Particulate organic matter controls benthic microbial N retention and N removal in contrasting estuaries of the Baltic Sea

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Abstract

Estuaries worldwide act as "filters" of land-derived nitrogen (N) loads, yet differences in their environmental settings can affect the N filter function. We investigated microbial N retention (nitrification, ammonium assimilation) and N removal (denitrification, anammox) processes in the aphotic benthic system (bottom boundary layer [BBL] and sediment) of two Baltic Sea estuaries differing in riverine N loads, trophic state, geomorphology, and sediment type. In the BBL, rates of nitrification (5–227 nmol N L^{-1} d^{-1}) and ammonium assimilation (9–704 nmol N L^{-1} d^{-1}) were not enhanced in the eutrophied Vistula estuary compared to the oligotrophic Öre estuary. No anammox was detected in the sediment of either estuary, while denitrification rates were twice as high in the eutrophied (352±123 µmol N m^{-2} d^{-1}) than in the oligotrophic estuary. Particulate organic matter (POM) was mainly of phytoplankton origin in the benthic systems of both estuaries. It seemed to control heterotrophic denitrification and ammonium assimilation as well as autotrophic nitrification by functioning as a substrate source of N and organic carbon. Our data suggest that in stratified estuaries POM is an essential link between riverine N loads and benthic N turnover and may furthermore function as a temporary N reservoir. During long particle residence times or alongshore transport pathways, increased time is available for the recycling of N until its eventual removal, allowing effective coastal filtering even at low process rates. Understanding the key controls and microbial N processes in the coastal N filter therefore requires to also consider the effects of geomorphological and hydrological features on the residence times of particulate and dissolved nutrients.

1 Introduction

Human nitrogen (N) utilization, especially in agriculture (Galloway and Cowling, 2002; Rabalais, 2002), has strongly increased riverine N inputs to coastal zones (Howarth et al., 1996) and therefore coastal eutrophication (Howarth and Marino, 2006; Nixon, 1995). The coastal zone of the semi-enclosed Baltic Sea annually receives ~680 kt of waterborne total N (TN, HELCOM, 2019) from its catchment area inhabited by >85 million people (Sweitzer et al., 1996). The Baltic coastal zone is

thus particularly prone to eutrophication resulting in oxygen deficiency and a loss of biodiversity (Conley et al., 2011; Diaz and Rosenberg, 2008; Rabalais, 2002; Richardson and Jørgensen, 2013).

Estuaries are the primary recipients of the riverine N load and intense biogeochemical cycling establishes them as "filters" of land-derived N on its way to the open sea (Nedwell et al., 1999; Soetaert et al., 2006). The N filter function consists of retention and removal, with N retention defined as the cycling of bioavailable N within a system for longer than its mean fresh water residence time, and N removal as the permanent removal of N from a system via burial and the production of gaseous forms (Asmala et al., 2017). Microbial processes that contribute to N retention include uptake into biomass, ammonification, nitrification, and dissimilatory nitrate reduction to ammonia (DNRA), while denitrification and anaerobic ammonium oxidation (anammox) lead to N removal. Nitrification, the aerobic oxidation of ammonium (NH_4^+) via nitrite (NO_2^-) to nitrate (NO_3^-), and denitrification, the stepwise anaerobic reduction of NO_3^- to nitrous oxide (N_2O) and di-nitrogen (N_2), are two key microbial processes in the coastal N cycle. Nitrification provides substrates not only for other N retention processes such as primary production and DNRA, but also for N removal via denitrification and anammox. While mainly regulated by oxygen and NH_4^+ availability (Ward, 2008), particulate organic matter (POM) is an additional important factor controlling nitrification in coastal systems (Bartl et al., 2018; Damashek et al., 2016; Hsiao et al., 2014). There, nitrifiers are often found attached to particles (Dang and Chen, 2017), where they utilize the NH_4^+ generated during POM degradation (Klawonn et al., 2015a; Marzocchi et al., 2018). Denitrification is the dominant N removal process in many coastal sediments (Dalsgaard et al., 2005) with anammox often contributing only up to 17% to N_2 production (Dale et al., 2009; Trimmer et al., 2003). Denitrification is mainly controlled by concentrations of the substrates NO_3^- and dissolved organic carbon (Piña-Ochoa and Álvarez-Cobelas, 2006), but equally important is the quantity of labile POM as the source of both N and organic carbon substrates (Bonaglia et al., 2017; Eyre et al., 2013; Hietanen and Kuparinen, 2008). The coupling of microbial N retention and removal processes such as nitrification and denitrification is especially intense in the benthic system, which comprises both oxic and anoxic portions of the sediment, and the overlying turbulent bottom boundary layer (BBL; Richards, 1990). The processes in these three compartments are closely linked via the exchange and diagenesis of solutes and particles (Boudreau and Jørgensen, 2001), thus making the benthic system a key component of the coastal N filter.

Baltic Sea estuaries are highly variable in terms of their riverine N load, stratification, water residence time, and sediment type (Asmala et al., 2017; Conley et al., 2011; Stepanauskas et al., 2002). All these environmental settings can impact the estuarine filter function. For instance, high riverine N loads are known to increase rates of microbial N processes (Seitzinger et al., 2006), whereas stratification of the water column may slow benthic N turnover as it limits the direct supply of riverine substrates from the surface water (Hellemann et al., 2017). A long water residence time, facilitated by geomorphological boundaries, increases the proportion of N removed in the sediment relative to the riverine N load (Finlay et al., 2013; Nixon et al., 1996; Seitzinger et al., 2006). Similarly, it may also increase the proportion of N retained via nitrification or DNRA, yet thorough investigations are still lacking. The sediment type influences the transport of substrates into, through, and out of the sediment, and thus the microbial N processes therein. In cohesive sediments, diffusive and fauna-induced fluxes govern solute exchange, while in sandy, permeable sediments advective pore-water flow is usually the dominant transport process (Huettel et al., 2003; Thibodeaux and Boyle, 1987). Pore-water flow leads to an increased supply of oxygen, oxidized solutes, and particles into the sediment, as well as to the build-up of a complex redox zonation (Huettel et al., 1998, 2003, 2014), in sum resulting in increased microbial turnover of organic matter (Boudreau et al., 2001) and potentially enhances nitrification and denitrification rates. The various combinations of these environmental settings may strongly influence, how effectively microbial processes retain or remove N, yet detailed comparisons of contrasting estuaries are scarce.

Based on a compilation of denitrification rates across different coastal types in the Baltic Sea, Asmala et al. (2017) estimated that the entire Baltic coastal zone removes ~16% of annual land-derived TN loads via denitrification, while the remaining 84%

is probably retained within the coastal zone or exported to the open sea. Model results indicate, however, that the export of riverine N to the open Baltic Sea accounts for only a minor share of the TN load (Radtke et al., 2012), suggesting that most N remains within the coastal zone. So far, however, actual rate measurements of N retention processes in coastal benthic systems of the Baltic Sea are rare (e.g. Bonaglia et al., 2014; Jäntti et al., 2011). Therefore, in this study, we examined microbial N removal (denitrification, anammox) and N retention (nitrification, ammonium assimilation) processes in the aphotic benthic systems of two Baltic estuaries with contrasting environmental settings. The small, northern Öre estuary receives low riverine N loads (430 t TN yr^{-1}, Table 1) from a catchment area mainly consisting of forests and bogs (Wikner and Andersson, 2012). Its oligotrophic state is reflected in its low concentrations of nutrients and total organic carbon as well as low rates of primary production (Ask et al., 2016; Wikner and Andersson, 2012). By contrast, the 12-fold larger southern Vistula estuary receives high riverine N loads (97 000 t TN yr^{-1}, Table 1) from a catchment area of intensively cultivated cropland, which has led to high concentrations of nutrients and organic matter (Pastuszak et al., 2012), high primary production rates (Wielgat-Rychert et al., 2013; Witek et al., 1999), and thus the eutrophied state of the estuary. The estuaries further differ in their geomorphology and sediment type, but share similarity of peak riverine N loads in spring. In previous studies we showed that POM is an important factor controlling denitrification in the sediment of the Öre estuary (Hellemann et al., 2017) and nitrification in the BBL of the Vistula estuary (Bartl et al., 2018). In the present work, we combined new environmental data and process rates with the published data from the Öre estuary (Hellemann et al., 2017) and the Vistula estuary (Bartl et al., 2018; Thoms et al., 2018; Supplement Table S1) to identify the impact of contrasting environmental conditions on microbial N turnover and to estimate the role of POM in the coastal N filter function.

2 Materials and Methods

2.1 Study areas and sampling

The Öre estuary (ÖE) is located on the Swedish coast of the Quark Strait, northern Baltic Sea (Fig. 1). It covers an area of ~71 km^2 and has a volume of ~1 km^3 (SMHI, 2003). Inputs to the estuary originate from the Öre River, whose mean discharge of 36 m^3 s^{-1} creates a river plume of 2–3 m vertical and up to 10 km horizontal extent. The estuary is framed by an archipelago to the east and by land to the west, and has a basin-like bottom topography (Brydsten, 1992, Fig. 1). The outlet of the Öre estuary, located in the south, is relatively wide at its surface but narrows at water depths >20 m (Brydsten, 1992; Malmgren and Brydsten, 1992). A small elevation at ~25−30 m water depth separates the estuarine bottom waters from the open sea (Brydsten, 1992, Fig. 1). The water column of the estuary is oxic throughout the year, with concentrations ranging from ~250 µmol L^{-1} in summer to ~450 µmol L^{-1} in spring (DBotnia, 2016; SMHI, 2003). The estuarine soft sediments (21 km^2) consist of silts as well as non-permeable very fine and fine sands (Hellemann et al., 2017).

The Vistula estuary (VE), part of the Polish Bay of Gdansk, southern Baltic Sea (Fig. 1), covers an area of ~825 km^2 and has a volume of ~20 km^3. It receives inputs from the Vistula River, whose mean discharge of 1080 m^3 s^{-1} results in a river plume of 0.5–12 m vertical and 4–30 km horizontal extent (Cyberska and Krzyminski, 1988). Due to the absence of topographical restrictions, the Vistula estuary merges freely with the adjacent coastal and offshore waters of the Bay of Gdansk (Fig. 1). It can nevertheless be distinguished from adjacent offshore waters at ~50 m water depth, where the sediment changes from sand to silt and the isotopic signature of N in the sediment from anthropogenic to marine sources (Thoms et al., 2018; Fig. 1). The water column of the Vistula estuary is oxic throughout the year albeit with small seasonal differences (~380 µmol L^{-1} in spring and ~240 µmol L^{-1} in summer; Bartl et al., 2018). Under specific conditions, such as floods or high respiration rates during stagnant stratification, coastal hypoxia may develop (Conley et al., 2011; Hansson et al., 2011), although this did not happen during the cruises of this study.

Water and sediment samples from both estuaries were taken in spring and summer during four campaigns in 2014–2016 with the RV *Lotty* (ÖE I, ÖE II) and RV *Elisabeth Mann Borgese* (VE I, VE II; Table 1). Water samples were obtained at three to six depths, from surface (0–2.5 m) to bottom, using either a rosette water sampler (5 L) connected to a conductivity-temperature-depth probe (CTD; VE) or Niskin bottles (5 L or 10 L; ÖE) after the CTD cast. Water samples from immediately above the sediment (20–40 cm) were taken from the overlying water of intact sediment cores. To assign bottom water and core water samples to the BBL, the vertical BBL extent was identified based on the change in the potential density over the change in depth (Supplement Figure S1). Since turbulent boundary layer flow leads to a constant potential density within the BBL (Turnewitsch and Graf, 2003), the vertical extent of the BBL is defined as the uppermost point in the water column (viewed from the sediment surface) where the variation of the change in potential density exceeds a threshold of 0.01 kg m^{-3} (Holtermann and Umlauf, 2012). In the Vistula estuary, the vertical BBL extent was 3.2±1.1 m in spring and 3.4±1.4 m in summer (Bartl et al., 2018), and in the Öre estuary 2.9±0.6 m and 1.9±0.6 m, respectively (Supplement Table S2). Sediment samples were collected using a Gemini twin corer (core iØ 8 cm, length 80 cm; silt, ÖE), a multi-corer (core iØ 10 cm, length 60 cm; silt and fine sand, VE), and a HAPS bottom corer (core iØ 14 cm, length 30 cm; sand, all campaigns) with a vibration unit (KC Denmark; vibration time 10–15 s). Surface sediment slices (0–2 cm) were taken for basic sediment characteristics. Subsamples for denitrification rate measurements (n = 12 per station, except VE I: n = 20) and pore-water oxygen profiles (n = 3 per station) were collected in acrylic cores (iØ 2.3 cm, length 15 or 20 cm). The cores were pushed gently into the sediment so that 30% (silt) to 50% (sand) of their volume was filled with sediment, the remaining volume consisting of overlying water, and closed without a gas headspace.

2.2 Environmental data

2.2.1 Water column

Water column measurements were carried out with CTD-probes (VE: SBE911plus; ÖE I: SBE19plus; ÖE II: SBE19plus V2; all Seabird Scientific), equipped with either an additional sensor for dissolved oxygen (SBE43, Seabird-Scientific, VE) or a separate oxygen optode (4330, Aanderaa) attached to a second CTD-probe (Seaguard Aanderaa, ÖE). Dissolved oxygen in the overlying core water was determined via Winkler titration (Grasshoff et al., 1999). Concentrations of dissolved inorganic N species (NO$_2^-$, NO$_3^-$, NH$_4^+$, µmol L^{-1}, with the sum defined as DIN) were measured colorimetrically using a continuous segmented flow analyser (QuAAtro, Seal Analytical; ÖE) following Grasshoff et al. (1999) and HELCOM guidelines (2014) or as described in Bartl et al. (2018; VE). Background subtraction of the colorimetric signals in Öre estuary samples was used to account for the high dissolved organic matter content colouring the water. Concentrations of chlorophyll *a* (Chl.*a*, µg L^{-1}) were measured using an optical sensor (Cyclops 7, Turner Designs) attached to a CTD probe (Seaguard, Aandeera; ÖE) and by high-performance liquid chromatography (Lumi Haraguchi, unpublished data; ÖE), or according to the fluorometric method (Edler, 1979; Wasmund et al., 2006, VE). Particulate organic nitrogen and carbon concentrations (PON, POC; µmol L^{-1}) and the natural isotopic composition of POC (δ^{13}C-POC; ‰) were measured using a continuous-flow isotope ratio mass spectrometer (IRMS; Delta V Advantage, Thermo Fisher Scientific) as described in Hellemann et al. (2017; ÖE) and Bartl et al. (2018; VE). The contribution of different POM sources to the total estuarine POM pool was estimated using a two-component mixing model (Goñi et al., 2003; Jilbert et al., 2018) with terrestrial POM (C:N of 20) and phytoplankton-derived POM (C:N of 8) as end-members (Hellemann et al., 2017). Since high C:N ratios can also indicate degraded POM due to the preferential utilization of PON over POC (Savoye et al., 2003), δ^{13}C-POC values were used to distinguish between terrestrial (δ^{13}C-POC <−28‰ in Baltic rivers; Maksymowska et al., 2000; Rolff and Elmgren, 2000) and degraded POM. The degradation state of POM was analysed based on the mass ratio of POC:Chl.*a* (µg µg^{-1}) and the molar ratio of particulate C:N (µmol µmol^{-1}), both of which increase simultaneously during degradation (Savoye et al., 2003). POC:Chl.*a* ratios <200 indicate newly produced phytoplankton POM, and >200 degraded POM (Cifuentes et al., 1988).

2.2.2 Sediment

Sediments were characterized by grain size distribution, porosity, and loss on ignition (LOI), using standard methods as described in Hellemann et al. (2017; ÖE) and Thoms et al. (2018; VE). Permeability (K_m) of the sandy sediments was analysed according to the constant head method as described in Hellemann et al. (2017). Sediments with $K_m \geq 2.5 \times 10^{-12}$ m^2 were considered sufficiently permeable to enable advective pore-water flow with significant effects on sediment biogeochemistry in the Baltic Sea, while in sediments with $K_m < 2.5 \times 10^{-12}$ m^2 these effects were shown to be negligible and the sediments were hence defined as non-permeable (Forster et al., 2003).

Oxygen pore-water concentration profiles were obtained at in situ temperature using Clark-type microelectrodes (ÖE, VE I: 200- to 250-µm vertical resolution, OX-100; VE II: 500-µm vertical resolution, OX-250; all Unisense) as described in Hellemann et al. (2017). The oxygen penetration depth (OPD) in the sediment was determined from each profile with the sediment surface identified by a characteristic break in the profile curve and by additional visual estimates. Profiles affected by fauna were discarded (max. 12–16 %).

Samples for the determination of pore-water NH_4^+ concentrations were taken from intact sediment cores, either by core slicing (resolution: 1 cm) under N_2 atmosphere followed by centrifugation and filtration (fine silts ÖE) or according to Thoms et al. (2018; VE) using Rhizons^{TM} (Rhizosphere Research Products; resolution: 1 cm at 1- to 5-cm depth, 2 cm at 5- to 11-cm depth; coarse silts and fine sands ÖE). Pore-water NH_4^+ samples were immediately frozen and kept at −20°C until colorimetric measurement (Grasshoff et al., 1999), either manually, using a spectrophotometer (UV-Vis 1201 LAMBDA2, Shimadzu, accuracy 5%; fine silts ÖE) or automated, using a continuous segmented flow analyser (QuAAtro, Seal Analytical, accuracy 5–10%; coarse silts and fine sands ÖE). The concentrations were vertically integrated for the surface (0–2 cm) and subsurface (2–10 cm) sediment layers to yield total pools of pore-water NH_4^+ (µmol m^{-2}; Table 3).

2.3 Quantification of N-transformation processes

2.3.1 Nitrification and ammonium assimilation rates in the BBL

Nitrification and ammonium assimilation were determined in ^{15}N-NH_4^+ tracer incubations (Damashek et al., 2016; Ward, 2011). Water samples were collected from the bottom water and the sediment overlying core water and processed as described by Bartl et al. (2018). Briefly, six polycarbonate bottles were filled with water (core water: 170 mL, except VE II 100 mL; bottom water: 625 mL) and sealed gas-tight. The samples were amended with ^{15}N-NH_4Cl (98 atom% ^{15}N, Sigma Aldrich) to yield a sample enrichment of 0.05 µmol L^{-1} (ÖE, VE I) or 0.20 µmol L^{-1} (VE II). Three samples were filtered immediately through pre-combusted glass-fiber filters (GF/F Whatman, 3 h at 450°C), while the remaining triplicates were incubated for 5–7 h (ÖE, VE I) or 3 h (VE II) in the dark at in situ temperature. The short incubation time minimized isotope dilution via ammonification during the incubation (Ward, 2011). The incubation was terminated by filtration, and both the filtrates and the filters were stored at −20°C until the analysis. The ^{15}N content of NO_3^-+NO_2^- in the filtrate was measured according to the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), using a continuous-flow IRMS (Delta V Advantage, Thermo Fisher Scientific) connected to a Finnigan GasBench II (calibration against the standards IAEA-N3 and USGS-34, accuracy: ±0.14‰). Nitrification rates were calculated according to Veuger et al. (2013). Since the ^{15}N content of both NO_2^- and NO_3^- is measured simultaneously, the calculated nitrification rate is a bulk rate that includes NH_4^+ oxidation and NO_2^- oxidation. The concentration and ^{15}N content of PON was measured from the filters as described by Bartl et al. (2018) using the same continuous-flow IRMS. Ammonium assimilation rates were calculated according to Dugdale and Wilkerson (1986).

2.3.2 Gaseous N production in the sediment

Benthic N_2 and N_2O production was measured using the revised isotope pairing technique (r-IPT; Risgaard-Petersen et al., 2003), which accounts for the contributions of denitrification and anammox to total N_2 production. All non-permeable sediment samples from the two estuaries were incubated using a diffusive set-up, in which the overlying water in the acrylic cores was enriched with $K^{15}NO_3$ (98 % ^{15}N, Cambridge Isotope Laboratories) to final concentrations of 40, 80 and 120 µmol L^{-1} (n = 4 per concentration, except n = 12 for 120 µmol L^{-1} VE I; isotope enrichment in the water [Fn]: 84–100%; ÖE, VE I) or 30, 60, 90 and 120 µmol L^{-1} (n = 3 per concentration; Fn: 86–100%; VE II). Subsequently, the samples were incubated in the dark for 3–5 h at in situ temperatures under gentle water mixing by magnetic stirrers. The permeable sediment samples of VE II were also incubated this way, since advective pore-water flow was most likely negligible during sampling (see Section 4.1.3). The permeable sediment samples of VE I were incubated with an advective set-up, in which bottom water, enriched with $K^{15}NO_3$ (98% ^{15}N, Cambridge Isotope Laboratories) to final concentrations of 40, 80, and 120 µmol L^{-1} (n = 5–7 per concentration; Fn: 98–100%), was pumped through the advective sediment layer, which was determined from previously measured oxygen profiles and used as approximation of the sediment depth affected by advective pore-water flow (Gihring et al., 2010; Supplement Fig. S2). The pumping rate (0.25 mL min^{-1}; IPC high-precision tubing pump, ISMATEC) at site-specific porosities led to pore-water velocities of ~7.6 cm h^{-1}. The ^{15}N-NO_3^- enriched water was pumped from the top into the acrylic cores and drawn out of the cores through holes pre-drilled at two opposing core sides (vertical resolution 5 mm). This outflow was adjusted in each core to ~5 mm above the approximated oxic-anoxic interface in the sediment to ensure that the flow reached the interface where denitrification occurred but did not affect deeper layers. In- and outflow ports were sealed with rubber plugs through which Tygon® tubing (ST R-3603/R-3607, iØ 2.3 mm) was inserted; all connecting interfaces were tightened with Teflon® tape. During a pre-incubation (2.5–3 h), all resident pore-water in contact with the estimated advective sediment layer was exchanged with ^{15}N-NO_3^- enriched water. Subsequently, one core per concentration was sampled to obtain the start values, while the tubing of the remaining cores was connected to a closed circulation for each core and incubated for ~5 h (Supplement Fig. S1). Incubations were stopped by gently mixing the sediment with the overlying water. After brief sediment settling, 12-mL subsamples were placed into gastight glass vials (Exetainer, Labco Scientific) with 0.5 mL of $ZnCl_2$ (100 % w/v, Merck). A 5-mL helium headspace was created and the isotopic compositions of N_2 and N_2O were analysed using a continuous-flow IRMS (IsoPrime 100, Isoprime; standard gas: N_2, >99.999 % purity, AGA) interfaced with a gas pre-concentrator system (TraceGas, Isoprime) and an automated liquid handler (GX-271, Gilson) at the Department of Environmental Sciences, University of Jyväskylä, Finland (ÖE, VE I) or with a continuous-flow IRMS (Delta V Plus, Thermo Scientific, standard gas: Oztech N_2, i.e. $\delta^{15}N$ vs. air = −0.61, Oztech Trading Co.) interfaced with a gas bench and a pre-concentrator system (Precon, Thermo Scientific) at the Stable Isotope Facility, University of California, Davies, USA (VE II).

According to the r-IPT, a contribution of anammox to the measured N_2 production is indicated when the production rate of ^{14}N-N_2 (D14, calculated according to Nielsen, 1992) correlates positively with the added ^{15}N-NO_3^- concentrations. In this case, the calculation of N_2 production needs to distinguish between denitrification and anammox rates and follows Risgaard-Petersen et al. (2003). If D14 does not correlate positively with the added ^{15}N-NO_3^- concentrations, denitrification is assumed to be the only process producing N_2 and the calculations follow Nielsen (1992). Valid application of the method further requires a linear dependency between the production rate of ^{15}N-N_2 (D15) and increasing $^{15}NO_3^-$ concentrations. All dependencies were tested with a regression analysis (significance level: p<0.05). Denitrification of NO_3^- from the bottom water (Dw) and from nitrification within the sediment (Dn, coupled nitrification-denitrification) was calculated from D14 and the ratio of ^{15}N-NO_3^- to ^{14}N-NO_3^- in the water phase (Nielsen, 1992; Risgaard-Petersen et al., 2003).

2.4 Statistical analyses

The significance of the differences between the factors 'site' (Öre estuary, Vistula estuary), 'season' (spring, summer) and 'sediment type' (permeable, non-permeable) was tested using the non-parametric Mann-Whitney U-test (2 factors, $n \geq 3$) or the non-parametric Kruskal-Wallis (KW) test (>2 factors, $n \geq 3$) combined with Dunn's post-hoc test (all SigmaPlot, version 13.0). Multivariate correlation analyses (Kendall's τ, $n \geq 5$) were done between environmental variables and rates of nitrification (ÖE II), ammonium assimilation (ÖE II, VE), and denitrification (ÖE II, VE) using SAS (version 9.4). The ÖE I data could not be analysed in correlation analyses because the sample size was too small ($n \leq 4$). In all analyses, the significance level was $p < 0.05$.

3 Results

3.1 Environmental variables

3.1.1 Water column

The plumes of the Öre and Vistula rivers, identified from their low salinity, extended vertically to ~2 m (ÖE) and ~5 m (VE) in spring and to ~6 m (ÖE) and ~1 m (VE) in summer (Figs. 2, 3). Horizontally, the river plumes covered $\leq 50\%$ of the respective estuarine area (not shown). The water column below the river plumes was well-mixed in spring (Fig. 2) and characterized by a thermohaline stratification in summer (Fig. 3). In both estuaries, oxygen conditions differed seasonally but all water layers were oxic with >230 μmol L^{-1} (Supplement Table S2). In spring, DIN concentrations were more than 30 times higher in the Vistula than in the Öre river plume and estuarine surface waters, while concentrations in the BBL differed by a factor of two (Fig. 2; Supplement Table S2). In summer, DIN concentrations in the river plumes and surface waters of both estuaries was <2.0 μmol L^{-1} (Fig. 3; Supplement Table S2). In the BBL of the Öre estuary, summer NH_4^+ concentrations were two to three times lower (U-test, $p < 0.001$) and the $NO_3^- + NO_2^-$ concentrations two times higher (U-test, $p < 0.001$) than in the Vistula estuary (Fig. 3; Supplement Table S2). The POC and PON concentrations in the BBL of both estuaries were two to four times higher in summer than in spring (ÖE: U-test, $p = 0.037$; VE: Bartl et al., 2017; Table 2), whereby summer concentrations were more than twice as high as in the Öre than in the Vistula estuary (POC: U-test, $p = 0.040$; PON: U-test, $p = 0.048$; Fig. 3; Table 2).

The POM of the Öre River and its plume contained a large share of terrestrial organic matter in both spring and summer, as reflected by the high C:N ratios and depleted δ^{13}C-POC values (Table 2). By contrast, in the Vistula River and its plume, POM was mainly phytoplankton-derived (Table 2). In the coastal water column (river and river plume excluded) phytoplankton-derived POM dominated in both estuaries and in both seasons (Table 2), which was also reflected in the elevated Chl.*a* concentrations measured in the entire water column in spring and in the surface water in summer (Table 2; Fig. 2 and 3). The particulate C:N ratio was similar in the surface water of the two estuaries during spring and summer, but significantly higher in the BBL of the Öre than the Vistula estuary in summer (U-test, $p = 0.005$; Fig. 4, Table 2). In both estuaries, POC:Chl.*a* ratios were <200 throughout the water column in spring and >200 in the BBL in summer, whereby the summer ratio in the Öre estuary was seven times larger than in the Vistula estuary (Fig. 4, Table 2).

3.1.2 Sediment

Permeable sediments were estimated to cover ~56% of the Vistula estuary (Supplement Fig. S3), whereas the sediments in the Öre estuary were non-permeable (Hellemann et al., 2017). LOI differed significantly between permeable and non-permeable sediments (U-test, $p < 0.001$) but was similar both between the non-permeable sediments of the two estuaries and during spring and summer (Table 3). The oxygen profiles in the permeable sediments of the Vistula estuary in spring were sigmoidal, with nearly constant oxygen concentrations in the top millimetres of the sediment, and nearly parabolic in summer, similar to the profiles of the non-permeable sediments in both seasons (Fig. 5). Thus, the mean OPD in the permeable sediments in summer

was 60% lower than in spring (U-test, p=0.003) and similar to the summer OPD in the non-permeable sediments (Table 3). In addition, pore-water NH_4^+ pools differed seasonally in the permeable surface sediments of the Vistula estuary, with ~73% more NH_4^+ in summer than in spring (U-test, p=0.016). The deep NH_4^+ pool of the non-permeable sediments was significantly higher in the Vistula than in the Öre estuary (U-test, p=0.008) but similar between seasons (Table 3).

3.2 Nitrogen transformation processes

3.2.1 Nitrification and ammonium assimilation in the BBL

Nitrification rates did not significantly differ between estuaries or seasons (KW-test, p=0.478; Table 4). In both estuaries, the nitrification rates correlated positively with the PON and POC concentrations in summer (VE: Kendall's τ: 0.81, p=0.01, n=7 [Bartl et al., 2018]; ÖE: Kendall's τ: 0.71, p=0.02, n=7; Fig. 6A). In the Öre estuary, the summer nitrification rates showed a negative trend with the particulate C:N ratio (Kendall's τ: −0.53, p=0.10, n=7; Fig. 6B). Ammonium assimilation rates differed seasonally in the Vistula estuary (spring<summer; U-test, p=0.006) but not in the Öre estuary (Table 4). In spring, ammonium assimilation rates were three times higher in the Öre than in the Vistula estuary (U-test, p=0.044), whereas in summer- rates were similar (Table 4). Summer rates correlated positively with the PON and POC concentrations in both estuaries (VE: Kendall's τ: 0.61, p=0.02, n=9; ÖE: Kendall's τ: 0.71, p=0.02, n=7; Fig. 6C), and negatively with the particulate C:N ratio in the Öre estuary (Kendall's τ: −0.71, p=0.02, n=7; Fig. 6D).

3.2.2 Denitrification and anammox in the sediment

Anammox was not detected at any of the sites, indicating that N_2 production in both estuaries originated entirely from denitrification. N_2O production during denitrification was ≤1.8% of total N_2 production in all samples, and denitrification rates are presented as the sum of N_2 and N_2O. Denitrification rates in the Öre estuary were not detectable in spring and were ≥60% lower than in the Vistula estuary in summer (U-test, p<0.001). In the Vistula estuary, spring denitrification rates were 50% lower in the permeable than in the non-permeable sediment but did not differ in summer (Table 4). In both estuaries, denitrification was primarily coupled to nitrification in the sediment (Dn, spring:- ~80 %; summer: ≥90 %). Dn correlated positively with LOI in the surface sediments of the Vistula estuary in summer (Kendall's τ: 0.73, p=0.04, n=6, one non-permeable site excluded) but not in spring (spring: Kendall's τ: 0.40, p=0.33, n=5) nor in the Öre estuary (Kendall's τ: 0.14, p=0.70, n=6; Fig. 6E). Dn correlated negatively with the particulate C:N ratio in the Öre estuary (Kendall's τ: −0.80, p=0.05, n=5; Fig. 6F) but not in the Vistula estuary (spring: Kendall's τ: 0.20, p=0.63, n=5; summer: Kendall's τ: 0.24, p=0.45, n=7).

4 Discussion

4.1 Environmental settings of the Vistula and Öre estuaries

4.1.1 Site-specific and seasonal environmental settings

The main difference between the estuaries is their trophic state (eutrophied vs oligotrophic) based on the two magnitudes higher nutrient load of the Vistula River than the Öre River (Table 1). The corresponding high nutrient availability in the photic zone of the Vistula estuary supports an annual primary production rate that is ~6 times higher (225 g m^{-2} y^{-1}; Witek et al., 1999) than in the nutrient-limited Öre estuary (39 g m^{-2} y^{-1}; Ask et al., 2016). In both seasons of this study, this difference was reflected by the higher concentrations of Chl.*a* and POM in the surface water of the Vistula estuary (Table 2). Furthermore, the mainly phytoplankton-derived POM of the Vistula River and its plume can easily enter the coastal N cycle and thus be related to the eutrophied state of the estuary (Maksymowska et al., 2000). The large share of terrestrial POM in the Öre River and its plume is likely refractory and was observed to settle right at the river mouth (Forsgren and Jansson, 1992), thus not enhancing biological N turnover in the Öre estuary. Interestingly, despite the different primary production rates and POM

sources, in both estuaries >60% of the benthic POM is phytoplankton-derived though degraded to different degrees. In the Vistula estuary, the continuous input of labile POM likely results in the less degraded state of benthic summer POM, determined from lower C:N and POC:Chl.a ratios than in the Öre estuary (Fig. 4C). Extensive degradation of the POM presumably accounted for the greater accumulation of NH_4^+ not only in the BBL in summer (Fig. 3), but also on a long-term scale as reflected by the large NH_4^+ pools in the non-permeable sediment of the Vistula estuary (Table 3). In the Öre estuary, by contrast, low river loads and estuarine primary production result in comparatively small inputs of phytoplankton-derived POM to the benthic system, where it seems to be effectively degraded over the course of the year (Hellemann et al., 2017) resulting in the significantly more degraded state of benthic summer POM compared to the Vistula Estuary (Fig. 4C).

In contrast, the different trophic state was not reflected in the quantity of accumulated POM in the BBL, which was surprisingly higher in the Öre estuary in summer. This points to the influence of estuarine geomorphology which determines particle and water residence times (Seitzinger et al., 2006; Statham, 2012). The basin-like topography of the Öre estuary (Fig. 1, see also section 2.1) and a particle residence time of up to one year (Brydsten and Jansson, 1989) likely allow enhanced accumulation of settled POM during the productive seasons. Also, the summer NO_3^-+NO_2^- concentrations were higher in the BBL of the Öre than of the Vistula estuary, furthermore, indicating a long bottom water residence time due to the restricted water exchange across the elevation at the Öre estuary's outlet (Brydsten and Jansson, 1989). However, at the same time, the NH_4^+ concentrations remain lower than in the Vistula estuary. The low input of labile POM as well as the lower NH_4^+ pools in the non-permeable sediments of the Öre estuary suggest reduced NH_4^+ release from POM degradation and from the sediment. Indeed, spring NH_4^+ fluxes are significantly lower in the Öre estuary (5.4 μmol m^{-2} d^{-1}; core incubations; Nedwell et al., 1983) than in the Vistula estuary (930 μmol m^{-2} d^{-1}; in situ chamber incubations; Thoms et al., 2018). Thus, effective NH_4^+ assimilation and nitrification during a long water residence time could result in the accumulation of the end products, PON and NO_3^-, but not of NH_4^+. Also, the release of up to 300 μmol NO_3^- m^{-2} d^{-1} from the sediments of the Öre estuary (core incubations; Nedwell et al., 1983), further supports potential NO_3^- accumulation in the BBL. In contrast, the open shape of the Vistula estuary may limit the accumulation of benthic POM as unrestricted lateral transport could lead to its export, which may the reason for the lower POM concentrations compared to the Öre estuary. In addition, the large area of permeable sediments, that can experience advective pore-water flow likely added to the degradation of POM in the sediment of the Vistula estuary (Boudreau et al., 2001; Huettel and Rusch, 2000).

The two estuaries also share similar features related to the seasonal stratification of their water columns and the corresponding distributions of DIN and POM. In spring, when the riverine nutrient loads are highest, haline stratification prevents the direct contact of river plume DIN with the benthic system. Instead, DIN remains in the photic surface layer where it is likely taken up by primary producers. The newly produced POM settles to the aphotic benthic system, as suggested by the elevated Chl.a concentrations in the BBL in spring compared to the summer (Table 2) or the winter season (< 1 μg L^{-1}; Bartl et al., 2018; DBotnia, 2016), and by the dominance of phytoplankton-derived POM in the BBL (Table 2). In summer, reduced vertical mixing and thermohaline stratification allow enhanced benthic remineralization of the accumulated POM, thus slightly lowering the oxygen concentrations and increasing the NH_4^+ concentrations in the BBL of both estuaries compared to spring (Table S2). Sediment oxygen consumption is a proxy for benthic remineralisation activity and the rates measured in previous studies of the two estuaries were at least twice as high in summer than in spring (Nedwell et al., 1983; Witek et al., 1999). Consequently, in both estuaries, riverine DIN is supplied to the benthic system indirectly, via POM build-up and sedimentation which uncouples the peak river N load in spring from enhanced N turnover in the benthic system in summer (Hellemann et al., 2017).

4.1.2 Permeable sediments of the Vistula estuary

Permeable sediments are known to experience advective pore-water flow, which significantly influences nutrient and organic matter turnover (Huettel et al., 2014). In the permeable sediments of the Vistula estuary, advective pore-water flow was indicated in spring by the sigmoidal shape of the oxygen profiles (Revsbech et al., 1980) and the low pore-water NH_4^+ pools, similar to the subtidal permeable sediments in the North Sea (Ehrenhauss et al., 2004; Lohse et al., 1996). These low-NH_4^+ pore-water pools likely result from enhanced nitrification in the large oxic sediment layer and/or enhanced NH_4^+ release through advection (Huettel et al., 1998). However, the strikingly higher NH_4^+ pools, the nearly parabolic shape of the oxygen profiles and the shallow OPDs in summer (Table 3) rather suggest NH_4^+ accumulation and the dominance of diffusive transport despite the permeable character of the sandy sediments in that season. Similar seasonally differing oxygen profiles have also been found in the permeable sediments of the German Bight, North Sea, where the parabolic profile shape in summer is attributed to the "absence of a turbulent water column" (Lohse et al., 1996). The authors of that study also observed that oxygen consumption in the sediment can distort the shape of originally advective (sigmoidal) oxygen profiles within 30–60 min at a diffusive oxygen uptake (DOU) rate of 6.7 mmol m^{-2} d^{-1}. In our study, oxygen profiles were measured within ~30 min of the first sampling and had a much lower summer DOU (0.6±0.3 mmol m^{-2} d^{-1}, n=21). It is therefore unlikely that the observed parabolic profile shape resulted from strong oxygen utilization occurring prior to the measurements. Instead, we assume that the pressure gradients at the sediment surface in summer were too low to induce advective pore-water flow. Such pressure gradients mainly originate from waves or from the interaction of near-bottom flow and the bottom topography (Santos et al., 2012). Hence, we used modelled near-bottom flow velocity data of our sampling period to examine whether the interaction of this flow with a topographic object could, at least theoretically, create pressure gradients sufficient to drive advection (see supplements). The modelled near-bottom flow velocity was very low (<2.5 cm s^{-1}) and resulted only in minor pressure gradients (<0.15 Pa) at a 3-cm-high mound (Table S3). The calculated Peclet number was below the threshold for pore-water advection within the sediment (≥5, Bear, 1972; Table S3). We therefore suggest that, at the time of the summer cruise, the pressure gradients at the sediment surface of the Vistula estuary were too low to induce an advective pore-water flow able to significantly affect sediment biogeochemistry; leaving diffusion and fauna-induced fluxes as the main transport processes during that time. Presumably, this temporary switch between transport regimes is more likely to occur in low-energy environments, such as the non-tidal Baltic Sea. Further research is needed to evaluate the frequency of such changes and their impact on biogeochemical processes.

4.2 Effects of contrasting environmental settings on benthic microbial N turnover

4.2.1 Nitrification and ammonium assimilation in the BBL

Nitrification rates are often higher in eutrophied than in oligotrophic estuaries, due to the increased availability of the substrate NH_4^+ and higher concentrations of POM (Bianchi et al., 1999; Dai et al., 2008; Damashek et al., 2016). Yet, rates of coastal nitrification cover an extremely large range (0.2–14400 nmol L^{-1} d^{-1}; Brion et al., 2008; Bristow et al., 2015; Damashek et al., 2016; Heiss and Fulweiler, 2016; Hsiao et al., 2014). While the nitrification rates determined in this study are in the lower range of other globally acquired rates, they are similar to previously reported nitrification rates in the Baltic Proper (0−84 nmol L^{-1} d^{-1} at a water depth of 80–117 m, Hietanen et al., 2012). The similar ranges of nitrification rates in the two estuaries are unexpected, given the difference in their trophic states. However, they might be explained by a recent study that found similar gene and transcript abundances as well as similar community compositions of ammonium-oxidizing archaea and bacteria in the BBL of the Vistula and Öre estuaries (Happel et al., 2018). In both estuaries, the positive correlations between the nitrification rates and the concentrations of PON and POC imply the regulation of nitrification by particle-attached nitrifiers (Karl et al., 1984; Phillips et al., 1999), which profit from the direct NH_4^+ supply during PON degradation (Bartl et al., 2018; Hsiao et al., 2014; Klawonn et al., 2015). Furthermore, recent studies found nitrifying species capable of degrading organic

nitrogen compounds to obtain NH_4^+ directly (Kuypers et al., 2018; Yager et al., 2012). Such organisms may also contribute to the positive correlation between nitrification rates and PON in our study.

The only difference between the BBLs of the two estuaries that seems to influence nitrification was the quality of the POM, as defined by its C:N ratio. This was also shown to be the case for nitrification in soils (Bengtsson et al., 2003) and may apply to coastal systems as well. With increasing PON concentration, the increase in nitrification was stronger in the Vistula than in the Öre estuary (Fig. 6), likely due to the less degraded state of the POM in the former (Fig. 4). By contrast, the more degraded POM in the Öre estuary limits nitrification due to the limited availability of organic N as a potential NH_4^+ source, which is reflected by the negative correlation between nitrification rates and the C:N ratio (Fig. 6). Hence, a combination of the concentrations of POC and PON and their ratio, i.e. the POM quality, likely influenced nitrification in the Öre estuary. In addition to PON, a second source of NH_4^+ might have been sedimentary NH_4^+ release. Corresponding total NH_4^+ fluxes measured by Thoms et al. (2018) in the Vistula estuary in spring 2016 (same cruise) did not correlate with the here presented nitrification rates (not shown). These total NH_4^+ fluxes were measured with in situ chamber incubations, which, however, neglect advective pore-water flow (Thoms et al., 2018), and hence additional rate and flux data are needed to thoroughly determine the contribution of sedimentary NH_4^+ release as a substrate source for nitrification in the BBL.

Ammonium assimilation is both a substrate- and a temperature-dependent heterotrophic process (Baer et al., 2014; Hoch and Kirchman, 1995). The ammonium assimilation rates measured in this study represent typical coastal rates, similar to rates determined in the surface waters of the Delaware estuary (13–930 nmol L^{-1} d^{-1}; Hoch and Kirchman, 1995) and in the bottom waters of the Washington coast (500 nmol L^{-1} d^{-1}; Ward et al., 1984). The eutrophied state of the Vistula estuary did not result in higher ammonium assimilation rates which further showed the same correlation patterns with PON, POC, and C:N as determined for the nitrification rates (Fig. 6). This suggests that POM also plays an important role as a substrate source for NH_4^+-assimilating microbes and that its quality is especially important in the oligotrophic Öre estuary.

4.2.2 Denitrification in the sediment

Denitrification rates are commonly enhanced in eutrophied ecosystems due to the greater availability of organic C and NO_3^- (Seitzinger et al., 2006). This was also the case for the Vistula estuary, where denitrification rates were more than 2-fold higher than in the Öre estuary (Table 4) and similar to rates from other eutrophied estuaries of the Baltic Sea (320–360 µmol N m^{-2} d^{-1}, Bonaglia et al., 2014; 90–910 µmol N m^{-2} d^{-1}, Silvennoinen et al., 2007; 290–350 µmol N m^{-2} d^{-1}, Nielsen and Glud, 1996). The higher availability of labile POM in the benthic system supplied organic C and N, with the latter one serving as source for ammonification subsequently driving coupled nitrification-denitrification (Dn). As a result denitrification in the Vistula estuary increased significantly with increasing organic matter concentrations as also reported for other coastal systems (Finlay et al., 2013; Jäntti et al., 2011; Seitzinger and Nixon, 1985). By contrast, the more degraded state of the POM in the Öre estuary reduced the availability of organic N and C as substrates which led to the negative correlation between denitrification and the particulate C:N ratio (Fig. 6F). The results from both estuaries are consistent with previous findings of a dependency of denitrification on the quality of organic matter (Eyre et al., 2013; Hietanen and Kuparinen, 2008).

The limited denitrification rates in the colder spring season can be attributed to the low availability of labile organic C (Bradley et al., 1992; Hellemann et al., 2017) as denitrification uses organic C and NO_3^- in a 1:1 ratio (Taylor and Townsend, 2010). While newly produced POM was present in both benthic systems during the spring samplings (Fig. 4), low bottom water temperatures (Fig. 2) likely slowed its degradation to dissolved C components suitable for denitrification. Such limitation has been found previously also in other coastal sediments of the Baltic Sea in the same season (Hietanen and Kuparinen, 2008; Jäntti et al., 2011).

In both estuaries and both seasons, denitrification mainly used NO_3^- from nitrification in the sediment and not NO_3^- from the BBL, which is common in coastal sediments with sufficiently deep oxygen penetration and low NO_3^- concentrations in the water overlying the sediment (Rysgaard et al., 1994). This was also true for the permeable sediments under advective pore-water flow in the Vistula estuary and is in agreement with the results of Rao et al. (2008) and Marchant et al. (2016). Advective pore-water flow can favor Dn over Dw by enhancing nitrification through an increase of the oxic sediment volume (Gihring et al., 2010; Huettel et al., 1998; Marchant et al., 2016) and by increasing the oxic-anoxic interface across which NO_3^- and NH_4^+ are exchanged (Cook et al., 2006; Precht et al., 2004). However, because advective pore-water flow affects sediment biogeochemistry in complex ways, there is no consistent pattern yet regarding a general favouring of Dn or Dw in permeable sediments (Kessler et al., 2013; Gihring et al., 2010; Marchant et al., 2016; Rao et al., 2007).

4.2.3 Measurement of denitrification rates in the permeable Vistula sediment

The permeable sediments along the southern coast of the Baltic Sea may account for substantial N removal as a result of high N turnover related to pore-water flow (Korth et al., 2013; Voss et al., 2005a), similar to permeable sediments in the North Sea and Atlantic Bight (Gao et al., 2012; Rao et al., 2007). In this study, the permeable sediments of the Vistula estuary in spring experienced advective pore-water flow, and denitrification rates were correspondingly measured using an advective incubation design. The determined rates were lower than those of the non-permeable sediments during the same season, presumably due to the limitations of our incubation design in representing advective pore-water flow. During the incubation, pore-water flow velocities were within the range of those in sediments underlying high-energy waters (Huettel et al., 1996; Precht et al., 2004) and therefore probably too high to realistically represent Baltic Sea conditions. Over the course of the incubation, the flow increased the initial OPD in most of the investigated sediment cores (data not shown), leading to the oxygenation of formerly anoxic sediment layers and a downwards shift of the oxic-anoxic interface. The delay until the microbial community adapted to the new conditions might explain the measured low rates of denitrification. Yet, at the time of the spring cruise, denitrification was limited by the low availability of labile dissolved organic C. It is therefore unlikely that in situ denitrification rates in the permeable sediment would have been significantly higher than those measured in the non-permeable sediment, even with a better simulation of advective pore-water flow.

4.3 Key drivers of the coastal N filter in the Öre and Vistula estuaries

In the two here studied estuaries, POM was found to be an essential link between land-derived DIN in the surface waters and the spatially and temporally separated benthic processes nitrification, ammonium assimilation, and denitrification. Through benthic-pelagic coupling, POM likely functions as a carrier and temporary reservoir of organic N and C that controls the process rates of benthic N retention and removal (Hellemann et al., 2017).

To better understand this coupling, we estimated the amount of riverine DIN potentially taken up by primary production. In the Öre estuary, N uptake in April 2015 was calculated using a primary production rate of 0.39 g C m^{-2} d^{-1} (DBotnia, 2016), the Redfield C:N ratio of 6.6, and the estuarine area of 71 km^2. The resulting areal N uptake rate of 4.9 t d^{-1} was an order of magnitude higher than the riverine DIN load during the same period (0.53 t d^{-1}). Thus, it is likely that all riverine DIN and also riverine DON (Stepanauskas et al., 2002) were readily consumed by phytoplankton. A considerable amount of this easily degradable POM sinks to the bottom and may remain in the benthic system for over a year (Brydsten and Jansson, 1989). Thus N could undergo cycles of retention via ammonification, nitrification, re-assimilation to PON, and DNRA before it is removed via sedimentary denitrification (Hellemann et al., 2017). Thus, even at low process rates, the estuary may be an effective coastal N filter, which is mainly accomplished through its geomorphology that allows long particle residence times (Fig. 7).

In the Vistula estuary, primary production rates, estimated from the riverine DIN load in March 2016 (453 t d^{-1}), would need to be as high as 3.1 g C m^{-2} d^{-1} to result in the complete consumption of riverine DIN. However, known primary production

rates are lower with 0.3−2.8 g C m^{-2} d^{-1} (March–May, Voss et al., 2005b; Witek et al., 1999) and would consume 10–90% of the Vistula DIN input in March 2016. Hence, it is possible that not all riverine DIN is taken up by primary production but instead remains in the surface waters. Due to the open shape of the estuary, unrestricted water exchange may reduce the residence time of both DIN and newly produced POM allowing their export out of the Vistula estuary (Fig. 7). Residence times

475 and transport in the surface water of the Vistula estuary strongly depend on wind direction and speed (Matciak and Nowacki, 1995; Voss et al., 2005b). Short-term eddy formations during southerly and south-easterly winds have been observed to transport small amounts of riverine DIN out into the open Baltic Sea (Voss et al., 2005b), whereas the predominant south-westerly and westerly winds lead to alongshore eastward coastal currents, so that DIN and POM could largely remain within the coastal rim of the southern Baltic zone (Radtke et al., 2012; Siegel et al., 1996; Voss et al., 2005a, 2005b). We assume that

480 the predominant alongshore transport of DIN and POM extends the N filter of the Vistula estuary to the adjacent coastal zones where further DIN uptake, POM sedimentation and benthic microbial N retention and removal facilitate a coastal filter function over a larger area and a longer time scale. However, to thoroughly understand the N filter function and efficiency of the Vistula estuary and adjacent coastal zones, the effects of wind conditions not only on current dynamics, transport, and residence times in the surface water, but also in intermediate and bottom water layers needs to be resolved. Furthermore, the microbial N

485 processes studied here are not sufficient to elucidate the role and magnitude of N retention in the Öre and Vistula estuaries since actual rate measurements of DIN uptake by primary producers, ammonification, nitrification and DNRA in the sediment as well as in situ fluxes across the sediment water interface are lacking (Fig. 7). Especially nitrification in the sediment and DNRA were focus in a few recent studies of Baltic coastal systems where the rates varied extremely between ~20–700 μmol m^{-2} d^{-1} in nitrification (Bonaglia et al., 2014; Jäntti et al., 2011) and 1–487 μmol m^{-2} d^{-1} in DNRA (Bonaglia et al., 2014,

490 2017; Jäntti and Hietanen, 2012; Jäntti et al., 2011). These rates cover the same range as denitrification rates which emphasizes their significant role in retaining N in coastal ecosystems.

4.4 Revisiting coastal filter efficiency

The efficiency of the coastal N filter is often evaluated by estimating the N removal efficiency (e.g., Asmala et al., 2017; Deek et al., 2013; Khalil et al., 2013), which is an extrapolation of the denitrification rates to a specific area, divided by the riverine

495 TN load. To determine the N removal efficiency of the Vistula and Öre estuaries, we extrapolated the denitrification rates (Table 4) to the respective estuarine sediment areas (ÖE: 21 km^2; VE: 462 km^2 permeable sediment; 363 km^2 non-permeable sediment, Supplement Figure S3) and sampling months (31 days), and divided them by the riverine TN load (converted to mol month^{-1}) of the same month (Table 1). Despite their significantly different denitrification rates, the two estuaries each removed only ~5% of the riverine TN loads in the respective summer months, and even less in spring (0.2%, Vistula estuary only).

500 These values are at the lower end of N removal efficiencies estimated for temperate estuaries (3–26%; Deek et al., 2013; Fear et al., 2005; Jäntti et al., 2011; Seitzinger and Nixon, 1985; Silvennoinen et al., 2007). Asmala et al. (2017) calculated that ~16% of the riverine TN load entering the Baltic coastal zone is removed by denitrification, and concluded that the Baltic coast is a less efficient N filter than the open Baltic Sea. The authors' compilation of denitrification rates across different coastal types, however, lacks denitrification measurements from sandy, permeable sediments, which cover large areas of the southern

505 Baltic coastal zone coinciding with the region of highest riverine N loads (HELCOM, 2018). Thus, the question remains whether the removal efficiency could be underestimated and additional denitrification measurements from sediments experiencing advective pore-water flow are needed for future estimations.

Based on our results, we emphasize the fact that the N removal efficiency alone is not a sufficient indicator of the N filter efficiency in coastal zones. The time-delay of the riverine N load in the surface and its removal in the sediment make the direct

510 relation of N input to N removal only sensible for longer, i.e. annual and decadal timescales (Edman et al., 2018). On shorter, i.e. seasonal timescales the N filter efficiency would rather depend on the transport and residence time of N which provide time for N storage in POM and for retention processes to recycle N several times until it eventually enters the removal pathway.

Hence, to better quantify the coastal N filter efficiency, an additional measure of a N recycling efficiency is needed that not only considers the role and magnitude of microbial N retention processes, but also quantifies transport and residence times of nutrients and POM, as all of these factors may facilitate N preservation in the coastal system.

5 Conclusion

Contrary to our expectations, the different trophic states of the Vistula and Öre estuaries influence only the denitrification rates in the sediment, but not the rates of ammonium assimilation and nitrification in the BBL. In both estuaries, all three processes depend on the availability of easily degradable, phytoplankton-derived POM as a substrate source. Due to its build-up through primary production and subsequent sedimentation, POM is the essential link between riverine DIN loads and the spatially and temporally separated benthic microbial N processing in stratified estuaries such as of the Vistula and Öre rivers. In addition, POM can function as a temporary N reservoir through long particle residence times (Öre estuary) or alongshore transport (Vistula estuary), which are both governed by the geomorphological and hydrological features of coastal zones. Consequently, the efficiency of a coastal N filter depends not only on the rates of microbial N removal (removal efficiency), but also on transport and residence time of nutrients and POM as well as on the rates of microbial N retention (recycling efficiency). Especially in the southern Baltic coastal zone, where riverine TN loads are consistently high and water residence times or benthic N process rates are largely unknown, we still lack knowledge whether the coastal filter works efficiently. Our findings have important implications in our understanding of the coastal N filter function and highlight the need for holistic approaches combining microbial N process quantifications with investigations on current dynamics, transport and residence times. This would give crucial information for the application of appropriate agricultural and coastal management measures.

Author contributions

Ines Bartl and Dana Hellemann: Study conceptualization, investigation, formal analysis, and data visualization; writing of the original draft of the manuscript, as well as its review and editing

Christophe Rabouille, Kirstin Schulz, Petra Tallberg: Support for investigation; writing, review, and editing of the manuscript

Susanna Hietanen and Maren Voss: Support of the study's conceptualization; funding acquisition; investigation support; resource provision; writing, review, and editing of the manuscript

Competing interests

The authors have no conflicts of interest to declare.

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Tables

Table 1: Sampling details of the field campaigns, as well as river discharge and nitrogen (N) loads (TN = total N, DIN = dissolved inorganic N, PON = particulate organic N) during the sampling months, and the annual average.

Site	Cruise	Date	Season	River discharge[a] $(m^3\ s^{-1})$	TN load $(t\ month^{-1})$	DIN load (% of TN)	PON load (% of TN)
Öre estuary	ÖE I	20–24/04/2015	Spring	66	98	17	29
	ÖE II	03–07/08/2015	Summer	26	26	3	22
			Annual average	36	36[b]	16[b]	26[c]
Vistula estuary	VE I	28/02/–10/03/2016	Spring	1500	16172	87	6
	VE II	04–15/07/2014	Summer	932	2621[d]	3[d]	10[f]
			Annual average	1080	8100[e]	63[e]	8[g]

[a] Öre River: www.vattenwebb.smhi.se (annual average: 2004–2014); Vistula River: annual average discharge (1951-1990; Pastuszak and Witek, 2012); discharge of VE I and VE II from Polish national monitoring by the Institute of Meteorology and the Water Management National Research Institute
[b] http://miljodata.slu.se/mvm/ (1967–2014, without 1975)
[c] Average of spring and summer
[d] Polish national monitoring by the Institute of Meteorology and the Water Management National Research Institute
[e] Average loads from Pastuzak and Witek (2012; period 1988-2011) and from Polish national monitoring by the Institute of Meteorology and the Water Management National Research Institute (period 2014-2015)
[f] Stepanauskas et al. (2002)
[g] Average of spring and summer

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Table 2: Characteristics of particulate organic matter in the Öre and Vistula estuaries in spring and summer. The contribution of POM sources (terrestrial and phytoplankton) was estimated based on a two-component mixing model following Jilbert et al. (2018), using end members from Goñi et al. (2003). Values are average and standard deviation of each water layer. The number of replicates is shown in parentheses, n.a. = not available.

Site	Season	Location	POC (µmol L⁻¹)	PON (µmol L⁻¹)	δ¹³C-POC (‰)	C:N (molar)	Chl.a (µg L⁻¹)	POC:Chl.a (mass)	Terrestrial POM (%)	Phytoplankton POM (%)
Öre estuary[a]	Spring	River	153.6	11.2	-29.1	13.7.	n.a.	n.a.	71	29 (1)
		River plume	53.7	5.1	-29.5	10.6	3.3 ± 1.2 (4)	196	44	55 (1)
		Surface	40.2 ± 13.5	4.3 ± 1.4	-25.7 ± 1.0	9.3 ± 0.8 (8)	5.7 ± 0.2 (6)	89 ± 27 (5)	19 ± 16	83 ± 16 (8)
		BBL	36.8 ± 14.1	4.2 ± 1.5	-25.0 ± 1.0	8.7 ± 1.1 (10)	5.3 ± 1.8 (5)	79 ± 28 (5)	19 ± 16	81 ± 16 (10)
	Summer	River	67.2	5.7	-30.2	11.7	n.a.	n.a.	56	44 (1)
		River plume	46.9 ± 0.7	4.1 ± 0.7	-28.7 ± 0.2	11.8 ± 1.9 (3)	2.6 ± 0.7 (6)	214	55 ± 16	45 ± 16 (3)
		Surface	34.1 ± 7.9	4.0 ± 0.8	-26.5 ± 0.6	8.5 ± 0.7 (13)	2.4 ± 0.6 (7)	181 ± 87 (4)	15 ± 11	85 ± 11 (13)
		BBL	135.9 ± 85.5	13.1 ± 8.4	-26.1 ± 0.3	10.2 ± 0.9 (9)	0.6 ± 0.0 (3)	4596 ± 1447 (3)	38 ± 11	62 ± 11 (9)
Vistula estuary[b]	Spring	River	164.2	16.5	-25.7	10.0	3.48	567	37	63 (1)
		River plume	61.1 ± 25.9	6.9 ± 2.5	-26.5 ± 1.4	8.9 ± 1.5 (8)	6.8 ± 2.8 (8)	121 ± 54 (8)	25 ± 14	75 ± 14 (8)
		Surface	45.6 ± 15.8	5.8 ± 2.4	-24.8 ± 0.7	8.1 ± 1.2 (6)	7.0 ± 2.1 (6)	79 ± 17 (6)	10 ± 16	90 ± 16 (6)
		BBL	25.4 ± 13.6	2.6 ± 1.3	-25.6 ± 0.8	9.8 ± 1.9 (18)	2.1 ± 1.3 (18)	164 ± 77 (18)	31 ± 24	69 ± 24 (18)
	Summer	River	n.a.	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	n.a.
		River plume	103	10.2	-25.8	10.1	3.1	402	33	67 (1)
		Surface	73.6 ± 34.6	8.3 ± 3.7	-25.7 ± 0.6	8.8 ± 0.6 (7)	4.6 ± 2.0 (7)	200 ± 62 (7)	20 ± 10	80 ± 10 (7)
		BBL	46.9 ± 30.7	5.3 ± 5.5	-25.4 ± 0.8	8.9 ± 0.3 (11)	0.8 ± 0.6 (7)	630 ± 307 (5)	15 ± 10	85 ± 10 (9)

BBL-bottom boundary layer; POC-particulate organic carbon; PON-particulate organic nitrogen; δ¹³C-POC- natural isotopic composition of POC; C:N-particulate carbon to nitrogen ratio; Chl.a-Chlorophyll a; POC:Chl.a-ratio of particulate organic carbon to chlorophyll a

[a] POC, PON, δ¹³C-POC, C:N, terrestrial POM and phytoplankton POM from Hellemann et al. (2017)

[b] POC, PON, C:N from Bartl et al. (2018)

Table 3: Sediment characteristics in the Öre and Vistula estuaries in spring and summer. Permeability (K_m), porosity (ϕ), and loss on ignition (LOI) are determined from the pooled surface sediment (0–2 cm), NH_4^+ pools are derived from vertically integrated pore-water concentrations over the surface (0–2 cm) and the subsurface (2–10 cm) sediment layer, oxygen penetration depth (OPD) is derived from oxygen profiles. All data as average and standard deviation (except for bottom depth), with the number of replicates in parentheses.

Site	Season	Sediment	Bottom depth (m)	K_m (10^{-12} m^2)	Sediment type	ϕ	LOI (dw %)	OPD (mm)	NH_4^+ surface pool (µmol m^{-2})	NH_4^+ deep pool (µmol m^{-2})
Öre estuary[a]	Spring	Non-permeable	18–37	0.1 ± 0.1 (2)	Silt (Sandy) very coarse silt (Silty) very fine sand	0.8 ± 0.1 (6)	7.8 ± 4.3 (6)	7.2 ± 0.9 (13)	360 ± 232 (3)	4743 ± 1845 (6)
	Summer	Non-permeable	18–34	0.2 ± 0.1 (2)	Silt (Silty) very fine sand (Silty) fine sand	0.7 ± 0.1 (6)	4.8 ± 3.2 (6)	3.5 ± 0.9 (38)	473 ± 309 (7)	4079 ± 2331 (7)
Vistula estuary[b]	Spring	Permeable	22–36	6.9 ± 3.6 (7)	Fine sand Medium sand	0.4 ± 0.0 (8)	0.9 ± 0.3 (8)	10.1 ± 4.5 (40)	92 ± 48 (4)	2899 ± 1103 (4)
		Non-permeable	16–59	-	(Silty) very fine sand Fine sand	0.6 ± 0.2 (3)	2.8 ± 1.9 (3)	3.2 ± 0.9 (21)	428 ± 173 (2)	15 362 ± 5996 (2)
	Summer	Permeable	25–49	9.0 ± 8.1 (5)	Fine sand Medium sand Coarse sand	0.4 ± 0.0 (5)	1.2 ± 0.7 (5)	4.1 ± 1.3 (20)	336 ± 183 (5)	4596 ± 1432 (5)
		Non-permeable	17–50	0.7 ± 0.2 (2)	Very fine sand Fine sand	0.6 ± 0.1 (3)	6.3 ± 4.7 (3)	3.2 ± 1.2 (13)	574 ± 284 (3)	11 422 ± 7108 (3)

[a] Data from Hellemann et al. (2017)
[b] Sediment type, porosity, LOI from Thoms et al. (2018)

5   **Table 4: Rates of ammonium assimilation and nitrification in the bottom boundary layer (BBL), and denitrification in the sediments of the Öre and Vistula estuaries in spring and summer. Öre estuary sediments are a non-permeable, thus no rates available in the permeable sediments (n.a.), denitrification in the Öre estuary in spring was not detectable (n.d.). All rates as average and standard deviation, with the number of replicates in parentheses; the maximum rate is shown below. %Dn gives the share of coupled nitrification-denitrification in total denitrification.**

| Site | Season | Ammonium assimilation BBL | Nitrification BBL | Denitrification | | | |
| | | | | Permeable sediment | | Non-permeable sediment | |
		$(nmol\ L^{-1}\ d^{-1})$	$(nmol\ L^{-1}\ d^{-1})$	$(\mu mol\ N\ m^{-2}\ d^{-1})$	%Dn	$(\mu mol\ N\ m^{-2}\ d^{-1})$	%Dn
Öre estuary[a]	Spring	92 ± 70 (4) 211	21 ± 7 (4) 29	n.a.	n.a.	n.d.	n.d.
	Summer	218 ± 107 (7) 304	49 ± 30 (7) 98	n.a.	n.a.	138 ± 47 (65) 290	93
Vistula estuary[b]	Spring	36 ± 16 (9) 73	41 ± 22 (11) 84	72 ± 37 (19) 162	81	140 ± 52 (50) 285	79
	Summer	319 ± 232 (10) 704	64 ± 72 (7) 227	354 ± 127 (49) 652	97	349 ± 117 (21) 584	90

[a] Denitrification rates from Hellemann et al. (2017)
[b] Nitrification and ammonium assimilation rates from Bartl et al. (2018)

Figures
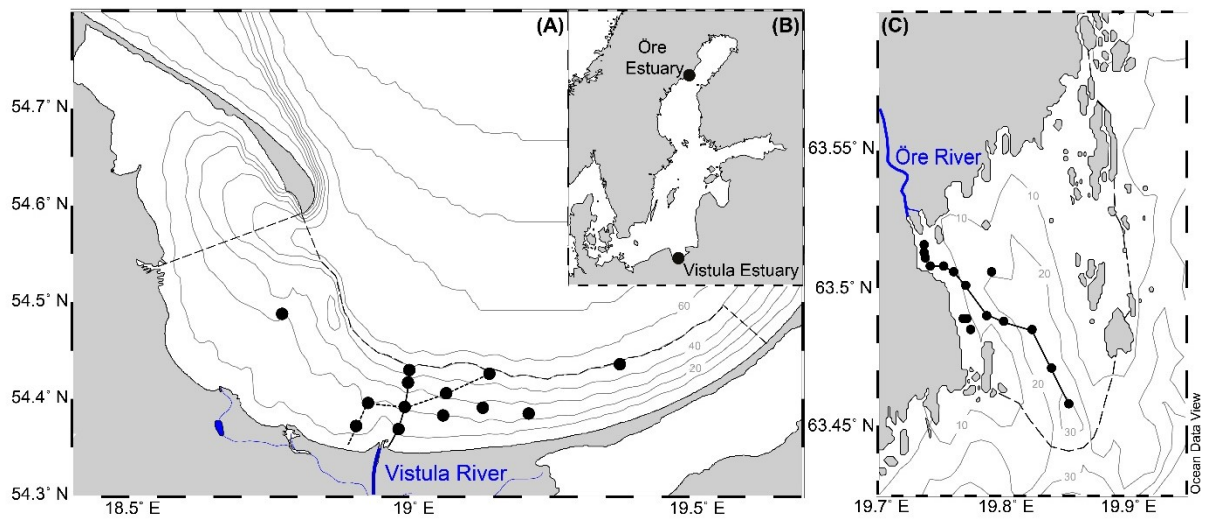
Figure 1: Map showing the locations of the Vistula estuary (A) and Öre estuary (B) in the Baltic Sea (C). The boundaries of the estuaries are indicated by the dashed lines (see Section 2.1 for details). Lines along the station points represent the transects shown in Figures 2 and 3. Vistula estuary: VE I (solid line), VE II (dotted line).
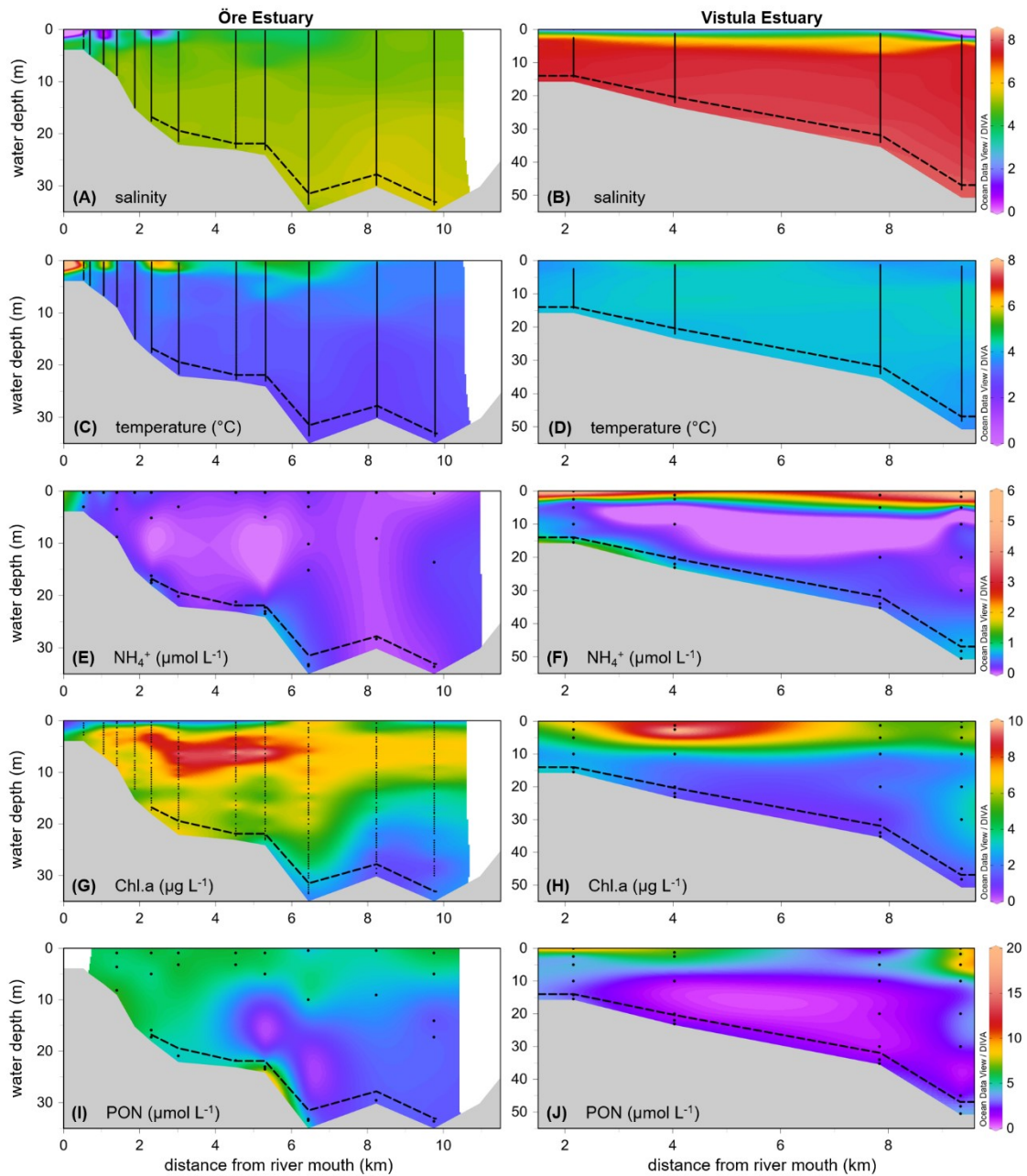
Figure 2: Environmental variables of the water column along a sampling transect (vertical line or points) from the river mouth to the outlets of the Öre (left) and Vistula (right) estuaries in spring. Note that, due to different optical properties of the water and different measurement methods, the chlorophyll-a (Chl.*a*) concentrations are not directly comparable between the two estuaries; rather, the figures provide qualitative information on the presence/absence of phytoplankton. Bottom topography was estimated from the water depths of the stations. The dashed line represents the vertical extent of the bottom boundary layer (BBL, see Section 2.1.1). The plots were derived from 12 (Öre estuary) and 4 (Vistula estuary) profiles using DIVA-gridding in Ocean Data view (Schlitzer, 2015). Plots of salinity, temperature and particulate organic nitrogen (PON) in the Öre estuary are reproduced from Hellemann et al. (2017).
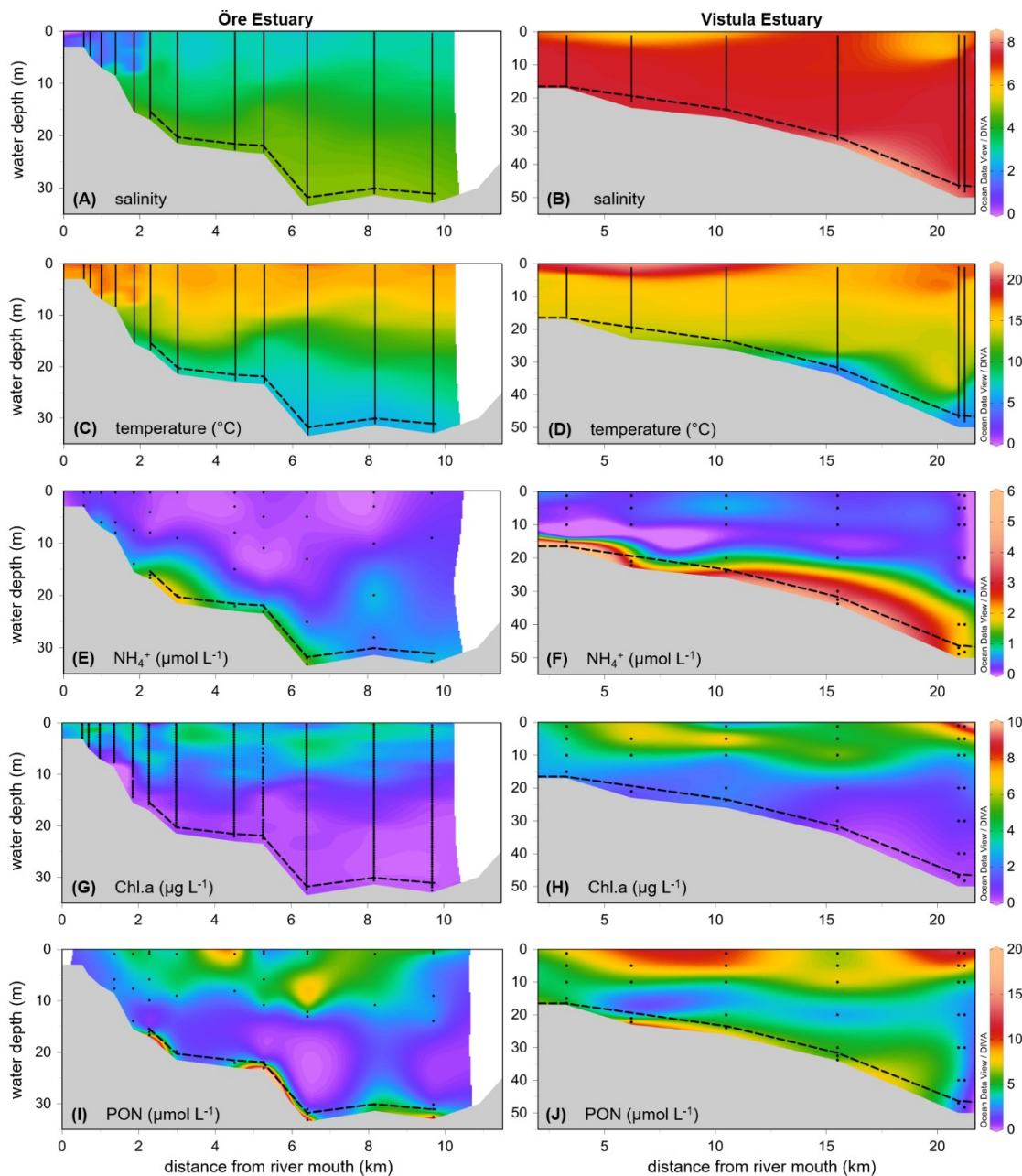
Figure 3: Environmental variables of the water column along a transect (vertical line or points) from the river mouth to the outermost station in the Öre (left) and Vistula (right) estuaries in summer. Note that, due to different optical properties of the water and different measurement methods, the Chl.*a* concentrations are not directly comparable between the two estuaries; rather, the figures provide qualitative information on the presence/absence of phytoplankton. Bottom topography was estimated from the water depths of the stations. The dashed line represents the vertical extent of the BBL (see Section 2.1.1). The plots were derived from 12 (Öre estuary) and 6 (Vistula estuary) profiles using DIVA-gridding in Ocean Data view (Schlitzer, 2015). Plots of salinity, temperature and particulate organic nitrogen (PON) in the Öre estuary are reproduced from Hellemann et al. (2017).
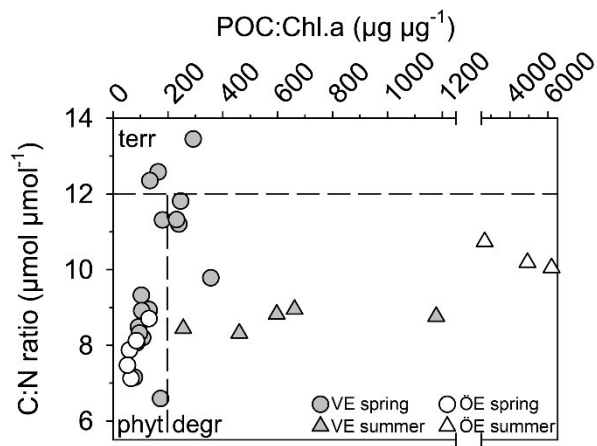
Figure 4: Ratio of particulate organic carbon to nitrogen (C:N ratio) plotted against the ratio of particulate organic carbon (POC) to Chl.*a* in the bottom boundary layer (BBL) of the Vistula and Öre estuaries in spring and summer. According to Savoye et al. (2003), a C:N ratio of >12 is assigned as terrestrial (terr) particulate organic matter (POM); according to Cifuentes et al. (1988), a POC:Chl.*a* ratio <200 indicates newly produced phytoplankton POM (phyt), and a ratio of >200 degraded phytoplankton POM (degr).

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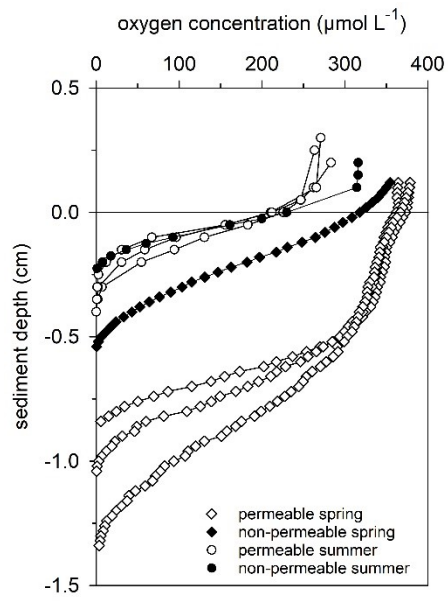
45   **Figure 5: Pore-water oxygen concentration profiles in the permeable (n=3) and non-permeable (n=1) sediments of representative stations of the Vistula estuary in spring and summer. The zero line indicates the sediment surface.**
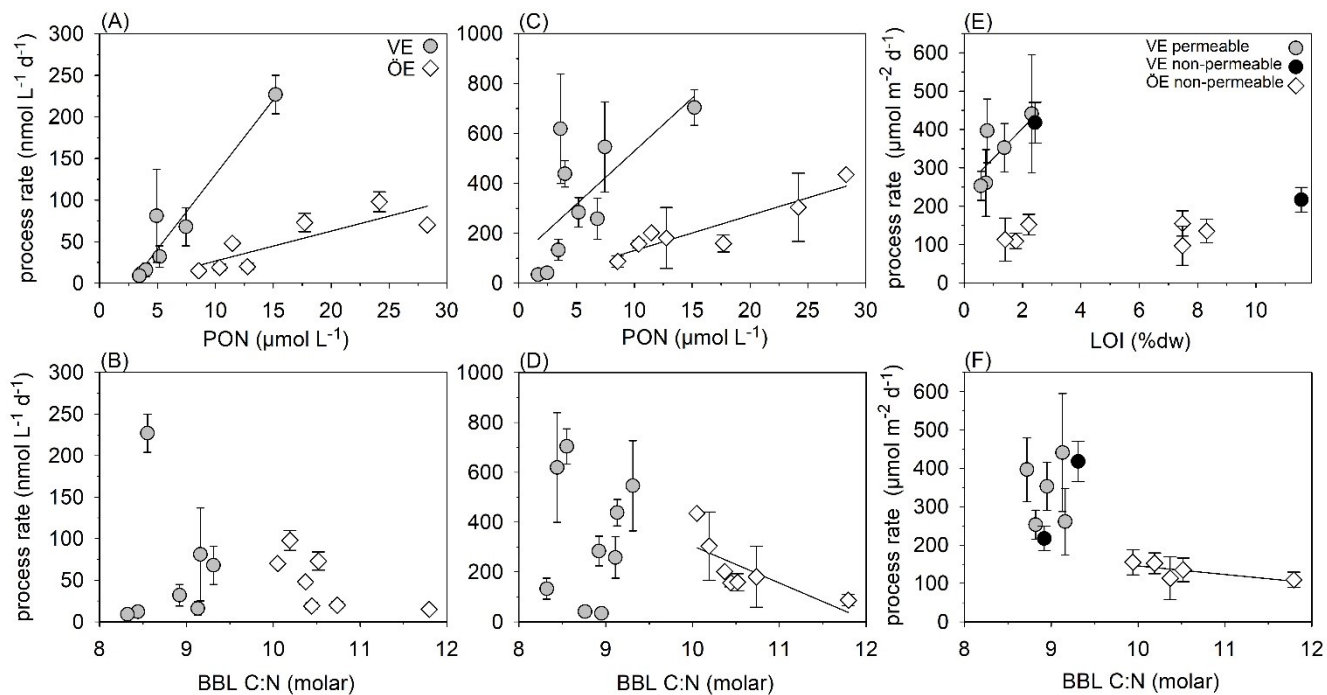
Figure 6: Correlations of the nitrification rates in the bottom boundary layer (BBL) with the particulate organic nitrogen (PON) concentration (A) and particulate C:N ratio (B); ammonium assimilation rates in the BBL with the PON concentration (C) and particulate C:N ratio (D); and coupled nitrification-denitrification rates in the sediment with loss on ignition (LOI) (E) and the particulate C:N ratio (F). Solid lines indicate significant correlations.

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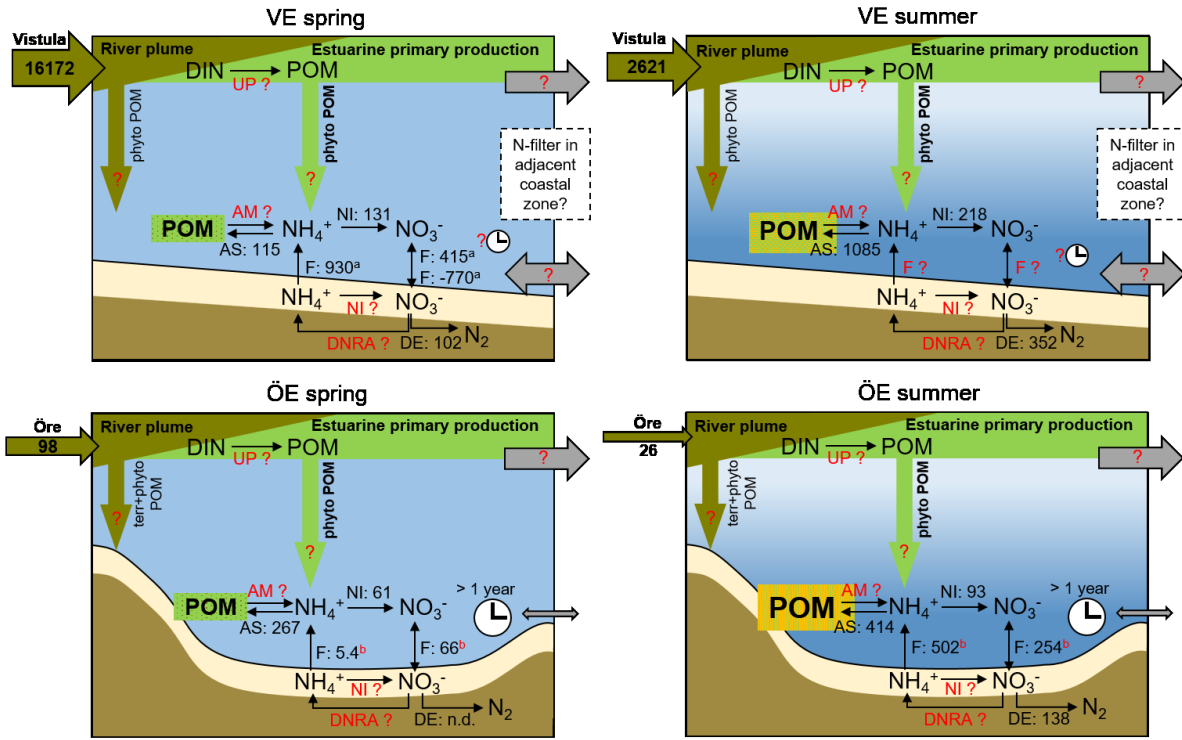
Figure 7: Schematic of the N-filter in the Vistula (top) and Öre (bottom) estuaries. The riverine total N loads are given in t month⁻¹ in the horizontal brown arrows. The process rates of nitrification (NI), ammonium assimilation (AS) and denitrification (DE) determined in this study are given in μmol m⁻² d⁻¹. Volumetric nitrification and ammonium assimilation rates are integrated over the vertical BBL extent (given in section 2.1). Fluxes of NH₄⁺ and NO₃⁻ (F) in the Vistula estuary are from Thoms et al. (2018; in situ incubations) and in the Öre estuary from Nedwell et al. (1983; core incubations, not in situ). Other microbial N retention process rates such as N uptake in the surface (UP), benthic ammonification (AM), nitrification (NI) and dissimilatory reduction to ammonia (DNRA) in the sediment, as well as sedimentation rates of particulate organic matter (POM), transport rates, and the particle (VE) and nutrient (VE, ÖE) residence time (white clock) are still unknown for these two estuaries (marked in red). In both estuaries, riverine DIN is supplied to the benthic system indirectly, via POM build-up and sedimentation which uncouples the peak river N load in spring from enhanced N turnover in the benthic system in summer. In the Öre estuary, the limited bottom water exchange and hence the long particle residence time results in a high efficiency of the estuarine N-filter. In the Vistula estuary, the unrestricted bottom topography may lead to the enhanced alongshore transport of DIN and POM and thus to a potential extension of the coastal filter function over a larger area and a longer time scale. Please note, this figure is not intended to present a closed N budget for these coastal zones.