KLAIPĖDA UNIVERSITY

MINDAUGAS ŽILIUS

OXYGEN AND NUTRIENT EXCHANGE AT THE SEDIMENT-WATER INTERFACE IN THE EUTROPHIC BOREAL LAGOON AT THE BALTIC SEA

Doctoral dissertation
Biomedical sciences, ecology and environmental sciences (03B)

Klaipėda, 2011

TABLE OF CONTENTS

INTRODUCTION

Scope of study

Nutrients of terrestrial origin undergo a series of biogeochemical transformations when they pass through transition zones such as estuaries and lagoons (Wollast, 1983; Seitzinger, 1988; Nixon et al., 1996; Ogilvie et al., 1997). They can be incorporated into benthic and pelagic primary producers, grazed by herbivores and rapidly recycled to the water column or they can be retained in surface sediments as buried organic matter or precipitated with other elements (Howarth, 1988; Conley & Malone 1992; Kemp et al., 1992; Cowan & Boynton 1996; Conley et al., 2009). The coupling of these processes can significantly delay the delivery of nutrients to coastal areas, but sudden release and export of temporary trapped elements can also occur (Jensen et al., 1990).

Sediment biogeochemistry and nutrient exchange are strongly regulated by the availability, vertical distribution and dynamics of dissolved oxygen (Rasmussen & Jørgensen, 1992). Oxic sediment layer has been recognized as an important controlling factor of nitrification and denitrification processes (Christensen et al., 1990; Jensen et al., 1994), overall preservation or mineralization of organic matter (Hartnett et al., 1998), P and S^{2-} mobility (Giordani et al., 1996) and with implication for oxidation of anaerobic metabolism end-products (De Wit et al., 2001; Bartoli et al., 2009). In eutrophic water bodies and coastal areas algal blooms can cause a massive influx of labile particulate matter to the surface sediment. Such organic matter input may result in progressive oxygen depletion due to consumption rates exceeding diffusion from the water column. This can ultimately affect oxygen concentration in the near-bottom waters as well as nitrogen and phosphorous cycling and stoichiometry (Kemp et al., 1992).

When oxygen becomes depleted, reactive phosphate is released from iron bound complex in sediments (Jensen et al., 1995). On the other hand, when denitrification is based on nitrate transport from the overlaying water, reduced oxic zone may increase denitrification rates due to decreased NO_3^- diffusion path (Christensen et al., 1990; Jensen et al., 1994; Rysgaard et al., 1995). Therefore enhanced internal loading of phosphorus leads to the lower nitrogen to phosphorus ratio in water column and may effectively promote blooms of N_2-fixing cyanobacteria. These coupled processes of internal loading, nitrogen removal, and the prevalence of N_2-fixing cyanobacteria were described as a self-sustaining ”vicious circle”, which links increased sedimentation of organic material with increasing extent of anoxic bottoms and subsequently increasing internal phosphorus load (Vahtera et al., 2007).

The present study was carried out in the highly eutrophic boreal lagoon, which suffers from plankton blooms and seasonal inputs of labile organic matter to the bottom sediment (Galkus & Jokšas 1997; Jokšas et al. 1998; Olenina 1998; Pilkaitytė and Razinkovas 2006, 2007).

The goal of study

This study aims to quantify dynamics of dissolved oxygen and nutrient exchange at the sediment–water interface in the Curonian Lagoon.

The main objectives:

1. to microprofile oxygen distribution in the surface sediment and quantify oxygen exchange at the sediment–water interface in the principal lagoon environments during distinctive seasons;
2. to estimate porewater nutrient stocks and to determine diffusive and total fluxes at the sediment–water interface;
3. to evaluate capacity of sediment to remove nitrogen from the Curonian lagoon ecosystem in transition from spring to summer;
4. to identify environmental factors responsible for denitrification control and regulation of oxygen, and nutrient fluxes at the sediment water–interface;
5. to assess potential activity of benthic microalgae;

The novelty of study

This study is assessing dynamics of biogeochemical processes in the Curonian lagoon, and provides integrated view on nutrients exchange at the sediment–water interface and its relation to the seasonal phytoplankton succession and algae. Denitrification measurements using revised isotope pairing technique have been carried out in the Curonian lagoon for the first time and provide new knowledge about sediment potential to remove nitrogen from this largest boreal lagoon in Europe. Furthermore, study results supply new information on the role of sediment in controlling water quality of this heavily eutrophicated lagoon.

Scientific and practical significance of the results

Results of this study provide additional knowledge on importance of internal loading in the Curonian lagoon, which significantly contributes to the general understanding of nutrient loading effects needed for effective ecosystem management and its restoration. Study results indicate, that bottom sediment has potential to remove, retain or release nutrient from/to the water column, and consequently to influence eutrophication processes. Thus, study supply information about benthic-pelagic coupling and it role in the ecosystem functioning at the Curonian lagoon. Field measurements carried out during this study have been integrated with phytoplankton and zooplankton observations, therefore collected datasets are ready for development of biogeochemical part in ecological model of the Curonian lagoon.

Defensive statements:

1. Organic matter supply to the sediments in the Curonian lagoon is driven by pelagic processes, however locally benthic microalgae can be important.
2. Sediment oxygen demand is increasing towards summer and largely depends on OM supply.
3. Total oxygen uptake rates in organic-rich sites do not exceed those in poor organic sandy sediment. After sedimentation pulses benthic metabolism in shallow sands with low organic content is higher than in deeper organic-rich sites.

4. Seasonal dynamics of chlorophyll *a* is tightly coupled with temperature and nutrient availability is important complex driving nutrient exchange processes.
5. Seasonal differences in denitrification rates are primarily shaped by external NO_x^- load into lagoon.
6. Benthic microalgae and deposited viable phytoplankton cells are locally important for oxygen and nutrient exchange at the sediment water interface.

Scientific approval

The results of this study were present at conference:

2nd, Lithuanian scientific and practical conference on "Marine and Coastal Research", Palanga, Lietuva April 9-11, 2008.

3rd regional student conference on "Biodiversity and functioning of aquatic ecosystems in the Baltic Sea regeon", Judkrantė, Lithuania, October 9-13, 2008.

3rd, Lithuanian scientific and practical conference on "Marine and Coastal Research", Nida, Lietuva April 8-10, 2009.

4th European Conference on Coastal Lagoon Research, Montpellier, France December 14-18, 2009.

BONUS EEIG–Annual Conference 2010, Vilnius, Lithuania January 19-21, 2010.

4th Lithuanian scientific and practical conference on "Marine and Coastal Research", Palanga, Lithuania April 13-16, 2010.

EUTRO 2010, Nyborg, Denmark July 15-18, 2010.

5th European Conference on Coastal Lagoon Research, Aveiro, Portugal July 25-30, 2011.

Publications on the dissertation topic:

1. **Zilius**, **M**., Bartoli M., Daunys D., Pilkaityte R. & Razinkovas A., (2011). Benthic oxygen uptake in the shallow eutrophic Curonian lagoon (Baltic Sea). Hydrobiologia, (accepted).
2. Bresciani, M., Claudia Giardino C., Stroppiana D., Pilkaitytė R, **Zilius M**., Bartoli M. & Razinkovas A., 2011. Retrospective analysis of spatial and temporal variability of chlorophyll-a in the Curonian Lagoon. Coastal Monitoring (accepted).
3. **Zilius**, **M**., Daunys D., Bartoli M. & Razinkovas A. Seasonal nutrient exchange at sediment–water interface in the eutrophic boreal lagoon (The Baltic Sea), Journal of Limnology (submitted).
4. Bartoli, M., Nizzoli D., **Zilius M**., Razinkovas A., Longhi D., Fulweiler R., Sundbäck K. & Viaroli P. Benthic processes with special emphasis on nitrogen transformations in the surface sediments of the Curonian Lagoon (Baltic Sea, Lithuania), (in preparation).

Volume and structure of the thesis. Dissertation is presented in the following chapters: Introduction, Literature review, Study area, Material and Methods, Results, Discussion, Conclusions, References and

Appendix1. The dissertation volume is 99 pages, it contains 36 figures and 18 tables. References include 255 sources.

Acknowledgments

These thesis would not have been possible without the help of numerous people, to whom I am sincerely grateful; I grateful thank my superadvisor Darius Daunys, who had trusted in me and let by myself plan field activity and experiments. His numerous constructive and skillful comments on writing this thesis let achieved present state of thesis. Thanks advisor Artūras Razinkovas-Baziukas, who turned me in biogeochemistry of Curonian lagoon and permanently shared a many of idea. Without his financial support was impossible to be performed this study. Sincerely thanks Marco Bartoli for opportunity to learn flux and denitrification measurements, for helping to obtain and calculating denitrification rates in lagoon. Also would like to thank Marco Bartoli for good time spent in Parma and helping to start my scientific carrier today. I am indebted to a head of analytical laboratory of sewage treatment Nijolė Domarkienė and other staff for nutrient analysis. I would like also thank director of my host institute CORPI Zita Rasuolė Gasiunaitė for supporting idea and opportunity to construct some device, Ričardas Paškauskas for initial inspiration and introduction to Curonian lagoon system, Daniele Nizzoli and Daniele Longhi for skilful assistance in the laboratory and helping to collect part of sample, Saulius Gulbinskas for grain size analysis. Tomas Ruginis, Kasparas Bagdonas for numerous times spent to assisting in field and laboratory experiments, Renata Pilkaityte for measuring water and sediment chlorophyll *a* concentrations, Rasa Butkutė for analysis of dissolved organic carbon, Ingrida Bagdonavičiutė for design of bottom sediments map, Igoris for help to constructing experimental setup, Shipping repair company “Garant” for constructed microprofiling table and hand-corer, Captain Algimantas Žemaila and crew of the R/V Puta for their assistance during field activity. Also would like to thank Prof. Pierluigi Viaroli for hospitability and possibility to perform some measurements in Parma University.

Especially I would like thank my darling wife Rūta, for her awareness and permanent contribution during study.

This study financially was supported in frame of BONUS ERA-NET PLUS project AMBER, COLAR, EU LIFE projects.

Abbreviations used in thesis

Chl a –chlorophyll *a*
Dn – coupled nitrifcation–denitrifiacation
DOC – dissolved organic carbon
DOU – diffusive oxygen uptake
Dtot – Total denitrification
TOM – total organic matter
TOU – total oxygen uptake

Dw – denitrification on diffused NO_3^- from water

N – nitrogen

NH_4^+ – ammoniums

NO_2^- – nitrite

NO_3^- – nitrate

NO_x^- – nitrate+nitrite

O_2 – oxygen

OM – organic matter

OPD – oxygen penetration depth

P – phosphorus

PC – principal component

PCA – principal component analysis

POM – particulate organic matter

RDA – redundancy analysis

TCO_2 – total inorganic carbon

LTERATURE REVIEW

1.1. Main biogeochemical cycles in shallow sediments

Organic matter mineralization. Shallow sediments commonly stand a primary site for the mineralization of deposited organic material (OM) (Hammond et al., 1985; Jørgensen, 1996), which mainly comes from phytoplankton production (Jørgensen, 1996). On the other hand, also microphythobenthos can deliver relevant input of organic carbon to the sediment (Underwood & Kromkamp, 1999; Middelburg et al., 2000).

Organic material within sediments is mediated by an array of aerobic and anaerobic microbial processes in surface sediment with a concurrent release of inorganic nutrients (Mackin & Swider, 1989; Canfield et al., 1993) (Fig. 1.1). Mineralization of the rapidly leachable fraction of the fresh sedimentated material occurs quickly and with the same constant rate regardless of the electron acceptor availability (Kristensen & Holmer, 2001). However, more refractory organic material undergoes the oxic and anoxic mineralization, with faster decomposition in oxic conditions (Kristensen et al., 1995), therefore the later is considered to be more efficient and the most important pathway of organic material mineralization (Jørgensen & Sørensen, 1985; Hansen & Blackburn, 1991). In spite of this, significance of oxic mineralization in the estuarine sediments is comparable to that taking placing in the anoxic layers, which are prevailing due to very low oxygen penetration depth in coastal sediments (Fig. 1.1) (Revsbech et al. 1980). Relative importance of a given organic matter oxidation pathway depends also on organic matter load (Graf et al., 1982; Sloth et al., 1995; Conley & Johnstone, 1995), sediment and water chemistry (Jørgensen & Sørensen, 1985; Christensen et al., 1990) as well as organic matter oxidation pathway have been found to dominate in different environment (Jørgensen & Sørensen, 1985; Glud et al., 2000; Warnken et al., 2008). Furthermore, mixing processes (*e.g.* bioturbation or resuspension) result in high heterogeneity of sediment and different oxidation pathways can be highly overlapping in their vertical division (Hansen & Blackburn, 1992; Canfield et al., 1993; Banta et al., 1999; Kostka et al., 1999; Warken et al., 2008). Moreover temporal transition of sediments from oxic to anoxic state results in a profound modification of the benthic microbial community with significant changes in stratification of vertical processes (Holmer, 1999; Bartoli et al., 2009).

Vertical distribution of electron acceptors determines thickness of the oxic zone, which vary from less than 1 millimeter to a few centimeters in the upper sediment. Oxygen penetration depth is strongly regulated by the availability, vertical distribution and dynamics of dissolved oxygen (Rasmussen & Jørgensen, 1992), water temperature (Thamdrup et al., 1998), organic carbon load (Caffrey et al., 1993; Candfield et al., 1993), thickness of the diffusive boundary layer (Jørgensen & Revsbech, 1985), micro- or macrophythobenthos primary production (Olesen & Lundsgaard, 1995; Barranguet et al., 1996; Pasqualini et al., 1998; Lorenzen et al., 1998) and benthic fauna (Aller, 1998; Kristensen, 2000). In oxic zone using O_2 as electron acceptor organic carbon can be completely metabolized to CO_2 and H_2O (Fig. 1.1). During this aerobic degradation other oxygen–containing radicals (*e.g.* $-O_2^-$, $-H_2O_2$, -OH) can also assist and ultimately depolymerize refractory organic compounds (Canfield, 1994).

Furthermore the oxidized zone that extends just below the upper oxic zone in sediments is frequently referred to the 'suboxic zone' (Froelich et al., 1979). Thus zone functions as a barrier for the reduced compounds (NH_4^+, Mn_2^+, Fe_2^+ and S^{2-}) diffusing from deeper layer, where anaerobic oxidation occurs (Thamdrupt et al., 1994; Maeyer et al., 2001). In the lower part of oxic zone occurring reduced compounds (*e.g.* NH_4^+) oxidation is the most relevant to further biogeochemical cycling in anoxic zone due to increased availability of electron acceptors.

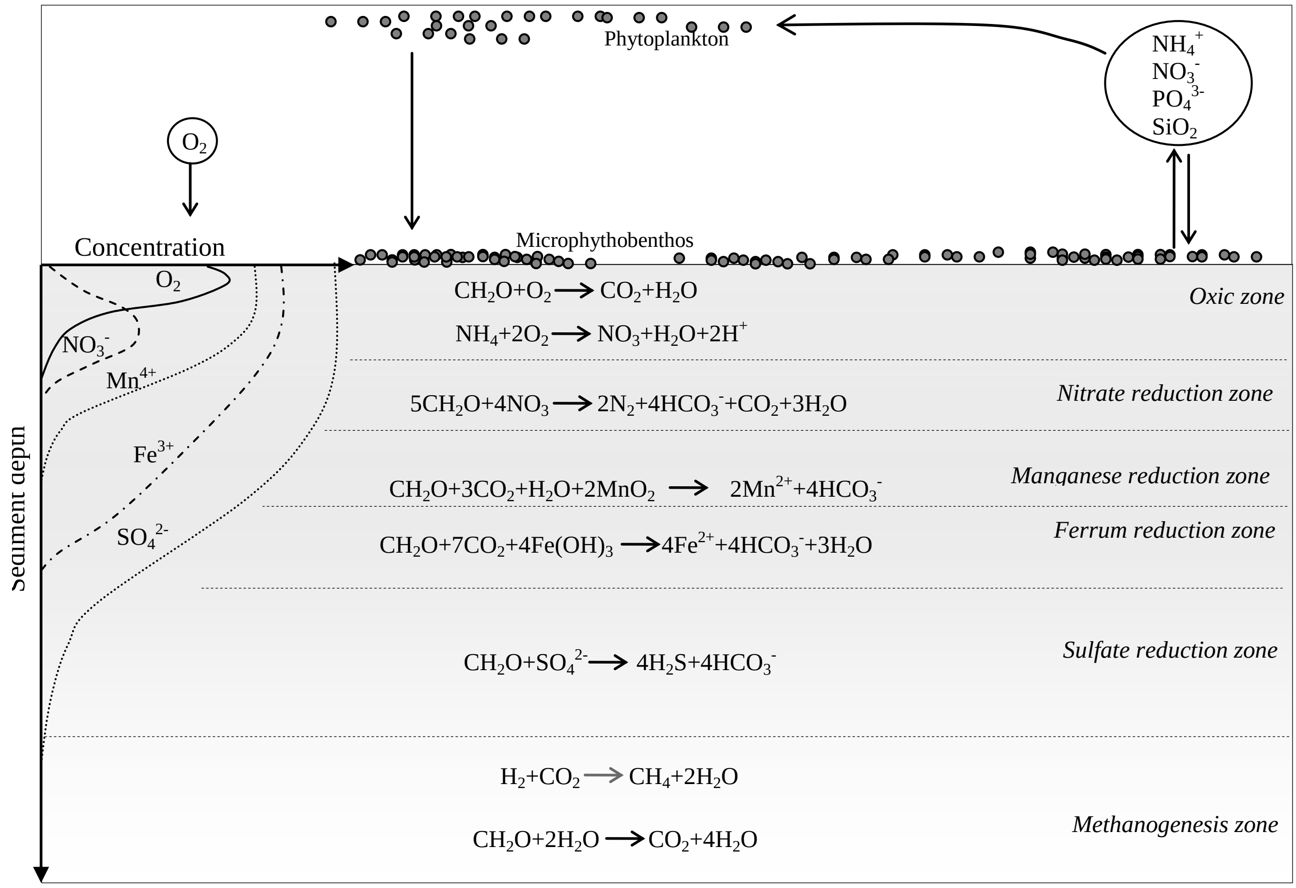


Figure 1.1. Schematic presentation of some important diagenetic processes in coastal sediments (modified from Fenchel & Jørgensen 1977; Froelich et al., 1979; Canfield et al. 1993).

The nitrate reduction zone primarily occurs bellow the oxic/anoxic interface (Jensen et al., 1993; Lorenzen et al., 1998) (Fig. 1.1) and organic matter mineralization here is carried out by facultative anaerobic bacteria, using NO_3^+ as electron acceptors (Seitzinger, 1988). Denitrification is fueled by diffusing nitrates from lower part of oxic zone where nitrification occurs or from overlaying water column (Seitzinger 1988; Maeyer et al., 2001). Modeling study showed that in well–mixed waters denitrification is mainly coupled with nitrification within the sediment, while influx of NO_3^- from overlaying water is the most important nitrate source under stratified water column conditions (Soetaert & Middelburg, 2009). Numerous authors (Jørgensen & Revsbech, 1985; Christensen et al., 1990; Nielsen et al., 1990; Ogilvie et al., 1997; Stockenberg &

Jonhstone, 1997; Mayer et al., 2001) recognize, however, that NO_3^- concentration in the overlaying water column is primary controlling factor to denitrification.

If metal oxides Mn and Fe are available in deeper anaerobic sediments the transfer of electrons from organic matter to Fe(III) and Mn(IV) can be an important pathway for OM decomposition (Froelich et al., 1979; Lovley et al., 1986; Jakobsen & Postma, 1999; Vandieken et al., 2006) (Fig. 1.1). In temperate zone shelf areas and arctic fjords sediment dissimilatory Mn(IV) and Fe (III) reduction is dominant processes of anaerobic carbon mineralization in the upper 10 cm of sediment, whereas in deeper sediments the importance of hydrooxides is decreasing (Canfield et al., 1993; Thamdrupt et al., 1994; Vandieken et al., 2006). Bellow is situated sulfate reduction zone, where in diagenetic OM process SO_4^{2-} serves as electron acceptor with further H_2S accumulation (Capone & Kiene, 1988; Thamdrup et al., 1994). Most of produced H_2S is precipitated as iron sulfide and S^0 by reaction with Fe (Thamdrup et al., 1994). Availability of sulfate ion (SO_4^{2-}) is a primary factor in the distribution of microbial activities in the anoxic sediments (Jørgensen & Sørensen, 1985; Holmer, 1999). Sulfate concentration is the highest in estuarine environments with seawater inflows and consequently sulfate reduction typically exceeds methanogenesis there (Capone & Kiene, 1988). In freshwater dominated estuaries, however, sulfate reduction can rapidly decline and the methanogenesis become generally the most important terminal process in overall carbon mineralization (Holmer, 2001). Though sulfate reducing bacteria and methane producing bacteria may coexist (Lomans et al., 1999), the former group out-competes often fermenting and methanogenetic bacteria due high affinity for the most common substrates in sediments (Li et al., 1996). Number of studies performed in nearshore and estuarine environments demonstrate sulfate reduction being the major pathway of OM mineralization in sediments (Howarth & Giblin, 1983; Mackin and Swider, 1989).

Nitrogen biogeochemical cycling. Nitrogen transformation is typically carried out by consortium of bacteria within oxic and anoxic sediment zones (Herbert, 1999) (Fig. 1.2), and coupling of these zones has been recognized as a relevant controlling factor for nitrogen cycling within sediment: e.g. nitrification and denitrification (Risgaard-Petersen et al., 1994; Lorenzen et al., 1998; Meyer et al., 2001).

The most of dissolved inorganic nitrogen prevailed is ammonium yielded from OM (e.g. dissolved organic nitrogen and urea) ammonification deeper below oxic zone (Jensen, 1993). Due to gradient–driven diffusion NH_4^+ transported from anoxic zone is oxidized to nitrate in the oxic environment (Jensen, 1993) (Fig. 1.2). Conventionally nitrification is a strictly aerobic process during which chemoautotrophic bacteria derive energy from the oxidation of ammonium, which is used to fix inorganic carbon. Though thickness of the oxic zone, where nitrification occurs may be extended from less than 1 mm to over several centimeters, it is strongly is regulated by organic matter load (Billen, 1982), oxygen concentration (Jensen et al., 1993), sediment bioturbation (Kristensen 2000; Nielsen et al., 2004; Stief & de Beer, 2006) and photosynthesis/respiration of microphythobenthos (Jensen et al., 1993; Lorenzen et al., 1998; Meyer et al., 2001) and its competition with bacteria’s for N (Risgaard-Petersen et al., 2004b).

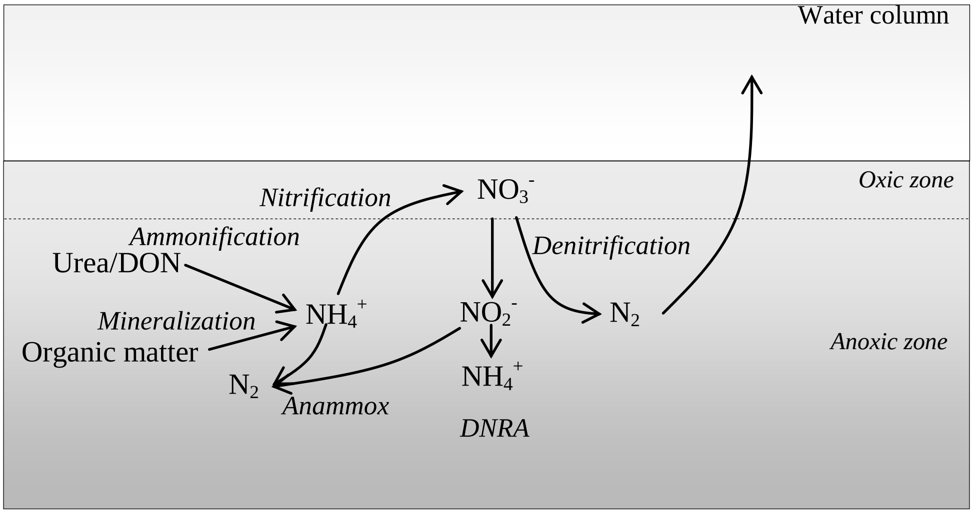


Figure 1.2. Major pathways of N cycle in sediments

Reduction of dissimilatory oxidized nitrogen to gaseous N_2 (denitrification) is another significant nitrogen cycling pathway (Fig. 1.2). It is the major pathway which supports the loss of nitrogen from marine, estuarine and freshwater systems (Seitzinger, 1988; Thamdrupt & Dalsgaard, 2002; Dalsgaard et al., 2003; Rysgaard et al., 2004; Engström et al., 2005; Hietanen & Kuparinen, 2008). The regulation of denitrification and its coupling to nitrification is complex due to the involvement of bacteria in oxic and anoxic zone. The general concept of coupled benthic nitrification and denitrification is usually assumed to follow strict sequence of vertically stratified diagenetic reactions with nitrification in the oxic zone and denitrification just bellow in the suboxic or uppermost part of the anoxic sediment layer (Henriksen & Kemp, 1988). Otherwise denitrification can be maintained by nitrate diffusing from the overlaying water column (Seitzinger, 1988).

In shallow estuarine sediments denitrification is commonly suppressed due presence of microphythobenthos (Sundbäck & Mile, 2000). Inhibition of denitrification by photosynthetically active sediment firstly occurs due to extended oxic zone which prolongs diffusive path length of the NO_3^- from overlaying water to denitrification site (Rysgaard et al., 1995; Meyer et al., 2001). Moreover, microphythobenthos could strongly compete with denitrifiers for NO_3^- present in porewater (Risgaard-Petersen et al., 2004b).

Instead of being denitrified, under high OM loading (e.g. from fish farms) a substantial part of nitrate may alternatively be converted to ammonium via dissimilatory nitrate reduction to NH_4^+ (DNRA) with intermediate NO_2^- (Fig. 1.2) (Christensen et al., 2000). In this case inorganic nitrogen is retained within the aquatic environment (Koike & Hattori, 1978). Recent studies confirmed that DNRA rates can represent significant pathway of nitrate in comparison to denitrification in shallow estuaries and marine sediments (Dong et al., 2000; Hietanen, 2007).

Finding of previously unknown nitrogen removal via anaerobic NH_4^+ oxidation by NO_2^- (anammox) encouraged to revisit N_2 removal balance in numerous marine and estuarine systems (e.g. Thamdrupt &

Dalsgaard, 2002; Dalsgaard et al., 2003; Rysgaard et al., 2004; Engström et al., 2005; Hietanen & Kuparinen, 2008). Anaerobic NH_4^+ oxidation with NO_2^- as an electron acceptor is mediated by monophyletic group of bacteria that branches deeply in the phylum *Planctomecetes* (Strous et al., 1999). In marine environment anammox bacteria have "microaerotolerant lifestyle" therefore thrives at low levels of O_2 up to ~10 µmol l^{-1} (Jensen at al., 2008). The anammox reaction occurs with stoichiometric ratio 1:1 through pairing of NH_4^+ and NO_2^- atoms (Thamdrupt & Dalsgaard, 2002). Recently, field experiments have indicated that coupled NO_3^- reduction to NO_2^- or NH_4^+ and ammonia oxidation may significantly contribute to N_2 gas production in aquatic ecosystems (Thamdrup & Dalsgaard, 2002). Hence high NO_3^- concentration in the overlying water and a greater availability of organic carbon may regulate NO_2^- supply via NO_3^- reduction and modulate greater anammox rates (Trimmer et al. 2003; Meyer et al., 2005; Risgaard-Petersen et al., 2005; Nicholls & Trimmer, 2009). This suggested that if NO_3^- availability is low, the loss of NO_2^- from denitrifiers would probably be insignificant and insufficient to support a population of anammox bacteria. Temperature seems to be another important factor which regulates anammox in marine and estuarine sediments, because numbers of studies confirmed presence of anammox process in temperate zone (Dalsgaard & Thamdrup 2002; Ryssgaard et al. 2004; Hietanen & Kuparinen, 2008; Dong et al., 2009; Nicholls & Trimmer, 2009).

Phosphorus biogeochemical cycling. In contrast to nitrogen, phosphorus cycling generally is a chemical process, not mediated by bacteria. In coastal marine sediments was found that phytoplankton sedimentation delivers a large part of phosphorus into coastal marine sediments, where it undergoes biogeochemical transformations (Jensen et al., 1995). This mainly include conversions from a dissolved to a solid state: anion adsorption, precipitation/co-precipitation with elements such as calcium, iron and aluminum and assimilation of organic forms by microbes and plants (Sundby et al., 1992; Jensen et al., 1995; Slomp et al., 1998; Holmer et al., 2006). Therefore phosphorus speciation in sediments greatly depends on geochemical reactions of phosphate with these sediment components (Krom & Berner, 1981). Under anoxic conditions non-refractory organic and Fe-bound phosphorus contribute to soluble reactive phosphorus (SRP) regeneration via organic matter decomposition and the reduction of ferric iron species, while iron oxidation processes are responsible for phosphorus retention within sediment under oxic conditions (Jensen et al., 1995; Gunnars & Blomqvist, 1997; Golterman et al., 2001; Rozan et al., 2002). In experiments was demonstrated that in sediment porewater a large part of SRP is derived by reduction of ferric oxides or lost binding sites to ferric compounds due to its precipitation with sulfides (Jensen et al., 1995; Gunnars & Blomqvist, 1997; Rozan et al., 2002).

1.2. Ecosystem elements and processes linked to sediment biogeochemistry

Ecosystem level factors such as microphythobenthos, macrofauna activity, sediment resuspension, temperature, organic matter supply and quality, nutrient loading and salinity have been shown to be important for regulation of biogeochemical processes and solute transport across sediment–water interface

(Graf et al. 1982; Boynton and Kemp, 1985; Jensen et al. 1990; Sundbäck & Miles, 2000; Stahlberg et al., 2006 and et cetera). Simultaneously, water temperature cannot be excluded as the single controlling factor for benthic metabolism and solute transport; the external seasonal loading of nutrient by rivers, benthic microalgae activity and seasonal inputs of labile organic material to the sediments seem to be more important parameter to consider (Graf et al., 1982; Arnosti et al., 1998, Franco et al., 2009). Temperature is rather set of all factors that could shape biogeochemical cycling and nutrient exchange at sediment–water interface (Cowan & Boynton 1996).

Microphythobenthos. Benthic microalgae (microphythobenthos) are significant driver in organic matter turnover and nutrient cycling in the temperate shallow estuarine environments (Risgaard-Petersen et al., 1994; Middelburg et al., 2000; Sundbäck & Miles, 2000). Microphythobenthos is responsible for significant fraction of oxygen consumption and nitrogen retention (Christensen et al., 1990; Lorenzen et al, 1998; Mayer et al., 2001; Köster et al., 2005). Labile carbon produced by microphybenthos can be rapidly recycled and indirectly cause increased oxygen consumption (Middelburg et al., 2000; Köster et al., 2005). Additionally, microphythobenthos photosynthetic activity can increase the oxic zone by 1–2 mm (Lorenzen et al, 1998; Mayer et al., 2001) and deeper oxygen penetration may stimulate nitrification and nitrification–denitrification coupling due to increased availability (Risgaard-Petersen et al., 1994). In fact, the thickness of the oxic sediment layer directly determines the length of the nitrate diffusion pathway from the water to the denitrification zone, and higher rates of dissimilative nitrogen loss are expected when oxygen is limiting in surface sediment (Rysgaard et al., 1995). On the other hand, this may lead to decoupling of nitrification–denitrification processes in estuarine sediments (Risgaard-Petersen, 2003, Risgaard-Petersen et al., 2004b). Nitrogen assimilation by the microphythobenthos affects NH_4^+ availability to nitrifying bacteria and overcomes denitrifiers due to lack nitrates. NO_3^- or NH_4^+ fluxes from microphythobenthos inhabited sediments to water column can be less than 12% of the release from unvegetated sediments (Risgaard-Petersen, 2003). Comparing N uptake by microphythobenthos and denitrification become evident that denitrification has minor role as sink particularly in low latitude situated sediments (Sundbäck et al., 2000; Risgaard-Petersen, 2003). Similarly, anaerobic ammonium oxidation capacity of sediments could be considerably altered by microphythobenthos. Reduced activity of anammox bacteria in sediments is most likely linked to the ability of microphythobenthos to hinder the supply of NO_x^- and thereby the supply of NO_2^- to the anoxic sediment strata harboring the process (Risgaard-Petersen, 2004a). Furthermore, microphythobenthos affects the net nutrient regeneration to the water column and may result in a temporary trap of inorganic nitrogen, phosphate and silicate (Sundbäck & Graneli, 1988; Sundbäck et al., 2000, Thorton et al., 2002; Bartoli et al., 2003). Due to reoxidation of Fe(II) microphytobenthos could indirectly retain soluble reactive phosphorus and/or reduce its efflux from sediments (Sundbäck & Graneli, 1988). Microphythobenthos can also contribute substantially to the carbon flux to sediments (Underwood & Kromkamp, 1999; Middelburg et al., 2000) due to release of in the form of carbohydrates (Smith &

Underwood, 2000), which can be rapidly incorporated into hetrotrophic bacterial biomass (Middelburg et al., 2000; Köster et al., 2005).

Macrofauna activity. Macrofauna has profound impact on benthic fluxes via burrowing and irrigation activities (Kristensen, 1988, 2000). Burrowing may significantly extend the sediment-water interface, and decrease diffusion distances at burrow walls (Kristensen 1984; Nielsen et al., 2004; Pelegri & Blackburn, 1995; Svensson & Leonhardson, 1996). Exchange of solutes between the pore water and the overlying water column may be increased at least several times (Archer & Devol, 1992; Glud et al., 2003; Nielsen et al., 2004; Wenzhoeper & Glud, 2002). On the other hand, sediment bioturbation can reduce inorganic soluble phosphorus and silica exchange at the sediment-water interface due increased sediments oxygenation and subsequent chemical precipitation (Tuominen et al., 1999).

Mosaic of oxic and anoxic niches created by the network of burrow walls within the uppermost sediment horizons, expands the sediment–water interface, where important biogeochemical processes, namely aerobic mineralization, nitrification and denitrification and iron reoxidation can occur (Nielsen et al., 2004; Pelegri & Blackburn, 1995; Mayer et al., 1995; Fenchel, 1996, Bartoli et al., 2001). Simultaneously, burrow ventilation by macrofauna can increase supply of fresh organic material, redistribute electron acceptors in the deeper sediment and subsequently change a balance between aerobic and anaerobic respiration (Sloth et al., 1995; Banta et al., 1999). Experiments showed that intensive bioturbation can significantly decrease anaerobic respiration e.g. sulfate reduction (up to 66% of initial rate) and increase aerobic process (Banta et al., 1999; Heilskov & Holmer, 2001).

Macrofauna activity influences nitrogen cycling in burrow microenvironments and nitrogen flux across sediment-water interface due to excretion of labile N-compounds (e.g. urea) (Pelegrí & Blackburn, 1995; Mayer et al., 1995). Bioturbation stimulates nitrification and sediment oxygen uptake to an equivalent extent, while coupled nitrification-denitrification could be stimulated twice as much as oxygen consumption (Pelegrí et a1., 1994; Stief & de Beer, 2006). Therefore increased oxygen uptake and nitrate reduction in burrow microenvironments can be several magnitudes higher comparing to exchange at the sediment–water interface (Nielsen et al., 2004; Wenzhöfer & Glud, 2004).

Sediment resuspension. In shallow estuarine environments wind driven resuspension of sediment alter both sediment biogeochemical processes and organic matter, and nutrient pool in the water column, which can stimulate phytoplankton growth and productivity as well as cause shifts of pelagic community from autotrophic to heterotrophic status (Simon, 1989; Lawrence et al., 2004; Stahlberg et al., 2006; Almroth-Rosell et al., 2011). Sediment flushing results in transfer of porewater to the water column and promoted desorption of ammonium from sediment particles (Simon, 1989; Marinelli et al. 1998; Mortminer et al., 1998; Warnken et al., 2000). Morin and Morse (1999) found that about 2/3 of ammonium released from resuspended sediment originated from desorption rather than dilution of pore water. Increased oxygen consumption as a result of resuspension may lead to extension of anoxic/suboxic bottom waters with subsequently increased benthic flux of phosphate and ammonium (Almroth et al., 2009). Obviously resuspension driven pore water can induce higher inputs than the benthic diffusive flux (Simon, 1989). On the hand resuspension can redistribute organic matter in the system: modeling results showed that due to shallow sediment resuspension organic matter is transferred to water column, with later accumulation in deeper stagnant areas, where resuspension is considerable lower (Almroth-Rosell et al., 2011).

Rather short term resuspension events can influence more carbon and nutrient availability and cycling within sediments than either event occurring often (Stahlberg et al., 2006).

Organic matter load. In shallow hypereutrophic coastal waters, repeated microalgae blooms cause a massive influx of labile particulate matter to the sediment surface. Such organic matter input can result in the progressive depletion of oxygen as consumption rates exceed diffusion from the water column. This can ultimately affect oxygen concentration in near-bottom waters (Jensen et al., 1990; Kemp et al., 1992; Sloth, 1995). A subsequently developing hypoxia has numerous feedbacks to biogeochemistry of sediments, which could lead eutrophication (Conley et al., 2009; Vahtera et al., 2007).

Furthermore, translocation of fresh labile organic matters from water column to the benthos is followed by a gradual recovery of dissolved inorganic N, P and Si concentrations in pore water and thereafter their high release rates from sediment (Cowan & Boynton, 1996; Grenz et al., 2000; Jensen et al., 1990; Conley & Johnstone, 1995; Jensen et al., 1995).

The increased organic matter loading to sediments significantly affects the oxic/anoxic interface and overall balance between aerobic and anaerobic processes (Jensen et al., 1990; Caffrey et al., 1993; Jørgensen 1996; Herbert, 1999). Higher organic matter load supports reduced condition and affects fate of N and P (Jensen et al., 1990; Jensen et al., 1995; Sloth, 1995; Conley & Johnstone, 1995). Conventional nitrogen removal through denitrification can be replaced by nitrate reduction to ammonium with its subsequent retention in the ecosystem (Christensen et al., 2000). On the other hand, inorganic phosphorus is released from iron-bound phosphorus in sediment (Jensen et al., 1995), and combined ammonium and inorganic phosphorus flux will result in negative feedback processes and stimulation of pelagic production (Conley et al., 2009a; Eyre & Ferguson, 2009; Vahtera et al., 2007).

Nutrient loading. Estuaries and lagoons are transition zones playing an important role in transformation of nitrogen and phosphorus flow from rivers into the sea (Wollast, 1983; Seitzinger, 1988; Ogilvie et al., 1997). External nutrient inputs into estuaries and lagoons have increased by 6–50 times for the N load from pristine conditions to present, whereas 18–180 times increase has been observed in the P load (Conley et al., 2000). Received nutrients here rapidly can be incorporated into benthic and pelagic primary producers, grazed by herbivores and rapidly recycled to the water column or they can be retained in surface sediments as buried organic matter or precipitated with other elements (Howarth, 1988; Conley & Malone 1992; Kemp et al., 1992; Cowan & Boynton 1996; Conley et al., 2009).

On the other hand the fraction of derived nutrients can obviously stimulate biogeochemical nutrient and OM cycling; know that at higher concentrations, NO_3^- diffuse downward to sediments and serve as electron acceptor during denitrification or being reduced to NO_2^- with positive effect to anammox activity (Trimmer et al., 2000; Dong et al., 2000; Mayer et al., 2001; Rysgaard, 2004).

Salinity. Conventionally that in estuarine environment along salinity gradient is common use to approximate process occurring in ecosystem level (Boynton & Kemp, 1985; Trimmer et al., 1998; Rysgaard et al., 1999). From biogeochemical point of view sediment becomes more complexly and it role in ecosystem functioning is changing along salinity gradient (Boynton & Kemp, 1985). It is broadly recognized that salinity factor has potential to control nutrient flux and cycling in sediment (Gardner et al., 1991; Gunnars & Blomqvist, 1997; Rysgaard et al., 1999; Rich et al., 2008).

In estuarine environment fluctuating salinity seems affect ion exchange capacity: at higher salinities ion pairing enhance NH_4^+ realise from the sediment, with follow limitation to the nitrifying bacteria (Gardner et al., 1991; Rysgaard et al., 1999). Thereafter was demonstrated that coupled nitrification–denitrification decrease with increasing salinity (Rysgaard et al., 1999). But it could be also explained by salinity inhibitory effect on microorganisms (Rysgaard et al., 1999). Stehr et al. (1995) and Cebron et al. (2003) contribute that salinity is important in controlling abundance of ammonium oxidation bacteria.

Salinity has also indirectly potential to control inorganic phosphate flux (Gunnars & Blomqvist, 1997). In estuarine environment where seawater inflows sulfate concentration is the highest and consequently there sulfate reduction occurs with following terminal production of sulfide (Capone & Kiene, 1988), which can mobilize ferric bounded phosphate due reduction and precipitation of ferric (Gunnars & Blomqvist, 1997).

1.3. Biogeochemistry of estuaries versus freshwater and marine ecosystems

Salinity is main conventional parameter distinguishing freshwater, estuarine and marine systems. From chemical standpoint, an estuarine environment maybe defines as one in which sea marine water is substantially diluted with freshwater entering from watershed. Therefore estuaries and lagoons being at the interface between marine and freshwater environment has both their characteristics which predetermine biogeochemical OM and nutrient cycling. Carbon production, quality and decomposition, and nutrient cycling, as well as removal of nitrogen can be useful to characterize differences between freshwater, estuarine and marine systems (Capone & Kiene, 1988; Seitzinger, 1988) (Fig. 1.3). Therefore comparisons among different ecosystem types can provide additional insights, which are not readily apparent from comparition of similar systems (Seitzinger, 2000).

In all marine, estuarine and freshwater systems large part of autochthonous and allochthonous organic carbon is decomposited in sediments (e.g. Graf, 1982; Kemp et al., 1992; Jørgensen 1996; Grenz et al., 2000). But the sources, quality and quantity of organic matter changes from freshwater to estuarine and marine systems (Capone & Kiene, 1988) (Fig. 1.3). In freshwater systems and particularly in areas with large terrestrial input a greater fraction of organic matter consist of complex structural and refractory polymers with high C/N ratio (Ittekkot & Laane, 1991; Bianchi, 2007). In contrast, in estuarine environments due to lower amount of terrestrial C_{org} delivered by rivers and relative dominance of phytoplankton and microphythobenthos, a high quality organic matter (low C/N ratio) is supplied for OM diagenesis (Underwood & Kromkamp, 1999; Middelburg et al., 2000). In marine systems organic matter is qualitively different: phytoplankton dominated organic carbon is a main source for benthic metabolism (Middelburg et al., 1996; Grenz et al., 2000).

In contrast to continental shelf sediment aerobic mineralization in estuarine sediments takes place in relative thin 0–5 mm surface sediment layer (Dedieu et al., 2007; Denis & Grenz, 2003; Jørgensen et al., 2005; Loshe et al., 1996; Mayer et al., 2001; Rabouille et al., 2003; Rasmussen & Jørgensen, 1992). In eutrophic freshwater systems (e.g. lakes and streams) thickness of oxic layer is comparable to estuarine waters (Jensen et al., 1993; Steaf & de Beer, 2006), however the later are commonly inhabited by microphythobenthos and macrofauna specimens capable to extend the oxic zone by the several millimeters (Lorenzen et al, 1998; Mayer et al., 2001). Relatively thick oxic zone (from several millimeters up centimeters) in marine sediment is primarily determined by lower load of organic carbon, intensive sediment bioirrigation (Glud, 2002; Glud et al., 2003; Jørgensen et al., 2005) and active pore water advection (Cook et al., 2006), therefore volume of marine sediment characterized by aerobic respiration is higher if compared to estuarine and freshwater. While rates of total oxygen uptake in estuarine sediment are relatively higher than thus marine sediment, primarily due to more active organic material deposition to bottom sediments, less extension of advection and bioturbation processes (Rasmussen & Jørgensen, 1992; Mayer et al., 2001; Glud et al., 2003; Rabouille et al., 2003; Jørgensen et al., 2005; Dedieu et al., 2007).

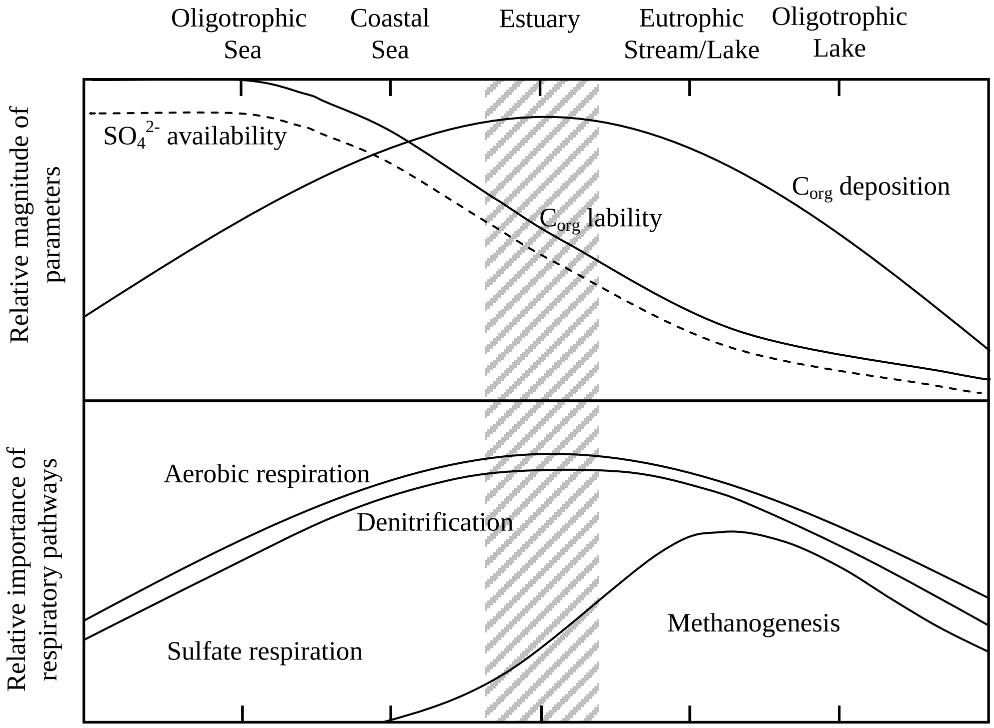


Figure 1.3. Conceptual model of relative importance of respiratory modes in sediments of different aquatic system (below) with relevant characterizing features (top) (redraw from Capone & Kiene, 1988)

In the presence of sea water, sulfate reduction can be dominant carbon oxidation pathway in anoxic sediment and exceed methanogenesis (Capone & Kiene, 1988; Canfield, 1993). The importance of methanogenesis in sediment metabolism increases with decreasing salinity and sulfate concentration. Low concentration of sulfate in freshwater systems is one of important factors determining low rates of sulfate reduction (Capone & Kiene, 1988; Sinke et al., 1992). The relative importance of sulfate reduction in estuarine sediment metabolism is influenced by sulfate transport to the sediment which in combination with the low sulfate concentration in the water column determines the depth of the sulfate reduction zone (Jørgensen & Sørensen, 1985).

Similarly estuaries tend to have greater potential of denitrification comparing to freshwater and coastal marine habitats due the carbon availability and nutrient loading (Seitzinger, 1988; Dong et al., 2009). However a comparison of denitrification in marine, estuarine and freshwater sediments revealed unexpected differences that in estuarine and marine N_2 efflux from sediment may reach up to 50-70% of the total nitrogen flux in estuarine and marine sediment, while N_2 release from freshwater sediments is much more actively (from 75 to 100% of the total nitrogen flux) (Seitzinger, 1988; Rysgaard et al., 1993; Trimmer, 1999). The percentage of nitrogen inputs that are removed by denitrification in estuaries sediments strongly depends on water residence time (Nixon et al., 1996). In estuarine and freshwater ecosystems NO_3^- transported from the overlying water may account for 20–100% of the total NO_3^- needed by denitrification (Rysgaard et al., 1993; Trimmer et al., 1998). In marine habitats NO_3^- concentration in overlaying water is relative less important for denitrification due to thicker oxic zone and longer diffusive path (Rao et al., 2008), and hence denitrification in marine sediments is primarily coupled with nitrification (Laursen & Seizinger, 2002; Rao et al., 2008). However in fluctuating salinity environment like estuaries and lagoons nitrification and it coupling with denitrification can be reduced due ion paring increased NH_4^+ flux to near bottom water.

Higher NO_3^- loading into estuaries with relatively high and stable concentrations of NO_3^- in the water column subsequently supports higher rates of anaerobic ammonium oxidation (Rysgaard-Petersen et al., 2005), in comparison to nitrate poor coastal marine environments (Rich et al., 2008; Dong et al., 2009; Nicholls &Trimmer, 2009). The highest anammox contribution accounts up 67% of the net N_2 production in temperate marine sediments of the continental shelf (Thumdrupt & Dalsgaard, 2002), while in estuarine environment anammox contributes in rage from 0 to 30% of net N_2 flux (Rysgaard-Petersen et al., 2003; Trimmer et al., 2003; Hietanen, 2007; Hietanen & Kuoparinen, 2008; Rich et al., 2008; Dong et al., 2009; Nicholls &Trimmer, 2009; Jäntti et al., 2011) and has a minor role in freshwater systems (Zhang et al., 2007).

Sediment capacity to retain nutrient pool also differs across the systems primarily due to water composition. Mobilization of phosphorus from sediments into overlaying oxic water becomes more effective in marine and estuarine environment in comparison to freshwater (Gunnars & Blomqvist, 1997) (Fig. 1.4). The relatively low release rate in freshwater systems suggests that in these systems sediments immobilize a large fraction of P released during decomposition of organic material, while in most marine and brackish systems, essentially all the remineralized P is returned to the water column (Caraco et al., 1990). Mobilization of phosphorus primarily occurs due to lost bound with Fe during its precipitation with H_2S (Gunnars & Blomqvist, 1997).

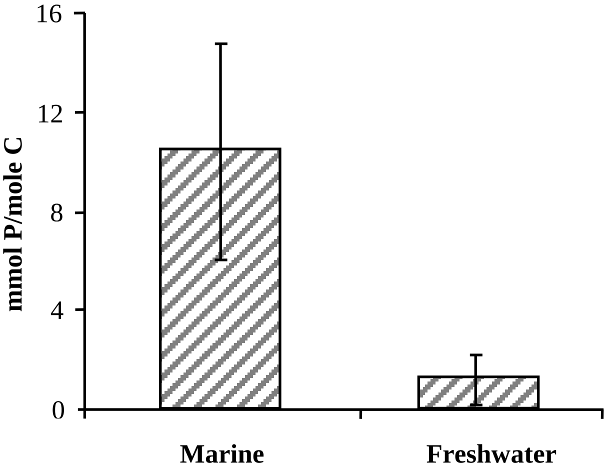


Figure 1.4. Average (with 95% confidence limits) theoretical phosphorus release in sediment of brackish and coastal marine systems (marine) and freshwater systems (freshwater) (redrawn from Caraco et al. 1990).

1.4. Methodological approaches in the biogeochemistry of estuarine sediment

Organic matter, nutrient loading and self ecosystem regulation to prevent eutrophication processes, rates of benthic metabolism and sedimentary nutrient pool is conventionally studied from non–tidal to intertidal coastal systems like estuaries, fjords and shallow bays (Rasmussen & Jørgensen, 1992; Nedwell & Trimmer, 1996; Cabriba & Brotas, 2000; Dong et al., 2000; Sundbäck et al., 2000; Meyer et al., 2001; Magalhães et al., 2002; Rysgaard-Petersen, 2003; Sundbäck et al., 2004; Sundbäck et al., 2006).

Benthic flux measurements. Measurements of benthic oxygen and nutrient exchange across the sediment–water interface can be used as a net measure of organic matter decomposition pathways, benthic production and nutrient cycling occurring in the sediment, assuming steady state condition (Boynton & Kemp, 1985; Banta et al., 1999; Hammond et al., 1999; Meyer et al., 2001; Eyre & Ferguson, 2002; Sundbäck et al., 2000, 2006; Ferguson et al., 2007).

The most straightforward method to measure respiration is the total sediment oxygen uptake (TOU) method. Here the initial O_2 decrease rate of an overlying well–mixed water phase is approximately linear, and the TOU is calculated, accounting for the enclosed area and the water volume (Fig. 1.5) (Glud, 2008). If measured in dark, TOU is yield respiration of benthic community, which includes organic matter mineralization, reoxidation of reduced metabolic products, respiration of microphythobenthos and macrofauna. Hence approximation of TOU rates to early diagenesis of carbon follows the assumption that production and oxidation of reduced solutes from anaerobic degradation are at steady state and respiration of microphythobenthos and macrofauna is minor (Glud, 2008; Glud et al., 2002). Simultaneously measuring oxygen exchange at the sediment–water interface at illumination is possible get estimation of benthic gross net production (e.g. Eyre & Ferguson, 2002; Sundbäck et al., 2000).

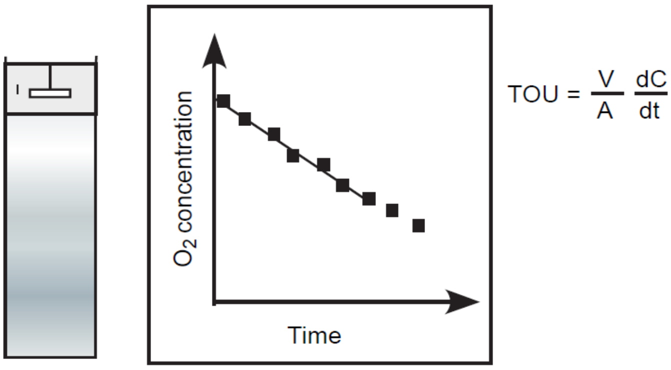


Figure 1. 5. The most common procedure for quantifying benthic O_2 exchange rates is an enclosed sediment core and the discrete recordings of an O_2 sensor inserted into the well-mixed overlying water phase. The TOU is calculated from the area of the enclosed sediment (A) and the volume of the enclosed water (V) and the rate by which O_2 is consumed (from Glud, 2008).

Dissolved inorganic carbon (DIC) is the ultimate product of organic matter oxidation in aerobic and anaerobic pathways (Hulth et al., 1997). The ratio between simultaneously determined TCO_2 and O_2 exchange rates can provide information on extent of production and oxidation of reduced species from anaerobic mineralization at steady state conditions (Ferguson et al., 2007; Therkildsen & Lomstein, 1993). Converting O_2 exchange rates into carbon oxidation rates the TCO_2/O_2 exchange ratio is typically assumed to be in range between 0.8 and 1.2, though can fluctuate temporally (Therkildsen & Lomstein 1993; Hammond et al., 1996; Roden & Wetzel 1996).

Measured nutrient flux and its stoichiometric ratio with TOU can be useful for determining cycling pathways e.g. nitrification and denitrification (Boynton & Kemp, 1985; Cowan & Boynton, 1996). Ratio of nutrient fluxes in light and dark together with benthic oxygen flux can be also used to quantify autotrophic/heterotrophic assimilation of nutrients (Sundbäck & Miles, 2000; Ferguson et al., 2007). However, interpretation of dissolved inorganic phosphorus and silicate flux is complicated due to their adsorption/desorption processes; for instance only small amount of remineralizated phosphorus can be realise to water column (Jensen et al., 1995).

Incubation setup to measure benthic fluxes at the sediment–water interface using intact cores vary widely according to the size of transparent Pexiglass® tubes (24–65 cm long and 5.2–15 cm diameter) (Dalsgaard et al., 2000; Nielsen et al., 2001; Nedwell & Trimmer, 1996; Magalhães et al., 2002; Sundbäck et al., 2000), sediment height in cores (6-20 cm), number of incubated cores (3-5 replicates) (Dalsgaard et al., 2000; Magalhães et al., 2002; Nedwell & Trimmer, 1996; Sundbäck et al., 2000), sampling design (intial-end or time series) (Sundbäck et al., 2000; Nielsen et al., 2001; Magalhães et al., 2002; Nedwell & Trimmer, 1996), incubation time (from 1 to 21 h depending on the season) (Sundbäck et al., 2000; Magalhães et al., 2002) and dark–light regime (Sundbäck et al., 2000; Nielsen et al., 2001). To prevent water stratification cores are always stirred during incubations.

In situ measurements with benthic chambers (Hall et al., 1989) and sediment profiling with microelectrodes (Rasmussen & Jørgensen, 1992; Rabouille et al., 2003) are alternatively used to laboratory core incubations. Recent studies demonstrated higher TOU rates measured *in situ* than in the laboratory incubations due to fluctuation of environmental conditions and exclusion of larger fauna in relatively small sediment cores (Glud et al., 1994; Nielsen & Glud, 1996; Glud et al., 2003).

Porewater profiling. Microprofiles and profiles are commonly used for identification of vertical stratification of the biogeochemical process and quantification of their rates and nutrient stocks within the sediment (Rebsvech, 1989; Jensen et al., 1994; Lorenzen et al., 1998; Meyer et al., 2001; Denis & Grenz, 2003; Rysgaard et al., 2004; Rysgaard-Petersen et al., 2004).

Conventional porewater sampling methods are based on centrifugation (Denis & Grenz, 2003), pressurization (Bartoli et al., 2003; Rysgaard et al., 2004), microprofiling (Rasmussen & Jorgensen, 1992; Jensen et al., 1994; Lorenzen et al., 1998; Glud et al., 2003; Risgaard-Petersen et al., 2004a, c), diffusion samplers and peepers (Mesnage et al., 2007; Bally et al., 2004). Methodologies based on cores slicing and further centrifugation or porewater pressuring lead to coarser resolution (only millimeter scale is possible) and break chemical stratification. During the last decades O_2, N_2O, NH_4^+ microsensors and NO_2^-/NO_3^- biosensors became widely used tools for accurate porewater measurements without destructive profiling (Binnerup et al., 1992; De Beer et al., 1991; Jensen et al., 1994; Larsen et al., 1997; Lorenzen et al., 1998). Applying diffusion reaction modeling to the profiles it is possible to quantify diagenetic processes such as oxic respiration, denitrification (Berg et al., 1998).

Denitrification measurement technique. To evaluate sediment capacity to remove nitrogen direct N_2 flux measurement, microprofiling with biosensor or isotope pairing techniques are applied (De Beer & Sweert, 1989; Koike & Hatori, 1978; Seitzinger et al., 1980; Nielsen, 1992; Kana et al., 1994). Most of studies during last decades, however, focused on use of isotope paring technique (IPT) (e.g. Nielsen, 1992; Ogilvie et al., 1997; Sundbäck et al., 2000; Trimmer et al., 2003; Tuominen et al., 1998; Rysgaard-Petersen et al., 2003; Jäntti et al., 2011). By applying stable isotope tracers the method allows splitting total denitrification into denitrification from the water column (D_w) and denitrification of nitrate produced within the sediment due to nitrification (D_n). Isotope paring technique is based on $^{15}NO_3^-$ tracer, which is added into overlaying water and diffuses downward into anoxic sediment layer, where denitrification occurs (Fig. 1.6). $^{15}NO_3^-$ mixes with the $^{14}NO_3^-$ in the water column and the upper sediment layer and denitrification (D_{tot}) of this nitrate trace mixture ($^{15}NO_3^-$ and $^{14}NO_3^-$) produces N_2 molecules with possible molecular mass of 28, 29 and 30 according to the tracer isotopic signature of tracer mixture. The concentration of ^{28}N, ^{29}N and ^{30}N is determined by gas chromatography/mass spectrometry (Risgaard-Petersen & Rysgaard, 1995).

In sandy sediments, however, denitrification could be underestimated with IPT due to established thick oxic zone, which increase $^{15}NO_3^-$ diffusion path to anoxic sediments (Cook et al., 2006; Rao et al., 2008). In some cases this could explain low and delayed production of ^{29}N and ^{30}N after addition of $^{15}NO_3^-$ in comparison to high ^{28}N production (Rao et al., 2008). On the other hand, heterogeneous coastal sediments with isolated oxic microzones impedes $^{15}NO_3^-$ diffusion to denitrification sites (Rao et al., 2008), therefore IPT requires a long time after $^{15}NO_3^-$ tracer addition to reach steady state within sediment (Cook et al., 2006).

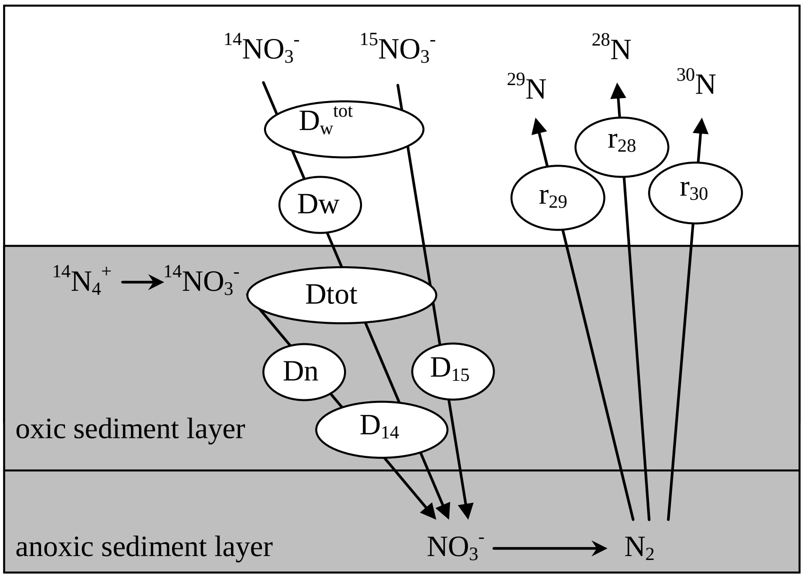


Figure 1.6. Schematic representation of the denitrification during a $^{15}NO_3^-$ *tracer experiment.* Dw^{tot} *- total denitrification of both in situ and labeled nitrate from the water column. Dw - denitrification of nitrate from the water column without tracer addition. Coupled nitrification-denitrification is given as Dn. Dtot refers to the total denitrification rate during the tracer experiment. The specific denitrification rates of* ^{15}N *and* ^{14}N *nitrate are given as* D_{15} *and* D_{14}*, respectively, and the production rates of* N_2 *with masses of 28, 29, and 30 are represented by* r_{28}, r_{29}, *and* r_{30}*, respectively (redraw from Steingruber et al., 2001*).

In contrast to isotope pairing technique, the direct N_2 flux measurement based on N_2:Ar method is independent from adding labeled $^{15}NO_3^-$ and its diffusion path length to denitrification site. N_2 flux gives only net benthic denitrification, the sum of Dw and Dn (Kana et al., 1994). Also net N_2 flux is a balance of denitrification and benthic N_2–fixing with assumption on negligible anammox (Ferguson et al., 2007). N_2:Ar method and IPT in muddy sediment gave comparable results, however due instrumental artifact caused by O_2 interference, N_2 production can be overestimated with N_2:Ar method (Eyre et al., 2002). In low-respiration sediments subject to bioturbation, where coupled nitrification–denitrification dominates, IPT greatly underestimated denitrification, compared to N_2:Ar, (Ferguson & Eyre, 2007). Nevertheless N_2:Ar method applied to permeable sandy sediments with non-homogeneous sediment porewater flushing can lead to overestimated net N_2 flux (Cook et al., 2006).

Recent findings of anammox in marine environment (Thamdrup & Dalsgaard, 2002) suggested that nitrogen removal by denitrification in most cases is overestimated with IPT approach, since its central assumptions (i.e. independence between added $^{15}NO_3^-$ and $^{14}N^{14}N$ production and binomial distribution of produced $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ (Risgaard- Petersen et al. 2003) have been violated. Recently Risgaard-Petersen et al. (2003; 2004c) revised isotope pairing technique (r-IPT) and proposed estimation of $^{14}N^{14}N$ production rate using the production rates of $^{14}N^{15}N$ and $^{15}N^{15}N$ pairs in different concentrations and concentration ratios. Additionally, slurries incubation technique (Thamdrupt & Dalsgaard, 2002) based on collecting the sediment layer from 0 to 2 cm depth (Rysgaard et al., 2004; Rich et al., 2008; Dong et al., 2009), where anammox may potentially occur was developed. According to this technique following three treatments are performed: (1) addition of $^{15}NO_3^-$, (2) addition of $^{15}NH_4^+$, (3) addition of $^{15}NH_4^+$and $^{14}NO_3^-$ at different time intervals (0.1–7 days) (Rysgaard et al., 2004; Rich et al., 2008). And the finally $^{14}N^{15}N$ and $^{15}N^{15}N$ abundance and concentrations are analyzed. In contrast to r-IPT technique in slurries incubations, a new methodological approach based on ^{15}N-labelling of N_2O allows denitrification and anammox to be quantified in intact sediment cores using techniques similar to those already established in IPT (Trimmer et al., 2006). However this technique is prone to understanding anammox and subsequently overestimating the true N_2 production rate (Trimmer et al., 2006).

2. STUDY AREA

The Curonian Lagoon (Fig. 2.1), with a total surface of 1584 km^2, is the largest lagoon in Europe, situated in the south–eastern part of the Baltic Sea. It is shallow non-tidal (mean depth 3.8 m) water body almost entirely separated from the Baltic Sea by a narrow (0.4 km) strait.

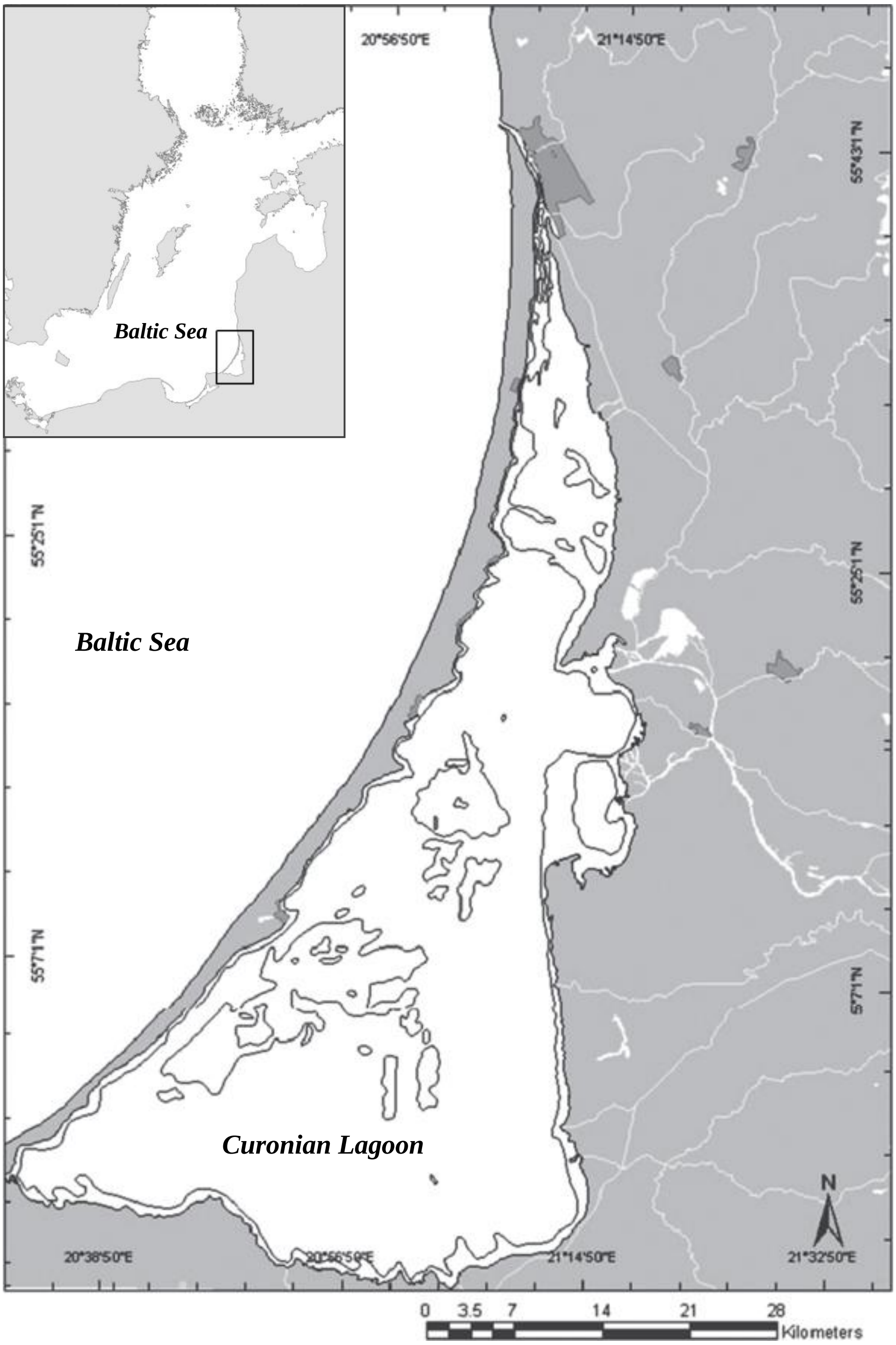


Figure 2.1. Location of the the Curonian lagoon and its physiographic boundaries.

2.1. Hydrological features

From the hydrological point of view, the Curonian lagoon is divided into three principal areas (Ferrarin et al., 2008; Razinkovas et al., 2005): 1) *transitory northern part* with active sea–lagoon water exchange and river runoff; 2) *stagnant or limnic part* characterized by poor water renewal and intensive sedimentation which result in extensive fine sediment bottoms; and 3) *intermediate and complex central part*, directly exposed to the freshwater runoff. Water residence time in the northern part ranges from 10 to 40 days, while in the central and southern parts water renewal takes significantly longer – over 100 days (Fig. 2.2) (Ferrarin et al., 2008).

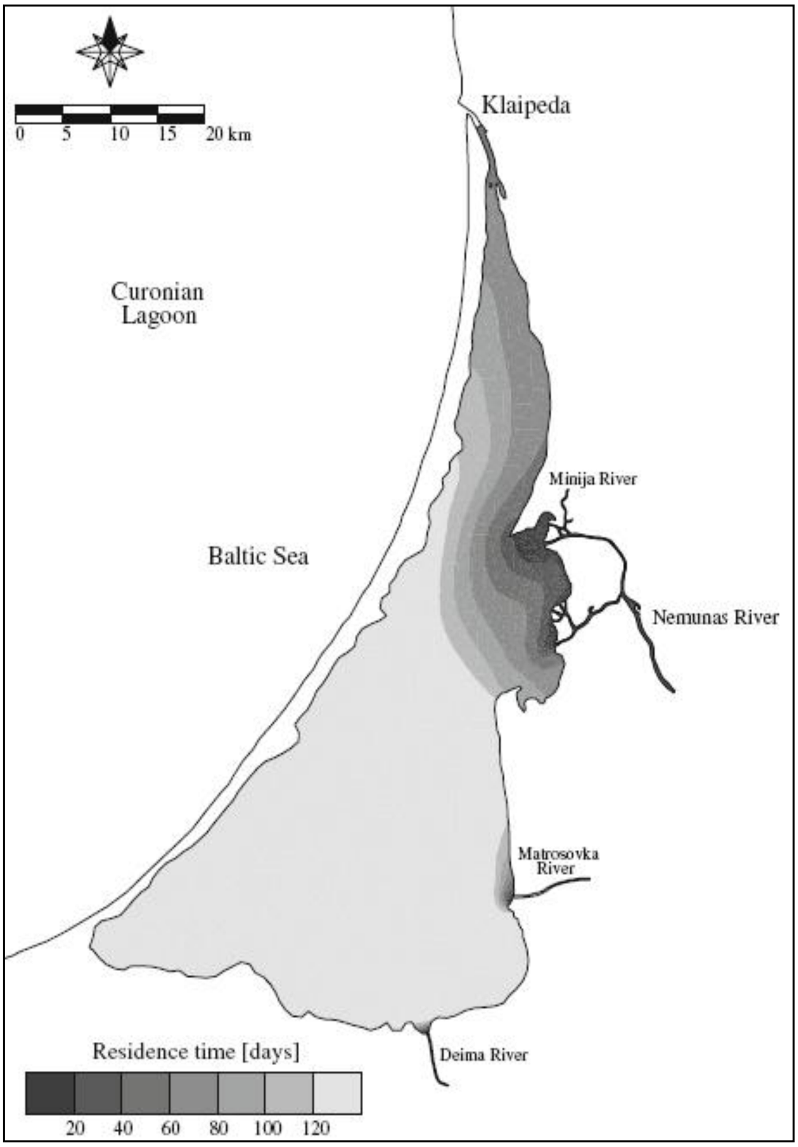


Figure 2.2. Modeled average residence time of the Curonian Lagoon (Ferrarin et al. 2008).

Due to high dominance of river runoff in the lagoon water balance, this system is mainly fresh water. Nemunas River discharge makes up to 90% of the total riverine runoff (22.1 km^3 year^{-1}) contributing approx.

77% to the lagoon water balance (Gailiušis et al., 2005; Razinkovas et al., 2008), whereas inflows from the Baltic Sea and precipitation have considerably lower inputs to the lagoon (18.7 and 4.4% respectively) (Gailiušis et al., 2005). Typically seawater inflows take place on about 29% days per year in the northern part of the lagoon (Dailidienė & Davulienė, 2008).

In 2009 freshwater input to the lagoon exhibited a strong seasonal pattern with two peaks during snowmelt and flood season in March–April and during intensive precipitation in November–December (Fig. 2.3). Riverine input into the lagoon was the lowest during January and May–October.

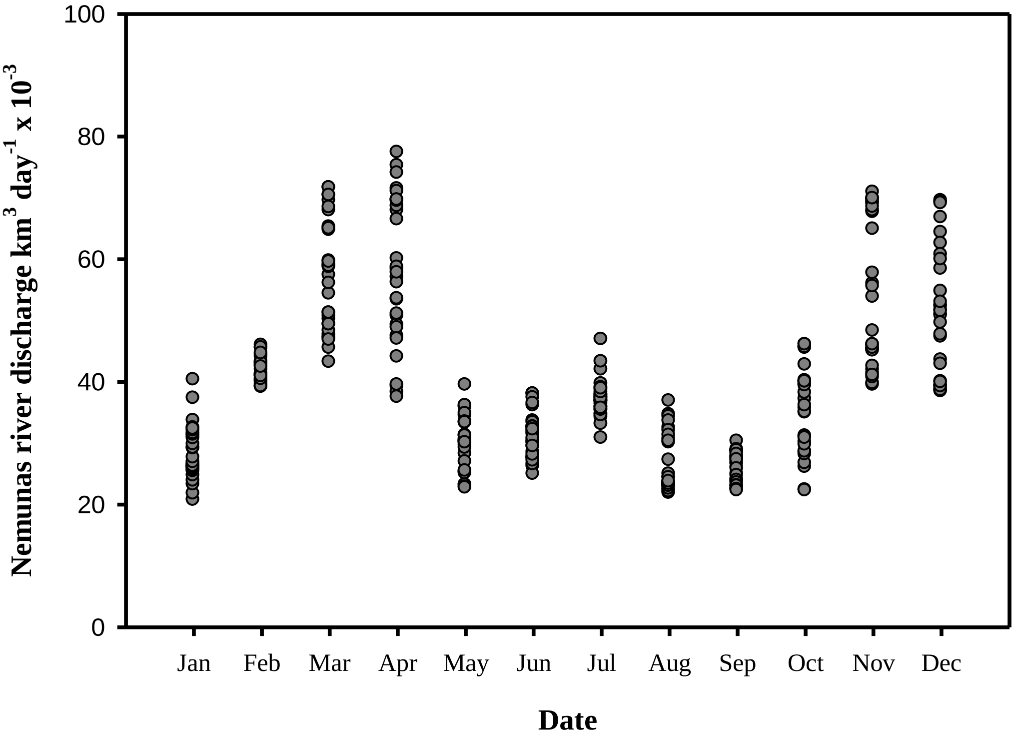


Figure 2.3. Average daily discharge of Nemunas River in 2009 (LHMT, 2009).

2.2. Water column characteristics

<u>Salinity</u>. Due to restricted exchange with the Baltic Sea and dominance of the river runoff, salinity fluctuations in range from freshwater up to 8‰ are limited to the northern part of the lagoon (Dailidienė & Davulienė, 2007). Seawater intrusions can rarely reach the central part of lagoon (Dailidienė & Davulienė 2007; Jurevičius, 1956) (Fig. 2.4), therefore annual salinity average varies from 2.6‰ at the entrance to the sea down to 1.2‰ in the northern part and less than 0.1‰ in the central part (Dailidienė & Davulienė, 2007; Jurgėlenaitė & Šarauskienė, 2007). Seasonal salinity variations depend on regional climate, affecting river discharge and wind driven brackish water inflows from the Baltic Sea (Daunys, 2001; Dailidienė & Davulienė, 2007, 2008).

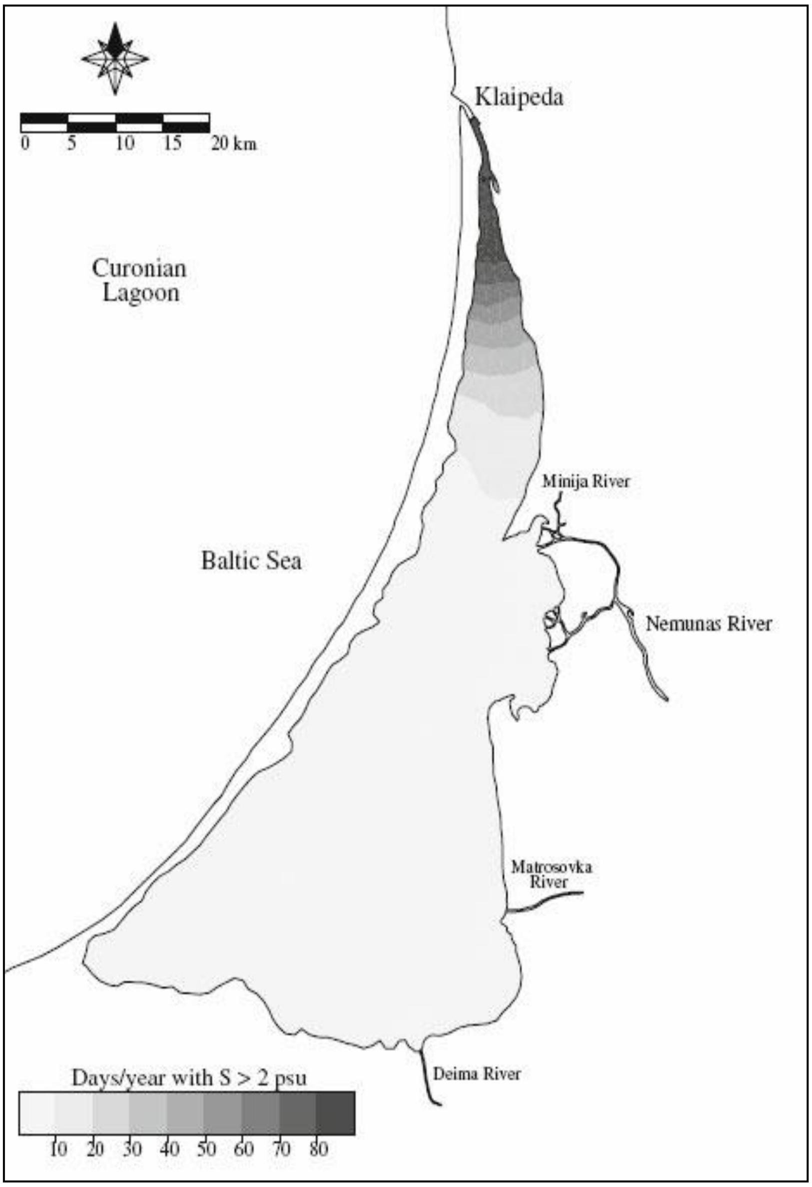


Figure 2.4. Simulated average number of days per year with salinity higher than 2 psu, (Ferrarin et al. 2008).

Temperature. Water temperature dynamics is typical for shallow temperate water bodies, with annual amplitude from 0.1 up to 25–29°C (Žaromskis, 1996). Due to wind effects and shallow nature of the lagoon, temperature stratification of the water column is weak and unstable. Occasionally temperature of the near-bottom water layer is 1–2 °C lower than in the surface layers (Pustelnikovas, 1998). The Klaipeda strait is always ice free, while in the rest of the lagoon ice cover is present for 110 days on average.

Dissolved oxygen. Dissolved oxygen saturation of the water column fluctuates spatially and temporally (both diurnally and seasonally) (Jurevičius, 1959) and generally varies between 20 and 115% (Pilkaitytė, 2003). Oxygen concentrations decrease during the ice cover period as well as during calm weather days in summer, when elevated water temperatures and intensive microalgae vegetation facilitate the transient establishment of hypoxia or anoxia particularly during night hours (Jurevičius, 1959; MRC, 2006; Zilius, unpublished data). Although widely recognized, the later phenomena of hypoxic-anoxic conditions in summer period are relatively poorly supported by empirical data.

Nutrients. Nutrient dynamics is typical for temperate and boreal transitional waters with strong riverine inputs (Gasiunaite, 2000). In spite of agriculture collapse in 1991 and subsequently decreased ammonium and phosphate loads by Nemunas River, nitrate concentrations remained elevated and agriculture in the catchment area and municipal sewage remained the main nutrient sources for the Curonian lagoon (Sileika et al., 2006; Šileika & Gaigalis, 2006). Moreover, during vegetation period N_2–fixing cyanobacteria can contribute up to 43% of nitrogen brought by river runoff (Langas et al., 2010).

Seasonal nutrient variation in the lagoon is mainly associated with the river runoff, microalgae vegetation periods, nutrient remineralization and sediment resuspension (Razinkovas & Pilkaitytė, 2002; Zilius, unpublished). Due to intensive runoff high amounts of nitrogen, phosphate and silica are delivered to the lagoon from the catchment area in spring, however concentrations of these nutrients rapidly decrease during diatom vegetation period (Razinkovas & Pilkaityte, 2002). In summer, nutrient stocks in the water column are gradually recovering most likely due to organic matter mineralization (Razinkovas & Pilkaitytė, 2002). Wave induced sediment resuspension may additionally contribute to the water column nutrient pool by mixing surface sediment and transferring large part of nutrients from porewater to the water column (Zilius, unpublished).

Water chlorophyll a. The lagoon is characterized as a hypereutrophic system, with repeated diatom and cyanobacteria blooms (Pilkaityte, 2003). Diatom blooms start early in spring and are gradually replaced by cyanobacteria (primary diazotrophic *Aphanizomenon flos-aquae*) in summer (Olenina, 1998). Cyanobacteria blooms are typically extended till late autumn (Olenina, 1998; Pilkaitytė & Razinkovas, 2007).

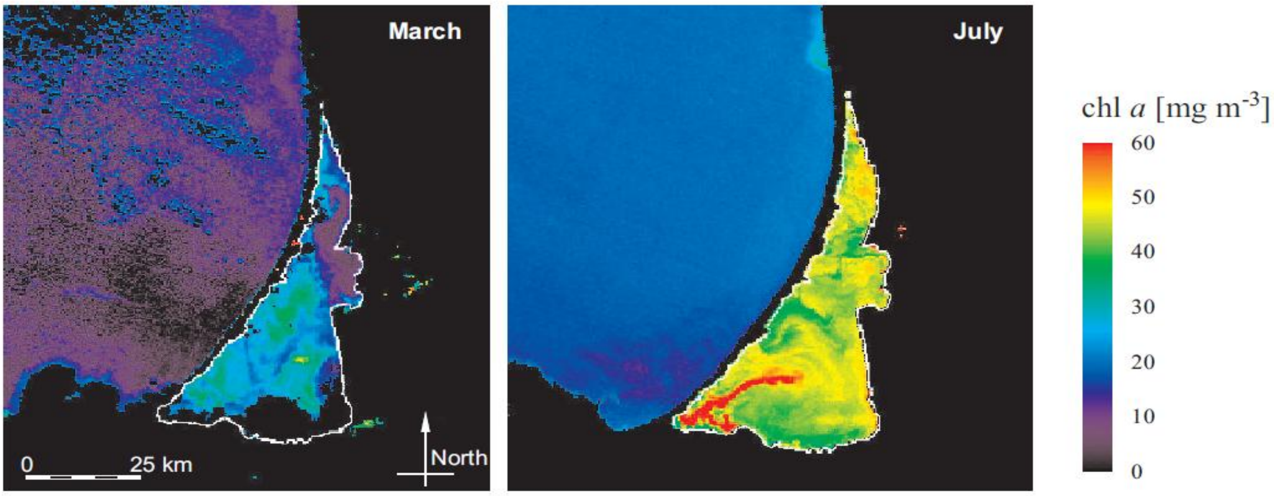


Figure 2.5. Distribution of chlorophyll a in the Curonian Lagoon according to MERIS data from March and July in 2009 (modified from Gardino et al., 2010).

During summer vegetation period phytoplankton biomass is the highest and chlorophyll *a* concentrations can exceed 100 µg l^{-1} (Olenina, 1998; Pilkaitytė, 2003; Krevs et al., 2007). Average chlorophyll *a* concentration positively correlates with the total phosphorus concentration and is negatively related to the nitrogen and phosphorus ratio (Langas et al., 2010). Large scale distribution of phytoplankton in surface waters is mainly determined by lagoons circulation system and the highest concentrations are typically found in active sedimentation zones along western–south sector (Fig. 2.5) (Gardino et al., 2010).

2.3. Sedimentary environment

Bottom sediments. Grain size composition is a major criterion characterizing the Curonian lagoon sediments (Pustelnikovas & Gulbinskas, 2002). Distribution of grain size fractions in the sediment is determined by hydrodynamic factors and accumulation of thin dispersed autochthonous and allochthonous material from water column (Pustelnikovas, 1998). Sediments include a broad spectrum of sands, silts and clay (Trimonis & Gulbinskas, 2003), however fine sand is the most widespread and dominant fraction in the northern and central parts of the Curonian lagoon (Fig. 2.6). In the western part fine sand is separated from the coast by belt of medium sand or silty sediments (Trimonis & Gulbinskas, 2003). Distribution of fine silty mud is restricted to the main sedimentation zones, situated in the frontal area of the Nemunas River delta, relatively deep sheltered bays along the Curonian spit (*e.g.* Nagliu Bay) and open southern part.

Bottom areas in the central part of the lagoon are predominantly covered by shell deposits (more than 50% sediment volume) and predominated by *Dreissena polymorpha* (Trimonis & Gulbinskas, 2003; Zaiko et al., 2009) (Fig. 2.6).

Sediment organic and nutrient content. Distribution of organic carbon is tightly linked to the sediment type; the highest organic carbon content sediment exceeding 10% dry weight is recoreded in areas of active sedimentation (Pustelnikovas et al., 1983; Pustelnikovas, 1998; Galkus, 2004), whereas considerably lower values (0.5-0.8% of dry weight) are typical for transitional environments dominated by sandy sediment.

The distribution of $CaCO_3$ follows similar patterns as organic carbon and its amount in fine sand and silty mud differ at least by order of magnitude (from 1.3% to 32% respectively) (Pustelnikovas, 1998).

The highest nutrient content in porewater is observed in depositional environments associated with organic rich muddy sediments (Pustelnikovas, 1998).

Benthic communities. Bottom sediments of the Curonian Lagoon are mainly dominated by freshwater macrofauna species characterized by higher species diversity and relatively large biomass (Daunys 2001; Zettler & Daunys, 2007). Salinity is the main factor predetermining benthic species composition and distribution of marine species in the lagoon (Daunys, 2001).

In the northern part of the lagoon sediments are inhabited by oligochaetes, chironomids and the invasive polichaete communities (Daunys, 2001), while the remaining central and southern parts are mostly colonized by community of chironomids and oligochaetes. In the central part of the lagoon occurrence of chironomids–

oligochaetes is overlaid with colonies of suspension feeders *Dreisena polymorpha* (Daunys, 2001; Zaiko, 2009).

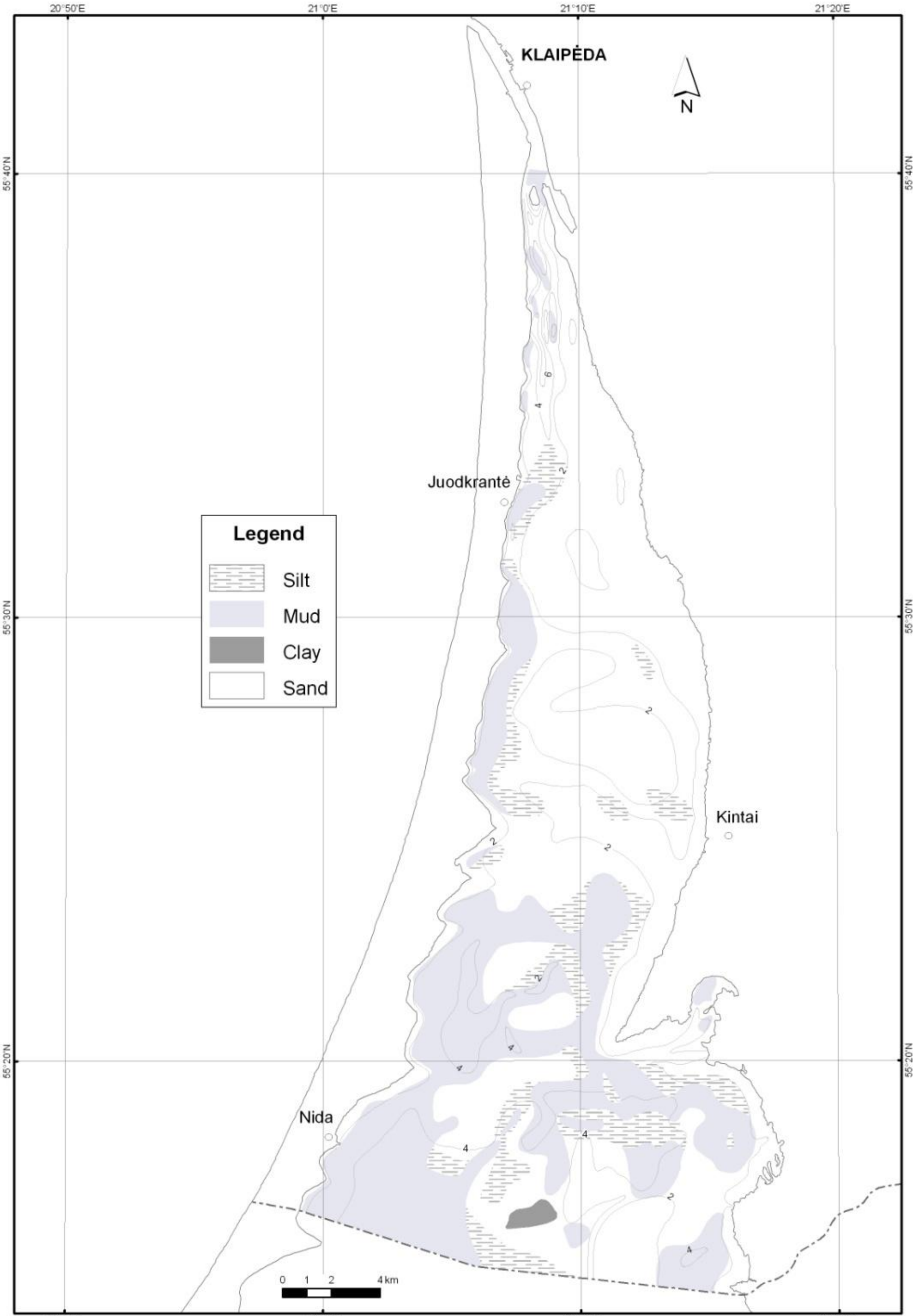


Figure 2.6. Distribution of main sediment types in the Curonian Lagoon.

Generally sediments are poorly bioturbated by large macrofauna since the dominant community consists of oligochaetes and chironomids that exhibit relatively low burrowing activities down to 10-14 cm (Daunys, 2001). Patchy distributed polychaetes *Nereis diversicolor* and *Marenzelleria neglecta* may significantly extend bioturbated sediment layer down to 20-25 cm depth and even at low polychaete densities the total volume of reworked sediment can increase 2-4 times in depths of ~5-10 cm below the sediment surface (Daunys, 2001).

Freshwater macro- and microphybenthos mainly prevails in the shallow eastern part of the Curonian lagoon, where Nemunas River outflow dominates (Plokštienė, 2002; Vaikutienė, 2004; Kasperovičiene & Vaikutienė, 2007). However their distribution is limited due to the high light attenuation predetermined by phytoplankton, hydrodinamical patterns and sediment resuspension (Minkevičius & Pipinys, 1978; Vaikutienė, 2004).

2. Sedimentation features

Main source of sedimentation matter is thin suspended particulate matter originating from local biological production, riverine input and sediment resuspension, whereas other sources such as atmospheric input or terrigenous sources play minor role in the overall budget (Galkus & Jokšas, 1997; Jokšas et al. 1998) (Fig. 2.7). The estimated C/N and stable isotope ratios in suspended particulate organic matter (POM) suggest that the largest proportion of suspended particulate organic matter comes from primary production (Lesutienė, 2009), which strongly depends on season (Jokšas et al., 1998; Lesutienė, 2009). Autochthonous particulate organic matter contributes from 10 to 25% to the total suspended particulate matter in spring and summer respectively, while in autumn this amount is decreasing and reaches the lowest values in winter (Jokšas et al., 1998).

Measurements of phytoplankton primary production indicated, that during bloom periods phytoplankton community in the Curonian lagoon produces from 1.22 to 2.11 million tons of organic matter per year, from 1.1 to 2.0% of the total annual phytoplankton production in the Baltic Sea (Александров, 2003). Thus major source is phytoplankton, which contributes two thirds of the total POM (69%) in the Curonian lagoon (Fig. 2.7). However, only minor part of phytoplankton organic matter is transferred to the higher trophic levels due high bioproduction and respiration ratio in the water column and low phytoplankton grazing capacity (Razinkovas & Gasiūnaitė, 1999; Александров, 2003; Krevs et al., 2007). Hence a large amount of phytoplankton organic matter tends to settle down to the surface sediment. Approximately 74% of phytoplankton production and received both autochthonous and allochthonous POM accumulates in Curonian lagoon during sedimentation. The remaining 26% of total POM (it includes 29% of both riverine and lagoon autochthonous POM) outflow to the sea. Interestingly, that most allochthonous detritus (89%) tends accumulate in the lagoon.

POM transport and accumulation in the Curonian lagoon is predetermined by combined effect of hydrodynamics and bottom topography. Considering to hydrodynamic conditions, the northern part of the lagoon is a transitory zone for POM transport (Pustelnikovas & Gulbinskas, 2002), while the western-south parts are distinguished by long residence time and current circulation scheme supporting POM accumulation.

Suspension feeder *Dreissena polymorpha* may also enhance deposition by 10-30% of the total riverine particulate matter inputs (Daunys et al., 2006).

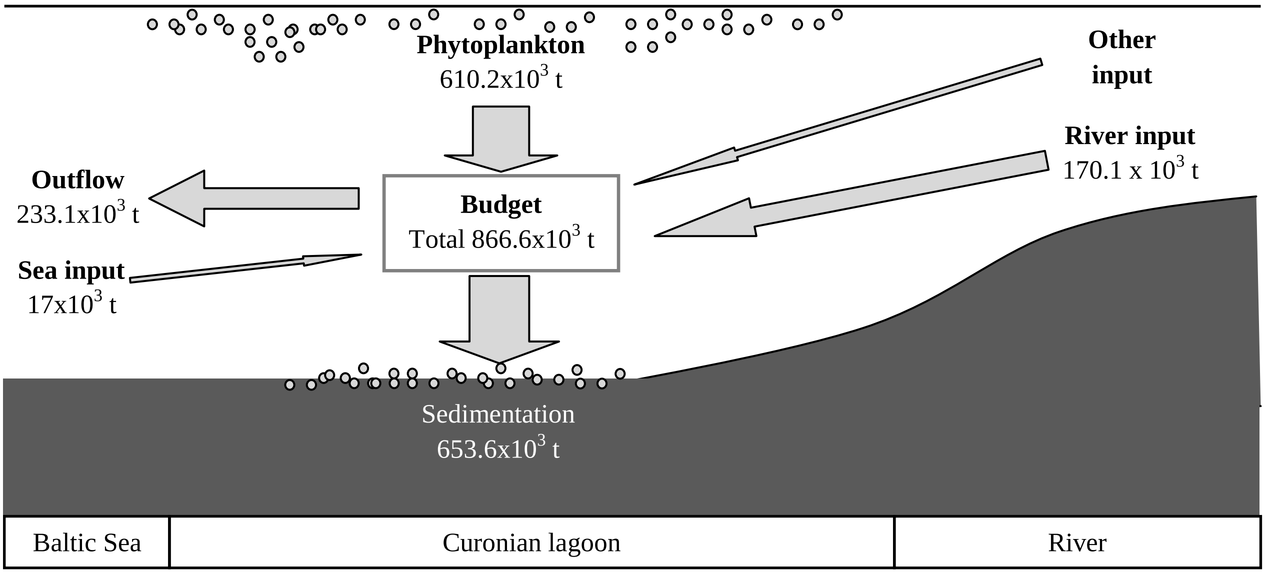


Figure 2.7. Annual total particulate organic matter (TPOM) budget for the Curonian lagoon. Data summarized from Galkus & Jokšas (1997) and Jokšas et al. (1998).

Recently Mažeika et al. (2008) showed that an average sedimentation rate vary from 9.5 to 12.4 mm year^{-1} in the deeper muddy areas. According to the seasonal origin of suspended matterial Jokšas et al. (1998) identified that s accumulation type in spring is present terrigenous, during summer–autumn period dominates biogenous and in winter again – terrigenous. During vegetation period sedimentation of phytoplankton bloom-derived organic material to the bottom is the major pathway of nutrient burial and sediment organic enrichment (Jokšas et al., 1998; Galkus, 2004).

3. Material and Methods

3.1. Sampling sites

This study is quantitatively evaluating oxygen and nutrient exchange processes at the sediment–water interface by means of field measurements and core incubations. In order to simplify the overall complexity of the Curonian lagoon, three principal sedimentary environments were distinguished according to hydrodynamic, depths and particle sorting (Pustelnikovas & Gulbinskas, 2002; Ferrarin et al., 2008): the littoral sand, the open lagoon muddy sand and the open lagoon mud (Fig. 3.1).

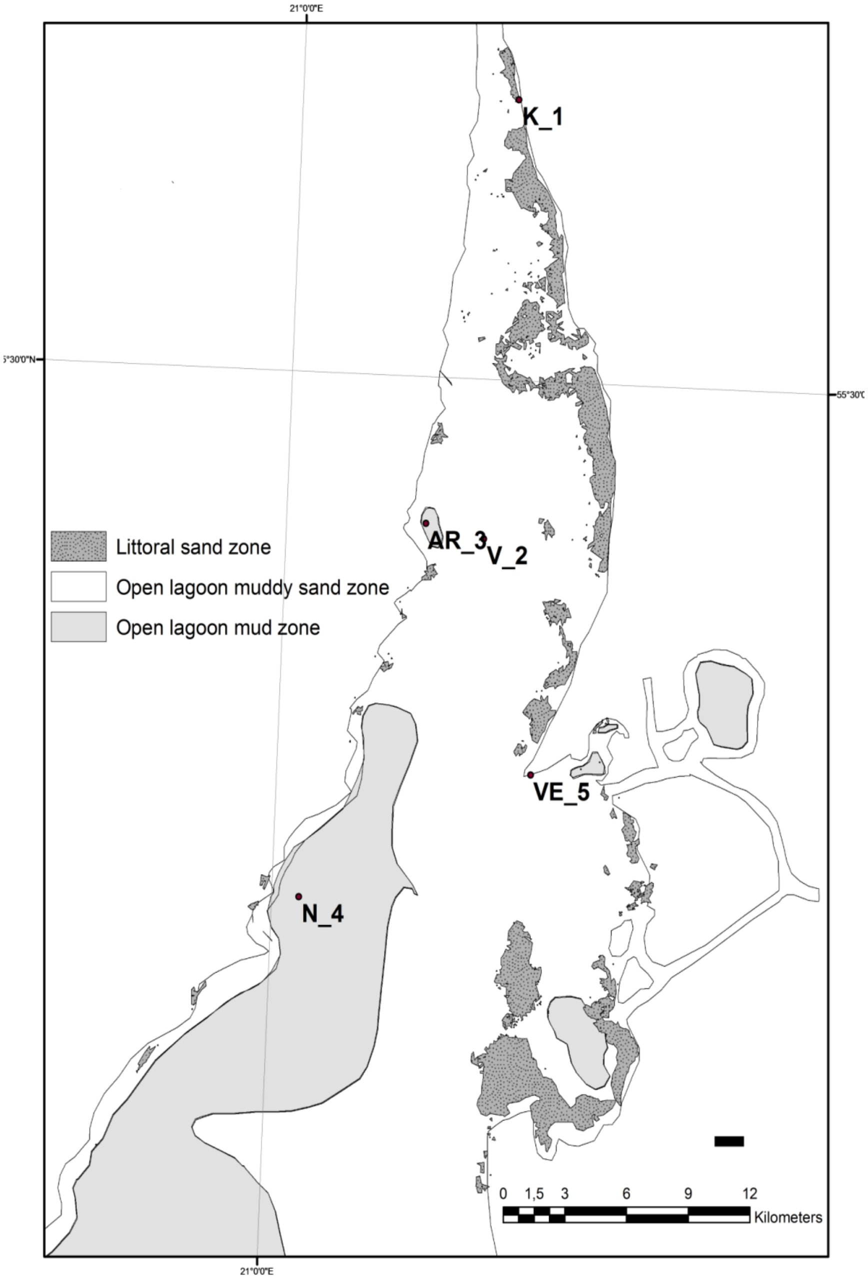


Fig. 3.1. Location of sampling sites in the Curonian Lagoon (southeastern Baltic Sea).

Littoral sand zone is shallowest environment, most likely favourable for benthic primary producers (*e.g.* microphythobenthos).

Relative deeper open lagoon muddy sand area covers the largest part of lagoon and is characterized by relatively low water residence time (<40 day on average), shallow depth (mean depth 1.7 m) and high bottom shear stress (Ferrarin et al., 2008, Razinkovas pers. com.), which prevent effective accumulation of organic material. During calm weather conditions, however flocculent layer of freshly deposited phytoplankton can develop on surface sediment. Benthic productivity is likely limited (Razinkovas & Pilkaityte, 2002) due to high turbidity and low light availability at the sediment surface during vegetation period.

Open lagoon mud zone is relatively deep (2.5-3.5m), therefore during bloom periods sediments are enriched by intensive inputs of fresh labile organic matter, which makes sediments fluffy structure.

All measurements in the Curonian Lagoon were performed during 2009 in March (after ice melt), May, July and October at 5 sites: sites LitS_1N and LitS_5S (littoral sand), site OLms_2 (open lagoon muddy sand) and sites ShM_3 and ExpM_4 (open lagoon mud) (Fig. 3.1, Table 3.1).

Table 3.1. Main characteristics of sampling sites and areal extent of corresponding sediments in the Curonian Lagoon.

Sedimentary environment	**Littoral sand zone**		**Open lagoon muddy sand**	**Open lagoon mud**	
Relative area in the lagoon (%)	<1		~54	~44	
Study site	LitS_1N	LitS_5S	OLms_2	ShM_3	ExpM_4
Water depth (m)	1	1	1.7	2.5	3.5

3.2. Measurement of water column characteristics

In every sampling occasion water column temperature, conductivity and oxygen concentration were measured *in situ* at each station and on every sampling occasion by means of an YSI 460 multiple probe while chlorophyll a concentrations were measured by a FluoroProbe II. The later device was also used to differentiate 'spectral groups' of cyanobacteria, green algae, cryptophytes, diatoms and dinoflagellates according to their distinctive accessory pigments (Beutler et al., 2002).

Water samples were collected near the water–sediment interface with a Ruttner bottle, immediately filtered through GF/C filters (pore diameter 0.45 μm) and transferred to plastic vials; they were then frozen at -20^{o}C for later nutrient analyses in the laboratory. Water samples for soluble reactive phosphorus determination were filtered, transferred into 10 ml glass tubes and analyzed within 12 hours.

3.3. Sediment core sampling and maintenance

During each sampling occasion 14–16 intact sediment cores were collected at each station by hand corer and approximately 80 l of water per station were collected for core maintenance during transportation, pre-incubation and incubation periods. Ten cores (i.d. 8 cm, height 30 cm) were collected for determination of total dark–light oxygen and nutrient fluxes at the sediment–water interface and denitrification measurements. Three smaller cores (i.d. 4.6 cm, height 25 cm) were collected for oxygen microprofiling and sediment characterization. Additionally, 1–3 cores (i.d. 8 cm, height 30 cm) per site were sampled for extraction pore water. Only cores with visually undisturbed sediments and clear overlaying water were accepted for further treatment. Sediment level of collected cores was adjusted to 20 cm, leaving an overlaying water column of about 10 cm. Within 4 hours of sampling cores were transferred to large laboratory tanks containing *in situ* water at ambient temperature and left overnight.

In the laboratory each of five intact cores for light and dark treatment were placed into the incubation tank with *in situ* water (Fig. 3.1). Rotating teflon-coated magnet was fixed to the inner wall of each core approx. 6 cm above the sediment for gentle water mixing (40 rpm) avoiding sediment resuspension. Water was stirred during the whole pre-incubation and incubation periods. For a more detailed description of employed materials, pre-incubation and incubation techniques see Dalsgaard et al. (2000).

3.4. Total flux oxygen and nutrient measurements at the sediment-water interface

Dark and light oxygen flux rates and exchange of inorganic nutrients (ammonium NH_4^+, a sum of NO_2^- and NO_3^- (denoted as NO_x^-) and soluble reactive phosphorus SRP) between sediment and near bottom water were measured after overnight pre-incubation. The day after sampling, the water inside the incubation cores was replaced with fresh *in situ* water and incubations were started by installing plexiglas lids on the tops of the cores. Water samples were collected from each core in triplicate with plastic 60 ml syringes at the beginning and at the end of incubation. Part of sampled water was transferred into 12 ml glass tubes (Exatainers, Labco, UK) and fixed with reagents for dissolved oxygen analysis, which was carried out within a few hours. GF/C filtered (pore size 0.45 µm) water was transferred into 20 ml plastic vials and frozen at -20°C for later analysis of inorganic nitrogen. Additional 10 ml were transferred into glass tubes for analysis of soluble reactive phosphorus, which was performed within 12 hours.

Incubations in the light were carried out simulating *in situ* irradiance at the sediment–water interface, attenuating the intensity of outside lightning with mesh. Incubation time varied between 3 (May and July) and 5 hours (March and October) and was set to keep oxygen concentration within 20% of initial values. Fluxes were calculated according to the equation (1):

$$F_x = \frac{(C_f - C_i) \times V}{A \times t} \qquad \text{(eq. 1)}$$

where F_x (µmol $m^{-2}h^{-1}$) is the a flux of chemical species x, C_i and C_f (µmol/l) are concentrations of chemical species x at the beginning and at the end of incubation, respectively, V (l) is the water volume in the core, A (m^2) is the surface of the sediment and t (h) is incubation time.

Measured oxygen flux under light conditions represented net primary production (NPP) of benthic microalgae, while gross primary production (GPP) was calculated as NPP minus community respiration

(CR) measured in the dark (Sundbäck et al., 2000). Constant CR under light and dark regime was assumed. Benthic trophic status index (BTSI; Rizzo et al., 1996) was applied by plotting oxygen flux values under light regime against values obtained in the dark regime.

Daily nutrient fluxes (mmol m^{-2} d^{-1}) were calculated in order to evaluate water column nutrient budget, according to equation:

$$\text{net } F_x = (\text{hourly dark flux x } h_D) + (\text{hourly light flux x } h_L) \quad \text{(eq. 2)}$$

where h_D and h_L are the number of dark and light hours during sampling period, respectively.

Figure 3.1. Sediment intact core incubation systems (left) and sediment microprofiling setup (right).

3.5. Denitrification measurement with $^{15}NO_3$ isotope pairing technique

Denitrification measurements in sediment were performed with isotope pairing technique (Nielsen, 1992), which allowed to distinguish denitrification (Dw) supported by overlaying water NO_3^- and denitrification coupled with nitrification (Dn). Standard 15 µM $^{15}NO_3^-$ stock solution (98% of $^{15}KNO_3$, Cambridge Isotope Laboratories, MA, USA) was added to the water column of the same cores used for nutrient flux measurements. The NO_3^- concentration was measured prior to the addition of $^{15}NO_3^-$ and within 15–30 minutes (in July and March respectively) after $^{15}NO_3^-$ addition at the time the cores were closed in order to calculate the $^{14}N/^{15}N$ ratio in the NO_3^- pool. Cores were incubated under dark conditions as described for nutrient flux measurements. At the end of incubations, bacterial activity was stopped by adding 2 ml of $ZnCl_2$ (7M) to the water column; then sediment and water were gently mixed. Part of slurries were transferred to gastight, 12 ml glass vials (Exetainer, Labco, High Wycombe, UK) and fixed with 250 µl 7 M $ZnCl_2$. $^{14}N^{15}N$ and $^{15}N^{15}N$ analysis of samples was carried out in National Environmental Research Center, using gas chromatography column coupled with a triple-collector of isotopic mass ratio spectrometer

(RoboPrep G^+ in line with Tracer-Mass, Europa Scientific, Crewe, UK), as described in Rysgaard et al. (1995).

To isotope pairing technique application was checked by applying concentration and time series gradient experiments, respectively in March and July (Bartoli et al., in prep.).

Production rates of isotope pairs were calculated for combined volume of the water column and porewater (calculated by multiplying the sediment volume by the porosity). Denitrification rates were estimated from the production rates according to Risgaard-Petersen et al. (2003, 2004) in order to avoid overestimation in presence of anammox:

$$p_{14} = 2r_{14}[p^{29}N_2 + p^{30}N_2(1 - r_{14})] \qquad \text{(eq. 3)}$$

where r_{14} is the ratio between $^{14}NO_3^-$ and $^{15}NO_3^-$ in the NO_3^- reduction zone, and $p^{29}N_2$ and $p^{30}N_2$ are the production rate of $^{14}N^{15}N$ and $^{15}N^{15}N$, respectively. The ratio between $^{14}NO_3^-$ and $^{15}NO_3^-$ in the NO_3^- reduction zone (r_{14}) can be estimated from:

$$r_{14} = \frac{(1-ra)\cdot R^{29} - ra}{(2-ra)} \qquad \text{(eq. 4)}$$

where R^{29} is the ratio between $^{14}N^{15}N$ and $^{15}N^{15}N$ production rates, and *ra* is the contribution of anammox to N_2 production. The contribution of anammox to N_2 production (*ra*) in the Curonian lagoon was derived from the slurry incubation experiments (Bartoli et al., in prep.).

3.6. Sediment microprofiling

Oxygen profiles were measured at randomly selected sites within each core by Clark-style microsensors (Unisense, DK), equipped with a guard cathode and an internal reference (Revsbech, 1989). The microelectrodes had a 100 µm diameter sensing tip, 1.5 % stirring sensitivities and a 90% response time of less than 5 s. The sensors were mounted on a manual micromanipulator; the sensor current was measured with a picoamperometer connected to an A/D converter which transferred the signal to computer (Fig. 2.2). Oxygen profiles were measured with a depth resolution of 100 µm. All microprofiles were measured in the laboratory, placing sediment cores in an aquarium containing *in situ* water maintained at ambient oxygen concentration and temperature. A total of 120 oxygen microprofiles were performed in the cores collected in May, July and October.

Linear calibration of microelectrodes was carried out in anoxic sediment layer and near-bottom water by measuring oxygen concentrations using Winkler titration.

3.7. Porewater extraction

Porewater extraction was carried out in the laboratory within 8 hours from sampling. Before slicing the sediment, overlying water was removed down to the lowest possible level above the sediment surface. Then sediment were extruded and sliced in 0.5 cm intervals down to 2 cm sediment depth and 2-3, 3-5 and 5-10 cm layers in deeper sediment. Porewater was obtained by N_2 squeezing of sediment slices (under 2-3 bar pressure) and directly filtered through GF/C filters (pore size 0.45 µm) when collecting into plastic vials. The samples were immediately frozen and stored in -20°C for later analysis.

3.8. Analytical procedures

Both porewater and overlying water samples were analyzed using following methods: 1. dissolved oxygen concentration was measured by Winkler titration (Grashoff, 1983); 2. ammonium nitrogen (NH_4^+) was analyzed by manual salicylate and hypochlorite method using nitroprusiate as catalyst (Bower & Holm-Hansen, 1980); 3. nitrate - nitrite nitrogen (NO_x^-), nitrite (NO_2^-) and soluble reactive phosphorus (SRP) were analyzed by a flow injection analyzer (FIAstar™ 5000, Foss, Denmark) using standard colorimetric methods (Grashoff, 1983); 4. nitrate (NO_3^-) was calculated as a difference between NO_x^- and NO_2^-; dissolved organic carbon (DOC) was analyzed by high temperature (680 °C) combustion catalytic oxidation/NDIR method using Shimadzu TOC 5000 analyzer. Dilution factor of 2-30 was applied for porewater samples.

3.9. Measurements of sediment characteristics

3.9.1 Exchangeable ammonium

In October sediment cores were taken from each of five sites for determination of exchangeable ammonium $NH_4^+{}_{ex}$ ($NH_4^+{}_{adsorbed}$ + $NH_4^+{}_{pore\ water}$). The cores were extruded and sliced in following layers 0-1, 1-2, 2-3, 3-5 cm. Each slice was immediately homogenised and 1 cm³ sample (wet volume) was transferred to sterile flasks containing 20 ml 1M KCl solution. The slurries were vigorously shaken for 1 h and later centrifuged at 3000 rpm for 8 min. Supernatant were GF/C filtered and immediately frozen (-20°C) for later NH_4^+ determination as described above. Production of $NH_4^+{}_{ex}$ calculated according equation (5):

$$\mathrm{NH}_{4\ \mathrm{ex}} = \frac{(\mathrm{C_{slurries}} - \mathrm{C_{KCl}})\ \mathrm{V}}{\mathrm{V_{sediment}}} \qquad \text{(eq. 5)}$$

where $NH_{4\ ex}$ (µmol NH_4^+ cm^{-3}) is production of exchangeable ammonium, $C_{slurries}$ (µM) is concentration of NH_4^+ in slurries after extraction, C_{KCl} (µM) is concentration of NH_4^+ in KCl solution, V (ml) is volume of KCl solution, $V_{sediment}$ (cm³) is volume of added wet sediment.

3.9.2. Sediment chlorophyll *a* and total organic matter

Sediment chlorophyll a (sediment chl *a*) samples were collected in triplicate sediment cores for analysis of fresh labile organic matter and microphythobenthos biomass. 1cm³ of the upper 0–1 cm section of each core was removed and stored frozen into 15 ml centrifuges tubes for later analysis. Chlorophyll *a* was extracted by adding 96% ethanol to sediment samples (Jespersen & Christoffersen, 1972). After 24 h samples were centrifuged and obtained supernatant analyzed spectrophotometrically according to Lorenzen (1967).

Total organic matter content (TOM) was estimated from weight loss after ignition of dried and powdered uppermost 1 cm sediment layer (~1 g) at 430 °C for 3 hours:

$$\mathrm{TOM}(\%\ \text{dry weight}) = \frac{\text{net dry sediment}_{70}(\text{g}) - \text{net dry weight}_{430}\ (\text{g})}{\text{net dry sediment weight}_{70}\ (\text{g})} \times 100 \qquad \text{(eq. 6)}$$

3.9.3. Total nitrogen and phosphorus

Total nitrogen (TN_k) and phosphorus (TP) were determined in 0–2 and 2–5 cm sediments slices taken from small intact cores (i.d. 4.6 cm, length 25 cm). Homogenized slices were immediately sub-sampled for TN_k and TP analysis. Total nitrogen analysis was carried out by Kjeldahl method described in Bremner (1965) using Kjeltec autoanalyzer. TP was measured spectrophotometrically as soluble reactive phosphorus after HCl extraction (Aspila et al., 1976).

3.9.4. Physical properties

All physical sediment characteristics are referred in the upper 0-1cm layer.

Water content. The sediment water content was obtained by the loss of weight during drying to constant weigth at 70°C for 24 hours and calculated as follows:

$$\text{Water content}\ (\%) = \frac{\text{net wet weight (g)} - \text{net dry weight (g)}}{\text{net dry weight (g)}} \times 100 \qquad \text{(eq. 7)}$$

Density. The density of sediment was determined as:

$$\text{Density}\ (\text{cm}^3\text{mg}^{-1}) = \frac{\text{Volume of wet sediment sample}}{\text{Wet weight of sediment sample}} \qquad \text{(eq. 8)}$$

Porosity. Porosity was determined from weight loss of a known wet sediment volume, after drying at 70°C to constant weight for 24 h:

$$\text{Porosity} = \frac{\text{water content}\ (\%) \times \text{wet weight (g)} \times \text{sediment} - \text{dw}}{\text{volume of sediment}\ (\text{cm}^3)} \qquad \text{(eq. 9)}$$

Grain size. A coarser (2.0–0.125 mm) sandy fraction was determined by sieving. Silty fraction (0.125–0.001 mm) was quantified gravimetrically.

3.10. Numerical data analysis

3.10.1. Diffusive oxygen uptake

Diffusive oxygen uptake rates were calculated from the measured oxygen microprofiles assuming zero-order consumption kinetics and homogeneous respiration within the oxic sediment layer (Rasmussen & Jørgensen, 1992) (equation 10). This assumption is particularly valid for sediments where oxygen penetration is less than 1 mm:

$$R_{vol} = D_s d^2C/dz^2 \qquad \text{(eq. 10)}$$

where R_{vol} (µmol $cm^{-3}h^{-1}$) is the volume-specific O_2 consumption rate within sediment; D_S (cm^2s^{-1}) is the diffusion coefficient of oxygen in sediments; C is oxygen concentration (µM); and z (cm) is the depth in sediments. D_S was determined from porosity (φ) using the relationship proposed by Iversen & Jørgensen (1993):

$$D_s = [1 + n(1 - \varphi)]^{-1} D \qquad \text{(eq. 11)}$$

where, *D* is the molecular diffusion coefficient taken from Broecker and Peng (1974) and corrected for temperature with the Stokes-Einstein relation (Li & Gregory, 1974); φ is the average porosity measured in the upper 1 cm sediment layer. Values of the empirical factor *n* were 2 and 3 for sandy and for clayish-silty sediments respectively (Iversen & Jørgensen, 1993). A second order polynomial function was fitted to all oxygen profiles and concentration gradient was calculated according to Nielsen et al. (1990). The total oxygen consumption within the oxic zone was determined per unit area multiplying oxygen consumption rates (per unit volume of sediment) by thickness of the oxic zone (Rasmussen & Jorgensen, 1992).

In March (when profiling was not performed) oxygen penetration depth in sediments (z_{max}) was calculated according to Revsbech et al. (1980) and Rasmussen & Jorgensen (1992):

$$z_{\max} = 2\ \mathrm{C}\ \mathrm{D_s}\varphi/\mathrm{J} \qquad \text{(eq. 12)}$$

where *J* is the flux of oxygen into the sediment measured during core incubations. This equation was applied to oxygen flux data from May, July and October and calculated oxygen penetration varied between 0.2 and 1.07 mm, in agreement with experimentally found oxygen penetration values.

3.10.2. Diffusive nutrient transport

Diffusive fluxes of ammonium, nitrate and nitrite nitrogen and soluble reactive phosphorus at the sediment water-interface were calculated from nutrient profiles in the sediment by applying Fick's first law (Berner, 1983):

$$J=-\phi D_s\ (dC/dx)_{x=0} \qquad \text{(eq. 13)}$$

where *J* (mmol m^{-2} d^{-1}) is diffusive flux of a nutrient species; ϕ is the porosity); D_S (m^{-2} d^{-1}) is the diffusion coefficients of nutrients within sediments, *dC/dx* (mmol cm^{-4}) is nutrient concentration gradient across the sediment-water interface. D_S was determined according to Lerman (1979):

$$Ds=D_w^0/\ \Theta^2 \qquad \text{(eq. 14)}$$

where, D_w^0 is infinitive molecular diffusion coefficients for NH_4^+, $NO_x^-(NO_3^-+NO_2^-)$ and SRP in water taken from Broecker & Peng (1974); Θ^2 is turtosity obtained from the equation (Boudreau, 1996):

$$\Theta^2=1-2\ln\phi \qquad \text{(eq. 15)}$$

D_w^0 coefficients were corrected for temperature with the Stokes-Einstein relation (Li & Gregory, 1974). Diffusive flux was calculated according to the concentration change between the near-bottom and sediment layer, which supports the best linear fit.

3.10.3. Theoretical denitrification model

Prediction of denitrification rates of bottom–water NO_3^- in the anoxic sediments was based on a model developed by Christensen et al. (1990):

$$Dw = \mathrm{F_{O2}} \times 0.8 \times \left[\sqrt{\left(1 + \frac{\mathrm{D(NO_3^-)} \times \mathrm{C_{NO_3^-}}}{\mathrm{D(O_2)} \quad \times \mathrm{C_{O_2}}} \times \frac{1}{0.8}\right)} - 1\right] \qquad \text{(eq. 16)}$$

where *Dw* is the rate of denitrification of NO_3^- from the water column; and F_{O2} is the sediment O_2 uptake rate (taken from total flux measurements). D (NO_3^-) and D (O_2) represent the diffusion coefficients of NO_3^- and O_2, respectively.

3.10.4. Multivariate analysis

Principal component analysis (PCA) was used to define statistically independent groups of water and sediment characteristics in order to reduce the number of environmental variables in the subsequent analysis. Then, redundancy analysis (RDA) was applied in order to determine relationships between environmental characteristics and nutrient fluxes at the sediment–water interface. The significance of each RDA axis was statistically tested by unrestricted Monte Carlo permutations with forward selection.

Two–way analysis of variances (ANOVA) was used to test significance of season, light–dark regime and studied sites (including interaction of two factors) for total O_2, NH_4^+, NO_x^- fluxes for each studied occasion. Homogeneity of variance was checked using Cochran's test ($p<0.001$) and data were transformed if significant heteroscedascity was found. Variance homogeneity could not be reached for SRP dark flux data, therefore general linear model with Generalized Least Squares method was applied to test significance seasons and sites. If significant effects were found, a pair–wise comparison of means was carried with *post hoc* Tukey test. Statistical significance was set at p level lower than $p<0.05$.

Pearson correlation was used to check for relationship between variables. Data normality was assessed using a Kolmogorov-Smirnov goodness-of-fit test. All the analyses were performed and data visualized using Brodgar 2.6.6, STATISTICA 7 and SigmaPlot 11.0 software.

4. RESULTS

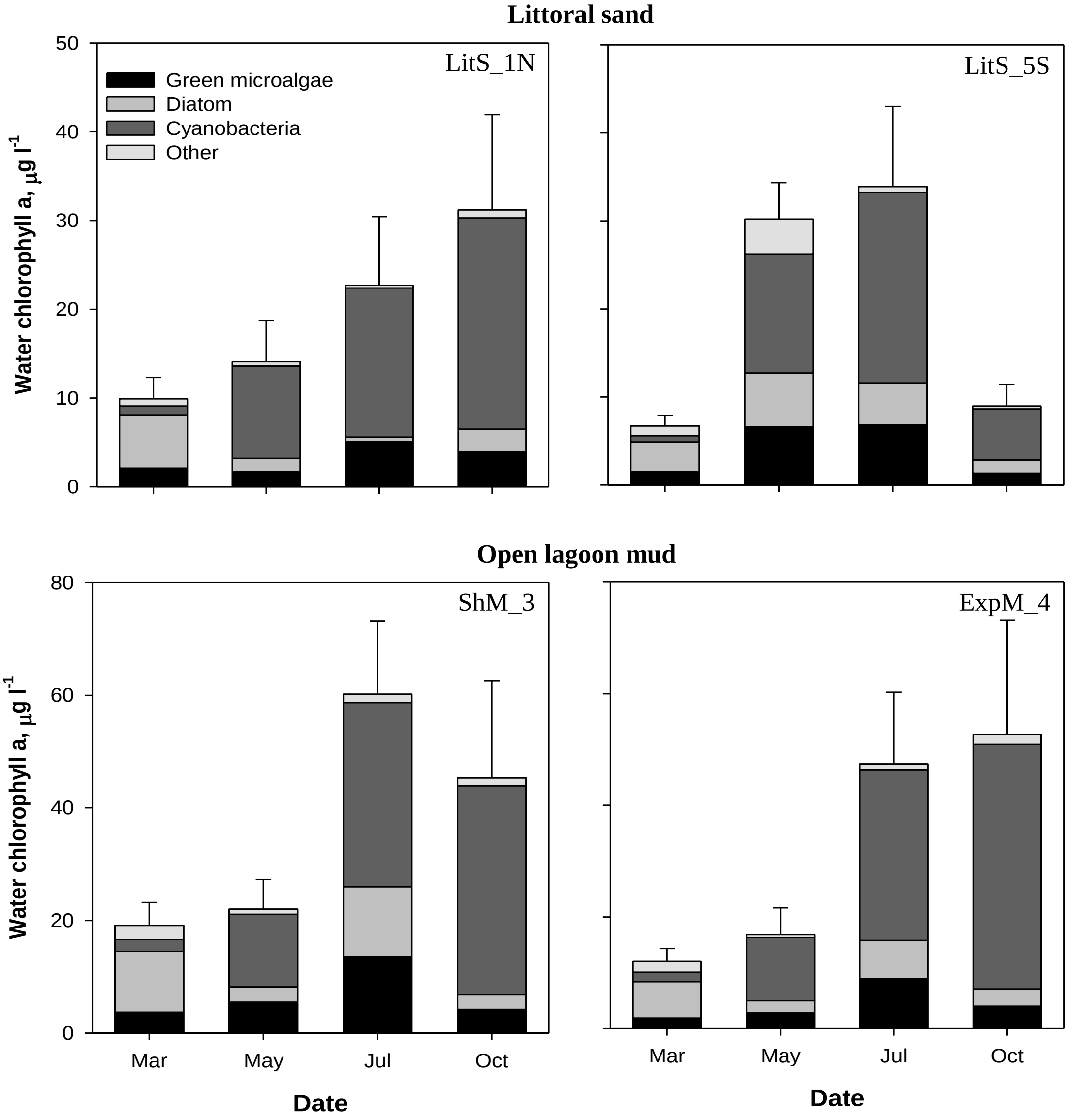
4.1. Water column and sediment characteristics of the studied sites

The Curonian Lagoon was mostly freshwater during sampling occasions, except in the littoral sand zone of site LitS_1N where salinity reached 2‰ in May and October (Table 4.1). Water temperature varied from 2–3 (March) to 18–20°C (July).

Table 4.1. Main water column characteristics of the sampling sites; data refer to average values (± standard deviation) from 3 replicates.

Sedimentary environment	**Littoral sand zone**		**Open lagoon muddy sand**	**Open lagoon mud**	
Study site	LitS_1N	LitS_5S	OLms_2	ShM_2	ExpM_4
Temperature (^{o}C)					
Mar	2	3	2	2	3
May	17	17	17	17	17
Jul	19	19	20	18	18
Oct	9	9	9	8	8
Salinity (‰)					
Mar	0	0	0	0	0
May	2	0	0	0	0
Jul	0	0	0	0	0
Oct	2	0	0	0	0
O_2 (µM)					
Mar	302.2	290.0	293.9	285.6	287.2
May	232.5	229.1	244.9	227.6	212.7
Jul	244.9	253.9	242.5	237.0	232.2
Oct	348.9	391.8	261.6	253.9	246.6
O_2 saturation (%)					
Mar	70	60	68	66	68
May	76	76	81	75	71
Jul	86	89	85	80	79
Oct	91	103	56	69	67
NH_4 (µM)					
Mar	1.9	2.1	3.1	4.5	2
May	5.4	2.2	2.7	3.1	3.9
Jul	4.2	2.2	3.8	2.4	3.9
Oct	7.5	10.4	10.1	13.3	14.5
NO_x^- (µM)					
Mar	87.0	126	72.4	86.5	198.0
May	0.3	1.0	0.7	0.5	2.8
Jul	4.5	4.8	3.8	3.1	3.2
Oct	7.5	60.6	15.7	13.6	13.4
SRP (µM)					
Mar	0.4	0.4	0.5	0.5	1.1
May	0.7	0.4	0.5	0.3	0.3
Jul	0.9	0.1	0.6	0.1	0.5
Oct	0.1	0.4	0.4	0.4	0.3
DIN/SRP					
Mar	222	320	156	182	182
May	8	8	7	12	34
Jul	10	70	8	55	14
Oct	150	178	65	67	93

Water chlorophyll *a* exhibited different patterns at the study sites and generally lower concentrations were observed at the littoral sites than in the open lagoon sites. Cyanobacteria gradually replaced diatoms at all study sites towards the summer and dominated the phytoplankton community till late autumn. Other phytoplankton groups such as green algae and *Cryptophyta* contributed a minor part to the total chlorophyll *a* during the study period. Chlorophyll *a* concentrations varied between 7 and 21 µg l^{-1} in March (average 14±6 µg l^{-1}) (Fig. 4.1). Thereafter, chlorophyll *a* values increased and peaked in summer up to maximum values of 50-60 µg l^{-1} at the open lagoon sites, while remaining in range of 30-40 µg l^{-1} in the littoral sandy areas (Fig. 4.1). At the open lagoon sites, chlorophyll *a* remained elevated also in October.



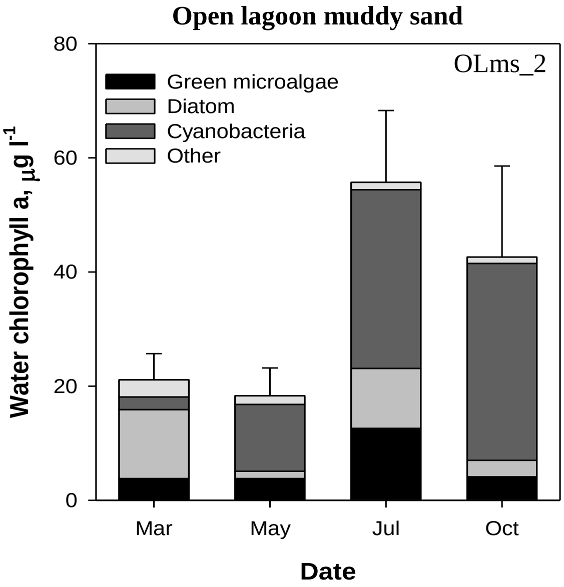


Figure 4.1. Average (±SD, n=3) contribution of different phytoplankton groups to the total chlorophyll a content during four measurement periods at five study sites. Note scale differences in y-axis

During all sampling periods dissolved oxygen saturation, measured during daylight, was typically below 100% at all sampling sites (except the littoral site LitS_5S in October), but anoxic events were not recorded (Table 4.1). Oxygen saturation in the littoral zone increased from March (65% on average) to October (97%). Similarly, in the open lagoon sites oxygen saturation increased from March to July (67±1 and 81± 3% on average), but approached spring values in October (64±7%).

Ammonium concentration (NH_4^+) in the water column ranged between 1.9 and 14.5 µM during sampling occasions (Table 4.1). In the most of sites (except LitS_1N in May and OLms_2 in July) NH_4^+ concentrations were consistent from March to July (4.4±1.7 µM and 3.9±0.7 µM respectively), however peaked up to 3 folds in October (11.2±2.5 µM). During the course of seasonal sampling the highest concentrations in range between 3.9 and 14.5 µM were typical for the deepest open lagoon mud site ExpM_4.

An average oxidized dissolved nitrogen concentration (NO_x^-) in the water column was the highest in March 114.0±51.0 µM (Table 4.1). After spring bloom in May, however, NO_x^- was depleted and concentrations dropped close to zero in all sampled sites (1.5±1.5 µM). Despite repeated cyanobacterial blooms concentration considerably increased from 3.3±1.6 µM in July to 22.2±21.7 µM in October. More than 95% of NO_x^- pool was in the form of nitrate and spatial heterogeneity reflected freshwater inputs from the Nemunas River and complex circulation patterns within the Curonian Lagoon.

Contrary to the dissolved inorganic nitrogen forms, soluble reactive phosphorus (SRP) slightly decreased with time, from 0.6±0.3 µM in early spring to 0.3±0.1 µM in late autumn. During entire sampling period SRP ranged between 0.1–1.1 µM, with relatively higher concentrations measured in open lagoon sites OLms_2 and ExpM_4 (Table 4.1).

Calculated dissolved inorganic nitrogen (DIN=NH_4^++NO_x^-) and SRP ratio decreased after spring bloom (Table 4.1); at the end of spring (May) and midsummer (July) approached the Redfield ratio (16) in the most of sites.

Sediment characteristics considerably differed between sampling sites depending on sediment type and sampling period (Table 4.2). The higher concentrations of total nitrogen (8.2-13.1% dry weight) and total phosphorus (0.72-1.11% dry weight) were associated with organic rich sediments (TOM ranged between 12.5 and 17.9%) of higher porosity (0.81-0.86) and lower density (1.03-1.11 cm^3 g^{-1} on average) in open lagoon fine silt sediment.

In contrast, sandy sediments had lower total nitrogen (0.5-0.7% dry weight) and phosphorus amount (0.01-0.08% dry weight) and typically were characterized by higher density (between 1.73 and 1.82 cm^3 g^{-1}), primary dominance of fine sand particles and significantly lower total organic matter content (0.4-0.7 % dry weight) (Table 4.2).

Table 4.2. Average values of main sediment characteristics (± standard deviation, n=3) of the sampling sites.

Sedimentary environment	**Littoral sand zone**		**Open lagoon muddy sand**	**Open lagoon mud**	
Study site	LitS_1N	LitS_5S	OLms_2	ShM_2	ExpM_4
Type of sediment	Fine sand		Fine muddy sand	Fine silty mud	
Median grain size (mm)	0.223	0.241	0.171	0.028	0.048
Porosity	0.34±0.03	0.43±0.05	0.40±0.05	0.84±0.05	0.81±0.03
Density (cm^3 g^{-1})	1.82±0.05	1.73±0.03	1.75±0.07	1.03±0.09	1.11±0.03
TOM (%)					
Mar	0.6±0.1	0.54±0.1	0.6±0.1	15.5±0.8	14.6±0.6
May	0.6±0.1	0.68±0.1	0.7±0.1	17.9±0.9	16.8±1.0
Jul	0.5±0.1	0.40±0.1	0.4±0.1	12.5±0.5	12.5±1.2
Oct	0.4±0.1	0.52±0.1	0.6±0.1	14.2±0.8	14.2±0.6
TN at 0-2 cm (%)					
May	0.7	0.6	0.6	12.6	13.1
Jul	0.6	0.5	0.5	8.2	10.6
Oct	0.8±0.1	0.7±0.1	0.6±0.1	11.1±1.4	11.5±1.4
TP at 0-2 cm (%)					
May	0.09	0.13	0.01	0.91	1.07
Jul	0.03	0.11	0.07	0.85	0.90
Oct	0.07±0.01	0.14±0.02	0.07±0.01	1.03±0.02	1.11±0.06

Concentration gradients between surface sediment and near bottom water show sediment being a source of dissolved organic carbon (DOC) to the overlaying water (except site ShM_3 in July) (Fig. 4.2). DOC was relatively low in organic rich sediments, while in sandy sediments (sites LitS_1N, LitS_5S and OLms_2) three times higher porewater concentrations were determined (Fig. 4.2). Furthermore, porewater profiles demonstrate increasing DOC concentrations between May and October in all sampled sites. During studied periods DOC concentrations were highly variable within upper 2 cm sediment layer in the most of sites, whereas deeper sediment in this respect was much more uniform.

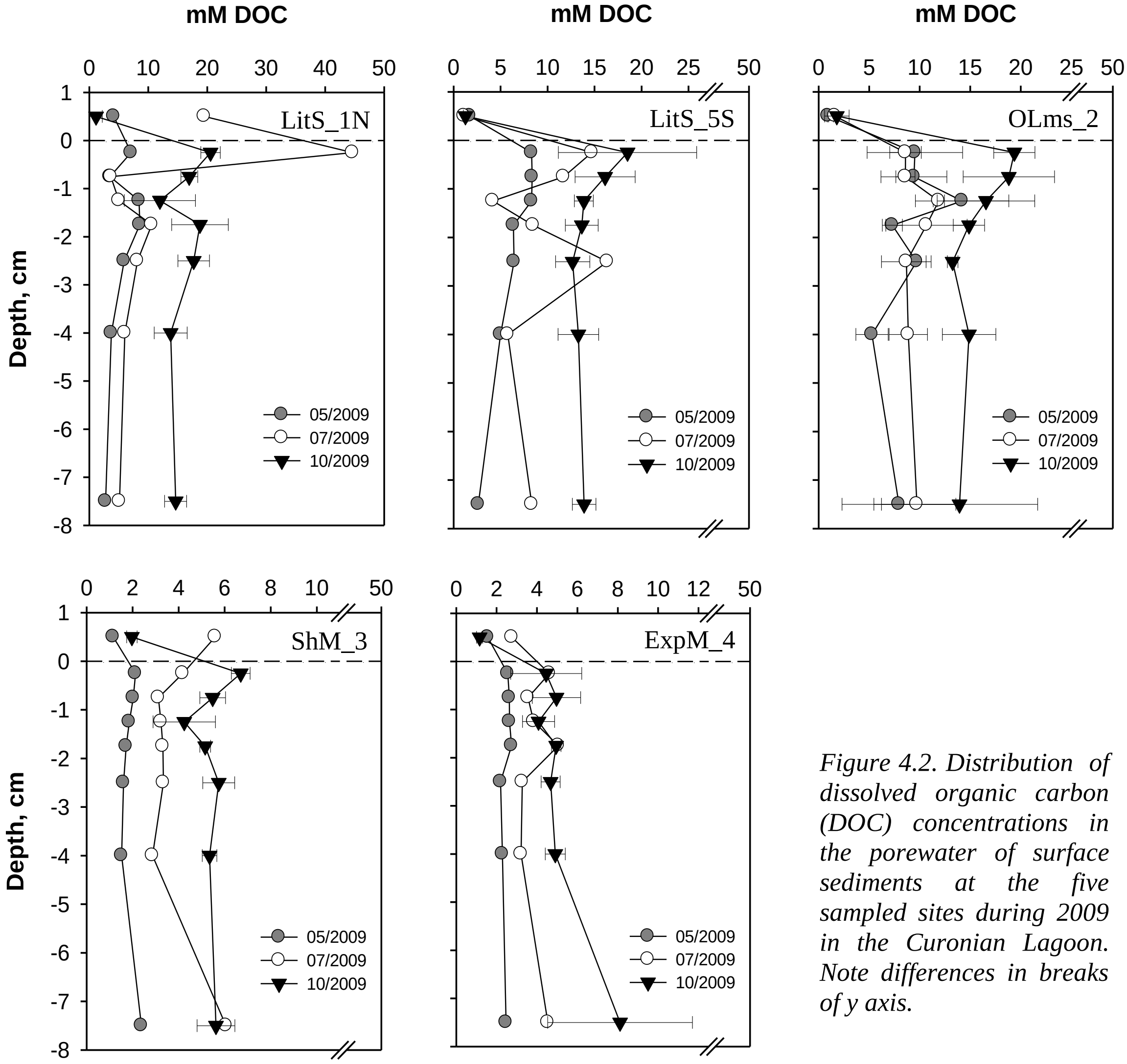


Figure 4.2. Distribution of dissolved organic carbon (DOC) concentrations in the porewater of surface sediments at the five sampled sites during 2009 in the Curonian Lagoon. Note differences in breaks of y axis.

The amount of exchangeable ammonium, which accounts for both porewater and adsorbed ammonium fractions, differed between sediment types (Fig. 4.3). Considerably higher amount (0.83±0.41 µmol NH_4^+ cm^{-3} on average) was extracted from the open lagoon mud, while sandy sediments (except site LitS_1N) contained seven times lower concentrations (0.12±0.08 µmol NH_4^+ cm^{-3} on average). Sediments in the littoral site LitS_1N, however, had 5 folds higher capacity to retain ammonium comparing to others sandy sites, and extracted exchangeable ammonium content (0.60±0.08 µmol NH_4^+ cm^{-3} on average) there was similar to that found in muddy sediment. Exchangeable ammonium content within the muddy sediment increased towards the deeper sediment layers, whereas in sandy sediment it was relatively homogeneously distributed along the vertical profile (Fig. 4.3).

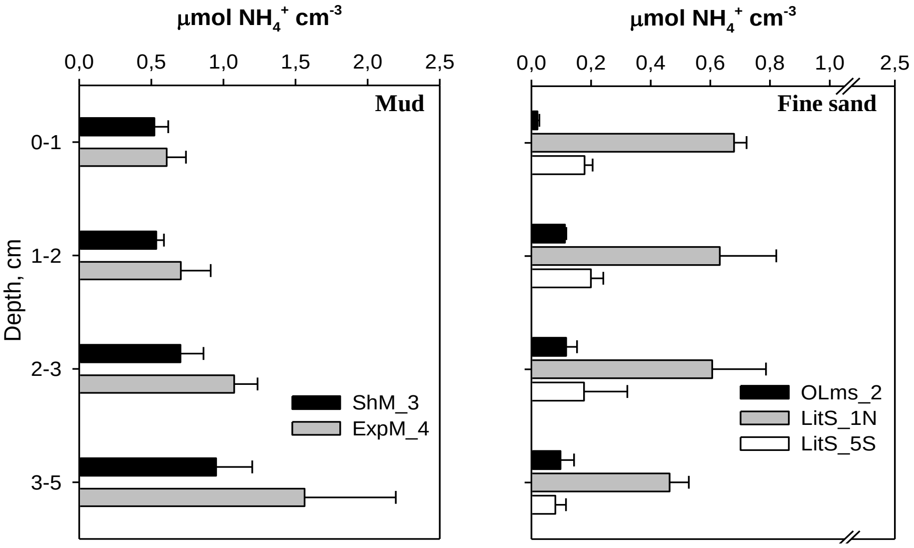


Figure 4.3. Average content (±SD, n=3) of exchangeable ammonium ($NH_4^+{}_{ex}$) in the sediments at five study sites in October, 2009.

Chlorophyll *a* concentrations at the surface sediment layer varied considerably in time and increasing pattern was typical from March to October (from 85±26 to 153±17 mg m^{-2} on average) for all studied sites (Fig. 4.4). Relative lower sediment chlorophyll *a* concentration 86±36 mg m^{-2} on average was determined in the open lagoon muddy sand comparing to the other investigated areas during spring–summer period. In autumn sediment chlorophyll *a* concentrations measured at all sites were already comparable.

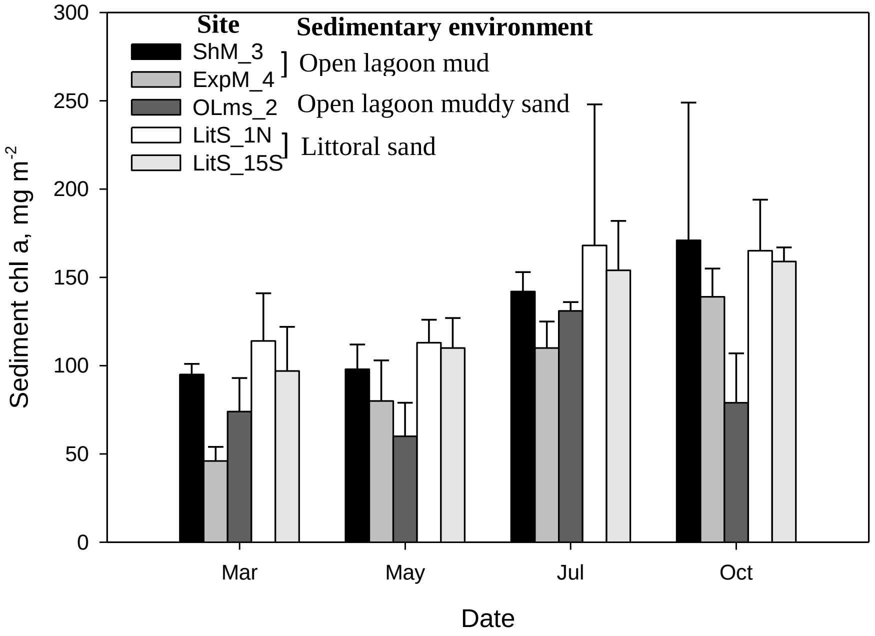


Figure 4.4. Average (±SD, n=3) chlorophyll a content in the surface sediments during four measurement periods at five study sites.

In order to integrate 16 environmental characteristics described above principal component analysis (PCA) was carried out. Analysis results showed first four principal components (PCs) with eigenvalues greater than 1 (Table 4.3) accounting for 80.8% of the total variance.

Table 4.3. Eigenvalues of the correlation matrix, proportion of variance explained by each PC and cumulative variation for the PCA.

PC	Eigenvalues	% Variation	Cum. % Variation
1	6.066	37.9	37.9
2	3.443	21.5	52.4
3	2.282	14.3	73.7
4	1.131	7.1	80.8

First PC accounting for 37.9% of the total explained variance was positively related to the sediment density and dissolved organic carbon in the upper 2 cm sediment layer (DOC_0-2), and negatively related to the porosity, total phosphorus (TP_0-2), total nitrogen (TNk_0-2) and organic matter (TOM) content in the uppermost 2 cm surface sediment were (Table 4.4). This demonstrates that sediment total nitrogen and total phosphorus concentrations were primary linked to the low density organic rich fine silt particles of higher porosity. Consequently, high density sandy sediment was poor in total organic matter and consequently showed low content of total nitrogen and total phosphorus.

Table 4.4. Loadings of environmental variables for principal components (PC) derived by Principal Component Analysis. The highest loadings are bolded.

Variables	PC1	PC2	PC3	PC4
Density	**0.395**	-0.038	-0.051	0.082
DOC_0-2	**0.319**	-0.098	0.209	-0.209
TOM	**-0.355**	0.078	0.054	-0.014
TNk_0-2	**-0.392**	0.051	0.069	-0.018
TP_0-2	**-0.394**	0.033	0.114	-0.018
Porosity	**-0.394**	0.034	0.083	-0.055
NOx	0.059	**0.462**	0.243	-0.076
SRP	0.023	**0.373**	-0.058	0.207
Water_chl_a	-0.158	**-0.371**	0.007	-0.128
Season	-0.004	**-0.445**	0.295	-0.134
NH4	-0.102	-0.076	**0.506**	0.049
O2_conc	0.207	0.134	**0.467**	-0.068
Sed_chl_a	0.062	-0.330	**-0.347**	0.080
Temp	-0.021	-0.371	**-0.412**	-0.021
Salinity	0.136	-0.118	0.071	**0.752**
NH4ex	-0.218	-0.078	0.084	**0.533**

PC2 accounted for 21.5% of the total variance and four water column variables such as sum nitrate and nitrite (NOx), and soluble reactive phosphorus (SRP) concentrations, temperature (Temp), water chlorophyll *a* (Water_chl_a), and seasonality (Season) were the main contributors to this axis (Table 4.4). This confirms that annual dynamics of water chlorophyll *a* is tightly coupled with seasonal variation of temperature and nutrient concentrations.

PC3 explained 14.3% of variation (Table 4.4) and was related to the sediment chlorophyll *a* content (Sed_chl_a), temperature, ammonium (NH4) and water column oxygen (O2_conc) concentrations. These environmental variables shaped the autumn picture. Increased ammonium concentrations in the water column are likely the result of sediment resuspension and porewater flushing which are common in the shallow lagoon in autumn. Simultaneously intensive water mixing and decreasing temperature predetermines typically higher O_2 solubility in the water. On the other hand, large influx of labile organic matter to the sediments was still sustained in the end of summer vegetation period.

The lowest contribution of PC4 accounting only for 7.1% of the total variability in environmental data is mainly related to the salinity (Salinity) and sediment exchangeable ammonium pool (NH4ex). This axis reflects higher concentrations of exchangeable ammonium during brackish water inflows in the lagoon.

3.2. Sedimentary oxygen microprofiles and flux at the sediment-water interface

4.2.1. Oxygen microprofiles

Oxygen distribution in the surface sediment indicated a sharp decline immediately below the water–sediment interface in May, July and October and oxygen penetration depth was generally less than 1 mm (Fig. 4.5). During warmer periods (May and July) the thickness of the oxic layer was comparable at all sampling sites and confined to the upper 0.4 mm of the surface sediment. In October oxygen penetration was relatively higher in the littoral sites, than in the other sites (0.5-0.8 mm versus 0.3-0.4 mm). Oxygen penetration calculated for March indicated much higher oxygen penetration depth of 6-8 mm at all sampling sites.

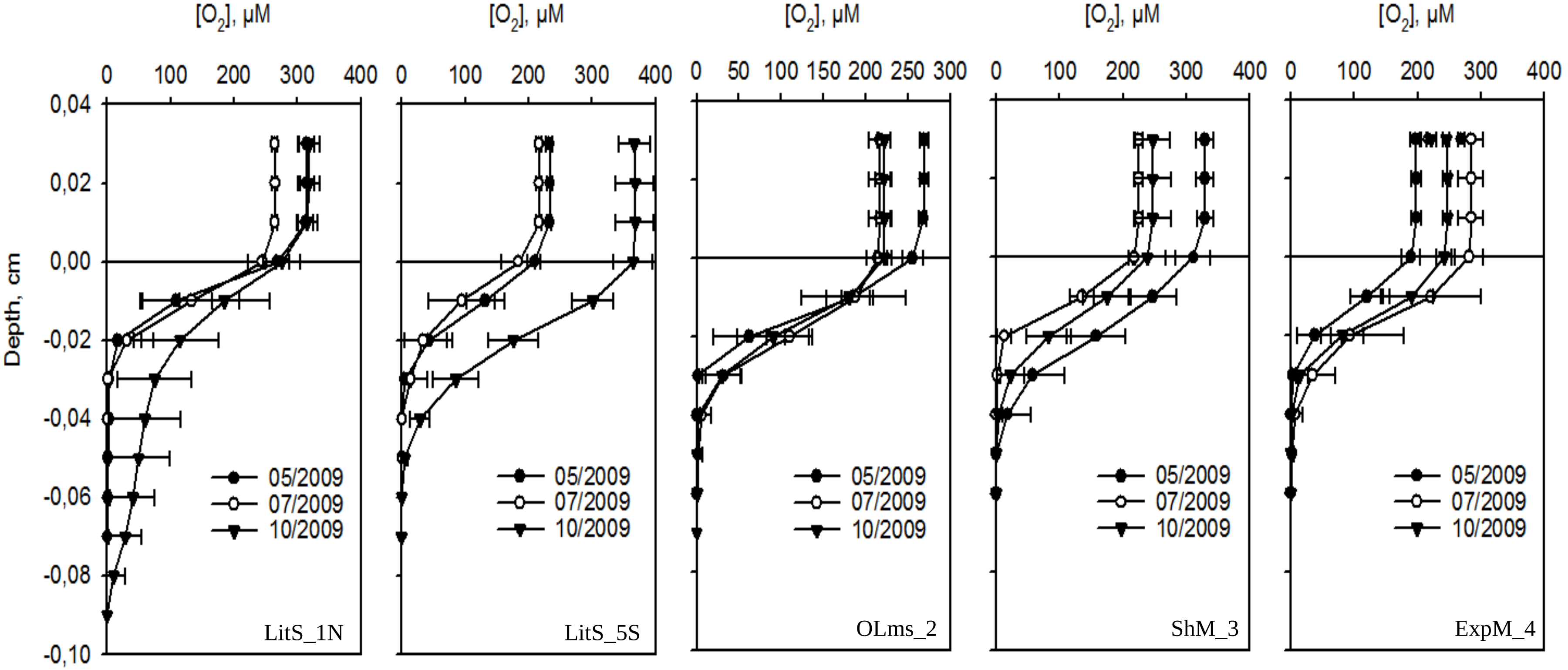


Figure 4.5. Oxygen microprofiles (average concentrations ± SD, n=3-9) measured in the Curonian Lagoon surface sediment in May, July and October, 2009.

4.2.2. Total and diffusive oxygen uptake

Total sediment oxygen uptake (TOU) varied between stations and sampling periods by a factor 8, with a minimum of 0.27±0.10 mmol O_2 m^{-2} h^{-1}, measured in March at the sandy station LitS_5S, and a maximum of 2.14±0.29 mmol O_2 m^{-2} h^{-1}, measured in July at the littoral station LitS_1S (Fig. 4.6).

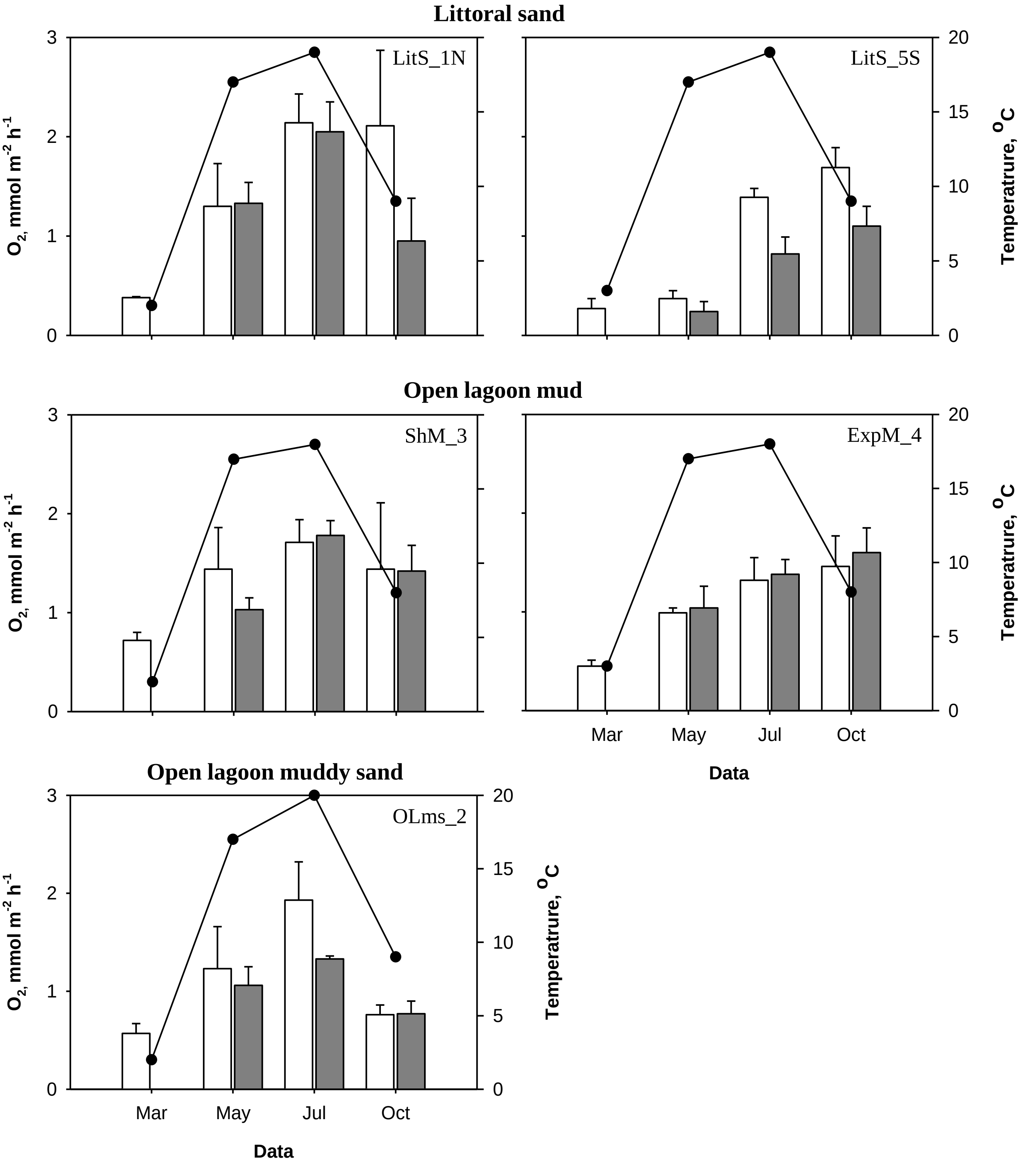


Figure 4.6. Average (±SD, n=5) total and diffusive oxygen oxygen uptake (±SD, n=3-9) (TUO and DOU respectively) and temperature values measured in the Curonian Lagoon in March, May, July and October. Diffusive fluxes were not calculated for March due to missing measurements of oxygen profiles.

At all sites (except OLms_2) TOU increased from March to July and remained elevated till October, despite sharp decrease of water temperature (Fig. 4.6). In the open lagoon site OLms_2, however, TOU values reflected changes in the water temperature and were approximately two times lower in October than in July. Concequently, two-way ANOVA indicated significantly different average TOU rates between stations (F=68.6, p<0.001) and sampling periods (F=9.1, p<0.001) with significant interaction between both factors (F=5.9, p<0.001).

Diffusive O_2 uptake rates calculated from oxygen microprofiles varied between 0.25 and 2.05 mmol O_2 m^{-2} h^{-1} and were comparable to the range of TOU variation (Fig. 4.6). The ratio between TOU and DOU was reasonably close to 1 at both muddy sites (ShM_3 and ExpM_4) and at the open lagoon muddy sand site OLms_2 during all sampling periods. In the shallow littoral sandy areas, however, total oxygen flux was considerably higher than diffusive transport: at LitS_5S site total to diffusive flux ratio was permanently in range between 1.5 and 1.7, whereas at LitS_1N site ratio of 2.2 was observed only in October.

According to the results of the redundancy analysis (RDA), seven environmental characteristics employed in the analysis explain 54% of the variation of DOU, TOU and oxygen penetration depth (OPD) (Fig. 4.7).

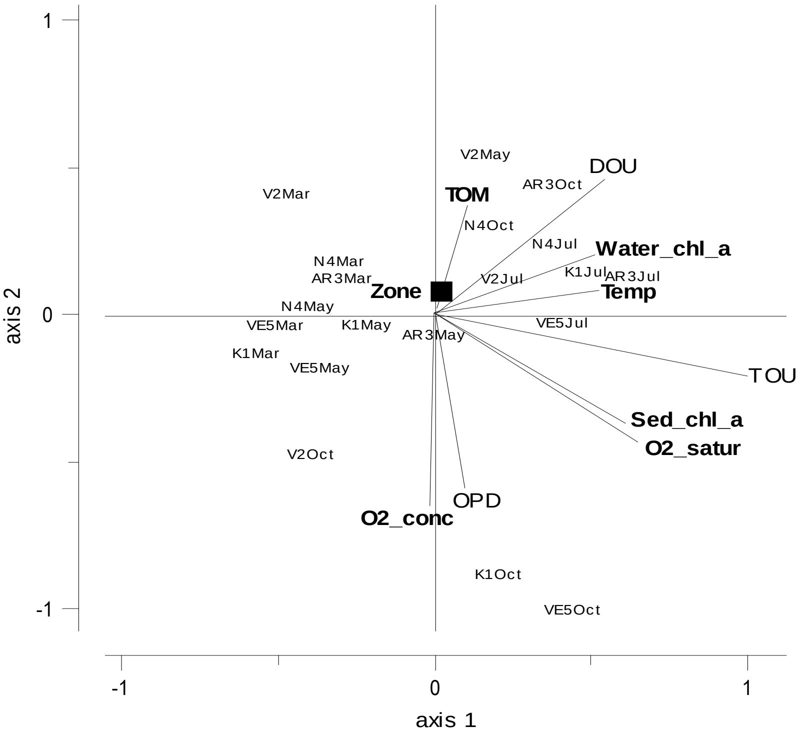


Figure 4.7. Redundancy analysis (RDA) triplot showing relationships between three response variables (DOU - dissolved oxygen uptake; TOU - total oxygen uptake; OPD - oxygen penetration depth) and seven explanatory variables (TOM – total organic matter content in sediment; O2_satur – water column oxygen saturation; O2_conc – water column oxygen concentration; Water_Chl_a – water chlorophyll a concentration; Sed_Chl_a – chlorophyll a concentration in the sediment surface layer; TEMP – water temperature; Zone – type of sedimentary sedimentary environment). Data labels correspond station title (K1-LitS_1N, VE5-LitS_5S, V2-OLms_2, AR3-ShM_3 and N4-ExpM_4) and sampling periods (Mar-March, May, Jul-July, Oct-October).

Permutation tests revealed that oxygen saturation (*F*=3.52, *p*=0.010) and water chlorophyll a concentration (*F*=2.36, *p*=0.090) were the most significant factors describing oxygen dynamics. Sediment chlorophyll *a* and temperature had highest eigenvalues next to oxygen saturation if a single factor tests were run with environmental variables individually. This demonstrates a complex regulation of oxygen uptake by environmental factors, which can be aggregated into three major groups (Fig. 4.7): 1) water oxygen concentration and sediment total organic matter (TOM), 2) water temperature and water chlorophyll a; and 3) water oxygen saturation and sediment chlorophyll *a*.

TOM and oxygen concentration were strongly linked to the measured OPD values and reflected well our principal division of 5 study sites into three sedimentary environments. OPD values were positively related to the water oxygen concentrations and negatively to the sediment TOM content. On the other hand, sediment TOM dynamics was not related to the measured TOU values, but higher values were reflected in accelerated DOU rates. Two other groups of environmental parameters directly and indirectly affected rates of both TOU and DOU; Temperature driven water chlorophyll *a* was equally important for both DOU and TOU, whereas sediment chlorophyll *a* and oxygen saturation were positively linked to TOU and OPD (Fig. 4.7).

4.2.3. Oxygen exchange at the sediment-water interface under different illumination regimes

Oxygen exchange at the sediment–water interface was highly dependent on light regime in the Curonian lagoon (Fig. 4.8, Table 4.5). During daytime measured net primary production (NPP) fell in range between <0.1 and 2.2 mmol m^{-2} h^{-1} with the average 0.3±0.9 mmol m^{-2} h^{-1}, while in the dark mean flux rate was -1.2±0.7 mmol m^{-2} h^{-1}. Moreover, results demonstrated better illuminated littoral sand and open lagoon muddy sand were mostly autotrophic (NPP>0). Significantly (Tukey HSD test, p<0.05) higher NPP rates (0.5±1.0 mmol m^{-2} h^{-1}) were observed in site LitS_5S, whereas open lagoon deep mud sites (ShM_3 and ExpM_4) functioned as to oxygen sink (<0.1 mmol m^{-2} h^{-1}). Here more than 70% of measured flux rates fell in range between -2.6 and -0.1 mmol m^{-2} h^{-1}, with the average uptake rate of -0.3±0.6 mmol m^{-2} h^{-1}.

Although seasonal NPP rates highly varied between studied sites located in different sedimentary environments (Table 4.5), pooled data showed significantly higher rates (Tukey HSD test, p<0.05) in March (0.3±0.9 mmol m^{-2} h^{-1} on average). In spite of increasing chlorophyll *a* in the water column, benthic microalgae photosynthetically activity remained relatively constant (0.8±0.6 mmol m^{-2} h^{-1}) in shallow sandy sites (except site OLms_2 in July), obviously while in deeper (> 2 m) sites (-0.5±0.6 mmol m^{-2} h^{-1}, on average).

Applied Benthic Trophic Status Index (BTSI) attributed lagoon sediments to net autotrophic (BTSI 3) and net heterotrophic (BTSI 1), categories in spring and summer–autumn months respectively. According to the BTSI classification shallower littoral and open lagoon muddy sand sediment was mostly autotrophic (site

LitS_1N in May and site OLms_2 in July), while open lagoon mud was consistently of the net heterotrophic status.

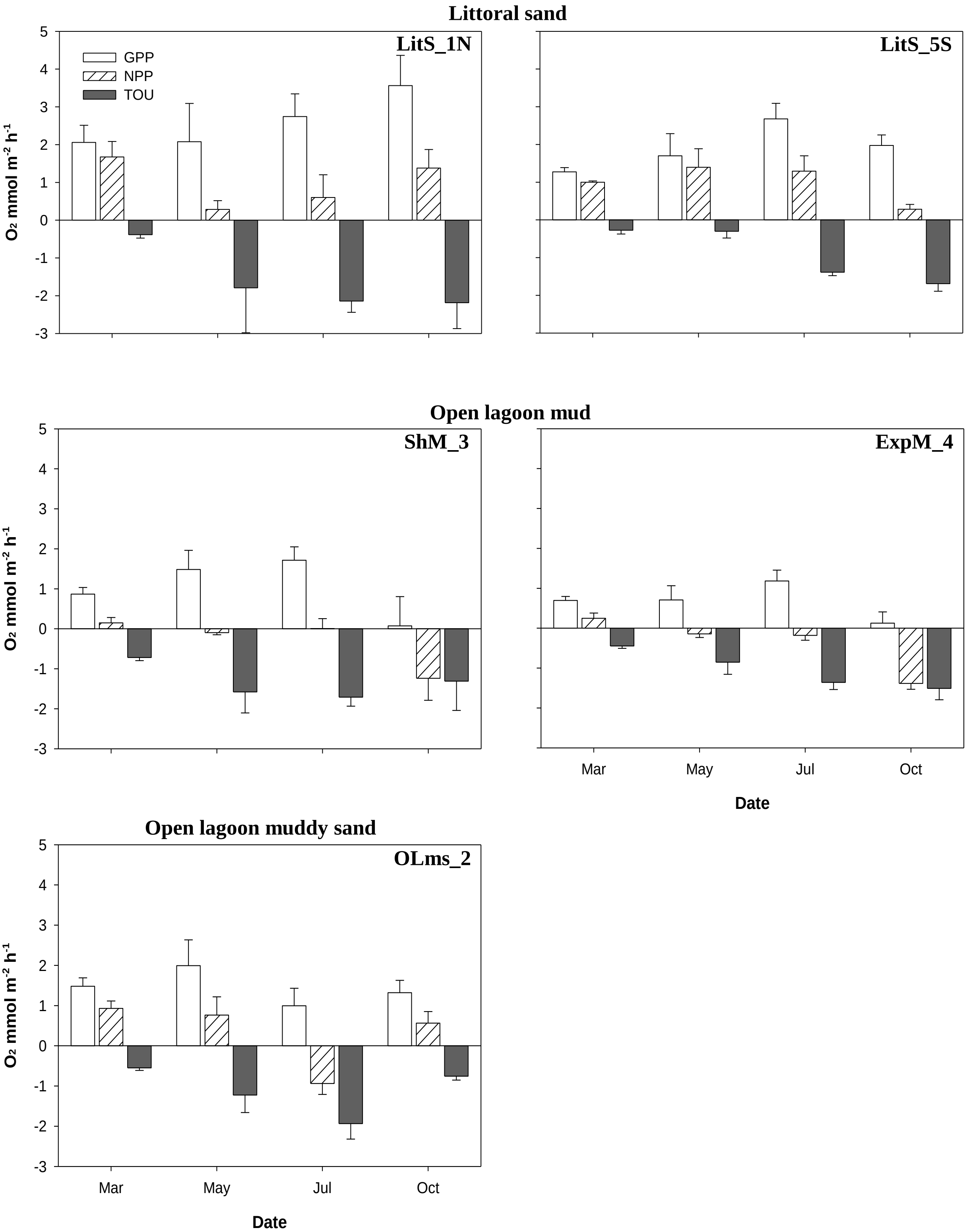


Figure 4.8. Average (±SD, n=5) gross primary production (GPP), net primary production (NPP), and community respiration (CR) in different sedimentary environments in the Curonian Lagoon in March, May, July and October in 2009.

The mean benthic microalgae gross primary production (GPP) was in range between <0.1 and 3.6 mmol m^{-2} h^{-1} (Fig. 4.8) and decreased with water depth. The highest rates were calculated in the littoral sandy sediments (2.0±1.0 mmol m^{-2} h^{-1} on average), while in relative deeper open lagoon muddy sand GPP was 25% lower over studied periods. In the deepest mud sites GPP rate was found to be less than 50% of that measured in the littoral sand.

Table 4.5. Two-way ANOVA results ($log(x^2)$ transformation was applied to NPP data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p-significance level, where $p<0.05$.

Factor	**Df**	**SS**	**MS**	**F**	***p***
March					
Site	4	8.3	2.1	7.2	<0.001
Light/Dark	1	0.0	0.0	0.1	0.724
Site x Light/Dark	4	18.1	4.5	15.5	<0.001
Residual	40	11.6	0.3		
Total	49	38.1	0.8		
May					
Site	4	12.4	3.1	12.4.9	<0.001
Light/Dark	1	31.7	31.7	126.3	<0.001
Site x Light/Dark	4	3	0.8	3.0	0.030
Residual	40	10.0	0.3		
Total	49	57.1	1.2		
July					
Site	4	9.7	2.4	24.2	<0.001
Light/Dark	1	43.3	43.4	432.0	<0.001
Site x Light/Dark	4	6.7	1.8	16.7	<0.001
Residual	40	4.0	0.1		
Total	49	63.8	1.3		
October					
Site	4	13.1	3.3	18.1	<0.001
Light/Dark	1	24.9	24.9	138.5	<0.001
Site x Light/Dark	4	21.0	5.3	29.2	<0.001
Residual	40	7.2	0.2		
Total	49	66.2	1.4		

Calculated daily flux (Appendix 1) demonstrated, that littoral site LitS_5S and open lagoon muddy sand site OLms_2 sediments were autotrophic during studied spring–autumn period (22.2±17.6 and 6.4±6.1 mmol m^{-2} h^{-1} on average respectively), with exception in July for site OLms_2 and autumn for site LitS_5S when they shifted to heterotrophic status. Other sites were characterized by fully heterotrophic sediments in day period (except in March).

4.3. Ammonium concentration profiles and exchange at the sediment-water interface

Ammonium (NH_4^+) concentration in the surface sediment was typically higher than in the overlaying water (except mud sediment in October) (Fig. 4.9) and was mostly accumulated in the organic rich mud sediment.

Amount of extracted NH_4^+ from these sediment showed that concentration was approx. 2 times higher in sheltered area (site ShM_3) than in exposed one (ExpM_4).

The mean NH_4^+ concentrations in the porewater were highly variable between and within sites during study occasions (Fig. 4.9). In the littoral sediment (LitS_1N and LitS_5S) NH_4^+ concentrations fluctuated between 21.4 and 292.9 µM with negative correlation between sites. In the open lagoon muddy sand (OLms_2) porewater concentrations in the upper 2 cm in the sediment peaked in midsummer (up to 322.6 µM) (Fig. 4.9), while lower values (20.5–97.6 µM) in the porewater were observed in spring and autumn. In open lagoon mud sites (ShM_3 and ExpM_4) the mean NH_4^+ concentrations were relative consistent in porewater of the 2 cm sediment layer during spring and midsummer (Fig. 4.9). However, autumn, minimum values were reached in the porewater.

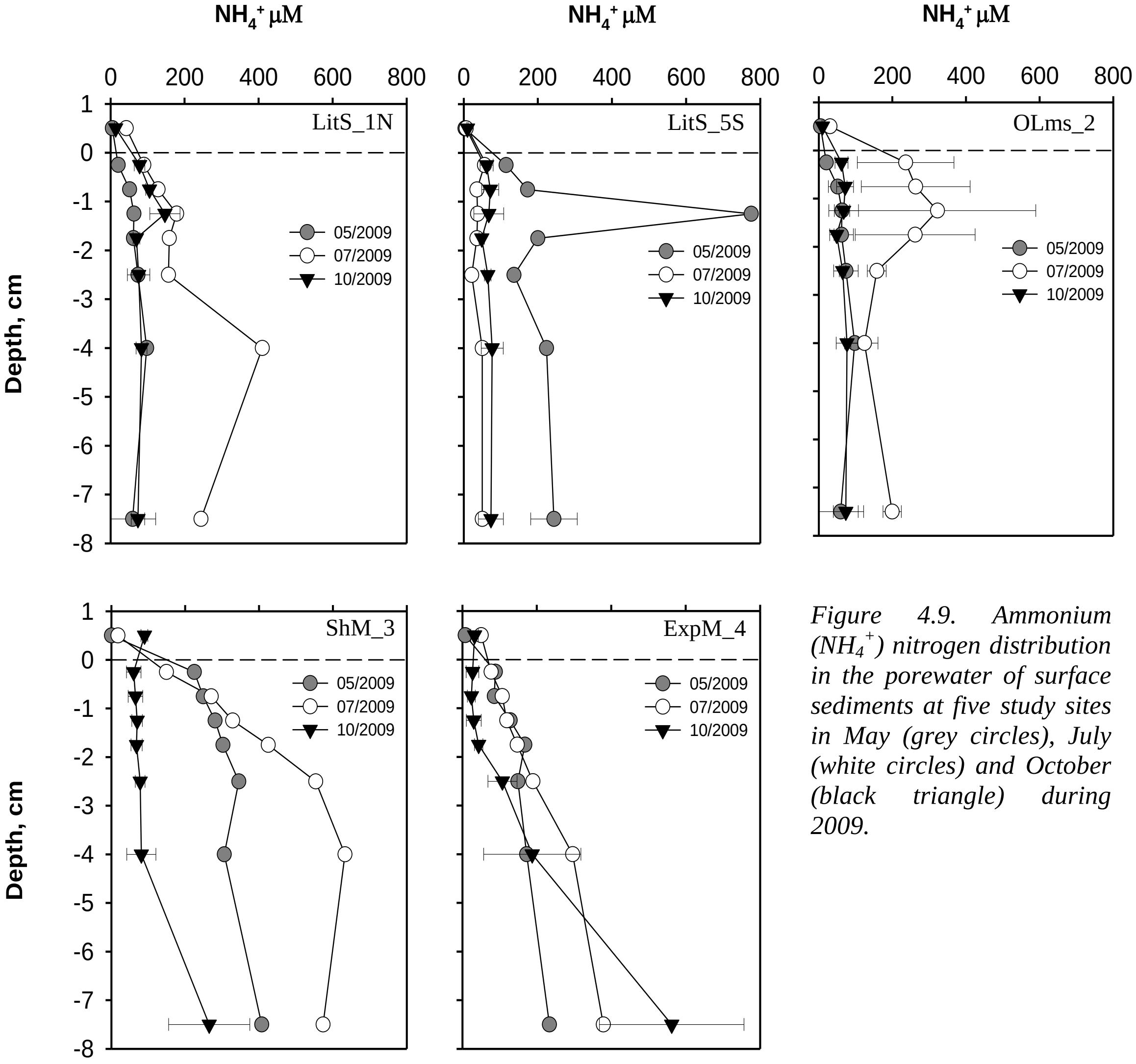


Figure 4.9. Ammonium (NH_4^+) nitrogen distribution in the porewater of surface sediments at five study sites in May (grey circles), July (white circles) and October (black triangle) during 2009.

Furthermore, shape of NH_4^+ profiles indicate the highest rates of ammonium production and consumption processes occurring in the upper 2 cm sandy sediment layer, while deeper in the sediment rates were negligible (except in site LitS_1N). In mud sediment NH_4^+ concentration consistently increased (up to 632.9 µM) with depth (Fig. 4.9).

Ammonium diffusive transport was related to the degree of concentration gradient at the sediment–water interface. In littoral sandy zone NH_4^+ was permanently released from sediment to near-bottom water, with elevated rates in summer and autumn (Table 4.6). In the open lagoon muddy sand the highest rates of NH_4^+ transport to the near-bottom water were observed in July (Table 4.6), while in mud diffusive NH_4^+ flux from the sediment decreased from spring towards autumn.

Table 4.6. Diffusive NH_4^+ flux rates (n=1–3) at the sediment–water interface in three different sedimentary environments in the Curonian Lagoon.

Sedimentary enviroment		**Littoral sand**		**Open lagoon mudy sand**	**Open lagoon mud**	
Sites		LitS_1N	LitS_5S	Olms_2	ShM_3	ExpM_4
Date	May	1.2	0.6	20.3±18.7	603.2	211.4
	July	137.2	148.3	708.7±371.1	501.3	67.9
	October	142.4±19.0	115.2±32.4	115.9±31.4	-67.5±17.4	-37.6±71.9

Total ammonium flux rates at the sediment–water interface significantly differed between sites and seasons (Table 4.7). In different studied environments (open lagoon muddy sand and mud) NH_4^+ efflux to the near-bottom water increased from March to October in range between -67.2 and 741.5 µmol m^{-2} h^{-1} (Fig 4.10) and seasonality was the main driving factor (Table 4.7). Significantly ($p<0.05$) lower ammonium exchange rates was observed in the March (11.4±20.5 µmol m^{-2} h^{-1}). However, the mean NH_4^+ flux rate considerable varied between open lagoon sites (Table 4.7).

Table 4.7. Two-way ANOVA results (*log(1+x²)* transformation was applied to NH_4^+ data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p-significance level, where *p*<0.05.

Factor	**Df**	**SS**	**MS**	**F**	***p***
Site	4	31.4	7.9	23.0	<0.001
Season	3	71.7	23.9	69.9	<0.001
Site x Season	12	38.4	3.2	9.4	<0.001
Residual	80	27.3	0.3		
Total	99	168.8	1.7		

In contrast to the open lagoon sediments (Tukey HSD test, $p<0.05$), NH_4^+ flux in shallow littoral sand was always low (-35.5–88.7 µmol m^{-2} h^{-1} range) showing NH_4^+ uptake under dark regime (Fig. 4.10). In open lagoon muddy sand ammonium release to the near–bottom water was highly variable with flux rates of 3.7–315.5 µmol m^{-2} h^{-1} on average, though increasing from March to October (Fig. 4.10). Similarly, in the deeper open lagoon mud NH_4^+ also showed efflux to the near–bottom water with average rate of 27.0±53.7 µmol m^{-}

^{2} h^{-1} during spring–summer. In October NH_4^+ efflux steeply increased by 90% (up to 741.5 µmol m^{-2} h^{-1}) (Fig. 4.10).

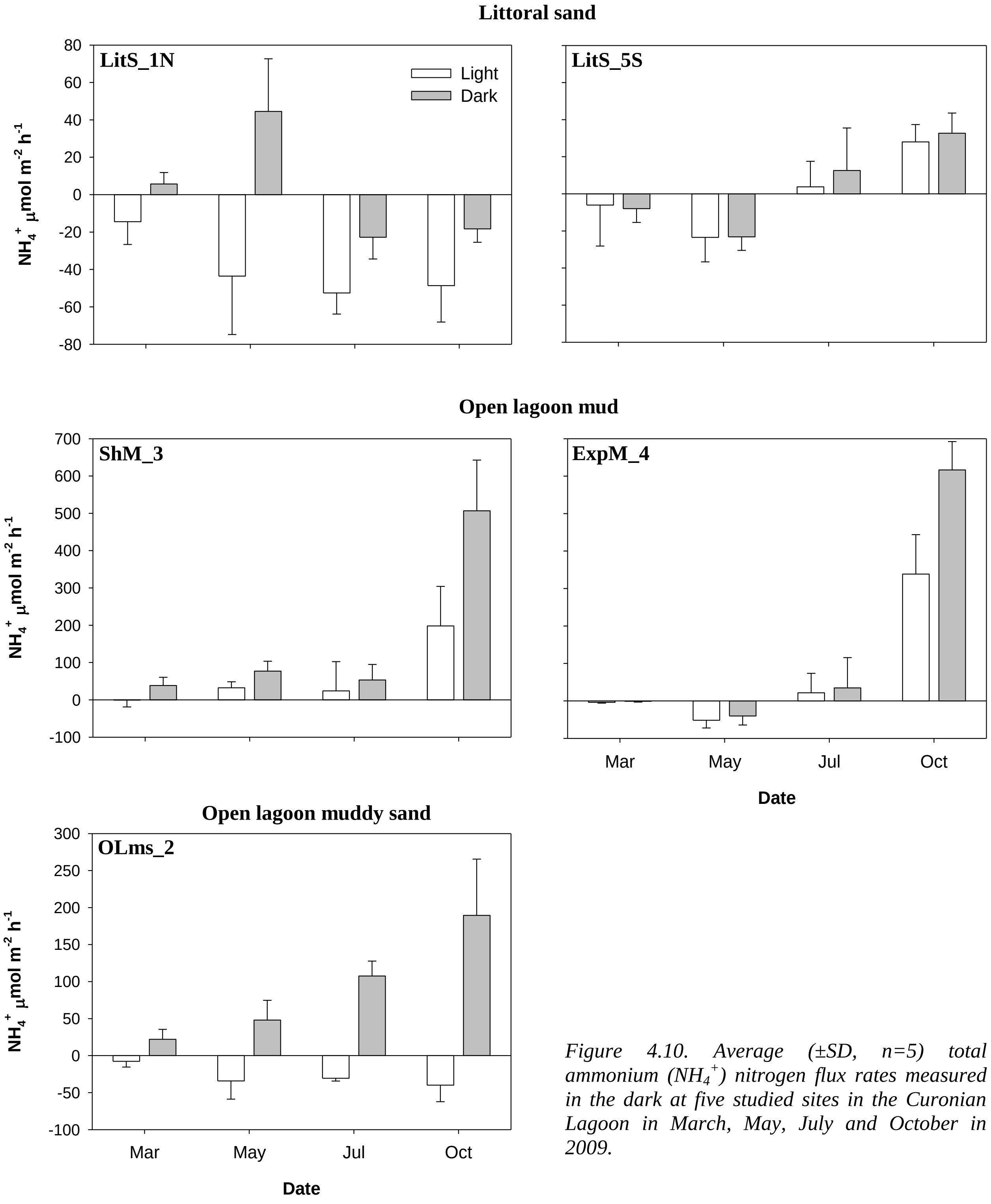


Figure 4.10. Average (±SD, n=5) total ammonium (NH_4^+) nitrogen flux rates measured in the dark at five studied sites in the Curonian Lagoon in March, May, July and October in 2009.

Significant differences in NH_4^+ fluxes rates between light and dark regimes (Tukey HSD test, $p<0.05$) was found for all studied periods except March (Table 4.8). However, importance of interaction with the site factor demonstrates significant variation of illumination effect between studied sites (Table 4.8). NH_4^+ uptake was increased up to -97.1 µmol m^{-2} h^{-1} during day time particularly in sandy sediment (with some exceptions in littoral sediment). Moreover, in some occasions ammonium was taken up even by relatively deep open lagoon mud (Fig. 4.10), while in open lagoon muddy sand, NH_4^+ was consistently taken up by sediments at a rate of 28.1±20.2 mmol m^{-2} h^{-1} during day time and released to the near bottom water in the dark.

Table 4.8. Two-way ANOVA results (*$log(x^2)$* transformation was applied to NH_4^+ data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p- significance level, where $p<0.05$.

Factor	**Df**	**SS**	**MS**	**F**	***p***
			March		
Site	4	6.8	5.3	10.2	<0.001
Light/Dark	1	0.4	0.4	0.7	0.426
Site x Light/Dark	4	11.4	2.9	2.9	0.006
Residual	40	26.9	0.7		
Total	49	66.0	1.4		
			May		
Site	4	56914.4	14228.6	26.9	<0.001
Light/Dark	1	25721.5	25721.5	48.5	<0.001
Site x Light/Dark	4	15916.4	3979.1	7.5	<0.001
Residual	40	21196.5	529.9		
Total	49	119748.8	2443.9		
			July		
Site	4	41071.0	10267.8	5.6	0.001
Light/Dark	1	23992.4	23992.4	13.0	<0.001
Site x Light/Dark	4	28773.4	7193.4	3.9	0.009
Residual	40	74031.3	1850.8		
Total	49	167868.2	3425.9		
			October		
Site	4	1973219.5	493304.9	92.4	<0.001
Light/Dark	1	362057.6	362057.6	67.8	<0.001
Site x Light/Dark	4	203030.1	50757.5	9.5	<0.001
Residual	40	213622.4	5340.6		
Total	49	2751929.6	56161.8		

4.4. Nitrate and nitrite nitrogen concentration profiles and exchange at the sediment-water interface

The porewater profiles of nitrate and nitrite (NO_x^-) nitrogen demonstrated sandy and muddy sediment being a source of these nutrients to the near bottom water in late spring, summer and autumn (except open lagoon sites in autumn), when nitrification rates were the highest (Fig. 4.11). There was always a surface maximum in porewater concentrations with the mean NO_x^- concentration in the upper 2 cm sediment layer between 19.3 and 290.6 µM. However, concentrations always significantly dropped down in deeper layers.

Nitrate was the dominant (>70%) nitrogen form in the porewater of the studied sediment comparing to nitrite.

The NO_x^- profiles also showed that in littoral sandy sediment (LitS_1N and LitS_5S) the concentrations in the porewater of the upper 2 cm increased from spring to autumn (Fig. 4.11). In open lagoon muddy sand (OLms_2) the mean NO_x^- concentrations in the porewater was the highest in July (up to 174.2 μM), while in other periods were recorded 90% lower values. NO_x^- concentration values in open lagoon mud sediments rarely exceeded more than 12 μM during studied seasons (Fig. 4.11), though slight peaks of NO_x^- was observed down to 2 cm depth.

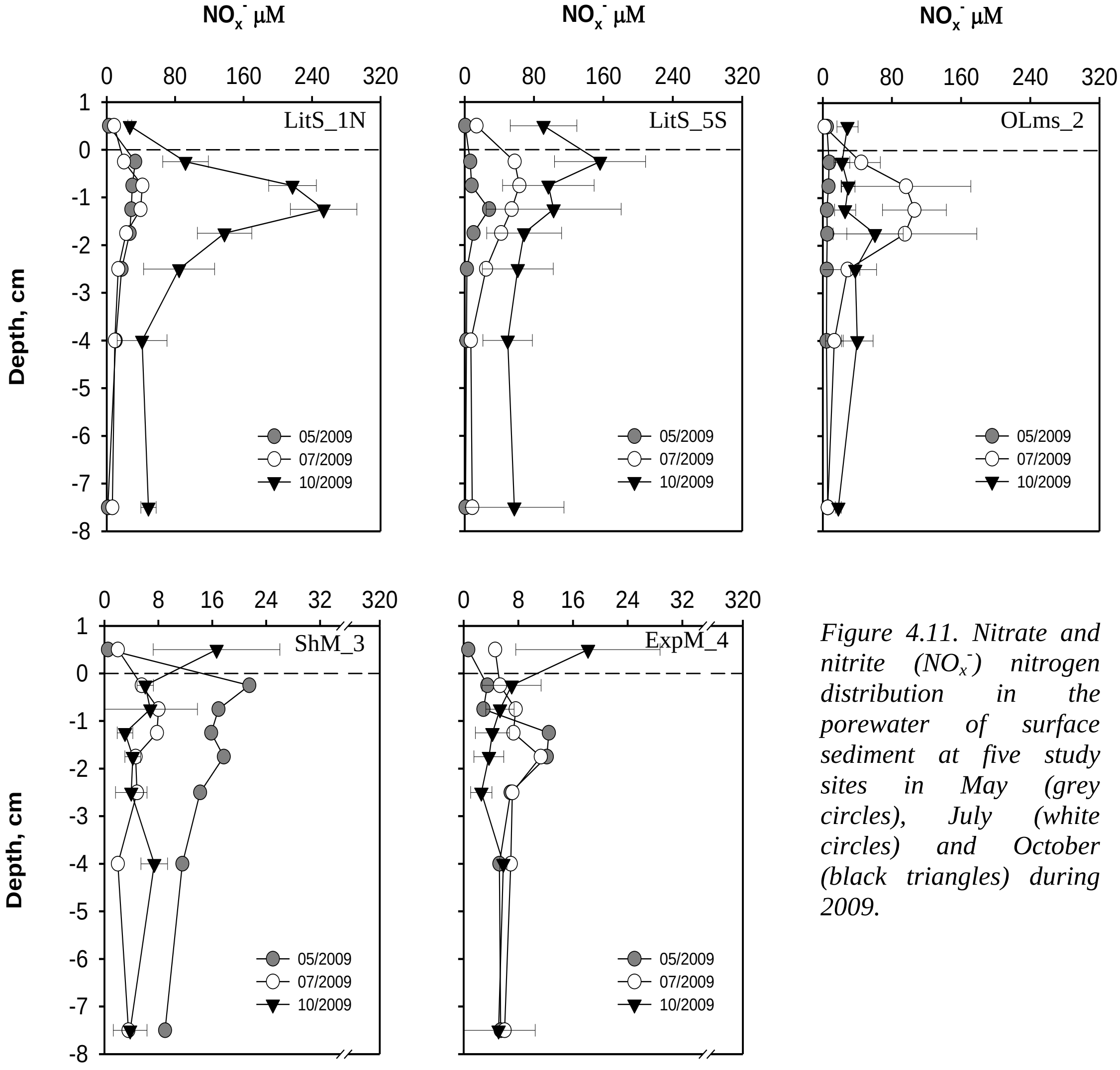


Figure 4.11. Nitrate and nitrite (NO_x^-) nitrogen distribution in the porewater of surface sediment at five study sites in May (grey circles), July (white circles) and October (black triangles) during 2009.

Active nitrification promoted NO_x^- efflux to the near bottom water in littoral sand and open lagoon muddy sand in late spring and midsummer (Table 4.9). In autumn littoral sand still remained a source of NO_x^- to the near-bottom water, while downward diffusive flux to the sediment was observed in muddy sand. In the open lagoon mud diffusive NO_x^- transport to the near-bottom water was relatively low and decreased towards autumn (Fig. 4.9).

Table 4.9. Diffusive nitrate and nitrite (NO_x^-) flux at the sediment–water interface at five studied sites during 2009 in the Curonian Lagoon.

Sedimentary enviroment		**Littoral sand**		**Open lagoon mudy sand**	**Open lagoon mud**	
Sites		LitS_1N	LitS_5S	Olms_2	ShM_3	ExpM_4
Date	May	5.8	22.6	6.4±12.5	58.4	4.4
	July	102.3	385.2	139.4±41.9	8.8	0.6
	October	160.4±51.1	108.1±31.7	-13.4±21.6	-22.0±17.5	-22.0±12.0

The NO_x^- dark flux rate at the sediment–water interface was in range between -569.3–315.6 µmol m^{-2} h^{-1} at the studied areas (Fig. 4.12), and different lagoon areas simultaneously were functioning as a sink or source of nitrate to the overlaying water. In general downward flux of nitrate and nitrite was dominant in spring and autumn, while release from sediment to the near-bottom water was mainly observed in midsummer. Similarly to ammonium exchange, seasonality was also the most important driving factor in NO_x^- exchange at the sediment–water interface (Table 4.10). Furthermore, seasonality significantly interacted with the site factor (Table. 4.10), indicating different seasonal trends in mean flux rates between studied sites (Fig. 4.12). During spring (March–May) the most of the lagoon sediment functioned as a sink for NO_x^- (-154.6±239.7 and -13.6±10.8 µmol m^{-2} h^{-1} on average respectively), although uptake rates decreased considerably in late spring. In summer period open lagoon sediments were a source of NO_x^- to the overlaying water (47.3±69.7 µmol m^{-2} h^{-1} on average). In autumn mud sediment shifted to a sink of NO_x^- (-25.6±17.3 µmol m^{-2} h^{-1} rate on average) as response to increased near-bottom water concentrations, whereas open lagoon muddy sand remained a source of NO_x^- with elevated flux rates.

Table 4.10. Two-way ANOVA results (*$log(x^2)$* transformation was applied to NO_x^- data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p- significance level, where $p<0.05$.

Factor	**Df**	**SS**	**MS**	**F**	***p***
Site	4	7.0	1.7	4.8	0.002
Season	3	68.4	22.8	61.0	<0.001
Site x Season	12	51.4	4.3	11.4	<0.001
Residual	80	29.4	0.4		
Total	99	156.7	1.6		

In spite of active NO_x^- production in the littoral sand, the mean NO_x^- exchange rates were relatively low (-137.5–157.5 µmol m^{-2} h^{-1}) and mainly indicated uptake processes. Moreover NO_x^- exchange at the sediment–water interface in the littoral sand was less pronounced in comparison to the open lagoon sediment.

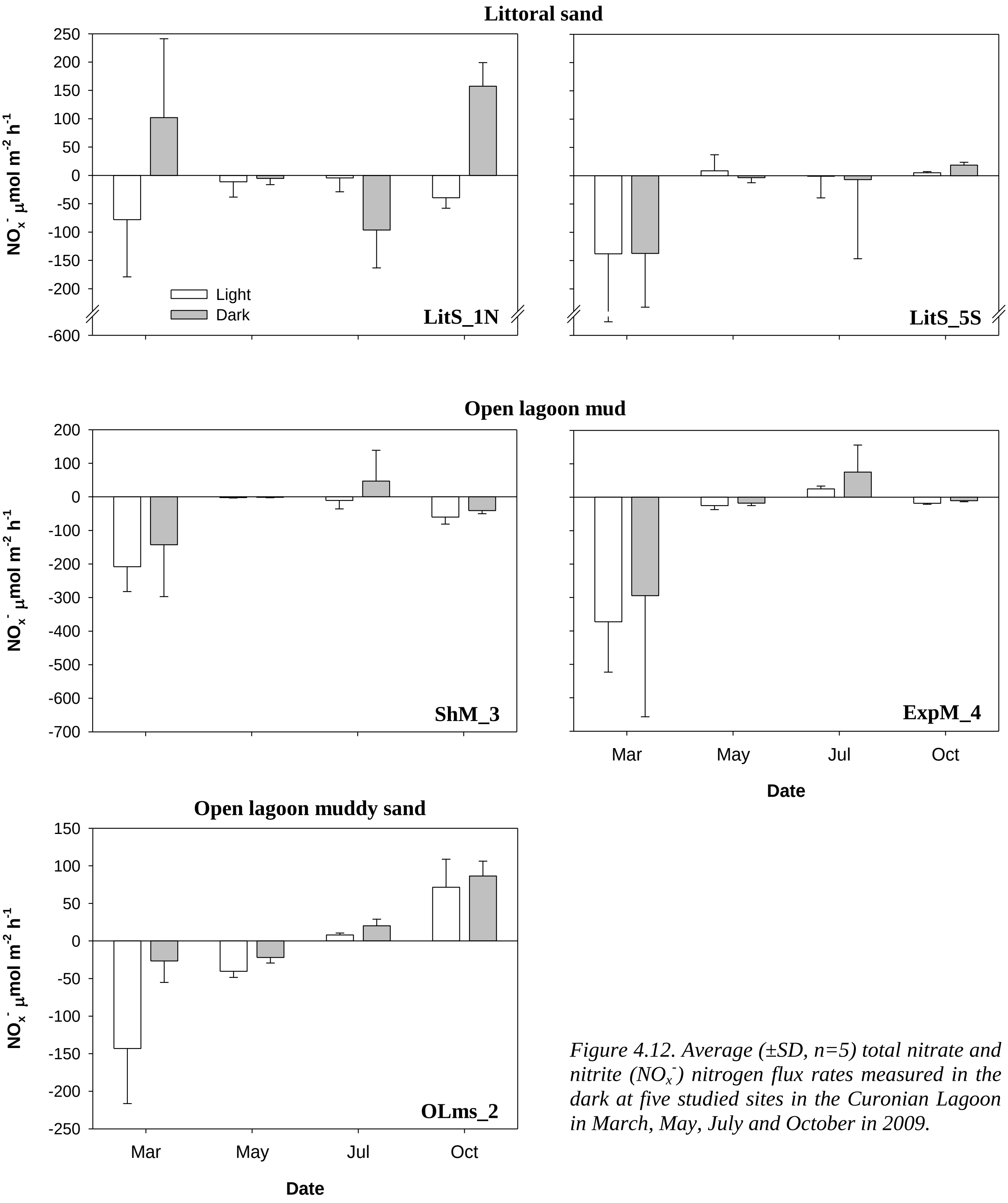


Figure 4.12. Average (±SD, n=5) total nitrate and nitrite (NO$_x^-$) nitrogen flux rates measured in the dark at five studied sites in the Curonian Lagoon in March, May, July and October in 2009.

During the study, differences between light and dark fluxes of NO$_x^-$ were found only in March and October (Table 4.11). Significant factor interaction indicates that flux differences between light and dark regimes depended on site. In March NO$_x^-$ uptake rates were up to five times higher under light regime than in the dark in sites OLms_2 and LitS_5S (Fig. 4.12). In October sediment of both littoral sites, were a sink of NO_x^- under light conditions and functioned as a source in dark. Even at the deeper ExpM_4 site significantly higher uptake rate (Tukey HSD test, p<0.05) was induced by sediment illumination.

Table 4.11. Two-way ANOVA results (*log(x^2)* transformation was applied to NO_x^- data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p-significance level, where *p*<0.05.

Factor	**Df**	**SS**	**MS**	**F**	***p***
March					
Site	4	16.5	4.1	11.1	<0.001
Light/Dark	1	3.6	3.6	9.6	0.004
Site x Light/Dark	4	4.8	1.2	3.2	0.021
Residual	40	14.8	0.4		
Total	49	39.7	0.8		
May					
Site	4	7813.1	1953.3	9.5	<0.001
Light/Dark	1	211.1	211.1	1.0	0.316
Site x Light/Dark	4	1237.4	309.4	1.5	0.218
Residual	40	8204.3	205.1		
Total	49	17465.9	356.5		
July					
Site	4	54176.4	13544.1	3.2	0.022
Light/Dark	1	237.8	237.8	0.1	0.813
Site x Light/Dark	4	35812.8	8953.2	2.1	0.094
Residual	40	167745.2	4193.6		
Total	49	5264.7	5264.7		
October					
Site	4	28.65	7.2	79.4	<0.001
Light/Dark	1	1.6	1.6	18.1	<0.001
Site x Light/Dark	4	6.4	1.6	18.0	<0.001
Residual	40	3.6	0.1		
Total	49	40.3	0.8		

4.5. Soluble reactive phosphorus concentration profiles and exchange at the sediment-water interface

Similarly to the NH_4^+ distribution in the Curonian lagoon, higher concentrations of soluble reactive phosphorus (SRP) were also attributed to the mud sediment (Fig. 4.13). In this sediment SRP concentrations gradually increased with the sediment depth and reached maximum in deeper horizons (up to 58.7 µM). Although higher concentrations (in range 5.2–56.9 µM) were measured in sand the upper 3 cm sediment layer, they considerably decreased with sediment depth (Fig. 4.13).

A comparison of porewater profiles revealed distinct seasonal SRP dynamics in different environments of the study area. In the upper 3 cm of the littoral sandy sediment SRP concentrations decreased considerably from late spring towards autumn. In the muddy sediment SRP concentration was the lowest and uniformly distributed in May, but increased up to 2 times on average in summer, however in the open lagoon mud SRP decreased at least 80% over the entire sediment profile in October.

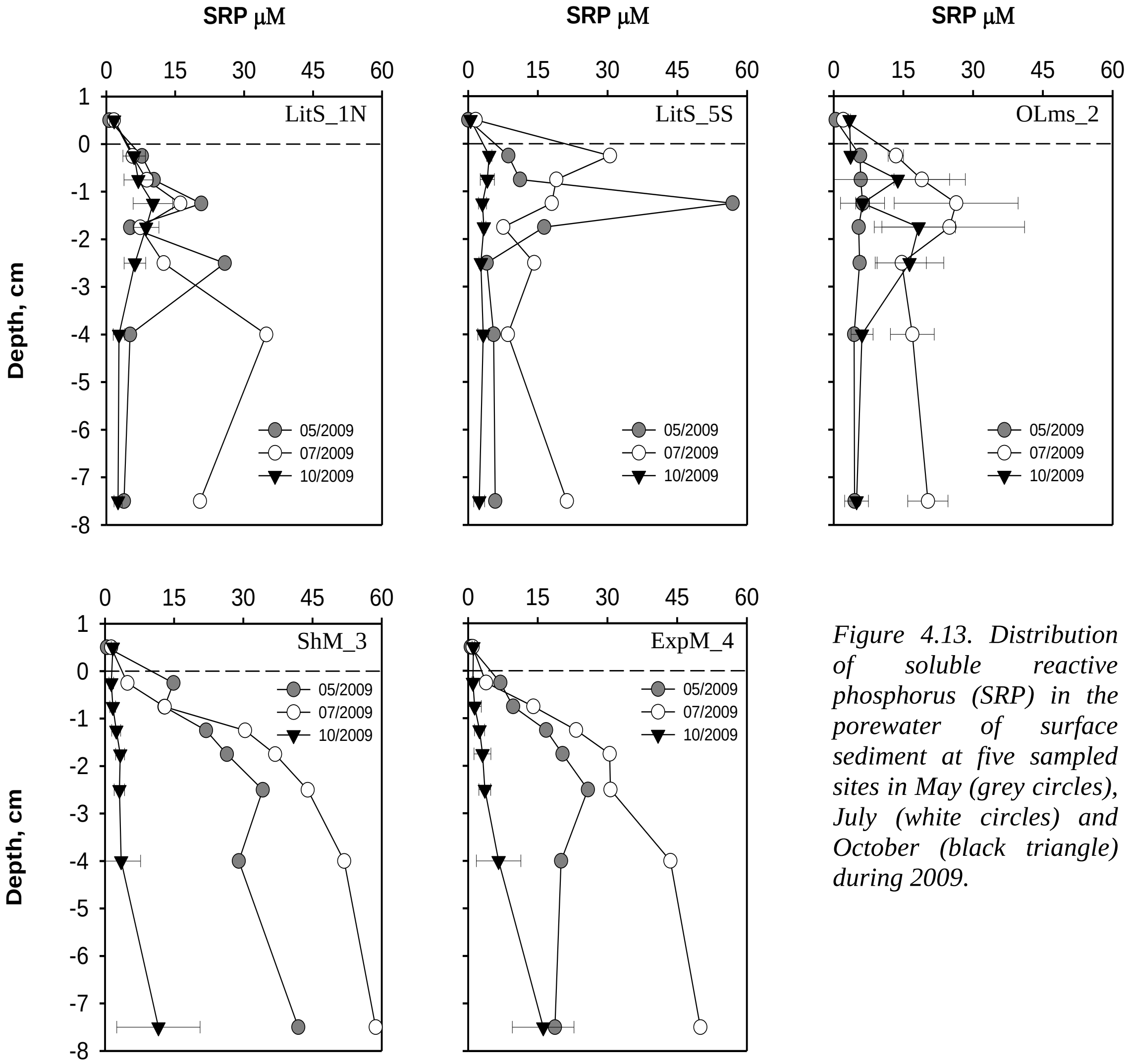


Figure 4.13. Distribution of soluble reactive phosphorus (SRP) in the porewater of surface sediment at five sampled sites in May (grey circles), July (white circles) and October (black triangle) during 2009.

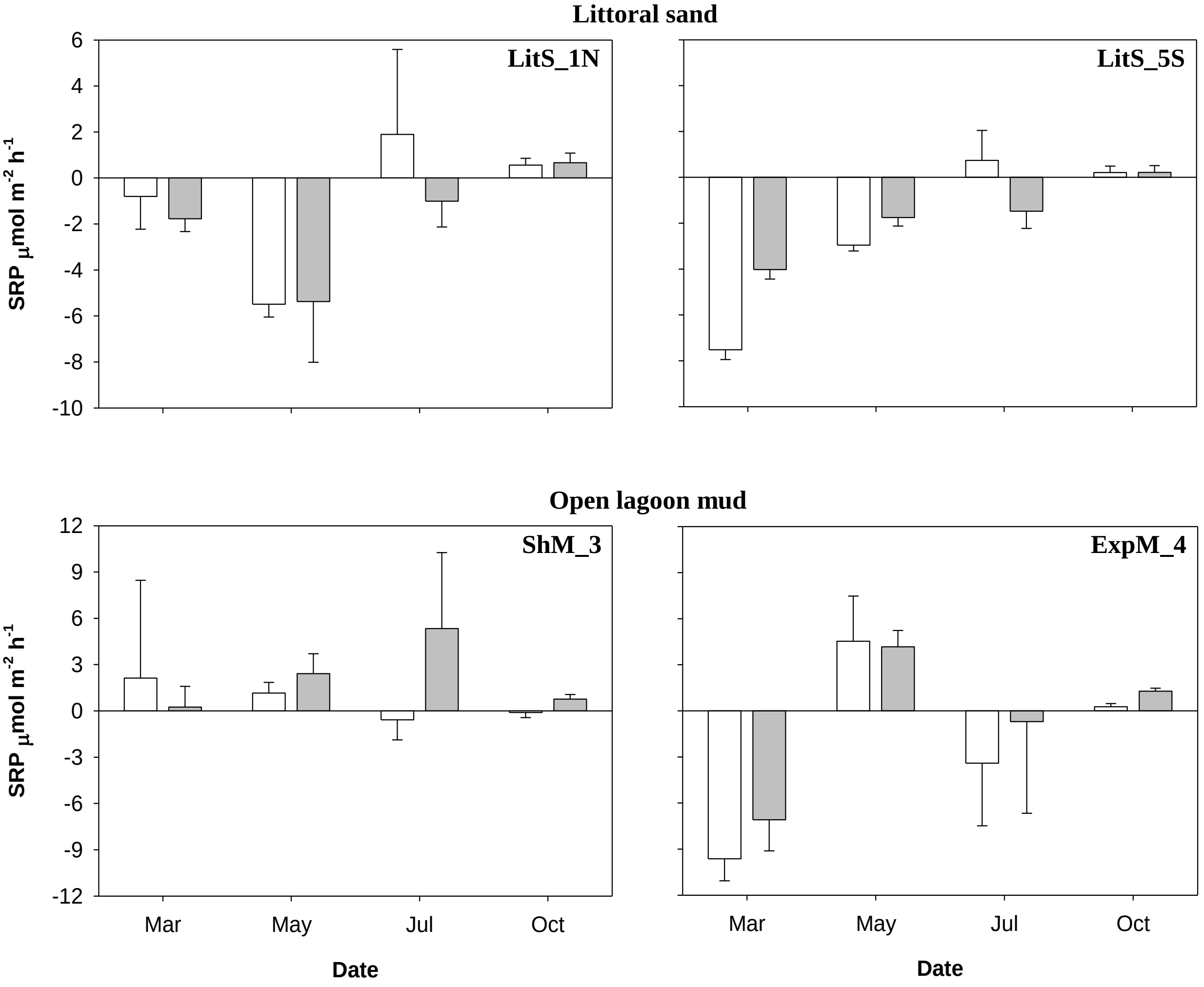
Table 4.12. Diffusive soluble reactive (SRP) flux at the sediment–water interface at the five studied sites during 2009 in the Curonian Lagoon.

Sedimentary enviroment		**Littoral sand**		**Open lagoon mudy sand**	**Open lagoon mud**	
	Sites	LitS_1N	LitS_5S	Olms_2	ShM_3	ExpM_4
Date	May	5.1	2.83	4.58±0.35	6.7	5.1
	July	7.3	19.3	9.4±3.6	8.5	7.8
	October	2.1±0.7	2.1±0.3	0.13±0.16	-0.3±0.2	-0.01±0.03

SRP concentration gradient across the sediment–water interface was reflected in the diffusive transport, which always showed SRP release from the lagoon sediment (except open lagoon sites in October) (Table

4.12). SRP efflux increased from late spring to midsummer and decreased at least four times in autumn with SRP adsorption in mud sediment (Table 4.12).

Total SRP flux rate at the sediment–water interface varied in range from -9.0 to 11.8 µmol m^{-2} h^{-1} at the studied sites (Fig 4.14). Although most of the core incubations showed SRP uptake by sediment on average, replicate measurements indicated both SRP uptake and release from sediment in different cores at the same time. Applied general linear model, with Generalized Least Squares method showed that SRP flux differed significantly (F=64.0, p<0.001) between sites. Flux measurements showed sandy sediment being a typical SRP sink environment (-7.8 – -0.1 µmol m^{-2} h^{-1}) (few exceptions in littoral sites only), while open lagoon mud was mainly SRP source (up to 11.8 µmol m^{-2} h^{-1}) (except in July at the ExpM_4).



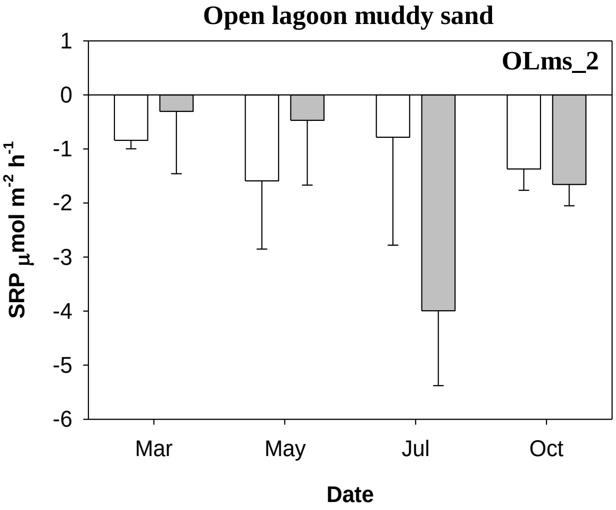


Figure 4.14. Average (±SD, n=5) total soluble reactive phosphorus (SRP) flux rates measured in the dark at five studied sites in the Curonian Lagoon in March, May, July and October in 2009.

Table 4.13. Two-way ANOVA results (*$log(1+x^2)$* transformation was applied to SRP data when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p-significance level, where *p*<0.05.

Factor	**Df**	**SS**	**MS**	**F**	***p***
			March		
Site	4	628.0	157.0	30.1	<0.001
Light/Dark	1	7.0	7.0	1.3	0.255
Site x Light/Dark	4	51.8	12.9	2.5	0.059
Residual	40	208.5	5.2		
Total	49	895.2	18.3		
			May		
Site	4	6.9	1.7	15.4	<0.001
Light/Dark	1	0.1	0.1	0.6	0.415
Site x Light/Dark	4	1.1	0.3	2.4	0.067
Residual	40	4.5	0.1		
Total	49	12.5.	0.3		
			July		
Site	4	151.3	37.8	3.7	0.011
Light/Dark	1	0.0	0.0	0.0	0.948
Site x Light/Dark	4	165.1	41.3	4.1	0.007
Residual	40	404.7	10.1		
Total	49	721.1	721.1		
			October		
Site	4	33.9	8.5	83.0	<0.001
Light/Dark	1	1.5	1.5	14.3	<0.001
Site x Light/Dark	4	3.2	0.8	7.8	<0.001
Residual	40	4.1	0.9		
Total	49	42.7	0.9		

Prevailing SRP downward flux to sandy sediment varied seasonally between littoral and open lagoon zones. In the littoral sand the highest uptake rates were measured during spring, while in the open lagoon muddy sand uptake rates peaked in midsummer (-3.0±2.3 and -4.0±1.4 µmol m^{-2} h^{-1} respectively). Moreover, SRP uptake was 25% higher in the open lagoon than in the littoral sandy sediment.

In the open lagoon mud (ExpM_4) SRP was released from the sediment most of the time from the late spring to the autumn (2.2±3.6 µmol m^{-2} h^{-1}) and transport rates were considerably lower than in sheltered mud site (ShM_3).

Data analysis revealed that illumination was weakly related to the SRP exchange at the sediment–water interface (Fig. 4.14). Significant differences between light and dark fluxes were found in midsummer and autumn and were more evident in more shallow sandy sites (Table 4.13). There SRP uptake was more active in the light conditions in comparison to dark. Even if light was limited SRP uptake was observed in deeper mud sediment as well.

4.6. Nitrogen removal in the Curonian lagoon sediments

Total denitrification rate (Dtot) and denitrification of water column nitrate (Dw) were significantly different between sites and sampling seasons (Table 4.14), while denitrification of nitrate produced via nitrification within the sediments (Dn) differed only between studied sites.

Table 4.14. Two-way ANOVA results *sqrt* transformation was applied to Dtot and Dw data, and division from dispersion to Dn when significant heteroscedascity was found). Df- degrees of freedom, SS- sum of squares, MS- mean square; F-F value, p-significance level, where $p<0.05$.

Factor	**Df**	**SS**	**MS**	**F**	***p***
Total denitrification [Dtot]					
Site	3	169.8	56.6	114.1	<0.001
Season	1	7.4	7.4	14.9	<0.001
Site x Season	3	3.4	1.1	2.3	0.096
Residual	32	15.9	0.5		
Total	39	196.5	5.0		
Denitrification from water column NO_3^- [Dw]					
Site	3	154.6	51.4	29.2	<0.001
Season	1	91.4	91.4	51.8	<0.001
Site x Season	3	79.1	26.4	14.9	<0.001
Residual	32	56.5	1.8		
Total	39	381.5	9.8		
Coupled nitrification-denitrification [Dn]					
Site	3	3.0	1.0	15.8	<0.001
Season	1	0.0	0.0	0.0	0.935
Site x Season	3	0.3	0.1	1.6	0.206
Residual	32	2.0	0.1		
Total	39	5.3	0.1		

Dtot varied between 4.9 and 108.6 µmol N $m^{-2}h^{-1}$ in March and between 5.0 and 66.8 µmol N $m^{-2}h^{-1}$ in July. Deeper mud sites in the open lagoon exhibited higher denitrification rates compared to shallow littoral sandy sites during both sampling periods (Fig. 4.15). The different relative importance of Dw to the Dtot reflected variable availability of nitrate in the water column during two sampling periods. In March, denitrification was mainly sustained by Dw, which represented >90% and 46-67% of Dtot at muddy and sandy sites respectively, while in July denitrification was mainly coupled to nitrification within the sediment (>70% of Dtot, with LitS_1N being the only exception).

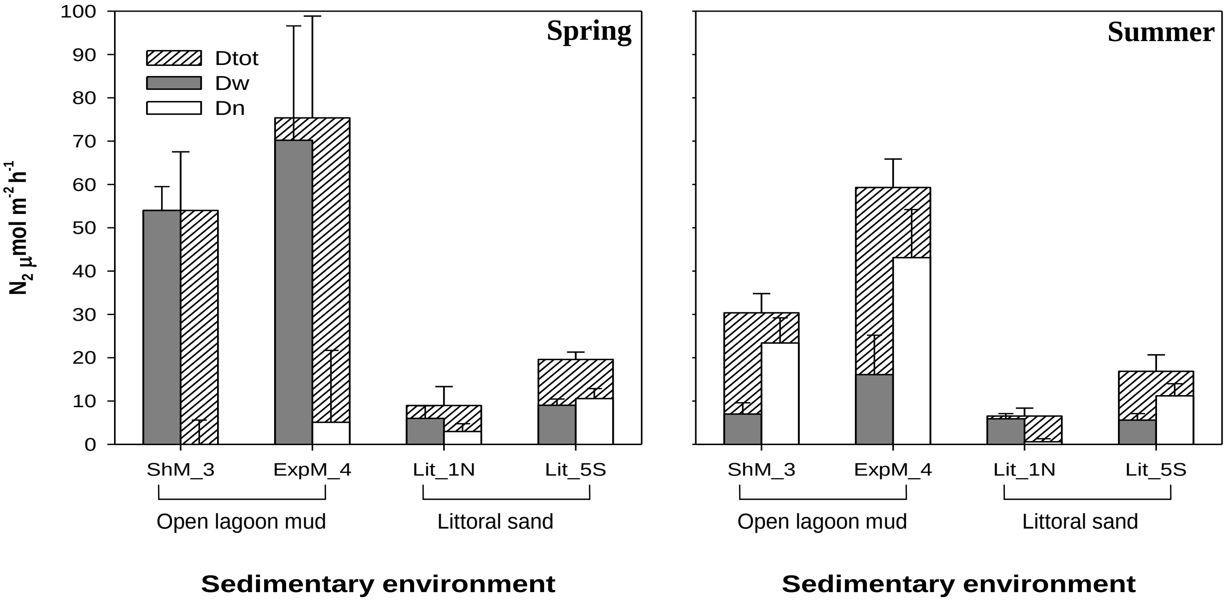


Figure 4.15. Average (±SD, n=5) total denitrification (Dtot; stripped bars), denitrification on diffused NO_3^- from water (Dw; grey bars) and coupled nitrification–denitrification (Dn; white bars) at four studied sites in the open lagoon deep muddy sediments and shallow littoral sandy sediment in the Curonian Lagoon during spring and summer.

5. DISSCUSION

5.1. What contributes to the sedimentary organic matter pool in the lagoon?

Curonian lagoon is characterized by high productivity and the dominance of pelagic production (Александров, 2003). Due to low efficiency of organic carbon flow to the higher trophic levels and favorable hydrolological conditions a large part of primary production is intensively accumulating in the bottom sediments (Galkus & Jokšas, 1997; Jokšas et al., 1998; Razinkovas & Gasiunaitė, 1999; Александров, 2003; Krevs et al., 2007; Ferrarin et al., 2008). Estimated stable isotope ratio in the settled particulate organic matter confirms that large part of it is supplied by autochthonous phytoplankton (Lesutiene, 2009). Similarly, after estimating suspended matter budget for the Curonian lagoon, Galkus et al. (1998) also suggest that autochthonous material can contribute significantly to the sedimentary organic carbon pool.

The origin and quality of settling particles is a key factor in understanding temporal variability of the benthic metabolism (Eyre &Ferguson, 2005). Using chlorophyll *a* as a tracer for highly labile organic matter in the sediment, the quality of the incoming organic carbon can be identified. Conventionally chlorophyll *a* is an indicator of the microphybenthos biomass in the shallow illuminated sediments (Sundbäck & Miles, 2000), while in deeper systems it is used to justify an amount of labile material settling to the surface sediments (Banta et al., 1995; Cowan & Boynton, 1996; Hopkinson et al., 2001; Eyre & Ferguson, 2005). In both cases it accounts for readily available organic carbon in the benthic food web (Middelburg et al., 2000; Köster et al., 2005).

Present study was carried out in three different sedimentary environments of the Curonian lagoon (shallow littoral sand, open lagoon muddy sand and relatively deep open lagoon mud) and revealed main sources of organic material and its distribution patterns. In the littoral sand and open lagoon muddy sand excess accumulation of organic material is prevented by relatively low water residence time (<40 days on average) and high bottom shear stress (Ferrarin et al., 2008). Although flocculent layers of freshly deposited phytoplankton can occasionally develop on surface sediments during calm weather conditions, these zones are primarily dominated by poor in organic matter fine sand. Steeply increased sediment chl *a* in summer is likely a consequence of phytoplankton deposition in the open lagoon muddy sand, however water chlorophyll *a* is weakly related to the sediment chlorophyll *a* values (Fig. 5.1) and may reflect presence of benthic microalgae as well. It was also supported by recorded net primary production in this sediment (Fig. 4.8) and preliminary revision of surface sediments (Sundbäck pers. com.). Köster et al. (2005) proposed that in contrast to deeper sediments with low light availability and predominant phytoplankton accumulation, labile organic carbon produced by benthic microalgae in the shallow sediment can be rapidly recycled and lead to low standing stocks of organic matter.

Open lagoon mud is typically associated with relatively deep depressions, where high water residence time results in intensive accumulation of suspended material from the water column (Pustelnikovas, 1998; Ferrarin et al., 2008). Sediment chlorophyll *a* seems to be a good predictor of water chlorophyll *a* in such environment (Fig. 5.1). In mud sediment pigment concentrations were consistent to water chlorophyll *a* values during spring–autumn period and this finding is in a good agreement with statements, that phytoplankton pigments are better indicators of the deposition of fresh and labile phytodetritus than bulk sediment parameters (Banta et al., 1995; Cowan & Boynton, 1996; Hopkinson et al., 2001).

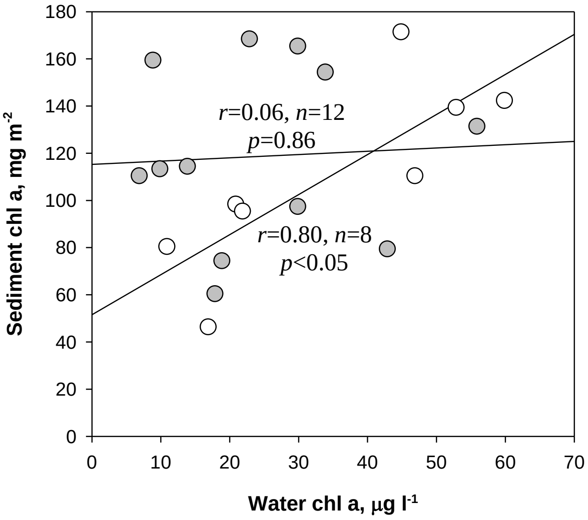


Figure 5.1. Relationship between sediment chlorophyll a and water chlorophyll a in the Curonian lagoon littoral and open lagoon sandy bottoms (grey circles) and open lagoon mud zone (open circles).

Total organic matter content (TOM) appeared to be less informative sedimentary characteristic for indication of organic matter pool and its turnover rate. The lack of relationship between TOM content and benthic metabolism, TOM is unsuitable measure of labile organic matter since mainly reflects the preservation of bulk refractory carbon (Banta et al., 1995; Soetaert et al., 1997), particularly in areas with periodically occurring sediment resuspension (Cowan & Boynton, 1996). Furthermore, increase of organic material in marine sediment leads to decreasing degradability (Köster et al., 2005). In contrast to TOM, dissolved organic carbon had opposite distribution patterns in the Curonian lagoon, what shows fine sandy sediments being a primary site for accumulation of dissolved organic carbon.

In general, organic matter supply to the Curonian lagoon sediments is the net result of different inputs, including both pelagic and benthic sources, controlled by light climate, phytoplankton biomass and hydrodynamic forcing. Since carbon production and its further mineralization can be main regulators of a quantity and a quality of the benthic nutrient cycling and fluxes (Eyre & Ferguson, 2002), all these factors should be considered when evaluating sedimentary oxygen uptake and nutrient cycling in the sediments of the Curonian lagoon.

5.2. Patterns of benthic oxygen uptake in the eutrophic lagoon

Surface sediments in estuarine systems display large variability of oxygen demand due to seasonal evolution of water temperature, organic matter input and variable bottom water oxygenation (Rasmussen & Jørgensen, 1992; Jørgensen, 1996; Rysgaard et al., 1998; Thamdrup et al., 1998; Glud et al., 2003; Eyre & Ferguson, 2005). Furthermore, other environmental and biological factors such as development of microphythobenthos and distribution of benthic macrofauna can amplify the small-scale spatial variability of benthic processes (Jørgensen, 1996; Bartoli et al., 2003; Eyre & Ferguson, 2005; Nizzoli et al., 2007). In the present study, however, measured TOU and calculated DOU rates were characterized by relatively low level of variability (coefficients of variation 20.6±10.7 and 18.6±11.2% respectively) suggesting low spatial heterogeneity and confirming sufficient accuracy of sampling, incubation and microprofiling procedures.

Seasonality and frequent ice cover in winter time is a typical feature of the Curonian lagoon, (Žaromskis, 1996); therefore strong seasonal variation of water temperature could be expected as main controlling factor of total sediment oxygen consumption. Dramatic algal blooms start in early spring and extend over the summer and autumn months ensuring a prolonged input of fresh organic matter to the sediment (Olenina, 1998; Pilkaitytė & Razinkovas, 2006, 2007). In this context 2009 was an exceptional year, with cyanobacterial bloom still present in late October (Fig. 3.1). The eight-fold increase of sediment oxygen demand from March to July is likely due to a combination of higher water temperatures and increased organic matter input to the surface sediments after spring phytoplankton bloom. However, despite the steep drop in temperature from July to October the sediment oxygen uptake decreased very little in the littoral zone and open lagoon muddy areas, confirming complex interaction of factors in shaping biogeochemical cycling and nutrient exchange at the sediment–water interface (Banta et al., 1995; Cowan & Boynton, 1996). Similar tendencies have also been found in polar, temperate and tropical coastal systems (Banta et al., 1995; Rysgaard et al., 1998; Eyre & Ferguson, 2005).

Results of multivariate analysis showed water chlorophyll *a* having a significant impact on the oxygen uptake, therefore settled fresh phytoplankton plays an important role in determining high sediment oxygen uptake rates. Sediment microbial communities can utilize labile phytodetritus independently from temperature (Rysgaard et al., 1998; Eyre & Ferguson, 2005), however microphythobenthos can also supply heterotrophs with labile organic matter (Middelburg et al., 2000) and could be a significant component of benthic oxygen uptake during night (Christensen et al., 1990; Margalhães et al., 2002). The analysis of littoral surface sediment collected in March and July suggest the presence of microphythobenthos (Sundbäck, personal communication) and sediment chlorophyll *a* was an important explanatory variable when a single factor effects on sediment oxygen dynamics were considered. Weakly related water and sediment chlorophyll *a* values in shallow sandy sediment also demonstrate that microphythobenthos can be abundant in these sites, however further quantitative analysis is required to estimate its potential contribution to the total sediment oxygen uptake.

According to RDA results, sediment oxygen uptake rates in this study were also tightly related to oxygen saturation in the overlying water. During the sampling period in the Curonian lagoon oxygen saturation values were typically below 100% and this may well explain low oxygen penetration depth in the sediment. This relationship is also supported by data from both littoral sites, where high oxygen saturation values reaching 90-100% in October coincide with the highest measured oxygen penetration depth values. Regulation of oxygen penetration depth and sediment oxygen uptake by the water column oxygen saturation was also found in temperate estuarine system (Rasmussen & Jørgensen, 1992; Glud et al., 2003).

The sediment TOM was negatively related to OPD and its pool in sandy bottoms was lower by a factor >10 when compared to deeper mud dominated sites. In spite of this, TOM seems to be a weak predictor of oxygen uptake in the Curonian Lagoon sediments. Elevated oxygen uptake rates measured in sandy sediments were comparable or even higher than those measured at organic-rich sites. This demonstrates faster benthic metabolism response and possibly higher turnover rates of fresh organic matter in shallow littoral sand rather than in deeper areas after sedimentation pulses of pelagic organic matter. Similarly, other authors demonstrated (Hopkinson et al., 2001; Köster et al., 2005; Ferguson et al., 2007; Pusceddu et al., 2009), that microbial and faunal metabolism is driven by the macromolecular quality of organic matter and its availability rather than by the total organic pool.

Although the Curonian lagoon is characterized by generally low number and patchy distribution of large burrowers (Daunys, 2001, Gasiūnaitė et al., 2008), estimated TOU to DOU ratios in range between 1.5 and 2.2 at shallow sandy sites suggest the possible influence of benthic fauna mediated oxygen uptake, which may include both faunal respiration and oxygen uptake around the burrow walls. Occasional increase of total to diffusive ratio in October at the site closest to the lagoon mouth was most likely associated with temporary sediment colonization by the brackish water polychaete *Marenzelleria neglecta*, since species distribution and abundance in the lagoon is highly dependent on seawater inflows (Daunys et al., 2000). Higher total to diffusive flux ratio may be subject to local immigration of this deep burrowing (up to 30 cm) species, while relatively constant total to diffusive rates (1.4-1.5) in freshwater littoral sites were most likely caused by burrowing and respiration activity of *Stichochironomus*, the only bioturbating taxa present in these sediments. According to the data on benthic macrofauna in study sites on March and July (Ruginis, not published), *Stichochironomus* individuals were exclusively associated with shallow sediment and their average density was relatively stable during the two sampling periods (1230±200 ind m^{-2} and 1290±220 ind m^{-2} in March and July, respectively). Sandy and muddy open lagoon sites, however, appeared to be poorly bioturbated and diffusive oxygen uptake was very similar to the total oxygen demand (except in the open lagoon sandy sediments in July). This is supported by existing knowledge on distribution of benthic macrofauna (Daunys, 2001) and low numbers of burrowers (mainly small chironomids) in these bottoms.

5.3 Denitrification in the lagoon sediment: early spring and midsummer cases

Conventionally sedimentary denitrification is the most important nitrogen removal pathway in estuarine environment (Seitzinger, 1988; Risgaard-Petersen et al., 2003, 2004b; Hietanen, 2007; Jäntti el al., 2011). In temperate coastal marine and estuarine environments, denitrification typically shows maximum in spring with decreasing rates towards summer and then a next peak in late autumn with low rates during winter (Jørgensen & Sørensen, 1985; Jensen et al., 1988; Jørgensen, 1989). In boreal environments the highest N_2

production rates dominate in autumn–early winter and the lowest in spring (Hietanen & Kuparinen, 2008; Jäntti el al., 2011). Seasonal and spatial patterns of denitrification are shaped by a set of environmental factors such as organic matter supply, NO_3^- concentration in the overlaying water column, nitrification, oxygen penetration depth and microphythobenthos (Christensen et al., 1990; Risgaard-Petersen et al., 1994; Sundbäck & Mile, 2000; Mayer et al., 2001; Risgaard-Petersen, 2003; Pinã-Ochoa & Álvarez-Cobelas, 2006; Trimmer & Nicholls, 2009 and references therein).

In the Curonian lagoon large seasonal variations in denitrification primarily occurred due to the dramatic variations in the NO_3^- load (RDA analysis, Fig. 5.3). Negative correlation between water chlorophyll *a* and NO_x^- concentration (r=-0.74, p<0.05) suggest that phytoplankton may strongly compete for nitrates with denitrifiers. Hence, denitrification driven by nitrate diffusion from the overlaying water was decreased up to 87% in transition between spring and midsummer and this led to approx. 30% lower total denitrification rates (Dtot) in the dark (Fig. 4.15). Eyre and Ferguson (2002) proposed, that decreasing denitrification rates reflect NO_3^- availability and this agrees well with observations in other systems, where relationships between NO_3^- supply and denitrifying activity are justifying nitrate availability being a major controlling factor for denitrification (Christensen et al., 1990; Nielsen et al. 1990; Pinã-Ochoa & Álvarez-Cobelas, 2006). Typically NO_3^- arrives into denitrification zone either from the near bottom water layer or is supplied by sediment nitrification. In temperate systems with nitrate concentrations in range of 20–200 µM in water column, denitrification is supported by NO_3^- diffusion from the overlaying water (Christensen et al., 1990; Nielsen et al., 1990; Rysgaard et al., 1995; Ogilvie et al., 1997; Mayer et al., 2001). At low nitrate concentrations in summer (<10-25µM), however, the main NO_3^- source for denitrification is nitrification (Rysgaard et al., 1993, 1995; Stockenberg & Jonhstone, 1997; Hietanen & Kuparinen, 2008). In the Curonian lagoon denitrification was fueled by NO_3^- from overlaying water column at concentrations of 72.4–198.0 µM in spring, while in midsummer at NO_x^- concentrations below 5 µM denitrification was primarily maintained by nitrates produced through nitrification.

Oxic conditions in the surface sediment favour denitrification, if it is coupled to the sediment nitrification (Jensen et al., 1994; Lorenzen et al., 1998). On the other hand, when denitrification is based on nitrate transport from the overlaying water, thick oxic zone may reduce denitrification rate due increased diffusion path of NO_3^- (Christensen et al., 1990; Jensen et al., 1994; Rysgaard et al., 1995). In the Curonian lagoon, however, the thickness of the oxic zone plays minor role in control of both nitrification–denitrification coupled and water column supported denitrification. In spring benthic respiration was negligible due to low water temperature and this led to the thick oxic zone (up to 6 mm). Consequently, low ammonification rate most likely limited nitrification and its coupling to the denitrification. Due to high NO_x^- concentrations in the water column and low benthic metabolism NO_x^- deeply penetrated into sediments supporting water column driven denitrification pathway. In midsummer, however, extremely decreased NO_3^- concentrations and thin oxic zone (<1mm) favoured nitrification–denitrification coupling in all studied sites.

The Christensen et al. (1990) model applied to predict denitrification based on NO_x^- transport from the overlaying water in the dark gave relatively consistent results (r^2=0.85, p<0.05) with the rates measured in the deeper mud in the Curonian lagoon (Fig. 5.2.). Although the model overestimated denitrification rates in the range between 60 and 90 µmol m^{-2} h^{-1}, the main results indicate that water column denitrification can be predicted reasonably well on the basis of only few variables. For sandy sites, however, the correlation between Christensen model results and measured data was very weak (r^2=0.1, p=0.67), and expected nitrogen removal is much higher as compared to measured rates. Furthermore, the model predicts that increased NO_3^- concentration in the overlaying water will increase denitrification activity in the muddy sediments.

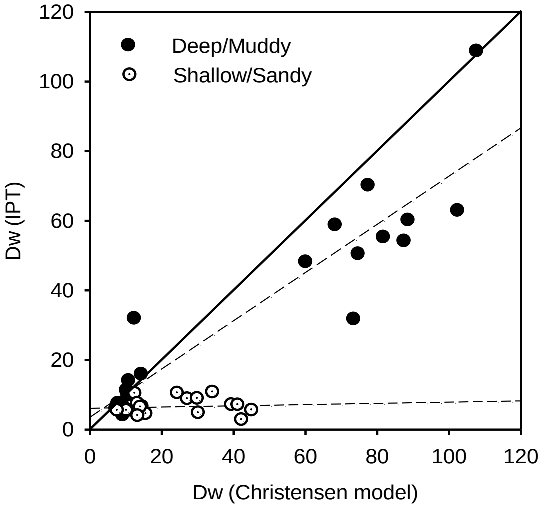


Figure 5.2. Relationship between measured denitrification by isotope pairing technique (Dw (IPT)) and predicted by Christensen et al. (1990) (Dw (Christensen model)); black circles represent mud, open circles - shallow sandy sediments and lines indicate trends.

In spite of substantially higher (>80%) NO_x^- porewater concentrations in the shallow littoral autotrophic sediment, denitrification rates coupled with sediment nitrification were more than 80% lower as compared to the relatively deep heterotrophic sediment (Fig. 4.15). Negative relationship (r=-0.74, p<0.05) between sediment chlorophyll *a* and total denitrification rates (primary coupled nitrification–denitrification in midsummer) may indicate microphythobenthos activity. Data from 18 European estuarine systems demonstrate (Risgaard-Petersen, 2003), that denitrification coupled with nitrification in autotrophic sediments is significantly lower than in heterotrophic in case of 90% of all measurements (median 4.2 versus 20.3 µmol N m^{-2} h^{-1} respectively,). Measurements in shallow sediments revealed that microphybenthos can successfully compete with denitrifiers for nitrates (Rysgaard et al., 1994; Risgaard-Petersen, 2003; Sundbäck et al., 2000, 2006), therefore denitrification could be less important pathway of nitrogen removal in sediments inhabited by microphythobenthos (Sundbäck & Miles, 2000; Risgaard-Petersen, 2003). Sundbäck and Miles (2000) found that rates of nitrogen assimilation by microphythobenthos were greater than those by denitrification by 1-2 orders of magnitude in temperate sediments. Moreover, in our study denitrification coupled with nitrification was found 90% lower in at site (Lit_1N) impacted directly by seawater inflows. It known, that fluctuating salinity can affect ion exchange capacity by enhancing the NH_4^+ transport rate, and decreasing availability to nitrifying bacteria (Gardner et al., 1991; Rysgaard et al., 1999). However that can be also explained by salinity inhibitory effect on relevant groups of microorganism (Rysgaard et al., 1999). Stehr et al. (1995) and Cebron et al. (2003) also showed that salinity is important in controlling abundance of ammonium oxidizing bacteria.

5.4. Seasonal changes in nutrient cycling and exchange at sediment–water interface

Nutrient cycling and exchange at the sediment–water interface exhibited a considerable seasonal variation in the Curonian lagoon (Fig. 4.10-15). According to the results of redundancy analysis (RDA), 13 selected environmental characteristics explain 58.2% of the total variance in nutrient exchange at the sediment–water interface (Fig. 5.3). Applied permutation tests revealed that water column nutrient and chl *a* concentrations, along with sediment total organic matter content are the most significant factors for nutrient cycling and exchange at the sediment water interface in the Curonian lagoon (see to Table 5.1). Temperature was also important when a single factor tests were run with environmental variables individually.

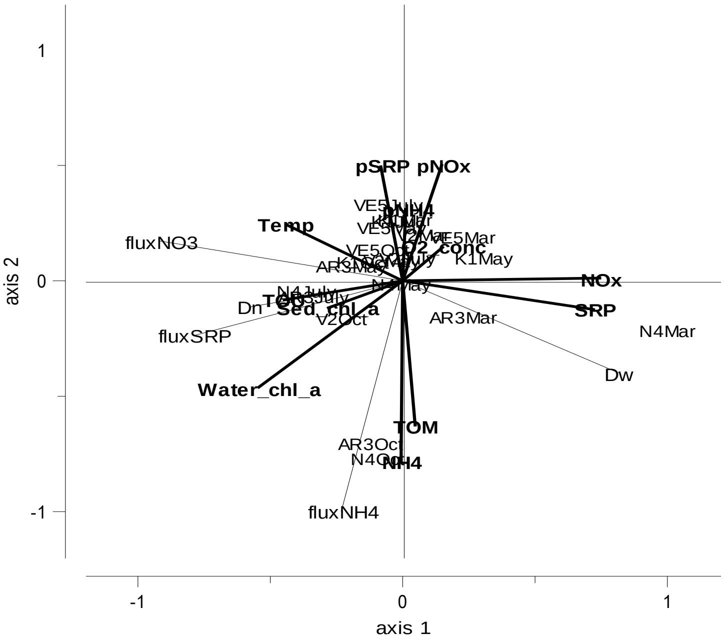


Figure 5.2. Redundancy analysis (RDA) triplot showing relationships between six response variables (fluxNH4 – ammonium flux; fluxNO3 – flux of nitrate; fluxSRP – flux of soluble reactive phosphorus; Dn – denitrification coupled with nitrification; Dw – denitrification coupled nitrates from overlaying water) and 11 explanatory variables (Sed_chl_a – chlorophyll a concentration in the sediment surface layer; TOM – total organic matter content; Temp – water temperature; Water_chl_a – water chlorophyll a concentration; O2_conc – water column oxygen concentration; NH4 – water column ammonium concentration; NOx – water column nitrate+nitrite concentration; SRP - water column soluble reactive phosphorus concentration; TOU – total oxygen uptake; pNH4 – porewater ammonium concentration; pNO3 - porewater nitrate concentration; pSRP – porewater soluble reactive phosphorus;). Data labels correspond sampling sites (K1-LitS_1N, VE5-LitS_5S, V2-OLms_2, AR3-ShM_3 and N4-ExpM_4) and sampling periods (Mar-March, May, Jul-July, Oct-October).

Table 5.1. Numerical output of redundancy analysis (RDA) results; Sed_chl_a – chlorophyll *a* concentration in the sediment surface layer; TOM – total organic matter content; Temp – water temperature; Water_chl_a – water chlorophyll *a* concentration; O2_conc – water column oxygen concentration; NH4 – water column ammonium concentration; NOx – water column nitrate+nitrite concentration; SRP - water column soluble reactive phosphorus concentration; TOU – total oxygen uptake; pNH4 – porewater ammonium concentration; pNO3 - porewater nitrate concentration; pSRP – porewater soluble reactive phosphorus.

Variables	**Eigenvalue as %** (of sum all eigenvalues)	**Marginal effects**	**Conditional effects**	**F-statistic**	***p***
SRP	**27.91**	**0.24**	**0.24**	**5.634**	**0.005**
NOx	**25.50**	**0.22**	**0.08**	**3.618**	**0.015**
Water_chl_a	**19.68**	**0.17**	**0.09**	**3.143**	**0.030**
NH4	**15.46**	**0.13**	**0.13**	**3.536**	**0.015**
TOM	**15.07**	**0.13**	**0.11**	**3.463**	**0.025**
Temp	11.41	0.10	0.03	1.405	0.315
TOU	9.61	0.08	0.01	0.539	0.665
pNOx	8.78	0.08	0.05	1.768	0.155
pSRP	8.63	0.07	0.05	2.236	0.115
Sed_chl_a	6.45	0.06	0.02	0.917	0.400
O2_conc	3.04	0.03	0.03	1.178	0.290
pNH4	2.98	0.03	0.01	0.541	0.650

Multivariate analysis demonstrated that seasonal dynamics of water chlorophyll *a* is tightly coupled with seasonal variation in temperature variation and nutrient availability into lagoon, both forming a main driving force for biogeochemical nutrient cycling and exchange processes (Fig. 5.3). Intensive snow melting in the river catchment delivers high amount of bio-available nitrogen into the lagoon during spring (Table 4.1) and triggers the diatom bloom. Thriving diatoms result in a flux of fresh labile organic matter to the surface sediments, which mostly include vital cells (mainly *Thalassiosira* and *Fragilaria* species; Sundbäck pers. com.). This confirms earlier findings on capability of deposited diatoms to remain active and function as benthic microalgae (Lomstein et al., 1990; Eyre & Ferguson, 2005). Measured net primary production and observed differences between light and dark nutrient fluxes at the sediment–water interface (particularly increased NH_4^+ and NO_x^- uptake in light) support the fact that physiologically active settled diatoms effectively assimilate nutrients turning the bottom sediment in a net sink of nitrogen and phosphorus in March (Fig. 4.10, 4.12 and 4.14). Lomstein et al. (1990) suggested that deposited diatoms in Arhus Bay can even persist throughout summer and continue their assimilation of nutrient from bottom water and porewater. On the other hand, benthic metabolism and organic matter mineralization rates in the Curonian lagoon were extremely low in early spring as indicated by low sediment oxygen uptake and ammonium nitrogen transport rates (Fig. 4.6, 4.10). High NO_x^- flux into the sediments during this period was probably a result of suppressed nitrification due to low ammonium concentration within the thick oxic zone. In absence of nitrification–denitrification coupling in the sediment, NO_x^- transported from the water column can be taken up by denitrifiers (Meyer et al., 2001). This pathway contributed up to 38% of the total NO_x^- uptake by sediment. The established thick oxic layer can also successfully increase sediment capacity to trap soluble reactive phosphorus from porewater (Jensen et al., 1995).

Nevertheless, nutrients incorporated into pelagic primary producers were transferred to the surface sediment, where they can be buried or rapidly remineralized with sudden nutrient release to the bottom water. Experimental simulations of spring deposition of diatoms demonstrated that efflux rates of NH_4^+, SRP and uptake of NO_x^- are immediate increasing (Conley & Johnston, 1995). As a result, in the end of spring extremely reduced oxic layer can obviously decrease nitrification activity but these processes, however, were not reflected in the dynamics of sediment NH_4^+ and NO_x^-. In spite of extremely decreased thickness of oxic zone, diffusive transport of oxidized nitrogen was still measured likely as a result of nitrification. Therefore, in spite of NO_x^- depletion in the water column after the diatom bloom at the end of spring, enhanced NO_x^- uptake could be maintained by benthic microalgae due to low water chlorophyll *a* concentrations and increased transparency.

Temperature and water chlorophyll *a* concentrations increase in midsummer was followed by the increased sediment chlorophyll *a* and higher oxygen uptake rates, particularly in the open lagoon sites. In the open lagoon mud, elevated water chlorophyll *a* concentrations resulted in more intensive inputs of fresh organic material and considerably enhanced total oxygen uptake by sediments (r=0.83, p<0.05). Increased total oxygen uptake in these sediment significantly reduced oxic layer with positive feedback to release of soluble reactive phosphorus (TOU *vs* SRP flux, r=0.72, p<0.05; Fig. 5.3). It is widely accepted, that inorganic P tends to be released to the water column from reduced sediments (Jensen et al., 1995), and such phenomena is well documented in the adjacent Baltic Sea during anoxic periods (Westman et al., 2003; Vahtera et al., 2007). Enhanced SRP release from open lagoon mud most likely sustained N_2–fixing cyanobacteria growth, which in turn supports high influx of organic material to the surface sediment. Such sequence obviously demonstrate part of self – sustaining ”vicious circle”: intensive sedimentation of organic material → increasing extent of anoxic bottoms → enhanced phosphorus release (Vahtera et al., 2007).

Delivered phytodetritus was rapidly mineralized and was positively related to the increased ammonium release from the sediment (sediment chl *a* *vs* NH_4^+ flux, r=0.74, p<0.05), which in turn was reflected in higher NH_4^+ concentrations in the water column (r=0.93, p<0.05). RDA analysis showed that higher NH_4^+ release rates coincided with lower amounts of oxidized nitrogen forms in porewater (Fig. 5.3). Since nitrification is strongly regulated by oxygen availability (Maeyer et al., 2001), this suggest unfavorable reduced conditions for nitrification in mud. In spite of extremely thin oxic zone the elevated NO_x^- concentrations were detected at sediment depth of 0.5–2 cm, while nitrification typically occurs only in the lowest part of the oxic zone (Maeyer et al., 2001). This could be explained by high numbers of actively irrigating chironomids (density up to 4190 ind m^{-2}, Ruginis, pers. comm.) that could enhance oxygen penetration depth and accelerate nitrification (Stief et al., 2005; Stief & de Beer, 2006). On the other hand, elevated NO_x^- concentrations in the deeper layers could be also partly attributed to the sediment removal by core extruder and subsequent slicing effects, which could have forced downward transport of solutes as demonstrated by small–scale measurements (Rysgaard et al., 2004). In spite of this, estimated total fluxes at the sediment water–interface in midsummer showed that most of sediments type became a source of NO_x^- to the overlaying water. Multivariate analysis revealed that depleted NO_x^- concentration in the water column can significantly elevate its transport from the sediment (r=-0.96, p<0.05) particularly in the open lagoon mud sediment.

Autumn period in the Curonian lagoon is primarily characterized by lower temperatures, increased nutrient concentrations in the water column and still relatively high water chlorophyll *a* values. In spite of decreasing temperature benthic metabolism remained elevated in the littoral sand and open lagoon mud (Fig. 4.6). However, in spite of intensive benthic metabolism nutrient concentrations in the porewater considerably decreased in open lagoon mud. This presumably was caused by porewater flushing and slower nutrient accumulation in sediment during autumn. This is supported by the high NH_4^+ and NO_x^- concentrations in the water column, which cannot be explained by low riverine nitrogen supply, which are still low in this period. Our *in situ* observations in the Curonian lagoon demonstrated that stormy winds and subsequent sediment resuspension could cause up to 8 fold concentration increase in the water column within hours (Zilius, unpublished data).

In the open lagoon muddy sand, lower water temperature and sediment chlorophyll *a* imposed lower rates of total oxygen uptake and consequently lower rates of nutrient remineralization and accumulation within the sediments (Trimmer et al., 1998; Sundbäck et al., 2000). Nevertheless, results obtained from shallow littoral sand and open lagoon muddy sand demonstrate complex nutrient cycling and exchange at the sediment–water interface, mainly controlled by organic carbon producers. Single positive relationship between sediment chlorophyll *a* and NH_4^+ flux (r=0.70, p<0.05) suggest that OM produced by benthic microalgae can be remineralized and transferred to the water column, therefore benthic microalgae can be also important in exchange processes.

5.5. Do benthic microalgae play an important role in nutrient exchange in the turbid estuary?

Benthic microalgae conventionally are the driving component in benthic metabolism and nutrient exchange in temperate shallow and illuminated sediments (Risgaard-Petersen et al., 1994; Rysgaard et al., 1995; Sundbäck et al., 2000; Köster et al., 2005). Previous studies showed that sandy sediments particularly may function as sink for nutrients during winter until early summer, when nutrient assimilation and retention by benthic microalgae is more important than heterotrophic pathways (Sundbäck & Miles, 2000; Sundbäck et al., 2006). However, in highly productive shallow coastal areas the equilibrium between pelagic and benthic primary production is generally controlled by turbidity and light penetration (Gerbersdorf et al., 2005; Sundbäck et al., 2004; Köster et al., 2005). In the Curonian lagoon high phytoplankton concentrations reduce near bottom irradiance level (up to ~99 % of surface water) down to 6–20 $\mu E\ m^{-2}\ s^{-1}$ in less than 2 m depth (Zilius, unpublished data.). Although benthic microalgae remain viable at such irradiance levels (Sundbäck et al. 2004), light in deeper lagoon area is attenuated close to zero (Zilius unpublish.) and the role of benthic microalgae in assimilation of remineralized nutrient is negligible.

Interesting fact, that most of physiologically active “benthic microalgae” in shallow sand area early in spring were mostly attributed to the deposited planktonic diatoms in early spring, whereas toward to summer this type of sediment was mainly inhabited by typical benthic microalgae towards the summer (Sundbäck pers. com.). In deeper open lagoon mud, however, the settled vital planktonic species were recorded during the entire study period.

Applied benthic trophic state index (BTSI) (Rizzo et al., 1998) for the Curonian lagoon sediment showed that shallow littoral and open lagoon sand were from highly atrophic to net autotrophic during the study period, while open lagoon mud was primarily net heterotrophic. Net annual primary production from gross primary production values (photosynthetic quotient=1.2; Glud et al., 2002) between 2.8 and 105.4 mg C m^{-2} h^{-1} indicate, that benthic organic carbon production contributed less than <1% of pelagic production measured in water column in midsummer (Krevs et al., 2007). However, integration of daily oxygen flux values showed that lagoon sediments were heterotrophic during studied period, except the single sandy site in the littoral. Nevertheless light stimulates benthic respiration activity by accelerating release of photosynthetically produced organic carbon (Köster et al., 2005). Peaks of dissolved organic carbon concentration in the first millimeters of the upper sediment suggests that deposited microalgae or living microphythobenthos possibly produced measureable amount of labile carbon, which can affect sediment oxygen uptake directly (Köster & Meyer-Reil, 2001).

Benthic microalgae can remain viable even if they are not exposed to light for long periods and can start photosynthesizing when the water column becomes more transparent (Lomstein et al., 1990; Glud et al., 2002). In arctic sediment settled diatoms can efficiently optimize their photosynthetic apparatus under existing light conditions (Glud et al., 2002). Our measurements of seasonal nutrient exchange at the sediment–water interface by means of light and dark incubation of intact sediment cores demonstrated nitrogen uptake from the water column by benthic microalgae in most of littoral and open lagoon sandy sites.

The observed SRP exchange rates were relatively uniform (Fig. 4.14) in March, May and October, however, in July the variability between replicates has doubled. This variation could be attributed to a number of processes including SRP release from adsorbed ferric hydrooxides and precipitation due to extended oxic layer of bioturbating macrofauna and benthic microalgae or vital sedimentated phytoplankton cells activity. Known, that microphythobenthos activity may also result in temporary trap of inorganic phosphate by direct assimilation or indirect retention of soluble reactive phosphorus efflux from sediments due to reoxidation of Fe(II) (Sundbäck & Graneli, 1988). Even if light is limited, SRP can be taken up by settled phytoplankton cells, as it was observed in mud sediment.

Difference between estimated diffusive nutrient transport rates and measured total flux at the sediment–water interface can be at least partly attributed to a presence of benthic microalgae (Fig. 5.4-5.6). In general nutrients were taken up from both overlaying water and porewater in all three studied sedimentary environments. Obtained differences between measured total and calculated diffusive fluxes, excluding macrofauna activity, show that benthic microalgae in surface sediment can retain up to 20.2 N mmol m^{-2} d^{-1}

and 0.3 P mmol m^{-2} d^{-1}, what makes a 70-100% and 50-100% of N and P respectively diffusing towards near-bottom water. The most active nutrient assimilation was calculated for littoral sands, where sediment permanently acted as sink for nutrients (Fig. 5.4). In the open lagoon muddy sand high benthic microalgae activity was also observed, however, but the most of nutrient were assimilated in midsummer. Results show that benthic microalgae can modify N:P ratio of regenerated nutrients in surface sediment. Assimilation of nitrogen in late spring reduced N:P ratio in the open lagoon mud sediment to 1:4, which favour cyanobacteria blooms., In summer and autumn, however, N:P ratio was increased due to higher P utilization in comparison to N.

5.6. Importance of sediment in benthic pelagic–coupling

Many studies focus on functioning of estuarine and lagoon ecosystems as traps of nutrient between land–seas and oceans (Wollast, 1983; Seitzinger, 1988; Nixon et al., 1996; Ogilvie et al., 1997). This research became particularly relevant in the northern hemisphere where external nutrient sources are commonly present (Jørgensen & Sørensen, 1985; Ogilvie et al., 1997; Trimmer et al., 1998). Nutrients of terrestrial origin undergo a series of biogeochemical transformations when they pass through transitions zones as estuaries and lagoons (Wollast 1983, Seitzinger 1988, Ogilvie et al. 1997). They can be incorporated into benthic and pelagic primary producers, grazed by herbivores and rapidly recycled to the water column or they can be retained in surface sediments as buried organic matter or co-precipitated with other elements (Howarth, 1988; Conley & Malone 1992; Kemp et al., 1992; Cowan & Boynton 1996; Conley et al., 2009). In contrast, irreversible biogeochemical nutrient removal from ecosystem is largely related to the eutrophication issues (Seitzinger, 1988).

Capacity of the Curonian lagoon sediment to remove oxidized nitrogen from the water column was positively related with NO_x^- concentrations in water column. In the end of spring up to 70% of NO_x^- was taken up by sediment and further denitrified or assimilated by benthic microalgae (Fig. 5.4-5.6). In summer different types of sediment functioned as a source of NO_x^- to the water column and daily balance of NH_4^+ and NO_x^- shows, that sediment could increase the concentration in the overlaying water column concentration by 14% per day. However, sediment role in removing or enriching water column is strongly regulated by water residence time (Nixon et al., 1996; Silvennoinen et al., 2008), therefore open lagoon mud, with average residence time of overlying water column of 100 days, can be important to eutrophication processes. Although mean water residence time is lower in shallow littoral and open lagoon muddy sand areas (Ferrarin et al., 2008), active benthic-pelagic coupling processes may also occur due to low depths (Fig. 5.4 and 5.5).

Sandy sites in the Curonian lagoon were typically acting as a sink for soluble reactive phosphorus, and sediment removed up to 4% of SRP daily amount in the overlaying water during the entire period (Fig. 5.4 and 5.5).

LITTORAL SAND (1 m depth)

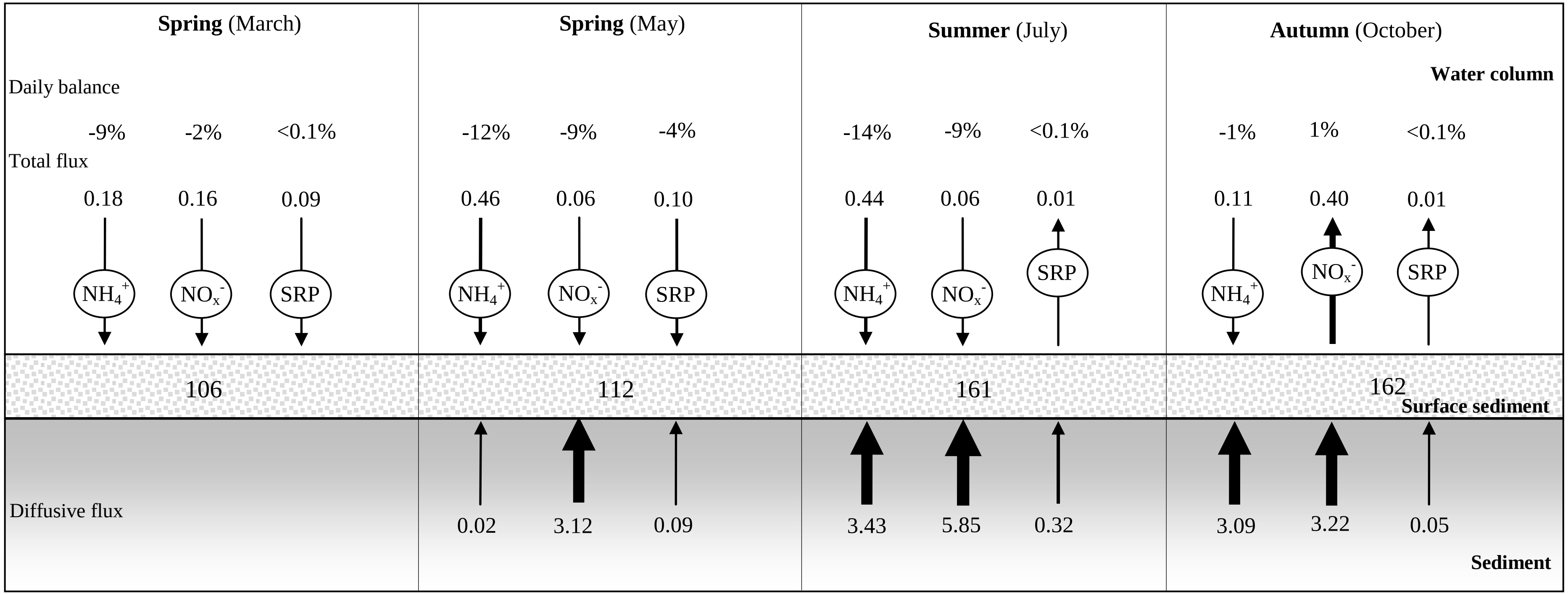


Figure 5.4. Total and diffusive fluxes (mmol m^{-2} d^{-1}) at the sediment–water interface and their impact to the nutrient concentrations in the overlaying water column (1.0 m); chlorophyll *a* content (mg m^{-2}) shown in surface sediment layer.

OPEN LAGOON MUDDY SAND (1.7 m depth)

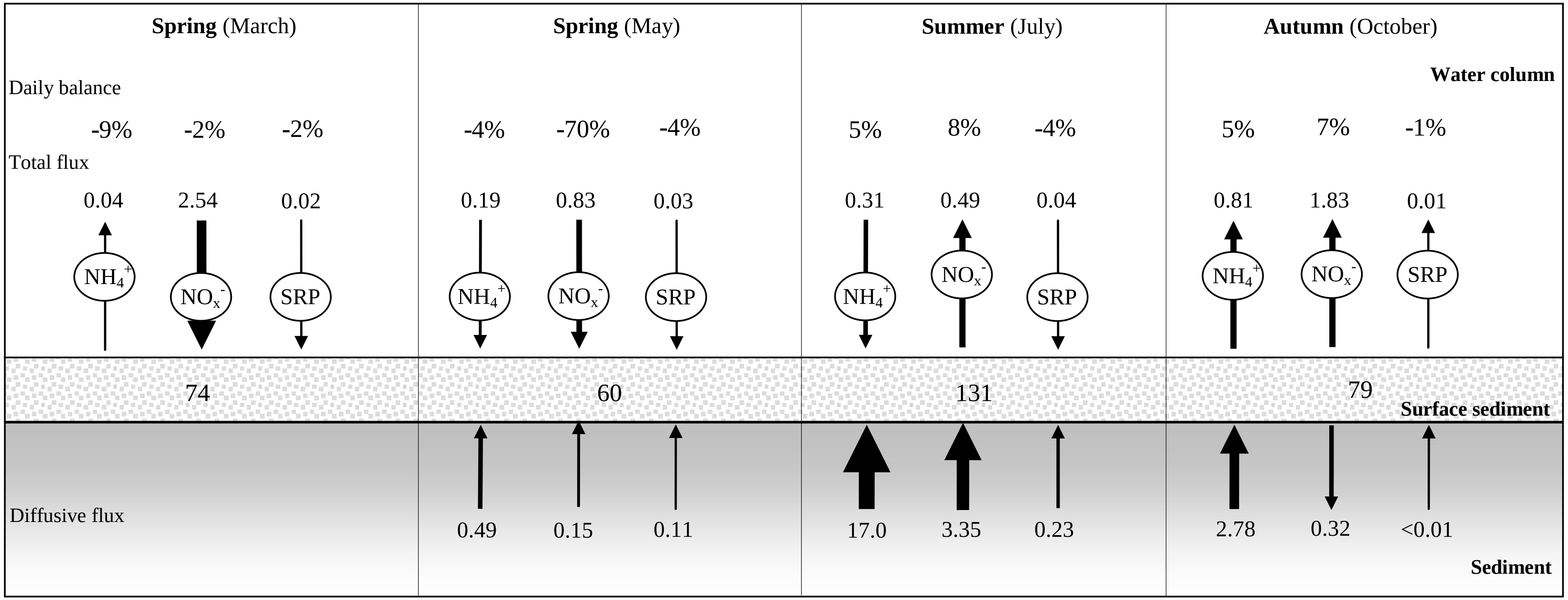


Figure 5.5. Total and diffusive fluxes (mmol m^{-2} d^{-1}) at the sediment–water interface and their impact to the nutrient concentrations in the overlaying water column (1.7 m); chlorophyll *a* content (mg m^{-2}) shown in surface sediment layer.

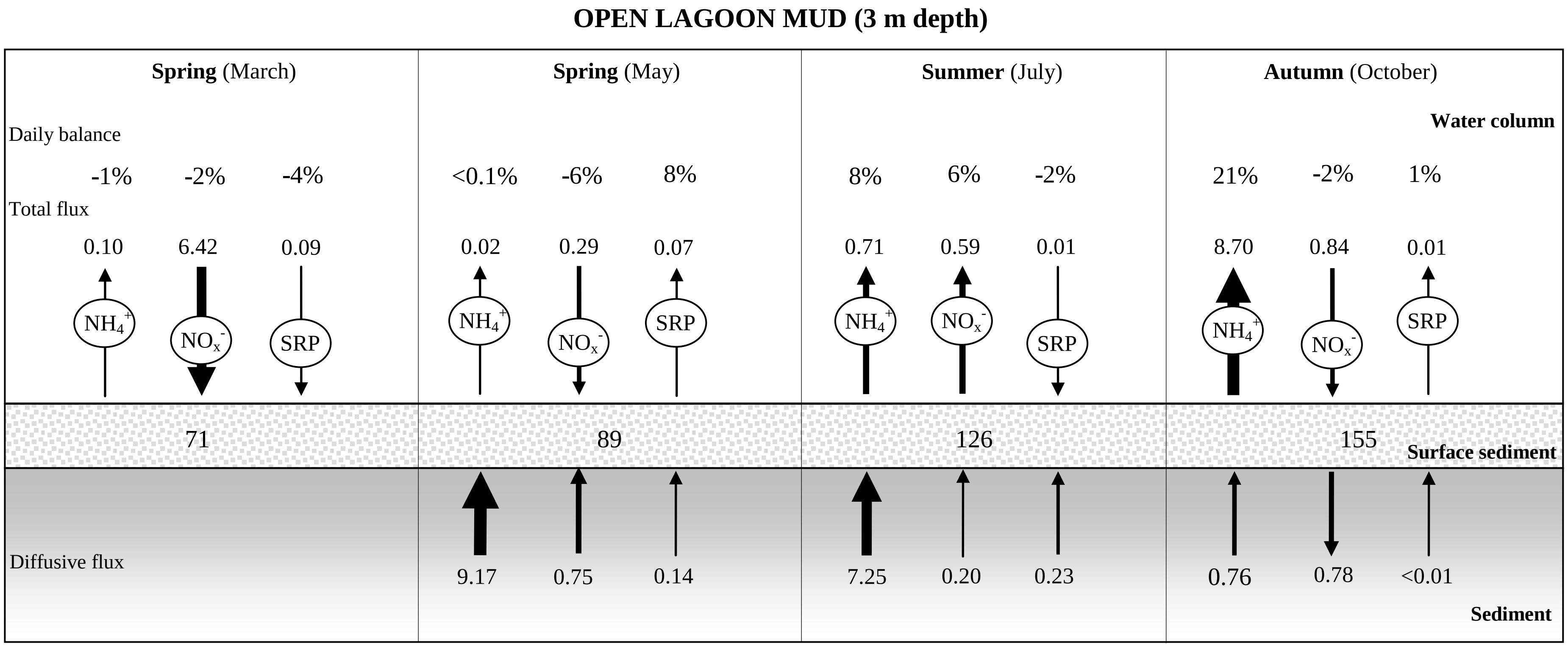


Figure 5.6. Total and diffusive fluxes (mmol m^{-2} d^{-1}) at the sediment–water interface and their impact to the nutrient concentrations in the overlaying water column (3.0 m); chlorophyll *a* content (mg m^{-2}) shown in surface sediment layer.

Muddy sediment, was both acting as SRP source or sink to SRP depending on season. In late spring SRP release enhanced the concentration in the overlaying water column by 8% and could accelerate summer cyanobacterial bloom, since tight coupling between water chlorophyll *a* and seasonal nutrient changes was observed. Generally sediment role shifted from source to sink along the depth gradient, being source in deep and sink in shallow sites. The role of shallow sandy sediment as a sink for nutrients is in a good agreement with results from other studies (Sundbäck et al., 2000; Eyre & Ferguson, 2002).

It is widely accepted, that mineralization of organic matter produced during spring bloom may fuel summer hypoxia or anoxia (Malone et al., 1986). In the Curonian lagoon high water column productivity can potentially initiate hypoxia due to increased sediment oxygen demand. However, in 2009, oxygen uptake by the Curonian lagoon sediment alone (assuming average water column of 3.8 m and dissolved oxygen concentrations varying between 200 and 300 µM) is not likely to result in oxygen depletion unless it is combined with high water column respiration occurring during cyanobacterial blooms when calm climatic condition and higher temperatures prevail. Under such circumstances, with chlorophyll *a* values exceeding 100 µg l^{-1}, the respiration in the water column could play an important role (Krevs et al., 2007) and simultaneously with benthic oxygen uptake may significantly contribute to developing hypoxia particularly during nighttime. Oxygen profiles suggest that oxygen penetration is extremely low for 6 months period from May to October having deep implications for phosphorous cycling (Giordani et al., 1996). Theoretically hypoxia or anoxia could also be established during ice cover periods, when primary production is strongly limited by light and re-aeration is prevented. However, high oxygen penetration depths estimated for March in the study area do not support such a hypothesis.

5.7. Benthic metabolism and denitrification in a context of the Baltic Sea estuaries and bays

This study was carried out in the Curonian lagoon, a transitional system characterized by short term seawater inflows, shallow depths and large seasonal freshwater inflow. This coastal water body is hypertrophic and suffers from plankton blooms, with diatom communities dominating in early spring and cyanobacteria being more abundant in summer. These blooms result in massive inputs of labile organic matter to the bottom sediment (Pilkaitytė & Razinkovas, 2006, 2007). In spring and autumn the algal blooms are fuelled by nutrients from the Nemunas River, whereas remineralization processes in the sediment can drive nutrient supply in summer.

The Curonian lagoon features unique and complex hydraulic circulation patterns including seasonal transition between lake, river and estuarine-like system (Ferrarin et al., 2008). On the other hand extremely low depths increase the role of wind, which impedes water column stratification and maintains elevated oxygen concentration in the near-bottom water layer. Since these features have large spatial and temporal variability, patterns of benthic metabolism in the Curonian lagoon cannot be directly predict from existing knowledge about coastal marine, estuarine and freshwater environments (Jørgensen & Sørensen, 1985; Rasmussen & Jørgensen, 1992; Svensson & Leonardson, 1996 and references therein).

Daily rates of total oxygen consumption (-7 to -46 mmol m^{-2} d^{-1}) in the Curonian lagoon are in range of those reported for other enclosed Baltic areas: e.g. -36.6– -43.0 mmol m^{-2} d^{-1} in Norsminde fjord (Jørgensen & Sørensen, 1985); -19.7– -21.8 mmol m^{-2} d^{-1} in Laholm Bay in the west coast of Sweden (Enoksson & Samuelsson, 1987), -24– -57 mmol m^{-2} d^{-1} in the Gulf of Bothnia (Nedwell et al., 1983), -27 mmol m^{-2} d^{-1} on average in Gulf of Finland (Silvennoinen et al., 2007), -24 mmol m^{-2} d^{-1} on average in Archipelago Sea (Silvennoinen et al., 2007) or -12– -55 mmol m^{-2} d^{-1} in other small brackish bays (Sundbäck et al., 2003).

The highest measured denitrification rates in the Curonian lagoon were typically two-three times higher than in other Baltic Sea areas and neighboring regions (Table 5.2) with the only exception being the Szczecin lagoon, where high denitrification rates have been determined by high external nutrient loading (Dahlke et al., 1998).

Although theoretically denitrification can be overestimated in the coastal sediments of the Baltic Sea due to recently described nitrogen removal throughout anammox process (Hietanen, 2007; Hietanen & Kuparinen, 2008), potential anammox contributes less than 10% to the total N_2 production in the Curonian lagoon bottom sediments (Bartoli et al., in prep.). Similar contribution of anammox was found in other estuarine environments in temperate latitudes (Risgaard-Petersen et al., 2003; Trimmer et al., 2003). Indeed the denitrification remains the main pathway of nitrogen removal in this lagoon, even taking into account high spatio-temporal heterogeneity. Furthermore, denitrification during the year is shifting from being maintained by water column NO_3^- in spring to denitrification coupled with sediment nitrification in summer. Due to the high water residence time in the Curonian lagoon, the capacity to remove nitrogen is much enchanced in comparison to the other estuarine systems in the Baltic Sea.

Table 5.2. Overview of denitrification rates (µmol N_2 m^{-2} h^{-1}) in sediments of the Baltic Sea and other neighboring regions. Measurements obtained by laboratory incubations of intact cores (*- benthic lander), **- annual rates are provided.

Studied area	Denitrification rate	Method	References
Curonian lagoon	6.5-75.3	Isotope pairing	Present study
Szczecin lagoon	83.3**	-	Dahlke et al., 1998
Gulf of Riga	2.8-6.6	Isotope pairing	Sundbäck et al., 1998
Gulf of Finland	3.8-16.7	Isotope pairing	Hietanen & Kuoparinen, 2008
Archipelago Sea	3.8-37.9	Isotope pairing	Silvennoinen et al., 2007
Bothnian Bay, river estuaries	13.8-37.7	Isotope pairing	Silvennoinen et al., 2007
Northern Baltic proper	<1-12.5	Isotope pairing	Tuominen et al., 1998
Southern Baltic and Baltic proper	0.5-28.7	Isotope pairing	Deutsch et al., 2010
Southeast Baltic Sea	0.0-6.6	Isotope pairing	Sundbäck et al., 2006
NE Kattegat	<1-40	Isotope pairing	Sundbäck et al., 2000
Gullmar Fjord (Skagerrak)	0.4-23	Isotope pairing	Sundbäck et al., 2004
Arhus Bay	14.5-19.8*	Isotope pairing	Nielsen & Glud, 1996

CONCLUSIONS

1. Organic matter supply to the lagoon sediments is the net result of different inputs. In deeper open lagoon mud sediment chlorophyll *a* seems to be a good predictor (r=0.80, p<0.05) of water chlorophyll *a*, thus sediment pigment is indicator of the deposition of fresh labile phytodetritus concentrations during spring–autumn period. However water chlorophyll *a* was weakly related (r=0.06, p=0.86) to the sediment chlorophyll *a* values in sandy areas reflecting importance of benthic microalgae.

2. The eight-fold increase of sediment oxygen demand from March (2-3 ^{o}C) to July (18-20 ^{o}C) is likely due to a combination of higher water temperatures and more than 30% increased organic matter input to the surface sediments after spring phytoplankton bloom. However, despite the steep drop in temperature from July to October (7 ^{o}C) the sediment oxygen uptake decreased very little in the littoral zone and open lagoon muddy areas, confirming complex interaction of factors in shaping biogeochemical cycling and nutrient exchange at the sediment–water interface.

3. Elevated oxygen uptake rates measured in organic poor (TOM<1% dw) sandy sediments were comparable or even higher than those measured at organic-rich sites (TOM=12-18% dw). This demonstrates faster benthic metabolism response after sedimentation pulses and possibly higher turnover rates of fresh organic matter in shallow littoral sands than in deeper areas.

4. Multivariate analysis results showed water chlorophyll *a* having a significant impact on the oxygen uptake, which in turn played an important role in reduction of the oxic layer thickness with positive feedback to release of soluble reactive phosphorus (TOU *vs* SRP, r=0.72, p<0.05).

5. Large seasonal variations in denitrification primarily occurred due to the dramatic variations in the NO_x^- load. Denitrification driven by NO_x^- diffusion from the overlaying water was decreased up to 87% in transition between spring and midsummer and this led to approx. 30% lower total denitrification rates.

6. Nutrient exchange measurements at the sediment–water interface by means of light and dark incubation and differences between estimated diffusive and total nutrient transport rates can be at least partly attributed to a presence of benthic microalgae in most of littoral and open lagoon sandy sites. Recorded net primary production and observed differences between light and dark nutrient fluxes at the sediment–water interface (increased by mean 93% and 55%, respectively NH_4^+ and NO_x^- uptake in light) supported the fact that physiologically active settled diatoms effectively assimilated nutrients and caused the bottom sediment functioning as net sink of nitrogen and phosphorus in March.

7. The most of studied shallow sandy sites were functioning as sink to NH_4^+ and SRP on day basis, while deeper mud sediments were a source of nutrient to the water column. Curonian lagoon sediment capacity to remove oxidized nitrogen from the water column was positively related to NO_x^-. In the end of spring up to 70% of NO_x^- was taken up by sediment and further denitrified or assimilated by benthic microalgae.

REFERENCES

1. Aller, R. C., 1998. Benthic fauna and biogeochemical processes in marine sediments: the role of burrow structure. In: Blackburn, T. H. & J. Sørensen, (Eds) Nitrogen cycling in coastal marine environments. John Wiley & Sons, Chichester: 301-338.
2. Almroth, E., A. Tengberg, H. Andersson, S. Pakhomova & P.O.J. Hall, 2009. Effects of resuspension on benthic fluxes of oxygen, nutrients, dissolved inorganic carbon, iron and manganese in the Gulf of Finland, Baltic Sea. Continental Shelf Research 29: 807-818.
3. Almroth-Rosell, E., K. Eilola, R. Hordoir, H.E. M. Meier & P.O.J. Hall, 2011. Transport of fresh and resuspended particulate organic material in the Baltic Sea – a model study. Journal of Marine Systems 87: 1-12.
4. Aplinkos apsaugos agentūra, 2010. Tarpinių ir priekrantės vandenų būklė, ją įtakojantys veiksniai ir būklės gerinimo priemonės.
5. Archer, D. & A. Devol, 1992. Benthic oxygen fluxes on the Washington shelf and slope: a comparison of in situ microelectrode and chamber flux measurements. Limnology and Oceanography 37: 614-629.
6. Arnosti, C., B.B. Jørgensen, J. Sageman & B. Thamdrup, 1998. Temperature dependence of microbial degradation of organic matter in marine sediments: polysaccharide hydrolysis, oxygen consumption, and sulfate reduction. Marine Ecology Progress Series 165: 59-70.
7. Aspila, K.I., H. Agemian & A.S.Y. Chau, 1976. A semi-automated method for the determination of inorganic, organic, and total phosphate in sediments. Analyst 101:187-197.
8. Bally, G., V. Mesnage, J. Deloffre, O. Clariss, R. Lafite & J.-P. Dupont**,** 2004. Chemical characterization of porewaters in an intertidal mudflat of the Seine estuary: relationship to erosion–deposition cycles. Marine Pollution Bulletin 49(3): 163-173.
9. Banta, G.T., A.E. Giblin, J. E. Hobbie & J. Tucker, 1995. Benthic respiration and nitrogen release in Buzzards Bay, Massachusetts. Journal of Marine Research 53: 107-135.
10. Banta, G.T., M. Holmer, M.J. Jensen & E. Kristensen, 1999. The effect of 2 polychaete worms, *Nereis diversicolor* and *Arenicola marina*, on decomposition in an organic-poor and an organic-enriched marine sediment. Aquatic Microbial Ecology 19: 189-204.
11. Barranguet, C., M.-R. Plante-Cuny & E. Alivon, 1996. Microphytobenthos production in the Gulf of Fos, French Mediterranean coast. Hydrobiologia 333: 181-193.
12. Bartoli, M., D. Nizzoli, P. Viaroli, E. Turolla, G. Castaldelli, E. A. Fano & R. Rossi, 2001. Impact of Tapes philippinarum farming on nutrient dynamics and benthic respiration in the Sacca di Goro. Hydrobiologia 455: 203-212.
13. Bartoli, M., D. Nizzoli & P. Viaroli. 2003. Microphytobenthos activity and fluxes at the sediment-water interface: interactions and spatial variability. Aquat Ecology, 37: 341-349.
14. Bartoli M., L. Vezzull, D. Nizzoli, R. Azzoni, S. Porrello, M. Moreno, M. Fabiano & P. Viaroli, 2009. Short-term effect of oxic to anoxic transition on benthic microbial activity and solute fluxes in organic-rich phytotreatment ponds. Hydrobiologia 629:123-136.
15. Berg, P., N. Risgaard-Petersen, & S. Rysgaard, 1998. Interpretation of measured concentration profiles in sediment pore water. Limnology and Oceanography 43:1500-1510.
16. Berner, R.A. 1980. Early Diagenesis: A Theoretical Approach. Princeton University Press, Princeton, New York.
17. Beutler, M., K.H. Wiltshire, B. Meyer, C. Moldaenke, C. Lüring, M. Meyerhöfer, U.-P. Hansen & H. Dau, 2002. A fluorometric method for the differentiation of algal populations in vivo and in situ. Photosynthesis Research 72: 39-53.
18. Binnerup, S.J., K. Jensen, N.P. Revsbech, M.H. Jensen & J. Sørensen, 1992. Denitrification, dissimilatory reduction of nitrate to ammonium, and nitrification in a bioturbated estuarine sediment as measured with 15N and microsensor techniques. Applied and Environmental Microbiology 58: 303-313.
19. Boudreau, B.P., 1997. Diagenetic Models and their Implication: Modeling Transport and Reactions in Aquatic Sediments. Springer, Berlin.
20. Bower, C.E. & T. Holm-Hansen. 1980. A salicylate-hypochlorite method for determining ammonia in seawater. Canadian Journal of Fisheries and Aquatic Sciences 37: 794-798.
21. Boynton, W.R. & W.M. Kemp, 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Marine Ecology Progress Series 23: 45-55.
22. Bremner, J.M, 1965. Total nitrogen. Agronomy 9:1149-1178.
23. Broecker, W.S. & T.H. Peng, 1974. Gas exchange rates between air and sea. Tellus, 26: 21-35.
24. Cabrita, M.T. & V. Brotas, 2000. Seasonal variation in denitrification and dissolved nitrogen fluxes in intertidal sediments of the Tagus estuary, Portugal. Marine Ecology Progress Series 202: 51-65.

25. Caffrey, J.M., N.P. Sloth, H.F Kaspar & T.H. Blackburn, 1993. Effect of organic loading on nitrification and denitrification in a marine sediment microcosm. FEMS Microbiology Ecology 12: 159–167.
26. Callender, E. & D.E. Hammond, 1982. Nutrient exchange across the sediment-water interface in the Potomac River estuary. Estuarine, Coastal and Shelf Science 15(4): 395-413.
27. Canfield, D.E., B.B. Jørgensen, H. Fossing, R.N. Glud, J.K. Gundersen, B. Thamdrup, J.W. Hansen, L.P. Nielsen & P.O.J. Hall, 1993. Pathways of organic carbon oxidation in three continental margin sediments. Marine Geology 113: 27-40.
28. Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. Chemical Geology 114: 315-329.
29. Caraco, N., J. Cole & G.E. Likens, 1990. A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems Biogeochemistry 9: 211-290.
30. Capone, D.G. & R.P. Kiene, 1988. Comparative microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. Limnology and Oceanography 33: 725-749.
31. Cebron, A., T. Berthe & J. Garnier, 2003. Nitrification and nitrifying bacteria in the Lower Seine River and Estuary (France). Applied and Environmental Microbiology 69: 7091-7100.
32. Conley, D.J. & T.C. Malone, 1992. Annual cycle of dissolved silicate in Chesapeake Bay: implications for the production and fate of phytoplankton biomass. Marine Ecology Progress Series 81: 121-128.
33. Conley, D. J. & Johnstone, R. W. 1995 Biogeochemistry of N, P and Si in Baltic Sea sediments: response to a simulated deposition of a spring diatom bloom. Marine Ecology Progress Series 122: 265-276.
34. Conley, D., J. Carstensen, R. Vaquer-Sunyer & C.M. Duarte, 2009. Ecosystem thresholds with hypoxia. Hydrobiologia 629: 21-29.
35. Christensen, P.B., L.P. Nielsen, J. Sørensen & N.P. Revsbech, 1990. Denitrification in nitrate-rich streams: diurnal and seasonal variation related to benthic oxygen metabolism. Limnology and Oceanography 35:640-651.
36. Cook, P.L.M., F. Wenzhofer, S. Rysgaard, O.S. Galaktionov, F.J.R. Meysman, B.D. Eyre and others, 2006. Quantification of denitrification in permeable sediments: insights from a two-dimensional simulation analysis and experimental data. Limnology and Oceanography: Methods 4: 294-307.
37. Cowan, J.L.W. & W.R. Boynton, 1996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: seasonal patterns, controlling factors and ecological significance. Estuaries, 19: 562–580.
38. Dailidienė, I. & L. Davulienė. 2007. Long-term mean salinity in the Curonian Lagoon in 1993-2005. Acta Zoologica Lituanica, 17(2): 172-181.
39. Dailidienė, I. & L. Davulienė. 2008. Salinity trend and variation in the Baltic Sea near th Lithuanian coast in the Curonian Lagoon in 1984-2005. Journal of Marine Systems 74: 520-529.
40. Dahlke, S., C. Wolf & H.W. Bange, 1998. Mikrobieller N-, S- und C- Umsatz und die Emission von N_2O, und CH_4 im Greifswalder Bodden und im westlichen Teil des Oderastuars. In: Lampe R (ed) Greifswalder Bodden und Oder Astuar-Austauschprozesse (GOAP), Synthesebericht des Verbundprojektes. Greifs Geogr Arb 16: 370-402.
41. Dalsgaard, T. & others, 2000. Protocol handbook for NICE—Nitrogen Cycling In Estuaries: A project under the EU research programme: Marine Science and Technology (MAST III). National Environmental Research Institute.
42. Dalsgaard, T., D.E. Canfield, J. Petersen, B. Thamdrup & J. Acuna-Gonzalez, 2003. N_2 production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica. Nature 422: 606-608.
43. Daunys, D., D. Schiedek & S. Olenin, 2000. Species strategy near its boundary: the *Malenzelleria* cf. *viridis* (Polychaeta, Spionidae) case in the southeastern Baltic Sea. International Review of Hydrobiology 85: 639-651.
44. Daunys, D., 2001. Patterns of the bottom macrofauna variability and its role in the shallow coastal Lagoon. Summary of PhD dissertation, Klaipėda University, Klaipėda.
45. Daunys, D., P. Zemlys, S. Olenin, A. Zaiko & C. Ferrarin, 2006. Impact of the zebra mussel Dreissena polymorpha invasion on the budget of suspended material in a shallow lagoon ecosystem. Helgoland Marine Research 60 (2): 113-120.
46. De Beer, D. & J.P.R. Sweerts, 1989. Measurement of nitrate gradients with an ionselective microelectrode. Analytica Chimica Acta 219: 351-356.
47. De Beer, D., J.P.R.A. Sweerts & J.C. van den Heuvel, 1991. Microelectrode measurement of ammonium profiles in freshwater sediments. FEMS Microbiology Ecology 86: 1-6.
48. Dedieu, K., C. Rabouille, G. Thouzeau, F. Jean, L. Chauvaud, J. Clavier, V. Mesnage, & S. Ogier. 2007. Benthic O_2 distribution and dynamics in a Mediterranean lagoon (Thau, France): An in situ microelectrode study. Estuarine, Coastal and Shelf Science 72: 393-405.
49. Denis, L. & C. Grenz, 2003. Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean Sea). Oceanologica Acta 26: 373-389.
50. Dettmann, E., 2001. Effect of Water Residence Time on Annual Export and Denitrification of Nitrogen in Estuaries: A Model Analysis. Estuaries 24 (4): 481-490.

51. Deutsch, B., S. Forster, M. Wilhelm, J.W. Dippner & M. Voss, 2010. Denitrification in sediments as a major nitrogen sink in the Baltic Sea: an extrapolation using sediment characteristics. Biogeosciences Discussions 7: 2487–2521.
52. De Wit, R., L.J. Stal, B.Aa. Lomstein, R.A. Herbert, H. Van Gemerden, P. Viaroli, V.U. Ceccherelli, F. Rodriguez-Valera, M. Bartoli, G. Giordani, R. Azzoni, B. Schaub, D.T. Welsh, A. Donnelly, A. Cifuentes, J. Anton, K. Finster, L.B. Nielsen, A.-E. Underlien Pedersen, A. Turi Neubauer, M. Colangelo & S.K. Heijs, 2001. ROBUST: the role of buffering capacities in stabilising coastal lagoon ecosystems. Continental Shelf Research 21: 2021-2041.
53. Dong, L.F., D.C.O. Thornton, D.B. Nedwell & G.J.C. Underwood, 2000. Denitrification in sediments of the River Colne estuary, England. Marine Ecology Progress Series 203: 109-122.
54. Dong L.F., J. C.J. Smith, S. Papaspyrou, A. Stott, A. M. Osborn & D.B. Nedwell, 2009. Changes in Benthic Denitrification, Nitrate Ammonification, and Anammox Process Rates and Nitrate and Nitrite Reductase Gene Abundances along an Estuarine Nutrient Gradient (the Colne Estuary, United Kingdom). Applied and Environmental Microbiology 75(10): 3171-3179.
55. Engström, P., T. Dalsgaard, S. Hulth & R.C. Aller, 2005. Anaerobic ammonium oxidation by nitrite: Implications for N_2 production in coastal marine sediments. Geochimica et Cosmochimica Acta 69(8): 2057-2065.
56. Eyre, B.D. & A.J. Ferguson, 2002. Comparison of carbon production and decomposition, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgal and macroalgal dominated warm temperate Australian lagoons. Marine Ecology Progress Series 229: 43-59.
57. Eyre, B.D. &, S. Rysgaard, T. Dalsgaard & P.B. Christensen, 2002. Comparison of isotope pairing and N_2/Ar methods for measuring sediment denitrification rates—assumptions, modifications and implications. Estuaries 25: 1077-1087.
58. Eyre, B.D. & A.J.P. Ferguson, 2005. Benthic metabolism and nitrogen cycling in a subtropical east Australian estuary (Brunswick): Temporal variability and controlling factors. Limnology and Oceanography 50(1): 81-96.
59. Eyre, B.D. & A.J.P. Ferguson, 2009. Denitrification efficiency for defining critical loads of carbon in shallow coastal ecosystems. Hydrobiologia 629: 137-146.
60. Fenchel, T., 1996. Worm burrows and oxic microniches in marine sediments. 1. Spatial and temporal scales. Marine Biology 127: 289-295.
61. Ferguson, A.J.P., B.D. Eyre, J.M. Gay, N. Emtage & L.O. Brooks, 2007. Benthic metabolism and nitrogen cycling in a sub-tropical embayment: spatial and seasonal variability and controlling factors. Aquatic Microbial Ecology 48(2): 175-195.
62. Ferrarin, C., A. Razinkovas, S. Gulbinskas, G. Umgiesser & L. Bliūdžiutė 2008 Hydraulic regime-based zonation scheme of the Curonian Lagoon. Hydrobiologia 611 (1): 133-146.
63. Froelich, P.N., G.P. Klinkhammer, M.L., Bender, N.A. Luedtke, G.R. Heath, D. Cullen, P. Dauphin, D. Hammond, B.Hartman & V. Maynard, 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica et Cosmochimica Acta 43: 1075-1090.
64. Gasiūnaitė Z.R. 2000. Coupling of the limnetic and brackishwater plankton crustaceans in the Curonian lagoon (Baltic Sea). International Review of Hydrobiology 85: 649-657.
65. Gasiūnaitė Z.R., D. Daunys, S. Olenin & A. Razinkovas, 2008. The Curonian Lagoon. In: U. Schiewer, (Eds.) Ecology of the Baltic Coastal Waters. Ecological Studies 197. Springer-Verlag, Berlin Heidelberg: 197-215.
66. Gailiušis, B., M. Kovalenkovienė & J. Kriaučiūnienė, 2005. Hidrological and Hydraulic investigation of water area in the Curonian lagoon between island Kiaulės nugaros and Alksnynės. Energetika 4: 34-41. [in Lithuanian]
67. Galkus, A. & K. Jokšas, 1997 Nuosėdinė medžiaga tranzitinėje akvasistemoje. Vilnius. 198 psl. [in Lithuanian]
68. Galkus, A., 2004. Peculiarities of sedimentary environment of most polluted bottom sediments in the Lithuanian waters of Curonian lagoon. Geografijos metraštis: 37.
69. Gardner, W.S., S.P. Seitzinger & J.M. Malczyk, 1991. The effects of sea salts on the forms of nitrogen released from estuarine and freshwater sediments: Does ion pairing affect ammonium flux? Estuaries 14:157-166.
70. Gerbersdorf, S.U., J. Meyercordt & L.-A. Meyer-Reil, 2005. Microphytobenthic primary production in the Bodden estuaries, southern Baltic Sea, at two study sites differing in trophic status. Aquatic Microbial Ecology 41: 181-198.
71. Giardino, C., M. Bresciani, R Pilkaityte, M. Bartoli & Arturas Razinkovas, 2010. In situ measurements and satellite remote sensing of case 2 waters: first results from the Curonian Lagoon. Oceanologia 52(2): 197-210.
72. Giordani, G., M. Bartoli, M., M. Cattadori & P. Viaroli, 1996. Sulphide release from anoxic sediments in relation to iron availability and organic matter recalcitrance and its effects on inorganic phosphorus recycling. Hydrobiologia 329: 211-222.
73. Glud, R.N., N. Risgaard-Petersen, B. Thamdrup, H. Fossing & S. Rysgaard, 2000. Benthic carbon mineralization in a high-Arctic sound (Young Sound, NE Greenland) 206: 59-71.

74. Glud, R.N., J.K. Gundersen, B.B. Jørgensen, N.P. Revsbech & H.D. Schulz, 1994. Diffusive and total oxygen uptake of deep-sea sediments in the eastern South Atlantic Ocean: In situ and laboratory measurements. Deep-Sea Research 41: 1767-1788.
75. Glud, R.N., M. Kuhl, F. Wenzhöfer & S. Rysgaard, 2002. Benthic diatoms of a high Arctic fjord (Young Sound, NE Greenland): importance for ecosystem primary production. Marine Ecology Progress Series 238:15-29.
76. Glud, R.N., J.K. Gundersen, H. Røy, B.B. Jørgensen, 2003. Seasonal dynamics of benthic O_2 uptake in a semi-enclosed bay: importance of diffusion and fauna activity. Limnology and Oceanography 48: 1265-1276.
77. Glud, R.N, 2008. Oxygen dynamics of marine sediments. Marine Biology Research 4: 243-289.
78. Graf, G., W. Bengtsson, U. Diesner, R. Schultz, & H. Theede, 1982. Benthic response to sedimentation of a spring phytoplankton bloom. Process and budget. Marine Biology 67: 201-208.
79. Grenz, C., Cloern, J., Hager, S.W., B.E. Cole, 2000. Dynamics of nutrient cycling and related benthic nutrient and oxygen fluxes during a spring phytoplankton bloom in south San Francisco Bay (USA). Marine Ecology Progress Series 197: 67-80.
80. Grasshoff, K., M. Ehrhardt & K. Kremling, 1983. Methods of Seawater Analysis, 2nd eds. Verlag Chemie, Berlin.
81. Gunnars, A. & S. Blomquist, 1997. Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions-an experimental comparison of freshwater and brackish marine systems. Biogeochemistry 37: 203-206.
82. Hall, P.O.J, L.G. Anderson, M.M. Rutgers van der Loeff, B. Sundby & S.F.G. Westerlund, 1989. Oxygen uptake kinetics in the benthic boundary layer. Limnology and Oceanography 34(4): 734-746.
83. Hammond, D.E., C. Fuller, D. Darmon, B. Hartman, M. Korsec, L.G. Miller, R. Rea, S. Warren, W. Berelson & S.W. Hager, 1985. Benthic fluxes in San Francisco Bay. Hydrobiologia 129: 69-90.
84. Hammond, D.E., J. McManus, W. Berelson, T. Kilgore & R. Pope, 1996. Early diagenesis of organic carbon in the equatorial Pacific: rates and kinetics. Deep Sea Research 43: 1365-1412.
85. Hammond, D.E., P. Giordani, W. Berelson & R. Poletti, 1999. Diagenesis of carbon and nutrients in sediments of the Northern Adriatic Sea. Marine Chemistry 66: 53-79.
86. Hansen, L.S. & T.H. Blackburn, 1991. Aerobic and anaerobic mineralization of organic material in marine sediment microcosms. Marine Ecology Progress Series 75: 283-291.
87. Hansen, L.S. & Blackburn T.H., 1992. Effect of algal bloom deposition on sediment respiration and fluxes. Marine Biology 112: 147-152.
88. Heilskov, A.C. & M. Holmer, 2001. Effects of benthic fauna on organic matter mineralization in fish-farm sediments: importance of size and abundance. Ices Journal of Marine Science 58: 427-434.
89. Henriksen, K. & W.M. KEMP, 1988. Nitrification in estuarine and coastal marine sediments. In: T.H. Blackburn & J. Sorensen, (Eds.) Nitrogen cycling in coastal marine environments. John Wiley & Sons, Chichester: 207-249.
90. Herbert, R.A., 1999. Nitrogen cycling in coastal marine ecosystems. FEMS Microbiology Reviews 23: 563-590.
91. Hietanen, S., 2007. Anaerobic ammonium oxidation (anammox) in sediments of the Gulf of Finland. Aquatic Microbial Ecology 48:197-205.
92. Hietanen, S. & J. Kuparinen, 2008. Seasonal and short-term variation in denitrification and anammox at a coastal station on the Gulf of Finland, Baltic Sea. Hydrobiologia 596: 67-77.
93. Holmer, M., 1999. The effect of oxygen depletion on anaerobic organic matter degradation in marine sediments. Estuarine, Coastal and Shelf Science 48: 383-390.
94. Holmer, M., F. Ø. Andersen, N. Holmboe, E. Kristensen & N. Thongtham, 2001. Spatial and temporal variability in benthic processes along a mangroveseagrass transect in the Bangrong Mangrove, Thailand. Wetlands Ecology and Management. 9: 141-158.
95. Hopkinson, C.S., A.E. Giblin & J. Tucker, 2001. Benthic metabolism and nutrient regeneration on the continental shelf of Eastern Massachusetts, USA. Marine Ecology Progress Series 224: 1–19.
96. Hulth, S., A. Tengberg, A. Landen & P.O.J. Hall, 1997. Mineralization and burial of organic carbon in sediments of the southern Weddell Sea (Antarctica). Deep-Sea Research Part I-Oceanographic Research Papers 44, 955-981.
97. Howarth, R.W. & A.E. Giblin, 1983. Sulfate reduction in the salt marshes at Sapelo Island, Georgia. Limnology and Oceanography 28: 70-80.
98. Howarth, R.W., 1988. Nutrient limitation of net primary production in marine systems. Annual Review of Ecology and Systematics 19: 89-110.
99. Ittekkot., V. & R. Laane,1991. Fate of riverine particulate organic matter. In: D.E. Kempe & R. Richey, (Eds.) Biogeochernistry of Major World Rivers. John Wiley and Sons, New York: 233-242.
100. Iversen, N. & B.B. Jørgensen, 1993. Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. Geochimica et Cosmochimica Acta 57: 571-578.
101. Jakobsen, R. & D. Postma, 1999. Redox-zoning, rates of sulfate reduction and interaction with Fe-reduction and methanogenesis in a shallow sandy aquifer, Romo, Denmark. Geochimica et Cosmochimica Acta 63: 137-151.
102. Jäntti, H., F. Stange, E. Leskinen & S. Hietanen, 2011, Seasonal variation in nitrification and nitrate-reduction pathways in coastal sediments in the Gulf of Finland, Baltic Sea. Aquatic Microbial Ecology. 26 (63): 171-181.

103. Jensen, M. H., E. Lomstein, & J. Sørensen, 1990. Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. Marine Ecology Progress Series 61: 87-96.
104. Jensen, K., N.P. Revsbech & L.P. Nielsen, 1993. Microscale distribution of nitrification activity in sediment determined with a shielded microsensor for nitrate. Applied and Environmental Microbiology 59: 3287-3296.
105. Jensen, H.S., P.B. Mortensen, F.Ø. Andersen, E. Rasmussen & A. Jensen, 1995. Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. Limnology and Oceanography 40: 908-917.
106. Jensen K, Sloth NP, Risgaard-Petersen N, Rysgaard S, Revsbech NP. 1994. Estimation of nitrification and denitrification from microprofiles of oxygen and nitrate in model sediment systems. Applied and Environmental Microbiology 60: 2094-2100.
107. Jensen, M. M., M.M.M. Kuypers, G. Lavik & B. Thamdrup, 2008. Rates and regulation of anaerobic ammonium oxidation and denitrification in the Black Sea. Limnology and Oceanography 53: 23-36.
108. Jespersen, A.M. & K. Christoffersen, 1987. Measurements of chlorophyll a from phytoplankton using ethanol as extraction solvent. Archiv Hydrobiologia 109: 445-454.
109. Jokšas, K., A. Galkus & R. Stakėnienė, 1998. Geocheminiai Kuršių marių dugno nuosėdų ypatumai ir juos formuojantys veiksniai. Geografijos metraštis 31: 123-144. [in Lithuanian].
110. Jurgelėnaitė, A. & D. Šarauskienė, 2007. The impact of Klaipėda strait permeability on the process of sea water inflow into the Curonian lagoon. Energetika 53 (2):52–56. [in Lithuanian].
111. Jørgensen, B.B. & J. Sørensen, 1985. Seasonal cycles of O_2, NO_3^- and SO_4^{2-} reduction in estuarine sediments: The significance of a nitrate reduction maximum in Spring. Marine Ecology Progress Series 24: 65-74.
112. Jørgensen, B.B. & N.P. Revsbech, 1985. Diffusive boundary layers and the oxygen uptake of sediments and detritus. Limnology and Oceanography 30: 111-122.
113. Jørgensen BB (1996) Case study—Aarhus Bay. In B.B. Jørgensen & K. Richardson (eds). Coastal and estuarine studies-eutrophication in coastal marine ecosystems. American Geophysical Union, Washington, DC. 137-154.
114. Jørgensen B.B, R.N. Glud & O. Holby, 2005. Oxygen distribution and bioirrigation in Arctic fjord sediments (Svalbard, Barents Sea). Marine Ecology Progress Series 292: 85-95.
115. Kana T.M., C. Darkangelo, M.D. Hunt, J.B. Oldham, G.E. Bennett & J.C. Cornwell, 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N_2, O_2, and Ar in environmental water samples. Analytical Chemistry 66: 4166-4170.
116. Kasperovičienė, J. & G. Vaikutienė, 2007. Long–term changes in diatom communities of phytoplankton and the surface sediments in the Curonian Lagoon (Lithuanian part). Transitional Waters Bulletin 1: 27-37.
117. Kemp, W.M., P.A. Sampou, J. Garber, J. Tuttle & W.R. Boynton, 1992. Seasonal depletion of oxygen from bottom waters of Chesapeake Bay: relative roles of benthic and planktonic respiration and physical exchange processes. Marine Ecology Progress Series 85: 137-152.
118. Koike, A. & A. Hattori, 1978. Denitrification and ammonium formation in anaerobic coastal sediments. Applied and Environmental Microbiology 35: 278-282.
119. Krevs, A., J. Koreiviene, R. Paskauskas & R. Sulijiene, 2007. Phytoplankton production and community respiration in different zones of the Curonian lagoon during the midsummer vegetation period. Transitional Waters Bulletin 1 (1): 17-26.
120. Kristensen, E., 1984. Effect of natural concentrations on nutrient exchange between a polychaete burrow in estuarine sediment and the overlying water. Journal of Experimental Marine Biology and Ecology 75: 171–190.
121. Kristensen, E., 1988. Benthic fauna and biogeochemical processes in marine sediments: Microbial activities and fluxes. In: T.H. Blackburn & J. Sørensen, (Eds.) Nitrogen cycling in coastal marine environments. John Wiley & Sons, Chichester: 275-299.
122. Kristensen, E., S. I. Ahmed & A. H. Devol, 1995. Aerobic and anaerobic decomposition of organic matter in marine sediment: which is fastest? Limnology and Oceanography 40: 1430-1437.
123. Kristensen, E., 2000. Organic matter diagenesis at the oxic/anoxic interface in coastal marine sediments, with emphasis on the role of burrowing animals. Hydrobiologia 426: 1-24.
124. Kristensen, E. & M. Holmer, 2001 Decomposition of plant material in marine sediment exposed to different electron acceptors (O^2, NO_3^- and SO_4^{2-}), with emphasis on substrate origin, degradation stage and the role of bioturbation. Geochimica et Cosmochimica Acta 65: 419-433.
125. Kostka, J.E., B. Thamdrup, R.N. Glud, D.E. Canfield, 1999. Rates and pathways of carbon oxidation in permanently cold Arctic sediments. Marine Ecology Progress Series 180:7-21.
126. Krom, M.D. & R.A. Berner, 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta 45: 207-216.
127. Köster, M. & L.A. Meyer-Reil, 2001. Characterization of carbon and microbial biomass pools in shallow water coastal sediments of the southern Baltic Sea (Nordrügensche Bodden). Marine Ecology Progress Series 214:25-41.
128. Köster M., S. Dahlke & L.-A. Meyer-Reil, 2005. Microbial colonization and activity in relation to organic carbon in sediments of hypertrophic coastal waters (Nordrügensche Bodden, Southern Baltic Sea). Aquatic Microbial Ecology 39: 69-83.

129. Langas, V., D. Daunys, R. Paškauskas, P.Zemlys, R. Pilkaitytė, A. Razinkovas & S. Gulbinskas, 2010. Tarpinių ir pakrantės vandenų būklė, ją įtakojantys veiksniai ir būklės gerinimo priemonės. Vilnius; 136.
130. Larsen, L.H., T. Kjaer, N.P. Revsbech, 1997. A microscale NO_3^- biosensor for environmental applications. Analytical Chemistry 69: 3527-3531.
131. Laursen, A.E. & S.P. Seitzinger, 2002. The role of denitrification in nitrogen removal and carbon mineralization in Mid- Atlantic Bight sediments. Continental Shelf Research 22: 1397-1416.
132. Lawrence, D., M.J. Dagg1, H. Liu, S.R. Cummings, P.B. Ortner & C. Kelble, 2004. Wind events and benthic–pelagic coupling in a shallow subtropical bay in Florida. Marine Ecology Progress Series 266: 1-13.
133. Lesutienė, J., 2009. Food web of the Curonian lagoon: Organic matter sources and Feeding of Mysids. Summary of PhD dissertation, Klaipėda University, Klaipėda.
134. Lerman, A., 1979. Geochemical Processes: Water and Sediment Environments. John Wiley & Sons, New York.
135. Li., Y.H. & S. Gregory, 1974. Diffusion of ions in deep-sea sediments. Geochimica Cosmochimica Acta 38: 703-714.
136. Li, Y.-Y., S. Lam & H.H.P. Fang, 1996. Interactions between methanogenic, sulfate-reducing and syntrophic acetogenic bacteria in the anaerobic degradation of benzoate. Water Research 30(7): 1555-1562.
137. Lorenzen, C.J., 1967. Determination of chlorophyll and pheo-pigments: spectrophotometric equations. Limnology and Oceanography 12: 343–346.
138. Lorenzen, J., L.H., Larsen, T. Kjaer & N.P. Revsbech, 1998. Biosensor determination of the microscale distribution of nitrate, nitrate assimilation, nitrification, and denitrification in a diatom-inhabited freshwater sediment. Applied and Environmental Microbiology 64: 3264-3269.
139. Lomans, B.P., H.J.M. OP, D. Camp, A. Pol, C. Van Der Drift & G.D. Vogels, 1999. Role of Methanogens and Other Bacteria in Degradation of Dimethyl Sulfide and Methanethiol in Anoxic Freshwater Sediments. Applied and Environmental Microbiology 65(5): 2116-2121.
140. Lohse L., Epping E. H. G., Helder W., and van Raaphorst W. (1996). Oxygen porewater profiles in continental shelf sediments of the North Sea: Turbulent vs. molecular diffusion. Marine Ecology Progress Series 145: 63-75.
141. Lomstein, E., M.H. Jensen, J. Sørensen, 1990. Intracellular NH_4^+ and NO_3^+ pools associated with deposited phytoplankton in a marine sediment (Aarhus Bight, Denmark). Marine Ecology Progress Series 61: 97-105.
142. Lovley, D.R. & E.J.P Phillips, 1986. Organic Matter Mineralization with Reduction of Ferric Iron in anaerobic Sediments. Applied and Environmental Microbiology 51: 683-689.
143. Mackin, J.E., K.T. Swider, 1989. Organic matter decomposition pathway and oxygen consumption in coastal marine sediments. Journal of Marine Research 47: 681-716.
144. Magalhães, C.M., A.A. Bordalo & W.J. Wiebe, 2002. Temporal and spatial patterns of intertidal sediment-water nutrient and oxygen fluxes in the Douro River estuary. Portugal. Marine Ecology Progress Series 233: 55-71.
145. Malone. T.C., 1992. Effects of water column processes on dissolved oxygen: nutrients, phytoplankton, and zooplankton. In: Smith, D., M. Leffler & G. Mackiernan, (Eds.) Oxygen dynamics in Chesapeake Bay. A synthesis of results. Maryland Sea Grant, College Park: 61-148.
146. Mayer, M.S., L. Schaffner & W.M. Kemp, 1995. Nitrification potentials of benthic macrofaunal tubes and burrow walls: effects of sediment NH_4^+ and animal irrigation behavior. Marine Ecology Progress Series 121: 157-169.
147. Mažeika, J., R. Paškauskas & J. Taminskas, 2008. 210Pb and 137Cs – indicators for sediment age assessment in the Curonian lagoon. In proceedings of “Coastal research”. Klaipėda University. Klaipėda. [in Lithuanian]
148. Marinelli, R.L., R.A. Jahnke, D.B. Craven, J.R. Nelson & J.E. Eckman, 1998. Sediment nutrient dynamics on the South Atlantic Bight continental shelf. Limnology and Oceanography 43:1305-1320.
149. Mesnage, V., S. Ogier, G. Bally, J.-R. Disnar, N. Lottier, K. Dedieu, C. Rabouille & Y. Copard, 2007. Nutrient dynamics at the sediment-water interface in a Mediterranean lagoon (Thau, France): influence of biodeposition by shellfish farming activities. Marine Environmental Research 63(3), 257-277.
150. Meyer, R.L., T. Kjær & N.P. Revsbech, 2001. Use of NO_x^- microsensors to estimate the activity of sediment nitrification and NO_x^- consumption along an estuarine salinity, nitrate, and light gradient. Aquatic Microbial Ecology 26: 181-193.
151. Meyer, R.L., N. Risgaard-Petersen,., D.E Allen,., and Dv (2005) Correlation between anammox activity and microscale distribution of nitrite in a subtropical mangrove sediment. *Applied and Environmental Microbiology* 71: 6142-6149.
152. Middelburg, J.J., C. Barranguet, H.T.S. Bushker, P.M.J. Herman & T. Moens, 2000. The fate of intertidal microphythobenthos carbon: an in situ ^{13}C-labelling study. Limnology and Oceanography 45: 1224-1234.
153. Minkevičiu, A. J. Pipinys, 1978. Augalija. Kuršių marios. Vilnius: 65-77.
154. Morin, J. & J.W. Morse, 1999. Ammonium release from resuspended sediments in the Laguna Madre estuary. Marine Chemistry 65: 97-110.
155. Mortimer, R.J.G., M.D. Krom, P.G. Watson, P.E. Frickers, J.T. Davey & R.J. Clifton, 1998. Sediment–water exchange of nutrients in the intertidal zone of the Humber estuary, UK. Marine Pollution Bulletin 37: 261-279.
156. MRC, 1996. Annual report of scientific work. Center of Marine research, Environmental Protection Ministry: 94.

157. Nedwell, D.B., M. Trimmer, 1996. Nitrogen fluxes through the upper estuary of the Great Ouse, England: the role of the bottom sediments. Marine Ecology Progress Series 142: 273-286.
158. Nicholls, J.C. & M. Trimmer, 2009. Widespread occurrence of the anammox reaction in estuarine sediments. Aquatic Microbial Ecology 55(2): 105-113.
159. Nielsen, L.P., P.B. Christensen, N.P. Revsbech & J. Sørensen, 1990. Denitrification and oxygen respiration in biofilms studied with a microsensor for nitrous oxide and oxygen. Microbial Ecology 19: 63-72.
160. Nielsen, L.P., 1992. Denitrification in sediment determined from nitrogen isotope paring. FEMS Microbial Ecology 86: 357-362.
161. Nielsen, L.P. & R.N. Glud, 1992. Denitrification in a coastal sediment measured in situ by nitrogen isotope pairing technique applied to a benthic flux chamber. Marine Ecology Progress Series 137: 181-186.
162. Nielsen, O.I., B. Gribsholt, E. Kristensen & N.P. Revsbech, 2004. Microscale distribution of oxygen and nitrate in sediment inhabited by *Nereis diversicolor*: spatial patterns and estimated reaction rates. Aquatic Microbial Ecology 34: 23-32.
163. Nixon, S.W., J.W. Ammerman, L.P. Atkinson, V.M. Berounsky, G. Billen, W.C. Boicourt, W.R. Boynton, T.M. Church, D.M. DiToro, R. Elmgren, R.H. Garber, A.E. Giblin, R.A. Jahnke, N.J.P. Owens, M.E.Q. Pilson & S.P. Seitzinger, 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141-180.
164. Ogilvie, B., D.B. Nedwell, R.M. Harrison, A. Robinson & A. Sage. 1997. High nitrate, muddy estuaries as nitrogen sinks: the nitrogen budget of the River Colne estuary (United Kingdom). Marine Ecology Progress Series 150: 217-228.
165. Olenina, I., 1998. Long-term changes in the Kuršių Marios lagoon: eutrophication and phytoplankton response. Ekologija 1: 56-65.
166. Olesen, M. & C. Lundsgaard, 1995. Seasonal sedimentation of autochthonous material from the euphotic zone of a coastal system. Estuarine, Coastal and Shelf Science 41: 475-490.
167. Rabouillle, C., L. Denis, K. Dedieu, G Stora, B. Lansard & C. Grenz, 2003. Oxygen demand in coastal marine sediments: comparing in situ microelectrodes and laboratory core incubations. Journal of Experimental Marine Biology and Ecology 285-286:49-69.
168. Rao, A.M.F., M.J. Mccarthy, W.S Gardner & R.A. Jahnke, 2008. Respiration and denitrification in permeable continental shelf deposits on the South Atlantic Bight: N_2:Ar and isotope pairing measurements in sediment column experiments. Continental Shelf Research 28: 602-613.
169. Rasmussen, H. & B.B. Jørgensen, 1992. Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion. Marine Ecology Progress Series 81: 289-303.
170. Razinkovas, A. & R. Pilkaitytė, 2002. Factors limiting phytoplankton development in the Curonian lagoon, Jūra ir aplinka, 1 (6): 39-46. [in Lithuanian]
171. Razinkovas, A. & Z.R. Gasiūnaitė, 1999. The potential grazing by zooplankton and nektobenthic species on phytoplankton in an estuarine system: the Kurshiu Marios (Curonian) lagoon. Finnish Environment 263: 44-51.
172. Razinkovas, A., L. Bliudziute, A. Erturk, C. Ferrarin, C. Lindim, G. Umgiesser & P. Zemlys, 2005. Curonian lagoon: a modelling study- Lithuania. In: Russo, R.C., (Eds.) Modeling Nutrient Loads and Response in River and Estuary Systems. Report No. 271. Committee on the Challenges of Modern Society, North Atlantic Treaty Organization, Brussels: 194-222.
173. Razinkovas, A., Z. Gasiūnaitė, P. Viaroli & J.M. Zaldívar 2008. Preface: European lagoons—need for further comparison across spatial and temporal scales. Hydrobiologia 611 (1): 1-4.
174. Revsbech, N.P., J. Sørensen, T.H. Blackburn & L.P Lomholt, 1980. Distribution of oxygen in marine sediments measured with microelectrodes. Limnology and Oceanography 25: 403-411.
175. Revsbech, N.P., 1989. An oxygen microsensor with a guard cathode. Limnology and Oceanograph 34: 474-478.
176. Rich, J.J., O.R. Dale, B. Song & B.B. Ward, 2008. Anaerobic ammonium oxidation (anammox) in Chesapeake Bay sediments. Microbial Ecology 55: 311-320.
177. Risgaard-Petersen, N., S. Rysgaard, L.P. Nielsen & N.P. Revsbech, 1994. Diurnal variation of denitrification and nitrification in sediments colonized by benthic microphytes. Limnology and Oceanography 39: 573-579.
178. Risgaard-Petersen, N., 2003. Coupled nitrification-denitrification in autotrophic and heterotrophic estuarine sediments: On the influence of benthic microalgae. Limnology and Oceanography 48: 93-105.
179. Risgaard-Petersen, N., L.P. Nielsen, S. Rysgaard, T. Dalsgaard & R.L. Meyer, 2003. Application of the isotope pairing technique in sediments where anammox and denitrification coexist. Limnology and Oceanography: Methods 1: 63-73.
180. Risgaard-Petersen, N. & S. Rysgaard, 1995. Nitrate reduction in sediments and waterlogged soil measured by ^{15}N techniques. In: Alef, K. & P. Nannipieri, (Eds.) Methods in applied soil and microbiology. Academic: 287–295.
181. Risgaard-Peterson, N., R.L. Meyer, M. Schmid, M.S.M. Jetten, A. Enrich-Prast, S. Rysgaard & N.P. Revsbech, 2004a. Anaerobic ammonium oxidation in an estuarine sediment. Aquatic Microbial Ecology 36: 293-304.

182. Risgaard-Petersen, N., M.H. Nicolaisen, N.P. Revsbech, & B.A. Lomstein, 2004b. Competition between ammonia-oxidizing bacteria and benthic microalgae. Applied and Environmental Microbiology 70(9): 5528-5537.
183. Risgaard-Petersen, N., L.P. Nielsen, S. Rysgaard, T. Dalsgaard & R.L. Meyer, 2004c. Erratum: Application of the isotope pairing technique in sediments where anammox and denitrification co-exist. Limnology and Oceanography: Methods 2: 315.
184. Risgaard-Peterson, N., R.L. Meyer, & N.P. Revsbech, 2005. Denitrification and anaerobic ammonium oxidation in sediments: effects of microphythobenthos and NO_3^-. Aquatic Microbial Ecology 40: 67-76.
185. Rizzo, W.M., S.K. Dailey, G.J. Lackey, R.R. Christian, B.E. Berry & R.L. Wetzel, 1996. A metabolism-based trophic index for comparing the ecological values of shallow-water sediment habitats. Estuaries 19: 247-256.
186. Roden E. E. & R.G. Wetzel, 1996. Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. Limnology and Oceanography 41(8): 1733-1748.
187. Rozan T.F., M. Taillefert, R.E. Trouwborst, B.T. Glazer, S. Ma, J. Herszage, L. M. Valdes, K.S. Price & G. W. Luther, 2002. Iron–sulfur–phosphorus cycling in the sediments of a shallow coastal bay: Implications for sediment nutrient release and benthic macroalgal blooms Limnology and Oceanography 47(5): 1346-1354.
188. Rysgaard, S., N. Risgaard-Petersen, L.P. Nielsen & N.P. Revsbech, 1993. Nitrification and denitrification in lake and estuarine sediment measured by the ^{15}N dilution technique and isotope pairing. Applied and Environmental Microbiology 59: 2093-2098.
189. Rysgaard, S., P.B. Christensen & L.P. Nielsen, 1995. Seasonal variation in nitrification and denitrification in estuarine sediment colonized by benthic microalgae and bioturbating infauna. Marine Ecology Progress Series 126: 111-121.
190. Rysgaard, S., B. Thamdrup, N. Risgaard-Petersen, H. Fossing, L.P. Nielsen, P.B. Christensen & T. Dalsgaard, 1998. Seasonal carbon and nutrient mineralization in a high-Arctic coastal marine sediment,Young Sound, Northeast Greenland. Marine Ecology progress Series 175: 261-276.
191. Rysgaard, S., P. Thastum, T. Dalsgaard, P.B. Christensen & N. P. Sloth, 1999. Effects of salinity on NH_4^+ adsorption capacity, nitrification, and denitrification in Danish estuarine sediments. Estuaries and Coasts 22(1): 21-30.
192. Rysgaard, S., R.N. Glud, N. Risgaard-Petersen & T. Dalsgaard, 2004. Denitrification and anammox activity in Arctic marine sediments. Limnology and Oceanography 49: 1493-1502.
193. Pasqualini, V., C. Pergent-Martini, P. Clabaut & G. Pergent, 1998. Mapping of Posidonia oceanica using aerial photographs and side scan sonar: application off the Island of Corsica (France). Estuarine, Coastal and Shelf Science 47: 359-367.
194. Pusceddu, A., A. Dell'Anno, M. Fabiano & R. Danovaro, 2009. Quantity and bioavailability of sediment organic matter as signatures of benthic trophic status. Marine Ecology Progress Series 375: 41-52.
195. Pelegri, S.P., L.P. Nielsen & T.H. Blackburn, 1994. Denitrification in estuarine sediment stimulated by the irrigation activity of the amphipod *Corophium volutator*. Marine Ecology Progress Series 105: 285-290.
196. Pelegri, S.P. & T.H. Blackburn, 1995. Effect of bioturbation by Nereis sp., Mya arenaria and Cerastoderma sp. on nitrification and denitrification in estuarine sediments. Ophelia 42: 289-299.
197. Pilkaityte, R., 2003. Phytoplankton seasonal succession and abundance in the eutrophic estuarine lagoons. Summary of Doctoral Dissertation. Klaipėda University, Klaipėda.
198. Pilkaitytė, R. & A. Razinkovas, 2007. Seasonal changes in phytoplankton composition and nutrient limitation in a shallow Baltic lagoon, Boreal Environmental Research, 12(5): 551-559.
199. Plokštienė, D., 2002. Development and changes of the vegetation of the Kuršių marios lagoon. Sea and Environment 2, 33–41. [in Lithuanian]
200. Pustelnikovas, O., 1983. Peculiarities of recent sedimentation and of distribution of the elements (and pollutants) in the basin of the lagoon Marios. Moscow, 'Litologya i poleznye iskopaemye', 6:54-69. [in Russian]
201. Pustelnikovas, O., 1998. Geochemistry of Sediments of the Curonian Lagoon (Baltic Sea). Institute of Geography, Vilnius.
202. Pustelnikovas, O. & S. Gulbinskas, 2002. Lithology and chemical composition of recent sediments of the Curonian Lagoon. In: Emelyanov, E., (Eds.) Geology of the Gdansk Basin. Baltic Sea. Yantarny skaz, Kaliningrad: 316-327.
203. Seitzinger, S.P., 1990. Denitrification in aquatic sediments. In: Revsbech N.P. & J. Sørensen, (Eds.) Denitrification in soil and sediment. FEMS Symposium No 56. Plenum Press, New York:291-300.
204. Seitzinger, S.P., 1988. Denitrification in freshwater and coastal marine ecosystem: ecological and geochemical significance. Limnology and Oceanography 33: 702-724.
205. Seitzinger, S.P., 2000. Scaling up: Site specific Measurements to global – scale estimates of denitrification. J.H. Hobbie (eds), Estuarine science: a synthetic approach to research and practice. Island press, Washington, DC. 211-240.

206. Sileika, A. S., P. Stalnacke, S. Kutra, K. Gaigalis & L. Berankiene, 2006. Temporal and spatial variation of nutrients levels in the Nemunas River (Lithuania and Belarus). Environmental monitoring and assessment 122(1-3): 335-354.
207. Simon, N.S., 1989. Nitrogen cycling between sediment and the shallow-water column in the transition zone of the Potomoac River and estuary. II. The role of wind-driven resuspension and adsorbed ammonium. Estuarine, Coastal and Shelf Science 28:53 1-547.
208. Silvennoinen, H., S. Hietanen, A. Liikanen, C.F. Stange, R. Russow, J. Kuparinen & P. J. Martikainen, 2007. Denitrification in the River Estuaries of the Northern Baltic Sea. Ambio 36(2): 134-140.
209. Slomp, C.P., S.J. Van der Gaast & W. Van Raaphorst, 1996. Phosphorus binding by poorly crystalline iron oxides in North Sea sediments. Marine Chemistry 52: 55-73.
210. Slomp, C.P., J.F.P. Malschaert & W. Van Raaphorst, 1998, The role of adsorption in sediment-water exchange of phosphate in North Sea continental margin sediments. Limnology and Oceanography 43(5): 832-846.
211. Sloth, N.P., H. Blackburn, L.S. Hansen, N. Risgaard-Peteresen & B.A. Lomstein, 1995. Nitrogen cycling in sediments with different organic loading. Marine Ecology Progress Series 116: 163-170.
212. Smith, D.J. & G.J.C. Underwood, 2000. The production of extracellular carbohydrates by estuarine benthic diatoms: the effects of growth phase and light and dark treatment. Journal of Phycology 36: 321-333.
213. Soetaert, K. & J.J. Middelburg, 2009. Modeling eutrophication and oligotrophication of shallow-water marine systems: The importance of sediments under stratified and well-mixed conditions. Hydrobiologia 629: 239-254.
214. Soetaert, K., .J. Vanaverheke, C. Heip, P.M.J. Herman, J.J. Middelburg, A. Sandee & G. Duineveld 1997. Nematode distribution in ocean margin sediments of the Goban Spur (North-East Atlantic) in relation to sediment geochemistry. - Deep-Sea Research. 44: 1671-1683.
215. Stahlberg, C., D. Bastviken, B.H. Svensson & L. Rahm, 2006. Mineralisation of organic matter in coastal sediment at different frequency and duration of resuspension. Estuarine, Coastal and Shelf Science 70: 317-325.
216. Stehr, G., B. Bottcher, P. Dittberner, G. Rath & H-P. Koops, 1995. The ammonia-oxidizing nitrifying population of the River Elbe estuary. FEMS Microbiology Ecology 17:177-186.
217. Steingruber, S., J. Freidrich, R. Gächter & B. Wehrli, 2001. Measurements of denitrification in sediments with the ^{15}N isotope pairing technique. Applied and Environmental Microbiology 67: 3771-3778.
218. Stief, P. & D. De Beer, 2006. Probing the microenvironment of freshwater sediment macrofauna: Implications of deposit-feeding and bioirrigation for nitrogen cycling. Limnology and Oceanography 51 (6): 2538-2548.
219. Stief, P., L. Nazarova & D. De Beer. 2005. Chimney construction by *Chironomus riparius* larvae in response to hypoxia: Microbial implications for freshwater sediments. Journal of the North American Benthological Society 24 (4): 858-871.
220. Stockenberg, A. & R.W. Johnstone, 1997. Benthic denitrification in the Gulf of Bothnia, Estuarine, Coastal and Shelf Science 45, 835-843
221. Strous, M., J.G. Kuenen & M.S.M. Jetten, 1999. Key physiology of anaerobic ammonium oxidation," Applied Environmental Micorbiology 65:3248-3250.
222. Sundbäck, K. & W. Graneli, 1988. Influence of microphytobenthos on the nutrient flux between sediment and water: a laboratory study. Marine Ecology Progress Series 43: 63-69.
223. Sundbäck, K., V. Enoksson, W. Graneli & K. Pettersson, 1991. Influence of sublittoral rnicrophytobenthos on the oxygen and nutrient flux between sedunent and water: a laboratory continuous-flow study. Marine Ecology Progress Series 74: 263-279.
224. Sundbäck, K., C. Nilsson, A. Stockenberg, 1998. Microphytobenthic primary productivity and bacterial nitrogen turnover in the littoral sediments of the Gulf of Riga. Final Report, Nordic Council of Ministers, Goteborg.
225. Sundbäck, K., A. Miles & E. Göransson, 2000. Nitrogen fluxes, denitrification and the role of microphythobenthos in microtidal shallow-water sediments: an annual study. Marine Ecology Progress Series 200: 59-76.
226. Sundbäck, K., A. Miles, 2000. Balance between denitrification and microalgal incorporation of nitrogen in microtidal sediments, NE Kattegat. Aquatic Microbial Ecology 22: 291-300.
227. Sundbäck, K., F. Linares, F. Larson, A. Wulff & A. Engelsen, 2004. Benthic nitrogen fluxes along a depth gradient in a microtidal fjord: the role of denitrification and microphytobenthos. Limnology and Oceanography 49: 1095-1107.
228. Sundbäck, K., A. Miles, F. Linares, 2006. Nitrogen dynamics in non-tidal littoral sediments: role of microphytobenthos and denitrification. Estuaries and Coasts 29: 1196-1211.
229. Sundby, B., C. Gobeil, N. Silverberg, A. Mucci, 1992. The phosphorus cycle in coastal marine sediments. Limnology and Oceanography 37(6): 1129-1145.
230. Svensson J.M. & L. Leonardson, 1996. Effects of bioturbation by tube-dwelling chironomid larvae on oxygen uptake and denitrification in eutrophic lake sediments. Freshwater Biology 35: 289-300.
231. Šileika, A.S., & K. Gaigalis, 2006. Fosforo kaitos Nemuno ir kai kurių jo intakų vandenyje tendencijos ir priežastys. Vandens ukio inžinerija 30 (50): 15-27.[in lithuanian]

232. Thamdrup, B., F. Fossing & B.B. Jørgensen, 1994. Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochimica et Cosmochimica Acta 58: 5115-5129.
233. Thamdrup, B & S. Fleischer, 1998. Temperature dependence of oxygen respiration, nitrogen mineralization, and nitrification in Arctic sediments. Aquatic Microbial Ecology 15: 191-199.
234. Thamdrup, B. & T. Dalsgaard, 2002. Production of N2 through anaerobic ammonium oxidation coupled to nitrate reduction in marine sediments. Applied and Environmental Microbiology 68: 1312-1318.
235. Therkildsen, M.S. & B.A. Lomstein, 1993. Seasonal variation in net benthic C-mineralization in a shallow estuary. FEMS Microbiology Ecology 12: 131-142.
236. Thornton, D.C.O., L.F. Dong, G.J.C. Underwood & D.B. Nedwell, 2002. Factors affecting microphytobenthic biomass, species composition and production in the Colne estuary (UK). Aquatic Microbial Ecology 27:285-300.
237. Trimmer, M., D.B. Nedwell, D.B. Sivyer & S.J. Malcolm, 1998. Nitrogen fluxes through the lower estuary of the river Gt. Ouse, England: the role of the bottom sediments. Marine Ecology Progress Series 163: 109-124.
238. Trimmer, M., D.B. Nedwell, D.B. Sivyer & S.J. Malcolm, 2000. Seasonal benthic organic matter mineralisation measured by oxygen uptake and denitrification along a transect of the inner and outer River Thames estuary, UK. Marine Ecology Progress Series 197: 103-119.
239. Trimmer, M., J.C. Nicholls & B. Deflandre, 2003. Anaerobic ammonium oxidation measured in sediments along the Thames Estuary, United Kingdom. Applied and Environmental Microbiology 69: 6447-6454.
240. Trimmer, M., N. Risgaard-Petersen, J.C. Nicholls & P. Engström, 2006. Direct measurement of anaerobic ammonium oxidation (anammox) and denitrification in intact sediment cores. Marine Ecology Progress Series 326: 37-47.
241. Trimonis, E., S. Gulbinskas & M. Kuzavinis, 2003. The Curonian Lagoon bottom sediments in the Lithuanian water area. Baltica 16: 13-20.
242. Tuominen L., A. Heinanen, J. Kuparinen, L.P. Nielsen, 1998. Spatial and temporal variability of denitrification in the sediments of the northern Baltic Proper. Marine Ecology Progress Series 172: 13-24.
243. Tuominen, L., K. Mäkelä, K.K. Lehtonen, H. Haahti, S. Hietanen & J. Kuparinen, 1999. Nutrient Fluxes, Porewater Profiles and Denitrification in Sediment Influenced by Algal Sedimentation and Bioturbation by *Monoporeia affinis*. Estuarine, Coastal and Shelf Science (1999 49: 83-97.
244. Underwood, G.J.C. & J. Kromkamp, 1999. Primary production by phytoplankton and microphythobenthos in estuaries. In: Nedwell, D.B. & D.G. Raffaelli, (Eds.) Advances in Ecological Research e Estuaries 29. AcademicPress, New York: 93-153.
245. Vahtera, E., D.J. Conley, B.G. Gustafsson, H. Kuosa, Pitka¨nen, H.; Savchuk, O. P.; Tamminen, T.; Viitasalo, M.; Voss, M.; Wasmund, N.; Wulff, F. 2007. Internal ecosystem feedbacks enhance nitrogen-fixing cyanobacteria blooms and complicate management in the Baltic Sea. Ambio 36: 186-194.
246. Vandieken, V., N. Finke & B.B. Jørgensen, 2006. Pathways of carbon oxidation in an Arctic fjord sediment (Svalbard) and isolation of psychrophilic and psychrotolerant Fe(III)-reducing bacteria 322: 29-41.
247. Zaiko, A., 2009. The habitat engineering role of the invasive bivalve Dreissena polymorpha (Pallas) in the boreal lagoon ecosystem. Summary of Doctoral Dissertation. Klaipėda University, Klaipėda.
248. Zettler, M.-L. & D. Daunys, 2007. Long-term macrozoobenthos changes in a shallow boreal lagoon: Comparison of a recent biodiversity inventory with historical data. Limnologica 37: 170-185.
249. Žaromskis, R., 1996. Oceans, Seas, Estuaries. Debesija, Vilnius. [in Lithuanian]
250. Warnken, K.W., G.A. Gill, P.H. Santschi & L.L. Griffin, 2000. Benthic exchange of nutrients in Galveston Bay, Texas. Estuaries 23:647-661.
251. Warnken, K.W., P.H. Santschi, K. A.Roberts & G.A. Gill, 2008. The cycling and oxidation pathways of organic carbon in a shallow estuary along the Texas Gulf Coast. Estuarine, Coastal and Shelf Science 76(1): 69-84.
252. Wenzhöfer, F. & R.N. Glud, 2004. Small-scale spatial and temporal variability in benthic O_2 dynamics of coastal sediments: impact of fauna activity. Limnology and Oceanography 49: 1471-1481.
253. Wenzhöfer, F. & R.N. Glud, 2002. Benthic carbon mineralization in the Atlantic: a synthesis based on in situ data from the last decade. Deep-Sea Research I 49: 1255-1279.
254. Westman, P., J. Borgendahl, T.S. Bianchi & N. Chen, 2003. Probable Causes for Cyanobacterial Expansion in the Baltic Sea: Role of Anoxia and Phosphorus Retention. Estuaries 26: 680-689.
255. Wollast, R., 1983. Interactions in estuaries and coastal waters. In: Bolin, B. & R.B. Cook, (Eds.) The Major Biogeochemical Cycles and their Interactions. John Wiley & Sons, Chichester. 385-407.
256. Александров С. В., 2003. Первичная продукция планктона в Вислинском и Куршском заливах Балтийского моря и ее связь с рыбопродуктивностью: Дис. канд. биол. наук: 03.00.18: Санкт-Петербург, 195 с. РГБ ОД, 61:04-3/722

APPENDIX 1

Calculated daily oxygen and nutrient fluxes (mmol m^{-2} d^{-1}) at studied sites in the Curonian lagoon; data refer to average values (± standard deviation) from 5 replicates.

Zone	Littoral sand		Open lagoon muddy sand	Open lagoon mud	
Site / **Data**	LitS_1N	LitS_5S	Olms_2	ShM_3	ExpM_4
March	0,02±0,02	14,43±0,79	10,91±2,91	-2,51±2,89	0,45±2,77
May	-0,03±0,01	42,01±17,78	4,02±8,04	-34,06±15,65	-10,56±4,92
July	-0,01±0,02	10,38±6,72	-29,98±5,74	-12,75±4,45	-11,81±2,97
October	-0,01±0,01	-21,81±1,59	-4,96±3,51	-31,12±15,36	-35,08±4,87