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High Resolution Measurements of Nitrous Oxide (N_2O) in the Elbe Estuary

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Nitrous oxide (N_2O) is one of the most important greenhouse gases and a major sink for stratospheric ozone. Estuaries are sites of intense biological production and N_2O emissions. We aimed to identify hot spots of N_2O production and potential pathways contributing to N_2O concentrations in the surface water of the tidal Elbe estuary. During two research cruises in April and June 2015, surface water N_2O concentrations were measured along the salinity gradient of the Elbe estuary by using a laser-based on-line analyzer coupled to an equilibrator. Based on these high-resolution N_2O profiles, N_2O saturations, and fluxes across the surface water/atmosphere interface were calculated. Additional measurements of DIN concentrations, oxygen concentration, and salinity were performed. Highest N_2O concentrations were determined in the Hamburg port region reaching maximum values of 32.3 nM in April 2015 and 52.2 nM in June 2015. These results identify the Hamburg port region as a significant hot spot of N_2O production, where linear correlations of AOU-N_2O_{xs} indicate nitrification as an important contributor to N_2O production in the freshwater part. However, in the region with lowest oxygen saturation, sediment denitrification obviously affected water column N_2O saturation. The average N_2O saturation over the entire estuary was 201% (*SD*: ±94%), with an average estuarine N_2O flux density of 48 μmol m^{-2} d^{-1} and an overall emission of 0.18 Gg N_2O y^{-1}. In comparison to previous studies, our data indicate that N_2O production pathways over the whole estuarine freshwater part have changed from predominant denitrification in the 1980s toward significant production from nitrification in the present estuary. Despite a significant reduction in N_2O saturation compared to the 1980s, N_2O concentrations nowadays remain on a high level, comparable to the mid-90s, although a steady decrease of DIN inputs occurred over the last decades. Hence, the Elbe estuary still remains an important source of N_2O to the atmosphere.

Keywords: nitrous oxide, N_2O, estuary, Elbe River, trace gases, emissions, laser spectroscopy

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INTRODUCTION

Nitrous oxide (N_2O) is one of the most important atmospheric greenhouse gases (IPCC, 2013) and a major precursor for stratospheric ozone depletion (Crutzen, 1970; WMO, 2014). At present, the global average atmospheric dry mole fraction of N_2O is ∼324 ppb, with an annual growth rate of ∼0.25% (IPCC, 2013). N_2O is predominantly released via microbial processes, such as nitrification (oxidation of ammonium to nitrate) and denitrification (reduction of nitrate to dinitrogen, N_2).

Both processes occur in soils, sediments, or water bodies, and release in total ∼10–12 Tg N_2O-N per year (Davidson and Kanter, 2014). During the first step of nitrification (i.e., the oxidation of ammonium to nitrite via hydroxylamine), N_2O can be produced as a side product of hydroxylamine oxidation (Ritchie and Nicholas, 1972; Poughon et al., 2001). During denitrification, N_2O is an obligate intermediate that can be further reduced to N_2 (Knowles, 1982).

However, the yield of N_2O production during nitrification and denitrification strongly depends on the prevailing oxygen (O_2) concentrations, which is especially relevant in aquatic systems: Hypoxic to anoxic conditions lead to high N_2O production by both nitrification and denitrification, whereas N_2O is consumed by denitrification under anoxic conditions (Bakker et al., 2014). Coastal regions receive inputs of nitrogen (N) that fuel both nitrification and denitrification. Moreover, eutrophication via N inputs also promotes hypoxia or anoxia (Howarth et al., 2011) which, in turn, may lead to additional N_2O production (see e.g., Naqvi et al., 2010). In line with this, estuaries are known to release high amounts of N_2O from nitrification and/or denitrification (e.g., Bange, 2006; Barnes and Upstill-Goddard, 2011; Murray et al., 2015).

The Elbe estuary has undergone a long history of eutrophication and remediation and was highly polluted until the 1990s. Since then, ecological conditions in the Elbe estuary have improved significantly due to a better management of municipal and industrial sewage and an overall reduction of pollution (Adams et al., 2001; Langhammer, 2010). As a consequence, the O_2 regime improved and O_2 concentrations rarely decrease below 2 mg L^{-1} (62.5 μM), which comes along with a decrease of ammonium and nitrate concentrations in the Elbe (Amann et al., 2012).

In an early study from the late 1980s, Hanke and Knauth (1990) found N_2O saturations of up to 1,600% in the Elbe estuary which they attributed mostly to denitrification in the port region and its sediments. In a follow-up study by the BIOGEST project in the 1990s, N_2O saturations of <400% were reported (data from J. Middelburg published in Barnes and Upstill-Goddard, 2011).

Here we present the results of high-resolution measurements of dissolved N_2O along the Elbe estuary in April and June 2015. This study was performed in order (i) to decipher the N_2O distribution and its saturations along the transect and (ii) to identify hot spots of N_2O production and potential N_2O production pathways in the Elbe estuary. Moreover, we compare our results with those of previous studies (iii) to elucidate how management measures that changed the ecological conditions of the Elbe estuary over the past 20 years have affected N_2O pathways and emissions.

METHODS

Study Site

The Elbe River runs from the Czech Republic through Germany and discharges into the German Bight/North Sea. Its catchment area of about 148.300 km^2 is inhabited by nearly 25 million people (Simon, 2005). The Elbe estuary extends over ∼140 km, from a weir at stream km 586 that separates the tidal estuary from the river, through the Port of Hamburg to the port of Cuxhaven (stream km 730), where the estuary opens into the German Bight. The salinity gradient starts around stream km 670. The estuary is well mixed (Middelburg and Herman, 2007) and with an annual load of 2.9 kt P and 88 kt N (mostly as nitrate), it is the largest nutrient source to the German Bight (RBC Elbe, 2010). From the Port of Hamburg (∼ stream km 620) to the German Bight, the estuary has an average water depth of >10 m and ∼15 m in the navigational route and it is heavily dredged on a regular basis to ensure access for large container ships to the port (Schöl et al., 2014).

Transect Sampling

Samples were taken during two research cruises with the research vessel *Ludwig Prandtl* during 28/29 April 2015 and 9–11 June 2015. All sampling and on-line measurements were done during ebb tide to ensure comparable current and mixing conditions. Transects and locations of sampling stations were similar in April and June (**Figure 1**), but sampling started further downstream (stream km 626) in April compared to June (stream km 609). Distinct samples for nutrient analyses were taken at 16 stations in April 2015 and at 20 stations in June 2015.

The ship's membrane pump continuously pumped water from 2 m water depth and supplied a Ferry-Box system (Petersen et al., 2003) and the equilibrator of the N_2O measurement system with a continuous flow rate of 1 L min^{-1}. Additionally, discrete samples for nutrient analysis were taken from a separate outlet of the ship's pump. O_2 concentration (μM), O_2 saturation (%), salinity, and temperature (°C) data were recorded with the Ferry-Box system.

Nutrient Measurements

Water samples for nutrient analyses were filtered immediately (GFF, 0.45 μm), and stored frozen (−18°C) for later analyses in the shore-based laboratory. Dissolved nitrate, nitrite and ammonium concentrations were measured with a continuous flow auto analyzer (AA3, SEAL Analytical) using standard colorimetric techniques (Hansen and Koroleff, 2007).

Equilibrator Based N_2O Measurements and Calculations

An N_2O analyzer (Model 914-0022, Los Gatos Res. Inc., San Jose, CA, USA) was used to measure gas phase mole fractions of N_2O, as well as water vapor (H_2O), using off-axis integrated cavity output spectroscopy (OA-ICOS; Baer et al., 2002).

The N_2O analyzer was connected to a seawater/gas equilibrator which is described in detail by Körtzinger et al. (1996).

Comparable setups show a very good agreement with discrete measurements of dissolved CH_4 and N_2O using traditional gas chromatographic system (Gülzow et al., 2011; Arévalo-Martínez et al., 2013) and have been successfully deployed during various campaigns to the Atlantic and Pacific Oceans and the Baltic Sea (Gülzow et al., 2013; Grefe and Kaiser, 2014; Arévalo-Martínez et al., 2015, 2017).

The general principle of dynamic equilibration systems is based on a continuous flow of water passing through an

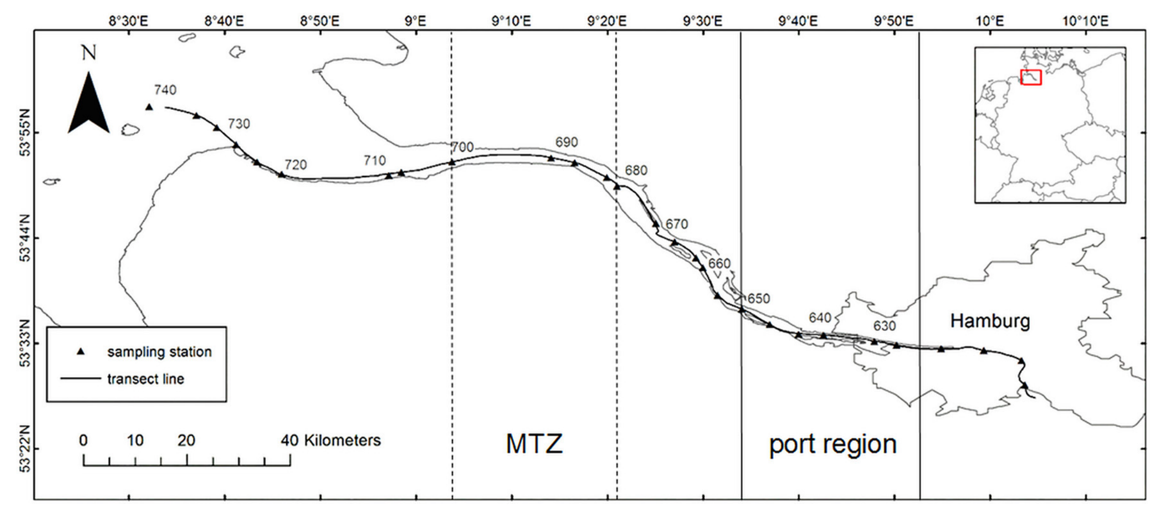

FIGURE 1 | The Elbe estuary with river stream km, transect line (black line) and stations for distinct sampling (triangles); MTZ, maximum turbidity zone.

equilibration chamber which is open to the atmosphere. This allows equilibration at ambient pressure at any time of the measurements. The continuous re-circulation of a fixed volume of headspace air ensures a permanent equilibrium with the constantly renewed water phase. For a quick equilibration, water is dripped down along the glass tube of the headspace in combination with a "shower head and laminary flow" to enlarge the surface sample gas to water ratio (Körtzinger et al., 1996). The gas stream from the headspace was dried in a Nafion® tube embedded in silica gel beads before it reached the inlet of the analyzer (**Figure 2**). The equilibration time of N_2O for the equilibrator applied in our study was determined to 7 min (according to Gülzow et al., 2011) and was taken into account for data processing.

The N_2O analyzer covers a N_2O mole fraction range from 300 to 100 ppm. Its internal precision is ±0.2 ppb for N_2O (1σ, 100 s integration time, $N_2O > 300$ ppb). Furthermore, the instrument's software uses the parallel measured water vapor to calculate N_2O dry mole fractions. Laboratory dilution experiments covering a N_2O mole fraction range from 300 to 5 ppm showed an analytical precision of gas phase measurement of N_2O from ±0.2 ppb (at 300 ppb N_2O) to ±3 ppb (at 5 ppm N_2O) which corresponds to an overall precision of ±0.06–0.07%.

For validation of the N_2O measurements, standard gas mixtures of N_2O in synthetic air (Standard 1: 312.9 ppb N_2O and Standard 9: 573.8 ppb N_2O, prepared by Deuste Steininger GmbH, Mühlhausen, Germany) were measured regularly during the campaigns. In addition, a bottle of pressurized air (337 ppb N_2O) in the lab was used for on-site calibration of the system. Standard measurements had a precision of 0.5 ppb and an accuracy of 0.9 ppb. During our transect measurements, no drift was detected, and thus, no drift correction was performed.

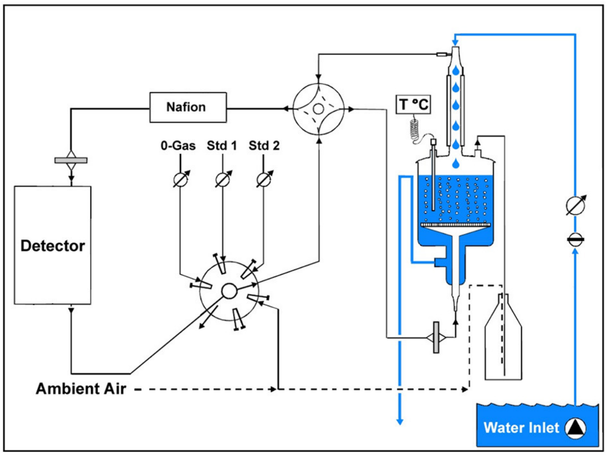

FIGURE 2 | Scheme of the N_2O measurement system.

For further data analyses, we calculated 1 min averages of N_2O dry mole fractions (ppb). The dry mole fractions were measured from the recirculating the headspace air of the equilibrator, and N_2O water concentrations (N_2O_{cw}; *SD*: ± 0.15 nM) were calculated from these, using the Bunsen solubility function of Weiss and Price (1980) and taking into account temperature differences between sample inlet and equilibrator (Rhee et al., 2009). N_2O saturations (s) were calculated as shown in Equation (1), based on N_2O_{cw} and atmospheric N_2O (N_2O_{air}).

$$s = 100 \times \left(\frac{N_2O_{cw}}{N_2O_{air}} \right) \qquad (1)$$

Atmospheric N_2O was determined in regular measurements along the two transects. The average atmospheric N_2O dry mole fractions were 331 ppb (*SD*: ±0.5 ppb) in April 2015 and 325 ppb (*SD*: ±0.8 ppb) in June 2015. The comparably high mean N_2O mole fraction in April was most probably resulting from agricultural activities such as manure-and N-fertilization (Lampe et al., 2003; Hellebrand et al., 2008). Computations of 48 h air mass backward trajectories (data not shown) imply that the measured air masses originated from the agricultural regions of western Germany, the Netherlands and Belgium.

The gas transfer coefficient (k) (Equation 2), expressed in m d^{-1}, was calculated based on Borges et al. (2004) using the average wind speed at 10 m height above water surface ($u_{10} = 7.41 \pm 2.26\,m\,s^{-1}$ in April, $u_{10} = 5.05 \pm 1.31\,m\,s^{-1}$ in June) and the Schmidt number (Sc), which is the ratio of the kinematic viscosity of water (Siedler and Peters, 1986) to the diffusivity of N_2O in water (Rhee, 2000). Air-sea flux densities (f in μmol m^{-2} d^{-1}; Equation 3) were calculated according to Equation (3):

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

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

RESULTS

Transect Measurements

Based on the N_2O concentration peaks, as well as on the lowest O_2 concentrations found between km 620 and 650, we in the following refer to this region of the Elbe estuary as the Hamburg port region. Its upper boundary coincides with the intensely dredged deep water section (>10 m, navigational route: ∼15 m) of the Port of Hamburg (Schöl et al., 2014).

N_2O and O_2 Concentrations

In general, N_2O and O_2 concentrations were inversely correlated (**Figure 3A**). N_2O was low in the upstream part of the transect (only sampled in June 2015), rose further downstream and peaked in the Hamburg port region, with maximum values of 32.3 and 52.2 nM in April and June, respectively. N_2O concentrations then decreased and remained relatively constant between stream km 650 and 700 with average values of 18.6 ± 0.5 nM in April and 18.2 ± 1.9 nM in June. In the Elbe mouth, the N_2O concentrations decreased with increasing salinity to a final concentration of ∼10 nM N_2O in April and June, which is near the equilibrium concentration calculated for dissolved N_2O in water based on the measured N_2O atmospheric mole fractions.

Upstream of the port region, the O_2 concentration was high (up to 424 μM) and supersaturated (>140%). The concentrations then decreased to 324 μM and approached saturation when entering the port region. In April 2015, sampling started slightly further downstream, and the O_2 saturation at the beginning of the transect was only 72% (230 μM). In the port region, the O_2 concentrations decreased to minimum values of 185 μM (April) and 153 μM (June), corresponding to saturations of 58 and 53%, respectively. Downstream of the port region, the O_2 concentrations rose again, reaching ∼330–350 μM in both months in the Elbe mouth, which was equivalent to 100% saturation in April and a slight oversaturation of 105% in June.

DIN Distribution

Dissolved inorganic nitrogen (DIN, i.e., NO_3^-, NO_2^-, and NH_4^+) concentrations were generally higher in April than in June (**Figure 3B**). NO_3^- concentrations increased from the beginning of each transect up to the MTZ (Maximum Turbidity Zone, located between stream km 680–700), and then decreased with increasing salinity. Maximum concentrations of NH_4^+ (19 μM) and NO_2^- (4 μM) were measured in April around stream km 640 in the port region. In June, the peaks were located slightly further upstream at stream km ∼630 to ∼635 in the port region, and maximum values were 7 μM for NH_4^+ and 2 μM for NO_2^-. Further downstream, ammonium and nitrite concentration fell below the detection limit (<0.5 μM). In April, a slight increase in ammonium and nitrite concentration (4 and 0.6 μM, respectively) was visible in the mouth of the estuary (stream km 710–740).

N_2O Saturations and Emissions to the Atmosphere

The N_2O saturations were always highest in the Hamburg port region (**Figure 4**) with median N_2O saturations of 237 ± 32% and 386 ± 105% in April and June, respectively. Downstream, the mean saturations dropped to 155 ± 5% in April and 175 ± 11% in June. Toward the end of the transect, at the onset of the salinity gradient, saturations decreased further and approached equilibrium (i.e., 100%) in the German Bight/North Sea region.

Similar to the N_2O saturations, the N_2O sea-to-air flux densities were highest between stream km 620 and 650, i.e., in the section of the estuary where the port of Hamburg is located (100 and 199.8 μmol m^{-2} d^{-1} in April and June, respectively). To get an integrated picture of N_2O emissions along the estuary, we divided the transect into different sections, the Port region (stream km 620–650), the residual freshwater part (stream km 650–680), beginning of salinity gradient up to the North Sea (stream km 680–740). We then calculated mean fluxes for each section, and, based on the respective surface area (J. Kappenberg, pers. comm.), calculated the flux for the entire estuary. This calculation yielded an average sea-to-air flux density of 48 μmol m^{-2} d^{-1} (*SD*: ± 41.4 μmol m^{-2} d^{-1}) over the entire estuary, which is equivalent to an N_2O emission of 0.18 Gg N_2O y^{-1} (*SD*: ± 0.01 Gg N_2O y^{-1}).

DISCUSSION

N_2O Source Regions in the Estuary

N_2O and DIN concentrations were low upstream of the port, where the water column was oversaturated with respect to O_2. In this region of the Elbe, intense phytoplankton growth led to an obvious increase of dissolved oxygen concentration (Amann et al., 2012, 2015; Schöl et al., 2014), and this clearly was also the reason for the observed O_2 oversaturations during our sampling campaign in early summer.

Especially in June 2015, the O_2 concentrations decreased sharply around stream km 620, where a sudden increase in channel depth marks the beginning of the deep Hamburg port region (Schöl et al., 2014). Due to a reduction of light availability in the port, and an increase of suspended particulate matter, primary production is inhibited in this region (Goosen et al., 1995; Wolfstein and Kies, 1999), and the fresh phytoplankton biomass brought in by the Elbe water is an optimal source for remineralization by heterotrophic bacteria (Kerner, 2000). Enhanced remineralization and decreasing

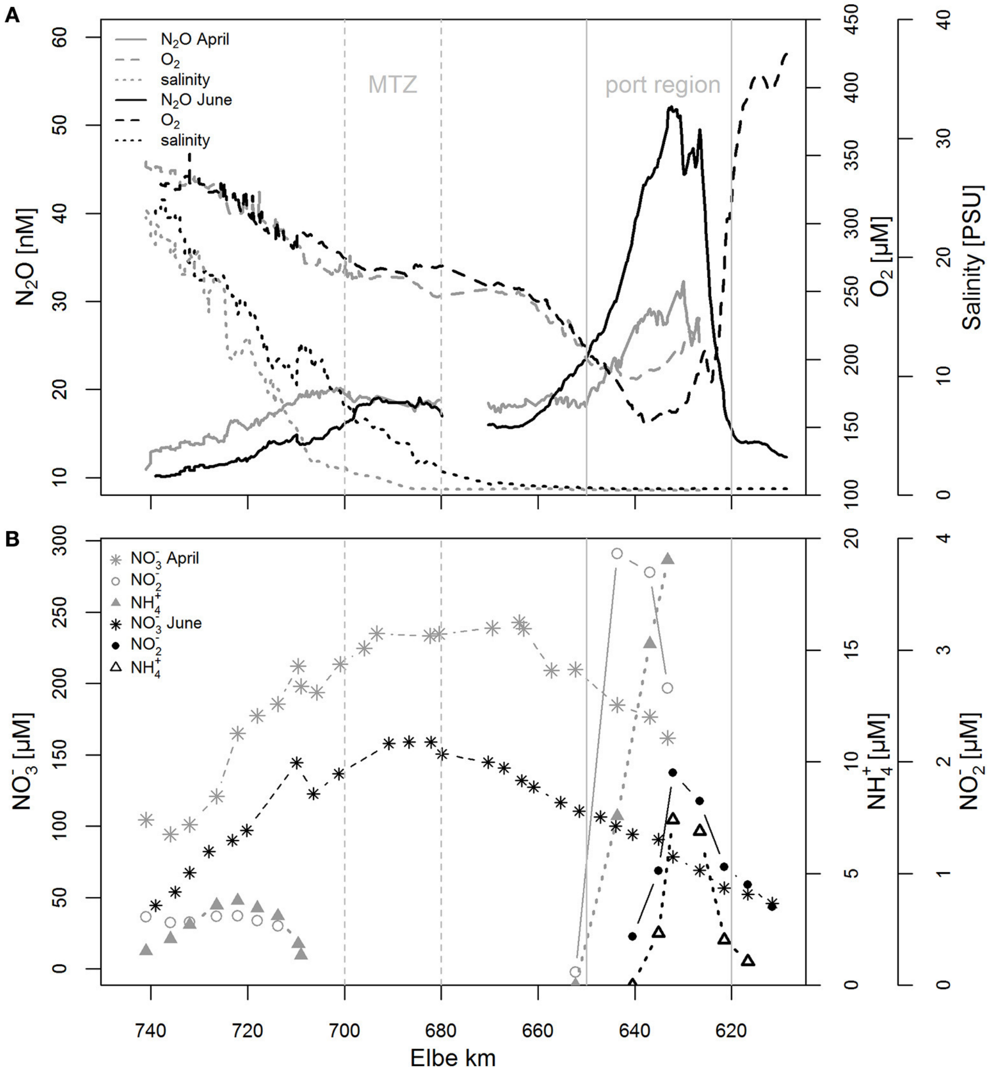

FIGURE 3 | Transect measurements in April 2015 and June 2015 from Elbe stream km 609 to 745. **(A)** Continuous measurements of N_2O, O_2 and salinity, **(B)** Concentrations of DIN: NO_3^-, NH_4^+, and NO_2^-; vertical lines indicate the Hamburg port region according to **Figure 1**, the dashed line localized the area of the MTZ.

phytoplankton activity leads to increased O_2 consumption and a decrease of O_2 production, respectively, leading to the observed minimal O_2 concentrations in the deep Hamburg port region (Schöl et al., 2014).

Furthermore, these high remineralization rates (Kerner and Spitzy, 2001; Schöl et al., 2014) can contribute to elevated ammonium concentrations (**Figure 3B**). This ammonium is the substrate for ammonia oxidation during the first step of nitrification (Kerner and Spitzy, 2001). Based on stable isotope investigations, Dähnke et al. (2008) concluded that nitrification played an important role in the estuary.

Intriguingly, recent rate measurements revealed that both nitrification and denitrification can occur at high rates in the port region: Deek et al. (2013) found highest denitrification rates in the sediments at stream km ~630, and Sanders et al. (2017) found highest nitrification rates in the water column in the same section of the estuary. This implies that both processes can potentially contribute to N_2O production in the region of the Hamburg port where the O_2 minimum is most pronounced.

In addition, N_2O production either due to nitrification and/or denitrification is enhanced under lower oxygen conditions (e.g., Goreau et al., 1980; Codispoti et al., 2001; de Bie et al., 2002), also seen in N_2O concentration differences between June and April. Furthermore, an increase of nitrification and denitrification rates and thus N_2O release, is fueled by warmer temperatures (e.g., Nowicki, 1994; Gödde and Conrad, 1999) which were also measured in June (20 vs. 14°C in April) in the port region.

Beside this obvious hot spot of N_2O production, we also aimed to evaluate N_2O production in the downstream part of the Elbe estuary. The low concentrations of NH_4^+ and NO_2^- measured in April when entering the Elbe mouth may indicate biological N-turnover, but there was no obvious relationship with the N_2O

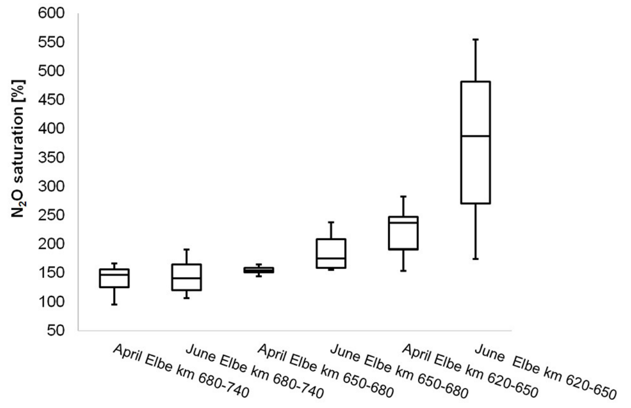

FIGURE 4 | N_2O water saturations (%) of different transect parts with according Elbe stream km, including the Hamburg port area (km 620–650), the Elbe river (km 650–680) and beginning of salinity gradient of the Elbe estuary up to the North Sea (km 680–740).

concentrations which decreased steadily. Upstream of the Elbe mouth, between stream km 680 and 700, the MTZ is located, and in many estuaries, this is regarded as a hot spot of biogeochemical processing (e.g., Barnes and Owens, 1998; Kerner, 2000; Harley et al., 2015) due to intense decomposition of organic matter at rising salinity. This decomposition is often coupled to intense N_2O production (e.g., Barnes and Owens, 1998; de Wilde and de Bie, 2000; Barnes and Upstill-Goddard, 2011). In our study, however, we only see a slight increase of 3–6 nM N_2O at the beginning of the salinity gradient in the MTZ. This indicates that the MTZ at the time of our measurements was not a site of enhanced N_2O production.

Thus, in contrast to other European estuaries, we find that the MTZ is only of minor importance with regards to estuarine N_2O emissions, which leaves the Hamburg port region as the most important hot spot of N_2O production in the Elbe estuary.

Assessment of Nitrification and of Denitrification as N_2O Sources

If we assume that significant N_2O production occurs mainly in the deeper part of the Hamburg port region, this still leaves an open question as to whether this N_2O production is dominated by nitrification (in the water column or in surface sediments) or by sedimentary denitrification.

The relationship of DIN and nitrous oxide can be useful tools to evaluate the origin of N_2O. Denitrification intensity is regulated by the presence of nitrate and nitrite (Dong et al., 2004). Thus, with ample nitrate present, the setting for sedimentary denitrification is ideal, and nitrous oxide may well stem from denitrification. However, the importance of nitrification in the estuary is obvious: in the most upstream part of the transect (June: stream km 611–633), a distinct parallel increase of NO_3^- and N_2O concentration and a positive correlation ($r^2 = 0.90$) suggests that N_2O production and NO_3^- production are linked to each other to some extent. Furthermore, the sharp increase in N_2O concentrations coincided with high NH_4^+ concentrations during both sampling campaigns (April: $r^2 = 0.95$, $p \ll 0.05$, June: $r^2 = 0.67$, $p \ll 0.05$) and provides additional evidence for N_2O produced during nitrification (de Wilde and de Bie, 2000). Downstream the N_2O concentration peak, NO_3^- concentration continues to increase up to the MTZ, likely due to ongoing nitrification, resulting in an overall negative correlation of both parameters. This highlights that the exact setting and nutrient distribution in an individual estuary must be taken into account, and that processes cannot be quantified based on correlations alone (cf. Harley et al., 2015).

Thus, to assess the role of nitrification vs. denitrification, we investigated the correlation of excess N_2O (N_2O_{xs}) and apparent oxygen utilization (AOU). Nitrification consumes oxygen, and a linear correlation of AOU and N_2O_{xs} is usually regarded as an indicator for a dominant role of nitrification in N_2O production (e.g., Cohen and Gordon, 1979; Nevison et al., 2003; Walter et al., 2004). N_2O_{xs} was calculated based on the difference between the N_2O concentration in the water (N_2O_{cw}) and the theoretical equilibrium concentration (N_2O_{air}):

$$N_2O_{xs} = N_2O_{cw} - N_2O_{air} \tag{4}$$

This can be correlated to the apparent oxygen utilization (AOU in μM) defined as Equation (5),

$$AOU = O_2^{'} - O_2 \tag{5}$$

where O_2 is the dissolved O_2 measured in the water phase and O_2' is the theoretical equilibrium concentration of the water body with respect to atmospheric O_2 concentration (Garcia and Gordon, 1992).

In our study, mixing along the salinity gradient obviously exerts a major control on both AOU and N_2O_{xs}, and when mixing is dominant, the correlation of both parameters cannot be used as a proxy for nitrification. Therefore, only parts of the data can be used to investigate the correlation of AOU and N_2O_{xs}. All stations with clearly rising salinities are disregarded due to dominant mixing effects, and so are all upstream stations that showed an oversaturation in O_2. Hence, only the freshwater part of the Elbe was plotted [stream km 620, where mean water depth decreases due to dredging (Schöl et al., 2014), up to stream km 670], **Figure 5**.

AOU-N_2O_{xs} cross plots showed a significant linear relationship in most parts of the transect (**Figure 5**), which only breaks down at lowest O_2 concentrations, where N_2O production is elevated (blue symbols in **Figure 5**). Such a linear relation is regarded as an indicator for a dominant role of nitrification in N_2O production (Cohen and Gordon, 1979; Walter et al., 2004). The slope itself generally reflects the biological N_2O yield per mole O_2 consumed (Cohen and Gordon, 1979; Najjar, 1992; Suntharalingam and Sarmiento, 2000). As we find a linear correlation throughout most of the transect, we thus conclude that nitrification dominates N_2O production in the Elbe estuary.

Regression slopes were remarkably similar in the upstream part of the river in April and June. Furthermore, in June, the slopes upstream and downstream of the O_2 minimum are also

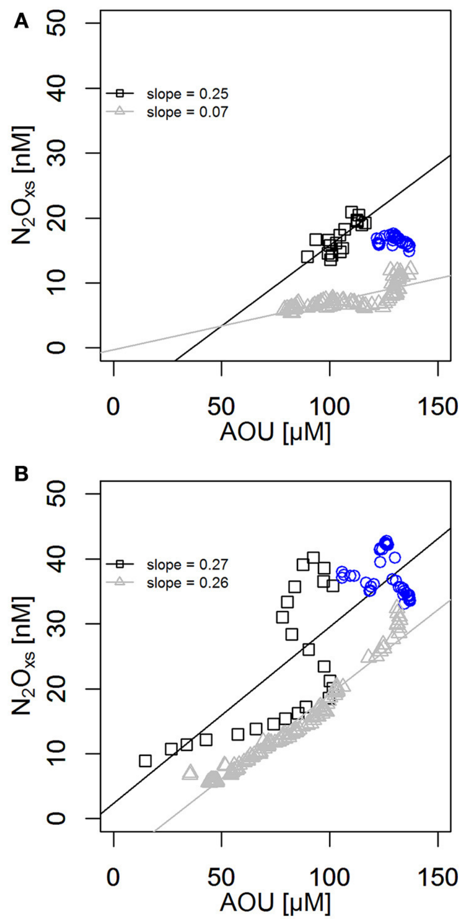

FIGURE 5 | Relationship between N_2O excess (N_2O_{XS}) and apparent oxygen utilization (AOU) in the Elbe river with according regression slopes in April **(A)** and June **(B)**. □, Elbe river upstream of the region with lowest O_2 concentration; Δ, Elbe river downstream of the region with lowest O_2 concentration region; o, within the oxygen minimum.

comparable. For nitrification, regression slopes of 0.08 to 0.3 nM N_2O/µM O_2 have been calculated (Suntharalingam and Sarmiento, 2000), in our study, the slopes (0.25–0.27) are thus in the high end of this range, reflecting a high relative N_2O yield. In the light of comparatively low O_2 concentrations in our study, this is in line with an expected increase of nitrous oxide production with decreasing O_2 (Bakker et al., 2014).

We note that the slopes can also be affected by mixing processes (Suntharalingam and Sarmiento, 2000; Nevison et al., 2003), and assume that this is the case in June 2015, where we, despite significant linearity (**Figure 5B**—black symbols, $r^2 = 0.39$, $p \ll 0.05$), see a curved pattern of AOU vs. N_2O_{xs}. We assume that this reflects local mixing with water masses from adjacent harbor basins and/or waste water discharge by a neighboring waste water treatment plant (stream km ~630). We also note that in estuarine regions like in the Elbe estuary, oxygen consumption is fueled not only by nitrification, but that remineralization also can contribute to an increased AOU. Hence, the strong linear correlation cannot be taken as an indicator of nitrification alone. Nevertheless, nitrification contributes to oxygen consumption, is tightly coupled to remineralization in the Elbe estuary (Kerner and Spitzy, 2001), and obviously increases the nitrate load massively throughout the estuary. This co-occurrence of nitrate production, in combination with the linear correlation of AOU and N_2O_{xs} suggests a large portion of nitrous oxide that is produced in the freshwater section of the estuary from stream km 620 onwards stems from nitrification (Cohen and Gordon, 1979; Walter et al., 2004).

While we did not perform N_2O measurements in the sediment, at minimum O_2 concentrations, we find that the linear correlation of N_2O_{xs} and AOU breaks up (**Figure 5**). Our measured O_2 concentration which was measured at 2 m water depth is too high to allow denitrification in the water column. But the break-up of linearity is accompanied by high AOU values, which indicate high O_2 consumption in water masses and/or sediment of the Elbe River, either due to nitrification and/or due to respirational processes (Schöl et al., 2014; Amann et al., 2015). Therefore, we speculate that the resulting hypoxic conditions can favor denitrification as an additional contributor to N_2O in the Elbe estuary and previous studies showed that denitrification in sediments is highly active in this region (Schroeder et al., 1990; Deek et al., 2013). It is thus plausible that a portion of the N_2O that is apparently produced in the sediment during denitrification escapes to the water column. In consequence, this would affect linearity of N_2O_{xs}/AOU by increasing the relative amount of N_2O, which is exactly what we find in our measurements. Hence, we assume that the additional N_2O_{xs} in the oxygen minimum region must be explained by sedimentary denitrification contributing to an elevated concentration of N_2O in the water column. This break-up of linearity occurred at lowest oxygen concentrations and in a smaller part of the transect (~stream km 627/633–638/640) in the port region. Thus, we conclude that sedimentary denitrification is an additional contributor to N_2O concentration beside nitrification.

Trends in N_2O Saturation in the Estuary and Emissions

In comparison to other European estuaries, N_2O saturation in the Elbe appears to be in the midrange of values reported so far, even if seasonal variability can affect the comparison. The mean N_2O saturation of 201% (*SD*: ±94%) in the Elbe is high compared to Tamar, Temmesjoki, Gironde, and Tagus estuaries, but relatively low compared to the Schelde and the Humber (UK) estuary (**Table 1**), where nitrification is the main source of N_2O (Barnes and Owens, 1998; de Wilde and de Bie, 2000; de Bie et al., 2002). In addition, de Bie et al. (2002) also speculated that additional N_2O may derive from denitrification, which occurs at high rates in the inner Humber estuary (Barnes and Owens, 1998).

Despite the moderate N_2O saturations in the Elbe estuary, we found very high sea-to-air fluxes which are closer to those measured in the Schelde and the Humber estuary than to other European estuaries. While a major uncertainty derives from

TABLE 1 | Comparison of N_2O saturations, fluxes and emissions from European estuaries.

Estuary/ Country	N_2O saturation (%)	N_2O flux (μmol m^{-2} d^{-1})	N_2O emissions (Gg N_2O y^{-1})	Area (km^2)	References
Elbe, Germany	200.9	48.1	0.18	371.85	This study
Elbe, Germany	199–1600	n.a.	n.a.	n.a.	Hanke and Knauth, 1990
Elbe, Germany	202	33.6	0.12	224	BIOGEST—Barnes and Upstill-Goddard, 2011
Humber Estuary, UK	395.7	77.5	0.41	303.6	Barnes and Upstill-Goddard, 2011
Tamar, UK	145	8.03	0.006	39.6	Barnes and Upstill-Goddard, 2011
Schelde, The Netherlands	710	66.2	0.28	269	de Wilde and de Bie, 2000; de Bie et al., 2002
Temmesjoki, Finland	136	14.7	0.09	407.6	Silvennoinen et al., 2008
Gironde, France	132	n.a.	0.18	442	Bange et al., 1996; Barnes and Upstill-Goddard, 2011
Tagus, Portugal	125	5.8	0.03	320	Gonçalves et al., 2010
European estuaries	327	45.7	1.35	1,840	Barnes and Upstill-Goddard, 2011

estimations of gas transfer velocity, which highly depends on wind, water currents, turbulences, etc. (Zappa et al., 2003; Abril et al., 2009), the average sea-to-air flux density of 48.1 μmol m^{-2} d^{-1} still suggests that the Elbe is a significant source for N_2O. The calculated total N_2O emissions of 0.18 Gg N_2O y^{-1} are rather comparable to the Gironde (France) (**Table 1**) than to the Humber estuary (0.41 Gg N_2O y^{-1}), even though the DIN concentrations in the Elbe are comparable to those of the Humber estuary. Zhang et al. (2010) showed that DIN and N_2O emissions are often correlated, and the Elbe data from our study nicely match the correlation they show.

Thus, as this correlation holds, and because nutrient loads in the Elbe Estuary have decreased during the last decades, we compared trends in nutrient loads and N_2O concentrations over time. Previous investigations in the 1980s (Hanke and Knauth, 1990) found N_2O saturations from 199 to 1,600%, which were much higher than the saturation range from 139 to 374% reported in the BIOGEST study from the 1990s (Barnes and Upstill-Goddard, 2011). One main reason for the difference between the results of Hanke and Knauth (1990) and later studies including ours probably is the reduced nutrient load of the Elbe estuary and the increased oxygen concentration (**Figure 6A**). Hanke and Knauth (1990) reported ammonium concentrations of ∼15–110 μM along the whole transect, while in our study ammonium concentrations were below 19 μM. In line with high nutrient loads and low oxygen saturation at that time, Hanke and Knauth (1990) concluded that denitrification was the dominant contributor to N_2O production. The importance of denitrification appears to have ceased in the contemporary Elbe estuary since then (Dähnke et al., 2008), and our data support that this also affects N_2O production: Beside the obvious nitrate production in the freshwater section, the clear correlation of N_2O_{xs} and AOU also points toward nitrification as an important N_2O source in the contemporary estuary.

Since the study by Hanke and Knauth (1990), the DIN load decreased markedly, and a significant improvement of the environmental condition in the Elbe estuary occurred as a consequence of reduced nutrient inputs (**Figure 6B**). A reduced input of DIN correlates with a reduction in N_2O production (Zhang et al., 2010), and we thus expected to find lower N_2O concentrations than during the BIOGEST study in the 1990s (**Figure 6**). However, in comparison to the BIOGEST data, it is remarkable that N_2O saturations have obviously not decreased any further some 20 years later, even though a steady decrease of the total nitrogen load occurred over the last decades (Pätsch and Lenhart, 2004; Radach and Pätsch, 2007; see also **Figure 6A**). It is yet unclear why N_2O saturations remained unchanged at this high level, but it appears plausible that internal N-cycling, i.e., intense nitrification, and denitrification in the port region, may compensate for the reduction in overall nutrient loads.

CONCLUSIONS

N_2O saturations in the range from 118 to 554% and high sea-to-air fluxes were observed along two transects along the salinity gradient of the Elbe estuary in April and June 2015, indicating that the Elbe estuary was a moderate source of N_2O to the atmosphere. We found highest N_2O concentrations in the Hamburg port area, which was a hot spot of biological N_2O production with maximum sea-to-air flux densities of 100 and 200 μmol m^{-2} d^{-1} April and June, respectively. Our DIN and O_2 measurements suggest that intense remineralization and respiration took place in this area leading to maximum ammonium concentrations, which serve as a substrate for nitrification. Moreover, nitrification was identified to be mainly responsible for N_2O production as indicated by linear correlations of apparent oxygen utilization and N_2O_{xs} throughout much of the transect in the freshwater part. However, we found that the linear correlation of AOU-N_2O_{xs} breaks up at highest N_2O concentrations associated with the lowest measured O_2 concentrations, which shows a signal of N_2O production by sedimentary denitrification as an additional contributor to N_2O concentration in parts of the port region.

In comparison to previous studies, our data indicate that the main N_2O production pathway with respect to the whole Elbe estuary freshwater part has changed from predominant denitrification in the 1980s to nitrification in the present estuary. Although a significant reduction in N_2O saturations (and its subsequent emissions to the atmosphere) occurred since the 1980s, the Elbe estuary remains an important source of N_2O,

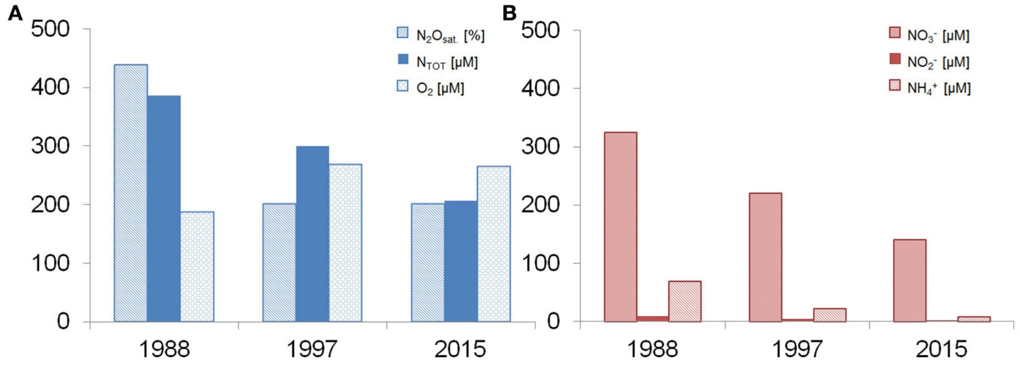

FIGURE 6 | Comparison of Elbe transect measurements for the years 1988, 1997, and 2015. **(A)** Average N_2O saturation, and annual average total N and O_2 concentrations. **(B)** Annual average concentrations of dissolved NO_3^-, NO_2^-, and NH_4^+. Nutrient and O_2 data are available at: http://www.elbe-datenportal.de/FisFggElbe/content/start/BesucherUnbekannt.action.

especially as nutrient reduction measures do not seem to further reduce N_2O production. Thus, the future development of the Elbe estuary as a greenhouse gas source is unclear, and the seasonality of N_2O production as well as determining factors should be evaluated in future studies.

AUTHOR CONTRIBUTIONS

LB contributed to the concept of the work and analytical design, analyzing, and interpretation of the data and draft the manuscript. HB and KD contributed to interpretation of the data and critical discussion. RL contributed to analytical design and critical discussion. TS contributed to critical discussion and first data interpretation. KD conceived this study, and also helped to structure and draft the manuscript.

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