Seasonal variability of nitrous oxide concentrations and emissions ~~along the Elbe estuary~~in a temperate estuary

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Abstract

Nitrous oxide (N_2O) is a greenhouse gas, with a global warming potential 298 times that of carbon dioxide. Estuaries can be sources of N_2O, 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_2O and ~~N_2O~~ its emissions along the Elbe ~~e~~Estuary (Germany), a well-mixed temperate estuary with high nutrient loading from agriculture. During nine research cruises ~~done~~ performed between 2017 and 2022, we measured dissolved N_2O concentrations, as well as dissolved nutrients and oxygen concentrations along the estuary and calculated N_2O saturations, flux densities and emissions. We found that the estuary was a year-round source of N_2O, with highest emissions in winter when dissolved inorganic nitrogen (DIN) loads and wind speeds are high. However, in spring and summer, N_2O saturations and emissions did not decrease alongside lower riverine nitrogen loads, suggesting that estuarine in-situ N_2O production is an important source of N_2O. ~~We found intense N_2O production along the Elbe estuary that compensated the effect of decreasing dissolved inorganic nitrogen (DIN) loads since the 1990s.~~ We identified ~~T~~two hot-spots areas of N_2O ~~production~~ production~~have been identified in the estuary~~: the Port of Hamburg, a major port region, and the mesohaline estuary near the ~~estuarine~~ maximum turbidity ~~maximum~~ zone (MTZ). N_2O production was enhanced by warmer temperatures and was fueled by decomposition of riverine organic matter in the Hamburg Port and by~~or~~ marine organic matter in the MTZ. A comparison with previous measurements in the Elbe Estuary revealed that N_2O saturation did not decrease alongside with DIN concentrations after a significant improvement of water quality in the 1990s that allowed for phytoplankton growth to reestablish in the river and estuary. This effect of phytoplankton growth and the overarching control of organic matter on N_2O production, highlights that eutrophication and agricultural nutrient input can increase N_2O emissions in estuaries. ~~Surprisingly, estuarine N_2O emissions where equally high in winter and summer. In winter, high riverine N_2O concentrations led to high N_2O emissions from the estuary, whereas in summer, estuarine biological N_2O production led to equally high N_2O emissions. Overall, we find that the Elbe estuary is a year-round source of N_2O with estimated annual emissions of 0.24 ± 0.06 Gg yr^{-1}.~~

1 Introduction

Nitrous oxide (N_2O) 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, 2000; Crossland et al., 2005; Bouwman et al., 2013), and a potential source of N_2O (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_2O-N of the annual global budget of 16.9 Tg N_2O-N (Murray et al., 2015; Tian et al., 2020). N_2O 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_2O emission estimates.

Nitrification and denitrification are the most important N_2O production pathways in estuaries. Under oxic conditions, N_2O 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_2O (e.g. Wrage et al., 2001; Bange, 2008). Denitrification takes place under anoxic conditions and mostly acts as a source of N_2O, but can also reduce N_2O to N_2 (e.g. Knowles, 1982; Bange, 2008). In estuaries, denitrification ~~mainly~~ can occur~~s~~ in anoxic sediments, the anoxic water column or anoxic microsites of particles, whereas ~~oxic~~ nitrification and nitrifier-denitrification take place in the oxygenated water column (Beaulieu et al., 2010; Murray et al., 2015; Ji et al., 2018; Tang et al., 2022).

In estuaries, the most important factor controlling N_2O emissions are considered to be oxygen availability and dissolved inorganic nitrogen loads (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)~~ Since N_2O measurements in estuaries are scarce, global N_2O emissions can be estimated by using emission factors and considering dissolved inorganic nitrogen (DIN) or total nitrogen (TN) loads, where it is assumed that higher loads lead to higher N_2O emissions (Kroeze et al., 2005, 2010; Ivens et al., 2011; Hu et al., 2016). However, several studies instead reported no obvious relationship between nitrogen concentrations and N_2O emissions (Borges et al., 2015; Marzadri et al., 2017; Wells et al., 2018), highlighting the need to understand the causes for variability of the relationship between nitrogen loads and N_2O emissions (Wells et al., 2018). ~~.~~

The Elbe E~~e~~stuary is a heavily managed estuary with high agricultural nitrogen inputs that hosts the third ~~biggest~~ largest port in Europe (e.g. Radach and Pätsch, 2007; Bergemann and Gaumert, 2008; Pätsch et al., 2010; Quiel et al., 2011). It has been identified as a N_2O source, with a hotspot of N_2O production in the Port of Hamburg (Hanke and Knauth, 1990; Brase et al., 2017). We aimed to investigate drivers for N_2O emissions along the estuary, specifically the N_2O and DIN ratio (N_2O:DIN). ~~However, the seasonal variability of N_2O along the estuary is largely unknown so far~~ To do so, we ~~objectives study were~~ (1) ~~to detect a~~looked for potential long~~-~~-term ~~trend~~ changes in ~~of~~ N_2O ~~concentrations~~saturations, (2) ~~to decipher the~~investigated potential production hotspots as well as the spatial and temporal distribution of N_2O ~~concentrations~~ saturations~~along the Elbe estuary during different seasons~~, ~~and (3) to identify hotspots and drivers for N_2O production~~and (3) used the N_2O:DIN ratio for a comparison with other estuaries that receive similar high agricultural nutrient inputs. ~~To this end, we present here measurements of dissolved N_2O as well as dissolved nutrients and oxygen from nine research cruises along the Elbe estuary from August 2017 to March 2022.~~

2 Methods

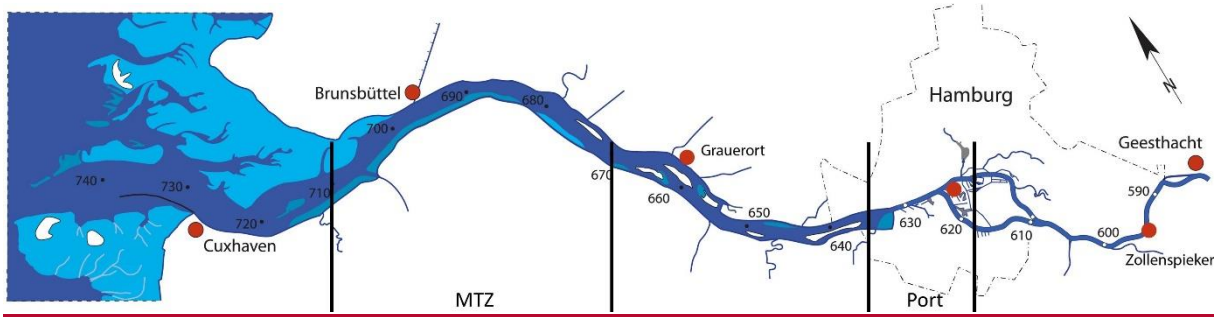
2.1 Study site

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 R~~r~~iver is 140 268 km² (Boehlich and Strotmann, 2019), with

74 % urban and agricultural land-use (Johannsen et al., 2008).~~This makes the~~The Elbe is 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 E~~e~~stuary is a well-mixed temperate estuary, which begins at stream kilometer 586 at a weir in Geesthacht and ~~flows~~ stretches through the Port of Hamburg, entering the North Sea near Cuxhaven at~~,~~ 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 E~~e~~stuary has a length of 142 km (Boehlich and Strotmann, 2019) and a mean annual discharge of 712 $m^3 s^{-1}$ (measured at gauge Neu Darchau at stream kilometer 536; ~~of 712 $m^3 s^{-1}$ with a mean variation range of 276 $m^3 s^{-1}$ to 1960 $m^3 s^{-1}$ (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~~ rang~~inges~~ from ~72 days during times of low discharge (300 $m^3 s^{-1}$) to ~10 days ~~with~~ during times of high discharge (2000 $m^3 s^{-1}$; Boehlich and Strotmann, 2008). The estuary has an annual nitrogen load of 84 Gg-N (FGG Elbe, 2018). Point sources along the estuary provide only small part of the total nitrogen input to the Elbe Estuary (Hofmann et al., 2005; IKSE, 2018). Oxygen concentrations in the Elbe ~~e~~E~~s~~tuary ~~shows a high seasonal variability~~ vary seasonally, with oxygen depletion during the summer months and oxygen minimum zones regularly experiencing concentrations below 94 µmol O_2 L^{-1} ~~In summer months, oxygen depletion and low oxygen zones occur regularly reaching concentrations below 3 mg O_2 L^{-1}~~ (Schroeder, 1997; Gaumert and Bergemann, 2007; Schöl et al., 2014).

The Elbe E~~e~~stuary is dredged year-round ~~on a regular~~ to maintain a water depth of 15 – 20 m and to grant access for large container ships to the Port of Hamburg (Boehlich and Strotmann, 2019; Hein et al., 2021)~~, which is the third biggest largest port in Europe (HAFEN HAMBURG, 2021)~~. Construction work for further deepening of the fairway was carried out ~~in~~ during our study period, from 2019 to early 2022. Upstream of the Port of Hamburg water depth is less than 10 m (Hein et al., 2021).



~~**Figure 1: Map of the Elbe estuary sampled during the research cruises with stream kilometers indicated (wsv.de, last access: 12.09.2022). Background map: © OpenStreetMap contributors 2021. Distributed under the Open Data Commons Open Database License (ODbL) v1.0. The Hamburg Port region stretches from stream kilometer 620 – 635 and is shown between the two grey dashed lines. The typical position of the maximum turbidity zone (MTZ) is shown between the dotted grey lines (Bergemann, 2004).**~~

Figure 1: Map of the Elbe Estuary sampled during our research cruises with stream kilometers. The vertical black lines indicate the Hamburg Port region and a typical position for the maximum turbidity zone (MTZ, ~~(~~Bergemann, 2004).

2.2 Transect sampling and measurements

We performed nine sampling campaigns along the estuary with the research vessel *Ludwig Prandtl* (Tab~~.~~le 1). Most ~~of the~~ cruises took place during ~~the~~ spring and summer ~~seasons~~, with water temperatures > 10 °C (May to September), ~~while~~ two cruises were conducted ~~in~~ during ~~colder~~ winter ~~months~~ (early March, water temperature < 6 °C~~;~~) ~~(~~Tab~~.~~le 1). Transects ~~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). To ensure comparable current and mixing conditions, ~~T~~transect sampling ~~always~~ was ~~performed~~ always done after high-tide, ~~steaming~~ with the ship travelling upstream against the ~~outgoing~~ tide. For comparison to previous measurements, we included summer data from a previous study in 2015 (Brase et al., 2017).

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

Campaign Dates	Stream kilometers (km)	Water temperature (°C)	Wind speed 10 m ($m\ s^{-1}$)	Average discharge ($m^3\ s^{-1}$)	Average DIN load ($\mu mol\ L^{-1}$)
28.-29.04.2015	627 – 741	12.3 ± 1.0	~~11.8 ± 0.3~~7.4 ± 2.3	595	191.0 ± 45.0
02.-04.06.2015	609 – 739	17.4 ± 1.7	5.0 ± 1.3	276	105.9 ± 36.2
01.-02.08.2017	621 – 749	20.9 ± 0.7	3.6 ± 1.5	607	79.2 + 30.2
04.-05.06.2019	610 – 750	18.7 ± 2.2	4.0 ± 1.7	423	108.3 ± 35.9
30.07.-01.08.2019	609 – 752	22.6 ± 1.0	4.2 ± 1.4	171	60.8 ± 38.6
19.-20.06.2020	609 – 747	19.8 ± 1.4	5.8 ± 1.2	331	74.6 ± 33.8
09.-11.09.2020	607 – 745	18.9 ± 0.6	5.9 ± 2.8	305	93.1 ± 32.7
10.-12.03.2021	609 – 748	5.4 ± 0.5	9.3 ± 2.6	862	324.4 ± 83.8
04.-05.05.2021	610 – 751	10.5 ± 0.8	11.0 ± 3.1	411	85.7 ± 36.6
27.-28.07.2021	621 – 751	22.2 ± 0.7	5.2 ± 1.3	721	139.8 ± 58.4
01.-02.03.2022	610 – 752	5.6 ± 0.2	2.9 ± 1.0	1282	238.0 ± 74.7

An onboard membrane pump continuously provided water ~~from~~ at 1.2 m depth to an on-line in-situ FerryBox system and to an equilibrator used for the measurements of N_2O dry mole fraction (Section 2.4). The FerryBox system continuously measured water temperature, salinity, oxygen concentrations, pH and turbidity. We corrected the ~~oxygen measurements using the~~ salinity corrected optode measurements using~~in~~ comparisons to Winkler titrations of distinct samples. ~~The corrections of the individual cruises are listed in the~~See Table S1 for further details.

Discrete water samples (30-40 samples for each cruise) were ~~taken~~ collected 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 were ~~stored~~ frozen in acid washed PE-bottles until analysis. The filters were also stored frozen (-20 °C) and subsequently analyzed for ~~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~~ methods (Hansen and Koroleff, 1999) for dissolved nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) concentrations. Detection limits were 0.05 µmol L^{-1}, 0.05 µmol L^{-1}, and 0.07 µmol L^{-1} for nitrate, nitrite and ammonium, respectively.

2.4 Equilibrator based N_2O measurements and calculations

Equilibrated dry mole fractions of N_2O were measured by an N_2O 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. Twice a day, ~~-~~two standard gas mixtures of N_2O in synthetic air (500.5 ppb ± 5 % and 321.2 ppb ± 3 %) were analyzed to validate our measurements. No drift was detected during our cruises.

We calculated the dissolved N_2O concentrations in water with the Bunsen solubility function of Weiss and Price (1980), using 1 min averages of the measured N_2O dry mole fraction (ppb). Temperature differences between the sample inlet and the equilibrator were taken into account for the calculation of the final N_2O concentrations Rhee et al. (2009). N_2O saturation were calculated based on N_2O concentrations in water (N_2O_{cw}) and the ~~in the air~~atmospheric equilibration concentrations ($N_2O_{eq\text{~~air~~}}$~~;~~) ~~(~~Eq. 1). ~~During each cruise, A~~Atmospheric N_2O dry mole fractions were measured before and after each transect cruises using an air duct from the deck of the research vessel.

$$s = 100 \times \frac{N_2O_{cw}}{N_2O_{eq\text{~~air~~}}} \quad (1)$$

The gas transfer coefficients (k) were determined based on Borges et al. (2004, Eq. 3), ~~(~~Nightingale et al.~~,~~ (2000), ~~(~~Wanninkhof~~,~~ (1992) and ~~(~~Clark et al.~~,~~ (1995), using ~~–~~ ~~taking~~ the Schmidt number (Sc) and wind speeds (u_{10}) measured at ~~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_2O 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).~~Cruise wind speeds (Table 1) varied significantly from average annual wind speeds of the two federal states, in which the Elbe Estuary is located (4.7 m s^{-1}, Schleswig-Holstein u. Hamburg: Mittlere Windgeschwindigkeit (1986-2015)* | Norddeutscher Klimamonitor, 2023), and also compared to seasonal average wind speeds determined for the stations Cuxhaven and Hamburg (Rosenhagen et al., 2011). Thus, to estimate uncertainties due to varying wind conditions during our cruises, we used 1) the in-situ wind speeds measured on board the *R/V Ludwig Prandtl* at 10 m height by a MaxiMet GMX600 (Gill Instruments Limited, Hampshire, UK), 2) the average annual wind speed (Schleswig-Holstein u. Hamburg: Mittlere Windgeschwindigkeit (1986-2015)* | Norddeutscher Klimamonitor, 2023), and 3) the seasonally averaged wind speeds (Rosenhagen et al., 2011). ~~Flux densities were calculated according to Equation 3.~~ The flux densities in the main text were calculated using Eq. 3 and the wind speeds measured on board the vessel. Results of the other calculations are listed in the supplementary material (Table S2).

$$k = 0.24 \times (4.045 + 2.58u_{10}) \times \left(\frac{Sc}{600}\right)^{-0.5} \quad (2)$$

$$f = k \times (N_2O_{cw} - N_2O_{air}) \quad (~~3~~3)$$

~~For emission calculations we used an area of 371.85 km² for the Elbe estuary in line with Brase et al. (2017). We calculated seasonal averages for winter and spring/summer based on our transect cruises, which we used for estimation of annual emissions.~~

To estimate N_2O emissions, we separated the Elbe Estuary into five regions: limnic (stream kilometer 585 to 615), Port of Hamburg (stream kilometer 615 to 632), oligohaline (stream kilometer 632 to 704), mesohaline (stream

kilometer 704 – 727) and polyhaline (stream kilometer 727 to 750), see Table S3. Respective areas were provided by the German Federal Waterways Engineering and Research Institute (BAW, pers. Comm., Oritz, 2023) and (Geerts et al., (2012). In order to account for seasonality, cruises were defined as: winter (March), spring (April and May), summer (June and July) and late summer/autumn (August and September). We then calculated daily N_2O emissions per section and season. For upscaling, we used calculated monthly emissions to estimate annual emissions (winter: November to March, spring: April to May, summer: June to July and late summer/autumn: August to October). To address uncertainties, we calculated N_2O emissions based on different parametrizations and wind speeds as described above.

2.5 Excess N_2O and apparent oxygen utilization

The correlation between excess N_2O (N_2O_{xs}) and apparent oxygen utilization (AOU) can provide insights into N_2O production (Nevison et al., 2003; Walter et al., 2004). We calculated N_2O_{xs} as the difference between the N_2O concentration in water (N_2O_w) and the theoretical equilibrium concentration (N_2O_{eq}) (Eq. 4). AOU was determined using Eq. equation 5, where O_2 is the measured dissolved oxygen concentration, and O_2' is the theoretical equilibrium concentration between water and atmosphere calculated according to Weiss (1970).

$$N_2O_{xs} = N_2O_w - N_2O_{eq} \quad (4)$$

$$AOU = O_2' - O_2 \quad (5)$$

A linear relationship between AOU and N_2O_{xs} is usually an indicator for nitrification (Nevison et al., 2003; Walter et al., 2004).

2.6 Statistical analysis

All statistical analyses were done using R packages. The packages ggpubr v.0.6.0 (Kassambara, 2023) and stats v.4.0.2 (The R Stats Package, Version 4.0.2, 2021) were used to calculate Pearson correlations (R) and p-values.

3 Results

3.1 Hydrographic properties and DIN distribution

Discharge ranged between 171 $m^3\ s^{-1}$ and 1282 $m^3\ s^{-1}$ during our cruises (ZDM, 2022), with higher discharge in winter and lower discharge in summer (Table. 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 (Table 1). For the further evaluation, March 2021 and 2022 cruises will be were regarded as winter cruises (water temperature < 6°C), whereas all cruises with higher water temperature were 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 of nitrate (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 ± 85.7 µmol L^{-1} and 230.9 ± 76.2 µmol L^{-1} in 2021 and 2022, respectively. During summer, nitrate concentrations were lower, with. The nitrate concentrations averages were between 151.0 ± 58.1 µmol L^{-1} in May 2021 and 63.3 ± 38.8 µmol L^{-1} in July 2019 (Fig. 2a and b).

Nitrite and ammonium concentrations were usually low (< 1 µmol L^{-1}) ~~along~~ throughout the Elbe ~~e~~Estuary, but peaked ~~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 µmol L^{-1} (July 2019) to concentrations below the detection limit ~~(< 0.05 µmol L^{-1})~~ (Fig. 2c and d). The highest ammonium concentration was measured in March 2021 at ~~with~~ 23.5 µmol L^{-1} ~~. Over large stretches of the estuary, ammonium was below the detection limit (< 0.07 µmol L^{-1}) in winter as well as in spring and summer~~ (Fig. 2e and f).

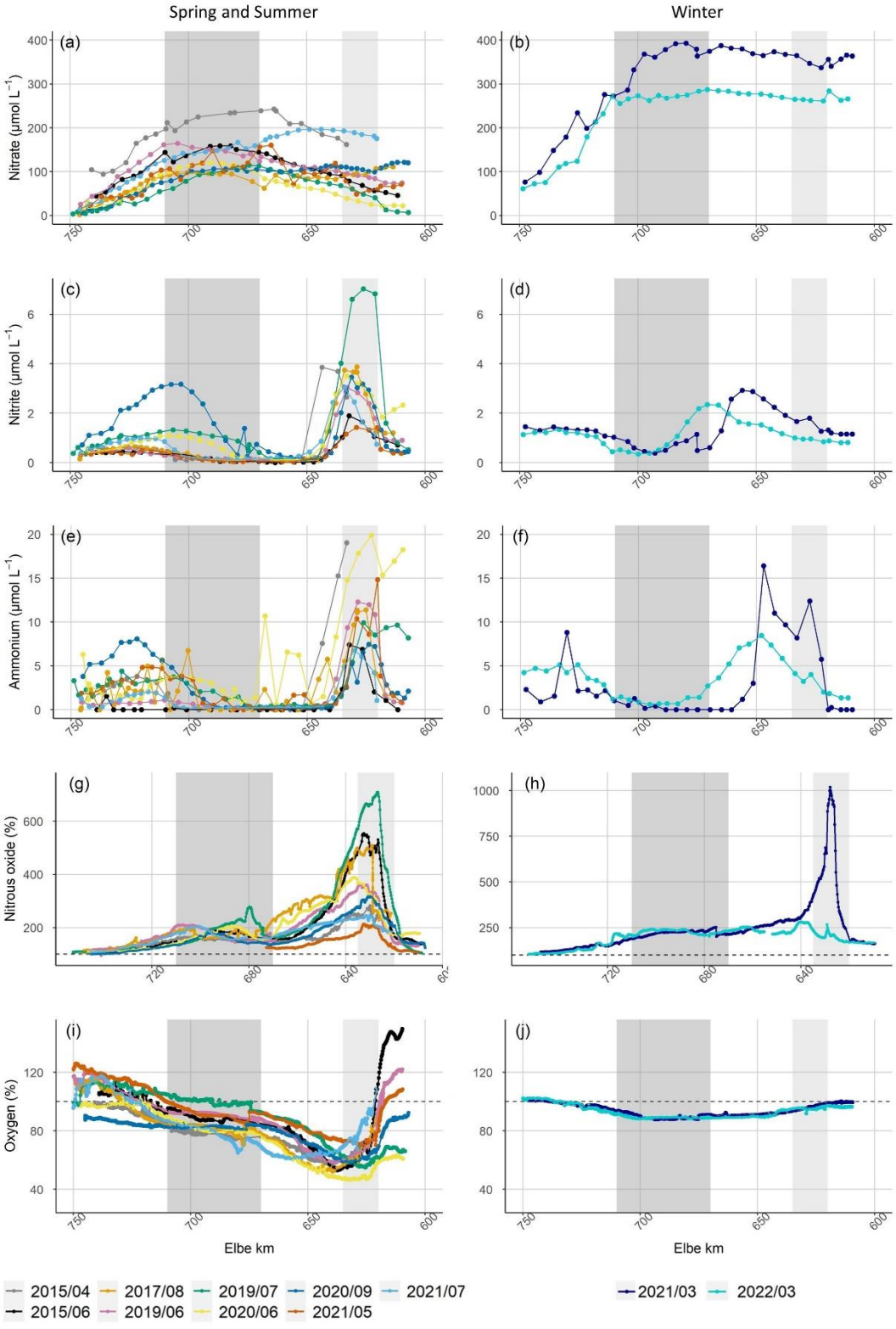


Figure 2: Nitrate concentration ~~in µmol L^{-1}~~ along the Elbe ~~estuary~~ Estuary (a) in spring/summer, (b) in winter. Nitrite concentration ~~in µmol L^{-1}~~ along the Elbe ~~estuary~~ Estuary (c) in spring/summer and (d) in winter. Ammonium concentration ~~in µmol L^{-1}~~ along the Elbe ~~estuary~~ Estuary (e) in spring/summer and (f) in winter. N_2O ~~concentration~~ in % saturation~~nmol L^{-1}~~ along the Elbe ~~estuary~~ Estuary (g) in spring/summer, (h) in winter. Dissolved oxygen in % saturation ~~in % saturation~~ along the Elbe ~~estuary~~ Estuary (i) in spring/summer and (j) in winter. All ~~values~~ variables are ~~ppl~~plotted against Elbe stream kilometers (Elbe km). Light grey shading denotes ~~T~~the Hamburg Port region, dark grey shading ~~is shown with light grey background. t~~The typical position of the maximum turbidity zone (MTZ,~~) is shown with a dark grey (~~Bergemann, 2004). Note the difference in Y-axis scales ~~differ~~ for the plots of ~~N_2O concentrations~~ (g) and (h). The dashed black lines in (g) and (h), as well as (i) and (j) indicate ~~an oxygen~~ saturation of 100 % for nitrous oxide and dissolved oxygen, respectively.

3.2 Atmospheric ~~and dissolved~~ N_2O and N_2O saturation

The average atmospheric N_2O dry mole fractions ranged from 325 ppb in June 2015 to 336 ppb in July 2022 (Table~~.~~ 2). The differences between our measurements and the mean monthly N_2O mole fraction measured at the Mace Head atmospheric monitoring station ~~Mace Head~~ (Ireland; Dlugokencky et al., 2022) were always less than 1.5 %, indicating a good agreement with the monitoring data.

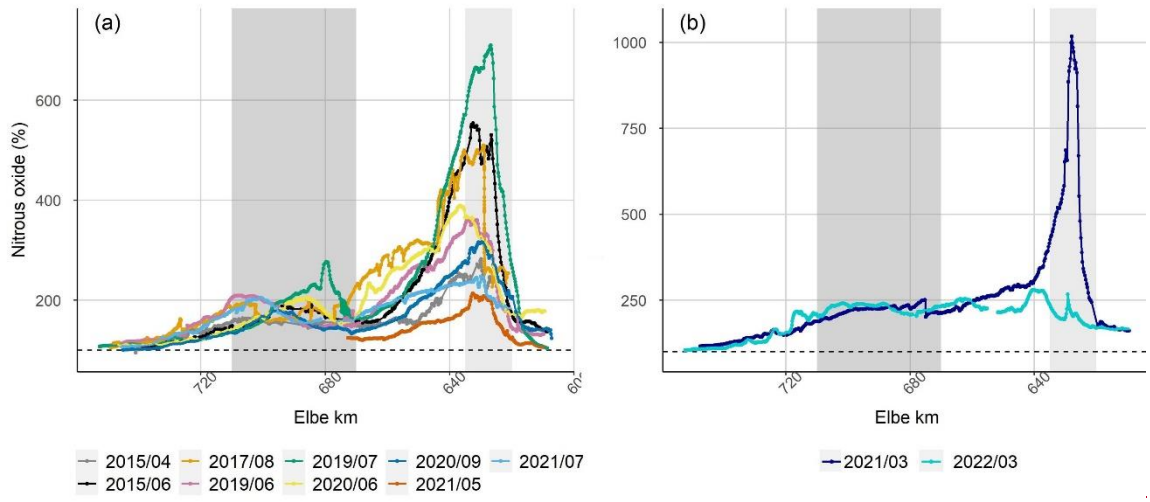
~~Comparable to the nutrient concentrations, N_2O varied seasonally (Fig. 2): In spring and summer, riverine N_2O (i.e., inflow into the estuary, stream kilometer <589) ranged from 8 nmol L^{-1} to 15 nmol L^{-1}. At the onset of the estuary, spring and summer N_2O concentrations usually showed a steep increase and peak values between 27 nmol L^{-1} and 58 nmol L^{-1} (~stream kilometer 620-635). Further downstream, N_2O 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}. N_2O concentrations dropped towards equilibrium concentrations of 8 – 12 nmol L^{-1} in the North Sea (Fig. 2g).~~

~~In winter, riverine N_2O concentrations were elevated (~ 25 nmol L^{-1}) compared to spring and summer riverine concentrations. In 2021, a steep increase of N_2O concentrations occurred in the Hamburg Port region, (stream kilometer 620 – 635) leading to exceptionally elevated N_2O concentrations of up to 158 nmol L^{-1} (Fig. 2h). In March 2022, N_2O increased to 44 nmol L^{-1} in this region. Further downstream, N_2O 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 N_2O saturations and flux densities~~

During all cruises, the Elbe ~~e~~Estuary was supersaturated in N_2O in the freshwater region (Fig. ~~3~~2g, h). The average N_2O saturation over the entire transect ranged between 146 % and 243 % with an overall average of 197 % for all cruises. Highest N_2O ~~saturations~~ occurred in the Hamburg Port region in spring and summer with an average N_2O peak of 402 % saturation and a maximum supersaturation of 710 % in July 2019. The distributions of N_2O ~~saturations~~ during ~~the~~ winter cruises were significantly different: In March 2022, highest N_2O ~~saturation~~ (280 % saturation) occurred at stream kilometer 640. In contrast, i~~I~~n March 2021, ~~in contrast,~~ we found an extraordinarily high peak with a saturation of 1018 % at stream kilometer 627. Between stream kilometer 680 and 720, a supersaturation of up to 277 % occurred in spring and summer ~~months~~. Further towards the North Sea, N_2O ~~saturation~~ decreased, ~~and~~ approaching equilibrium with the atmosphere.

~~3.4~~3.3 N_2O flux densities and N_2O emissions



~~**Figure 3: (a): N_2O saturation along the Elbe estuary for cruises in spring/summer, (b) N_2O 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.**~~

For N_2O flux densities, we in the following present calculated values after Borges et al. (2004, Table 2). See Table S2 for results of other parametrizations. The N_2O flux densities were usually highest in the Hamburg Port area, with an average of 95.0~~95.1~~ ± ~~113.6~~97.9 µmol m^{-2} d^{-1} and lowest towards the North Sea, with an average of 3.9 ± 3.0 µmol m^{-2} d^{-1} (Elbe stream kilometers > 735). The average N_2O flux density of all cruises was ~~37.8~~39.9 ± ~~51.4~~6.90 µmol m^{-2} d^{-1}. (~~Tab. 2~~calculated~~(Borges et al., 2004)~~ ,with in-situ wind speeds measured during the- cruises).

Table 2: Calculated average N_2O saturation, sea-to-air fluxes calculated following Borges et al. (2004) and atmospheric N_2O dry mole fractions during our cruises in~~for~~ the Elbe E~~e~~stuary

Campaign Dates	Average saturation (%)	N_2O Flux densities (µmol m^{-2} d^{-1})			Average atmospheric dry mole fraction (ppb)
		In-situ wind	Annual wind	Seasonal wind	
28.-29.04.15	160.8 ± 37.9	33.1 ± 21.0	23.1 ± 14.7	25.4 ± 16.1	331 ± 0.5
02.-04.06.15	203.8 ± 112.7	39.0 ± 42.7	37.2 ± 40.7	37.8 ± 41.4	325 ± 0.8
01.-02.08.17	221.0 ± 106.5	35.6 ± 31.8	43.2 ± 38.5	44.1 ± 39.3	331 ± 1.2
04.-05.06.19	192.6 ± 66.0	29.7 ± 21.5	33.5 ± 24.2	34.0 ± 24.6	332 ± 0.2
30.07.-01.08.19	232.5 ± 155.3	42.0 ± 50.1	45.7 ± 54.5	47.4 ± 56.4	327 ± 1.0
19.-20.06.20	193.9 ± 74.1	39.2 ± 31.6	33.3 ± 26.9	33.9 ± 27.3	330 ± 0.6
09.-11.09.20	160.5 ± 53.6	26.0 ± 23.5	21.8 ± 19.7	24.5 ± 22.1	331 ± 0.7
10.-12.03.21	242.5 ± 141.6	100.7 ± 101.2	58.1 ± 58.4	71.0 ± 71.4	331 ± 1.3
04.-05.05.21	145.6 ± 28.8	35.6 ± 22.5	17.8 ± 11.2	18.5 ± 11.7	331 ± 0.8
27.-28.07.21	172.6 ± 37.2	28.0 ± 14.6	25.9 ± 13.6	26.9 ± 14.1	334 ± 3.8
01.-02.03.22	196.5 ± 47.0	27.8 ± 13.9	39.0 ± 19.5	47.7 ± 23.8	333 ± 0.7

N_2O emission estimates varied significantly depending on the used parametrization and wind speeds. Note that we calculated emission twice: 1) including (w 03/2021) and 2) deliberately excluding (w/o 03/2021) the N_2O peak saturation measured in the Port of Hamburg in March 2021, using a linear interpolated concentrations in the

respective. Highest emissions were calculated following methods by Borges et al. (2004) and using in-situ wind speeds, resulting in emissions of 0.25 ± 0.16 Gg-N_2O yr^{-1} and 0.23 ± 0.12 Gg-N_2O yr^{-1} with and without the N_2O peak in March 2021, respectively. Lowest emissions of 0.08 Gg-N_2O yr^{-1} arose with parametrization of (Nightingale et al., (2000) and (Wanninkhof, (1992), and using annual wind speeds (Table 3).

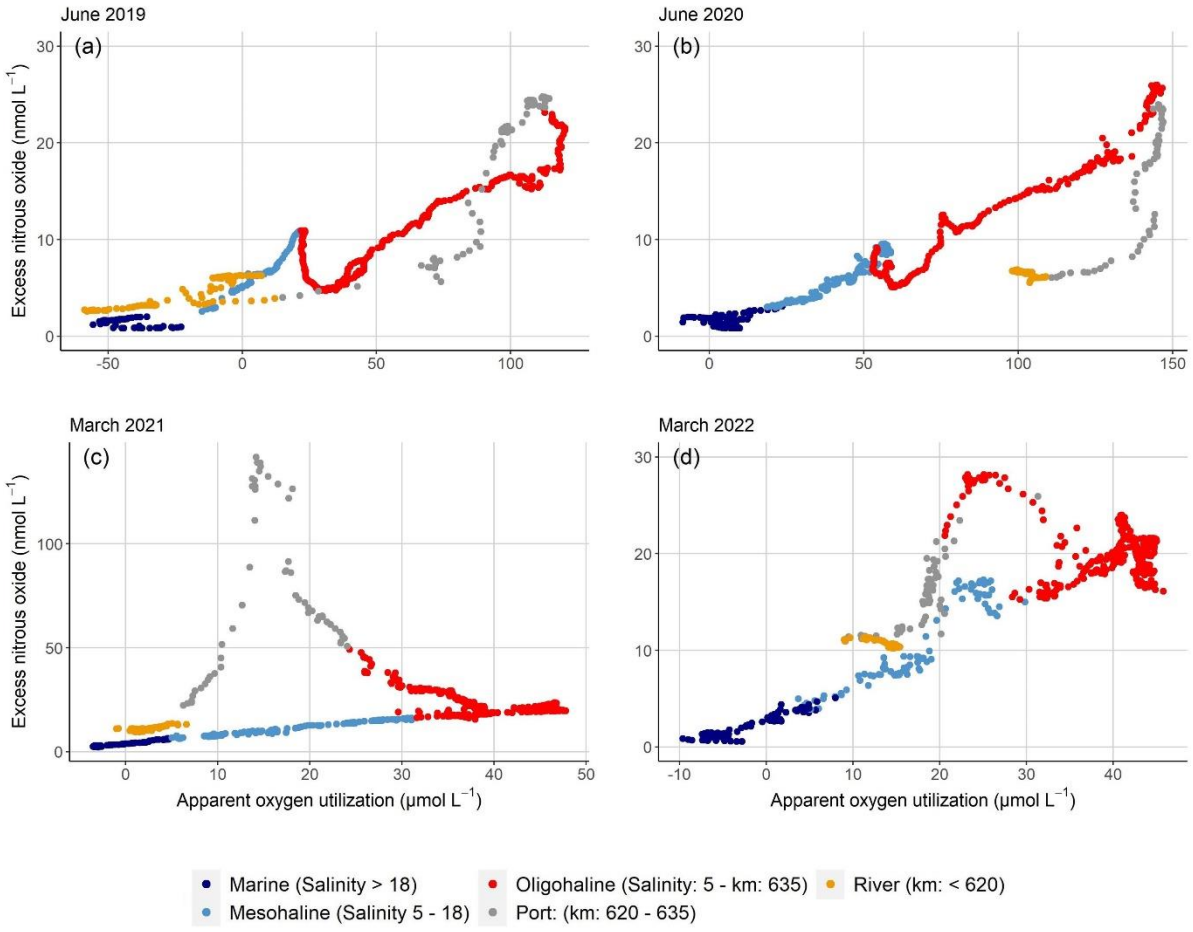
Table 3: Annual N_2O emission estimates in Gg-N_2O yr^{-1} calculated with different parametrizations and wind speeds

		Emissions in Gg-N_2O yr^{-1}			
		Borges et al. (2004)	(Nightingale et al., (2000)	(Wanninkhof, (1992)	(Clark et al., (1995)
w 03/2021	In-situ wind	0.25 ± 0.16	0.14 ± 0.12	0.17 ± 0.15	0.16 ± 0.12
	Annual wind	0.21 ± 0.11	0.08 ± 0.04	0.09 ± 0.05	0.09 ± 0.05
	Seasonal wind	0.24 ± 0.12	0.11 ± 0.06	0.13 ± 0.06	0.12 ± 0.06
w/o 03/2021	In-situ wind	0.23 ± 0.12	0.13 ± 0.09	0.15 ± 0.11	0.14 ± 0.09
	Annual wind	0.20 ± 0.08	0.08 ± 0.03	0.08 ± 0.03	0.09 ± 0.04
	Seasonal wind	0.22 ± 0.09	0.11 ± 0.04	0.12 ± 0.04	0.12 ± 0.04

3.53.4 Dissolved oxygen saturation

Average oxygen saturation varied between 76 and 95 in % saturation with an oxygen minimum in the Hamburg Port area. Winter cruises varied littleshowed 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 supersaturated in oxygen (> 100 % saturation). In the Hamburg Port region, oxygen saturation generally decreased. Lowest values occurred in June 2020 with 47 % saturation. The along-estuary oxygen minimum oxygen in summer months (June to 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_2O (N_2O_{xs}) and apparent oxygen utilization (AOU) revealed excess N_2O along the entire estuary (Fig. 3). During all cruises, elevated riverine N_2O_{xs} entered the estuary (stream kilometer < 620). A linear positive relationship between N_2O_{xs} and AOU suggested nitrification as main production pathway in large sections of the estuary (Nevison et al., 2003; Walter et al., 2004). However, in summer, a change of slope in the Port of Hamburg as well as in the mesohaline section of the estuary suggested either increased in-situ N_2O production or external N_2O input. In winter, we found an increasing slope in the Hamburg Port region and in the oligohaline part of the Elbe Estuary (Fig. 3h, k).Plots of excess N_2O (N_2O_{xs}) and apparent oxygen utilization (AOU) (Fig. 4) revealed excess N_2O along the entire estuary (Fig. 4 and supplementary material S2). During all cruises, elevated riverine N_2O_{xs} concentrations entered the estuary (stream kilometer < 620). In spring and summer, steep, non-linear increases of N_2O_{xs} in the Port of Hamburg suggested in-situ N_2O production (Fig. 4a, 4b). This production extended into the oligohaline estuary (stream kilometer > 635 and salinity < 5) followed by a linear decrease of N_2O_{xs} reduction in the transition region to the mesohaline section of the estuary (salinity: 5-18), N_2O_{xs} increased again, followed by a decrease to 0 nmol L^{-1} towards the North Sea. In winter, we found a linear relationship of N_2O_{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_2O_{xs}/AOU plots for summer (4 a, b) and winter (4 c, d) are shown (see supplementary material: Fig. S2 for all plots).


June 2019
(a)
June 2020
(b)
March 2021
(c)
March 2022
(d)
Excess nitrous oxide (nmol L^{-1})
Apparent oxygen utilization (µmol L^{-1})
Marine (Salinity > 18)
Mesohaline (Salinity 5 - 18)
Oligohaline (Salinity: 5 - km: 635)
Port: (km: 620 - 635)
River (km: < 620)

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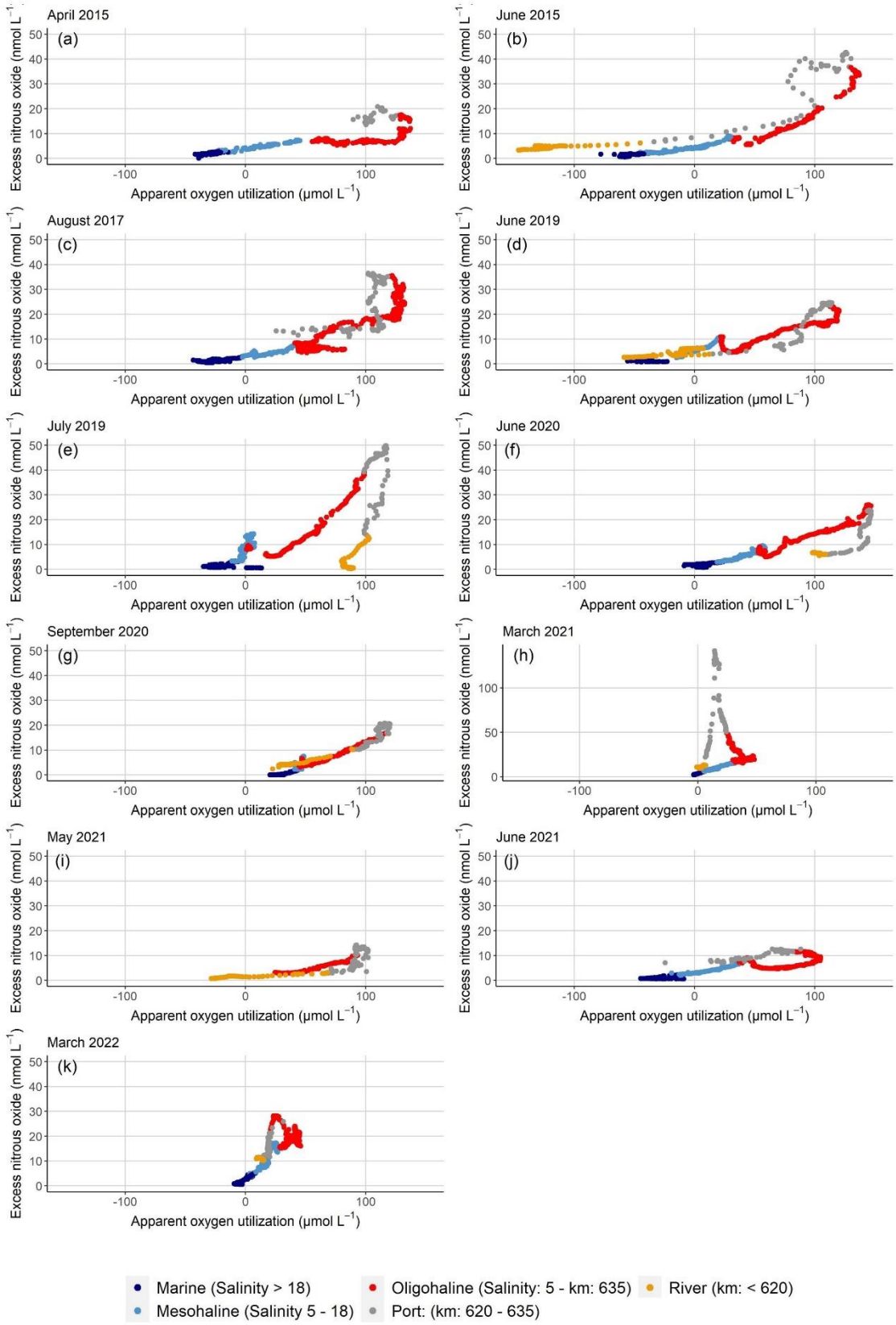


Figure 43: ~~Representative p~~Plots of N_2O_{xs} vs AOU for (a) ~~June 2019~~April 2015, (b) June 2015~~ June 2020~~, (c) ~~March 2021~~August 2017~~ and~~, (d) ~~March 2022~~ June 2019, (e) July 2019, (f) June 2020, (g) September 2020, (h) March 2021, (i) May 2021, (j) June 2021 and (k) March 2022. 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 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. 4~~c~~3h.

3.5 Statistical analysis

We performed a statistical analyses to identify potential N_2O production pathways and controlling factors. Table 4 summarizes the results for the entire data set with further separation into spring and summer cruises (sp/su), as well as separation according to presence of a salinity gradient (salinity > 1) or freshwater regions (salinity < 1). Further, we performed corresponding analysis to assess the significance of correlations between for average values of different parameters for each cruise (Table 5).

Table 4: Pearson correlation coefficients (R) for N_2O saturation (%) with temperature (T in °C), pH value, oxygen (O_2 in %), ammonium concentrations (NH_4^+ in µmol L^{-1}), nitrite concentrations (NO_2^- in µmol L^{-1}), nitrate concentrations (NO_3^- in µmol L^{-1}), SPM concentrations (SPM in mg L^{-1}), C/N values, particulate carbon fraction (PC in %) and particulate nitrogen fraction (PN in %) for the entire data set, spring and summer cruises (sp/su), data with salinity > 1, spring and summer cruises with salinity > 1, data with salinity < 1 and spring and summer cruises with salinity < 1. The significance is shown as ** for p-value < 0.001, * for p-values < 0.01 and + for p-values < 0.05.

N_2O saturation %	T °C	pH	O_2 %	NH_4^+ µM	NO_2^- µM	NO_3^- µM	SPM mg	C/N	PC %	PN %
Entire data	0.06	-0.47**	-0.56**	0.27**	0.48**	0.23	0.10	0.60	-0.05	-0.13+
sp/su	0.33*	-0.59**	-0.65**	0.23**	0.53**	0.09	0.02	0.24**	-0.09	-0.13+
Sal>1	0.03	-0.40**	-0.53**	-0.32**	-0.05	0.71**	0.32**	0.11*	-0.24	-0.39**
Sal<1,	0.01	-0.41**	-0.42**	0.28**	0.51**	-0.00	-0.08	0.15	-0.25*	-0.24*
Sal>1, sp/su	-0.10	-0.21+	-0.52**	-0.28**	0.01	0.62**	0.02	0.39**	-0.31**	-0.41**
Sal<1, sp/su	0.30**	-0.60**	-0.57**	0.21+	0.58**	-0.23*	-0.16`	0.11	-0.30*	-0.27*

Table 5: Pearson correlation coefficients (R) for average N_2O saturation (%) with average discharge (Q in m^3 s^{-1}) temperature (T in °C), pH value, oxygen (O_2 in %), ammonium concentrations (NH_4^+ in µmol L^{-1}), nitrite concentrations (NO_2^- in µmol L^{-1}), nitrate concentrations (NO_3^- in µmol L^{-1}), SPM concentrations (SPM in mg L^{-1}), C/N values, particulate carbon fraction (PC in %) and particulate nitrogen fraction (PN in %) for the entire data set, spring and summer cruises (sp/su), data with salinity > 1, spring and summer cruises with salinity > 1, data with salinity < 1 and spring and summer cruises with salinity < 1. The significance is shown as ** for p-value < 0.001, * for p-values < 0.01 and + for p-values < 0.05.

N_2O saturation %	Q m^3s^{-1}	T °C	pH	O_2 %	NH_4^+ µM	NO_2^- µM	NO_3^- µM	SPM mg	C/N	PC %	PN %
Entire data	0.13	0.06	-0.65	-0.39	0.02	0.48	0.27	-0.31	0.53	0.12	-0.16
sp/su	-0.26	0.76+	-0.82+	-0.32	0.01	0.35	-0.40	-0.92*	0.15	0.18	0.31
Sal>1	-0.07	-0.14	-0.38	-0.43	-0.18	0.23	0.52	-0.19	0.46	-0.18	-0.38
Sal<1,	-0.21	0.29	-0.59	-0.39	0.26	0.76*	-0.11	-0.57	0.12	0.61	0.47
Sal>1, sp/su	-0.07	-0.70+	-0.41	-0.26	-0.42	0.03	0.05	-0.81+	-0.04	-0.10	0.14
Sal<1, sp/su	-0.48	0.72+	-0.80	-0.46	0.29	0.77+	-0.58	-0.87+	-0.17	0.69	0.67

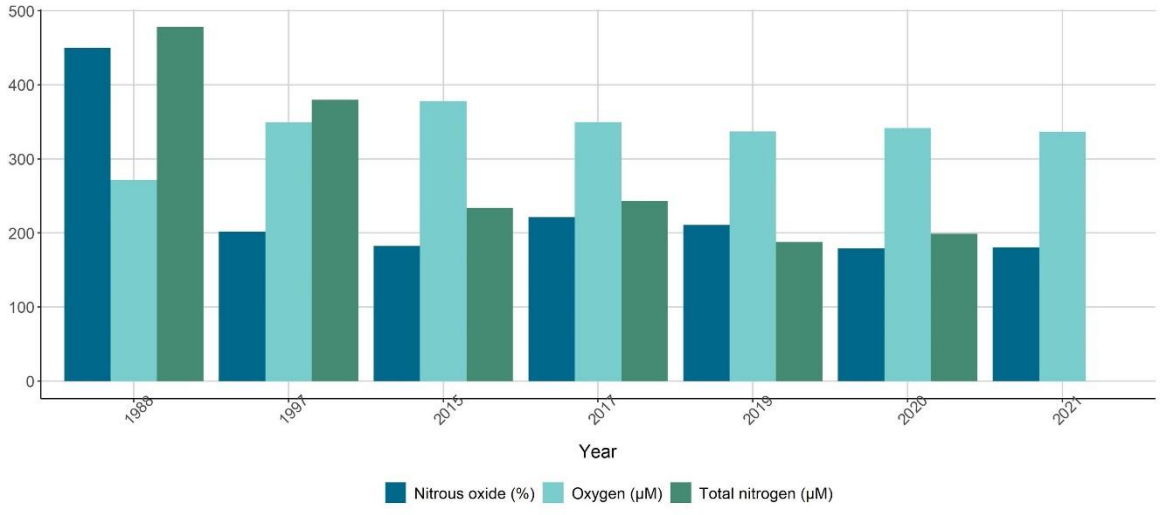
4 Discussion

4.1 N_2O saturation and flux densities of the Elbe Eestuary

The average N_2O saturation and flux density were 197 % and 39.9 ± 46.9 ~~39.68~~ µmol m^{-2} d^{-1}, respectively. The N_2O flux densities from the Elbe ~~estuary~~ 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} (Garnier et al., 2006; Gonçalves et al., 2010; Murray

et al., 2015) and ~~.~~average N_2O saturations fitted to values determined by ~~(~~Reading et al.~~,~~ (2020) for highly modified urban systems. ~~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_2O_{xs} and AOU for most of the regions of the Elbe estuary. Therefore, large sections in the estuary~~ The relationship of N_2O_{xs} and AOU (Fig. 3), with changing slopes in the Port of Hamburg and mesohaline estuary, ~~were influenced~~was determined by either initial riverine N_2O production, or in-situ production along the estuary. During spring and summer, we found ~~enhanced~~ increasing N_2O concentrations in ~~two regions:~~ the Hamburg Port region (see also Brase et al. (2017)), and in the salinity gradient (stream kilometer 680 – 700, salinity ~5). Both N_2O peaks varied in magnitude ~~height~~ and spatial extension, suggesting in-situ biological production (Fig. 2g~~, 3a~~). This matches ~~previous~~ earlier research linking estuarine N_2O fluxes to in-situ generation (e.g. Bange, 2006; Barnes and Upstill-Goddard, 2011; Murray et al., 2015).

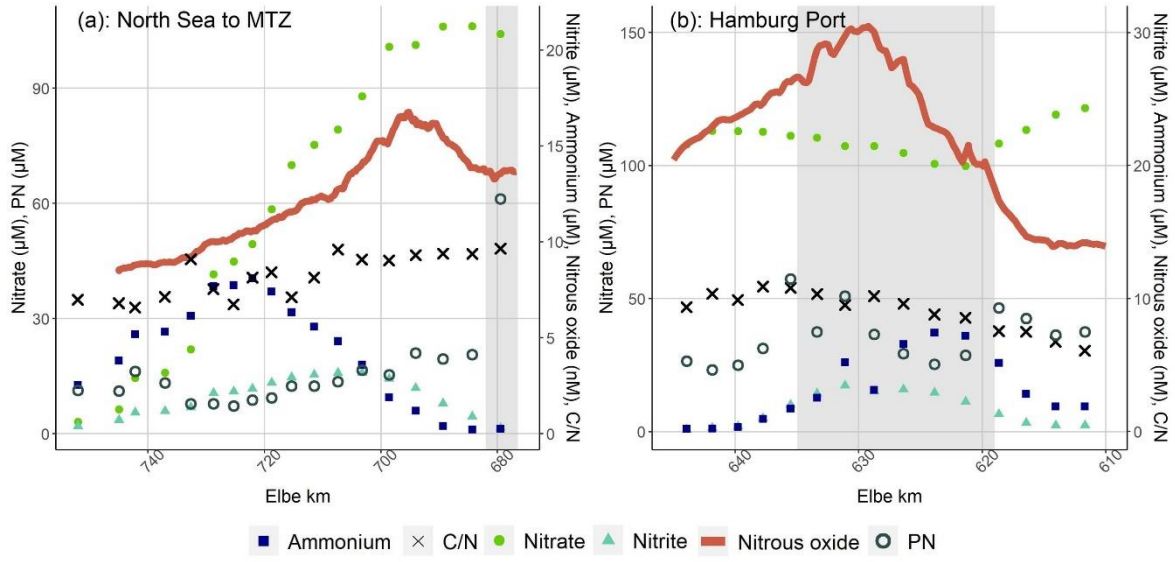
Previous measurements of N_2O saturation and flux densities in the Elbe E~~e~~stuary between the 1980s and 2015 (Hanke and Knauth, 1990; Barnes and Upstill-Goddard, 2011; Brase et al., 2017) showed a significant reduction of N_2O saturation due to the reduced riverine nutrient load and higher dissolved oxygen concentrations (Brase et al., 2017). However, ~~S~~since the BIOGEST study in 1997 (Barnes and Upstill-Goddard, 2011), N_2O remained relatively stable at ~ 200 % saturation despite a concurrent decrease in TN concentration from ~400 µmol L^{-1} to around 200 µmol L^{-1} (Fig. S2; Hanke and Knauth, 1990; Barnes and Upstill-Goddard, 2011; Brase et al., 2017; Das Fachinfomrationssystem (FIS) der FGG Elbe, 2022). As N_2O saturation did not decrease in scale with riverine nitrogen input, this suggests ~~suggesting~~ that in-situ N_2O production along the estuary is important ~~(Fig. 5)~~. Dähnke et al. (2008) showed a shift from dominating denitrification towards significant nitrification in the Elbe Estuary due to the significant improvement of water quality after the reunification of Germany in 1990. In the following sections, we investigate the biogeochemical controls of this in~~-~~-situ production. For this purpose, we discuss ~~both~~ the two zones of intense N_2O production separately and also distinguish between ~~biological active~~ cruises in spring and summer (water temperature > 10 °C) and in winter (water temperature < 6 °C).



~~**Figure 5: Comparison of average N_2O saturation transect measurements with previous research from the Elbe estuary. Average annual oxygen concentration and total nitrogen concentration are shown for the station Zollenspieker at the beginning of the estuary (stream kilometer 598.7) and publicly available (Das Fachinfomrationssystem (FIS) der FGG Elbe, 2022).Values for 2022 and total nitrogen concentration for 2021 are not presented as the data is not publicly available yet.**~~

4.2 N_2O production in spring and summer in the mesohaline estuary

The N_2O peak in the transition between oligohaline and mesohaline estuary was accompanied by a sudden change ~~from a decreasing to an increasing trend between~~in the slope of the AOU ~~and~~ vs N_2O_{xs} plots (Fig. ~~4a, 4b~~3), pointing towards N_2O production in the oxic water column. ~~Interestingly, we find that small peaks~~Peaks of nitrite and ammonium concentrations coincided with the elevated nitrous oxide saturations ~~peak~~ between Elbe km 680–700, with an ammonium peak around stream kilometer ~720, and a nitrite peak at ~700 (Fig. 4a). Highest N_2O 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~~4a, September 2020, and Fig. S3-S13). This co-occurrence of nitrite accumulation and increased N_2O saturation has been interpreted as signs for N_2O production via denitrification (e.g. Wertz et al., 2018; Sharma et al., 2022). However, denitrification does not seem likely in this oxic water column. ~~S~~Such a succession of nitrite and ammonium peaks is also typical for remineralization and nitrification, and the slight decrease of oxygen concentrations around the higher N_2O saturation ~~peak~~ (Fig. 2g and i) suggests ~~that~~ oxygen consumption, possibly caused by ~~nitrification~~these two processes.~~, occured.~~ Sanders et al. (2018) measured small but detectable nitrification rates ~~(of~~ 1 – 2 µmol L^{-1} d^{-1}) for this region of the Elbe Eestuary, suggesting that N_2O ~~in this region~~ may be a side product of nitrification.



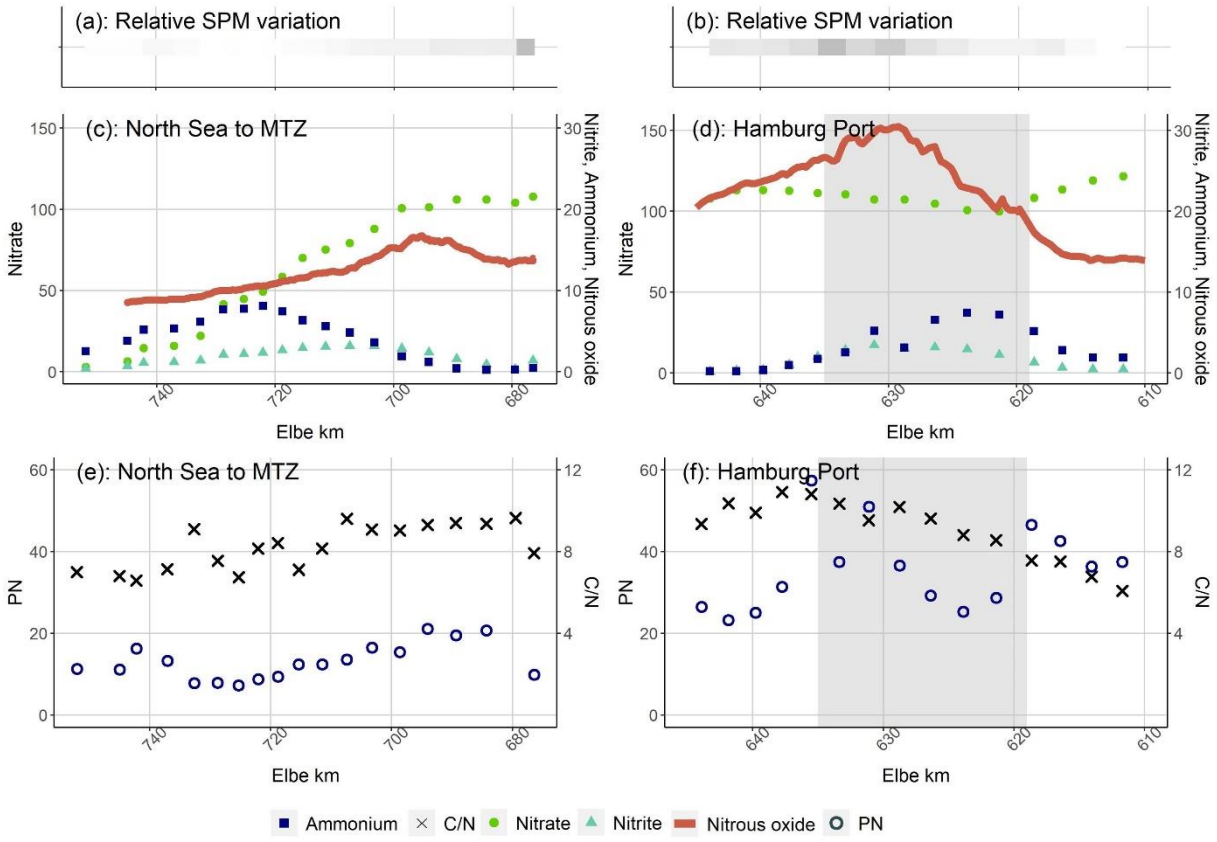


Figure ~~64~~: ~~(a)~~ Succession of N-bearing substances coming from the North Sea and in the Port of Hamburg in September 2020: Relative change of SPM concentrations (a) from the North Sea and (b) in the Port of Hamburg. Nitrate in µmol L^{-1}, nitrite in µmol L^{-1}, ammonium in µmol L^{-1} and nitrous oxide concentrations in nmol L^{-1} plotted against Elbe stream kilometers (c) from the North Sea and (d) in the Port of Hamburg. Particulate nitrogen concentrations in µmol L^{-1} and C/N values plotted against stream kilometers (e) from the North Sea and (f) in the Port of Hamburg. ~~.~~ The grey area in (f) and (f) shows the position of the ~~MTZ~~Port of Hamburg. ~~(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 µmol L^{-1} are presented as green circles and particulate nitrogen (PN) concentrations as unfilled circles in µmol L^{-1}. The right y-axis shows nitrite concentrations in µmol L^{-1} as light blue triangles, ammonium concentration in µmol L^{-1} as dark blue squares, nitrous oxide concentration in nmol L^{-1} as a red line and C/N ratios as grey crosses.**~~

~~However, t~~This suggests 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 a concentrations in the polyhaline part of the Elbe ~~e~~Estuary by input of freshly produced ~~marine~~ particulate matter of marine origin. Generally, ~~the occurrence of an MTZ is unique to each estuary and is~~maximum turbidity zones are generated by the balance between river-induced flushing and upstream transport of marine SPM, as a ~~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_2O 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_2O saturation (R = -0.81, Table 5), and found that the N_2O peak was located downstream of the MTZ, and upstream of increasing nitrite and ammonium concentrations (Fig. ~~6~~4a). This ~~(1)~~ suggests that (1) the mere concentration of SPM is not the driving factor of nitrification as a source of N_2O, but that organic matter quality is key to biological

turnover (Dähnke et al. 2022), and (2) ~~speaks in favor the of~~ material transport from the North Sea upstream towards the MTZ (Kappenberg and Fanger, 2007; Schoer, 1990) is a main mechanism for N_2O generation ~~(?) (Kappenberg and Fanger, 2007; Schoer, 1990)~~. 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 N_2O peaks (Fig. 4a~~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 N_2O peak in the salinity gradient of the Elbe ~~estuary~~Estuary. This production was mainly fueled by fresh organic matter entering the estuary from the North Sea.

4.3 Hamburg Port: N_2O 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, Norbisrath 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 N_2O peaks of our study were located in the Port of Hamburg. Brase et al. (2017) identified the port region as a hotspot of N_2O production and hypothesized that simultaneous nitrification and denitrification were responsible. We use our expanded dataset to further evaluate this hypothesis.~~During all cruises, we measured highest N_2O saturation in the Port of Hamburg. These peaks can be caused by input from a waste water treatment plant, by deepening and dredging operations, enhanced benthic production or by in-situ production in the water column.

Point sources generally play a minor role in the Elbe Estuary (Hofmann et al., 2005; IKSE, 2018). We estimated the wastewater discharge fraction of stream flow according to Büttner et al. (2020) for the waste water treatment plant (WWTP) Köhlbrandhöft, which treats the waste water from the Hamburg metropolitan region, with less than 5 % even under low fresh water inflow. Thus, point sources seemed not to be the cause for the elevated N_2O concentrations.

Dredging can be a potential source of N_2O in the water column. The estuary is continuously deepened and dredged to grant access for large container ships, which stirs up bottom sediments. Ammonium concentrations in the sediment pore water are high (Zander et al., 2020, 2022) and N_2O can be produced by nitrifier-denitrification in the sediments (Deek et al., 2013). However, we found no correlation of high SPM concentrations and N_2O saturation, indicating no major influence on N_2O dynamics from channel dredging and deepening.

Several studies identified the Hamburg Port region as a hotspot of biogeochemical turnover: Deek et al. (2013) showed ~~ongoing~~ denitrification,~~;~~ where Sanders et al. (2018) measured intense nitrification.~~anthe s, as,. ;~~ Norbisrath et al. (2022) determined intense total alkalinity generation, and Dähnke et al. (2022) found that nitrogen turnover ~~were~~was driven by high particulate organic matter in this region. ~~The highest N_2O peaks of our study were located in the Port of Hamburg.~~ Brase et al. (2017) identified the~~the~~ Hamburg~~Hamburg~~ port region as a hotspot of N_2O production and hypothesized that simultaneous nitrification and sediment denitrification were

responsible. We use our expanded dataset to further evaluate this hypothesis and to identify drivers for N_2O production in the port region.

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~~4b). Several researchers did address the nitrogen turnover and this~~,~~ accumulation of nitrite and ammonium assuming that the sudden increase of water depth in the Port leads to a light limitation and decomposition of riverine organic material (Schroeder, 1997; Schöl et al., 2014). This in turn raises ammonium and nitrite concentrations and fosters nitrification in the port region (Sanders et al., 2018; Dähnke et al., 2022).

~~-~~High nitrite concentrations are favorable for~~of~~ N_2O production by nitrification and ~~of~~ nitrifier-denitrification (Quick et al., 2019), ~~and~~ while low-oxygen conditions facilitate ~~made~~ both nitrification and denitrification ~~plausible in this region~~. We found that N_2O saturation~~s~~ increased with decreasing discharge (R = -0.48, Table 5) during spring and summer. This further points towards in-situ N_2O production, because denitrification and nitrification are more intense during longer ~~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 showed the succession of ammonium, nitrite and N_2O production (Fig. 4b and supplementary material S3-S13) confirming simultaneous sedimentary denitrification and nitrification in the water column responsible pathways for N_2O production in the Port of Hamburg (Brase et al. 2017).~~Overall, our data show that the correlations of ammonium, nitrite and N_2O are significant and confirm that simultaneous denitrification and nitrification likely are responsible for N_2O production.~~

~~A correlation analysis for the Hamburg Port region (stream kilometer 610 – 645) revealed a strong negative correlation of N_2O 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~~between N_2O_{xs} and AOU in the Hamburg Port (Fig. 3). This may result from combined N_2O production by nitrification and denitrification. However, oxygen saturation and N_2O saturation were inversely correlated in ~~the~~ Hamburg Port (~~R = -0.58~~Table 4 and 5), suggesting that N_2O production was controlled by oxygen concentrations, and thus was related to~~by~~ oxygen consumption in the port region. Most (75 %) of this oxygen consumption is caused by respiration whereas the remaining 25 % stem from nitrification (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~~linking estuarine N_2O production to river eutrophication. ~~(~~Fabisik et al.~~,~~ (2023) showed that algae could additionally contribute to N_2O production. In the Elbe, f~~F~~resh organic matter from the ~~Elbe r~~River with low C/N values as well as high PN and PC contents 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~~. This organic material was ~~where it~~ rapidly ~~got~~ degraded in the Hamburg Port region (Fig. S1). Dähnke et al. (2022) found that labile organic matter ~~strongly~~ fueled nitrification but also denitrification in the fresh water part of the Elbe E~~e~~stuary, which, as shown in our study, results in high N_2O production in the Hamburg Port, ~~region~~ leading to the reported negative correlations of PC and PN content with N_2O saturation. ~~(Zander et al., 2022)~~

Overall ~~in spring and summer~~, oxygen conditions mainly controlled N_2O production in the Hamburg Port region in spring and summer. Since respiration of organic matter dominates oxygen drawdown in the port region, we

deduced that N_2O production there was is linked to the decomposition of phytoplankton produced in the upstream Elbe River regions.

4.4 Hamburg Port: N_2O production in winter

In winter, low water temperature (< 6 °C) should hamper biological production (Koch et al., 1992; Halling-Sorensen and Jorgensen, 1993). Indeed, we did not detect a N_2O peak in the MTZ in winter, but we find high N_2O concentrations in the port region. Intriguingly, we also find high N_2O 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_2O production, we did not detect an N_2O peak during either March cruise. With water temperatures below 6 °C, biological processing likely was inhibited (Koch et al., 1992; Halling Sorensen and Jorgensen, 1993). For March 2022, we found a linear increase of N_2O_{xs} and AOU along with oxygen consumption and increasing ammonium, nitrite and PN concentrations indicating nitrification in the Hamburg Port port region producing N_2O. Unlike in summer, N_2O 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_2O, with a peak concentration that by far exceeded internal biological sources in summer (Fig. 2h). Also, anAn ammonium peak in the water column coincided with the N_2O maximum (Fig. 2f and supplementary material Fig. S10S11). If microbial activity is mostly temperature--inhibited, a point local source of N_2O in the port seems the most likely cause.. (Zander et al., 2020, 2022)(Deek et al., 2013)Ammonium and N_2O concentrations are high in the pore water of underlying sediments, so one potential source of elevated N_2O may be the deepening and dredging works in the Hamburg Port region, stirring up sediment. Indeed,

We considered intensified deepening operations in the Port of Hamburg one potential source of elevated N_2O saturation. Ddeepening and dredging work occurred in the Hamburg Port region in 2021 (HPA, pers. Comm., Karrasch 2022). butHowever, this also applied to 2022, when we saw no sharp N_2O peak (Fig. 2h). Furthermore, the regions of deepening and dredging operation did not match the region of high N_2O concentrations, and since turbidity at the time of sampling did not change significantly compared to other cruises. Jointly, this also speaks against a major signal from suggests that channel dredging and deepening was not the primary cause for the 2021 winter N_2O peak. Thus, we conclude that sediment input most likely was not the source of N_2O in the water column in winter 2021.

Another possible source of N_2O 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 that joins the sampled stretch main estuary at stream kilometer 626 (Fig. 1), matching the N_2O peak at stream kilometer 627 (Fig. 2h and 3b). As explained above (section 4.3), the effect of this WWTP on N_2O saturations under normal conditions should be negligible. This peak can be the result of an extraordinary event during our sampling. We indeed found out that aggravated operation conditions in the WWTP at the time of sampling were caused bythat an extreme rain event occurred on March 11th 2021 (HAMBURG WASSER, pers. Comm., Laurich 2022) with a statistical recurrence probability of one to five years (https://sri.hamburgwasser.de/, last access: 04.04.2023). This rare event caused aggravated operation conditions in the WWTP at the time of sampling. While the operators could still meet the limits for the effluent levels of nitrate and ammonium, higher than usual ammonium loads exited left the treatment plant during the March 2021 campaignat this time. We assume that theseis elevated ammonium WWTP loads from the WWTP, were rapidly converted to N_2O as the warmer and biologically active waste water entered the Elbe

Estuary ~~most likely was the cause of the unexpected high N_2O peak~~ in March 2021. ~~-~~An important factor for aggravated conditions was a temperature drop in the WWTP caused by cold rain water, we hypothesize that a similar rain event in warmer months would not lead to comparable N_2O peaks. ~~,~~

Therefore, we argue that our March 2021 cruise likely represents an exception due to an extreme weather situation, ~~and that typical~~whereas normal winter conditions in the ~~Elbe~~ estuary comply with the N_2O production, ~~as~~ like in March 2022.

4.5 Seasonally ~~varying~~changes of ~~N_2O emissions~~ N_2O:DIN dynamic

We calculated annual N_2O emissions of the Elbe Estuary ranging from 0.08 ± 0.03 Gg-N_2O yr^{-1} to 0.25 ± 0.16 Gg-N_2O yr^{-1}, which varied from recent N_2O summer emission estimate of 0.18 ± 0.01 Gg-N_2O yr^{-1} by Brase et al. (2017). Estuarine N_2O emissions are affected by tides, diel variations and currents (Barnes et al., 2006; Baulch et al., 2012; Gonçalves et al., 2015), all of which we did not address in our study. Range of possible parametrizations of gas transfer coefficients further complicates a direct comparison of fluxes between studies (Hall Jr. and Ulseth, 2020; Rosentreter et al., 2021), which were reflected in the big differences of our emission estimates (Table 2). Therefore, a direct comparison to other studies is difficult.

In a more general approach, the relationship between N_2O and DIN (N_2O:DIN) is used for global estimates of N_2O emissions (Kroeze et al., 2005, 2010; Ivens et al., 2011; Hu et al., 2016). Using publicly available data (Table S4 and S5), we calculated the amount of the annual nitrogen load released as N_2O. Depending on the parametrization used for the gas transfer coefficients, 0.14 % to 0.67 % of the annual DIN loads of the Elbe Estuary were released as N_2O (0.11 % to 0.57 % for TN loads). This is significantly less than the 1 % predicted by Kroeze et al. (2005), but matches results from other estuaries with high agricultural input, e.g. Wells et al. (2018) with 0.3 % to 0.7 % (0.1 % for TN loads) and Robinson et al. (1998) with 0.5 % (0.3 % for TN loads) as well as the 0.11 % to 0.37 % estimated by (Maavara et al.~~,~~ (2019), who used TN loads to predict global estuarine emissions.

At our site, highest emissions were estimated in winter (Fig. 5b) along with highest DIN loads (Fig. 5c). In spring, summer and late summer, N_2O emissions reduced along with DIN loads (Fig. 5b, c). However, N_2O release did not scale with the seasonal change of DIN. In winter, 0.10 % to 0.32 % of DIN were released as N_2O, whereas during the other seasons, up to 1.26 % were emitted. Thus, our results corroborate that there is a deviating relationship between DIN and N_2O (Borges et al., 2015; Marzadri et al., 2017; Wells et al., 2018) showing that this relationship even varies seasonally on site due to changing drivers for N_2O production and emissions.

Next to DIN loads, we find that organic matter is an important driver for N_2O production by providing substrate for nitrification. Furthermore, the comparison of our results with previous measurements in the Elbe Estuary revealed that N_2O saturation stopped to scale with DIN input after the 1990s (section 4.1). The significant regime change after the 1990s enabled phytoplankton growth to reestablish in the river (Kerner, 2000; Amann et al., 2012; Hillebrand et al., 2018; Rewrie et al., submitted) and led to high nitrification rates in the estuary (Dähnke et al., 2008; Sanders et al., 2018), supporting the overarching control of organic matter on N_2O production and emissions along the Elbe Estuary.

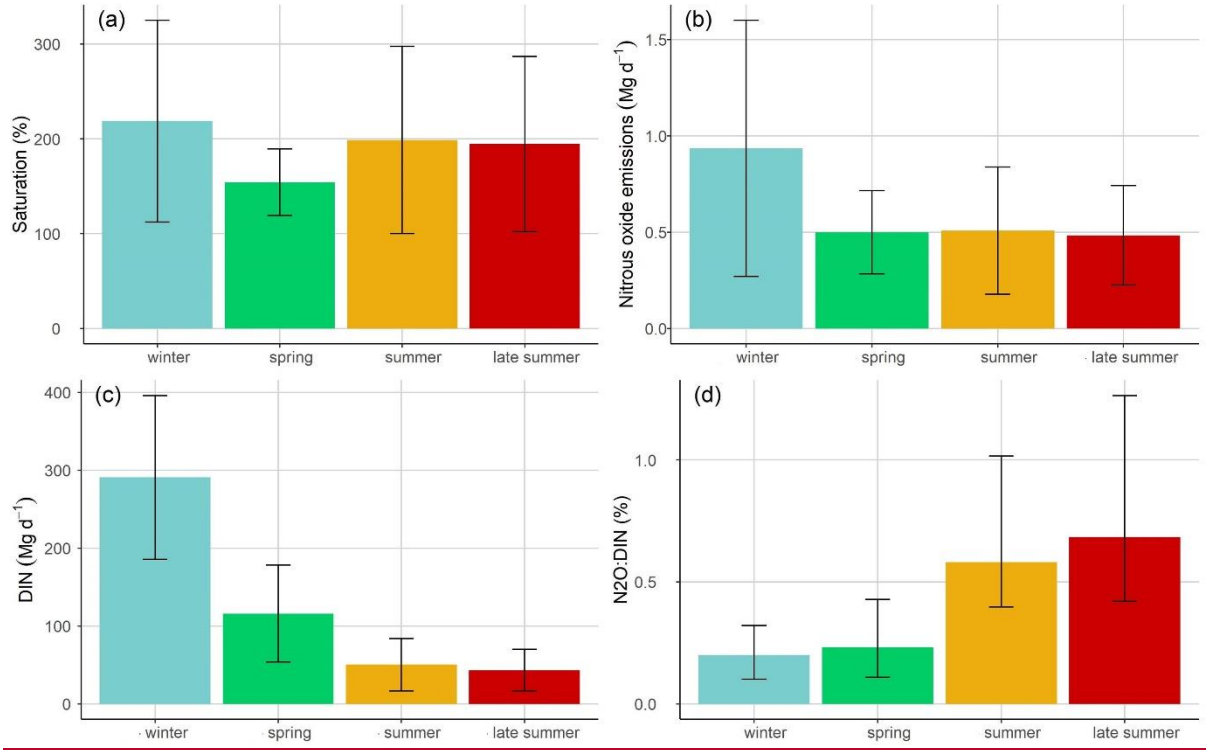
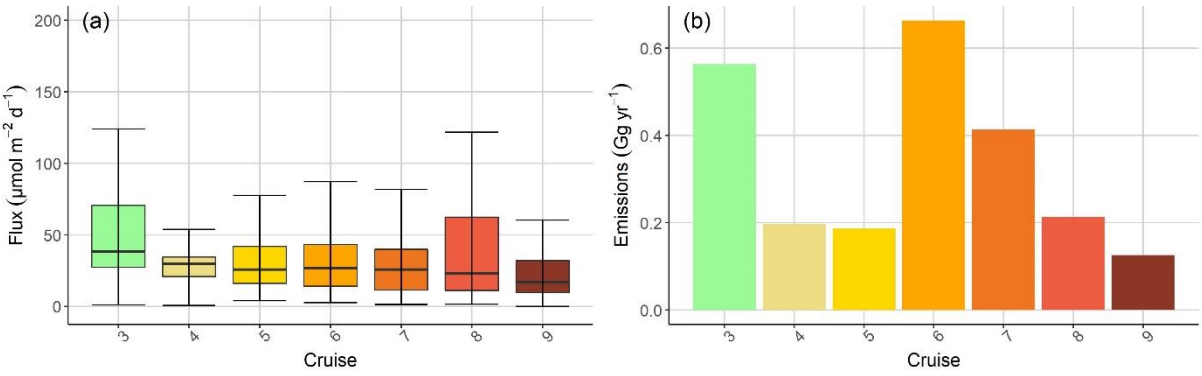


Figure 5: (a) Average nitrous oxide saturation for each season, (b) average nitrous oxide emissions for each season calculated after Borges et al. (2004), (c) average DIN loads for each season and (d) ratio of nitrous oxide emissions and DIN loads (N_2O:DIN) for each season. The error bars represent the standard deviations for (a), (b) and (c). The N_2O:DIN ratios is shown as average values calculated for each parametrization and wind speeds with error bars representing their variability.

~~(Kerner, 2000; Amann et al., 2012; Hillebrand et al., 2018; Rewrie et al., submitted)~~

~~For an accurate assessment of annual estuarine N_2O emissions, we first evaluate their seasonal distribution. In March, average N_2O emissions were 0.28 ± 0.17 Gg yr^{-1}. Note that we deliberately excluded the N_2O 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_2O emissions in March 2021 (Tab. 3). March 2022 (0.16 ± 0.08 Gg yr^{-1}) only slightly deviated from average N_2O emissions in spring and summer (0.20 ± 0.05 Gg yr^{-1}). Overall, we calculated average annual emissions using the seasonal averages (Tab. 3) resulting in 0.24 ± 0.06 Gg yr^{-1}, thus exceeding the recent summer N_2O emission estimates of 0.18 ± 0.01 Gg yr^{-1} by Brase et al. (2017).~~

~~Enhanced microbial N_2O production can lead to high N_2O 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_2O emissions originated from 1) high wind speeds with increased sea-air exchange, 2) nitrification in the Hamburg Port and 3) elevated riverine N_2O 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_2O concentrations remained high until mixing with water from the North Sea, which resulted in a decrease and in outgassing to the atmosphere.~~



~~**Figure 7: (a) Monthly variation of N_2O flux density in μmol m^{-2} d^{-1}, (b) monthly variation of N_2O emissions in Gg yr^{-1}.**~~

~~The high riverine N_2O input into the estuary is intriguing and may be caused by high nitrate discharge from soils and groundwater fueling N_2O production, which was found in other streams and rivers (Beaulieu et al., 2009; Clough et al., 2011). Agricultural fertilizer application might also affect winter N_2O concentrations (Murray et al., 2015), since it can lead to high DIN and N_2O concentrations in estuaries. In the 1990s, Hanke and Knauth (1990) also measured high riverine N_2O concentrations in the Elbe estuary in winter, albeit at higher DIN concentrations. Other temperate estuaries showed high N_2O emissions with the dominant control on N_2O concentrations being freshwater delivery, rather than in-situ production (Barnes and Owens, 1999; Robinson et al., 1998; Murray et al., 2020). In combination with a higher probability of strong winds in winter, it is clear that winter N_2O emissions in the Elbe estuary should not be neglected, as they can potentially even exceed summer emissions.~~

~~Overall in winter, large nitrogen loads from the Elbe catchment caused high riverine N_2O concentrations, which led to high N_2O emissions in the adjacent estuary (Fig. 7). In summer, reduced riverine N_2O input was compensated by in-situ N_2O production processes. We find that both effects are currently balanced, leading to year-round high N_2O emissions in this estuary.~~

~~**Table 3: Average N_2O 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 km^2 was taken into account (Brase et al., 2017).**~~

~~TSeason~~	~~Average N_2O flux densities~~	~~N_2O emissions~~
~~Spring and summer~~	~~33.5 ± 7.8 μmol m^{-2} d^{-1}~~	~~0.20 ± 0.05 Gg yr^{-1}~~
~~March~~	~~47.3 ± 28.1 μmol m^{-2} d^{-1}~~	~~0.28 ± 0.17 Gg yr^{-1}~~
~~Annual average~~	~~40.3 ± 14.3 μmol m^{-2} d^{-1}~~	~~0.24 ± 0.06 Gg yr^{-1}~~

5 Conclusions

Overall, the Elbe is a year-round source of N_2O to the atmosphere, with highest emission occurring in winter, along with high DIN loads and high wind speeds. However, summer N_2O saturation and emissions did not decrease with lower riverine nitrogen input suggesting variable relations of DIN and N_2O (Borges et al., 2004; Marzadri et al., 2017; Wells et al., 2018), and seasonal variability of this ratio caused by changing drivers for N_2O production and emissions. Two hot-spots of N_2O production were found in the Elbe eEstuary: the Port of Hamburg and the mesohaline estuary near the estuarine turbidity maximum. Biological N_2O production was enhanced by warmer temperatures and fueled by riverine organic matter in the Hamburg Port or marine organic matter in the MTZ. ~~more~~A comparison with historical N_2O measurements in the Elbe Estuary revealed that N_2O saturation ~~scaled~~did

not decrease with DIN input after the 1990s. The improvement of water quality in the Elbe Estuary allowed phytoplankton growth after the reunification of Germany in 1990s (Kerner, 2000; Amann et al., 2012; Hillebrand et al., 2018; Rewrie et al., submitted) and led to a switch from dominant denitrification to high nitrification (Dähnke et al., 2008; Sanders et al., 2018), supporting the overarching control of organic matter on N_2O production along the Elbe Estuary~~(Dähnke et al., 2008; Sanders et al., 2018)~~. Thus, our findings indicate that DIN availability is not the sole control of N_2O production ~~in N2O emissions~~ in estuaries with high agricultural input. High organic matter availability due to phytoplankton blooms driven by river eutrophication fuels nitrification and subsequent ~~and this are also essential,~~ N_2O emissions, causing a decoupling of the N_2O:DIN ratio. Therefore, N_2O emissions in heavily managed estuaries with high agricultural loads are clearly linked to eutrophication.~~was~~

Consequently, reducing nitrogen input alone is not sufficient to minimize N_2O emissions from estuaries. Further measures are needed to prevent the developments of intense phytoplankton blooms in rivers and estuaries. Especially considering climate change projections of more frequent and extensive draughts and warmer temperatures (IPCC, 2022), which potentially fuel phytoplankton growth (e.g. Scharfe et al., 2009; Kamjunke et al., 2021; IPCC, 2022). ~~Overall, we found enhanced N_2O concentrations along the entire Elbe estuary, which point towards in-situ N_2O production that compensated the effect of decreasing DIN loads since the 1990s. Two hot-spots of N_2O production were found in the estuary: the Port of Hamburg and the mesohaline estuary near the estuarine turbidity maximum. Biological N_2O 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 N_2O emissions, despite seasonal variations in in-situ N_2O production: In winter, high riverine N_2O input led to high N_2O saturation and emissions in the estuary, whereas in summer, high N_2O emissions were controlled by in-situ production. Overall, the Elbe estuary is a year-round perennial source of N_2O, with estimated annual emissions of 0.24 ± 0.06 Gg yr^{-1}. In conjunction with the overarching control of N_2O production by organic matter quality, this highlights that a holistic approach of water quality improvement and nutrient mitigation is needed to further reduce N_2O 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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