## Seasonal variability of nitrous oxide concentrations and emissions along the Elbe estuary

## 4 S1: Oxygen corrections

Table S1: Applied oxygen correction for each cruise: The corrections were made using the salinity corrected optode
 measurements from the FerryBox (O2) in comparison with Winkler titrations. Changes in oxygen corrections arose due
 to several optode changes in the time period from 2017 to 2022.

Cruise	Correction	Winkler titrations	$\mathbb{R}^2$
2017/08	$+24.05\pm1.52$	7	
2019/06	$+35.19\pm5.97$	9	
2019/07	$+35.19\pm5.97$	9	
2020/06	-2.38	19	0.99
2020/09	-2.38	19	0.99
2021/03	$0.97\times O2+43.91$	22	0.94
2021/05	$1.12 \times O2 + 13.41$	36	0.97
2021/07	$1.12 \times O2 + 13.41$	36	0.97
2022/03	$1.12 \times O2 + 13.41$	36	0.97



10 Figure S1: Salinity along the Elbe estuary (a) in spring/summer and (b) in winter. Suspended particulate matter (SPM) 11 concentration in (mg L<sup>-1</sup>) along the Elbe estuary in (c) spring/summer and (d) in winter. Particulate carbon to nitrogen 12 ratio (C/N) along the Elbe estuary in (e) in spring/summer and (f) in winter. Particulate nitrogen (PN) content in (%) 13 in (g) spring/summer and (h) winter. Particulate carbon (PC) content in (%) in (i) spring/summer and (j) winter. All 14 values are potted against stream kilometers. The Hamburg port region is shown with a gray background. C/N ratios 15 were measured with an Elemental Analyzer (Eurovector EA 3000) calibrated against a certified acetanilide standard 16 (IVA Analysentechnik, Germany). The standard deviation was 0.05% and 0.005% for carbon and nitrogen respectively. 17 Please note that there are no data for the suspended particulate matter composition in 2015.



Figure S2: Plots of  $N_2O_{xs}$  vs AOU for (a) April 2015 (b) June 2015, (c) August 2017, (d) June 2019, (e) July 2019, (f) June (2020), (g) September 2020, (h) March 2021, (i) May 2021, (j) July 2021 and (k) March 2022. The values are colored to distinguish between different regions of the estuary. Values upstream of stream kilometer 620 are yellow. In the Hamburg port region (km: 620 – 635), points are colored green. Red points mark the region downstream of the port with low salinity (km: 635 – salinity 5). Up to stream kilometer 720, points are light blue (mesohaline part, salinity: 5 – 18) and everything further out in the North Sea is a dark blue (salinity > 18).





Figure S3: (a) Exemplary nitrogen cascade coming from the North Sea shown for April 2015. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.





Figure S4: (a) Exemplary nitrogen cascade coming from the North Sea shown for June 2015. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares, nitrous

40 oxide concentration in (nmol  $L^{-1}$ ) as a red line and C/N ratios as grey crosses.





Figure S5: (a) Exemplary nitrogen cascade coming from the North Sea shown for August 2017. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in ( $\mu$ mol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in ( $\mu$ mol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in ( $\mu$ mol L<sup>-1</sup>) as light blue triangles, ammonium concentration in ( $\mu$ mol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.

Ammonium × C/N • Nitrate A Nitrite Nitrous oxide O PN





Figure S6: (a) Exemplary nitrogen cascade coming from the North Sea shown for June 2019. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.





Figure S7: (a) Exemplary nitrogen cascade coming from the North Sea shown for July 2019. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in ( $\mu$ mol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in ( $\mu$ mol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in ( $\mu$ mol L<sup>-1</sup>) as light blue triangles, ammonium concentration in ( $\mu$ mol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.



Figure S8: (a) Exemplary nitrogen cascade coming from the North Sea shown for June 2020. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in ( $\mu$ mol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in ( $\mu$ mol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in ( $\mu$ mol L<sup>-1</sup>) as light blue triangles, ammonium concentration in ( $\mu$ mol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.





Figure S9: (a) Exemplary nitrogen cascade coming from the North Sea shown for September 2020. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in ( $\mu$ mol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in ( $\mu$ mol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in ( $\mu$ mol L<sup>-1</sup>) as light blue triangles, ammonium concentration in ( $\mu$ mol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.





Figure S10: (a) Exemplary nitrogen cascade coming from the North Sea shown for March 2021. The grey area shows the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in ( $\mu$ mol L<sup>-1</sup>) are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in ( $\mu$ mol L<sup>-1</sup>). The right y-axis shows nitrite concentrations in ( $\mu$ mol L<sup>-1</sup>) as light blue triangles, ammonium concentration in ( $\mu$ mol L<sup>-1</sup>) as dark blue squares, nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.



Ammonium × C/N • Nitrate A Nitrite Nitrous oxide O PN



Figure S11: (a) Exemplary nitrogen cascade coming from the North Sea shown for May 2021. The grey area shows the
position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area
shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented as green
circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows nitrite
concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares, nitrous
oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.



Figure S12: (a) Exemplary nitrogen cascade coming from the North Sea shown for July 2021. The grey area shows the
position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey area
shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented as green
circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows nitrite
concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares, nitrous
oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.



Figure S13: (a) Exemplary nitrogen cascade coming from the North Sea shown for March 2022. The grey area shows
the position of the MTZ. (b) Exemplary nitrogen cascade in the Port of Hamburg shown for September 2020. The grey
area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in (µmol L<sup>-1</sup>) are presented
as green circles and particulate nitrogen (PN) concentrations as unfilled circles in (µmol L<sup>-1</sup>). The right y-axis shows
nitrite concentrations in (µmol L<sup>-1</sup>) as light blue triangles, ammonium concentration in (µmol L<sup>-1</sup>) as dark blue squares,
nitrous oxide concentration in (nmol L<sup>-1</sup>) as a red line and C/N ratios as grey crosses.