Phosphorus dynamics in sediments of Darß-Zingst Bodden Chain, a eutrophic estuary in the southern Baltic Sea

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…, die den Autor schon zu der Aussage verleitet haben, dass die Variabilität in Zeit und Raum die einzige Konstante in diesem Brackwasserlebensraum darstellt.“

(ARNDT, 1994)

Content

List of figures VI

List of tables XI

List of abbreviations XIII

Summary XV

Zusammenfassung XVI

1 Introduction 1

2 Material and Methods 6

2.1 Sampling location 6

2.2 Sediment & pore water sampling 8

2.3 Macrozoobenthos 11

2.4 Incubations 12

2.4.1 Undisturbed core incubations 13

2.4.2 Phosphate release 14

2.4.3 Phosphate adsorption 15

2.5 Chemical analysis 17

2.6 Conversions 20

3 Results 23

3.1 Sediment characteristics 23

3.2 Amounts of selected elements in the sediment 27

3.3 Chlorophyll and Macrozoobenthos 33

3.4 Nutrient pore water distribution 35

3.5 Incubation fluxes 37

3.5.1 Undisturbed core incubation 37

3.5.2 Phosphate release 39

3.5.3 Phosphate adsorption 41

4 Discussion 44

4.1 TP inventories versus organic matter content 46

4.2 Influence of macrophytes and infauna on porewater nutrient concentration and dynamics 54

4.3 Diffusive versus incubation phosphate fluxes 59

4.4 Mass balance 64

5 Conclusion 69

References 71

Danksagung 80

Declaration / Selbständigkeitserklärung................ **Fehler! Textmarke nicht definiert.**

List of figures

Figure 1: Schematic phosphorus cycling in shallow aquatic ecosystems. 2

Figure 2: Phosphorus load in tons of the three main inflows to the DZBC (Bachor et al., 2014). 3

Figure 3: Map of the Darß-Zingst Bodden Chain (DZBC) with sampling locations. 6

Figure 4: Map and depth profile of transect stations in Dabitz, Grabow (© 2009 GeoBasis-DE/BKG, Google). 7

Figure 5: Map of sampling stations along the German Baltic coast (© 2009 GeoBasis-DE/BKG, Google). 8

Figure 6: Timeline of the tube incubation experiment, indicating times of aliquots withdrawal. 15

Figure 7: Schema of the tube incubation with different phosphate concentrations of 0; 0.1; 0.5; 1; 2; 5; 10; 25 and 50 µmol L^{-1}) 16

Figure 8: Timeline of the phosphate addition experiment, indicating time of water sampling and phosphate additions to about 50 µmol L^{-1} each time. 16

Figure 9: Blank control chart of PO_4^{3-} determination 2014-2016 with detection limit (black line). 17

Figure 10: Extinction (E) at 690 nm wavelength against 885 nm wavelength for phosphate concentration from 0 to 10 µmol L^{-1} in a 1 cm cuvette. 19

Figure 11: Water content (WC) and porosity (phi) (left) and dry bulk density (DBD) (right) along the depth transect in the Grabow (Gra) from March 2014. 23

Figure 12: Loss on Ignition (LOI) displayed in percentage of sediment dry weight (left) and sediment wet weight (right) along the depth transect in the Grabow form March 2014. 24

Figure 13: Correlation between total carbon concentration (TC) and Loss on Ignition (LOI) displayed in percentage of sediment wet weight (correl. coeff. = 0.958, p<0.001). 24

Figure 14: Sediment depth profiles of porosity (phi) and loss on ignition (LOI) in % DW from 0.5 m (filled circles, n=12) and 2 m station (open triangles, n=8), Grabow (mean, whiskers show SD). 25

Figure 15: Sediment depth profile of porosity (phi) and loss on ignition (LOI) in % DW from the Bodstedter Bodden (n=8, mean, whiskers show SD). 26

Figure 16: Median grain size of sediments from estuaries along the German Baltic Coast (GB-Gelting Bay, OB-Orther Bay, SH-Salzhaff, VB-Vitter Bodden, SW-Spandowhagener Wiek, Gra-Grabow, BoB-Bodstedter Bodden). 27

Figure 17: Total phosphorus (TP), total carbon (TC) and total nitrogen (TN) content, related to the sediment dry weight (left) and concentrations, related to sediment bulk volume (right) in the surface sediment (0-1cm) of transect stations in the Grabow (black) and Bodstedter Bodden (grey) from March 2014 (TP: n=3, whiskers show SD; TC, TN single measurement). 29

Figure 18: Total phosphorus (TP) content (left) and TP concentration (right) in relation to LOI displayed in percentage of sediment dry weight (DW) or sediment wet weight (WW) in sediments of 0.5 m (filled circles) and 2 m (open triangle) station, Grabow. 30

Figure 19: Sediment depth profile of total phosphorus (TP) displayed in two different ways. TP content related to sediment dry weight (left) and TP concentration related to sediment bulk volume (right) from 0.5 (filled circles, n=4, whiskers show SD) and 2 m (open triangles, single measurement) station, Grabow. Symbols above depth 0 indicate water column concentrations in mol m^{-3} (data: Schumann, unpublished). 30

Figure 20: Total Phosphorus (TP) and Total Carbon (TC) concentration in surface sediments (0-2 cm) of 7 stations along the German Baltic Coast (GB-Gelting Bay, OB-Orther Bay, SH-Salzhaff, VB-Vitter Bodden, SW-Spandowhagener Wiek, Gra-Grabow, BoB-Bodstedter Bodden) along the southern Baltic Coast. Indices a and b indicate significant differences (n=5; p<0.05). 31

Figure 21: Sediment depth profile of total phosphorus (TP) concentration from 0.5 m station (left) and 2 m station (right), Grabow from March 2015. Measured manually (dashed lines) with persulfate digestion or via ICP-OES after HCL digestion (black lines). 32

Figure 22: Sediment depth profile of total amount of Fe (a), Mn (b) and Al (c) displayed as concentration related to sediment bulk volume from 0.5 station (filled circles) and 2 m station (open triangles), Grabow from March 2015. 33

Figure 23: Chlorophyll depth profile from 0.5 m (filled circles) and 2 m station (open triangles), Dabitz from March 2015 (n=5, whiskers show SD). Symbols above depth 0 indicate water column concentrations (data: Schuman, unpublished). 34

Figure 24: Mean abundances (left) and biomass displayed as ash-free dry weight (AFDW) (right) of macrofauna species at 0.5 m and 2 m station, Grabow, during 2014 (n=5). Numbers indicate percentages of total abundance or biomass of main contributors 35

Figure 25: Mean pore water concentrations (black) of phosphate (a), ammonium (b) and nitrate (c) at the 0.5 m (filled circles) and 2 m (open triangles) station at Grabow during 2014 and 2015. Light grey lines show single measurements at different months throughout the years for phosphate and ammonium, whiskers show SD for triplicate measurement of nitrate in March 2015. Symbols above depth 0 indicate water column concentrations (data: Schumann). 36

Figure 26: Mean pore water concentration of phosphate and ammonium at 0.5 m station, Bodstedter Bodden during 2014, light grey lines show single measurements at different months throughout the years. 37

Figure 27: Oxygen, phosphate and ammonium fluxes in different laboratory incubation experiments on sediment cores from 0.5 m station (black) and 2 m station (grey); lt-a – long-term, anoxic; st-o – short-term, oxic; lt-o – long-term, oxic). Dashed line display mean oxygen flux and the resulting expected phosphate flux (see text). (different n result from loss of single cores, whiskers show SE) 38

Figure 28: Development of pore water phosphate and ammonium inventories during 46 days of tube-incubation, considering the uppermost 10 cm of sediment at 0.5 m and 2 m station, Grabow (n=2, whiskers show SE) 39

Figure 29: Inventories considering the uppermost 10 cm of sediment (left) and percentage (right) of different P fractions in sediments from 0.5 m (n=12) and 2 m station (n=8), Grabow (mean, whiskers show SD). NaCl – loosely bound phosphorus extractable by natrium chloride, BD – metal bound phosphorus

extractable by bicarbonate dithionite, PS- remaining phosphorus digested by acid persulphate. 41

Figure 30: Equilibrium phosphate concentration after shaking a sediment-water-mixture with different initial concentrations for 24h with sediments from 0.5 m (filled circles) and 2 m (open triangles) station, Grabow. (n=3, whiskers show SD, black line=mean) 42

Figure 31: left: Change of phosphate concentration in overlying water after phosphate addition in two 50 µM pulses (arrows) on sediment cores of 0.5 (filled circles) and 2 m (open triangles) station, Gra. right: Phosphate fluxes into sediment after addition of different phosphate concentrations to the overlying water (n=3; whiskers show SD) 43

Figure 32: Bathymetry of the DZBC with the area down to 1 m water depth marked as potentially inhabited by macrophytes. (Karstens and Kruse, unpublished) 45

Figure 33: Some basic relationships between sediment volume, dry bulk density (or mass concentration), water content, porosity, and pore-water volume for pure sand (0% silt fraction), a sand-mud mixture (50% silt fraction), mud (100% silt fraction) and sediment of the 0.5 and 2 m station, Grabow (bold). Images at top display the volumetric relationships between pore water and solids in a defined volume of sediment. Redrawn from Flemming & Delafontaine (2000). 48

Figure 34: Relationship of POC/TC concentration and POC/TC content in sediments from Nordrügenschen Bodden (left, Flemming & Delafontaine 2000) and the Grabow, DZBC (right, this study, n=10) 51

Figure 35: Relationship of POC concentration and POC content in surface sediments from the Gotland Basin and Arkona Basin, Baltic Sea (n=192) (Leipe et al., 2011).Table 8: comparison of weight specific TP content (TP Cw) of surface sediments and surface related TP inventories (TP i) considering the uppermost 10 cm of sediment of the Baltic Sea published by different authors, re-calculated from given data (see text). 51

Figure 36: C/N (grey) and C/P (black) ratio [mol/mol] in surface sediment (0-1 cm) of transect stations along a depth transect in the Grabow. Dashed lines mark corresponding Redfield ratios. 53

Figure 37: Sediment cores of 0.5 m (left) and 2 m (right) station, Gra showing influence of bioturbation and macrophytes on sediment, light brown sediment indicating oxidized conditions. 56

Figure 38: DIN/SRP ratio in porewater of 0.5 m (closed symbols) and 2 m (open symbols) station at Grabow. Symbols above depth 0 indicate water column concentrations (data: Schumann, unpublished) 59

Figure 39: Seasonal variation of calculated diffusive phosphate (filled circles) and ammonium (open rectangles) fluxes at the 2 m station, Grabow. Whiskers show a deviation of 55% estimated from core to core variation in March 2015 60

Figure 40: Phosphours fluxes (blue) and pools (black) in the Grabow 69

List of tables

Table 1: Overview on different incubation experiments with experimental conditions, sampling date, core diameter in cm, sampled stations and number of replicates, incubation time and abbreviations used in f 13

Table 2: Mean values of sediment parameters of surface sediment (0-1 cm), measured 6-9 times from 2013 to 2015 ± SE. Gra- Grabow, BoB – Bodstedter Bodden 25

Table 3: Mean amounts of total phosphorus (TP), carbon (TC) and nitrogen (TN) of surface sediments (0-1 cm) as weight specific contents, volume specific concentrations and surface related inventories of the uppermost 10 cm of sediment. Measured in March and May 2014 ± SE., Gra-Grabow, BoB-Bodstedter Bodden.. 28

Table 4: Mean release rates of phosphate and ammonium in mmol m^{-2} d^{-1} from sediment at 0.5 m and 2 m station, Grabow (± SE)................................... 39

Table 5: Phosphate and ammonium release potential (Pt_{Re}), in mmol m^{-2}, considering the uppermost 10 cm of sediment at 0.5 m and 2 m station, Grabow (± SE). 40

Table 6: Phosphate adsorption and release potential (P_{Ad}) from different experiments (exp.) related to sediment surface considering the uppermost 10 cm in mmol m^{-2} at 0.5 m and 2 m station, Grabow (± SE). Negative numbers indicate fluxes into the sediment, positive numbers indicate effluxes from the sediment.. 43

Table 7: Comparison of weight specific TP content (TP Cw) of surface sediments and surface related TP inventories (TP i) considering the uppermost 10 cm of the sediment of the DZBK published by different authors, re-calculated from given data (see text). 50

Figure 35: Relationship of POC concentration and POC content in surface sediments from the Gotland Basin and Arkona Basin, Baltic Sea (n=192) (Leipe et al., 2011).Table 8: comparison of weight specific TP content (TP Cw) of surface sediments and surface related TP inventories (TP i) considering the uppermost 10 cm of sediment of the Baltic Sea published by different authors, re-calculated from given data (see text). 51

Table 9: Calculated mass balances between P demand for primary production and potential P release from the sediments for the Grabow. Details see text. .. 67

Table 10: Calculated mass balances for the whole DZBC, details see text 68

List of abbreviations

A	area of sediment cores
ads	adsorption experiment (tube incubation)
AFDW	ash-free dry weight
BACOSA	Baltic Coastal System Analysis and Status Evaluation
BD	Bicarbonat-Dithionite
BD-P	metal bound phosphorus extractable with Bicarbonat-Dithionite
BoB	Bodstedter Bodden
C	carbon
c	concentration
Ca-P	Calcium bound phosphorus
C_V	volume specific concentration
C_W	weight specific content
DBD	dry bulk density
DCZBC	Darß-Zings Bodden Chain
DW	dry weight of sediment
GB	Gelting Bay
Gra	Grabow
i	area specific inventory
k	permeability
LOI	loss on ignition
lt-a	long time and anoxic incubation
lt-o	long time and oxic incubation
LUNG	Landesamt für Umwelt, Naturschutz und und Geologie, Mecklenburg-Vorpommern (environmental agency of Mecklenburg-Western Pomerania)
N	nitrogen
NaCl	sodium chloride
NaCl-P	loosely sorbed phosphorus extractable with NaCl solution
NH_4^+	ammonium
OB	Orther Bay
P	phosphorus
P-Campus	Science Campus Phosphorus Research, Rostock

phi	porosity of sediment
PO_4^{3-}	phosphate
Pt	potential
rel	release experiment (tube incubation)
S	salinity
SD	standard deviation
SE	standard error
SH	Salzhaff
SRP	soluble reactive phosphorus
st-o	short time and oxic incubation
st-oi	short time and oxic in-situ incubation
SW	Spandowhagener Wiek
T	temperature
TC	total carbon
TN	total nitrogen
TP	total phosphorus
upt	uptake experiment
VB	Vitter Bodden
WC	water content of sediment
WW	wet weight of sediment

Summary

The Darß-Zingst Bodden Chain (DZBC), a shallow estuary of the southern Baltic Sea, is highly eutrophicated. High nutrient input from intense agriculture since the 1960s induce an ecosystem shift from a macrophyte dominated system to a phytoplankton dominated one. The reduction of nutrient input since the 1980s could not induce a reduction of phytoplankton biomass and turbidity. Macrophytes recur in the DZBC in the regions shallower than one metre water depth.

It is hypothesized, that the sediments provide nutrients, especially phosphate, to the overlying water column and therefore support the persistent eutrophicated status.

In the framework of the joint research project BACOSA (Baltic Coastal System Analysis and Status Evaluation) the role of sediment in nutrient cycling in the DZBC was analysed in the present study, with focus on phosphorus (P) dynamics in the sediment and at the sediment water interface.

Seasonal measurements of phosphorus and phosphate concentrations in the sediment and the pore water as well as different incubation experiments were conducted on sediments from mainly two stations in 0.5 m and 2 m depth in the Grabow, representing the two main sediment types in the DZBC.

Based on weight specific total phosphorus (TP) contents it was a long-time assumption that phosphorus accumulates in fine grained organic rich sediments in the deeper Bodden areas (below 1 m). This could not be confirmed, if TP was displayed as volume specific concentration. The TP concentrations of 4.8 mol m^{-3} on the 0.5 m station and 3.6 mol m^{-3} on the 2 m station show that TP is deposited at the shallow site with sandy sediments at least to the same extent as in muddy sediments.

Phosphate release from sediments occurs under anoxic conditions only. The release potential represents the absolute amount of P, which is potentially liberated from a defined sediment surface area. A maximum release potential of 2.4 and 3.1 mmol m^{-2} was measured at sediment of the 0.5 and 2 m station respectively. Only on the 2 m station a mean diffusive flux of 15 µmol m^{-2} d^{-1} could be calculated from pore water concentration gradients. This would result in a phosphate efflux of 2.6 t a^{-1} from the muddy sediment in the Grabow, which could account for less than 19 % of P-demand for phytoplankton and macrophyte production.

Moreover, due to the shallow character of the DZBC the water column is well mixed during the year and the sediment surface is mostly well oxygenated. Under these oxic conditions, P adsorbs onto iron oxyhydroxids. In incubation experiments it could be shown, that the adsorption potential of 4.6 mmol m^{-2} at the 0.5 m station and 5.6 mmol m^{-2} at the 2 m station surmounts the release potential. Therefore, the oxidized sediment surface acts as effective barrier for PO_4^{3-} diffusion upwards from anoxic sediment layers.

From the results of the present study it can be concluded, that the sediments of the DZBC do not act as source for P sufficient to explain the persistence of high phytoplankton biomass in the system. Due to the high adsorption capacity, they may rather act as sink for P.

Zusammenfassung

Die Darß-Zingster Boddenkette (DZBK), ein flaches Ästuar der südlichen Ostseeküste, ist durch intensive Landnutzung und der daraus folgenden hohen Nährstoffbelastung seit den 1960er Jahren stark eutrophiert. Eine deutliche Reduktion der Nährstofffrachten seit den 1980er erbrachte aber keine Verbesserung im Ökosystem. Der ursprüngliche von Makrophyten dominierte Zustand konnte bisher nicht wieder erreicht werden. Das System verbleibt im trüben von Phytoplankton dominierten Zustand, wobei aber auch ein Wiederauftreten von Makrophyten in den flachen (unter 1 m Wassertiefe) Bereichen der DZBK beobachtet werden kann.

Es wird angenommen, dass die Sedimente Nährstoffe, insbesondere Phosphat, an die darüber liegende Wassersäule abgeben und damit den anhaltenden Eutrophierungszustand erhalten.

Im Rahmen des Verbundprojektes BACOSA (Baltic Coastal System Analysis and Status Evaluation) wurde in der vorliegenden Arbeit die Rolle des Sediments im Nährstoffkreislauf der DZBK untersucht. Hierbei lag der Hauptfokus auf der Phosphordynamik im Sediment sowie an der Sediment-Wasser-Grenzfläche.

Es wurden saisonal Messungen der Phosphor- und Phosphatkonzentration im Sediment und Porenwasser, sowie verschiedene Inkubationsexperimente an Sedimenten, von hauptsächlich zwei Stationen in 0.5 m und 2 m Wassertiefe im Grabow durchgeführt, welche die beiden vorwiegenden Sedimenttypen der DZBK repräsentieren.

Basierend auf gewichtsspezifischen Totalphosphor (TP)-Gehalten wurde lange Zeit angenommen, dass P in feineren, organikhaltigen Sedimenten in den tieferen Boddenbereichen (unter 1 m Wassertiefe) akkumuliert.

Mit Betrachtung der volumenbezogenen TP-Konzentrationen im Sediment konnte diese Annahme nicht bestätigt werden. Die TP-Konzentrationen von 4.8 mol m^{-3} auf der 0.5 m Station und 3.6 mol m^{-3} auf der 2 m Station zeigen, dass in den flachen Bereichen mit sandigem Sediment mindestens genauso viel TP abgelagert wird, wie in schlickigen Sedimenten.

Nur unter anoxischen Bedingungen wird Phosphat mit einem maximalen Freisetzungspotential von 2.4 mmol m^{-2} auf der 0.5 m Station und 3.1 mmol m^{-2} auf der 2 m Station aus den Sedimenten freigesetzt. Aber nur auf der 2 m Station konnte aus den Konzentrationsgradienten im Porenwasser ein diffusiver Efflux von 15 µmol m^{-2} d^{-1} berechnet werden. Das entspricht einem jährlichen P-Fluss von 2.6 t a^{-1} von den Schlickflächen des Grabow, deckt jedoch den P-Bedarf für die Primärproduktion von Phytoplankton und Makrophyten zu nicht mal 19%.

Zudem führt der flache Charakter der DZBK zu einer ständig durchmischen Wassersäule und damit zu einer guten Sauerstoffversorgung des Oberflächensediments. Unter oxischen Bedingungen bindet P an Eisen-Oxyhydroxide. In Inkubations-Experimenten konnte gezeigt werden, dass das Adsorptionspotential von 4.6 mmol m^{-2} auf der 0.5 m Station und 5.6 mmol m^{-2} auf der 2 m Station das jeweilige Freisetzungsspotential übertrifft. Die gut oxidierte Sedimentoberfläche fungiert damit als effektive Barriere für das aus anoxischen Sedimentschichten aufwärts diffundierende Phosphat.

Die Ergebnisse der vorliegenden Arbeit zeigen, dass die Sedimente der DZBK keine ausreichende Quelle für den P-Bedarf der anhaltend hohen Phytoplanktonbiomasse darstellen, sondern eher eine P-Senke im System sind.

1 Introduction

Phosphorus (P) is one of the essential nutrients for life on earth. It is an important component in DNA, RNA and in body structures like bones and teeth. Phospholipids build up the cell membrane and in the form of ATP phosphorus mediates the energy transfer in cells and organisms. Plants take up phosphorus in its dissolved form as phosphate ion (PO_4^{3-}), integrate it into their biomass and therefore make it available for the upper trophic levels. Due to a rising world population and the increasing need for food, also the demand for phosphate in agriculture increases. But the P-rock, used as resource for mineral P-fertilizer, is limited and will be exhausted in a foreseeable future (van Dijk et al., 2016).
The low efficiency of P assimilation in various stages of food production and consumption as well as insufficient recycling leads to high P losses. On one hand, due to limited P resources, these losses will become an increasing economic problem. On the other hand, the “lost” P causes large environmental problems through eutrophication in aquatic ecosystems.
In the need of closing the economic P cycle towards greater sustainability and to understand the environmental P impacts for appropriate environment and watershed management, the Science Campus Phosphorus Research in Rostock (P-Campus) supports interdisciplinary and international research focused on P. This science network includes research on different chemical forms of P, the efficient use and recycling possibilities of P as well as P cycling in the environment.

In aquatic ecosystems PO_4^{3-} is taken up by phytoplankton during primary production and incorporated into biomass. This organic matter is later decomposed by bacteria and nutrients are regenerated. In shallow ecosystems the remineralization of nutrients mostly takes place in the sediment since the benthic and pelagic realms are closely coupled (Sundby et al., 1992). In contrast to deep water regions, in coastal and shallow ecosystems a large amount of fresh organic matter reaches the sediment surface (Jensen et al., 1995). The deposited organic matter is consumed fast in the benthic food web (Graf, 1987) and finally nutrients are remineralized and released back to the water column (Figure 1).

Furthermore the water column is influenced by resuspension of organic matter and inorganic sediment from the bottom, increasing the turbidity and exchange rates between sediment and overlying water (Almroth et al., 2009; Kleeberg et al., 2013).

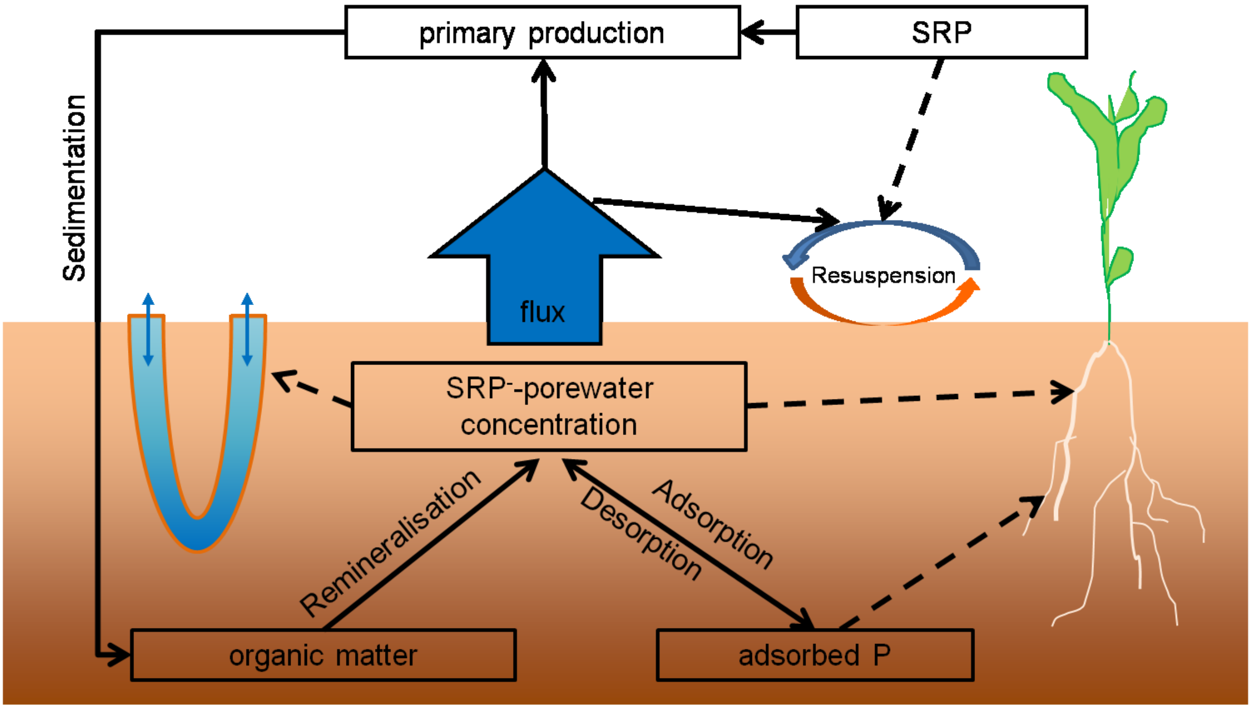

Figure 1: Schematic phosphorus cycling in shallow aquatic ecosystems.

The PO_4^{3-} remineralized in the sediment is released to the pore water from which it can be transported to the overlying water column, reprecipitated in an authigenic form (Ca-P, Apatite) or adsorbed onto sediment particles (Figure 1). In oxygenated sediments the adsorption onto metal oxyhydroxides plays an important role in sediment P cycling (Sundby et al., 1992). However, whether phosphorus is liberated to the overlying water column or retained in the sediment depends mostly on redox conditions in the sediments (Krom and Berner, 1981; Mort et al., 2010; Reed et al., 2011; Sundby et al., 1992). Under hypoxic and anoxic conditions the sediment may act as internal P source to the water, as reported by various authors for the Baltic Sea (Balzer, 1984; Conley et al., 2002; Jensen et al., 1995; Mort et al., 2010; Pitkänen et al., 2001), whereas under oxic conditions adsorption in the oxidized surface sediment likely decreases or blocks phosphate fluxes from the sediment to the overlying water (Sundby et al., 1992 references therein).

The Darß-Zingst Bodden Chain (DZBC) is a shallow estuary of the southern Baltic Sea. It consists of a string of four partially enclosed basins (Figure 3). The main fresh water input to the system is supplied by the rivers Recknitz and Barthe. In the east, the DZBC opens to the adjacent Baltic Sea by a narrow connection, which allows only limited water exchange. This results in a distinct salinity gradient from east to west.

Due to the intensification of agriculture and excessive use of fertilizer the DZBC was subject to massive nutrient input from the catchment area since the 1960s (Selig et al., 2006). This led to an anthropogenic eutrophication and a system shift from a macrophyte dominated to a phytoplankton dominated system (Schiewer, 2006). Since the beginning 1980s until the 1990s nutrient input was reduced by about 60% and remains stable until today (Figure 2, Bachor, 2005; LUNG, 2013; Selig et al., 2006).

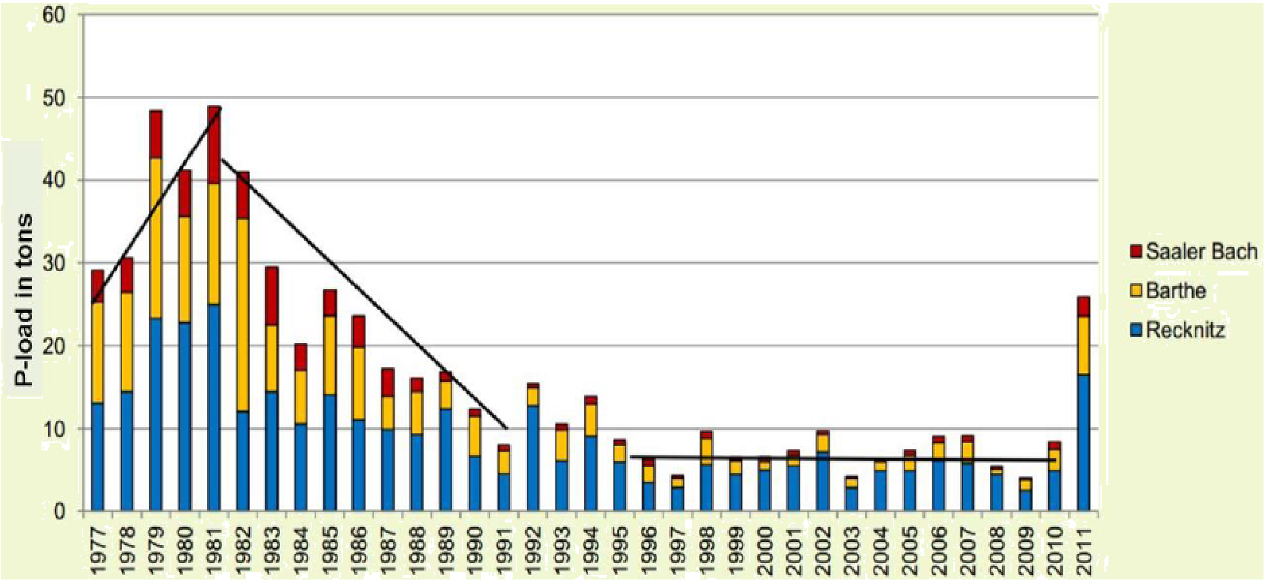

Figure 2: Phosphorus load in tons of the three main inflows to the DZBC (Bachor et al., 2014).

Nevertheless, the phytoplankton biomass, dominated by cyanobacteria and chlorophyceae, and the turbidity in the water column did not decrease (Schumann and Karsten, 2006). Meanwhile macrophyte biomass increases again (Piepho and Schubert, 2015; Yousef and Schubert, 2001).

It is hypothesized, that the sediments provide nutrients to the overlying water column (Biele et al., 2007; Dahlke, 2006; Schlungbaum et al., 2001; Selig et al., 2006). This paradigm results from in-situ bell jar experiments conducted under finally anoxic conditions by Baader and Schlungbaum (1982). In these experiments a maximal efflux of phosphate from the sediment of 14.53 mg P m^{-2} d^{-1} was measured and compared to the efflux of 19 mg P m^{-2} d^{-1} measured by Balzer (1984) in a similar experiment in Kiel Bight. Both these values from different regions and sediment types were probably averaged to a general P-release value of 16.7 mg P m^{-2} d^{-1} (Baader and Schlungbaum, 1982). The value 16.7 mg P m^{-2} d^{-1} (0.54 mmol m^{-2} d^{-1}) is often cited in literature thereafter (Schlungbaum et al., 2001, 1994b; Selig, 2005) and led to the assumption, that the sediments of the DZBC provide an internal nutrient load that surmounts the external P load (Biele et al., 2007; LUNG, 2008).

In contrast, Schlungbaum (1982) also showed that the sediments have a high adsorption capacity with 1.1 mg P g^{-1} DW (1.8 mmol m^{-2}) for silty sediments and 0.05 mg P g^{-1} DW (0.24 mmol m^{-2}) for “mineralic” sediments. They also found that this capacity to adsorb soluble reactive phosphorus (SRP) from water onto sediment particles is not exploited under natural SRP concentrations of 0 to 6 µmol L^{-1} in the Bodden waters. But these results or the idea that sediments adsorption capacity may exceed the SRP supply were neither considered in the following literature nor related to potential P release from sediments.

Furthermore most of the former studies focused on muddy and organic rich sediments from deeper basins of the DZBC, but only 40-50% of the whole Bodden area is covered by this sediment type (Schlungbaum et al., 1994a). At least 26% of the DZBC area is shallower than 1 m water depth (LUNG, 2015), potentially influenced by macrophytes and well oxygenated. Thus, the role of sediments in P cycling in DZBC may have been misjudged to a considerable extent.

Another problem in former evaluations of sediment nutrient status is the widespread confusion of the terminology, i.e. the concepts of “content” and “concentration” (Flemming and Delafontaine, 2000). The amount of total phosphorus (TP) in sediments is often related to sediment mass and given in mg P per g of sediment dry mass, and therefore does not take into account how much water is contained in the sediment. This led to the assumption, that organic matter and TP contents are correlated and TP accumulates in the deeper basins of the DZBC (Nausch and Schlungbaum, 1993;

Schlungbaum et al., 2001, 1994; Selig et al., 2006). In contrast, the concentration is volume related and considers the higher water content in muddy compared to sand sediments. Therefore, the use of TP concentration seems to be more appropriate when comparing different sediment types to evaluate the P status of the sediment and calculate the P balance in the ecosystem.

The influence of re-established macrophytes on the nutrient status and phytoplankton development were analysed in the joint research project BACOSA (Baltic Coastal System Analysis and Status Evaluation) to evaluate the ecosystem services of the DZBC.

The present study, conducted in the framework of the BACOSA project, focuses on the nutrient exchange processes at the sediment-water interface. Especially the P dynamics in the sediment was analysed and compared at two main stations along a depth transect at 0.5 m and 2 m in the Grabow representing the main sediment types that occur in the DZBC. On one hand, the station in the shallow area (0.5 m) consist of sandy sediments with less organic matter content (LOI < 5 %), which are influenced by macrophytes and bioturbation by high macrozoobenthic biomass. On the other hand, muddy sediments with high organic matter content (LOI > 5%) occur on the station in the deeper region (2 m) of the DZBC, where fine material accumulates.

The aim of the present study is to estimate the extent of sedimentary P load and to elucidate if the nutrient supply via the sediments could account for ongoing eutrophication. Therefore, the following main questions should be answered:

1. How much P is stored in the sediments of the DZBC?
2. Which portions of the P-pool are potentially desorbable?
3. How much SRP is liberated from sediment to the overlying water column and under which conditions?
4. Which factors regulate the P fluxes between sediment and water column?

2 Material and Methods

2.1 Sampling location

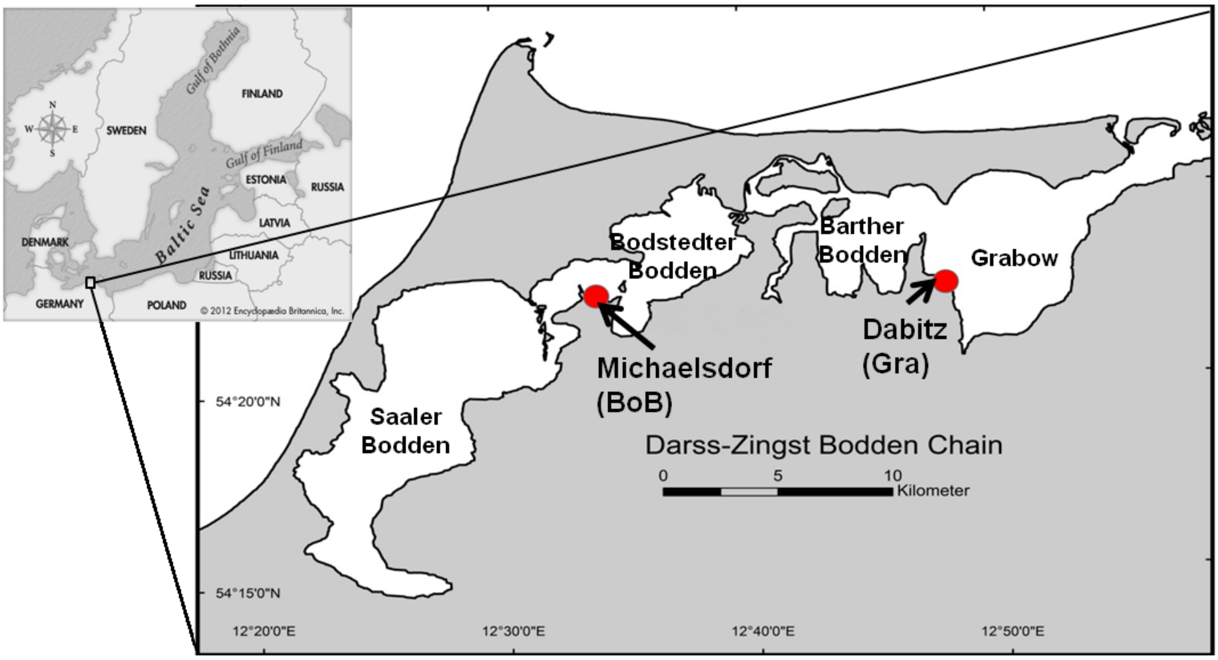

Figure 3: Map of the Darß-Zingst Bodden Chain (DZBC) with sampling locations.

The DZBC is part of the graded shoreline ("Ausgleichsküste") in the southern Baltic Sea. It is separated from the adjacent Baltic Sea by the Fischland-Darß-Zingst peninsula. The DZBC consists of a string of four partially enclosed basins with an average depth of 2 m (Figure 3). The central connection of the Zingster Strom is narrowed by small islands and a draw-bridge and therefore separates the eastern part (Grabow, Barther Bodden) from the western part (Bodstedter Bodden, Saaler Bodden). The DZBC is connected to the Baltic Sea by the narrow Gellenstrom in the east of the lagoon system, resulting in a distinct salinity decrease from east to west, in which the eastern parts are affected by higher fluctuations than the western ones (Schlungbaum et al., 2001).

The sampling sites were situated in Dabitz at the southwestern shore of the Grabow (Gra) and in Michaelsdorf at the southern shore of the Koppelstrom, which is part of the Bodstedter Bodden (BoB) (Figure 3). The salinity varied between 7 and 8.5 at Gra and between 2.5 and 6 at BoB during the sampling period from 2013 and 2015. The samples at each site were taken at 10 stations along a transect perpendicular to the shoreline with increasing water depth (Figure 4). Due to hydrographic conditions, it was not possible to sample along a distinct depth gradient at BoB, therefore sampling was reduced to one station subsequently.

Based on early results from the transect program in 2014 the sampling later focused on two stations in the Grabow in different water depths with different sediment types (see section 3.1). The sediment at the 0.5 m station is influenced by macrophytes, mainly *Stuckenia pectinata*, *Ruppia* sp. and *Chara baltica* (Piepho and Schubert, 2015). At the station in 2 m water depth no or very few macrophytes occur (Blindow and Meyer, 2015) due to the prevailing light conditions (0.25-1.2 m Secchi depth; LUNG, 2013; Piepho et al., 2016).

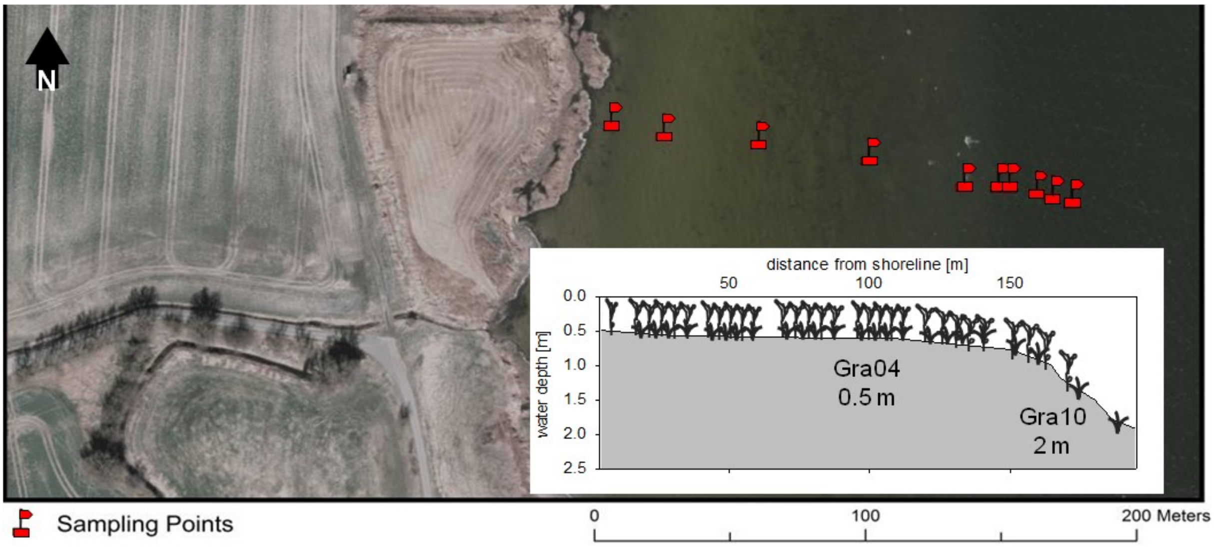

Figure 4: Map and depth profile of transect stations in Dabitz, Grabow (© 2009 GeoBasis-DE/BKG, Google).

In June and July 2013, in preparation of the intense sampling program in the DZBC in 2014 sediment was additionally sampled from five stations along the German Baltic coast (Figure 5) and analyzed for sediment parameters, TP, TC and TN content.

All sampling spots were situated in shallow water environments and partly influenced by macrophytes. Gelting Bay (GB), Orther Bay (OB) and Salzhaff (SH) show a similar salinity of 10 to 11.5 and salinity dropped down to 8 at Vitter Bodden (VB) and 3 at Spandowhagener Wiek (SW).

Figure 5: Map of sampling stations along the German Baltic coast (© 2009 GeoBasis-DE/BKG, Google).

2.2 Sediment & pore water sampling

In 2013 a preliminary sampling took place at Gra in roughly 0.5 m water depth, 500 m southwards from the later transect, during a master thesis (Gebhardt, 2013) and at Gra and BoB in the frame of a comparison to different stations along the outer coastline of the southern Baltic Sea (see section 2.1, Figure 5).

In 2014 within the scope of the central transect program in BACOSA sediment was sampled 5 times per year at Gra and BoB. In March 2015 three parallel cores each were taken at the two focus stations at Gra. Unfortunately, in November 2015 dense fog prohibited sampling at the 2 m station and samples could only be taken at the 0.5 m station.

On the 10 stations along the transect at Gra and BoB small sediment cores with a diameter of 3.6 cm were sampled in March and May 2014 and in September 2014 at Gra only. Sediment cores with a diameter of 10 cm and a sediment depth of 10 to 25 cm were sampled on one station at BoB, and at the two stations in 0.5 m and 2 m water depth at Gra. Up to 0.7 m water depth sediment cores were taken hand-operated with beveled Plexiglas tubes. In greater water depth (> 0.7 m) the samples were taken from the research boat "Pomi" (Biological Station Zingst, University of Rostock). In September 2014, the depth transect was extended once to include two more stations in 2.5 and 3.1 m water depth. Here sediment cores with a diameter of 6 cm were taken with a single tube gravity corer.

One 10 cm core per station and time was sliced in 2 x 0.5 cm, 4 x 1 cm and 6 x 2 cm consecutive layers. The layers were homogenized and subsamples of 5 cm³ were weighed fresh, after drying at 60 °C and after combusting at 500°C for determination of water content (WC) and porosity (phi, equ. 1, 2), dry bulk density (DBD, equ. 3) and loss on ignition (LOI).

$$\mathbf{Vol\%} = \frac{\frac{\mathbf{WW - DW}}{\boldsymbol{\rho}_{\mathbf{H_20}}} * \mathbf{100}}{\frac{\mathbf{WW - DW}}{\boldsymbol{\rho}_{\mathbf{H_20}}} + \frac{\mathbf{DW}}{\boldsymbol{\rho}_{\mathbf{Sed}}}}$$

equ. 1

$$\mathrm{phi} = \frac{\mathrm{Vol\%}}{100}$$

equ. 2

$$\mathrm{DBD} = \frac{\mathrm{DW}}{\mathrm{V_{Sed}}}$$

equ. 3

Vol% = water content in percentage of volume
phi = Porosity
DBD = dry bulk density [g cm^{-3}]
WW = sediment wet weight [g]
DW = sediment dry weight [g]
ρ_{H_20} = density of water = $f(T,S)$ [g cm^{-3}] (Ramsing and Gundersen, 2001)
ρ_{Sed} = density of quartz = 2.65 [g cm^{-3}]
V_{Sed} = volume of sediment sample = 5 cm³

An accurate language would require the use of the term wet mass (WM) and dry mass (DM) of sediment. But to stay in consensus with common literature and to avoid irritation the more frequently used terms wet weight (WW) and dry weight (DW) are used in this work.

The grain-size distribution was determined by wet sieving of mixed sediment of the uppermost three centimeters, over a $\log_2$-set of sieves (1000, 500, 250, 125, 63 µm). The pore water was gained by centrifugation (3 min, 3000 rpm) of wet sediment over glass microfiber filters (GF/F-filters) (Saager et al., 1990) and analysed for soluble reactive phosphate (SRP), ammonium (NH_4^+) and in March 2015 also for nitrate (see section 2.5).

According to Fick's first law a diffusive flux (F_{diff}) was calculated from the pore water concentration gradient of the upper 2 cm.

$$F_{diff} = phiD_S \times \frac{dC}{dz}$$

equ. 4

F_{diff} = diffusive flux [µmol m^{-2} d^{-1}]

dC/dz = slope from linear regression of concentration versus sediment depth

phi = porosity

D_S = Diffusion coefficient in sediment [cm^2 s^{-1}]

The diffusion coefficient in sediment was calculated from the Infinite-Dilution Diffusion Coefficient in water, correcting for temperature and tortuosity following Boudreau (1996)

$$D_S = \frac{D_0}{\theta^2}$$

$$D_0 = (m_0 + m_1 \times T) \times 10^6$$

$$\theta^2 = 1 - \ln(phi^2)$$

equ. 5

D_0 = Infinite-Dilution Diffusion Coefficient [cm^2 s^{-1}]

θ = tortuosity

m_0 and m_1 = parameter of linear regression against temperature (T) in °C (Boudreau, 1996; tab. 4.7 and 4.8)

The small sediment cores with a diameter of 3.6 cm were sliced into an 'a'-horizon corresponding to the uppermost 1 cm, and a 'b'-horizon from 1-5 cm sediment depth. From the homogenized layers subsamples for WC, phi, DBD and LOI were taken and treated as described before. From every layer 0.05 g of the dried sediment was analyzed in a Carlo Erba NC 2500 Elemental Analyzer for TC and TN content and 0.1 g of the combusted sediment was digested for TP analysis (see section 2.5).

The permeability (k) was analyzed by falling head permeability test in July 2014 on three replicates (3.6 cm sediment cores) from the 0.5 m station of Gra.

$$\mathrm{k_f} = \mathrm{L} \times \frac{\ln\left(\frac{\mathrm{h_1}}{\mathrm{h_2}}\right)}{\Delta \mathrm{t}}$$

equ. 6

$$\mathrm{k} = \mathrm{k_f} * \frac{\mu}{\mathrm{g}} \times \rho_{\mathrm{H_20}}$$

equ. 7

k_f = hydraulic conductivity [cm s^{-1}]
k = permeability [cm^{-2}]
L = height of sediment column [cm]
h_1, h_2 = upper and lower water level corresponding to one time interval [cm]
Δt = recorded time of water level changing from h_1 to h_2 [s]
µ = dynamic viscosity [g cm^{-1} s^{-1}]
g = acceleration of gravity = 9.81 m s^{-2}
ρ_{H_20} = density of water = $f(T,S)$ [g cm^{-3}]

Several further analyses like chlorophyll concentration, TP content, sequential fractioning of phosphorus binding forms and elemental analysis of sediment as well as nitrate concentration in pore water, were conducted at the sediment cores taken in March 2015.

2.3 Macrozoobenthos

Macrozoobenthos was sampled by sieving one sediment core (10 cm diameter) for each station and point of time over a 500 µm mesh. The fauna was preliminarily preserved in 4% formalin. For longer storage preservation solution was changed to 70% ethanol. The macrozoobenthos samples from 2013 and 2014 were analyzed in the frame of two bachelor theses (Hoppe, 2014; Rach, 2015).

2.4 Incubations

Different incubation experiments were conducted with sediments from the 0.5 m and 2 m station (Table 1): (1) undisturbed core incubation to investigate phosphate fluxes under nearly natural conditions, (2) tube incubation on anoxic sediment to analyze the release potential of the sediment and (3) core incubation with phosphate addition to the overlying water column to investigate the adsorption behavior of the sediment surface.

Until incubations, the sediment cores were aerated and stored in the dark in a temperature controlled (10 °C) water bath. The conditions and height of the overlying water column were monitored regularly and water was restocked if necessary. Laboratory incubations take place in the dark and at roughly 10°C. A rotating disc or stirring magnets inside the incubation chamber ensured the mixing of the overlying water. Water samples from the overlying water of sediment cores were taken at least at the beginning and end of the incubation.

After core incubations, the sediment cores were sliced as described above (section 2.2) and pore water was gained and analyzed. The fluxes were calculated by relating the concentration differences in the overlying water between the beginning and end of the incubation to the core surface and the incubation time.

$$\mathbf{F} = \frac{(\mathbf{c_{tn}} - \mathbf{c_{tn-1}}) \times \mathbf{V}}{\mathbf{A} \times \Delta \mathbf{t}} \times \mathbf{24}$$

equ. 8

F = flux [µmol m^{-2} d^{-1}]

c_{tn} = concentration at time point n [µmol L^{-1})

V = volume of overlying water [L]

A = sediment surface [m^{-2}]

Δt = duration of the incubation [h]

Table 1: Overview on different incubation experiments with experimental conditions, sampling date, core diameter in cm, sampled stations and number of replicates, incubation time and abbreviations used in following figures: lt: long term, st: short term, a: anoxic, o: oxic, i: in-situ, rel: release, upt: uptake

abbr.	conditions	Sampling date	core Ø	station (n)	incubation time
1) Undisturbed core incubations					
lt-a	long-term, anoxic, dark, closed	13/10	20	0.5 m (3)	95 h
st-o i	short-term, oxic, in-situ; light, closed	14/04	10	0.5 m (4)	5 h
st-o	short-term, oxic, dark, closed	14/09	10	0.5 m (3)	5 h
st-o	short-term, oxic; dark, closed	14/11	10	0.5 m (3), 2 m (3)	5-6 h
lt-o	long-term, oxic, dark, open	15/03	10	0.5 m (4), 2 m (3)	7-9 d
2) release in tube incubations					
rel	long-term, anoxic, dark, closed	14/04	tubes	0.5 m (2), 2 m (2)	46 d
3) adsorption					
3a) tube incubation					
ads	short-term, oxic, PO_4^{3-}addition (0-50 µM), light, closed	14/07	tubes	0.5 m (3) 2 m (3)	24 h
3b) core incubation					
upt100	short-term, oxic, PO_4^{3-} addition (100 µM), dark, closed	14/11	10	0.5 m (3), 2 m (3)	6 h
upt50	long-term, oxic, PO_4^{3-} addition (2 x 50 µM), dark, open	15/03	10	0.5 m (3), 2 m (3)	51-115 h

2.4.1 Undisturbed core incubations

To investigate how much SRP could be released from sediments under anoxic conditions a preliminary experiment was conducted. Sediment cores with a diameter of 20 cm, taken in October 2013 near the 0.5 m station were sealed with tight lids and incubated for roughly 100 h. Oxygen was completely depleted in the overlying water roughly 50 hours after the start of incubation. Oxygen concentration was measured continuously with an oxygen optode (PreSens Oxy-4 mini) (Glud et al., 1996; Woelfel et al., 2009).

In April 2014, an in situ incubation was conducted on the 0.5 m station, Gra. Four cylindrical benthic chambers with a diameter of 20 cm were placed on the sediment surface, inserted into the sediment to approximately 15 cm depths and enclosing a water column of 20-25 cm height. A rotating disc inside the chamber ensured the mixing of the water column (Janssen et al., 2005). The chambers were incubated for roughly 5 h in light conditions. Water samples were taken at the beginning and end of the incubation and exact start and end times were noted.

Based on the findings from the in-situ incubation in November 2014 three sediment cores with a diameter of 10 cm each from the 0.5 m and the 2 m station were taken to the laboratory and incubated for roughly 5 h as described above (see section 2.4). To find out if SRP is taken up by plankton or adsorbed by particles in the water column the incubations were conducted with unfiltered as well as with filtered habitat water.

During long time incubations, even small fluxes should be detected. Therefore, in March 2015 three sediment cores from both stations were taken and incubated for several days in the laboratory without lid and a reduced water column (~ 5 cm) to ensure oxidized conditions on the sediment surface even during long term incubations. With the reduced water volume, the dilution of released SRP should be avoided to detect small concentration changes. Water samples were taken at different times during the incubation to monitor SRP concentrations changes with time.

2.4.2 Phosphate release

To analyze the release potential of phosphate in the sediment an anoxic tube incubation was conducted in July/August 2014 on sediments from the 0.5 and 2 m station, collected in April 2014. For each station 10 aliquots of 50 ml sediment from 1-5 cm sediment depth was enclosed free from air bubbles in 50 ml centrifugation tubes and incubated for overall 46 days. The tubes were incubated at 10 °C and buried in a container with sediment to ensure dark and anoxic conditions.

After the start of the incubation two aliquots each were sacrificed to gain pore water as described in section 2.2 and analyzed for SRP concentration on day 16, 25, 31, 40 and 46 (Figure 6).

Additionally, duplicate subsamples were taken from each aliquot for sequential extraction of phosphorus. The different physicochemical fractions of phosphorus were analyzed following an extraction scheme modified after Jensen and Thamdrup (1993) (see section 2.5).

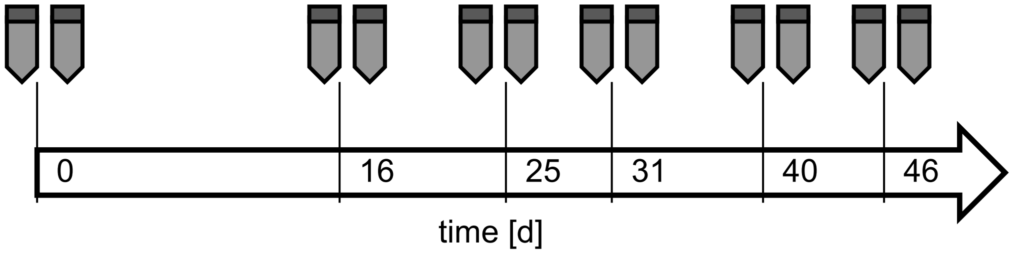

Figure 6: Timeline of the tube incubation experiment, indicating times of aliquots withdrawal.

2.4.3 Phosphate adsorption

Another tube incubation was conducted to analyze the adsorption capacity of resuspended sediment. Therefore 15 ml of water with different phosphate concentrations (0; 0.1; 0.2; 0.5; 1; 2; 5; 10; 25; 50 µmol L^{-1}) was added to roughly 2.5 g of wet sediment from the surface of 0.5 and 2 m station collected in April 2014. The sediment-water mixture was shaken for 24 hours in 50 ml centrifugation tubes (Figure 7). The experiment was conducted with triplicate samples for each concentration and sediment type combination. The SRP concentration in the water was measured at the beginning and end of the experiment, after sediment had settled again. Before the experiment, the surface sediments from each station were analyzed for water and TP content and a sequential fractioning was conducted. Because these analyzes are very time consuming the sediment of one single replicate only was used for TP analysis and sequential fractioning at the end of the experiment.

In the remaining two replicates, the phosphate enriched water was replaced by distilled water and the sediment-water mixture was shaken again for 24 hours, to investigate if the SRP adsorbed before, will be desorbed again from the sediment. The SRP concentration in the water was measured at the end of the experiment. The sediment of one replicate was used for sediment analyzes (TP, WC and sequential fractioning). The very labour intensive analysis of TP digestion and sequential fractioning were only conducted at some selected samples during the whole project period.

Therefore, the results of all the sediment analyzes during seasonal measurements as well as from different incubation experiments were used together to characterize both main sediment types on average.

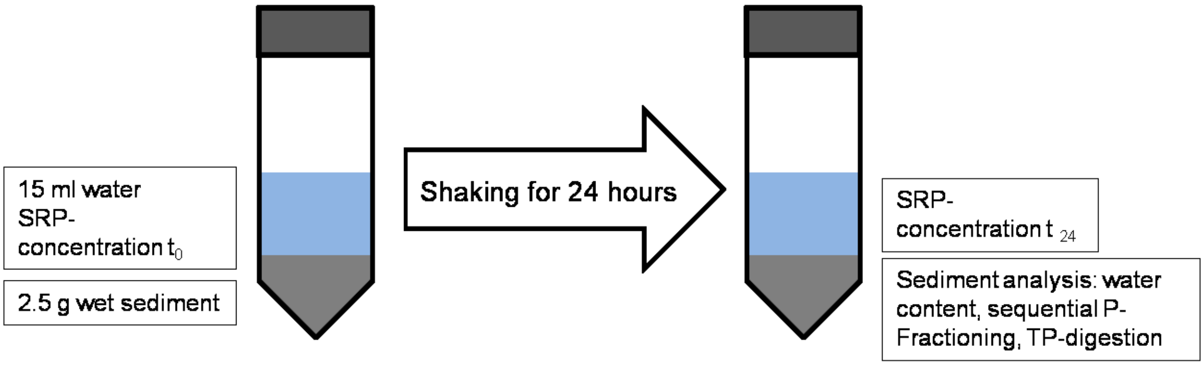

Figure 7: Schema of the tube incubation with different phosphate concentrations of 0; 0.1; 0.5; 1; 2; 5; 10; 25 and 50 µmol L^{-1})

To measure the adsorption behavior of the intact sediment surfaces, sediment cores were incubated with phosphate enriched overlying water. Three cores from the 0.5 m and 2 m station respectively, taken in November 2014, were incubated in December 2014 for roughly 6 h with a concentration of 100 µmol L^{-1} SRP in the overlying water. Another incubation experiment was conducted in April 2015 on three sediment cores from each station, taken in March 2015. The incubation was conducted without a lid and a low water column (1-5 cm) as described above (see section 2.4.1). Phosphate was added in two steps with a concentration of about 50 µmol L^{-1} each in the overlying water and incubated for overall 7 days. Water samples were taken at various times during incubation. The second phosphate pulse was added on day 2 of the incubation (Figure 8).

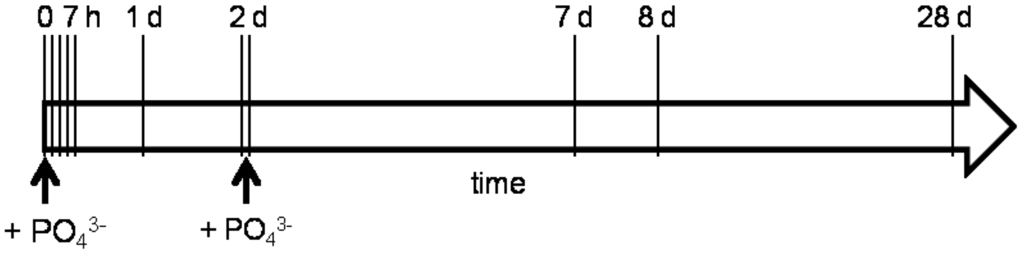

Figure 8: Timeline of the phosphate addition experiment, indicating time of water sampling and phosphate additions to about 50 µmol L^{-1} each time.

2.5 Chemical analysis

The SRP concentrations in all extracts, overlying water and pore water samples and the ammonium concentrations in overlying water and pore water samples were measured photometrically by the molybdenum blue method and the indophenols blue method (Hansen and Koroleff, 1999). The extinctions were measured at 885 nm and 630 nm respectively in a Spectronic® Genesys 5 photometer with a 1 cm cuvette. One blank and standard concentrations of 5 and 10 µmol L^{-1} NH_2PO_4 and NH_4Cl were measured with every analysis. The method allows a detection limit of 0.2 µmol L^{-1} for phosphate (n=56 blanc determinations, mean=0.07 µmol L^{-1}, SD = 0.06 µmol L^{-1}) (Figure 9) and 2.3 µmol L^{-1} for ammonium (n=21 blanc determinations, mean=0.82 µmol L^{-1}, SD=0.75), determined here as three times the standard deviation of all measured blanks (IUPAC, 1997)

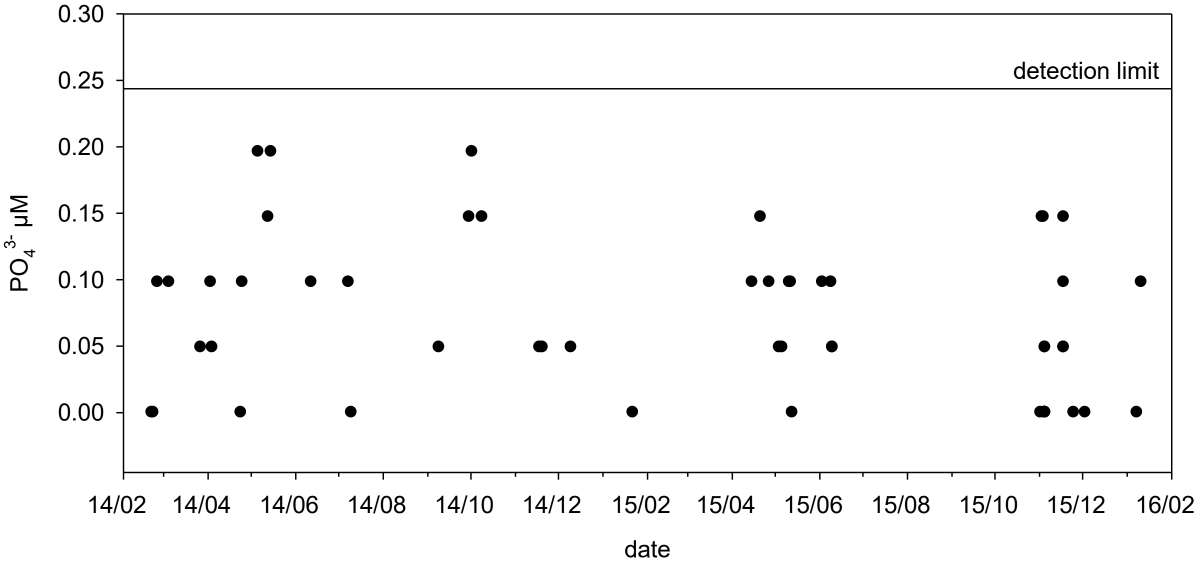

Figure 9: Blank control chart of PO_4^{3-} determination 2014-2016 with detection limit (black line).

Pore water nitrate concentrations were measured at the biological station, Zingst (University of Rostock) by reducing nitrate to nitrite over a reduction column filled with copper-coated cadmium granules. Nitrite concentration was measured as azo dye at 540 nm (Grasshoff et al., 1983) in a continuous Flow Analyzer (Alliance Instruments).

To analyse the total phosphate content 0.1 g of combusted sediment was suspended in 15 ml distilled water and digested with 1.5 ml acidic persulphate for 24h at 90°C (Berthold et al. 2015). The extracts were neutralized with 1 to 2 ml NaOH and diluted for photometrical phosphate analyses, if necessary.

Phosphorus binding fractions were analyzed by following the first two steps of the sequential extraction scheme modified after Jensen and Thamdrup (1993). In step one, the loosely bound phosphorus was extracted by adding 15 ml 0.46 M NaCl solution to 0.5 g wet sediment and centrifuged for 10 min at 3000 RPM after 1 h aeration with N_2. The supernatant was collected and 0.6 ml 1 M H_2SO_4 was added to avoid iron and manganese co-precipitation. The sample was washed with another 15 ml NaCl solution, centrifuged and the supernatant was cumulated with the former one. For analysis of metal-bound phosphorus in step two the sediment pellet was resuspended with15 ml Bicarbonat-Dithionite (BD)-reagent and aerated for 1 h with N_2. After centrifugation and collecting the supernatant as before, one BD and one NaCl wash followed and 1 ml 1M H_2SO_4 was added to the cumulated supernatant. The extracts were oxidized by shaking for 1 to 2 h, with open lids to prevent cross-reactions of the molybdenum with the remaining dithionite. Due to formation of elemental sulphur during the molybdenum blue reaction, which interferes with photometric determination, the molybdenum blue complex had to be extracted from the turbid analytical solution. Therefore, a mixture of 95% hexanol and 5 % isopropanol was added to the sample in 1:1 relation, mixed and separated from aqueous solution by centrifugation. Subsequently the extinction was measured at 690 nm (Jensen and Thamdrup, 1993). Between 0 and 5 µmol L^{-1} (extinction (E) = 0.1; Figure 10) the calibration showed the same results as with 885 nm. Because the measured concentrations in the analytical solution never exceed this concentration the same qualitative limits could be assumed as for standard SRP determinations. Finally, the remaining sediment pellet was digested with acidic persulphate like described above for TP content analysis.

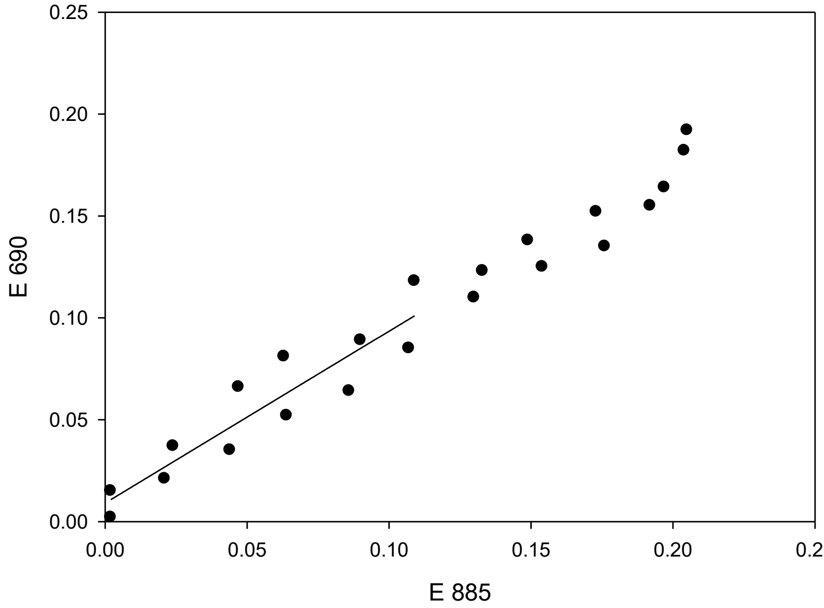

Figure 10: Extinction (E) at 690 nm wavelength against 885 nm wavelength for phosphate concentration from 0 to 10 µmol L^{-1} in a 1 cm cuvette.

An elemental analysis of sediment was conducted on sediment cores from March 2015 at the Leibniz-Institute of Baltic Sea Research. 50 mg of dried sediment of each layer was digested by incubating the samples for 1h at 50°C with 65% HNO_3 first and for another 12 hours at 185°C with a 1:1 mixture of 70% $HClO_4$ and 40% HF. In the following the samples were vaporized at 180°C and washed three times with 6 M HCl. Another 2 ml of 2 % HNO_3 were added prior to decanting the sample to a HNO_3 conditioned flask and restock to 50 mg with HNO_3. Standard solutions were added and the elemental composition of the samples was measured at the ICP-OES (inductively coupled plasma optical emission spectrometry).

The Chlorophyll concentration was determined fluorometrically and is reported as chlorophyll pigment equivalents (CPE; equ. 9). Therefore, sediment slices were stored frozen. After defrosting 1 cm³ of each homogenized slice was suspended in 9 ml acetone and treated mechanically in a cell mill for disruption of cells and better extraction of pigments. After centrifugation (10min, 4000rpm) chlorophyll concentration in the extract was measured at a TD-700 fluorometer (Turner Designs). The extract was treated with 250 µl 1N HCl and measured again to determine the amount of phaeopigments in total chlorophyll content (Holm-Hansen et al., 1965).

$$CPE = \frac{\big(Fv - (Fn \times 1.03)\big) \times \left(\frac{AF}{(AF-1)}\right) \times CF \times V_{Ext}}{V_{Sed}\ x\ L}$$

equ. 9

CPE = chlorophyll pigment equivalents [µg ml^{-1}]
Fv = fluorescence before acidification
Fn = fluorescence after acidification
AF = acidification factor = Fv/Fn of standard concentration
CF = calibration factor [µg cm^{-2}]
V_{Ext} = extraction volume [ml]
V_{Sed} = sediment volume [cm³]
L = optical path [cm]

Oxygen concentration in the overlying water was measured at start and end of the incubation by Winkler titration (Grasshoff et al., 1983) or continuously during incubation using optodes (Glud et al., 1996; Woelfel et al., 2009).Therefore a fluorophore spot was fixed on the underside of the chamber lids and connected to a four channel measuring system (PreSens Oxy-4 mini) via optical fiber (Gebhardt, 2013).

2.6 Conversions

Various units for phosphorus amounts in sediments are given in literature. Most common are weight specific contents whereas fluxes are related to the sediment surface area. To make these values comparable with each other as well as to calculate mass balances, a conversion to volume specific concentrations or area specific inventories is mandatory.

Phosphate concentrations in the analytical solutions, which are original solute samples as well as extracts of solid phase after digestion, were determined in µmol L^{-1}. For the overlying water as well as for pore water samples this equates to the SRP concentration. Multiplied with porosity of the sediment the concentration in the pore water can be related to sediment bulk volume.

The phosphate concentration in the extracts of solid phase after the different sediment digestion steps was routinely first related to sediment dry mass as weight specific phosphorus content.

The P levels detected in solid sediment phase in defined sediment layers or physicochemical fractions as well as the P concentrations in the water (overlying or pore water) should be given in the same unit. The different compartments are connected to each other and exchange processes take place between the particulate P in the sediment and the dissolved P in the water, displayed as fluxes via the sediment surface. Therefore, weight specific contents were recalculated as volume specific concentrations related to sediment volume or inventories related to sediment surface.

The weight specific content of TP, TC and TN (C_W) was converted to volume specific concentration (C_V) by using the dry bulk density (DBD) of the sediment.

$$C_V\,[mol\ m^{-3}] = C_W[\mu mol\ g^{-1}] \times DBD[g\ cm^{-3}]$$

equ. 10

By multiplication of the concentration (C_V) with the height of considered sediment column (h = 0.1m) concentrations were converted into surface specific inventories (i; units: mol m^{-2}).

$$i = C_V[mol\ m^{-3}] \times h[m]$$

equ. 11

Furthermore, to compare the phosphate adsorption and release fluxes to each other, they are presented as potentials (Pt) related to the sediment surface (A).

$$Pt_{Ad} = \frac{(c_{tn} - c_{tn-1}) \times V}{A}$$

equ. 12

$$Pt_{Re} = (c_{tn} - c_{tn-1}) \times phi \ \times h$$

equ. 13

Pt_{Ad} or Pt_{Re} = Potential [mmol m^{-2}]

c_{tn} = concentration in overlying water or pore water at time point n [mmol L^{-1}]

V = volume of overlying water [L]

A = sediment surface area [m^2]

phi = porosity

h = height of considered sediment column = 0.1 m

3 Results

3.1 Sediment characteristics

In the Grabow sediment characteristics changed markedly with increasing water depth. With increasing percentage of silt fraction (<63 µm) water content and sediment porosity (phi) increased too, while the dry bulk density (DBD) decreased (Figure 11).

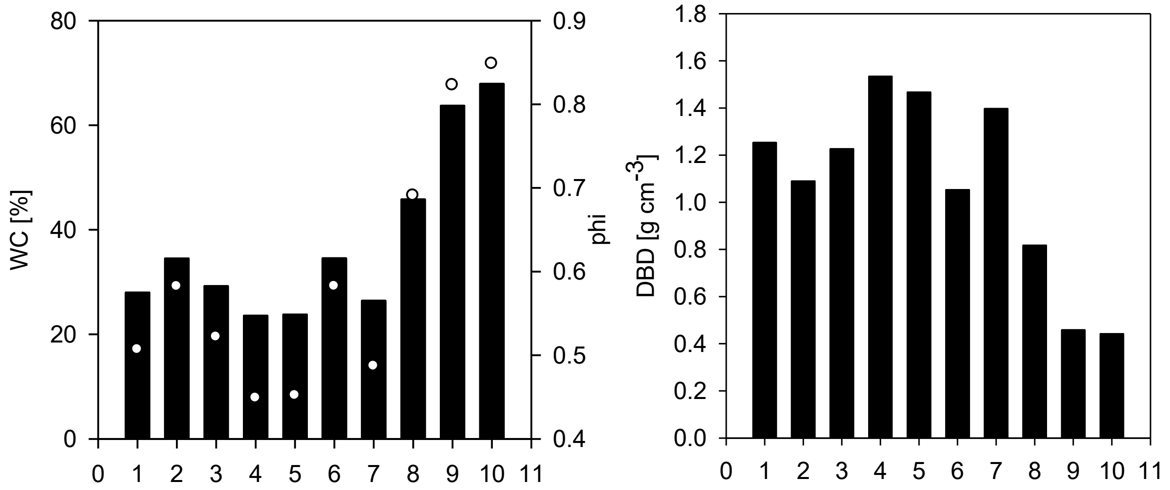

Figure 11: Water content (WC) and porosity (phi) (left) and dry bulk density (DBD) (right) along the depth transect in the Grabow (Gra) from March 2014.

The Loss on Ignition (LOI) displayed in percentage of sediment dry weight usually is used as indicator for organic matter content and increased on the deeper stations as well (Figure 12). But LOI displayed in percentage of sediment wet weight also correlated well with the total carbon concentration (Figure 13).

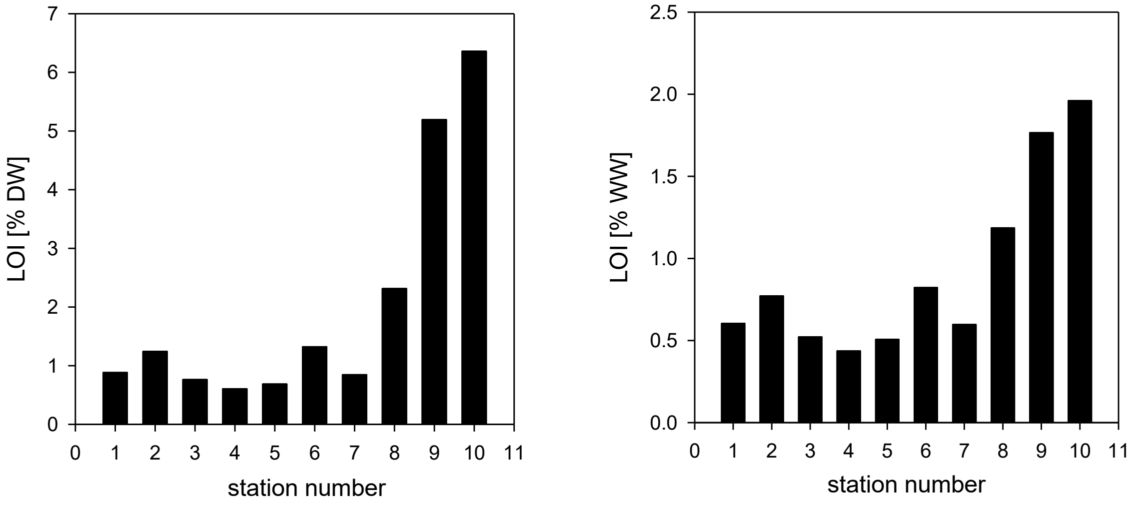

Figure 12: Loss on Ignition (LOI) displayed in percentage of sediment dry weight (left) and sediment wet weight (right) along the depth transect in the Grabow form March 2014.

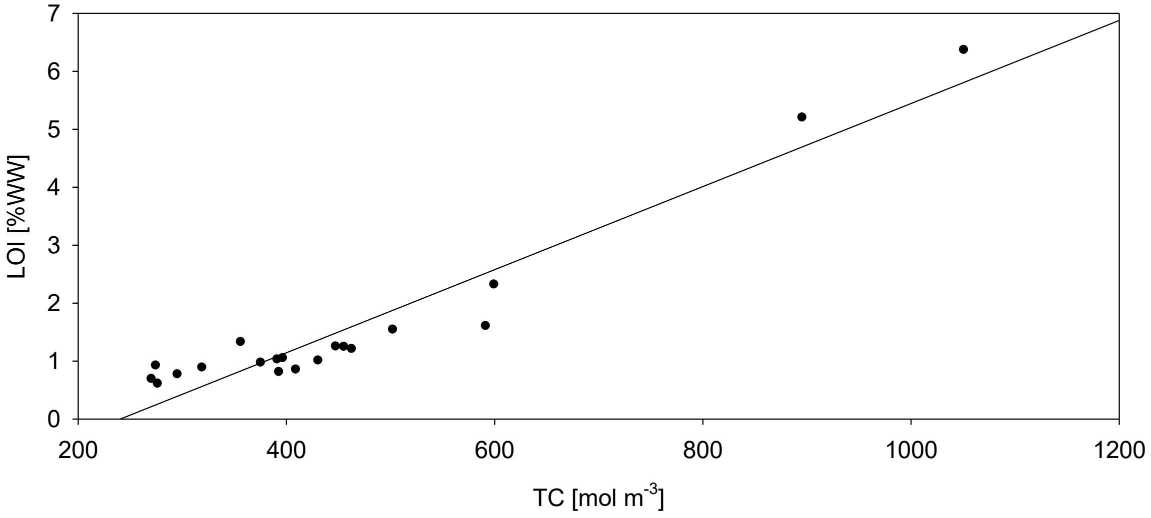

Figure 13: Correlation between total carbon concentration (TC) and Loss on Ignition (LOI) displayed in percentage of sediment wet weight (correl. coeff. = 0.958, p<0.001).

The two focus stations at Gra in 0.5 m and 2 m depth represent well the main sediment types of DZBC (Table 2), as can be seen in the sediment characteristics.

The sediment in 0.5 m water depth was characterized as fine to medium sand with low percentage of silt fraction. Nevertheless the sediment was practically impermeable with measured permeabilities of 0.2 to 6*10^{-12} m² (n=3) and two out of three measurements below the threshold for possible pore water advection of 1 - 3*10^{-12} m² (Forster and Bitschofsky, 2015). The LOI value of roughly 0.7 % DW indicated low organic matter content and it remained constant along the sediment depth profile (Figure 14). The sediment at this station was influenced by macrophytes growing in different densities, mainly *Stuckenia pectinata*, *Ruppia* spec. and *Chara baltica* (Piepho and Schubert, 2015).

Table 2: Mean values of sediment parameters of surface sediment (0-1 cm), measured 6-9 times from 2013 to 2015 ± SE. Gra- Grabow, BoB – Bodstedter Bodden

Parameter	Station	**Gra-0.5 m**		**Gra-2 m**		**BoB-0.5 m**	
		mean	±	**mean**	±	**mean**	±
Median grain size [µm]		**232**	57	**80**	0.3	**197**	14
Silt fraction (<63 µm) [%]		**3.8**	1.3	**34.1**	1.7	**3.9**	0.8
Water content [%]		**24.0**	1.8	**74.1**	4.4	**30**	1.9
Porosity		**0.44**	0.04	**0.87**	0.05	**0.54**	0.06
Dry bulk density DBD [g cm^{-3}]		**1.5**	0.1	**0.3**	0.1	**1.4**	0.1
Loss on Ignition [% dw]		**0.7**	0.1	**9.1**	1.8	**1**	0.1

In 2 m water depth, fine grained material accumulated and the sediment was characterized as silty sand with high water content and therefore a high porosity, which decreased with increasing sediment depth. The organic matter content in this type of sediment was much higher than at the shallow station and decreased from 8.9% DW at the surface down to 2.5 % DW in deeper sediment layers (Figure 14). Due to the prevailing light conditions hardly any macrophytes can be found (Blindow and Meyer, 2015).

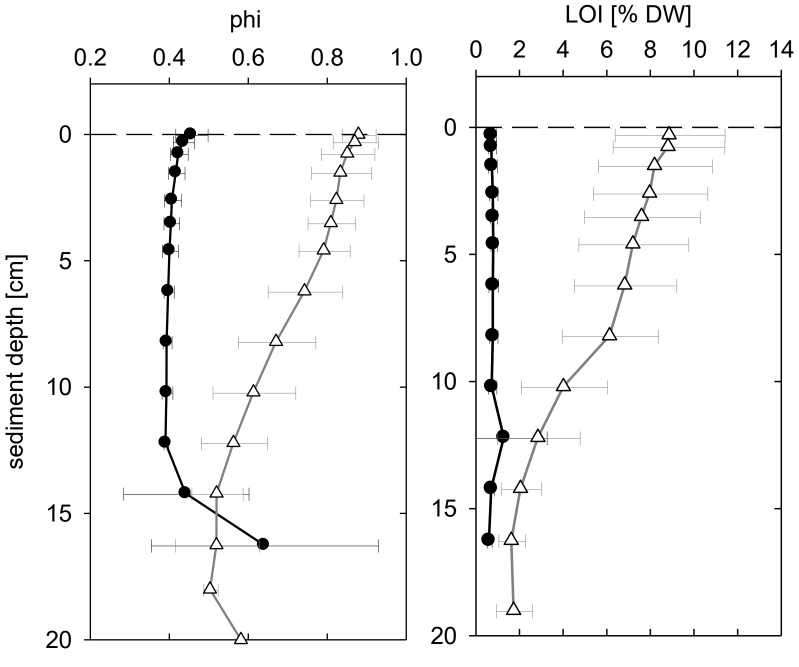

Figure 14: Sediment depth profiles of porosity (phi) and loss on ignition (LOI) in % DW from 0.5 m (filled circles, n=12) and 2 m station (open triangles, n=8), Grabow (mean, whiskers show SD).

The sediments from the Bodstedter Bodden resembled those of the shallow station sediments from the Grabow. But in contrast LOI increased at 4-6 cm sediment depth due to a layer of peat and refractory reed material (Figure 15).

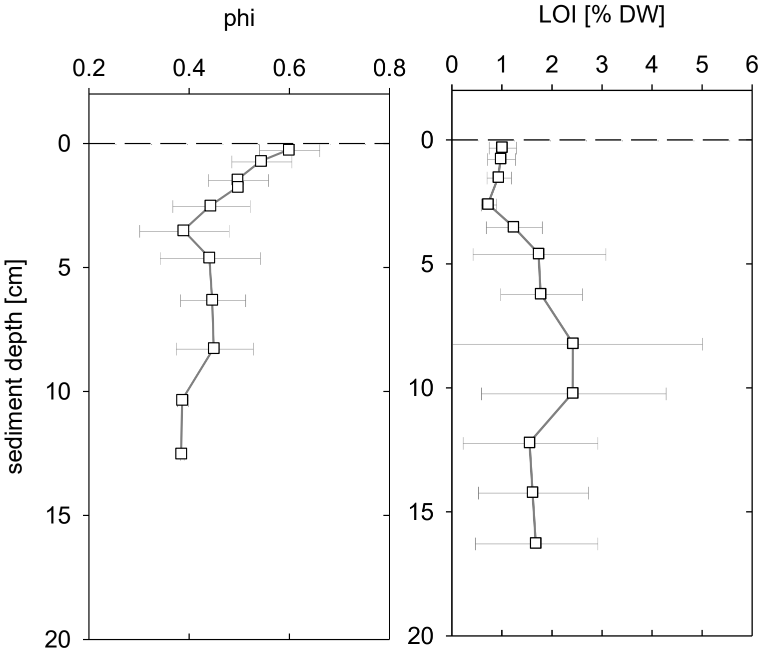

Figure 15: Sediment depth profile of porosity (phi) and loss on ignition (LOI) in % DW from the Bodstedter Bodden (n=8, mean, whiskers show SD).

The sediments from the DZBK (Gra 0.5 and BoB) were comparable to the sediments of other shallow water environments along the German Baltic Coast (Figure 5) investigated in the present study. Except for the Salzhaff (SH), all sediments could be classified as fine sand with average median grain size of 187 ± 47 µm (Figure 16), 5.6 ± 2.8 % silt fraction, water content of 26 ± 10 % and LOI of 1 ± 0.3 % DW. At station SH finer sediment occurred with a median grain size of 93 µm and 11.35 % silt fraction. Sediments showed no differences in their characteristics, whether they were inhabited by macrophytes or not.

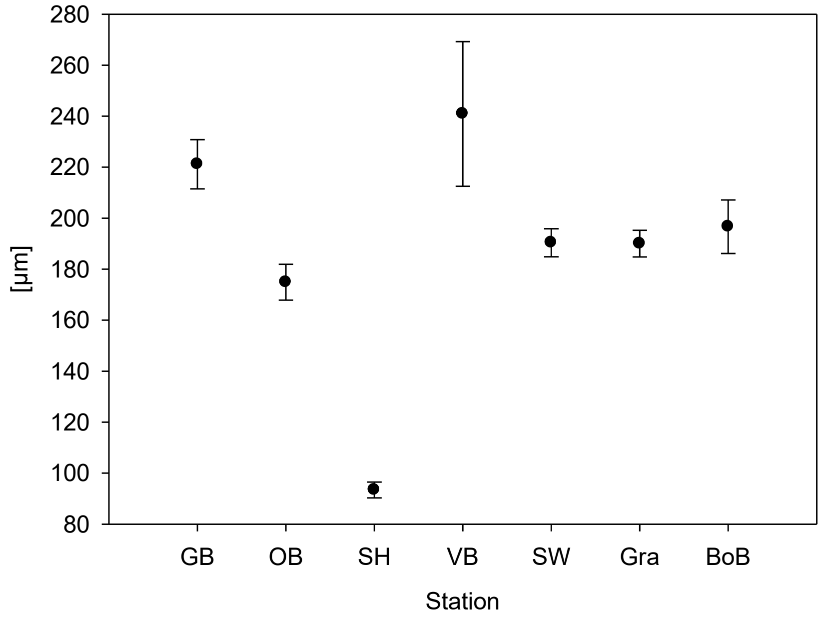

Figure 16: Median grain size of sediments from estuaries along the German Baltic Coast (GB-Gelting Bay, OB-Orther Bay, SH-Salzhaff, VB-Vitter Bodden, SW-Spandowhagener Wiek, Gra-Grabow, BoB-Bodstedter Bodden).

3.2 Amounts of selected elements in the sediment

Beside the physical parameters of sediments, also the chemical composition is characteristic for the different sediment types.

Depending on whether they are displayed as weight specific content or volume specific concentration the relations between total carbon, nitrogen and phosphorus amounts contained in the different sediment types vary markedly.

In the Grabow the TC, TN and TP contents increased with increasing water depth along transect sampling stations (Figure 17), indicating a correlation between TP and organic matter content (Figure 18). Also in sediment depth profiles, the differences in TP content between both focus stations were evident (Figure 19). At the Bodstedter Bodden sampling site the water depth did not increase along the 10 subsampling stations, therefore TC, TN and TP contents are similar at all stations (Figure 17, grey bars). But at the first transect stations close to the reed belt a slightly higher TP content was observed in the Grabow as well as in the Bodstedter Bodden indicating an influence of the reed belt on adjacent sediment (Figure 17). Due to the high variations between parallel samples of these stations, these differences are not significant.

The element contents related to the sediment dry weight does not consider that the water content as well as the porosity also increase with increasing water depth. To value and compare the element masses present in different sediment types it is necessary to relate them to sediment volume. Therefore, the DBD is used to calculate volume related element concentrations (Table 3).

Table 3: Mean amounts of total phosphorus (TP), carbon (TC) and nitrogen (TN) of surface sediments (0-1 cm) as weight specific contents, volume specific concentrations and surface related inventories of the uppermost 10 cm of sediment. Measured in March and May 2014 ± SE., Gra-Grabow, BoB-Bodstedter Bodden.

station	**Gra-0.5 m**		**Gra-2 m**		**BoB-0.5 m**	
	mean	±	**mean**	±	**mean**	±
TP content [µg g^{-1} DW]	**99.2**	23.8	**337.0**	98.9	**39.2**	14.8
TP content [µmol g^{-1} DW]	**3.2**	0.8	**10.9**	3.2	**1.3**	0.5
TP concentration [mol m^{-3}]	**4.8**	1.1	**3.6**	1.1	**1.8**	0.7
TP inventory [mol m^{-2}] (upper 10 cm)	**0.5**	0.1	**0.4**	0.1	**0.2**	0.1
TC content [mg g^{-1} DW]	**3.1**	1.1	**36.4**	7.8	**4**	1.9
TC content [mmol g^{-1} DW]	**0.3**	0.1	**3.0**	0.7	**0.3**	0.2
TC concentration [mol m^{-3}]	**384**	135	**1013**	218	**474**	230
TC inventory [mol m^{-2}] (upper 10 cm)	**38.4**	13.5	**101.3**	21.8	**47.4**	23
TN content [mg g^{-1} DW]	**0.4**	0.2	**4.6**	1.5	**0.4**	0.1
TN content [µmol g^{-1} DW]	**26.0**	12.0	**325.5**	104.5	**27.9**	6.9
TN concentration [mol m^{-3}]	**38.6**	17.9	**108.7**	34.9	**39.5**	9.7
TN inventory [mol m^{-2}] (upper 10 cm)	**3.9**	1.8	**10.9**	3.5	**4**	1

With these recalculated concentrations the relation between the different stations changes, because of decreasing DBD with increasing water depth (Figure 11).

At Gra the TC and TN concentration still showed an increase with water depth, consistent with increasing LOI. In contrast, the TP concentrations did not show any dependency on water or sediment depth (Figure 17, 19). Therefore, no correlation occurred between TP concentrations and LOI for the Grabow samples (Figure 18). To calculate inventories related to the sediment surface area the uppermost 10 cm of sediment are considered (equ. 11). On average of all TP measurements during 2013 and 2015, the 0.5 m and 2 m station at Gra have a similarly TP inventory of 0.5 and 0.4 mol m^{-2} respectively. The TP inventory at BoB is 0.2 mol m^{-2}, and somewhat lower than at Gra (Table 3).

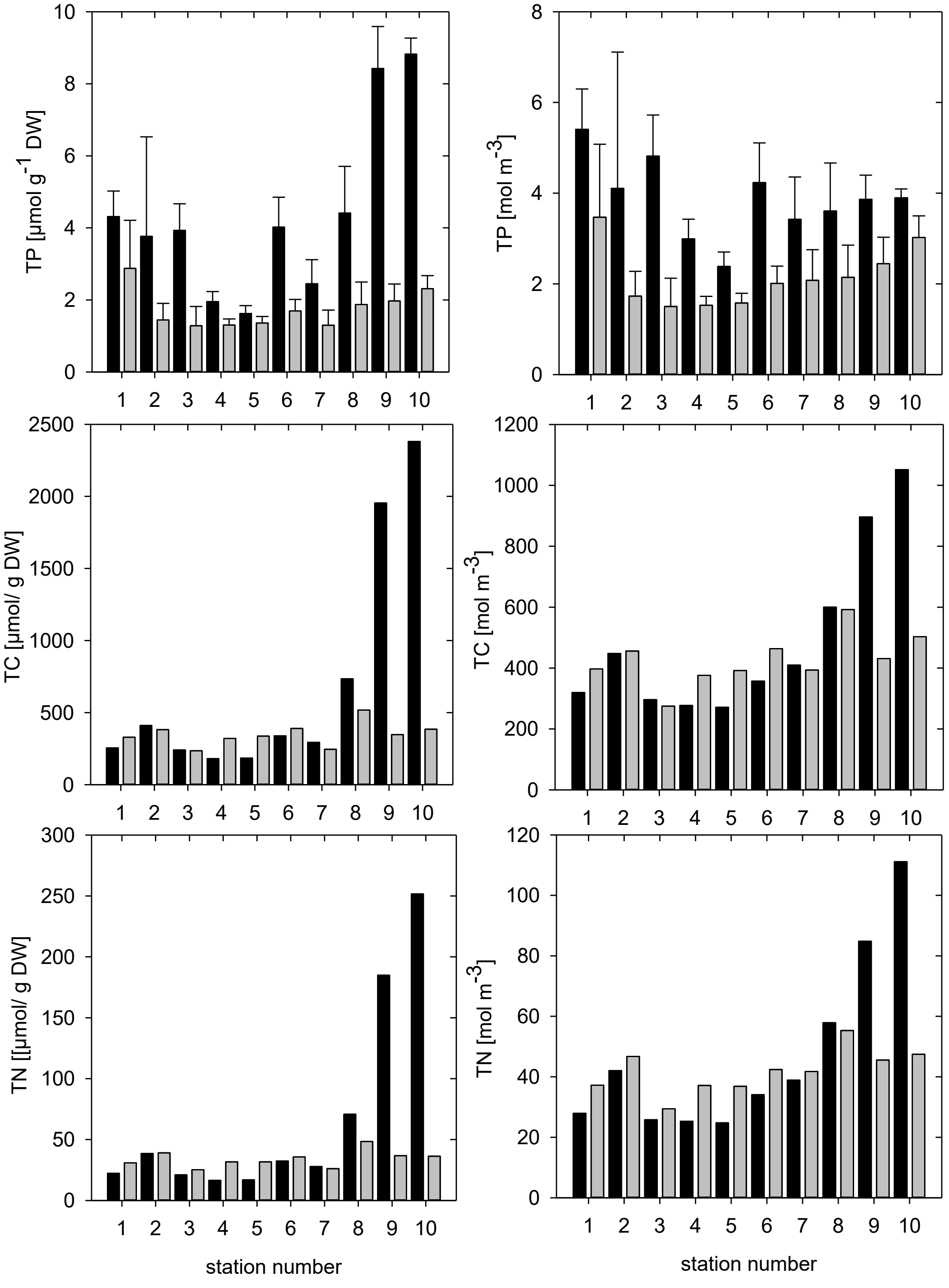

Figure 17: Total phosphorus (TP), total carbon (TC) and total nitrogen (TN) content, related to the sediment dry weight (left) and concentrations, related to sediment bulk volume (right) in the surface sediment (0-1cm) of transect stations in the Grabow (black) and Bodstedter Bodden (grey) from March 2014 (TP: n=3, whiskers show SD; TC, TN single measurement).

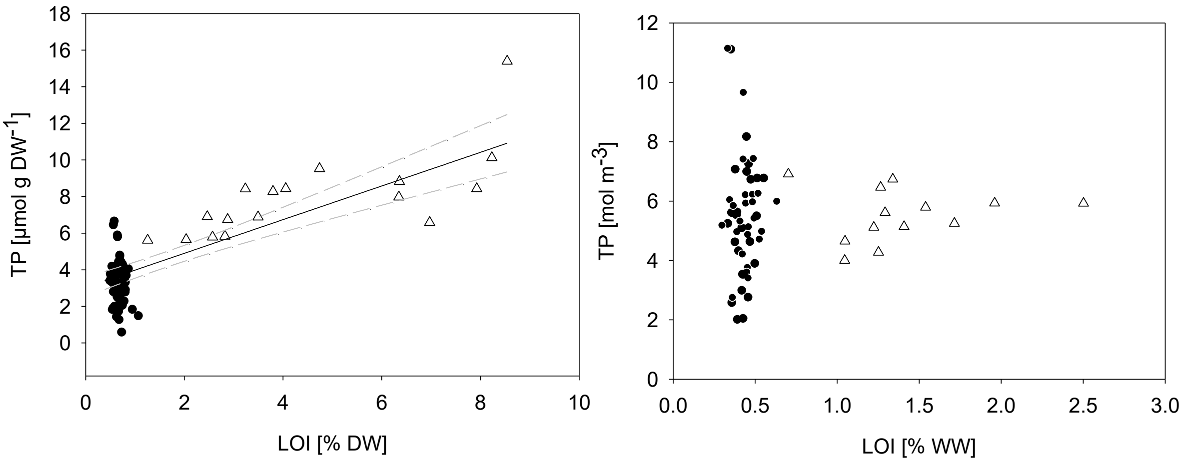

Figure 18: Total phosphorus (TP) content (left) and TP concentration (right) in relation to LOI displayed in percentage of sediment dry weight (DW) or sediment wet weight (WW) in sediments of 0.5 m (filled circles) and 2 m (open triangle) station, Grabow.

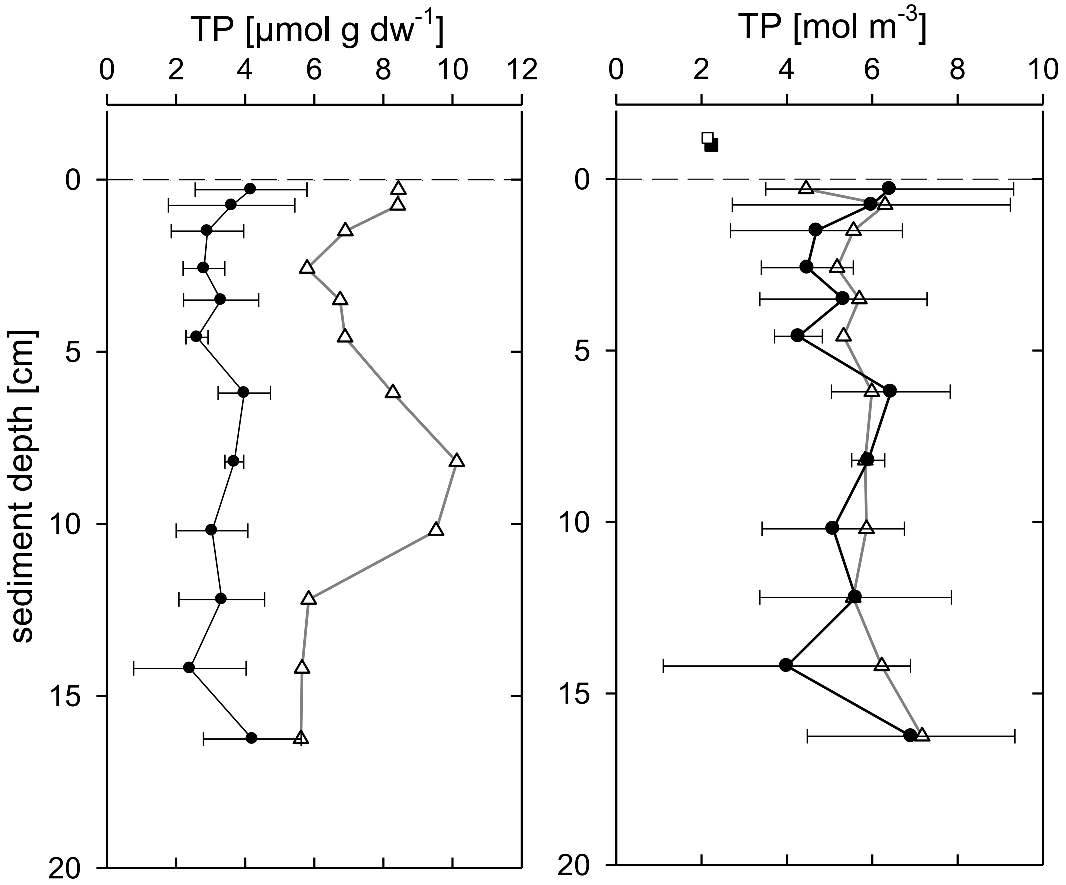

Figure 19: Sediment depth profile of total phosphorus (TP) displayed in two different ways. TP content related to sediment dry weight (left) and TP concentration related to sediment bulk volume (right) from 0.5 (filled circles, n=4, whiskers show SD) and 2 m (open triangles, single measurement) station, Grabow. Symbols above depth 0 indicate water column concentrations in mol m^{-3} (data: Schumann, unpublished).

In comparison with sediments of other estuaries along the German Baltic Coast the DZBC sediments show similar TP concentrations at the sediment surface, even if the TC concentrations show significant differences (Figure 20). The sediment at Gelting Bay (GB), Spandowhagener Wiek (SW) and Grabow (Gra) showed significant higher TC concentrations without corresponding increase in TP concentration.

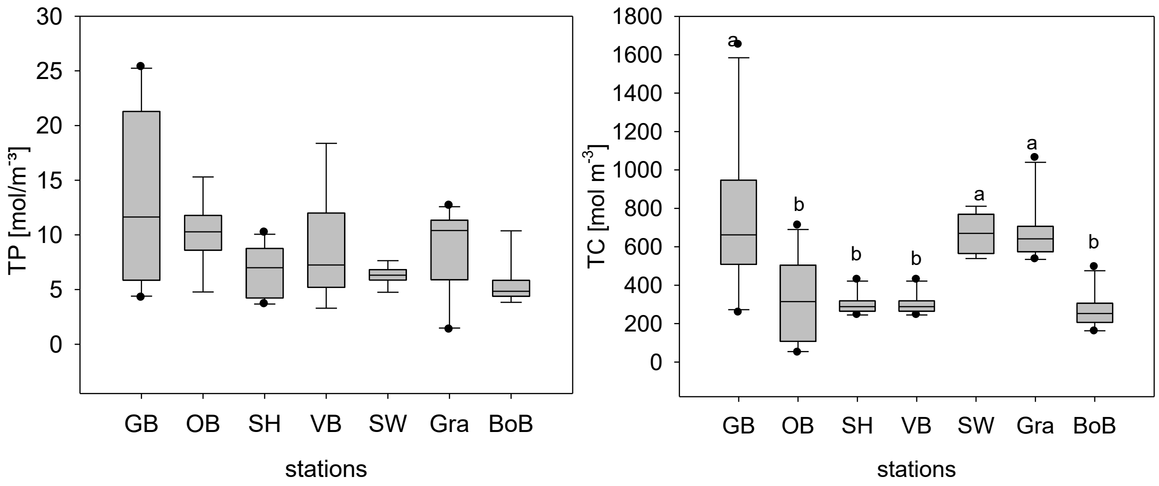

Figure 20: Total Phosphorus (TP) and Total Carbon (TC) concentration in surface sediments (0-2 cm) of 7 stations along the German Baltic Coast (GB-Gelting Bay, OB-Orther Bay, SH-Salzhaff, VB-Vitter Bodden, SW-Spandowhagener Wiek, Gra-Grabow, BoB-Bodstedter Bodden) along the southern Baltic Coast. Indices a and b indicate significant differences (n=5; $p<0.05$).

Additionally, to the manual TP measurement after persulfate digestion, TP values in sediments from March 2015 were also measured by elemental analysis with ICP-OES and HCL digestion. Within the limits of accuracy, the results correspond well to each other (Figure 21). At the 0.5 m station the results of manual digestion and ICP-OES show greater differences. Due to high variability between replicate measurements of persulfate digestion observed at this station, these differences are within the limits of standard deviation of the mean TP profile (24-69%, Figure 19). A TP peak of 9.7 µmol m^{-3} was found in 10 cm depth in the results of ICP-OES which outrange the standard deviations.

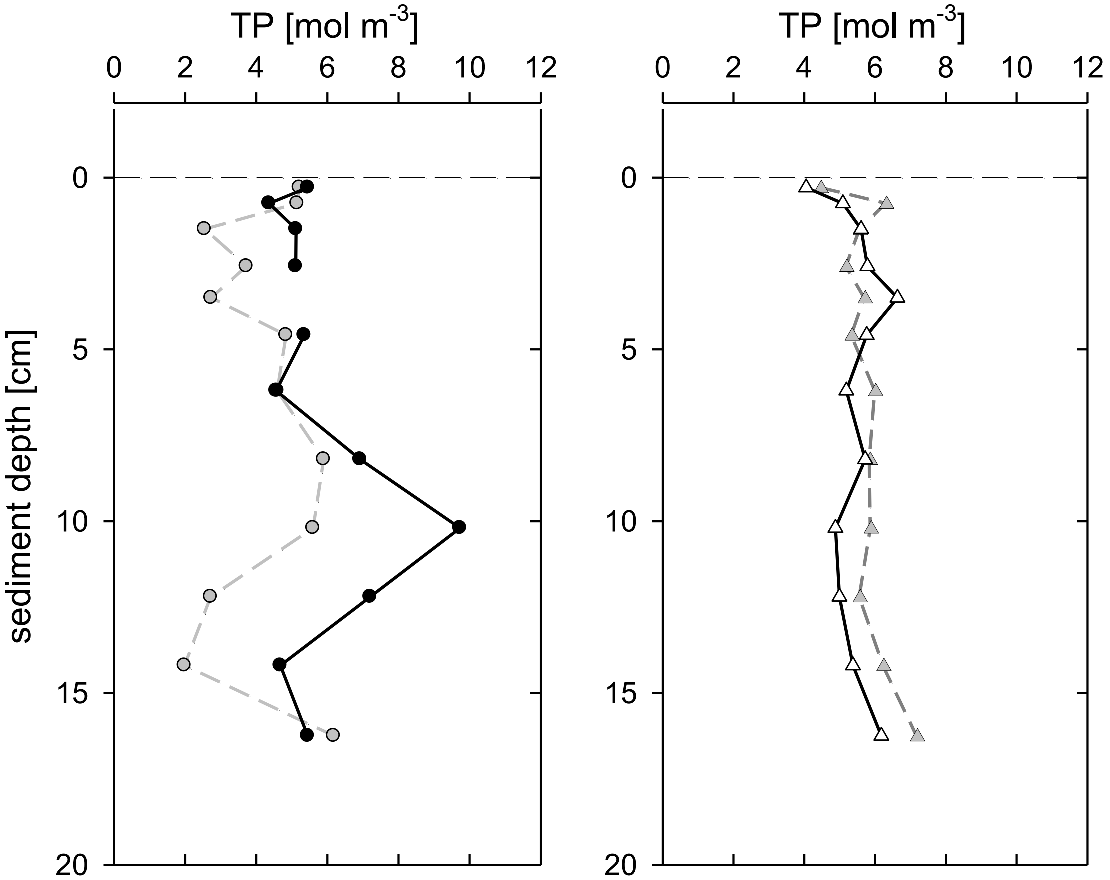

Figure 21: Sediment depth profile of total phosphorus (TP) concentration from 0.5 m station (left) and 2 m station (right), Grabow from March 2015. Measured manually (dashed lines) with persulfate digestion or via ICP-OES after HCL digestion (black lines).

Additionally, to the TP content the ICP-OES analyses provides further information on elemental composition of the sediment. Iron, manganese and aluminium are meaningful elements for phosphorus dynamics in the sediment, because phosphorus potentially adsorbs onto the oxidized forms of these metals. At the 2 m station the total iron and manganese concentration was higher than at the 0.5 m station. It slightly increased in the first 2-3 cm, stayed constant until roughly 10 cm and increased sharply from 10 to 12 cm sediment depth. At the 0.5 m station a distinct subsurface concentration peak of Fe and Mn occurred in 2-3 cm sediment depth. In contrast, the total aluminium concentration is lower at the 2 m station compared to the 0.5 m station but shows the same pattern as described before. At the 0.5 m station the subsurface peak of Al is located in the first centimetre and less pronounced than in the Fe and Mn depth profile (Figure 22).

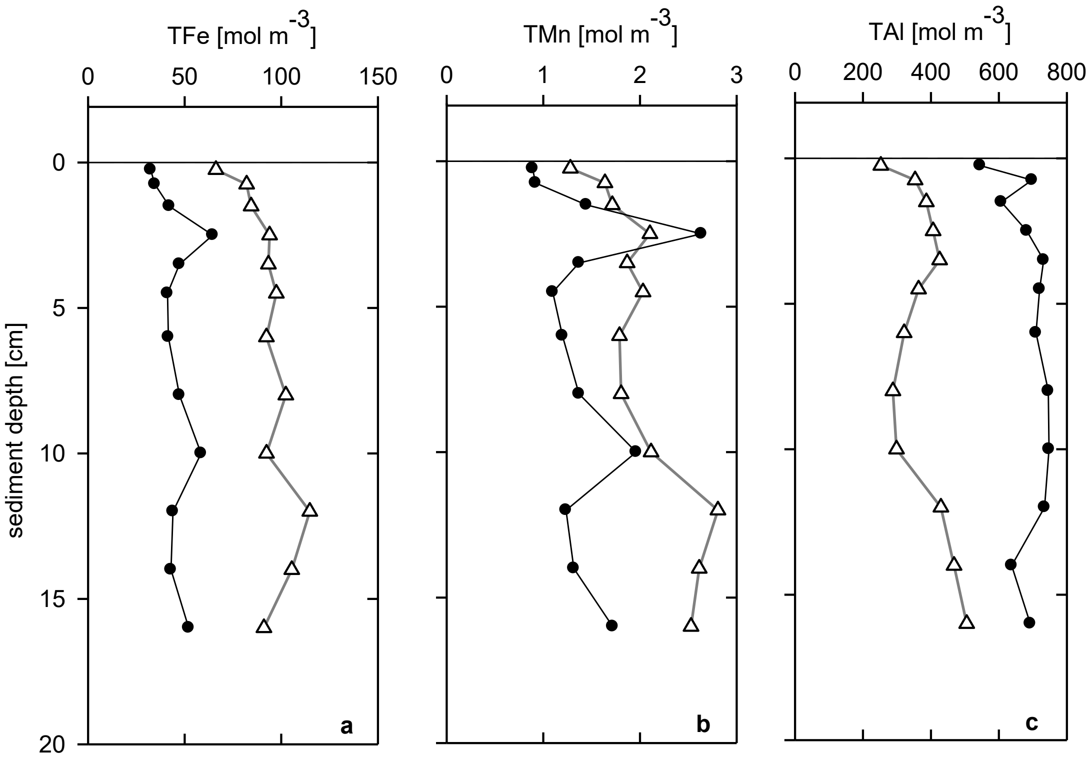

Figure 22: Sediment depth profile of total amount of Fe (a), Mn (b) and Al (c) displayed as concentration related to sediment bulk volume from 0.5 station (filled circles) and 2 m station (open triangles), Grabow from March 2015.

3.3 Chlorophyll and Macrozoobenthos

The Chl a concentration in the sediment and its changes with sediment depth can be used as an indicator for bioturbation activity (Sun et al., 1991) and microphytobenthic production. On both stations, the Chl a concentration in the overlying water is similar with 0.04 µg cm^{-3} on the 0.5 m station and 0.03 µg cm^{-3} on the 2 m station in March 2014 (Schuman, unpublished). Assuming a complete settling of the Chl a from the respective water column this would lead to a concentration of 2.15 µg cm^{-3} at the 0.5 m station and 6.4 µg cm^{-3} at the 2 m station in the sediment surface. At the 2 m station the measured Chl a concentration of 7.1 µg cm^{-3} (same season in 2015) in the sediment surface corresponds very well to this theoretical value. In the sediment surface of the 0.5 m station the Chl a concentration of 19.4 µg cm^{-3} is roughly nine-fold higher than expected from Chl a concentration in the water column, indicating benthic primary production.

The Chl a depth distribution in the sediment at both stations (Figure 23) indicated an enhanced particle mixing. Without any particle mixing the Chl a concentration would decrease to zero in the sediment within the first centimeter, due to its degradation. Therefore the slope in Chl a depth profile is an indicator for the bioturbation intensity. In comparision of both stations it can be assumed that the bioturbation impact on the 0.5 m station is higher than on the 2 m station (Figure 23).

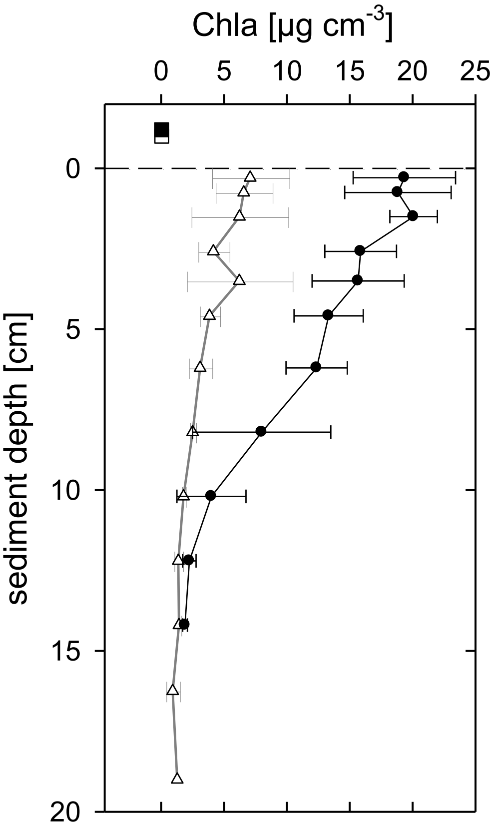

Figure 23: Chlorophyll depth profile from 0.5 m (filled circles) and 2 m station (open triangles), Dabitz from March 2015 (n=5, whiskers show SD). Symbols above depth 0 indicate water column concentrations (data: Schuman, unpublished).

The macrozoobenthic community at the 0.5 m station comprise 16 taxa with a total abundance of 7675 Ind. m^{-2} (Figure 24, left). Five of these taxa (6970 Ind. m^{-2}), mainly *Hediste diversicolor* and olygocheata, were assumed to have an important influence on exchange processes (Bitschofsky et al., 2015). At the 2 m station 14 species with 3369 Ind. m^{-2} were identified of which only 1711 Ind. m^{-2} were indicated as important bioturbators, mainly *Marenzelleria neglecta* and as well *H. diversicolor* and oligochaeta. At both stations *Hydrobia spp.* occured in high abundances, which could influence the uppermost millimeters of the sediment by grabbing and grazing activities. The mean biomass (AFDW) of 9.2 g m^{-2} at the 0.5 m station is dominated by *H. diversicolor*. At the 2 m station the polychaets *H. diversicolor* and *M. neglecta* contribute mainly to the mean biomass of 5.4 g m^{-2} (Figure 24, right).

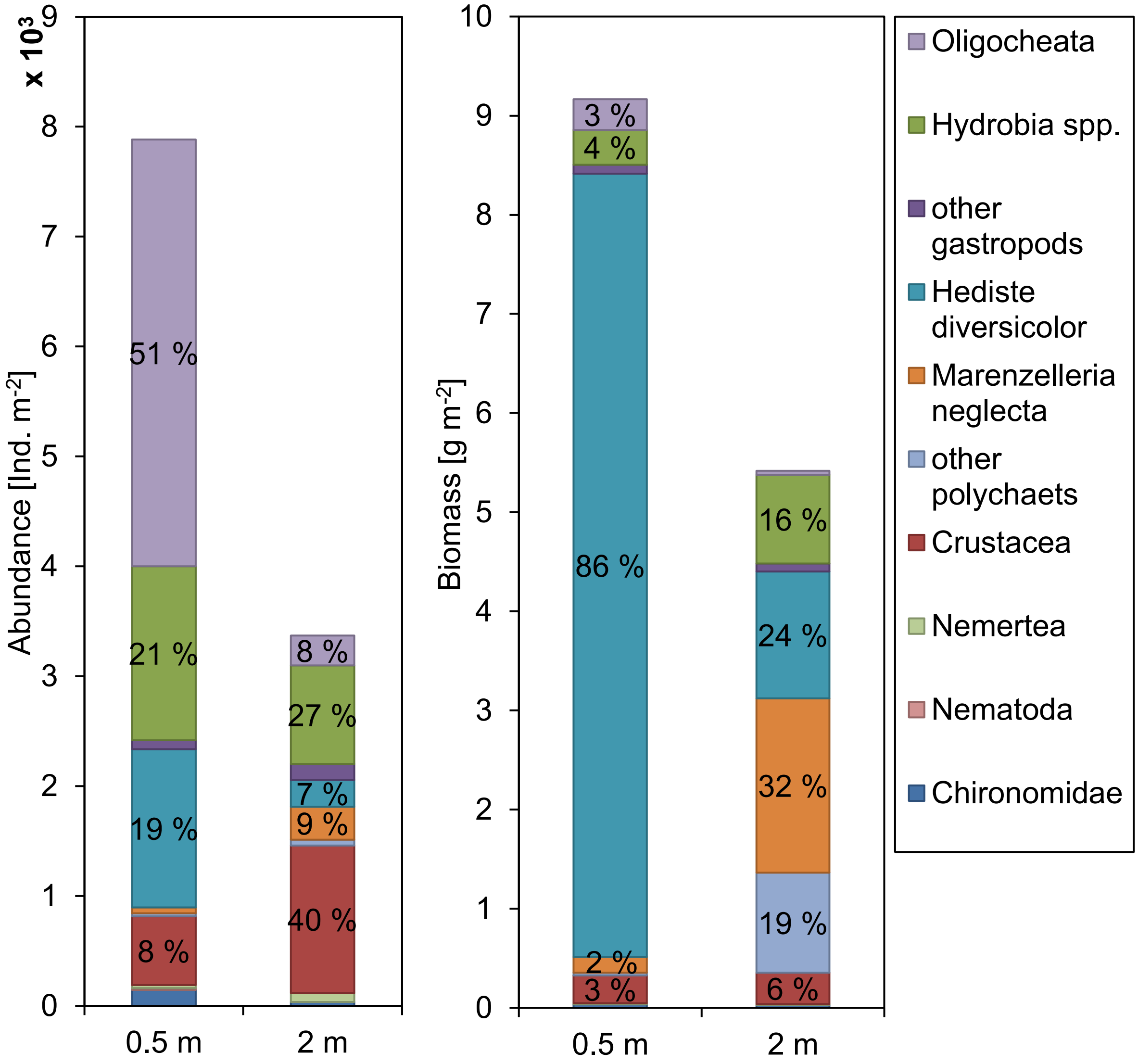

Figure 24: Mean abundances (left) and biomass displayed as ash-free dry weight (AFDW) (right) of macrofauna species at 0.5 m and 2 m station, Grabow, during 2014 (n=5). Numbers indicate percentages of total abundance or biomass of main contributors

3.4 Nutrient pore water distribution

With roughly 2 µmol L^{-1} the phosphate pore water concentration at the 0.5 m station was constantly low over depth and time, while the ammonium concentration increased slightly with sediment depth from 12.7 µmol L^{-1} to a maximum of 63 µmol L^{-1} (Figure 25 a, b).

At the 2 m station the mean phosphate concentrations at the sediment surface (0.5 cm) was 3.3 µmol L^{-1} and similar to that of the 0.5 station but increased up to 46.2 µmol L^{-1} in deeper anoxic sediment layers. The ammonium concentration increased from 96.4 to 446.1 µmol L^{-1} (Figure 25 a, b).

The concentration gradients of the uppermost 2 cm at the 2 m station indicated a mean diffusive efflux of 14.8 ± 13 µmol m^{-2} d^{-1} of phosphate and 857.5 ± 558 µmol m^{-2} d^{-1} of ammonium averaged over all pore water profiles during the sampling period. The pore water concentrations, especially at the 2 m station, underlie high variability, which cannot clearly be identified as spatial or temporal under the given sampling circumstances. The nitrate concentration at the 2 m station decreased rapidly from 92.5 µM to 6.2 µM. At the 0.5 m station a higher nitrate concentration of roughly 125 µM reached a sediment depth of 3 cm before it decreased in a less sharp gradient down to 23.4 µM, indicating nitrification at least until this sediment depth (Figure 25 c).

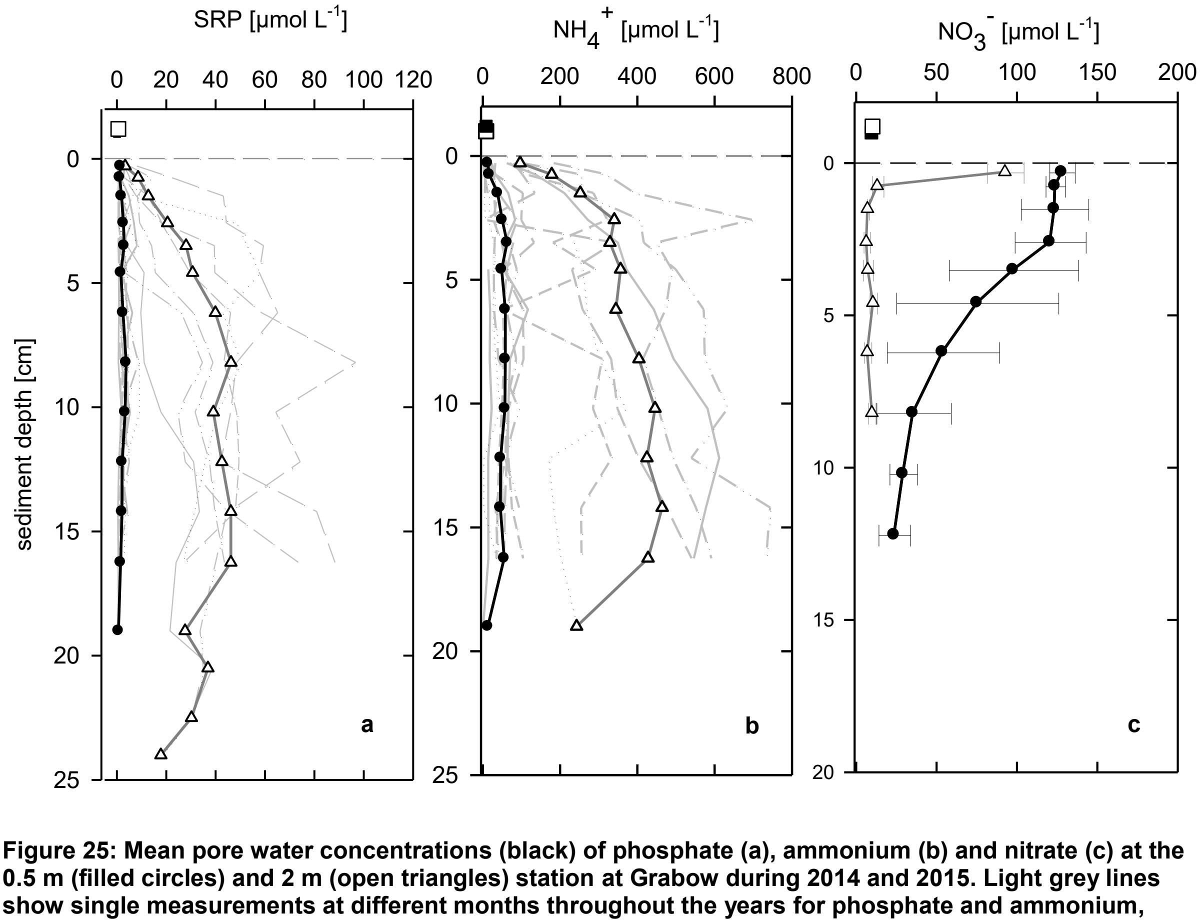

Figure 25: Mean pore water concentrations (black) of phosphate (a), ammonium (b) and nitrate (c) at the 0.5 m (filled circles) and 2 m (open triangles) station at Grabow during 2014 and 2015. Light grey lines show single measurements at different months throughout the years for phosphate and ammonium, whiskers show SD for triplicate measurement of nitrate in March 2015. Symbols above depth 0 indicate water column concentrations (data: Schumann).

The pore water phosphate concentrations in the sediment surface at the Bodstedter Bodden are like that at the 0.5 station in the Grabow, but increase to a maximum of 7.8 µM in 10 cm sediment depth (Figure 26 a). However, with a mean of 89 ± 27 µM and a maximum peak of 251 µM in 5-6 cm the ammonium concentration is much higher compared to the 0.5 m station at Gra (Figure 26 b). The sharp increases in ammonium and phosphate concentration below 5 cm correspond well with a layer of peat and refractory plant material with high organic matter content (Figure 15).

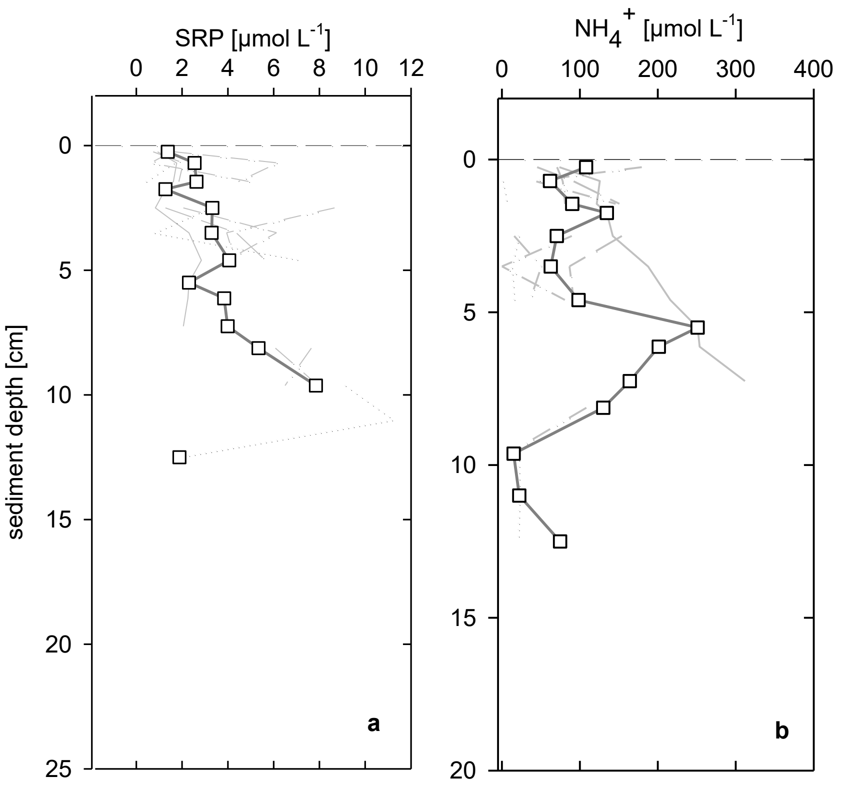

Figure 26: Mean pore water concentration of phosphate and ammonium at 0.5 m station, Bodstedter Bodden during 2014, light grey lines show single measurements at different months throughout the years.

3.5 Incubation fluxes

3.5.1 Undisturbed core incubation

The oxygen depletion in different incubation experiments on undisturbed sediment cores from the 0.5 m and 2 m station was almost consistent with a mean of 32.3 ± 18.3 mmol m^{-2} d^{-1} (Figure 27). Assuming a respiratory quotient of 0.85 and a C/P ratio in organic matter of 125:1 (Balzer, 1984) a phosphate remineralization and therefore a potential efflux of 0.2 ± 0.1 mmol PO_4^{3-} m^{-2} d^{-1} could be expected.

Only in the incubation with finally anoxic conditions in the incubation chamber a phosphate efflux of 0.24 ± 0.11 mmol m^{-2} d^{-1} was detected, which corresponds to the expectation (Figure 27). Under oxic conditions the differences between the end and start concentration of phosphate in the overlying water, measured in the laboratory as well as in situ (data not shown) incubations, did not differ significantly from zero, and therefore no valid fluxes could be calculated (Figure 27).

The ammonium fluxes showed a high core to core variability from -5.5 to 5.5 mmol m^{-2} d^{-1}, which makes it impossible to differentiate the ammonium fluxes in the different incubation approaches (Figure 27).

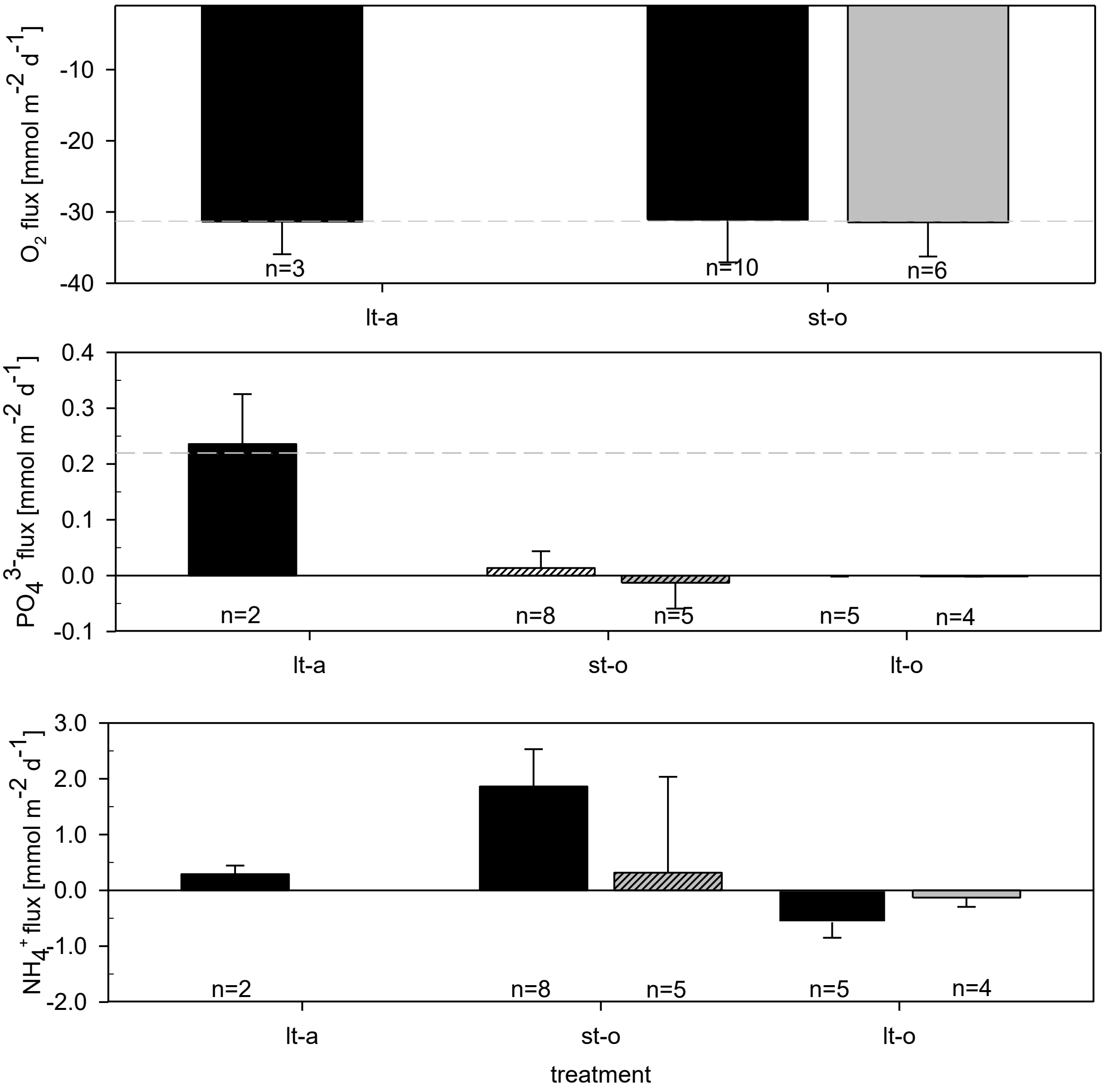

Figure 27: Oxygen, phosphate and ammonium fluxes in different laboratory incubation experiments on sediment cores from 0.5 m station (black) and 2 m station (grey); lt-a – long-term, anoxic; st-o – short-term, oxic; lt-o – long-term, oxic). Dashed line display mean oxygen flux and the resulting expected phosphate flux (see text). (different n result from loss of single cores, whiskers show SE)

3.5.2 Phosphate release

In consequence of the findings in the undisturbed core incubation, a tube-incubation under anoxic conditions was conducted. The phosphate concentration in the pore water of sediments from both stations increased during the first 30 days of incubation reaching 50-60 µmol L^{-1} and stagnated during the subsequent measurements.

The ammonium concentration increased over the whole incubation time, and reached a maximum of 2667 µmol L^{-1} on the 0.5 m station and 915 µmol L^{-1} on the 2 m station. The phosphate and ammonium pore water concentrations were converted to inventories for the uppermost 10 cm, considering the porosity of the different sediment types (equ. 12). A linear regression was calculated for the change of inventory over time and the regression slope corresponding to the mean release rates (Figure 28, Table 4).

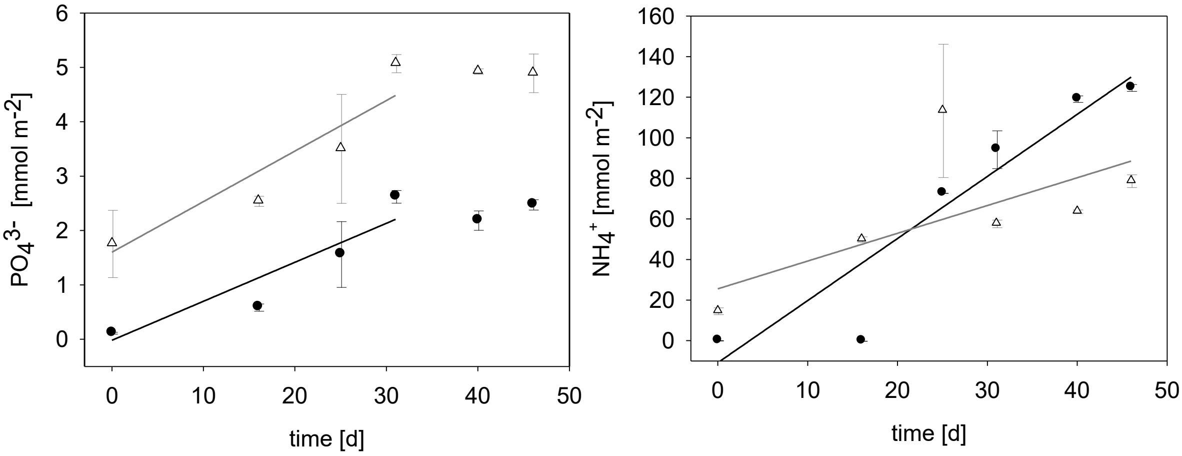

Figure 28: Development of pore water phosphate and ammonium inventories during 46 days of tube-incubation, considering the uppermost 10 cm of sediment at 0.5 m and 2 m station, Grabow (n=2, whiskers show SE)

Table 4: Mean release rates of phosphate and ammonium in mmol m^{-2} d^{-1} from sediment at 0.5 m and 2 m station, Grabow (± SE).

station	Gra-0.5 m		Gra-2 m	
	mean	±	**mean**	±
Phosphate	**0.07**	0.01	**0.09**	0.02
Ammonium	**3.06**	0.3	**1.37**	0.4

These release rates refer to a P exchange between sediment particles and pore water and not necessary to an exchange between sediments surface and overlying water column. Therefore, the term potential is introduced to compare different incubations (tube or core incubations) which differ in incubations time and initial concentrations differences. The release potentials (Pt_{Re}) were estimated from absolute differences in inventories between the end and start of incubation (Table 5).

Table 5: Phosphate and ammonium release potential (Pt_{Re}), in mmol m^{-2}, considering the uppermost 10 cm of sediment at 0.5 m and 2 m station, Grabow (± SE).

station	**Gra-0.5 m**		**Gra-2 m**	
	mean	±	**mean**	±
Phosphate	**2.4**	0.2	**3.1**	0.9
Ammonium	**124.7**	1.9	**64.1**	6.6

The sequential fractioning of different phosphate-binding forms at the beginning of the experiment showed that 1-2 % of total phosphorus inventory is loosely bound on particle surfaces and extractable with a NaCl solution. Another 2-4% of TP is BD-extractable and therefore potentially desorbable, when sediment redox potential shifts from oxic to anoxic. The release potential of 2.4 - 3.1 mmol m^{-2} found in this experiment finally represents less than 1% of TP. This indicates that the extractable P pool which in total amount to 3-6 % of TP is not exploited, even under persistent anoxic conditions. The results of sequential fractioning at the beginning of the experiment are typical for both sediment types. On average of all sequential fractioning analysis conducted during investigation period (2013-2015) in different experiments and on selected natural sediment samples, only 1-3% of total phosphorus belongs to the NaCl-fraction in both sediment types. While 6% on the 0.5 m station and 2.3 % on the 2 m station of the total phosphorus pool is bound in the redox-sensitive DB-fraction containing the metal bound phosphorus (Figure 29). Overall the higher amount of metal bound phosphorus indicates a better oxygenation at the 0.5 m station and therefore a higher adsorption potential.

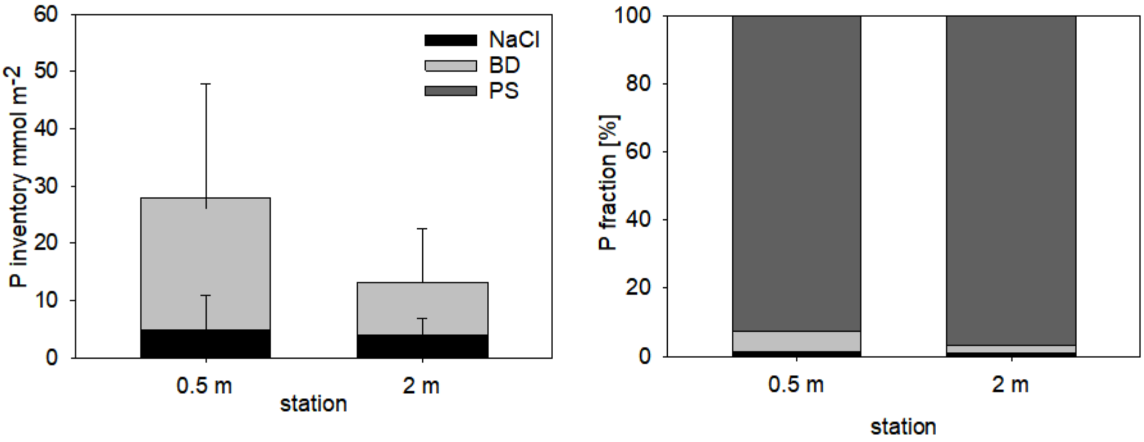

Figure 29: Inventories considering the uppermost 10 cm of sediment (left) and percentage (right) of different P fractions in sediments from 0.5 m (n=12) and 2 m station (n=8), Grabow (mean, whiskers show SD). NaCl – loosely bound phosphorus extractable by natrium chloride, BD – metal bound phosphorus extractable by bicarbonate dithionite, PS- remaining phosphorus digested by acid persulphate.

3.5.3 Phosphate adsorption

In the tube incubation, the final phosphate concentration in the water after 24 h of sediment resuspension was consistent with a mean of 1.6 ± 0.8 µmol L^{-1} independent of different initial concentration. This refers to an equilibrium concentration where neither adsorption nor desorption processes occur (Figure 30). The difference between the maximal initial concentration of 50 µmol L^{-1} and this equilibrium concentration of 1.6 µmol L^{-1} corresponds to the amount of P that changed from the dissolved form in the water to particulate form in the sediments. This amount related to sediment bulk volume corresponds to a potential adsorption onto sediment particles of roughly 0.7 mol m^{-3} for both sediment types. And it is evident that the maximum adsorption capacity is not reached so far.

The adsorbed P could not be desorbed again, when shaking the sediment for another 24 h with distilled water and the equilibrium concentration was almost stable.

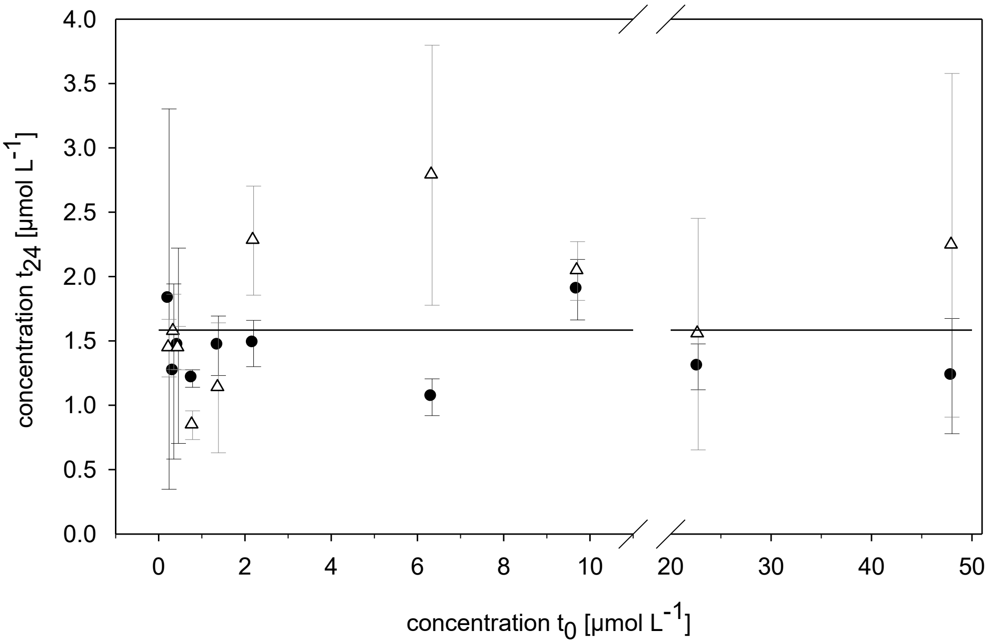

Figure 30: Equilibrium phosphate concentration after shaking a sediment-water-mixture with different initial concentrations for 24h with sediments from 0.5 m (filled circles) and 2 m (open triangles) station, Grabow. (n=3, whiskers show SD, black line=mean)

To understand the adsorption behavior of intact sediment surfaces and their ability to bind phosphate from the overlying water column, different phosphate concentrations were added to intact sediment cores.

After a phosphate addition with a final concentration of 100 µmol L^{-1} in the overlying water, about 15 % of the phosphate disappeared from the water column within 6 h of incubation. This corresponds to an influx of 21.3 mmol m^{-2} d^{-1} and 11.7 mmol m^{-2} d^{-1} for the sediment of the 0.5 m and 2 m station, respectively (Figure 31, right). A phosphate pulse of 50 µmol L^{-1} results in a slower uptake than with high initial concentration, but finally the phosphate concentration in the overlying water drops to nearly zero after 2 days of incubation. Even a second 50 µmol L^{-1} pulse added to the same sediment was taken up completely by the sediment after another 2 days of incubation (Figure 31 left). This results in influxes of 0.6 to 1.3 mmol m^{-2} d^{-1} (Figure 31, right).

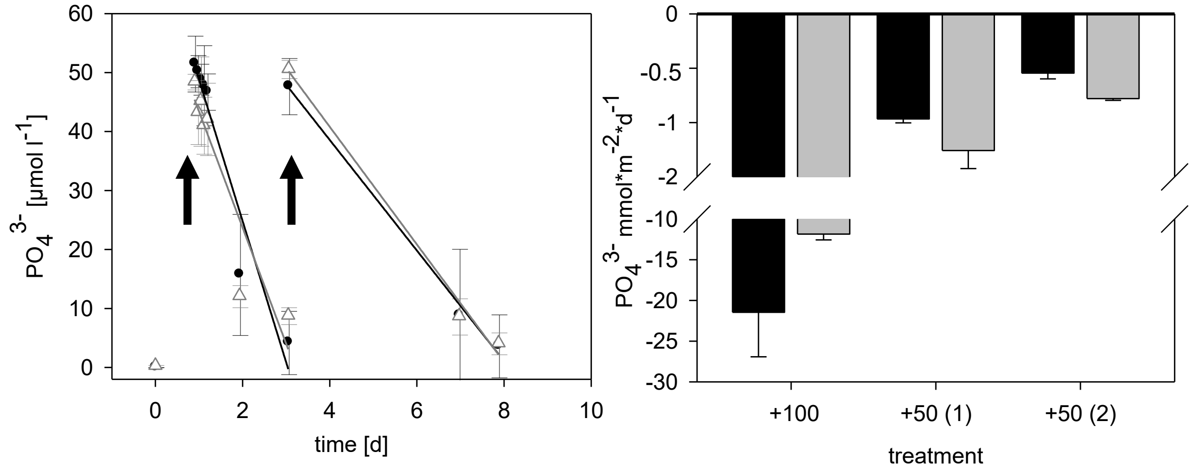

Figure 31: left: Change of phosphate concentration in overlying water after phosphate addition in two 50 µM pulses (arrows) on sediment cores of 0.5 (filled circles) and 2 m (open triangles) station, Gra. right: Phosphate fluxes into sediment after addition of different phosphate concentrations to the overlying water (n=3; whiskers show SD)

The adsorption potential per m² (P_{Ad}) resulting from the absolute concentration difference related to the uppermost 10 cm (equ. 13) of the sediments clearly surmounts the phosphate release potential (Table 6).

Table 6: Phosphate adsorption and release potential (P_{Ad}) from different experiments (exp.) related to sediment surface considering the uppermost 10 cm in mmol m^{-2} at 0.5 m and 2 m station, Grabow (± SE). Negative numbers indicate fluxes into the sediment, positive numbers indicate effluxes from the sediment.

station	**Gra-0.5 m**		**Gra-2 m**	
treatment	**mean**	±	**mean**	±
adsorption, tube exp.	**-70**	0.7	**-68**	2
uptake +100, core exp.	**-5.3**	1.4	**-2.9**	1.7
uptake +50, core exp.	**-4.6**	0.2	**-6.5**	0.4
Release, tube exp.	**2.4**	0.2	**3.1**	0.9

4 Discussion

The two focus stations in 0.5 m water depth and 2 m water depth represent two main sediment types in the DZBC. From 1977 to 1990 the structure and dynamics of the sediment in the DZBC was already analyzed (Schlungbaum et al., 1994a; Selig et al., 2006). Based on the percentage of organic matter content Schlungbaum et al. (1994a) differentiated two types of sediment: the mud complex with > 5 % LOI and the mineral complex with < 5 % LOI. The sediments from the shallow station at Gra as well as at BoB correspond to the mineral complex while the sediment on the 2 m station corresponds to the mud complex. This matches the findings of Schlungbaum et al. (1994a) that sediments in shallow water areas (< 1 m) almost entirely belong to the mineral complex, while the finer sediment and organic matter accumulates in the deeper basins and river mouths. At least 50 to 60% of the whole area of the DZBC and 59% of the Grabow belong to mineral complex (Schlungbaum et al., 1994a). Even if the different sediment types are well characterized and analysed in former studies, the meaning of the different physical properties was underestimated by using weight specific contents to evaluate the nutrient status of the sediments. Flemming and Delafontaine (2000) underline the importance of sediment composition, water content and dry bulk density to quantify sediment related substances, since the common confusion between a volume specific concentration and weight specific content may lead to serious misinterpretation.

Another conspicuous difference between both stations is the occurrence of submersed macrophytes In the Saaler Bodden and Bodstedter Bodden the macrophyte distribution is limited to areas above 1 m water depth, due to higher turbidity and limited light availability. In the Grabow the distribution limit is reached at a maximum of 1.8 m water depth (Piepho et al., 2016). Therefore in the Grabow roughly 36.5% of the total area could potentially be inhabited by submersed macrophytes (Piepho et al., 2016) (Figure 32).

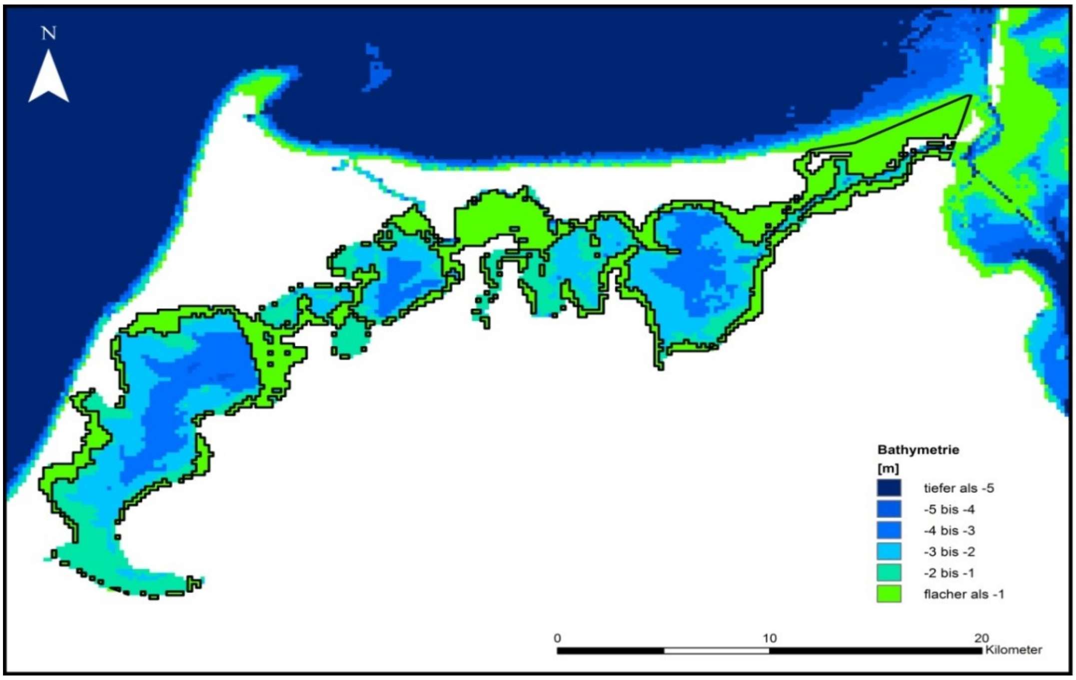

Figure 32: Bathymetry of the DZBC with the area down to 1 m water depth marked as potentially inhabited by macrophytes. (Karstens and Kruse, unpublished)

The macrophytes increase the small scale spatial heterogeneity and reduce the current velocity (Dietz, 2015). It is known from lakes, that macrophytes stabilize a clear water state by storing nutrients and preventing phytoplankton blooms (Kleeberg, 2015; Piepho et al., 2016). Due to high nutrient input macrophyte populations in the DZBC collapsed in the 1970s and the system shifted to a phytoplankton dominated one. Since the late 1990s the macrophyte biomass increases again (Yousef and Schubert, 2001) without a decrease of phytoplankton biomass or turbidity.

Phytoplankton and macrophytes compete for nutrients and light. Piepho & Schubert (2015) explained the coexistence by a time shift between maximum macrophyte production and phytoplankton bloom during the year 2013. On the other hand Berthold (2016) found no reduction of phytoplankton biomass, indicated by high chlorophyll a and suspended matter concentration, in mesocosms experiments with macrophytes in comparison to mesocosms without. These results indicate that against the theory of two alternative stable states (Blindow et al., 1993) macrophytes and phytoplankton may coexist in a eutrophicated ecosystem.

Macrophytes meadows are also a refuge for fishes and macrozoobenthic species. Therefore, in the sediment of the 0.5 m station the abundance and biomass of macrofauna is much higher than on the 2 m station (Figure 24) indicating a stronger bioturbation impact.

In the Baltic Sea a similar sediment distribution occurs, with predominance of sandy sediments in the shallow areas and an accumulation of organic matter and silty sediments in the deeper basins (Carman and Cederwall, 2001). In contrast to the DZBC in the deep basins of the Baltic Sea sub- or anoxic conditions appear enhancing phosphate desorption and release to the overlying water column (Balzer, 1984; Conley et al., 2009; Hille et al., 2005; Jensen et al., 1995; Pitkänen et al., 2001; Viktorsson et al., 2013).

In the DZBC anoxia may appear only under stable ice coverage over several weeks. This was reported the last time in 1995 (Schumann, personal communication). Apart from that oxygen deficiency in the bottom water did not occur. Therefore, the sediment surface even in the deeper basins is well oxygenated.

The results found in the present study about the exchange processes at the sediment water interface of both different sediment types should clarify the question if the sediments act as internal phosphorus source. Since the DZBC is an intermediate ecosystem between freshwater and seawater these findings are also partly assignable to freshwater ecosystems, as well as to the brackish system of the Baltic Sea.

4.1 TP inventories versus organic matter content

Several authors (Lehtoranta, 2003; Nausch and Schlungbaum, 1993; Schlungbaum et al., 2001, 1994; Selig et al., 2006) suggested, that the phosphorus content of sediments correlates with mud and organic matter content. This assumption was accepted by many authors and environmental agencies thereafter (Dahlke, 2006; Karstens et al., 2015; LUNG, 2008; Schumann et al., 2006).

The weight specific TP, TC and TN contents at Gra confirm this assumption (Figure 18, left) .The mean TP content of 3.2 µmol g^{-1} DW at the 0.5 m station and 10.9 µmol g^{-1} DW at the 2 m station are similar to TP contents reported by Schlungbaum et al. (1994) with 5.2 µmol g^{-1} DW (0.16 mg g^{-1} DW) for sediment of mineral complex (LOI < 5% DW) and 16.1 µmol g^{-1} DW (0.5 mg g^{-1} DW) for sediment of mud complex (LOI = 5-10% DW) in the Grabow.

The TP, TC and TN content at BoB do not vary along transect sampling stations since there are no variations in depth and sediment properties. Schlungbaum et al. (1994)

reported a TP content of 5.5 µmol g^{-1} DW (0.17 mg g^{-1} DW) in sediments of mineral complex (LOI <5%) in the Bodstedter Bodden. The mean TP content for BoB found in this study of 1.2 µmol g^{-1} DW is lower than these literature data and also lower than the Gra values, even though the sediment at BoB is similar to the 0.5 m station at Gra. These differences may be explained by different topography and land use of the hinterland (Karstens et al., 2016). While at Gra fertilized cropland border directly to the reed belt, at BoB the wetland is separated by a dyke from sheep pasture.

TP-contents increase slightly towards the reed belt, probably due to refractory plant material accumulating in the sediment. At BoB the mean TP content of 2.8 µmol g^{-1} DW at the first station next to the reed belt was about two times higher than at the following stations. At Gra the TP content of 4 µmol g^{-1} DW is also elevated at the first three stations in comparison to station 4 and 5 which showed the lowest TP contents of roughly 1.8 µmol g^{-1} DW along the transect (Figure 17). In the framework of the BACOSA project Karstens et al. (2015a; 2016) show TP accumulation in the reed belt as consequence of high biomass production by *Phragmites australis* and high litter abundances with long residence time. Inside the reed belt TP content decreases from the basin to the fringe zone. Nevertheless, the TP content in the surface sediment of the wetland fringe zone with 14 ± 5 µmol g^{-1} DW at Gra and 4.8 ± 1.6 µmol g^{-1} DW at BoB (Karstens et al., 2016) is markedly higher than in the adjacent sediment. Even if particle transport is suppressed by dense *Phragmites* stands (Karstens et al., 2015b) the sediment in front of the reed belt seemed to be affected by slightly higher nutrient contents originating from the reed belt.

The picture changes if the mass related contents are converted to volume specific concentrations. TC and TN still increase with increasing water depth (Figure 17 right), indicating an accumulation of carbon and nitrogen contained in organic matter in the deeper and muddy parts of the Grabow. In contrast, the TP concentration did not show any dependency on water depth or mud content and therefore seems to be decoupled from organic matter content (Figure 18, right).

Flemming and Delafontaine (2013, 2000) discussed the differences between the term “content” and “concentration” (

Figure 33). They stated that these terms are often confused in literature and misused for quantitative comparisons between parameters with different physical dimensions that should not be compared on this basis, which lead to misinterpretations of relationships.

Since exchange processes across the sediment water interface are related to the sediment surface, it seems reasonable to calculate sediment TP-, TC- and TN-mass in relation to the sediment surface, too. To calculate surface related inventories units of concentration related to volume of sediment are needed, which can be integrated over a certain depth below the sediment surface (Table 3).

Figure 33 illustrates the meaning of the different physical sediment properties and shows that one litre of sand contain 5 times more dry material than mud. The TP content related to sediment dry mass is more than three times higher at the 2 m stations than at the 0.5 m station. But comparing this dry mass related TP contents between sand and mud would mean comparing 1 L of sand with 5 L of mud. Therefore the amount of water in a volume of sediment has to be considered.

1 litre of different sediment type	pure sand	**0.5 m station**	muddy sand	**2 m station**	mud
silt fraction [%]	0	**3.8**	50	**34.1**	100
dry bulk density [g cm^{-3}]	1.5	**1.5**	0.9	**0.3**	0.3
dry mass per litre [g]	1500	**1500**	900	**300**	300
water content [weight-%]	23	**24**	45	**74**	74.5
porosity	0.45	**0.44**	0.75	**0.87**	0.88
pore water volume per litre [ml]	450	**440**	750	**870**	880
TP per sediment dry weight [µmol g^{-1}]		**3.2**		**10.9**	
TP per sediment volume [mol m^{-3}]		**4.8**		**3.6**	

Figure 33: Some basic relationships between sediment volume, dry bulk density (or mass concentration), water content, porosity, and pore-water volume for pure sand (0% silt fraction), a sand-mud mixture (50% silt fraction), mud (100% silt fraction) and sediment of the 0.5 and 2 m station, Grabow (bold). Images at top display the volumetric relationships between pore water and solids in a defined volume of sediment. Redrawn from Flemming & Delafontaine (2000).

Due to the high water content at the 2 m station TP is reduced to rougly the same concentration than at the 0.5m station. This leads to the conclusion that below one m²

of sediment a similar total mass of P exists at both locations. The physical variations of different sediment types make it difficult to compare and interpret TP data found in this study with literature data. TP is often given as mass related content in mg g^{-1} DW without sufficient information on volume or surface related data. In order to convert such literature data for further comparison the given TP contents are converted first to µmol g^{-1} by dividing by the molar mass of 30.97 g mol^{-1}. Next the content is converted to a volume related concentration per one m³ of sediment by using the dry bulk density (DBD see section 2.6, equ. 10) and then TP mass is related to 1 m² by multiplying with 0.1m integrating the uppermost 10 cm of sediment (see section 2.6, equ. 11).
Unfortunately the DBD is not given in most of the studies. Some studies use wet bulk density but refer to it as "sediment density" or "bulk density" (Berghoff et al., 2000; Carman and Wulff, 1989; Dahlke, 2006; Wranik et al., 2012). This terminology is not exact and wet bulk density certainly is inappropriate to calculate TP inventories from TP content given per g sediment drymass. The wet bulk density gives a density for the water saturated sediment, but gives no information on the water content itself. Due to the density of water the wet bulk density is never below 1 g cm^{-3}.

According to the importance of the relation between water and dry mass in a defined volume of sediment (
Figure 33) the DBD had to be calculated, following Flemming & Delafontaine (2000), if data were given for water content in the respective publications:

$$DBD = 2.6596369 - 0.088614WC + 0.0088041WC^{1.5} - 0.000259WC^{2}$$

equ. 14

Alternatively DBD could be calculated from porosity according to Avnimelech et al. (2001):

$$DBD = (\varphi - 1) \times \rho_p$$

equ. 15

with ρ_p = particle density = 2.65 g cm^{-3} for quarz.

TP contents reported from literature and recalculated as inventories following eq. 10, 11, 14 and 15 are presented in Table 7 for DZBC and in Table 8 for Baltic Sea sediments. The values show that even if TP content differs for different sediment types of the DZBC between 0.17 and 30.7 µmol g^{-1}, the TP inventories are much more similar to one another with values between 0.14 and 0.62 mol m^{-2}. These findings contradict the longtime assumption, that P accumulates in the deeper basins of DZBC.

Table 7: Comparison of weight specific TP content (TP Cw) of surface sediments and surface related TP inventories (TP i) considering the uppermost 10 cm of the sediment of the DZBK published by different authors, re-calculated from given data (see text).

Author	location	LOI [% dw]	DBD [g/cm³]	TP C_w [µmol g^{-1}]	TP i [mol m^{-2}]
Schlungbaum 1982	Barther Bodden	1.1	1	0.17	0.56
	Bodstedter Bodden	12.8	0.2	1.12	0.62
Schlungbaum et al. 1994	Grabow	<5		5.2	
	Grabow	5-10		16.1	
	Bodstedter Bodden	<5		5.5	
Berghoff et al. 2000	Kirr-Bight summer	2	1.1	5.7	0.6
	autumn	2.5	1	8.6	0.8
Dahlke 2006	Grabow (2.8 m)	5-20	0.2	30.7	0.58
	Grabow (3 m)	5-20	0.3	13.7	0.35
Wranik et al. 2012	Kirr-Bight mM/oM[1]	1.5/10	1/0.1	3.1/6.5	0.3/0.05
	Barther Strom mM/oM[1]	1.8/2.2	1/0.6	1.6/2.3	0.15/0.14
this study 2014/2015	Grabow (0.5 m)	0.7	1.5	3.2	0.5
	Grabow (2 m)	9.1	0.3	10.9	0.4
	Bodstedter Bodden	1	1.4	1.2	0.2
Karstens et al. 2016	Grabow reed belt fringe zone	9.9	0.6	14	0.84
	Bodstedter Bodden reed belt fringe zone	4.8	0.8	4.9	0.39

[1] mM = with macrophytes; oM = without macrophytes

Flemming and Delafontaine (2000) found similar relationships between POC concentration and POC content in a re-evaluation of data from Köster et al. (1997) from the Nordrügenschen Bodden (Figure 34 left). They show that the POC concentration in muddy sediment with high POC content (10-15% DW) is similiar to POC cocentrations found in sandy sediments with lower POC contents (1.5%) DW. In Baltic Sea surface sediments Leipe et al. (2011) similarly found highest POC concentrations in the range of intermediate POC contents (3-7 % DW) (Figure 35). The TC contents in the surface sediments of the Grabow range between 0.2 and 2.8 % DW and the relationship between TC concentration and TC content is linear indicating an accumulation of organic matter in the muddy sediments in deeper Bodden regions. (Figure 34, right).

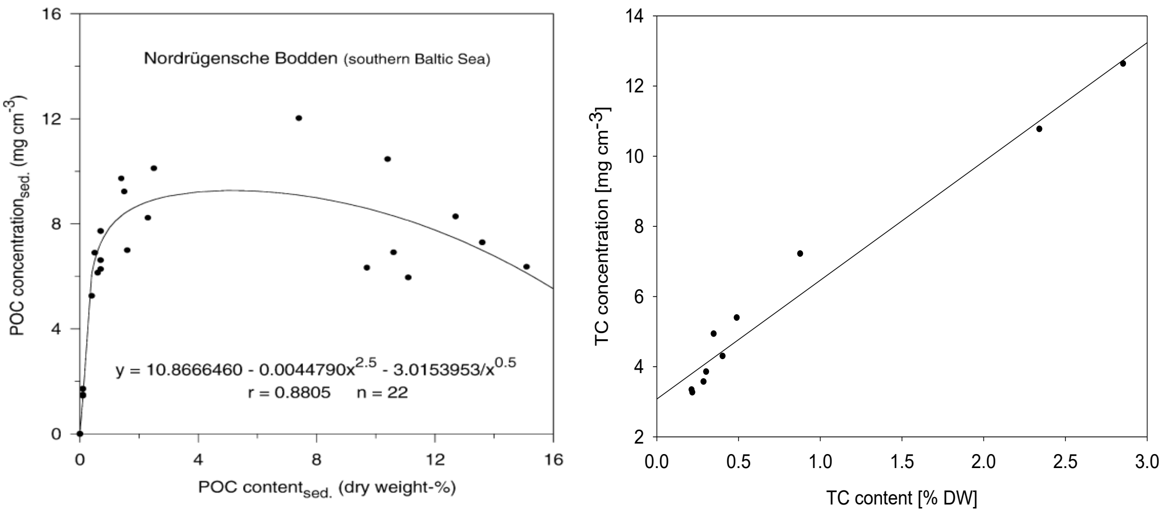

Figure 34: Relationship of POC/TC concentration and POC/TC content in sediments from Nordrügenschen Bodden (left, Flemming & Delafontaine 2000) and the Grabow, DZBC (right, this study, n=10)

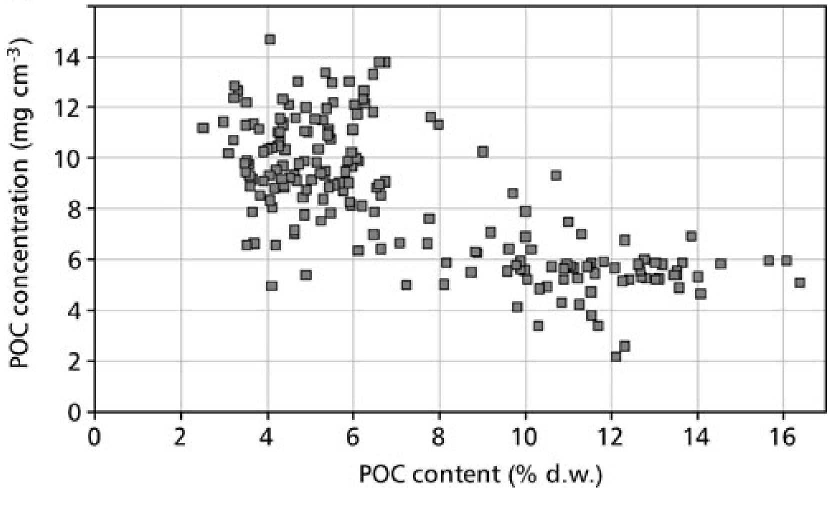

Figure 35: Relationship of POC concentration and POC content in surface sediments from the Gotland Basin and Arkona Basin, Baltic Sea (n=192) (Leipe et al., 2011).

Table 8: comparison of weight specific TP content (TP Cw) of surface sediments and surface related TP inventories (TP i) considering the uppermost 10 cm of sediment of the Baltic Sea published by different authors, re-calculated from given data (see text).

Author	location	LOI [% dw]	DBD [g/cm³]	TP Cw [µmol g^{-1}]	TP i [mol m^{-2}]
Balzer 1986	Kiel Bight			15.3	
Carman & Wulff 1989	Baltic proper 47 m	2.7	1.3	29.5	3.69
	Baltic proper 82 m	15.6	0.2	50.3	0.94
Carman & Jonsson 1991	Baltic proper offshore	21.7	0.1	31.2	0.28
	Baltic proper nearshore	4.3	0.8	17.2	1.42
	Baltic proper Archip.	12.8	0.2	38.2	0.7
Jensen et al. 1995	Aarhus Bay (Kattegat)	10.7	0.5	49	2.34
Lehtoranta 2003	Gulf of Finland	17.05	0.1	103.3	1.19
Pitkänen et al. 2001	Gulf of Finland	>15	0.1	83.95	0.53
Lukawska-Matuszewska & Bolalek 2008	Gulf of Gdansk, (<30m)	n.a	0.9	13	1.13
	Gulf of Gdansk, (>30m)	12.4	0.3	17.7	0.6
	Gdansk Deep	20	0.1	647.7	7.56
Rydin et al. 2011	Stockh. Archip., oxic	14	0.1	2.84	1.02
	Stockh. Archip., anoxic	23	0.1	1.37	0.35
this study 2014/2015	Grabow (0.5 m)	0.7	1.5	3.2	0.51
	Grabow (2 m)	9.1	0.3	10.9	0.54
	Bodstedter Bodden	1	1.4	1.2	0.2

Compared to DZBC, higher TP contents of 13 to 648 µmol g^{-1} occur in the sediments of the Baltic Sea, with higher amounts in silty and organic rich sediments. The TP inventories vary between 0.53 and 7.56 mol m^{-2} (Table 8). In contrast to the idea of P-accumulation in fine-grained sediments in the deeper basins, the more sandy sediments (DBD~1) in shallow areas often show higher inventories than the silty ones (Carman and Jonsson, 1991; Carman and Wulff, 1989; Łukawska-Matuszewska and

Bolałek, 2008), except for the Gdansk Deep, where Lukawska-Matuszewska and Bolalek (2008) reported extremly high TP contents.

The data presented in Table 8 and Figure 18 emphasize the meaning of physical sediment properties for interpretation of elemental composition and mass balances. It shows that neither in the DZBC nor in the Baltic Sea phosphorus accumulates with muddy organic rich sediments in the deeper basins.

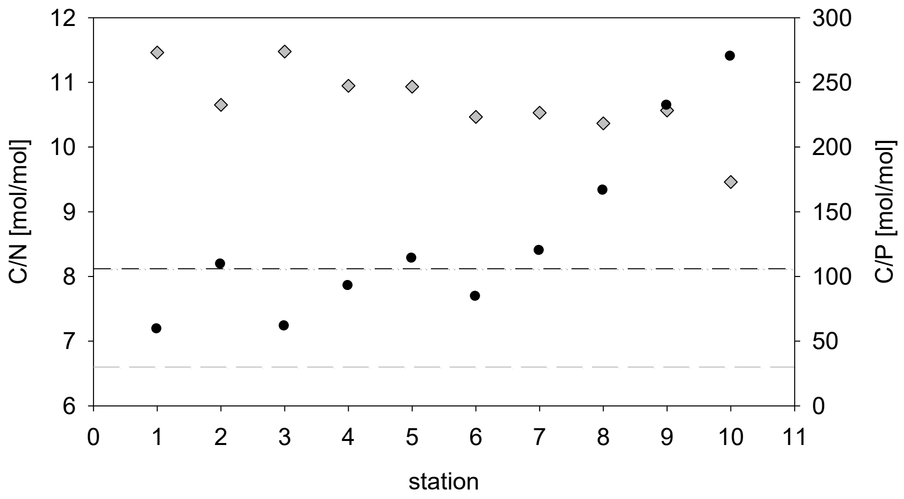

Figure 36: C/N (grey) and C/P (black) ratio [mol/mol] in surface sediment (0-1 cm) of transect stations along a depth transect in the Grabow. Dashed lines mark corresponding Redfield ratios.

The enrichment of carbon in relation to phosphorus is also reflected in the C:P ratio of surface sediments increasing strongly at the last three stations along the depth transect at Gra (Figure 36). This indicates an accumulation of organic matter originating from macrophytes from shallower regions with C:P ratio of 235. For anoxic Baltic Sea sediments Emeis (2000) described a depletion of TP relative to TC and TN indicating a loss of P due to redox-dependent desorption and liberation of dissolved phosphate to the water column. But since the overlying water and sediment surface is well oxygenated in the DZBC a preferential liberation of P to the porewater of surface sediment and to the overlying water column is not reflected in the DIN/DIP ratio in porewater profile (Figure 38 and discussion below).

The decrease of C:P below Redfield ratio on the shallow stations rather indicates a mechanism proposed by Shaffer (1979) called “phosphate pump”. Dissolved phosphate released from anoxic sediments to the water column is reaccumulated by adsorption to well oxygenated sediments. This lateral transport mechanism is observed by Carman and Jonsson (1991) in the Baltic Proper, where the potential adsorption of P onto oxygenated sediments may surmount the release from reduced sediments. Additionally to the lateral transport of dissolved phosphorus from the deeper basins to the shallow areas, this mechanism may also work vertically in DZBC sediments, where the oxygenated surface of the sediment act as trap for phosphate diffused upwards from anoxic sediment layers.

4.2 Influence of macrophytes and infauna on porewater nutrient concentration and dynamics

Despite the similar total phosphorus inventory the concentration of SRP as well as ammonia and nitrate in the pore water of the different sediment types differ markedly (Figure 25). The SRP pore water concentration at the 0.5 m station and at BoB is constantly low over sediment depth. The ammonium concentration increases slightly with sediment depth indicating degradation of organic matter. High nitrate concentration at 0.5 m station Gra, indicate nitrification processes in the sediment. At BoB the sharp increase of ammonium concentration at 5-6 cm sediment depth could be explained by a layer of peat and refractory plant material, where organic matter content (Figure 26) and therefore probably remineralisation activity increase. The nutrient distribution in pore water of the 2 m station at Gra differs markedly. SRP as well as ammonium increase with sediment depth and resulting concentration gradient indicates a mean diffusive efflux of phosphate and ammonium (Figure 25).

Beside the physical sediment properties, the influence of macrophytes and macrozoobenthic fauna may explain these pronounced differences between the two focus stations at Gra. The chlorophyll concentration at the sediment surface at the 0.5 m station indicates microphytobenthic growth, which may influence the sediment, too. The chlorophyll distribution in the sediment can be used as tracer for bioturbation activity (Sun et al., 1991). From the slope of chlorophyll decrease with sediment depth a diffusion analogue mixing could be assumed at both stations. Without any particle mixing the chlorophyll concentration would reach zero within the first centimetre of sediment. The deep penetration of chlorophyll on the 0.5 m station shows enhanced mixing of sediment particles and indicates a higher bioturbation impact compared to the 2 m station (Figure 23).

These findings agree with mean macrozoobenthic abundances as well as biomass, which are much higher on the 0.5 m station than on the 2 m station (Figure 24). The species distribution in the DCBC shows high spatial and temporal variability depending on sediment structure, salinity and temperature (Arndt, 1994; Zettler, 1995). Due to this high variability between samples and the small number of samples analysed, Rach (2015) could not find any significant differences between both stations during his Bachelor thesis.

Nevertheless the 0.5 m station is densely populated by different bioturbating species at any time. In Bitschofsky et al. (2015) the tube dwelling worms *H. diversicolor*, *M. neglecta* and oligochaets as well as *Hydrobia spp.* that occur in high abundances are classified as important for exchange processes. Additionally, the invasive species *Rithropanopeus harrisii* may become more important for bioturbation processes. According to biomass (Figure 24 right) *H. diversicolor* is the dominant species at the 0.5 m station influencing the sediment strongly by bioturbation. The polychaetes builds branched tubes up to 30 cm depth (Zettler et al., 1994). Due to ventilation activity oxygen is transported to deeper sediment layers, supporting the microbial nutrient remineralisation and enhancing solute exchange with the overlying water (Davey and Watson, 1995). Mortimer et al. (1999) found *H. diversicolor* to reduce phosphate release as a consequence of oxygen introduction into the sediment which leads to an increase of adsorption sites along their oxidised burrow walls. Lewandowski et al. (2007) described a similar effect along irrigated chironomid burrows, where oxygen import results in nitrification of ammonium, oxidation of iron(II) and a co-precipitation of phosphate. Karlson et al. (2007) showed decreasing phosphate liberation to the overlying water with increasing macrofauna density.

Visual inspections of the cores show a light brown sediment surface, indicating oxidized conditions down to 3-4 cm (Figure 37). Influence of burrows surrounded by light brown sediment could reach down to a maximum 14 cm.

Along the oxic walls of irrigated burrows nitrifying bacteria could grow (Hansen et al., 1981) causing oxidation of ammonium to nitrate below the oxygen penetration depth. Gilbert et al. (2003) hypothesized that macrofaunal burrows would increase denitrification coupled to nitrification along oxidized burrow walls, also indicated by elevated nitrate levels in the pore water of such burrowed sediment layers. It is evident that the activity of macrofauna in the sediment stimulates microbial processes by providing organic matter and nutrients to deeper sediment layers but also by introducing oxygen into the sediment and in consequence creating oxygenated sediment surfaces. Thereby the adsorption sites for phosphate are increased and the SRP flux from the sediment to the overlying water is reduced or partly suppressed.

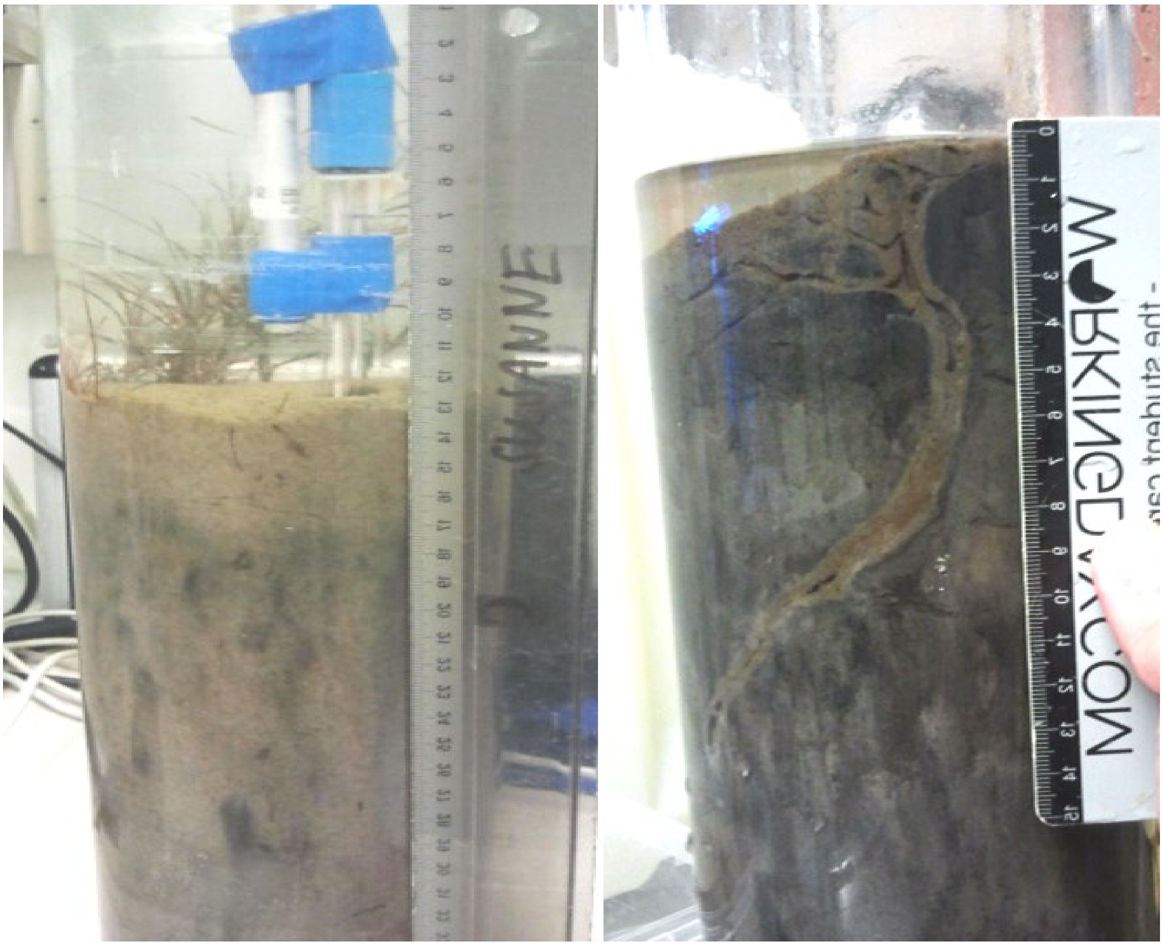

Figure 37: Sediment cores of 0.5 m (left) and 2 m (right) station, Gra showing influence of bioturbation and macrophytes on sediment, light brown sediment indicating oxidized conditions.

Along with the macrozoobenthic community also the submerged macrophytes, only growing on the 0.5 m station, interact with the sediment. At Gra mainly *Stuckenia pectinata*, *Chara sp.* and *R. cirrhosa* occur. The macrophytes biomass reaches a maximum of 266 g DW m^{-2} in the summer month and shows a distinct seasonality (Piepho et al., 2016; Piepho and Schubert, 2015).

Selig (2007) described a decline of charophytes in macrophytes communities with increasing organic matter and nutrient content in sediment expressing the influence of sediment properties on macrophyte community composition. On the other hand Wranik (2012) interpreted the strongly reduced TP contents in sediments inhabited by macrophytes in the DZBC as P uptake by the plants. Considering the TP inventories (Table 3) this effect is negated here.

Nevertheless it's evident from several authors that submersed rooted macrophytes obtain their nutrient supply largely from the sediment (Barko and Smart, 1981; Barko et al., 1991; Carignan and Kalff, 1980; Howard-Williams and Allanson, 1981). Wigand (1997) reported that submersed macrophytes could turn over the porewater phosphate pool in the order of hours to days depending upon sediment type and plant species.

To gain nutrients, rooted macrophytes influence the biogeochemical conditions in the rhizosphere (Kleeberg, 2015). Oxygen is transported from shoots to roots and oxygenates the surrounding sediment on the microscale, resulting in enhanced microbial activity, nutrient remineralisation, but also P-adsorption (Karjalainen et al., 2001; Sorrell et al., 2002; Wigand et al., 1997). Sand-Jensen et al. (1982; see also Laskov et al., 2006) found a radial oxygen loss (ROL) of 19-38 µmol h^{-1} g^{-1} root DW for *P. pectinatus* (now: *Stuckenia pectinata*). With a mean root biomass of *Stuckenia pectinata* of 0.5-8 g m^{-2} measured in June 2014 (Meyer, unpublished) this would lead to an introduction of 0.23 – 7.3 mmol O_2 m^{-2} d^{-1} to the sediment.

Additionally some macrophyte species are associated with mycorrhiza providing nutrients to macrophyte roots (Karjalainen et al., 2001; Wigand et al., 1998). By excreting organic acids micorrhiza could desorbed P even from iron hydroxids and therefore make it available to the plants (Bolan, 1991; Kleeberg, 2015). Overall, the uptake into plants and/or oxidation of sediments through root systems further reduces the likelihood of SRP escaping to the overlying water.

During plant decay organic matter and nutrients are leached and released to sediment or overlying water again (Kleeberg, 2015). By returning P to the water column macrophytes may enhance phytoplankton productivity in P-limited systems (Barko and Smart, 1980). In contrast, Howard-Williams and Allanson (1981) could not detect any increase in littoral SRP during plant decomposition, since SRP is rapidly trapped again by filamentous epiphytic algae and the *Potamogeton*-periphyton complex.

Release of phosphate during decomposition depends on C:P ratio of available plant material. According to Canfield (2005) virtually no net phosphate mineralization occurs if C:P ratio of organic matter is above 80, because all phosphorus is assimilated and incorporated into microbial biomass The C:P ratio of macrophyte biomass at Gra is 235 (Piepho et al., 2016) and far beyond this threshold. Additionally simultaneously released metals may contribute to P binding and decrease P availability and release to the water column (Kleeberg 2013; 2015). The constantly low SRP concentrations found in the water column as well as in the pore water at the 0.5 station during the year supports the idea that on average the macrophytes do not enhance P mobilization and translocation from sediment to the water column.

On the 2 m station where the sediment is inhabited by less macrofauna and where no macrophytes occur due to light limitation (Blindow and Meyer, 2015; LUNG, 2015) only the upper 0.5-1.5 cm of the sediment is oxidized. The oxidized surface is extended by some single burrows of *H. diversicolor*, *M. neglecta* or oligochaeta, at this station, too (Figure 24). Nevertheless, phosphate and ammonium concentration increase in deeper sediment layers due to remineralisation of organic matter and, in the case of phosphate, additionally due to desorption from iron oxyhydroxides under reduced conditions. In contrast nitrate concentration decreases rapidly within the first centimetre at the 2 m station due to reductive pathways of anaerobic microbial metabolism such as DNRA or denitrification. On the other hand, at the 0.5 m station the nitrate concentration in the pore water is constantly high until 3 to 4 cm sediment depth indicating an intensified N-cycle and strong activity of nitrifying bacteria, due to availability of oxygen in deeper sediment layers.

But even if there is a phosphate release under anoxic conditions, the oxidized sediment surface at both sites may trap the phosphate liberated from anoxic sediment layers due to their high phosphate adsorption potential (Table 6).

The elemental ratios of N to P in the porewater, as depicted in the DIN/SRP ratios, are far beyond Redfield ratio in the sediment and reflect the shortage of dissolved P in relation to N, especially at the 0.5 m station, but also in the surface of the 2 m station (Figure 38). This relation can also be seen in the effluxes of the respective solute ions. Ammonium and phosphate effluxes result in a mean $NH4^+/PO_4^{3-}$ ratio of 66 for the 0.5 station and 81 for the 2 m station. Karlson (2007) et al. found an efflux N:P ratio of 0.75 in anoxic sediment in contrast to N:P ratios of 11 and 12 in bioturbated sediments as result of increased retention of mineralized P in the later, while efflux of inorganic N species (ammonium, nitrate) was enhanced by bioturbation activity. In Baltic Sea sediments, Jilbert et al. (2011) found high NH_4^+/PO_4^{3-} ratios of 19 and 83 characteristic for sediments with an oxygenised sediment surface containing iron oxyhydroxides.

Therefore, the very high DIN:SRP efflux ratios found in the present study indicate an effective P-retention.

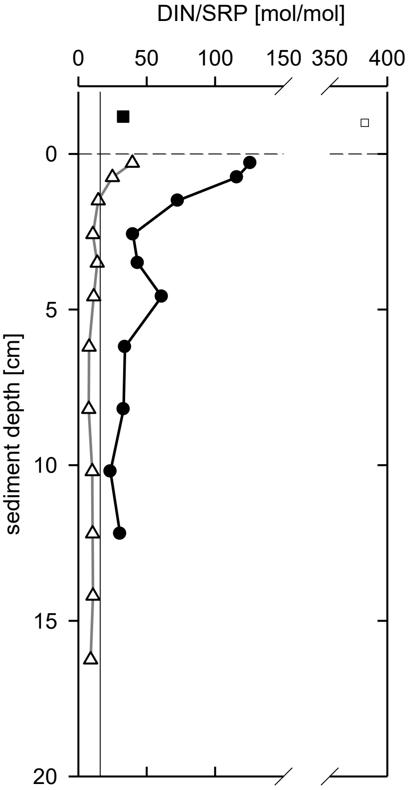

Figure 38: DIN/SRP ratio in porewater of 0.5 m (closed symbols) and 2 m (open symbols) station at Grabow. Symbols above depth 0 indicate water column concentrations (data: Schumann, unpublished)

4.3 Diffusive versus incubation phosphate fluxes

In the present study two different methods were used to estimate the nutrient exchange between sediment and the overlying water column. On one hand, the fluxes are calculated from the gradient in porewater concentration following Fick’s First Law (equ. 4). On the other hand, the fluxes are measured as change of concentration over time in the overlying water during sediment incubation experiments (equ. 8).

At the 0.5 m station (Gra) and at BoB the porewater concentration of SRP and ammonium was constantly low without a distinct gradient (Figure 25 a, b; 26) and therefore no diffusive fluxes could be calculated. Only at the 2 m station (Gra) a gradient in porewater SRP and ammonium concentration occurs (Figure 25 a, b), indicating a diffusive efflux. The calculated fluxes vary between 1.2 and 28.3 µmol SRP m^{-2} d^{-1} and 556.3 and 1856 µmol NH_4^+ m^{-2} d^{-1} during 2014 - 2015.

Under the given sampling circumstances with only one measurement for each point of time, the variability of fluxes could not clearly be identified as spatial or temporal. A measurement on three parallel cores in March 2015 indicating a high core to core variability with a mean diffusive flux of 28.3 ± 15.2 µmol SRP m^{-2} d^{-1} and 556.2 ± 301 µmol NH_4^+ m^{-2} d^{-1}. This corresponds to a core to core variability of roughly 55 %. Assuming the same percentage of variability for all measurements during the year a seasonal variability could not completely be excluded (Figure 39). Enhanced organic matter supply after spring bloom or macrophyte degradation may trigger microbial activity and therefore remineralization of nutrients. The phosphate remineralization may also be influenced by temperature, since microbial activity increase with increasing temperatures (Klump and Martens, 1989). More analyses over a longer period of time are necessary to answer the question how seasonal variation is reflected in porewater nutrient concentration.

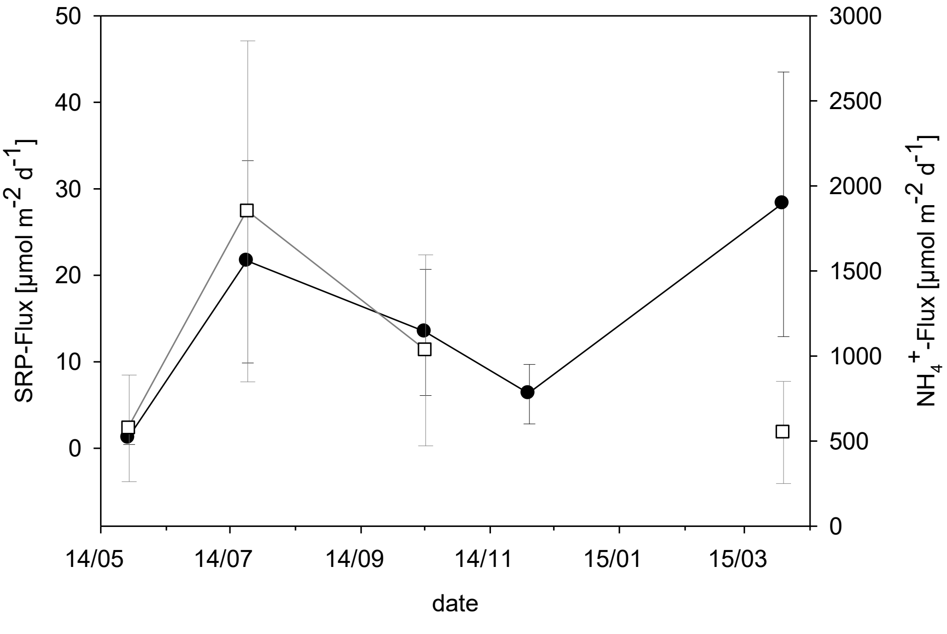

Figure 39: Seasonal variation of calculated diffusive phosphate (filled circles) and ammonium (open rectangles) fluxes at the 2 m station, Grabow. Whiskers show a deviation of 55% estimated from core to core variation in March 2015

The diffusive fluxes calculated from pore water gradients assume a steady state situation and, moreover, only reflect the vertical distribution of pore water concentration. They do not consider horizontal heterogeneity. Additionally, the vertical resolution of 0.5 to 1 cm may underestimate the steepness of the gradient at the sediment water interface and therefore the flux (Viktorsson et al., 2012). Mortimer et al. (1999) stated that diffusive fluxes calculated from pore water concentration gradient are in general significantly lower than in incubation experiments directly measured fluxes, indicating an enhancement of diffusion by processes like bioirrigation. Similar to the present study Mortimer et al. (1999) also found very low phosphate concentrations in pore waters from Humber estuary resulting in diffusive fluxes of -29 to 15 µmol m^{-2} d^{-1}. Nevertheless, their measured phosphate fluxes during incubations were also small and mostly insignificant.

In this study phosphate fluxes determined during oxic sediment incubation from concentration differences in the overlying water never exceed the analytical detection limit and therefore are not significant different from zero (Figure 27). Assuming a mean diffusive flux of 15 µmol m^{-2} d^{-1}, found at the 2 m station, an incubation time of nearly 7 days would have been necessary to reach a reliably measurable concentration difference above 0.4 µmol L^{-1} (detection limit: 0.2 µmol L^{-1}) in a sediment core with 10 cm diameter and 6 cm water column height (0.5 L). Only in the experiment with finally anoxic conditions in the overlying water at sediments from the 0.5 m station, the mean measured flux of 0.24 mmol m^{-2} d^{-1} exceeds the mean calculated diffusive fluxes of 0.015 mmol m^{-2} d^{-1} (Figure 27). By contrast in incubations with oxic conditions the diffusive fluxes could not be confirmed. These results indicate, that the oxygenation of sediment surface seems to prevent phosphate liberation from sediments to the overlying water column.

After a 42 d in-situ incubation which induced hypoxic conditions in the chambers Baader and Schlungbaum (1982) measured a maximum phosphate release of 0.47 mmol m^{-2} d^{-1} (14.53 mg P m^{-2} d^{-1}) within three days under anoxic conditions on mineralic sediments (LOI 1.3%). Similar effluxes from 0 up to 1.25 mmol m^{-2} d^{-1} have been reported from hypoxic and anoxic regions of the Baltic Sea (Balzer, 1984; Jensen et al., 1995; Lehtoranta, 2003; Pitkänen et al., 2001; Viktorsson et al., 2013, 2012) where the sediments were shown to be an internal nutrient source. This is generally not true for oxic bottoms in the Baltic Sea, where measured fluxes are mostly negative or zero and vary between -0.06 and 0.07 mmol m^{-2} d^{-1} (Lehtoranta, 2003; Viktorsson et al., 2013, 2012).

Phosphate release from the sediment is the result of remineralisation, ad- and desorption processes and strongly dependent on redox conditions at the sediment surface. Due to ad- and desorption onto/from iron-oxyhydroxids the BD-P pool is supposed to be the most important exchangeable P pool in the sediments and mainly controls the pore water SRP concentration (Jensen and Thamdrup, 1993). Additionally the accumulation of phosphorus as polyphosphate in microorganisms under oxic conditions and their consumption and therefore PO_4^{3-} release under hypoxic and anoxic conditions (Stigebrandt et al., 2014) may intensify the redox dependency.

In the sediments of the Grabow 3-7% of the TP pool are potentially desorbable including loosely bound P (NaCl-fraction) and metal-bound P (BD-fraction). This equates a potentially desorbable P-inventory of 13 mmol m^{-2} at the 2 m station and 28 mmol m^{-2} at the 0.5 m station. Due to better oxygenation of the sediment at the 0.5 m station more P is retrained in the metal-bound P pool. However, in the anoxic tube incubation the maximum pore water phosphate inventory of roughly 3 mmol m^{-2} at the 0.5 m station and 5 mmol m^{-2} at the 2 m station reached after 30 days of incubation corresponds to only 8 % and 25 % of the potentially desorbable phosphate pool respectively and therefore less than 1% of the TP pool. After this time, an equilibrium or saturation state with a maximum concentration of 50 to 60 µmol L^{-1} seems to be reached (Figure 28). Also, the mean pore water profile (Figure 25) at the 2 m station shows a more or less constant SRP concentration below 10 cm sediment depth of about 40 µmol l^{-1}. Balzer (1984) found a “saturation” value of about 25 µmol l^{-1} in sediments of Kiel Bight, Western Baltic. A constant concentration at depth reflects the equilibrium concentration of sorption kinetics, which Pant & Reddy (2001) determine with 24.2 µmol L^{1} under anaerobic conditions in similar sediments of an Indian River Lagoon. Additional phosphate released into the pore water by remineralisation diffuses upwards into the oxic sediment layer, where adsorption capacity is much higher, and therefore equilibrium concentration decreases (1.6 µmol l^{-1}, Pant and Reddy, 2001; 1.6 µmol l^{-1} present study, see Figure 30)

Jensen (1992) found the phosphate release to be dependent on total Fe:P ratio in surface sediments in Danish lakes and stated that sediments with a molar Fe:P ratio above 8.5 were capable of retaining phosphate. Surprisingly the Fe:P ratio at the sediment surface of the 0.5 m station is 5.9 and below that value, while the ratio at the

2 m station is 16.3. Unfortunately, the total Fe amount gives no information how much iron is available in its oxidized form. Additionally, the Fe measurement took only place once during the study period and is therefore only a snapshot in temporal and spatial variability. But since the Fe (III) oxyhydroxides precipitate phosphate with a lower limiting molar Fe:P ratio of 2 (Gunnars et al., 2002), one can suggest that the amount of Fe available for adsorption in the sediment is not saturated with phosphate.

The phosphate adsorption capacity for sediments of the DZBC was determined by Schlungbaum (1982) with 0.048 mg P g^{-1} DW for "mineralic" sediments, which is similar to the sediment of the 0.5 m station, and 1.13 mg P g^{-1} DW for sediments of mud complex, which correspond to sediment of the 2 m station. Depending on the different DBD these values correspond to 0.24 mmol m^{-2} (0.5 m station, DBD=1.5 g cm^{-3}) and 1.8 mmol m^{-2} (2 m station, DBD=0.5 g cm^{-3}), respectively.

In this study the surficial sediments absorbed much more phosphate in the adsorption experiments conducted on intact sediment cores (Table 6) than expected from Schlungbaum (1982) data, however, depending on the phosphate concentration in the overlying water. Thus, adsorption by the sediment surface surmounts the potential phosphate release (Table 6). The sediment surface could act as barrier for SRP diffusing upwards from deeper sediment layers and therefore prevent liberation of SRP to the overlying water column (Rydin et al., 2011; Sundby et al., 1992). This may explain why the expected diffusive pore water flux at the 2 m station could not be confirmed in incubation experiments. Because the oxygenated surface layer at this station comprises roughly 0.5 cm sediment depth, it is not detected in pore water profile resolution. Under oxygen deficiency this barrier disappears due to dissimilatory reduction of iron oxides and liberation of phosphate (Reed et al., 2011; Sundby et al., 1992). But in this shallow and well mixed lagoon system the summer oxygen concentration in the bottom waters is above 0.19 mmol l^{-1} (6 mg l^{-1}) and oxygen deficiency may occur only on spatial and temporal limited locations/spots (LUNG, 2013). Anoxia has only been reported under ice coverage over several weeks in 1995 in the DZBC (Schumann, personal communication).

Furthermore, if there is dissolved phosphate in the water column, resuspended oxidized sediment particles could act as trap by adsorption on e.g. iron oxyhydroxids (Almroth-Rosell et al., 2012; Lenzi, 2010; Tengberg et al., 2003). Such an effect was observed during the initial phase of in situ incubations and was reported several times in the literature (Baader and Schlungbaum, 1982; Balzer, 1984; Holmer et al., 2003).

Besides the adsorption on iron-oxyhydroxides, the storage of polyphosphates in bacteria strengthens the redox-dependent P-binding in the sediment (Stigebrandt et al., 2014). It has been shown, that the sulphur bacteria of the genera *Beggiatoa* have a high phosphate accumulation capacity due to a 'luxury uptake' of phosphate under oxic conditions (Brock and Schulz-Vogt, 2011).

It can be concluded so far, that the oxygenized sediment surface acts as effective trap for dissolved phosphate from the pore water as well as from the overlying water column. Therefore, the theoretical calculated diffusive fluxes from pore water concentration gradients could not be confirmed in incubation experiments. This indicates the sediments to be rather a sink than a source for dissolved phosphorus.

4.4 Mass balance

For the DZBC different authors suggested that the sediment provides nutrients to the water column and that this internal loading might surmount the external load brought to the Bodden Chain via runoff (Biele et al., 2007; Dahlke, 2006; Schlungbaum et al., 2001; Selig et al., 2006). Dahlke (2006) assumed on average 53% of sediment TP as bioavailable including the metal bound phosphorus as well as the organic phosphorus, extractable with BD and NaOH. He thus calculated an internal load of 0.53 to 1.45 g m^{-2} a^{-1} for the whole DZBC in the uppermost 30 cm of sediment, in contrast to an external load of 0.14 g m^{-2} a^{-1}.

These values for internal load are probably overestimated. Berghoff (2000) also reported an amount of 30-50% of TP as bioavailable in surface sediments at the Kirr Bight. But the values decrease to 7-14% in 9-10 cm sediment depth. In contrast De Jonge (1993) found only the loosely adsorbed NaCl-fraction and the metal-bound BD-fraction to be bioavailable contributing 16-50% to TP. In this study only 3-7% contributed to these two fractions (Figure 29). Nevertheless, the BD and as well the NaOH fraction is mostly redox depended and will therefore only be released from sediment under hypoxic conditions at the sediment surface. Therefore, the values correspond to a potentially internal load, which is not realized under oxic conditions. Additionally, in previous studies only muddy sediments were analysed and finally extrapolated to the whole Bodden area, without considering the adsorption capacity of sediments.

Since the values reported from Dahlke (2006) and Biele (2007), as well as the data from Schlungbaum et al. (2001), are still used in reports of federal environmental agencies giving implications for watershed management, they shall be re-evaluated and related to the results of the present study.

Recalculating the data of Dahlke (2006) for the silt area of the Grabow, and only considering the uppermost 10 cm of sediment (equ. 10, 11), leads to an internal load of 0.08-0.22 g m^{-2} a^{-1}. In the present study, a desorbable P pool of 3-7 % of TP (instead of 53% in Dahlke 2006) was detected. Assuming the same decay rate as Dahlke (2006, references therein) of 0.1 or 0.3 a^{-1} these values would lead to a potential P release of 0.03 to 0.12 g m^{-2} a^{-1}. Finally, the release potentials of 2.4 mmol m^{-2} at the 0.5 m station and 3.1 mmol m^{-2} on the 2 m station (Table 5) measured in anoxic tube incubation corresponds to less than 1 % of TP. This indicates that a much smaller part of sediment bound TP could be desorbed from particles and liberated to the overlying water column than expected from former studies as well as from sequential fractioning presented in this study.

In contrast the mean measured release rate of roughly 0.1 mmol P m^{-2} d^{-1} (2.8 mg P m^{-2} d^{-1}) measured during the first days of the anoxic tube experiments (Table 4) would lead to an annual release of 1 g m^{-2} a^{-1} and is roughly 5 times higher than the values found by Dahlke (2006) indicating a high and fast phosphate release when changing from oxic to anoxic conditions until equilibrium is reached. But in this case phosphate was released from sediment particles to the pore water and this did not necessarily represent an exchange through the sediment surface to the overlying water. Therefore, these rates are inappropriate for estimates about the nutrient supply to the water column via the sediments.

Otherwise, if the mean calculated diffusive efflux of the 2 m station (see section 3.4) is assumed to be constant over the year, this would result in an internal phosphate input from the sediment to the overlying water of the Grabow of 5 mmol m^{-2} a^{-1} (0.15 g m^{-2} a^{-1}) which corresponds well to the data of Dahlke (2006), recalculated for the Grabow and 10 cm sediment depth. This indicates that the sediment depth of 10 cm considered in the present study represents the sediment layer responsible for exchange processes better than the 30 cm sediment depth assumed by Dahlke. Extrapolating the mean diffusive efflux to the silt area of the Grabow of 17 km² (41% of total area, Schlungbaum et al. 2001) results in a total phosphate flux of $85*10^3$ mol a^{-1} (2.6 t a^{-1}). This value is much below the assumption of Dahlke (2006) that in the Grabow 122-226 t P a^{-1} are potentially liberated from the sediment to the water.

Even if the diffusive flux reaches the overlying water column (see discussion above, section 4.3) it is questionable if this provides a sufficiently large phosphate source for primary production in the Grabow. In Table 9 the different approaches of P release are related to the P demand of primary producers (phytoplankton, macrophytes) as well as to the P adsorption.

Piepho et al. (2016) reported a primary production in the Grabow of 1321 t C a^{-1} of phytoplankton and 161 t C a^{-1} of macrophytes resulting in a P demand of 12.5 and 1.5 t P a^{-1} respectively. Therefore, the potential internal input calculated from mean diffusive flux at the 2 m station could account for 19% of whole P demand. In different scenarios Wranik et al. (2012) calculated a P-assimilation by macrophytes of 1.2 - 5.9 t a^{-1} suggesting that macrophyte production alone would take up the whole P disposal estimated by Dahlke (2006) .

Table 9: Calculated mass balances between P demand for primary production and potential P release from the sediments for the Grabow. Details see text.

		production [t C a^{-1}]		P demand [t P a^{-1}]	
Piepho et al. 2016	phytoplankton	1321		12.5	
	macrophytes	161		1.5	
	sum	**1482**		**14**	
		g P m^{-2} a^{-1}	area km²	t P a^{-1}	% of demand
Dahlke 2006	P release max.	0.25	17	4.3	30.4
present study	P release mean	0.15	17	2.6	18.6
	P release (anoxic)	1.13	17	19.2	137.1
present study	P adsorption min.	6.8	24.5	166	
	P adsorption max.	14.7	24.5	359	

Furthermore the minimum adsorption flux measured on the 0.5 m station of -0.6 mmol m^{-2} d^{-1} (Table 6) extrapolated to 59% of total area of the Grabow, which corresponds to sediment of mineral complex (Schlungbaum et al., 2001), results in phosphate loss of $-5.36*10^{6}$ mol a^{-1} (-166 t a^{-1}). Since the natural SRP concentrations in water are much lower than the 50 µM used in the adsorption experiment, these high adsorption values would not occur in the field, but it shows the high adsorption capacity of the sediment. On one hand, the phosphate probably released from silty area could easily be adsorbed in sandy sediment areas. On the other hand, it confirms that the oxidized sediment layer may act as effective barrier for phosphate diffusing upwards from deeper anoxic sediment layers.

In Table 10 the balances presented in Table 9 are extrapolated to the whole Bodden area and related to the external P input via rivers and rain.

The Saaler Bodden (including the Ribnitzer See) is not investigated in the present study. It is strongly influenced by nutrient input from the river Recknitz and therefore subject to stronger eutrophication impact than the western Bodden parts. Therefore, the sediment in this Bodden part may contribute more to the overall P input than the sediments from the Grabow. This effect is not considered in the calculations presented in Table 10 and therefore the total P input is probably underestimated.

Nevertheless, it can be assumed that the adsorption potential measured in the Grabow can be extrapolated to the sandy areas of the whole DZBC. Regarding that even the minimal adsorption potential of 619 t a^{-1} surmounts the presented mean total input of 33.8 t a^{-1} roughly 18 times, an additional P input from the sediments of the Saaler Bodden could easily buffered by adsorption on sandy sediments.

Table 10: Calculated mass balances for the whole DZBC, details see text

		production [t C a^{-1}]		P demand [t P a^{-1}]	
Piepho et al. 2016	phytoplankton	8059		76	
	macrophytes	876		8.3	
	sum	**8935**		**84.3**	
		g P m^{-2} a^{-1}	area km²	t P a^{-1}	% of demand
Dahlke 2006	P release max.	0.25	74.6	18.7	22.2
this study	P release mean	0.15	74.6	11.2	13.3
	P release (anoxic)	1.13	74.6	84.2	99.8
LUNG 2008	external load mean 2003-2006[1]			22.6	26.8
	sum (external+mean release)			**33.8**	**40.1**
this study	P adsorption min.	6.78	91.3	619	
	P adsorption max.	14.7	91.3	1342	

[1] including mean (1996-2012) input of 3.1 t a-1 via rain (Schumann)

While external TP-input to water of DZBC decreased since the 1980’s by about 31% (LUNG 2013,), the sediment TP inventories in surface sediments seem to be constant since 1982 (Table 7).This relation supports the idea that the sediments posses an effective P accumulation potential and that the sediments in the DZBC rather act as P sink than as source (Table 10).

5 Conclusion

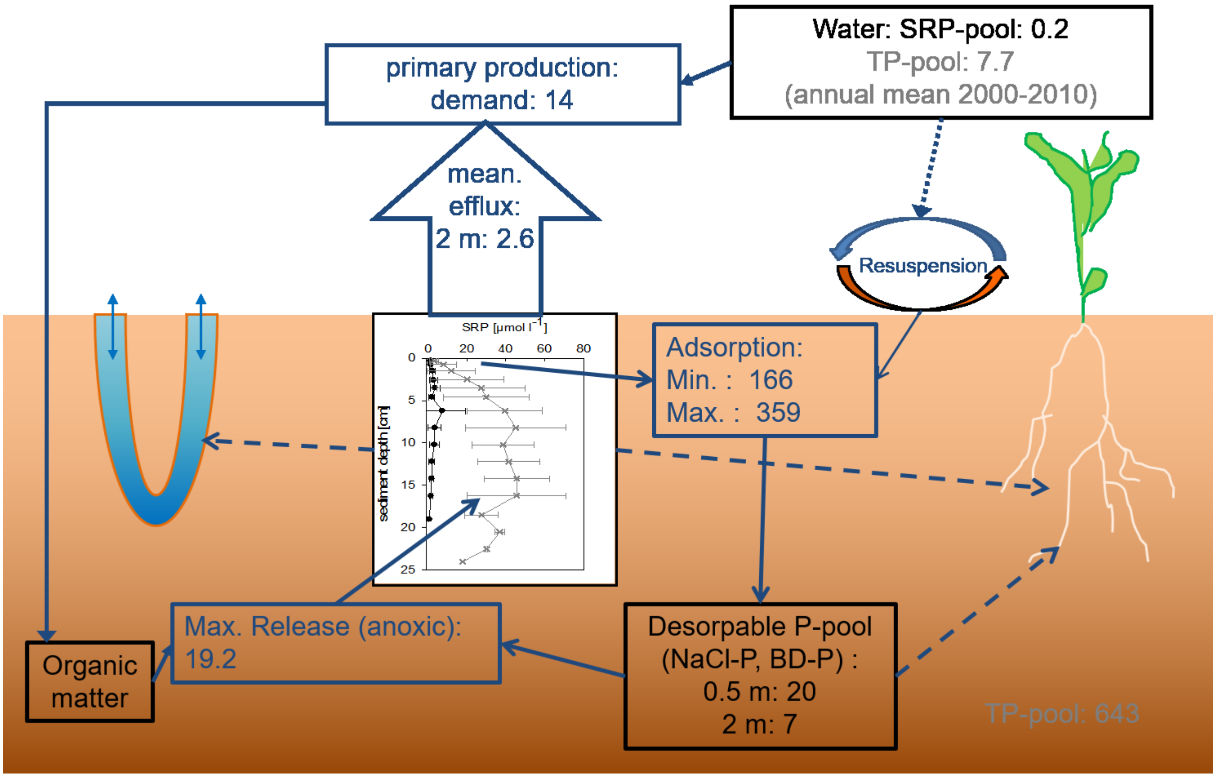

Figure 40: Phosphours fluxes (blue) and pools (black) in the Grabow

According to Table 9 the P fluxes and pools of the Grabow are presented in Figure 40, summarizing the results of the present study.

The following conclusions could be made:

1. The sediments along the depth transect at 0.5 and 2 m water depth in the Grabow belong to two main sediment types. Sandy sediment with low organic matter content (LOI < 5%) occur on the shallow erosion site, influenced by macrophytes and high macrozoobentic biomass. In the deeper basins, where fine material accumulates the sediment is muddy, with higher contents of organic matter (LOI < 5%)
2. The TP contents of 10.9 µmol g^{-1} DW at the 2 m station are more than three times higher than at the 0.5 m station with 3.2 µmol g^{-1} DW.
3. If TP is displayed as volume specific concentration, the TP-concentrations on both stations are similar with 4.8 mol m^{-3} on the 0.5 m station and 3.6 mol m^{-3} on the 2 m station. The TP concentration does not correlate to mud or organic matter content in the sediments.

4. TP is deposited at the sandy shallow site to at least the same extent than in muddy sediments, even if organic matter accumulates in the deeper basins of the DZBC.
5. Three to five percent of the TP inventory in the sediments are potentially desorbable including the loosely bound P (NaCl-fraction) and the metal-bound P (BD-fraction).
6. Under anoxic conditions phosphate is released from sediment with a maximum release potential of 2.4 and 3.1 mmol m^{-2} at the 0.5 and 2 m station, respectively. These potentials contribute to less than 1% of the TP inventory.
7. A diffusive efflux resulting from pore water concentration gradient could only be calculated for sediments of the 2 m station. The mean efflux of roughly 15 µmol m^{-2} d^{-1} would result in a yearly amount of 2.6 t P released from this sediment, which could account for roughly 19% of the P demand for phytoplankton and macrophyte primary production.
8. Under oxic conditions P adsorbs onto iron oxyhydroxides. The adsorption potential of the sediment surface of 4.6 mmol m^{-2} at the 0.5 m station and 6.5 mmol m^{-2} at the 2 m station surmounts the release potential. Therefore, the oxidized sediment surface may act as effective barrier for PO_4^{3-} diffusing upwards from anoxic sediment layers.
9. Due to bioturbation impact and influence of macrophytes the oxidized sediment surface is enlarged, increasing the adsorption capacity especially at the 0.5 m station.

Summarized the results of the present study contradict the longtime assumption that the sediments of the DZBC provides a P source for the overlying water column. Along with a well-mixed water column and therefore a good oxygenation of the bottoms the sediment act rather as P sink than as source.

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