



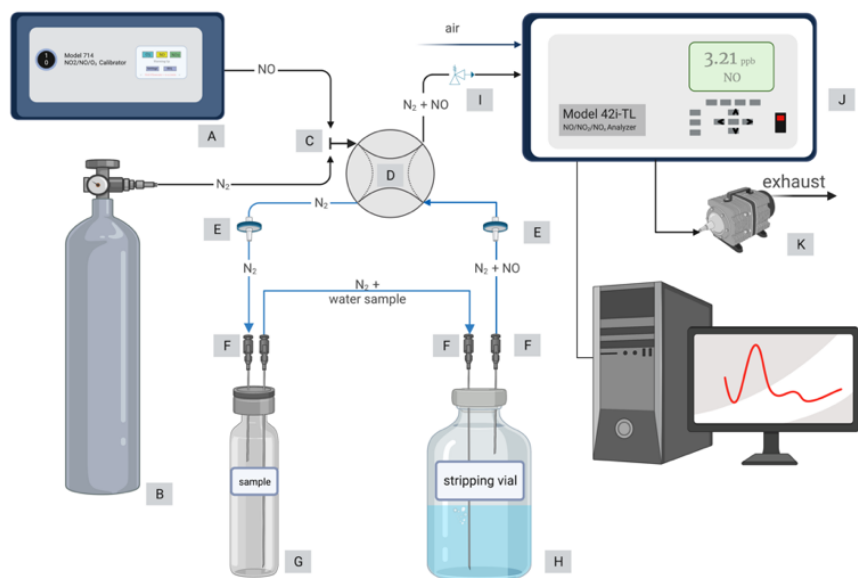
*Supplement of*

## **Dissolved nitric oxide in the lower Elbe Estuary and the Port of Hamburg area**

**Riel Carlo O. Ingeniero et al.**

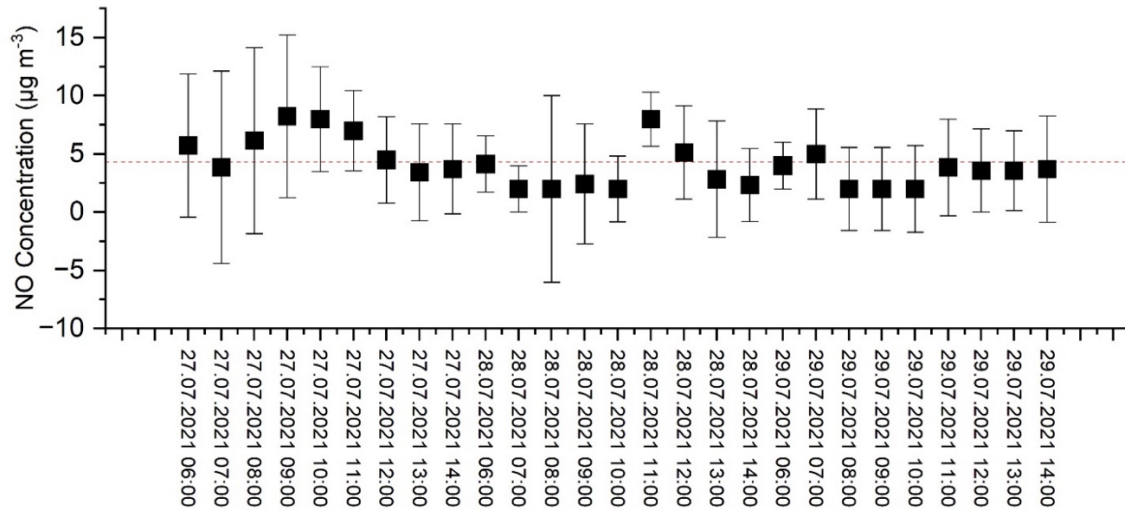
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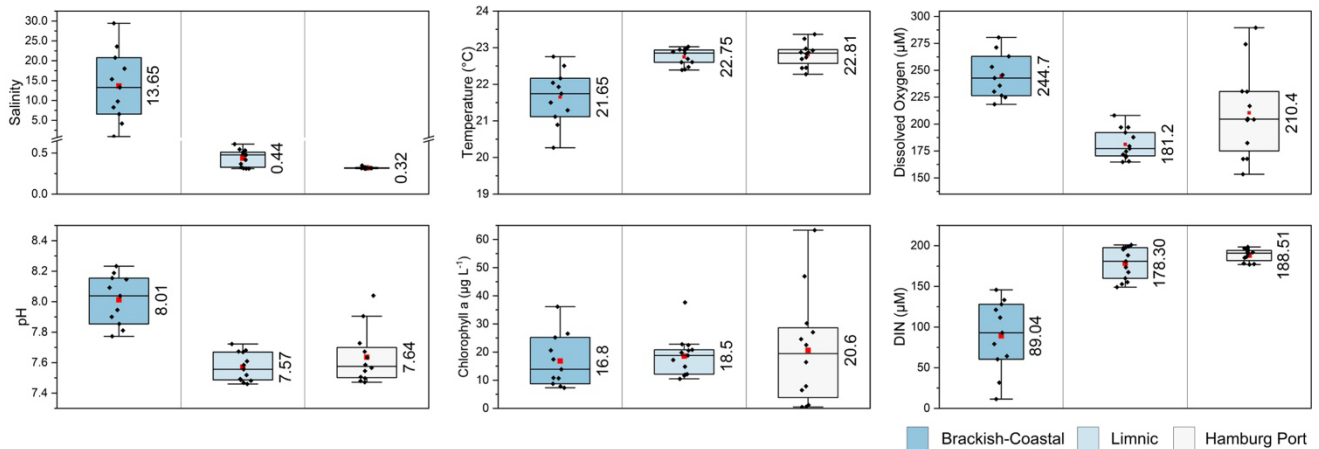
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**Figure S1: Schematic diagram of the updated NO measurement system. The system consists of a chemiluminescence detector connected to a stripping unit, including A: portable nitric oxide calibrator, B: nitrogen gas source connected to a mass flow controller, C: three-way gas valve to switch between NO calibrator gas and nitrogen gas source, D: four-way valve to switch between calibration mode and analysis mode, E: inline filters, F: Luer lock valve to close and isolate the line from the atmosphere when moving to the next sample, G: 50 mL sample vial, H:100 mL stripping vial, I: needle valve, J: NO detector, K: vacuum pump.**

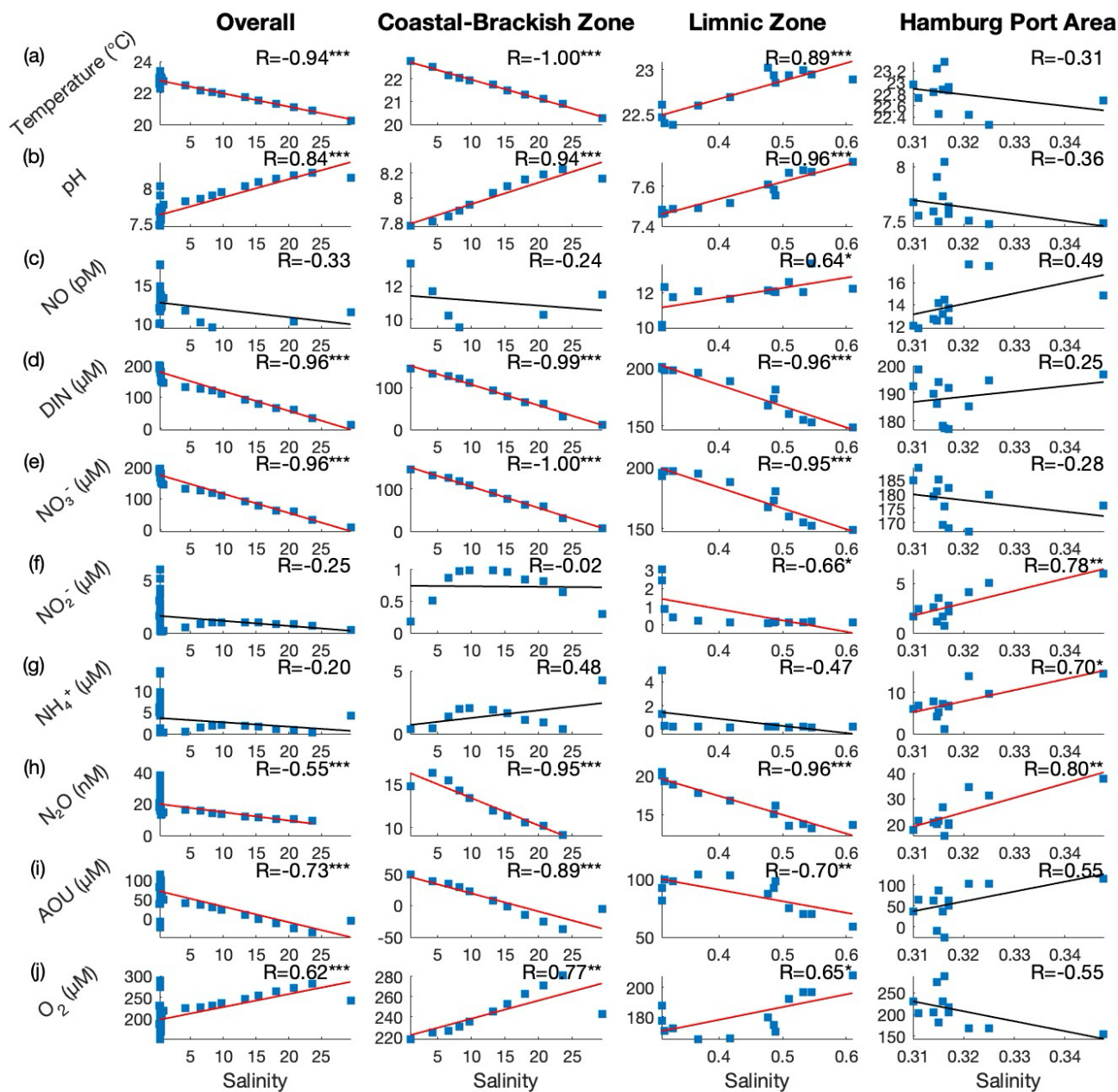


10 **Figure S2: Average hourly atmospheric NO concentration ( $\mu\text{g m}^{-3}$ ) measured in seven background monitoring stations near the Elbe Estuary (AltonaElbhag, Billbrook, FinkenwerderAirbus, FinkenwerderWest, HafenKlGrasbrook, Veddel, and Wilhelmsburg) in Hamburg representative of the time of sampling. Note that the error bars represent the standard deviation. Shown in the red dashed line is the average concentration of  $4.3 \mu\text{g m}^{-3}$ . These data were obtained from <https://luft.hamburg.de/> (last accessed on 2 May 2023).**

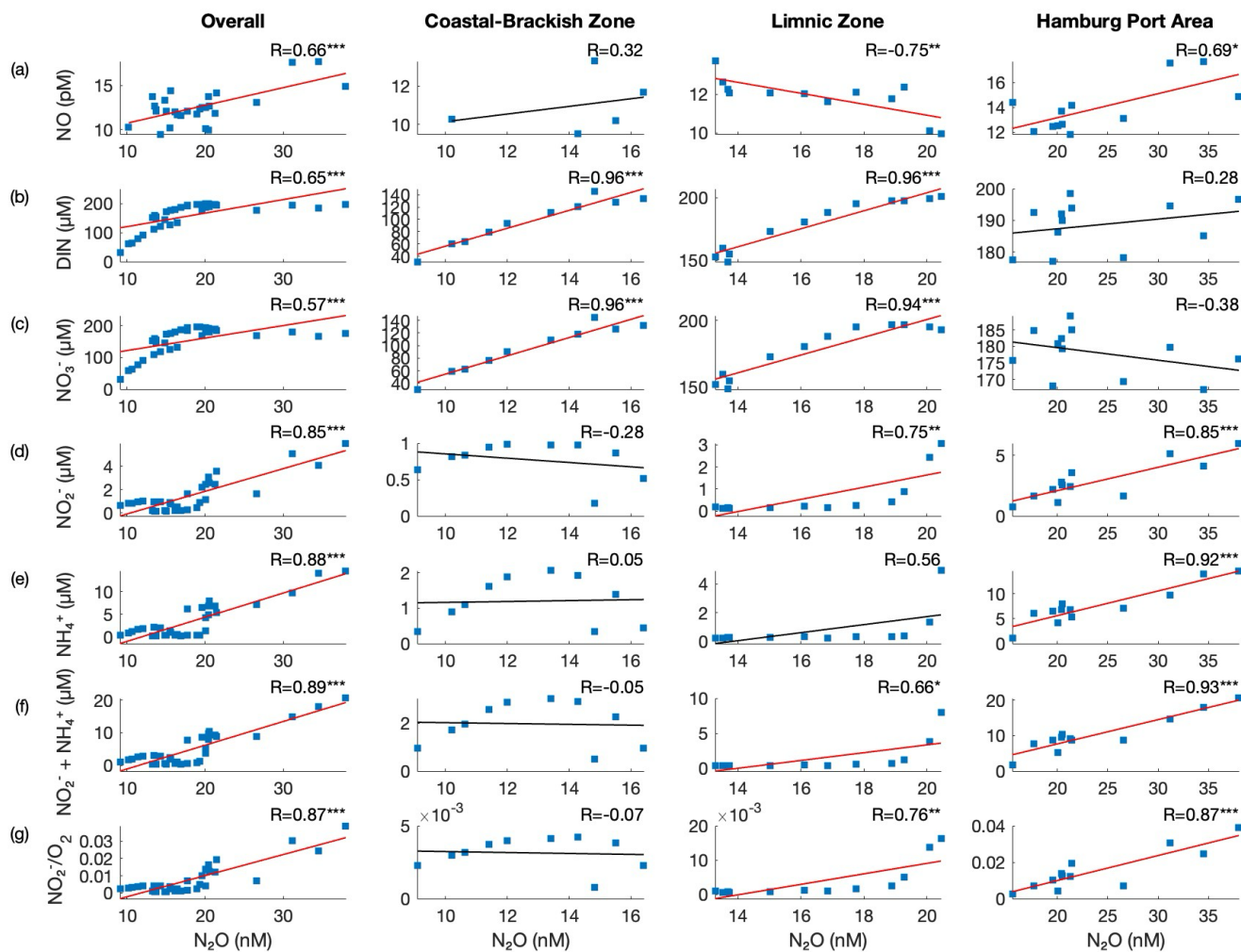
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**Figure S3: Boxplot of selected biogeochemical parameters measured in the different sampling stations along the Elbe Estuary during the campaign.**



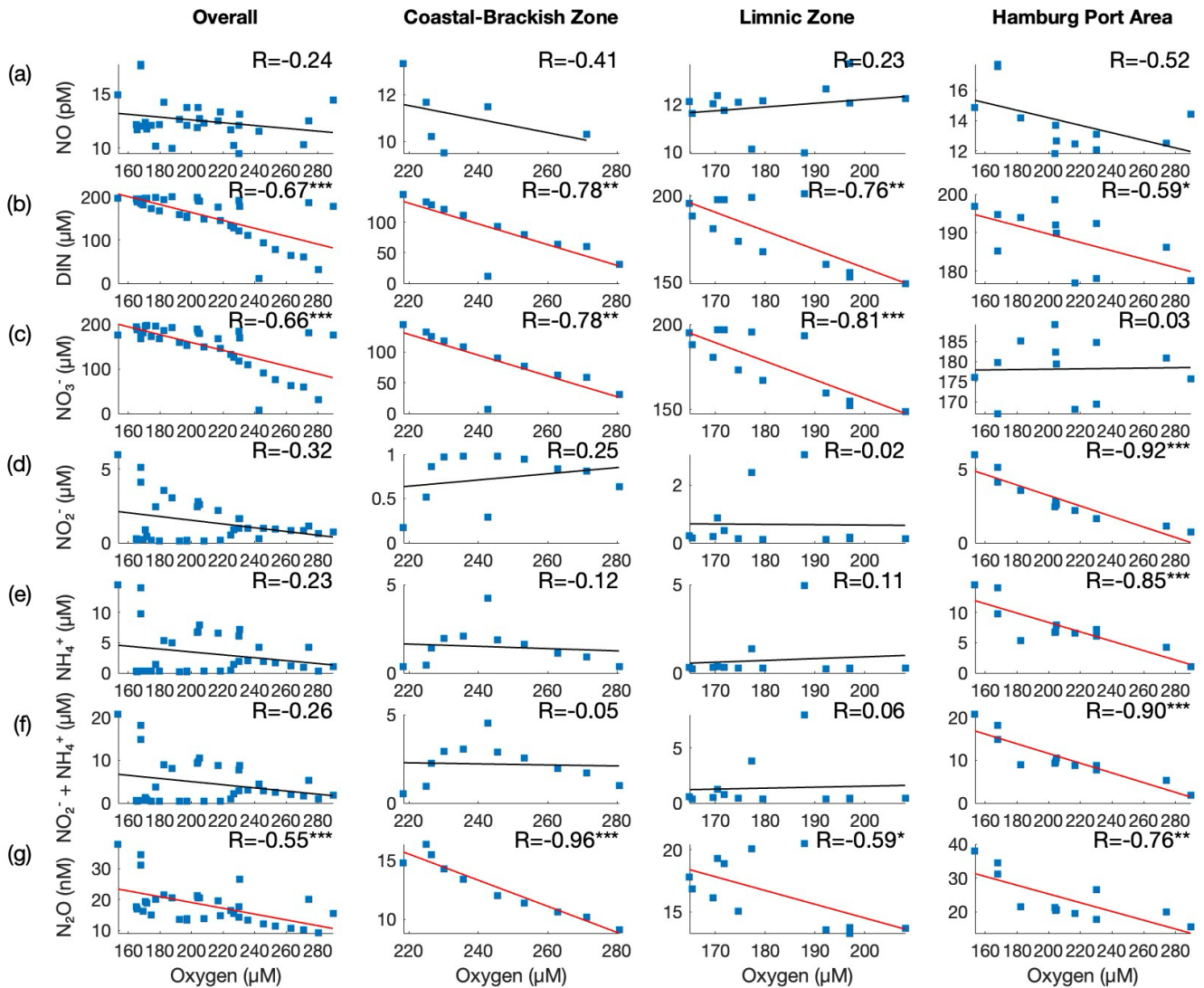
20 **Figure S4:** Scatter plot and linear regression of salinity vs selected biogeochemical parameters in the Elbe Estuary and each salinity zone. Pearson correlation coefficient (R) for each plot is denoted above each subplot. Significant correlations are denoted with a red regression line. Note that the superscripts on the R-value indicate a significant correlation at \*\*\* $p < 0.001$ , \*\* $p < 0.01$ , and \* $p < 0.05$ .



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Figure S5: Scatter plots and linear regression between  $N_2O$  (nM) and NO (pM), DIN ( $\mu$ M),  $NO_3^-$  ( $\mu$ M),  $NO_2^-$  ( $\mu$ M),  $NH_4^+$  ( $\mu$ M), sum of  $NO_2^-$  and  $NH_4^+$  ( $\mu$ M), and  $NO_2^-/O_2$  ratio. Pearson correlation coefficient (R) for each plot is denoted above each subplot. Significant correlations are denoted with a red regression line. Note that the superscripts on the R-value indicate a significant correlation at \*\*\* $p < 0.001$ , \*\* $p < 0.01$ , and \* $p < 0.05$ .

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**Figure S6:** Scatter plots and linear regression between dissolved O<sub>2</sub> (µM) and NO (pM), DIN (µM), NO<sub>3</sub><sup>-</sup> (µM), NO<sub>2</sub><sup>-</sup> (µM), NH<sub>4</sub><sup>+</sup> (µM), sum of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (µM), and N<sub>2</sub>O (nM). Pearson correlation coefficient (R) for each plot is denoted above each subplot. Significant correlations are denoted with a red regression line. Note that the superscripts on the R-value indicate a significant correlation at \*\*\*p < 0.001, \*\*p < 0.01, and \*p < 0.05.

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**Table S1: Summary statistics of various biogeochemical parameters measured in the different sampling stations along the Elbe Estuary during the campaign. Note that values less than the detection limit and blanks were not included in the calculation of the mean and median.**

Biogeochemical Parameters	Mean	Minimum	Maximum	Standard Deviation	Median
Salinity	4.43	0.31	29.43	7.77	0.45
Temperature (°C)	22.43	20.27	23.37	0.69	22.65
pH	7.73	7.46	8.23	0.24	7.67
Dissolved oxygen (μM)	210.4	153.5	289.6	37.6	204.6
Oxygen saturation (%)	80.2	57.1	115.6	16.5	76.5
Ammonium (μM)	3.22	0.23	14.62	3.89	1.37
Nitrite (μM)	1.40	0.12	5.99	1.48	0.86
Nitrate (μM)	149.82	6.85	196.89	49.88	168.78
DIN (μM)	154.43	11.35	201.03	51.49	177.17
Chlorophyll a (μg L <sup>-1</sup> )	18.7	0.5	63.3	12.9	17.3
N <sub>2</sub> O (ppm)	0.70	0.37	1.46	0.24	0.64
N <sub>2</sub> O (nM)	18.04	9.09	38.00	6.51	16.63
N <sub>2</sub> O saturation (%)	210.12	110.14	440.46	75.17	192.35
N <sub>2</sub> O flux density (μmol m <sup>-2</sup> d <sup>-1</sup> )	44.12	3.37	133.01	32.53	35.10
Wind Speed (m s <sup>-1</sup> )	5.78	1.76	13.11	2.12	5.02
NO (pM)	12.5	9.5	17.7	1.9	12.1
NO flux density (mol cm <sup>-2</sup> s <sup>-1</sup> )	2.40 × 10 <sup>-17</sup>	3.08 × 10 <sup>-19</sup>	5.52 × 10 <sup>-17</sup>	1.54 × 10 <sup>-17</sup>	2.21 × 10 <sup>-17</sup>
NO saturation (%)	194	147	275	29	188

**Table S2: Pearson correlation coefficient (R) between salinity and some biogeochemical parameters at each salinity zone. Note that significant correlations are in bold font, and the superscripts indicate significant correlation at \*\*\*p < 0.001, \*\* p < 0.01, and \*p < 0.05.**

	Overall	Coastal-Brackish	Limnic	Hamburg Port
Temperature (°C)	<b>0.8897***</b>	<b>0.9936***</b>	<b>0.7912***</b>	0.0966
pH	<b>0.7056***</b>	<b>0.8770***</b>	<b>0.9187***</b>	0.1263
Chlorophyll a ( $\mu\text{g L}^{-1}$ )	0.0016	0.2650	0.0332	0.0668
DIN ( $\mu\text{M}$ )	<b>0.9139***</b>	<b>0.9878***</b>	<b>0.9256***</b>	0.0628
$\text{NO}_3^-$ ( $\mu\text{M}$ )	<b>0.9286***</b>	<b>0.9907***</b>	<b>0.9001***</b>	0.0793
$\text{NO}_2^-$ ( $\mu\text{M}$ )	0.0622	0.0006	<b>0.4392*</b>	<b>0.6146**</b>
$\text{NO}_2^-/\text{O}_2$ ratio	-0.2672	-0.1534	-0.6801	<b>0.8272*</b>
$\text{NH}_4^+$ ( $\mu\text{M}$ )	0.0408	0.2276	0.2230	<b>0.4906***</b>
$\text{NO}_2^- + \text{NH}_4^+$ ( $\mu\text{M}$ )	-0.2198	0.4538	<b>-0.5704*</b>	<b>0.7502**</b>
$\text{O}_2$ ( $\mu\text{M}$ )	<b>0.3895***</b>	<b>0.5988**</b>	<b>0.4214*</b>	0.3055
$\text{O}_2$ saturation (%)	<b>0.7312***</b>	<b>0.8828***</b>	<b>0.6829*</b>	-0.5448
AOU ( $\mu\text{mol L}^{-1}$ )	<b>0.5266***</b>	<b>0.7864***</b>	<b>0.4873**</b>	0.2972
$\text{N}_2\text{O}$ (nM)	<b>0.2977***</b>	<b>0.9098***</b>	<b>0.9248***</b>	<b>0.6403*</b>
$\text{N}_2\text{O}$ saturation (%)	<b>-0.5349**</b>	<b>-0.9454***</b>	<b>-0.9634***</b>	<b>0.8005**</b>
$\text{N}_2\text{O}/\text{NO}_2^-$ ratio	-0.2855	<b>-0.6505<sup>c</sup></b>	<b>0.8151<sup>b</sup></b>	-0.3166
$\text{N}_2\text{O}/\text{NH}_4^+$ ratio	-0.2210	-0.4213	0.4192	-0.1390
$\text{N}_2\text{O}/(\text{NO}_2^- + \text{NH}_4^+)$ ratio	-0.2560	-0.5910	<b>0.7077*</b>	-0.1788
NO (pM)	0.1073	0.0598	<b>0.4122*</b>	0.2366
NO flux density ( $\text{mol cm}^{-2} \text{s}^{-1}$ )	<b>0.2846*</b>	0.3185	0.0557	0.0771
NO saturation (%)	0.1073	0.0598	<b>0.4122*</b>	0.2366



45 **Table S3: Pearson correlation coefficient (R) between NO concentration and some biogeochemical parameters at each salinity zone. Note that significant correlations are in bold font, and the superscripts indicate significant correlation at \*\*\*p < 0.001, \*\*p < 0.01, and \* p < 0.05.**

	Overall	Coastal-Brackish	Limnic	Hamburg Port
Temperature (°C)	0.2395	0.2742	0.4991	<b>-0.6102*</b>
pH	-0.2875	-0.3408	<b>0.6174*</b>	-0.3437
Oxygen (µM)	-0.2407	-0.4052	0.2258	-0.5204
Oxygen saturation (%)	-0.2735	-0.3509	0.2515	-0.5204
AOU (µmol L <sup>-1</sup> )	0.2769	0.3646	-0.2614	0.5257
Chlorophyll a (µg L <sup>-1</sup> )	-0.0439	0.1488	-0.3420	-0.2240
Salinity	-0.3276	-0.2446	<b>0.6420*</b>	0.4864
DIN (µM)	0.3263	0.1630	<b>-0.6576*</b>	0.0677
NO <sub>2</sub> <sup>-</sup> (µM)	<b>0.5425**</b>	<b>-0.9419**</b>	<b>-0.8379***</b>	<b>0.6570*</b>
NO <sub>3</sub> <sup>-</sup> (µM)	0.2552	0.1715	<b>-0.5998*</b>	-0.3726
NH <sub>4</sub> <sup>+</sup> (µM)	<b>0.6051***</b>	-0.2267	<b>-0.7322**</b>	0.5558
NO <sub>2</sub> <sup>-</sup> + NH <sub>4</sub> <sup>+</sup> (µM)	<b>0.6005***</b>	-0.4396	<b>-0.8011***</b>	<b>0.6060*</b>
NO <sub>2</sub> <sup>-</sup> /O <sub>2</sub>	<b>0.5692***</b>	<b>-0.9212**</b>	<b>-0.8404***</b>	<b>0.6711*</b>
N <sub>2</sub> O (µM)	<b>0.6609***</b>	0.3164	<b>-0.7527**</b>	<b>0.6940*</b>
N <sub>2</sub> O/NO <sub>2</sub> <sup>-</sup>	-0.1196	<b>0.9422*</b>	<b>0.6064***</b>	-0.2644
N <sub>2</sub> O/NH <sub>4</sub> <sup>+</sup>	-0.1833	<b>0.9589**</b>	<b>0.7569**</b>	0.0195
N <sub>2</sub> O/ (NO <sub>2</sub> <sup>-</sup> + NH <sub>4</sub> <sup>+</sup> )	-0.155	<b>0.9881**</b>	<b>0.7014*</b>	-0.0409