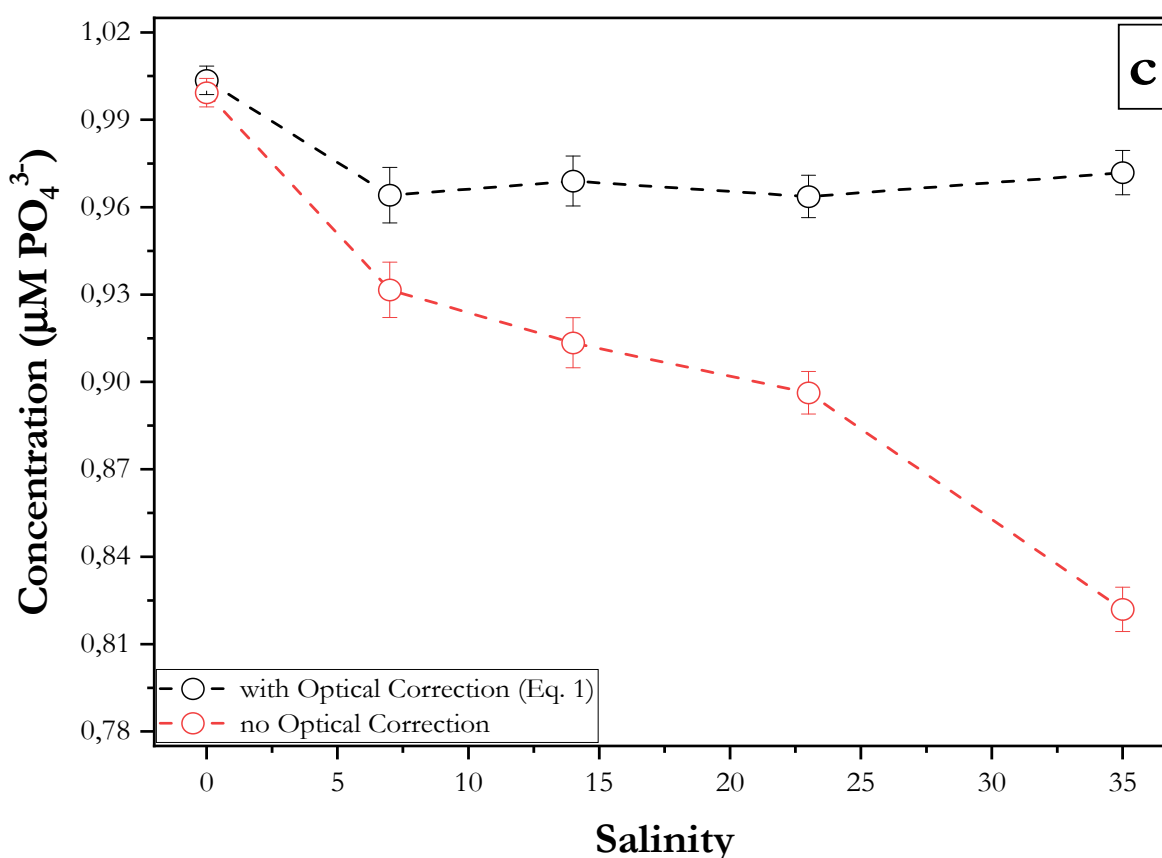
<sup>d</sup> port 13: STD1, port 14: STD2, port 2: STD3



**Figure S1.** Effect of reaction time in minutes on (a) the absorbance of 10  $\mu\text{M}$   $\text{NO}_3^-$  and (b) the reduction efficiency (%) which defined as the ratio of the absorbance of 10  $\mu\text{M}$   $\text{NO}_3^-$  and the absorbance of 10  $\mu\text{M}$   $\text{NO}_2^-$ .





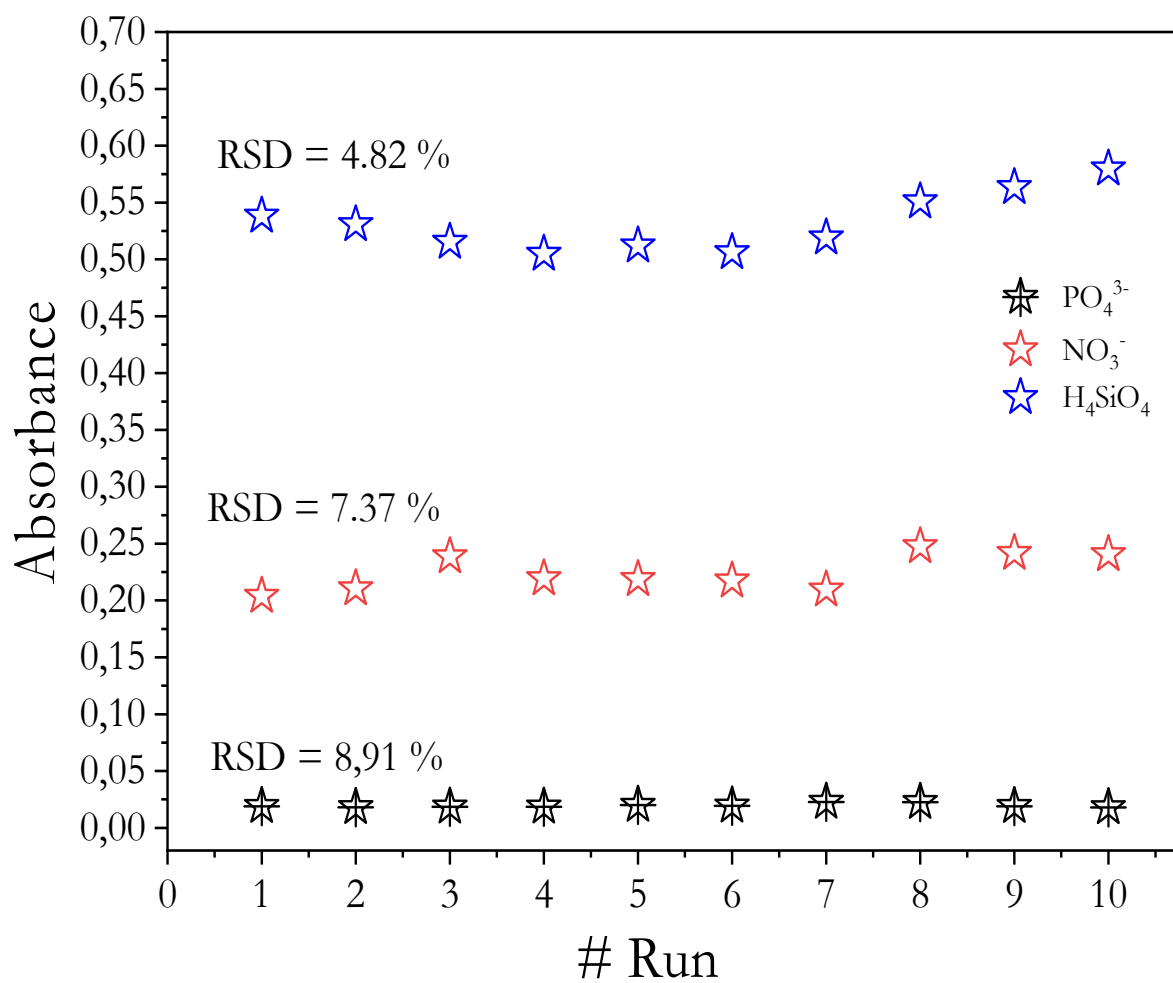


**Figure S2.** (a) calculated concentrations of 5  $\mu\text{M}$   $\text{NO}_3^-$ , (b) calculated concentrations of 5  $\mu\text{M}$   $\text{H}_4\text{O}_4\text{Si}$  and (c) calculated concentrations of 1  $\mu\text{M}$   $\text{PO}_4^{3-}$  samples with different salinity (0, 7, 14, 23, 35) based on calibration curves of (0, 1, 5 and 10  $\mu\text{M}$   $\text{NO}_3^-$ ), (0, 1, 5, 10  $\mu\text{M}$   $\text{H}_4\text{O}_4\text{Si}$ ) and (0, 0.5, 1, 2  $\mu\text{M}$   $\text{PO}_4^{3-}$ ), respectively. The raw data were processed using equation 1 (black circles) and the red circles represent the data processed using the traditional Beer's Law equation ( $A = -\log_{10}(\frac{I}{I_0})$ ). Error bar ( $\pm 1$  SD),  $n = 10$ .

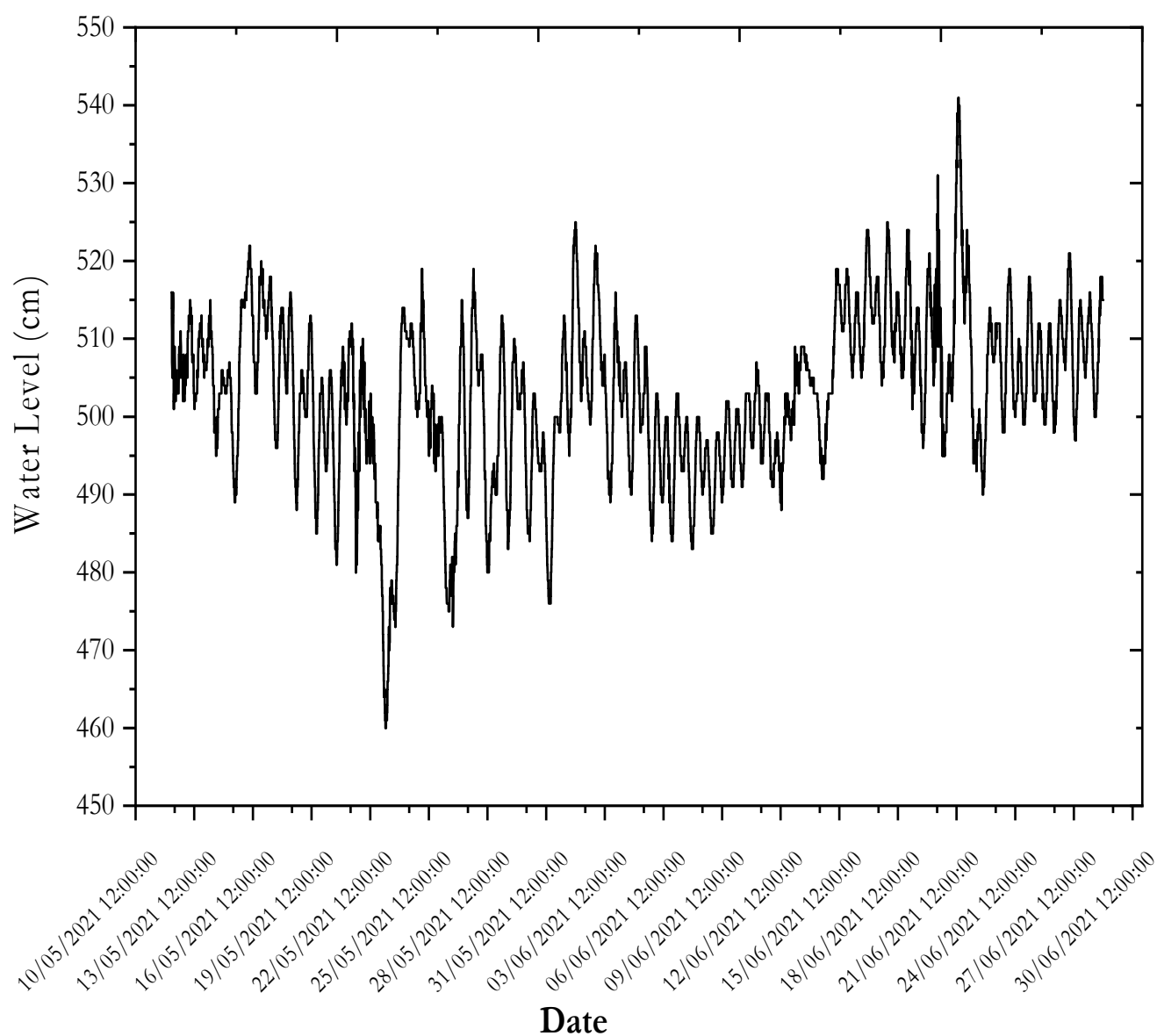
**Table S2.** Slopes and intercepts including their standard deviations, t-values and the probabilities for the calibration curves in Figure 6.

		Value	Standard deviation	t-value	Probability
$\text{NO}_3^-$	Int.	0.06876	$6.85 \times 10^{-4}$	100.42	$1.079 \times 10^{-13}$
	Slp.	0.00614	$9.76 \times 10^{-5}$	62.94	$4.51 \times 10^{-12}$
$\text{NO}_2^-$	Int.	0.04061	0.00228	17.77	$1.028 \times 10^{-7}$
	Slp.	0.01202	$2.94 \times 10^{-4}$	40.87	$1.414 \times 10^{-10}$
$\text{PO}_4^{3-}$	Int.	0.00191	$4.88 \times 10^{-4}$	3.9	0.00294
	Slp.	0.01211	$8.46 \times 10^{-5}$	143.1	$5 \times 10^{-10}$
$\text{H}_4\text{SiO}_4$	Int.	-0.00632	0.00351	-1.8	0.10199
	Slp.	0.02377	$6.48 \times 10^{-4}$	36.65	$5.44 \times 10^{-12}$

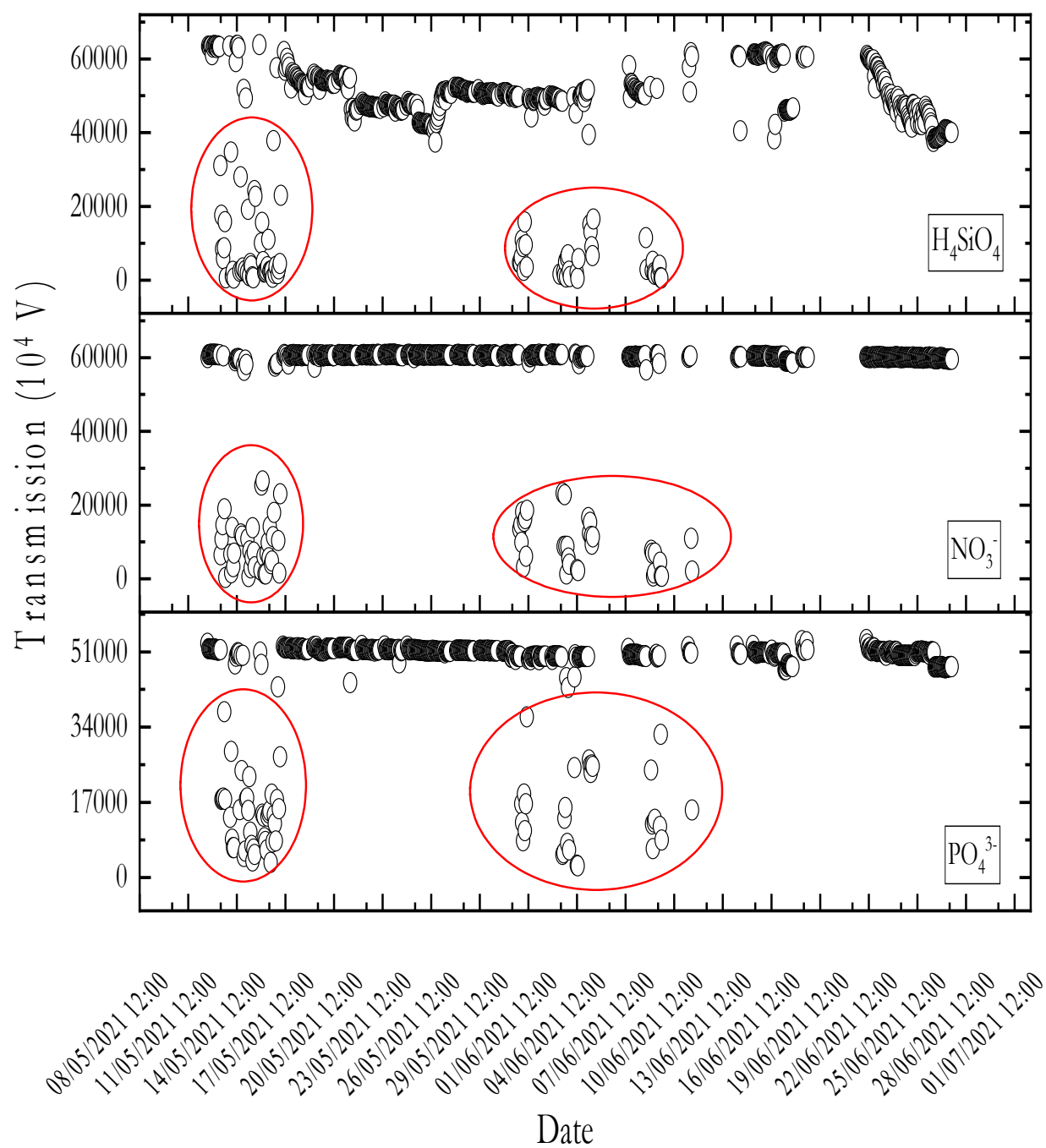
Int.: Intercept, Slp.: Slope.



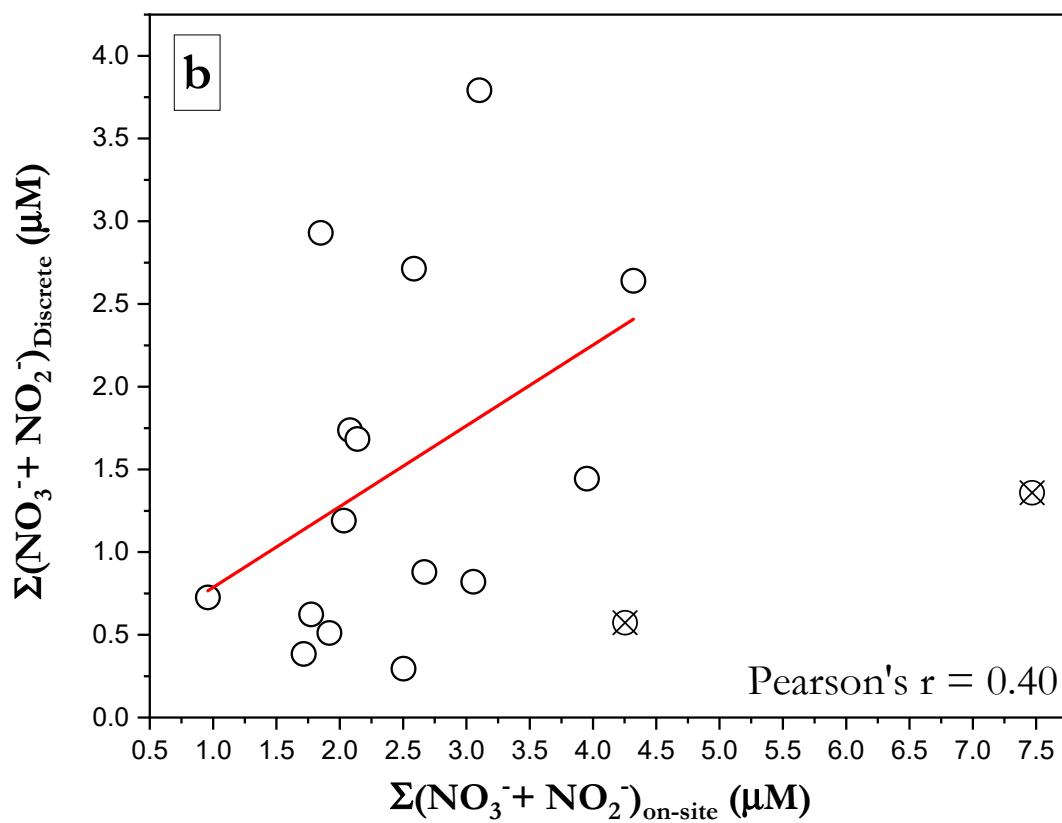
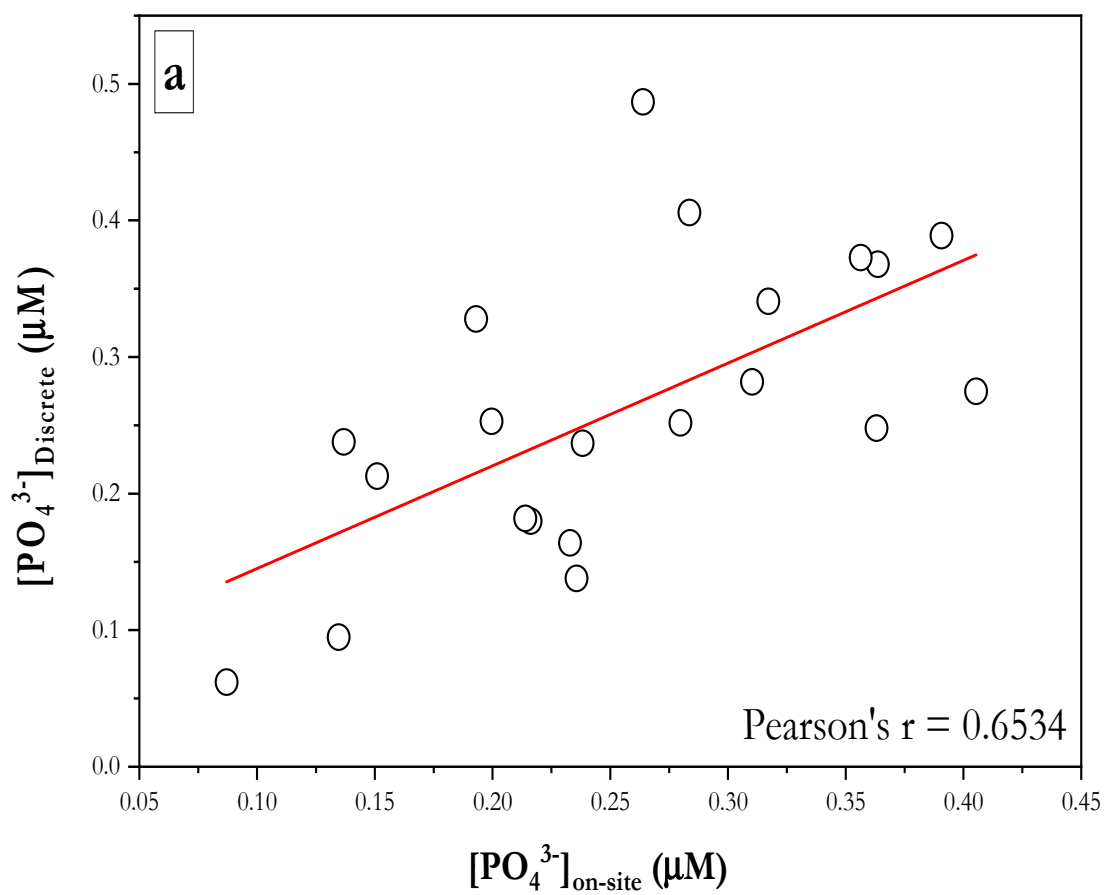
**Figure S3.** The measured absorbance value of KANSO CRM for nutrients for 6 consecutive runs of PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, and H<sub>4</sub>O<sub>4</sub>Si with RSD (relative standard deviation) value. The Certified value for CRM is  $23.7 \pm 0.2 \mu\text{M}$  for NO<sub>3</sub><sup>-</sup>,  $56.4 \pm 0.5 \mu\text{M}$  for H<sub>4</sub>O<sub>4</sub>Si, and  $1.7 \pm 0.02 \mu\text{M}$  for PO<sub>4</sub><sup>3-</sup>.

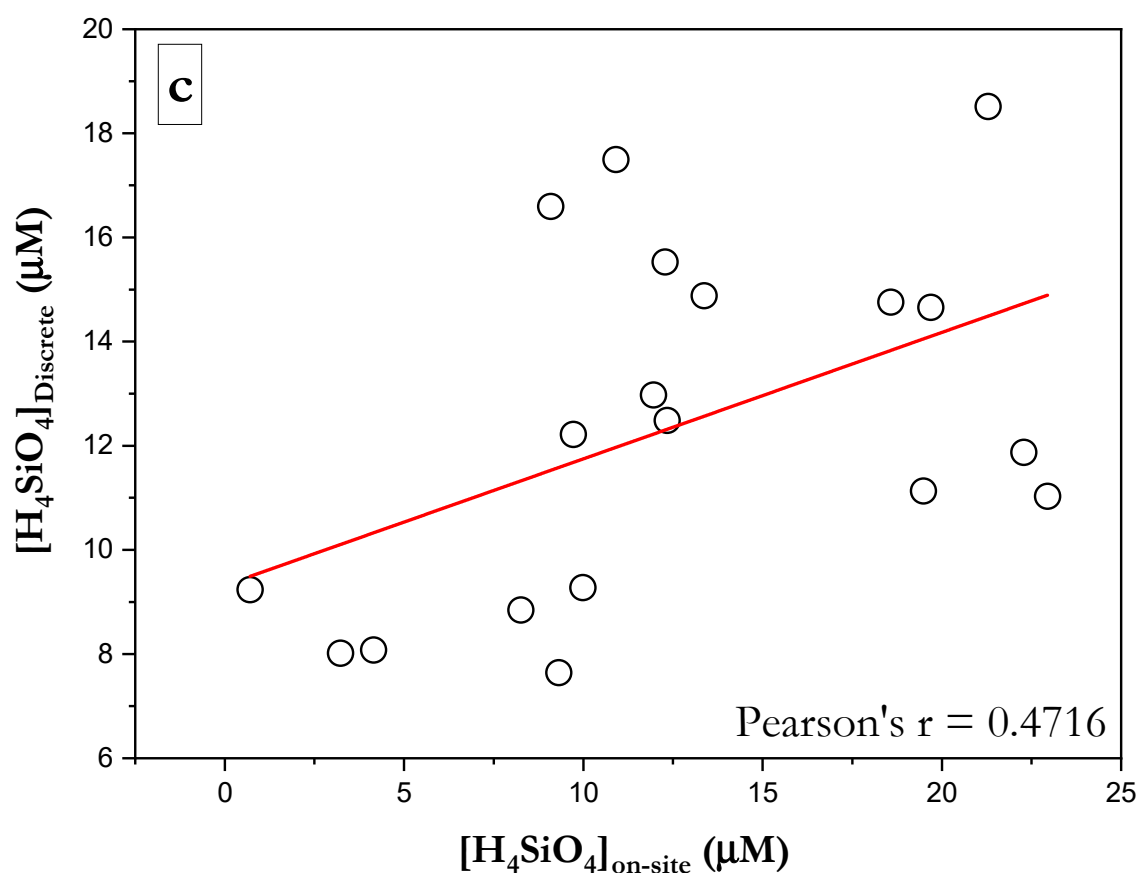


**Figure S4.** Time series data for the period from May 12 to June 28, 2021, for water level data at the kiel-Holtenau station obtained from the Federal Waterways and Shipping Administration (WSV).

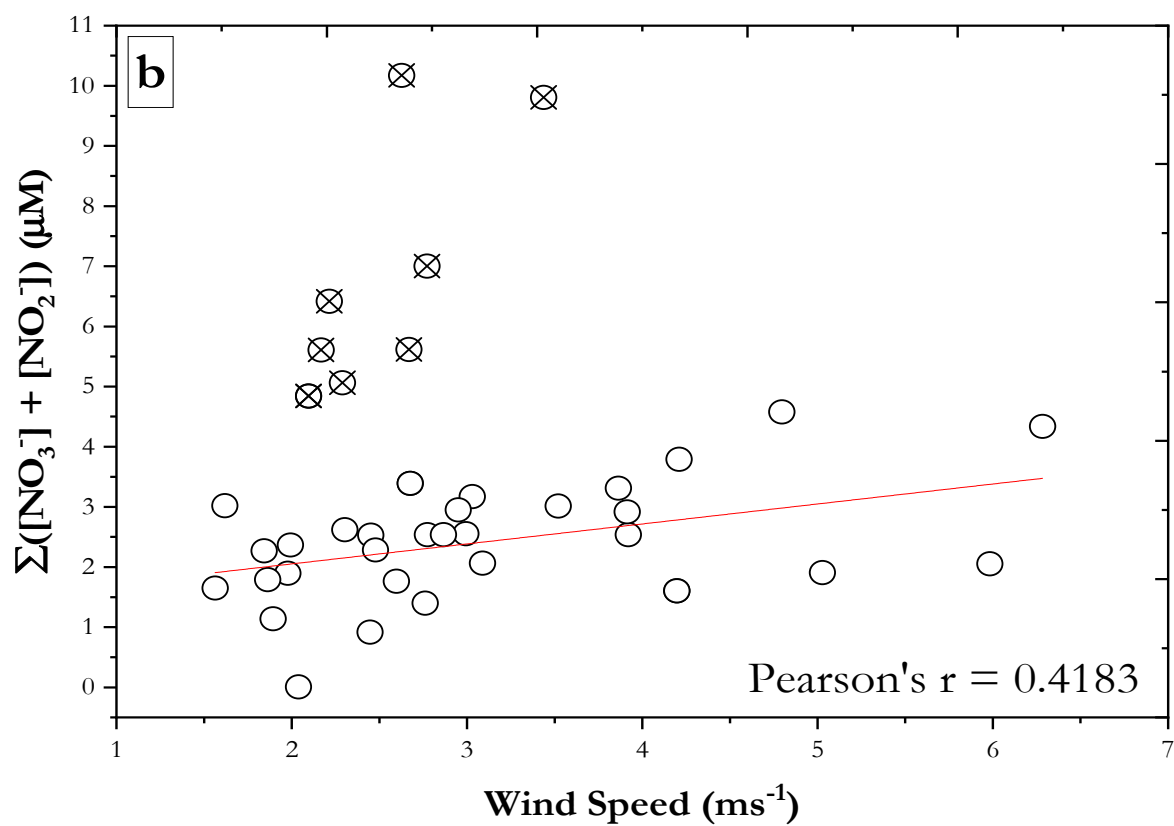
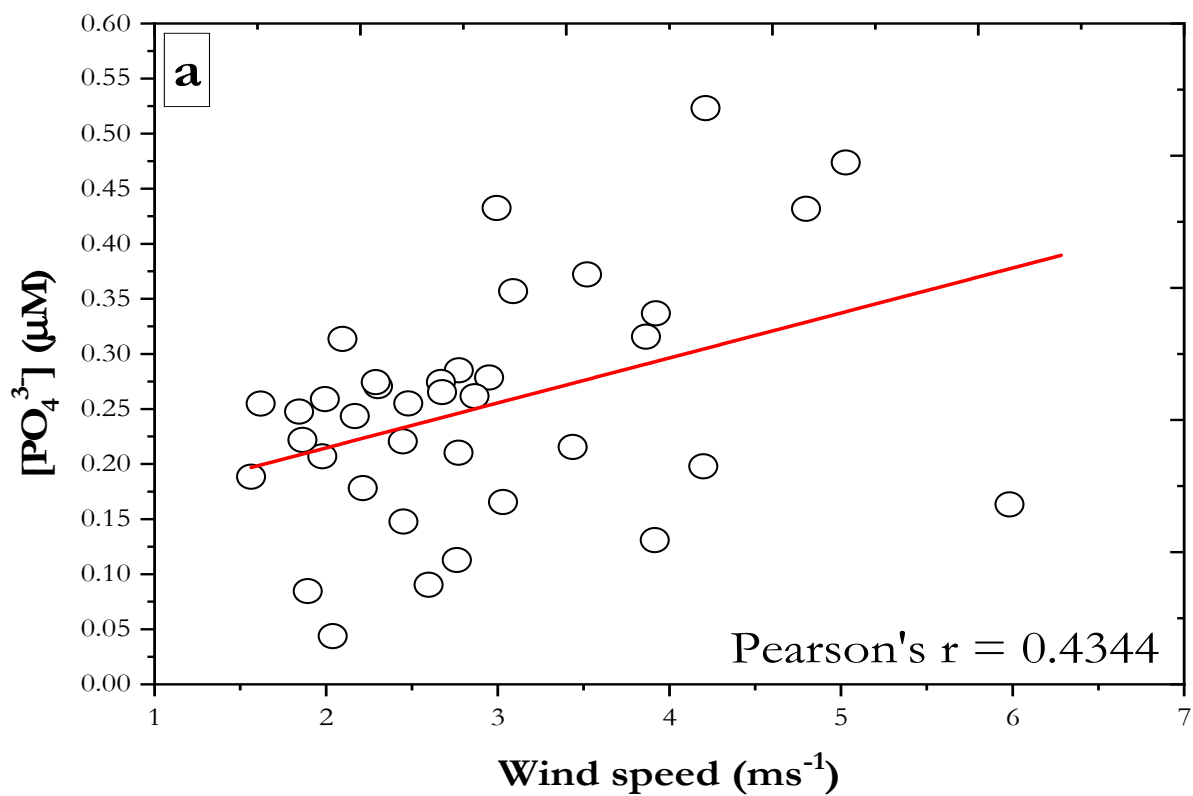


**Figure S5.** Time series data from May 12 to June 26, 2021, of  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , and  $\text{H}_4\text{O}_4\text{Si}$  photodiode detector readout; the points in red circles refer to the drop-down of the transmission values due to air bubbles trapped into the flow cell.

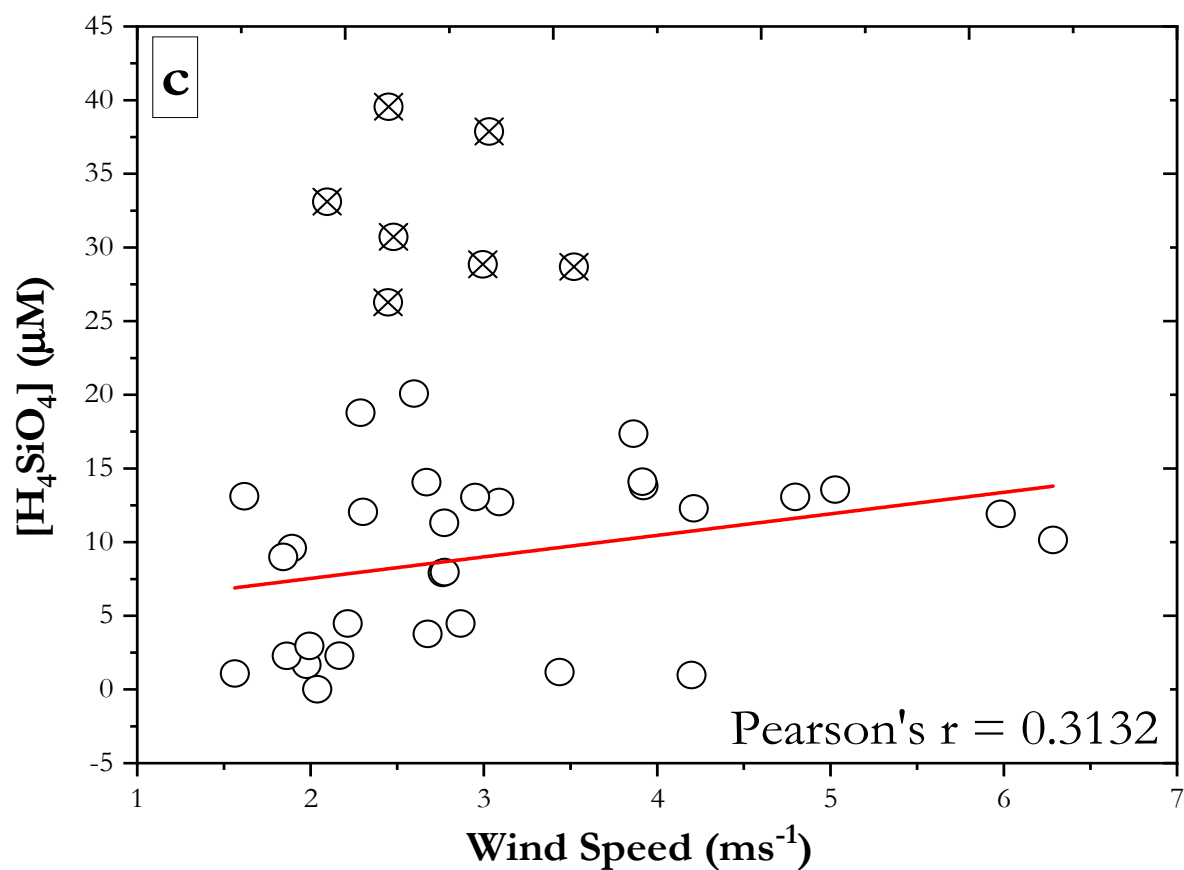




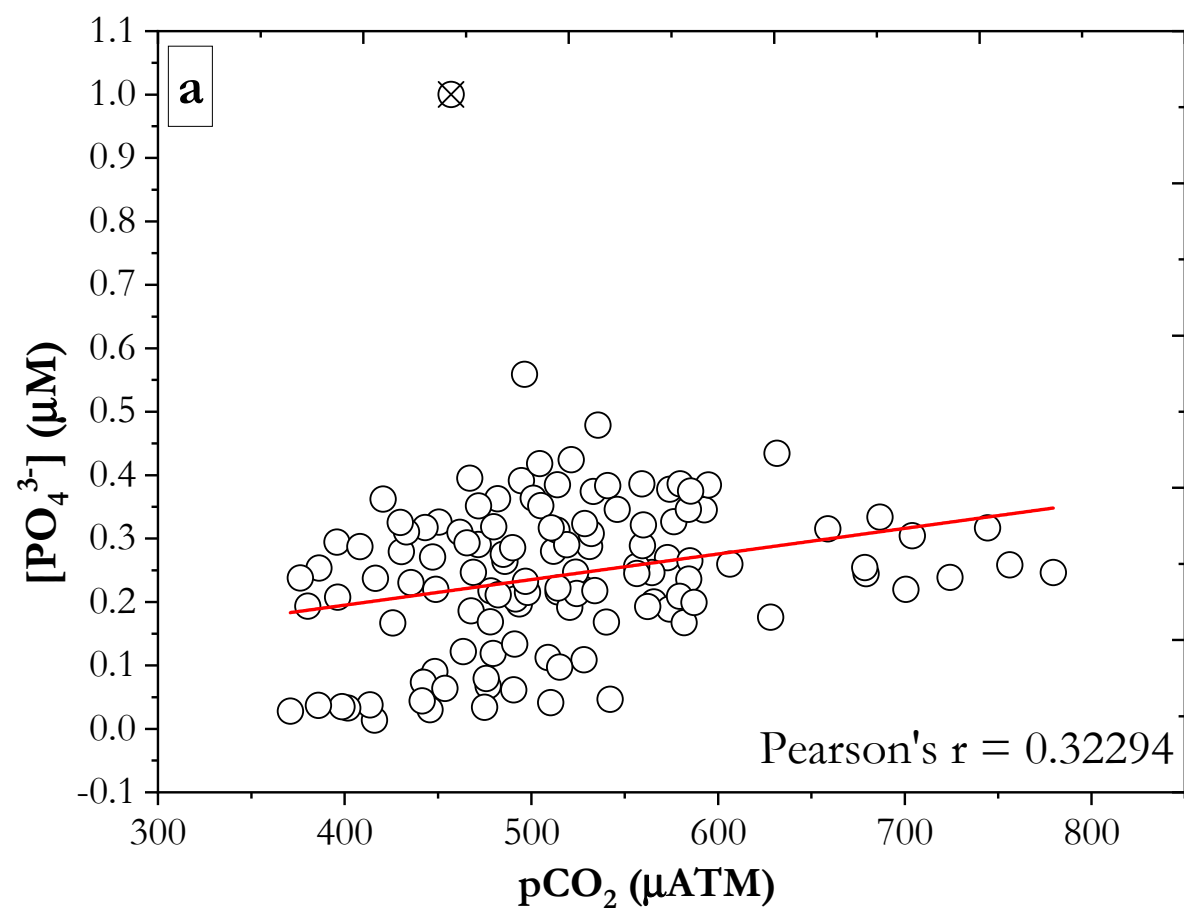
**Figure S6.** Property-to-property plots for (a)  $\text{PO}_4^{3-}$  in  $\mu\text{M}$  measured on-site with the AutoLAB analyser compared to synchronised  $\text{PO}_4^{3-}$  in  $\mu\text{M}$  measured with the air-segment analyser in the laboratory for discretely collected samples pearson's  $r = 0.6534$ ,  $n = 21$ , (b)  $\Sigma(\text{NO}_3^- + \text{NO}_2^-)$  in  $\mu\text{M}$  measured on-site with the AutoLAB analyser compared to synchronised  $\Sigma(\text{NO}_3^- + \text{NO}_2^-)$  in  $\mu\text{M}$  with the air-segment analyser in the laboratory for discretely collected samples, pearson's  $r = 0.4$ ,  $n = 17$ , two clear outliers ( $\times$ ) were removed and (c)  $\text{H}_4\text{SiO}_4$  in  $\mu\text{M}$  measured on-site with the AutoLAB analyser compared to synchronised  $\text{H}_4\text{SiO}_4$  in  $\mu\text{M}$  measured with the air-segment analyser in the laboratory for discretely collected samples, pearson's  $r = 0.4716$ ,  $n = 19$ .

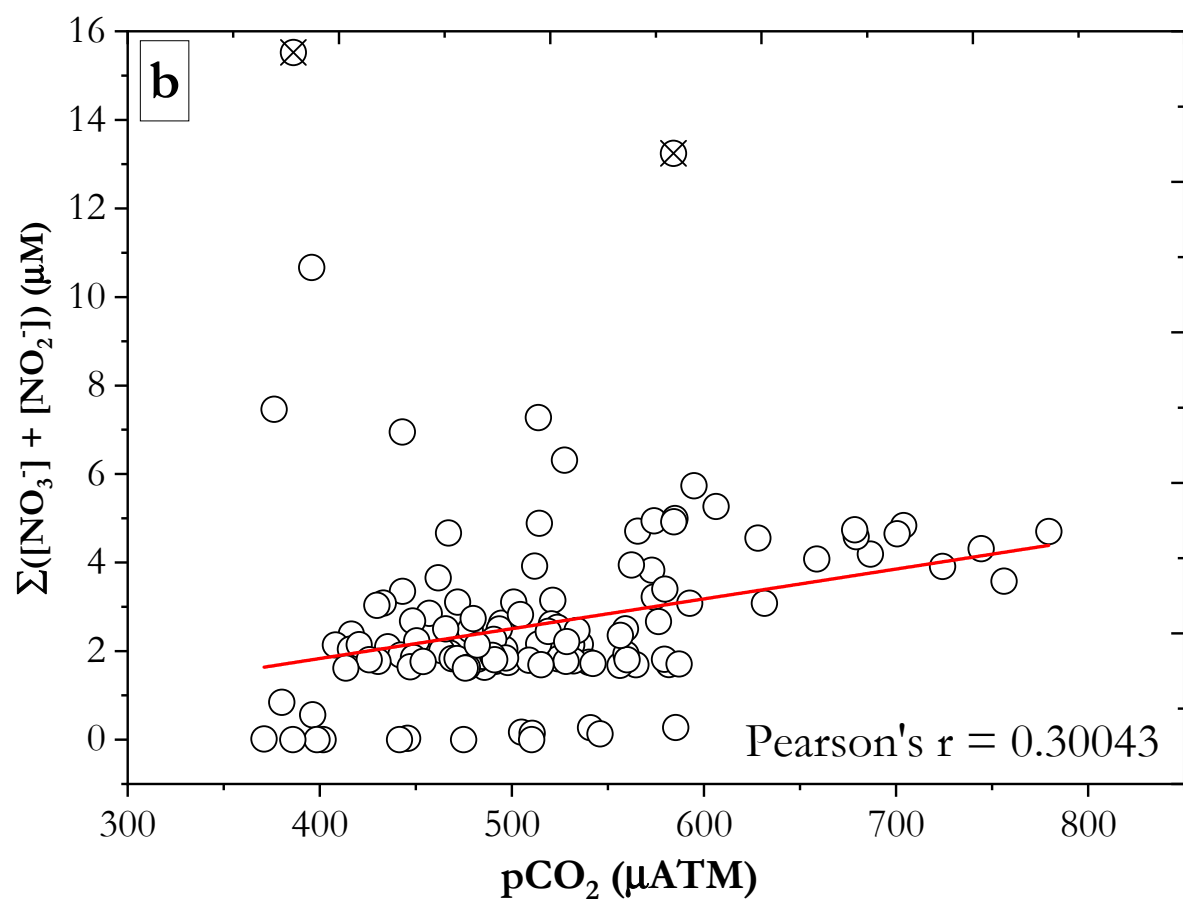


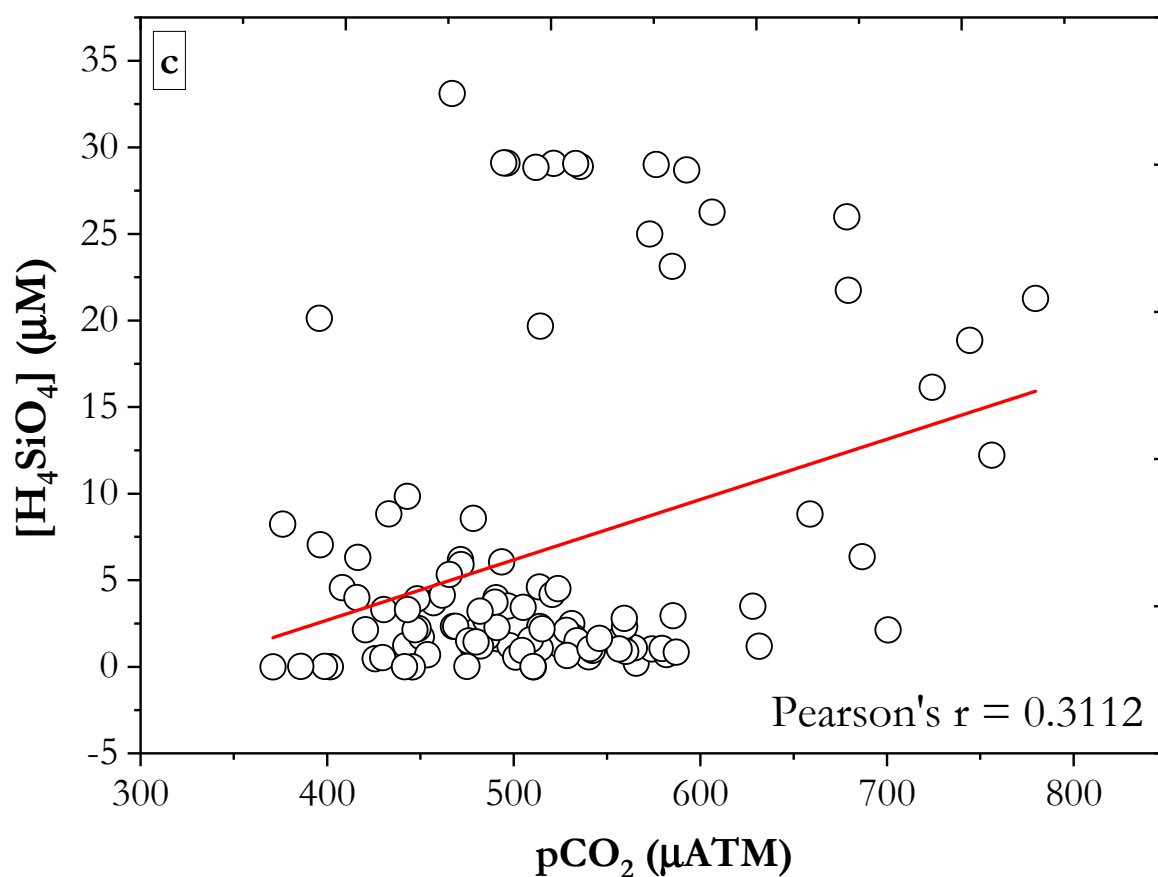




**Figure S7.** Plot-by-plot plots from 12 May to 27 June 2021 for (a) the daily average of on-site  $\text{PO}_4^{3-}$  concentration in  $\mu\text{M}$  versus the daily average of wind speed in  $\text{ms}^{-1}$ , (b) the daily average of on-site  $\Sigma(\text{NO}_3^- + \text{NO}_2^-)$  concentration in  $\mu\text{M}$  versus the daily average of wind speed in  $\text{ms}^{-1}$ , excluding clear outliers (9 points) (x), and (c) the daily average of  $\text{H}_4\text{SiO}_4$  concentration in  $\mu\text{M}$  measured on site compared to the daily average of wind speed in  $\text{ms}^{-1}$ , excluding clear outliers (7 points) (x).







**Figure S8.** Plot-by-plot plots for the 11-day period from June 4 to June 9 and from June 18 and June 22 to June 27, 2021 for (a) in situ  $p\text{CO}_2$  data compared to on-site  $\text{PO}_4^{3-}$  measured by AutoLab with a unique outlier ( $\times$ ) was excluded (pearson's  $r = 0.32294$ ,  $n = 122$ ), (b) in situ  $p\text{CO}_2$  data compared with on site  $\Sigma(\text{NO}_3^- + \text{NO}_2^-)$  measured by AutoLab with two clear outliers ( $\times$ ) excluded (pearson's  $r = 0.30034$ ,  $n = 122$ ), and (c) in situ  $p\text{CO}_2$  data compared with on site  $\text{H}_4\text{SiO}_4$  measured by AutoLab (pearson's  $r = 0.3112$ ,  $n = 108$ ).