KLAIPĖDA UNIVERSITY

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PHOSPHORUS POOL VARIATIONS IN THE CURONIAN LAGOON AND ITS IMPLICATION TO EUTROPHICATION

Doctoral dissertation

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INTRODUCTION

Relevance of the study

Coastal lagoons and estuaries have been defined by the European Commission as transitional waters to describe the continuum between freshwaters and coastal waters (McLusky and Elliott, 2007). By their definition, transitional waters are strongly influenced by the human-enriched nutrient inputs from the anthropogenic activities located in the watershed (Howarth, 2011; Newton et al., 2014). Seasonally dissolved and particulate nutrients are transformed, retained within the system and outflowed to the Sea (Conley et al., 1995; Humborg et al., 2003). Phosphorus is the key element in estuarine systems. In many cases, phosphorus retention and cycling is controlling eutrophication processes and, ultimately, the water quality both in transitional waters and coastal areas. Since phosphorus does not have gaseous form (excluding phosphine, which is expected not to be important in estuarine P cycling), it has high capacity to flow in the system as particulate matter (Ruttenberg, 2003), consequently, transitional waters can become efficient traps and filters for this element.

The delivered composition and amount of nutrients (nitrogen, phosphorus and silica) from rivers sustain the seasonal productivity of estuaries (Burford et al., 2011). Different phytoplankton groups, such as diatoms, green algae and cyanobacteria, can dominate depending on the delivered nutrient stoichiometry ratio to estuaries (Vahtera et al., 2007; Lilover and Stips, 2008; Pearl, 2008). By dominating high water temperature, calm weather and low DIN:DIP ratio (Kanoshina et al., 2003), cyanobacteria are intensively proliferate and form huge biomass and by settling to sediments become rapidly degrading organic matter. Afterwards microbial decomposition processes are being supported by the consumption of electron acceptors (O_2, NO_x, Mn(III/IV), Fe(III), SO_4^{2-}). Consequently, it keeps hypoxia/anoxia at the bottom water layers, leads to the mortality of macrofauna, and degrades the water quality. Intensive organic matter mineralization and bottom hypoxic/anoxic conditions regenerate phosphorus from sediments by supporting nitrogen fixing cyanobacteria bloom (Humborg et al., 2000; Coelho et al., 2004).

In the present study the focus is on the role of phosphorus cycling on the development of cyanobacteria blooms which are the most common and important phenomenon related to the water quality degradation in the South Baltic coastal lagoons and the Curonian lagoon in particular.

Aim and objectives of the study

The aim of the study is to describe the variation of phosphorus pools by identifying the mobility of reactive forms in the sediments along with their release rates to the water column during the vegetation periods and to define the role of these processes in sustaining cyanobacteria blooms.

The main objectives are:

1. Identify the variation of phosphorus forms in the water column of the Curonian lagoon during the vegetation period;
2. Analyse the phosphorus forms reactivity in the sandy and muddy sediments;
3. Identify the factors controlling the fluxes of phosphorus across sediment-water interface;
4. Measure and compare the uptake and release of inorganic phosphorus under the oxic and anoxic conditions;
5. Evaluate the phosphorus cycling potential to sustain the cyanobacteria blooms.
6. Assess the balance of phosphorus in the Curonian lagoon

Novelty of the study

This study presents a detailed report on the variation of phosphorus forms and cycling in the main sedimentary environments of the Curonian lagoon during the vegetation period. The speciation of inorganic phosphorus pools in the typical bottom sediments of the Curonian lagoon allows assessing the potential release of phosphorus during cyanobacteria bloom. The analytical phosphorus budget was constructed by quantitative estimation of the internal cycling processes during the vegetation period.

Scientific and practical significance of the results

The results of this study extend the knowledge of the interaction between the phosphorus loads, the benthic-pelagic fluxes and the cyanobacteria proliferation in the Curonian lagoon. This study has confirmed that the hypoxic/anoxic events can occur even in such turbid shallow systems as the Curonian lagoon by enhancing the release of phosphorus from the sediment to water column. By this study, the Curonian lagoon has been described as a biogeochemical phosphorus filter between the Nemunas River and the Baltic Sea. The results of the study provide a theoretical basis for management efforts to control the eutrophication process in the Curonian lagoon.

Statements to be defended

1. The organic phosphorus comprises the major fraction of total phosphorus in the water column during the vegetation period.
2. The difference of sedimentation rate leads to the fact that the pool of reactive P is higher in muddy than sandy sediments.
3. The phosphorus fluxes across sediment-water interface depend on hydrodynamic conditions and biological processes.
4. The phosphorus release from sediments to the water column is associated with organic matter degradation rates and authigenic Ca-bound phosphorus dissolution under anoxic conditions.
5. The low DIN:DIP ratio in the riverine supply can promote summer cyanobacteria bloom which can in turn stimulate internal phosphorus loads from anoxic sediments and ultimately leading to a self-sustaining cycle.
6. Shallow estuarine lagoon can be considered as a sink for the dissolved inorganic phosphorus but serves as an additional source of particulate phosphorus transported to the Baltic Sea.

Scientific approval

The results of this study were presented at six conferences:

1. The 5th European coastal lagoon symposium, Aveiro, Portugal, July of 2011.
2. ECSA 50th Conference „Today's Science for Tomorrow's Management“, Venice, Italy, June of 2012
3. ECSA 51th International Symposium "Research and management of transitional waters", Klaipėda, Lithuania, September 2012.
4. Scientific-practical conference “Sea and Coastal research– 2013”, Klaipėda, Lithuania, April 2013.
5. Baltic Sea Science Congress New Horizonts for Baltis Sea Science, Klaipėda, Lithuania, August 2013.
6. Scientific-practical conference “Sea and Coastal research– 2014”, Klaipėda, Lithuania, April 2014.

The material of this dissertation was presented in 3 original publications:

1. M. Zilius, M. Bartoli, M. Bresciani, M. Katarzyte, T. Ruginis, **J. Petkuviene**, I. Lubiene, C. Giardino, P. A. Bukaveckas, R. deWit, A. Razinkovas-Baziukas. (2014) Feedback Mechanisms Between Cyanobacterial Blooms, Transient Hypoxia, and Benthic Phosphorus Regeneration in Shallow Coastal Environments. *Estuaries and coasts, 37*(3), 680-694.
2. Zilius, M., Giordani, G., **Petkuviene, J**., Lubiene, I., Ruginis, T., and Bartoli, M. (2015). Phosphorus mobility under short-term anoxic conditions in two shallow eutrophic coastal systems (Curonian and Sacca di Goro lagoons). *Estuarine, Coastal and Shelf Science, 164*, 134-146.
3. **J. Petkuviene**, M. Zilius, I. Lubiene, T. Ruginis, G. Gordani, A. Razinkovas-Baziukas, M. Bartoli. Phosphorus cycling in a freshwater estuary impacted by cyanobacterial bloom. *Estuaries and coasts* (submitted after revision)

Volume and structure of the thesis

The dissertation is presented in the following chapters: Introduction, Literature Review, Study Area, Material and Methods, Results, Discussion, Conclusions, References and Appendix. The dissertation volume is 124 pages (including 4 pages of appendixes); it contains 27 figures and 16 tables. References include 250 sources. It is written in English with Lithuanian summary.

Abbreviations used in the study

CS – confined site
Chl-*a* – chlorophyll *a*
DIN – dissolved inorganic nitrogen
DIP – dissolved inorganic phosphorus
DO/O_2 – dissolved oxygen
DOP – dissolved organic phosphorus
DS – dissolved sulphide
DW – dry weight
Fe^{2+} - dissolved reduced iron
Fe(III) – dissolved oxidized iron
I/IN – inflowing study site
IP – inorganic phosphorus
LOI – weight loss after ignition
Mn^{2+} – dissolved reduced manganesium
Mn(III/IV) – dissolved oxidized manganesium
NH_4^+ - ammonium
NO_x – nitrogen oxides (nitrate and nitrite)
O/OUT – outflowing study site
OP – organic phosphorus
OPD – oxygen penetration depth
P – phosphorus
PIP – particulate inorganic phosphorus
POP – particulate organic phosphorus
PP – particulate phosphorus
TS – transitional site
TDP – total dissolved phosphorus
TP – total phosphorus

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1. LITERATURE REVIEW

1.1 Phosphorus forms present in water ecosystem

Phosphorus (P) circulates in the estuarine systems in three phases: particulate (solid), dissolved and gaseous (negligible amount); and in two chemical states: inorganic and organic (Fig. 1.1) (Compton et al., 2000; Reddy et al., 2005). This classification is based on the operational method analysis. All these forms are available in water and sediments.

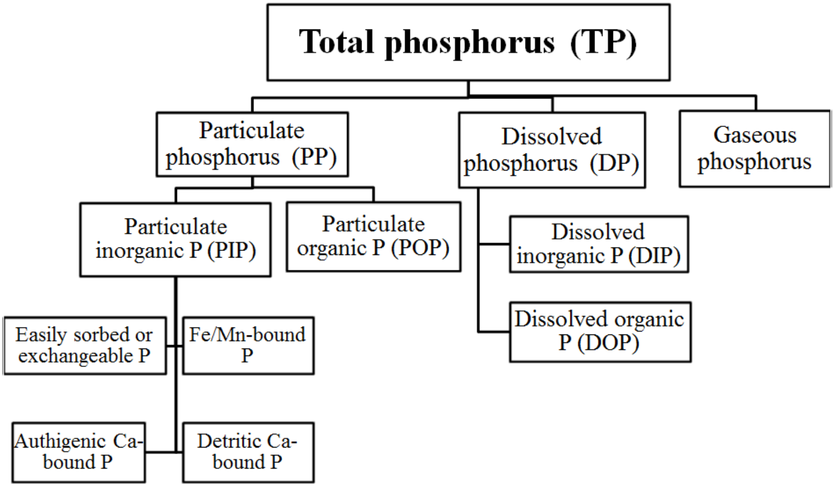


Fig. 1.1 *Basic phosphorus forms in water column and sediments*

Considering the total pool, the most of phosphorus is in the particulate fraction, where inorganic forms are dominant (PIP) and commonly associated with ions, such as Mg^{2+}, Ca^{2+}, F^- and Fe^{3+} (Compton et al., 2000; Slomp, 2011). PIP can also be divided in 3 parts: (i) orthophosphate easily adsorbed onto mineral particles (exchangeable P), (ii) phosphorus bounded to Fe^{3+} or Mn^{3+} ions

(Fe/Mn-bound P), (iii) and different phosphorus bounded to calcium compounds. Calcium sorbed phosphorus pool can be separated in authigenically formed phosphorus (i.e., *in situ,* authigenic Ca-bound P) and detritic phosphorus (detritic Ca-bound P). The authigenic Ca-bound P forms are carbonatefluorapatite (CFA), hydroxyapatite, fluorapatite, calcium carbonate and biogenic P. Detritic calcium bound P is mainly the mineral particles, usually weathered from the rock, land, and it is considered as an insoluble/unreactive P form (Ruttenberg, 1992; Ruttenberg and Berner, 1993; Slomp, 2011). Particulate organic phosphorus (POP) is the phosphorus incorporated into organic compounds, as phospholipids, nucleic acids, and phosphonates. Particulate phosphorus forms (PIP and POP) are not directly available for primary producers (Table 1.1, Reddy et al., 2005).

Table 1.1 Phosphorus forms availability and media

Phosphorus form	Examples	Present	Availability for biota
Particulate inorganic phosphorus (PIP)	Fe/Mn bound P; Authigenic Ca-bound P; Detritic Ca-bound P;	Water and sediments	No
Particulate organic phosphorus (POP)	phospholipids, nucleic acids, etc.	Water and sediments	No
Dissolved organic phosphorus (DOP)	Small organic particles (DNA, RNA)	Water and sediments	No/Yes
Dissolved inorganic phosphorus (DIP)	H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}	Water and sediments	Yes
Gaseous phosphorus (GP)	PH_3	Anaerobic sediments	No

Dissolved organic phosphorus (DOP) is mainly composed by the small organic particles (DNA, RNA), released from organic matter mineralisation or degradation. Dissolved inorganic phosphorus (DIP) is phosphorus associated with oxygen and hydrogen, which is denoted as PO_4^{3-} and called orthophosphate. DIP is the form of phosphorus used by primary producers for assimilation (Aydin et al., 2009). However, under the absence of DIP phytoplankton, it can utilize dissolved organic phosphorus (DOP) by means of phosphatases (Van Boekel et al., 1992).

The only gaseous phosphorus form (PH_3) is called phosphine, which is reduced form and produced under anaerobic conditions. It reacts rapidly with oxygen in oxic conditions forming DIP and consequently, it is not detected in the water column (Gassmann, 1994; Feng et al., 2008; Reddy et al., 2005).

1.2 Phosphorus sources and cycling in the transitional water

1.2.1 The main sources of phosphorus in the transitional waters

Phosphorus can be delivered to the transitional water bodies from four main sources: (i) physical erosion and chemical weathering of rock producing soils, (ii) riverine transport, (iii) soil drain and transportation by groundwater, (iv) atmospheric deposition (Ruttenberg, 2003). The delivery of phosphorus to rivers or directly to transitional waters is also associated with natural and anthropogenic run-off (Whiters and Jarvie, 2008). Composition (concentration, speciation, and bioavailability) and timing of delivery (continuous, seasonal or episodic) make all the sources different and variable during the scale of time (Withers and Jarvie, 2008).

During weathering and erosion, particulate inorganic phosphorus (PIP), such as apatite, vivianite, wavellite, phosphorites (Ruttenberg, 2003; Aydin et al., 2009) and particulate organic P (POP), as leaves, tree parts and other organic matter from the land, can reach the water bodies. During the rainy seasons, dissolved and particulate phosphorus run-off their intense, especially in anthropogenic areas, like over fertilized agricultural land, pasture, gardens and livestock farms (Ellison and Brett, 2006; Aydin et al., 2009). By these ways and from sewage treatment plants, high amount of dissolved inorganic phosphorus (DIP) are discharged straight to the rivers or to the transitional water systems (Withers and Jarvie, 2008).

About 10–60 % of phosphorus, which is delivered to the rivers, is retained within these systems, while the rest is outflowed to the transitional waters, mainly in the particulate forms (90 %, Froelich, 1988; Benitez-Nelson, 2000; Jarvie et al., 2002; House, 2003; Ruttenberg, 2003). On average 20–40 % of the particulate phosphorus delivered to the transitional waters is in organic form, while majority of the rest is sorbed onto ferric oxy-hydroxides and apatite (Ruttenberg, 2003). The proportion of particulate organic phosphorus increases in the summer.

Phosphorus’ inputs from groundwater depend on the soil properties and composition as well as concentration in the aquifers (Holman et al., 2008). In the areas with shallow, permeable coastal aquifers or intensive sewage disposal and with high rates of ground water, recharge the input of P can be significant to support the transitional water phosphorus resources (Lapointe et al., 1990; Slomp, 2004). However, P concentrations in the ground water is minor, if during filtration trough the soil P is efficiently retained by adsorption or co-precipitation with calcium carbonate, or iron (II/III) and aluminium hydro-oxides (Lapointe et al., 1990; Ruttenberg, 2003; Slomp, 2011).

Phosphorus can circulate in the atmosphere only as small particles from crust weathering, insect remains, pollen, spores, leaf fragments, etc. (Föllmi, 1996; Ashley et al., 2011). It is calculated that atmospheric phosphorus deposition consists of only 5 % of P budget (Benitez-Nelson, 2000). Higher input of P from atmosphere was recorded in the regions close to working volcanoes, due to P volcanic emissions, but this is only a local phenomenon, as globally P input from the atmosphere is minor (Yamagata et al., 1991; Benitez-Nelson, 2000; Ruttenberg, 2003).

1.2.2 Phosphorus cycling in the transitional waters

The concentrations of different phosphorus forms in transitional ecosystems are controlled by the inputs and internal cycling processes (Fig. 1.2; Bennion and Smith, 2000; Søndergaard et al., 2002).

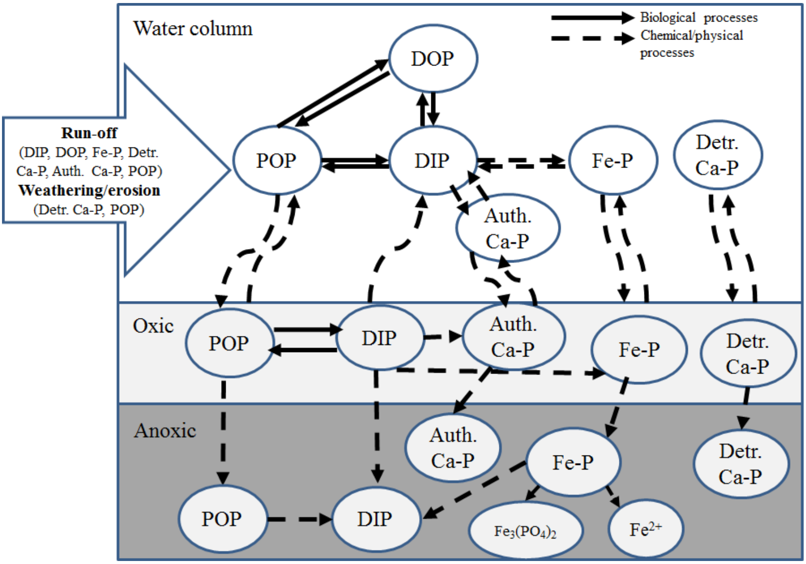


Fig. 1.2 *Phosphorus cycle in the water column and sediment (modified from Reddy et al., 2005)*

Usually DIP does not show strong seasonal variations, as observed for nitrogen. Higher concentrations were found in winter, due to riverine discharge and the internal recycling processes. In the temperate areas, other peaks of DIP were observed in spring, after the post-winter floods, while the lowest values were measured during vegetation period (Cadée and Hegeman, 1993). However, DIP concentrations are limited, because it is quickly incorporated in particulate forms, or sorbed with suspended particles (Froelish, 1988; Fox, 1993; House, 2003; Withers and Jarvie, 2008). According to House (1995; 2003), the initial reaction of P sorption in oxic condition is very fast, and 60 % of P was taken up in the first 30 min. Dominant DIP transformation creates stable or unstable phosphorus buffering (Ruttenberg, 2003; Correll, 1998). Unstable buffer capacity is when the large part of P is assimilated by primary producer or adsorbed on reactive inorganic P (exchangeable P, Fe/Mn bound P or authigenic Ca-bound bound P), while stable buffers are the detritic Ca-bound P or complex authigenic phosphorus forms (Ruttenberg, 2003). Particulate inorganic phosphorus forms are dominant in spring and autumn, while organic P fraction is abundant during vegetation periods. Particulate phosphorus concentrations in the water column are lower in winter and twice higher in the vegetation time (Søndergaard et al., 1999; 2002).

Phosphorus can be recycled internally by mineralization and desorption processes, which are affected by salinity, redox and pH changes. In the river–sea water continuum (which includes the transitional waters as well), the higher TP concentrations are generally measured at the river mouth, and decrease along the salinity gradient, due to the sea dilution effect (Lebo et al., 1994; Zwolsman, 1994; Nixon et al., 1996; Pustelnikovas, 1998; Fang, 2000; Krüger et al., 2006; van der Zee et al., 2007). Moreover, as salinity increases, the capacity to adsorb DIP onto Fe oxy-hydroxides decreases, resulting in a shift from Fe-bound P to easily exchangeable P or Ca-bound P (Zwolsman, 1994; van der Zee et al., 2007).

This is related to the lower supply of Fe^{3+} in marine inputs, comparing to the fresh waters (Blomquist et al., 2004). The decrease of TP is related to the estuarine capacity, to retain particulate matter in sediments. Another factor affecting P cycling in estuaries is the variation of pH. $H_2PO_4^-$ is dominating form in the fresh water, and HPO_4^{2-} – in seawater (Zwolsman, 1994; Bianchi, 2007; Krüger et al., 2007). Saline water intrusion to the fresh zone of transitional water leads to increase in water alkalinity, by inducing the shift of DIP species from $H_2PO_4^-$ to HPO_4^{2-}. The pH changes affect the iron oxy-hydroxides by competing Fe oxides with OH^- and HPO_4^{2-} and desorbing DIP (Zwolsman, 1994; Gomez et al., 1999; Bianchi, 2007). However, the alkaline water, which is the result of elevated pH during intensive photosynthesis up to 10, can accelerate DIP co-precipitation with calcium carbonate, if dissolved Ca^{2+} is available (Reddy et al., 2005). At the contrary, the decrease of pH below 8 can induce solubilisation of calcium-bound P and increase the absorption capacity of Fe(OOH) (Seitzinger, 1991; Gomez et al., 1999; Coelho et al., 2004; Reddy et al., 2005).

Phosphorus cycling in water column is associated with seasonal changes in transitional waters, such as river discharge, vegetation development and recycling of phosphorus from dissolved to particulate forms and vice versa. Autochthonous and allochthones particulate P can be transported from the water column to the sea or settled to the sediments (Föllmi, 1996; Benitez-Nelson, 2000; Ruttenberg, 2003). According to Slomp et al. (1996) and Benitez-Nelson (2000) 70-90% of estuarine particulate phosphorus is buried in the sediment.

1.3 Phosphorus cycling in the sediments

The sediment is constituted by compressed particles filled with a small amount of water, which is called porewater. Phosphorus retained in the sediment undergoes through a complex cycles of burial, dissolution (biological, chemical), upward migration (diffusion, resuspension), and re-precipitation several times per year (Sundby et al., 1992; Reddy et al., 2005; Da-Peng and Yong, 2010) by changing forms, and resulting release of DIP into the porewater or to overlaying water.

In the sediment particulate phosphorus is accumulated in the organic, Fe/Mn-bound, authigenic and detritic Ca-bound P and in other minor compounds, depending on the quality of riverine discharges and *in situ* processes.

Organic matter oxidation. Oxic sediments prevent DIP release to bottom or porewater (Froelich, 1988; Sundby et al., 1992), while the opposite situation is detected in anoxic sediments (Fig. 1.2), for example, strong negative relationships between the oxygen and DIP concentrations were found in the Baltic Sea (Conley et al., 2002).

Under both, oxic and anoxic conditions, the most reactive P form in the sediments is organic (Ruttenberg and Berner, 1993; Slomp, 2011). Labile organic matter (lipids, nucleic acids, tracers of di-esters, tri-esters and phosphatidylcholine) is primarily mineralised releasing DIP (Föllmi, 1996). However, the refractory forms of organic matter, as humic and fluvic acids, can be buried in the sediments for decades (Reddy et al. 2005; Ellison and Brett, 2006). During the early diagenetic processes, organic matter (including incorporated organic phosphorus) is decomposed by bacteria using various electron acceptors (O_2, NO_x, Mn-OH, Fe-OOH). During intensive mineralization and after depletion of primary oxidants (O_2, NO_x), Mn- and Fe-oxide/hydroxides bound P can serve as electron acceptors for OM mineralisation, by breaking down the Fe/Mn-bound P compounds and releasing DIP (Sundby et al., 1992; Jensen et al., 1995; Lovley and Chapelle, 1995; Slomp et al., 1996; Föllmi, 1996; Anschutz et al., 2007).

$$\mathrm{OM + Mn\text{-}OOH\text{-}PO_4 \rightarrow HCO_3^- + Mn^{2+} + H_2PO_4^-} \qquad (1)$$

$$\mathrm{OM + Fe\text{-}OOH\text{-}PO_4 \rightarrow HCO_3^- + Fe^{2+} + H_2PO_4^-} \qquad (2)$$

Under anoxia, in sulphide rich environment, the strong interactions of iron–sulphur–phosphorus cycles take place and Fe-bound phosphorus is desorbed by the iron–sulphide formation (Fig. 1.3, Sundby et al., 1992; Giordani et al., 1996; Paludan and Morris, 1999; Andrieux-Loyer and Aminot, 2001; Gächter and Müller, 2003; Da-Peng and Yong, 2010).

Roden and Edmonds (1997) suggested a scheme for DIP release from Fe-bound P compounds under anaerobic sulphate, and sulphate-free conditions. Sulphate-reducing bacteria are promoting the reduction of Fe-bound P (#1) in the saline water. Additionally, DIP can be released during conversion of the Fe(II)-P compounds to iron-sulphide (#2), and during dissolved Fe^{2+} trapping by precipitating in iron-sulphide and preventing the Fe(II)-P compound formation (#3). Under anaerobic sulphide-free environment, DIP release from Fe-bound P is promoted only by direct activity of Fe(III)-reducing bacteria during the organic matter mineralisation.

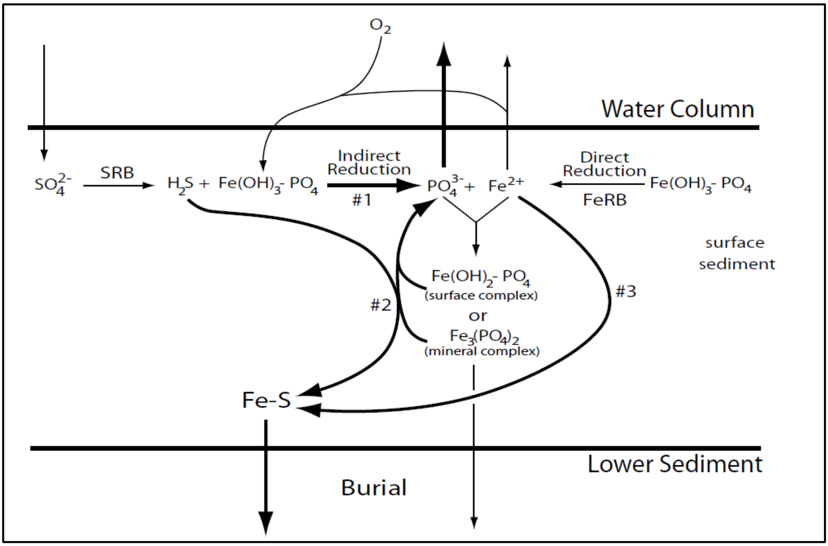


Fig. 1.3 *Fresh to marine waters Fe-reducing aerobic bacteria convert amorphous Fe(III) into Fe(II), releasing Fe-associated* PO_4^{3-}*. SRB – sulfate reducing bacteria; FeRB – Fe(III)-reducing bacteria;* $Fe(OH)_3$ *– amorphous Fe(III)oxide;* $Fe(OH)_2$ *– Fe(II)hydroxide. (taken from Bianchi 2007)*

In the methane rich sediments, Fe-$(OH)_3$-P can react by releasing bioavailable phosphorus to the near bottom water layers or sediment porewater (3, Azzoni et al., 2005; Slomp et al., 2013).

$$CH_4 + 8Fe(OH)_3\text{-}PO_4 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 21H_2O \quad (3)$$

However, the Fe/Mn bound P settled to sediments under oxic condition is rather buried (Jilbert and Slomp, 2013).

Due to the increase of pH, as a result of intensive photosynthesis, the solubility of iron-phosphate compounds increases (Søndergaard et al., 1999). Apatites are considered as stable P burial forms in particular, as detrital apatite of igneous or metamorphic origin (detrital

Ca-bound P). $CaCO_3$ bound P, which is freshly formed authigenic Ca-bound P, is soluble under low pH (Gomez et al., 1999). Authigenic carbonate fluorapatite is abundant in marine systems and it needs aproximatley10 years to form complex structure (Ruttenberg, 1992; Ruttenberg and Berner, 1993; Gomez et al., 1999). Moreover, microorganisms directly or indirectly (as by-product) can extract organic acids and solubilise authigenic from bearing shells, skeletons, and fish hard parts (Föllmi, 1996; Reddy et al., 2005). Mineralization of organic matter pH decreases and apatite can also become soluble (Gomez et al., 1999).

Easily adsorbed P can be released mainly by ion exchange, induced, for example, by salinity variations in tidal estuarine systems. The sedimentary phosphorus forms differ along saline gradient, where Fe-bound P decreases by factor 2, while organic and exchangeable P increases by factor 2 and 5 respectively with increased salinity (Jordan et al., 2008; Hartzell et al., 2010). Since marine water has more carbonate and such minerals as Ca^{2+}, Mg^{2+}, free DIP is usually adsorbed onto $CaCO_3$ by forming stable authigenic fluorapatite (Coelho et al., 2004). Salinity changes also affect the refractory phosphorus burial in the sediment. Phosphorus can be buried as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), organic P or detritic Ca-bound P in freshwater, while in saltwater carbonate fluorapatite is the main burial phosphorus form (Ruttenberg, 1992; Ruttenberg and Berner, 1993; Paludan and Morris, 1999; Gunnar et al., 2002; Jordan et al., 2008; Hartzell, 2010).

DIP released to the sediment porewater can escape by molecular diffusion or resuspension to overlaying water, and also can be assimilated by microphytobenthos (incorporated in OM) or macrophytes in upper sediment layers or accumulated back in the sediment porewater (Ruttenberg and Berner, 1993; Slomp et al., 1996; Ruttenberg, 2003; Anschutz et al., 2007). DIP concentration increases with sediment depth (Föllmi, 1996). According to Benitez-Nilson (2000) 90 % of the settled P is remineralized and released into sedimentary porewater.

Sedimentary phosphorus can be affected by the diagenetic redistribution, so called “sink-switching” processes, under which it undergoes the transformation of organic P to authigenic Ca–P, from Fe-oxide-bound P to vivianite and burial (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1994; Slomp et al., 1996; Delaney, 1998; Benitez-Nelson, 2000; Slomp 2011). This sink-switching process is important, because authigenic minerals, such as apatite and vivianite often act as a permanent sinks for P in sediments (Slomp, 2011). Organic phosphorus is mainly dominant on sediment surface, due to deposition and stable authigenic P forms becomes dominant with sediments depth (Sundby et al., 1992; Ruttenberg, 2003).

Wind induced resuspension. Physical forces can affect sedimentary phosphorus cycle mainly by sediment resuspension and DIP flushing from the porewater. Since DIP concentration is much higher in porewater comparing to the bottom water layer, DIP concentration consequently increases 20–30 times during the resuspension, which is much higher than DIP release from undisturbed sediments (Sundby et al., 1992; Søndergard et al., 1992). P redistribution causes negative or very low DIP fluxes across sediment-water interface after resuspension (Christiansen et al., 1997; Tengberg et al., 2003; Da-Peng and Yong, 2010). Resuspension of DIP from the sediments can enhance phytoplankton development (Søndergaard et al., 1992). Settled P after resuspension can also undergo chemical changes; according to Da-Peng and Yong (2010), after resuspension the share of apatite has been increased, while exchangeable P, Fe/Mn-bound P has been decreased. Wind induced stress can oxidize the sediments, but the oxygen penetration depth was found to be lower after resuspension, presumably, due to the increased oxygen consumption, induced by the resuspension, i.e. intensive oxidation of reduced agents (Fe^{2+}, Mn^{2+}, NH_4^+) and increased organic matter degradation (Christiansen et al., 1997; Ståhlberg et al., 2006; Almroth et al., 2009).

Primary producers and macrofauna (Biota). Primary producers of the water (phytoplankton, macrophytes) and macrofauna can influence P forms by its activity.

They are directly controlling P concentration in the water by up taking DIP during the vegetation and are releasing DIP during the decay (Witheras and Jarvie 2008). Primary producers influence P cycle indirectly during the intensive phytoplankton vegetation periods, when active photosynthesis reduces the concentration of CO_2 and HCO_3^- and increases pH. In such conditions Ca^{2+} and DIP are released from the dissolution of calcite (House, 2003). Sediments coated with microphytobenthos prevent DIP release from sediments by assimilating DIP from porewater and incorporating organic P. At the opposite, high abundance of phytoplankton or macroalgae can settle and cover sediments by thick labile organic matter enhancing microbial activities and reducing oxygen penetration into the deeper sediment (Bartoli et al., 1996). The oxygen shortage can change redox conditions and cause release of DIP, as discussed above (Andrieux-Loyer and Aminot, 2001; Anderson and Taylor, 2001; Anschutz et al., 2007; Zhu et al., 2011). Moreover, macrophytes transport oxygen to deeper sediment layers with roots and prevent P release to water column (Witheras and Jarvie, 2008).

Bacteria and fungi participate in P cycle as decomposers of organic P. Moreover, they regulate the fluxes of P across the sediment–water interface either through the active uptake, the alteration of redox conditions at the sediment surface, and the production of refractory organic P compounds that become terminally buried (Gächter and Meyer, 1993; McDowell, 2003).

Macrofauna can alter metabolism through direct consumption of organic matter, excretion, and bioturbation (Kemp and Boynton, 1981; Cowan and Boynton, 1996; Fulweiler et al., 2010). For example, oligochaetes and chironomids change the chemical, physical and microbiological sediment condition by bioirrigation, bioturbation, ingestion, digestion, defecation, and excretion, by affecting phosphorus cycling in the sediments (Lewandowski and Hupfer 2005). Burrowing fauna by scavenging to sediments, ventilating can bring dissolved oxygen to deeper sediment layers, increase the oxic zones around the tubes and stimulate bacterial growth. Sediment surface oxygenation induces oxidation of reduced agents (Fe^{2+}, Mn^{2+},

S^-) and increase mineralisation of organic matter (Aller and Aller, 1998; Kristensen and Mikkelsen, 2003). During the burrowing activity burrowing fauna pump water through burrows and enhance solute exchange between the overlaying water and porewater by removing the metabolites of mineralization processes to the overlaying water. Bioirrigation decrease the DIP concentration in porewater due to the oxygenation and incorporation of phosphate in Fe(III) oxy-hydroxides (Gunnars et al., 2002). After the ingestion and digestion of taken particles, they are defecated in more labile compounds and excreted DIP can stimulate bacterial growth, and thus, mineralization.

Filter feeders play the role of ecological engineers by filtrating water column particles and incorporating nutrients in biomass or in the surface sediments (Caraco et al., 2000, 2006). Approximately 87 % of the total removed material has been deposited in the form of faeces and pseudofaeces, while the rest 13 % has been assimilated into the body weight of mussels (Daunys et al., 2006). On the other hand, filter feeders are seen as organisms contributing rather to the degradation than improvement of water quality by increasing the benthic respiration rate with labile organic matter and augmenting the risk of hypoxia and DIP release (Effler and Siegfried, 1994; Caraco et al., 2000; Bartoli et al., 2001).

The composition of burial P depends on hydrodynamic factors as accumulation, residence time and influence of the rivers. More organic phosphorus is extensively buried in more accumulative zone, while in erosive zone the detritic P is more abundant. Environmental condition changes under oxygen, salinity, pH variations, which can increase the exchange of DIP between the sediments and the overlaying water. High water productivity generates high amount of labile organic matter, which can settle and increase oxygen consumption releasing DIP. Much more DIP in saline environment liberates due to the combination of sulphate reduction, iron-sulphide formation and microbial Fe(III)oxide reduction (Roden and Edmonds, 1997; Conley, 2000). pH variations can convert Fe/Mn-bound P form to authigenic Ca-bound P and vice versa.

1.4 Eutrophication processes in transitional water and its causes

Phosphorus is an important constituent of biological systems involved in genetic material (RNA, DNA), membrane structure and energy transfer molecules (ATP) (Ruttenberg, 2003; Reddy et al., 2005; Bianchi, 2007; Conley et al., 2009; Ashley et al., 2011). Moreover, phosphates are necessary to create a stiff structure, and about 85% of phosphorus is found as a structural component of bones and teeth bound with calcium (Tzaphlidou, 2008). Due to the phosphorus importance for biota, it is one of the most necessary nutrients, which can cause seasonal or continual P limitation to water productivity (Ruttenberg, 2003; Brandes et al., 2007; Aydin et al., 2009, Ashley et al., 2011). High phosphorus fluxes give short term benefit by increasing productivity of water ecosystem, but in the long term have negative affect by causing water eutrophication.

Water eutrophication is the response of ecosystem to the nutrient enrichment (nitrogen and/or phosphorus), to the water system from the untreated waste water, over fertilised fields, etc. (Paerl et al., 2004; Andersen et al., 2006; Smith et al., 2006). Eutrophication process is not the short term water quality deterioration, but it can cause continued water conditions disturbances over the loss of habitat and natural resources, and severe hypoxia (Rabalais et al., 2009). Eutrophication process starts from the increase of nutrients input by rivers to the coastal zone, and the enhancement of nutrient concentrations in the coastal area (Fig. 1.4), which determines the increase of water productivity the harmful phytoplankton bloom.

The bloom can destabilize the equilibrium of the system resulting in outspread of one or few phytoplankton species (Tubay et al., 2013). Harmful phytoplankton can cause harm either due to the direct toxin production and development of high biomass leading scums (Anderson et al., 2002). N-fixing cyanobacteria are presented as common phytoplankton species, as a consequence of eutrophication, as they have competitive advantage under the calm warming conditions. They can proliferate quickly with the available phosphorus and fixing gaseous nitrogen (Correll, 1998; Helbling et al., 2015). High abundance of the phytoplankton covers water surface and light cannot penetrate in the deeper layers by preventing the growth of seagrass. The increase of biomass sustains trophic chain by increasing zooplankton → fish populations. The high amount of labile organic matter, produced during the bloom, settles in the sediments and improves the food quality for benthic animals for short period. The intensive mineralisation of settled organic matter causes oxygen deficiency and toxic hydrogen sulphide formation losing benthic abundance and diversity in sulphate rich areas (Correll, 1998; Glibert et al., 2005; Díaz and Rosenberg, 2008; Helbling et al., 2015).

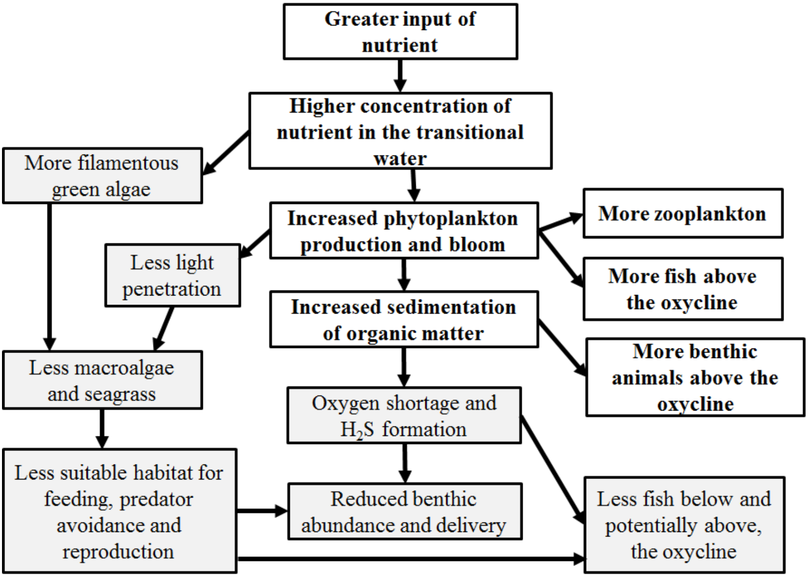


Fig. 1.4 *Schematic representation of cascading effects of the eutrophication process. Grey box represents the harmful effect. (modified from Rönnberg and Bonsdorff 2004 and Rabalais et al. 2009)*

Additionally, the increased respiration processes and consequent CO_2 release in eutrophic shallow marine areas enhance global warming (Föllmi, 1996). Global warming may sustain eutrophication process by the increasing water temperature, which leads to more susceptible development of hypoxia through enhanced stratification, decreased oxygen solubility, increased metabolism and remineralization rates, increased production of organic matter, and increased inflows of freshwater and nutrients to the coastal water (Rabalais et al., 2009). Moreover, the increased temperature is changing into more calm weather and extended to more cloudy cover (Verity et al., 2006)

1.5 Water quality and management

Water management strategies have to be taken for water quality improvement and mitigation of eutrophication process. There is a debate whether one or both nutrients (N and P) should be controlled (Conley et al., 2009). Phosphorus is considered as the most common cause of eutrophication in freshwater, lakes and oligohaline estuaries, while nitrogen is the key nutrient controlling primary production in the seas and oceans (Andersson et al., 1996; Nixon et al., 1996; Correll, 1998; Blomqist et al., 2004). The excess of both P and N is related to the eutrophication problems, where the shift of nutrient accessibility affects the seasonal evolution of phytoplankton communities (Correll, 1998; Paerl, 2008; Wang and Wang, 2009). P limitation is observed in spring and autumn, while in summer season N is limiting primary producers (Correll, 1998; Conley et al., 2009). Moreover, the different phytoplankton communities are controlled by certain nutrients. Green algae is N or N and P limited, diatoms are silica limited, while N fixing phytoplankton is P limited (Correll, 1998). Transitional water, dominated by N-fixing cyanobacteria, is expected to be P controlled at least in summer (Pilkaityte and Razinkovas, 2006; 2007). According to recommendations of Daunys et al. (2007) and Langas et al. (2010), TP is an indicator for the water quality of transitional water. The classification is based on the TP concentration values during the period from June to September (Table 1.2, Remeikaitė-Nikienė et al., 2013).

Table 1.2 Ecological state classes according to physico-chemical quality elements for transitional waters (values in µM) (Langas et al., 2010)

Water quality status	**Boundary values of TP at the plume of Curonian lagoon in the Baltic sea zone (µM)**	**Boundary values of TP at northern part of the Curonian lagoon (µM)**	**Boundary values of TP at southern part of the Curonian lagoon (µM)**	**N:P ratio**
Reference	<0.90	<1.52	<1.55	>40
High good	0.91 – 1.18	1.53 – 1.90	1.56 – 1.94	40–35
Good	1.19 – 1.71	1.91 – 2.58	1.94 – 2.55	34–30
Moderate	1.72 – 2.71	2.58 – 4.39	2.56 – 4.19	29–20
Poor	2.72 – 5.65	4.40 – 10.06	4.20 – 8.97	19–10
Bad	>5.66	>10.06	>8.98	<10

Water pollution can be improved by implementing P mitigation approaches. Pollution by P from point source can be reduced by implementing P removal tools. Three types of removal exist: first is precipitation with cations, the second is assimilation by plant or microorganisms (activated sludge plants) and the third is by magnetic or ion exchange process. Chemical precipitations and biological approaches are widely used in the waste water treatment plants. During the chemical dosing, different salts are used as calcium, magnesium ammonium (later can be used in agriculture as fertilizer), iron and aluminium compounds (products are not used for fertilization) (Smil, 2000; Jarvie et al., 2008). For non-point pollution, several mitigation approaches are used the formation of buffer zones, construction of wetlands and ponds, due to the surface run-offs and erosion. The reduced autumn tillage also minimizes the pollution of P from agriculture land (Ulún et al., 2007; Jarvie et al., 2008). In addition to this, the reed cultivation and filter feeder introduction to transitional water can be the approach to minimise the particulate and dissolved pollution (Li et al., 2003; Caraco et al., 2006; Zhou and

Hosomi, 2008; Schernewski et al., 2012; McLaughlan and Aldridge, 2013). The last mentioned approach is on the debate, because filter feeders are filtering water and reducing particulate concentration in the water. However, filter feeders extract with faeces and pseudofaeces dissolved and labile organic matter, which can promote blooming and change biogeochemistry of surrounding sediments (Zhang et al., 2011 Effler and Siegfried, 1994; Caraco et al., 2000; Bartoli et al., 2001, Ruginis et al., 2014).

In many cases, the water quality was not improved after the adoption of watershed-based protection programs through last decades (Jarvie et al., 2013; Meals et al., 2010; Sharpley et al. 2013). The protection actions were undertaken to minimise nutrient losses from point and diffusive sources (Sharpley et al., 2013) in such systems as the Chesapeake Bay watershed (Reckhow et al., 2011), Mississippi River basin (Dale et al., 2010), the Lake Erie basin (Sharpley et al., 2012) 20 to 30 years ago. But water quality was not improved and eutrophication process took place. The N and P riverine loads to the Baltic Sea were reduced by 50 %, but N-fixing blooms were occurring in summer (HELCOM, 2009). Many scientists are postulating that the sedimentary phosphorus is a cause of cyanobacteria bloom even if the external P loads are minimised (Hamilton, 2012; Meals et al., 2010; Spears et al., 2012; Sharpley et al., 2013). Since phosphorus gaseous form is negligible in aquatic systems, P has capability to accumulate in water system sediment. Moreover, P can be remobilised or recycled within the water system and can act as a continuing source to downstream water bodies for years, decades, or even centuries (Sharpley et al., 2013).

2. STUDY AREA

The Curonian Lagoon is situated in the south–eastern part of the Baltic Sea (Fig. 2.1) and with total surface of 1584 km^2 is the largest lagoon in Europe (Žaromskis, 1996; Pustelnikovas, 1998).

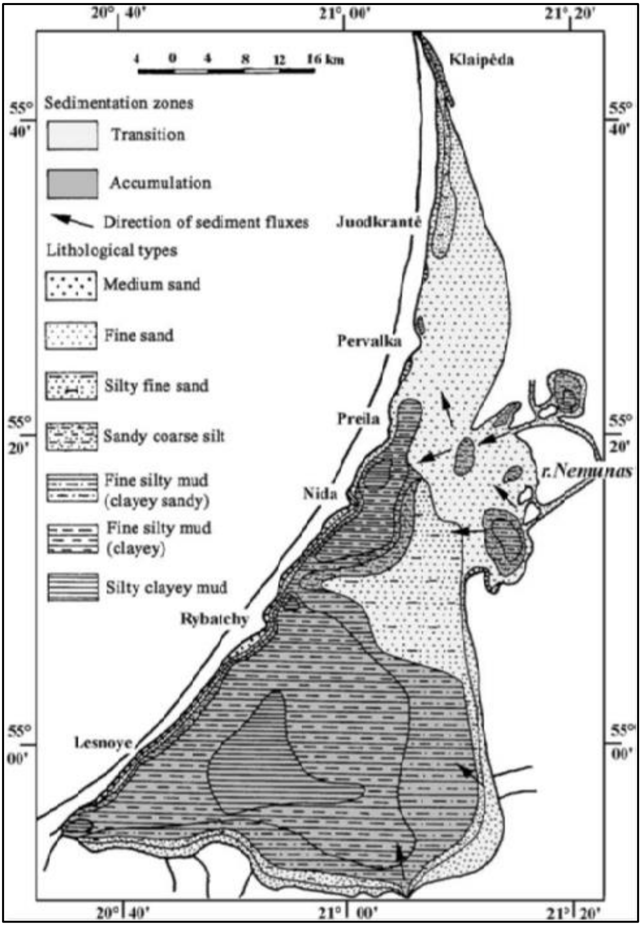


Fig. 2.1 *Curonian lagoon map based on sedimentation zones (taken from Gulbinskas, 1995)*

Curonian lagoon is non-tidal water body almost entirely restricted from the Baltic Sea except for a narrow connection (0.4 km wide) located in the north corner (Žaromskis, 1996; Gasiūnaite et al., 2008). Curonian lagoon is mainly freshwater except for the northern part, where salinity vary around 6–8 (Dailidienė and Davulienė, 2007). Curonian lagoon is traditionally divided into three zones: northern, central and southern (Žaromskis, 1996). Klaipeda strait is the part that is strongly affected by anthropogenic activities including dredging and intensive shipping. Consequently this part is treated as a separate zone of Curonian lagoon (Žaromskis, 1996).

It is a shallow lagoon with a mean depth of 3.8 m; the southern part is the deepest (average depth ~5 m), while the northern part of the lagoon is more shallow (1–2 m). Klaipeda strait is the deepest part of the lagoon with depths up to 12–14 m (Pustelnikovas, 1998).

Water circulation in the lagoon. Curonian lagoon is fed by four main rivers (Nemunas River, Matrosovka, Minija and Deima). Nemunas River is considered the main water source to the lagoon (Žaromskis, 1996; Gailiušis et al., 2005; Jakimavičius, 2012) and modelling data showed that river in the Russian part of the lagoon (Matrosovka and Deima) do not influence water circulation (Ferrarin et al., 2008). The highest discharge of Nemunas is recorded in the November–May period with an annual average discharge of 487±206 and 541±312 $m\,s^{-1}$ in 2011 and 2013, respectively (Fig. 2.2). According to Pustelnikovas (1998), Nemunas River input to the Curonian lagoon is highest in spring (41.6 % of all discharge) and lowest in summer. The same pattern is observed for outflows from the lagoon.

Water circulation is triggered by wind speed / direction and Nemunas discharge (Fig. 2.3). The northern part of the lagoon is influenced by Nemunas River, while southern part is more affected by wind (Ferrarin et al., 2008). South-west, west, and south-east are the wind dominant directions on the Lithuanian coast (Davulienė et al., 2002).

The wind action creates water circulation by dividing lagoon in subsystems. In the highest discharge period during the spring floods, the south–north currents moves water from the river mouth to the Baltic Sea through Klaipėda Strait.

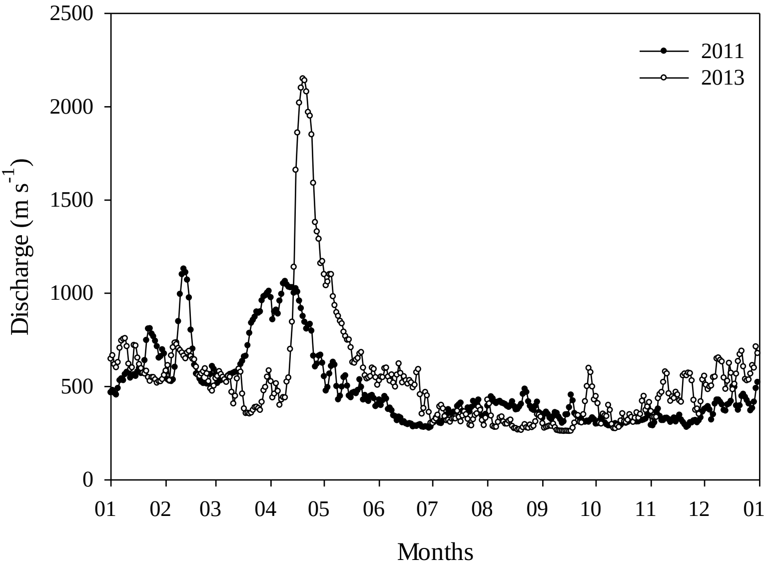


Fig. 2.2 *Nemunas River discharge in 2011 and 2013 (data from Marine Research Department)*

When strong north and north-west winds blow, brackish sea water enters the lagoon and salinity could be traced down to the central part of the lagoon (Ferrarin et al., 2008). Model simulations showed that the Baltic Sea water influences the northern part (up to 20 km from the sea entrance) of the lagoon and has negligible effects at the distance of about 20 km to south (Ferrarin et al., 2008; Zemlys et al., 2013).

The residence time is lowest in Klaipeda strait area; the northern part of lagoon has values of 10–40 days. The residence time in the central and the southern parts is >100 days. In general residence time (water renewal) is related to fresh water discharge intensity (Ferrarin et al., 2008).

Sedimentation and sediment types in the Curonian lagoon. The Curonian lagoon is collecting the runoff material from Nemunas and other minor rivers, 49 % of the total particulate matter (Table 2.1) being of terrigenous origin, 45 % of particulate matter is produced within the Curonian lagoon and only 2 and 4 % of particulate material is coming from the sea and from the weathering, respectively (Pustelnikovas, 1998).

Table 2.1 Balance of sedimentary material of the Curonian lagoon (modified from Pustelnikovas, 1998)

Elements	Total particulate matter (thous. tons y^{-1})	Total particulate matter (% of total input/output)	Terrigenous material (% of element value)	Biogenous substance (% of element value)
Total input	1346.3			
River discharge	660.6	49	60	40
From sea and air	22.5	2	32	68
Bioproductivity	610.2	45	-	100
Abrasion, erosion and eolic transport	53	4	94	-
Total output	1346.3			
To the sea	424.0	32	28	72
Dissolution/ mineralisation	523.1	38	-	100
Accumulation	399.2	30	99	1

About 30 % of the incoming particulate matter settles in the southern part of the Curonian lagoon (Pustelnikovas, 1998), whereas 32–40 % is carried through the Klaipeda Strait to the Baltic Sea (Pustelnikovas, 1998; Daunys et al., 2006). About 72 % of the particulate matter outflowing to the Baltic Sea is of biogenous origin

(Pustelnikovas, 1998). However, the largest part of biogenous particulate matter is mineralized within the lagoon.

Table 2.2 Quantitative distribution of suspended matter in the water column (taken from Pustelnikovas, 1998)

Sedimentation zone	**Sample number**	**Content of suspension (mg l^{-1})**	
		Limit of changes	**Mean**
Rivers	15	11.0–54.1	28.6
Curonian lagoon, total including:	73	10.0–85.2	30.3
Southern	17	13.9–51.4	30.1
Central	26	13.0–85.2	31.0
Northern	30	10.0–52.4	31.1
Near mouth area of Baltic Sea	21	0.9–21.8	6.6

The formation of sediment is associated with particulate matter quantity and quality (Table 2.2), internal particulate matter formation, sedimentation rates and watershed hydrodynamic activities. Small particles are mostly transported to the Baltic Sea, while the bigger ones are settled near the river mouths. Since the southwest corner of the Curonian lagoon is the most hydraulically stagnant part of the lagoon, small particles of silt and clay settled there and, consequently, sediments are mostly fine silty mud. The medium sand is the dominant fraction in the northern part of the lagoon (Fig. 2.1, Galkus, 1995; Gulbinskas, 1995; Žaromskis, 1996; Pustelnikovas, 1998).

3. MATERIAL AND METHODS

3.1. Sampling sites

Four sampling sites were chosen for the study in the Curonian lagoon (Fig. 3.1).

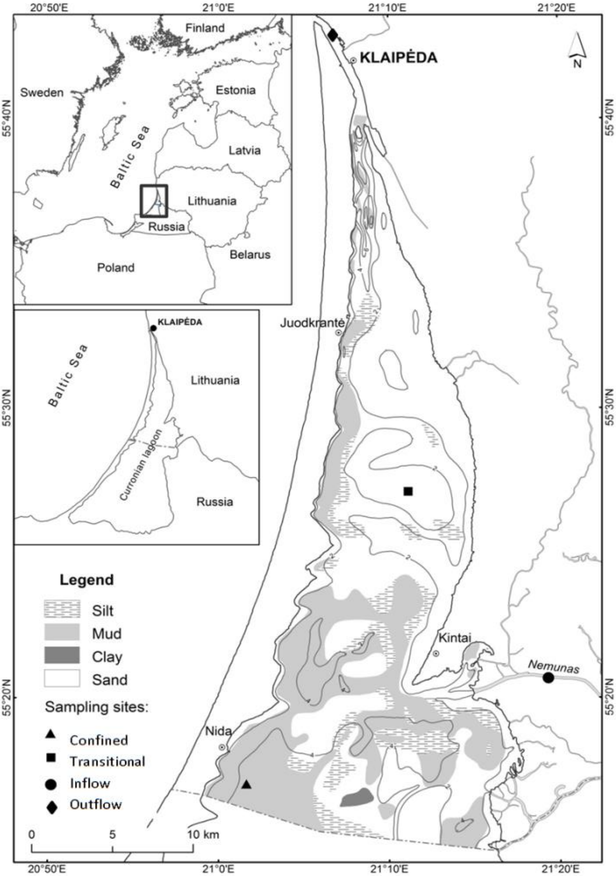


Fig. 3.1 *Location and map of the Lithuanian part of the Curonian Lagoon, with indicated the sampling sites, the sediment composition and the water depth*

At two sampling sites: transitional (TS) and confined (CS), samples of surface and bottom waters and sediment were taken during monthly campaigns from April to September in 2011 and in 2013 (Fig. 3.1; Table 3.1).

Transitional and confined sampling sites represent different sedimentary and hydrodynamic areas in the lagoon. The transitional site is shallow (mean depth 1.5 m) and sandy; it is influenced by riverine discharges and brackish water intrusions from the Baltic Sea. This site has low water residence time and frequent resuspension prevent organic matter accumulation (Ferrarin et al., 2008).

Table 3.1. The summary of parameters measured in the transitional (TS), confined (CS), inflow (I) and outflow (O) sites in 2011 and 2013

No.	Parameters	Periods of sampling		Layers	Samples No.	St.
		Years	Months			
1	2	3	4	5	6	7
Water column						
1	Temperature, DO, pH, salinity	2011, 2013	04–09	surface, bottom	24^1	TS, CS
2	**TP***, *DIP*	2011*, 2013	04–09	surface, bottom	24^3	TS, CS
3	**TP***, *DIP*, DIN**	2011*, 2013	01–12	surface	24^3	I, O
4	**DOP, PIP, POP**	2013	04–09	surface	6^3	TS, CS
		2013	01–12	surface	12^3	I, O
5	Photic zone	2011, 2013	04, 07, 09	through all depth	6^3	TS, CS
6	***Chl-a and phytoplankton groups***	2011, 2013	04–09	surface	12^3	TS, CS
Sediments						
7	**Density, porosity, WC, LOI, TP, OP, IP**	2011, 2013	04–09	6 layers	72^3	TS, CS

Table 3.1, continuation

1	*2*	3	4	5	6	7
8	*Grain size*	2011, 2013	04, 07, 09	1 layer	6^3	TS, CS
9	**IP fractions**	2013	06, 09	5 layers	10^3	TS, CS
10	*Oxygen penetration depth*	2011, 2013	04, 07, 09	through all depth	6^3	TS, CS
11	*DIP in porewater*	2011	04–09	8 layers	48^3	TS, CS
		2013	04, 06, 07, 09	6 layers	24^3	TS, CS
12	*Net DIP fluxes*	2011, 2013	04–09	-	12^5	TS, CS
Assessment of hypoxia risk						
13	*DO*	2011	04–09	surface	12^3	TS, CS
14	**Net DO fluxes**	2011	04–09	-	6^5	TS, CS
Experiment of Anoxia						
15	*DO, DIP,* Fe^{2+}, Mn^{2+}, *DS*	2013	07	surface	9^4	CS
16	*DIP,* Fe^{2+}, Mn^{2+} *in porewater*	2013	07	6 layers	12^1	CS
17	**IP fractions**	2013	07	2 layers	4^3	CS

*data was taken from Marine Research Department;

^{1,3,4,5} in the column “Number of samples” – the number of replicates

Bold – analysis performed by the author;

Italic – analysis performed by other scientists (dr. Diana Vaičiūtė, dr. Gianmarco Giordani, Ilona Minevičiūtė, Irma Lubienė, dr. Marco Bartoli, dr. Marija Kataržytė, dr. Mindaugas Žilius)

The confined site (mean depth 3.5 m) is characterized by higher water residence time >100 days and silt-muddy deposits (Ferrarin et al., 2008).

Additional sampling sites were selected to characterize inflow (I) and outflow (O) water characteristics in order to assess external P inputs and outputs. Sampling campaigns were organized monthly from January to December in 2013. For 2011 data collected by the Marine Research Department were used.

3.2 Measurements of water column characteristics

In situ temperature, pH, salinity and dissolved oxygen (DO) concentrations were measured at the surface (0.3 m depth) and bottom water layers (0.5 m above the sediment) at two sites using YSI 460 multiple probe. In addition, seasonal photic zone depth was measured with the LI-192S underwater quantum sensor connected to a LI-COR 1400 data logger. The limit of the euphotic zone (Z_{eu}) is considered when radiation is 1 % of surface PAR. Phytoplankton was separated into "spectral groups" of green algae, diatoms, cyanobacteria and cryptophytes by using FluoroProbe II instrument according to their distinctive accessory pigments (Beutler et al., 2002). Moreover, the microscopic analyses were performed to identify whether N-fixing or non N-fixing species were dominant in the water column during the cyanobacteria bloom.

Dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen ($DIN=NO_x+NH_4^+$), total dissolved phosphorus (TDP), total phosphorus (TP) and chlorophyll *a* (Chl-*a*) concentrations were measured in all water samples. Aliquots for DIP and TDP measurements were immediately filtered through *Whatman GF/F*, while unfiltered water samples were used for TP measurement. For particulate and inorganic phosphorus (PP and PIP) water samples were filtered on the *Whatman GF/F* and filters were frozen for later analysis.

3.3 Sediment sampling and analysis

During each sampling event, eight intact sediment cores (Ø, 8 cm, 30 cm length) and three smaller intact cores (Ø, 4.6 cm, 25 cm length) were collected using the hand corer at the transitional and confined sites. Of the 8 larger cores, 5 were used for net DIP flux measurements while the remaining cores were used for porewater extraction. The smaller cores were sliced in the following sediment layers: 0-1, 1-2, 2–3, 3–5, 5–7 and 7–10 cm for physical and chemical sediment characteristics. Density (eq. 1), porosity (eq. 2) and water content (eq. 3) were calculated after sediment drying at 60 ^{o}C for 48 hours. Organic matter (LOI) expressed as weight loss after ignition is calculated according to the 4th equation.

$$Density = \frac{W_W}{V} \qquad \text{(eq. 1)}$$

$$Porosity = \frac{W_W - W_D}{V} \qquad \text{(eq. 2)}$$

$$Water\ content = \frac{W_W - W_D}{W_D} \times 100 \qquad \text{(eq. 3)}$$

$$Weight\ loss\ after\ ignition = 100 - \frac{W_I \times 100}{W_D} \qquad \text{(eq. 4)}$$

where W_w is a wet weight of sediment (g), W_D – dry weight of sediment (g), W_I – weight after ignition (g), V – volumn of taken sediment sample (ml).

Additional sediment samples were taken for total and inorganic phosphorus analysis (TP and IP) and in 2013 for inorganic phosphorus pools analysis. Sediment samples for TP and IP were dried at 60 °C for 48 hours and incinerated at 550 °C for 4 hours (only TP). TP and TIP pools were extracted with 37 % HCl and measured spectrophotometrically after neutralization with 10N NaOH, following Valderrama (1981). Organic P (OP) was calculated as difference between TP and the sum of sedimentary P pools that are considered as IP.

A detailed analysis of sedimentary P pools was conducted seasonally in 2013 (in June and September) when sediment samples were collected under anoxic conditions, homogenised and aliquots of approximately 6–10 g subsamples (wet weight) were transferred to N_2 pre-flushed centrifuge tubes. Sedimentary P pools analysis was conducted following the four–step sequential extraction scheme described by Ruttenberg (1992) and modified by Anderson and Delaney (2000). The extractions were carried out at room temperature (21 ^{o}C) under continuous shaking with the extracting solutions and for the time reported in Table 3.2. First two steps were performed under anoxic conditions.

Table 3.2 Steps of sequential sediment phosphorus extraction procedure

Steps	**Extractants**	**Extraction time**	**Extracted phosphorus (P) phase**
1	20 ml 1 M $MgCl_2$ (pH 7.5–8) 20 ml 1 M $MgCl_2$ (pH 7.5–8) 20 ml distilled water	2 h 2 h 5 min	Exchangeable P (Exch.~P)
2	10 ml CDB* 10 ml 1 M $MgCl_2$ (pH 7.5–8) 10 ml distilled water	6 h 2 h 5 min	Fe/Mn-bound P (Fe/Mn~P)
3	10 ml 1 M Na-acetate (pH 4) 20 ml 1 M $MgCl_2$ (pH 7.5–8) 20 ml 1 M $MgCl_2$ (pH 7.5–8) 20 ml distilled water	2 h 2 h 2 h 5 min	Authigenic Ca-bound P + $CaCO_3$-bound P +Biogenic apatite (Auth. Ca~P)
4	20 ml 1 N HCl	16 h	Detrital Ca-bound P (Detr. Ca~P)

*CDB is Citrate–Dithionite–Bicarbonate solution (0.22 M Na-citrate; 1 M $NaHCO_3$; 0.033 M Na-dithionite)

After each extraction, samples were centrifuged at 3000 rpm for 5 min and the supernatants were collected for DIP measurements. Furthermore, sediment grain size was measured with Frisch Lazer Particle Sizer Analysette 22.

3.4 Oxygen penetration depth microprofiles

Depth of oxygen penetration was measured in triplicate in intact core (n=3) by Clark-style microsensors (50 µm diameter, Unisense, DK), equipped with a guard cathode and an internal reference (Revsbech, 1989). The sensors were mounted on a motor driver micromanipulator which performed measurements with a depth resolution of 50 µm. The sensor current was measured with a multimeter connected to PC. All microprofiles were measured in the laboratory, placing the sediment cores in an aquarium containing *in situ* water maintained at ambient oxygen concentration and temperature. Two-point linear calibration of O_2 sensors was achieved in air saturated water (100 %) and 0.1 M alkaline solution of sodium ascorbate (0 %).

3.5 Dissolved inorganic phosphorus extraction from porewater

Sediment porewater samples for DIP were obtained by anoxic sediment squeezing. Sediment was extruded from the cores (n=3) in a glove bag under nitrogen atmosphere and sliced in the following depth layers: 0–0.5, 0.5–1, 1–1.5, 1.5–2, 2–3, 3–5, 5–7 and 7–10 cm in 2011 and 0–1, 1–2, 2–3, 3–5, 5–7 and 7–10 cm in 2013. Porewater was obtained by gentle N_2 squeezing of discrete sediment slices (under 2.5 – 3 bar pressure) and directly filtered through GF/F filters into 12 ml exetainers, acidified with few drops of concentrated H_2SO_4 and analysed within 24 hours.

3.6 Net dissolved inorganic phosphorus flux measurements

During each sampling event, five intact sediment cores (Ø, 8 cm, 30 cm length) were collected using the hand corer at the transitional and confined sites to measure DIP and DO (as TOU) fluxes as described in Zilius et al. (2014). Intact cores were transported to laboratory and submerged in the experimental chambers with water from the site at ambient temperature. Sedimentary fluxes were measured in the dark after overnight pre-incubation as described in Dalsgaard et al. (2000). Incubation times varied between 2 and 8 hours depending on the water temperature in order to keep final O_2 concentration within 20 % of initial value. Water subsamples were collected from each core with plastic 50 ml syringes at the beginning and at the end of incubation. Aliquots for DIP analyses were filtered using *Whatman GF/F* filters and transferred into 10 ml glass tubes. Fluxes were calculated according to the 5th equation:

$$F = \frac{(C_f - C_i) \times V}{A \times t} \qquad \text{(eq. 5)}$$

where F is the DIP and DO flux, C_i and C_f are initial and final concentrations of DIP and DO, V is the water volume overlying the core, A is the surface area of the sediment and t is incubation time.

3.7 Design of anoxia experiment

Water and sediment samples were collected at the confined site in 25/07/2013 (Fig. 3.1). During the sampling campaign, eight intact sediment cores (Ø, 8 cm, 30 cm length) were collected using the hand corer. In addition, 50 liters of water were collected for core maintenance and incubations. Intact cores were transferred to the laboratory within 4 hours where they were left to settle overnight at the *in situ* temperature submerged in incubation tanks with unfiltered, well-mixed and aerated water from the confined site. After one day, 4 cores were used for DS microprofiling and sliced under N_2 atmosphere for the analysis of porewater DIP, dissolved iron (Fe^{2+}), manganese (Mn^{2+}) and sedimentary particulate P pools. The rest of the cores were incubated, after replacing the water in the tank and providing each liner with magnetic stirrer.

At zero time, four replicates water samples (ca. 15 ml) were collected from the incubation tank and the cores were closed with rubber stoppers and were left in the dark. The second water sampling was conducted after 3 hours of incubation in order to keep the dissolved oxygen (DO) concentration within 20–30 % of the initial value. The following samplings were conducted at about ~5 hour intervals. The dark incubation lasted until anoxia conditions were maintained for some hours to avoid the extreme and unrealistic conditions. The experiment finished after about 40 hours.

Table 3.3 Summary of experimental activities in the confined site.

Type of activity	Sampling design	Measures
Water column analyses	Time series	DO, DIP, Mn^{2+} and Fe^{2+}
Porewater extraction	initial and final	DIP, Mn^{2+} and Fe^{2+}
Sequential P extraction	initial and final	IP pools
Microprofiling	initial and final	DS

At each sampling event, DO concentrations were measured with a microelectrode (Unisense, DK) and water subsamples of 15 ml were collected, filtered and acidified for DIP, Fe^{2+} and Mn^{2+} analyses. Sediment microprofiles of DS were done in triplicates and cores were sliced for porewater extraction and sedimentary inorganic P pools at the end of the experiment. The summary of experimental activities is shown in Table 3.3.

Net fluxes (µmol or mmol $m^{-2}h^{-1}$) of all measured solutes across the sediment–water interface during the oxic–anoxic transitions were calculated according to net flux measurements presented in section 3.4. The flux of DO is referred therein as total sediment oxygen uptake (TOU).

3.8 Hypoxia risk assessment

The risk of transient hypoxia was assessed in 2011 in bottom water layer under calm weather conditions by calculating the number of hours required to reduce oxygen concentrations below 62.5 µmol l^{-1}, taking into account pelagic and benthic respiration and assuming an initial oxygen content of 100 % saturation (more in Zilius et al., 2014).

Pelagic community respiration measurements were performed in 2011. Rates of community respiration (CR) in the water column were measured by the light–dark bottle technique. Six replicate 115 ml Winkler glass bottles were filled with pooled water from surface and bottom layers. Three replicates were immediately fixed with Winkler reagents for dissolved oxygen analysis (T_o); the remaining three bottles were used for dark incubation. CR was measured in Winkler bottles transferred to opaque plastic bags and incubated in situ. Incubation length was between 3 and 7 h, depending on water temperature and for Chl-*a* concentration to have measureable differences in dissolved oxygen, avoiding excess of oxygen production or consumption. After incubation water was immediately fixed with Winkler reagents for final dissolved oxygen analysis (T_f). Pilot incubations were carried out in the laboratory to set appropriate incubation times, in order to limit dissolved oxygen variations within 20–30 % of the initial value. Rates of CR were calculated from the differences in dissolved oxygen concentrations at the start (T_o) and end of the incubation periods (T_f) and expressed in units of micromoles per cubic meter per hour.

Benthic respiration was evaluated from the intact core incubation by measuring dissolved oxygen concentration at the start and the end of incubation. The rate of benthic respiration was calculated by using the 5th equation.

3.9 Analytical methods

Water samples from *in situ* sampling, extractions and incubations were analysed for DIP and DIN concentrations with the continuous flow analyser (San++, Skalar, sensitivity 0.3 µM); only DIP samples obtained from TIP analysis were measured spectrophotometrically at 885 nm (Grasshoff et al., 1983). TP and TDP were analysed spectrophotometrically at 700 nm after acid persulphate oxidation

(Grasshoff et al., 1983). Dissolved organic phosphorus (DOP) was calculated by subtracting DIP from TDP values. TPP was calculated as difference between TP and TDP. Inorganic and organic fractions of particulate P were calculated from total particulate phosphorus (PP) and particulate inorganic phosphorus (PIP) analyses. Filters were dried at 60 °C for 24 h, incinerated at 550 °C for 4 h (only for PP) and analysed spectrophotometrically at 880 nm after dissolution into 1M of HCl for 2 h (Aspila et al., 1976). Chl-*a* was extracted from the filters with 5 ml of 90 % acetone for 24 h at 4 °C, extracts were centrifuged and Chl-*a* was measured spectrophotometrically according to Lorenzen (1967).

3.10 Numerical data analysis

3.10.1 Diffusive dissolved inorganic phosphorus transport

Diffusive flux of DIP at the sediment water-interface was calculated from DIP profiles in the sediment porewater by applying Fick‘s first law (Berner, 1980):

$$J = -\varphi \times D_S \times (\frac{dC}{dx})_{x=0} \qquad \text{(eq. 6)}$$

where J (µmol $m^{-2}d^{-1}$) is diffusive flux of DIP, φ is the average porosity measured in the upper 1 cm sediment layer), D_S ($m^2\,d^{-1}$) is the diffusion coefficients of DIP within sediments and *dC/dx* (mmol m^{-4}) is nutrient concentration gradient across the sediment-water interface. *DS* was determined according to Lerman (1979):

$$D_S = \frac{D_w^0}{\theta^2} \qquad \text{(eq. 7)}$$

where D_w^0 is coefficient corrected for temperature with the Stokes–Einstein relation (Li and Gregory, 1974). Infinitive molecular diffusion coefficient for DIP in water taken from Broecker and Peng

(1974) and Θ^2 is tortuosity obtained from the equation (Boudreau, 1997):

$$\theta^2 = 1 - 2ln\varphi \qquad \text{(eq. 8)}$$

Diffusive flux was calculated according to the concentration change between the near bottom and sediment layer, which supports the best linear fit.

3.10.2 Shear stress calculation

The resuspension condition before and during the sampling was identified by calculating wind induced bottom shear stress (according to Laenen and le Tourneau, 1996). The wind speed and direction data from Vente meteorological station provided by Marine Research Department were used. The fetches at different wind directions were calculated using eq. 9 (Gons et al., 1986):

$$F = \frac{\sum_{i=1}^{15} x_i (cos\alpha)^2}{13.5} \qquad \text{(eq. 9)}$$

where F is the effective fetch; x_i is the distance from a point in the lagoon to the shore; α is the angle from the wind direction azimuth, in 60 increments from 42^o to -42^o. Later the fetches were extrapolated by using QGIS GIS software for 2 sampling sites.

The calculation of bottom shear stress requires the computation of wave period (T), wave length in shallow water (L_o) and wave height (H). These equations are as follows:

$$T = 7.54\left(\frac{U_A}{g}\right) tanh\left(0.833\left(\frac{gh}{U_A^2}\right)^{0.375}\right) tanh\left(\frac{0.0379\left(\frac{gF}{U_A^2}\right)^{0.333}}{tanh\left(0.833\left(\frac{gh}{U_A^2}\right)^{0.375}\right)}\right) \qquad \text{(eq. 10)}$$

where T is the wave period; U_A is the wind speed; g is gravity; F is effective fetch, h is the water depth.

$$L_o = \left(\frac{gT^2}{2\pi}\right) tanh\left(\frac{2\pi h}{\left(\frac{gT^2}{2\pi}\right)}\right) \qquad \text{(eq. 11)}$$

where L_o is the wave length in shallow water.

$$H = 0.283\left(\frac{U_A^2}{g}\right) tanh\left(0.530\left(\frac{gh}{U_A^2}\right)^{0.75}\right) tanh\left(\frac{0.00565\left(\frac{gF}{U_A^2}\right)^{0.5}}{tanh\left(0.530\left(\frac{gh}{U_A^2}\right)^{0.75}\right)}\right) \text{(eq. 12)}$$

where H is the wave height.

Calculation of the maximum horizontal velocity at edge of the bottom boundary layer determines bottom shear stress which is described by the equation (Sheng and Lick, 1979):

$$u_m = \frac{\pi H}{Tsinh\left(\frac{2\pi h}{L_o}\right)} \qquad \text{(eq. 13)}$$

where u_m is the maximum bottom boundary velocity.

$$\tau = \rho f u_m^2 \qquad \text{(eq. 14)}$$

where τ is the bottom shear stress, ρ is water density = 1, f is a dimensionless skin friction coefficient $1/R_e$. Where R_e is a Reynolds number from 15–30 (f=0.04 in the lagoon).

3.10.3 Phosphorus mass balance calculation

Phosphorus budgets were calculated on seasonal and annual basis for 2011 and 2013 using monthly sampling data of dissolved and particulate P forms and daily water discharges of the Nemunas River provided by the MRD. Since the Nemunas River is supplying the Curonian lagoon by 98 % of the incoming water (Jakimavičius, 2012) it is considered to be the only water input. Precipitation and water evaporation are generally in equilibrium and were not considered in the water (and P) balance (Gailiušis et al., 2005; Jakimavičius and

Kraučiuniene, 2011). Thus it is assumed that the water outflow from the lagoon is similar to the river discharge since brackish water intrusion was negligible (during the sampling campaigns no saline water intrusions were recorded). The daily P concentrations (C_n) were extrapolated from the measured monthly values in inflowing and outflowing water. P daily loads (L_n) were calculated as the product of C_n and D_n (the corresponding daily river water discharge of the day n). The same approach was applied for DIN:DIP loads calculations.

Annual and seasonal P budgets were calculated using a black box approach, assuming the lagoon to be in steady state and normalizing inflowing and outflowing loads on a square meter basis. The internal P transformations ($\mathit{\Delta L}$) were calculated as:

$$\Delta L = L_{out} - L_{in} \quad \text{(eq. 15)}$$

where L_{out} and L_{in} are the outflow and inflow loads per m^{-2}, respectively. Negative $\mathit{\Delta L}$ is an indication that the lagoon acts as a sink for P, while positive values, indicate that the lagoon is a P source.

Seasonal budgets were calculated separately for the spring (April–May), summer (June–August) and autumn (September) periods in order to compare rates with measured sediment fluxes. The average sediment–water fluxes of inorganic P were calculated combining data from the muddy (confined) and sandy (transitional) zones, which represent 44 % and 54 % of the total lagoon area, respectively.

3.10.4 Statistical analysis

Different types of statistical analyses were applied in the study. The descriptive statistic was performed for all data used in the thesis (except for such parameters as water temperature, salinity, pH and dissolved oxygen concentration). The multivariate analysis was employed to analyse variability and relationship between phosphorus and environmental parameters (Table 3.4). Water column and sediment characteristics, DIP in porewater and fluxes were tested for normality using the Kolmogorov–Smirnov test.

Table 3.4 Statistical methods applied in the thesis

	Objective	Years	Study site	Data	Transformation.	Statistical analysis
	1	2	3	4	5	6
4.1	Comparison between years	2011 2013	TS, CS	Temperature Chl-*a*	- -	T–test
	Comparison between the study sites	2011 2013	TS, CS	Temperature	-	T–test
4.2	Comparison between years and sites	2011 2013	TS, CS	TP DIP	Square root	Two–way ANOVA
	Relationship between response and explanatory variables	2011 2013	TS, CS	Responses: TP, DIP 7 explanatory: 2 nominal.	-	Redundancy analysis (RDA)
	Comparison between sites	2011 2013	TS, CS	Sedimentary TP	-	T–test
	Comparison between years and months	2011 2013	TS	Sedimentary TP	-	Two–way ANOVA
	Comparison between years and months	2011 2013	CS	Sedimentary TP	-	Two–way ANOVA
	Comparison between sites	2011 2013	TS, CS	DIP porewater	- -	T–test
	Comparison between stations	2011 2013	TS, CS	density, porosity, LOI, TP, IP, OP, DIPpw	-	Multidimensional scaling (MDS)

Table 3.3, continuation

	1	2	3	4	5	6
4.3	Comparison between years, months, sites	2011 2013	TS, CS	Net DIP fluxes	Log(x^2)	Three–way ANOVA
	Correlation between DIP fluxes and Chl-*a*	2011 2013	CS	Net DIP fluxes and Chl-*a*		Spearman correlation
	Correlation between DIP fluxes and TP loads	2011 2013	TS	Net DIP fluxes and TP loads		Spearman correlation
	Comparison of diffusive and net fluxes	2011 2013	TS, CS	DIP measured and calculated fluxes	-	Mann–Whitney Rank Test
4.4	Comparison of treatment	2013	CS	DIP Fe^{2+} Mn^{2+}	- - -	Repeated ANOVA
	Comparison between oxic and anoxic conditions	2013	CS	Fe^{2+} Mn^{2+}	- -	T–test
	Comparison between oxic and anoxic conditions	2013	CS	Exchangeable P Fe/Mn-bound P Authigenic Ca-bound P Detritic Ca-bound P	- - - -	T–test

If the parameters were not normally distributed, they were transformed by square root or log(x^2) before statistical tests.

Differences between years or sites were tested applying T–test for normally distributed or Mann–Whitney Rank Test for not normally distributed parameters. Two–way ANOVA was applied to delineate temporal differences and differences between the sites TP, DIP and sedimentary TP distribution in the water and sediments, respectively. The Redundancy analysis (RDA) was applied to establish the relationship between the environmental characteristics and phosphorus different forms in the water. For the dissimilarities of sites regarding to sediment composition the Multidimensional scaling (MDS) was applied with the ANOSIM statistical ranking. Three–way ANOVA was used to test the significance of years, months and sites for DIP net flux. For the significant factors, *post hoc* pair-wise comparisons were performed using the Tukey HSD test. Statistical significance was set at $p < 0.05$. Finally, repeated ANOVA was applied for solutes (DIP, Fe^{2+}, Mn^{2+}) changes during oxygen depletion.

All the analysis was performed and data visualized using *Brodgard 2.7.4, R 3.0.2, Primer 6* and *SigmaPlot 12.5* software.

4. RESULTS

4.1 Characteristics of study environment

4.1.1 Water column characteristics

During the sampling period no brackish water intrusions from the Baltic Sea were detected. The salinity was <1 ‰ in all samples (both at surface and bottom water layers) (Table 4.1). Temperature didn't show statistically significant difference between years (t–test, $t=0.74$, $df=22$, $p>0.05$) or study sites (t–test, $t=0.18$, $df=22$, $p>0.05$). Temperature varied seasonally in the range of 2.0–15.4 ^{o}C in April–May, 19.1–26.3 ^{o}C in June–August and 11.2–15.5 ^{o}C in September. Despite the shallowness of the lagoon, thermal stratification was observed in July of 2011 at the confined site during the calm weather conditions. During this event temperature was 26.3 ^{o}C at the surface and 20.9 ^{o}C in the bottom water layer. The average surface water pH was 9.0±0.3 in 2011 and 8.6±0.2 in 2013 with highest value (pH 9.4) in July of 2011 at the confined site (Table 4.1) during phytoplankton bloom (Fig. 4.1). The average surface DO concentration varied from 210 to 786 μM in 2011 and from 294 to 564 μM in 2013. Thermal stratification occurred in July of 2011 at confined site and was coupled to DO depletion in the bottom water layer (786 μM DO at the surface and 68.4 μM in the bottom).

There were differences in seasonal phytoplankton succession (i.e. Chl-*a* concentration and dominant phytoplankton groups) between studied years (t–test, $t=2.7$, $df=12.8$, $p<0.05$) (Fig.4.1). Chl-*a* concentrations were 3 times higher in 2011 comparing to 2013. Higher Chl-*a* concentrations were measured in summer 2011 (122.5±66.2 μg l^{-1}) with peak of 236.6 μg l^{-1} in July at the confined site.

Table 4.1 Surface and near bottom water characteristics at studied sites in the Curonian Lagoon during 2011 and 2013; (n=1)

Date	Temperature (^{o}C)		Salinity (‰)	pH	Dissolved oxygen (μM)	
	Surface	Near bottom	Surface	Surface	Surface	Near bottom
Transitional site						
04/2011	7.1	7.1	0.2	-	274.9	257.5
05/2011	13.5	13.5	0.2	8.7	368.8	368.8
06/2011	19.8	19.2	0.5	9.0	330.6	332.5
07/2011	22.7	20.9	0.2	9.1	607.8	370.0
08/2011	19.7	19.7	0.2	9.2	352.5	352.5
09/2011	14.9	14.9	0.2	8.5	296.9	296.9
04/2013	3.6	3.6	0.2	8.7	550.6	550.6
05/2013	15.4	15.3	0.2	8.4	302.2	300.2
06/2013	19.1	19.0	0.2	8.6	286.9	280.1
07/2013	20.9	20.0	0.3	8.5	290.6	274.6
08/2013	20.0	19.9	0.2	9.2	342.2	338.5
09/2013	11.2	11.2	0.4	8.5	402.2	385.9
Confined site						
04/2011	8.3	8.3	0.2	-	210.4	198.2
05/2011	13.5	13.5	0.2	8.5	381.4	381.3
06/2011	21.0	18.9	0.2	9.2	502.8	282.5
07/2011	**26.3**	**20.9**	0.1	9.4	**785.6**	**68.4**
08/2011	19.7	19.7	0.2	9.0	320.3	320.3
09/2011	15.5	15.5	0.2	9.0	320.5	320.6
04/2013	2.0	2.0	0.2	8.6	502.2	497.2
05/2013	14.4	14.4	0.2	8.7	389.1	384.4
06/2013	19.7	19.5	0.2	8.7	305.9	283.7
07/2013	21.9	21.0	0.2	8.5	309.4	271.3
08/2013	19.4	19.3	0.2	8.6	372.8	345.7
09/2013	11.8	11.8	0.2	8.5	425.0	331.9

Spectral analysis of functional phytoplankton groups revealed noticeable prevalence of cyanobacteria (51.2±32.6 %) in 2011 and green algae (38.6±14.6 %) in 2013. Nitrogen fixing cyanobacteria were dominant in both years.

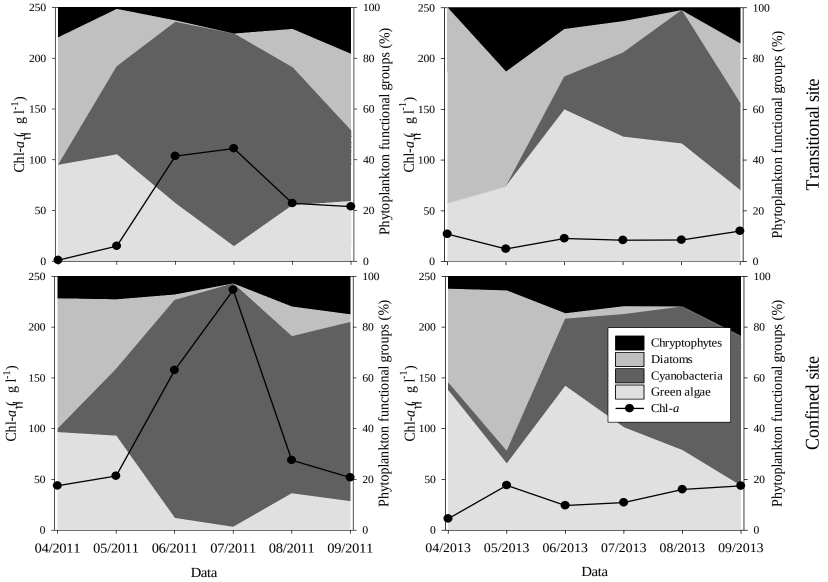


Fig. 4.1 *Chl-a and phytoplankton functional groups during study years at transitional and confined sites*

Penetration of solar radiation into the water column (Z_{eu}=1 % of surface PAR) was extended to 0.4–1.8 m and 1.4–2.0 m at confined and transitional sites, respectively, representing 13–53 % and 75–95 % of water column in 2011 (data not shown). The cyanobacterial bloom observed in July 2011 turned the lower 87 % of the water column aphotic, while in 2013, the euphotic zone comprised 99.5 % and 56–71 % of water column at transitional and confined sites, respectively.

4.1.2 Sediment characteristics

Transitional site was located in the riverine plume area and had an erosive sediment type, characterized by medium grain size sand, high density, low porosity and water content (Table 4.2). These physical parameters remain more or less constant in the whole sediment profile (Appendix 1).

Table 4.2 Sedimentary features of sampling sites (2011 and 2013 averages). Data referred to 0–1 cm layer (average±SD, n=36)

	Transitional site	Confined site
Grain size	Medium sand[1] (74±8 %)	Silt[2] (80±1 %)
Density (g ml^{-1})	1.8±0.1	1.1±0.1
Porosity	0.4±0.1	0.9±0.1
Water content (%)	23.0±3.0	87.9±1.4
LOI[3] (%)	0.9±0.4	18.1±1.0
Oxygen penetration depth (mm)	0.2±0.04<OPD<4±0.5	0.1±0.04<OPD<1.8±0.7

[1] grain size 500-125 μm; [2]grain size <63 μm; [3] Weight Lost After Ignition (LOI);

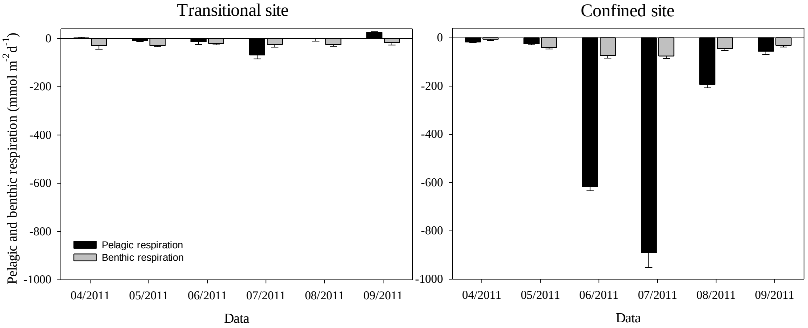
Confined site was dominated by fine silt particles typical for accumulative sediment types (Table 4.2). The average density was low and increased with sediment depth. Porosity and water content were higher at the sediment surface and decreased with sediment depth (at 10 cm depth were 0.8 and 78.6 % respectively).

Organic matter (expressed in weight loss after ignition (LOI)) content was about 0.87 % at the surface of the transitional site but was 20 times higher at the confined site where it decreased with the sediment depth (from 18 % at the surface to 14 % at 10 cm depth).

Oxygen penetration depth (OPD) in sediments (Table 4.2) showed seasonal variations and ranged from 0.2 to 4 mm at the transitional site and 0.1–1.8 mm at the confined site. The lowest value was observed in July of 2011 during the cyanobacteria bloom (Fig. 4.1).

4.1.3 Hypoxia risk in the Curonian lagoon

Water column net dissolved oxygen fluxes (production–respiration) varied from 25.2 (in September) to -68.3 mmol $m^{-2}d^{-1}$ (in July) at the transitional site (Fig. 4.11). Benthic respiration was almost constant during the study period and was in the range of -17.3 (in September) to -29.8 mmol $m^{-2}d^{-1}$ (in April). The most of the respiration was benthic and only in July pelagic respiration share increased up to 73.8 % of total respiration at this study site.


Transitional site

Confined site

Fig. 4.2 Pelagic and benthic respiration in the Curonian lagoon in 2011(average±SD, n=3–5)

At the confined site, higher rates of both pelagic and benthic respiration were observed. During summer, when Chl-a concentration was the highest, pelagic respiration increased up to 890.9 and 193.0 mmol $m^{-2}d^{-1}$ in July and August, respectively. At this station, net water column community (or pelagic) respiration was lower in spring and autumn (from -17.1 to -55.3 mmol $m^{-2}d^{-1}$). Benthic respiration intensity had the same pattern as pelagic respiration and higher oxygen consumption rates were detected in summer (about -74.4 mmol $m^{-2}d^{-1}$). On average, pelagic respiration was higher comparing to benthic respiration (92 % of all respiration in July).

Table 4.3 The assessment of seasonal hypoxia risk in the near bottom layer (0.5 m) at two sampling sites during the calm weather conditions (wind speed below 2 m/s) and their variations throughout the year

	Transitional site		Confined site	
Months	Hours needed to reach hypoxia in the 0.5 m bottom layer (h)	Area of the lagoon where risk of hypoxia is higher than at the sampling site (percentage of site (km^2))	Hours needed to reach hypoxia in the 0.5 m bottom layer (h)	Area of the lagoon where risk of hypoxia is higher than at the sampling site (percentage of site (km^2))
April	111.9		281.5	
May	71.8		58.5	
June	47.5	81	14.1	76
July	22.2	73	10.0	60
August	53.7	96	33.6	95
September	128.4		67.7	

At the transitional site and during non-bloom periods, the time required to reach hypoxia was longer (from 30 to >200 h).

4.1.4 Wind-induced shear stress to sediments

Wind in shallow systems such as Curonian lagoon is an important driving force for sediment resuspension. The annual average wind speed was slightly higher in 2011 (7.0 ± 2.8 m s^{-1}) comparing to 2013 (6.1 ± 2.5 m s^{-1}). In more than 20 % of days during the study, the dominant wind direction was south–east and north–west. In 2013, in more than 20 % days during investigation periods wind direction was south–east>north–west> north–east. The highest shear stress to sediments is expected to be under the southern wind directions at the transitional site, while both south, north east and south east directions were important to wind induced sediment shear stress at the confined site (Appendix 2). In 2011, more intensive wind stimulated higher effect of turbulence and resulted in stronger shear stress to sediment surface (Fig. 4.3).

In 2011, the average shear stress to sediments was $2.2\pm1.6\cdot10^{-5}$ and $1.5\pm1.1\cdot10^{-5}$ N m^{-2} during the sampling time at the transitional and confined sites, respectively. In 2013 the shear stress was twice lower at both sites ($1.1\pm1.4\cdot10^{-5}$ and $0.8\pm1.0\cdot10^{-5}$ ^{5} N m^{-2} at transitional and confined sites, respectively).

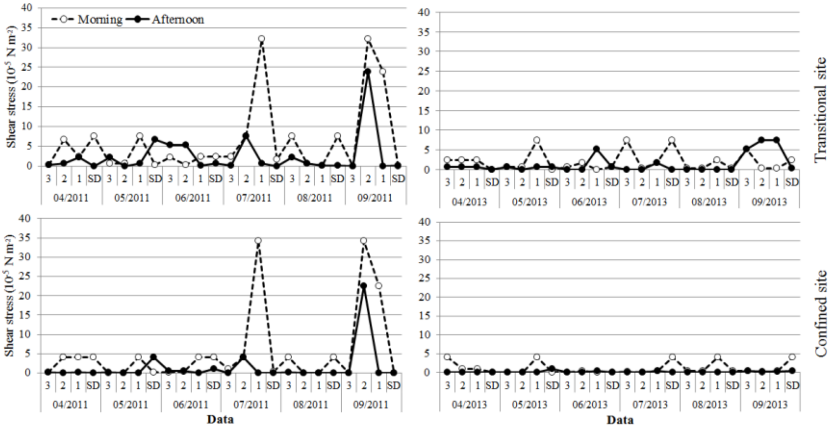


Fig. 4.3 *Wind induced shear stress at transitional and confined sites in 2011 and 2013 (SD – sampling days; numbers (1, 2, 3) of days before sampling at morning (6 am) and afternoon (6 pm))*

The highest shear stress to sediments before sampling was calculated in July and September 2011 for both stations. The calculated shear stress reached $33.3\cdot10^{-5}$ and $28.2\cdot10^{-5}$ N m^{-2} at transitional and confined sites, respectively. However, at the sampling date, it was lower than $0.01\cdot10^{-5}$ N m^{-2} at both study sites. The calm weather lasted for 21 hours at confined site in July 2011. The maximum shear stress was calculated at transitional site ($7.5\cdot10^{-5}$ N m^{-2}) in May and July before the sampling periods in 2013.

4.2 Phosphorus forms variation in water column and sediments

4.2.1 Phosphorus forms variation in water column

Total phosphorus concentration was statistically different between 2011 and 2013 (F=15.9, $p<0.05$). The difference between stations was not statistically reliable and TP distribution was not statistically dependent on years and sites together (Table 4.4). Lower TP concentrations were detected in April (1.1–1.5 µM in 2011 and 1.3–1.7 µM in 2013). TP concentrations were increasing during the following months and reached peak in July (5.8–6.8 µM in 2011 and 2.6–3.3 µM in 2013) and afterwards it declined (Fig. 4.4).

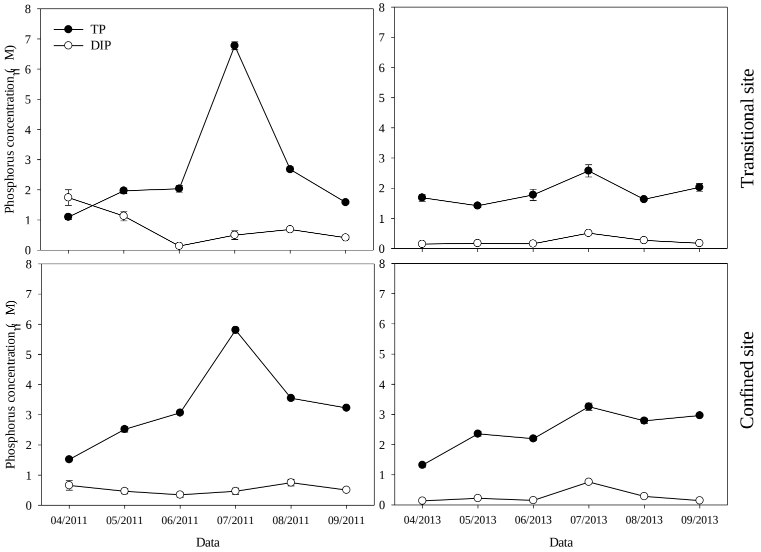


Fig. 4.4 *Total (TP) and dissolved inorganic (DIP) phosphorus concentration in water column (2011 TP concentrations were provided by Marine Research Department, data interpolation was*

conducted in order to get values for each sampling day; average±SD; n=3)

Table 4.4 Two-Way ANOVA results (square root transformation was applied to TP and DIP data when significant heterogeneity was found). Df – degrees of freedom, F – F value, p – significant level, where $p<0.05$.

Factors	Df	F	p
Total phosphorus			
Years	1	15.9	<0.05
Sites	1	1.5	0.23
Years x Sites	1	2.0	0.16
Residual	68		
Dissolved inorganic phosphorus			
Years	1	35.5	<0.05
Sites	1	0.6	0.45
Years x Sites	1	1.7	0.2
Residual	68		

This form increased from April (0.8±0.03 µM) to September (2.5±0.03 µM) at the confined site, while at the transitional site PP concentration didn't show clear seasonal pattern and fluctuated in the 0.7–1.8 µM range. Organic phosphorus was 64.8±5.1 % and 62.2±3.0 % of PP at transitional and confined sites, respectively.

Total dissolved phosphorus (TDP) concentrations in the water column varied gradually in the range of 0.4–0.8 µM at the transitional site and 0.5–1.0 µM at the confined site (Fig. 4.5). This P form contributed to 33.8±8.6 % of total phosphorus at the transitional site and 27.1±8.9 % at the confined site with lowest proportion during summer. Dissolved organic phosphorus (DOP) was the main dissolved form dominating water column at both study sites (60.3±19.1 % of TDP). The only exception was observed in July, when DIP reached 74 and 68 % of DP at transitional and confined sites, respectively.

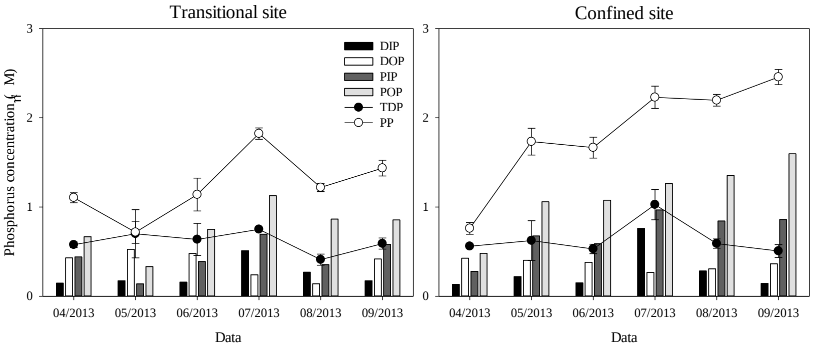


Fig. 4.5 *Seasonal concentrations of phosphorus forms (DIP – dissolved inorganic phosphorus, DOP – dissolved organic phosphorus, PIP – particulate inorganic phosphorus, POP – particulate organic phosphorus, TDP – total dissolved phosphorus, PP – total particulate phosphorus) in water column of the Curonian lagoon (average±SD; n=3)*

According to the results of redundancy analysis (RDA), ten explanatory variables explained 46 % of the DIP and TP variation in the water column (Fig 4.6). Permutation tests indicated that Chl-*a* (F=7.45, p=0.02) and bottom dissolved oxygen concentration (F=1.9, p=0.19) were the most significant variables describing phosphorus (TP and DIP) variation.

Total phosphorus loads by Nemunas River and months have marginal effect on TP and DIP dynamic. This analysis demonstrates that phosphorus variation in the water column was regulated by Chl-*a* concentration, near bottom oxygen concentration and total phosphorus loads by Nemunas River which were changing seasonally (months). DIP concentrations are strongly correlated to DIP loads from the Nemunas River and negatively to O_2 concentrations in the bottom water layer and sedimentary TP concentrations.

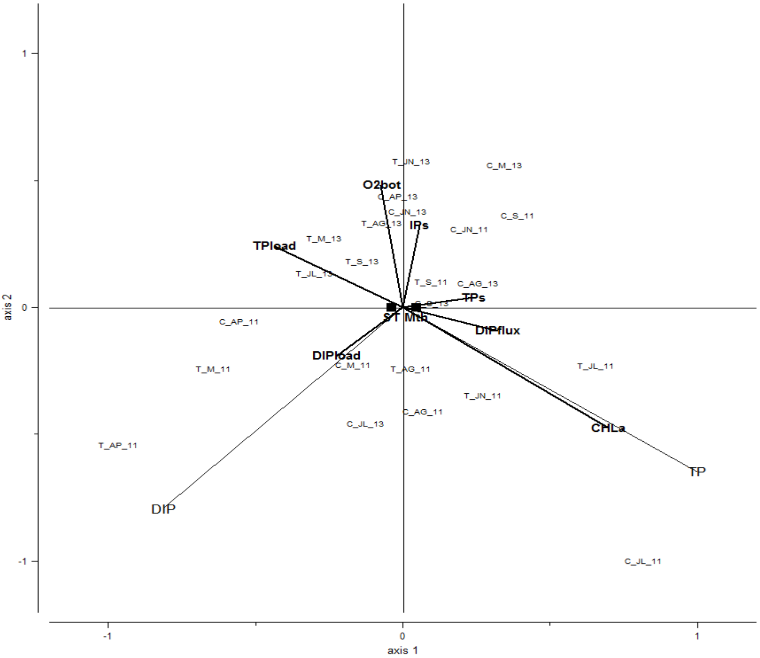


Fig. 4.6 *Redundancy analysis (RDA) triplot showing relationship between two response variable of water column (TP – total phosphorus; DIP – dissolved inorganic phosphorus) and ten explanatory variables (CHLa – chlorophyll a, O2bot – oxygen concentration at near bottom layer, IPs – sedimentary inorganic phosphorus, TPs – sedimentary total phosphorus, DIPflux – fluxes of dissolved inorganic phosphorus, DIPload – loads of dissolved inorganic phosphorus, TPload – loads of total phosphorus) and two nominal variables (Stations and Months). Data labels correspond study sites (T – transitional, C – confined), sampling months (AP – April, M – May, JN – June, JL – July, AG – August, S – September) and study years (11 – 2011, 13 – 2013).*

Since studies were performed in the period from April to September (dry season) TP concentration was related to Chl-*a* concentrations in the water column and negatively to TP loads to the lagoon.

4.2.2 Phosphorus forms variation in sediments

The sandy and muddy sedimentary environments were different in total phosphorus (TP) concentrations in the surface sediments (Fig. 4.7) which were significantly higher (9 times) at the confined site comparing to the transitional one (T–test, t=21.1, df=20, $p<0.05$).

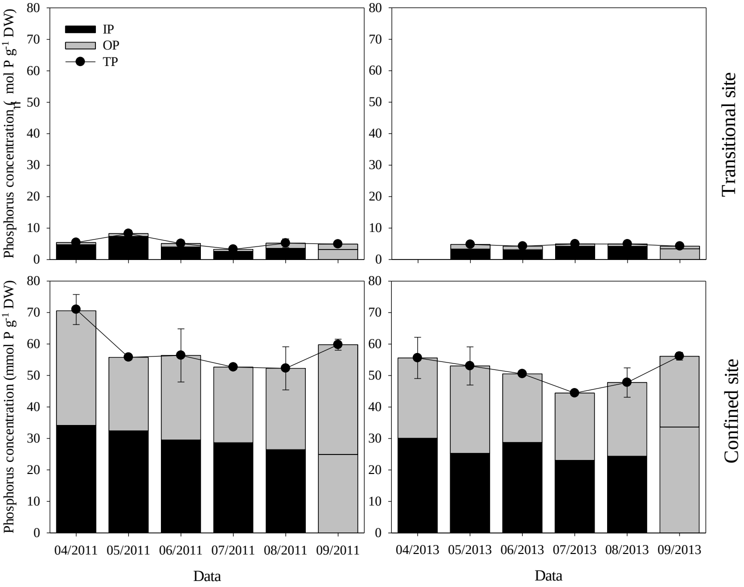


Fig. 4.7 *Inorganic (IP) and organic (OP) phosphorus (column) and total phosphorus (TP, line) variation during study periods in the surface of sediments of transitional and confined sites (average±SD; n=3)*

Total phosphorus concentrations at sediment depth of 0–1 cm did not change seasonally and were in the range of 3.3–8.3 μmol g^{-1}DW in 2011 and 4.2–5.0 μmol g^{-1}DW in 2013. The differences between years (F=6.8, $p<0.05$) and the interaction between years and months (F=8.7, $p<0.05$) were statistically significant at the transitional site. The 79±8 % of TP was in an inorganic form.

At the confined site statistically significant changes of TP were observed yearly (F=21.3, $p<0.05$) and monthly (F=8.9, $p<0.05$) and the higher concentration was detected in 2011 (Table 4.6). Seasonal changes were observed at the confined site where the highest concentration was found in April. Further it decreased from May to August and in September, after the phytoplankton vegetation period, the accumulation of TP started (Fig. 4.7). Total phosphorus comprised 53±5 % of inorganic and 47±5 % of organic phosphorus forms at the confined site.

Table 4.5 Two-Way ANOVA results for total phosphorus in sediments. Df – degrees of freedom, F – F value, p – significant level, where $p<0.05$.

Factors	Df	F	p
Transitional site			
Years	1	6.8	$p<0.05$
Months	4	8.9	$p<0.05$
Year x Months	4	8.7	$p<0.05$
Residual	20		
Confined site			
Years	1	21.3	<0.05
Months	5	8.9	<0.05
Year x Months	5	1.5	0.23
Residual	24		

Total phosphorus concentration was decreasing with sediment depth. At both study sites TP concentrations at the depth of 10 cm were approximately 30 % lower than at the surface (Fig. 4.8). The variation in the average TP concentrations during the two years were in the rage of 5.1±1.6 to 3.7±1.4 μmol g^{-1}DW, whereas at the confined site TP concentration decreased with depth from 54.5±8.1 to 36.3±5.8 μmol g^{-1}DW. Organic phosphorus forms were abundant at the surface sediments and decreased with the sediment depth. Consequently, the proportion of inorganic P increased with depth.

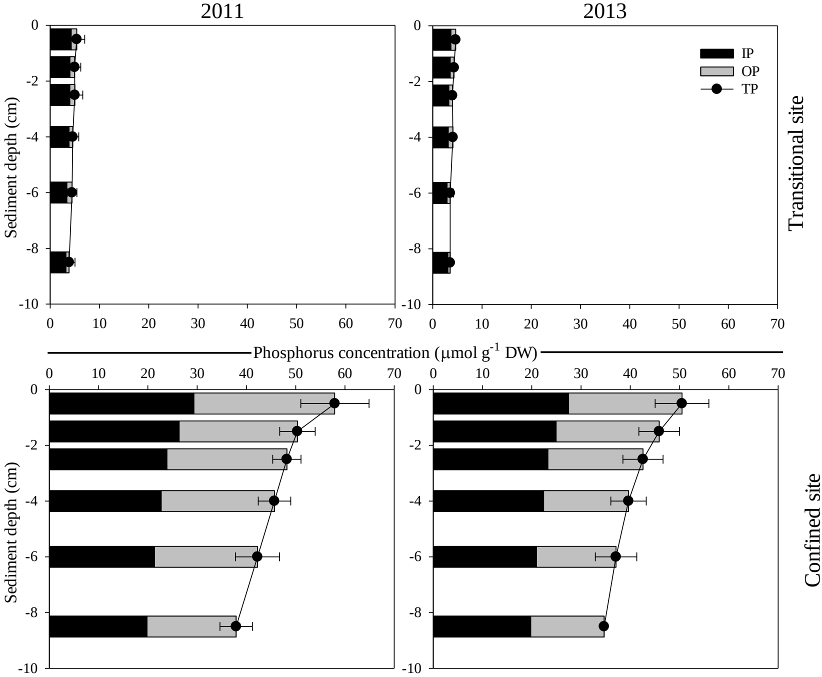


Fig. 4.8 The average inorganic (IP) and organic (OP) phosphorus (column) and total phosphorus (TP, line) variation with sediment depth at the transitional and confined sites (average±SD; n=36)

The major inorganic phosphorus fraction was the detritic Ca-bound P at both sites, where it constituted 57±4 and 32±29 % of TIP at the transitional and confined sites, respectively (Fig. 4.9). This stable form increased with the sediment depth. About 28±9 and 26±30 % of TIP was consisted of Fe/Mn-bound P at the transitional and confined sites, respectively. Other forms were minor at the transitional site, while sediments at the confined site were rich in exchangeable P and authigenic Ca-bound P forms (21±2 and 21±1 %, respectively.

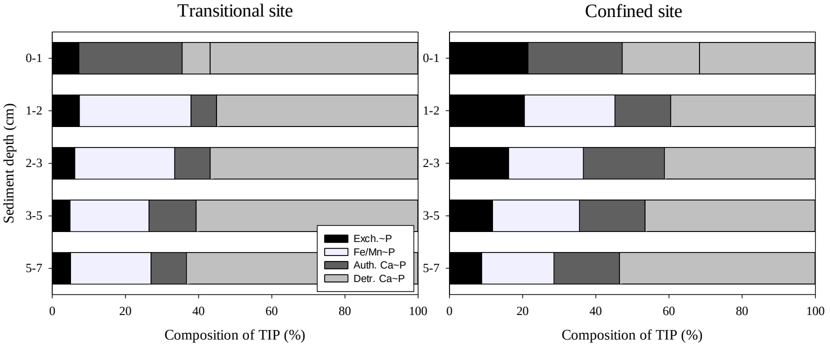


Fig. 4.9 *Inorganic phosphorus forms (TIP) in transitional and confined sites with sediment depth in 2013 (the average of June and September values)*

The reactive phosphorus pool consisted mostly of organic and Fe/Mn-bound P at the transitional site. Confined site reactivity was related to the organic P as well but also to the exchangeable P, Fe/Mn bound P and authigenic Ca-bound P pools (Appendix 3 and 4).

4.2.3 Dissolved inorganic phosphorus distribution in sediment porewater

Sediment porewater at the confined site had DIP concentration higher by a factor from 1 to 36 comparing to the transitional site (T–test, t=6.5, df=94, p<0.05) (Fig. 4.9). At the transitional site the mean DIP concentration in porewater was relatively constant across the entire sandy layer (0–10 cm) during both years. DIP concentration in the porewater varied from 4.4±1.6 µM at the surface and the highest concentrations were found at 2 cm sediment depth (5.7±1.4 µM). The decrease of DIP concentration until 4.0±2.0 µM was measured deeper in the sediments.

The porewater DIP concentrations gradually increased with the sediment depth (from 6.1±5.8 at the surface to30.4±15.5 µM at 5–7 cm depth) at the confined site. The highest concentrations of DIP were measured in the deeper sediment layers (up to 80.16 µM at 3–4 cm depth) at the confined site. On a yearly basis, DIP concentrations were higher in spring and summer of 2011 than of similar season in 2013, while in the autumn concentrations were similar in both years. High accumulation of DIP in the porewater was observed in July 2013 at the confined site.

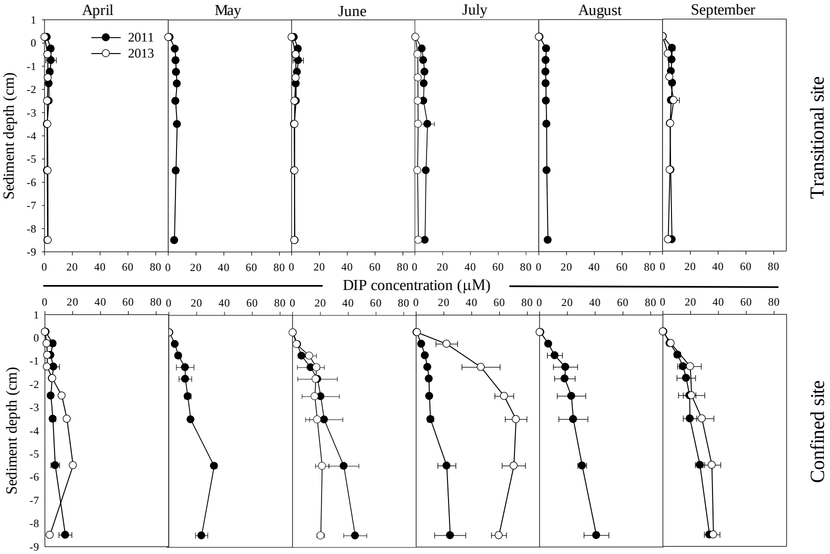


__Fig. 4.10__ Dissolved inorganic phosphorus (DIP) concentration in porewater of sediments in the Curonian lagoon (average±SD, n=3)

A strong DIP concentration gradient was formed between DIP concentration in the bottom water and DIP concentration in first layers of sediment porewater. 3–44 times higher concentrations were detected in the first layers of the porewater at both sites (Fig. 4.10).

The analysis of Multidimensional scaling (MDS) showed that according to seven sediment characteristics (density, porosity, LOI, total, inorganic and organic phosphorus, DIP concentrations in porewater) the study sites were separated as different sedimentary environments (Fig. 4.11).

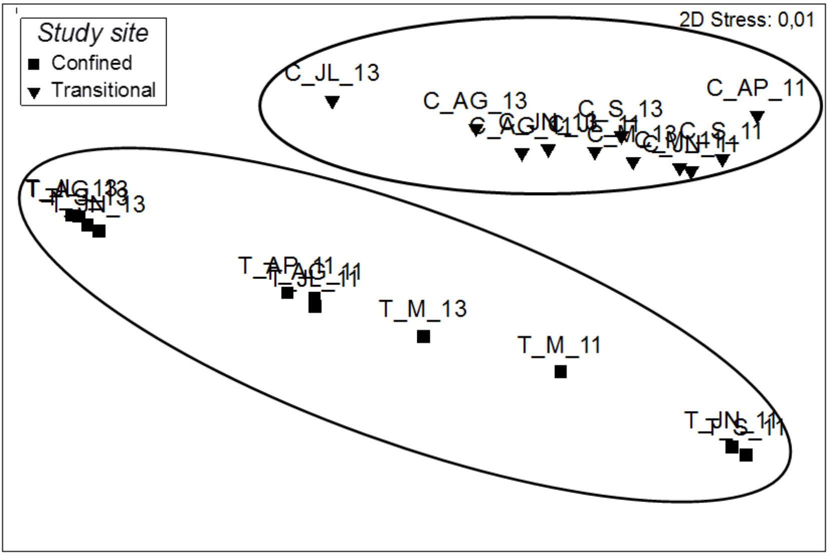


Fig. 4.11 *Multidimensional scaling (MDS) analysis of sedimentary characteristics. Data labels corresponding study sites (T – transitional, C – confined), sapling months (AP – April, M – May, JN – June, JL – July, AG – August, S – September) and years (11 – 2011, 13 – 2013).*

ANOSIM analysis confirmed the dissimilarity of sedimentary characteristics at different study sites as well (R=0.58, p< 0,05).

4.3 Pelagic-benthic coupling: diffusive and net fluxes

Study sites were functioning as sink (negative flux value) or source (positive flux value) of DIP to the overlaying water depending on season and year of sampling (Three-way ANOVA, year x month x site, F=3.0, p<0.014). DIP fluxes (Table 4.6) were in the range from -6.0 to 43.0 µmol $m^{-2}h^{-1}$ at the confined site and from -6.1 to 5.8 µmol $m^{-2}h^{-1}$ at the transitional site. Year effect (F=57.7, p<0.001) was the most significant factor in differences in DIP exchange at the sediment-water interface. Pairwise comparisons showed significantly highest efflux (Turkey HSD test, $p<0.05$) in June 2011, with a mean rate of 33.0±7.7 µmol $m^{-2}h^{-1}$ at the confined site.

Table 4.6 Measured (M_f) and calculated diffusive (C_f) fluxes and delta (Δ) during 2011 and 2013 (average±SD, n=3-5)

Data	**Transitional site**			**Confined site**		
	M_f	**C_f**	**Δ**	**M_f**	**C_f**	**Δ**
04/2011	-3.7±0.2	1.4±0.6	2.3	-2.2±2.7	11.9±4.2	-14.1
05/2011	1.7±2.4	2.1±0.3	-0.4	5.1±2.0	11.7±1.7	-6.6
06/2011	2.4±2.1	4.1±1.2	-1.7	30.3±13.8	10.1±1.0	20.2
07/2011	-1.5±5.3	3.8±0.3	-4.3	13.4±11.7	13.5±1.0	-0.1
08/2011	-1.7±0.8	3.7±1.5	-5.4	3.9±2.7	9.9±9.1	-6.0
09/2011	0.5±1.9	4.2±1.2	-3.7	-3.0±0.8	14.5±1.8	-17.5
04/2013	-0.4±0.1	0.6±0.0	-1.0	0.0±0.2	1.7±0.0	-1.7
05/2013	-3.4±1.1	-	-	0.2±1.4	-	-
06/2013	0.4±1.1	1.8±1.5	-2.0	0.0±0.6	11.0±0.8	-11.0
07/2013	-0.2±1.1	1.0±0.1	-1.2	-1.1±5.4	90.3±32.7	-91.4
08/2013	-0.2±0.9	-	-	0.0±1.9	-	-
09/2013	3.0±2.4	1.8±0.6	1.2	-1.5±3.7	16.0±3.2	-17.5

Muddy sediments were functioning as a source of DIP, particularly in the summer of 2011. However, this was not the case for the sediment-water interface fluxes at the transitional site. DIP efflux was significantly (Turkey HSD test, $p<0.05$) lower and more erratic at both study sites in 2013. DIP fluxes were negatively and statistically significantly correlated to TP loads at the transitional site ($r=-0.6$, $p=0.05$), while the DIP fluxes positively correlated to Chl-*a* concentration in the water column ($r=0.8$, $p<0.05$) at the confined site.

Theoretical diffusive DIP fluxes at the sediment-water interface calculated from the porewater profiles varied between 0.6 and 90.3 µmol $m^{-2}h^{-1}$ with lower rates at the transitional site (Table 4.6). Calculated diffusive fluxes were always positive (i.e. from the sediment to the water column) and higher than measured net fluxes except in June and April 2011 at the confined and transitional site, respectively (Mann–Whitney Rank Sum Test, $p<0.001$).

Differences among the calculated and measured fluxes suggest, with few exceptions, the occurrence of biogeochemical processes confined to the upper sediment layer that are able to buffer regenerated DIP and prevent its diffusion in the water column. Calculated potential positive fluxes (up to 90 μmol $m^{-2}h^{-1}$) were attenuated or reversed (Table 4.6). Only in June 2011 calculated diffusive fluxes were lower than the measured DIP release by nearly 20 μmol $m^{-2}h^{-1}$.

4.4 Effect of hypoxic/anoxic condition changes to phosphorus release from muddy sediment

4.4.1 Concentration changes and fluxes during the development of anoxia

The experiment was carried out to evaluate the strength of sediment buffer for the DIP release from sediments at the confined site. Sedimentary metabolism was weak and, consequently, anoxia was created in experimental chambers only after 30 hours of incubation.

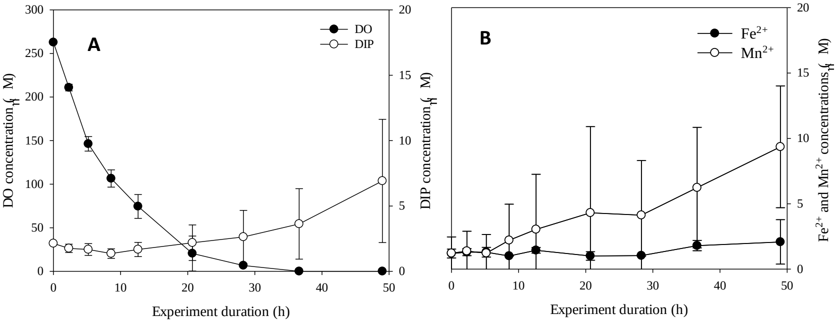


Fig. 4.12 *Dynamics of dissolved oxygen (DO) and inorganic phosphorus (DIP, A), iron and manganesium (B) concentrations in near-bottom water during oxic and anoxic incubations of sediment cores from Curonian lagoon (average±SD, n=4)*

Dissolved oxygen (DO) depletion followed the increase in DIP concentration in the overlaying water from 2.1±0.1 to 6.9±4.7 µM (Fig. 4.12). Reduced iron (Fe^{2+}) concentration was almost constant during the experiment. Mn^{2+} concentration exhibited high variation with a slight increase from 1.2±1.3 to 9.4±4.7 µM. The repeated ANOVA measurement showed that solutes (DIP, Fe^{2+}, Mn^{2+}) concentrations were statistically different between the treatments ($F=4.4$, $p=0.005$).

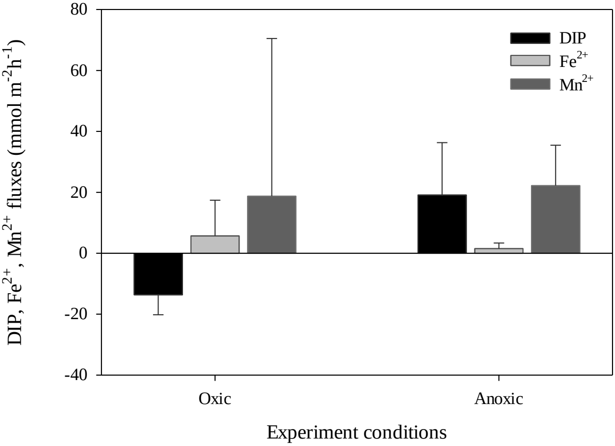


Fig. 4.13 *The average net fluxes of DIP,* Mn^{2+}*,* Fe^{2+} *before and after anoxia establishment in the Curonian lagoon (average±SD, n=4)*

The low measured values of the total oxygen uptake (TOU) by sediments (2.9±0.2 mmol $m^{-2}h^{-1}$) indicated the formation of anoxic conditions. DO shortage shifted the sediment role (expressed as DIP fluxes) from the sink to source (from -22.2±18.5 to 19.9±18.5 µmol $m^{-2}h^{-1}$, respectively) (Fig. 4.13).

Fe^{2+} release was not related to the induced redox shift, as lower fluxes were measured in the absence of oxygen (1.5±1.8µmol $m^{-2}h^{-1}$). Mn^{2+} fluxes calculated in the oxic and anoxic incubations were lower than 100 µmol m^{-2} h^{-1} and exhibited a modest increase during the transition (Fig. 4.13).

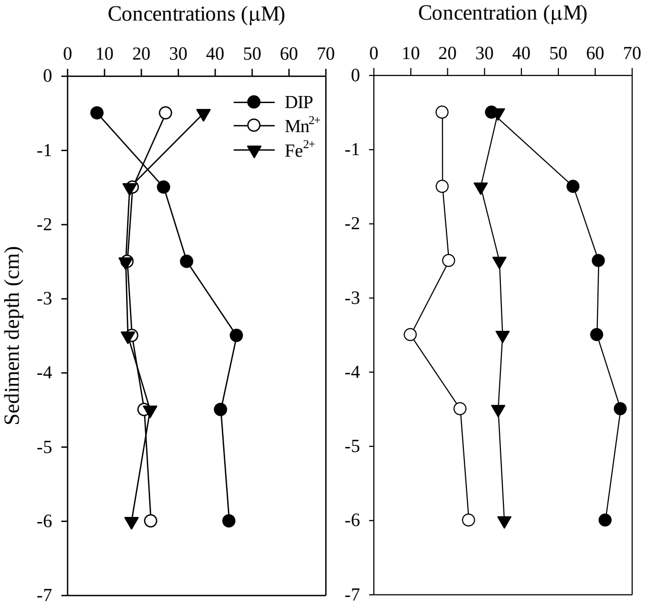


Fig. 4.14 *Porewater profiles of DIP, Mn^{2+} and Fe^{2+} in oxic and anoxic conditions in confined site sediment (average±SD, n=3)*

Fe^{2+} and Mn^{2+} shift from the oxic to anoxic was statistically not significant (t=0.7, df=6, p=0.5 and t=0.1, df=6, p=0.9, respectively).

4.4.2 Sedimentary condition changes due to anoxia

Under oxic conditions, DIP concentrations gradually increased with depth and reached maximum values in the porewater of deeper sediment layers (39.4±6.2 μM) (Fig. 4.14). DIP was increased by a factor of 4 in the 0–3 cm depth sediment layer after the establishment of anoxic conditions, while in deeper sediment layers increase was not so pronounced.

Porewater Mn^{2+} concentrations were not affected by anoxia as exhibited similar patterns in both oxic and anoxic conditions

(Fig. 4.14). Anoxia stimulated the production of Fe^{2+} which increased from 15.9±2.4 to 29.1±2.7 µM along the entire sediment depth. Dissolved sulphides were not detected in the sediments in all conditions.

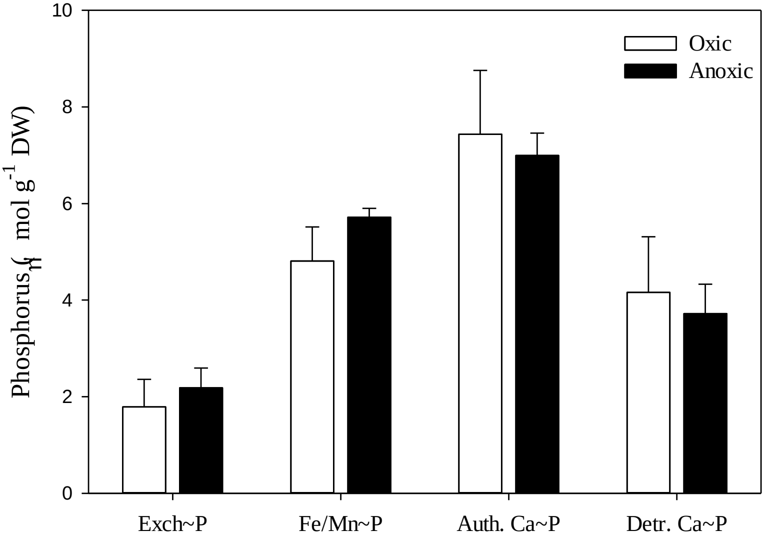


Fig. 4.15 *Sedimentary inorganic phosphorus pools before and after anoxia creation in the surface of sediments (average±SD, n=3)*

The sediments used for the experiment had high proportion of authigenic Ca-bound P and Fe/Mn-bound P. Due to the environmental changes, authigenic and detritic Ca-bound P pools have declined by 3 %, while reactive forms as exchangeable and Fe-bound P have increased by 2 and 4 %, respectively (Fig. 4.15). These changes, however, were not statistically significant (Appendix 5).

4.5 Phosphorus loads from the river to the lagoon and exchange with the Baltic Sea

On average the Nemunas River discharged 3.3 tTP day^{-1} in 2011 and 4.3 tTP day^{-1} in 2013 to the lagoon (Fig. 4.16). The highest loads were observed during the flood season, which occurred in February (10.3 t day^{-1}) and April (8.6 t day^{-1}) in 2011 and in May 2013 (20.2 t day^{-1}). Much lower P loads were measured during the summer. The export of TP to the Baltic Sea was 17 and 23 % lower than inflows in 2011 and 2013, respectively, with a net retention of nearly 200 and 360 t of TP per year.

DIP loads showed annual and seasonal variations with a mean daily DIP load (calculated on a two years basis) of 1.4±0.8 t day^{-1}. The highest DIP loads were observed in the autumn-spring periods with peaks of 4.5 t day^{-1} in February 2011 and 3.5 t day^{-1} in September of 2013. Lowest inputs of DIP from Nemunas River were observed in summer with minimal values of 0.25 t day^{-1} in June 2011. Seasonal patterns of inflowing and outflowing DIP were overlapping except for the summer-autumn periods (from June to November) when DIP outflow was 54 % lower than inflow.

A clear difference in the seasonal composition of P loads was observed in 2013 (Fig. 4.17). During the wet period (September–April), DIP was the main component of TP river discharge (42.8±16.0 %), while in the dry period (May–August) particulate phosphorus was dominant (74.0±5.7 % of TP), being mainly in the organic P form (57.5±2.5 % of PP, Fig. 4.17).

Particulate phosphorus was the main component during both seasons in the outflowing water (52.2±20.4 and 73.0±4.3 % of TP in the wet and dry period, respectively). The exported particulate pool was richer in inorganic P in the wet season 55.9±10.4 % of PP) and in organic P in the dry season (58.2±5.0 % of PP, Fig. 4.17)

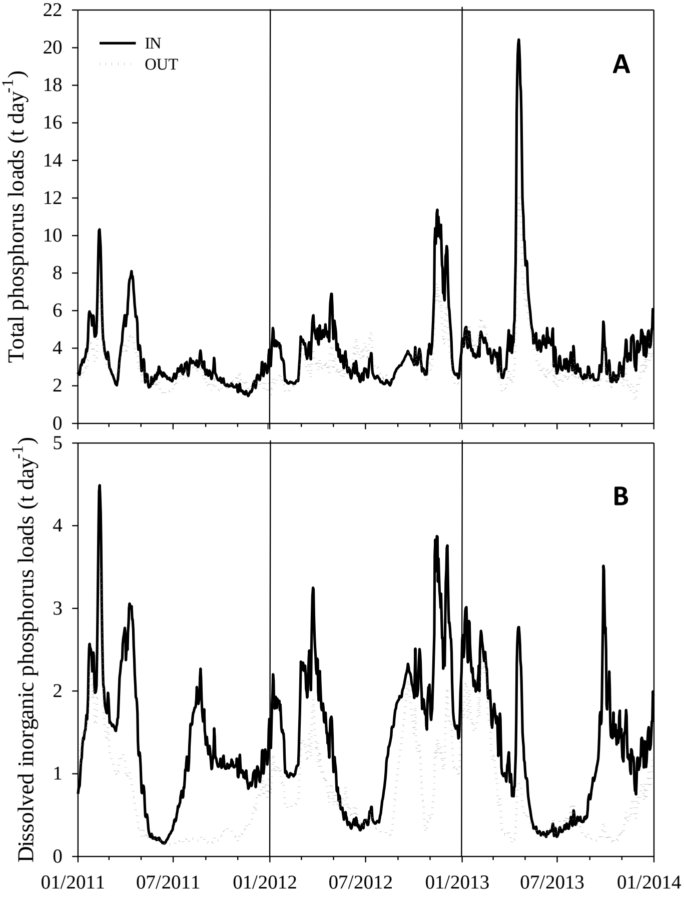


Fig. 4.16 *Total (TP; A) and dissolved inorganic (DIP; B) phosphorus loads inflowing to (IN) and outflowing from (OUT) the Curonian lagoon in 2011–2013. Note different Y scales.*

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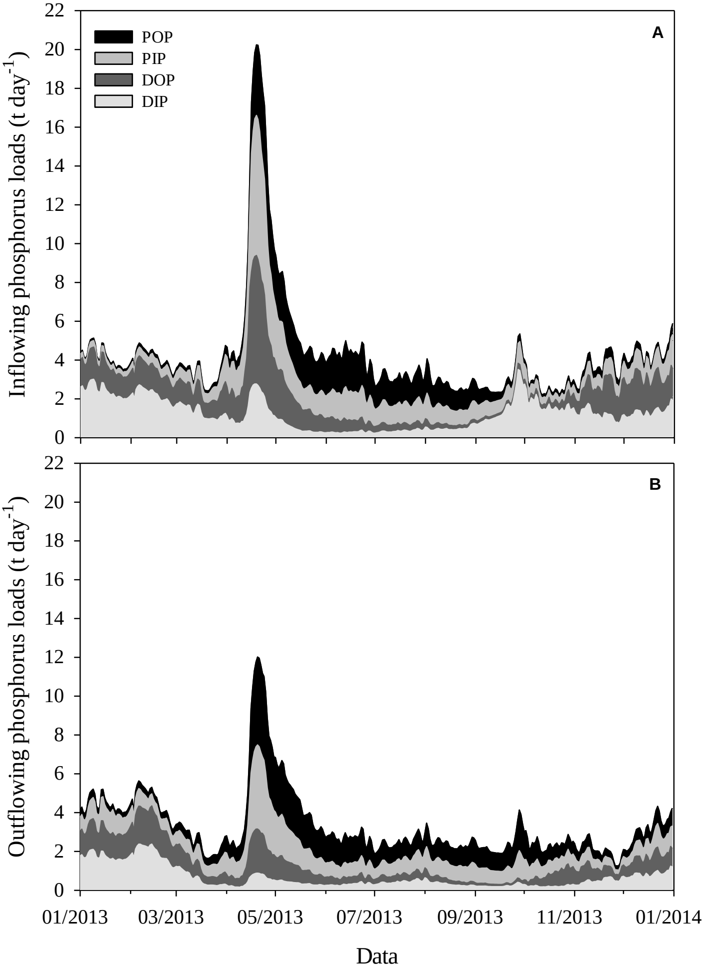

Fig. 4.17 *Speciation of phosphorus (P) forms in inflowing (A) and outflowing (B) loads in 2013. POP – particulate organic P, PIP – particulate inorganic P, DOP – dissolved organic P and DIP – dissolved inorganic P*

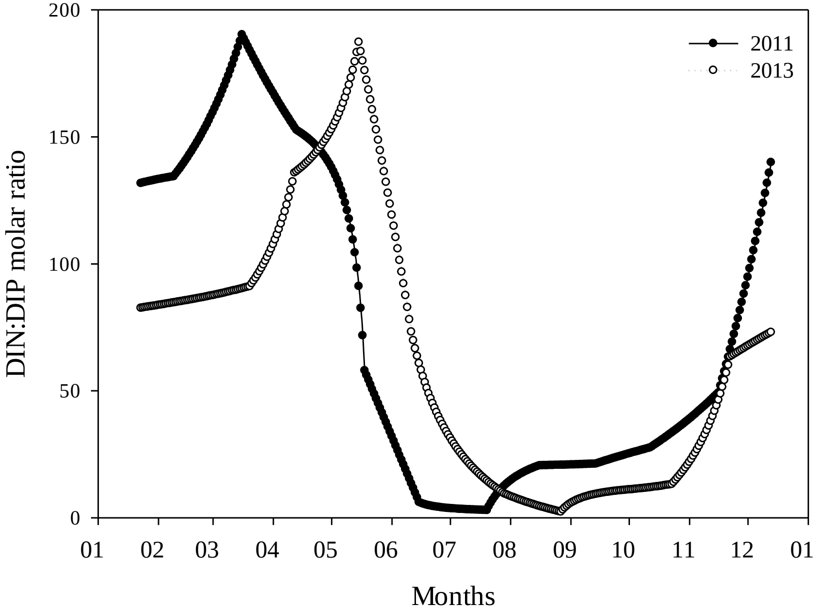

Fig. 4.18 *Molar ratios of dissolved inorganic nitrogen (DIN) and phosphorus (DIP) calculated in the Nemunas River water at the closing section in 2011 (black circle) and 2013 (open circle)*

The molar ratio of DIN:DIP varied in the inflowing water during the study period, with higher values being found during flood periods and the lower values in summer (Fig. 4.18). The average DIN:DIP molar ratio was 73.0±62.4 in 2011 (min 2.9, max 190.2) and 63.6±51.9 in 2013 (min 2.2, max 187.3). There was difference in timing of the flood occurrence between years: in 2011 the highest flood was in March, while in 2013 it was in May.

5. DISCUSION

5.1 Environmental condition changes and phosphorus pool in the water column

Annual phosphorus cycling in the water strongly depends on climatological and hydrological regime (Malmaeus et al., 2006). This study was carried out in two different years characterized by different river discharge, spring flood timing and temperature regime. Annual water discharge values were lower in 2011 (414±114 $m^3 s^{-1}$), while the spring flood had two peaks in February and March–April (average 862±157 $m^3 s^{-1}$, Fig. 2.2). Meanwhile in 2013 the average discharge values were higher (535±377 $m^3 s^{-1}$) and the spring flood was very late featuring one huge peak in April (1375±485 $m^3 s^{-1}$). According to Jakimavičius and Kovalenkovienė (2010) and Jakimavičius and Kriaučiūnienė (2013), Nemunas River discharge and, especially spring floods, have decreased from 1960 to 2009, presumably in in the connection with air temperature increase. In 2011 surface water was 2.5 ^{o}C warmer than in 2013, and in July thermal stratification was observed at the confined site with a temperature difference between the surface and the bottom of 5.4 ^{o}C (Table 4.1). However, according to Pustelnikovas (1998), it is a very rare phenomenon in the Curonian lagoon.

Coastal environment trophic state can vary due to the hydro-meteorological conditions, changes of nutrient loads, and the most common trophic state indicator is the Chl-*a* concentration (Phillips et al., 2008; Bresciani et al., 2012). Phosphorus availability in transitional systems is evidently promoting phytoplankton growth (Phillips et al., 2008). However, internal phosphorus cycling is complex due to the temporal variability in the sources of phosphorus supply (Fang, 2000), and diversity of factors regulating the transformation of phosphorus within estuary (Conley et al., 2002). Curonian lagoon is a eutrophic transitional water system with clear inter-annual and seasonal variability in Chl-*a* concentrations and relative abundance of different phytoplankton groups which are mainly related to temperature and hydrological events (Pilkaitytė, 2007; Bresciani et al., 2012).

According to our data, the combination of climatic and hydrological factors have caused the lower phosphorus loads by Nemunas River in 2011 and, therefore, the conditions were much favourable for phytoplankton development and, subsequently, higher Chl-*a* concentrations were observed in 2011 (79.5±59.6 μg l^{-1}) comparing to 2013 (27.1±6.2 μg l^{-1}, Fig. 4.1). The peak of Chl-*a* concentrations was mostly related to the high cyanobacteria abundance and coincided with the elevated temperature and calm weather conditions (Kanoshina et al., 2003). Calm weather conditions are advantageous for buoyant cyanobacteria which can move toward the euphotic zone in the response of reduced turbulent mixing (Kanoshina et al., 2003; Jöhnk et al., 2008; Wynne et al., 2010); this was also demonstrated in previous studies in the Curonian lagoon (Pilkaitytė and Razinkovas, 2006). In July 2011, community respiration rates were high, and, in the night rapidly consumed the oxygen, leading to the bottom hypoxia conditions. According to Žaromskis (1996), hypoxia was measured only during the winter when the lagoon was covered by ice and there were only occasional signs pointing toward oxygen decrease during the summer in the southern (dominated by muddy sediments) part of the lagoon. In general, hypoxia phenomena are widely studied water bottom conditions across-systems, from deep stratified bays to estuaries or lagoons (Diaz, 2001; Rabalais et al., 2002; Hagy et al., 2004; Chen et al., 2007; Kemp et al., 2009; Tyler et al., 2009; Steckbauer et al., 2011), though in shallow environments hypoxia is less expected due to the vertical mixing induced by tides, waves, and wind action (Kemp et al., 2009). However, the combination of several environmental factors such as elevated temperature, calm weather conditions, minimal vertical mixing of the water column and increased supply of labile organic matter to sediments can promote sediment oxygen demand and hypoxia can establish rapidly (within hours) (Conley et al., 2007; Park et al., 2007; Tyler et al., 2009). However, in 2013 phytoplankton community was dominated mostly by green algae and diatoms, so neither huge peaks of Chl-*a* hypoxia were observed.

Internal phosphorus cycling in the water column includes a wide range of processes such as assimilation, degradation, mineralisation, sorption, desorption by holding available P in favourable concentration for phytoplankton vegetation (Froelish, 1988; Fox, 1993). According to Conley et al. (2002) variation in internal water column phosphorus stock is 1–2 order of magnitude larger than the variation observed in external P inputs to the Baltic Sea.

The phosphorus inflow from Nemunas River in 2011was mostly DIP (40 %), while in 2013, when phosphorus loads were much higher, DIP constituted only the 20 % of TP. Most of the coming phosphorus was in particulate form and, during the vegetation period in 2013, it was mostly in organic form (Fig. 4.5). The constant DIP concentration (18.0±14.9 and 15.2±10.6 % of TP at transitional and confined sites, respectively) demonstrated the buffering capacity of the Curonian lagoon to assimilate or absorb the DIP in the particulate matter in the water. The equilibrium between the dissolved and the particle-bound phosphorus (Froelich, 1988) is restraining the accumulation of dissolved inorganic P and increasing the abundance of the particulate form either bound to mineral particles or in the organic forms in the water (Lebo, 1991; Sundby, 1994; Howart et al., 1995; Anschutz et al., 1998). Our study demonstrates strong correlation between Chl-*a* concentration and TP during the vegetation period as well (Spearman Rank Order Correlation, $r=0.7$, $p<0.05$).

The particulate phosphorus forms were dominant at both study sites in 2013 (more than 54 % of TP), while the share of organic forms was higher than in the Chesapeake Bay (Conley et al., 1995). POP pool can support internal P re-cycling especially during the intensive microbial activity via mineralisation of particulate organic phosphorus in the water column (Selig et al., 2002; Deborde et al., 2007). This process is so fast that the mineralisation of lying cyanobacteria cells during the night could support new vegetation during the next day. Particulate inorganic phosphorus is sensitive to surrounding environmental changes of salinity and pH and exchangeable P, Fe/Mn-bound P and authigenic Ca-bound P can desorb releasing DIP or DOP (Scheldt Estuary, Zwolsman, 1994; Gunnars et al., 2002). Bottom hypoxia which was observed in July 2011 can also contribute to DIP availability in the water column as a result of mineral P dissolution. PP forms can include phytoplankton cells during the vegetation period (April–September), while in colder period (October–March) the inorganic forms can be dominant (Selig et al., 2002). This study, however, did not investigate the lability of PP which is a topic for future research.

The high portion of DOP in the total dissolved phosphorus (Fig. 4.4) observed in 2013 indicated intensive mineralisation rates (Jensen and Andersen, 1992; Søndergard et al., 1999). DOP compounds can be used directly by phytoplankton or bacteria regeneration (Wetzel, 1983; Cotner and Wetzel, 1992; Selig et al., 2002). When DIP is depleted, cyanobacteria are able to uptake DOP by enhancing alkaline phosphatase activity (Granéli et al., 1990; Nausch and Nausch, 2006).

Since P in the Curonian lagoon is found mainly in particulate form, the pathway of TP should follow in general the fate of particulate matter in the lagoon. According to Pustelnikovas (1998) 32 % of particulate matter are transported to the Baltic Sea, 38 % are recycled in the water column and 30 % are retained and accumulated in the sediment, mostly in the southern and central part of the lagoon (Table 2.1).

Summarizing, the Curonian lagoon waters are an effective buffer for DIP transported from the river to the Baltic Sea. The TP concentration in the water column is related to Chl-*a*, i.e. phosphorus is mostly represented by labile organic forms that can be easily recycled by microorganisms, and, ultimately, can support vegetation in the water column by DIP.

5.2 The reactivity of phosphorus pools in the different sedimentary environments

The Curonian lagoon is a heterogenic environment with dominant sediment types such as sand, mud and sandy mud (Gulbinskas, 1995).

The distribution of different sediment types is mostly a result of the riverine influence and could be differentiated by the water residence time, wind induced shear stress and sedimentation rates (Ferrarin et al., 2008). In the transitional zone sediments are dominated by the coarser particles, while in stagnant zone fine organic particles accumulated. This, in turn, leads to differences in distribution of phosphorus other compounds under variable riverine exposure (Carman and Cederwal, 2001; Dias et al., 2002; Lukarri et al., 2008; Slomp, 2011).

Sedimentary phosphorus analyses revealed different patterns of phosphorus distribution at the study sites as muddy sediments had 9 times higher TP concentration than sandy sediments (Fig. 4.7 and 4.8). However, these values are in the range of TP concentrations found in other coastal zones of the Baltic Sea, where mean TP concentrations range from 40 to 90 and from 3 to 20 μmol g^{-1} DW in muddy and sandy sediments, respectively (Emelyanov 2001; Lukarri et al., 2008; Łukawska–Matuszewska and Bolałek, 2008; Rydin et al., 2011).

Table 5.1 Overview of total phosphorus (μmol g^{-1} DW) in sediments of the Baltic Sea

Study area	TP concentration	Sediment type	Reference
The Archipelago of the Baltic sea	27.1–229.0	muddy	Puttonen et al., 2014; Malmaeus et al., 2012; Rydin et al., 2011
Gulf of Finland	16.0–66.8	sandy and muddy	Lukkari et al., 2009; Viktorsson et al., 2012
Aarhus Bay	36–60	mud	Jensen et al., 1995
Gulf of Gdansk	3.1–4.8	sand	Lukawska-Matuszewska and Bolalek, 2008

Phosphorus mobility and recycling are mainly related to the three reactive TIP fractions (Exch~P + Fe/Mn~P + Auth Ca~P) and the amount of labile organic phosphorus lying on the sediment surface (Slomp, 2011). The reactivity of sedimentary phosphorus is controlled by early diagenesis processes, intensity of organic matter accumulation, degradation, bioturbation, frequency of resuspension and changes of salinity, redox and pH (Sundby et al., 1992; Ruttenberg and Berner, 1993; Canfield, 1994; Jensen et al., 1995; Slomp et al., 1998; Andrieux-Loyer and Aminot, 2001).

Since transitional waters are traps for river delivered particles, the sediments consist of both allochthones and autochthonous particulate matter (Zhang et al., 2004). According to Pustelnikovas (1998) 30 % of all lagoon particulate matter retained in sediments is of terrigenous origin. At the transitional site, sandy sediments are under the riverine influence and accumulation is based on the terrestrial particles (Galkus and Jokšas, 1997; Pustelnikovas, 1998, Ferrarin et al., 2008). This was reflected in the P composition where 57±20 % of TP was in reactive phosphorus forms (22 % of TP Fe/Mn-bound P + 23 % of TP organic P) and it was relatively rich in the detritic Ca-bound P forms (about 43 % of sedimentary TP) which are important form for P burial in this system (Appendixes 4). High residence time facilitates particulate matter sedimentation rates and accumulation at the deeper confined site (Galkus and Jokšas, 1997; Pustelnikovas, 1998). Consequently, muddy sediments were rich in reactive P forms and mostly in organic P, while other reactive forms contributed to ~12 % of TP. Small part of detritic Ca-P (about 18 % of TP) demonstrated that the riverine effect was less pronounced. Moreover, the origin of particulate matter changed seasonally; terrigenous forms were most abundant in winter and spring, while in summer autochthonous biogenous material dominated (Jokšas et al., 1998). TIP analysis performed in June and September confirms these early findings: the terrigenous P form was dominant in both sites in June (Appendix 3), while the concentrations of Fe/Mn bound and authigenic formed apatite increased at the end of the vegetation period. Organic P fractions increased with autotropic production intensity in the lagoon, which resulted mainly in labile organic matter production, which, in turn, could be quickly mineralised by intense microbial activity (Jensen et al., 1995; Lukarri et al., 2008; Rydin et al., 2011). The labile organic matter concentration in sandy and muddy sediments increases after the phytoplankton bloom (Jokšas et al., 1998; Lesutiene, 2009; Zilius, 2011). Transitional site lays in the shallow zone so, according to Köster et al. (2005), the organic matter accumulation in sediments declines with decreasing water depth. Furthermore, Zilius (2011) demonstrated that labile organic matter mineralisation is much faster in sandy sediments comparing to the muddy ones. In a long perspective, the remaining organic P is in refractory form and can be buried in the sediment (Zilius et al., submitted). Deeper confined site has much higher sediment organic matter content and the rate of accumulation is much higher as compared to sandy sediments.

P reactivity can be influenced by redox changes in the near bottom water layer or sediments. In simulated hypoxia risk experiment conducted during the bloom periods (June and July), hypoxia could occur within 10–14 (confined site) and 20–40 h (transitional site) after the onset of low-wind conditions which can cover 60–95 % of the area of the confined site (Table 4.3). The time required to attain hypoxia was longer at the transitional site and during non-bloom periods (30 to >200 h), so the likelihood of its occurrence would be precluded by the frequency of wind mixing events.

Resuspension as a physical force affects the reactivity of sediments, redistribution of phosphorus from reactive to unreactive forms and burial rates (Christiansen et al., 1997; Tenberg et al., 2003; Almroth et al., 2009; Da-Peng and Young, 2010). Earlier (Ferrarin, 2006) and this study showed that higher resuspension as a consequence of higher bottom shear stress values induced by wind is expected in the norther part of lagoon, where sandy sediments (the average of two year $4.2 \pm 6.1 \cdot 10^{-5}$ N m^{-2}) are dominant, comparing to deeper site ($2.4 \pm 4.9 \cdot 10^{-5}$ N m^{-2}, Fig. 4.3). From 0.1 to 2.0 cm of upper sediment layer (Kristensen et al., 1992; Schallenberg and Burns, 2004) could be affected during the resuspension depending of the sediment properties and exposure intensity, where sediments with low density, high water content and organic matter sediments are resuspended more easily than coarser-grained sediments (Jepsen and Lick, 1997; Christiansen et al., 1997). Resuspension redistribute organic particles from deeper layers to surface, oxidize reduced elements (Almroth et al., 2009) and during the intensive vegetation periods it could increase organic P concentrations in the surface due to the DIP assimilation during resuspention (Fanning et al., 1982), which also increases the mineralisation of organic matter (Stählberg et al., 2006), decreases dissolved phosphorus increased adsorbed (Fe/Mn bound P, $CaCO_3$ particles, clay minerals) or organic P (Tenberg et al., 2003; Da-Peng and Young, 2010). In general, TP concentration decreases with sediment depth and shift from reactive to unreactive, indicating the stability of this resources and burial rates (Lukarri et al., 2009; Slomp et al., 1996). At both stations TP concentration was decreased of about 30 % at 10 cm depth, this gradient being an indication of frequent resuspension events.

Moreover, benthic macrofauna, which was abundant at the transitional site, can have significant role in increasing phosphorus burial via bioturbation, (Zilius et al., 2014). According to Canfield et al. (1993) and Boström et al. (1982), burrowing animals move oxic agents to reduced zones, increasing sediment re-oxidation and preventing the desorption of Fe/Mn~P forms. The reactivity of sandy sediments is lower due to high content of oxidized metals (Fe/Mn) of terrigenous origin. Foreseen future environmental changes, such as more frequent saline water intrusion due to the sea level rise and the decrease in Nemunas River discharge (Jakimavičius, 2011; Zemlys et al., 2013), can enhance DIP liberation due to the iron–sulphur–phosphorus cycles interaction (Caraco et al., 1990; Roden and Edmonds, 1997) in the transitional area.

In general, the reactivity of sedimentary phosphorus is related to the organic P and Fe/Mn bound P at the transitional site, but, due to high hydrodynamic activity this site can become a phosphorus source only as a consequence of organic P mineralisation aftermath a the phytoplankton bloom. The sediments at the confined site have important role in providing P to overlaying water due to the high content of reactive forms and other favourable conditions as being deeper, less influenced by wind higher accumulation rate of organic matter and hypoxia risk.

5.3 Regulation of phosphorus fluxes across the sediment–water interface

Phosphorus retained in sediments undergoes through a complete cycle of burial, dissolution (biological, chemical), upward migration (diffusion, resuspension), re-precipitation for several times per years by changing P forms and releasing DIP to overlaying water or in the sediment porewater (Sundby et al., 1992; Ruttenberg, 2003; Reddy et al., 2005; Da-Peng and Yong, 2010; Slomp, 2011).

The sandy sediments in the transitional site were rich in stable P forms and during the studied period lower Chl-*a* concentration with no hypoxia events or thermal stratification were observed (Table 4.1, Fig. 4.6 and 4.8). Muddy sediments were rich of reactive P forms and subjected to wide changes of oxygen and Chl-*a* concentrations, depending upon stratification and blooms at the confined site. This is reflected in DIP distribution in porewater and fluxes to the overlaying water. Transitional site had low porewater DIP concentrations, with slight increment with depth (Fig. 4.10) and low measured (-3.7 to 2.4 µmol $m^{-2}h^{-1}$) and calculated (0.6–4.2 µmol $m^{-2}h^{-1}$) fluxes from the sediments. Higher calculated diffusive fluxes comparing to low or negative release of net fluxes were indication of an effective biogeochemical barrier (e.g. microphytobenthos) at the subsurface sediment layer (Zilius, 2011, Zilius et al., 2012). Diatoms deposited after the spring bloom can be another effective sink because of the summer nutrient assimilation (Lomstein et al., 1990). On the opposite, muddy sediments have shown steep gradients of porewater DIP along the depth profiles (Fig. 4.10) and high benthic fluxes (both measured and calculated; Table 4.6). This study site is a potential internal source of P as it was observed in summer 2011. The conditions, when this internal source can be activated is a critical point for the P balance of the whole lagoon and it can be only speculated which P forms are responsible and which conditions promote these fluxes.

The highest DIP fluxes were measured during the phytoplankton bloom (Table 4.6). They can be promoted by the deposition of labile OM on the sediment surface and recycling of the P organic fraction. The following consumption of oxygen or other electron acceptors can ultimately cause hypoxic/anoxic conditions and acidification in the near bottom layer (Spagnoli and Bergamini, 1997; Ståhlberg et al., 2006; Almroth et al., 2009; Chen et al., 2014). This fact was also confirmed by the high benthic oxygen consumption measured at the confined site in July 2011 when oxygen penetration depth (OPD) reached the minimum (0.11±0.04 mm) in experimentally maintained oxic conditions. The consumption of electron acceptors can result in low redox conditions facilitating the dissolution of Fe-bound pool, sediment acidification with consequent pH decrease and dissolution of some carbonate apatite included in the authigenic Ca-bound pool. Surprisingly higher fluxes were observed in June rather than in July, when hypoxia was observed. However, the low DIP concentrations measured in porewater in July of 2011 are expected to be a consequence of resuspension event which have redistributed DIP from porewater to overlaying water layers. Calculation of the wind-induced shear-stress to sediments in July 2011 based on the climatic data confirmed this hypothesis; just 21 hours before the sampling event the sediments were exposed to strong wind wave derived shear stress (Fig. 4.3), which was high enough to resuspend the sediments and flush DIP from sediment porewater to overlaying water and, consequently, the sediment porewater had limited time to recover its initial nutrient content (Reddy et al., 1996; Tengberg et al., 2003; Da-Pengand and Yong, 2010).

Consequently, it can be stated that the DIP release, was facilitated by a combination of several factors: i) mineralization of the labile organic pool enriched by fresh OM deposition; ii) DIP release from authigenic Ca-bound P due to the pH decrease and from Fe/Mn-bound P due to the low redox conditions (Table 4.1) and iii) wind/wave resuspension of surficial sediment (Fig. 4.3). The TIP fractions were not analysed during the first year of the study (2011) so it was not possible to determine if TIP forms had significant changes due to DIP release from the muddy sediments at the confined site. However, there are many studies on the redox dependency of P cycling, stating that oxygen depletion stimulates the reduction of Fe oxides with subsequent P liberation in sediment porewater and overlying bottom waters (Jensen et al., 1995; Giordani et al., 1996; Gunnars and Blomqvist, 1997; Rozan et al., 2002). On the other hand, it cannot be excluded that the organic P is an important source of DIP in the muddy sediments of the Curonian lagoon. However, the anoxia experiment conducted in July 2013 to assess the sediment buffer capacity related to Fe/Mn-bound P under low labile OM content, showed that short-term anoxia have stimulated DIP release over 19.9 μmol $m^{-2}h^{-1}$ (Fig. 4.12). At the confined muddy site, most of the identified P was in the authigenic Ca-bound (such as carbonate fluorapatite or more unstable calcite) and organic pools at the confined muddy site. Typically, under oxygen shortage, organic matter mineralization is being driven by the sequential reduction of NO_3^-, Mn(IV), Fe(III) and SO_4^{2-}, with rates that depend upon the relative abundances of the various chemical species (Canfield, 1994; Kristensen and Holmer, 2001; Middelburg and Levin, 2009). Moreover, during the intensive mineralisation, the pH of sediments can decrease fostering the dissolution of authigenic Ca-bound P pool (Gomez et al. 1999; Coelho et al. 2004; Reddy et al. 2005), release of DIP (Slomp et al., 1996) and increase the adsorption capacity of Fe(OOH)) (Seitzinger, 1991, Gomez et al., 1999, Søndergaard et al., 1999). Exchangeable and Fe-bound P pools increased during the course of the incubation, suggesting that Mn^{2+} diffusion from the bottom sediment can support Fe oxidation and DIP removal in the top sediment layers in the Curonian lagoon (Fig. 4.13). Rozan et al. (2002) showed that Fe(III) oxides formed in subsurface sediment can act as an effective barrier to upwards DIP fluxes. The porewater Fe^{2+}/DIP ratio in the upper sediment layer was decreased from 4.6 to 1.0 during the incubation mostly due to the DIP accumulation, while Fe^{2+} remained constant (Fig. 4.14). This process can be explained by gradient-driven upward molecular diffusion of DIP from deeper sediments. Gunnars and Blomqvist (1997) suggested that sulphide production via microbial sulphate reduction is one of the possible explanatory variables for Fe^{2+} and DIP mobilization. However, in the Curonian lagoon, where salinity is generally <1, sulphate concentrations are low and NO_3^- is depleted in the summer, methanogenesis becomes the most important OM degradation pathway in absence of oxygen (Zilius et al., 2012; Zilius et al., submitted). There still is a theoretical possibility of methane re-oxidation via Fe(III) reduction in freshwater sediments (Roden and Wetzel, 1996). Oxygen depletion had no clear stimulation on Mn^{2+} net fluxes at the sediment–water interface that remained similar in the both two conditions. Similar results were also obtained for Fe^{2+}. Lovley and Phillips (1988) demonstrated that Mn(IV) oxide reduction can inhibit iron reduction, and thereby net accumulation of Fe^{2+} starts when the oxidized pool of Mn is exhausted (Kristiansen et al., 2002; Kristensen et al., 2003). In coastal sediments, Mn(IV) oxides can be reduced to Mn^{2+} either via microbial respirations or through the chemical oxidation of reduced iron and sulphur species (Canfield et at., 1993; Thamdrup et at., 1994; Thamdrup, 2000; Schippers and Jørgensen, 2001; Ferro et al., 2003). Our data indicates that metal redox–reactions (Mn and Fe) under oxic to anoxic conditions also could be significant for DIP cycling (e.g. Kristiansen et al., 2002; Kristensen et al., 2003). Future research should address more detailed role of Mn when O_2 is depleted; this metal in fact discriminates processes occurring in the river plume areas and in organic-enriched sites due to the different availability, reactivity and different interactions with other biogeochemical processes. Manganese reduction makes the mechanisms regulating P mobility more complex, in particular under varying concentrations of bottom water nitrate. Anoxia did not stimulate DIP or Fe^{2+} fluxes (Fig. 4.13) but rather did the decrease of authigenic Ca-bound P (Fig. 4.15).

Results show that the Curonian lagoon sediments act as an efficient P trap, but it can turn to a DIP source when high phytoplankton biomass accumulates in the water column over the confined muddy site. However, other potentially important process, such as sediment resuspension which redistributes phosphorus from the sediments was not directly assessed.

5.4 Is internal phosphorus cycling promoting cyanobacteria blooms?

Study results demonstrate that the sort of self-sustaining system presented by Vahtera et al. (2007) can also be present in the early cyanobacteria proliferation stage in the Curonian lagoon which sustains fast phosphorus internal recycling. Since cyanobacteria has a competitive advantage in fixing atmospheric N, its abundance in the water column is likely to be controlled by the availability of dissolved inorganic P (Lilover and Strips, 2008; Conley et al., 2009).

The Curonian lagoon has clear seasonal succession of phytoplankton functional groups; diatoms and green algae are dominant in spring, while the cyanobacteria prevail over other groups in summer (Olenina, 1998; Pilkaityte and Razinkovas, 2006). Seasonal phytoplankton community changes are affected by N or P limitation, while most of the phytoplankton is N limited, cyanobacteria capable to fix nitrogen from atmosphere is P limited (Smith, 1984; Kahru et al., 1994; Finni et al., 2001; Vahtera et al., 2007; Lilover and Stips, 2008; Pearl, 2008). Jensen et al. (1994) and Hyenstrand et al. (1999, 2000) showed that phytoplankton community shift from green algae to cyanobacteria is strongly correlated with DIN:DIP ratio decrease, i.e. P enrichment. The beginning of phytoplankton bloom is generally driven by high temperature and river discharges enriched of both nitrogen and phosphorus. High molar DIN:DIP ratio indicated high availability of nitrogen and low DIN:DIP ratio indicated that the water is rich of phosphorus, but nitrogen limited. Differences in planktonic community composition in 2011 and 2013 can depend on DIN:DIP ratios of incoming waters (Fig. 4.1; Fig. 4.18). DIN:DIP ratio decreased by more than order of magnitude from March (~190) to June (~4) and cyanobacteria concentration in the water column increased in the beginning of June in 2011 (Fig. 5.1).

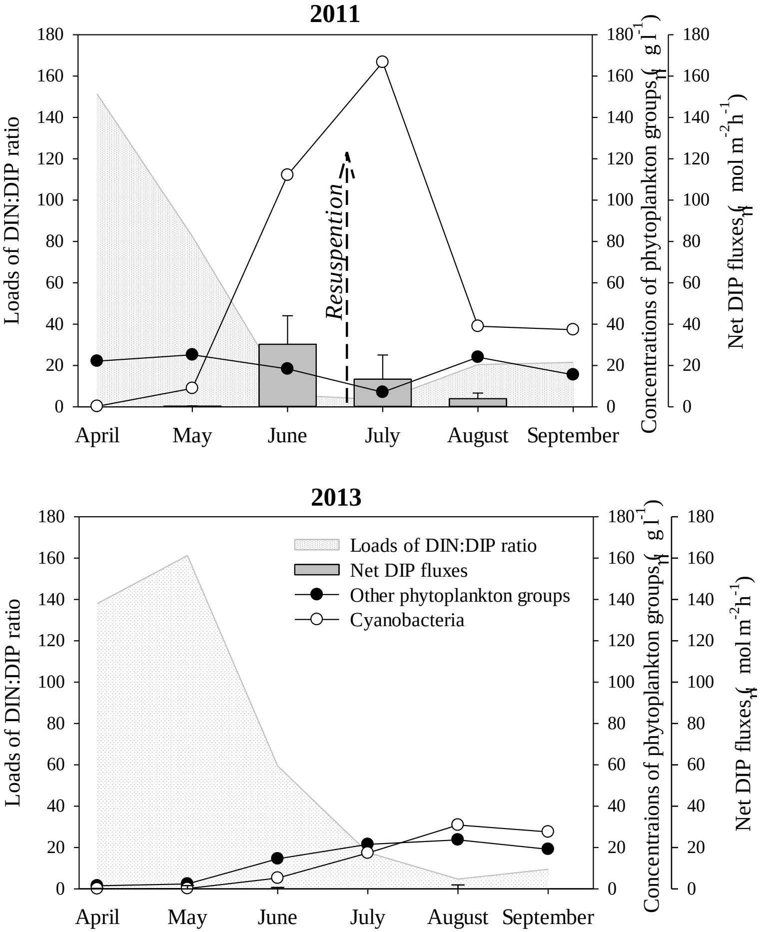

***Fig. 5.1** Loads of DIN:DIP ratio, net DIP fluxes and concentration changes of phytoplankton groups, in 2011 and 2013 at the confined site*

DIN:DIP ratio dropped 2 months later, from May (~187) to August (~2) and low DIN:DIP ratio was maintained for a shorter period in

2013. Under such specific circumstances, cyanobacteria cannot outcompete other phytoplankton groups, especially green algae, which become dominant during the summer in 2013.

Additionally, our data underline differences in biogeochemical processes in 2011 and 2013. 2011 was characterized by a strong summer peak of Chl-*a*, higher percentage of cyanobacteria and large summer efflux of inorganic P from the confined site sediments. Moreover, physical resuspension can drastically increase the P exchange between the porewater and the water column, also oxidizing the surficial sediment. Calculated wind-induced shear stress to sediments, 21 hours before sampling (Fig. 4.3), was high enough to resuspend the sediments and promote DIP effluxes, stimulating planktonic primary producers in July 2011 (Søndergaard et al., 1992). Fanning et al. (1982) found that even 1 mm of resuspended sediments can stimulate productivity in the water column from 100 to 200 %. This is not only due to the higher DIP release but also due to the liberation of iron, which is necessary for cyanobacteria growth, from porewater (Hyenstrand et al., 1999, 2000). The Chl-*a* concentration was increased up to 237 $\mu g\ l^{-1}$ after the anticipated sediment resuspension event in the Curonian lagoon. Settled blooms enhance oxygen consumption and can lead to anoxia, under calm weather conditions and water stratification. Under such conditions, organic or mineral P can be released from the sediments and support further proliferation of N-fixers, keeping the water column DIN/DIP ratio low and forming self-sustaining “vicious circle” (Jensen et al., 1994; Hyenstrand et al., 1999, 2000; Vahtera et al., 2007). Contrastingly, limited algal bloom in summer was followed by minor cyanobacteria blooms in autumn and, accordingly, sedimentary DIP release was very low at confined site in 2013 (Fig. 5.1).

This study results suggest that nutrient loads and stoichiometry from the watershed can trigger development of huge cyanobacteria blooms and, these N-fixing organisms can promote their self-sustainment facilitating the internal P recycling.

5.5 Phosphorus balance in Curonian lagoon and implication to water management

The study presents a preliminary mass balance of P for the Curonian lagoon, combining seasonal DIP and TP inflows and outflows (Fig. 4.16) with fluxes measured at the sediment–water interface (Table 4.6). This budget was constructed to assess the role of the Curonian Lagoon as a net sink or source of phosphorus in 2011 and 2013 and to evaluate the relevance of sediment diffusive DIP fluxes as a budget term. The Nemunas River has been considered as the only external P input to the lagoon. Since sewage treatment plants and minor rivers from both Lithuanian and Russian sides were not included, input terms could have been slightly underestimated. Outflowing P concentrations could also have been affected by brackish water intrusions as the associated dilution effects were not considered. However, during the sampling period salinity was always lower than 1, suggesting the low relevance of brackish water exchange. Moreover, brackish water intrusions are important only when the wind is very strong (>14 m s^{-1} according to Beaufort wind scale) and coming from the west or northwest directions (Zemlys et al., 2013). These conditions occurred only during 7–14 days in 2011 and 5–10 days in 2013, resulting in a general negligible effect (data from Marine Research Department of Lithuanian Ministry of Environment).

According to our estimates the Curonian Lagoon was a net sink of TP in 2011 and 2013, with a mean retention rate spanning from 0.40 to 1.77 µmol TP $m^{-2}h^{-1}$ (Table 5.2, Appendix 6). Seasonal DIP budgets were always negative and exceeding TP budgets (except for spring) even despite summer regeneration from sediments of 6.33 µmol DIP $m^{-2}h^{-1}$ in 2011. Taking this fact into consideration, we suggest that dissolved inorganic forms were converted into particulate ones within the lagoon. The high values of Chl-*a* data, indicating cyanobacteria blooms during 2011, confirm such hypothesis. Similar situation with net retention of DIP was recorded in 2013. Particulate P, measured in 2013, was net retained in 2 out of 3 seasons, suggesting either sedimentation or turnover into dissolved organic or inorganic fractions. During the autumn of 2013, characterized by minor cyanobacterial blooms, PP forms were net exported to the open sea (Fig. 4.1 and Fig. 5.2).

Total phosphorus loads coming from the Nemunas River are 2, 4 and 8 times lower comparing to other large Baltic Sea rivers as Neva, Oder and Vistula, respectively (Witek et al., 2003; Pastuszak et al., 2005; HELCOM, 2014). Vistula river water has twice higher concentrations of DIP than Nemunas. In both years DIP was assimilated or adsorbed in the Curonian lagoon except in the summer of 2013, when the DIP portion of TP in outflowing water was higher than in inflowing water. The Oder lagoon receives twice more DIP, which indicates high rates of DIP assimilation and regeneration within the estuary. DIP loads to the Curonian lagoon in 2011 were high (Fig. 4.13, Table 4.4) but only 20 % of this DIP amount was reaching the Baltic Sea, while the rest has been possibly transformed within the system by biological assimilation processes (Fig. 4.1). The relevance of measured net DIP fluxes from sediments was very different between two investigated years. The intensive sediment regeneration drove the whole annual budget and produced a net annual efflux, averaging 2.14 µmol DIP $m^{-2}h^{-1}$ during the summer in 2011. Such efflux was particularly important considering the outflow–inflow DIP budget. Being part of European Union and HELCOM signatory, Lithuania has obligations to improve water quality in the lagoon (to reach a good ecological status by 2015) and reduce the input of TP from Nemunas watershed to the Baltic Sea (down to 880 tP per year until 2021) (Borja and Elliott, 2007; HELCOM, 2009).

New approach for European water quality assessment was proposed after the enforcement of Water Framework Directive (WFD) which was adopted in the European Union in 2000. The strong relationship between Chl-*a* and total phosphorus was found by combining historical data, ecological relevance of nutrients concentration and phytoplankton parameters and expert judgment.

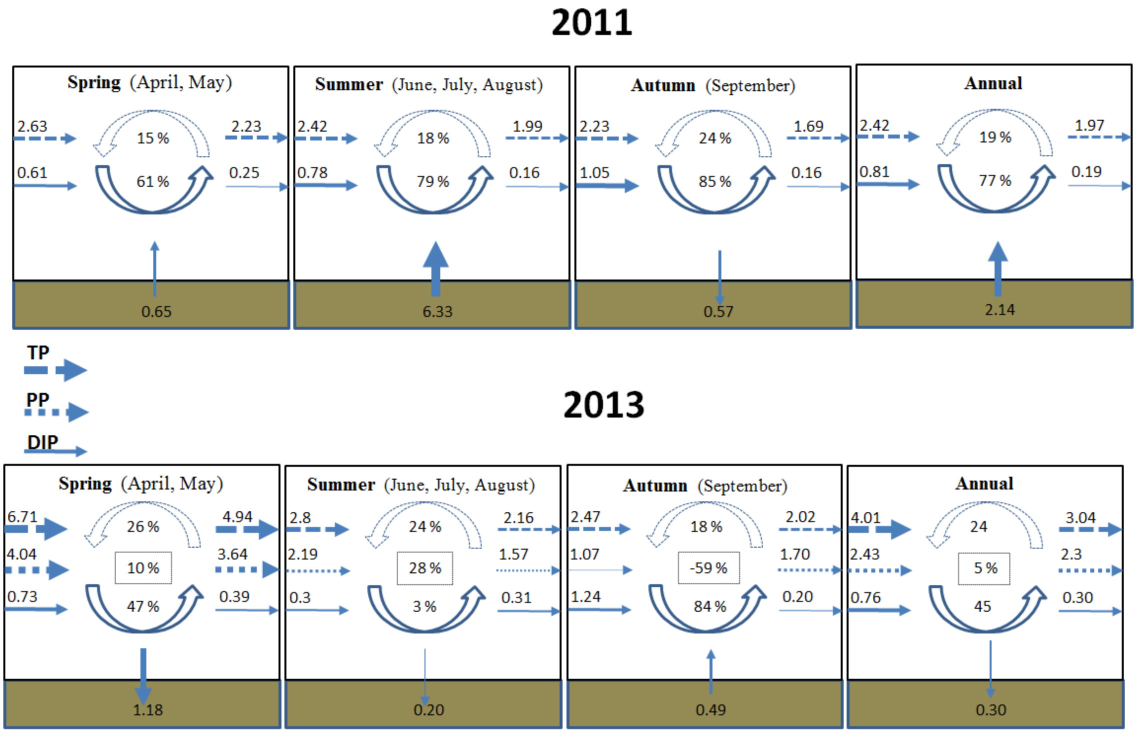

Fig. 5.2 *Preliminary seasonal budgets of DIP and TP in Curonian lagoon in 2011 and 2013, Units µM m*$^{-2}$*day*$^{-1}$

Therefore, the DIN:DIP ratio was selected as indicative value for reference conditions for Lithuanian transitional waters (Daunys et al., 2007, Langas et al., 2010). There was already a suggestion that to improve water quality and keep cyanobacteria abundance low in Lithuanian transitional waters by reduction of TP concentrations from June to September. Different class boundaries were proposed for the northern and central parts of the Curonian lagoon (Table 1.2, Daunys et al., 2007; Langas et al., 2010; Remeikaitė–Nikienė et al., 2013). DIP, however, was not considered as reference parameter as it does not have reliable relationship with Chl-*a*.

Table 5.2. TP concentrations in the Baltic Sea lagoons and estuaries

Lagoon, estuary	**Study months**	**Chl-*a* ($\mu g\ l^{-1}$), dominant phytoplankton group**	**TP, µM**	**References**
Curonian lagoon Lithuanian part	April–September	1.2–236.6 cyanobacteria	1.1–6.8	Our study
Curonian lagoon Russian part	Summer	45.0–186.0	2.8–8.2	Aleksandrov 2010
Szczecin lagoon	January–December	-	3.5–9.2	Bangel et al. 2004
Vistula lagoon Russian part	April–October	30.0–48.0 Cyanobacteria	3.5–4.8	Aleksandrov 2010
Neva estuary	May–October	Green algae	2.6–11.6	Berezina 2008

In general, Remeikaite–Nikienė et al. (2013) referred the Curonian lagoon as having “moderate” or “bad” water quality in terms of total phosphorus concentration in the water. Our study demonstrates that transitional site could be regarded as having “good” (in 2013) or “moderate” (in 2011) status, while the status of confined site could be described as “moderate” in both years. However, the threshold values determining the water quality classes are country specific (Daunys et al., 2007) and application of Lithuanian water quality criteria’s to other Baltic Sea lagoons could result in classifying the Neva estuary and Szczecin (Oder) lagoon into “very bad” water quality class in regard of TP concentrations (Table 5.2).

According to the calculated phosphorus budgets in 2011 and 2013, out of 1204 and 1570 tons of phosphorus that have entered the Curonian lagoon, 19 and 24% were retained.

According to Sileika et al. (2006) the loads to the Curonian lagoon are decreasing but this study demonstrates that the sediments (internal recycling) could contribute to the increase of TP loads and, subsequently, lead to higher discharges of TP into the Baltic Sea.

According to the HELCOM commitments, the outflow of P should be reduced down to 880 tP per year, i.e. the reduction should be by 24 % of presently measured loads from the Lithuanian territory to the Baltic Sea. Therefore, the reduction of phosphorus loads in the river drainage basin including point sources should be selected as a priority (ban of P-containing detergents, reduction of application in fertilizers, construction of wetlands and ponds, reduced autumn tillage). Local mitigation measures such as chemical precipitation, cultivation of zebra mussels and reed harvesting could be considered as well (Smil, 2000; Li et al., 2003; Caraco et al., 2006; Ulún et al., 2007; Jarvie et al., 2008; Jarvie et al., 2008), but rather as accompanying activities.

CONCLUSIONS

1. Total phosphorus was mainly in organic forms (68 %) in the lagoon water during the vegetation period and its concentration was statistically different between the study years ($F=15.9$, $p<0.05$), which positively correlated with Chl-*a* concentration ($r=0.7$, $p<0.05$).
2. The total sedimentary phosphorus concentrations was statistically different between sites (T-test, $t=21.1$, $df=20$, $p<0.05$), due to the differences in sedimentary characteristics, i.e. the accumulative muddy sediments had 9 times higher phosphorus concentrations, from which 83 % is in reactive forms. The transitional sandy sediments are poorer in total phosphorus, which is being mostly represented as stable inorganic phosphorus.
3. The more intensive phosphorus fluxes across sediment–water interface were observed in muddy sediments comparing to sandy sediments ($F=5.8$, $p<0.05$). The phosphorus fluxes from muddy sediments were positively correlated to Chl-*a* concentrations in water.
4. During the experiment phosphorus concentration increased by 3 times at the bottom water layer under the anoxic conditions comparing to oxic conditions.
5. Low DIN:DIP ratio (<5) has promoted the cyanobacteria development in the late spring of 2011 (from 14.0 in May to 135.3 $\mu g\ l^{-1}$ in June), while further bloom (236.6 $\mu g\ l^{-1}$ in July) was sustained by the sediment efflux of dissolved inorganic phosphorus (13.4–30.3 $\mu mol\ m^{-2}h^{-1}$).
6. On average, 69 % of the inflowing DIP from the Nemunas River is assimilated in the Curonian lagoon, however, about 97 % of inflowing DIP could be as well directly transported to the Baltic Sea during the intensive river discharge events (as in June 2013). 76 % of outflowing phosphorus from the Curonian lagoon to the Baltic Sea is in particulate form.

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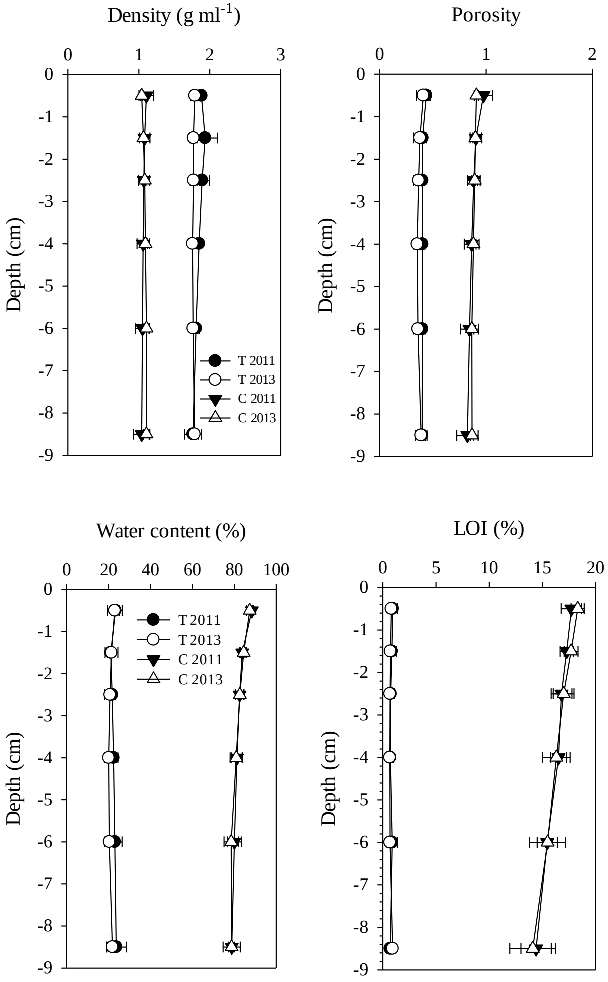
APPENDIXES

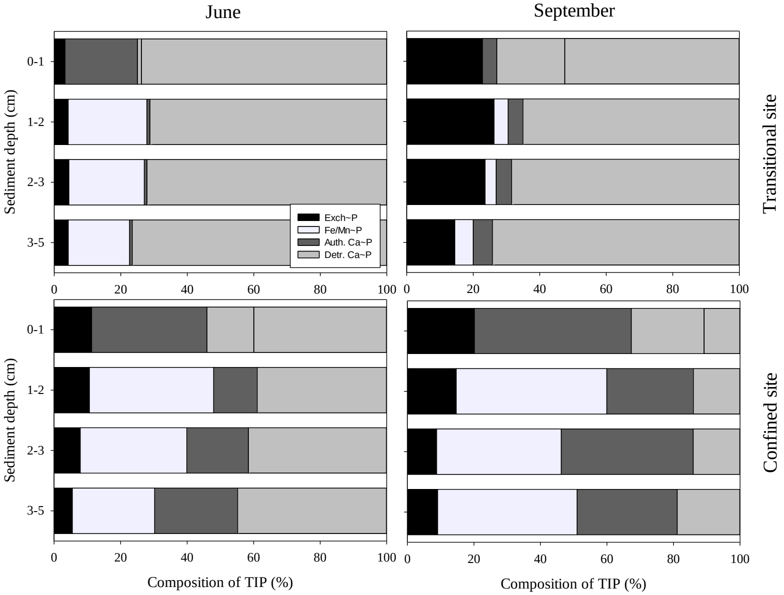
Appendix 1. Sedimentary characteristics (porosity, density, water content and LOI) distribution at transitional (circle) and confined (triangle) in 2011 (black) and in 2013 (white)



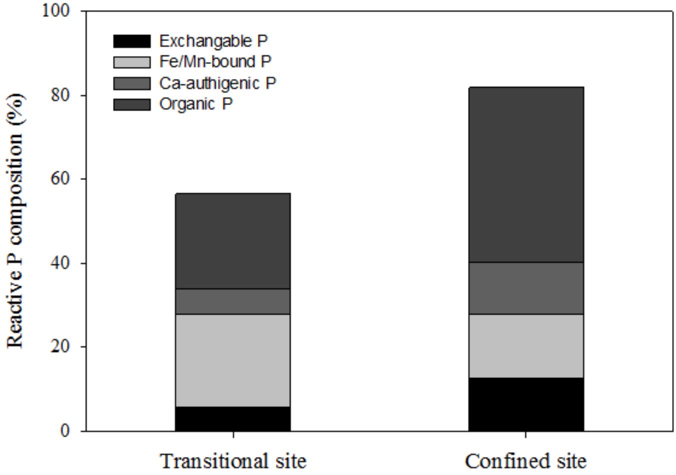
Appendix 2. Wind direction induced effective fetches for transitional and confined sites

Sites/wind direction	N	NE	E	SE	S	SW	W	NW
Transitional	15	7	4	15	70	7	2	4
Confined	10	30	15	30	42	15	5	5

Appendix 3 Total inorganic phosphorus fraction at the transitional and confined sites in June and September 2013



Appendix 4. The reactive phosphorus forms at the transitional and confined sites



Appendix 5. Results of statistical comparison (T-test) of phosphorus forms concentration (average±SD, µmol ml^{-1}) in the oxic and anoxic conditions. Statistically significant differences are indicated with asterisks.

	Oxic	**Anoxic**	**t value**	**Degree of freedom**
Exchangable P	0.26±0.08	0.31±0.06	-0.97	4
Fe/Mn-bound P	0.69±0.10	0.82±0.03	-2.15	4
Authigenic Ca-bound P	1.07±0.19	1.00±0.07	0.55	4
Detritic Ca-bound P	0.59±0.17	0.53±0.09	0.59	4

Appendix 6. Preliminary seasonal mass balance of DIP and TP in Curonian lagoon for 2011 and 2013 years, Unites μM $m^{-2}day^{-1}$

Seasons	**Sources**	**2011**		**2013**		
		DIP	**TP**	**DIP**	**PP**	**TP**
Spring	**Input:** Nemunas River	0.61	2.63	0.73	4.04	6.71
	Output: Baltic Sea	0.25	2.23	0.39	3.64	4.94
	ΔL*	**-0.36**	**-0.40**	**-0.34**	**-0.4**	**-1.77**
	Sediments	0.65	n.d.	-1.18	n.d.	n.d.
Summer	**Input:** Nemunas River	0.78	2.42	0.32	2.19	2.86
	Output: Baltic Sea	0.16	1.99	0.31	1.57	2.16
	ΔL*	**-0.62**	**-0.43**	**-0.01**	**-0.62**	**-0.70**
	Sediments	6.33	n.d.	-0.20	n.d.	n.d.
Autumn	**Input:** Nemunas River	1.05	2.23	1.24	1.07	2.47
	Output: Baltic Sea	0.16	1.69	0.2	1.70	2.02
	ΔL*	**-0.89**	**-0.54**	**-1.04**	**0.63**	**-0.45**
	Sediments	-0.57	n.d.	0.49	n.d.	n.d.
Annual	**Input:** Nemunas River	0.81	2.42	0.76	2.43	4.01
	Output: Baltic Sea	0.19	1.97	0.30	2.30	3.04
	ΔL*	**-0.62**	**-0.45**	**-0.46**	**-0.13**	**-0.97**
	Sediments	2.14	n.d.	-0.30	n.d.	n.d.

***Delta (Δ) is accumulation (-) or transportation (+) in/from lagoon**