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

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Abstract
Nitrous oxide (N\textsubscript{2}O) is a greenhouse gas, with a global warming potential 298 times that of carbon dioxide. Estuaries can be sources of N\textsubscript{2}O, but their emission estimates have significant uncertainties due to limited data availability and high spatiotemporal variability. We investigated the spatial and seasonal variability of dissolved N\textsubscript{2}O and N\textsubscript{2}O emissions along the Elbe estuary (Germany). During nine research cruises done between 2017 and 2022, we measured dissolved N\textsubscript{2}O concentrations, as well as dissolved nutrients and oxygen concentrations along the estuary and calculated N\textsubscript{2}O saturation, flux densities and emissions. We found intense N\textsubscript{2}O production along the Elbe estuary that compensated the effect of decreasing dissolved inorganic nitrogen (DIN) loads since the 1990s. Two hot-spots areas of N\textsubscript{2}O production have been identified in the estuary: the Port of Hamburg and the mesohaline estuary near the estuarine turbidity maximum (MTZ). N\textsubscript{2}O production was enhanced by warmer temperatures and fueled by riverine organic matter in the Hamburg Port or marine organic matter in the MTZ. Surprisingly, estuarine N\textsubscript{2}O emissions where equally high in winter and summer. In winter, high riverine N\textsubscript{2}O concentrations led to high N\textsubscript{2}O emissions from the estuary, whereas in summer, estuarine biological N\textsubscript{2}O production led to equally high N\textsubscript{2}O emissions. Overall, we find that the Elbe estuary is a year-round source of N\textsubscript{2}O with estimated annual emissions of 0.24 ± 0.06 Gg yr\textsuperscript{-1}.

1 Introduction
Nitrous oxide (N\textsubscript{2}O) is an important atmospheric trace gas that contributes to global warming and stratospheric ozone depletion (WMO, 2018; IPCC, 2021). Estuaries are important regions of nitrogen turnover (Middelburg and Nieuwenhuize, 2001; Crossland et al., 2005; Bouwman et al., 2013), and a potential source of N\textsubscript{2}O (Bange, 2006; Barnes and Upstill-Goddard, 2011; Murray et al., 2015). Together with coastal wetlands, estuaries contribute between 0.17 and 0.95 Tg N\textsubscript{2}O-N of the annual global budget of 16.9 Tg N\textsubscript{2}O-N (Murray et al., 2015; Tian et al., 2020). N\textsubscript{2}O emission estimates from estuaries are associated with significant uncertainties due to limited data availability and high spatiotemporal variability (e.g. Bange 2006; Barnes and Upstill-Goddard 2011; Maavara et al. 2019), presenting a big challenge for the global N\textsubscript{2}O emission estimates.

Nitrification and denitrification are the most important N\textsubscript{2}O production pathways in estuaries. Under oxic conditions, N\textsubscript{2}O is produced as a side product during the first step of nitrification, the oxidation of ammonia to nitrite (e.g. Wrage et al. 2001; Barnes and Upstill-Goddard 2011). At low oxygen (but not anoxic) conditions, nitrifier-denitrification may occur, during which nitrifiers reduce nitrite to N\textsubscript{2}O (e.g. Wrage et al. 2001; Bange...
2008). Denitrification takes place under anoxic conditions and mostly acts as a source of N₂O, but can also reduce N₂O to N₂ (e.g. Knowles 1982; Bange 2008). In estuaries, denitrification mainly occurs in anoxic sediments whereas oxic nitrification and nitrifier-denitrification take place in the oxygenated water column (e.g. Beaulieu et al. 2011; Murray et al. 2015). Beside oxygen availability, temperature, substrate availability, pH and water level can also control nitrous oxide production (Murray et al., 2015; Quick et al., 2019).

The Elbe estuary is a heavily managed estuary that hosts the third biggest port in Europe (e.g. Radach and Pätsch 2007; Bergemann and Gaumert 2010; Pätsch et al. 2010; Quiel et al. 2011). It has been identified as a N₂O source, with a hotspot of N₂O production in the Port of Hamburg (Hanke and Knauth, 1990; Brase et al., 2017). However, the seasonal variability of N₂O along the estuary is largely unknown so far. Therefore, the objectives of our study were (1) to detect a long-term trend of N₂O concentrations, (2) to decipher the spatial and temporal distribution of N₂O concentrations along the Elbe estuary during different seasons and (3) to identify hotspots and drivers for N₂O production. To this end, we present here measurements of dissolved N₂O as well as dissolved nutrients and oxygen from nine research cruises along the Elbe estuary from August 2017 to March 2022.

2 Methods

2.1 Study site

The Elbe River stretches over 1094 km from its spring in the Giant Mountains (Czech Republic) to the North Sea (Cuxhaven, Germany). The catchment of the Elbe river is 140 268 km² (Boehlich and Strotmann, 2019), with 74 % urban and agricultural land-use (Johannsen et al., 2008). This makes the Elbe the second largest German river discharging into the North Sea, as well as the largest source of dissolved nitrogen for the German Bright, which is heavily affected by eutrophication (van Beusekom et al., 2019).

The Elbe estuary begins at stream kilometer 586 at a weir in Geesthacht and flows through the Port of Hamburg, entering the North Sea near Cuxhaven, stream kilometer 727 (Fig. 1). Estuaries are commonly structured along their salinity gradient into an oligohaline section (salinity: 0.5 – 5.0), a mesohaline section (salinity: 5.0 – 18.0) and polyhaline section (salinity > 18.0) (US EPA, 2006). The Elbe estuary has a length of 142 km (Boehlich and Strotmann, 2019) and a mean annual discharge of 712 m³ s⁻¹ with a mean variation range of 276 m³ s⁻¹ to 1960 m³ s⁻¹ (measured at gauge Neu Darchau at stream kilometer 536) (HPA and Freie und Hansestadt Hamburg, 2017). The average water residence time is ~32 days and ranges from ~72 days during low discharge (300 m³ s⁻¹) to ~10 days with high discharge (2000 m³ s⁻¹) (Boehlich and Strotmann, 2008). The estuary has an annual nitrogen load of 84 Gg-N (FGG Elbe, 2018). Oxygen concentrations in the Elbe estuary shows a high seasonal variability: In summer months, oxygen depletion and low oxygen zones occur regularly reaching concentrations below 3 mg O₂ L⁻¹ (Schroeder, 1997; Gaumert and Bergemann, 2007; Schiöel et al., 2014).

The Elbe estuary is deepened and dredged on a regular basis to grant access for large container ships to the Port of Hamburg (Boehlich and Strotmann, 2019), which is the third biggest port in Europe (HAFEN HAMBURG, 2021). Construction work for further deepening of the fairway was carried out in our study period, from 2019 to early 2022.
2.2 Transect sampling and measurements

We performed nine sampling campaigns along the estuary with the research vessel Ludwig Prandtl (Tab. 1). Most of the cruises took place during the spring and summer seasons, with water temperatures > 10 °C (May – September), while two cruises were conducted in colder winter months (early March, water temperature < 6 °C) (Tab. 1). Transect sampling started in the German Bright, close to the island Scharhörn and continued along the salinity gradient, through the Port of Hamburg to Oortkaten (stream kilometer 609). Transect sampling always was performed after high-tide, steaming upstream against the outgoing tide. For comparison, we included summer data from a previous study in 2015 (Brase et al., 2017).
An onboard membrane pump continuously provided water from 1.2 m depth to an on-line in-situ FerryBox system and to an equilibrator used for the measurements of N₂O dry mole fraction (Section 2.4). The FerryBox system continuously measured water temperature, salinity, oxygen concentration, pH and turbidity. We corrected the oxygen measurements using the salinity corrected optode measurements in comparisons to Winkler titrations. The corrections of the individual cruises are listed in the Tab. S1 of the supplementary material. Discrete water samples were taken every 20 min from a bypass of the FerryBox system. For nutrient analysis water samples were filtered immediately through combusted, pre-weighted GF/F Filters (4 h, 450 °C), and stored frozen in acid washed PE-bottles until analysis. The filters were stored frozen (-20 °C) and used for the later analysis of suspended particulate matter (SPM), particulate nitrogen fraction (PN), particulate carbon fraction (PC) and C/N ratios (supplementary material Fig. S1).

### 2.3 Nutrient measurements

Filtered water samples were measured in triplicates with a continuous flow auto analyzer (AA3, SEAL Analytics) using standard colorimetric and fluorometric techniques (Hansen and Koroleff 2007) for dissolved nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonium (NH₄⁺) concentrations.

### 2.4 Equilibrator based N₂O measurements and calculations

Equilibrated dry mole fractions of N₂O were measured by a N₂O analyzer based on off-axis integrated cavity output (OA-ICOS) absorption spectroscopy (Model 914-0022, Los Gatos Res. Inc., San Jose, CA, USA), which was coupled with a sea water/gas equilibrator using off-axis cavity output spectroscopy. Brase et al. (2017) described the set-up and instrument precision in detail. We regularly analyzed two standard gas mixtures of N₂O in synthetic air (500.5 ppb ± 5 % and 321.2 ppb ± 3 %) to validate our measurements. No drift was detected during our cruises.

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**Table 1: Campaign dates with the sampled Elbe estuary sections shown via stream kilometers, average discharge during each cruise measured at the Pegel Neu Darchau, averages and standard deviations for water temperature (°C), wind speed (m³ s⁻¹) in 10 m height, dissolved inorganic nitrogen (DIN) concentrations (µmol L⁻¹) for each campaign.**

<table>
<thead>
<tr>
<th>Campaign Dates</th>
<th>Stream kilometers (km)</th>
<th>Water temperature (°C)</th>
<th>Wind speed (m s⁻¹) in 10 m</th>
<th>Average discharge (m³ s⁻¹)</th>
<th>Average DIN load (µmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.-29.04.2015</td>
<td>627 – 741</td>
<td>12.3 ± 1.0</td>
<td>11.8 ± 0.3</td>
<td>595</td>
<td>191.0 ± 45.0</td>
</tr>
<tr>
<td>02.-04.06.2015</td>
<td>609 – 739</td>
<td>17.4 ± 1.7</td>
<td>5.0 ± 1.3</td>
<td>276</td>
<td>105.9 ± 36.2</td>
</tr>
<tr>
<td>01.-02.08.2017</td>
<td>621 – 749</td>
<td>20.9 ± 0.7</td>
<td>3.6 ± 1.5</td>
<td>607</td>
<td>79.2 ± 30.2</td>
</tr>
<tr>
<td>04.-05.06.2019</td>
<td>610 – 750</td>
<td>18.7 ± 2.2</td>
<td>4.0 ± 1.7</td>
<td>423</td>
<td>108.3 ± 35.9</td>
</tr>
<tr>
<td>30.07.-01.08.2019</td>
<td>609 – 752</td>
<td>22.6 ± 1.0</td>
<td>4.2 ± 1.4</td>
<td>171</td>
<td>60.8 ± 38.6</td>
</tr>
<tr>
<td>19.-20.06.2020</td>
<td>609 – 747</td>
<td>19.8 ± 1.4</td>
<td>5.8 ± 1.2</td>
<td>331</td>
<td>74.6 ± 33.8</td>
</tr>
<tr>
<td>09.-11.09.2020</td>
<td>607 – 745</td>
<td>18.9 ± 0.6</td>
<td>5.9 ± 2.8</td>
<td>305</td>
<td>93.1 ± 32.7</td>
</tr>
<tr>
<td>10.-12.03.2021</td>
<td>609 – 748</td>
<td>5.4 ± 0.5</td>
<td>9.3 ± 2.6</td>
<td>862</td>
<td>324.4 ± 83.8</td>
</tr>
<tr>
<td>04.-05.05.2021</td>
<td>610 – 751</td>
<td>10.5 ± 0.8</td>
<td>11.0 ± 3.1</td>
<td>411</td>
<td>85.7 ± 36.6</td>
</tr>
<tr>
<td>27.-28.07.2021</td>
<td>621 – 751</td>
<td>22.2 ± 0.7</td>
<td>5.2 ± 1.3</td>
<td>721</td>
<td>139.8 ± 58.4</td>
</tr>
<tr>
<td>01.-02.03.2022</td>
<td>610 – 752</td>
<td>5.6 ± 0.2</td>
<td>2.9 ± 1.0</td>
<td>1282</td>
<td>238.0 ± 74.7</td>
</tr>
</tbody>
</table>

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We calculated the dissolved N\textsubscript{2}O concentrations in water with the Bunsen solubility function of Weiss and Price (1980) using 1 min averages of the measured N\textsubscript{2}O dry mole fraction (ppb). Temperature differences between sample inlet and equilibrator were taken into account for the calculation of the final N\textsubscript{2}O concentrations (Rhee et al., 2009). N\textsubscript{2}O saturation were calculated based on N\textsubscript{2}O concentrations in water (N\textsubscript{2}O\textsubscript{cw}) and in the air (N\textsubscript{2}O\textsubscript{air}) (Eq. 1). During each cruise, we regularly measured the atmospheric N\textsubscript{2}O dry mole fractions.

\begin{equation}
S = 100 \times \frac{N_2O_{cw}}{N_2O_{air}}
\end{equation}

The gas transfer coefficients (k) were determined based on Borges et al. (2004) taking the Schmidt number (Sc) and wind speed in 10 m height (u_10) into account (Eq. 2). The Schmidt number was calculated as ratio of the kinematic viscosity in water (Siedler and Peters, 1986) to the N\textsubscript{2}O diffusivity in water (Rhee, 2000). Wind speeds were measured on board in 10 m height of the R/V Ludwig Prandtl by a MaxiMet GMX600 (Gill Instruments Limited). Flux densities were calculated according to Equation 3.

\begin{equation}
k = 0.24 \times (4.045 + 2.58u_{10}) \times \left(\frac{Sc}{600}\right)^{-0.5}
\end{equation}

\begin{equation}
f = k \times (N_2O_{cw} - N_2O_{air})
\end{equation}

For emission calculations we used an area of 371.85 km\textsuperscript{2} for the Elbe estuary (Eq. 1). During each cruise, we regularly measured the atmospheric N\textsubscript{2}O dry mole fractions.

\begin{equation}
AOU = O_2^* - O_2
\end{equation}

A linear relationship between AOU and N\textsubscript{2}O\textsubscript{n} is usually an indicator for nitrification (Nevison et al., 2003; Walter et al., 2004).

### 3 Results

#### 3.1 Hydrographic properties and DIN distribution

Discharge ranged between 171 m\textsuperscript{3} s\textsuperscript{-1} and 1282 m\textsuperscript{3} s\textsuperscript{-1} during our cruises (ZDM, 2022), with higher discharge in winter and lower discharge in summer (Tab. 1). Average water temperature over the entire estuary ranged from 5.4 ± 0.5 °C in March 2021 to 22.6 ± 1.0 °C in August 2017 (Tab. 1). For the further evaluation, March 2021 and 2022 cruises will be regarded as winter cruises (water temperature < 6°C), whereas all cruises with higher water temperature are jointly regarded as spring and summer conditions.

Nitrate was the major form of dissolved inorganic nitrogen (DIN) during all cruises. In winter, high nitrogen concentrations entered the estuary from the river. Towards summer, the riverine input (stream kilometer < 620)
decreased, but along the estuary nitrate concentrations increased up to approximate stream kilometer 700, then decreased again towards the North Sea. Nitrate concentrations were highest during both March cruises with averages of $319.0 \pm 85.7 \mu\text{mol L}^{-1}$ and $230.9 \pm 76.2 \mu\text{mol L}^{-1}$ in 2021 and 2022, respectively. During summer, nitrate concentrations were lower. The nitrate concentrations averages were between $151.0 \pm 58.1 \mu\text{mol L}^{-1}$ in May 2021 and $63.3 \pm 38.8 \mu\text{mol L}^{-1}$ in July 2019 (Fig. 2a and b).

Nitrite and ammonium concentrations were usually low along the Elbe estuary, but showed peaks in the Hamburg Port region and around stream kilometer 720 (Fig. 2c and 2e). We measured pronounced variations in nitrite concentrations during most of our cruises, ranging from $> 6.0 \mu\text{mol L}^{-1}$ (July 2019) to concentrations below the detection limit ($< 0.05 \mu\text{mol L}^{-1}$) (Fig. 2c and d). The highest ammonium concentration was measured in March 2021 with $23.5 \mu\text{mol L}^{-1}$. Over large stretches of the estuary, ammonium was below the detection limit ($< 0.07 \mu\text{mol L}^{-1}$) in winter as well as in spring and summer (Fig. 2e and f).
Figure 2: Nitrate concentration in µmol L$^{-1}$ along the Elbe estuary (a) in spring/summer, (b) in winter. Nitrite concentration in µmol L$^{-1}$ along the Elbe estuary (c) in spring/summer and (d) in winter. Ammonium concentration in µmol L$^{-1}$ along the Elbe estuary (e) in spring/summer and (f) in winter. N$_2$O concentration in nmol L$^{-1}$ along the Elbe estuary (g) in spring/summer, (h) in winter. Dissolved oxygen in % saturation along the Elbe estuary (i) in spring/summer and (j) in winter. All values are plotted against stream kilometers. The Hamburg Port region is shown with light grey background. The typical position of the maximum turbidity zone (MTZ) is shown with a dark grey (Bergemann, 2004) Y-axis scales differ for the plots of N$_2$O concentrations (g) and (h). The dashed black lines in (i) and (j) indicate an oxygen saturation of 100%.
3.2 Atmospheric and dissolved N₂O

The average atmospheric N₂O dry mole fractions ranged from 325 ppb in June 2015 to 336 ppb in July 2022 (Tab. 2). The differences between our measurements and the mean monthly N₂O mole fraction measured at the atmospheric monitoring station Mace Head (Ireland) (Dlugokencky et al., 2022) were always less than 1.5 %, indicating a good agreement with the monitoring data.

Comparable to the nutrient concentrations, N₂O varied seasonally (Fig. 2): In spring and summer, riverine N₂O (i.e., inflow into the estuary, stream kilometer <589) ranged from 8 nmol L⁻¹ to 15 nmol L⁻¹. At the onset of the estuary, spring and summer N₂O concentrations usually showed a steep increase and peak values between 27 nmol L⁻¹ and 58 nmol L⁻¹ (~stream kilometer 620-635). Further downstream, N₂O concentrations decreased towards a local minimum (~ stream kilometer 670). A second peak was located along the salinity gradient at salinity ~ 5 (~ stream kilometer 680 - 700) ranging from 17 nmol L⁻¹ to 22 nmol L⁻¹. N₂O concentrations dropped towards equilibrium concentrations of 8 – 12 nmol L⁻¹ in the North Sea (Fig. 2g).

In winter, riverine N₂O concentrations were elevated (~ 25 nmol L⁻¹) compared to spring and summer riverine concentrations. In 2021, a steep increase of N₂O concentrations occurred in the Hamburg Port region, (stream kilometer 620 – 635) leading to exceptionally elevated N₂O concentrations of up to 158 nmol L⁻¹ (Fig. 2h). In March 2022, N₂O increased to 44 nmol L⁻¹ in this region. Further downstream, N₂O concentrations remained relatively constant at ~ 35 nmol L⁻¹ during both cruises, and dropped to near equilibrium concentrations between stream kilometer 700 and the coastal ocean.

3.3 N₂O saturations and flux densities

During all cruises, the Elbe estuary was supersaturated in N₂O in the freshwater region (Fig. 3). The average N₂O saturation over the entire transect ranged between 146 % and 243 % with an overall average of 197 % for all cruises. Highest N₂O saturations occurred in the Hamburg Port region in spring and summer with an average N₂O peak of 402 % and a maximum supersaturation of 710 % in July 2019. The distribution of N₂O saturations during the winter cruises were significantly different: In March 2022, highest N₂O saturation (280 %) occurred at stream kilometer 640. In March 2021, in contrast, we found an extraordinarily high peak with a saturation of 1018 %.

Between stream kilometer 680 and 720, a supersaturation of up to 277 % occurred in spring and summer months.

Further towards the North Sea, N₂O saturation decreased, and approaching equilibrium with the atmosphere.
Figure 3: (a): N\textsubscript{2}O saturation along the Elbe estuary for cruises in spring/summer, (b) N\textsubscript{2}O saturation for the cruises done in March. The dashed black lines in both plots indicate a saturation of 100 %. The Hamburg Port region is shown with a background in light grey. The typical position of the maximum turbidity zone (MTZ) is shown with a dark grey (Bergemann, 2004). Y-axis scales differ for both plots.

The N\textsubscript{2}O flux densities were usually highest in the Hamburg Port area with an average of 95.1 ± 113.6 µmol m\textsuperscript{-2} d\textsuperscript{-1} and lowest towards the North Sea with an average of 3.9 ± 3.0 µmol m\textsuperscript{-2} d\textsuperscript{-1} (stream kilometers > 735). The average N\textsubscript{2}O flux density of all cruises was 37.8 ± 51.0 µmol m\textsuperscript{-2} d\textsuperscript{-1}.

Table 2: Calculated average N\textsubscript{2}O saturation, sea-to-air fluxes and atmospheric N\textsubscript{2}O dry mole fractions during our cruises for the Elbe estuary

<table>
<thead>
<tr>
<th>Campaign Dates</th>
<th>Average saturation (%)</th>
<th>N\textsubscript{2}O Flux densities (µmol m\textsuperscript{-2} d\textsuperscript{-1})</th>
<th>Average atmospheric dry mole fraction (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.-29.04.15</td>
<td>160.8</td>
<td>-2.5</td>
<td>33.1 ± 21.0</td>
</tr>
<tr>
<td>02.-04.06.15</td>
<td>203.8</td>
<td>2.6</td>
<td>45.5 ± 49.8</td>
</tr>
<tr>
<td>01.-02.08.17</td>
<td>221.3</td>
<td>1.5</td>
<td>35.8 ± 31.8</td>
</tr>
<tr>
<td>04.-05.06.19</td>
<td>192.9</td>
<td>3.4</td>
<td>26.6 ± 16.1</td>
</tr>
<tr>
<td>30.07.-01.08.19</td>
<td>228.6</td>
<td>1.3</td>
<td>41.7 ± 49.7</td>
</tr>
<tr>
<td>19.-20.06.20</td>
<td>194.1</td>
<td>3.7</td>
<td>38.9 ± 30.8</td>
</tr>
<tr>
<td>09.-11.09.20</td>
<td>163.9</td>
<td>-0.1</td>
<td>21.1 ± 15.7</td>
</tr>
<tr>
<td>10.-12.03.21</td>
<td>244.2</td>
<td>9.1</td>
<td>105.6 ± 119.2</td>
</tr>
<tr>
<td>04.-05.05.21</td>
<td>123.5</td>
<td>-0.5</td>
<td>15.1 ± 19.9</td>
</tr>
<tr>
<td>27.-28.07.21</td>
<td>174.8</td>
<td>2.5</td>
<td>27.4 ± 14.7</td>
</tr>
<tr>
<td>01.-02.03.22</td>
<td>196.5</td>
<td>1.1</td>
<td>27.3 ± 13.6</td>
</tr>
</tbody>
</table>

3.4 Dissolved oxygen saturation

Average oxygen saturation varied between 76 and 95 in % saturation with a minimum in the Hamburg Port area. Winter cruises showed only little variation, with oxygen remaining relatively constant along the estuary (> 88 % saturation). During most spring and summer cruises, water from the river coming into the estuary was high in oxygen. In the Hamburg Port region, oxygen saturation generally decreased. Lowest values occurred in June 2020 with 47 % saturation. The along-estuary minimum oxygen in summer months (June - August) was always below
61 % saturation. In spring and summer, oxygen increased towards the North Sea and reached 100 % saturation (Fig. 2i and j).

Plots of excess N\textsubscript{2}O (N\textsubscript{2}O\textsubscript{xs}) and apparent oxygen utilization (AOU) (Fig. 4) revealed excess N\textsubscript{2}O along the entire estuary (Fig. 4 and supplementary material S2). During all cruises, elevated riverine N\textsubscript{2}O\textsubscript{xs} concentrations entered the estuary (stream kilometer < 620). In spring and summer, steep, non-linear increases of N\textsubscript{2}O\textsubscript{xs} in the Port of Hamburg suggested in-situ N\textsubscript{2}O production (Fig. 4a, 4b). This production extended into the oligohaline estuary (stream kilometer > 635 and salinity < 5) followed by a linear decrease of N\textsubscript{2}O\textsubscript{xs} reduction in the transition region to the mesohaline section of the estuary (salinity: 5-18), N\textsubscript{2}O\textsubscript{xs} increased again, followed by a decrease to 0 nmol L\textsuperscript{-1} towards the North Sea. In winter, we found a linear relationship of N\textsubscript{2}O\textsubscript{xs} and AOU along the estuary, with a decoupling in the Hamburg Port and the oligohaline part of the Elbe estuary. In Figure 4, representative N\textsubscript{2}O\textsubscript{xs}/AOU plots for summer (4 a, b) and winter (4 c, d) are shown (see supplementary material: Fig. S2 for all plots).

Figure 4: Representative plots of N\textsubscript{2}O\textsubscript{xs} vs AOU for (a) June 2019, (b) June 2020, (c) March 2021 and (d) 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 grey. 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). Y-axis scale differ for Fig. 4c.
4 Discussion

4.1 N$_2$O saturation and flux densities of the Elbe estuary

The average N$_2$O saturation and flux density were 197 % and 39.68 µmol m$^{-2}$ d$^{-1}$, respectively. The N$_2$O flux densities from the Elbe estuary were in the mid-range of flux densities of other European estuaries ranging from 2.9 µmol m$^{-2}$ d$^{-1}$ to 96.5 µmol m$^{-2}$ d$^{-1}$ (e.g. Garnier et al. 2006; Gonçalves et al. 2010; Murray et al. 2015). But they were significantly lower than observed medians for tidal environments with high DIN loads (72 µmol m$^{-2}$ d$^{-1}$ and 168 µmol m$^{-2}$ d$^{-1}$) (Murray et al., 2015). As shown in Fig. 4, there was no linear relationship between N$_2$O$_{xs}$ and AOU for most of the regions of the Elbe estuary. Therefore, large sections in the estuary were influenced by either initial riverine N$_2$O production, or in-situ production along the estuary. During spring and summer, we found enhanced N$_2$O concentrations in two regions: the Hamburg Port region (see also Brase et al. (2017)), and the salinity gradient (stream kilometer 680 – 700, salinity ~5). Both N$_2$O peaks varied in height and spatial extension suggesting in-situ biological production (Fig. 2g, 3a). This matches previous research linking estuarine N$_2$O fluxes to in-situ generation (e.g. Bange 2006; Barnes and Upstill-Goddard 2011; Murray et al. 2015).

Previous measurements of N$_2$O saturation and flux densities in the Elbe estuary between the 1980s and 2015 (Hanke and Knauth, 1990; Barnes and Upstill-Goddard, 2011; Brase et al., 2017) showed a significant reduction of N$_2$O saturation due to the reduced riverine nutrient load and higher dissolved oxygen concentrations (Brase et al., 2017). Since the BIOGEST study in 1997 (Barnes and Upstill-Goddard, 2011), N$_2$O saturation did not decrease in scale with riverine nitrogen input suggesting that in-situ N$_2$O production along the estuary is important (Fig. 5). In the following sections, we investigate the biogeochemical controls of this in-situ production. For this purpose, we discuss both zones of intense N$_2$O production separately and also distinguish between biological active cruises in spring and summer (water temperature > 10 °C) and winter (water temperature < 6 °C).

![Figure 5: Comparison of average N$_2$O saturation transect measurements with previous research from the Elbe estuary.](image)

4.2 N$_2$O production in spring and summer in the mesohaline estuary

The N$_2$O peak in the transition between oligohaline and mesohaline estuary was accompanied by a sudden change from a decreasing to an increasing trend between AOU and N$_2$O$_{xs}$ (Fig. 4a, 4b), pointing towards N$_2$O production...
in the oxic water column. Interestingly, we find that small peaks of nitrite and ammonium coincided with the nitrous oxide peak between km 680 -700, with ammonium around stream kilometer ~720, and a nitrite peak at ~700. Highest N\textsubscript{2}O concentrations were usually measured between the nitrite peak and the region with highest turbidity (see Fig. 6 for an example, supplementary material Fig. S3-S13), as seen for our cruise in September 2020 in Fig. 6a. Such a succession of nitrite and ammonium peaks is typical for remineralization and nitrification, and the slight decrease of oxygen concentrations around the N\textsubscript{2}O peak (Fig. 2g and i) suggests that oxygen consumption, possibly caused by nitrification, occurred. Sanders et al. (2018) measured small but detectable nitrification rates of 1 – 2 \mu\text{mol L}^{-1} d^{-1} for this region of the Elbe estuary, suggesting that N\textsubscript{2}O in this region may be a side product of nitrification.

![Figure 6: (a) Succession of N-bearing substances coming from the North in September 2020. The grey area shows the position of the MTZ. (b) Succession of N-bearing substances in the Port of Hamburg in September 2020. The grey area shows the position of the Port of Hamburg. On the left y-axis nitrate concentrations in \mu\text{mol L}^{-1} are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in \mu\text{mol L}^{-1}. The right y-axis shows nitrite concentrations in \mu\text{mol L}^{-1} as light blue triangles, ammonium concentration in \mu\text{mol L}^{-1} as dark blue squares, nitrous oxide concentration in nmol L\textsuperscript{-1} as a red line and C/N ratios as grey crosses.](https://doi.org/10.5194/bg-2023-35)

However, this suggest input of particulate matter from the North Sea and upstream particle transport towards the maximum turbidity zone of the estuary (MTZ). This transport mechanism is in line with Wolfstein and Kies (1999), who explained organic matter contents and chlorophyll \textalpha concentrations in the polyhaline part of the Elbe estuary by input of fresh marine particulate matter. Generally, the occurrence of an MTZ is unique to each estuary and is generated by the balance between river-induced flushing and upstream transport of marine SPM as well as a function of estuarine geomorphology, gravitational circulation and tidal flow, trapping the particles in the MTZ (Bianchi, 2007; Sommerfield and Wong, 2011; Winterwerp and Wang, 2013). Other studies detected N\textsubscript{2}O production from water column nitrification in estuarine MTZs (e.g. Barnes and Owens 1999; de Wilde and de Bie 2000; Bange 2006; Barnes and Upstill-Goddard 2011; Harley et al. 2015), caused by high bacterial numbers, particulate nitrogen availability and long residence times (Murray et al., 2015).

For the selected dataset, we calculated a negative correlation between average SPM concentrations and N\textsubscript{2}O saturation (R = -0.81), and found that the N\textsubscript{2}O peak was located downstream of the MTZ, and upstream of increasing nitrite and ammonium concentrations (Fig. 6). This (1) suggests that the mere concentration of SPM is not the driving factor of nitrification as a source of N\textsubscript{2}O, but that organic matter quality is key to biological turnover (Dähnke et al. 2022), and (2) speaks in favor of material transport from the North Sea upstream towards the MTZ.
We find organic matter with low C/N ratios, and with relatively high PN and PC contents in the outermost samples (ranging from 5.9 in June 2020 to 8.8 August 2017), indicating fresh and easily degradable organic matter (supplementary material Fig. S1, e.g. Redfield et al. 1963; Fraga et al. 1998; Middelburg and Herman 2007). Towards the MTZ, C/N values, PN and PC contents decreased, indicating remineralization in the water column. This remineralization and subsequent nitrification can then cause the observed succession of ammonium, nitrite and N₂O peaks (Fig. 6), contributing to the already high nitrate concentrations in the MTZ coming from the upper estuary, where high C/N values (9 – 11/16) indicate low organic matter quality (e.g. Hedges and Keil 1995; Middelburg and Herman 2007).

Overall, we conclude that remineralization of marine organic matter, followed by nitrification, produced the N₂O peak in the salinity gradient of the Elbe estuary. This production was mainly fueled by fresh organic matter entering the estuary from the North Sea.

### 4.3 Hamburg Port: N₂O production in spring and summer

Several studies identified the Hamburg Port region as a hotspot of biogeochemical turnover: Deek et al. (2013) showed ongoing denitrification, Sanders et al. (2018) measured intense nitrification, Norbirsath et al. (2022) determined intense total alkalinity generation, and Dähnke et al. (2022) found that nitrogen turnover were driven by particulate organic matter. The highest N₂O peaks of our study were located in the Port of Hamburg. Brase et al. (2017) identified the port region as a hotspot of N₂O production and hypothesized that simultaneous nitrification and denitrification were responsible. We use our expanded dataset to further evaluate this hypothesis.

During all our cruises in spring and summer, we measured ammonium and nitrite peaks in the Hamburg Port region (Fig. 2c and e, exemplary for September 2020 in Fig. 6b). High nitrite concentrations are favorable of N₂O production by nitrification and of nitrifier-denitrification (Quick et al., 2019), and low-oxygen conditions made both nitrification and denitrification plausible in this region. We found N₂O saturations increased with decreasing discharge (R = -0.48) during spring and summer. This further points towards in-situ N₂O production, because denitrification and nitrification are more intense at higher residence times (e.g. Nixon et al. 1996; Pind et al. 1997; Silvennoinen et al. 2007; Gonçalves et al. 2010). Overall, our data show that the correlations of ammonium, nitrite and N₂O are significant and confirm that simultaneous denitrification and nitrification likely are responsible for N₂O production.

A correlation analysis for the Hamburg Port region (stream kilometer 610 – 645) revealed a strong negative correlation of N₂O saturation with pH (R = -0.60), nitrite concentrations (R = 0.58), oxygen saturation (R = -0.58), particulate carbon (PC) content (R = -0.53) and particulate nitrogen (PN) content (R = -0.49).

In spring and summer, we found no linear relationship of N₂O₅ and AOU in the Hamburg Port. This may result from combined N₂O production by nitrification and denitrification. However, oxygen saturation and N₂O saturation were inversely correlated in the Hamburg Port (R = -0.58), suggesting that N₂O production was controlled by oxygen concentrations, and thus by oxygen consumption in the port region. Most (75 %) of this oxygen consumption is caused by respiration (Schöl et al., 2014; Sanders et al., 2018). This respiration in turn is determined by remineralization of algal material from the upstream river that is transported to and respired within the port region (Schroeder, 1997; Kerner, 2000; Schöl et al., 2014), and this directly links estuarine N₂O production to river eutrophication. Fresh organic matter from the Elbe River entered the estuary, showing up in low C/N values ranging from 6.6 in July 2019 to 10.8 in August 2017 as well as in high PN and high PC contents, where it rapidly got degraded in the Hamburg Port region (supplementary material Fig. S1). Dähnke et al. (2022) found...
labile organic matter strongly fueled nitrification but also denitrification in the fresh water part of the Elbe estuary, which, as shown in our study, results in high N\textsubscript{2}O production in the Hamburg Port region leading to the reported negative correlations of PC and PN content with N\textsubscript{2}O saturation.

Overall in spring and summer, oxygen conditions mainly controlled N\textsubscript{2}O production in the Hamburg Port region. Since respiration of organic matter dominates oxygen drawdown in the port region, we deduced that N\textsubscript{2}O production was linked to the decomposition of phytoplankton produced in the upstream Elbe river regions.

### 4.4 Hamburg Port: N\textsubscript{2}O production in winter

Intriguingly, we also find high N\textsubscript{2}O concentrations in the port region in winter, at a time when low water temperature should hamper biological production. In the MTZ, the other identified region of intense estuarine N\textsubscript{2}O production, we did not detect an N\textsubscript{2}O peak during either March cruise. With water temperature below 6 °C, biological processing likely was inhibited (Koch et al., 1992; Halling-Sørensen and Jorgensen, 1993). For March 2022, we found a linear increase of N\textsubscript{2}O\textsubscript{a} and AOU along with oxygen consumption and increasing ammonium, nitrite and PN concentrations indicating nitrification in the port region producing N\textsubscript{2}O. Unlike in summer, N\textsubscript{2}O concentrations showed a flat increase extending far into the oligohaline section of the estuary (Fig. 2, 4d, supplementary material Fig. S1).

However, in March 2021, we found a sharp and sudden increase in N\textsubscript{2}O, with a peak concentration that by far exceeded internal biological sources in summer (Fig. 2h). Also, an ammonium peak in the water column coincided with the N\textsubscript{2}O maximum (Fig. 2f and supplementary material Fig. S10). If microbial activity is mostly temperature-inhibited, a point source of N\textsubscript{2}O in the port seems the most likely cause. Ammonium and N\textsubscript{2}O concentrations are high in the pore water of underlying sediments, so one potential source of elevated N\textsubscript{2}O may be the deepening and dredging works in the Hamburg Port region, stirring up sediment. Indeed, deepening and dredging work occurred in the Hamburg Port region in 2021 (HPA, pers. Comm., Karrasch 2022). However, this also applied to 2022, when we saw no sharp N\textsubscript{2}O peak (Fig. 2h). Furthermore, the regions of deepening and dredging operation did not match the region of high N\textsubscript{2}O concentrations, and since turbidity at the time of sampling did not change significantly compared to other cruises, this also speaks against a major signal from channel dredging and deepening. Thus, we conclude that sediment input most likely was not the source of N\textsubscript{2}O in the water column in winter 2021.

Another possible source of N\textsubscript{2}O is the waste water treatment plant (WWTP) Köhlbrandhöft, which treats the waste water from the Hamburg metropolitan region. The WWTP outflow in the Southern Elbe joins the sampled stretch at stream kilometer 626 (Fig. 1), matching the N\textsubscript{2}O peak at stream kilometer 627 (Fig. 2h and 3b). We indeed found out that aggravated operation conditions in the WWTP at the time of sampling were caused by an extreme rain event on March 11\textsuperscript{th} 2021 (HAMBURG WASSER, pers. Comm., Laurich 2022). While the operators could still meet the limits for the effluent levels of nitrate and ammonium, higher than usual ammonium loads left the treatment plant during the March 2021 campaign. We assume this elevated ammonium loads from the WWTP most likely was the cause of the unexpected high N\textsubscript{2}O peak in March 2021. Therefore, we argue that our March 2021 cruise likely represents an exception due to an extreme weather situation, and that typical winter conditions in the Elbe estuary comply with the N\textsubscript{2}O production, as in March 2022.
4.5 Seasonal changes of N$_2$O emissions

For an accurate assessment of annual estuarine N$_2$O emissions, we first evaluate their seasonal distribution. In March, average N$_2$O emissions were $0.28 \pm 0.17$ Gg yr$^{-1}$. Note that we deliberately excluded the N$_2$O peak in March 2021 and interpolated the concentrations in this region to exclude the effect of a point source (Section 4.4). Nonetheless, high wind speeds still led to high N$_2$O emissions in March 2021 (Tab. 3). March 2022 ($0.16 \pm 0.08$ Gg yr$^{-1}$) only slightly deviated from average N$_2$O emissions in spring and summer ($0.20 \pm 0.05$ Gg yr$^{-1}$). Overall, we calculated average annual emissions using the seasonal averages (Tab. 3) resulting in $0.24 \pm 0.06$ Gg yr$^{-1}$, thus exceeding the recent summer N$_2$O emission estimates of $0.18 \pm 0.01$ Gg yr$^{-1}$ by Brase et al. (2017).

Enhanced microbial N$_2$O production can lead to high N$_2$O flux densities in summer (Usui et al., 2001; Allen et al., 2011; Murray et al., 2015; Quick et al., 2019), as is the case for the Elbe estuary in spring and summer (Fig. 7). However, winter flux densities were unexpectedly high (Fig. 7). Elevated winter N$_2$O emissions originated from 1) high wind speeds with increased sea-air exchange, 2) nitrification in the Hamburg Port and 3) elevated riverine N$_2$O inputs into the estuary, with 25 nmol L$^{-1}$ (161.9 % saturation) and 26 nmol L$^{-1}$ (165.3 % saturation) in March 2021 and 2022, respectively, well above summer riverine input concentrations. Since the Elbe estuary acted as a transport channel, rather than a bioreactor in the winter months, due to temperature inhibited biological processing (Koch et al., 1992; Halling-Sorensen and Jorgensen, 1993), the N$_2$O concentrations remained high until mixing with water from the North Sea, which resulted in a decrease and in outgassing to the atmosphere.
Table 3: Average N₂O flux densities and emissions for spring and summer, winter and per year. For the winter, only the March 2022 cruise was used due to the extreme peak in 2021 that was most probably caused by a point-source influx of ammonium and an extreme weather event. For the emissions calculation, the area of the Elbe estuary of 371.85 km² was taken into account (Brase et al., 2017).

<table>
<thead>
<tr>
<th>Season</th>
<th>Average N₂O flux densities</th>
<th>N₂O emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring and summer</td>
<td>33.5 ± 7.8 µmol m⁻² d⁻¹</td>
<td>0.20 ± 0.05 Gg yr⁻¹</td>
</tr>
<tr>
<td>March</td>
<td>47.3 ± 28.1 µmol m⁻² d⁻¹</td>
<td>0.28 ± 0.17 Gg yr⁻¹</td>
</tr>
<tr>
<td>Annual average</td>
<td>40.3 ± 14.3 µmol m⁻² d⁻¹</td>
<td>0.24 ± 0.06 Gg yr⁻¹</td>
</tr>
</tbody>
</table>

5 Conclusions

Overall, we found enhanced N₂O concentrations along the entire Elbe estuary, which point towards in-situ N₂O production that compensated the effect of decreasing DIN loads since the 1990s. Two hot-spots of N₂O production were found in the estuary: the Port of Hamburg and the mesohaline estuary near the estuarine turbidity maximum. Biological N₂O production was enhanced by warmer temperatures and fueled by riverine organic matter in the Hamburg Port or marine organic matter in the MTZ.

We saw no seasonality in N₂O emissions, despite seasonal variations in in-situ N₂O production: In winter, high riverine N₂O input led to high N₂O saturation and emissions in the estuary, whereas in summer, high N₂O emissions were controlled by in-situ production. Overall, the Elbe estuary is a year-round perennial source of N₂O, with estimated annual emissions of 0.24 ± 0.06 Gg yr⁻¹. In conjunction with the overarching control of N₂O production by organic matter quality, this highlights that a holistic approach of water quality improvement and nutrient mitigation is needed to further reduce N₂O emission from the Elbe estuary.

Data availability

The dataset generated and/or analyzed in this study are currently available upon request from the corresponding author and will be made publicly available under coastMap Geoportal (www.coastmap.org) connecting to PANGAEA (https://www.pangaea.de/) with DOI availability in the near future.

Authors contribution

GS, TS and KD designed this study. GS did the sampling and measurements for cruises from 2020 to 2022 as well as the data interpretation and evaluation. TS was responsible for the sampling and measurements for cruises done in 2017 and 2019. YGV provided the oxygen data correction from the FerryBox data. KD, HWB, YGV and TS contributed with scientific and editorial recommendations. GS prepared the manuscript with contributions of all co-authors.

Competing interest

The authors declare that they have no conflict of interest.
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