KLAIPĖDA UNIVERSITY

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LOADS, TRANSPORT AND TRANSFORMATIONS OF NUTRIENTS N, P AND SI ALONG THE RIVER-LAGOON-SEA CONTINUUM

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MAISTINGŲJŲ MEDŽIAGŲ N, P IR SI SRAUTAI, PERNAŠA IR VIRSMAI UPĖS–LAGŪNOS–JŪROS KONTINUUME

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Abstract

Nutrient loads (N, Si and P) and their ecological stoichiometry (*sensu* Redfield) were analyzed along the Nemunas River-Curonian Lagoon (CL)-Baltic Sea continuum, and budgets were calculated. The mechanisms linking nutrient loads and the lagoon functioning were also analyzed by means of laboratory experiments. It was hypothesized that 1) seasonal variability of nutrient stoichiometry regulates algal communities; 2) cyanobacteria blooms affect the functioning of the CL; 3) blooms are self-promoting through anoxia and benthic P release that affect N-retention in the lagoon. The first and second hypotheses were tested through 5 years, using monthly analysis of nutrient loads to and from the CL and by whole system budgets. The third hypothesis was validated through measurement of P fluxes under anoxia and of N-related processes in the benthic and pelagic compartments.

The results of the study suggest a significant drop in total P loads to the lagoon as compared to historical data, while N loads remain high. Interestingly, P loads showed limited interannual fluctuations, while N loads varied by 50 %, suggesting short-term control of their genesis and export. Despite P reduction, a regular, strong limitation of N and Si occurs in the summer, favoring the diatoms-cyanobacteria shift. Mass balance calculations suggest that large cyanobacteria blooms impact the nutrient retention capacity of the CL, due to large export of particulate matter and regeneration of nutrients from sediments, as confirmed by laboratory experiments. Under a scenario of climatic and socio-economic changes, the regular monitoring of nutrient loads and stoichiometry along the Nemunas River-CL-Baltic Sea continuum must be conducted further.

Key words

Curonian Lagoon, nutrients, ecological stoichiometry, retention, phytoplankton blooms.

Reziumė

Maistingųjų medžiagų srautas (N, Si ir P) ir jo ekologinė stechiometrija (t. y. Redfyldo santykis (Redfield ratio)) buvo analizuojami Nemuno upės–Kuršių marių–Baltijos jūros kontinuume, vėliau – sudarant maistingųjų medžiagų balansą. Siekiant nustatyti mechanizmus, lemiančius lagūnos funkcionavimą, buvo atlikti eksperimentai, tiriantys biogeocheminius maistingųjų medžiagų virsmus. Pagrindinės darbo hipotezės buvo šios: 1) maistingųjų medžiagų stechiometrijos pokyčiai sezono metu lemia planktono bendrijos dinamiką, 2) melsvabakterių „žydėjimas" veikia Kuršių marių funkcionavimą ir 3) planktono „žydėjimas" gali palaikyti pats save, sukeldamas deguonies trūkumą, dėl ko P atsipalaiduoja iš dugno nuosėdų, o tai lemia N sulaikymą sistemoje. Pirma ir antra hipotezės buvo patikrintos atliekant maistingųjų medžiagų srauto į Kuršių marias ir iš jų matavimą 5 metų laikotarpyje, vėliau – sudarant masių balansą. Trečia hipotezė patikrinta vertinant P apykaitą tarp nuosėdų ir vandens storymės deguonies trūkumo sąlygomis bei išmatuojant N mikrobiologinius virsmus mariose.

Lygindami su anksčiau publikuotais duomenimis, pastebime ženklų P srautų į Kuršių marias sumažėjimą, tuo tarpu N srautai tirtuoju periodu išliko dideli. Skirtingai nei P srautai, kurie nedaug skyrėsi tarp metų, N srautai svyravo apie 50 %. Šie svyravimai byloja apie intensyvius procesus, lemiančius N atsipalaidavimą ir pernašą upės baseine. Fosforo sumažėjimas ir vasaros metu susidaranti pastebima N ir Si limitacija lemia perėjimą nuo diatominių dumblių prie melsvabakterių „žydėjimo". Sudarytas masių balansas atskleidė, kad maistingųjų medžiagų sulaikymas mariose priklauso nuo melsvabakterių „žydėjimo" intensyvumo. Esant intensyviam „žydėjimui" padidėja organinės medžiagos išnešimas į jūrą ir ištirpusių maistingųjų medžiagų išsiskyrimas iš dugno nuosėdų. Šis darbas taip pat atskleidžia, kad besikeičiančio klimato ir socioekonominių pokyčių kontekste būtina tęsti maistingųjų medžiagų srautų ir jų stechiometrijos matavimus Nemuno upės–Kuršių marių–Baltijos jūros kontinuume.

Reikšmingi žodžiai

Kuršių marios, maistingosios medžiagos, ekologinė stechiometrija, sulaikymas, fitoplanktono žydėjimas.

Contents

List of original publications

The material of this study was presented in 5 original publications, published in peer-reviewed scientific journals and 1 manuscript, referred in the text by their Roman numbers:

I. Zilius, M., Giordani, G., Petkuviene, J., Lubiene, I., Ruginis, T., Bartoli, M., 2015. Phosphorus mobility under short-term anoxic conditions in two shallow eutrophic coastal systems (Curonian and Sacca di Goro lagoons). Estuarine, Coastal and Shelf Science, 164, 134-146.

II. Petkuviene, J., Zilius, M., Lubiene, I., Ruginis, T., Giordani, G., Razinkovas-Baziukas, A., Bartoli, M., 2016. Phosphorus Cycling in a Freshwater Estuary Impacted by Cyanobacterial Blooms. Estuaries and coasts, 39(5), 1386-1402.

III. Vybernaite-Lubiene, I., Zilius, M., Giordani, G., Petkuviene, J., Vaiciute, D., Bukaveckas, P. A., Bartoli, M., 2017. Effect of algal blooms on retention of N, Si and P in Europe's largest coastal lagoon. Estuarine, Coastal and Shelf Science, 194, 217-228.

IV. Vybernaite-Lubiene, I., Zilius, M., Saltyte-Vaisiauske, L., Bartoli, M., 2018. Recent trends (2012–2016) of the N, Si and P loads from the Nemunas River watershed. Water, 10(9), 1178.

V. Zilius, M., Vybernaite-Lubiene, I., Vaiciute, D., Petkuviene, J., Zemlys, P., Liskow, I., Voss, M., Bartoli, M., Bukaveckas, P.A. The influence of cyanobacteria blooms on nitrogen storage and retention in a Baltic coastal lagoon (Accepted in Biogeochemistry).

VI. Vybernaite-Lubiene, I., Zilius, M., Bartoli, M., Petkuviene, J., Zemlys, P., Giordani G. Net metabolism and nutrient budget studied with the LOICZ budget approach in the Curonian Lagoon. Manuscript.

Author's contributions

I. Vybernaite-Lubiene took part in the study design and data collection and was in charge of the analytical work; she also contributed to the writing.

II. Vybernaite-Lubiene took part in the study design and data collection and was in charge of the analytical work; she also contributed to the writing.

III. Vybernaite-Lubiene designed the sampling strategy, realized all samplings, analytical work and data analysis and wrote the manuscript draft. A large fraction of her time was spent to refine analytical procedures in order to improve the quality of data.

IV. Vybernaite-Lubiene designed the sampling strategy, realized all samplings, analytical work and data analysis and wrote the manuscript draft.

V. Vybernaite-Lubiene took part in the study design and data collection and was in charge of the analytical work; she also contributed to the writing.
VI. Vybernaite-Lubiene calculated the budgets and wrote the paper draft.

Abbreviations

Abbreviation	Explanation
Ar	Argon
BSi	Biogenic silica
BSAP	Baltic Sea Action Plan
C	Carbon
Chl-a	Chlorophyll *a*
CL	Curonian Lagoon
DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus
DNRA	Dissimilatory nitrate reduction to ammonium
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
DSi	Dissolved reactive silica
LOICZ	Land and Ocean Interaction at Coastal Zone
MIMS	Membrane inlet mass spectrometer
N	Nitrogen
N_2	Dinitrogen gas
NEM	Net Ecosystem Metabolism
NH_4^+	Dissolved ammonium
NO_3^-	Dissolved nitrates
NO_2^-	Dissolved nitrites
NO_x^-	Combined nitrites and nitrates
O_2	Oxygen
P	Phosphorus
PN	Particulate nitrogen
PP	Particulate phosphorus
Si	Silica
TDN	Total dissolved nitrogen
TDP	Total dissolved phosphorus
TN	Total nitrogen
TP	Total phosphorus
TSi	Total silica

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Introduction

Combined anthropogenic and climatic effects on N, Si and P export from large watersheds. In the last decades, the impact of human activities on biogeochemical cycles has increased in scale and for elements such as nitrogen (N), phosphorous (P) and silica (Si) such impact has now a recognized global scale (Bernot and Dodds, 2005; Mulholland et al., 2008; Paerl, 2009; Han and Allan, 2012). Inland and coastal waters have become more and more enriched with N and P due to intensive soil fertilization for agriculture and wastewater discharge (Galloway et al., 2008; Paerl, 2009). Nutrient excess can favour and accelerate eutrophication processes up to levels where phytoplankton or macroalgal growth cannot be controlled by pelagic or benthic grazing, resulting in algal biomass accumulation, organic enrichment and oxygen depletion (Carpenter et al., 1998; Rabalais et al., 2002). The simultaneous reduction of Si delivery to aquatic ecosystems has resulted in unbalanced nutrient stoichiometry, favouring harmful algal blooms and further impacting the functioning of benthic and pelagic compartments (Cloern, 2001; Yunev et al., 2007; Howarth et al., 2011; Bresciani et al., 2014).

Global changes of biogeochemical cycles have also altered the scale of analysis of processes (Lehner et al., 2006; Galloway et al., 2008). In the past, research in the field of eutrophication and aquatic biogeochemistry was traditionally analysing single water bodies or single nutrients. The modern approach couples aquatic ecosystems to their watersheds or to macroregions and considers simultaneously the trajectories of different elements (Chapin et al., 2002; Galloway and Cowling, 2002, Viaroli et al., 2015, HELCOM, 2015). Climatic anomalies and anthropogenic pressures in catchments such as agriculture, urbanization, landscape homogenization, and river damming may in fact produce a wide range of contrasting element-specific effects, either amplifying or reducing their delivery or retention and resulting in strong impact on their ecological stoichiometry (Bennet et al., 2001; Sternberg, 2006; Gruber and Galloway, 2008; Romero et al., 2016). A few studies have simultaneously analysed long-term changes of N, Si and P loads, despite the well-recognized role of their relative abundance on algal community composition (Billen et al., 2001). Silica genesis and export from watersheds was generally calculated from the lithology and assumed to vary mostly due to hydrological features (Billen et al., 2001; Garnier et al., 2002). The recent literature focusing on the terrestrial Si cycle stresses how agricultural activities may impact the delivery of this element to the coastal areas and should therefore be considered when analysing its budgets with respect to long-term variations of land use (Carey and Fulweiler, 2012).

The percentage of N load generated within a watershed, which is not exported via river discharge ranges between 70 and 95 %, with a substantial variability, observed between temperate and arid regions (Howarth et al., 2006; Schaefer et al., 2009; Lassaletta et al., 2012; Romero et al., 2016; Goyette et al., 2016). Retention includes processes such as storage in sediments through primary production uptake or loss to the atmosphere via denitrification or anaerobic ammonium oxidation with nitrites (anammox). Similar or even higher percentages (85 to 99 %) are reported for P retention (Han et al., 2011; Hong et al., 2012, Zhang et al., 2015), which might be coupled to those of Si via diatom blooms and nutrient uptake (Le et al., 2010). Studies focusing on Si are scarce as compared to those on N and P and global estimates of Si retention are affected by a large degree of uncertainty (Turner et al., 2003; Beusen et al., 2009; Seitzinger et al., 2010).

Several processes explain how N is retained within watersheds through uptake by crops and natural vegetation, storage in soils, percolation and accumulation in groundwater (Bartoli et al., 2012; Billen et al., 2013; Soana et al., 2017; Ascott et al., 2017). Microbially mediated N transformations in aquatic lakes, canals and rivers are measured and reported in several papers (Castaldelli et al., 2015), while methodological difficulties limit denitrification or N_2 fixation measurements in soils and groundwater (Groffman et al., 2006). The limited dataset of some soil-related processes limits our knowledge of how they are regulated or affected by climatic anomalies (i.e. drought or precipitation extremes), or agricultural practices (i.e. irrigation or land use) (Vagstad et al., 2004).

The increasing P accumulation in agricultural soils elevates the potential P erosion, runoff and percolation to surface and groundwater (Bennet et al., 2001; Prasuhn and

Sieber, 2005). Dissolved P losses can be significant in soils where iron, aluminium, and calcium absorption capacity is saturated, allowing P to move more readily toward aquatic ecosystems (Sims et al., 1998). Riparian buffers and wetland areas, impoundments, and conservation agriculture practices may trap some of the exported P, while the rest may contribute to eutrophication processes, and be retained via assimilation or incorporation within sediments (Bennet et al., 2001; Wang and Li, 2010; Canga et al., 2016; Kronvang et al., 2016).

Silica delivery to aquatic ecosystems was assumed to be regulated by processes as chemical weathering of silicate minerals in rocks and soils (Sommer et al., 2006; Struyf et al., 2009). However, anthropogenic pressures as hydrological alterations (Ittekkot et al., 2000; Frings et al., 2014) and the agricultural production loop (Vandevenne et al., 2012; Viaroli et al., 2013) were demonstrated to affect the biogeochemical Si cycle. Among hydrological alterations, river damming intensified during last century, favouring diatom growth and settling of their frustules in reservoirs, resulting in net upstream retention and less export of particulate Si to the coastal zone (Harrison et al., 2012; Maavara et al., 2014). Concerning the agricultural production loop, crops harvest results in a significant export of biogenic silica (BSi) from soil, which can determine a progressive depletion of bio-available silica due to intensive agricultural practices (Carey and Fulweiler, 2012; Vandevenne et al., 2012; Vandevenne et al., 2015; Carey et al., 2016). Manure spreading and burial of crop residues can increase BSi in soils, but these contributions remain understudied (Viaroli et al., 2015). For example, a very few data on livestock waste Si content are available (Song et al., 2014; Tsai and Liu, 2016).

Under a scenario of increased human and climatic perturbations, the understanding of the factors controlling N, Si and P export from watersheds to aquatic environments is becoming crucial. Perturbations may in fact differentially affect the cycling of three elements and alter their ecological stoichiometry, which regulates the composition of algal communities. Significant shifts from molar ratios as that of Redfield (C:Si:N:P=106:15:16:1; Brzezinski, 1985) may produce large changes in phytoplankton communities. Silica limitation for example favours the bloom of non-siliceous algae such as cyanobacteria or dinoflagellates (Yunev et al., 2007; Bresciani et al., 2014). In order to understand and contrast the trajectories of eutrophication processes, it seems important to couple aquatic ecosystems with their watersheds and to adopt a multi-element approach with the ecological stoichiometry as conceptual reference.

Nutrient loads, stoichiometry and their direct and indirect effect on lagoon functioning. Estuaries and lagoons, being situated at the interface between freshwater and marine environments, are peculiar environments characterized by very specific conditions, communities, chemical gradients and functioning (Howarth et al., 2011; Asmala et al., 2017). These ecotones were intensively studied in the last decades due to increasing transport of nutrients from rivers and eutrophication, resulting in green tides and dystrophy (Bennett et al., 2001; Anderson et al., 2002). Green tides were strongly affecting the functioning of these systems, with a spring net autotrophic period and a summer net heterotrophic phase (Viaroli et al., 2015). Extreme net autotrophy and net heterotrophy characterize unstable systems that are prone to sudden collapse of the production and where the respiration of the organic bulk produced in spring may exhaust oxygen (O_2) availability in the water column and produce huge crises, affecting benthic biodiversity and processes (Austen et al., 2002; Danovaro et al., 2008). The intense research activity that was produced during the 90's allowed a deep understanding of the synthesis and decomposition of the within lagoon organic matter, of internal biogeochemical buffers and of their saturation or carrying capacity (De Wit, 2011). Nitrogen was the main and most studied element in terms of uptake, storage, burial and loss via denitrification (NICE project, Nitrogen Cycling in Estuaries). Comparatively, phosphorous dynamics were less studied as considered less important in coastal versus inland water bodies while studies on silica are very scarce. Afterwards, research activities moved upstream, where loads of nutrients are generated and focused on basins and watersheds and in particular on agriculture, animal farming and sewage treatment plants (Seitzinger et al., 2010; Bosch et al., 2013). In Europe, a number of research programs were started in order to coordinate the political actions and target a significant reduction of exported loads to the coastal zone (e.g. the European Nitrogen Assessment, ENA, http://www.nine-esf.org/node/204/ENA.html). The Baltic macro region is a good example of geographical area where a political coordination among all the countries surrounding the Baltic Sea was established in order to define common targets aiming at the improvement of the trophic status of this menaced marine system (e.g. HELCOM, Baltic Sea Action Plan (BSAP)). After another decade of political actions, mostly targeting the terrestrial side, upstream the coastal area, significant results were obtained in a few regions, while in most impacted areas a large lag between political decisions, action and recovery/response of the system was demonstrated (Bouraoui and Grizzetti, 2011). What seems unavoidable is to keep simultaneously active research activities upstream and downstream the coastal area, in order to analyze how estuaries and lagoons react to variable (hopefully decreasing) nutrient loads from the terrestrial environments. It is in fact likely that political actions may differentially affect different nutrient genesis, transport and retention resulting in altered stoichiometry. An excess decrease of N loads compared to those of P for example may select and favor blooms of harmful algae, something which should be avoided. In watershed therefore political actions should target a balanced reduction of nutrients, in order to keep their stoichiometry (= relative availability) close the Redfield ratio, which promotes the dominance of diatoms. Under the scenarios of nutrient reduction, the analysis of estuarine and lagoon functioning, in terms of their ability to process nutrient, synthesize organic matter and keep equilibrated flows of energy and matter among different ecosystem compartments, seems important (e. g. via simple budgeting approach, Giordani et al., 2008). Such an investigation does not overlap with the one conducted two decades ago as the ongoing trajectories are opposite, along an oligotrophication path. It appears therefore extremely interesting to analyze nutrient budget within lagoons and estuaries under variable (decreasing) nutrient loads.

Estuaries and lagoons, due to dynamic mixing of nutrient-rich freshwater with oxygen-rich marine water, generally display high rates of biogeochemical activity (Nixon et al., 1996; Boyer and Howarth, 2008; Asmala et al., 2017). An important aspect of the ecosystem services provided by estuaries is their ability to transform and retain nutrients, thereby mitigating eutrophication of the coastal environment (Nedwell et al., 1999). It is important to quantify the role of estuaries as sources or sinks of nutrients, to better understand the processes that regulate nutrient retention, and to document how these processes respond to changing nutrient loads (Galloway et al., 2004; Boyer and Howarth, 2008; Li et al., 2014). In brackish areas, riverine nutrient loads are acted upon by a variety of processes and it is of particular interest to find factors, which drive estuarine processes and which govern nutrient loads to estuaries. Relevant estuarine processes include biotic assimilation by primary producers and bacteria, remineralization of organic matter, nitrification, denitrification, N_2 fixation, sorption/desorption, sedimentation/resuspension and burial (Bartoli et al., 2012; Loken et al., 2016). However, N cycling in estuaries has received considerable attention, but there remains a need to better understand the mechanisms governing N retention and storage, particularly with respect to quantifying sources of N supporting algal blooms (Wood et al., 2016). Estuaries and lagoons are considered to be net sinks for dissolved inorganic nutrients. However, export of particulate fractions may offset removal of dissolved inorganic forms, resulting in low net retention. The timing of nutrient delivery in relation to estuarine productivity cycles may be an important variable determining overall nutrient retention. The long residence time is expected to favour high rates of nutrient retention via biotic assimilation, burial within sediments and removal via denitrification (Nixon et al., 1996; Dettmann, 2001).

Blooms and their effect on N and P cycling. The previous paragraphs discuss the effect of global changes on nutrient transport to lagoons changing their loads in term of storage or gain, and timing of the delivery. The different patterns in nutrient retention or release within watersheds may have profound effects on downstream lagoons and coastal areas. For example, the loads delivered with unbalanced nutrient stoichiometry may stimulate blooms of specific phytoplankton groups, potentially harmful and toxic for other groups of organisms. Within lagoon ecosystems, phytoplankton blooms may alter biogeochemical cycling through sudden organic matter inputs to the sediment, resulting in bottom water anoxia, death of benthic communities and dystrophy. Coastal lagoons, due to these events, may switch from sink to source, and such a transition may have two consequences. The first is the increased export of dissolved and particulate nutrients to the open sea and the second is the maintenance of prolonged blooms.

Phytoplankton blooms are spreading worldwide (Conley et al., 2009; Qin et al., 2010) and harmful cyanobacteria blooms are especially common in the hypertrophic and shallow freshwater lagoons along the coast of the Baltic Sea (Nawrocka and Kobos, 2011; Bresciani et al., 2012). The Curonian Lagoon is one of these areas where the phytoplankton in summer months is dominated by cyanobacteria, representing up to 90 % of total chlorophyll a (Chl-a), with a high abundance of the N_2 fixing *Aphanizomenon flos aquae* (Pilkaityte and Razinkovas, 2007). High concentrations, exceeding 200 μg Chl-a l^{-1}, are frequent and spread over 70 % of the lagoon surface (Bresciani et al., 2012; Zilius et al., 2014). The frequent cyanobacteria blooms may considerably alter both riverine nutrient loads and their biogeochemical transformations. Cyanobacteria has positive buoyance due to gas vesicle and that allows them floating or being exported to the sea (Walsby, 1994; Chu et al., 2007). The lack of buoyance leads cyanobacteria accumulation in surface sediments. Decomposition of algal biomass results in oxygen depletion and altered redox conditions in sediments. This may affect the variety of N-related microbial processes. For example, under chemically reduced conditions denitrification is generally suppressed and the dissimilatory nitrate reduction to ammonium (DNRA) becomes the dominant process (Christensen et al., 2000). This offset loss of N through the denitrification or anammox, and subsequently creates self-sustaining phytoplankton blooms (Pant and Reddy, 2001; Zilius et al., 2014). Burial or mineralization of deposited organic matter also has impact on P cycling. Due to increase of respiration may lead to O_2 depletion and therefore iron reduction may liberate P, which was chemically bound in oxidized iron minerals. Sudden P release in excess to N or Si may further stimulate blooms of N_2 fixing organisms, which is a serious threat for ecological, recreational and economic aspects (Vahtera et al., 2007).

In cascade, the ecological stoichiometry of regenerated nutrients may potentially feedback on the growth of phytoplankton (Eyre and Ferguson, 2009). In a recent paper, Zilius et al. (2016) demonstrated that the burial of cyanobacteria within sediments stimulates large release of dissolved organic nitrogen (DON), which may be assimilated by phytoplankton creating another positive feedback. If nutrients affect algal primary production and community composition, blooms affect nutrient cycling. As demonstrated for opportunistic freshwater invasive species (e.g. pleustonic communities), the onset of cyanobacteria blooms may create a series of feedback mechanism that self-promote their occurrence. When cyanobacteria dominate Si is not assimilated and is exported from the lagoon, resulting in surface sediment layer devoid of this precious element. Floating cyanobacteria can also regulate the lack of N by fixing dissolved atmospheric dinitrogen (N_2). N_2 fixation during cyanobacteria booms can offset the losses via denitrification, also to support blooms when external loads are low. N_2 fixation also gains resulting in additional flux of this element to the sediment or to the open sea.

Aim and objectives

The general aims of the present study were to quantify the seasonal loads of the three nutrients N, Si and P delivered to the Curonian Lagoon from the Nemunas River watershed, and to analyse how the biological and physical processes occurring within the Curonian Lagoon affect these loads and their ecological stoichiometry along their path to the Baltic Sea.

The specific objectives of the thesis were:

1. To estimate timing and magnitude of N, Si and P loads generated from the Nemunas watershed, and to compare recent loads with previously published data;
2. To evaluate the effect of blooms on retention or net export of N, P and Si in the Curonian Lagoon;
3. To analyse the Curonian Lagoon net autotrophy (nutrient sink) or net heterotrophy (nutrient source) via the LOICZ budget approach;
4. To analyse in detail pelagic and benthic processes affecting nutrient transformations and fluxes, to provide a mechanistic interpretation of processes measured at the macro scale.

Novelty of the study

In the last decade, the knowledge about the biogeochemistry of N and P in the Curonian Lagoon has substantially been improved thanks to the PhD theses of M. Žilius (2011) and J. Petkuvienė (2015). Žilius and Petkuvienė works focussed mainly on mechanisms (benthic and pelagic dynamics of microbial and micro-algal activities) linking blooms to N and P sedimentary processes, respectively. They worked on a few representative stations within a very large estuary (1,584 km^2), and the upscaling of their results therefore is affected by a large degree of uncertainty. What was missing in the past and ongoing research activities in the Curonian Lagoon is a robust experimental validation of the effects of variable hydrologic loading rates and the occurrence of algal blooms on nutrient transformation and retention at the whole lagoon scale. A detailed temporal analysis of nutrient loads to the estuary and from the estuary to the sea, in all their forms, was also missing. This was contrasting with the need to validate political actions targeting, a significant reduction of N and P loads to coastal areas in the Baltic macro region, and in particular in Lithuania.

The novel aspects of this thesis deal with 1) frequent monitoring of dissolved and particulate forms of N, P and Si from a large watershed to the Curonian Lagoon over 5-years, 2) trend analysis of loads and ecological stoichiometry, 3) evaluation of how nutrient loads and stoichiometry and algal blooms affect the Curonian Lagoon whole-system functioning (in terms of sink-source role) and 4) provision of a mechanistic, experimental explanation of budgets. To the best of my knowledge, there are no previous works conducted in this geographical area where dissolved and particulate forms of N, Si and P, and their ecological stoichiometry were analysed simultaneously. Recent works stress that the ecological stoichiometry of N, Si and P, more than a single element analysis, is an important attribute of nutrient loads exported from a large watershed, as it affects algal communities and may trigger harmful algal blooms in adjacent estuarine and coastal areas (Conley et al., 2009; Pearl et al., 2011).

Scientific and applied significance of the results

An understanding of the dynamics and the processes regulating N, P and Si fluxes at the landscape scale is critical to management efforts aimed at reducing anthropogenic impacts on inland and coastal waters. Nutrient loads are acted upon by a variety of processes occurring in their path from the land to the sea, which alter the timing and magnitude of their delivery (Seitzinger et al., 2006; Boyer and Howarth, 2008; Luu et al., 2012). It is anticipated that climate change will increase the frequency and intensity of precipitation and storm events; therefore, it is important to understand how the delivery of nutrient loads to aquatic environments will be altered in future climate conditions (Cross et al., 2005). It is also important to analyse the impact of ongoing policy implementation on water quality BSAP and Water Framework Directive, and quantify how effective measures such as the nitrate (NO_3^-) or urban wastewater directives are at reducing the Nemunas River nutrient loads to the Baltic Sea (Bouraoui and Grizzetti, 2011; Voss et al. 2011; Šileika et al., 2013; HELCOM, 2015). Thus, long-term monitoring actions are necessary due to these ongoing changes, in order to understand how ecosystems react to different land use under different climatic conditions. These monitoring actions are specifically needed in regions of the Baltic Sea undergoing deep socio-economic transformations (Sileika et al., 2006; HELCOM, 2015). The evaluation of nutrient loads generated in watersheds and their budgets in large estuarine systems is also critical to understand the amounts of N, Si and P that are delivered to the open sea.

The results of this work provide completely new information on three key nutrients (N, P and Si) concentration, stoichiometry and loads measured at the Nemunas River gauging section and at the Curonian Lagoon mouth. This large dataset has allowed 1) comparing recent trend of nutrient loads with the scattered information available for one of the most important river discharging in the Baltic Sea; 2) performing mass budget at the whole lagoon scale in order to understand the functioning of this system, and in particular its sink-source role, which is temporally variable and affected by blooms; 3) linking regular drops in N:P and N:Si stoichiometry with phytoplankton community composition, and understanding the trophic cascade consequences triggered by large cyanobacteria colonies; 4) providing a missing framework where multiple mechanistic, small scale experiments can be interpreted and upscaled; 5) drawing attention on critical N loads exported from the Nemunas River watershed, similar to those measured 20 years ago and far from N reduction plans.

This work is scientifically robust, as demonstrated by the number of publications that were produced or supported by the dataset. It also has applied relevance, as it indirectly targets the whole catchment of the Nemunas River and integrates socio-economic and climate effects on nutrient genesis, transformations and downstream transport. It demonstrates that political actions resulted in significant P abatement but such actions were not effective for N. It also demonstrated that TN and TP loads exported to the sea could differ considerably if measured at the gauging section of Nemunas River (lagoon entrance) or at the Curonian Lagoon mouth (lagoon exit). This emphasizes the need to review monitoring programs and international commitments, for example to the HELCOM provided BSAP. To date HELCOM prioritizes maximal allowable nutrient loads directly from catchments to Baltic Sea, excluding internal retention in the lagoons. The results of this thesis show that the N and P reduction targets can be achieved faster if retention processes in transitional (estuarine) waters are considered.

Scientific approval

Results of this study were presented in 5 international and 2 national conferences:

1. VI Eurolag & VII Lagunet Conference: “Coastal lagoon domain and properties: from fundamental research to policy implementation”. Lecce, Italy, December 2013.
2. Littoral 2014: “Facing Present and Future Coast Challenges”. Klaipėda, Lithuania, September 2014.
3. 10th Baltic Sea Science Congress. Riga, Latvia, June 2015.
4. ECSA 56, Coastal systems in transition: “From a ‘natural’ to an ‘anthropogenically-modified’ state conference”. Bremen, Germany, September 2016.
5. The 11th Baltic Sea Science Congress: “Living along gradients: past, present, future”. Rostock, Germany, June 2017.
6. Scientific-practical conference “Sea and Coastal research-2014”. Klaipėda, Lithuania, April 2014.
7. 10th national conference, “Marine and Coastal Research“. Palanga, Lithuania, April 2017.

2

Material and methods

2.1 Study sites

The Nemunas River is the largest river in Lithuania with a catchment area of 97,864 km^2 of which 46,695 km^2 lay in Lithuania, 45,389 km^2 in Belarus and the rest in Latvia, Poland and Kaliningrad area (Gailiušis et al., 2001) Cultivated lands and forested areas cover nearly 60 and 40 % of the Nemunas River basin, respectively (Vaitkuviene and Dagys, 2008). The annual precipitation in the Nemunas River watershed varies from 520 to 800 mm (Sileika et al., 2006). The Nemunas is a lowland river with a long-term mean flow of 700 $m^3 s^{-1}$ and with seasonally variable discharge driven in part by the timing of spring snowmelt. The Nemunas enters the Curonian Lagoon, which discharges to the Baltic Sea. The Nemunas River is the third largest tributary and an important nutrient source to the Baltic Sea (Jakimavičius and Kriaučiūnienė, 2013; HELCOM, 2015).

The Curonian Lagoon is a large (1,584 km^2), shallow (mean depth 3.8 m), microtidal estuary situated along the SE Baltic coast (Fig. 1). Freshwater input to the estuary is dominated by the Nemunas River, which has an annual average discharge of 21.8 km^3, and accounts for 96 % of total inputs (Jakimavičius and Kriaučiūnienė, 2013). Additional freshwater inputs are from smaller tributaries (Bolshaya, Malaya Morianka, Kalinovka, Deima, Rybnaya, Minija, Dane and Dreverna rivers) located along the Russian and Lithuanian borders. Runoff to the Curonian Lagoon exhibits a

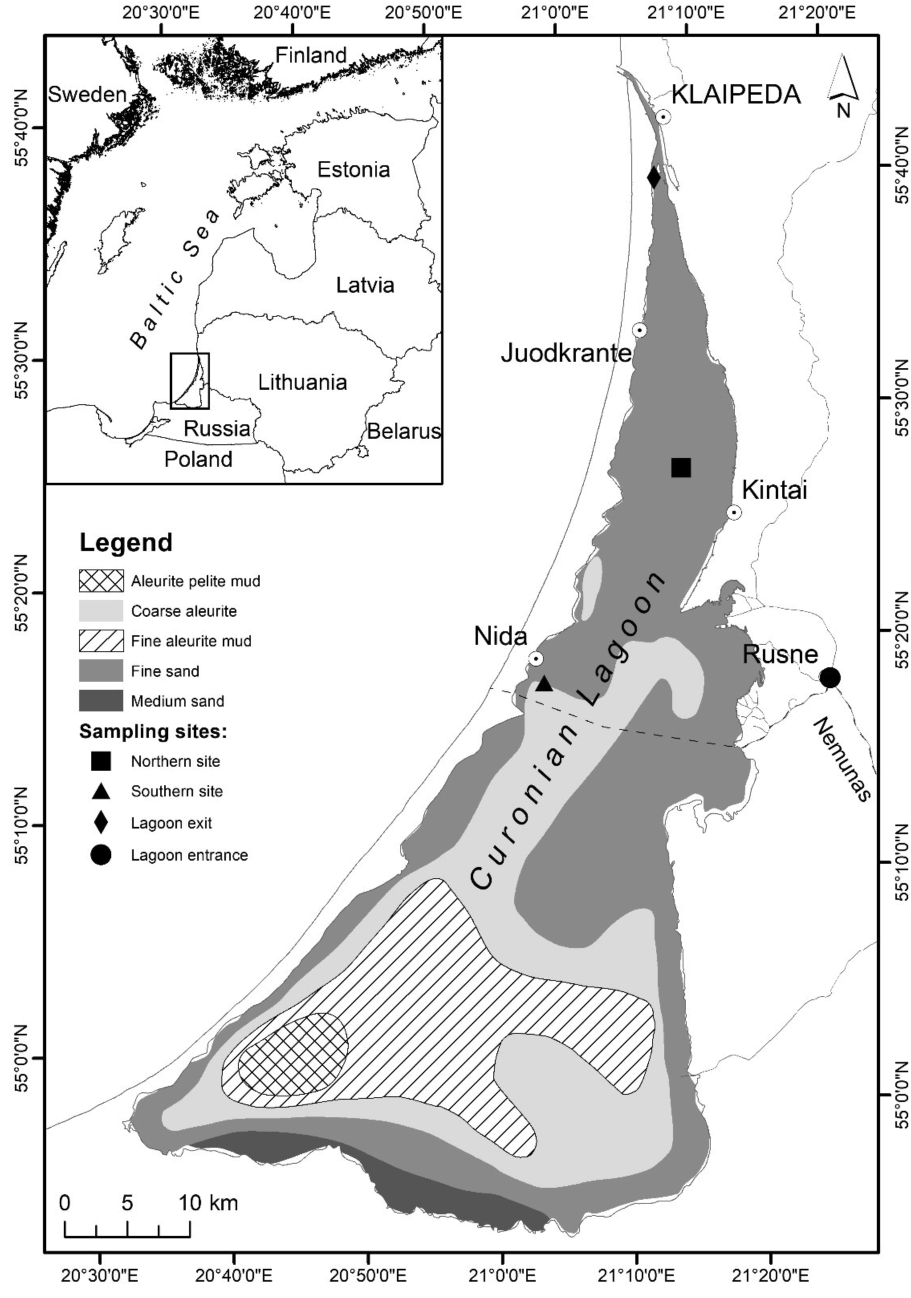

Fig. 1. Map of the Curonian Lagoon showing the distribution of sediment types and sampling locations (redrawn from Paper V).

seasonal pattern, peaking with snowmelt during March and April. The largest point source discharging to the lagoon is the sewage treatment plant for the city of Klaipeda (population = 200,000), which accounts for ~0.4 % (7.1 t P y^{-1}) of the annual Nemunas River input to the lagoon. The lagoon is connected to the Baltic Sea through a narrow strait and occasionally receives brackish water inputs from the sea during periods of wind–driven tidal forcing (Zemlys et al., 2013). These events are typically of short duration and result in small increases in salinity (in average 1–2, max. 7) in the northern portion of the lagoon.

The inflow of the Nemunas River divides the lagoon into northern and southern regions (54 and 44 % of the lagoon surface, respectively) that differ in water residence time, depth and sediment composition (Ferrarin et al., 2008; Zilius et al., 2014; Umgiesser et al., 2016). The northern part of the lagoon is characterized by shallow depths (1.5–2 m), short water renewal time (annual mean = 76 d; seasonal range = 50–100 d), and poor organic sandy sediments (Ferrarin et al., 2008; Zilius et al., 2014). The southern part of the lagoon is deeper (mean = 3.5 m), has a longer water renewal time (annual mean = 190 d; seasonal range = 100–250 d), high water Chl-a concentration in water column and organic–rich benthic deposits (predominantly silty sediments).

2.2 Sampling design

For riverine input analysis of three key macronutrients and their stoichiometry, samples were collected (5-years) at the Nemunas River gauging section (Lagoon Entrance, Fig. 1). For the mass balance analysis (2012–2015), water samples were collected additionally at outflow (Klaipeda Strait) of the lagoon (Lagoon Exit), and from an off-shore site in the Baltic Sea (55°55’13.1” N and 21°02’39.4” E), to estimate riverine inputs, lagoon export, and marine inputs, respectively. The internal processes for mass balance mechanistic explanation were measured at two sites: a northern site representing sandy substrates, and a southern site dominated by silty sediments (Fig. 1). The summary of performed activities is provided in Table 1.

Table 1. Summary of main activities carried in the Curonian Lagoon in the 2012–2016 period.

Type of activity	Sampling area	Sampling period	Measure	Frequency
Water characteristics	Lagoon	2013–2015	Temp., salinity, O_2, NH_4^+, NO_x^-, DON, PON, POC, DIP, DOP, TP, DSi DIP, DOP, TP, DSi, BSi, Chl-a, phytoplankton composition	Monthly/ biweekly

Type of activity	Sampling area	Sampling period	Measure	Frequency
Sediment characteristics	Lagoon	2015	C_{org}, PN_{sed}, $\delta^{13}C$, $\delta^{15}N$ and Chl-a	Seasonal
Benthic fluxes	Lagoon	2013/2015	NH_4^+, NO_x^-, DON, N_2, DIP	Seasonal
N_2 fixation	Lagoon	2015	$^{15}N_2$ uptake	Monthly/ biweekly
N-uptake	Lagoon	2015	Pelagic NPP	Seasonal
Loads	River/Lagoon exit/Sea	2012–2016	Temp., salinity, Chl-a, NH_4^+, NO_x^-, DON, PON $\delta^{15}N$, DIP, DOP, TP, DSi, BSi	Weekly-monthly

2.3 Main analytical chemical analysis

Dissolved nutrient analyses. In the laboratory, all water samples (n = 3 for each site) for dissolved nutrient analysis were filtered and transferred into tubes for inorganic and organic N and P, and inorganic Si spectrophotometric measurements. For detailed information about the methods, see Papers I–V.

Particulate nutrient and chlorophyll a analysis. The particulate fraction of nutrients and Chl-a were measured at each sample collection in triplicate by filtering variable water volumes, generally between 100 and 500 ml, depending upon turbidity. For detailed information about the methods, see Papers I–V.

Gas analysis. Dissolved dinitrogen (N_2) concentrations were measured with a membrane inlet mass spectrometer (MIMS, Bay instruments, MD, USA) at Ferrara University. Dissolved N_2 concentrations were calculated from N_2 : Ar ratios based on gas solubility equations (Weiss, 1970). For detailed information about the method, see Paper V.

2.4 Main experimental methods

Intact core collection and incubation. Intact sediment cores were collected using a hand corer at each of the two sites. Cores were pre-incubated and incubated in temperature-controlled (±0.5 °C) tanks with *in situ* water. For detailed information about the experimental activity, see Papers I, II and V.

N_2 fixation measurement. Rates of N_2 fixation in the water column were determined using the $^{15}N_2$ tracer method. Measurements of N_2 fixation followed methods described in Montoya et al. (1996). For detailed information about the experimental activity, see Paper V.

Pelagic N fluxes measurement. The net primary production and respiration in the water column were measured, using the light–dark bottle technique (e.g. Strickland, 1960). Production and respiration were estimated to derive rates of assimilatory and dissimilatory N fluxes in the water column (e.g. Knoll et al., 2016; Wood et al., 2016). For detailed information about the experimental activity, see Paper V.

2.5 Main statistical methods and calculations

The non-parametric Mann-Kendall test was employed to detect monotonic trends in a series of discharge and nutrient concentration data. The Seasonal-Mann-Kendall trend test was used to test the monotonic trends in a time series with seasonal variation. The partial Mann-Kendall trend test was used to examine the impact of incorporating information of covariates into the Seasonal-Mann-Kendall test to determine the trends of serially correlated data collected over several seasons, as suggested by Libiseller and Grimvall (2002). For detailed information about the statistical methods, see Paper III.

The monthly loads of dissolved and particulate nutrients were obtained by multiplying the concentrations measured at each sampling date by the mean monthly discharge according to HELCOM (2004). For detailed information about the calculations, see Papers III-IV.

Different types of statistics were applied for the data analysis such as parametric (t-test, Two- and Three-way ANOVA) and non-parametric (Mann-Whitney-Wilcoxon and Mann-Whitney Rank Test). For detailed information about the statistical methods, see Papers I-IV.

Seasonal and annual N budgets were calculated using measured input, output and internal fluxes (Nixon et al., 1996; Dettmann, 2001). For detailed information about the calculations, see Paper V.

2.6 LOICZ budget approach

The whole system sink/source role of the Curonian Lagoon was analyzed following the budget methodology developed in the context of the LOICZ (Land-Ocean Interaction in the Coastal Zone) project. Such mass balance budget is an efficient approach to describe, evaluate and summarize the inputs and outputs of nutrients in a specific system and in a specific period of time. It is based on accurate inventories of inputs and outputs, enabling to produce robust annual budgets and infer about dominant metabolic pathways. When the sum of all the outputs is greater than the sum of all the inputs, the system acts as a nutrient source; when it is lower the system is a sink. The black-box mass budget needs to quantify all the loads (inputs) and all the export (outputs) of a certain material for a confined system and for a specific period of time (year, season, month). Some materials as water and salt have conservative behavior, which means that their transformations within the systems are negligible. Other materials have not conservative behavior and mass balance can be used to evaluate their internal transformations, if the system is a net sink or source of a nutrient. Annual budget estimations for several years can give information on the intra-annual variations of loads and internal biogeochemical cycles and could represent a tool for the understanding of the effects of climate changes or other pressures. Some assumptions of the LOICZ approach must be carefully evaluated: 1) steady state conditions; 2) P internal fluxes can be considered as the result of biological transformations alone. The latter assumption is acceptable when suspended solids are low; 3) the differences between observed internal DIN fluxes and the ones expected by DIP fluxes can be considered as the net result of biological processes as denitrification and N_2 fixation. A major focus of this approach is to assess the Net Ecosystem Metabolism (NEM) with a simple calculation methodology: the magnitude of coastal ecosystem metabolism is specifically measured as the extent to which the coastal regions produce or consume organic carbon. NEM classifies a system as net autotrophic or net heterotrophic (Caffrey, 2003). For the detailed description of the LOICZ equations see Swaney and Giordani (2011).

3

Results and discussion

3.1 Recent trends of N, Si and P loads generated in the Nemunas River watershed

3.1.1 Discharge, nutrient concentrations, ecological stoichiometry and seasonal trends

During the 2012–2016 period the discharge from the Nemunas River was nearly 26 % below historical records (700 $m^3\ s^{-1}$, (Jakimavičius and Kriaučiūnienė, 2013)) and displayed seasonal and interannual variability. The highest monthly discharge was measured in April 2013 (2,200 $m^3\ s^{-1}$), and the lowest monthly discharge was measured from August to September 2015 (<200 $m^3\ s^{-1}$). The total annual discharge from the Nemunas River differed by 34 % during the 5-year period (2013 = 19.9 $km^3\ yr^{-1}$, 2015 = 13.1 $km^3\ yr^{-1}$). Most of the interannual differences were due to the peak flow measured from April–May 2013 and the exceptionally low discharge measured from August to September of 2015. The annual average discharge was 16.4 $km^3\ yr^{-1}$ (518.3 $m^3\ s^{-1}$).

At the Nemunas River closing section, the concentrations of dissolved inorganic N, P and Si displayed strong seasonality, with spring/summer minima and autumn/winter peaks (Fig. 2, left panel). After combining all of the data, only the concentrations of NO_3^- were found to be positively correlated with discharge ($[NO_3^-] = (0.62 \pm 0.06) \times$ Discharge, $p < 0.001$).

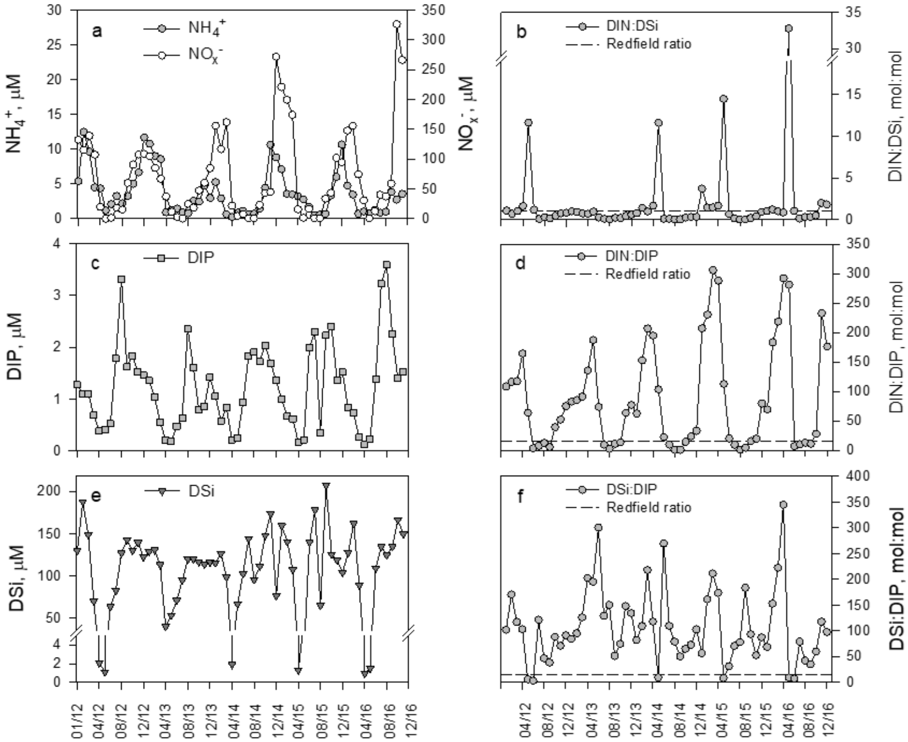

Fig. 2 Left panel: monthly concentrations of dissolved inorganic nitrogen (a), phosphorus (c), and silica (e) at the Nemunas River gauging station (Rusne station) during the 2012–2016 period. Right panel: The stoichiometric DIN:DSi (b), DIN:DIP (d), and DSi:DIP (f) ratios determined monthly during the 2012–2016 period at the Nemunas River gauging station. Dashed lines indicate the theoretical Redfield ratio (DIN:DSi = 16:15, DIN:DIP = 16:1 and DSi:DIP = 15:1) (redrawn from Paper IV).

The ratios of dissolved inorganic nutrients varied seasonally, with N in excess to P (80 < DIN:DIP) and Si (1 < DIN:DSi) in colder months and N limitation (below Redfield ratio) in warmer months (Fig. 2, right panel). However, the DIN : DSi ratio was < 1 during most of the study period, supporting the hypothesis of a prolonged summer N limitation in downstream aquatic ecosystems. The calculated DIN : DIP ratio suggests unbalanced nutrient stoichiometry (N in excess) that lasted for over 8 months per year and a strong N deficiency in summer, with DIN : DIP << 16.

Seasonality influenced the Nemunas River discharge, as well as the concentration of inorganic and particulate nutrients throughout the study period. The concentrations of PN, PP and BSi increased above the annual average during spring–summer months, likely due to algal growth and the conversion of inorganic to particulate nutrient forms within the river. The monthly concentration data series was tested for temporal trends by using both the seasonal and partial Mann-Kendall tests. A positive and statistically significant trend ($p < 0.05$) was detected for NO_3^-, while negative and statistically significant trends ($p < 0.05$) were detected for dissolved NH_4^+ and the Nemunas River discharge. Concerning particulate nutrient forms, PP temporal trends were statistically significant, positive and not dependent on the discharge. For more details, see Paper IV.

3.1.2 Nutrient loads: present and past data

Loads of dissolved inorganic and total nutrient forms varied substantially during 2012–2016 (Table 2, Paper IV). TN loads varied among years by 50 %, while TP and TSi displayed much smaller variations. The seasonal trends were stable for NH_4^+ and NO_3^-, while they were more variable for DIP and DSi. Within the study period, only annual NO_3^- loads increased significantly, a trend that is opposite to the predicted trend and desired political actions (Bauer, 2015). A major fraction of this N (and P) is generated from the section of the Nemunas River watershed that belongs to Belarus, while a minor fraction has a natural origin (Korth et al., 2013; Bauer, 2015).

Table 2. Annual loads of different forms of N, P and Si during the 2012–2016 period (from Paper IV).

Nutrient	Form	Annual nutrient loads (t yr^{-1})				
		2012	**2013**	**2014**	**2015**	**2016**
N	NH_4^+	1,290	1,528	564	808	786
	NO_2^-	190	310	208	186	268
	NO_3^-	18,889	15,254	14,274	23,792	34,934
	DON	15,763	28,267	12,353	5,853	23,167
	PN	6,128	5,011	4,353	3,337	3,525
	Total N	**42,260**	**50,370**	**31,752**	**33,976**	**62,680**
P	DIP	645	544	491	442	682
	DOP	276	411	193	161	214
	PP	848	687	607	633	900
	Total P	**1,769**	**1,642**	**1,291**	**1,236**	**1,795**
Si	DSi	49,611	57,044	43,242	39,194	59,097
	BSi		11,244	7,668	9,409	9,294
	Total Si		**68,288**	**50,910**	**48,603**	**68,39**

Compared to the previously published data, the NO_3^- loads decreased moderately, whereas the load reductions of NH_4^+ and DIP were much more noticeable from the early datasets (Table 3, Paper IV). Since riverine discharge remained relatively similar, we recommend addressing the substantial decrease in NH_4^+ and DIP through modernization of water treatment and construction of new sewage treatment plants after the accession of Lithuania to the European Union. Interestingly, the socio-economic changes in society such as the increasing use of phosphorus-free detergents will be responsible for further decrease of P inputs to natural environments from households (Saaltink et al., 2014). The trend in the DSi loads remains rather unclear, however, it was similar to those reported for rivers entering the Gulf of Riga (Laznik et al., 1999). Humborg et al. (2008) and Conley et al. (2008) showed that the DSi concentrations and loads tended to decrease during the past few decades in other large tributaries of the Baltic Sea due to river damming and other anthropogenic activities in catchments.

Table 3. Published average annual discharge and nutrient loads to the Baltic Sea measured in proximity to or at the mouth of the Nemunas River during the 1980–2016 period (from Paper IV).

Period	Flow (km^3 yr^{-1})	Nutrient loads (t yr^{-1})					DIN: DIP	Reference
		NO_3^-	NH_4^+	TN	DIP	TP		
1980–1993	20.5	31,650		58,340	4,140	5,410	8	Stålnacke et al., 1999
1986–1991		9,702	8,601		4,573		4	Sileika et al., 2006
1992–1996		20,604	5,983		969		27	Sileika et al., 2006
1997–2002	16.6*	25,048	2,202		636		43	Sileika et al., 2006
1997–2008	16.6*			46,335		2,635		HELCOM, 2015
2000–2006	15.9*			37,620				Šileika et al., 2013
2008–2010	18.3*			41,546		1,834		HELCOM, 2015
2012–2016	**16.4**	**21,429**	**995**	**44,208**	**561**	**1,547**	**40**	**This study**

*- long-term flow at the Nemunas River gauging station provided by The Lithuanian Hydrometeorological Service.

3.1.3 Local and macroregional implications

At the local scale (Nemunas River watershed - Curonian Lagoon continuum) mid-term (over some consecutive years) and frequent (at least monthly) monitoring of water discharge and chemistry at the closing section allows to provide reliable datasets to analyse what is exported, in which form and with which ecological stoichiometry. The results from this study suggest that the discharge and nutrient concentrations at the Nemunas River closing section displayed a strong and regular seasonality (see in Paper IV). The discharge is affected by a combination of precipitation patterns/intensities and evapotranspiration/ accumulation in groundwater, as well as by steep changes in temperature that either drive snow/ice melt or water freezing (Stankunavicius et al., 2007). The air temperature therefore co-regulates river discharge, and the discharge affects the pattern of nutrient delivery from the watershed to the river. Detailed knowledge of such trends allows inferring large scale processes at the watershed level and implication for algal communities downstream.

The results show that the seasonality of nutrient transport resulted in a variable ecological stoichiometry of N, Si, and P. In general, a large excess of N in autumn, winter, and spring (DIN : DIP > 16) but a marked N deficiency (and to a minor extent of Si) from May to August were observed during the five analysed years. With respect to the downstream water bodies (Curonian Lagoon and Baltic Sea), this strong N and Si summer limitation may favour the succession of phytoplankton communities from diatom-dominated (spring) to cyanobacteria-dominated (summer) (Bukaveckas et al., 2017). During warm months, cyanobacteria have a competitive advantage as they do not require silica for their exoskeleton and can fix relatively inert N_2 when N is limiting. Any P excess may therefore favour their development (Paerl et al., 2011). Recent findings suggest that cyanobacteria dominance can offset the attenuation of N load by the Curonian Lagoon via denitrification, anammox, uptake, and internal storage, while enhancing its export to the Baltic Sea (Paper V). Moreover, cyanobacteria blooms have large economic impacts in the Curonian Lagoon due to high rates of respiration in the water that can favour night-time hypoxia (<62.5 µM O_2, Zilius et al., 2014) and mortality of benthic organisms and fish (Zilius et al., 2014). The present study suggests that future political actions should target further P reductions in the Nemunas River watershed to tackle the unbalanced nutrient stoichiometry (HELCOM, 2015).

In Lithuania, the updated HELCOM compilation of trend analyses in nutrient loads projected a decrease of 1,142 t of TN and 63.4 t of TP during the 1995–2010 period (PLC 5.5, HELCOM, 2015). Results from this thesis show that until 2014, the annual loads of TN and TP followed this trend even faster than expected (Paper IV). However, the trend changed later, when TN started to increase. To meet the targets for sustainable total N and P loads to the Baltic Sea, Lithuania agreed to reduce annual TN and TP loads to 11,750 t and 880 t, respectively, by 2021 (HELCOM, 2007). These targets appear to be realistic for P, but they remain challenging for TN, as the mean load calculated in the present study exceeds the projected threshold by ~ 30 %. Šileika et al. (2013) suggests that converting 20 % of arable land to pasture, together with sewage treatment plant improvements, would reduce the yearly TN export to 12,000 t, which is close to the target set for Lithuania. A recent study proved that the improvement of agriculture practices would not necessary result in lower contribution to N loads because it largely depends on nutrient storage and immobilisation processes within soils (Romero et al., 2016; Garnier et al., 2018). In Soviet Union period the intensive usage of N fertilizers in agriculture likely caused soil pollution. Therefore, leaching of previously accumulated fertilizers can contribute to nutrient concentrations in rivers for decades as it was showed in southern Europe watersheds (Romero et al., 2016). However, the effect of previous fertilizer usage can be difficult to disentangle as it is confounded by ongoing changes in agricultural practices. According to the Lithuanian Department of Statistics, over the last decade, the pasture area has remained relatively constant and cattle number decreased by 7 % from 2004 to 2016, while croplands have increased by 42 % in the same period. The changes in agriculture practices coincided with new subsidies after acceding the European Union in 2004; since subsidies and market price increased for crops, therefore farmers maintained or improved this agricultural practice. However, land cover changes are accompanied by increased application of fertilizers, which can lead to higher leaching of N in dry year when crop yields are low (Huttunen et al., 2015). Modelled future intensification scenarios of agricultural practices for selected catchments in the Southeast Baltic region (Poland and Baltic States) reveal an increase in N loading by nearly 30 % (Andersen et al., 2016). Climate change may also result in increased crop production, especially in Belarus, further stimulating both the conversion of forests or pastures into arable land as well as the use of fertilizers. Under such a scenario the achievements of nutrient reduction plans become challenging for downstream countries as Lithuania due to major anthropogenic N and P loadings generated upstream, in Belarus. Nevertheless, trends in net anthropogenic N and P inputs can be confounded by ongoing regional changes of lifestyles (Hägg et al., 2014; Hong et al., 2012). Therefore, future studies addressing the genesis of nutrient loads in the Nemunas River watershed should integrate the combined effects of climate, agriculture and socio-economic changes.

3.2 Effects of algal blooms on nutrient retention

3.2.1 Chlrophyll a, nitrogen, phosphorous and silica retention: a black-box approach

Monthly input and output fluxes in the Curonian Lagoon were compared during two consecutive years characterized by the occurrence of cyanobacteria hyperbloom (2012) and by average algal concentrations (2013) to better understand how seasonal variability in the timing of nutrient inputs, and the occurrence of algal blooms affected nutrient transformation and retention.

Highest Chl-a concentrations were observed during a cyanobacteria (primarily of *A. flos aquae*) bloom in July 2012. Peak concentrations at the exit of the lagoon reached 472 µg l^{-1} during the bloom. By comparison, summer Chl-a did not exceed 100 µg l^{-1} in 2013. During 2012, the export of Chl-a from the lagoon exceeded input fluxes by

424 t y^{-1}, whereas in 2013, the lagoon was a modest sink for Chl-a (76 t y^{-1}). Based on fluorometric analysis, diatoms were the dominant group at the entrance site accounting for 60–80 % of Chl-a during April–October 2013. The community composition at the lagoon exit was dominated by diatoms in spring (60–80 % of Chl-a), chlorophytes in mid-summer (June–July) and cyanobacteria and diatoms in autumn (Paper III).

The export of dissolved N fractions was lower in comparison to inputs, indicating net retention within the lagoon. Annualized estimates for the retention of DIN were higher in 2012 (10,680 t y^{-1}) in comparison to 2013 (3,840 t y^{-1}), whereas retention of DON was similar in both years (4,900 and 5,600 t y^{-1}, respectively; Fig. 3). The proportion of DIN retained was 55 % (2012) and 30 % (2013). Retention of DIN was partially offset by net export of PN during bloom periods. PN export was generally less than 25 t d^{-1}, except during the July 2012 cyanobacteria bloom, when PN loads exported to the Baltic Sea were 170 t N d^{-1}. As a result, the annual export of PN in that year (15,700 t y^{-1}) was 3-fold higher than inputs (5,700 t y^{-1}). In the absence of large bloom events during 2013, inputs and outputs of PN were more closely balanced (4,200 and 5,900 t y^{-1}). During the bloom year (2012), the large export of PN (9,900 t y^{-1}) largely offset the retention of DIN and DON (15,600 t y^{-1}), resulting in net retention of TN of 5,630 t y^{-1}. During 2013, TN retention was higher (7,750 t y^{-1}), despite lower retention of the dissolved fractions (9,480 t y^{-1}), due to lower export of PN from the lagoon (1,730 t y^{-1}). The proportion of the TN load retained was 14 % (2012) and 19 % (2013).

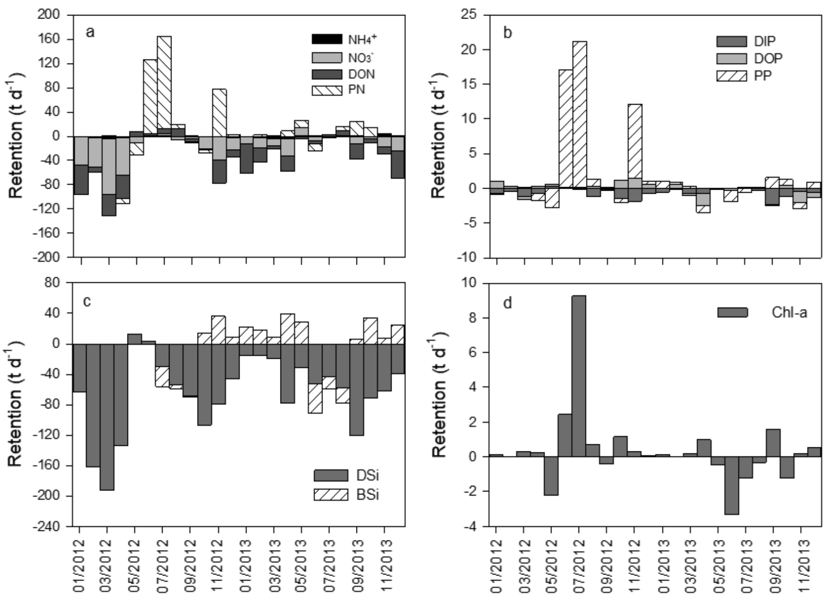

Fig. 3 Net retention on nitrogen (a), phosphorus (b), silica (c) and chlorophyll a (d) in the lagoon during 2012-2013. Negative values indicate net retention (sink), while positive values net export (source) (redrawn from Paper III).

On an annual basis, the lagoon was a sink for dissolved inorganic and organic P with a net retention of 328 and 330 t y^{-1} (2012 and 2013, respectively). Retention of the dissolved fractions was offset by net export of PP from the lagoon. In the bloom year (2012), export of PP (2,208 t y^{-1}) exceeded PP inputs (805 t y^{-1}), whereas in 2013, PP inputs (657 t y^{-1}) and outputs (672 t y^{-1}) were closely balanced. High export of PP during blooms in summer 2012 resulted in a net loss of TP from the lagoon because the export of particulate forms (1,403 t y^{-1}) exceeded the retention of dissolved fractions (328 t y^{-1}). In the absence of a large bloom event in 2013, the lagoon acted as a net sink for TP as retention of dissolved forms (330 t y^{-1}) exceeded net loss of particulate forms (14 t y^{-1}). In 2012, export of TP from the lagoon was equivalent to 165 % of inputs, whereas in 2013, export was 79 % of inputs.

In both years, the lagoon was a net sink for DSi retaining 28,053 and 18,372 t y^{-1} (2012 and 2013, respectively), which corresponded to 61 % and 41 % of the input load (respectively). Data from 2013 show that retention of the dissolved fraction was partially offset by a next export of BSi (3,464 t y^{-1}) resulting in an overall (TSi) retention of 27 %.

3.2.2 Shifts in algal dominance and shift in sink-source role of the Curonian Lagoon

The role of transitional waters such as the Curonian Lagoon in mitigating nutrient transport is a key issue for the on-going Baltic Sea Action Plan (HELCOM, 2007). The comparison of input-output fluxes suggests that blooms alter ecosystem mass balances by shifting the lagoon between source and sink states. During the cyanobacteria bloom of 2012, annual mass balances suggest that the Curonian Lagoon was a source of Chl-a, PN and PP to the Baltic Sea (Paper III). Enhanced export of particulate fractions during bloom conditions offset retention of dissolved forms of N and P. Prior studies have documented the important role of estuaries as nutrient sinks (Grelowski et al., 2000; Boynton et al., 2008; Bukaveckas and Isenberg, 2013). Results from this thesis show that the source-sink status of an estuary may be altered by the occurrence of blooms as the lagoon became a net source of TP during an extensive cyanobacteria bloom in 2012. The net export of TP in that year was equivalent to 3 years of retention as measured in the non-bloom year (2013). Bloom conditions may enhance the recycling of P from sediments (Slomp, 2011) which are subsequently exported from the lagoon in particulate form. It is shown in Paper I and Zilius et al. (2014) that blooms occur during stable (low wind) conditions and create feedback mechanisms that favor P recycling from sediments, due to the deposition of labile organic matter and occurrence of transient (night-time) anoxia in the water column. Nitrate concentrations were up to 15-fold lower at the lagoon exit compared with the entrance. Phytoplankton assimilation may contribute to NO_3^- removal (Dettmann, 2001; Voss et al., 2010; Zilius, 2011), but minor increases in PN and Chl-a at the lagoon exit suggest limited phytoplankton growth and inorganic N assimilation during winter. Denitrification is likely to be more important than phytoplankton uptake at this time, as it is supported by the elevated denitrification rates measured in winter–spring 2009 (1200 µmol N m^{-2} d^{-1}, Zilius, 2011). These rates are among the highest reported for shallow coastal sites in the Baltic region (e.g. Silvennoinen et al., 2007; Hietanen and Kuparinen, 2008; Bonaglia et al., 2014) and could account for 20–50 % of NO_3^- delivered to the Curonian Lagoon. Summer peaks of PN measured in June and July 2012 indicate a large conversion of N into microalgal biomass. During this bloom event, differences between PN at the lagoon entrance and exit exceeded 400 µM. External inputs are inadequate to support phytoplankton N demand at this time, and suggest a large internal recycling of N (i. e. NH_4^+ or DON release from sediments) and/or biological fixation of N_2.

A large drop in DSi concentration and conversion into particulate forms occurs within the Curonian Lagoon, where a 40 % reduction, consistent with data showing the importance of diatoms to the Lagoon's phytoplankton community, was measured (Humborg et al., 2006; Struyf and Conley, 2012; Hölker et al., 2015). Input-output comparison suggests a large conversion of DSi into diatom biomass, with subsequent sequestration into sediment and little regeneration. Si dissolution from diatoms frustules has not been studied in this system, but previous studies suggest that such recycling is more dependent upon chemical than biological transformations and is therefore much slower (Dugdale and Wilkerson, 2001). The results for the Curonian Lagoon serve to illustrate the linkages by which nutrient loads influence phytoplankton community composition, and how shifts in community composition subsequently influence the transformation and retention of N, P and Si.

The findings of this study show that the Curonian Lagoon is an important site for nutrient retention and transformation due to a combination of element-specific (i.e. denitrification, BSi burial and sediment P release) and common (i. e. algal uptake) estuarine processes. Future work might adopt a combined mass balance and modeling approach (e. g., Robson et al., 2008) that would allow us to assess the importance of marine intrusions and to constrain other processes such as net exchange with the atmosphere (via N-fixation and denitrification) and between the water column and sediments.

3.2.3 LOICZ biogeochemical approach

Annual budgets for N, P and Si were calculated for the 2013–2015 study period. The Curonian Lagoon behaviour differs for the three nutrients. For dissolved N, the system sink/source role changes widely both seasonally and inter-annually, as demonstrated in Paper IV with simple annual outflow and inflow load comparison. For dissolved DIP and DSi the lagoon acts consistently as a sink. Large differences are evaluated for the two areas of the lagoon, which differ for several environmental conditions. In the smaller transitional area, N_2 fixation results dominating over denitrification and thus it was a relevant net source of DIN while in the larger confined area, denitrification dominated and the fluxes were negative. The whole lagoon budgets depend on the relative contribution of the 2 areas; in 2013 – 2014, N_2 fixation was the dominant process while in 2015 denitrification dominated. The net ecosystem metabolism (NEM) indicates that the Curonian Lagoon is mainly autotrophic because of high net primary production rates with values up to 8 mmol C m^{-2} d^{-1} calculated for the transitional zone (Paper VI).

3.3 Alternating P and N sink-source role of the Curonian Lagoon: underlying mechanisms

Analyzing P cycling, results are indicative of positive feedbacks between P dynamics and pelagic primary producers in the Curonian Lagoon. As N_2 fixing cyanobacteria have a competitive advantage during periods of strong N-limitation, their abundance in the water column is likely to be controlled by the availability of DIP (Lilover and Stips, 2008; Conley et al., 2009). Moreover, N_2 fixing organisms may promote their self-sustainment by favoring internal P recycling (Fig. 4). Large blooms in fact enhance O_2 consumption and may lead, under calm weather conditions and water stratification, to the establishment of hypoxia/anoxia (Zilius et al., 2014). Under such conditions organic or mineral P may be released from sediments and feed new blooms of N-fixers, keeping the water column DIN : DIP ratio low (Jensen et al., 1994; Hyenstrand et al., 1999, 2000). Results from experimental studies targeting the mobility of DIP from sediments under anoxia, suggest that the Curonian Lagoon bottom acts generally as an efficient P trap. Benthic P mobility occurs only after prolonged hypoxic or anoxic conditions, and therefore stable climatic conditions (no wind for 3-5 days) are needed (Zilius et al., 2014). It is also concluded, that the respiratory activity of pelagic organisms is the main factor driving O_2 deficiency conditions, with a feedback for P regeneration. However, other potentially important processes, as sediment resuspension and bioturbation, may play an important role in P recycling, but they have not been assessed fully so far. Sedimentary P fluxes, under extreme conditions, could sustain the blooms, and even if limited in time they may offset the P sink role of the Curonian Lagoon (for more details see Paper II).

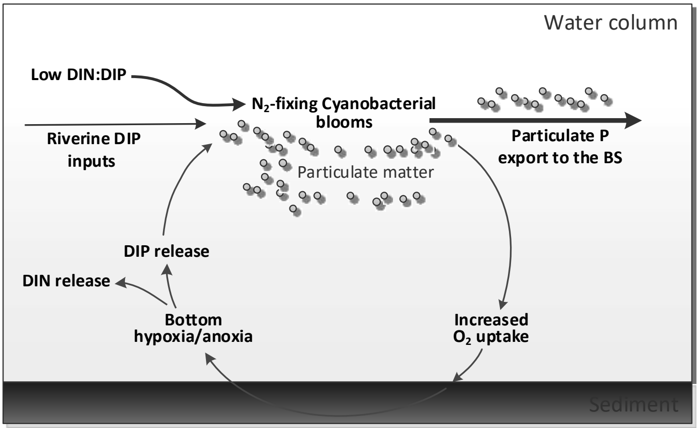

Fig. 4. Mechanisms linking external N and P loads with cyanobacteria blooms and the latter with anoxia and phosphorus release from sediments.

Also it was used the mass balance and process–specific measurements to align the processes regulating the transformation of N between particulate and dissolved fractions. Overall, findings from this work show that seasonal phytoplankton succession is relevant in regulating nutrient retention in the Curonian lagoon. Assimilation of DIN during the spring diatom bloom and subsequent sediment deposition seems the most important mechanism attenuating N fluxes through the Curonian Lagoon. While efflux of N_2 from sediments indicates that denitrification is the dominant mechanism of N export attenuation during winter. These N losses are offset by N_2 fixation during summer, resulting in a net balance for atmospheric N_2 exchange. In summer and fall, the Curonian Lagoon functions predominantly as a transformer of N with high rates of dissolved N uptake and PN production. During this period, pelagic N_2 fixation is large (exceeding riverine and marine DIN inputs), and the bulk of PN is re-mineralized or exported to the Baltic Sea, with little sediment storage.

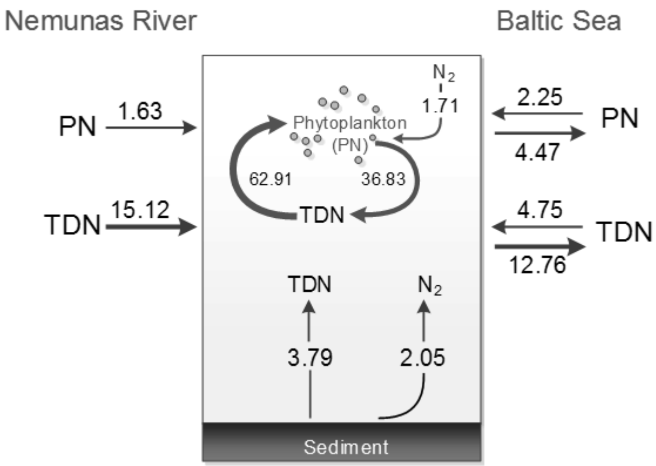

Fig. 5. Annual fluxes (all in mmol $m^{-2} d^{-1}$) to and from the Curonian Lagoon and within the pelagic and benthic compartments within the estuarine system (redrawn from Paper V).

These findings suggest that cyanobacteria blooms in the Curonian Lagoon influence the attenuation of N fluxes in two ways: N_2 fixation in summer offsets denitrification in winter, thus negating atmospheric loss as a mechanism of attenuation. Secondly, positive buoyancy of cyanobacteria favours export of algal N to the Baltic Sea during bloom periods, which, in combination with high sediment remineralization, results in minimal storage of N during peak phytoplankton production in summer. These findings suggest that factors favouring cyanobacteria dominance alter the fate of algal N and thereby reduce the attenuation of N by transitional waters while enhancing N export to marine coastal environments (Fig. 5) (for more details see Paper V).

4

Conclusions

1. During 2012-2016 loads generated in the Nemunas River watershed were significantly lower than historical (1980-1993) for P (decreased by 73 %), but not for N (decreased by 24 %). Such a difference is likely due to the improved sewage treatment plants removing P and to the continuous leaching of previously accumulated N fertilisers in soils.
2. Nutrient loads displayed a strong interannual variability, higher for N (up to 50 %) and lower for P (less than 10 %) and Si (up to 20 %), likely due to the complex regulation of soil N cycle, which is strongly affected by interannual changes in snowmelt period, precipitation timing and intensity, air temperature and vegetative season. All these factors may either favor nitrate production, solubilisation and export or its denitrification and permanent loss.
3. The ecological stoichiometry of inorganic nutrients delivered to the Curonian Lagoon from the Nemunas watershed revealed N excess in winter but strong and regular N and Si limitation in the summer period of all investigated years. It is likely that such a shift drives phytoplankton seasonal succession and triggers cyanobacteria bloom occurrence.
4. Lagoon's filter function varied annually and largely depended on algal (cyanobacteria) blooms. The shift in community composition influenced the transformation and retention of N, P and Si. During blooms the lagoon shifted be-

tween sink to source, as newly fixed N or mobilized DIP from sediments were exported to the Baltic Sea in PN and PP forms.

5. Diatoms and cyanobacteria have opposite effects on N storage. During spring diatom bloom, high nitrogen storage occurs due to large assimilatory uptake of diatoms and their sinking and incorporation within sediments. The change to cyanobacteria dominated phytoplankton community influenced the insignificant storage to sediments as cyanobacteria float, sink less and accumulate less within the sediments, resulting in a large export of PN to the Baltic Sea.
6. The importance of the internal recycling compared to the external loads increased in summer–autumn, when the river flow is the lowest. During this period, fluxes from sediments were the main source of DN and reactive P and this release was mainly occurring due to cyanobacteria bloom, by stimulating organic matter re-mineralization and by favoring anoxia.

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Santrauka

ĮVADAS

Temos aktualumas

Veiksnių, reguliuojančių azoto (N), fosforo (P) ir silicio (Si) srautus tarp sausumos ir vandens ekosistemų, supratimas yra labai svarbus siekiant sumažinti antropogeninį poveikį vidaus ir priekrantės vandenims. Maistingųjų medžiagų srautus iš sausumos į jūrą lemia įvairūs veiksniai, kurie keičia jų dydį ir intensyvumą (Seitzinger ir kt., 2006; Boyer ir Howarth, 2008; Luu ir kt., 2012). Prognozuojama, kad ateityje klimato kaita lems didesnį kritulių kiekį ir audrų dažnumą, todėl yra svarbu išsiaiškinti ir suprasti, kaip būsima klimato kaita paveiks maistingųjų medžiagų srautus į vandens telkinius (Cross ir kt., 2005). Taip pat svarbu suvokti, ar veikia priimti politiniai vandens kokybės gerinimo sprendimai (Baltijos jūros veiksmų planas (BSAP) ir Vandens pagrindų direktyva (WFD)) ir ar yra veiksmingos priemonės, tokios kaip Nitratų ar miesto nuotekų direktyvos, mažinant maistingųjų medžiagų srautus iš Nemuno upės į Baltijos jūrą (Bouraooui ir Grizzetti, 2011; Voss ir kt., 2011; Šileika ir kt., 2013; HELCOM, 2015). Dėl nuolatinių pokyčių yra labai svarbi ilgalaikė stebėsena, kuri padėtų suprasti, kaip priekrantės vandens ekosistemos reaguoja į skirtingą žemės panaudojimą ūkiuose ir besikeičiančias klimato sąlygas. Šie stebėsenos veiksniai ypač svarbūs Baltijos jūros regionuose, kuriuose vyksta tiek socialinių, tiek ir ekonominių pokyčių (Šileika ir kt., 2006; HELCOM, 2015).

Lagūnos ir estuarijos, esančios sandūroje tarp sausumos ir jūrinio vandens ekosistemų, yra svarbios sistemos, į kurias patenka dideli maistingųjų medžiagų kiekiai ir jose intensyviai vyksta biogeocheminiai procesai (Nixon ir kt., 1996; Boyer ir Howarth, 2008; Asmala ir kt., 2017). Estuarijose upių atneštos maistingosios medžiagos virsta kitomis formomis dėl įvairiausių vyksmų. Reikšmingiausi procesai, veikiantys jas, yra bakterijų ir pirminių augintojų asimiliacija, organinių medžiagų remineralizacija, nitrifikacija, denitrifikacija, sorbcija ir desorbcija, sedimentacija ir resuspensija ar užkonservavimas nuosėdose (Bartoli ir kt., 2012; Loken ir kt., 2016). Eutrofikuotose Baltijos jūros estuarijose pasikartojantis fitoplanktono žydėjimas gali gerokai pakeisti tiek patenkančius maistinių medžiagų srautus, tiek jų apykaitos ciklus dėl susidariusios fitoplanktono biomasės, jos patekimo į jūros aplinką arba dėl nusodinimo į dugno nuosėdas. Dumblių „žydėjimą“ lemia išoriniai veiksniai, kurie taip pat kontroliuoja maistinių medžiagų srautus, patenkančius iš upių, darydami poveikį jų transformacijai ir sulaikymui (Zilius ir kt., 2014). Dumblių biomasės skaidymas iki molekulių sukelia deguonies stoką, dėl kurios pakinta redukcinės ir oksidacinės sąlygos dugno nuosėdose, o tai palengvina maistinių medžiagų išsiskyrimą iš jų. Tokia vyksmų seka gali sukurti sistemą, palaikančią tolimesnį vandens žydėjimą (Pant ir Reddy, 2001; Zilius ir kt., 2014).

Šiame darbe analizuojamas penkerių metų laikotarpis (2012–2016), kurio metu buvo stebimi N, P ir Si srautai, patenkantys su Nemuno upės vandeniu per Kuršių marias į Baltijos jūrą. Taip pat buvo vertinamas fitoplanktono žydėjimo ir mikrobinių procesų poveikis maistingųjų medžiagų srautams bei jų ekologinei stechiometrijai Kuršių mariose, siekiant įvertinti šios estuarinės sistemos poveikį maistingųjų medžiagų sulaikymui ir eksportui į Baltijos jūrą.

Tyrimo tikslas ir pagrindiniai uždaviniai

Pagrindinis disertacijos tikslas – įvertinti trijų maistingųjų medžiagų (N, Si ir P) srautų iš Nemuno upės baseino į Kuršių marias sezoniškumą, išanalizuoti, kaip estuarinėje sistemoje vykstantys biologiniai ir fiziniai procesai veikia maistingųjų medžiagų kiekį ir jų stechiometriją pernašoje į Baltijos jūrą.

Šios disertacijos uždaviniai:

1. įvertinti N, Si ir P srautų iš Nemuno upės baseino į Kuršių marias dydį ir dinamiką, palyginti juos su anksčiau publikuotais duomenimis;
2. išanalizuoti dumblių žydėjimo poveikį N, Si ir P srautų sulaikymui Kuršių mariose arba jų išnešimui į Baltijos jūrą;
3. išanalizuoti Kuršių marių autotrofiškumą (maistingųjų medžiagų filtro vaidmuo) ir heterotrofiškumą (maistingųjų medžiagų šaltinio vaidmuo), panaudojant LOICZ metodologiją;

4. įvertinti procesus vandens storymėje ir dugno nuosėdose, turinčius įtakos maistingųjų medžiagų virsmams ir srautams, detalizuoti jų įtaką Kuršių marių funkcionavimui.

Darbo naujumas

Per pastarąjį dešimtmetį žinios apie azoto ir fosforo biogeocheminius ciklus pagausėjo dėl M. Žiliaus (2011) ir J. Petkuvienės (2015) apgintų disertacijų. M. Žiliaus ir J. Petkuvienės darbuose daugiausia dėmesio buvo skiriama paaiškinti ryšį tarp dumblių žydėjimo ir N bei P biogeocheminių procesų bei apykaitos tarp dugno nuosėdų. Jų darbai buvo paremti tyrimais reprezentacinėse Kuršių marių vietose, vėliau gautus rezultatus perskaičiuojant visam marių plotui (1584 km^2), o tai lėmė nemažai paklaidų. Tačiau vienas iš pagrindinių aspektų, kurių pasigendama praeities ir šiuolaikiniuose tyrimuose, – ištirti, kaip vandens srautų dinamika ir tuo pat metu vykstantis fitoplanktono žydėjimas veikia maistingųjų medžiagų virsmus ir jų sulaikymą sistemoje. Taip pat trūko išsamios analizės apie visų trijų maistingųjų medžiagų ir jų skirtingų formų srautus į Kuršių marias ir išnešimą į jūrą. Tai buvo svarbu siekiant efektyviai įgyvendinti politinius veiksmus, reikalingus taršai Baltijos jūroje mažinti. Ypač tai svarbu Lietuvai, kuri buvo įpareigota ženkliai sumažinti N ir P srautus į Baltijos jūrą.

Šio darbo nauji aspektai: 1) N, P ir Si dalelinių ir ištirpusių formų analizė Nemuno upės prietakoje į Kuršių marias per 5 metus; 2) maistingųjų medžiagų srautų ir ekologinės stechiometrijos tendencijų analizė; 3) įvertinimas, kaip maistinių medžiagų srautai ir ekologinė stechiometrija bei dumblių „žydėjimas“ veikia Kuršių marių funkcionavimą (nustatant šaltinio ar filtro vaidmenį); 4) suvokimas apie biogeocheminius procesus, kurie leistų paaiškinti masių balansą.

Kiek man žinoma, šioje geografinėje vietovėje nėra anksčiau atlikti tokie matavimai, kur dalelinės ir ištirpusios N, P ir Si formos bei jų ekologinė stechiometrija būtų nagrinėjamos vienu metu. Naujausi darbai atkreipia dėmesį, kad N, P ir Si ekologinės stechiometrijos vaidmuo reguliuojant fitoplanktono žydėjimą yra svarbesnis veiksnys nei pavienių maistingųjų medžiagų koncentracija (Conley ir kt., 2009; Pearl ir kt., 2011).

Rezultatų mokslinė ir praktinė reikšmė

Šio darbo rezultatai pateikia visiškai naują informaciją apie trijų pagrindinių maistingųjų medžiagų (N, P ir Si) koncentraciją, stechiometriją ir srautus, išmatuotus Nemuno upės žiotyse ir Klaipėdos sąsiauryje. Per penkerius metus sukauptas duomenų masyvas leido: 1) palyginti naujausius duomenis apie maistingųjų medžiagų srautus su anksčiau atskiruose šaltiniuose publikuota informacija apie vieną iš svarbiausių upių, teršiančių Baltijos jūrą; 2) sudaryti visoms Kuršių marioms masių balansą, kuris padėtų suvokti, kaip veikia sistema, ypač kada ji atlieka šaltinio ir filtro vaidmenį, kuris gali greitai keistis, ir kokią naudą turi dumblių žydėjimas; 3) susieti reguliarų N : P ir N : Si stechiometrinio santykio sumažėjimą su fitoplanktono bendrijos sudėtimi ir ištirti, kaip įsigalėjusios melsvabakterės sukelia trofinės kaskados griūtį; 4) pateikti trūkstamą analizės seką, kurią pasitelkus būtų galima eksperimentiškai nustatyti Kuršių marių funkcionavimo mechanizmus; 5) atkreipti dėmesį į kritinius N srautus Nemuno upėje, kurie išlieka panašūs, kaip ir išmatuota prieš 20 metų, o tai netenkina N mažinimo planų.

Kaip rodo publikacijų skaičius, šis darbas yra moksliškai pagrįstas. Jis taip pat yra aktualus, nes netiesiogiai susijęs su Nemuno upės baseinu integruodamas socialinį, ekonominį bei klimato poveikį maistinių medžiagų atsiradimui, transformavimui ir tolesniems srautams.. Rezultatai rodo, kad politiniai sprendimai lėmė reikšmingą P srautų sumažėjimą, bet jie buvo menkaverčiai mažinant N srautus. Darbas atskleidžia, kad bendrieji N ir P srautai į Baltijos jūrą gali būti skirtingi priklausomai nuo to, kur atliksime vertinimą: Nemuno žiotyse ar Klaipėdos kanale. Tai pabrėžia poreikį peržiūrėti monitoringo programas ir tarptautinius įsipareigojimus, pavyzdžiui, HELCOM (angl. *Baltic Marine Environment Protection Commission*). Iki šiol HELCOM nustato didžiausią leistiną maistinių medžiagų srautą tiesiai iš upės baseino į Baltijos jūrą, neatsižvelgdama į maistinių medžiagų sulaikymą Kuršių mariose. Galiausiai šio darbo rezultatai parodė, kad N ir P mažinimo tikslai gali būti pasiekti greičiau, jei bus atsižvelgiama į maistingųjų medžiagų sulaikymo procesus tranzitiniuose (estuariniuose) vandenyse.

TYRIMŲ MEDŽIAGA IR METODAI

Tyrimų rajonas

Nemunas yra didžiausia Lietuvos upė, kurios baseinas užima 97 864 km^2 , iš jų 46 695 km^2 yra Lietuvoje, 45 389 km^2 – Baltarusijoje, o likusi dalis – Latvijoje, Lenkijoje ir Kaliningrado srityje (Gailiušis ir kt., 2001). Metinis kritulių kiekis Nemuno upės baseine yra nuo 520 iki 800 mm (Šileika ir kt., 2006), ilgalaikis Nemuno upės debitas yra 700 m^3 s^{-1}. Nemunas yra trečia pagal dydį upė ir labai svarbus maistingųjų medžiagų šaltinis Baltijos jūrai (Jakimavičius ir Kriaučiūnienė, 2013; HELCOM, 2015).

Kuršių marios yra didelė (1 584 km^2), sekli (vidutinis gylis 3,8 m) estuarija pietrytinėje Baltijos jūros dalyje. Pagrindinis gėlo vandens šaltinis yra Nemuno upė, kuri sudaro 96 % bendro patenkančio vandens kiekio (Jakimavičius ir Kriaučiūnienė, 2013). Kuršių marios su Baltijos jūra susijungia siauru kanalu, Klaipėdos sąsiauriu, kuriuo, priklausomai nuo vėjo krypties ir Nemuno vandens lygio, priteka druskėto vandens (Zemlys ir kt., 2013).

Pagrindiniai cheminiai analitiniai metodai

Ištirpusių maistingųjų medžiagų analizė. Laboratorijoje visi vandens mėginiai (n=3 kiekvienai tyrimo vietai) maistingųjų medžiagų analizei buvo nufiltruoti ir supilstyti į atskirus mėgintuvėlius organinių ir neorganinių N, P ir S formų spektrofotometrinei analizei.

Dalelinių maistingųjų medžiagių ir chlorofilo a analizė. Dalelinės maistingųjų medžiagų formos ir chlorofilas *a* iš kiekvienos stoties buvo sukoncentruojami ant filtro nufiltruojant skirtingus mėginio tūrius (100–500 ml) priklausomai nuo drumstumo.

Statistinė analizė ir skaičiavimai

Neparametrinis Mano ir Kendalio (Mann-Kendall) testas buvo naudojamas identifikuoti monotonines tendencijas nuotėkio ir maistingųjų medžiagų laiko eilutėje. Sezoninis Mano ir Kendalio testas buvo naudojamas nustatyti tendencijas laiko eilutėse dėl sezoninės kaitos. Dalinis Mano ir Kendalio testas buvo taikomas patikrinti, ar sezoniniu Mano ir Kendalio testu aptiktos maistingųjų medžiagų koncentracijos tendencijos priklausė nuo Nemuno upės nuotėkio. Detalesnė informacija apie metodą pateikiama III publikacijoje.

Mėnesiniai ištirpusių ir dalelinių maistingųjų medžiagų srautai į Kuršių marias apskaičiuoti remiantis HELCOM (2004) metodika: konkrečios dienos koncentraciją padauginant iš vidutinio mėnesinio upės nuotėkio. Detalesnė informacija apie skaičiavimus pateikiama III ir IV publikacijose.

Duomenų analizei buvo panaudota aprašomoji ir daugiamatė statistika (dvifaktorė ir trifaktorė dispersinė analizė (ANOVA), *t*, Mano, Vitnio ir Vilkoksono (Mann-Whitney-Wilcoxon) bei Mano ir Vitnio (Mann-Whitney) rangų testai). Detalesnė informacija apie skaičiavimus pateikiama I–IV publikacijose.

Sezoninis ir metinis N masių balansas buvo sudarytas remiantis srautais į marias ir iš jų bei vidine apykaita tarp dugno nuosėdų, vandens storymės ir atmosferos (Nixon ir kt., 1996; Dettmann, 2001). Detalesnė informacija apie skaičiavimus pateikiama V publikacijoje.

LOICZ balanso metodas

Kuršių marių vaidmuo sulaikant ar praturtinant maistingųjų medžiagų srautus buvo analizuojamas panaudojant LOICZ (angl. *Land-Ocean Interaction in the Coastal Zone*) metodą. Šis masių balanso metodas, paremtas *juodosios dėžės* (angl. *black-box*) principu, yra efektyvus būdas kiekybiškai nustatyti ir apibendrinti tam tikros maistingosios medžiagos srautus į konkrečią sistemą ir iš jos pasirinktu laiko periodu (metai, sezonas ar mėnuo). Sudarydami metinius masių balansus keletą metų iš eilės galime spręsti apie metinius maistingųjų medžiagų srautų ir biogeocheminių procesų pokyčius, kurie leidžia identifikuoti platesniame kontekste vykstančius pokyčius dėl klimato kaitos ir žmogaus veiklos. Nepaisant metodo lankstumo, vis dėlto tam tikros prielaidos reikalingos tinkamam jo pritaikymui: 1) sistema yra *status quo* būsenos; 2) sistemoje P virsmai nulemti tik biologinių veiksnių (pastaroji prielaida galioja sistemose, kur suspenduotų dalelių kiekis vandens storymėje yra mažas); 3) ištirpusio neorganinio azoto pokyčiai yra pasekmė denitrifikacijos ir N_2 fikasacijos proceso. Viena iš galimybių naudojant šį metodą įvertinti bendrąjį ekosistemos metabolizmą (angl. *Net ecosystem Metabolism*, *NEM*), o tai leidžia įvertinti, kiek estuarinė sistema pagamina ar suvartoja anglies. Šis matas leidžia įvertinti, kiek sistema yra autotrofinė ir kiek heterotrofinė (Caffrey, 2003). Detalesnis metodo aprašymas yra publikuotas (Swaney ir Giordani, 2011).

REZULTATAI IR DISKUSIJA

Naujausios Nemuno upės baseine susidariusių N, P ir Si srautų tendencijos

Nemuno upės nuotėkis 2012–2016 metų laikotarpiu buvo beveik 26 % mažesnis nei ilgalaikis istorinis (700 $m^3\ s^{-1}$, Jakimavičius ir Kriaučiūnienė, 2013) ir kito tiek tarp sezonų, tiek tarp skirtingų metų. Didžiausias mėnesinis upės nuotėkis buvo apskaičiuotas 2013 metų balandį (2 200 $m^3\ s^{-1}$), o mažiausias – 2015 metais rugpjūčio–rugsėjo mėnesiais (<200 $m^3\ s^{-1}$).

Nemuno upės žiotyse išmatuota ištirpusių maistingųjų medžiagų (N, P, Si) koncentracija keitėsi sezoniškai: aukščiausia koncentracija buvo nustatyta rudens–žiemos laikotarpiu, o mažiausia – pavasarį–vasarą. Atlikus statistinę duomenų analizę paaiškėjo, kad tik nitratų (NO_3^-) koncentracija priklausė nuo upės nuotėkio dydžio ($[NO_3^-] = (0{,}62 \pm 0{,}06) \times$ upės nuotėkis, $p < 0{,}001$).

Ištirpusių neorganinių maistingųjų medžiagų stechiometrinis santykis keitėsi sezoniškai: santykis tarp N ir P (80 < DIN : DIP) ir Si (1 < DIN : DSi) buvo daugeliu atveju didesnis šaltuoju metų laiku, o vasarą – priešingai. Remiantis Redfyldo (Redfield) santykiu, šiuo periodu N visada buvo limituojanti maistingoji medžiaga. Apskaičiuotas didelis DIN : DIP santykis rodo nesubalansuotą maistinių medžiagų ryšį (N perteklius), kuris truko daugiau kaip 8 mėnesius per metus, o likusiu laikotarpiu (daugiausia vasarą) buvo fiksuojamos N trūkumo sąlygos (DIN : DIP << 16).

Suspenduotoje medžiagoje maistingųjų medžiagų (PN, PP ir BSi) koncentracija visada buvo didesnė pavasario–vasaros laikotarpiu, matyt, dėl intensyvaus fitoplankto augimo ir ištirpusių neorganinių maistinių medžiagų pavertimo į dalelinę formą upėje.

Skirtingų maistingųjų medžiagų formų srautai kito analizuojamuoju periodu (2012–2016 m.). Bendrojo N srautas skirtingais metais kito iki 50 %, o bendrojo P ir Si srautų pokyčiai nebuvo tokie ryškūs. Sezoniniai NO_3^- ir NH_4^+ srautai išliko gana pastovūs, o DIP ir DSi srautai kito. Nepaisant to, matavimų laikotarpiu tik NO_3^- srautai pastebimai padidėjo, nors buvo tikėtasi, kad dėl politinių sprendimų mažės (Bauer, 2015). Palyginus su anksčiau publikuotais duomenimis, NO_3^- srautai sumažėjo nežymiai, o NH_4^+ ir DIP srautai sumažėjo pastebimai. Upės nuotėkiui išlikus panašiam ar net sumažėjus, NH_4^+ ir DIP srautų sumažėjimą greičiausiai galima susieti su nuotekų valyklų modernizavimu Lietuvai įstojus į Europos Sąjungą (2004 m.). Įdomu ir tai, kad socialiniai bei ekonominiai pokyčiai visuomenėje (didėjantis ploviklių, kurių sudėtyje nėra fosforo, naudojimas) ateityje gali sumažinti fosforo patekimą į natūralius vandens telkinius (Saaltnik ir kt., 2014). Reikėtų atkreipti dėmesį į tai, kad nemaža dalis N ir P atnešama iš Nemuno baseino, esančio Baltarusijoje, taip pat dalis azoto patenka ir dėl natūralių procesų gamtoje (Korth ir kt., 2013; Bauer, 2015). Tuo tarpu Si srautų tendencijos išlieka gana neaiškios, bet panašios kaip ir didžiausioje Latvijos upėje Dauguvoje (Laznik ir kt., 1999). Kai kurie tyrėjai (Humborg ir kt., 2008; Conley ir kt., 2008) teigia, kad DSi koncentracija ir srautai upėse, įtekančiose į Baltijos jūrą, per pastaruosius kelis dešimtmečius sumažėjo dėl pastatytų užtvankų bei kitų antropogeninių veiksnių tų upių baseinuose.

Keletą metų iš eilės atliekant kasmėnesinius vandens nuotėkio ir chemijos matavimus galima surinkti patikimus duomenis, kuriais remiantis išanalizuojama, kokios maistingosios medžiagos, kokios formos būdamos, koks jų kiekis bei kokiu stechiometriniu santykiu patenka į tranzitinius priekrantės vandenis. Upės nuotėkio intensyvumas glaudžiai siejasi su iškritusių kritulių kiekiu ant žemės paviršiaus bei jų kaupimusi ar išgarinimu gruntiniuose vandenyse. Vandens judėjimas dirvožemio sluoksnyje gali reikšmingai keistis dėl meteorologinių sąlygų, pavyzdžiui, staigiai keičiantis temperatūrai, dėl kurios sniegas ar ledas gali ištirpti ar vanduo užšalti (Stankūnavičius ir kt., 2007). Dėl šios priežasties oro temperatūra reguliuoja upių nuotėkį, nuo kurio priklauso maistingųjų medžiagų patekimas iš baseino į upę.

Tyrimo rezultatai parodo, kad maistingųjų medžiagų srautų sezoninė kaita turi įtakos N, P ir Si ekologinei stechiometrijai. Apskaičiuota, kad šaltuoju metų laikotarpiu vyrauja azoto perteklius, tačiau per visą tyrimo laikotarpį nustatyta, kad gegužės–rugpjūčio mėnesiais atsirasdavo N (kartais ir Si) trūkumas. Taigi, vasaros metu esant žymiam N ir Si trūkumui gali pasikeisti dominuojanti fitoplanktono bendrijos sudėtis: iš pavasarį dominuojančių diatominių dumblių į vasaros metu klestinčias melsvabakteres (Bukaveckas ir kt., 2017). Šiltuoju metų laikotarpiu melsvabakterės turi konkurencinį pranašumą prieš kitas fitoplanktono grupes, nes joms yra nereikalingas silicis ir jos gali fiksuoti ištirpusį atmosferinį azotą, kai jos jaučia N trūkumą. Todėl bet koks fosforo perteklius gali palengvinti jų vystymąsi (Paerl ir kt., 2011). Naujausi tyrimai rodo, kad melsvabakterių dominavimas vasarą gali turėti įtakos N srautams ir virsmams Kuršių mariose. Pirmiausia dėl intensyvios organinės medžiagos produkcijos sumažėja N pašalinimas denitrifikacijos ir *anammox* procesų metu ir padidėja jos eksportas į Baltijos jūrą. Taip pat melsvabakterių žydėjimas turi didelį ekonominį poveikį Kuršių marioms, nes dėl didelio deguonies kiekio suvartojimo nakties metu gali susidaryti deguonies trūkumas – hipoksija (<62.5 μM O_2), o tai gali sukelti dugno organizmų žūtį ir žuvų kritimą (Zilius ir kt., 2014). Šio tyrimo rezultatai rodo, kad ateityje politiniai veiksmai turėtų būti nukreipti į tolimesnį P srautų mažinimą Nemuno upės baseine, siekiant išvengti nesubalansuotos maistingųjų medžiagų stechiometrijos (HELCOM, 2015).

Pagal atnaujintus skaičiavimus, HELCOM prognozavo, kad Lietuva 1995–2010 metais turėjo sumažinti maistingųjų medžiagų srautus atitinkamai 1 142 t TN ir 63,4 t TP (PLC 5.5, HELCOM, 2015). Remiantis šio darbo duomenimis, matyti, kad iki 2014 metų metiniai bendrojo N ir P srautai mažėjo pagal prognozes ar net greičiau, tačiau vėliau TN tendencija pasikeitė ir srautai padidėjo. Kad pasiektų galutinį tikslą mažindama N ir P srautus į Baltijos jūrą, Lietuva įsipareigojo iki 2021 metų sumažinti metinius bendrojo N ir P srautus atitinkamai iki 11 750 t ir 880 t (HELCOM, 2007). Tokie skaičiai atrodo įtikinamai fosforo, tačiau ne azoto atžvilgiu, nes pagal dabartinius rezultatus N vis dar viršija 30 %. Šileika ir kt. (2013) teigė, kad pavertus 20 % dirbamos žemės į ganyklas, taip pat kartu pagerinus nuotekų valyklų darbą, bendrojo N srautai sumažėtų iki 12 000 t, o tai beveik ir yra Lietuvos tikslas. Neseniai buvo įrodyta, kad žemės ūkio praktikos gerinimas nebūtinai sumažintų N patekimą į vandens telkinius, nes tai taip pat priklauso nuo to, kiek prieš tai buvo sukaupta maistingųjų medžiagų dirvožemyje ir kaip jos iš ten gali migruoti (Romero ir kt., 2016; Garnier ir kt., 2018). Sovietų Sąjungos laikotarpiu intensyvus azotinių trąšų naudojimas galėjo sukelti dirvožemio taršą. Todėl šių sukauptų trąšų išplovimas dešimtmečiais gali turėti įtakos N koncentracijai upeliuose, kurie glaudžiai ribojasi su žemės ūkio laukais, kaip tai buvo įrodyta Pietų Europos upių baseinuose (Romero ir kt., 2016). Pasak Lietuvos statistikos departamento, per pastarąjį dešimtmetį (2004–2016 m.) ganyklų plotai išliko nepakitę, galvijų skaičius padidėjo apie 7 %, o ariamos žemės plotai išaugo 42 %. Taigi, žemėnaudos pokyčiai yra susiję ir su padidėjusiu trąšų naudojimu, dėl kurio gali padidėti N išsiskyrimas sausringais metais, kai pasėlių derlius yra mažas (Huttunen ir kt., 2015). Sumodeliuoti ateities žemės ūkio intensyvumo scenarijai, kurie taikomi pasirinktiems Pietryčių Baltijos regionų (Lenkijos ir Baltijos šalių) upių baseinams, parodė, kad N srautai ateityje padidės beveik 30 % (Andersen ir kt., 2016). Klimato kaita taip pat gali padidinti augalininkystę, ypač Baltarusijoje, toliau skatinant miškų ir ganyklų vertimą į ariamas žemes, taip padidinant ir trąšų sunaudojimą. Esant tokiems scenarijams pasiekti reikiamus maistingųjų medžiagų srautų sumažinimo planus bus labai sudėtinga. Nepaisant visko, antropogeniniai N ir P srautai taip pat gali būti paveikti besikeičiančių gyvenimo sąlygų regionuose (Hägg ir kt., 2014; Hong ir kt., 2012).

Dumblių „žydėjimo“ poveikis maistingųjų medžiagų sulaikymui Kuršių mariose

Siekiant geriau suprasti, kaip maistingųjų medžiagų sezoninė kaita ir dumblių „žydėjimas“ veikia maistingųjų medžiagų sulaikymą ir transformacijas Kuršių mariose, 2012–2013 metais kartą per mėnesį buvo imami mėginiai įtekėjimo į marias (Nemuno upės žiotyse) ir ištekėjimo iš jų (Klaipėdos sąsiauryje) vietose. Didžiausia Chl-a koncentracija buvo užfiksuota 2012 metų liepą. Klaipėdos sąsiauryje didžiausia Chl-a koncentracija buvo 472 µg l^{-1}, o 2013 metų vasarą koncentracija buvo mažesnė nei 100 µg l^{-1}. Dėl intensyvaus žydėjimo 2012 metais iš Kuršių marių buvo išnešta apie 424 t Chl-a, o 2013 metais marios sulaikė 76 t Chl-a. Išmatavus ištirpusių N formų kiekį vandenyje, įtekančiame į marias ir ištekančiame iš jų, parodė, kad jų sulaikyta 55 % 2012 metais ir 30 % 2013 metais. Fitoplanktono žydėjimo metu DIN sulaikymas mariose buvo kompensuotas, nes jo metu dumblių biomasėje sukauptas azotas buvo išnešamas dalelinio N forma į Baltijos jūrą. Tais metais, kai buvo nustatytas intensyvus fitoplanktono žydėjimas, iš marių jo buvo išnešama tris kartus daugiau (15 700 t y^{-1}) nei pateko į jas. Tirtuoju periodu nustatyta, kad Kuršių marios nuolat sulaikė ištirpusį neorganinį ir organinį P. Tuo tarpu dalelinio P, kaip ir N srautai iš Kuršių marių, buvo gerokai didesni 2012 metais, kai žydėjo fitoplanktonas. Šiuo periodu į marias su upėmis pateko 805 t y^{-1} , o iš jų į Baltijos jūrą išnešta 2 208 t y^{-1}. 2013 metais, kai žydėjimas buvo nedidelis, palyginti su praėjusiais metais, dalelinio N ir P srautai į marias ir iš jų buvo beveik subalansuoti. Nepriklausomai nuo fitoplanktono žydėjimo, per metus Kuršių marios sukaupė 28 053 (2012 m.) ir 18 372 t y^{-1} (2013 m.) silicio, kuris sudarė atitinkamai 61 % ir 41 % patekusio su upe. Įeinančių ir išeinančių srautų palyginimas rodo, kad fitoplanktono žydėjimas gali reguliuoti marių vaidmenį sulaikydamas maistingąsias medžiagas. 2012 metų „žydėjimo“ metu sudarytas balansas parodė, kad Kuršių marios buvo šaltinis Chl-a, dalinio N ir P, patenkančių į Baltijos jūrą. Ankstesnių tyrimų rezultatai parodė, kad estuarijos dažniausiai veikia kaip maistingųjų medžiagų filtras, sumažinantis jų srautus į priekrantės vandenis (Grelowski ir kt., 2000; Boynton ir kt., 2008; Bukaveckas ir Isenberg, 2013). Šio darbo rezultatai rodo, kad estuarijos, kaip šaltinio ar filtro, vaidmuo gali keistis, priklausomai nuo fitoplanktono žydėjimo, kaip tai rodo 2012 metų tyrimai.

Dumblių „žydėjimas“ taip pat gali paskatinti neorganinio P išsiskyrimą iš dugno nuosėdų (Slomp, 2011), kuris vėliau yra asimiliuojamas į ląsteles ir išnešamas kaip dalelinis fitoplanktono biomasėje. Nitratų koncentracija buvo 15 kartų žemesnė iš marių ištekančiame vandenyje nei įtekančiame su Nemuno upės vandenimis. Žinoma, kad fitoplanktono asimiliacija estuarijose gali nulemti NO_3^- sumažėjimą (Dettmann, 2001; Zilius, 2011), tačiau kitu atveju nedidelis padidėjimas PN ir Chl-a iš marių ištekančiame vandenyje palyginti su įtekančiu rodo ribotas fitoplanktono galimybes asimiliuoti ištirpusį neorganinį N žiemos metu. Tikėtina, kad denitrifikacija yra svarbesnis procesas, sulaikantis nitratus, nei fitoplanktono asimiliacija šaltuoju periodu. 2009 metais atlikti tyrimai Kuršių mariose parodė, kad denitrifikacijos greitis yra didžiausias būtent žiemos–pavasario periodu (1 200 µmol N m^{-2} d^{-1}, Zilius, 2011). Įdomu ir tai, kad denitrifikacijos greitis yra vienas didžiausių Baltijos jūros regione (pvz., Silvennoinen ir kt., 2007; Hietanen ir Kuparinen, 2008; Bonaglia ir kt., 2014) ir gali sudaryti 20–50 % NO_3^- kiekio, atnešto į Kuršių marias.

Dalelinio azoto padidėjimas 2012 metų birželio ir liepos mėnesiais parodė didelę N akumuliaciją dumblių biomasėje. Šio dumblių žydėjimo laikotarpiu skirtumas tarp PN, išmatuoto marių įtekėjimo ir ištekėjimo vietose, siekė 400 µM. Akivaizdu, kad su Nemuno upe atnešamo N nepakankama patenkinti visų fitoplanktono poreikių maistingosiomis medžiagomis, todėl šiuo atveju svarbiu N šaltiniu tampa procesai, vykstantys mariose: NH_4^+ ar DON išskyrimas iš dugno nuosėdų ar biologinė azoto fiksacija.

Kuršių mariose pastebimas DSi koncentracijos sumažėjimas (iki 40 %) ir dalelinio Si padidėjimas, kuris sutampa su diatominių dumblių žydėjimo piku (Humborg ir kt., 2006; Struyf ir Conley, 2012; Hölker ir kt., 2015). Būtina atkreipti dėmesį, kad didžioji dalis asimiliuoto DSi į diatominių dumblių biomasę, nusėda į dugno nuosėdas dalelinio Si pavidalu. Dėl besikeičiančių sąlygų (temperatūros, pH) nusėdusioje biomasėje Si gali atsipalaiduoti į priedugnio vandenį DSi pavidalu. Kadangi Si atsipalaidavimas yra labiau cheminis nei biologinis procesas, todėl jis vyksta gamtoje daug lėčiau (Dugdale ir Wilkerson, 2001).

Šio darbo metu atlikti tyrimai atskleidžia, kaip glaudžiai siejasi maistingųjų medžiagų srautai su fitoplanktono bendrijos sudėtimi, kurios pasikeitimas iš diatominių dumblių į melsvabakterių dominavimą gali daryti nemažą įtaką N, P ir Si virsmams ir sulaikymui mariose, srautams į Baltijos jūros pakrantę. Tai atskleidžia, kad Kuršių marios yra svarbi sistema, kurioje dėl vykstančių procesų (denitrifikacijos, P išskyrimo iš dugno nuosėdų, dumblių asimiliacijos) Nemuno atneštų maistingųjų medžiagų kiekis gerokai pasikeičia.

Atliekant tyrimus Kuršių mariose taip pat buvo pritaikytas LOICZ metodas. Naudojant šį metodą 2013–2015 metų laikotarpiui buvo sudaryti N, P ir Si masių balansai. Rezultatai tik dar kartą patvirtino, kad Kuršių marios gali veikti skirtingai: tiek kaip maistingųjų medžiagų filtras, tiek ir kaip jų šaltinis. Jei kalbėsime apie azotą, tai marios gali jį ir sulaikyti, ir išskirti, priklausomai nuo metų. Tuo tarpu DIP ir DSi yra intensyviai sulaikomi Kuršių mariose. Siekiant reprezentuoti Kuršių marias, jos buvo padalytos į dvi dalis: pietinę akumuliacinę ir šiaurinę tranzitinę. Rezultatai parodė, kad tos dvi dalys ir veikia skirtingai. Pavyzdžiui, mažesnėje, t. y. tranzitinėje, dalyje N_2 fiksacija buvo intensyvesnė nei denitrifikacija, todėl ji buvo DIN šaltinis, o didesnėje, t. y. akumuliacinėje, dalyje viskas buvo priešingai. Apibendrinant Kuršių marių rezultatus, sudarytas abiejų dalių balansas parodė, kad 2013–2014 metais N_2 dominuojantis procesas buvo fiksacija, o 2015 metais – denitrifikacija.

Kuršių marių vaidmuo transformuojant N ir P: pagrindiniai mechanizmai

Analizuojant fosforo biogeocheminį ciklą, buvo pastebėtas teigiamas ryšys tarp fosforo koncentracijos pokyčių ir fitoplankto žydėjimo Kuršių mariose. Kadangi vasaros metu N_2, gebančios fiksuoti melsvabakterės, turi konkurencinį pranašumą azoto trūkumo sąlygomis, tai jų gausumas priklauso nuo vandenyje ištirpusio neorganinio P kiekio (Lilover ir Stips, 2008; Conley ir kt., 2009). Neseniai pastebėta, kad įsigalėjusios N_2, gebančios fiksuoti meslvabakterės, gali nulemti procesų seką, kuri tampa palanki jų klestėjimui. Dėl intensyvaus melsvabakterių žydėjimo susidaro dideli kiekiai lengvai skaidomos organinės medžiagos, kuri padidina deguonies suvartojimą. Esant ramioms sąlygoms deguonies patekimas į gilesnius sluoksnius gali būti ribotas dėl jo intensyvaus suvartojimo vandens storymėje (Zilius ir kt., 2014). Susidarius deguonies trūkumui priedugnio vandenyje, organinis arba mineralinis P gali išsiskirti iš nuosėdų ir kauptis storymėje. Dėl šių priežasčių atsiradęs P skatina N_2, fiksuojančių melsvabakterių augimą (Jensen ir kt., 1994; Hyenstrand ir kt., 1999, 2000). Atlikti eksperimentai parodė, kad įprastai Kuršių marių dugno nuosėdos efektyviai kaupia ir sulaiko P iš vandens storymės. Kad P pradėtų atsipalaiduoti ir išsiskirti iš dugno nuosėdų, prireikia keleto dienų trunkančio deguonies trūkumo (Zilius ir kt., 2014). Taip pat yra kitų procesų (dugno nuosėdų resuspensija, nuosėdų struktūros pakeitimas dėl besirausiančių uodo trūklio lervų), turinčių įtakos P ciklui, tačiau jie lieka iki galo neįvertinti. Nors ir fosforo srautai iš dugno nuosėdų gali palaikyti tolimesnį melsvabakterių žydėjimą nepaisant to, kad jie trumpalaikiai, vis dėlto jie gali kompensuoti mariose sulaikyto fosforo kiekį – melsvabakterėse sukauptas fosforas yra išnešamas į Baltijos jūros priekrantę.

Taip pat buvo svarbu nustatyti, kokie procesai Kuršių mariose reguliuoja N virsmus iš ištirpusių formų į dalelines organines arba priešingai. Todėl panaudojant masių balanso skaičiavimus ir specifinių biogeocheminių virsmų matavimą buvo siekiama įgyvendinti šį tikslą. Apibendrinus tyrimo rezultatus, pastebėta, kad sezoninė fitoplanktono suksecija ir diatominių dumblių asimiliacija bei jų vėlesnis nusėdimas ant dugno nuosėdų paviršiaus yra vienas iš pagrindinių mechanizmų, sulaikančių N Kuršių mariose. Tuo tarpu denitrifikacijos procesas, kurio metu susidaro N_2 dujos, yra svarbiausias procesas, kai N sulaikomas ir negrįžtamai pašalinamas iš ekosistemos. Nemaža dalis N, pasišalinusio dujų pavidalu, yra grąžinama į marias mikrobiologinės N_2 fiksacijos metu. Dėl intensyvios fitoplanktono asimiliacijos vasaros–rudens sezonais Kuršių marios funkcionuoja kaip azoto bioreaktorius. Šiuo laikotarpiu N_2 fiksacija vyksta labai intensyviai ir jos metu DIN į sistemą patenka daugiau nei su Nemuno ir jūros srautais. Biomasėje susikaupęs PN yra skaidomas vandens storymėje arba srovių išnešamas iš marių į Baltijos jūrą. Todėl jo kaupimasis dugno nuosėdose yra minimalus. Šios įžvalgos leidžia manyti, kad įsivyravusios melsvabakterės gali sumažinti N sulaikymą mariose dviem būdais. Pirma, vasarą vykstanti N_2 fiksacija kompensuoja žiemą denitrifikacijos proceso metu pašalintą azotą. Antra, teigiamas melsvabakterių plūdrumas vandens paviršiuje lengvai jas išneša iš marių į jūrą. Tuo pat metu dugno nuosėdose dėl intensyvios mineralizacijos išsiskiria didelis ištirpusio azoto kiekis, kuris taip patenka į jūrą. Šie atradimai leidžia manyti, kad melsvabakterės gerokai sumažina N sulaikymą mariose, padidindamos jo srautus į Baltijos jūros priekrantę.

IŠVADOS

1. Nuo 1980–1993 metų iki 2012–2016 metų laikotarpio N ir P srautai iš Nemuno upės baseino į Kuršių marias gerokai pasikeitė. Tikėtina, kad fosforo srautų sumažėjimą 73 % lėmė pagerėjęs nuotekų valymas modernizavus valymo įrenginius. Azoto srautų sumažėjo tik 24 % – tai lėmė anksčiau baseine sukauptų atsargų išplovimas.
2. Tyrimų laikotarpiu metiniai N, P ir Si srautai svyravo atitinkamai 50 %, < 10 % ir iki 20 %. Didžiausią įtaką N srautų dydžio svyravimui turėjo seka veiksnių, kurie nulėmė jo išplovimą iš dirvožemio: staigus sniego dangos ištirpimas, kritulių gausumas ir pasiskirstymas laike, oro temperatūra ir vegetacijos sezonas. Visa tai veikė nitratų susidarymą, tirpumą, migraciją dirvožemyje ir jų pašalinimą denitrifikacijos metu.
3. Išanalizavus maistingųjų medžiagų stechiometriją sraute į Kuršių marias, nustatytas N perteklius žiemos laikotarpiu, o vasarą N kartu su Si limitavo fitoplanktono augimą. Šie pokyčiai galimai lemia fitoplanktono bendrijos struktūrą ir sukuria palankias sąlygas įsigalėti melsvabakterėms.
4. Kuršių marių vaidmuo sulaikant maistingąsias medžiagas daugiausia priklausė nuo melsvabakterių žydėjimo intensyvumo. Fitoplanktono bendrijos struktūros pokyčiai turėjo įtakos N, P ir Si virsmams ir srautams mariose. Melsvabakterių žydėjimo metu padidėjus dalelinės medžiagos išnešimui į Baltijos jūros priekrantę, Kuršių marios tampa N ir P šaltiniu.
5. Diatominių dumblių ir melsvabakterių žydėjimas skirtingai veikia N kaupimąsi mariose. Pavasarinio diatominių dumblių žydėjimo metu N kaupiasi planktono biomasėje, kuri vėliau nusėda ant dugno. Tuo tarpu melsvabakterės išlieka vandens storymėje, todėl didžioji dalis jų biomasės yra išnešama į Baltijos jūrą.
6. Kuršių mariose vykstančių mikrobiologinių procesų svarba lyginant su išoriniais maistingųjų medžiagų srautais padidėja vasaros–rudens laikotarpiu, kai jų mažiausiai atnešama Nemuno upe. Vasaros melsvabakterių žydėjimo laikotarpiu dugno nuosėdos buvo svarbiausias ištirpusio N ir P šaltinis dėl organinės medžiagos mineralizacijos ir deguonies stygiaus.

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