Rewetting effects on nutrient cycling and export dynamics in coastal peatlands of the southern Baltic Sea

Dissertation

zur Erlangung des akademischen Grades

doctor rerum naturalium (Dr. rer. nat.)

der Mathematisch-Naturwissenschaftlichen Fakultät

der Universität Rostock

vorgelegt von

Anne Elisabeth Edith Breznikar

geb. am 09.01.1992 in Moers

Rostock, 2023

https://doi.org/10.18453/rosdok_id00004619

Gutachter:

 Gutachterin: Prof. Dr. Maren Voß Leibniz-Institut f
ür Ostseeforschung Warnem
ünde

Gutachter:
 Prof. Dr. Dominik Zak
 Universität Aarhus

Datum der Einreichung: 11.08.2023

Datum der Verteidigung: 26.01.2024

Table of Contents

| S | SummaryV ZusammenfassungVII | | | | | | | |
|----|--------------------------------|------------------|--|----|--|--|--|--|
| Z | | | | | | | | |
| 1. | | Introduction | | | | | | |
| 2. | | Mat | erial and methods | 13 | | | | |
| | 2.1 | Study sites | | | | | | |
| | 2.1 | .1 | Karrendorfer Wiesen | 14 | | | | |
| | 2.1 | .2 | Drammendorfer Wiesen | 14 | | | | |
| | 2.2 | San | npling | 14 | | | | |
| | 2.3 | Sample analysis | | 17 | | | | |
| | 2.3 | .1 | Nutrient concentrations | 17 | | | | |
| | 2.3 | .2 | Chlorophyll-a concentrations | 17 | | | | |
| | 2.3 | .3 | Particulate organic matter | 17 | | | | |
| | 2.3 | .4 | N and O isotopes in nitrate (¹⁵ N and ¹⁸ O) | 17 | | | | |
| | 2.3 | .5 | N ₂ O concentrations and saturations | 18 | | | | |
| | 2.3 | .6 | O isotopes in water (δ^{18} O-H ₂ O) | 18 | | | | |
| | 2.4 | Rate | e calculations | 19 | | | | |
| | 2.4 | .1 | Nitrification and NH4 ⁺ assimilation rates | 19 | | | | |
| | 2.4 | .2 | N ₂ production rates | 20 | | | | |
| | 2.5 | Ref | erence nutrient data from monitoring stations | 21 | | | | |
| | 2.6 | Nut | ent export calculation | 22 | | | | |
| | 2.7 | N ₂ C | flux calculations based on air-sea gas exchange parameterization | 24 | | | | |
| | 2.8 | Data | a processing and statistical analysis | 25 | | | | |
| 3 | | Res | ulte | 27 | | | | |
| 0. | 31 | Rev | vetting effects in Drammendorf | 27 | | | | |
| | 31 | 1 | Surface water properties (temperature salinity Ω_2 and Chlorophyll-a) | | | | | |
| | 3.1 | 2 | Nutrient dynamics and exports | 30 | | | | |
| | 3 | 3.1.2. | Pre- and post-rewetting spatiotemporal dynamics and comparison w | | | | | |
| | C | | nearby monitoring station | | | | | |
| 2 | | 3.1.2 | 2 Nutrient export from the rewetted peatland into the bay | | | | | |
| | 3.1 | .3 | N ₂ O concentrations and fluxes | | | | | |
| | 3.2 | Con | nparison of the two study sites | 34 | | | | |
| | | | | | | | | |

| | 3.2.1 | Physicochemical properties of the surface water (temperature, salinity, O_2 | | | | | |
|-------|----------|---|---|-----|--|--|--|
| | | sat | uration, pH) | | | | |
| | 3.2.2 | Nu | trient concentrations | | | | |
| | 3.2.2 | .1 | Surface water in the peatlands | | | | |
| 3.2.2 | | .2 | Porewater in the peatlands | | | | |
| | 3.2.2 | .3 | Spatial gradients in nutrient concentrations within the study sites | and | | | |
| | | | comparison to monitoring stations | | | | |
| 3.2.3 | | Nutrient exports | | | | | |
| | 3.2.4 | Bio | logical variables | | | | |
| | 3.2.4 | .1 | Chlorophyll-a and POM concentrations | | | | |
| | 3.2.4 | .2 | NH_4^+ assimilation rates and total dark NH_4^+ consumption | 41 | | | |
| | 3.2.4 | .3 | Nitrification rates and N_2O | | | | |
| | 3.2.4 | .4 | N ₂ production rates | | | | |
| | 3.3 Isot | ope | values of POM, NO ₃ -, and H ₂ O | 46 | | | |
| | 3.3.1 | Сa | and N isotopes in POM (δ^{13} C-POC and δ^{15} N-PON) | | | | |
| | 3.3.2 | N a | N and O isotopes in NO3^ ($\delta^{15}N\text{-}NO3^{-}$ and $\delta^{18}O\text{-}NO3^{-})$ and O isotopes in H2O | | | | |
| | | (δ ¹⁸ | ³ O-H ₂ O) | | | | |
| Δ | Die | CUE | sion | 53 | | | |
| т. | 4.1 Imn | nedi | ate effects of rewetting in the Drammendorfer Wiesen | 53 | | | |
| | 411 | Nut | lutrient dynamics and export | | | | |
| | 412 | N ₂ (|) dynamics | 55 | | | |
| | 413 | Co | nclusions | 57 | | | |
| | 4.2 Sho | ort-te | erm vs. Jong-term rewetting effects | 58 | | | |
| | 421 | Fac | ctors regulating the nutrient cycling in rewetted peatlands | 58 | | | |
| | 421 | 1 | Nutrient cycling in the surface water and porewater | 58 | | | |
| | 421 | 2 | Particulate organic matter cycling | 62 | | | |
| | 422 | .– Nut | trient exports into coastal areas and comparisons with rivers | | | | |
| | 423 | Co | nclusions | 65 | | | |
| | 4.3 Insi | ahts | ihts into processes and sources of POM and NO ₃ ⁻ by means of | | | | |
| | stat | ole is | le isotopes | | | | |
| | 4.3.1 | So | urces and transformations of POM. | | | | |
| | 4.3.2 | Na | and O isotopes in NO ₃ | | | | |
| | 4.3.2 | .1 | Identification of potential processes | | | | |
| | 4.3.2 | .2 | Identification of potential sources | | | | |
| | 4.3.3 | Co | nclusions | | | | |
| | | | | | | | |

| 5. | Final conclusions and outlook | 75 |
|-----------|-------------------------------|-------|
| 6. | References | 78 |
| Acknow | vledgements | XI |
| Publica | tions and Grant | XIII |
| List of I | Figures | XIV |
| List of | Tables | XVII |
| Append | lix | XVIII |
| Eidesst | attliche Erklärung | xxix |

Summary

The aim of this work was to investigate the long-term effects of rewetting coastal peatlands at the southern Baltic Sea, especially on their internal N cycle and potential nutrient export (N and P) to coastal waters. Two study sites in Mecklenburg-Vorpommern, northeastern Germany, were investigated: the Karrendorfer Wiesen (KW) near Greifswald, rewetted in 1993, and the Drammendorfer Wiesen (DW) on the Island of Rügen, rewetted in 2019. Both sites were drained and used for agriculture for decades, including fertilizer application.

Sampling was conducted at weekly to monthly intervals in 2019 and 2020 and thus, DW was sampled immediately after its rewetting. Variables such as water temperature, salinity, and oxygen concentration were measured on site. Surface water samples were analyzed for nutrients (nitrate, nitrite, ammonium, phosphate), particulate organic matter (POM as POC and PON, concentrations and isotopes), Chlorophyll-*a*, N₂O, nitrate isotopes (δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻), water isotopes (δ^{18} O-H₂O), nitrification rates, and ammonium assimilation rates. Porewater samples were analyzed for nutrients. Sediment cores were used to determine N₂ production rates, which provide information on denitrification potential. The objectives were 1) to investigate potential nutrient leaching at DW by comparing conditions before and after rewetting, 2) to compare N cycling and nutrient export from both study areas, and 3) to gain insight into POM and NO₃⁻ sources and processes by using stable isotopes.

The comparison of conditions before and after the rewetting of DW revealed that the highest nutrient concentrations occurred immediately after rewetting. In the bay off DW, nutrient concentrations increased significantly after rewetting and were higher than the long-term mean of a reference station, indicating a strong leaching of nutrients from the peatland and a pronounced water exchange between the peatland and the bay.

When comparing the two study sites, DW had significantly higher nutrient concentrations in the surface water and porewater than KW, with the highest nutrient concentrations occurring shortly after rewetting. Nutrient exports of DIN-N and PO₄-P occurred at both sites, although the DIN-N export was 75 % lower at KW. Compared to riverine inputs from the largest Baltic rivers, area-normalized exports from the two study sites were one to two

V

Summary

orders of magnitude higher. Phytoplankton growth, measured as Chlorophyll-*a* concentration, was ten times higher at DW than at KW, presumably due to the higher nutrient availability. Instead, the POM pool at KW was largely dominated by degraded phytoplankton and thus, a strong phytoplankton growth apparently did not occur. Despite the lower nutrient availability at KW, higher nitrification rates were measured than at DW, but N₂O saturations were overall lower. The highest measured N₂O saturation (up to 4000 %) occurred at DW immediately after rewetting. Possible reasons for these results and the suggestion that microbial activity was highest within the peat are discussed.

Stable isotope data of POM and NO₃⁻ not only confirmed the strong hydrological connection between the peatlands and their adjacent bays, but also indicated an intensive exchange between the surface water and the peat. The POM isotopes of both study sites were dominated by both terrestrial and marine sources. Significantly lower δ^{13} C-POC and pH values at DW in summer indicated strong remineralization of dying, inundated vegetation that had not been removed prior to rewetting. NO₃⁻ isotopes in both study sites clearly reflected their agricultural use, which is still detectable at KW even 30 years after rewetting. At KW, strong dynamics within the NO₃⁻ pool were observed during the growing season. Isotopic data showed that NO₃⁻ was likely both produced and consumed simultaneously, so that no dominant process could be identified. Hence, it is likely that biological processes such as assimilation, denitrification, and nitrification are closely linked at KW.

This thesis shows that small coastal areas such as rewetted coastal peatlands can contribute significantly to nearshore eutrophication, which was previously unknown. Although the highest nutrient exports likely occur shortly after rewetting, significant exports may still occur even after decades of rewetting. However, the results suggest that the natural filter function of peatlands to remove NO₃⁻ and to absorb N₂O can be restored over time.

VI

Zusammenfassung

Ziel dieser Arbeit war es, die langfristigen Auswirkungen der Wiedervernässung von Küstenmooren an der südlichen Ostsee zu untersuchen, insbesondere auf ihren internen N-Kreislauf und den potenziellen Nährstoffexport (N und P) in die Küstengewässer. Zwei Untersuchungsgebiete in Mecklenburg-Vorpommern, Nordostdeutschland, wurden untersucht: die Karrendorfer Wiesen (KW) bei Greifswald, die 1993 wiedervernässt wurden, und die Drammendorfer Wiesen (DW) auf der Insel Rügen, wiedervernässt in 2019. Beide Standorte wurden entwässert und jahrzehntelang landwirtschaftlich genutzt, einschließlich der Ausbringung von Düngemitteln.

Die Beprobungen wurden 2019 und 2020 in wöchentlichen bis monatlichen Abständen durchgeführt, sodass die DW unmittelbar nach der Wiedervernässung beprobt wurden. Variablen wie Wassertemperatur, Salzgehalt und Sauerstoffkonzentration wurden vor Ort gemessen. Oberflächenwasserproben wurden auf Nährstoffe (Nitrat, Nitrit, Ammonium, Phosphat), partikuläre organische Substanz (POM als POC und PON, Konzentrationen und Isotope), Chlorophyll-*a*, N₂O, Nitratisotope (δ^{15} N-NO₃⁻ und δ^{18} O-NO₃⁻), Wasserisotope (δ^{18} O-H₂O), Nitrifikationsraten und Ammoniumassimilationsraten untersucht. Porenwasserproben wurden auf Nährstoffe untersucht. Sedimentkerne wurden verwendet, um N₂-Produktionsraten zu bestimmen, die Aufschluss über das Denitrifikationspotenzial geben. Die Ziele dieser Arbeit waren 1) die Untersuchung einer möglichen Nährstoffauswaschung in den DW durch den Vergleich der Bedingungen vor und nach der Wiedervernässung, 2) der Vergleich des N-Kreislaufs und der Nährstoffexporte beider Untersuchungsgebiete und 3) die Gewinnung von Erkenntnissen über POM- und NO₃⁻-Quellen und -Prozesse mithilfe der Verwendung stabiler Isotope.

Der Vergleich der Bedingungen vor und nach der Wiedervernässung der DW ergab, dass die höchsten Nährstoffkonzentrationen direkt nach der Wiedervernässung auftraten. In der Bucht vor den DW stiegen die Nährstoffkonzentrationen nach der Wiedervernässung deutlich über das langjährige Mittel einer Referenzstation an, was auf eine starke Auswaschung von

VII

Nährstoffen aus dem Moorgebiet und einen ausgeprägten Wasseraustausch zwischen dem Moor und dem Bodden hindeutet.

Beim Vergleich der beiden Untersuchungsgebiete wiesen die DW deutlich höhere Nährstoffkonzentrationen im Oberflächenwasser und im Porenwasser auf als die KW, wobei die höchsten Nährstoffkonzentrationen kurz nach der Wiedervernässung auftraten. An beiden Standorten kam es zu einem Nährstoffexport von DIN-N und PO₄-P, wobei der DIN-Export in KW um 75 % geringer war. Im Vergleich zu Flusseinträgen der größten Ostseeflüsse waren die flächennormalisierten Exporte der beiden Untersuchungsgebiete um ein bis zwei Größenordnungen höher. Das Phytoplanktonwachstum, gemessen als Chlorophyll-a-Konzentration, war in den DW zehnmal höher als in den KW, vermutlich bedingt durch die höhere Nährstoffverfügbarkeit. Der POM-Pool in den KW war stattdessen größtenteils geprägt abgestorbenem Phytoplankton, von sodass dort offenbar kein starkes Phytoplanktonwachstum stattfand. Trotz der geringeren Nährstoffverfügbarkeit in den KW wurden dort höhere Nitrifikationsraten gemessen als in den DW, jedoch waren die N2O-Sättigungen insgesamt niedriger. Die höchste gemessene N2O-Sättigung (bis 4000 %) trat unmittelbar nach der Wiedervernässung in den DW auf. Mögliche Gründe für diese Ergebnisse und die Vermutung, dass die mikrobielle Aktivität innerhalb des Torfs am stärksten ausgeprägt war, werden diskutiert.

Die Zusammensetzung stabiler Isotope im POM und NO₃⁻ bestätigten nicht nur die starke hydrologische Verbindung zwischen den Mooren und den angrenzenden Bodden, sondern deuteten auch auf einen intensiven Austausch zwischen dem Oberflächenwasser und dem Torf hin. Die Isotopendaten des POM beider Untersuchungsgebiete wurden sowohl von terrestrischen als auch von marinen Quellen geprägt. Deutlich niedrigere δ^{13} C-POC und pH-Werte in den DW im Sommer deuteten auf eine starke Remineralisierung absterbender, überschwemmter Vegetation hin, die vor der Wiedervernässung nicht entfernt wurde. Die NO₃⁻ -Isotope beider Untersuchungsgebiete reflektierten eindeutig die landwirtschaftliche Nutzung, die in den KW auch 30 Jahre nach der Wiedervernässung noch nachweisbar ist. Während der Vegetationsperiode wurde in den KW eine starke Dynamik innerhalb des NO₃⁻ Pools

VIII

festgestellt. Die Isotopendaten legen nahe, dass NO₃⁻ gleichzeitig sowohl produziert, als auch verbraucht wurde, sodass kein dominanter Prozess identifiziert werden konnte. Dies deutet darauf hin, dass biologische Prozesse wie Assimilation, Denitrifikation und Nitrifikation in den KW eng miteinander verbunden sind.

Diese Arbeit zeigt, dass kleine Küstengebiete wie z. B. wiedervernässte Küstenmoore in erheblichem Maße zur küstennahen Eutrophierung beitragen können, was bisher nicht bekannt war. Obwohl die höchsten Nährstoffexporte wahrscheinlich kurz nach der Wiedervernässung auftreten, kann selbst nach Jahrzehnten der Wiedervernässung noch ein bedeutsamer Export stattfinden. Die Ergebnisse legen jedoch nahe, dass die natürliche Filterfunktion von Mooren zur Aufnahme von NO₃⁻ und N₂O mit der Zeit wiederhergestellt werden kann.

IX

1. Introduction

Peatlands display a very efficient long-term storage for organic and inorganic carbon (C) and nitrogen (N). Peat itself is most commonly defined as dead organic matter (OM) that contains at least 30 % of C (Joosten and Clarke, 2002). In their natural state, peatlands are able to take up dissolved inorganic nutrients like nitrate (NO_3), but also greenhouse gases (GHG) such as carbon dioxide (CO_2) and nitrous oxide (N_2O) by the uptake via plants, mosses and microorganisms. Worldwide, peatlands make up only ~3 % of the land surface (Parish et al., 2008), but they store ~550 Gt C which amounts one third of the global soil C and twice as much C as the world's forest biomass (Joosten and Clarke, 2002; Kaat and Joosten, 2009). The highest percentage of peatlands occurs in temperate areas of the Northern Hemisphere (Kaat and Joosten, 2009) which is due to a high precipitation (constant water supply) and low temperatures (less evaporation). Most peatlands are located in Asia, America (both 40.5 % of global peatland area) and Europe (13.2 % of global peatland area), in detail in South-East Asia, Canada, Alaska, Russia, Finland, and Sweden (Kaat and Joosten (2009) and references therein).

Peatlands are generally divided into oligotrophic and minerotrophic states which refer to the amount of nutrients within the peatland and their water and nutrient source (e.g., Succow and Joosten, 2001). Oligotrophic peatlands, called "bogs", are high-lying areas that are fed only by rainwater. The rainwater contains low nutrient concentrations and thus, fosters the growth of peat mosses like *Sphagnum*. On the other hand, minerotrophic peatlands, called "fens", are situated in land depressions. Their water and nutrient sources are rain and mainly groundwater. Due to groundwater intrusion, the nutrient concentrations in fens are slightly higher than in bogs which fosters the growth of sedges and reeds.

In general, the height of the water level determines the biogeochemical processes that occur in the peat layer. In a natural peatland, the water level is usually near the soil surface, ensuring permanently wet conditions. These wet conditions lead to the formation of anoxic zones within the peat, so that decaying organic matter is not fully decomposed and thus,

accumulates to new peat layers. Fully water-saturated, anoxic conditions within the peat are responsible for the ecosystem services provided by pristine peatlands, which are the uptake of CO₂ and occasionally N₂O, improvement of the water quality by retaining nutrients (Fisher & Acreman, 2004; Vikman et al., 2010), and provision of a unique habitat for a diverse flora and fauna.

Contrary to C, the N content of pristine peatlands is naturally low (e.g., Succow and Joosten, 2001). To sustain the growth of vegetation and the subsequent accumulation of organic matter (as C and N), the fixation of dinitrogen (N₂), which is the uptake of atmospheric N into biomass, was found to be an important source of N for pristine peatlands (e.g., Vile et al., 2014). However, anthropogenic activities have strongly increased the global input of reactive N into the environment and thus, the anthropogenic N fixation nowadays exceeds the natural one (e.g., Vitousek et al., 1997; Galloway et al., 2004). This anthropogenically introduced N excess is not only found in rivers and groundwater due to the intensive use of fertilizers, but also in the atmospheric deposition that affects all ecosystems worldwide (e.g., Duce et al., 2008). For peatlands it was reported that a chronic supply of reactive N by atmospheric deposition suppresses the biological N fixation and thus, greatly alters the internal biogeochemical cycling (Saiz et al., 2021). High N supplies were also found to significantly increase the emission of N₂O due to a higher substrate availability and an enhanced microbial activity (e.g., Augustin et al., 1998; Roughan et al., 2018).

N₂O production processes

N₂O is mainly produced by microbial processes such as nitrification, denitrification and nitrifierdenitrification (e.g., Stein and Yung, 2003; Kool et al., 2011; Figure 1). All these processes are highly dependent on the ambient oxygen (O₂) concentration within the peat, where nitrification needs oxic and denitrification hypoxic or anoxic conditions. Oxic/anoxic boundaries are hotspots for both processes (e.g., Marchant et al., 2016), because they favor the close spatial connection of processes that depend on each other.

 $\begin{array}{c} \mathsf{NH_4}^* \\ \mathsf{O_2} & \swarrow \\ \mathsf{NH_2}\mathsf{OH} & \longrightarrow & \mathsf{N_2}\mathsf{O} \quad (\mathsf{NN}) \\ \mathsf{H_2}\mathsf{O} & \swarrow \\ \mathsf{NO_2}^* & \longrightarrow & \mathsf{NO} & \longrightarrow & \mathsf{N_2}\mathsf{O} \quad (\mathsf{ND}) \\ \mathsf{H_2}\mathsf{O} & \swarrow \\ \mathsf{NO_3}^* & \to & \mathsf{NO_2}^* & \to & \mathsf{NO} & \to \mathsf{N_2}\mathsf{O} \quad (\mathsf{NCD}) \\ \mathsf{NO_3}^* & \to & \mathsf{NO_2}^* & \to & \mathsf{NO} & \to \mathsf{N_2}\mathsf{O} \quad (\mathsf{FD}) \end{array}$

Figure 1: Major N cycling pathways for the production of N_2O . NN = Nitrifier-nitrification. ND = Nitrifierdenitrification. NCD = Nitrification-coupled denitrification. FD = Fertilizer denitrification. NN and ND are conducted by nitrifiers and N_2O is produced as a by-product. NCD and FD are conducted by denitrifiers and thus, N_2O is produced as an intermediate (from Kool et al., 2011)

Nitrification is the two-step process of ammonium (NH₄⁺) oxidation to nitrite (NO₂⁻) by ammoniaoxidizing bacteria (AOB) or archaea (AOA), followed by a second step in which NO₂⁻ gets oxidized to NO₃⁻ by nitrite-oxidizing bacteria (NOB). The oxidation of NH₄⁺ in general and the contribution of AOB and AOA was found to be influenced e.g. by the pH in the soil (Nicol et al., 2008) or the NH₄⁺ concentration (Verhamme et al., 2011). Both steps are highly dependent on the ambient O₂ concentration which is why nitrification does not occur in deeper peat layers due to the lack of O₂. Therefore, nitrification is, if conducted at all, restricted to the peat surface where O₂ can potentially be provided from the atmosphere. Along the process, N₂O is produced as a side-product and therefore regularly released into the environment. However, nitrification in pristine peatlands with waterlogged conditions within the peat is usually rather low due to the lack of O₂ (Regina et al., 1996) which is one of the reasons why these peatlands are generally negligible sources of N₂O (Martikainen et al., 1993; Regina et al., 1996; Frolking et al., 2011).

Denitrification reduces NO_3^- to N_2 and thus, it needs hypoxic or anoxic conditions. However, due to the dependency on NO_3^- , denitrification often occurs in close vicinity to nitrification, as it provides NO_3^- as substrate. During denitrification, N_2O is produced as an intermediate. Thus, to be released, N_2O needs to be the end product of the process chain. Several factors lead to a partial denitrification, meaning that the process is not fully completed

up to N₂. For instance, the quality of organic C and the NO_3^- concentration were found to influence the denitrification rate, likely by affecting the N₂O reductase (Senbayram et al., 2012). If the activity of this enzyme is lowered, the N₂O/N₂ ratio increases and more N₂O can be released.

Besides nitrification and denitrification, the so-called nitrifier-denitrification is also of relevance for the production of N_2O (Wrage et al., 2001). This process is conducted by nitrifying microbes who firstly oxidize NH_4^+ to NO_2^- and secondly reduce NO_2^- to N_2O . It was shown that nitrifier-denitrification can be a significant source of N_2O under low O_2 conditions, contributing up to 66 % to the total N_2O production (Zhu et al., 2013), but as long as NO_3^- is available, denitrification is the dominating process of N_2O production in wet peatlands (Masta et al., 2022).

However, N_2O production is not only restricted to wet conditions, but is also of great importance in drained peatlands. Drainage of peatlands, mostly for agricultural purposes and forestry, has a long history around the world. Up to 10-20 % of the global peatland area has been reduced since 1800 due to human activities and climate change (Joosten and Clarke, 2002). In Europe, roughly 50 % of the original peatland area is lost (Joosten and Clarke, 2002), while the areal loss in Germany is even higher, amounting to ~85 % (Joosten and Clarke, 2002). Although drained peatlands make up only 0.3 % of the world's land surface, they emit \sim 5 % of the global anthropogenic C emissions (IPCC, 2019). This is due to the drastic change of biogeochemical processes within the peat after drainage. As described above, the water level is the most important driver of all processes in a peatland. If it permanently drops below the surface e.g. due to drainage, O_2 penetrates the peat and initializes its aerobic decomposition. The subsequent remineralization leads to high CO₂ and N₂O emissions due to an increased microbial activity that is fueled by higher substrate availabilities, originating from peat remineralization or fertilization (Augustin et al., 1998). N_2O emissions are usually smaller than CO₂ emissions, however, N₂O has a \sim 300 times larger global warming potential on a 100year timescale compared to CO_2 and is preserved in the atmosphere for 114 years (IPCC, 2007).

Nutrients in drained and rewetted peatlands

Besides GHG, also nutrients like NH₄⁺, NO₂⁻, NO₃⁻ and phosphate (PO₄³⁻) are produced by remineralization. Many incubation studies showed that drained peat, also if no fertilization was conducted, is highly enriched in nutrients that can be released if the water level rises (Van De Riet et al., 2013; Harpenslager et al., 2015). But even in a drained state, peatlands can be nutrient sources due to leaching via drainage ditches, being a risk for eutrophication of adjacent waters (Marttila et al., 2018). It was found that the topmost peat layer shows the highest degradation which is attributed to higher N concentrations (Cabezas et al., 2012) and N₂O emissions (Liu et al., 2019) compared to less degraded peat.

The high ecological value of peatlands has been recognized in the recent years and therefore, the rewetting of peatlands has gained great interest to stop GHG emissions, to fight climate change, and to restore their natural ecosystem services. The current literature shows that rewetting measures were conducted in many countries already. In general, rewetting is supposed to stop the peat degradation and thus CO₂ and N₂O emissions, while CH₄ emissions arise (e.g., Günther et al., 2020). The latter are offset by the uptake of CO₂ due to plant growth, so that a rewetted peatland displays a net C sink at least on a long-term perspective (Günther et al., 2020). Nevertheless, due to irreversible alterations of the density of drained peat, it was hypothesized that even after rewetting, highly degraded peatlands could still produce large amounts of N₂O if the water level is below ground surface (Liu et al., 2019).

Another positive aspect is that rewetting aims to bring back the unique biodiversity of these ecosystems. Moreover, by fostering the growth of different plant species, a rewetted peatland can potentially act as a nutrient sink due to plant uptake and microbial processes like denitrification within the peat (Fisher and Acreman, 2004), thus improving the water quality. However, if the drainage was long-lasting, there is a high risk that the damage could be too severe to be able to get back near the natural state (Kreyling et al., 2021). So far, mostly controlled laboratory experiments were conducted and showed the release of nutrients from rewetted peat (e.g., Zak and Gelbrecht, 2007; Van de Riet et al., 2013), that could potentially

be exported into adjacent waters. For instance, this release can be strongly affected by the salinity of the overlying water. Due to cation exchange, saline water induces the displacement of NH₄⁺, leading to its release from the soil (e.g., Rysgaard et al., 1999). Sulfate (SO₄²⁻), as being highly abundant in saline water, was shown to influence the biogeochemistry in anaerobic sediments, potentially leading to an increased N and phosphorus (P) mineralization in wetlands ("internal eutrophication"; Smolders et al., 2006). Additionally, SO₄²⁻ can also impact the P and iron (Fe) cycling, ultimately resulting in decreasing Fe:P ratios, so that P might be released into the water (Geurts et al., 2008; van Dijk et al., 2019, and references therein). To avoid nutrient leaching, topsoil removal (TSR) can be an effective measure to remove the largest stock of nutrients (Harpenslager et al., 2015; Zak et al., 2017). However, this measure is very cost intensive and not always feasible.

Coastal peatlands along the Baltic Sea

Peatlands constitute approximately 14 % of the total Baltic Sea drainage basin (Vasander et al., 2003). Many of these are located at the interface between terrestrial and marine ecosystems and thus, exposed to natural and anthropogenic pressures from both sites. Sea level rise is the most dominant threat to coastal peatlands in the future.

Most coastal peatlands are rather small, however, they display independently draining coastal catchments. Hannerz and Destouni (2006) updated the catchment area of the Baltic Sea and identified much more individual sub-catchments than previously considered. They calculated that unmonitored coastal sub-catchments, which are not connected to rivers, make up 13 % of the total Baltic Sea drainage basin, inhabiting 24 % (~20 million people) of the total population. This estimation is in line with reports from the Helsinki Commission (HELCOM). The Commission reported that nearly all coastal catchments are unmonitored concerning their nutrient inputs (HELCOM, 2019) and that their N retention capacity is currently unknown (HELCOM, 2018; Figure 2).



Figure 2: Left: Baltic Sea catchment area with monitored (green) and unmonitored (purple) subcatchments (from HELCOM, 2019). Right: Percentage of nitrogen retention of all sub-catchments. Areas with no data available are shown in gray (from HELCOM, 2018)

In Mecklenburg-Vorpommern (MV), northeastern Germany, where the study sites of this thesis are located, ~90 % of all peatlands have been drained for agriculture (Landesamt für Umwelt und Natur MV, 1997), from which drained coastal peatlands make up ~13 % by covering an area of ~360–400 km² (Bockholt, 1985; Holz et al., 1996). Today, more than 20 % of formerly agriculturally used coastal peatlands are already rewetted in MV (Schiefelbein, 2018). Due to drainage and subsequent peat shrinkage, these peatlands are nowadays low-lying (below mean sea level) and thus, highly vulnerable to rising sea levels. Additionally, the risk of flooding is even more pronounced in the southern Baltic Sea due to an isostatic subsidence of the coast (Johansson et al., 2014). Rewetting measures of coastal peatlands are therefore also intended to allow a controlled extension of the sea towards the land.

While nutrients originating from the terrestrial side are still increasing (e.g., Beusen et al., 2016), the marine side of the coast plays an enormously important role for the retention of nutrients, called the coastal filter (e.g., Asmala et al., 2017; Carstensen et al., 2020). The

Introduction

mechanism behind this filter is highly complex and regulated by several factors, such as for instance the sediment type, the biota and the physical environment (Carstensen et al., 2020). The two main processes behind the filter function are denitrification for N and burial for P, both happening mostly within the sediment.

It was shown that this coastal filter function can be highly efficient in the Baltic Sea, retaining 53 % of P, but only 16 % of N inputs from land (Asmala et al., 2017). However, estimates of coastal retention capacities are mostly based on data from rivers, estuaries and lagoons, whereas diffuse inputs are neglected. It can be assumed that these diffuse inputs add up quickly, displaying a large, currently unconsidered source of nutrients. This assumption of a large source is based on the two facts that (1) coastal areas were and are still used for agricultural purposes and (2) any potential retention capacity is highly limited due to the short spatial distance between the nutrient source and the coast, leading to a much shorter retention time for processes to occur.

Stable isotopes as tool to identify sources and processes

To gain knowledge of potential transforming processes and sources of elements such as N, the use of isotopes became widespread and established since a few decades (e.g., Kendall, 1998; Fry, 2006; Casciotti, 2016). Most elements such as C, N, sulfur or oxygen exist in different forms called isotopes. So-called heavy isotopes are forms of elements that contain one or more additional neutron in their nucleus, whereas light isotopes contain the same amount of protons and neutrons. Heavy isotopes are naturally rare compared to their lighter counterparts. For instance, ¹⁴N, the light isotope of molecular N with a mass number of 14, constitutes 99.635 %, whereas the heavy isotope ¹⁵N makes up 0.365 % of all N₂ within the atmosphere. For O₂, the ratio is 99.76 % (¹⁶O) to 0.1995 % (¹⁸O). Some heavy isotopes are non-radioactive and very stable, thus called stable isotopes. For instance, ¹⁵N and ¹⁸O are stable isotopes which can be used to disentangle the sources and processes that affect e.g. the in-situ NO₃ concentration. The ratio of stable isotopes is given in relation to an international standard and in delta (δ) notation, according to Eq. (1) as:

$$\delta \left[\%_{0}\right] = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000 \tag{1}$$

where R is the ratio of the heavy to the light isotope.

However, $\delta^{15}N$ and $\delta^{18}O$ are not constant, but rather affected by numerous biological and physical processes. The origin of varying isotope ratios for different processes and sources is based on the finding that usually the lighter isotopes are favored over the heavier ones, called kinetic fractionation (e.g., Mariotti et al., 1981). This preference for the lighter isotopes is based on a lower energy input to break up the weaker molecular bonds which makes the uptake more beneficial for plants and microbes. As a result, if the uptake of an N species occurs, the remaining pool of this species will become enriched, so that its $\delta^{15}N$ will increase due to the preferential uptake of ¹⁴N. On the other hand, the produced/transformed species will display a lowered $\delta^{15}N$ than the substrate.

In a closed system, the end product of a process is going to have the same isotope ratio as the substrate when a complete conversion of the substrate occurred. In an open system, however, a complete substrate conversion will never occur which is why it is necessary to know the fractionation factors of different processes and the δ ratios of different sources. Fractionation factors (" α ") can be calculated according to Eq. (2) by Fry (2006):

$$\alpha = \left(\frac{1000 + \delta_A}{1000 + \delta_B}\right) \tag{2}$$

where δ_A is the δ value of substance A (the substrate) and δ_B the δ value of substance B (the product). The corresponding enrichment factor (" ϵ ") displays the difference between the δ values of the substrate and the product and can be calculated according to Eq. (3):

$$\varepsilon = 1000 * (\alpha - 1) \tag{3}$$

Fractionation factors for microbial processes like nitrification and denitrification are usually determined by using pure cultures of bacteria and archaea in the laboratory to ensure controlled conditions. However, fractionation factors cover a range of values for each process,

Introduction

e.g. due to different physiological conditions across the species such as substrate affinity, different environmental conditions such as pH or different reservoir sizes. Additionally, single steps during the processes exhibit different fractionation factors which makes the interpretation even more difficult (e.g., Buchwald and Casciotti, 2010).

With regard to δ^{15} N, nitrification was found to have fractionation factors between 1.019 and 1.036 (Montoya, 1994), corresponding to enrichment factors of 19 – 36 ‰. For denitrification, fractionation factors between 1.017 and 1.029 (enrichment factors of 17 – 29 ‰) were determined (Montoya, 1994). It is noticeable that the range of values overlaps for these two processes. To be able to identify the dominant ongoing process, the additional use of the O isotopes (¹⁶O/¹⁸O) was established, the so-called dual isotope approach (e.g., Sigman et al., 2005). The idea behind this approach is to gain a more detailed insight into processes and sources by using two tracers that can be influenced by fractionation in a way that is characteristic for the respective process/source. For instance, if O₂ gets incorporated within a process, then the δ^{18} O of the product will be affected. During nitrification, O₂ will either be taken from the dissolved pool (δ^{18} O-O₂ of 24.2 ‰, Sigman et al., 2009, and references therein) or from the water itself (ranging from –24 ‰ to 4 ‰; Kendall et al., 2007). It was reported that nitrification seems to incorporate less than one out of six O atoms from dissolved O₂ (Casciotti et al., 2002; Sigman et al., 2009). To check if nitrification occurs, it is therefore helpful to additionally measure the δ^{18} O-H₂O to identify its potential influence on the δ^{18} O-NO₃⁻.

Measurements of Chlorophyll-*a*, particulate organic matter (POM, as N and C) concentrations and its isotopes (δ^{15} N-PON and δ^{13} C-POC) can be helpful to trace if phytoplankton is growing and if e.g. NO₃⁻ is assimilated. The uptake of any N species leads to changes in the remaining substrate pool (e.g., δ^{15} N-NO₃⁻) as well as in the uptaking organism (e.g., δ^{15} N-PON). Due to the preferential uptake of ¹⁴N, the substrate pool becomes enriched (increasing δ^{15} N), whereas the organism becomes depleted (decreasing δ^{15} N; e.g., Savoye et al., 2003). POC concentrations and δ^{13} C-POC values, together with Chlorophyll-a concentrations, can additionally be used to identify sources of the available POM. Freshly produced phytoplankton was reported to have POC:Chlorophyll-*a* ratios of < 200, while ratios

> 200 are characteristic for degraded phytoplankton (Cifuentes et al., 1988). δ^{13} C-POC can be used to distinguish between marine and terrestrial POM sources. Generally, low δ^{13} C-POC values around –30 ‰ are reported for terrestrial sources (e.g., Müller and Voss, 1999), whereas marine sources show higher, more ¹³C enriched values around –22 ‰ (e.g., Voss and Struck, 1997).

Isotope data of NO₃⁻ can not only be used to identify ongoing processes, but also to unravel its different sources. The dual-isotope approach has led to numerous publications dealing with the identification of NO₃⁻ sources (e.g., Mayer et al., 2002; Deutsch et al., 2006; Wankel et al., 2006). Kendall (1998) established a graphical scheme of different NO₃⁻ sources, consisting of nitrification, fertilizer, atmospheric deposition, soil N and manure/sewage (Figure 3). These five major sources can be distinguished by having distinctly different signatures of ¹⁵N-NO₃⁻ and ¹⁸O-NO₃⁻. Due to the high anthropogenic input of N into the environment, many studies revealed that high NO₃⁻ concentrations e.g. in rivers and streams were attributed to a high agricultural use in their catchment areas by using stable isotopes (e.g., Kaushal et al., 2011; Liu et al., 2018). However, to my knowledge, natural stable isotopes of NO₃⁻ were not yet used in peatlands to unravel its sources and cycling.



Figure 3: Scheme of $\delta^{15}N$ and $\delta^{18}O$ values of different NO₃⁻ sources (from Kendall, 1998)

Aims of this thesis

Overall, the long-term effects of rewetting on the N cycling in (coastal) peatlands is mostly unknown and understudied, especially regarding brackish environments. It also remains unclear if nutrients are not only released from the peat shortly after rewetting, but also exported into adjacent waters. If an export occurs, it is crucial to investigate the amounts and the duration of these additional nutrient inputs that are currently unmonitored. Additionally, insights into the internal N cycling are necessary to be able to estimate a potential retention of nutrients.

Therefore, this thesis examines the effects of rewetting in coastal peatlands, specifically on N dynamics and nutrient exports. By comparing two rewetted coastal peatlands in different stages, this thesis tries to reveal long-term effects of rewetting measures in the southern Baltic Sea region. In detail, the following hypotheses were addressed:

- Rewetting leads to the leaching of nutrients out of the peat and subsequently, to an export into adjacent waters.
- 2. The freshly rewetted peatland contains more nutrients within the peat, leading to more leaching and a higher N turnover than within the longer rewetted peatland.
- Local POM and NO₃⁻ sources and processes differ between the two rewetted peatlands due to their different rewetting stages as revealed by stable isotope signatures.

2. Material and methods

2.1 Study sites

Both study sites are located in the state of Mecklenburg-Vorpommern (MV) in northeastern Germany, approximately 25 km apart (Figure 4).



Figure 4: (a) Overview of the study sites location in the southern Baltic Sea. (b) Both study sites (red dots) and the respective monitoring stations (blue dots; used for nutrient data) at the northeastern German coast. (c) Stations in the longer rewetted peatland (Karrendorf, KW). (d) Stations in the recently rewetted peatland (Drammendorf, DW)

The climate is oceanic with a mean annual air temperature and precipitation height of 9.1°C and 626 mm (Deutscher Wetterdienst, DWD, 1991 – 2020). Both sites can be classified as highly degraded coastal peatlands (von Post degradation status H6–H8; Stanek and Silc, 1977). The overlying water matches the water level of the adjacent brackish Bodden with a salinity between 7 and 10. The remaining peat layers show a thickness of up to 2m. Topsoil removal was not conducted prior to rewetting at both study sites.

2.1.1 Karrendorfer Wiesen

The longer rewetted study site, the "Karrendorfer Wiesen" (KW), is located south of the Greifswalder Bodden and covers an area of approximately 3.5 km². It was diked around 1850 to be intensively used as cropland and, in low-lying areas, as pasture for cattle grazing. Fertilizer usage on the higher-elevated areas is documented between 1972 and 1989 and consisted of applications of N, P, and potassium (up to 80, 60, and 120 kg ha⁻¹ yr⁻¹, respectively; Seiberling, 2003). In 1993, the dike was partially removed to re-establish the water exchange with the Greifswalder Bodden. Some areas at KW are permanently inundated, resulting in water depths up to 50 cm, whereas others are irregularly flooded. After rewetting, land use shifted entirely to extensive cattle grazing, which is still conducted.

2.1.2 Drammendorfer Wiesen

The recently rewetted study site, the "Drammendorfer Wiesen" (DW), comprises approximately 0.9 km^2 and lies in the western part of the Island of Rügen, bordering on the Kubitzer Bodden. The dike was erected around 1900 and the area was used as grassland and pasture thereafter. From ~1980 until the rewetting, low-lying areas, permanently flooded today, were not fertilized and were used only for cattle grazing and mowing (three times per year). N fertilizer (~50 – 100 kg N ha⁻¹ yr⁻¹) was applied once per year in higher-elevated areas that were not later affected by the rewetting (Dr. M. Möller and S. Klatt, pers. comm., 2023). Rewetting was performed in November 2019 by removing parts of the dike, thus re-establishing a hydrological connection to the Kubitzer Bodden. The mean water depth of the permanently inundated area is ~50 cm, comparable to the inundated areas of the KW. Similar to the latter, DW is currently used for extensive cattle grazing.

Overall, the low-lying areas at both sites were used solely for cattle grazing, while areas of higher elevation were fertilized with similar amounts of N.

2.2 Sampling

At both study sites, surface water was sampled for nutrients (NO₃⁻, NO₂⁻, NH₄⁺ and PO₄³⁻), Chlorophyll-*a*, POM (consisting of POC and PON) concentrations and isotopes (δ^{13} C-POC and

 δ^{15} N-PON), H₂O isotopes (δ^{18} O), NO₃⁻ isotopes (δ^{15} N and δ^{18} O), N₂O concentrations, nitrification rates and NH₄⁺ assimilation rates. Porewater samples were taken for the analysis of nutrients (see above). Sediment cores ($\emptyset \sim 8$ cm, length 30 cm, 3 – 5 per sampling) were obtained to measure N₂ production rates.

At KW, surface water samples were taken monthly from April 2019 to September 2020, except of September 2019 and March 2020, by using a beaker (see Supplementary Table 1). The peatland site was sampled at two stations (KW3 in the channel, KW4 in the flooded area; Figure 4c) and the adjacent bay at three stations (KW1, KW2 and KW5; Figure 4c). Porewater samples for nutrients were taken at one peatland station (KW4) during each sampling. Sediment cores were obtained from the peatland and the bay in triplicates approximately every three months by using acrylic liners.

DW was sampled before and after its rewetting in November 2019. Prior to rewetting, surface water samples for nutrients (NO₃⁻, NO₂⁻, NH₄⁺, and PO₄³⁻) and Chlorophyll-*a* were collected from the bay off DW at station D1 (Figure 4d) and irregularly at a second station right in front of the removed dike section, which was abandoned after rewetting and therefore merged with station D1. Both stations were sampled from the land, and sampling was conducted monthly from June to November 2019, except for August.

After rewetting, DW was sampled with a small boat from December 2019 to December 2020 in different intervals. From December 2019 to January 2020, surface water samples were taken weekly, from February to September 2020 biweekly and from October to December 2020 monthly (see Supplementary Table 1) by using a horizontal 5 L Niskin bottle. For nutrient concentrations, the peatland site was sampled at six stations and the bay at 2 - 3 stations (Figure 4d). Samples for the other variables (see above) were taken at two stations in the peatland (D5, BTD8). In the bay, these samples were taken at three stations (D1, D3, D14; the latter from March 2020 on) until mid-July 2020 and afterwards at two stations (D1, D14). Porewater samples for nutrients were taken from July 2020 to December 2020 at 2 - 4 stations in the peatland. Sediment cores were obtained in triplicates only from bay station D1

approximately every three months by using acrylic liners. Cores could not be obtained from peatland stations at DW due to a very dense peat soil surface.

Porewater at KW was retrieved by using acrylic liners with drilled holes in regular distances to extract soil and to insert rhizons into the soil core (Rhizosphere Research Products B.V., The Netherlands; further details see Seeberg-Elverfeldt et al., 2005). At DW, a porewater lance was used (M.H.E. Products, USA). All porewater samples were immediately filtered with single-use 0.45 µm syringe filters in the field and stored frozen until the nutrient analysis was carried out.

Environmental variables such as surface water temperature, salinity, O_2 and pH were measured on site by using a HACH HQ40D multimeter (HACH Lange GmbH, Germany) equipped with three outdoor electrodes (LDO10105, CDC40105, PHC10105). The precision of the electrodes was $\pm 0.3^{\circ}$ C, $\pm 0.8 \%$, ± 0.1 and ± 0.02 for temperature, O_2 saturation, salinity, and pH, respectively.

Nutrient and NO₃⁻ isotope samples were filtered immediately onboard by using singleuse 0.45 µm syringe filters and stored frozen until analysis. Subsamples for the analysis of δ^{18} O-H₂O were filtered with single-use 0.45 µm syringe filters, collected in 1.5 ml glass vials sealed with a PTFE-coated septum cap and stored at 4°C in the dark until analysis. Water samples for POM, Chlorophyll-*a*, nitrification rates, and NH₄⁺ assimilation rates were taken with plastic canisters which were kept cool and dark until further processing in the lab. Samples for N₂O concentrations were taken with 250 ml glass crimp vials by using the overflow technique. All vials were crimp-sealed with butyl rubber stoppers onboard. In the lab, samples were treated with 500 µl saturated mercury chloride solution and stored at 4°C in the dark until analysis. For POM analysis, samples were filtered onto pre-combusted Whatman® GF/F filters (4 h at 450°C, poresize 0.7 µm) which were then stored frozen until analysis. For Chlorophyll-*a* analysis, non-combusted GF/F filters were used for filtration. Water for the determination of nitrification rates, NH₄⁺ assimilation rates and for sediment cores was stored bubbled and stirred overnight in the dark at 4°C (for nitrification rates and NH₄⁺ assimilation rates) and at in situ temperature (for sediment cores) to be processed on the next day.

2.3 Sample analysis

2.3.1 Nutrient concentrations

The nutrient analysis was carried out via photometry according to Grasshoff et al. (2009) by using a continuous segmented flow analyser (Seal Analytical QuAAtro, SEAL Analytical GmbH, Germany). Detection limits were 0.05 μ mol L⁻¹ for NO₂⁻, 0.1 μ mol L⁻¹ for PO₄³⁻, 0.2 μ mol L⁻¹ for NO₃⁻ and 0.5 μ mol L⁻¹ for NH₄⁺. For such measurements below the detection limit, using the actual values of these measurements is recommended (e.g., Fiedler et al., 2022) to achieve a robust statistical analysis. Since these data were not available for all measurements, random values between zero and the respective detection limit were generated with a uniform distribution for a robust statistical analysis.

2.3.2 Chlorophyll-a concentrations

Chlorophyll-*a* was analyzed fluorometrically after the pigment was extracted from GF/F filters by incubation with 96 % ethanol for 3 h (Wasmund et al., 2006). Measurements were conducted by using a fluorometer (TURNER 10-AU-005, Turner Designs, USA) at a wavelength of 670 nm.

2.3.3 Particulate organic matter

POM filters were dried at 60°C before analysis, packed into tin capsules and pelletized. PON and POC concentrations were measured by using an elemental analyzer (EA IsoLink, Thermo Fisher Scientific, USA). Calibration was done before each sample run by using acetanilide (Merck) with a C– and N–content of 71.09 % and 10.36 %, respectively. δ^{13} C-POC and δ^{15} N-PON analysis was carried out from the same filters. After combustion, the gas was injected via a split interface into an isotope ratio mass spectrometer (IRMS, Delta V Advantage, Thermo Fisher Scientific). IAEA-C3, -C6, -N1, -N2 and NBS 22 were used as reference standards and N₂ and CO₂ as reference gases. The accuracy of the isotopic analysis was ± 0.2 ‰.

2.3.4 N and O isotopes in nitrate (¹⁵N and ¹⁸O)

 NO_3^- isotopes ($\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$) were determined by using the denitrifier method according to Sigman et al. (2001) and Casciotti et al. (2002). Shortly, a denitrifying bacterium

(*Pseudomonas aureofaciens*), which is lacking the N₂O reductase, converts NO₃⁻ and NO₂⁻ to N₂O. The N₂O is then extracted by an autosampler, purified (Finnigan GasBench II) and analyzed by a continuous-flow IRMS (Delta V Advantage, Thermo Fisher Scientific). IAEA-N3 ($\delta^{15}N = 4.7 \%$, $\delta^{18}O = 25.6 \%$) and USGS-34 ($\delta^{15}N = -1.8 \%$, $\delta^{18}O = -28 \%$) were used as reference standards and were measured after every 10th sample. NO₂⁻ was not removed from any sample. The precision of the method is ± 0.2 ‰ (according to Sigman et al., 2001).

2.3.5 N₂O concentrations and saturations

N₂O concentrations were measured on two gas chromatographs (Shimadzu GC-2014, Shimadzu Corporation, Japan, and Agilent 7890B, Agilent Technologies, USA) using the purge and trap technique [for details see Pönisch (2018) and Sabbaghzadeh et al. (2021)]. For quality control, a N₂O calibration standard (1533 ppb for the Shimadzu and 1982 ppb for the Agilent GC) was measured twice per day, before and after the measurements. The standard deviation was < 1 %.

N₂O saturations were calculated from the measured N₂O concentrations in the surface water and the theoretical N₂O concentrations in brackish water at equilibrium with the atmosphere. The latter was calculated at standard atmospheric pressure (1 atm) with a dry mole fraction of 333.2 ppb-N₂O (World Meteorological Organization, 2021) by calculating the saturated water vapor pressure (at 100 % humidity) and using the solubility coefficients, following the descriptions of Weiss and Price (1980).

2.3.6 O isotopes in water (δ^{18} O-H₂O)

 δ^{18} O-H₂O isotopes were analyzed with a laser cavity-ring-down-spectroscopy system (CRDS; Picarro L2140-I; see Böttcher and Schmiedinger, 2021) and used to identify the potential contribution of nitrification to the production of NO₃⁻. This is possible due to the finding that during nitrification, less than one of six O atoms are derived from dissolved O₂, meaning that more than five of six O atoms are used from H₂O (Casciotti et al., 2002; Sigman et al., 2009). The theoretical δ^{18} O-NO₃⁻ can be calculated according to Eq. (4):

$$\delta^{18} \text{O-NO}_3^- = 5/6 \,\,\delta^{18} \text{O-H}_2 \text{O} + 1/6 \,\,\delta^{18} \text{O-O}_2 \tag{4}$$

where δ^{18} O-O₂ in the surface ocean is prescribed as 24.2 ‰ (Sigman et al., 2009). Finally, theoretical and measured values of δ^{18} O-NO₃⁻ were compared to reveal the importance of nitrification onto the NO₃⁻ pool.

2.4 Rate calculations

2.4.1 Nitrification and NH₄⁺ assimilation rates

Nitrification and NH₄⁺ assimilation rates were determined simultaneously by using the ¹⁵N-NH₄⁺ tracer incubation method (Ward, 2005; Veuger et al., 2013; Damashek et al., 2016). For each station, water was filled into six 300 ml polycarbonate bottles by using the overflow technique. All bottles were closed with a butyl septum to be able to inject the ¹⁵N-NH₄⁺ tracer into the bottles. The injection volume of ¹⁵N (as ¹⁵N-NH₄Cl, 98 atom%, SigmaAldrich) was adjusted for every batch of samples to ensure an enrichment of approximately 10 % of the ambient NH₄⁺ concentration. After injection, three bottles were filtered immediately to be used as t₀, while the other three were incubated for 15 – 23 h at in situ temperature in the dark (t_{final}). The incubation time for nitrification rates is usually shorter, however, a previous study showed that ¹⁵NO₃⁻ increased linearly during a 96 h incubation (Bartl et al., 2018), which justifies the longer incubation time of my measurements. After the incubation, triplicates were filtered with precombusted GF/F filters (4 h at 450°C). The filtrates and filters were stored frozen until analysis. Filtrates containing ¹⁵N of NO₂⁻ + NO₃⁻ were analyzed via the denitrifier method after Sigman et al. (2001) and Casciotti et al. (2002), as described above but with *Pseudomonas chlororaphis*, to calculate nitrification rates with Eq. (5):

$$NR = \frac{(15N - NO_x) x \frac{(NH_4^+)_{tot}}{(15N - NH_4^+)_{add}}}{\Delta t}$$
(5)

where ¹⁵N-NO_x is the excess concentration of ¹⁵N-NO₃⁻ + ¹⁵N-NO₂⁻, (NH₄⁺)_{tot} the total NH₄⁺ concentration (ambient + tracer), (¹⁵N-NH₄⁺)_{add} the added tracer concentration, and Δt the

incubation time. Nitrification rates are reported as the mean \pm standard deviation based on triplicates for t₀ and t_{final}.

Filters were used to determine PON concentrations and ¹⁵N-PON for the calculation of NH₄⁺ assimilation rates (AAR) according to Dugdale and Wilkerson (1986) by using Eq. (6):

$$AAR = V_m x \left[PON_m \right] \tag{6}$$

where V_m is the mean specific ¹⁵N uptake rate and PON_m the mean concentration of PON at the beginning and the end of the incubation. V_m was calculated as the mean of V_o and V_t, where V_o is based on the initial and final δ^{15} N-PON and V_t on the natural and final δ^{15} N-PON values. ¹⁵N-PON was determined by coupling the elemental analyzer (EA IsoLink, Thermo Fisher Scientific) to the IRMS (Delta V Advantage, Thermo Fisher Scientific). The precision of the isotope measurements was ± 0.1 ‰.

The sum of NH₄⁺ assimilation rates and nitrification rates yields the "total dark NH₄⁺ consumption". The contributions of both processes to the total dark NH₄⁺ consumption were calculated as means of all seasons to show a potential dominance of one process.

2.4.2 N₂ production rates

N₂ production rates were determined by measuring the ratio of N₂:Ar according to Kana et al. (1994). Sediment cores with fully oxygenated overlying water were stirred at low speed with a magnetic stirrer and incubated at in situ temperature in the dark. Samples were taken at the start and the end of the incubation. The incubation was started by closing the cores with rubber plugs to ensure no oxygen exchange with the environment. Incubation of control cores with only water was not conducted due to difficulties with water leakage. Thus, a potential gas exchange through the cores cannot be considered.

Water samples were taken with 12 ml Exetainer vials (Labco, High Wycombe, UK) and poisoned immediately with 100 μ l 7M zinc chloride solution. To ensure oxic conditions throughout the entire incubation, the incubation time was adjusted to keep the oxygen within ~20% of the initial concentration. Samples were analyzed with a membrane inlet mass spectrometer (MIMS; Bay Instruments, USA). Distilled water was measured as blank after

every 6th sample to calculate a drift factor for the correction of N₂:Ar ratios. To gain N₂ concentrations, the theoretical argon concentration (μ mol L⁻¹) of each sample based on the respective temperature and salinity was calculated according to Weiss (1970). Finally, the theoretical argon concentration was multiplied with the corrected N₂:Ar ratio to yield the N₂ concentration in μ mol L⁻¹. N₂ production rates were calculated according to Dalsgaard et al. (2000) with the simplified Eq. (7):

$$F_x = \frac{(C_f - C_i) * H}{t} * 10$$
(7)

where F_x is the flux of N₂ (µmol m⁻² h⁻¹), *Ci* and *C_f* are the concentrations of N₂ at the beginning and the end of the incubation (µmol L⁻¹), respectively, *H* is the height of the water column (cm) and t is the incubation time (h).

2.5 Reference nutrient data from monitoring stations

Nutrient monitoring data of one monitoring station (monitored by the Landesamt für Umwelt, Naturschutz und Geologie (LUNG) MV; station KB90 in the Kubitzer Bodden, see Figure 4) were used to compare these with the pre- and post-rewetting nutrient concentrations in the bay off DW. This comparison was conducted to see the potential export of nutrients out of the peatland after rewetting. Additionally, these data were used to calculate a total possible nutrient export. NO₃⁻, NO₂⁻, NH₄⁺, and PO₄³⁻ data from 2016 to 2020 were used.

To compare nutrient concentrations of the bays of both study sites with long-term monitoring data, a second monitoring station was used (GB1 in the Greifswalder Bodden, monitored by the LUNG MV; see Figure 4). For this, NO_3^- , NO_2^- , and NH_4^+ data of both monitoring stations were used for the years 1981 to 2020.

2.6 Nutrient export calculation

The chapter 2.6 is published in

Pönisch, D.L., Breznikar, A., Gutekunst, C.N., Jurasinski, G., Voss, M., and Rehder, G. (2023). Nutrient release and flux dynamics of CO₂, CH₄, and N₂O in a coastal peatland driven by actively induced rewetting with brackish water from the Baltic Sea. Biogeosciences, 20, pp. 295–323. https://doi.org/10.5194/bg-20-295-2023

Some sentences were adapted to match the scope of this thesis.

To calculate the bulk exchanges of dissolved inorganic nitrogen (DIN-N) and PO₄-P between the flooded peatland and the bay for both study sites, the water level was transformed to water volume by creating a hypsographic curve with increments of 0.1 m and a resolution of 1x1 m (see Supplementary Figure S1).

Water level data from nearby monitoring stations (for KW: "Stahlbrode", 54.23° N, 13.29° E; for DW: "Barhöft", 54.43° N, 13.03° E) and topography data with a resolution of 1x1 m were obtained from the Wasserstraßen- und Schifffahrtsamt Ostsee (WSA) and the Landesamt für innere Verwaltung MV, respectively. To ensure that the water level data of the monitoring stations were comparable with the actual water level within the study sites, on-site water level data of DW were compared with the data from the corresponding monitoring station. For data between August and December 2020, a strong correlation was found ($r_s = 0.95$, p < 0.001, 15–min intervals, Supplementary Figure S2). For KW, no on-site water level data were available.

A water level of -1.6 m above sea level, as the lowest recorded water level within the last 25 years, was used as the starting point to derive the cumulative water volumes of the peatlands. The water volumes were then assigned to the corresponding water levels to finally calculate the water volume changes (Q, in m³ s⁻¹) according to Eq. (8):

$$Q(t) = \frac{dV}{dt}$$
(8)

where *V* is the water volume and *t* the time. Positive volume changes (Q > 0) indicate an inflow of water into the peatland and vice versa. For each season, the mean inflow (Q_{in}) and outflow (Q_{out}) volumes were calculated, according to Eqs. (9) and (10):

$$Qin = \frac{1}{\Delta T} \int_{t}^{t+\Delta T} Q^{positive} dt \quad for \ Q > 0$$
(9)

$$Qout = \frac{1}{\Delta T} \int_{t}^{t+\Delta T} Q^{negative} dt \text{ for } Q < 0$$
(10)

where ΔT denotes the season length. Note that Q_{out} is negative. Seasonal mean values of nutrient concentrations (DIN and PO₄³⁻) were calculated and converted from µmol L⁻¹ to kg m⁻³ by using the molecular masses of the basic elements N and P to derive DIN-N and PO₄-P. After the conversion, nutrient masses of the peatland (c_{peatland}) and the bay (c_{bay}), respectively for each study site, were multiplied by Q_{out} and Q_{in} and integrated to calculate the net nutrient transport (NNT, in tonnes) according to Eq. (11):

$$NNT = \int_{t}^{t+\Delta T} Q_{in} c_{bay} dt + \int_{t}^{t+\Delta T} Q_{out} c_{peatland} dt$$
(11)

Negative values indicate a net nutrient export from the peatland into the bay, and positive values display a net nutrient import into the peatland. Uncertainty ranges for the seasonal NNT (u_{NNT} , as the 95 % confidence level) were calculated by using an error propagation, according to Eq. (12):

$$u_{NNT} = \sqrt{(c_{bay} \, dt \, u_{Qin})^2 + (c_{peat} \, dt \, u_{Qout})^2 + (Q_{out} \, dt \, u_{cpeat})^2 + (Q_{in} \, dt \, u_{cbay})^2} \tag{12}$$

where terms with "*u*" denote the respective 95 % confidence level. To derive the annual uncertainty range of the NNT, all seasonal errors were added up.

In January 2020, exceptionally high PO_4^{3-} concentrations of 7 µmol L⁻¹ were measured at KW during a high water level (~60 cm above local mean water level). For the export calculation, this high concentration was treated as an outlier and thus, not considered.

2.7 N₂O flux calculations based on air-sea gas exchange parameterization

The chapter 2.7 is published in

Pönisch, D.L., Breznikar, A., Gutekunst, C.N., Jurasinski, G., Voss, M., and Rehder, G. (2023). Nutrient release and flux dynamics of CO₂, CH₄, and N₂O in a coastal peatland driven by actively induced rewetting with brackish water from the Baltic Sea. Biogeosciences, 20, pp. 295–323. https://doi.org/10.5194/bg-20-295-2023

Some sentences were adapted to match the scope of this thesis.

The air–sea gas exchange (F; in g m⁻² h⁻¹) is a function of the gas transfer velocity (*k*) and the concentration difference between the bulk liquid (C_w) and the top of the liquid boundary layer adjacent to the atmosphere (C_a). It was calculated as reported in Wanninkhof (2014) and as shown in Eq. (13):

$$F = k \left(C_w - C_a \right) \tag{13}$$

where *k* was derived from an empirical relationship between a coefficient of gas transfer (0.251) and the wind speed (U^2 ; Wanninkhof, 2014) and Schmidt number (Sc), as expressed by Eq. (14):

$$k = 0.251 \, (U^2) (Sc/660)^{(-0.5)} \tag{14}$$

Wind speeds originated from the nearby (~15 km away) monitoring station of Putbus and were measured at 10m height (DWD; 54.3643° N, 13.4771° E; WMO-ID 10093). The average wind speed was defined as ± 3 h from midday because the wind speed over 24 h was lowest at night and highest at midday and because sampling was usually conducted within the selected time interval. The Schmidt number was approximated by a linear interpolation between the freshwater and seawater values. Atmospheric equilibrium conditions (C_a) were calculated using the atmospheric dry mole fraction of N₂O from the station of Mace Head (National University of Ireland, Galway; data from the NOAA Global Monitoring Laboratory (GML) carbon cycle cooperative global air sampling network; Lan et al., 2019). Due to its minor seasonality during the investigation period, an annual mean value of the atmospheric N₂O concentration

was used. Equilibrium concentrations were then calculated using the solubility coefficient (K_0) from Weiss and Price (1980). Flux calculations were conducted only for DW.

2.8 Data processing and statistical analysis

All data analyses and visualizations were performed in R (R Core Team, 2020), using functions of the packages *tidyverse* (Wickham et al., 2019), *psych* (Revelle, 2021), and *car* (Fox and Weisberg, 2019).

Potential relationships between the measured variables were investigated in linear regression analyses. The significance level was set to p < 0.05. To describe temporal patterns, meteorological seasons were assigned as follows: winter (December to February), spring (March to May), summer (June to August), and autumn (September to November). For the pre- and post-rewetting comparison of DW, data from summer and autumn 2019 (pre-rewetting) were compared with those from summer and autumn 2020 (post-rewetting) by using the Mann–Whitney–U–test.

General trends at the two study sites were statistically analyzed by merging (1) the data from individual stations within the peatland and bay areas at each study site and (2) KW data from 2019 and 2020.

The use of means for each area within the study sites (peatland and bay, respectively) was validated in a two-way analysis of variance (ANOVA, with factors "season" and "area"). If data were not normally distributed, a log-transformation was conducted. To compare seasons between the study sites, the Kruskal–Wallis–test was used.

The results showed that, within the study sites, the temporal variability was significantly higher than the spatial variability among the stations (p < 0.05). Thus, mean values and standard deviations are reported for the peatland and bay areas of both study sites. In Sect. 3.1 and 4.1, dealing with the immediate rewetting effects at DW, means for each sampling date are reported. In Sect. 3.2, 3.3, 4.2, and 4.3, dealing with the comparison of both study sites, means for each month are reported. Raw data (single values) can be found in the published data sets.

To validate pooling of data from 2019 and 2020 for KW, the local meteorology of the two years were compared with regard to air temperature and precipitation height data from two nearby monitoring stations (Putbus, WMO-ID 10093, and Greifswald, WMO-ID 10184; DWD; see Supplementary Figure S3). No significant differences between years were found (Mann–Whitney–U–test). To ensure detailed graphical insights into potential differences between the two years, monthly means (± standard deviations) of all variables are displayed separately for both years in the figures.

At DW, one of the stations in the bay (D3) was significantly different from the other bay stations regarding some variables. However, the more physically influenced variables (temperature, salinity, and O₂) were not differing. To obtain a larger data pool especially for the pre-rewetting period, D3 was included for the abovementioned physically influenced variables with regard to the pre- and post-rewetting comparison. For the comparison of DW and KW, D3 was excluded for any variable, as well as for the nutrient export calculation.

Porewater nutrient concentrations at KW and DW were compared based only on data from July to December, to ensure an overlap of the sampling. For KW, data from 2019 and 2020 were used.
3. Results

3.1 Rewetting effects in Drammendorf

The chapters 3.1.1 to 3.1.3 are published in

Pönisch, D.L., Breznikar, A., Gutekunst, C.N., Jurasinski, G., Voss, M., and Rehder, G. (2023). Nutrient release and flux dynamics of CO_2 , CH_4 , and N_2O in a coastal peatland driven by actively induced rewetting with brackish water from the Baltic Sea. Biogeosciences, 20, pp. 295–323. https://doi.org/10.5194/bg-20-295-2023

Some sentences were adapted to match the scope of this thesis.

3.1.1 Surface water properties (temperature, salinity, O₂, and Chlorophyll-*a*)

In the first year after rewetting, no significant differences between the peatland and the bay were found with respect to surface water temperature, salinity, and O₂ saturation (Figure 5a-c; Table 1), suggesting a pronounced water exchange between the peatland and the bay that was driven by frequent changes in the water level (Supplementary Figure S4).

Additionally, no significant differences between summer and autumn 2019 and summer and autumn 2020 were found in the bay. Temperature and salinity measurements near the peat surface showed no significant differences between the surface and bottom water over the year ($n_{surface} = 140$; $n_{bottom} = 86$; data not shown), which suggested that vertical exchange processes and mixing were highly pronounced. However, a significant difference in O₂ saturation between the surface and bottom water in summer (p < 0.01) indicated that local and temporary gradients are possible. Chlorophyll-*a* concentrations after rewetting showed clear seasonal and spatial differences, with significantly higher concentrations in the peatland in spring and summer (up to ~125 µg L⁻¹; Figure 5d; Table 1). A comparison of pre- and postrewetting Chlorophyll-*a* concentrations in the bay in summer and autumn showed higher concentrations after rewetting (pre-rewetting concentrations of 2.5 ± 0.9 µg L⁻¹; post-rewetting concentrations of 15.4 ± 11.5 µg L⁻¹).



Figure 5: Time series of the mean (a) temperature, (b) salinity, (c) O_2 saturation, and (d) Chlorophyll-a concentration (± standard deviation) in the surface water at Drammendorf from June 2019 to December 2020. Data from the flooded peatland (n = 6) are shown in blue and data from the bay in black (n = 2 or 3, as explained in Sect. 2.8). The vertical black line indicates the rewetting event. Figure adapted from Pönisch and Breznikar et al. (2023)

| variable | area | pre-rewetting | | post-rewetting | | | |
|-------------------------|------|------------------|------------------|-------------------------|---------------------------|--------------------|--------------------|
| | | summer 2019 | autumn 2019 | winter 2019 | spring 2020 | summer 2020 | autumn 2020 |
| temperature | peat | N/A | N/A | 3.73 ± 1.25 (45) | 12.03 ± 4.17 (35) | 19.85 ± 2.44 (30) | 12.94 ± 6.61 (30) |
| (C) | bay | 25.17 ± 3.27 (3) | 13.95 ± 3.59 (6) | 3.86 ± 0.99 (17) | 12.17 ± 4.09 (17) | 19.36 ± 2.68 (15) | 12.52 ± 6.58 (15) |
| | peat | N/A | N/A | 6.67 ± 0.68 (45) | 8.23 ± 0.66 (35) | 8.96 ± 0.50 (30) | 8.22 ± 0.33 (30) |
| sainny | bay | 9.21 ± 0.69 (4) | 8.39 ± 0.38 (6) | 6.99 ± 0.65 (17) | 8.27 ± 0.56 (17) | 8.86 ± 0.63 (15) | 8.13±0.32 (15) |
| O ₂ | peat | N/A | N/A | 11.19 ± 0.74 (45) | 11.72 ± 1.93 (35) | 8.60 ± 1.86 (30) | 9.34 ± 1.35 (30) |
| (mg L ⁻¹) | bay | 7.66 ± 1.70 (3) | 7.48 ± 3.87 (6) | 11.18 ± 0.67 (17) | 10.03 ± 3.48 (17) | 8.26 ± 2.26 (15) | 8.86 ± 1.80 (15) |
| chlorophyll-a | peat | N/A | N/A | 8.55 ± 10.80 (24) | 40.03 ± 26.39 (12) | 74.03 ± 29.01 (10) | 30.57 ± 37.50 (10) |
| (µg L ⁻¹) | bay | 2.66 ± N/A (1) | 2.42 ± 1.09 (3) | 4.76 ± 2.31 (8) | 13.52 ± 8.90 (8) | 21.91 ± 11.04 (10) | 8.83 ± 7.76 (10) |
| NO ₃ - | peat | N/A | N/A | 100.03 ± 57.66 (45) | 25.22 ± 46.03 (35) | 0.14 ± 0.10 (29) | 3.69 ± 3.99 (30) |
| (µmol L ⁻¹) | bay | 0.36 ± 0.30 (4) | 2.33 ± 2.80 (6) | 68.50 ± 40.67 (9) | 15.38 ± 30.68 (11) | 0.16 ± 0.12 (10) | 3.38 ± 3.56 (10) |
| NO ₂ - | peat | N/A | N/A | 1.49 ± 0.62 (45) | 0.43 ± 0.44 (35) | 0.23 ± 0.12 (29) | 0.99 ± 1.03 (30) |
| (µmol L ⁻¹) | bay | 0.11 ± 0.07 (4) | 0.19 ± 0.11 (6) | 1.04 ± 0.49 (9) | 0.29 ± 0.33 (11) | 0.16 ± 0.12 (10) | 1.11 ± 1.20 (10) |
| NH_4^+ | peat | N/A | N/A | 30.02 ± 26.13 (45) | 2.27 ± 1.56 (35) | 5.54 ± 6.48 (29) | 18.87 ± 19.50 (30) |
| (µmol L ⁻¹) | bay | 1.67 ± 1.33 (3) | 3.00 ± 1.70 (6) | 21.47 ± 23.42 (9) | 1.71 ± 1.13 (11) | 2.82 ± 3.87 (10) | 17.03 ± 21.78 (10) |
| PO4 ³⁻ | peat | N/A | N/A | 0.37 ± 0.41 (45) | 0.26 ± 0.28 (35) | 0.49 ± 0.26 (29) | 0.35 ± 0.33 (30) |
| (µmol L ⁻¹) | bay | 1.30 ± 1.90 (4) | 0.12 ± 0.08 (6) | 0.21 ± 0.21 (9) | 0.09 ± 0.13 (11) | 0.22 ± 0.21 (10) | 0.26 ± 0.28 (10) |
| N2O | peat | N/A | N/A | 85.53 ± 152.45 (46) | 15.42 ± 4.97 (35) | 6.95 ± 1.35 (30) | 14.34 ± 4.04 (30) |
| (nmol L ⁻¹) | bay | N/A | N/A | 26.74 ± 9.69 (7) | 13.13 ± 4.13 (11) | 8.76 ± 1.26 (10) | 16.68 ± 5.27 (10) |

Table 1: Seasonal comparison of the surface water means (± standard deviation) in the peatland at DW (peat) as opposed to the bay for all in situ variables. The number of observations is shown in parentheses, and significant seasonal differences (n < 0.05) between the bay and the peatland, are indicated in hold. N/A = not available.

3.1.2 Nutrient dynamics and exports

3.1.2.1 Pre- and post-rewetting spatiotemporal dynamics and comparison with a nearby monitoring station

In the bay, all N nutrient concentrations were substantially higher at the first sampling after rewetting than prior to rewetting, while PO₄³⁻ concentrations were only slightly higher postrewetting (Figure 6). This increase in N nutrients led to a drastic increase in the N:P ratio from ~73 in autumn 2019 before rewetting to ~1600 shortly after rewetting in winter 2019. A comparison of the same pre- and post-rewetting seasons (summer and autumn 2019/2020) showed generally higher N nutrient concentrations in the bay after rewetting, which could not be confirmed statistically (Mann–Whitney–U test; Table 1). During winter, all N nutrients were high in the peatland and bay. After a rapid decrease in spring, N nutrient concentrations reached their lowest values in summer, after which NH_4^+ and NO_2^- increased again in autumn. PO₄³⁻ concentrations followed a different pattern, with the highest concentrations determined in summer and fewer fluctuations over the year. The spatial differences in nutrient concentrations between the bay and the peatland after rewetting varied greatly between the nutrient species. From the N nutrients, only NO₂ concentrations were significantly higher once in winter, shortly after rewetting, whereas NH_4^+ and NO_3^- concentrations showed no significant differences in any season (Table 1). Significantly higher PO₄³⁻ concentrations in the peatland occurred during spring and summer (p < 0.05). Some significant correlations between nutrient species were found, especially between NO₂/NH₄⁺ and NO₃/NO₂, both in the peatland and the bay.

Nutrient concentrations of the monitoring station showed a low interannual variability during the years 2016–2020 and often lower concentrations than the bay off DW (Figure 7). A detailed comparison of nutrient data from the monitoring station with those from the bay showed that, before rewetting, only the NH₄⁺ concentrations were significantly higher in the bay. After rewetting, NO₃⁻ and NO₂⁻ concentrations in the bay increased and were significantly higher than at the monitoring station (p < 0.001 and p < 0.05, respectively). In spring, N nutrient concentrations were similar at the two locations, whereas in summer, all N nutrients were

significantly higher in the bay (p < 0.01). In autumn, NO₂⁻ and NH₄⁺ concentrations increased again and, thus, showed significantly higher concentrations in the bay. PO₄³⁻ again followed a pattern different to that of the N nutrients. Shortly before rewetting, its concentrations in the bay were significantly lower than those at the monitoring station (p < 0.05). After rewetting, PO₄³⁻ concentrations showed no significant differences in any season.



peatland ± standard deviation say ± standard deviation

Figure 6: Time series of the mean (± standard deviation) (a) PO_3^{4-} , (b) NO_3^{-} , (c) NO_2^{-} , and (d) NH_4^+ concentrations in the surface water at Drammendorf from June 2019 to December 2020. Data from the flooded peatland (n = 6) are shown in blue and data from the inner bay (until 11 March 2020, n = 1; thereafter, n = 2) in black. The vertical black line indicates the rewetting event. Figure adapted from Pönisch and Breznikar et al. (2023)

3.1.2.2 Nutrient export from the rewetted peatland into the bay

The rewetted peatland was a net source of DIN-N and PO₄-P for the bay (Supplementary Table 2). During the first year after rewetting, 10.8 ± 17.4 t DIN-N yr⁻¹ and 0.24 ± 0.29 t PO₄-P yr⁻¹ were exported into the bay (given as mean \pm 95 % confidence level). DIN-N export was highest during the winter directly after rewetting (8.6 \pm 9.9 t) and lowest during summer (0.3 \pm 0.5 t). DIN-N and PO₄-P were always exported from the peatland into the bay in all seasons.



Figure 7: Seasonal nutrient concentrations of (a) $NO_{3^{\circ}}$, (b) $NH_{4^{\circ}}$, (c) $NO_{2^{\circ}}$, and (d) $PO_{4^{3^{\circ}}}$ at the nearby monitoring station (red) and in the bay off Drammendorf (blue) from pre- to post-rewetting. The vertical black line indicates the rewetting event. Note that 5-year data (2016–2020) are shown for the monitoring station (see Sect. 2.5). ns stands for not significant, and the asterisks denote the following: * p < 0.05, ** p < 0.01, and *** p < 0.001 (Mann-Whitney-U-test). Figure adapted from Pönisch and Breznikar et al. (2023)

3.1.3 N₂O concentrations and fluxes

The highest N₂O concentration of 486.3 nmol L⁻¹ was measured in the peatland one week after rewetting (Figure 8), followed by 4–5 weeks of still-elevated N₂O concentrations between 19.9 and 91.8 nmol L⁻¹.

During winter, significant positive correlations were determined in the peatland between N₂O and NH₄⁺ (r_s = 0.61; n = 45; p < 0.001) and between N₂O and NO₂⁻ (r_s = 0.46; n = 45; p < 0.01). From spring onwards, N₂O decreased rapidly, both in the peatland and the bay, with the lowest values of 4.7 to 7.9 nmol L⁻¹ reached in summer. Other positive correlations of N₂O with N nutrients in the peatland included NO₃⁻ (r_s = 0.74; n = 35; p < 0.001) and NO₂⁻ (r_s = 0.70; n = 35; p < 0.001) in spring and all N species in autumn (NO₃⁻: r_s = 0.85, n = 30, p < 0.001; NO₂⁻: r_s = 0.70, n = 30, p < 0.001; NH₄⁺: r_s = 0.80, n = 30, p < 0.001). Spatial differences in N₂O concentrations between the bay and the peatland were low and not significant in winter, spring,

Results

or autumn, whereas significantly lower concentrations were measured in the peatland during summer (Table 1).

The rewetted peatland was a small source of N₂O, with an annual mean (\pm standard deviation) flux of 0.02 \pm 0.07 mg m⁻² h⁻¹ in the first year after rewetting (Supplementary Figure S5). The highest N₂O flux of 0.4 mg m⁻² h⁻¹ occurred one week after rewetting, followed by lower N₂O fluxes between 0.007 and 0.2 mg m⁻² h⁻¹ within the following 4–5 weeks. Afterwards, N₂O fluxes remained constantly close to zero. Negative fluxes, indicating N₂O uptake, were measured only in summer



peatland ± standard deviation say ± standard deviation

Figure 8: Time series of the mean N₂O concentration (cN_2O ; ± standard deviation) after rewetting in the surface water at Drammendorf from December 2019 to December 2020. Data from the flooded peatland (n = 6) are shown in blue and data from the bay in black (until 11 March 2020, n = 1; thereafter, n = 2). The vertical black line indicates the rewetting event. Figure adapted from Pönisch and Breznikar et al. (2023)

3.2 Comparison of the two study sites

3.2.1 Physicochemical properties of the surface water (temperature, salinity, O₂ saturation, pH)

The peatland areas of the two study sites showed similar environmental conditions across all seasons, but also some significant differences (Figure 9). At KW, the water temperatures were significantly higher in spring and summer compared to DW. The salinity at both sites fluctuated around 8 and increased towards summer where DW had significantly higher salinities. The lowest O_2 saturations around 85 – 90 % were found in winter and autumn at both sites, whereas highest O_2 saturations up to ~120 % occurred in spring. The pH fluctuated around 8 at both sites and showed significantly lower values down to 7.4 at DW in summer. Spatial differences between the peatland and bay areas within the study sites were overall low for all environmental variables (Supplementary Figure S6).

3.2.2 Nutrient concentrations

3.2.2.1 Surface water in the peatlands

Surface water nutrient concentrations differed between KW and DW (Figure 10). In particular the concentrations of dissolved inorganic N (DIN; sum of NO_3^- , NO_2^- and NH_4^+) were higher at DW than at KW, however, only the winter showed significantly higher concentrations. Winter was the first season after the rewetting of DW, with highest DIN concentrations of ~212.0, ~3.0 and ~91.0 µmol L⁻¹ for NO_3^- , NO_2^- and NH_4^+ , respectively. The typical seasonal pattern of lowest DIN concentrations in summer and increasing concentrations towards autumn was found at both sites.

 PO_4^{3-} concentrations fluctuated around ~0.5 µmol L⁻¹ at both sites and were frequently higher at KW, except in spring. The highest PO_4^{3-} concentration of ~7 µmol L⁻¹ was encountered only once at KW during a high water level in winter (~60 cm above local mean water level). In contrast to DIN, the lowest PO_4^{3-} concentrations occurred in spring and not in summer.



Figure 9: Monthly mean (\pm standard deviation) (a) water temperature, (b) salinity, (c) oxygen saturation, and (d) pH at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred). The dashed line in plot (c) shows the O₂ equilibrium with the atmosphere (100 % saturation). Winter was set as starting point for the timeline because it was the first season after the rewetting of DW



Figure 10: Monthly mean (\pm standard deviation) surface water nutrient concentrations of (a) NO₃⁻, (b) NO₂⁻, (c) NH₄⁺, and (d) PO₄³⁻ at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred). Winter was set as starting point for the timeline because it was the first season after the rewetting of DW

3.2.2.2 Porewater in the peatlands

Between July and December, porewater nutrient concentrations of the peat were generally higher at DW than at KW (Figure 11). NO_2^- , NH_4^+ and PO_4^{3-} showed significantly higher porewater concentrations at DW, whereas NO_3^- concentrations did not differ significantly between the study sites. Compared to the surface water measurements, NH_4^+ and PO_4^{3-} concentrations in the porewater of both study sites were one order of magnitude higher, while NO_2^- and NO_3^- concentrations were in the same order of magnitude.

If not only values between July and December, but all sampling events are considered, also NO_2^- concentrations were significantly higher in the porewater than in the surface water at both study sites. NO_3^- concentrations showed no significant differences between the porewater and the surface water at both sites.



Figure 11: Porewater nutrient concentrations of (a) $NO_{3^{\circ}}$, (b) $NO_{2^{\circ}}$, (c) $NH_{4^{\circ}}$, and (d) $PO_{4^{3^{\circ}}}$ at the peatland sides of Drammendorf (DW, blue) and Karrendorf (KW, orange). Only concentrations of the overlapping sampling months are considered (July to December). Numbers at the bottom of each boxplot display the number of used values. Significance levels of the site comparisons are shown on top (ns = not significant, ** = p < 0.01, *** = p < 0.001; Mann-Whitney-U-test)

3.2.2.3 Spatial gradients in nutrient concentrations within the study sites and

comparison to monitoring stations

Both study sites revealed different spatial gradients (peatland vs. bay) with regard to their nutrient concentrations (Supplementary Figure S7). At KW, nutrient concentrations did not differ significantly between the peatland and the bay in any season. At DW, significantly higher

Results

nutrient concentrations in the peatland were found for NO_2^{-1} in winter and PO_4^{3-1} in spring and summer.

Clear differences between the study sites were found for the nutrient concentrations of the bays. When compared to long-term means of nearby monitoring stations, NH_4^+ and NO_3^- concentrations revealed minor differences for KW (Figure 12). In contrast, NH_4^+ and NO_3^- concentrations in the bay off DW were often much higher than at the monitoring station, especially in winter and autumn, leading to concentrations far outside the 95 % confidence level.



Figure 12: Monthly mean concentrations of (a) NO_3^- and (b) NH_4^+ in the bay sites off Drammendorf (DW, blue) and Karrendorf (KW, orange) compared to mean concentrations of two nearby monitoring stations with data from 1981 to 2020 (LUNG, gray, with 95 % confidence level)

3.2.3 Nutrient exports

For both study sites, net DIN and PO_4^{3-} exports were calculated (Supplementary Table 2). At KW, a total of 6.1 ± 20.3 t DIN-N km⁻² yr⁻¹ and 0.04 ± 1.79 t PO₄-P km⁻² yr⁻¹ was released into coastal waters. The highest and lowest export of DIN-N occurred in autumn and summer, respectively. In contrast to DIN-N that was exported in all seasons, PO₄-P was imported during winter and spring.

At DW, a total of 21.6 \pm 34.8 t DIN-N km⁻² yr⁻¹ and 0.5 \pm 0.6 t PO₄-P km⁻² yr⁻¹ was exported into the Baltic Sea. The highest exports of DIN-N and PO₄-P were found in winter, while the lowest exports occurred in summer and autumn, respectively. Overall, DW exported roughly three times more DIN-N than KW, when the area-normalized exports are compared. PO₄-P exports were one order of magnitude higher at DW.

3.2.4 Biological variables

3.2.4.1 Chlorophyll-a and POM concentrations

Chlorophyll-*a* concentrations displayed a typical seasonality at both study sites, only the magnitude differed between the sites (Figure 13a). The highest Chlorophyll-*a* concentrations of up to 125 μ g L⁻¹, coinciding with high POC and PON concentrations, occurred in summer and were significantly higher at DW than at KW (Figure 13b and c). The particulate C:N ratios decreased from ~10 in winter to ~8 in summer and were not significantly different between the sites in any season (Figure 13d).

POC:Chlorophyll-*a* ratios, as indicators of fresh or degraded organic matter, displayed a clear distinction between the sites (Figure 13e). At KW, most POC:Chlorophyll-*a* ratios were > 200 in all seasons, whereas at DW most ratios were < 200, except in winter.



Figure 13: Monthly mean (± standard deviation) (a) Chlorophyll-a (Chla) concentrations, (b) PON concentrations, (c) POC concentrations, and (d) C:N ratios in particulate matter at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred). (e) Plot of POC:PON and POC:Chla ratios

3.2.4.2 NH₄⁺ assimilation rates and total dark NH₄⁺ consumption

NH₄⁺ assimilation rates varied between ~23 and ~4900 nmol L⁻¹ d⁻¹ at both study sites (Figure 14). The rates revealed a typical seasonality with the lowest activity in winter and the highest consumption in summer. Highest rates were found in summer at both sites (DW: mean \pm standard deviation of 1482.5 \pm 1849.9 nmol L⁻¹ d⁻¹; KW: mean \pm standard deviation of 303.2 \pm 242.0 nmol L⁻¹ d⁻¹), however, rates were significantly higher at DW than at KW.

At DW, NH₄⁺ assimilation rates correlated only in summer with the NH₄⁺ concentration, while the rates of KW were positively correlated with NH₄⁺ from winter to summer. At KW, nitrification accounted for 13.5 % and NH₄⁺ assimilation for 86.5 % of the total dark NH₄⁺ consumption, with the highest contributions of nitrification occurring in winter and autumn. At DW, nitrification accounted for 2.0 % and NH₄⁺ assimilation for 98.0 %. Due to NO₃⁻ + NO₂⁻ concentrations < 1 μ mol L⁻¹ and thus, no nitrification rate measurements of spring and summer for DW, a seasonal comparison was not possible.



Figure 14: Monthly mean (± standard deviation) NH4⁺ assimilation rates at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)

3.2.4.3 Nitrification rates and N₂O

Nitrification rates were generally higher at KW with an annual mean of 77.9 ± 161.3 nmol L⁻¹ d⁻¹, compared to 5.6 ± 9.1 nmol L⁻¹ d⁻¹ at DW (Figure 15a). However, nitrification rates at KW were only significantly higher in winter, as a result of only one sampling event during which a very strong resuspension with high PON and POC concentrations was observed.

Nitrification rates of both study sites correlated significantly positive with NH₄⁺ (KW: $r_s = 0.73$, n = 23, p < 0.001; DW: $r_s = 0.57$, n = 41, p < 0.001) and NO₃⁻ concentrations (KW: $r_s = 0.53$, n = 21, p < 0.05; DW: $r_s = 0.33$, n = 41, p < 0.05) when data of all seasons are combined.

The two study sites showed clear differences in the magnitude of N₂O saturations, but also in the temporal variability (Figure 15b). At DW, the rewetting led to the highest observed N₂O saturations of up to 4000 % in winter (mean: 486 ± 874 %), while N₂O saturations at KW were significantly lower (mean: 96 ± 3 %). From spring on, N₂O saturations in DW decreased strongly. During summer, DW showed a higher undersaturation compared to KW. Overall, the range of N₂O saturations at DW was between \sim 30 and \sim 4000 % and therefore much larger than at KW, where N₂O saturations ranged between \sim 80 and \sim 140 %.

N₂O concentrations (nmol L⁻¹) correlated positively with the nitrification rates in autumn at DW ($r_s = 0.94$, n = 6, p < 0.05), but not with rates at KW. At both sites, annual significant positive correlations occurred between N₂O and DIN (KW: $r_s = 0.63$, n = 31, p < 0.001; DW: $r_s = 0.83$, n = 147, p < 0.001) and N₂O and O₂ (in mg L⁻¹; KW: $r_s = 0.84$, n = 31, p < 0.001; DW: $r_s = 0.50$, n = 148, p < 0.001).

3.2.4.4 N₂ production rates

 N_2 production rates in the peatland site at KW varied between -500 and 1200 µmol m⁻² h⁻¹, indicating the occurrence of N_2 production (positive rates) and N_2 uptake (negative rates; Figure 16a). The highest N_2 production rate occurred in spring, while the highest uptake was observed in autumn. When referring to the means, four of six rates showed a net production of N_2 . No correlations between N_2 production rates and NO_3^- concentrations in the surface water and porewater were found.

 N_2 production rates in the bays of both study sites fluctuated between –200 and 1000 µmol m⁻² h⁻¹ and showed no clear seasonal trends (Figure 16b). Rates at KW were generally higher than at DW and all means indicated a net N_2 production.



Figure 15: Monthly mean (± standard deviation) (a) nitrification rates (in nmol L⁻¹ d⁻¹) and (b) N₂O saturations (in %) at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred). Nitrification rates with $NO_3^- + NO_2^-$ values < 1 µmol L⁻¹ were excluded, leading to a discontinous timeline in spring and summer. In (b), the dashed horizontal lines indicate the atmospheric equilibrium (100 % saturation)



Figure 16: Monthly mean (\pm standard deviation) N_2 production rates (a) in the peatland and (b) the bay sides at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)

3.3 Isotope values of POM, NO₃⁻, and H₂O

3.3.1 C and N isotopes in POM (δ^{13} C-POC and δ^{15} N-PON)

 δ^{13} C-POC values of both study sites ranged between –34 ‰ and –22 ‰, covering the entire range from terrestrial to marine values (Figure 17a, Figure 18). Between the sites, no significant differences were found in winter and spring, whereas summer and autumn showed significantly lower δ^{13} C-POC values at DW. At KW, the peatland and the bay did not differ in any season. At DW, the peatland site once showed lower δ^{13} C-POC values in summer compared to the bay (Supplementary Figure S8).



Figure 17: Monthly mean (± standard deviation) (a) δ^{13} C-POC and (b) δ^{15} N-PON values at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)

 δ^{15} N-PON values fluctuated between 4 ‰ and 32 ‰ (Figure 17b). At both sites, highest values were observed in winter, while lowest values occurred in spring (KW) and autumn (DW). Winter was the only season with significantly higher δ^{15} N-PON values at KW. At both study sites, no

correlations between δ^{15} N-PON and PON concentrations, NH₄⁺ assimilation rates, DIN concentrations or nitrification rates were found. Additionally, no significant differences between the respective peatland and bay occurred in either site (Supplementary Figure S8).



Figure 18: Plot of C:N ratio and δ^{13} C-POC at DW (blue) and at KW (orange). The reference values for marine and terrestrial POC and C3 plants are taken from Lamb et al. (2006)

3.3.2 N and O isotopes in NO₃⁻ (δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻) and O isotopes in H₂O (δ^{18} O-H₂O)

In spring and summer, isotope values of NO₃⁻ could often not be determined at both study sites due to NO₃⁻ + NO₂⁻ concentrations < 1 μ mol L⁻¹, leading to a discontinuous time series (Figure 19). Thus, seasonal comparisons between the study sites were only conducted for winter and autumn.

In general, KW showed a larger range of δ^{15} N-NO₃⁻ values (5.2 – 17.5 ‰) than DW (2.6 – 9.9 ‰), but the peatland sites were not significantly different in winter and autumn (Figure 19a). δ^{15} N-NO₃⁻ values at KW and DW were lowest in winter and autumn. At KW, they showed an increase of ~10 ‰ in spring that was preserved throughout summer. At DW, the

standard deviation of δ^{15} N-NO₃⁻ values was comparatively high in December. This was due to the merging of December 2019 and December 2020 which showed distinctly different δ^{15} N-NO₃⁻ values of 8.0 – 9.8 ‰ and 2.6 – 4.6 ‰, respectively. Differences between the peatland and the bay were only observed at KW in 2019, where δ^{15} N-NO₃⁻ values were constantly higher in the bay, except in May (Supplementary Figure S8). At KW, δ^{15} N-NO₃⁻ correlated significantly negative with nitrification rates (r_s = –0.60, n = 14, *p* < 0.05, all seasons). At DW, a significant positive correlation with δ^{15} N-PON occurred (r_s = 0.37, n = 29, *p* < 0.05, all seasons).

 δ^{18} O-NO₃⁻ values also showed a larger range at KW (1.6 – 43.1 ‰) than at DW (1.1 – 8.0 ‰; Figure 19b). The seasonal pattern was comparable at both sites, with low values in winter and autumn which were not significantly different between the sites. At KW, an increase of ~30 ‰ was observed in spring. Differences between the peatland and the bay were again only present at KW, with the bay permanently showing higher (~5 – 10 ‰) δ^{18} O-NO₃⁻ values compared to the peatland site (Supplementary Figure S8).

 δ^{18} O-H₂O values were quite similar in both sites, fluctuating between –6.6 and –3.0 ‰ (Figure 19c). Over the year, KW and DW had the lowest δ^{18} O-H₂O values in winter, while they increased towards spring and summer. During summer, δ^{18} O-H₂O values were significantly higher at DW. Unlike for the NO₃⁻ isotopes at KW, no consistent trend of differences between the peatland and the bay was observed (Supplementary Figure S8). By contrast, the peatland site of DW had higher δ^{18} O-H₂O values in spring and summer compared to its bay.

The correlation of NO₃⁻ concentration and δ^{15} N-NO₃⁻ was highly different between the peatland areas of the study sites (Figure 20a). At KW, a significant negative correlation was found over all seasons, while no significant correlation occurred at DW.

The correlation of δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ also showed differences between the sites (Figure 20b). Both NO₃⁻ isotopes were linearly correlated at KW, with a regression line slope of 2.4. The fractionation factor, based on all measured δ^{15} N-NO₃⁻ values, was calculated to be 1.012. At DW, no significant correlation was present and thus, no fractionation factor was calculated.



Figure 19: Monthly mean (± standard deviation) (a) δ^{15} N-NO₃⁻, (b) δ^{18} O-NO₃⁻, and (c) δ^{18} O-H₂O values at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)



Figure 20: Correlation plots of (a) δ^{15} N-NO₃⁻ and NO₃⁻ concentration and (b) δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ at Drammendorf (DW, blue) and Karrendorf (KW, orange)

Theoretical and measured δ^{18} O-NO₃⁻ values were compared to identify a potential influence of δ^{18} O-H₂O on δ^{18} O-NO₃⁻ during nitrification (Figure 21). Measured δ^{18} O-NO₃⁻ values were always higher than the theoretical ones, indicating that, in the water column, nitrification did not have a major impact on the NO₃⁻ pool.



Figure 21: Correlation plot of measured δ^{18} O-NO₃⁻ vs. theoretical δ^{18} O-NO₃⁻ at Drammendorf (DW, blue) and Karrendorf (KW, orange). The theoretical value is based on the assumption that during nitrification, approximately five out of six oxygen atoms are incorporated from H₂O (Casciotti et al., 2002; Sigman et al., 2009)

The identification of NO_3^- sources by using its isotopes revealed that KW and DW are supplied mostly by NO_3^- from the soil and from manure (Figure 22). At KW, some values could not be assigned to the defined sources.



Figure 22: Correlation plot of δ^{15} N-NO₃⁻ vs. δ^{18} O-NO₃⁻ including the isotopic ranges of different natural and anthropogenic NO₃⁻ sources (adapted from Kendall, 1998; Ding et al., 2014)

4. Discussion

4.1 Immediate effects of rewetting in the Drammendorfer Wiesen

4.1.1 Nutrient dynamics and export

The seasonal dynamics of nutrients followed a typical pattern throughout the year. After rewetting, NH_4^+ , NO_3^- , and NO_2^- concentrations in the surface water of the peatland were high in winter and autumn, which is usually due to mineralization of OM followed by nitrification (Voss et al., 2010). In contrast, the low DIN concentrations in spring and summer reflected the consumption of nutrients by plants and phytoplankton. The very high Chlorophyll-*a* concentration (up to 125 µg L⁻¹) in the peatland indicated a high abundance of phototrophic organisms, probably driven by the higher availability of nutrients compared to the bay. Lowest nutrient concentrations occurred in spring and summer and thus, rewetting during these seasons would likely be more beneficial to reduce a potential nutrient export into the bay, at least during the first few months after rewetting. However, although no significant differences between pre- and post-rewetting (summer and autumn 2019 vs. summer and autumn 2020) nutrient concentrations of the bay were found, the Chlorophyll-*a* concentrations were significantly higher after the rewetting, likely indicating an impact of nutrients from the peatland.

The export of nutrients from the peatland to the bay was confirmed by generally higher mean concentrations in the peatland, revealing that the peatland likely served as a nutrient source for the bay. The mineralization of upper, oxygenized peat layers is promoted by drainage and can lead to an accumulation of nutrients within the soil (Zak and Gelbrecht, 2007; Cabezas et al., 2012). If a drained peatland is rewetted, nutrient concentrations in the porewater and ultimately in the surface water increase (Van de Riet et al., 2013; Harpenslager et al., 2015; Zak et al., 2017). This nutrient leaching is driven by concentration differences across the soil–water interface, but it also depends on factors such as salinity (Rysgaard et al., 1999; Steinmuller and Chambers, 2018), the oxygen availability in the peat (Lennartz and Liu, 2019), and the effects of the latter on microbial processes (Burgin and Groffman, 2012), as well as on the degree of peat decomposition (Cabezas et al., 2012). Highly degraded peat,

such as at DW, can store and release more nutrients than less degraded peat (Cabezas et al., 2012), meaning that the highly degraded peat at DW was prone to leach considerable amounts of nutrients. Porewater nutrient concentrations in the peat revealed DIN and PO_4^{3-} concentrations up to one order of magnitude higher compared to the surface water, providing further support for the leaching of nutrients out of the peatland and ultimately, into the bay.

The annual nutrient exports (mean \pm 95 % confidence level) from the peatland were estimated to be high in relation to the small size (~0.5 km² at 0 m above sea level), yielding to absolute values of 10.8 \pm 17.4 t DIN-N yr¹ and 0.24 \pm 0.29 t PO₄-P yr¹. For comparison, the Warnow, a small river near the city of Rostock, MV, that flows into the Baltic Sea and drains an area of ~3300 km², had a mean annual DIN-N and PO₄-P export of 1200 \pm 500 and 19.9 \pm 7.6 t yr¹, respectively, over the last 25 years (HELCOM, 2019). Thus, the total nutrient export from the peatland to the bay accounted for ~1 % and ~3 % of the annual DIN-N and PO₄-P loads of the Warnow, respectively. When area-normalized, DW exported 21.6 t DIN-N km⁻² yr⁻¹ and 0.48 t PO₄-P km⁻² yr⁻¹, while the Warnow River exported only 0.36 t DIN-N km⁻² yr⁻¹ and 0.01 t PO₄-P km⁻² yr⁻¹.

The high uncertainty range of the calculated nutrient exports is due to several reasons. First, the exports derive from highly fluctuating nutrient concentrations in the surface water within the seasons, which is also visible in the high standard deviations (Table 1). Thus, also the 95 % confidence level of the nutrient exports is high and reflects the natural dynamic. Second, a default error propagation was conducted for the export calculation that leads to even higher ranges in addition to the high natural dynamic. Compared to the Warnow, a highly different range of uncertainties for the two sources is noticeable. While the uncertainties of my calculations are mostly higher and in the same order of magnitude compared to the means, the uncertainties of the data for the Warnow are one order of magnitude lower. The most likely reason for this is the different timescale of the two data sets. The export calculation for DW was conducted by taking only the first post-rewetting year into account in which the system was still transitioning, leading to very dynamic nutrient concentrations. By contrast, the uncertainties in the river exports were a result of using 25 years of data, leading to lower

uncertainties than using data from only one year. Additionally, uncertainty ranges of the river exports were calculated as standard deviation and not as 95 % confidence level, as was done for the exports of DW. Therefore, this must be taken into account when the uncertainty ranges are compared. Nevertheless, the results of this thesis highlight the importance of currently unmonitored and small, independently draining areas along the coastline of the southern Baltic Sea, especially those that become intentionally flooded (HELCOM, 2019).

4.1.2 N₂O dynamics

In addition to nutrient exports, GHG are also important in assessing the ecological consequences of rewetting. In the first year after rewetting, DW was a source of N₂O, although the mean annual N₂O flux of 0.02 \pm 0.07 mg m⁻² h⁻¹ was very low (Supplementary Figure S5). DW was expected to have a low N₂O flux, since permanent inundation leads to anoxic conditions in the peat and thus, prevents the production of N_2O by nitrification and denitrification, due to the lack of O₂ and NO₃, respectively (e.g., Succow and Joosten, 2001; Strack, 2008). However, in the first three months after rewetting (winter), a larger range of postrewetting N_2O fluxes was observed compared to the rest of the year, which indicated that N_2O was strongly and immediately affected by the rewetting, as shown elsewhere (Goldberg et al., 2010; Jørgensen and Elberling, 2012). One week after rewetting, the highest N₂O flux (0.4 mg m⁻² h⁻¹) and the highest NH₄⁺ concentration (78.0 µmol L⁻¹) were measured. In winter, a significant positive correlation between these two variables was found ($r_s = 0.61$, n = 45, p < 0.001). Additionally, N₂O correlated positively with NO₂⁻ in winter (r_s = 0.46, n = 45, p < 0.01), whereas no correlation with NO₃⁻ was found. N₂O, NO₂⁻, and NO₃⁻ accumulated in winter, which is generally interpreted as a result of shifting O_2 conditions in the freshly inundated ecosystem, favoring incomplete process chains of, for example, nitrification or denitrification (e.g., Rassamee et al., 2011). It seems likely that nitrification was responsible for the high N₂O concentrations in winter, due to the correlations of N₂O with its substrate (NH_4^+) and its main intermediate product (NO_2^-) , in addition to a trend of increasing $NO_3^$ concentrations towards spring.

During late spring and early summer, N₂O was undersaturated in the surface water, which pointed to its consumption within suboxic/anoxic zones of the peat. N₂O consumption in the surface water was unlikely because anoxic conditions were never observed near the peat surface. The change in O₂ conditions within the peat, from oxic to hypoxic/anoxic, was evidenced by the undersaturation of N₂O a few months after rewetting, turning DW into a N₂O sink, at least temporarily. Changing O₂ conditions were probably due to the higher availability of fresh OM (measured as Chlorophyll-*a*) in the peatland compared to the bay, resulting in significantly lower N₂O concentrations in the peatland in summer (*p* < 0.001; Table 1).

 N_2O fluxes from other drained peatlands were reported to range from 0.002 to 0.45 mg m⁻² h⁻¹, with a clear trend towards higher fluxes in fertilized or naturally N-rich areas (Flessa et al., 1998; Glatzel and Stahr, 2001; Augustin, 2003; Strack, 2008; Minkkinen et al., 2020). Augustin et al. (1998) investigated multiple degraded fens in MV and Brandenburg (Germany) and calculated N₂O fluxes of 0.04 to 0.10 mg m⁻² h⁻¹ in extensively and intensively used fen grasslands, respectively (Augustin et al., 1998). N₂O fluxes in drained peatlands are the result of a low water level, enabling the permanent penetration of atmospheric O₂ into the peat to enhance N₂O-producing processes that depend on O₂ (Martikainen et al., 1993; Regina et al., 1999).

Hence, it is likely that the drained peat of DW was a source of N₂O prior to rewetting, as the water level was permanently below the soil surface. The mean post-rewetting N₂O flux of DW ($0.02 \pm 0.07 \text{ mg m}^{-2} \text{ h}^{-1}$) is in the lower range of reported fluxes from drained peatlands. Thus, as shown in other studies (Succow and Joosten, 2001; Minkkinen et al., 2020), it seems reasonable that the rewetting probably reduced the N₂O fluxes, since they were likely high prior to rewetting. N₂O fluxes of rewetted peatlands are generally in the same range as fluxes from pristine ones (Minkkinen et al., 2020), indicating that rewetting can effectively reduce N₂O emissions back to near-natural levels. Literature values range from 0.01–0.02 mg m⁻² h⁻¹, for rewetted and undrained boreal peatlands (Minkkinen et al., 2020), respectively, to 0.08 mg m⁻² h⁻¹ for a rewetted riparian wetland near a freshwater meadow (Kandel et al., 2019). Although a comparison of N₂O fluxes at DW with those from other sites with different salinity,

hydrology, and history of use is difficult, the mean annual post-rewetting N_2O flux at DW is in the lower range of N_2O fluxes previously reported for rewetted and pristine peatlands.

4.1.3 Conclusions

Over one year, the immediate effects of rewetting a drained coastal peatland with brackish water and the subsequent formation of a permanently inundated area were studied.

Shortly after rewetting, a strong pulse of DIN leaching out of the peat was found, which led to a high DIN export in winter, the first season after rewetting. However, nutrient concentrations decreased rapidly in spring, likely due to biological consumption processes. Thus, the nutrient export after a rewetting in spring or summer would likely be lower compared to a rewetting in winter, at least during the first few months thereafter.

According to literature, drained peatlands were found to be large sources of N_2O due to their agricultural use and the remineralization of the peat, leading to a high nutrient availability. However, the permanent inundation of DW resulted in a rapid decrease of N_2O emissions and converted the peatland into a N_2O sink during summer, where the fluxes were similar to pristine peatlands.

At DW, the formation of salt grass meadows is ongoing and livestock farming will continue. However, it can be expected that the nutrient export and N₂O emissions will slowly decrease due to a decreasing reservoir of substrates. Nonetheless, this decrease will likely continue for decades, because the topsoil was not removed prior to flooding to diminish nutrients and OM. Nutrient exports from peatlands and the re-establishment of their filter function after rewetting are complex processes whose investigation requires long-term observations. The pronounced seasonal dynamics at DW highlight the need to conduct measurements with a high temporal resolution, such as achieved with sensor-based or eddy-supported measurements.

4.2 Short-term vs. long-term rewetting effects

4.2.1 Factors regulating the nutrient cycling in rewetted peatlands

4.2.1.1 Nutrient cycling in the surface water and porewater

Environmental variables such as salinity and O₂ saturation in the surface water were often comparable at the two study sites, suggesting similar impacts on nutrient biogeochemistry (Figure 9). O₂ saturation did not differ between KW and DW during any season and was therefore an unlikely driver of differences in microbial processes in the water column. Only water temperatures were slightly higher at KW in spring and summer, reaching up to 25°C which is not uncommon for shallow coastal bays (e.g., Broman et al., 2021).

Rewetting of a peatland can lead to high nutrient concentrations in the overlying water (Goldberg et al., 2010; Jørgensen and Elberling, 2012; Van De Riet et al., 2013; Harpenslager et al., 2015), as also observed in incubation studies (Zak and Gelbrecht, 2007; Cabezas et al., 2012). Nutrient concentrations (NO_2^- , NH_4^+ , and PO_4^{3-}) at both study sites were significantly higher in the porewater than in the surface water, indicating the peat itself as the main source of nutrients for the overlying water, even 30 years after rewetting. This suggests that previously farmed, highly degraded peat soils contain and are thus able to leach large amounts of nutrients, which is in line with the high surface water DIN concentrations determined at DW immediately after rewetting.

The high N₂O saturations (up to 4000 %) at DW one week after rewetting indicated high microbial activity (see Sect. 4.1.2), likely fueled by the release of nutrients (Figure 15). A previous study showed that the state of peat degradation influences N₂O emissions after rewetting, with a higher degree of degradation and therefore a lower C:N ratio resulting in higher emissions (Liu et al., 2019). Lower C:N ratios originate either from drainage and the preferential mineralization of C or from fertilization, ultimately leading to an enrichment of N in the peat (Berglund et al., 2010; Krüger et al., 2015). These high N loads can strongly increase the production of N₂O (e.g., Chmura et al., 2016; Roughan et al., 2018), as was observed at DW. In contrast to DW, N₂O saturation at KW did not reach a corresponding peak; instead, much lower deviations around the N₂O equilibrium with the atmosphere were determined,

which indicated a more balanced system that has mostly equilibrated with the atmosphere 30 years after rewetting. Other studies from rewetted peatlands also reported such low N₂O emissions, in some cases even lower than those from pristine peatlands (e.g., Minkkinen et al., 2020).

My results strongly suggest that the abiotic conditions and nutrient concentrations within the peat are among the most important drivers of N cycling. The high N₂O peak at DW immediately after rewetting indicated that the rapid increase in nutrient concentrations promoted microbial processes such as nitrification and denitrification, resulting in the production of N₂O. During nitrification, N₂O is produced as a side-product and therefore is more likely to be released into the environment than during denitrification, where it is an intermediate that is further reduced to N₂ (e.g., Stein and Yung, 2003). However, nitrification rates in the surface water remained low and other studies point to denitrification rather than nitrification as the dominant process of N₂O production in a fully water-saturated peat soil (Pihlatie et al., 2004; Masta et al., 2022), as was also present in my study sites due to a permanent inundation. Pihlatie et al. (2004) showed (1) that N₂O production was four orders of magnitude higher in fully water-saturated peat (100 % water-filled pore space, WFPS) than in less water-saturated peat (40 % WFPS) and (2) that the contribution of nitrification decreased with increasing water saturation. Thus, it is likely that denitrification was the dominant process of N₂O production in both study sites.

To gain an idea about the potential importance of denitrification on N₂O production, N₂ production rates were determined by measuring the change in N₂:Ar ratios in sediment core incubations. Sediment cores could only be obtained from KW and thus, a comparison of both peatlands cannot be conducted. At KW, four out of six measurements revealed a net N₂ production, which might have been due to denitrification. No correlation between N₂ production rates and N₂O concentrations was found, which suggests a spatial decoupling of the process (occurring in the sediment) and its potential product (measured in the overlying water). However, the general pattern of higher N₂ production rates in winter and autumn, coinciding with highest NO₃⁻ concentrations, and vice versa, was evident (e.g., Seitzinger and Nixon,

Discussion

1985; Deek et al., 2013). Negative N₂ production rates in summer and early autumn, indicating N₂ fixation, revealed that the system can temporarily fix new N although NO₂⁻ and NH₄⁺ were still present in the peat soil (e.g., Fulweiler et al., 2007).

Despite of the availability of NH₄⁺ in the peat, nitrification rates were rather low and did not seem to play a major role. These low nitrification rates at both sites are difficult to explain. especially since these are the first such measurements. Surprisingly, a higher NH₄⁺ availability at DW did not increase nitrification rates which were overall comparable to rates e.g. determined in the coastal waters of the Bay of Gdansk (Bartl et al., 2018). However, when strong resuspension occurs, high rates are possible (e.g., Happel et al., 2018), as was observed at KW, where nitrification rates reached ~600 nmol L⁻¹ d⁻¹ during a resuspension event. This high nitrification potential may be restricted to the availability of particulate matter, due to the preferential association of nitrifiers with particles (e.g., Brion et al., 2000; Kache et al., 2021). Another reason for overall low nitrification rates might have been the competition for NH₄⁺ between nitrification and heterotrophic NH₄⁺ assimilation. The latter is conducted by bacteria which were found to be temperature-dependent (Middelburg and Nieuwenhuize, 2000), whereas nitrification was revealed as being temperature-independent (Baer et al., 2014). Thus, heterotrophic NH₄⁺ assimilation rates are usually highest in summer (Baer et al., 2014; Bartl et al., 2018), restricting nitrification. At KW, nitrification accounted for 13.5 % (mean of all seasons) of the total dark NH₄⁺ consumption, with the highest contributions occurring in winter and autumn (15 – 26 %). At DW, nitrification accounted for only 2.0 % (mean of all seasons) of the total dark NH4⁺ consumption. These low contributions indicate that heterotrophic NH₄⁺ assimilation by bacteria outcompeted nitrification by far, likely contributing to the observed low nitrification rates. Finally, a third reason for low nitrification rates may be due to the sample processing. Bartl et al. (2018) found that the production of $^{15}N-NO_3^- + NO_2^$ via nitrification displayed a linear increase over 96 h. However, it is not possible to completely exclude the occurrence of ammonification that might have taken place during the incubation. Ammonification, the transformation of OM into NH_4^+ , can lead to the dilution of the tracer substrate (δ^{15} N-NH₄⁺) and ultimately, promote an underestimation of nitrification rates.

Both peatlands were not only sources but also occasionally sinks for NO₃⁻ and N₂O, as indicated by lower NO₃⁻ concentrations in the porewater than in the surface water and by N₂O saturations < 100 %. When the peat is constantly water-saturated, the O₂ saturation sinks and the soil very likely becomes hypoxic or anoxic. However, as no O₂ measurements in the soil were conducted, I can only speculate that O₂ was quickly depleted within the first few centimeters or even millimeters, as is known for wet peatlands (e.g., Joosten and Clarke, 2002). The occasional undersaturation of N₂O in the surface water at DW in spring and summer can be explained by a switch from oxic to hypoxic/anoxic conditions within the peat, favoring microbial processes that consume NO₃⁻ and N₂O, such as denitrification or dissimilatory NO₃⁻ reduction to NH₄⁺ (DNRA). Ultimately, these processes lead to the termination of N₂O emissions that occurs after rewetting measures (e.g., Regina et al., 1999; Strack, 2008), allowing rewetted peatlands to even become a sink for N₂O (Minkkinen et al., 2020), which is in agreement with my results.

Concerning the cycling of P, it was noticeable that the two study sites seemingly retained the majority of PO₄³⁻ in the peat throughout the year, as indicated by porewater PO₄³⁻ concentrations that were one order of magnitude higher than those in the surface water. This is in contrast to previous studies, which reported that the availability of SO₄²⁻, such as in brackish water, can lead to the mobilization of P and its subsequent leaching out of the soil (Lamers et al., 2002; Zak et al., 2009). Under oxic conditions, P is usually bound to Fe hydroxides and thus, stays in the sediment/soil. Under anoxic conditions and with a high availability of decomposable organic matter, however, SO₄²⁻ is reduced by sulfate-reducing microorganisms to hydrogen sulfide (H₂S), which is able to cause a reductive dissolution of Fe-P compounds (e.g., Zak et al., 2009). As a result, the dissolution leads to a lower availability of Fe(III) hydroxides and a lower binding capacity for P, so that P gets immobilized.

At DW, the inflow of SO_4^{2-} -containing brackish water may have had a short-term influence on the mobilization of P, as the highest PO_4^{3-} concentration in the surface water (mean of ~1.2 µmol L⁻¹) was measured one week after the rewetting. However, this highest surface water concentration did not reach the PO_4^{3-} concentrations of the porewater by far

(mean of ~40 µmol L⁻¹). At KW, the same pattern of a short-term impact was found. During one sampling, the highest observed water level (~60 cm above the local mean water level), among all the samplings I conducted, coincided with the highest PO_4^{3-} concentration of 7 µmol L⁻¹ in the surface water. This P release might have been due to the flooding of usually non-flooded areas, which released PO_4^{3-} after the intrusion of SO_4^{2-} into the peat. Since I did not conduct any O_2 , Fe, SO_4^{2-} , or H₂S measurements in the peat, I can only speculate that the intrusion of SO_4^{2-} led to a lower availability of Fe hydroxides so that P was ultimately released.

The overall low PO_4^{3-} concentrations in the surface water at both study sites indicated that most P was likely rather retained within the peat. This retention might have been due to the presence of microbial mats on the peat surface that accumulated PO_4^{3-} . At least at KW, filamentous microbial mats were found to significantly reduce the release of PO_4^{3-} into the surface water by accumulating it into polyphosphates (Choo et al., 2022). Although Choo et al. (2022) sampled other stations at KW, the presence of microbial mats at my stations seems likely since I occasionally observed some growth of filamentous bacteria in my sediment cores. Overall, it is likely that a combination of chemical and biological processes led to the pronounced gradient of PO_4^{3-} concentrations between the surface water and the porewater.

4.2.1.2 Particulate organic matter cycling

To identify the state and source of POM, C:N and POC:Chlorophyll-*a* ratios can be used to distinguish between marine vs. terrestrial and fresh vs. degraded POM.

A C:N ratio > 12 reflects terrestrial POM, and a ratio < 12 is attributable to phytoplankton-derived POM (Savoye et al., 2003). It is likely that during spring and summer, most of the POM at KW and DW originated from phytoplankton growth, since the majority of C:N ratios were < 12 (Savoye et al., 2003) and the Chlorophyll-*a* concentrations were high. In summer, Chlorophyll-*a* and POM concentrations were highest at both sites, however, concentrations were significantly higher at DW than at KW (Figure 13). The higher phytoplankton growth at DW was likely due to a higher nutrient availability, supporting my hypothesis that higher nutrient concentrations generate higher biomass production.
According to Cifuentes et al. (1988), a POC:Chlorophyll-*a* ratio < 200 indicates fresh phytoplankton and a ratio > 200 degraded phytoplankton. At DW, the majority of the POC:Chlorophyll-*a* ratios were < 200, consistent with the presence of fresh plankton. However, even during the highest phytoplankton growth, POM was probably actively degraded at the same time, as suggested e.g. by the low pH of 7.4 at DW during summer, attributable to the dominance of OM remineralization and the production of CO_2 (Figure 9; e.g., Zhou et al., 2021). At KW, POC:Chlorophyll-*a* ratios were mostly > 200 during all seasons, consistent with the availability of more degraded phytoplankton (Cifuentes et al., 1988).

Overall, the higher nutrient and OM availability at DW offer an explanation for the up to ten times higher phytoplankton growth than at KW. As noted above, the POM at DW derived mostly from freshly produced phytoplankton; however, there were also clear signs of the remineralization of POM during summer, likely due to the die-back of inundated vegetation. At KW, the POM pool was characterized by both fresh and degraded phytoplankton.

4.2.2 Nutrient exports into coastal areas and comparisons with rivers

Higher N nutrient concentrations (NO₃⁻ and NH₄⁺, as the most abundant species) in the bay off DW, compared to the monitoring stations, support my hypothesis of a nutrient export from the freshly flooded peatland into coastal waters (Figure 7; Figure 12). N nutrient concentrations in the bay off KW were at or below the 95 % confidence level of the concentrations recorded at the monitoring stations, whereas the concentrations at the bay off DW were often much higher than the 95 % confidence level. This strongly suggests that the higher nutrient concentrations in the bay off DW were caused by the rewetting and the subsequent outflow of nutrient-enriched waters.

The potential importance of rewetted peatlands as a diffuse source of nutrients in coastal regions is well demonstrated by a comparison of the annual DIN-N and PO₄-P exports from KW and DW. The area-normalized DIN-N export from KW was 6.1 ± 20.3 t km⁻² yr⁻¹ whereas at DW it was 3-fold higher with 21.6 ± 34.8 t km⁻² yr⁻¹ (Supplementary Table 2). The high uncertainty range derives mostly from the seasonal, but also from the spatial differences

within the peatland areas. Due to the lack of comparable studies on nutrient exports from similar rewetted sites, I compared my data with mean river loads of the largest rivers entering the Baltic Sea and with the Warnow. All river loads were much lower than the exports from my study sites when the area-normalized exports are compared (Table 2). Area-normalized DIN-N loads are highest in the Oder and Vistula rivers, with a mean of 0.3 ± 0.1 t DIN-N km⁻² yr⁻¹ from 1995 to 2019 for both rivers (HELCOM, 2021). The Warnow River, near Rostock, drains ~3300 km² of mostly agriculturally used land, but exports only 0.4 t DIN-N km⁻² yr⁻¹ (HELCOM, 2021). When converted to absolute loads, ~41000 t DIN-N yr⁻¹ are delivered by the Oder River (HELCOM, 2021), compared to 10.8 and 21.5 t DIN-N yr⁻¹ at DW and KW, respectively. Areanormalized PO₄-P exports of my study sites were 0.5 ± 0.6 (DW) and 0.04 ± 1.8 t km⁻² yr⁻¹ (KW), while the highest river exports were those of the Vistula and Daugava rivers with 0.01 and 0.008 t km⁻² yr⁻¹ for the Vistula River and ~700 t yr⁻¹ for the Daugava River (HELCOM, 2021), whereas the value at DW and KW was 0.2 t yr⁻¹, respectively.

| site | area (km²) | DIN-N export | | PO ₄ -P export | | reference |
|---------------------|---------------|-----------------------------------|---|-----------------------------------|---|------------------|
| | | absolute (t yr ⁻¹) | area- normalized (t km ⁻² yr ⁻¹) | absolute (t yr ⁻¹) | area- normalized (t km ⁻² yr ⁻¹) | |
| Karrendorf (KW) | ~3.5 | 21.5 ± 71.0 | 6.1 ± 20.3 | 0.2 ± 6.3 | 0.04 ± 1.8 | this study |
| Drammendorf (DW) | ~0.9 | 10.8 ± 17.4 | 21.6 ± 34.8 | 0.2 ± 0.3 | 0.5 ± 0.6 | this study |
| Oder | ~119000 | ~41000 ± 15000 | 0.3 ± 0.1 | ~855 ± 530 | 0.007 ± 0.004 | HELCOM (2021) |
| Vistula | ~194000 | ~59000 ± 19000 | 0.3 ± 0.1 | ~2800 ± 1500 | 0.014 ± 0.008 | HELCOM (2021) |
| Daugava | ~88000 | ~18000 ± 4700 | 0.2 ± 0.1 | ~690 ± 250 | 0.008 ± 0.003 | HELCOM (2021) |
| Warnow | ~3000 | ~1200 ± 500 | 0.4 ± 0.2 | ~20 ± 7.6 | 0.007 ± 0.003 | HELCOM (2021) |

Table 2: Comparison of nutrient exports from coastal peatlands (this study) and from major rivers of the Baltic Sea

The much lower area-normalized loads of the rivers are the result of N and P retention processes along the water flow from surface soils to groundwater and to the coast, which

reduce loads by > 80 % (e.g., Seitzinger et al., 2006; Asmala et al., 2017; Xenopoulos et al., 2017). When coastal areas such as my study sites drain directly to the coastline, the transport time of the water is much shorter, leaving nutrient loads mostly unprocessed. Overall, my finding that the area-normalized DIN-N and PO₄-P exports of my study sites were much higher than the exports of some major rivers of the Baltic Sea suggests that KW and DW are significant sources of local nutrient inputs to coastal waters.

To evaluate the potential magnitude of nutrient inputs from coastal peatlands in MV, mean area-normalized exports determined in this thesis (13.9 t DIN-N km⁻² yr⁻¹ and 0.3 t PO₄-P km⁻² yr⁻¹; means of annual exports from both study sites) were extrapolated to the total area of coastal diked and undiked (possibly wet) peatlands used for agricultural purposes, which is ~225 km² according to Schiefelbein (2018). Thus, potential nutrient exports are ~3100 t DIN-N km⁻² yr⁻¹ and ~60 t PO₄-P km⁻² yr⁻¹, which are significant loads compared to those of the above-mentioned rivers. However, this extrapolation is a maximum estimate of potential exports; the nutrient reservoirs of other coastal peatlands may well be different from those of KW and DW. Nonetheless, small coastal catchments directly connected to coastal waters may contribute significantly to nutrient inputs into the Baltic Sea, thus highlighting the need for better monitoring strategies following rewetting measures.

4.2.3 Conclusions

Two rewetted coastal peatlands, both formerly used for agriculture, clearly differed in their nutrient reservoirs and nutrient cycling. The recently rewetted DW was characterized by a high seasonal dynamic in the first year after rewetting. The larger nutrient reservoir in the peat at DW suggests that the reservoir at KW has decreased since rewetting in 1993, as both sites have a comparable fertilization history.

My results suggest high microbial activity (nitrification and denitrification) within the peat. At KW, the retention of nutrients, e.g. NH_4^+ via nitrification and NO_3^- via denitrification, and the apparently close connection of these microbial processes ensure a well-balanced N cycle, with surface water nutrient concentrations similar to those of the Bodden and low phytoplankton growth. At DW, by contrast, nutrients leached out of the soil rather than being

retained, thus supporting a high phytoplankton production in the surface water in spring and summer.

The strong hydrological exchange between the peatlands and their adjacent bays resulted in a net nutrient export out of both peatlands. However, as KW has been rewetted for 30 years, the area-normalized DIN export amounted to 6.1 ± 20.3 t km⁻² yr⁻¹, representing only ~25 % of the export at DW which amounted to 21.6 ± 34.8 t km⁻² yr⁻¹; PO₄-P exports from the two sites were much lower (0.04 to 0.5 t km⁻² yr⁻¹), likely due to a pronounced retention of P. Compared to riverine exports, these exports are high and suggest an intense coastal eutrophication potential.

My calculations show that, despite being rewetted for decades, a peatland can still export nutrients into its adjacent waters, but the export rates will be highest immediately after rewetting and decrease over time. However, these potentially high, currently unmonitored nutrient inputs should be monitored regularly as they contribute to nutrient inputs from former agricultural (peat) soils.

4.3 Insights into processes and sources of POM and NO₃⁻ by means of stable isotopes

4.3.1 Sources and transformations of POM

Stable isotopes of POM can give insights into its sources and biological transformations. δ^{13} C-POC values are commonly used to identify the origin of POM, with low values of around –30 ‰ originating from terrestrial and higher values of around –22 ‰ from marine sources, while δ^{15} N-PON values reveal biological processes like assimilation by phytoplankton or remineralization (e.g., McClelland and Valiela, 1998; Kendall et al., 2001; Remeikaitė-Nikienė et al., 2017). The C:N ratio, as well as the Chlorophyll-*a* concentration can additionally provide information on the status of POM (fresh vs. degraded), as discussed in Sect. 4.2.1.2. Generally, increasing C:N ratios indicate remineralization that leads to the preferential degradation of N and thus, higher C:N ratios (Cifuentes et al., 1988; Savoye et al., 2003).

At both study sites, δ^{13} C-POC values varied greatly over the year, ranging from –34 ‰ to –22 ‰ and thus, indicated the occurrence of both marine and terrestrial sources (e.g., Voss and Struck, 1997). This broad range likely reflected the highly dynamic water exchange with the Bodden, as was also indicated by similar environmental conditions in the peatlands and the respective bays of both study sites. While the values during winter were similar at both KW and DW, DW showed slightly higher δ^{13} C-POC values in spring which are indicative of marine POC, coinciding with elevated Chlorophyll-*a* concentrations. Thus, it seems reasonable that a marine phytoplankton bloom occurred at DW, probably fueled by the high nutrient availability.

During summer, δ^{13} C-POC values at KW and DW started to differ significantly due to decreasing values at DW and increasing values at KW. The low δ^{13} C-POC values at DW (around -32 %), together with the lowest pH of 7.4, suggested that most POC was remineralized (e.g., Zhou et al., 2021) and of terrestrial origin (Figure 17), possibly from the peat itself (-29.2 ‰; Müller and Voss, 1999), dead macrophytes such as *Phragmites australis* (-27.0 ‰; Müller and Voss, 1999), or grassland vegetation that died after the rewetting. However, highest Chlorophyll-*a* concentrations and decreasing C:N ratios during summer

indicated that phytoplankton growth occurred simultaneously with remineralization at DW, but the latter seemed to be the dominant process. At KW, increasing δ^{13} C-POC values (between -28 ‰ and -24 ‰), elevated Chlorophyll-*a* concentrations and lowest C:N ratios during summer were likely due to the inflow of growing marine phytoplankton. This contrasts with the definition of fresh vs. degraded POM by Cifuentes et al. (1988), which identified most POM at KW as degraded rather than freshly produced (see Sect. 4.2.1.2). However, previously reported δ^{13} C-POC values for growing, marine phytoplankton in nearby areas include -23.8 ‰ in the Arkona Basin (Voss and Struck, 1997) and -25.1 ‰ in the Greifswalder Bodden (Müller and Voss, 1999), fitting well to the observed values at KW.

During autumn, both sites showed the same pattern of increasing δ^{13} C-POC values and C:N ratios. This likely indicated the remineralization of POM originating from the Bodden. A potentially higher exchange with the adjacent Bodden is emphasized by the water level dynamics (see Supplementary Figure S4) that showed more frequent fluctuations and generally higher water levels during autumn.

 $δ^{15}$ N-PON values revealed a rather untypical seasonality, especially at KW, and did not correlate with any variable. In general, decreasing nutrient concentrations towards summer are accompanied by increasing $δ^{15}$ N-PON values (e.g., Savoye et al., 2003). This is due to the preferential uptake of ¹⁴N leading to an isotopically heavier DIN pool over time and thus to highest $δ^{15}$ N-PON values during the growing season in which this heavier pool is consumed by phytoplankton. However, this pattern was not observed in either of the two study sites. Instead, the highest $δ^{15}$ N-PON values were found in winter and autumn, accompanied by the highest nutrient concentrations and C:N ratios. There are two conceivable explanations for this pattern. As mentioned above, the amplitude of water level fluctuations was higher in winter and autumn (Supplementary Figure S4) and δ^{15} N-PON values were occasionally higher in the bay than in the peatland (Supplementary Figure S8). The local planktonic community of the Bodden may have had δ^{15} N-PON values similar to those determined for the Greifswalder Bodden (12.6 ‰) and for the Oder estuary (15.5 ‰) by Müller and Voss (1999), which are in the range of δ^{15} N-PON values found in both study sites. Hence, these findings indicate a stronger

hydrological exchange with the adjacent Bodden. In addition, high remineralization, which is known to increase δ^{15} N-PON (e.g., Möbius, 2013), may also has been involved in the increase of δ^{15} N-PON values in winter and autumn.

At KW, exceptionally high δ^{15} N-PON values of ~32 ‰ were observed once in January when the water level was unusually high. They coincided with the highest C:N ratio of ~10.5 and occurred about one month after a strong resuspension event. Müller and Voss (1999) investigated the isotopes of POM within a peat soil and reported a δ^{15} N-PON value of 4.9 ‰. Hence, the occurrence of resuspended peat as a potential source of high δ^{15} N-PON values can likely be excluded. To my knowledge, there is no literature reporting such high δ^{15} N-PON values. Therefore, it is not possible to trace the high values at KW back to a specific source.

During summer, the low δ^{15} N-PON values might have originated from the uptake of remineralized DIN species that derived from an intense nutrient cycling. This uptake was found to result in low ¹⁵N values and thus, leads to low ¹⁵N in phytoplankton communities (e.g., Savoye et al. (2003) and references therein). Although the nutrient concentrations were low throughout spring and summer, it seems reasonable that these were the result of intense nutrient cycling and uptake at both sites, rather than of constantly depleted nutrient pools with a low biological activity.

4.3.2 N and O isotopes in NO₃⁻

In the next two sections, I discuss the potential processes and sources of NO_3^- that may have had an impact on its isotopic values. However, it has to be considered that the data sets of DW and KW contain a different number of values (n = 29 and n = 14, respectively), where values of DW originate mainly from winter and autumn, while values of KW cover all seasons.

4.3.2.1 Identification of potential processes

When NO₃⁻ is assimilated or denitrified by primary producers or microorganisms, the remaining NO₃⁻ pool becomes isotopically enriched due to the preferential consumption of ¹⁴N by microbial processes and thus, the NO₃⁻ concentration decreases while δ^{15} N-NO₃⁻ increases with time (e.g., Fry, 2006). Taking also δ^{18} O-NO₃⁻ into account, NO₃⁻ assimilation and

denitrification yield to a regression line slope of 1 when δ^{15} N-NO₃⁻ is plotted against δ^{18} O-NO₃⁻ (Granger et al., 2004), while a slope of > 1 indicates nitrification (e.g., Wankel et al., 2007).

At KW, a significant negative correlation of the NO₃⁻ concentration vs. δ^{15} N-NO₃⁻ hinted towards assimilation or denitrification (Figure 20). δ^{15} N-NO₃⁻ did not correlate with Chlorophyll-*a* or δ^{15} N-PON and thus, the dominance of assimilation was not reflected when additional variables were considered. However, the fractionation factor of all δ^{15} N-NO₃⁻ values was 1.012, indicating NO₃⁻ uptake into POM (Montoya, 1994). Denitrification might also have been important, either happening in the water column or in the peat. According to Broman et al. (2021), denitrification is possible in an oxic water column if low-oxygen microniches such as organic particles are available, as was occasionally the case at both study sites due to resuspension. Denitrification likely played a major role in the peat as was indicated by lower NO₃⁻ concentrations in the porewater than in the overlying water and by highest N₂ production rates, as indicator of denitrification activity, during highest NO₃⁻ concentrations (winter and autumn).

The correlation of δ^{15} N-NO₃⁻ vs. δ^{18} O-NO₃⁻ at KW, however, yielded to a slope of 2.4 and thus, revealed a potential importance of nitrification. Its importance was further indicated by a negative correlation of nitrification rates with δ^{15} N-NO₃⁻ values and positive correlations of nitrification rates with NO₃⁻ and NH₄⁺ concentrations. Although nitrification rates were generally low at KW, it became clear that the potential for nitrification is very high, as was seen during a high resuspension event in December 2019 where the highest rates (up to 600 nmol L⁻¹ d⁻¹) were measured. As already discussed in Sect. 4.2.1, it seems likely that the highest nitrification activity did not occur in the water column, but in the peat soil. This is in line with other studies that have observed the highest nitrification rates in areas such as the maximum turbidity zone of rivers, due to the preferred particle attachment of nitrifiers (e.g., Xia et al., 2009; Damashek et al., 2016; Zhu et al., 2018; Kache et al., 2021).

 δ^{18} O-H₂O values can be used to further evaluate the potential importance of nitrification. During nitrification, approximately five out of six O atoms are incorporated from the water, while the sixth O atom is taken from dissolved O₂ (Casciotti et al., 2002; Sigman et al.,

2009). Taking this ratio and the isotopic values of both sources into account, the theoretical δ^{18} O-NO₃⁻ originating from nitrification can be calculated (see Sect. 2.3.6, Eq. 4). The comparison of theoretical and measured values showed that the latter were always higher and thus, nitrification seemingly did not have a major impact on δ^{18} O-NO₃⁻ at either site. Instead, it seems reasonable that the high δ^{18} O-NO₃⁻ values were caused by NO₃⁻ sources with different values, which will be discussed below.

At DW, NO₃⁻ concentrations did not correlate with δ^{15} N-NO₃⁻. Although the range of NO₃⁻ concentrations was much larger than at KW, δ^{15} N-NO₃⁻ values were less fluctuating. Additionally, no correlations were found for δ^{15} N-NO₃⁻ vs. δ^{18} O-NO₃⁻, theoretical vs. measured δ^{18} O-NO₃⁻ values, and δ^{15} N-NO₃⁻ vs. nitrification rates. This lack of correlations indicated that there was likely no single biological process shaping the NO₃⁻ isotopes. However, a small cluster of lower δ^{15} N-NO₃⁻ values was noticeable that could clearly be differentiated from all other values, likely originating from nitrification. These lower δ^{15} N-NO₃⁻ values were found in November and December 2020, separately assigned to autumn and winter. It can be assumed that NO₃⁻ production via nitrification was responsible for these values, since nitrification rates were highest during autumn. Low δ^{15} N-NO₃⁻ values could also have originated from N₂ fixation, which adds isotopically lighter NO₃⁻ to the N pool (e.g., Liu et al., 1996; Bourbonnais et al., 2009). However, N₂ fixation is generally known to be more likely to occur in pristine peatlands due to their naturally low N pool (e.g., Vile et al., 2014) and therefore, was an unlikely process at DW. Finally, the input of lower δ^{15} N-NO₃⁻ values from the bay off DW can be excluded since differences between the peatland and the bay were minor (Supplementary Figure S8).

4.3.2.2 Identification of potential sources

To identify potential NO₃⁻ sources, both N and O isotopes are commonly used to distinguish different sources such as nitrification, fertilizer, atmospheric deposition, soil N and manure/sewage (e.g., Kendall, 1998; Mayer et al., 2002; Kaushal et al., 2011).

For both study sites, the isotope data of NO₃⁻ revealed that NO₃⁻ derived mainly from manure and/or fertilization (Figure 22). Generally, these two sources have higher δ^{15} N-NO₃⁻ (manure) and δ^{18} O-NO₃⁻ (fertilizer) values compared to NO₃⁻ from natural sources like the soil

or nitrification. Consequently, they have been used to verify the impact of anthropogenic N inputs e.g. into coastal environments (e.g., Voss and Struck, 1997; Deutsch et al., 2006; Voss et al., 2006). NO₃⁻ from fertilizers is known to leach from soils because it is negatively charged like most soils in temperate regions and thus not retained in the soil (Di and Cameron, 2002). Therefore, due to the agricultural history of both study sites, including the use of fertilizers and manure, it seems reasonable that the isotopic signature of NO₃⁻ displays its anthropogenic origin.

At DW, a clearly distinguishable cluster of δ^{15} N-NO₃⁻ values < 5 ‰ was observed in autumn (November 2020) and winter (December 2020) and thus, one year after the rewetting. Although these values were still in the range of manure, there was a clear shift towards isotopically depleted NO₃⁻ which might have been the result of nitrification. This assumption is supported by the increasing NH₄⁺ and NO₂⁻ concentrations in autumn and the highest nitrification rate of ~28 nmol L⁻¹ d⁻¹ in November 2020. It is a hint towards a shift from NO₃⁻ just being present in the peat and released into the water to NO₃⁻ being produced internally, likely fueled by the huge reservoir of NH₄⁺ within the peat.

At KW, some data points did not match with the NO₃⁻ sources defined by Kendall (1998). During most seasons, except winter, some high δ^{15} N-NO₃⁻ values of 15 – 18 ‰ and δ^{18} O-NO₃⁻ values of 20 – 45 ‰ occurred. One or more of the following three reasons have likely been responsible for this finding: 1) some input of NO₃⁻ from atmospheric deposition/precipitation occurred, 2) biological processes led to an isotopic enrichment of both δ^{18} O-NO₃⁻ and δ^{15} N-NO₃⁻ and 3) NO₃⁻ within the peatland was mixed with NO₃⁻ from the bay, where δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ were generally higher in all seasons (Supplementary Figure S8). The influence of precipitation can be estimated by taking the precipitation heights of nearby monitoring stations into account (DWD data; stations "Putbus", WMO-ID 10093, and "Greifswald", WMO-ID 10184). The highest δ^{18} O-NO₃⁻ values occurred in summer (of 2019), however, the monthly precipitation heights in summer were lower than e.g. in autumn, where the δ^{18} O-NO₃⁻ values decreased again (Supplementary Figure S3). Daily precipitation data

revealed no heavy rainfalls shortly before the samplings (Supplementary Figure S9) and thus, it seems likely that precipitation did not have a major influence on the δ^{18} O of NO₃⁻.

Alternatively, biological processes could have influenced the isotopic composition of NO_3^- due to fractionation. As already discussed in Sect. 4.2.1 and 0.3.2.1, no clear signs of one dominating process were found. Instead, several correlations between different variables indicated the simultaneous occurrence of assimilation, nitrification, and denitrification, thus shaping the isotopes of NO_3^- collectively. However, since the data points that did not match the defined sources occurred during the growing season, it appears reasonable that NO_3^- consuming processes, such as assimilation or denitrification, have been responsible for the observed increase of $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values at KW towards summer.

4.3.3 Conclusions

The isotope data of POM and NO_3^- confirmed that the exchange between the peatlands and the bays, but also between the water and the peat soil was highly pronounced.

 δ^{13} C-POC values of the peatlands revealed a mixture of marine and terrestrial POC, highlighting the intense water exchange with the adjacent Bodden as source of marine POM. Lower δ^{13} C-POC values at DW during summer were likely due to the die-back and remineralization of inundated vegetation, which was not removed prior to rewetting.

 δ^{15} N-PON values displayed a rather untypical seasonality at both sites. Instead of increasing values towards summer, which are usually found due to decreasing N pools as a result of assimilation, δ^{15} N-PON values decreased and were lowest during the growing season. It is likely that this was the result of high remineralization, occurring together with high assimilation. A broader range of δ^{15} N-PON values at KW was indicative of a smaller N pool and more intense cycling that led to higher fluctuations than at DW.

 δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ values revealed a different internal NO₃⁻ cycling between both sites. At KW, some correlations indicated that NO₃⁻ was strongly influenced by simultaneously occurring biological processes like assimilation by phytoplankton or denitrification and nitrification by bacteria and archaea. At DW, NO₃⁻ was rather only leaching out of the peat in large amounts. No clear signs of biological transformations were found at DW, except for a

potential nitrification signal in the second winter after rewetting. Additionally, the historical farming and fertilization practices at both sites were clearly reflected in their isotope data. Especially in the colder seasons, the isotopic signature in both peatlands revealed the agricultural origin of NO_3^- . At DW, it was evident that the high amounts of NO_3^- in winter, right after rewetting, originated from the huge reservoir in the peat.

Overall, it needs to be considered that most isotope data of NO_3^- for DW originated from winter and autumn. Thus, the main growing seasons with the highest potential to biologically influence NO_3^- can neither be assessed, nor compared between the study sites.

5. Final conclusions and outlook

The importance of wet peatlands in terms of their long-term storage of C and N has gained global attention. Worldwide, many peatlands are drained for decades to be used for agricultural purposes, resulting in high emissions of CO₂ and N₂O due to the remineralization of the peat. Thus, rewetting measures are necessary to not only stop these GHG emissions, but to restore the natural capacity to take GHG up and to fight climate change.

Due to their agricultural history, including the use of fertilizers, drained peatlands are highly nutrient-enriched within the peat soil compared to their natural counterparts. While nutrient inputs from rivers are generally well-monitored, diffuse surface runoff from small catchments, such as peatlands along the coast, are mostly unconsidered. At the coast, lowlying, drained peatlands are prone to become affected by rising sea levels and increased storm surges in the future. Thus, their rewetting is conducted to re-establish buffer zones at the terrestrial-marine interface to mitigate more frequent storm surges and to restore their natural filter function. However, the consequences on nutrient cycling and potential leaching, especially to adjacent coastal waters, is not well-studied and still needs to be quantified.

This thesis aimed to unravel how the rewetting of coastal, formerly drained peatlands affects their N cycling and potential nutrient (DIN and PO₄³⁻) exports into adjacent coastal waters. To address this aim, three hypotheses were worked on: 1) Rewetting leads to the leaching of nutrients out of the peat and subsequently, into adjacent waters, 2) the freshly rewetted peatland (DW) contains more nutrients within the peat, leading to more leaching and a higher N turnover than within the longer rewetted peatland (KW), and 3) local POM and NO₃⁻ processes and sources differ between the two rewetted peatlands due to their different rewetting stages, as revealed by stable isotope signatures.

My results indicate that rewetting with brackish water led to an immediate leaching of nutrients shortly after rewetting. Nutrient concentrations were higher in the porewater than in the surface water and thus, nutrients likely originated from the formerly drained and fertilized peat. Ultimately, these nutrients were exported into adjacent coastal waters within weeks after

rewetting, as was indicated by higher nutrient concentrations in the bay off DW compared to pre-rewetting conditions and to data of an unaffected nearby monitoring station.

At both study sites, nutrient concentrations in the porewater, except of NO₃, were one order of magnitude higher than in the surface water. This suggests that peat soils can still be highly nutrient enriched, even if the rewetting was conducted 30 years ago. However, surface water concentrations at DW were significantly higher than those at KW only in winter, the first season after its rewetting. Both sites had a net nutrient export of both DIN and PO₄³⁻, with the highest exports occurring in winter and autumn. Annual DIN exports were 75 % lower at KW than at DW, revealing that the nutrient reservoir in the peat is still large enough to allow an export even after 30 years of rewetting. Since my nutrient export calculations were, to my knowledge, the first ones to quantify the eutrophication potential of coastal rewetted peatlands, no comparisons with similar sites are possible. Instead, I used riverine nutrient inputs to relate my calculations to these export numbers. As a result, I found that both study sites exported much more nutrients per area, especially DIN, than the biggest rivers entering the Baltic Sea.

The investigation of the internal N turnover revealed significant differences across both study sites. At DW, phytoplankton growth was much higher in summer, with up to ten times higher Chlorophyll-*a* concentrations than at KW. Both peatlands showed signs of simultaneous phytoplankton growth and remineralization, indicating that these processes were closely linked. δ^{13} C-POC values revealed both terrestrial and marine POM sources at both sites, however, DW was clearly dominated by terrestrial C in summer that likely originated from the remineralization of inundated vegetation. Surprisingly, nitrification rates were generally higher at KW than at DW, despite a lower nutrient availability. Together with the finding that the surface water nutrient concentrations at KW were always similar compared to the Greifswalder Bodden, it seems reasonable that microbial processes at KW are already established so that nutrients are rather retained than washed out. Isotope data of NO₃⁻ confirmed that, especially during the growing season, NO₃⁻ was strongly consumed and transformed at KW, with no clear signs of a single dominant process. Due to lacking isotope data of NO₃⁻ at DW, a direct comparison of the growing season is not possible.

In general, a highly pronounced exchange between the surface water and the peat, as well as an intense cycling within the peat was evident at both study sites. Nutrient exports at DW were much higher than at KW, suggesting that its internal turnover was not sufficient to fully retain the huge nutrient reservoir. However, both sites had in common that NO₃⁻ was at times obviously consumed within the peat and thus, removed from the system, as indicated by lower NO₃⁻ concentrations in the porewater. This demonstrates that nutrient species need to be investigated separately to be able to evaluate their different cycling patterns, influencing the assessment of the whole system. The main origin of NO₃⁻ at both study sites was clearly confirmed by their isotope data. As expected, the majority of NO₃⁻ originated from their former agricultural history, especially during winter. Additionally, the data revealed that biological transformations also had an influence on the NO₃⁻ pool at both sites, leading to deviations from the isotopic signature of manure.

Overall, this thesis revealed that rewetted coastal peatlands can contribute to coastal eutrophication by releasing high amounts of artificially enriched nutrients, mostly driven by their highly dynamic water exchange with the adjacent coast. Although most coastal peatlands are rather small compared to e.g. river catchment areas, their nutrient reservoirs and exports appear to be large. Topsoil removal is already known to be an efficient measure prior to rewetting to eliminate a large fraction of nutrients, however, this measure is not always feasible. Due to rising sea levels and actively induced rewetting measures, more coastal peatlands with huge reservoirs of nutrients will be flooded in the near future. Thus, future rewetting measures should monitor nutrient dynamics to be able to estimate and consider the eutrophication potential of coastal peatlands. Additionally, it needs to be considered that in contrast to rivers, nutrients from coastal peatlands are exported mostly unfiltered due to the close vicinity to the coast. Although the highest amount of nutrients is released right after rewetting, a nutrient export can occur even 30 years after rewetting. Nevertheless, it seems that rewetted coastal peatlands can slowly shift their nutrient cycling towards a system with a high retention and even removal potential, so that the natural filter function might be re-established within a few decades.

6. References

- Asmala, E., Carstensen, J., Conley, D. J., Slomp, C. P., Stadmark, J., & Voss, M. (2017). Efficiency of the coastal filter: Nitrogen and phosphorus removal in the Baltic Sea. *Limnology and Oceanography*, 62, S222–S238. https://doi.org/10.1002/lno.10644
- Augustin, J., Merbach, W., & Rogasik, J. (1998). Factors influencing nitrous oxide and methane emissions from minerotrophic fens in northeast Germany. *Biology and Fertility of Soils*, 28(1), 1–4. https://doi.org/10.1007/s003740050455
- Augustin, J. (2003). Gaseous emissions from constructed wetlands and (re)flooded meadows.
 In: International Conference: Constructed and Riverine Wetlands for Optimal Control of Wastewater at Catchment Scale, Mander, Ü., Vohla, C., and Poom, A. (Eds.), Tartu Univ. Press. ISBN 9985-4-0356-8
- Baer, S. E., Connelly, T. L., Sipler, R. E., Yager, P. L., & Bronk, D. A. (2014). Effect of temperature on rates of ammonium uptake and nitrification in the western coastal Arctic during winter, spring, and summer. *Global Biogeochemical Cycles*, 28, 1455–1466. https://doi.org/10.1111/1462-2920.13280
- Bartl, I., Liskow, I., Schulz, K., Umlauf, L., & Voss, M. (2018). River plume and bottom boundary layer Hotspots for nitrification in a coastal bay? *Estuarine, Coastal and Shelf Science*, 208, 70–82. https://doi.org/10.1016/j.ecss.2018.04.023
- Berglund, Ö., Berglund, K., & Klemedtsson, L. (2010). A lysimeter study on the effect of temperature on CO2 emission from cultivated peat soils. *Geoderma*, *154*(3–4), 211–218. https://doi.org/10.1016/j.geoderma.2008.09.007
- Beusen, A. H. W., Bouwman, A. F., Van Beek, L. P. H., Mogollón, J. M., & Middelburg, J. J. (2016). Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum. *Biogeosciences*, *13*(8), 2441– 2451. https://doi.org/10.5194/bg-13-2441-2016
- Bockholt, R. (1985). Flächen-. Ertrags- und Problemanalyse des Überschwemmungsgrünlandes der Ostsee-, Bodden- und Haffgewässer, Forschungsbericht Universität Rostock. 17 pp.
- Böttcher, M. E., & Schmiedinger, I. (2021). The impact of temperature on the water isotope (2H/1H, 17O/16O, 18O/16O) fractionation upon transport through a low-density polyethylene membrane. *Isotopes in Environmental and Health Studies*, 57(2), 183–192. https://doi.org/10.1080/10256016.2020.1845668
- Bourbonnais, A., Lehmann, M. F., Waniek, J. J., & Schulz-Bull, D. E. (2009). Nitrate isotope anomalies reflect N2 fixation in the Azores Front region (subtropical NE Atlantic). *Journal of Geophysical Research: Oceans*, *114*(3), 1–16. https://doi.org/10.1029/2007JC004617
- Brion, N., Billen, G., Guezennec, L., & Ficht, A. (2000). Distribution of nitrifying activity in the Seine River "France" from Paris to the estuary. *Estuaries*, 23(5), 669–682. https://doi.org/10.2307/1352893
- Broman, E., Zilius, M., Samuiloviene, A., Vybernaite-Lubiene, I., Politi, T., Klawonn, I., Voss, M., Nascimento, F. J. A., & Bonaglia, S. (2021). Active DNRA and denitrification in oxic hypereutrophic waters. *Water Research*, 194, 116954. https://doi.org/10.1016/j.watres.2021.116954
- Buchwald, C., & Casciotti, K. L. (2010). Oxygen isotopic fractionation and exchange during bacterial nitrite oxidation. *Limnology and Oceanography*, *55*(3), 1064–1074. https://doi.org/10.4319/lo.2010.55.3.1064
- Burgin, A. J., & Groffman, P. M. (2012). Soil O2 controls denitrification rates and N2O yield in a riparian wetland. *Journal of Geophysical Research: Biogeosciences*, *117*(1), 1–10. https://doi.org/10.1029/2011JG001799
- Cabezas, A., Gelbrecht, J., Zwirnmann, E., Barth, M., & Zak, D. (2012). Effects of degree of peat decomposition, loading rate and temperature on dissolved nitrogen turnover in rewetted fens. *Soil Biology and Biochemistry*, *48*, 182–191. https://doi.org/10.1016/j.soilbio.2012.01.027

- Carstensen, J., Conley, D. J., Almroth-Rosell, E., Asmala, E., Bonsdorff, E., Fleming-Lehtinen, V., Gustafsson, B. G., Gustafsson, C., Heiskanen, A. S., Janas, U., Norkko, A., Slomp, C., Villnäs, A., Voss, M., & Zilius, M. (2020). Factors regulating the coastal nutrient filter in the Baltic Sea. *Ambio*, 49(6), 1194–1210. https://doi.org/10.1007/s13280-019-01282-y
- Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. K., & Hilkert, A. (2002). Measurement of the oxygen isotopic composition of nitrate seawater and freshwater using the dentirifier method. *Anal. Chem.*, 74(19), 4905–4912. https://doi.org/10.1021/ac020113w
- Casciotti, K. L. (2016). Nitrogen and Oxygen Isotopic Studies of the Marine Nitrogen Cycle. Annu. Rev. Mar. Sci., Vol. 8, 379–407. 10.1146/annurev-marine-010213-135052
- Chmura, G. L., Kellman, L., Van Ardenne, L., & Guntenspergen, G. R. (2016). Greenhouse gas fluxes from salt marshes exposed to chronic nutrient enrichment. *PLoS ONE*, *11*(2), 1–13. https://doi.org/10.1371/journal.pone.0149937
- Choo, S., Dellwig, O., Wäge-Recchioni, J., Schulz-Vogt, H.N. (2022). Microbial-driven impact on aquatic phosphate fluxes in a coastal peatland. *Marine Ecology Progress Series, 702,* 19–38. https://doi.org/10.3354/meps14210
- Cifuentes, L. A., Sharp, J. H., & Fogel, M. L. (1988). Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnology and Oceanography*, *33*(5), 1102–1115. https://doi.org/10.4319/lo.1988.33.5.1102
- Dalsgaard, T. (ed.), Nielsen, L.P., Brotas, V., Viaroli, P., Underwood, G., Nedwell, D. B., Sundbäck, K., Rysgaard, S., Miles, A., Bartoli, M., Dong, L., Thornton, D.C.O., Ottosen, L.D.M., Castaldelli, G. & Risgaard-Petersen, N. (2000): Protocol handbook for NICE – Nitrogen Cycling in Estuaries: a project under the EU research programme: Marine Science and Technology (MAST III). National Environmental Research Institute, Silkeborg, Denmark. 62 pp.
- Damashek, J., Casciotti, K. L., & Francis, C. A. (2016). Variable Nitrification Rates Across Environmental Gradients in Turbid, Nutrient-Rich Estuary Waters of San Francisco Bay. *Estuaries and Coasts*, 39(4), 1050–1071. https://doi.org/10.1007/s12237-016-0071-7
- Deek, A., Dähnke, K., Van Beusekom, J., Meyer, S., Voss, M., & Emeis, K. (2013). N2 fluxes in sediments of the Elbe Estuary and adjacent coastal zones. *Marine Ecology Progress Series*, 493, 9–21. https://doi.org/10.3354/meps10514
- Deutsch, B., Mewes, M., Liskow, I., & Voss, M. (2006). Quantification of diffuse nitrate inputs into a small river system using stable isotopes of oxygen and nitrogen in nitrate. *Organic Geochemistry*, *37*(10), 1333–1342. https://doi.org/10.1016/j.orggeochem.2006.04.012
- Di, H. J., & Cameron, K. C. (2002). Nitrate leaching in temperate agroecosystems: Sources, factors and mitigating strategies. *Nutrient Cycling in Agroecosystems*, 64(3), 237–256. https://doi.org/10.1023/A:1021471531188
- Ding, J., Xi, B., Gao, R., He, L., Liu, H., Dai, X., & Yu, Y. (2014). Identifying diffused nitrate sources in a stream in an agricultural field using a dual isotopic approach. *Science of the Total Environment*, 484(1), 10–18. https://doi.org/10.1016/j.scitotenv.2014.03.018
- Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R. S., Geider, R. J., Jickells, T., Kuypers, M. M., Langlois, R., Liss, P. S., Liu, S. M., Middelburg, J. J., Moore, C. M., Nickovic, S., ... Zamora, L. (2008). Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science*, 320, 893–897. https://doi.org/10.1126/science.1150369
- Dugdale, R. C., & Wilkerson, F. P. (1986). the Use of N-15 To Measure Nitrogen Uptake in Eutrophic Oceans - Experimental Considerations. *Limnology and Oceanography*, 31(4), 673–689.
- Fiedler, J., Fuß, R., Glatzel, S., Hagemann, U., Huth, V., Jordan, S., Jurasinski, G., Kutzbach, L., Maier, M., Schäfer, K., Weber, T., & Weymann, D. (2022). *Measurement of carbon dioxide, methane and nitrous oxide fluxes between soil-vegetation-systems and the atmosphere using non-steady state chambers*.
- Fisher, J., & Acreman, M. C. (2004). Wetland nutrient removal: a review of the evidence. *Hydrology & Earth System Sciences*, *8*(4), 673–685.

- Flessa, H., Wild, U., Klemisch, M., & Pfadenhauer, J. (1998). Nitrous oxide and methane fluxes from organic soils under agriculture. *European Journal of Soil Science*, *49*(2), 327–335. https://doi.org/10.1046/j.1365-2389.1998.00156.x
- Fox, J. and Weisberg, S. (2019). An R Companion to Applied Regression. Third Edition. Thousand Oaks CA: Sage. https://socialsciences.mcmaster.ca/jfox/Books/Companion
- Frolking, S., Talbot, J., Jones, M. C., Treat, C. C., Kauffman, J. B., Tuittila, E. S., & Roulet, N. (2011). Peatlands in the Earth's 21st century climate system. *Environmental Reviews*, *19*(1), 371–396. https://doi.org/10.1139/a11-014
- Fry, B. (2006). Stable isotopes ecology. Springer, 308 pp. ISBN 978-0387-30513-4
- Fulweiler, R. W., Nixon, S. W., Buckley, B. a., & Granger, S. L. (2007). Reversal of the net dinitrogen gas flux in coastal marine sediments. *Nature*, 448(7150), 180–182. https://doi.org/10.1038/nature05963
- Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., & Vörösmarty, C. J. (2004). Nitrogen cycles: Past, present, and future. *Biogeochemistry*, *70*(2). https://doi.org/10.1007/s10533-004-0370-0
- Geurts, J. J. M., Smolders, A. J. P., Verhoeven, J. T. A., Roelofs, J. G. M., & Lamers, L. P. M. (2008). Sediment Fe:PO4 ratio as a diagnostic and prognostic tool for the restoration of macrophyte biodiversity in fen waters. *Freshwater Biology*, 53(10), 2101–2116. https://doi.org/10.1111/j.1365-2427.2008.02038.x
- Glatzel, S., & Stahr, K. (2001). Methane and nitrous oxide exchange in differently fertilised grassland in southern Germany. *Plant and Soil*, 231(1), 21–35. https://doi.org/10.1023/A:1010315416866
- Goldberg, S. D., Knorr, K. H., Blodau, C., Lischeid, G., & Gebauer, G. (2010). Impact of altering the water table height of an acidic fen on N2O and NO fluxes and soil concentrations. *Global Change Biology*, *16*(1), 220–233. https://doi.org/10.1111/j.1365-2486.2009.02015.x
- Granger, J., Sigman, D. M., Needoba, J. a., & Harrison, P. J. (2004). Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton. *Limnol. Oceanogr.*, *49*(5), 1763–1773. https://doi.org/10.4319/lo.2004.49.5.1763
- Grasshoff, K., Kremling, K., & Ehrhardt, M. (2009). *Methods of Seawater Analysis* (3. Edition). Wiley-VCH.
- Günther, A., Barthelmes, A., Huth, V., Joosten, H., Jurasinski, G., Koebsch, F., & Couwenberg, J. (2020). Prompt rewetting of drained peatlands reduces climate warming despite methane emissions. *Nature Communications*, *11*(1), 1–5. https://doi.org/10.1038/s41467-020-15499-z
- Hannerz, F., & Destouni, G. (2006). Spatial characterization of the Baltic sea drainage basin and its unmonitored catchments. *Ambio*, *35*(5), 214–219. https://doi.org/10.1579/05-A-022R.1
- Happel, E., Bartl, I., Voss, M., & Riemann, L. (2018). Extensive nitrification and active ammonia oxidizers in two contrasting coastal systems of the Baltic Sea. *Environmental Microbiology*, 20(8), 2913–2926. https://doi.org/10.1111/1462-2920.14293
- Harpenslager, S. F., van den Elzen, E., Kox, M. A. R., Smolders, A. J. P., Ettwig, K. F., & Lamers, L. P. M. (2015). Rewetting former agricultural peatlands: Topsoil removal as a prerequisite to avoid strong nutrient and greenhouse gas emissions. *Ecological Engineering*, 84, 159–168. https://doi.org/10.1016/j.ecoleng.2015.08.002
- HELCOM (2018). Sources and pathways of nutrients to the Baltic Sea. Baltic Sea Environment Proceedings No. 153
- HELCOM (2019). HELCOM Guidelines for the annual and periodical compilation and reporting of waterborne pollution inputs to the Baltic Sea (PLC-Water)
- HELCOM (2021). HELCOM PLC waterborne database. http://nest.su.se/helcom_plc/ (last access: 17 December 2022)

- Holz, R., Herrmann, C., & Müller-Motzfeld, G. (1996). Vom Polder zum Ausdeichungsgebiet: Das Projekt Karrendorfer Wiesen und die Zukunft der Küstenüberflutungsgebiete in Mecklenburg- Vorpommern, Natur und Naturschutz in MV, Schriftenreihe des Institutes für Landschaftsökologie und Naturschutz Greifswald, Band 32. pp. 5-27
- IPCC (2007). Changes in Atmospheric Constituents and in Radiative Forcing. [Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland (Eds.)]. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (Eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA
- IPCC (2019). Land Degradation. [Olsson, L., H. Barbosa, S. Bhadwal, A. Cowie, K. Delusca, D. Flores-Renteria, K. Hermans, E. Jobbagy, W. Kurz, D. Li, D.J. Sonwa, L. Stringer (Eds.)]. In: Climate Change and Land: an IPCC special report on climate change, desertification, land degradation, sustainable land management, food security, and greenhouse gas fluxes in terrestrial ecosystems [P.R. Shukla, J. Skea, E. Calvo Buendia, V. Masson-Delmotte, H.-O. Pφrtner, D. C. Roberts, P. Zhai, R. Slade, S. Connors, R. van Diemen, M. Ferrat, E. Haughey, S. Luz, S. Neogi, M. Pathak, J. Petzold, J. Portugal Pereira, P. Vyas, E. Huntley, K. Kissick, M. Belkacemi, J. Malley, (Eds.)]. https://doi.org/10.1017/9781009157988.006
- Johansson, M. M., Pellikka, H., Kahma, K. K., & Ruosteenoja, K. (2014). Global sea level rise scenarios adapted to the Finnish coast. *Journal of Marine Systems*, *129*, 35–46. https://doi.org/10.1016/j.jmarsys.2012.08.007
- Joosten, H., & Clarke, D. (2002). Wise use of mires and peatlands background and principles. www.wetlands.org/projects/GPI/default.htm
- Jørgensen, C. J., & Elberling, B. (2012). Effects of flooding-induced N2O production, consumption and emission dynamics on the annual N2O emission budget in wetland soil. *Soil Biology and Biochemistry*, *53*, 9–17. https://doi.org/10.1016/j.soilbio.2012.05.005
- Kaat, A., & Joosten, H. (2009). Fact book for UNFCCC policies on peat carbon emissions. Wetlands International
- Kache, S., Bartl, I., Wäge-Recchioni, J., & Voss, M. (2021). Influence of organic particle addition on nitrification rates and ammonium oxidiser abundances in Baltic seawater. *Marine Ecology Progress Series*, 674, 59–72. https://doi.org/10.3354/meps13797
- Kana, T. M., Darkangelo, C., Hunt, M. D., Oldham, J. B., Bennett, G. E., & Cornwell, J. C. (1994). *Membrane Inlet Mass Spectrometer for Rapid High-Precision Determination of N2*, 02, and Ar in Environmental Water Samples. 66(23), 4166–4170. https://doi.org/10.1021/ac00095a009
- Kandel, T. P., Lærke, P. E., Hoffmann, C. C., & Elsgaard, L. (2019). Complete annual CO 2, CH 4, and N 2 O balance of a temperate riparian wetland 12 years after rewetting. *Ecological Engineering*, 127(August), 527–535. https://doi.org/10.1016/j.ecoleng.2017.12.019
- Kaushal, S. S., Groffman, P. M., Band, L. E., Elliott, E. M., Shields, C. A., & Kendall, C. (2011). Tracking nonpoint source nitrogen pollution in human-impacted watersheds. *Environmental Science and Technology*, *45*(19), 8225–8232. https://doi.org/10.1021/es200779e
- Kendall, C. (1998). Tracing Nitrogen Sources and Cycling in Catchments. In: Isotope Tracers in Catchment Hydrology. C. Kendall and J.J. McDonnell (Eds.). Elsevier Science B.V. pp. 519-576
- Kendall, C., Silva, S. R., & Kelly, V. J. (2001). Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrological Processes*, 15(7), 1301–1346. https://doi.org/10.1002/hyp.216
- Kendall, C., Elliott, E. M., & Wankel, S. D. (2007). Tracing Anthropogenic Inputs of Nitrogen to Ecosystems. In: Stable Isotopes in Ecology and Environmental Science. R. Michener and K. Lajtha (Eds.) Blackwell Publishing Ltd. ISBN 978-1-4051-2680-9. pp. 375-449

- Kool, D. M., Dolfing, J., Wrage, N., & Van Groenigen, J. W. (2011). Nitrifier denitrification as a distinct and significant source of nitrous oxide from soil. *Soil Biology and Biochemistry*, 43(1), 174–178. https://doi.org/10.1016/j.soilbio.2010.09.030
- Kreyling, J., Tanneberger, F., Jansen, F., van der Linden, S., Aggenbach, C., Blüml, V., Couwenberg, J., Emsens, W. J., Joosten, H., Klimkowska, A., Kotowski, W., Kozub, L., Lennartz, B., Liczner, Y., Liu, H., Michaelis, D., Oehmke, C., Parakenings, K., Pleyl, E., ... Jurasinski, G. (2021). Rewetting does not return drained fen peatlands to their old selves. *Nature Communications*, *12*(1), 1–8. https://doi.org/10.1038/s41467-021-25619-y
- Krüger, J. P., Leifeld, J., Glatzel, S., Szidat, S., & Alewell, C. (2015). Biogeochemical indicators of peatland degradation - A case study of a temperate bog in northern Germany. *Biogeosciences*, 12(10), 2861–2871. https://doi.org/10.5194/bg-12-2861-2015
- Lamb, A. L., Wilson, G. P., & Leng, M. J. (2006). A review of coastal palaeoclimate and relative sea-level reconstructions using δ13C and C/N ratios in organic material. *Earth-Science Reviews*, 75(1–4), 29–57. https://doi.org/10.1016/j.earscirev.2005.10.003
- Lamers, L. P. M., Smolders, A. J. P., & Roelofs, J. G. M. (2002). The restoration of fens in the Netherlands. *Hydrobiologia*, 478, 107–130. https://doi.org/10.1023/A:1021022529475
- Lan, X., Dlugokencky, E.J., Mund, J.W., Crotwell, A.M., Crotwell, M.J., Moglia, E., Madronich, M., Neff, D. and Thoning, K.W. (2019). Atmospheric Nitrous Oxide Dry Air Mole Fractions from the NOAA. GML Carbon Cycle Cooperative Global Air Sampling Network, 1997-2019, https://doi.org/10.15138/53g1-x417
- Landesamt für Umwelt und Natur Mecklenburg-Vorpommern (1997). Landschafts-ökologische Grundlagen und Ziele zum Moorschutz in M-V. Gülzow. Schriftenreihe des Landesamtes für Umwelt und Natur, Heft 3
- Lennartz, B., & Liu, H. (2019). Hydraulic functions of peat soils and ecosystem service. *Frontiers in Environmental Science*, 7(JUN), 1–5. https://doi.org/10.3389/fenvs.2019.00092
- Liu, K. K., Su, M. J., Hsueh, C. R., & Gong, G. C. (1996). The nitrogen isotopic composition of nitrate in the Kuroshio water northeast of Taiwan: Evidence for nitrogen fixation as a source of isotopically light nitrate. *Marine Chemistry*, 54(3–4), 273–292. https://doi.org/10.1016/0304-4203(96)00034-5
- Liu, J., Shen, Z., Yan, T., & Yang, Y. (2018). Source identification and impact of landscape pattern on riverine nitrogen pollution in a typical urbanized watershed, Beijing, China. *Science of the Total Environment*, 628–629, 1296–1307. https://doi.org/10.1016/j.scitotenv.2018.02.161
- Liu, H., Zak, D., Rezanezhad, F., & Lennartz, B. (2019). Soil degradation determines release of nitrous oxide and dissolved organic carbon from peatlands. *Environmental Research Letters*, *14*(9). https://doi.org/10.1088/1748-9326/ab3947
- Marchant, H. K., Holtappels, M., Lavik, G., Ahmerkamp, S., Winter, C., & Kuypers, M. M. M. (2016). Coupled nitrification-denitrification leads to extensive N loss in subtidal permeable sediments. *Limnology and Oceanography*, 61(3), 1033–1048. https://doi.org/10.1002/Ino.10271
- Mariotti, a., Germon, J. C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, a., & Tardieux, P. (1981). Experimental determination of nitrogen kinetic isotope fractionation: Some principles; illustration for the denitrification and nitrification processes. *Plant and Soil*, 62(3), 413–430. https://doi.org/10.1007/BF02374138
- Martikainen, P. J., Nykänen, H., Crill, P., & Silvola, J. (1993). Effect of a lowered water table on N2O fluxes from northern peatland. *Nature*, *366*, 51–53.
- Marttila, H., Karjalainen, S. M., Kuoppala, M., Nieminen, M. L., Ronkanen, A. K., Kløve, B., & Hellsten, S. (2018). Elevated nutrient concentrations in headwaters affected by drained peatland. *Science of the Total Environment*, 643, 1304–1313. https://doi.org/10.1016/j.scitotenv.2018.06.278
- Masta, M., Espenberg, M., Gadegaonkar, S. S., Pärn, J., Sepp, H., Kirsimäe, K., Sgouridis, F., Müller, C., & Mander, Ü. (2022). Integrated isotope and microbiome analysis indicates dominance of denitrification in N2O production after rewetting of drained fen peat. *Biogeochemistry*, *161*(2), 119–136. https://doi.org/10.1007/s10533-022-00971-3

- Mayer, B., Boyer, E. W., Goodale, C., Jaworski, N. A., Van Breemen, N., Howarth, R. W., Seitzinger, S., Billen, G., Lajtha, K., Nadelhoffer, K., Van Dam, D., Hetling, L. J., Nosal, M., & Paustian, K. (2002). Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. *Biogeochemistry*, 57–58, 171–197. https://doi.org/10.1023/A:1015744002496
- McClelland, J. W., & Valiela, I. (1998). Linking nitrogen in estuarine producers to land-derived sources. *Limnology and Oceanography*, *43*(4), 577–585. https://doi.org/10.4319/lo.1998.43.4.0577
- Middelburg, J. J., & Nieuwenhuize, J. (2000). Uptake of dissolved inorganic nitrogen in turbid,tidal estuaries. *Marine Ecology Progress Series*, 192, 79–88.
- Minkkinen, K., Ojanen, P., Koskinen, M., & Penttilä, T. (2020). Nitrous oxide emissions of undrained, forestry-drained, and rewetted boreal peatlands. *Forest Ecology and Management*, 478(August), 118494. https://doi.org/10.1016/j.foreco.2020.118494
- Montoya, J. (1994). Nitrogen Isotope Fractionation in the Modern Ocean: Implications for the Sedimentary Record. In: NATO ASI Series, Vol. I 17: Carbon Cycling in the Glacial Ocean – Constraints on the Ocean's Role in Global Change. R. Zahn et al. (Eds.), Springer, pp. 259-279. ISBN 3-540-57594-4
- Möbius, J. (2013). Isotope fractionation during nitrogen remineralization (ammonification): Implications for nitrogen isotope biogeochemistry. *Geochimica et Cosmochimica Acta*, 105, 422–432. http://dx.doi.org/10.1016/j.gca.2012.11.048
- Müller, A., & Voss, M. (1999). The palaeoenvironments of coastal lagoons in the southern Baltic Sea, II. δ13C and δ15N ratios of organic matter - Sources and sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology, 145*(1–3), 17–32. https://doi.org/10.1016/S0031-0182(98)00095-9
- Nicol, G. W., Leininger, S., Schleper, C., & Prosser, J. I. (2008). The influence of soil pH on the diversity, abundance and transcriptional activity of ammonia oxidizing archaea and bacteria. *Environmental Microbiology*, *10*(11), 2966–2978. https://doi.org/10.1111/j.1462-2920.2008.01701.x
- Parish, F., Sirin, A., Lee, D., & Silvius, M. (2008). Assessment on Peatlands, Biodiversity and Climate Change. Main report, Global Environment Centre, Kuala Lumpur & Wetlands International, Wageningen, ISBN 978-983-43751-0-2
- Pihlatie, M., Syväsalo, E., Simojoki, A., Esala, M., & Regina, K. (2004). Contribution of nitrification and denitrification to N2O production in peat, clay and loamy sand soils under different soil moisture conditions. *Nutrient Cycling in Agroecosystems*, 70(2), 135–141. https://doi.org/10.1023/B:FRES.0000048475.81211.3c
- Pönisch, D.L. (2018). Methodenentwicklung und -anwendung zur Analytik von Methan und Lachgas in Seewasser, Leibniz Institute for Baltic Sea Research Warnemünde (IOW), Master Thesis, University of Rostock, 137 pp.
- Pönisch, D.L., Breznikar, A., Gutekunst, C.N., Jurasinski, G., Voss, M., & Rehder, G. (2023). Nutrient release and flux dynamics of CO2, CH4, and N2O in a coastal peatland driven by actively induced rewetting with brackish water from the Baltic Sea. *Biogeosciences*, 20, 295–323. https://doi.org/10.5194/bg-20-295-2023
- Rassamee, V., Sattayatewa, C., Pagilla, K., & Chandran, K. (2011). Effect of oxic and anoxic conditions on nitrous oxide emissions from nitrification and denitrification processes. *Biotechnology and Bioengineering*, *108*(9), 2036–2045. https://doi.org/10.1002/bit.23147
- R Core Team (2020). R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/ (last access: 10 January 2023)
- Regina, K., Nykänen, H., Silvola, J., & Martikainen, P. J. (1996). Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity. *Biogeochemistry*, 35(3), 401–418. https://doi.org/10.1007/BF02183033
- Regina, K., Silvola, J., & Martikainen, P. J. (1999). Short-term effects of changing water table on N2O fluxes from peat monoliths from natural and drained boreal peatlands. *Global Change Biology*, *5*(2), 183–189. https://doi.org/10.1046/j.1365-2486.1999.00217.x

- Remeikaitė-Nikienė, N., Lujanienė, G., Malejevas, V., Barisevičiūtė, R., Zilius, M., Vybernaitė-Lubienė, I., Garnaga-Budrė, G., & Stankevičius, A. (2017). Assessing nature and dynamics of POM in transitional environment (the Curonian Lagoon, SE Baltic Sea) using a stable isotope approach. *Ecological Indicators*, 82(November 2016), 217–226. https://doi.org/10.1016/j.ecolind.2017.06.035
- Revelle, W. (2021). psych: Procedures for Personality and Psychological Research. Northwestern University, Evanston, Illinois, USA. https://CRAN.Rproject.org/package=psych
- Roughan, B. L., Kellman, L., Smith, E., & Chmura, G. L. (2018). Nitrous oxide emissions could reduce the blue carbon value of marshes on eutrophic estuaries. *Environmental Research Letters*, 13(4). https://doi.org/10.1088/1748-9326/aab63c
- Rysgaard, S., Thastum, P., Dalsgaard, T., Christensen, P. B., & Sloth, N. P. (1999). Effects of salinity on NH4+ adsorption capacity, nitrification, and denitrification in Danish estuarine sediments. *Estuaries*, 22(1), 21–30. https://doi.org/10.2307/1352923
- Sabbaghzadeh, B., Arévalo-Martínez, D. L., Glockzin, M., Otto, S., & Rehder, G. (2021). Meridional and Cross-Shelf Variability of N2O and CH4 in the Eastern-South Atlantic. *Journal of Geophysical Research: Oceans*, 126(11). https://doi.org/10.1029/2020JC016878
- Saiz, E., Sgouridis, F., Drijfhout, F. P., Peichl, M., Nilsson, M. B., & Ullah, S. (2021). Chronic Atmospheric Reactive Nitrogen Deposition Suppresses Biological Nitrogen Fixation in Peatlands. *Environmental Science and Technology*, 55(2), 1310–1318. https://doi.org/10.1021/acs.est.0c04882
- Savoye, N., Aminot, A., Tréguer, P., Fontugne, M., Naulet, N., & Kérouel, R. (2003). Dynamics of particulate organic matter δ15N and δ13C during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France). *Marine Ecology Progress Series*, 255, 27–41. https://doi.org/10.3354/meps255027
- Schiefelbein, U. (2018). Was kam nach den Karrendorfer Wiesen? Über Ausdeichungen an der Ostseeküste Mecklenburg-Vorpommerns. *Natur Und Naturschutz in Mecklenburg-Vorpommern*, *46*, 19–34.
- Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., & Kölling, M. (2005). Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. *Limnology and Oceanography: Methods*, *3*(8), 361–371. https://doi.org/10.4319/lom.2005.3.361
- Seiberling, S. (2003). Auswirkungen veränderter Überflutungsdynamik auf Polder- und Salzgraslandvegetation der Vorpommerschen Boddenlandschaft.Doctoral Thesis, University of Greifswald, Germany. 224 pp.
- Seitzinger, S. P., & Nixon, S. W. (1985). Eutrophication and the rate of denitrification and N20 production in coastal marine sediments. *Limnology and Oceanography*, *30*(6), 1332–1339. https://doi.org/10.4319/lo.1985.30.6.1332
- Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B., Tobias, C., & Van Drecht, G. (2006). Denitrification across landscapes and waterscapes: A synthesis. *Ecological Applications*, *16*(6), 2064–2090. https://doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2
- Senbayram, M., Chen, R., Budai, A., Bakken, L., & Dittert, K. (2012). N2O emission and the N2O/(N2O+N 2) product ratio of denitrification as controlled by available carbon substrates and nitrate concentrations. *Agriculture, Ecosystems and Environment, 147*(1), 4–12. https://doi.org/10.1016/j.agee.2011.06.022
- Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Analytical Chemistry*, 73, 4145–4153. https://doi.org/10.1021/ac010088e
- Sigman, D. M., Granger, J., DiFiore, P. J., Lehmann, M. M., Ho, R., Cane, G., & van Geen, A. (2005). Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin. *Global Biogeochemical Cycles*, 19(4), 1–14. https://doi.org/10.1029/2005GB002458

- Sigman, D. M., DiFiore, P. J., Hain, M. P., Deutsch, C., Wang, Y., Karl, D. M., Knapp, A. N., Lehmann, M. F., & Pantoja, S. (2009). The dual isotopes of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen. *Deep-Sea Research Part I: Oceanographic Research Papers*, 56(9), 1419–1439. https://doi.org/10.1016/j.dsr.2009.04.007
- Smolders, A. J. P., Lamers, L. P. M., Lucassen, E. C. H. E. T., Van Der Velde, G., & Roelofs, J. G. M. (2006). Internal eutrophication: How it works and what to do about it - A review. *Chemistry and Ecology*, 22(2), 93–111. https://doi.org/10.1080/02757540600579730
- Stein, L. Y., & Yung, Y. L. (2003). Production, isotopic composition and atmospheric fate of biologically produced N2O. Annual Review of Earth and Planetary Sciences, 31(1), 329– 356. https://doi.org/10.1146/annurev.earth.31.110502.080901
- Steinmuller, H. E., & Chambers, L. G. (2018). Can Saltwater Intrusion Accelerate Nutrient Export from Freshwater Wetland Soils? An Experimental Approach. *Soil Science Society* of America Journal, 82(1), 283–292. https://doi.org/10.2136/sssaj2017.05.0162
- Strack, M. (Ed.) (2008). *Peatlands and climate change*. International Peat Society, 223 pp. ISBN 978-952-99401-1-0
- Succow, M. & Joosten, H. (2001). Landschaftsökologische Moorkunde. E. Schweizerbart'sche Verlagsbuchhandlung. 662 pp. ISBN 978-3-510-65198-6
- Van De Riet, B. P., Hefting, M. M., & Verhoeven, J. T. A. (2013). Rewetting drained peat meadows: Risks and benefits in terms of nutrient release and greenhouse gas exchange. *Water, Air, and Soil Pollution*, 224(4). https://doi.org/10.1007/s11270-013-1440-5
- Van Dijk, G., Lamers, L. P. M., Loeb, R., Westendorp, P. J., Kuiperij, R., van Kleef, H. H., Klinge, M., & Smolders, A. J. P. (2019). Salinization lowers nutrient availability in formerly brackish freshwater wetlands; unexpected results from a long-term field experiment. *Biogeochemistry*, 143(1), 67–83. https://doi.org/10.1007/s10533-019-00549-6
- Vasander, H., Tuittila, E.-S., Lode, E., Lundin, L., Ilomets, M., Sallantaus, T., Heikkilä, R., Pitkänen, M.-L., & Laine, J. (2003). Status and restoration of peatlands in northern Europe. Wetlands Ecology and Management, 11(February 2003), 51–63. http://doi.org/10.1023/A
- Verhamme, D. T., Prosser, J. I., & Nicol, G. W. (2011). Ammonia concentration determines differential growth of ammonia-oxidising archaea and bacteria in soil microcosms. *ISME Journal*, 5(6), 1067–1071. https://doi.org/10.1038/ismej.2010.191
- Veuger, B., Pitcher, A., Schouten, S., Sinninghe Damsté, J. S., & Middelburg, J. J. (2013). Nitrification and growth of autotrophic nitrifying bacteria and Thaumarchaeota in the coastal North Sea. *Biogeosciences*, 10(3), 1775–1785. https://doi.org/10.5194/bg-10-1775-2013
- Vikman, A., Sarkkola, S., Koivusalo, H., Sallantaus, T., Laine, J., Silvan, N., Nousiainen, H., & Nieminen, M. (2010). Nitrogen retention by peatland buffer areas at six forested catchments in southern and central Finland. *Hydrobiologia*, *641*(1), 171–183. https://doi.org/10.1007/s10750-009-0079-0
- Vile, M. A., Kelman Wieder, R., Živković, T., Scott, K. D., Vitt, D. H., Hartsock, J. A., Iosue, C. L., Quinn, J. C., Petix, M., Fillingim, H. M., Popma, J. M. A., Dynarski, K. A., Jackman, T. R., Albright, C. M., & Wykoff, D. D. (2014). N2-fixation by methanotrophs sustains carbon and nitrogen accumulation in pristine peatlands. *Biogeochemistry*, *121*(2), 317–328. https://doi.org/10.1007/s10533-014-0019-6
- Vitousek, P. M., Aber, J. D., Howarth, R. H., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., & Tilman, D. G. (1997). Human alteration of the global nitrogen cycle: Source and consequences. *Ecol Appl*, 7(3), 737–750. https://doi.org/10.1038/nn1891
- Voss, M., & Struck, U. (1997). Stable nitrogen and carbon isotopes as indicator of eutrophication of the Oder river (Baltic sea). *Marine Chemistry*, 59, 35–49. https://doi.org/10.1016/S0304-4203(97)00073-X
- Voss, M., Deutsch, B., Elmgren, R., Humborg, C., Kuuppo, P., Pastuszak, M., Rolff, C., & Schulte, U. (2006). Source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments. *Biogeosciences*, *3*, 663–676. https://doi.org/10.5194/bgd-3-475-2006

- Voss, M., Deutsch, B., Liskow, I., Pastuszak, M., Schulte, U., & Sitek, S. (2010). Nitrogen retention in the Szczecin Lagoon, Baltic Sea. *Isotopes in Environmental and Health Studies*, 1–15. https://doi.org/10.1080/10256016.2010.503895
- Wankel, S. D., Kendall, C., Francis, C. A., & Paytan, A. (2006). Nitrogen sources and cycling in the San Francisco Bay Estuary: A nitrate dual isotopic composition approach. *Limnology and Oceanography*, *51*(4), 1654–1664. https://doi.org/10.4319/lo.2006.51.4.1654
- Wankel, S. D., Kendall, C., Pennington, J. T., Chavez, F. P., & Paytan, A. (2007). Nitrification in the euphotic zone as evidenced by nitrate dual isotopic composition: Observations from Monterey Bay, California. *Global Biogeochemical Cycles*, 21(2), 1–13. https://doi.org/10.1029/2006GB002723
- Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography: Methods*, *12*, 351–362. https://doi.org/10.4319/lom.2014.12.351
- Ward, B.B. (2005). Temporal variability in nitrification rates and related biogeochemical factors in Monterey Bay, California, USA. Mar. Ecol. Prog. Ser. 292, 97–109. doi:10.3354/meps292097
- Wasmund, N., Topp, I., & Schories, D. (2006). Optimising the storage and extraction of chlorophyll samples Chlorophyll Methodology Extraction Storage Freezing. *Oceanologia*, *48*(1), 125–144.
- Weiss, R. F. (1970). The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research and Oceanographic Abstracts*, 17(4), 721–735. https://doi.org/10.1016/0011-7471(70)90037-9
- Weiss, R. F., & Price, B. A. (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*, *8*, 347–359. https://doi.org/10.1016/0304-4203(80)90024-9
- Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L. D., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T. L., Miller, E., Bache, S. M., Müller, K., Ooms, J., Robinson, D., Seidel, D. P., Spinu, V., Takahashi, K., Vaughan, D., Wilke, C., Woo, K., and Yutani, H.: Welcome to the tidyverse, Journal of Open Source Software, 4, 1686. https://doi.org/10.21105/joss.01686
- World Meteorological Organization (WMO, 2021). Greenhouse Gas Bulletin. The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2020. No. 17. https://library.wmo.int/doc_num.php?explnum_id=10904
- Wrage, N., Velthof, G. L., Van Beusichem, M. L., & Oenema, O. (2001). Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry*, 33(12–13), 1723–1732. https://doi.org/10.1016/S0038-0717(01)00096-7
- Xenopoulos, M. A., Downing, J. A., Kumar, M. D., Menden-Deuer, S., & Voss, M. (2017). Headwaters to oceans: Ecological and biogeochemical contrasts across the aquatic continuum. *Limnology and Oceanography*, 62, S3–S14. https://doi.org/10.1002/lno.10721
- Xia, X., Yang, Z., & Zhang, X. (2009). Effect of suspended-sediment concentration on nitrification in river water: Importance of suspended sediment - Water interface. *Environmental Science and Technology*, 43(10), 3681–3687. https://doi.org/10.1021/es8036675
- Zak, D. & Gelbrecht, J. (2007). The mobilisation of phosphorus, organic carbon and ammonium in the initial stage of fen rewetting (a case study from NE Germany). *Biogeochemistry*, 85(2), 141–151. https://doi.org/10.1007/s10533-007-9122-2
- Zak, D., Rossoll, T., Exner, H. J., Wagner, C., & Gelbrecht, J. (2009). Mitigation of sulfate pollution by rewetting of fens A conflict with restoring their phosphorus sink function? *Wetlands*, *29*(4), 1093–1103. https://doi.org/10.1672/09-102D.1
- Zak, D., Meyer, N., Cabezas, A., Gelbrecht, J., Mauersberger, R., Tiemeyer, B., Wagner, C., & McInnes, R. (2017). Topsoil removal to minimize internal eutrophication in rewetted peatlands and to protect downstream systems against phosphorus pollution: A case study from NE Germany. *Ecological Engineering*, 103, 488–496. https://doi.org/10.1016/j.ecoleng.2015.12.030

- Zhou, Y., Evans, C. D., Chen, Y., Chang, K. Y. W., & Martin, P. (2021). Extensive Remineralization of Peatland-Derived Dissolved Organic Carbon and Ocean Acidification in the Sunda Shelf Sea, Southeast Asia. *Journal of Geophysical Research: Oceans*, 126(6), 1–23. https://doi.org/10.1029/2021JC017292
- Zhu, X., Burger, M., Doane, T. a, & Horwath, W. R. (2013). Ammonia oxidation pathways and nitrifier denitrification are significant sources of N 2 O and NO under low oxygen availability. *Pnas*, *110*(16), 6328–6333. https://doi.org/10.1073/pnas.1219993110
- Zhu, W., Wang, C., Hill, J., He, Y., Tao, B., Mao, Z., & Wu, W. (2018). A missing link in the estuarine nitrogen cycle?: Coupled nitrification-denitrification mediated by suspended particulate matter. *Scientific Reports*, *8*(1), 1–10. https://doi.org/10.1038/s41598-018-20688-4

Acknowledgements

This thesis only exists due to the help of a lot of important people. I really view it as the final result of an absolutely great teamwork that I enjoyed over the entire time.

First and foremost, I want to thank **Maren Voß**. Thank you Maren for encouraging me to write a scholarship proposal to the DBU. It was a great idea and I am really glad it worked out. Thanks for your always valuable supervision that helped me to regain my focus countless times. I am happy to have been a part of your working group during the last six years.

Thanks to the **Deutsche Bundesstiftung Umwelt (DBU)** and in particular to **Dr**. **Volker Wachendörfer** for the opportunity to achieve my doctoral degree within the doctoral scholarship programme and for the highly appreciated help concerning all questions that arose during my work. I am very thankful to be a part of the inspiring DBU community.

Thanks to all colleagues of the **DFG graduate school "Baltic Transcoast"** to which I was associated. In particular I would like to thank Daniel Pönisch, Gerald Jurasinski and Gregor Rehder.

Thank you **Daniel** for our intensive and always joyful cooperation, not only during the writing of our shared manuscript, but especially during field work. I really enjoyed our collaboration and I am so glad that you initiated it. It was a great time. Thanks **Gerald** for always being motivating, being a great source of valuable input on all peatland-related topics and of course for being part of my thesis committee. Thank you **Gregor** for the opportunity to measure my N₂O samples in your lab and also for agreeing to be in my thesis committee.

All my findings would not have been possible without the help of lab chiefs. Thank you **Iris** (Liskow) for measuring the (almost) countless POM and ¹⁵N samples, for always being there to answer my technical questions and for watering my plants from time to time. Thank you **Christian** (Burmeister) for your reliable and much appreciated nutrient analyses. Thank you **Stefan** (Otto) for teaching me how to measure N₂O with the gas chromatograph and for helping me with upcoming questions.

XI

A big thank you to all colleagues of the N-cycle group. Thanks to **Jacqueline**, **Sophie**, **Tina**, **Noémie**, **Angelina**, **Kaja and again Iris** for your always motivating words, for valuable science-related input and discussions and for the very nice lunch breaks with a lot of non-science-related discussions. Thank you **Joachim** for calculating the water volumes of both study sites and for trying to improve my physical knowledge. Finally, I also want to thank **Henning** (Sack) – for your very much appreciated and very enjoyable help on many samplings. I was always looking forward to it and I think we have been a great team.

Thanks to all colleagues of the **IOW workshop**. Many important things would not have been possible without your technical help. Thank you for always having an open ear to my technical problems and also ideas and skills on how to adapt our technical items.

Thanks to **Marco Bartoli** (University of Parma), **Hans-Peter Grossart** and **Danny Ionescu** (both IGB Berlin) for your help on measuring my MIMS samples and for answering all my questions on the calculations.

Many thanks also go to several authorities for providing valuable data. To the Landesamt für Umwelt, Naturschutz und Geologie Mecklenburg-Vorpommern (LUNG MV), namely Mario von Weber, for nutrient monitoring data; to the Wasserstraßen- und Schifffahrtsamt Ostsee for water level data; to the Deutscher Wetterdienst (DWD) for meteorology data; and to the Landesamt für innere Verwaltung MV, Bereich Geodatenbereitstellung, for topography data.

Last, but definitely not least, I want to thank **my parents and friends**. I have always appreciated your encouraging words to stay on track and to not lose sight of my final goal. Thank you for always telling me that I am able to finish whatever I want.

XII

Publications and Grant

Articles in peer-reviewed journals

Pönisch, D.L., **Breznikar, A.**, Gutekunst, C.N., Jurasinski, G., Voss, M., and Rehder, G. (2023, shared first-authorship). Nutrient release and flux dynamics of CO₂, CH₄, and N₂O in a coastal peatland driven by actively induced rewetting with brackish water from the Baltic Sea. *Biogeosciences*, 20, pp. 295–323. https://doi.org/10.5194/bg-20-295-2023

Dataset: http://doi.io-warnemuende.de/10.12754/data-2022-0003

Submitted articles

Breznikar, A., Pönisch, D.L., Lorenz, M., Jurasinski, G., Rehder, G., and Voss, M. (under review) Rewetting effects on nitrogen cycling and nutrient export from coastal peatlands to the Baltic Sea. *Biogeochemistry*

Dataset: http://doi.io-warnemuende.de/10.12754/data-2023-0008

This thesis was financed by a doctoral scholarship from the Deutsche Bundesstiftung Umwelt (DBU), grant no. 20018/559.

List of Figures

Figure 3: Scheme of δ^{15} N and δ^{18} O values of different NO₃⁻ sources (from Kendall, 1998).11

Figure 5: Time series of the mean (a) temperature, (b) salinity, (c) O_2 saturation, and (d) Chlorophyll-a concentration (± standard deviation) in the surface water at Drammendorf from June 2019 to December 2020. Data from the flooded peatland (n = 6) are shown in blue and data from the bay in black (n = 2 or 3, as explained in Sect. 2.8). The vertical black line indicates the rewetting event. Figure adapted from Pönisch and Breznikar et al. (2023)......28

Figure 16: Monthly mean (\pm standard deviation) N₂ production rates (a) in the peatland and (b) the bay sides at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)....45

Figure 17: Monthly mean (± standard deviation) (a) δ^{13} C-POC and (b) δ^{15} N-PON values at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)......46

Figure 18: Plot of C:N ratio and δ^{13} C-POC at DW (blue) and at KW (orange). The reference values for marine and terrestrial POC and C3 plants are taken from Lamb et al. (2006)......47

Figure 19: Monthly mean (± standard deviation) (a) δ^{15} N-NO₃⁻, (b) δ^{18} O-NO₃⁻, and (c) δ^{18} O-H₂O values at Drammendorf (DW, blue) and Karrendorf (KW, orange and darkred)............49

| Figure 22: Correlation plot of δ^{15} N-NO ₃ ⁻ vs. δ^{18} O-NO ₃ ⁻ including the isotopic ranges of |
|--|
| different natural and anthropogenic NO ₃ -sources (adapted from Kendall, 1998; Ding et al., |
| 2014) |

List of Tables

| Table 2: Comparison of nutrient exports from coastal peatlands (this study) and from ma | ajor |
|---|------|
| rivers of the Baltic Sea | 64 |

Appendix



Supplementary Figure S1: Hypsographic curves of (a) Karrendorf and (b) Drammendorf in increments of 0.1 m



Supplementary Figure S2: Comparison of in-situ water level data at Drammendorf and water level data at a nearby monitoring station ("Barhöft"). This comparison was conducted to verify the use of monitoring data for the calculation of water volumes (see Sect. 2.6)



Supplementary Figure S3: Comparison of monthly (a) precipitation height and (b) air temperature data (bottom panel) at Karrendorf (2019, red, and 2020, blue) with long-term DWD data (1991-2020, black line ± standard deviation). No significant differences between the years occurred and thus, data of the two sampling years were merged (see Sect. 2.8)



Supplementary Figure S4: Time series of water level data from the monitoring station (a) near Karrendorf (KW) and (b) near Drammendorf (DW). The horizontal blue lines indicate the respective long-term (2010-2020) mean water level, while the red dots display the respective sampling days


Supplementary Figure S5: Time series of the mean N_2O fluxes (± standard deviation) for each sampling at Drammendorf from December 2019 to December 2020. The vertical black line indicates the rewetting event. Figure adapted from Pönisch and Breznikar et al. (2023)



Supplementary Figure S6: Monthly mean (\pm SD) (a and b) surface water temperature, (c and d) salinity, (e and f) oxygen saturation (in %), and (g and h) pH in the respective peatland and bay areas at Karrendorf (KW) and Drammendorf (DW)



Supplementary Figure S7: Monthly mean (± standard deviation) surface water nutrient concentration of (a and b) NO_{3^-} , (c and d) NO_{2^-} , (e and f) NH_{4^+} , and (g and h) $PO_{4^{3^-}}$ in the respective peatland ("peat") and bay ("bay") areas at Karrendorf (KW) and Drammendorf (DW). Note the different scales on the y-axes of the NO_{3^-} plots



Supplementary Figure S8: Monthly mean (± standard deviation) surface water values of (a and b) δ^{15} N-PON, (c and d) δ^{13} C-POC, (e and f) δ^{15} N-NO₃⁻, and (g and h) δ^{18} O-NO₃⁻, and (i and j) δ^{18} O-H₂O in the respective peatland ("peat") and bay ("bay") areas at Karrendorf (KW) and Drammendorf (DW)



Supplementary Figure S9: Time series of the daily precipitation height data from nearby monitoring stations (a) for Karrendorf (KW) and (b) Drammendorf (DW). The red dots display the respective sampling days

| Study site | season | | | | | |
|----------------------------|--|--|--|--|--|--|
| | winter | spring | summer | autumn | | |
| ĸw | 18.12.2019 28.01.2020 24.02.2020 | 24.04.2019 22.05.2019 23.04.2020 26.05.2020 | 25.06.2019 29.07.2019 26.08.2019 24.06.2020 27.07.2020 17.08.2020 | 09.10.2019 26.11.2019 14.09.2020 | | |
| DW (Pre- rewetting) | | | 19.06.2019 23.07.2019 | 12.09.2019 21.10.2019 19.11.2019 | | |
| DW (Post- rewetting) | 03.12.2020 12.12.2020 18.12.2020 08.01.2020 16.01.2020 21.01.2020 29.01.2020 13.02.2020 27.02.2020 08.12.2020 | 11.03.2020 31.03.2020 09.04.2020 24.04.2020 07.05.2020 28.05.2020 | 09.06.2020 24.06.2020 08.07.2020 22.07.2020 04.08.2020 | 01.09.2020 16.09.2020 07.10.2020 17.11.2020 | | |

Supplementary Table 1: Sampling dates at KW and DW, listed for all seasons

Supplementary Table 2: Mean seasonal water volume exchanges (Q_{in} / Q_{out} ; m³ s⁻¹) and nutrient masses (kg m⁻³) in the bay (c_{bay}), peatland ($c_{peatland}$), and the resulting net nutrient transport (NNT; in tonnes) for DIN-N and PO₄-P at KW and DW. Negative values of NNT indicate an export from the peatland into the bay, and vice versa. All errors are given as the 95 % confidence level. Data of DW are obtained from Pönisch and Breznikar et al. (2023)

| season | Q _{in} (m³ s⁻ ¹) | Q _{out} (m ³ s ⁻¹) | C _{bay} DIN-N (kg m ⁻³) | C _{peatland} DIN-N (kg m ⁻³) | NNT DIN-N (t) | C _{bay} PO ₄ -P (kg m ⁻³) | C _{peatland} PO ₄ -P (kg m ⁻³) | NNT PO₄-P (t) |
|---|---------------------------------|---|--|---|------------------|---|--|------------------|
| winter | 19.4 ± 1.3 | -19.1 ± 1.3 | 249 x 10 ⁻⁶ ± 56.6 x 10 ⁻⁶ | 278 x 10 ⁻⁶ ± 88.5 x 10 ⁻⁶ | -3.8 ± 17.4 | 46.8 x 10 ⁻⁶ ± 46.2 x 10 ⁻⁶ | 77.2 x 10 ⁻⁶ ± 105 x 10 ⁻⁶ | 0.55 ± 1.52 |
| spring | 14.1 ± 0.8 | -14.2 ± 0.8 | 29.1 x 10 ⁻⁶ ± 6.6 x 10 ⁻⁶ | 50.8 x 10 ⁻⁶ ± 23.8 x 10 ⁻⁶ | -1.1 ± 4.8 | 5.6 x 10 ⁻⁶ ± 2.8 x 10 ⁻⁶ | 4.3 x 10 ⁻⁶ ± 2.5 x 10 ⁻ 6 | 0.03 ± 0.71 |
| summer | 13.2 ± 0.7 | -13.2 ± 0.7 | 43.5 x 10 ⁻⁶ ± 16.9 x 10 ⁻⁶ | 47.6 x 10 ⁻⁶ ± 24.4 x 10 ⁻⁶ | -0.7 ± 6.4 | 22.6 x 10 ⁻⁶ ± 6.8 x 10 ⁻⁶ | 24.2 x 10 ⁻⁶ ± 11.2 x 10 ⁻⁶ | -0.43 ± 2.84 |
| autumn | 15.3 ± 1.0 | -15.4 ± 1.0 | 107 x 10 ⁻⁶ ± 49.0 x 10 ⁻⁶ | 287 x 10 ⁻⁶ ± 257 x 10 ⁻⁶ | -15.9 ± 42.5 | 16.1 x 10 ⁻⁶ ± 2.79 x 10 ⁻⁶ | 19.2 x 10 ⁻⁶ ± 6.2 x 10 ⁻ 6 | -0.31 ± 1.20 |
| total Karrendorfer Wiesen -21.5 ± 71.0 | | | | | | -0.16 ± 6.26 | | |
| total per area (t km ⁻² yr ⁻¹) -6.1 ± 20.3 | | | | | | -0.04 ± 1.79 | | |
| | | | | | | | | |

| season | Q _{in} (m³ s⁻ ¹) | Q _{out} (m ³ s ⁻¹) | C _{bay} DIN-N (kg m⁻³) | c _{peatland} DIN-N (kg m⁻³) | NNT DIN-N (t) | C _{bay} PO ₄ -P (kg m ⁻³) | c _{peatland} PO₄-P (kg m⁻³) | NNT PO4-P (t) |
|---|---------------------------------|---|--|--|------------------|---|--|------------------|
| winter | 1.9 ± 0.1 | −1.9 ± 0.1 | 1270 x 10 ⁻⁶ ± 506 x 10 ⁻⁶ | 1840 x 10 ⁻⁶ ± 267 x 10 ⁻⁶ | -8.6 ± 9.9 | 6.5 x 10 ⁻⁶ ± 5.0 x 10 ⁻⁶ | 11.5 x 10 ⁻⁶ ± 3.7 x 10 ⁻⁶ | -0.08 ± 0.10 |
| spring | 1.3 ± 0.1 | −1.3 ± 0.1 | 243 x 10 ⁻⁶ ± 289 x 10 ⁻⁶ | 391 x 10 ⁻⁶ ± 220 x 10 ⁻⁶ | -1.5 ± 3.8 | 2.8 x 10 ⁻⁶ ± 2.8 x 10 ⁻⁶ | 8.1 x 10 ⁻⁶ ± 3.1 x 10 ⁻⁶ | -0.05 ± 0.04 |
| summer | 1.1 ± 0.1 | −1.1 ± 0.1 | 44.0 x 10 ⁻⁶ ± 38.2 x 10 ⁻⁶ | 82.7 x 10 ⁻⁶ ± 34.6 x 10 ⁻⁶ | -0.3 ± 0.5 | 6.8 x 10 ⁻⁶ ± 4.7 x 10 ⁻⁶ | 15.2 x 10 ⁻⁶ ± 3.1 x 10 ⁻⁶ | -0.07 ± 0.05 |
| autumn | 1.2 ± 0.1 | −1.2 ± 0.1 | 301 x 10 ⁻⁶ ± 218 x 10 ⁻⁶ | 328 x 10⁻ ⁶ ± 104 x 10⁻ ⁶ | -0.4 ± 3.2 | 8.1 x 10 ⁻⁶ ± 6.2 x 10 ⁻⁶ | 10.9 x 10 ⁻⁶ ± 3.7 x 10 ⁻⁶ | -0.04 ± 0.10 |
| total Drammendorfer Wiesen | | | | −10.8 ± 17.4 | | | -0.24 ± 0.29 | |
| total per area (t km ⁻² yr ⁻¹) | | | | | -21.6 ± 34.8 | | | -0.48 ± 0.58 |

Eidesstattliche Erklärung

Ich habe eine Dissertation zum Thema

Rewetting effects on nutrient cycling and export dynamics in coastal peatlands of the southern Baltic Sea

an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock angefertigt. Dabei wurde ich von Frau Prof. Dr. Maren Voß betreut.

Ich gebe folgende Erklärung ab:

- Die Gelegenheit zum vorliegenden Promotionsvorhaben ist mir nicht kommerziell vermittelt worden. Insbesondere habe ich keine Organisation eingeschaltet, die gegen Entgelt Betreuerinnen/Betreuer f
 ür die Anfertigung von Dissertationen sucht oder die mir obliegenden Pflichten hinsichtlich der Pr
 üfungsleistungen f
 ür mich ganz oder teilweise erledigt.
- 2. Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe. Dazu habe ich keine außer den von mir angegebenen Hilfsmitteln und Quellen verwendet und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen habe ich als solche kenntlich gemacht.

Rostock, 11.08.2023