

# **The influence of phosphorus on the eutrophication process in the Darß-Zingst Bodden chain**

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**List of abbreviations**

°C	degree Celsius
°K	degree Kelvin
µg	microgramme
µmol	micromole
a	year
AFDM	ash-free dry mass
Al	aluminium
ASS	alternative stable states
BACOSA	Baltic Coastal System evaluation and Status Analysis
BB	Barther Bodden
BO	Bodstedter Bodden
BSZ	Biological Station Zingst
C	carbon
Chl <i>a</i>	chlorophyll <i>a</i>
cm	centimetre
d	day
DCMU	3-(3,4-dichlorophenyl)-1,1-dimethylurea
DL	determination limit
DM	dry mass
DZBC	Darß-Zingst Bodden chain
e.g.	<i>exempli gratia</i>
EPS	extrapolymeric substances
EU-MSFD	European Union marine strategy framework directive
EU-WFD	European Union water framework directive
Fe	iron
FL	fluffy layer
g	gramme
GB	Grabow
H	hydrogen
H <sub>2</sub> SO <sub>4</sub>	sulphuric acid
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	potassium peroxodisulphate
l	litre
m	metre

m <sup>2</sup>	square metre
m <sup>3</sup>	cubic metre
ml	millilitre
mmol	millimole
Mn	manganese
Mt	megatons
N	nitrogen
NaOH	sodium hydroxide
nm	nanometre
O	oxygen
P	phosphorus
PO <sub>4</sub>	phosphate
rfu	relative fluorescence unit
RM	Recknitz River mouth
rpm	revolutions per minute
RS	Ribnitzer See
s	seconds
S	sulphur
SB	Saaler Bodden
TN	total nitrogen
TP	total phosphorus
UV	ultraviolet
WB	Werder/Bock
ZS	Zingster Strom

## 1 Introduction

The human species is nowadays the only known on earth, which alters and restructures intentionally complete biogeochemical cycles and ecosystems. This influence has changed many ecosystems to such an extent that geologists discuss about a new era called Anthropocene (Crutzen, 2002; Ellis and Trachtenberg, 2014). One of these alterations is due to the demand for resources and elements, which affect nutrient cycles.

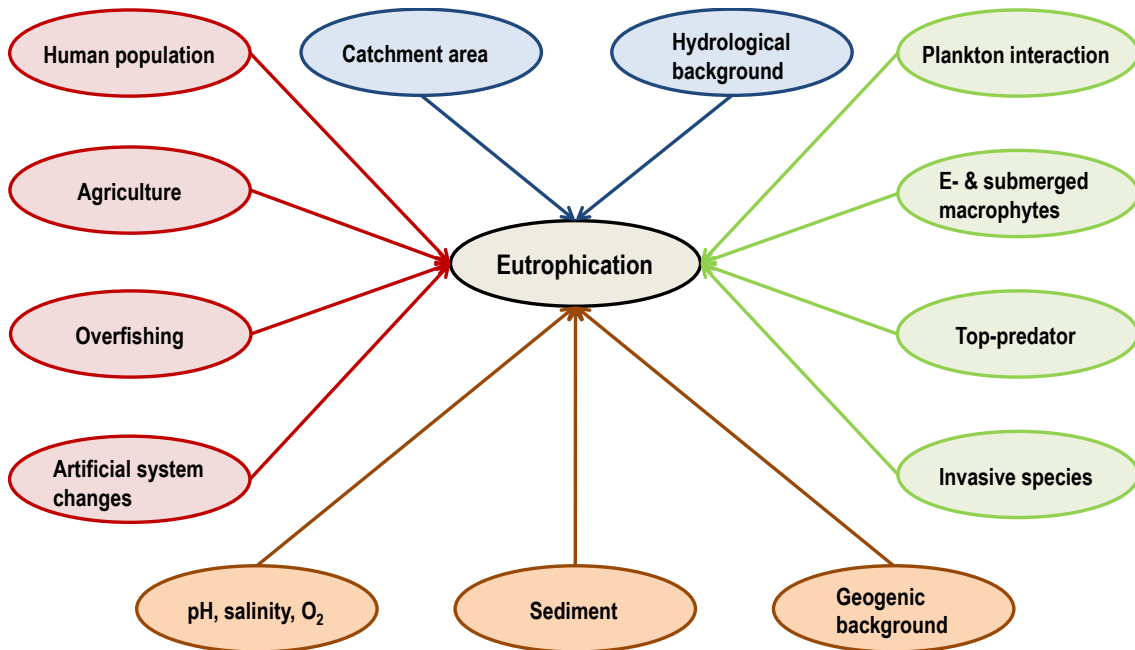
Terrestrial and aquatic ecosystems depend on exclusive macro- and micronutrients. All life that we know is built up with the essential elements carbon (C); nitrogen (N), phosphorus (P), oxygen (O), hydrogen (H), and sulphur (S). All organisms depend on the permanent availability of those elements for growth and reproduction. The Law of the Minimum states that one missing nutrient cannot be replaced by other nutrients in higher concentrations. Growth is limited by the least available nutrient (Liebig, 1842). P is one of these limiting nutrients in terrestrial and aquatic ecosystems. The cause is the geological time scale of the P cycle, which lasts in e.g. sediments between 42 to 200 million years (Lerman et al., 1975; Mackenzie et al., 1993). P itself has no important atmospheric phase except particulate P through atmospheric deposition (Mackenzie et al., 1993). The fact that there is no important gaseous P form, distinguishes it from N, which can be fixed biological from the atmosphere (Howarth et al., 1988a, 1988b). P is mostly bound as apatite in sediments and rocks (most common calcium fluorophosphate –  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) and is released by sediment decomposition, or bioleaching by microbial activity in terrestrial sediments (Becquer et al., 2014; Frossard et al., 1995). Afterwards, P is transported by precipitation, erosion, or groundwater into aquatic systems (e.g. Lemley et al., 2014; Lillebø et al., 2012; Magnien et al., 1992). There, P supports primary production. P circulates through all trophic levels. The only bioavailable form of P in water bodies is phosphate ( $\text{PO}_4$ ).  $\text{PO}_4$  itself can bind to several reaction partners in aquatic systems, like aluminium (Al), iron (Fe), manganese (Mn) or organic acids. Metal-phosphate compounds are only stable during positive redox potentials e.g. high oxygen saturation or nitrate concentrations (Hupfer et al., 1995; Jensen and Andersen, 1992). These compound characteristics are important in water body circulation and will be described further below.  $\text{PO}_4$  can mineralise with Ca and F as apatite again and precipitate to marine and limnic sediments (Frossard et al., 1995). The P residence time in the ocean last for up to 10 000 years (Froelich et al., 1982).

However, human demand for P cut this cycle short. Demand and use rose permanent since the 1950ies. The use of P is up to 90 % relevant for agricultural production as mineral fertiliser or food additive in the European Union (van Dijk et al., 2016). The new knowledge by the Law of the Minimum resulted in an increased application to agricultural land. Geological deposits were made accessible. High consumption as fertiliser led to a strong accumulation in agricultural used soils (Bennett et al., 2001).

P binds fast in clay-, metal-, and organic rich sediments after output in terrestrial systems. The mobilisation is reduced (Lajtha and Harrison, 1995), but erosion and precipitation flush it into aquatic systems continuously (Mackenzie et al., 1993). Main ways are drainages, groundwater, and rivers (Correll, 1998; Correll et al., 1999). Already in the mid of the 20<sup>th</sup> century anthropogenic sources added up to 12 – 14 Mt a<sup>-1</sup>, whereas the natural mobilisation was estimated up to three Mt a<sup>-1</sup>, (Cordell, 2010; Falkowski et al., 2000). This surplus of the limiting nutrient led to an increased reaction in aquatic ecosystems already in the 1930ies (Hasler, 1947). A change in aquatic systems was first described for lakes (Hasler, 1947). The higher availability of P led to an increase of primary production in former P limited systems. This process is described as eutrophication. Eutrophy of aquatic systems is the third of five levels in the trophic system (oligo-, meso-, eu-, poly- and hypertrophy). It is defined as follows: “The state of trophy is equal the intensity of primary production” (according to Schwoerbel, 1993). This means, that not the amount of detectable nutrients is important, but biomass increase of primary producers. This affects submerged macrophytes, as well as macro- and microalgae (e.g. Burkholder et al., 2007; Granéli and Solander, 1988; Lin et al., 1996; Örnólfsson et al., 2004).

There is a difference between the processes of natural and anthropogenic influenced eutrophication. Natural eutrophication is part of the succession of lakes. Although eutrophication is no sign for lake aging per se, but a description for biotic interactions, water retention time, and differed hydrological background (Whiteside, 1983). Nonetheless, with increasing lake age, the resuspension capacity rises by lowered water levels. This increases the potential for nutrient dissolution. Primary production increases during this time due to slowly P accumulation from natural geogenic inputs. The anthropogenically induced eutrophication happens much faster. The change of trophic levels accelerates due to the proportional higher nutrient inputs,

compared to the natural background. Eutrophication is influenced by many different factors. A general overview for major influencing factors is visualised in Figure 1.



**Figure 1 Selection of main influencing factors onto eutrophication.** Colours: Red – anthropogenic influence, Blue – hydrological influence, green – Biotic influence, brown – Abiotic influence.

However, not every factor does influence eutrophication to the same extent. During the eutrophication process, some factors may change to such an extent, that they can inhibit or elevate the eutrophication process further (see Table 1 for examples). The amount of possible influencing factors makes it necessary to investigate factors alone, or in a controlled environment. Such controlled environments can be mini- and mesocosms.

**Table 1** Factors that influence eutrophication directly or indirectly. Factors are sorted by abiotic and biotic parameters. Exemplary sources are listed by influencing factor.

Factor	Influence by	Source
<b>Abiotic parameters</b>		
<b>Water depth</b>	High resuspension in shallow waters results in nutrient reflux from sediments; Water stratification in deep waters results in oxygen depletion	(Niemistö et al., 2011; Søndergaard et al., 1992)
<b>pH</b>	High pH (>8.5) raise nutrient reflux from sediments	(Gomez et al., 1999; Niemistö et al., 2011)
<b>Oxygen saturation</b>	Low oxygen saturation resolve redox-sensitive nutrients from sediments	(Bartoli et al., 1996; Correll, 1999; Roy et al., 2011)
<b>Nitrate concentration</b>	High NO <sub>3</sub> concentration can stimulate overall microbial activity and prevent phosphate re-solution	(Jensen and Andersen, 1992; Lunau et al., 2013)
<b>Catchment area</b>	Background of nutrient inputs depends on land usage	(Bailey-Watts and Kirika, 1999; Krämer et al., 2011; Selig et al., 2006)
<b>Water retention time</b>	Long retention time results in higher trophic states	(Correll, 1999)
<b>Sediment</b>	Nutrient resolution and O <sub>2</sub> demand depends on sediment background; mineral vs. high organic content	(Christophoridis and Fytianos, 2006; Mort et al., 2010)
<b>Biotic parameters</b>		
<b>Phytoplankton</b>	Phytoplankton with high ratio of volume:surface are favoured in nutrient uptake Cyanobacteria can fix nitrogen	(Friebele et al., 1978; Howarth et al., 1988b; Smith, 1990)
<b>Emerged and submerged macrophytes</b>	Reduce sediment resuspension; Sedimentation trap for seston Nutrient sink during phytoplankton growth season	(Blindow et al., 2014; Kufel and Kufel, 2002)
<b>Food webs</b>	Systems with high predatory fish population are controlled top-down	(Stephen et al., 1998)

The accelerated eutrophication process results in a transformation of many aquatic systems. These transformations are connected to the concept of alternative stable states (ASS). ASS postulates that either submerged macrophytes, or phytoplankton dominate an aquatic system (Blindow et al., 1993). An aquatic system in the state of macrophyte dominance shows low turbidity, low phytoplankton biomass, and dense colonisation of different macrophyte species (Blindow et al., 2014 and

sources cited therein). Macrophytes take over several functions in this state. They are a retreat for zooplankton, create regions of reduced flow velocity, act as a sediment stabiliser, and are in case of charophytes direct competitors to phytoplankton for dissolved nutrients (Blindow et al., 2014, 1993; Kufel and Kufel, 2002). However, in case of elevated nutrient inputs into the system, phytoplankton can outcompete submerged macrophytes due to nutrient competition, light limitation, and O<sub>2</sub> depletion by decayed biomass (Granéli and Solander, 1988; Scheffer et al., 1997; Weisner et al., 1997). Elevated phytoplankton growth can lead to a light limitation of all aquatic phototrophs (Cloern, 1999). This self-shading affects both, phytoplankton and submerged macrophytes. A cascading reaction occurs in the system, when this condition lasts too long. Macrophytes in deeper zones die off and decay. Oxygen consumption increases because of the biomass degradation, of both submerged macrophytes and phytoplankton (Grenz et al., 2000; Nichols and Shaw, 1986). This results in resolution of sediment bound nutrients, like ferric phosphate due to the changed redox potential. This further fuels the eutrophication process. The system loses zones of reduced flow, which result in higher turbidity through resuspension. The zone of light limitation is expanded to lower water levels. Additionally, zooplankton loses its refugium and suffers a higher grazing pressure. This reduces grazing pressure on phytoplankton and can stabilise the phytoplankton biomass. Thus, a macrophyte-dominated system can switch within a relatively short time (<20 years) into a phytoplankton-dominated system (Blindow et al., 1993). This change includes the loss of previous biodiversity, higher turbidity, and altered food webs.

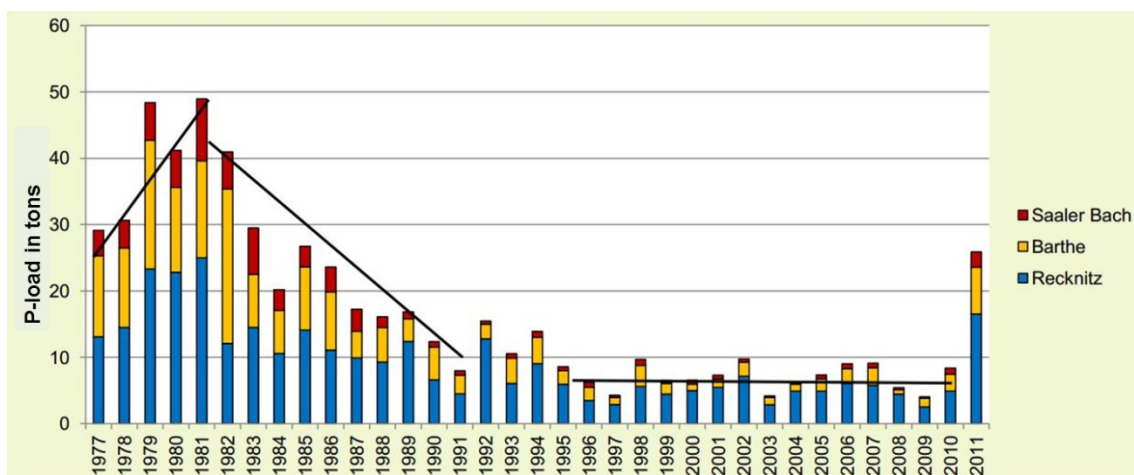
Consequently, counteractions were conducted to reverse or decelerate this process. Examples for counteractions are nutrient reduction through point sources, elevated water exchange, and chemical precipitation of nutrients (Gulati and Donk, 2002; Hupfer and Hilt, 2008). The legal basis for these counteractions is the EU water framework directive (EU-WFD). The “good ecological status” shall be accomplished by means of the EU-WFD: “[...] *Member states should aim to achieve the object of at least good water status by defining and implementing the necessary measures within integrated programmes of measures, taking into account existing Community requirements. [...]*” (European Community, 2000). However, a slight anthropogenic impact needs to be considered, because humans are part of the ecosystem, too. The attainment of the “good ecological status” can be determined best by analysis of monitoring data before and during the anthropogenic impact (Dale and Beyeler, 2001).

Therefore, an evaluation of long-term data can identify future ecosystem developments (Maier et al., 2009). These developments can be used to set specific instructions for the system restoration, or catchment area rehabilitation. This worked already for some systems, like Lake Veluwemeer and Lake Schlachtensee (Sas, 1989a). However, dense monitoring programmes are rare. Therefore, the evaluation of such dense programmes in model ecosystems can help to transfer the knowledge to other systems.

These successful counteractions so far worked mainly for deep lakes. However, rivers, shallow lakes, and estuaries are implemented in the EU-WFD as well. Shallow lakes or estuaries suffer especially from high nutrient inputs. Shallow lakes are prone to the effects of eutrophication because of their special ratio of surface to water depth to catchment area. Resuspension of sediment and phytoplankton biomass can happen more often. In estuaries, eutrophication events can develop due to their large catchment areas, zones of reduced flow, geogenic backgrounds, and brackish waters. Brackish waters stress all aquatic organisms by unfavourable osmotic conditions, which can decrease grazing on phytoplankton (Bisson and Kirst, 1995; Fu and Bell, 2003). Zones of reduced flow can promote phytoplankton bloom forming (Correll, 1999). Estuaries as final part of catchment areas receive all the accumulated nutrient inputs.

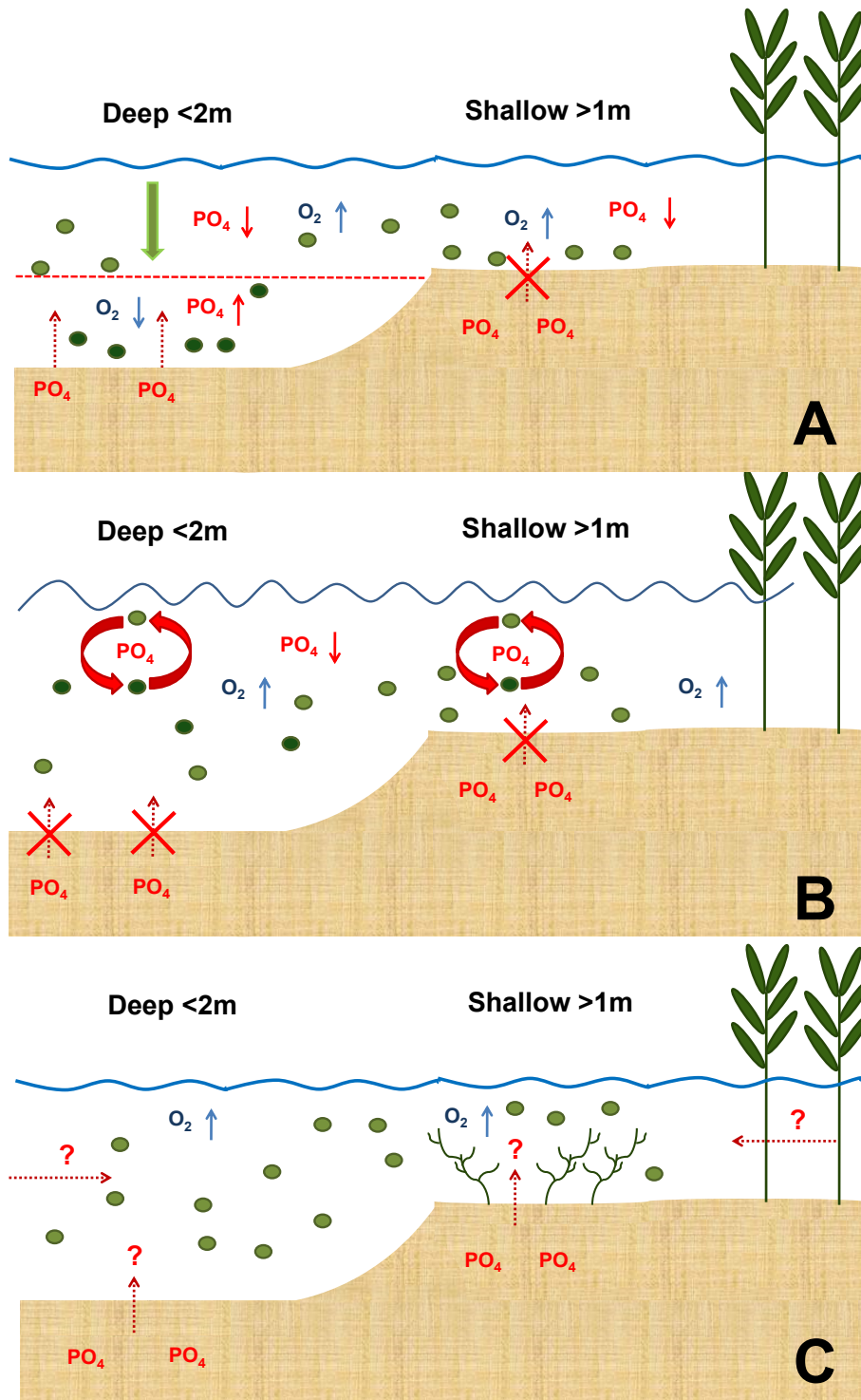
Examples for geologically young aquatic systems (~ 3000 years) are the “Bodden” and “Haffe” in the Southern Baltic Sea (Schlungbaum and Voigt, 2001 and sources cited therein). These systems are shallow lagoons. The exchange to the Baltic Sea is reduced due to the formation of islands and peninsulas parallel to the coastal line. The word “Bodden” comes from the Low-German word for “bottom”. The Bodden combine different hydrological and morphological characteristics from shallow lakes and estuaries. One of those systems is the Darß-Zingst Bodden chain (DZBC), which was in the focus of the present study. The DZBC is a shallow estuary, typical for the Southern Baltic Sea (Schlungbaum, 1994). Originally, the system had several connections to the open Baltic Sea. Those connections were closed as recorded in 1395, 1874 and 1905 - 1960 (Schlungbaum and Voigt, 2001). This altered the systems hydrology and shaped it to the present Bodden chain. Main characteristics can be found in chapter 2.1 Study site Table 2 (see below). The main river inputs come from the Recknitz River and the Barthe with 669 km<sup>2</sup> (42 %) and 292 km<sup>2</sup> (18 %) of the total catchment area, respectively. Water exchange is mainly controlled by Bodden water line, Baltic Sea water line, annual precipitation in catchment area, wind direction and duration (Baudler, 2004; Schumann et al., 2006).

The DZBC is described as a naturally mesotrophic to eutrophic system, according to its geogenic background (Schlungbaum et al., 2000) and catchment to surface area of 8:1 (Schiewer, 2007). First signs of eutrophication were described in the Saaler Bodden during the 1930ies (Wundsch 1968 in Schlungbaum et al., 2000, p. 44-a). The nutrient input increased during the following decades, mostly by extended fertiliser use in the catchment area. This resulted in a loss of submerged macrophytes and a permanently high phytoplankton biomass. This biomass consists mostly of small cyanobacteria since the late 1980ies (Schumann, 1993). However, the nutrient inputs via Recknitz River and Barthe declined since 1983. The total P-input into the system was reduced further until it remained stable since the 1990ies (Figure 2). This was mostly due to the construction of water treatment plants and changed land use after the German reunification.



**Figure 2 Phosphorus load in tons via the main river inputs into the Darß-Zingst Bodden chain.** The Recknitz flows into Ribnitzer See, Saaler Bach into Saaler Bodden, Barthe into Barther Bodden (modified after Bachor et al., 2007).

The nutrient reduction did not result in lower turbidity or phytoplankton biomass, even though  $\text{PO}_4$  concentrations are very low since that time (Data Biological Station Zingst and this work). The postulated opinions were that sediment or fast microbial activities maintain phytoplankton biomass, as an autochthonous nutrient source (Schiewer, 2007; Schlunbaum et al., 2000). Even without a change, the macrophyte population began to establish again during the last years. This reoccurrence of submerged macrophytes, and the fact, that the polymictic environment makes it difficult to assign direct nutrient inputs, made a re-evaluation of the systems development necessary. This was one of the main tasks for the joint project BACOSA (Baltic Coastal System Analysis and Status Evaluation). The work presented here was one part of the project BACOSA. It focused especially on the interactions between pelagic zone, sediment, and macrophytes. The different hypotheses on phytoplankton biomass sustainment are visualised in Figure 3.



**Figure 3 Hypotheses on the enduring eutrophication process in the Darß-Zingst Bodden chain.** A – Sediment as autochthonous phosphorus source supports phytoplankton biomass as stated by Schlungbaum. Phosphorus is released in deeper parts of the Bodden by low oxygen concentration, or by resuspension. B – High microbial activity and turn-over rate of phosphorus sustains the permanent high phytoplankton biomass as stated by Schiewer. C – Hypothesis that the processes alone of A or B do not sustain phytoplankton biomass. Focus lies particular on long-term phosphorus development and internal competition of macrophytes and phytoplankton.

According to one hypothesis, the sediment became enriched to such an amount with P during the last decades that the regular resuspension constantly supports phytoplankton in all parts of the DZBC. Schlungbaum stated this by analysing P fractions of Bodden sediments (e.g. Schlungbaum, 1982; Schlungbaum et al., 1994). Schlungbaum did measure potential P releases of sediment, but he never analysed biological uptake rates by phytoplankton (e.g. Baader and Schlungbaum, 1982). He concluded that the phytoplankton production depends on occasional nutrient pulses by resuspension or direct uptake above the sediment. This uptake above the sediment includes uptake rates under conditions present in the deeper areas of the Bodden, like dark incubation. The 1 % light penetration depth is around 0.4 to 0.8 m water depth in the middle part of the DZBC (Schumann et al., 2012). To this date, no work was done to analyse the impact of P addition on phytoplankton for successive seasons. Therefore, special treatments will be conducted on phytoplankton, like dark and poison incubated phytoplankton.

Another hypothesis is the high turn-over of P due to enhanced microbial food webs (Schiewer, 2007 and sources cited therein). However, primary production was rather low close by the Zingster Strom (middle part of the DZBC), which made the system net-heterotrophic (Börner, 1984; Schumann et al., 2005). The high attenuation by seston caused the dominance of respiration over production. Nevertheless, algae could maintain a high potential production (Schumann et al., 2009). The impact of non-point sources, like sediment P release, would be negligible for phytoplankton production. According to this point of view, water samples without any treatment should sustain the same biomass after a long incubation compared to day 0. This hypothesis shall be verified by incubating unfertilised and fertilised samples for successive seasons.

As stated before, changes in an ecosystem can best be analysed by using long-term data. The Biological Station Zingst (BSZ) monitors the DZBC for almost four decades. This includes daily measurement at the Zingster Strom and a regular monitoring of all Bodden. Part of these data will be analysed and discussed in this work to evaluate the impact of P on biomass. In addition, the experimental data shall be contextualised to the long-term development in the DZBC. It is questioned, if trends are detectable affecting re-mesotrophication.

Further, the reasons for what triggered the reoccurrence of macrophytes in the DZBC are unknown. Mesocosm experiments were used to examine the changed system status induced by macrophytes. The question was, if submerged macrophytes have the ability to suppress permanently phytoplankton in shallow turbid areas of the DZBC under the prevailing circumstances.

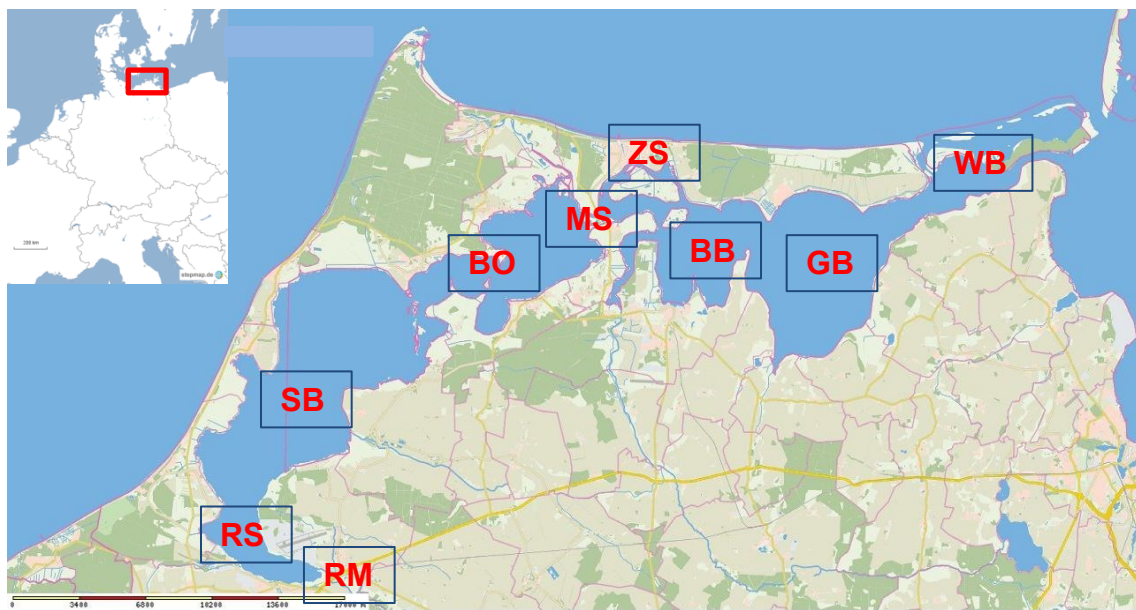
The following hypotheses can be formulated for this work:

1. The DZBC is still more influenced by allochthonous nutrient sources, as by autochthonous nutrient sources.
2. Phytoplankton is not phosphorus limited, even though bio-available  $\text{PO}_4$  is low.
3. Submerged macrophytes can regulate the system back to a clear water state under the prevailing circumstances.

## 2 Material and Methods

### 2.1 Study site

The Darß-Zingst Bodden chain (DZBC) is a highly eutrophic shallow lagoon in the Southern Baltic Sea (Figure 4). The system consists out of four consecutive lagoons: Saaler Bodden (SB), Bodstedter Bodden (BO), Barther Bodden (BB), and Grabow (GB). Additionally, there are some noteworthy sampling sites: Recknitz River mouth (RM), Ribnitzer See (RS), Meiningenstrom (MS), Zingster Strom (ZS) and Werder/Bock (WB).

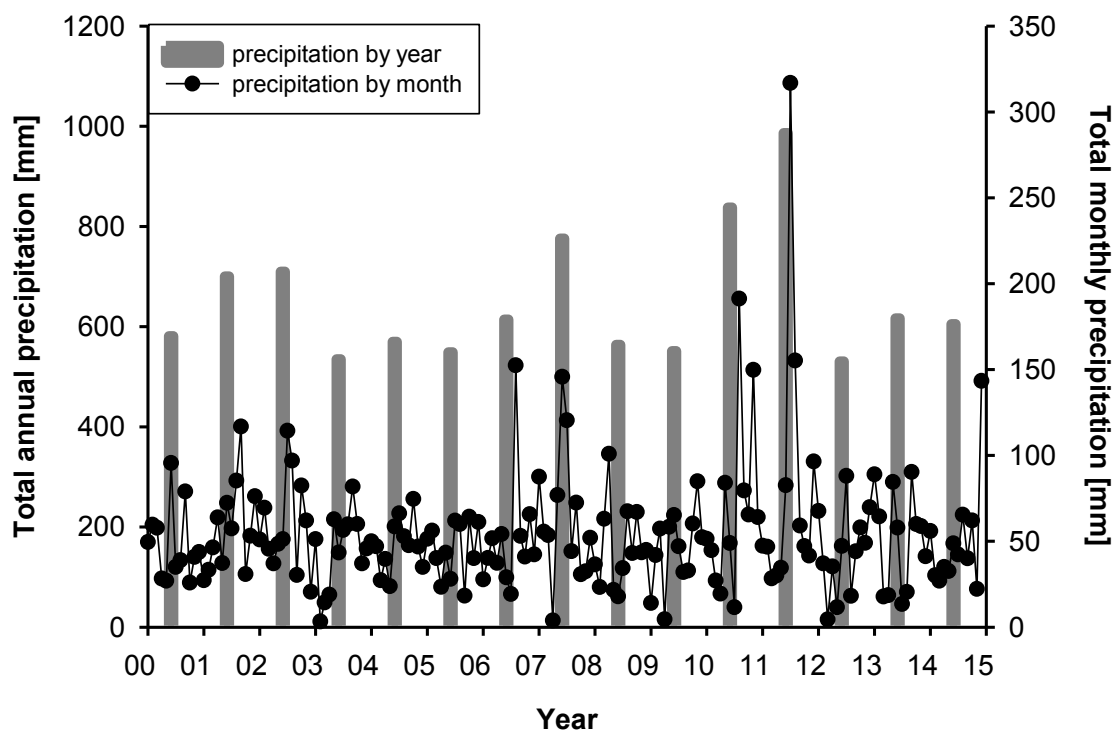


**Figure 4** Position of the Darß-Zingst Bodden chain in Central Europe and sampling sites in the Bodden chain for this work. From west to east: RM – Recknitz River mouth; RS – Ribnitzer See; SB – Saaler Bodden; BO – Bodstedter Bodden; MS – Meiningenstrom; ZS – Zingster Strom; BB – Barther Bodden; GB – Grabow; WB – Werder/Bock (Map Germany – stepmap.de; Map Bodden chain – GeoBasis-DE/M-V).

Table 2 and Figure 5 give an overview for hydrology, abiotic parameters and precipitation. Eutrophication and salinity follow a gradient (Schumann et al., 2006). The highest phytoplankton biomass and lowest salinity are found in the innermost (western) Bodden, called Ribnitzer See. The outermost Bodden in the east (Grabow), close to the Baltic Sea opening, has the lowest phytoplankton biomass and highest salinity. The inner Bodden SB is oligohaline, whereas all other Bodden are mesohaline. The mean depth is 2 m with the deepest zone of 16 m at the Meiningenstrom (Schlungbaum and Baudler, 2001). The catchment area is eight times higher, than the surface of the DZBC (Schiewer, 2007).

**Table 2** General abiotic and hydrological parameters for the main Bodden parts and the whole Darß-Zingst Bodden chain. Data for pH – Biological Station Zingst (BSZ), salinity – BSZ, Oxygen saturation – BSZ, Water renewal time, mean water depth, surface, volume – Schlungbaum (2000). All data from Biological Station Zingst median 2014 (n=365).

	Ribnitzer See	Saaler Bodden	Bodstedter Bodden	Barther Bodden	Grabow	Darß-Zingst Bodden chain
<b>pH</b>	8.54	8.67	8.51	8.46	8.4	
<b>Salinity</b>	2.7	4.0	5.7	7.3	8.3	
<b>Oxygen saturation (%)</b>	109.8	104.7	97.6	100.5	102.5	
<b>Water renewal time (a<sup>-1</sup>)</b>		6 – 7	33	57	32	7 – 8
<b>Mean water depth (m)</b>		2.2 (incl. Ribnitzer See)	1.9	1.8	2.3	2.0
<b>Surface (km<sup>2</sup>)</b>		80.9 (incl. Ribnitzer See)	24.1	19.4	41.5	196.8
<b>Volume (10<sup>6</sup> m<sup>3</sup>)</b>		174.5 (incl. Ribnitzer See)	46.8	34.1	93.8	397.1



**Figure 5** Total annual and monthly precipitation [mm] in the Zingster Strom from 2000 to 2014. The rain gauge had a collecting surface of 200 cm<sup>2</sup> and was checked every day for rain. The rain volume was determined with a calibrated graduated cylinder. Average precipitation per year: 649 mm (n=2519). Data set: Biological Station Zingst.

The study sites for the monitoring programme were at the described Bodden parts, except the Meiningenstrom (see 2.2). Other experiments were mainly conducted with samples from the ZS or RS. All experiments and data analyses can be found in Table 3.

**Table 3 Data set overview with duration and replicates for monitoring data and experiments.**

Sampling site	Duration	Data basis
Monitoring		
<b>Whole Darß-Zingst Bodden chain</b>	2000 – 2014	Zingster Strom n=20 – 24; all other Bodden n=10 – 12 data points per year
Phosphate uptake rates		
<b>Ribnitzer See</b> <b>Zingster Strom</b>	Ribnitzer See: 11.2013 – 11. 2014 Zingster Strom: 04.2013 – 11.2014	Ribnitzer See n=13 Zingster Strom n=32
Growth rates		
<b>Ribnitzer See</b> <b>Zingster Strom</b>	Ribnitzer See: 01.2014 – 11.2014 Zingster Strom: 01.2014 – 11.2014	Ribnitzer See n=11 Zingster Strom n=11
Mesocosms		
<b>Zingster Strom</b>	03.2014 – 10.2014 04.2015 – 09.2015	n=6

## 2.2 Monitoring and data analysis

The DZBC was monitored every two to four weeks by boat at definite locations (Table 4). Monitoring was cancelled only during heavy weather, or ice formation. The Zingster Strom is monitored daily (8 am CET) by the Biological Station Zingst. Data analysis includes only the monitoring on that date with the whole DZBC, to prevent misinterpretation by larger sampling at the Zingster Strom. Parameters of particulate matter include Chlorophyll *a* (Chl *a*), seston and total phosphorus (TP), which are measured since 2000 for the whole DZBC. The parameters seston, Chl *a*, and TP are included in the data analysis. The staff of the Biological Station Zingst compiled the complete monitoring data set, which is presented in this work. The sample processing will be described in 2.4 Abiotic parameters and 2.5 Biotic parameters. The main inflow (Recknitz River mouth) and outflow (Werder/Bock) are included. The main

interpretation will focus on the innermost Bodden part (Ribnitzer See), middle part (Zingster Strom) and outermost Bodden (Grabow). This selection allows a suitable insight on phytoplankton development due to increasing distance from the main freshwater inflow to the Baltic Sea. All additional figures and analysis will be added to the appendix of this thesis.

**Table 4 All monitored sampling sites and their coordinates.**

Sampling site	Coordinates
<b>Recknitz River mouth</b>	54° 14'52.2''N 12° 28'00.3''E
<b>Ribnitzer See</b>	54° 15'20.0''N 12° 24'37.0''E
<b>Saaler Bodden</b>	54° 21'00.3''N 12° 27'43.3''E
<b>Bodstedter Bodden</b>	54° 23'38.8''N 12° 37'25.6''E
<b>Zingster Strom</b>	54° 25'48.1''N 12° 41'18.8''E
<b>Barther Bodden</b>	54° 23'53.4''N 12° 44'58.0''E
<b>Grabow</b>	54° 23'43.9''N 12° 50'26.5''E
<b>Werder/Bock</b>	54° 25'48.9''N 12° 56'52.3''E

## 2.3 Experimental set-ups

### *Phosphate uptake rates*

P uptake was analysed in batch tubes. The water bath contained nine batch tubes (diameter 5 cm, volume 360 ml). Every experiment included one negative control, one positive control, and three replicates with PO<sub>4</sub>-pulses per sampling site. Negative controls were unfiltered plankton samples without a PO<sub>4</sub> pulse. Positive controls contained de-ionised water (<0.05 μS m<sup>-1</sup>), which received a 10 μmol l<sup>-1</sup> PO<sub>4</sub> pulse. Incubation started at least 8 hours (h) before treatment for acclimatisation to light and temperature. Water temperature was kept at 15 °C (±1 K) and photon fluxes at 100 μmol m<sup>-1</sup>s<sup>-2</sup> (16:8 h, Osram Lumilux Deluxe Daylight) inside the batch vessels. The PO<sub>4</sub>-pulse contained 3.45 ml of 1 mmol l<sup>-1</sup> PO<sub>4</sub> (Potassiumdihydrogenphosphate, Roth) for the treated batch (360 ml minus 15 ml for a pre-pulse sample of 15 ml). All sub-samples (15 ml) were filtered (GF6 glass fibre filters, Roth) right before, right after the pulse and after 1, 3, 5, 7 and 24 h for PO<sub>4</sub> quantification. Pulse experiments combined with growth experiments lasted for 7 days (d). Samples were analysed for TP, PO<sub>4</sub>, Chl *a* and seston on d 0 and after d 7.

*Phosphate uptake under special conditions*

Water samples were heated at 60 °C to analyse possible adsorptive processes to the batch tank walls or onto the seston in particles. These experiments were conducted additionally in November 2013 and January 2014. Poisoning with DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and sodium azide was used to determine the amount of PO<sub>4</sub> adsorbed by phytoplankton. The final concentrations for DCMU were 100 µmol l<sup>-1</sup> and 1 mmol l<sup>-1</sup> for sodium azide. Those toxins effectively inhibit energy production in algae (Metz et al., 1986; Nultsch et al., 1983; Wang and Priscu, 1994). The uptake velocity in deep, aphotic zones were imitated by cloaking water samples in aluminium foil and pre-incubate them for at least 12 h. Experiments with dark and poisoned samples were conducted in July 2013 and September 2014. All stated experiments had treated water samples without PO<sub>4</sub> addition and untreated water samples with PO<sub>4</sub> addition. The general procedures were the same, like stated in the previous paragraph.

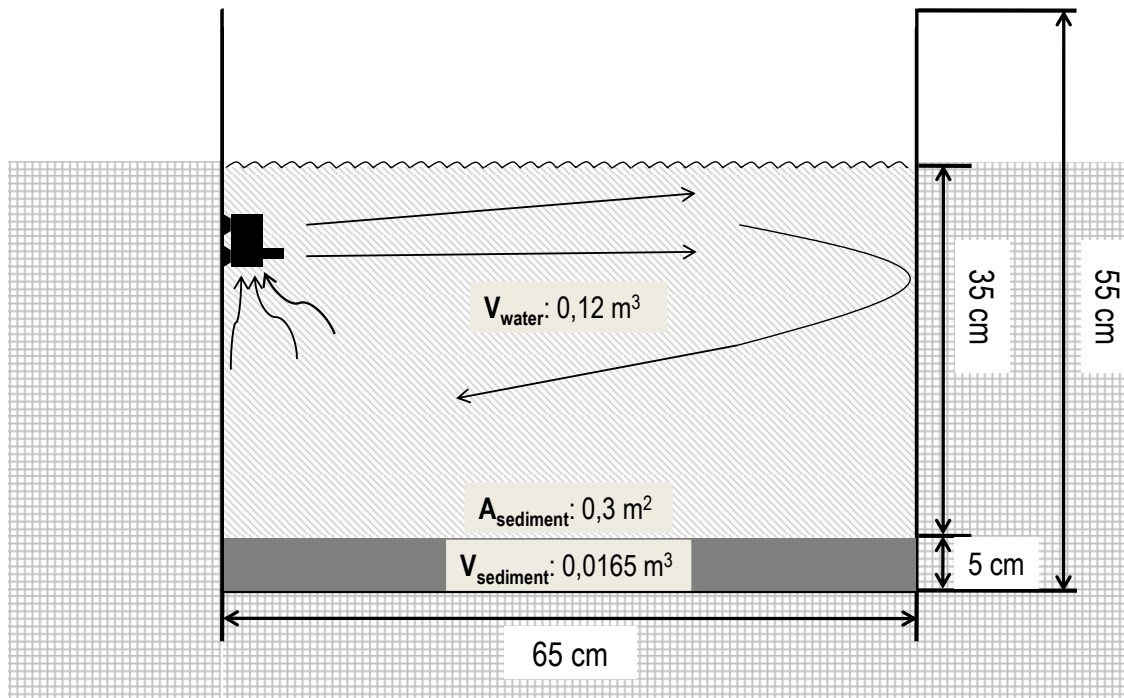
*Growth rates*

Samples from the Ribnitzer See and Zingster Strom were diluted 1:10 with the respective GF6 filtrates to prevent light limitation upon incubation. Diluted samples (20 ml) were placed into UV-C sterilised cuvettes (Licefa). Blanks contained only filtrates. Negative controls were samples without nutrient addition. PO<sub>4</sub>-stock solution (0.2 ml of 1 mmol l<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>) were added after the first measurement. Final concentrations were 10 µmol l<sup>-1</sup> PO<sub>4</sub>. Cuvettes were incubated at 15 °C (±1 K). Photon flux differed between 60 to 100 µmol m<sup>-2</sup>s<sup>-1</sup> (16:8 h) inside the incubator equipped by LED (Kunststofftechnik Rostock). There was no difference in growth rates between 50 and 110 µmol m<sup>-2</sup> s<sup>-1</sup> in earlier experiments (Schumann, personal observation). Nevertheless, cuvettes changed positions every day in a rotation scheme. Incubation started at least 12 h before the first measurement. Phytoplankton growth was followed *in vivo* with chlorophyll fluorescence as the biomass proxy (Gustavs et al., 2009) for 7 d. The fluorescence signal is stated in relative fluorescence units (rfu). All treatments were incubated and measured in five replicate cuvettes. They were shaken gently after each measurement to prevent accumulation of phytoplankton somewhere at the cuvette bottom. The fluorometer (MFMS, Hansatech) was calibrated by a Rhodamin-B standard (Karsten et al., 1996). Growth curves were fitted for a logistic growth (Schlegel, 1992)

by an iterative optimisation procedure (Excel Solver). The optimised parameter was the minimal accumulated deviance of measured and calculated biomasses, which were normalised by the calculated biomass. Biomass increases within 7 d were calculated from the curve parameters growth rate and capacity for each replicate separately.

### *Mesocosms*

The experimental set-up consisted of six barrels (polypropylene) with a total volume of 120 l, open to the atmosphere. The experiments were conducted *ex situ*. Therefore, the mesocosms were filled with sediment and water samples. Sediment was sampled at the ZS close to the Kirr bay, a shallow part of the lagoon with high macrophyte biomass (54° 25'38.2''N 12°41'23.3''E). The upper 5 cm of the sediment were sampled with a bottom grab sampler in February 2014 and stored until March 2014. It was assumed that only the upper 5 cm of the sediment contribute to a nutrient flux from sediment to water column. The total sediment height in the mesocosms was 5 cm (Figure 6). A water pump was used to fill the mesocosms with water from ZS in March 2014. No further Bodden water was filled in the mesocosms to prevent salt enrichment. Evaporated water was replaced by de-ionised water or rainfall. An internal water pump was necessary for water circulation (total pump volume per hour: 360 l). The total water column was turned over three times per hour. The mesocosms were buried up to 40 cm of the total height into the ground for temperature control. The growth of epiphytes was reduced by routinely cleaning of the mesocosm walls.



**Figure 6 Set-up for all mesocosm experiments.** Barrels (n=6) were placed 40 cm deep into the ground for temperature control. Sediment was sampled close to the Zingster Strom. Water samples were pumped from the Zingster Strom once in April 2014 and replaced in May 2015. The total water column was turned over three times per hour by an internal water pump.

Following the experimental approach three of six mesocosms had to stay free of macrophytes in 2014 and were therefore checked regularly. Then, all new macrophyte biomass was removed in these mesocosms. Macrophytes were determined on genus level. Each genus was pooled for dry mass (see 2.5 Biotic parameters). The other three mesocosms remained untouched, until October. Phytoplankton growth was not interfered in all mesocosms. Every two to four weeks samples were prepared for analysis of the abiotic parameters  $\text{PO}_4$ , TP, pH, salinity, turbidity and humic acid content. Biotic factors included Chl *a* in water samples and the total macrophyte biomass.

The mesocosm monitoring was intensified in 2015. The whole sampling procedure was repeated every two weeks. Macrophytes were not harvested throughout the season. There was no manipulation, except from water sampling. All mesocosms were assumed as black boxes with determined in- and outputs. Initial and final TP water concentration and TP through precipitation during the whole time were used as determined inputs. The difference was interpreted as P balance in the water column, whereas positive values showed a surplus of P and negative values a loss of P in the water column during the observation.

A Temperature/Light Logger (Hobo) measured the temperature inside the mesocosms. Rain was sampled separately by the Biological Station Zingst. The external TP inflow into the mesocosms was calculated with these values (Data Biological Station Zingst, unpublished). The O<sub>2</sub> saturation and concentration were measured in a 5 min interval between May and October by an optode (Hach-Lange Hq40). The ZS functioned as a control system. There, O<sub>2</sub> saturation was measured in a 10 min interval by an optode (Hach-Lange) (Data Biological Station Zingst, unpublished).

## 2.4 Abiotic parameters

### *pH, salinity, turbidity & oxygen*

A pH-electrode (Hach-Lange) measured pH. The electrode was regular two-point calibrated and stored in a 3 M potassium chlorid (KCl) solution. pH was determined in an aliquot right after sampling, or stored dark until analysis. Salinity was measured through conductivity at ambient temperatures (WTW Cond1970i). The measured values (mS cm<sup>-1</sup>) were transformed via conversion table (UNESCO, 1971) in salinity. Turbidity and humic acid content were both measured photometrically (Hach-Lange, DR 3900) in a 5 cm cuvette (optical glass, Helma) at 380 nm and 720 nm, respectively.

### *Phosphate*

PO<sub>4</sub> concentrations were determined with the molybdenum blue reaction according to Hansen and Koroleff (1999). Samples were filtered twice, with GF-6 and cellulose-acetate filters (Roth). Afterwards, samples were stored at –20 °C or instantly treated. Samples were incubated after addition of ascorbic acid and molybdenum-antimony reagents for 20 min. Samples were analysed automatically in a nutrient analyser (CFA, Alliance Instruments, Malcolm-Lawes and Wong, 1990), or by hand using a photometer at 885 nm (Hach-Lange DR 3900) in a 5 cm glass cuvette. The acid conditions upon the reaction may cleave some organically bound PO<sub>4</sub>, so that the result can be a bit overestimated and is usually named soluble reactive phosphorus. This results in elevated PO<sub>4</sub> concentrations, even though PO<sub>4</sub> is probably not determinable.

*Total phosphorus*

An alkaline persulphate solution digested water samples (seston) in tubes made of perfluoralkoxy-polymer (PFA). Oxisolv® (Merck) was used as digesting agent (Köthe and Bitsch, 1992) between 2000 and 2014. One spoon (delivered with the reagent powder, approx. 0.16 g) Oxisolv® was added to 15 ml sample (Hansen and Koroleff, 1999). The mixtures were digested in a laboratory microwave (Lavis-1000). Suspensions were heated up for 2 min at 120 °C and afterwards kept inside the microwave for 18 min intervals followed again by 2 min heating and 18 min waiting. Afterwards, the vessels were rather hot and under pressure depending on the initial vessel temperature for another 5 min or longer. Later, TP was digested in an alkaline persulphate solution (Hansen and Koroleff, 1999 modified by Berthold et al., 2015). A 100 ml persulphate solution with 5 g (ca. 0.2 mM)  $K_2S_2O_8$ , 3 g (ca. 0.5 mM)  $H_3BO_3$  and 1.5 g (0.375 mM) NaOH was used instead of Oxisolv®. The digestion solution (1.5 ml) was added to 15 ml digestion solution (Hansen and Koroleff, 1999). Fifteen ml of sample were mixed with 1.5 ml persulphate reagent and incubated at 90°C in PFA vessels for 24 h in an oven (Huang and Zhang, 2009). The samples were neutralised afterwards and stored at –20 °C until analysis. Neutralised samples were either analysed automatically in a nutrient analyser (CFA, Alliance Instruments, Malcolm-Lawes and Wong, 1990), or by hand using a photometer at 885 nm (Hach-Lange DR 3900) in a 5 cm glass cuvette (optical glass, Hellma) as a molybdenum blue complex.

An acid persulphate solution digested ash-free dry mass of macrophyte samples in glass tubes (Hansen and Koroleff, 1999 modified by Berthold et al., 2015). A 100 ml acid persulphate solution contained 5 ml  $H_2SO_4$  (4.5 mol l<sup>-1</sup>) and 5 g (ca. 0.2 mM)  $K_2S_2O_8$ . Samples were weighed and 15 ml de-ionised water were added. One and a half ml acid persulphate reagent was added and the samples were incubated at 90°C for 24 h in an oven (Huang and Zhang, 2009). The samples were neutralised afterwards and stored at –20 °C until analysis. Neutralised samples were analysed by hand using a photometer (Hach-Lange, DR 3900) at 885 nm in a 5 cm glass cuvette (optical glass, Helma) as a molybdenum blue complex.

## 2.5 Biotic parameters

### *Seston*

GF 6 filter (Roth) for seston content were precombusted at 450 °C in a muffle oven (Heraeus Instruments, Type M110) for 4 h. Water samples (n=3) were filtered and filters afterwards dried at 60 °C for 24 h. Blank filters were treated with filtrate. Filters were re-weighed after drying. Equation 1 was used to calculate the seston concentration.

**Equation 1 Formula to calculate seston content in water samples.**

$$\text{Seston [mg TM l}^{-1}\text{]} = \frac{(\text{filter}_{\text{sample } 60^{\circ}\text{C}} - \text{filter}_{\text{empty}}) - (\text{filter}_{\text{blank } 60^{\circ}\text{C}} - \text{filter}_{\text{empty}})}{\text{filtered volume [l]}}$$

### *Chlorophyll a*

The Chl *a* concentration was used as proxy for phytoplankton biomass. Water samples were filtered on GF 6 filters (Roth) and stored at –20 °C until analysis. Blank filters were treated with filtrate. Ethanol (EtOH, 96%, Roth) was used as extraction agent (Strickland and Parsons, 1972). Three ml EtOH were added to each filter and cold extracted at 8 °C in a fridge. This was the routine procedure until 2014. The new extraction procedure included to pestle the filters with 10 ml EtOH and addition of one spatula tip magnesium carbonate (MgCO<sub>3</sub>, Roth). The MgCO<sub>3</sub> removed any present acid, which will degrade the Chl *a* (Ritchie, 2006). Samples were centrifuged at 5000 rpm (revolutions per minute) for 5 min. Afterwards extinction was measured in 1 cm or 5 cm glass cuvettes (optical glass) at 665 nm and 750 nm. Equation 2 was used to calculate the Chl *a* concentration in µg l<sup>-1</sup> (DIN 38412, 1985; Strickland and Parsons, 1972).

**Equation 2 Formula to calculate Chlorophyll *a* content in water samples.**

$$\mu\text{g Chl } a \cdot \text{l}^{-1} = \frac{(E_{665} - E_{750}) \cdot v \cdot 10^6}{83 \cdot V \cdot d}$$

v – extraction volume in ml;

V – filtered volume in ml;

D – cuvette length in cm;

83 – absorption coefficient in EtOH.

### *Ratios*

Ratios were calculated out of Chl *a* to seston, seston to TP, and Chl *a* to TP. Growth can be determined by a changing composition between particulate organic matter and Chl *a*. However, the monitoring data set lacks on particulate organic matter concentrations. Further, the composition of particulate organic matter in the DZBC is rich on non-biomass related C (Görs et al., 2007; Schumann and Rentsch, 2001). Nausch and Setzkorn (2002) showed for the Oder estuary a possible approach of Chl *a*:seston. A ratio above 2 indicates freshly produced autochthonous material. A ratio above 1 indicates relatively fresh produced material, that was resuspended in the water column. However, the DZBC is polymictic and has a high concentration of particulate matter, which is not phytoplankton. Therefore, the ratio of above 1 will be used in this work to determine a possible biomass increase. The Chl *a*:TP ratio is a tool in lake monitoring (Sas, 1989a) and those parameters are correlated with each other in lakes. The Chl *a*:TP ratio usually correlates positive during summer months and under conditions of P or N limitations (Horn and Uhlmann, 1991 and sources cited therein). It will be used in this work to determine the utilisation of P by phytoplankton and a possible effect of dilution towards the Baltic Sea. Seston:TP ratios were used to estimate the influence of resuspension on the water column. If the sediment acts as nutrient source, an increase of seston will result in an increase of TP as well. In this case, seston and TP are positively correlated to each other.

### *Macrophyte biomass*

Macrophytes were sampled by hand. Species were determined onto genus level. The biomass was dabbed dry with paper towels and weighed as fast as possible. Afterwards biomass was dried for 24 h at 90 °C in an oven (Co. Heraeus). Dried samples were reweighed after 1 h incubation in a desiccator for dry mass (DM). The DM was used to calculate biomass per m<sup>2</sup>. Aliquots of what were taken and burned at 550 °C for 4 h. The remains were weighed again and used to calculate ash and ash-free dry mass (AFDM). Ash was used for TP extractions. Afterwards mg TP g<sup>-1</sup> in the ash was calculated to mg TP g<sup>-1</sup> DM of macrophyte biomass. Then, the calculated values were converted into macrophyte bound TP per m<sup>2</sup> (mg TP m<sup>-2</sup>).

*Animal biomass*

The mesocosms experiments in 2015 were densely populated by gammarids. Therefore, the gammarid biomass was determined, too. Gammarids were determined on species level. The whole water column and sediment was filtered through a mesh (mesh size 2 mm) to sample every individual. Afterwards, the gammarids were separated from remaining particulate matter by sieving. The biomass was dabbed dry with paper towels and weighed as fast as possible. The biomass was dried for 24 h at 90 °C in an oven (Co. Heraeus). Dried samples were reweighed after 1 h incubation in a desiccator for DM. The DM was used to calculate biomass per m<sup>2</sup>.

**2.6 Quality management***Determination limits and control charts*

Determination (also quantification) limits (DL) were calculated for all experiments (except long-term data). The blank method was used for DL calculation. Therefore, 10 blanks for PO<sub>4</sub>, TP, seston, and Chl *a* were measured at once (DIN 32645, 2008; Wellmitz and Gluschke, 2005). Blanks consisted of de-ionised water (<0.05 µS m<sup>-1</sup>). The DL amounted to 0.10 µmol l<sup>-1</sup> PO<sub>4</sub>, 0.3 µmol l<sup>-1</sup> TP, 0.45 mg l<sup>-1</sup> seston, and 1.05 µg l<sup>-1</sup> Chl *a* between 2013 and 2015. Standards were used as reference values for PO<sub>4</sub> determination. Glucose-6-phosphat and diphenylphosphate were used as standard by digestion reactions for TP. Potassiumdihydrogenphosphate was used as standard for direct PO<sub>4</sub> determinations. Blanks (n=3) and standards (n=1) were measured in every analytical series. Finally, the values were plotted in control charts (see Figure A 1 and Figure A 2). Standard deviations or spans were calculated from replicate sample measurements, normalised over the arithmetic means and were summarised in range control charts (Figure A 1 to Figure A 4). Average sample deviations of seston and Chl *a* (no standards available) were 8.2 % and 3.9 %, respectively for the duration of the experiments. The average deviation of standards from the nominal value was added to average standard deviation of sample replicates (Doerffel, 1990) to a combined standard deviation.

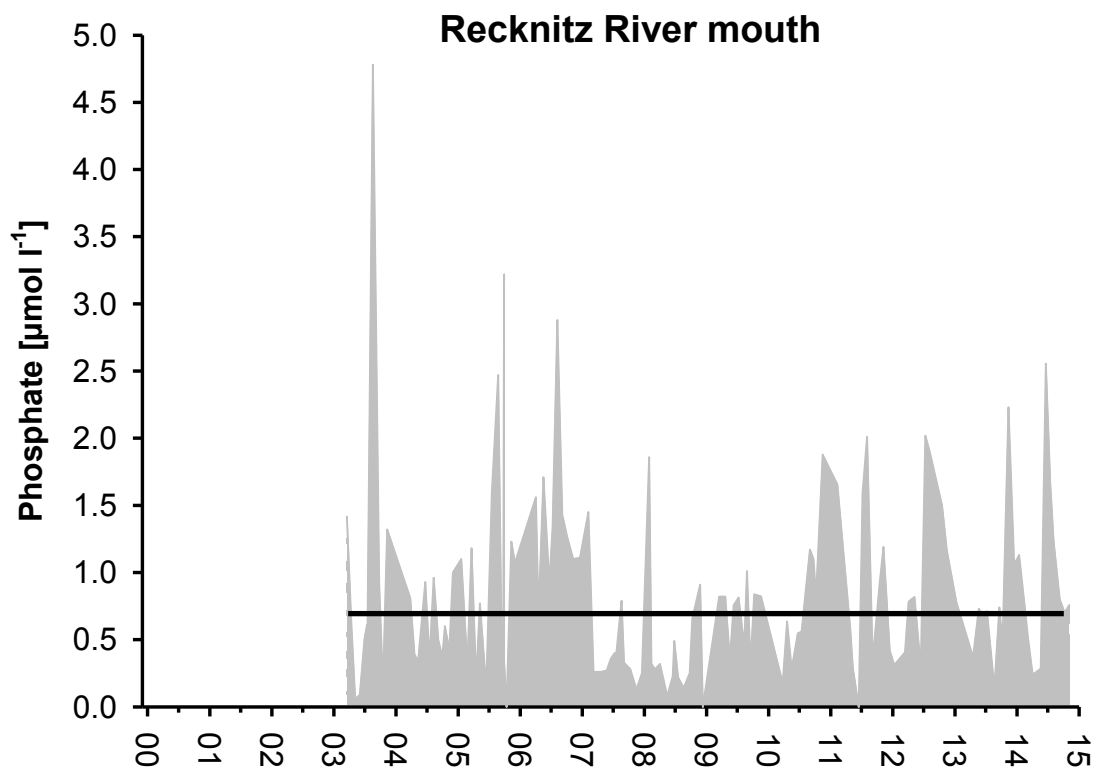
*Statistical analysis*

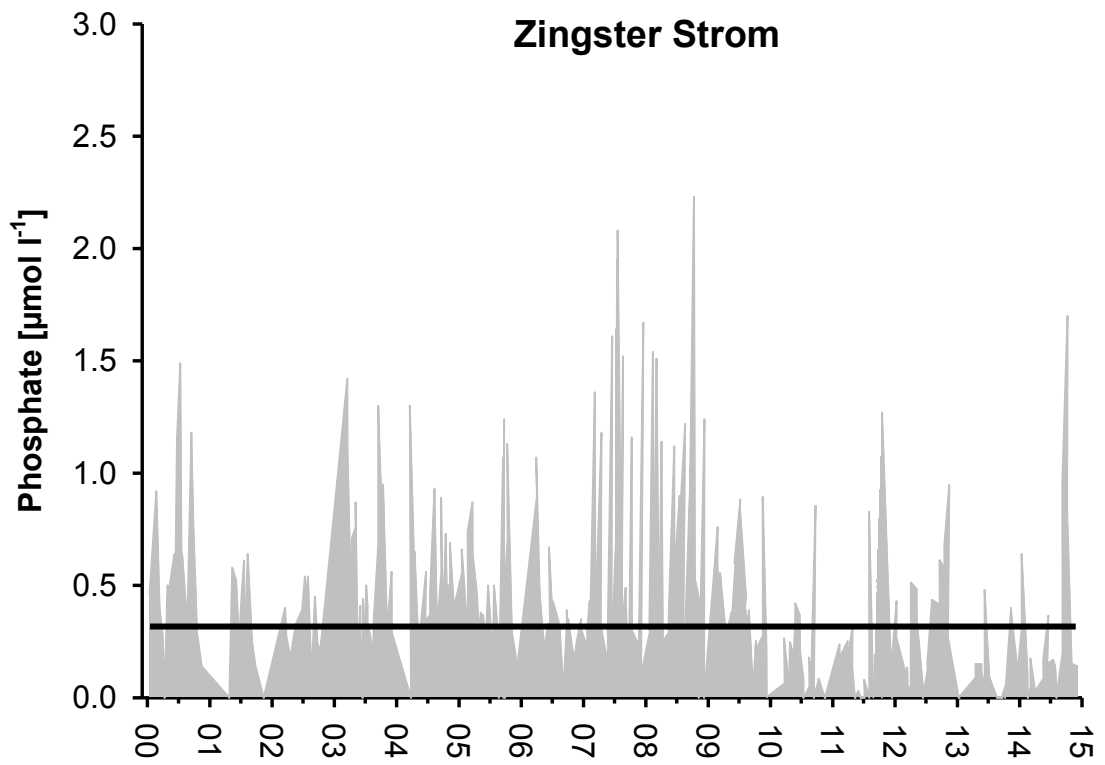
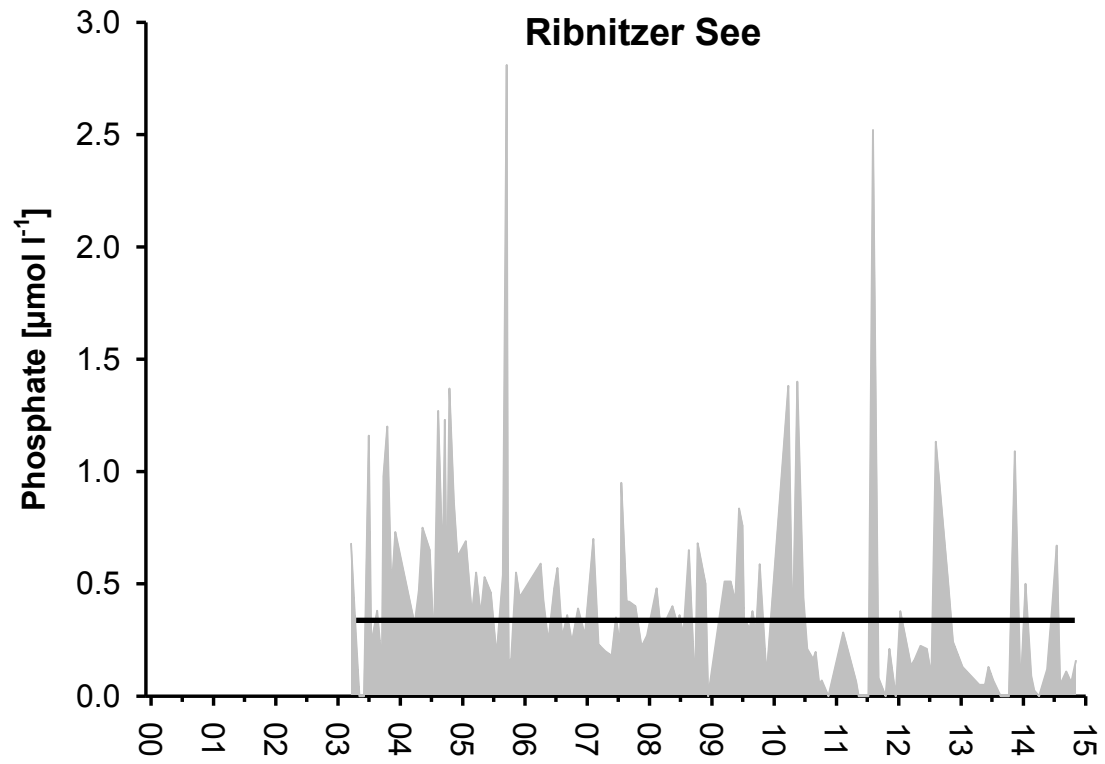
SigmaPlot 11 was used for statistical analysis. Whisker-Box plots were used as fast comparison between all sampling sites. The box plots show the median, data points between 10 to 90 % distribution, and individual outliers as points. Shapiro-Wilk-test tested all data for normal distribution. T-test was used to compare two sampling sites with each other. The paired t-test was used to compare experiments before and after treatment. Non-normal distributed treatments were analysed with the Wilcoxon-Signed-Rank-Test and non-normal distributed sampling sites with the Mann-Whitney-U-test. The correlation analysis used the Spearman-Rho-test for non-parametric data. All results stated with “significant” had a significance level of  $p \leq 0.05$  in this work. A star (\*) displays the significance level in figures.

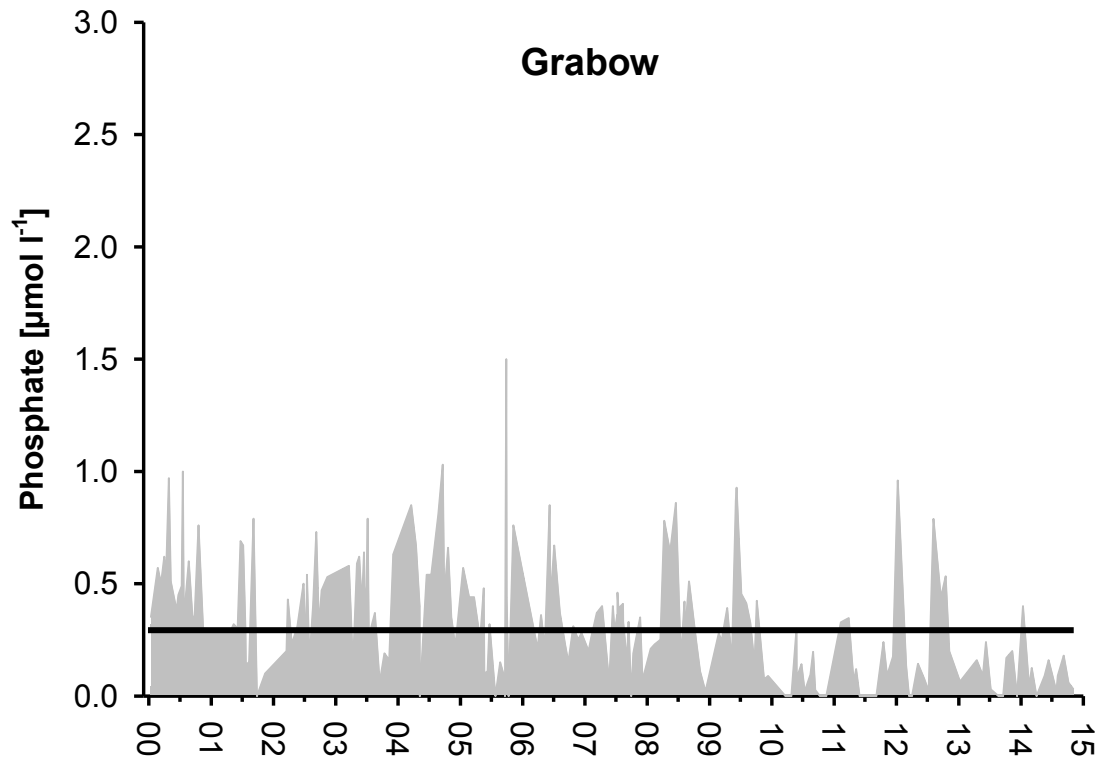
### 3 Results

#### 3.1 Long-term development of phosphorus between 2000 and 2014

The highest concentrations of bio-available  $\text{PO}_4$  were found in the station RM (Figure 7). High peaks with up to  $5 \mu\text{mol l}^{-1}$  were measured, but were a rare event. However, the mean  $\text{PO}_4$  concentration was with  $0.6 \mu\text{mol l}^{-1}$  twice as high, compared to the close by station RS with only  $0.3 \mu\text{mol l}^{-1}$ . The mean concentration of  $0.3 \mu\text{mol l}^{-1}$  was found also in all other Bodden parts (see Figure 7 and Figure A 5). The low concentration of  $0.3 \mu\text{mol l}^{-1}$  is close to the determination limit. Further,  $\text{PO}_4$  concentrations above  $1 \mu\text{mol l}^{-1}$  were found in 28 % of all samples in the RM, but only 1.5 – 9 % between GB and RS, respectively. High peaks were occasionally measured in all Bodden. It is noticeable, that the  $\text{PO}_4$  concentration showed no seasonality in all Bodden. Instead, there was an occurrence of high and low concentrations, independent of season. Years with high precipitation showed above average  $\text{PO}_4$  concentrations in the RM, but not at other sampling sites.

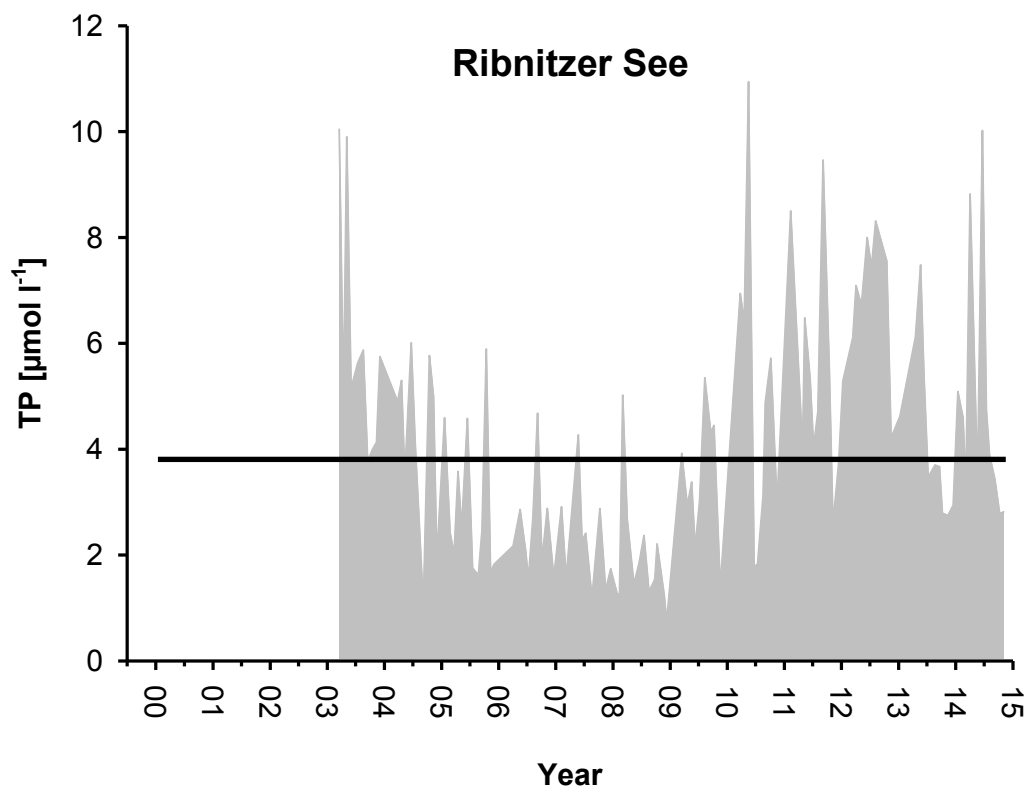
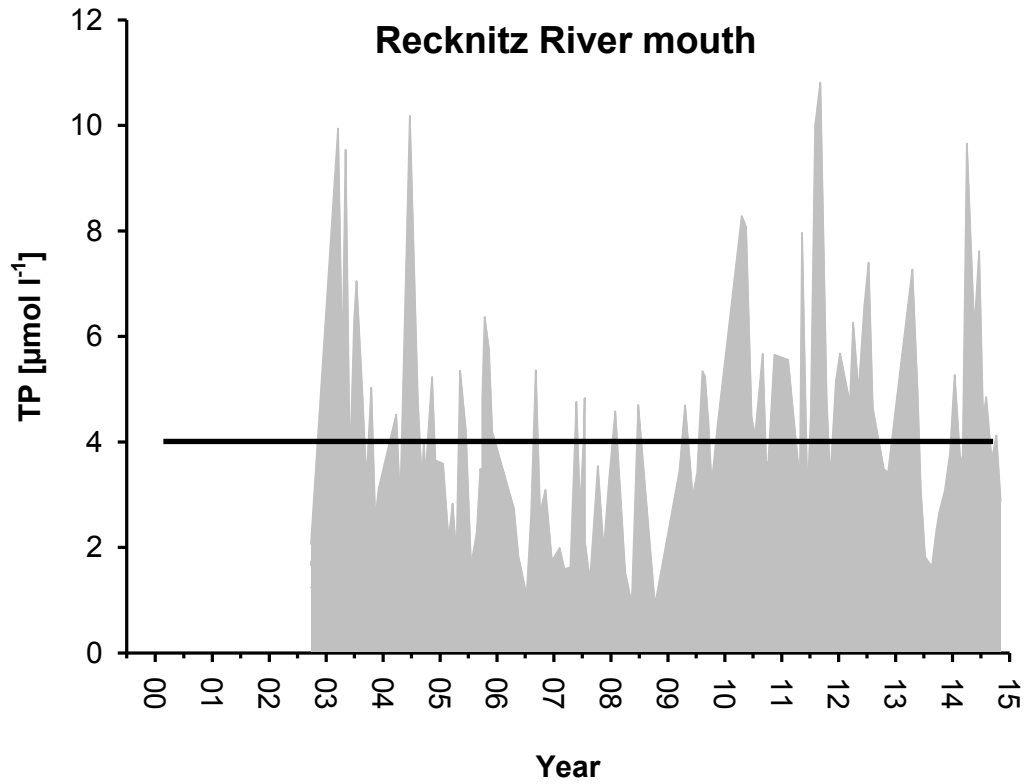


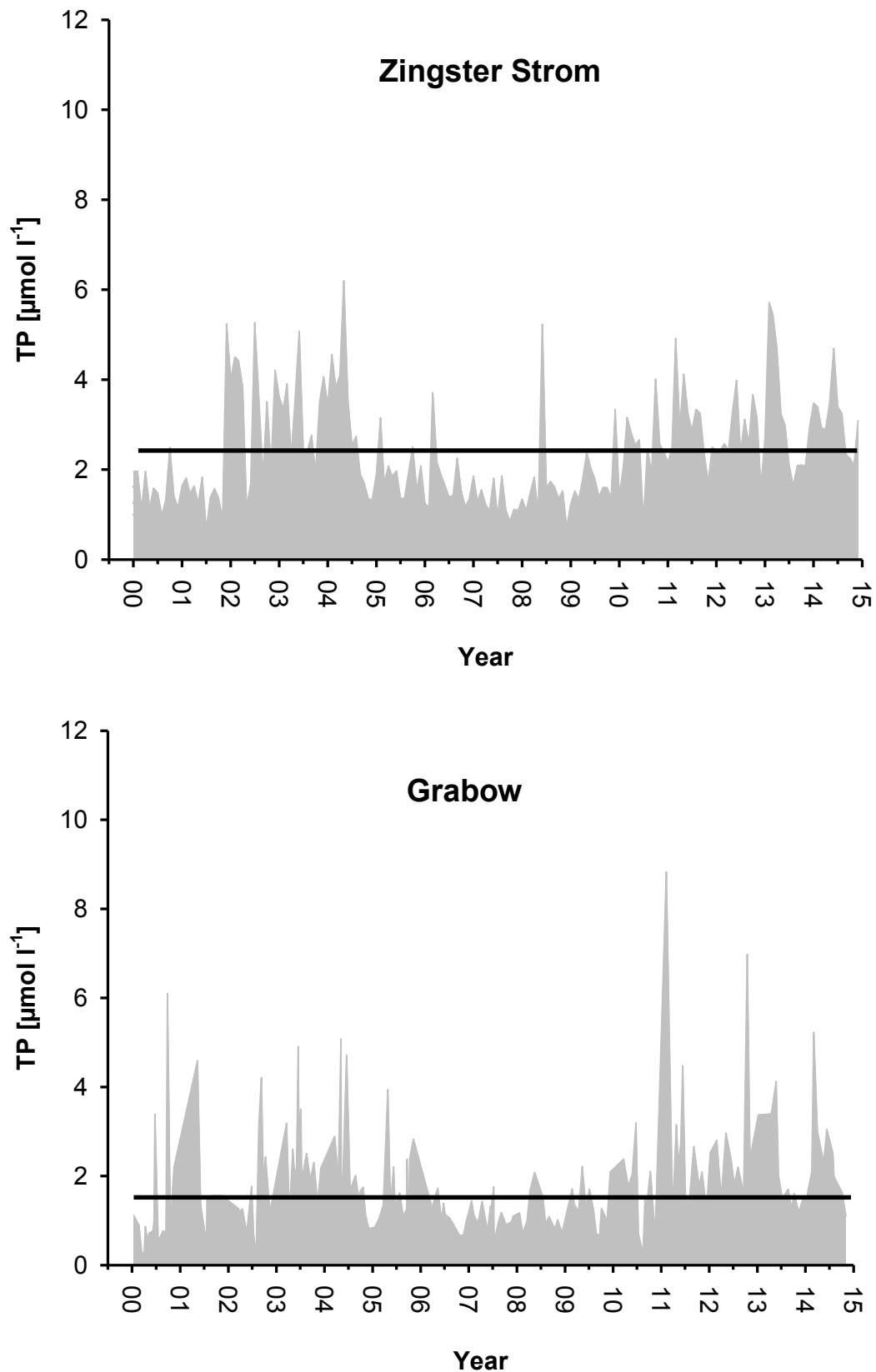




**Figure 7** Long-term development of phosphate ( $\text{PO}_4$ ) [ $\mu\text{mol l}^{-1}$ ] in the Recknitz River mouth, Ribnitzer See, Zingster Strom and Grabow during 2000 – 2014. Freshwater inflow – Recknitz River mouth (RM,  $n=132$ ), the innermost Bodden part – Ribnitzer See (RS,  $n=133$ ), middle part – Zingster Strom (ZS,  $n=342$ ), and outer part – Grabow (GB,  $n=163$ ). The solid black line shows median of all values during the sampling time. Data set: Biological Station Zingst.

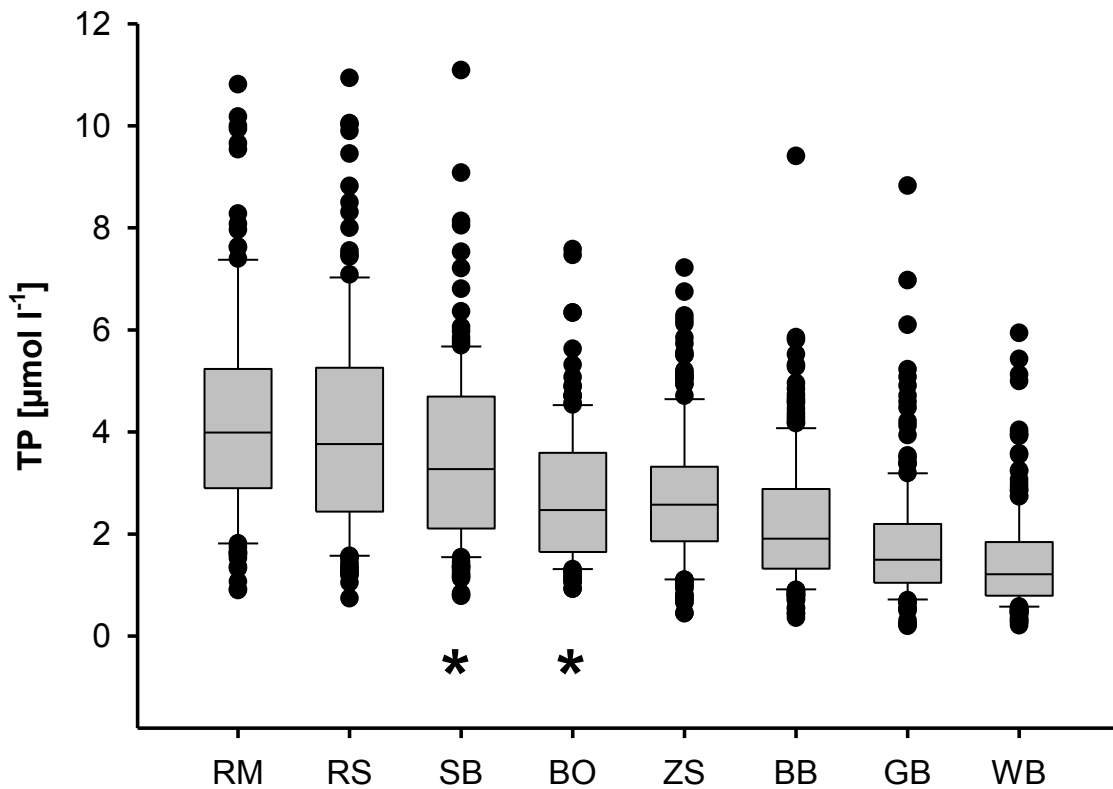
A similar pattern was found for the TP concentrations. Highest concentrations were measured in RM and RS (Figure 8). In contrast to  $\text{PO}_4$ , there was a clear difference between years with high and average precipitation. It is particularly striking, that there was a periodic oscillation. TP showed lowest concentrations during 2006 – 2009 with a sudden increase during 2011. These high concentrations remained in the RS for two additional years, whereas the concentrations were thinned out by sea water in the following Bodden parts. Additional, in years with high precipitation, peaks in TP concentration were still lower in Bodden parts located far away from the station RM. All other charts for  $\text{PO}_4$  and TP long-term development of other Bodden parts can be found in the appendix (see Figure A 5 and Figure A 6).





**Figure 8** Long-term development of total phosphorus (TP) [ $\mu\text{mol l}^{-1}$ ] in the Recknitz River mouth, Ribnitzer See, Zingster Strom and Grabow during 2000 – 2014. Freshwater inflow – Recknitz River mouth (RM, n=132), the innermost Bodden part – Ribnitzer See (RS, n=133), middle part – Zingster Strom (ZS, n=207), and outer part – Grabow (GB, n=163). The solid black line shows median of all values during the sampling time. Data set: Biological Station Zingst.

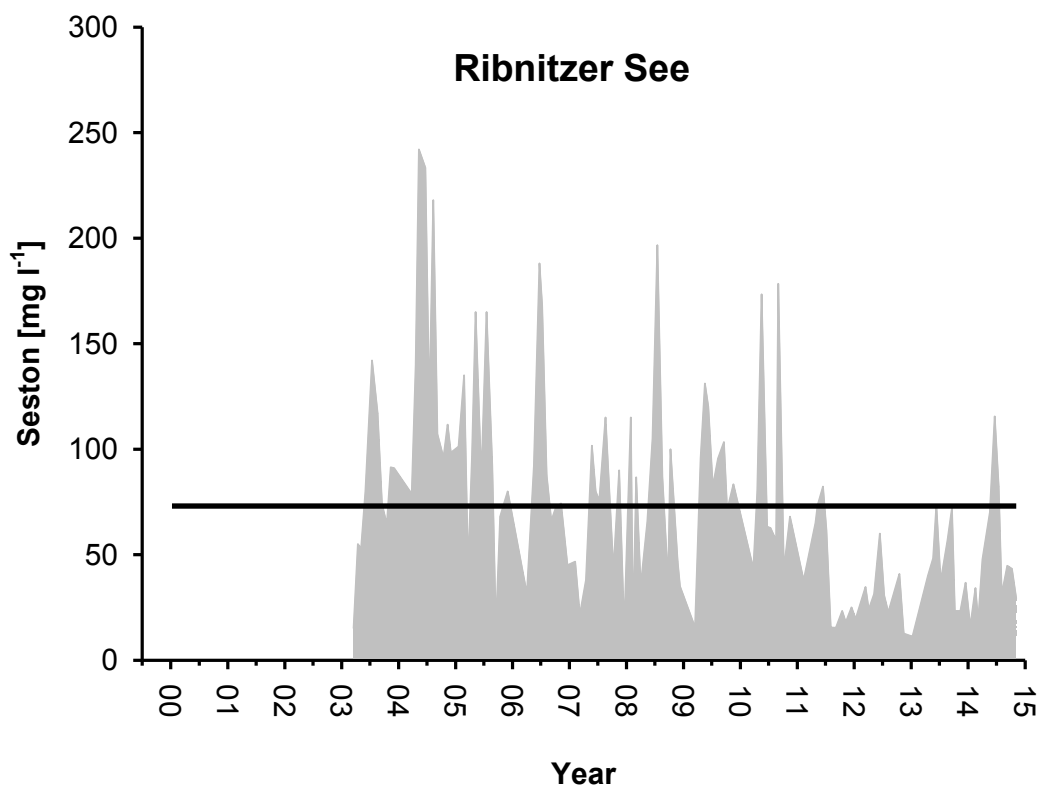
This gradient is visualised for all Bodden parts during the sampling time in Figure 9. Highest long-term mean concentrations were measured in RM and RS. The following sampling sites showed lower concentrations. The concentration divided in half at the GB and the variance became lower. However, high outliers were measured in all Bodden with concentrations up to  $12 \mu\text{mol l}^{-1}$  TP. The stations SB and BO differed significantly (Mann-Whitney-U-test;  $p \leq 0.001$ ,  $n=171-173$ ). This was not expected, because both Bodden are behind the narrow Meiningenstrom.

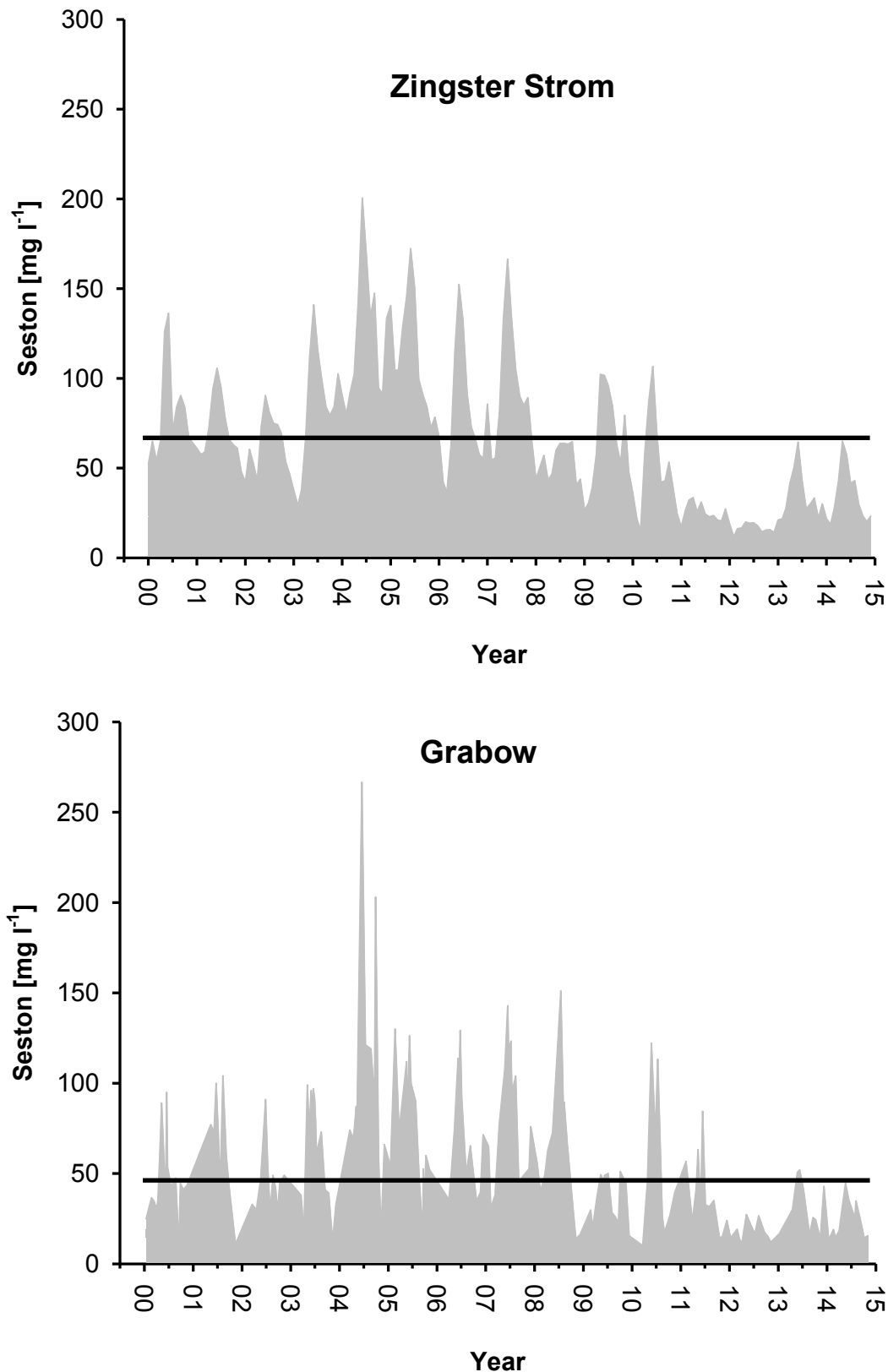


**Figure 9** Boxplot of total phosphorus concentration (TP) [ $\mu\text{mol l}^{-1}$ ] of all monitored sampling sites during 2000 – 2014. From west to east: RM – Recknitz River mouth ( $n=121$ ); RS – Ribnitzer See ( $n=133$ ); SB – Saaler Bodden ( $n=138$ ); BO – Bodstedter Bodden ( $n=142$ ); ZS – Zingster Strom ( $n=207$ ); BB – Barther Bodden ( $n=161$ ); GB – Grabow ( $n=163$ ); WB – Werder/Bock ( $n=162$ ). Star (\*) shows a significant difference between the stations (Mann-Whitney-U-test;  $p < 0.001$ ,  $n=171-173$ ). Data set: Biological Station Zingst.

### 3.2 Ecosystem responses to phosphorus loads between 2000 and 2014

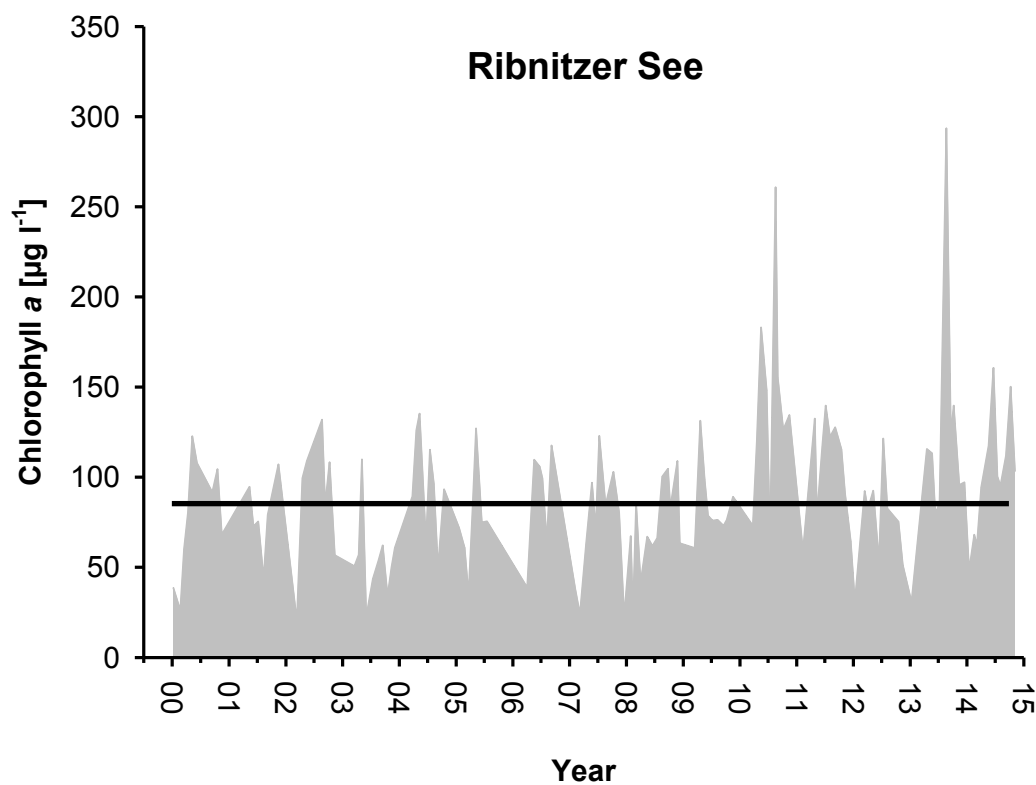
There were some remarkable reactions in the DZBC during the observation period. Highest seston concentrations were measured in all Bodden in 2003 and 2006 (Figure 10 Ribnitzer See, Zingster Strom and Grabow). Concentrations below the long-term median were measured during 2011 to 2013. In contrast to seston, TP showed lowest concentrations during 2006 – 2009 with a sudden increase during 2011 (see Figure 8, p.29). High TP concentrations remained in the RS for two additional years, whereas the seston concentrations were below average for the next three years in all other Bodden parts.

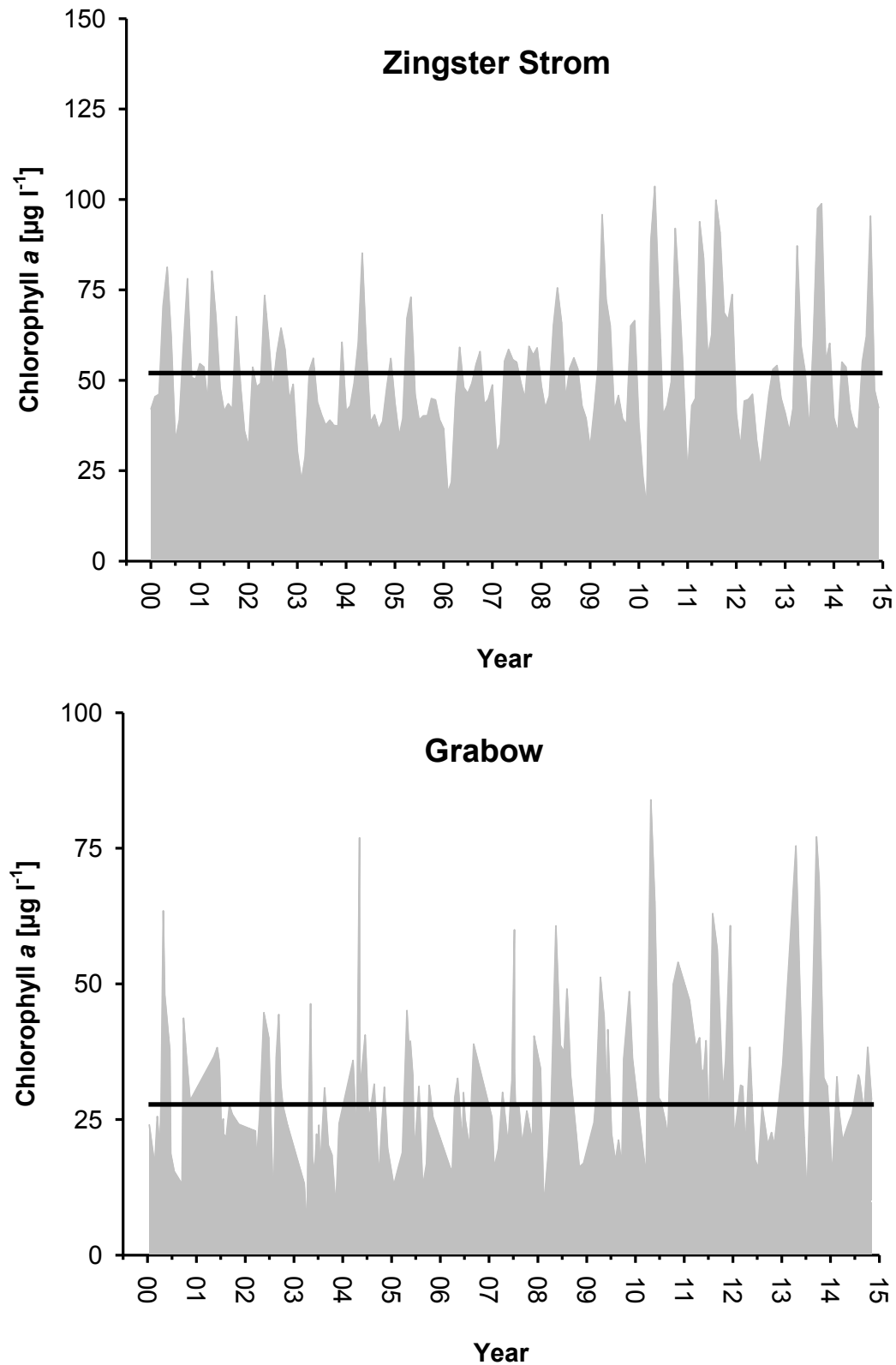




**Figure 10** Long-term development of seston [mg l<sup>-1</sup>] in the Ribnitzer See, Zingster Strom and Grabow during 2000 – 2014. Innermost Bodden part – Ribnitzer See (RS, n=135), middle part – Zingster Strom (ZS, n=332), and outer part – Grabow (GB, n=163). The solid black line shows median of all values during the sampling time. Data set: Biological Station Zingst.

This was not observed for the Chl *a* concentration during the same period (Figure 11). However, there was a high peak during 2010 with Chl *a* concentrations 2.5 times higher than the long term median. There was a following reduction in 2012 for all Bodden. It is recognisable that the sudden TP increase during 2011 overlapped with the Chl *a* increase in the same year. It is interesting that the Chl *a* concentration dropped again in 2012 even though there were still elevated TP concentrations. Surprisingly the Chl *a* concentration rose again in 2013, while the TP concentration decreased (see p.29 Figure 8). The long-term development charts of Chl *a* and seston for the other Bodden parts can be found in the appendix (Figure A 7 and Figure A 8).

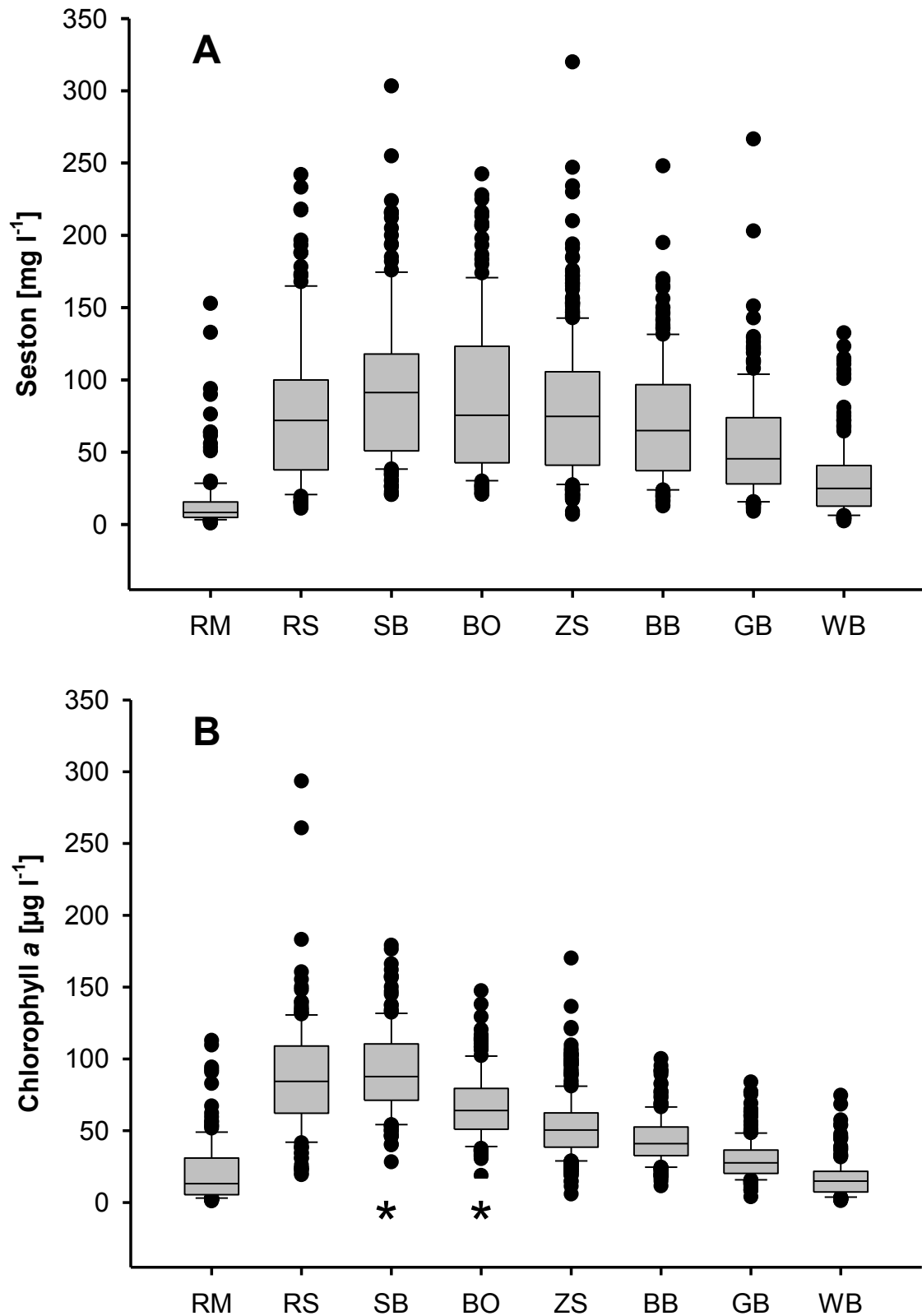




**Figure 11** Long-term development of Chlorophyll *a* [ $\mu\text{g l}^{-1}$ ] in the Ribnitzer See, Zingster Strom and Grabow during 2000 – 2014. Innermost Bodden part – Ribnitzer See (RS,  $n=151$ ), middle part – Zingster Strom (ZS,  $n=350$ ), and outer part – Grabow (GB,  $n=159$ ). The solid black line shows median of all values during the sampling time. Please note the different y-axes scaling for better visualisation of differences. Data set: Biological Station Zingst.

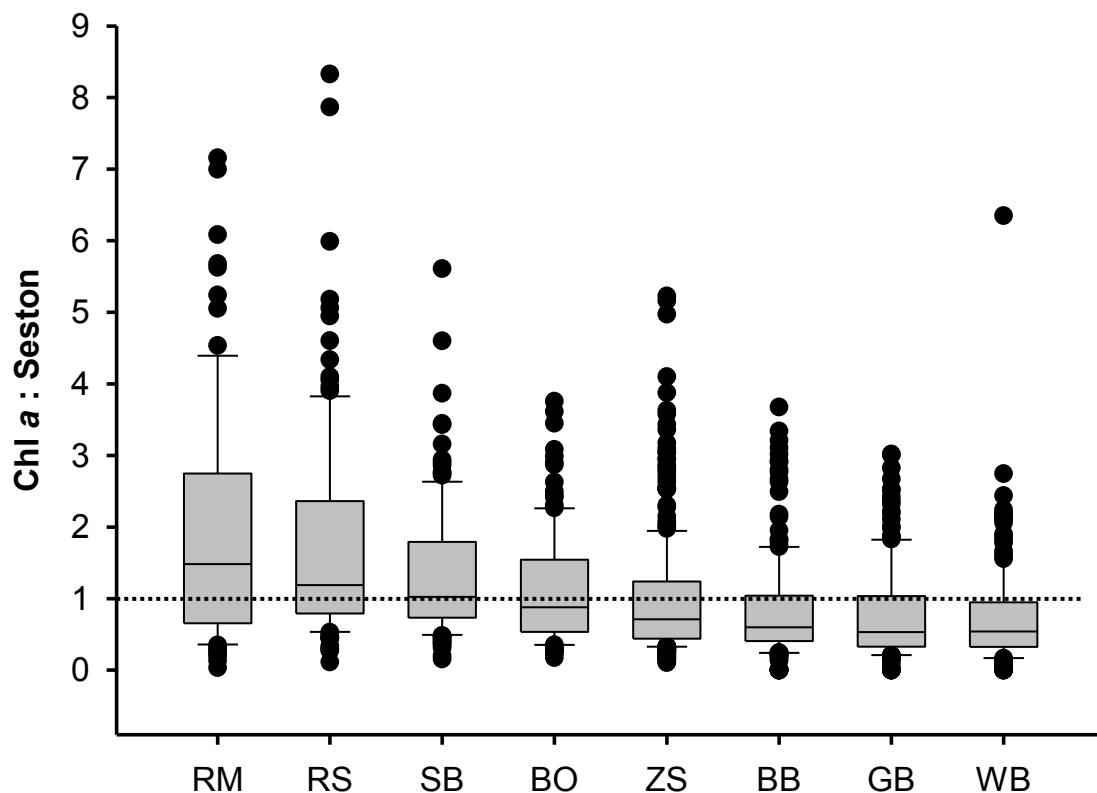
The development of all Bodden parts for Chl *a* and seston are visualised in Figure 12. The concentration of seston was always very low in the RM (Figure 12 A). The highest mean seston concentrations were found in the SB. Particular important are the great differences between RM and RS. This shows, that seston is not transported to the DZBC, but develops there. The median seston concentration was almost the same between BO (west) and BB (east) inclusive the ZS in between. There was no hydrological separation detectable between the ZS and BO through the Meiningenstrom in case of seston. Seston concentration thinned out eastwards to the GB with second lowest concentration at the Station WB, close to the Baltic Sea. However, the range of seston between the 25 – 75 % quartile was similar for all Bodden, expect for the inflow (RM) and outflow (WB).

The Chl *a* concentration showed a rather different distribution (Figure 12 B). Concentrations were lowest innermost at RM and outermost at WB. The highest Chl *a* concentrations were in the RS and SB. Interestingly the inner Bodden SB and BO were significantly different (Mann-Whitney-U test,  $p \leq 0.001$ ,  $n=171-173$ ) for Chl *a* but not for seston (Mann-Whitney-U test,  $p=0.147$ ,  $n=171-173$ ). The Chl *a* concentration at all sampling sites fluctuated between 30 – 100  $\mu\text{g l}^{-1}$  Chl *a*. In contrast to the seston concentrations, the dilution effect to the Baltic Sea was more prominent in the Chl *a* concentrations. Only 25 % of the highest Chl *a* concentrations from ZS to WB were close to the 25 % lowest Chl *a* concentrations of RS and SB.



**Figure 12** Different variables of particulate matter of all monitored sampling sites during 2000 – 2014. From west to east: RM – Recknitz river mouth; RS – Ribnitzer See; SB – Saaler Bodden; BO – Bodstedter Bodden; ZS – Zingster Strom; BB – Barther Bodden; GB – Grabow; WB – Werder/Bock.  
 A – seston concentration [mg l<sup>-1</sup>]: RM – n=133; ; RS – n=135, SB – n=140, BO – n=143, ZS – n=332, BB – n=163, GB – n=163, WB – n=161. Data set: Biological Station Zingst.  
 B – chlorophyll a concentration [µg l<sup>-1</sup>]: RM – n=149; RS – n=151, SB – n=157, BO – n=153, ZS – n=350, BB – n=159, GB – n=159, WB – n=157. Star (\*) shows a significant difference between the stations (Mann-Whitney-U-test; p<0.001, n=171-173). Data set: Biological Station Zingst.

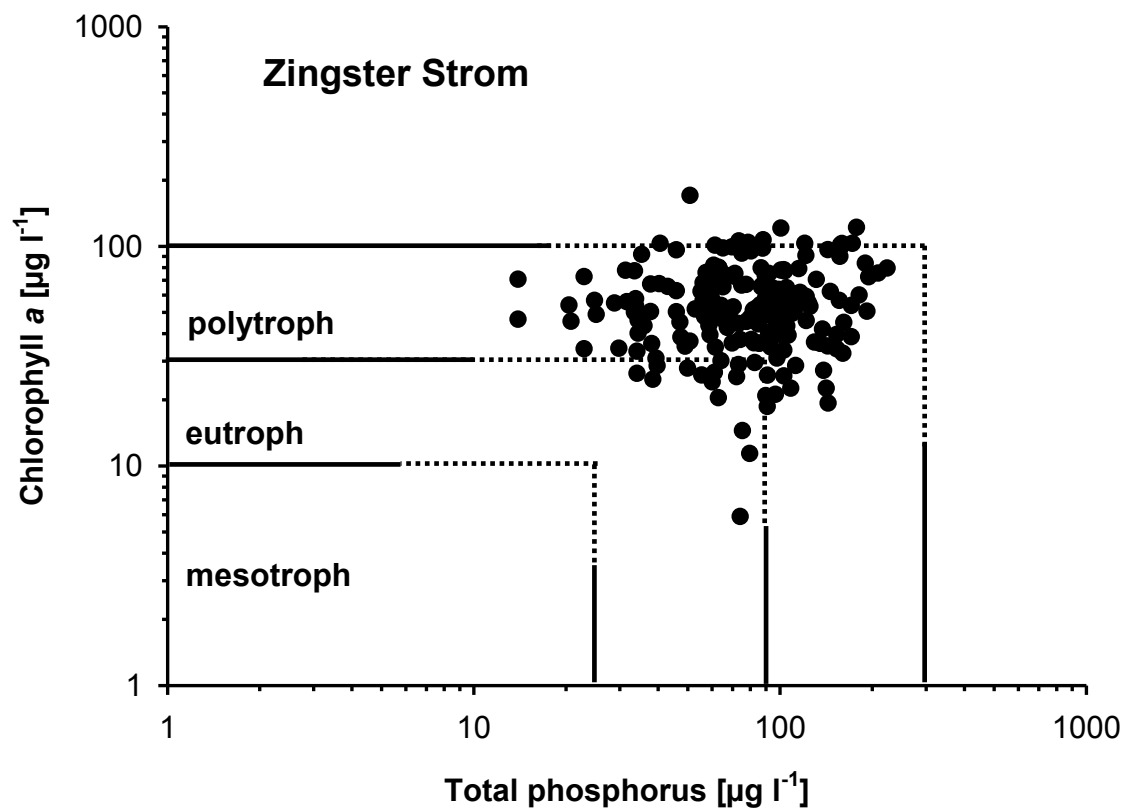
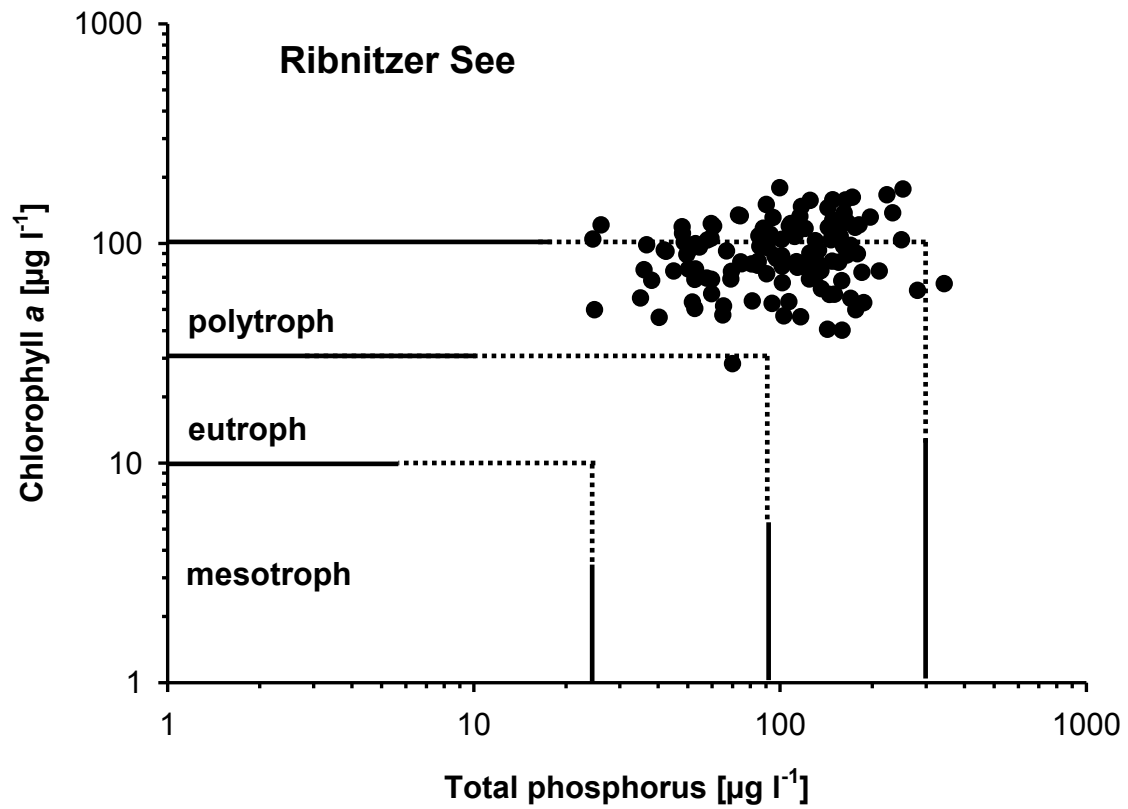
This becomes important, when looking at the growth proxies Chl *a*:seston and Chl *a*:TP. The median Chl *a*:seston ratio is for the stations RM, RS and SB during the whole sampling time above 1 (Figure 13). This shows, that there was most of the time a growth potential present. In contrast to the inner Bodden (RS, SB, BO), the ratio for BB, GB and WB was less than 25 % of the time close to this ratio. However, there was a significant difference between SB and BO (Mann-Witney-U-test,  $p=0.025$ ,  $n=171-173$ ). This shows, that not only the total concentrations of seston and Chl *a* is different between these Bodden parts, but the relative abundance changed as well.

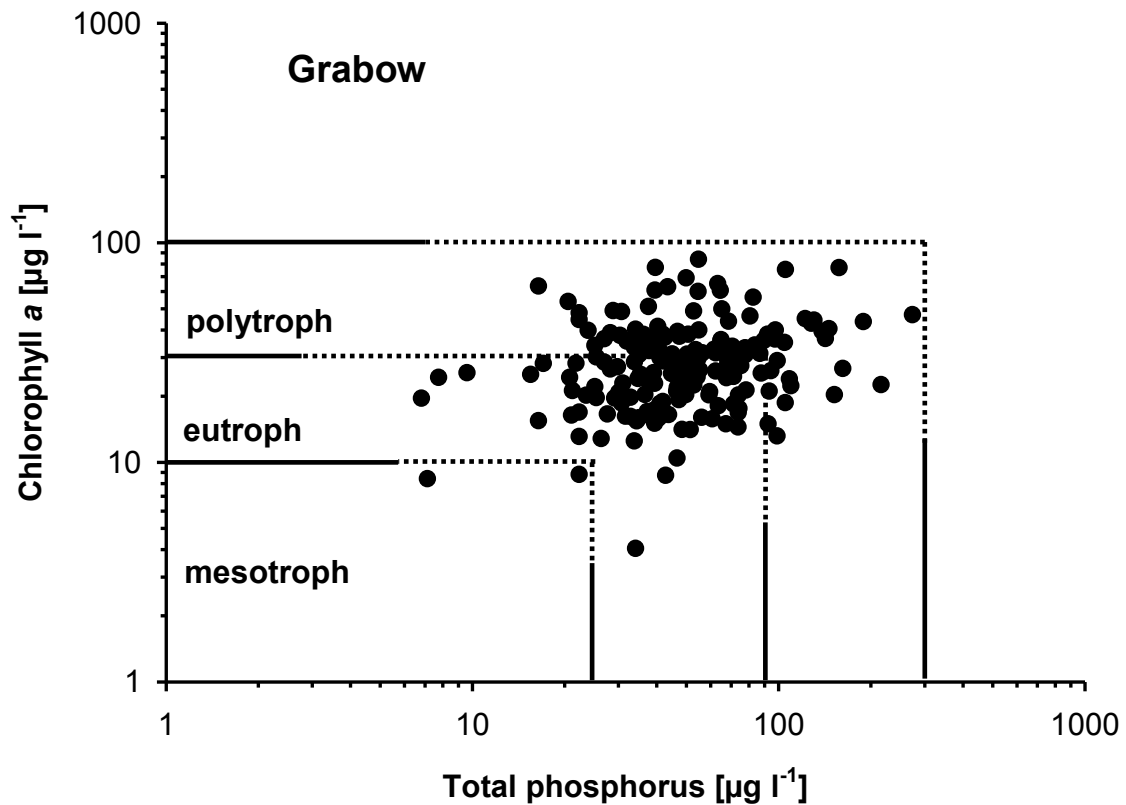


**Figure 13** Ratio of chlorophyll *a* concentration to seston concentration for all sampled sites during 2000 – 2014 presented as Whisker-Box plots. From west to east: RM – Recknitz River mouth ( $n=119$ ); RS – Ribnitzer See ( $n=122$ ); SB – Saaler Bodden ( $n=127$ ); BO – Bodstedter Bodden ( $n=130$ ); ZS – Zingster Strom ( $n=325$ ); BB – Barther Bodden ( $n=159$ ); GB – Grabow ( $n=163$ ); WB – Werder/Bock ( $n=157$ ). Dotted line shows a mean ratio of 1. Data set: Biological Station Zingst.

There was no clear correlation between Chl *a*:TP during the whole sampling time (Figure 14). All Bodden showed a eutrophic to polytrophic state for the whole sampling period. The trophic state decreased towards the Baltic Sea. However, this did not change the ratio of Chl *a* to TP. There was a clear span between actual TP concentration and obtained Chl *a* concentration in all Bodden parts. The same Chl *a* concentration of e.g.  $100 \mu\text{g l}^{-1}$  Chl *a* was obtained with TP concentrations between  $25 - 250 \mu\text{g l}^{-1}$  ( $0.8 - 8 \mu\text{mol l}^{-1}$ ). There is no prediction possible of phytoplankton biomass

with TP alone. The same pattern was already seen in the long-term development. The Chl *a*:TP charts for the other Bodden parts can be found in the appendix (Figure A 9).





**Figure 14** Chlorophyll *a* concentrations to total phosphorus concentrations ratio in  $\mu\text{g l}^{-1}$  as log-log plot for Ribnitzer See, Zingster Strom and Grabow. Scale limit for trophic level after Landerarbeitsgemeinschaft Wasser (LAWA), (1999). Data set: Biological Station Zingst.

The separation of the data set into seasons was more useful to analyse periodic effects. Chl *a* to TP of the SB was significantly correlated during spring in all years (Table 5). The RS and ZS showed never a significant correlation of Chl *a* to TP. All correlation coefficients for the ZS were rather low. The other Bodden parts BO, BB, GB and WB showed a significant correlation mostly during winter or for the whole sampling time.

Seston to TP showed a completely different pattern compared to Chl *a* to TP. Seston correlated negative to TP in all other Bodden parts, except the WB (Table 6). However, the negative correlation was only significant during autumn or winter and only for the stations ZS and SB. Surprisingly a seston increases did not induce an elevated TP concentration. Further, the years with high precipitation showed the lowest seston:TP ratios.

**Table 5 Overview of all correlation coefficients (Spearman-Rho) for chlorophyll *a* to total phosphorus separated in seasons and for the whole sampling time 2000 – 2014 for all Bodden parts.** Correlation coefficients were calculated with Spearman-Rho test. The seasons were separated in: Spring: March, April, May; Summer: June, July, August; Autumn: September, October, November; Winter: Dezember, January, February. The data set (Biological Station Zingst) was split into seasons to evaluate the effect of seasonality. Light grey shimmed rows show significant correlation. RS – Ribnitzer See, SB – Saaler Bodden, BO – Bodstedter Bodden, ZS – Zingster Strom, BB – Barther Bodden, GB – Grabow, WB – Werder/Bock.

	Spring			Summer			Autumn			Winter			All years		
	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N
RS	0.318	0.07	33	-0.077	0.636	40	0.125	0.493	32	-0.029	0.913	15	0.111	0.226	120
SB	0.404	0.022	32	-0.079	0.624	40	0.045	0.801	33	0.437	0.068	18	0.161	0.074	125
BO	0.185	0.286	35	-0.098	0.546	40	0.393	0.022	34	0.411	0.07	20	0.176	0.046	129
ZS	0.104	0.442	57	0.065	0.663	55	0.019	0.883	61	0.218	0.237	31	0.056	0.423	204
BB	0.220	0.170	40	0.01	0.538	40	0.23	0.147	41	0.423	0.049	23	0.29	<0.001	144
GB	0.249	0.081	50	0.056	0.665	61	0.0582	0.706	44	0.573	0.005	22	0.199	0.007	177
WB	-0.126	0.572	44	0.61	<0.001	43	0.249	0.107	41	0.314	0.045	22	0.376	<0.001	150

**Table 6 Overview of all correlation coefficients for seston to total phosphorus separated in seasons and for the whole sampling time 2000 – 2014 for all Bodden parts.** Correlation coefficients were calculated with Spearman-Rho test. The seasons were separated in: Spring – March, April, May; Summer – June, July, August; Autumn – September, October, November; Winter – Dezember, January, February. The data set was split into seasons to evaluate the effect of seasonality. Light grey shimmed rows show significant correlation. RS – Ribnitzer See, SB – Saaler Bodden, BO – Bodstedter Bodden, ZS – Zingster Strom, BB – Barther Bodden, GB – Grabow, WB – Werder/Bock. Data set: Biological Station Zingst.

	Spring			Summer			Autumn			Winter			All years		
	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N	Correlation	P-value	N
RS	-0.046	0.8	33	-0.172	0.279	41	0.065	0.686	41	-0.129	0.603	18	-0.067	0.443	133
SB	-0.224	0.201	34	-0.108	0.501	41	-0.326	0.0352	42	-0.349	0.118	21	-0.217	0.01	138
BO	-0.165	0.341	35	-0.025	0.878	41	-0.106	0.495	43	-0.483	0.019	23	-0.112	0.182	142
ZS	-0.203	0.13	57	-0.064	0.64	56	-0.335	0.008	61	-0.179	0.333	31	-0.211	0.002	205
BB	-0.11	0.492	41	-0.197	0.216	41	-0.053	0.731	44	-0.105	0.62	24	-0.109	0.183	150
GB	0.022	0.879	50	0.062	0.623	61	0.045	0.759	48	-0.424	0.045	23	-0.001	0.986	182
WB	0.352	0.02	44	0.156	0.31	44	0.296	0.05	44	-0.302	0.158	23	0.215	0.007	266

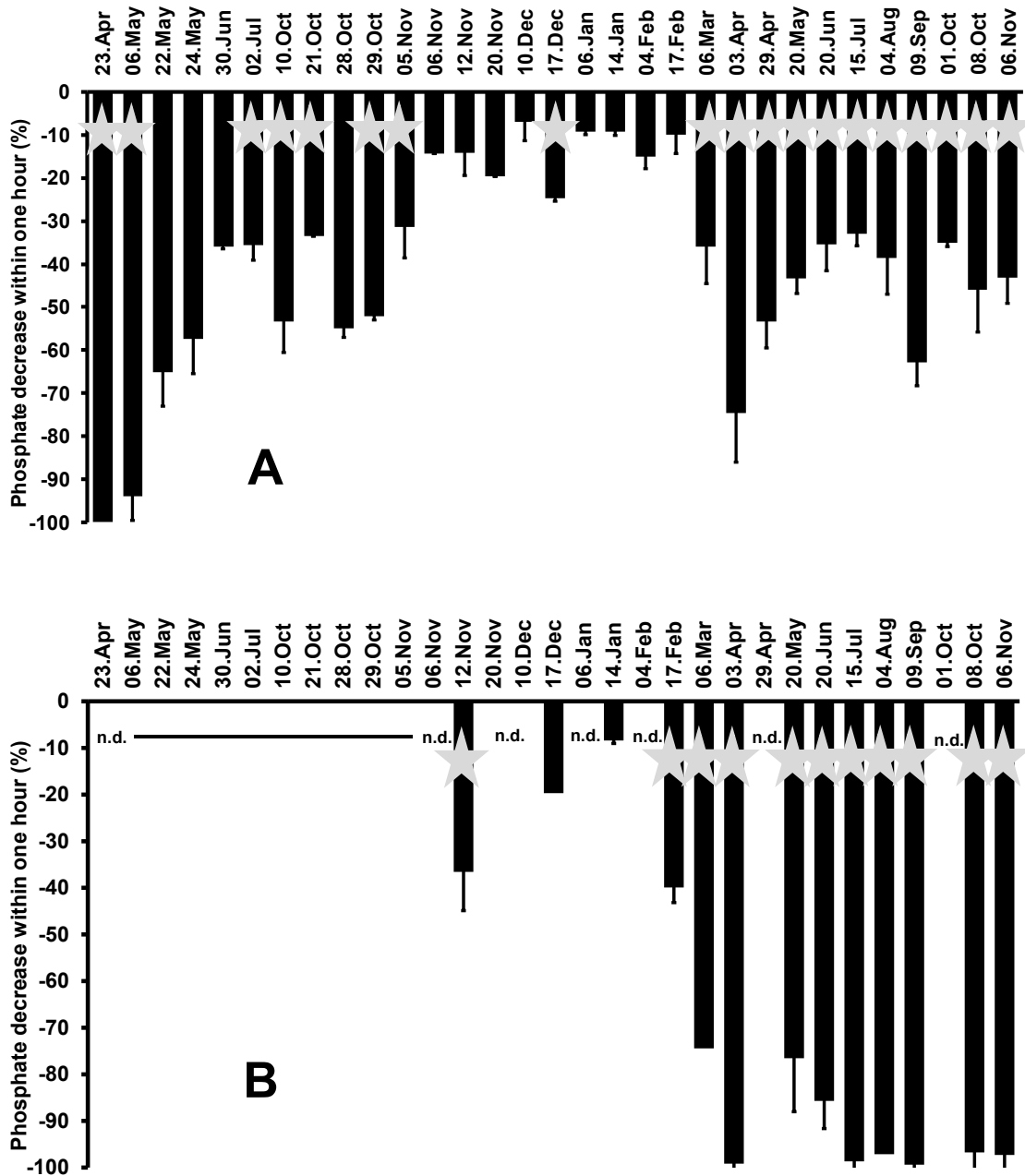
### 3.3 Velocity of pulsed nutrient inputs into particulate matter

Berthold & Schumann already implemented parts of the following chapter in the publication “Phosphorus dynamics in a polymictic eutrophic lagoon” 2016 (submitted). This includes Figure 15 and the referring text. The presented data are original from the author itself, if not stated otherwise.

#### *Seasonal patterns of pulsed nutrient inputs into particulate matter*

Fastest PO<sub>4</sub> decreases were measured during spring and autumn months in the ZS (Figure 15 A). The decrease of PO<sub>4</sub> ranged between 70 – 100 % for both years. There was a lower decrease in both years between May and August. PO<sub>4</sub> decreases ranged from 30 – 50 % in both years. Only one sample took up the whole 10 µmol l<sup>-1</sup> PO<sub>4</sub> pulse in one hour during the winter months. The complete pulse was taken up during all other months within 24 h (May & June 2013 not determined). The initial decrease rate in the first hour had no influence on the uptake in 24 h. The decrease rate in the RS (Figure 15 B), close to the freshwater influx of the Recknitz River, showed the same pattern. The initial uptake rates in the RS during the first hour were always higher compared to the ZS. However, there was no complete PO<sub>4</sub> decrease during December and January as well.

The PO<sub>4</sub> decrease at the ZS correlated positively with the Chl *a* (Spearman-Rho, coefficient=0.441, p=0.012, n=28) and seston concentration (Spearman-Rho, coefficient=0.584, p=0.001, n=28). There was no significant correlation in the RS for Chl *a* (Spearman-Rho, coefficient=0.396, p=0.173, n=13) or seston (Spearman-Rho, coefficient=0.527, p=0.06, n=13). The fast decreases in the RS were surprising because P inputs by the Recknitz River were very close (Figure 7 and Figure 8).



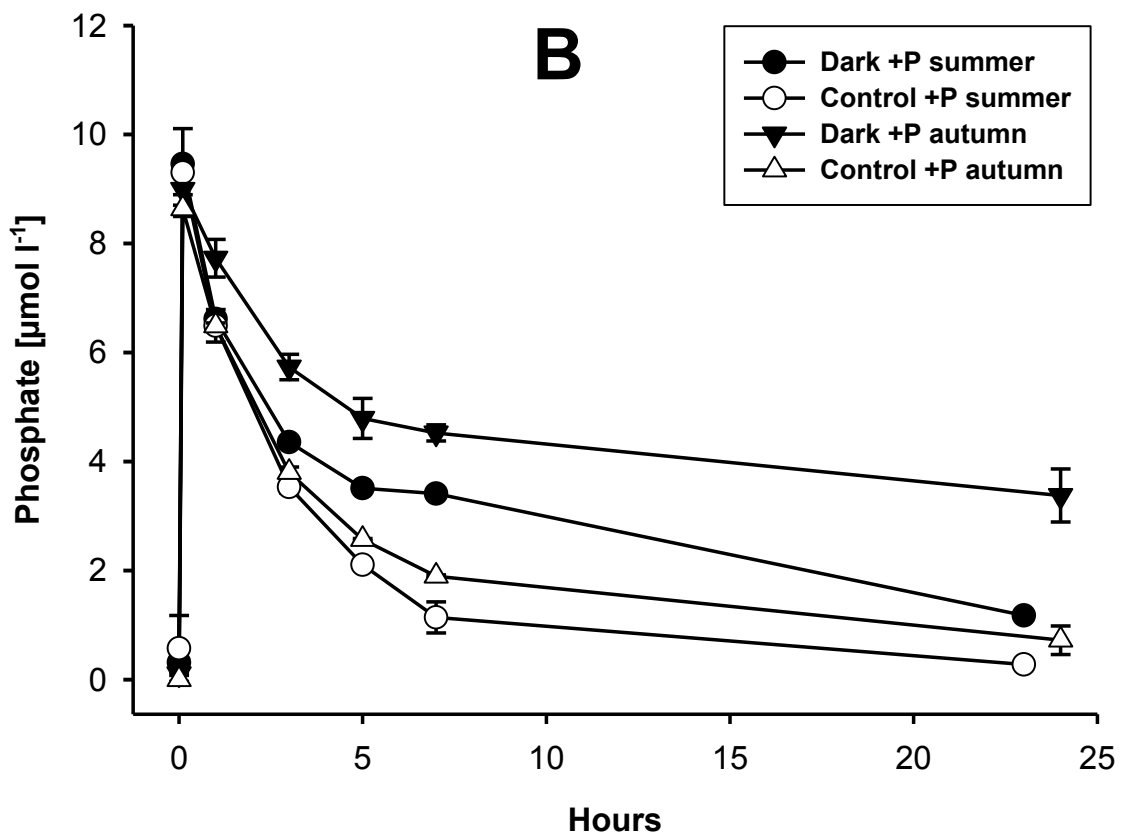
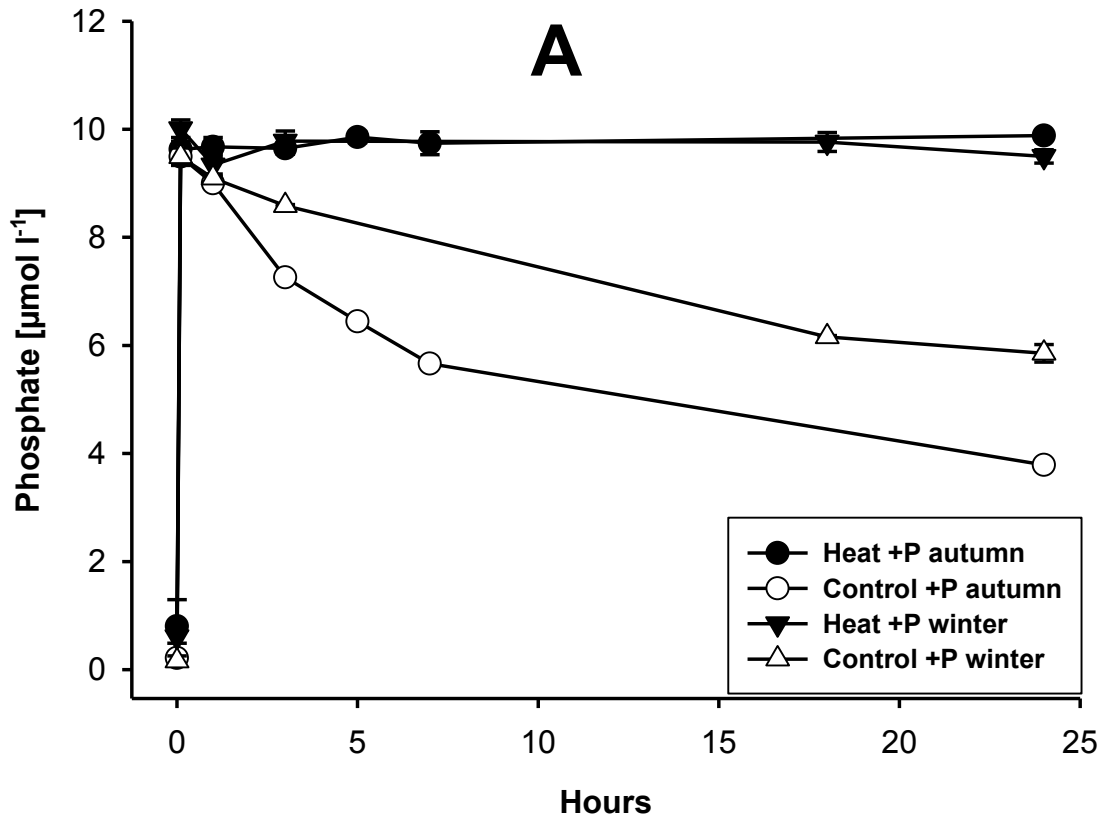
**Figure 15** Phosphate decrease (%) within the first hour after a  $10 \mu\text{mol l}^{-1}$  phosphate pulse. A: Zingster Strom, B: Ribnitzer See. Dates for A: April 2013 – Nov. 2014; Dates for B: Nov. 2013 – Nov. 2014. Bars labelled with a star had taken up the phosphate pulse in 24 h completely. Error bars are calculated as standard deviation ( $n=3$ ). Incubation in batch tanks at  $15 \text{ }^\circ\text{C}$  ( $\pm 1 \text{ }^\circ\text{K}$ ), photon flux  $100 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ , light:dark 16:8 hours.

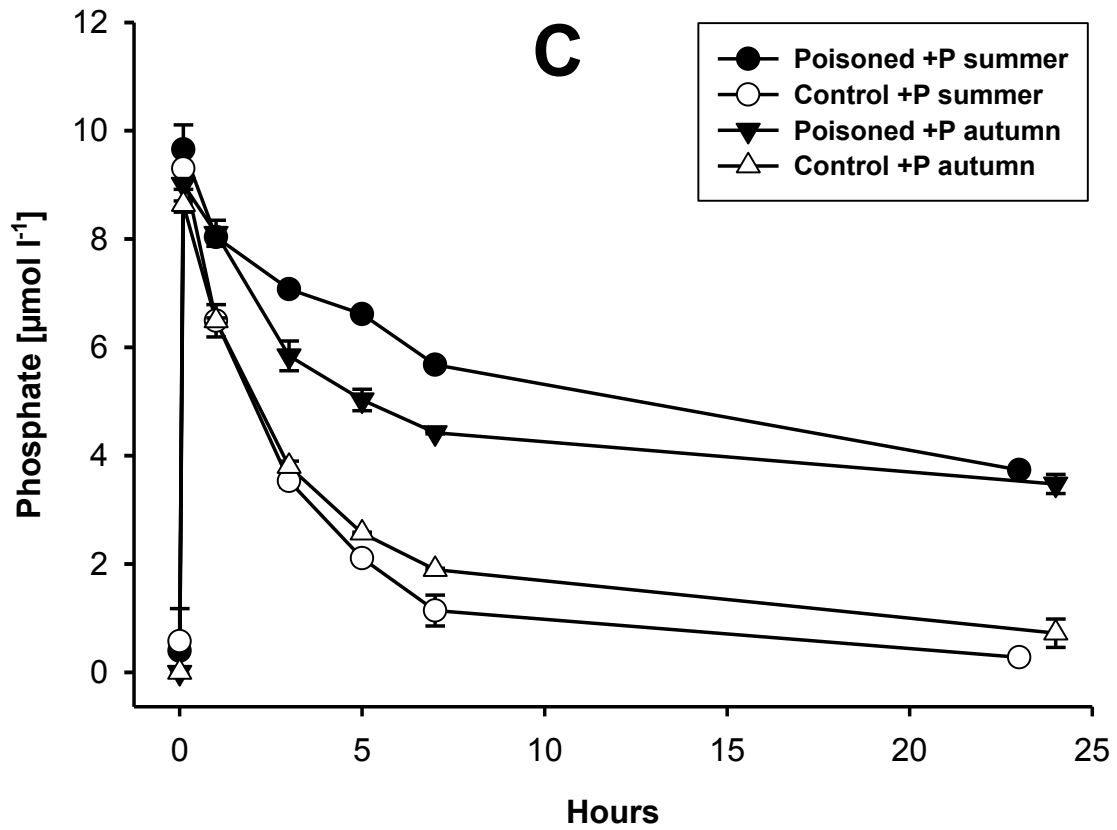
*Pulse velocities in heated, poisoned and dark incubated experiments*

The ways of the PO<sub>4</sub> pulses into seston were determined by treating seston samples with heat, poison, and dark incubation. The pulse velocities in treated experiments were rather different. There was no PO<sub>4</sub> decrease in heated samples (Figure 16 A). Simultaneously there was no PO<sub>4</sub> release in heated samples without PO<sub>4</sub> addition (data not shown). This shows that there was no overlapping effect through for instance lysis. Seston concentration remained the same after treatment (Seston<sub>before</sub>: 21.9±4.6 mg l<sup>-1</sup>, Seston<sub>after</sub>: 22.5±2.5 mg l<sup>-1</sup>). The Chl *a* concentration dropped from 34 µg l<sup>-1</sup> to 3.1 µg l<sup>-1</sup>. The absent PO<sub>4</sub> decrease excluded adsorptive processes from PO<sub>4</sub> to the batch tanks in general and non-living seston in particular.

The dark incubation showed a reduced phosphate decrease in dark incubated samples during summer and autumn (Figure 16 B). Dark incubations lost 10 to 40 % less PO<sub>4</sub> compared to the controls. This was surprising, because one of the main PO<sub>4</sub> nutrient fluxes are postulated to happen during dark conditions in the DZBC. Decrease of PO<sub>4</sub> during autumn differed significantly (t-test, P=0.006), but not during summer (t-test, p=0.057) compared to the controls. There was no release of PO<sub>4</sub> measured in dark incubated unpulsed samples (data not shown), which shows no increased PO<sub>4</sub> release by microbial activity during the duration of the experiments.

The same pattern was found during the phytoplankton poison experiments (Figure 16 C). Samples were incubated with a PS II inhibitor (DCMU) and respiratory chain inhibitor (sodium azide). The phosphate decrease was reduced up to 40 % compared to the untreated samples during both times. The reductions in the treated samples differed significantly from untreated ones (t-test, p<sub>summer</sub>=0.01, p<sub>autumn</sub>=0.05). This was the same decrease pattern, like in the dark incubated samples. This shows that there are some additional PO<sub>4</sub> demanding compartments in the plankton.





**Figure 16** Velocity of  $10 \mu\text{mol l}^{-1}$  phosphate pulses during the first 24 hours. All samples were from the Zingster Strom. A: Phosphate decrease after heating at  $60 \text{ }^\circ\text{C}$  ( $\pm 2 \text{ }^\circ\text{K}$ ) ( $n=2$ ) for 2 hours. Autumn 06.11.2013; Winter: 06.01.2014. B: Phosphate decrease after dark incubation for 12 hours. Summer sample  $n=1$ , autumn sample  $n=2$ . C: Phosphate decrease after intoxication with DCMU and sodium azide. Summer  $n=1$ , autumn  $n=2$ . B & C Summer: 02.07.2013; Autumn: 29.09.2014. Controls of all experiments were  $n=2$ . Error bars are calculated as standard deviation. Incubation in batch tanks at  $15 \text{ }^\circ\text{C}$  ( $\pm 1 \text{ }^\circ\text{K}$ ), photon flux  $100 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ , light:dark 16:8 hours.

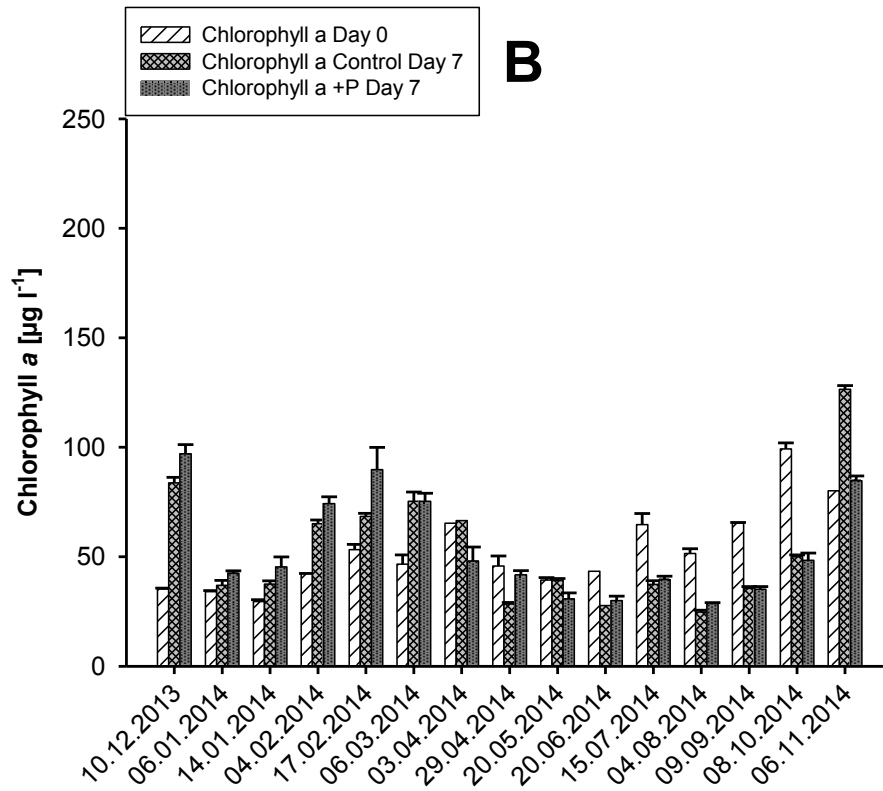
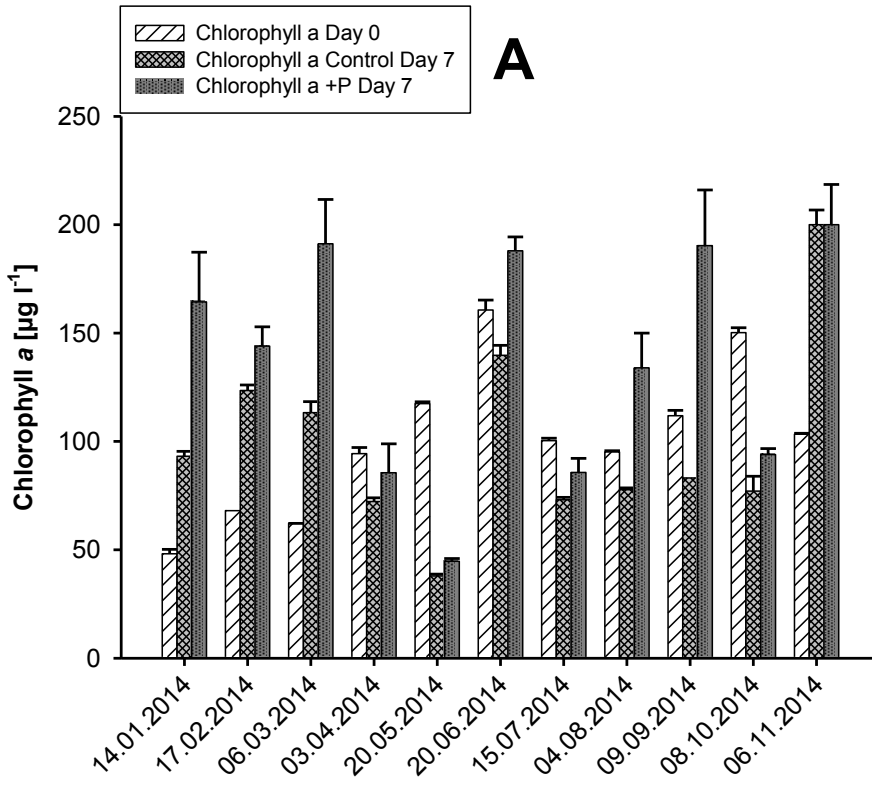
### 3.4 Utilisation of phosphorus pulses by phytoplankton

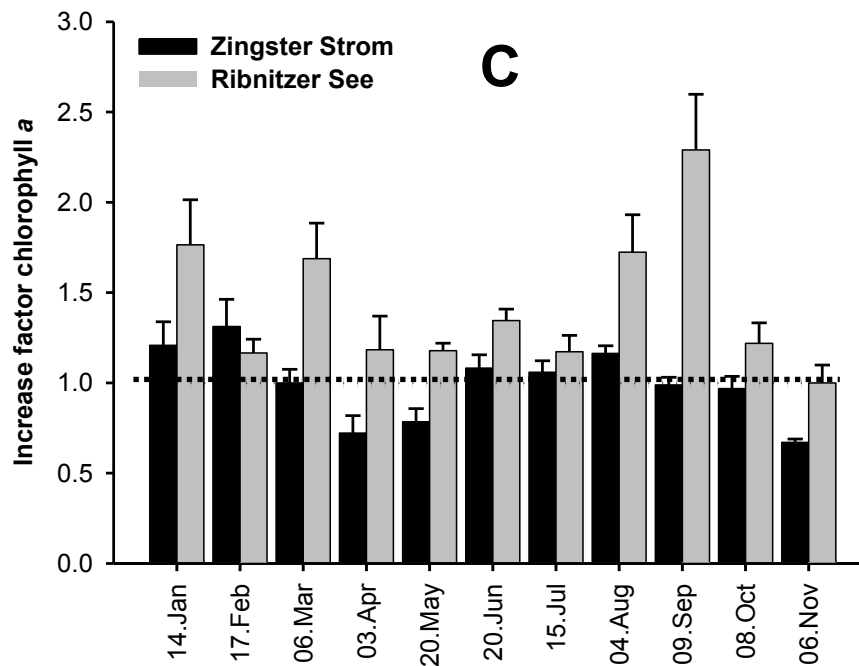
Berthold & Schumann already implemented parts of the following chapter in the publication “Phosphorus dynamics in a polymictic eutrophic lagoon” 2016 (submitted). This includes Figure 17 C, Figure 18 C, and Figure 19 C and the referring text. The presented data are original from the author itself, if not stated otherwise.

#### *Seston and Chl a development in batch tanks during seven days*

The increase of Chl *a* and seston was observed in fertilised samples with a  $10 \mu\text{mol l}^{-1} \text{PO}_4$  pulse and unfertilised samples. The highest increase in Chl *a* concentration was measured at least one month per season in the station RS (Figure 17 A). Chl *a* concentrations in fertilised incubations of the RS were in 7 out of 11 times higher after 7 d than the initial Chl *a* concentration (d 0). The Chl *a* concentrations in fertilised samples of the RS were in 10 out of 11 times higher compared to the unfertilised samples after 7 d. The increase of Chl *a* ranged between 17 and 128 % during the experiments (Figure 17 C). Interestingly, the Chl *a* concentrations never exceeded  $200 \mu\text{g l}^{-1}$  even though higher Chl *a* concentrations were observed during the long-term observation of the DZBC. This reaction was surprising because the TP concentrations in the system were never above  $10 \mu\text{mol l}^{-1}$  TP. The Chl *a* concentration could increase even though the  $\text{PO}_4$  decrease in the same sample was low (see Figure 15 and Figure 17).

This was not the case for the station ZS. Highest growth was observed between December 2013 and March 2014 (Figure 17 B) contrary to the lowest  $\text{PO}_4$  decrease during these months (see Figure 15 B). Chl *a* concentrations in fertilised incubations of the ZS were in only 5 out of 13 times higher after 7 d than the initial Chl *a* concentration (d 0). The Chl *a* concentrations in fertilised samples of the ZS were in 6 out of 13 times higher compared to the unfertilised samples after 7 d. The Chl *a* concentrations of both unfertilised and fertilised samples dropped below the initial Chl *a* concentration between April 2014 and October 2014, compared to the initial Chl *a* concentration. The increase of Chl *a* ranged between 15 and 30 % during the experiments (Figure 17 C). This was much lower compared to the RS and Chl *a* never exceeded  $100 \mu\text{g l}^{-1}$ . Surprisingly, growth was not induced the same, even though the initial  $\text{PO}_4$  concentrations were low, too.

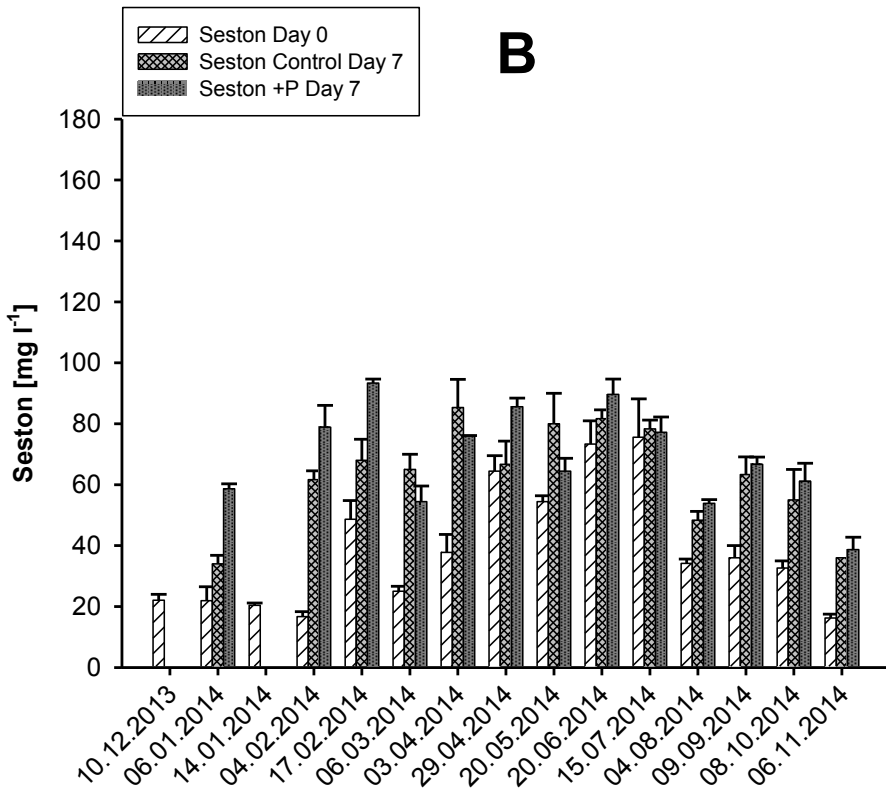
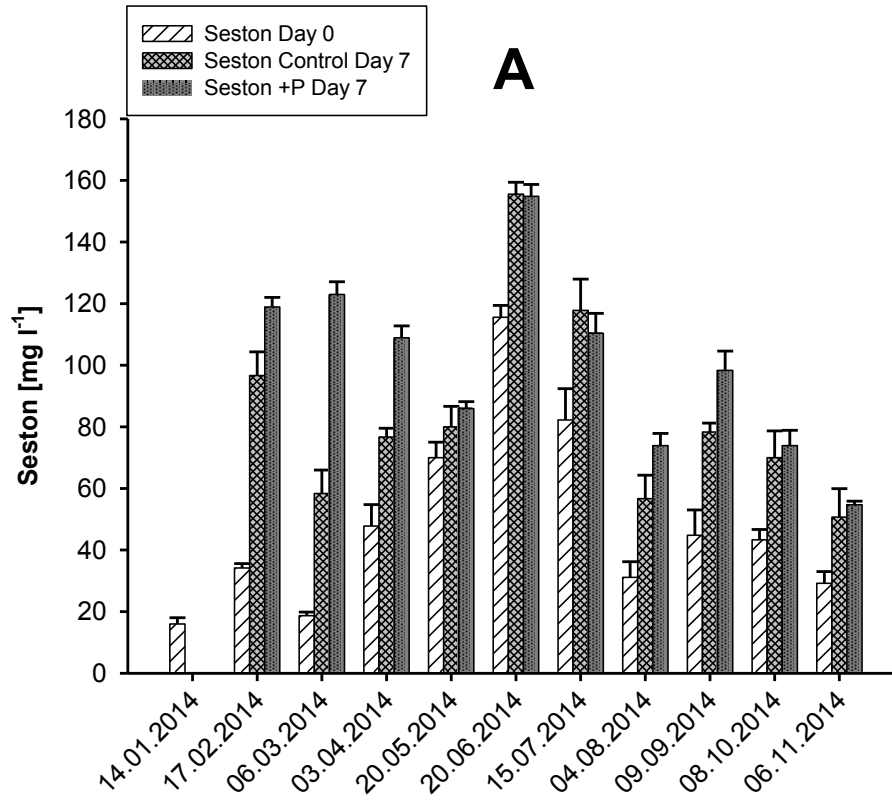


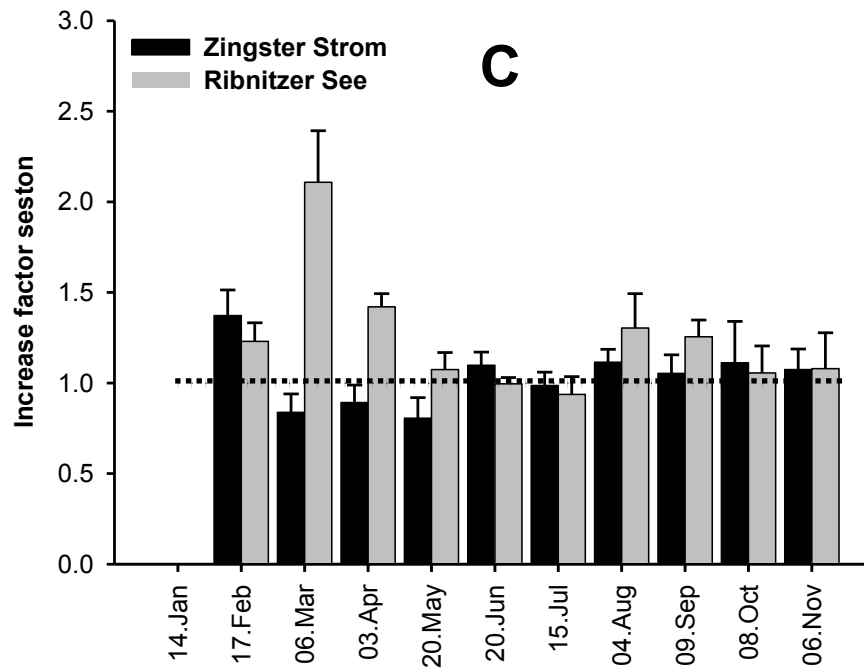


**Figure 17 Chlorophyll *a* concentration [ $\mu\text{g l}^{-1}$ ] after seven days in unfertilised and with phosphorus fertilised samples of the Zingster Strom and Ribnitzer See in 2014.** Samples were fertilised with a  $10 \mu\text{mol l}^{-1}$   $\text{PO}_4$  pulse at day 0. All samples of the Ribnitzer See (A) and Zingster Strom (B) were filtrated after seven days of incubation. The concentrations of day 0 were included as comparison. (C): Relative chlorophyll *a* concentration of samples with phosphorus addition to unfertilised samples; if bar is above 1.0 the fertilised sample had a higher concentration, compared to unfertilised samples. Incubation in batch tanks at  $15 \text{ }^\circ\text{C}$  ( $\pm 1 \text{ }^\circ\text{K}$ ), photon flux  $100 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ , light:dark 16:8 hours. Error bars in A and B are calculated as range ( $n=2$ ). Error bars in C are calculated as combined standard deviation ( $n=4$ ). Data Chlorophyll *a* was from the Biological station Zingst (unpublished).

Seston did not reflect Chl *a* development for both stations. The seston concentration increased between d 0 and d 7 for both, fertilised and unfertilised samples at the station RS almost every time (Figure 18 A). The pulsed samples had higher seston concentrations in 90 % (seston d 0) and 50 % (seston unfertilised d 7) of the time. The increase compared to the unfertilised samples ranged between 23 and 120 % during the experiments (Figure 18 C).

The same pattern was observed for the station ZS. The seston concentration increased in 90 % and 40 % during the time compared to d 0 and the unfertilised seston after d 7, respectively (Figure 18 B). The increase compared to the unfertilised samples ranged between 10 and 72 % during the experiments (Figure 18 C). It was surprising that there was a higher and more frequent increase of seston compared to d 0 even without Chl *a* increase.





**Figure 18** Seston concentration [ $\text{mg l}^{-1}$ ] after seven days in unfertilised and with phosphorus fertilised samples of the Zingster Strom and Ribnitzer See in 2014. Samples were fertilised with a  $10 \mu\text{mol l}^{-1} \text{PO}_4$  pulse at day 0. All samples of the Ribnitzer See (A) and Zingster Strom (B) were filtrated after seven days of incubation. The concentrations of day 0 were included as comparison. (C): Relative seston concentration of samples with phosphorus addition to unfertilised samples; if bar is above 1.0 the fertilised sample had a higher concentration, compared to unfertilised samples. Incubation in batch tanks at  $15 \text{ }^\circ\text{C}$  ( $\pm 1 \text{ }^\circ\text{K}$ ), photon flux  $100 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ , light:dark 16:8 hours. Error bars in A and B are calculated as standard deviation ( $n=3$ ). Error bars in C are calculated as combined standard deviation ( $n=6$ ). Data Seston day 0 was from the Biological station Zingst (unpublished).

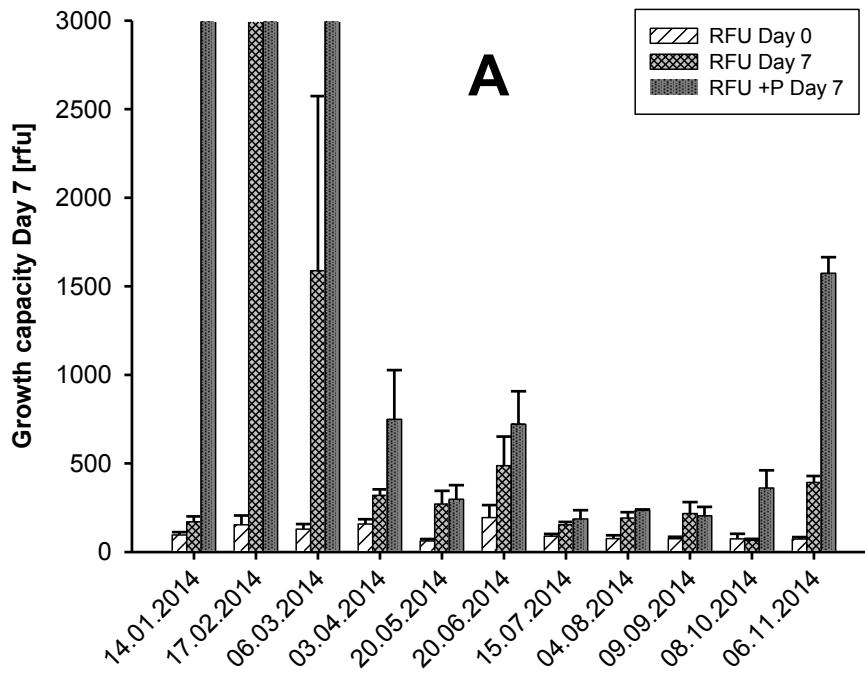
The comparison of Chl *a* and seston (Table 7) shows the Chl *a*:seston ratio for the sampling dates with available data. Obviously, the initial ratio of d 0 dropped by at least 60 % in RS and 75 % in ZS after 7 d. However, the fertilised samples in the station RS had during the whole summer and autumn a higher ratio compared to unfertilised samples after d 7. This shows, that the P addition could extend the time for growth. In contrast to RS, the ratios at the station ZS did not strongly differ between fertilised and unfertilised samples. This was surprising, because the ZS is even further away from the nutrient supply by a freshwater inflow. At least a sustainment of Chl *a*:seston was expected between d 0 and d 7.

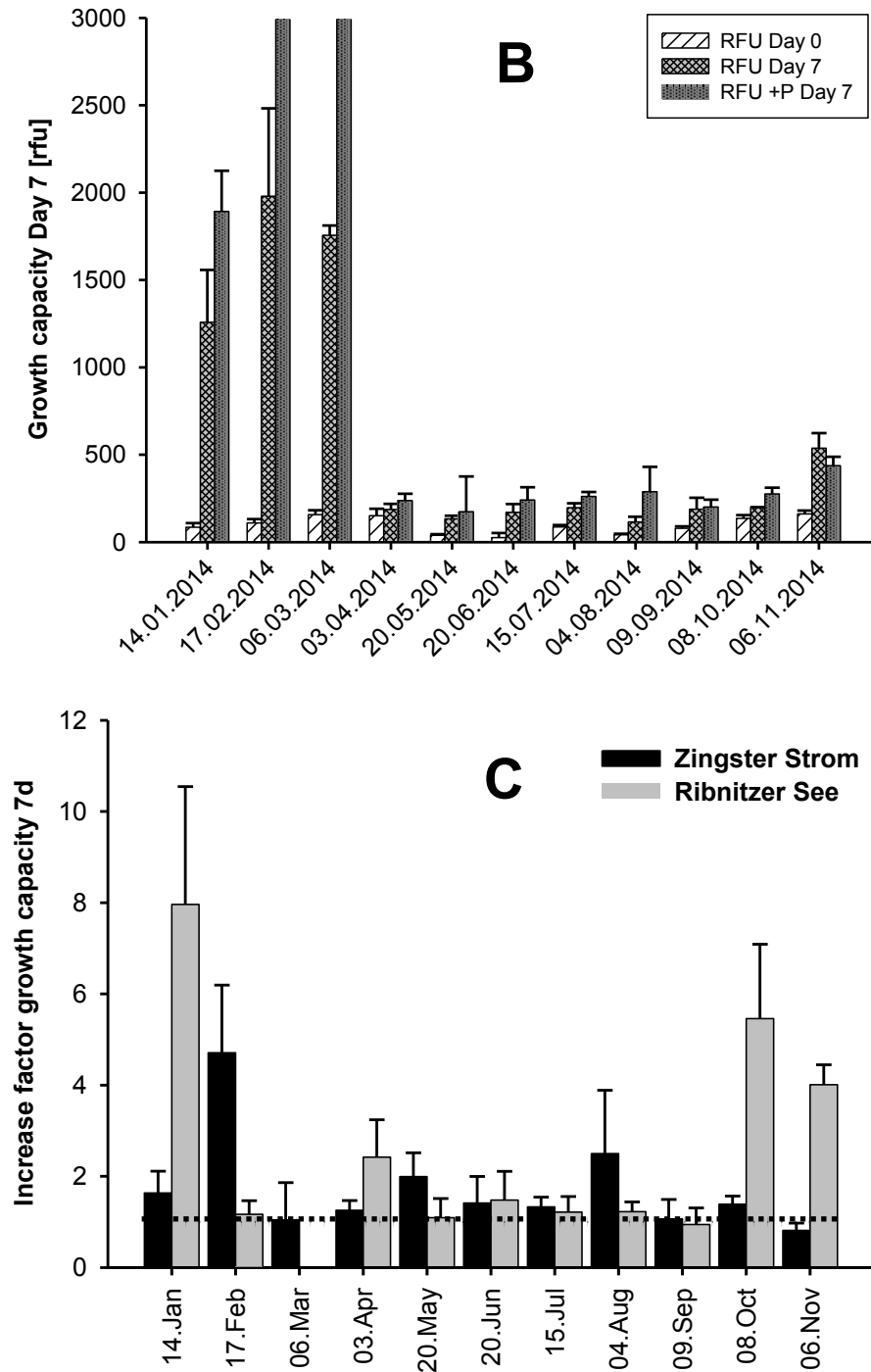
**Table 7 Overview of Chlorophyll *a* to seston ratios during pulse experiments between February and November 2014 for the sampling sites Ribnitzer See and Zingster Strom.** Day 0 – initial ratio, -P Day 7 – without nutrient addition after seven days, +P Day 7 – with 10  $\mu\text{mol l}^{-1}$  phosphate addition after seven days. Values Day 0: Biological station Zingst (unpublished); all other values: own data. Incubation in batch tanks at 15 °C ( $\pm 1$  °K), photon flux 100  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ , light:dark 16:8 hours.

Chl <i>a</i> :Seston	Ribnitzer See			Zingster Strom		
	Day 0	-P Day 7	+P Day 7	Day 0	-P Day 7	+P Day 7
17.02.	2.0	1.3	1.2	1.1	1.0	1.0
06.03.	3.3	1.9	1.6	1.9	1.2	1.4
03.04.	2.0	0.9	0.8	0.7	0.4	0.5
20.05.	1.7	0.5	0.5	0.7	0.5	0.5
20.06.	1.4	0.9	1.2	0.6	0.3	0.3
15.07.	1.2	0.6	0.8	0.9	0.5	0.5
04.08.	3.0	1.4	1.8	1.5	0.5	0.5
09.09.	2.5	1.0	1.9	1.8	0.6	0.5
08.10	3.5	1.1	1.3	3.0	0.9	0.8
06.11.	3.5	4.0	3.7	4.9	3.5	2.2

*Growth development of phytoplankton in the growth incubator*

The simultaneous performed growth experiments in an incubator showed a similar growth pattern as in the batch tanks. Growth capacities with P addition were significantly higher in the station RS (Wilcoxon-signed-rank,  $p=0.004$ ,  $n=11$ ) and in the station ZS (Wilcoxon-signed-rank,  $p=0.025$ ,  $n=11$ ) compared to untreated samples after d 7 (Figure 19). Obviously, there were very high capacities during the first months. At both stations, samples outgrew the measurement range in a couple of days. The values for cut bars can be found in the figure legend. Phytoplankton biomass in incubated samples consisted mostly of diatoms and less of cyanobacteria between January and March (personal observation). The station RS had always higher growth capacities after 7 d compared to the station ZS.



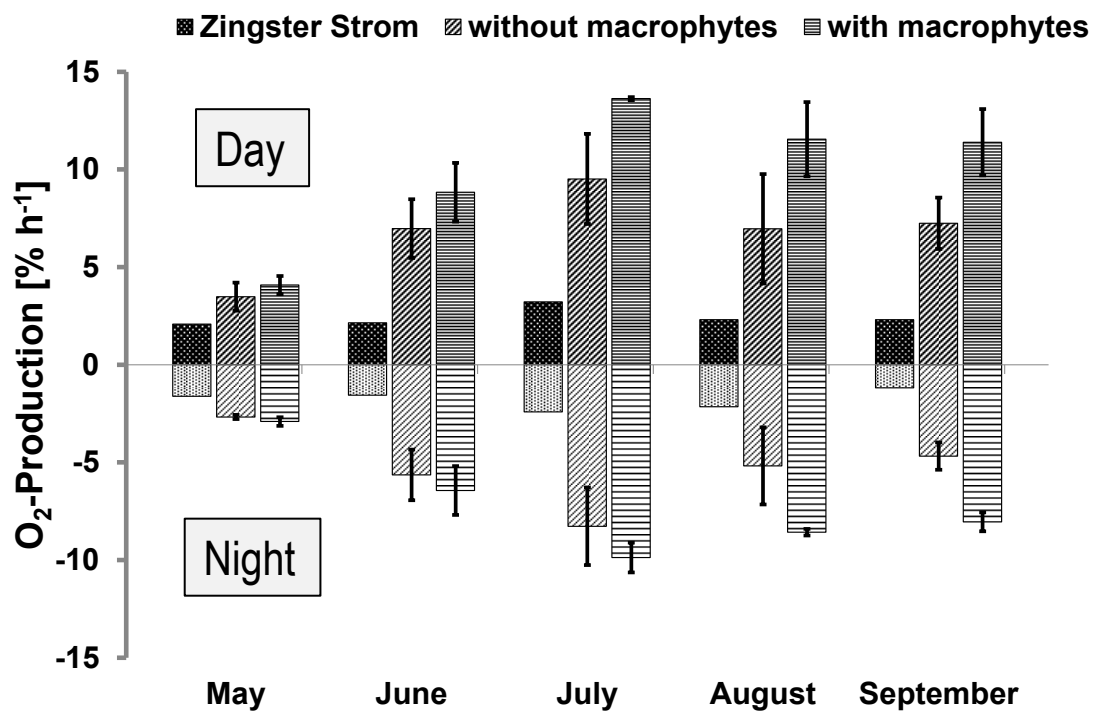


**Figure 19** Growth capacity after seven days in unfertilised and with phosphorus fertilised samples of the Zingster Strom and Ribnitzer See in 2014. Samples of the Ribnitzer See (A) and Zingster Strom (B) were measured for an increase in relative fluorescence units (rfu). Values were used to calculate the growth capacity after seven days. Values of day zero were added as comparison. Unfertilised samples were only diluted 1:10 with filtrate (RFU Day 7); fertilised samples had a phosphorus addition of  $10 \mu\text{mol l}^{-1} \text{PO}_4$  (RFU +P Day 7). (C): Relative growth of samples with phosphorus addition to unfertilised samples; if bar is above 1.0 the fertilised sample had a higher concentration, compared to unfertilised samples. Incubation in cuvettes in a growth incubator at  $15 \text{ }^\circ\text{C}$  ( $\pm 1 \text{ }^\circ\text{K}$ ), photon flux  $60 - 100 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ , light:dark 16:8 hours. Error bars in A and B are calculated as standard deviation  $n=5$ . Error bars in C are calculated as combined standard deviation  $n=5$ . Missing values A: 14.01.  $5974 \pm 2778$  rfu; 17.02. Day 7  $4497 \pm 3611$  rfu; +P  $9542 \pm 3287$  rfu; 06.03. +P  $17671 \pm 3439$  rfu. B: 17.02. +P  $10221 \pm 3037$  rfu; 06.03. +P  $4091 \pm 1882$  rfu. C: 06.03. Ribnitzer See  $11.1 \pm 7.2$ .

### 3.5 Interactions of submerged macrophytes and phytoplankton

#### *Oxygen saturation in mesocosms with and without macrophytes in 2014*

The mesocosms in 2014 had two different approaches. One set of mesocosms was sampled permanently free of macrophytes ( $n=3$ ), whereas the other set had undisturbed macrophyte growth conditions ( $n=3$ ). The  $O_2$  production in both mesocosm preparations started at the same level. Mesocosms with macrophytes increased their  $O_2$  production during June 2014 (Figure 20). The highest  $O_2$  production per hour was measured in mesocosms with submerged macrophytes during July 2014. The  $O_2$  production remained high afterwards, whereas the production in phytoplankton mesocosms already dropped in August. The production at day exceeded the loss during night in all set-ups. The water column never fell below 60 %  $O_2$  saturation, but could rise up to more than 200 %. These conditions would inhibit redox-sensitive nutrient release. The  $O_2$  production for both set-ups was always higher, than in the station ZS.

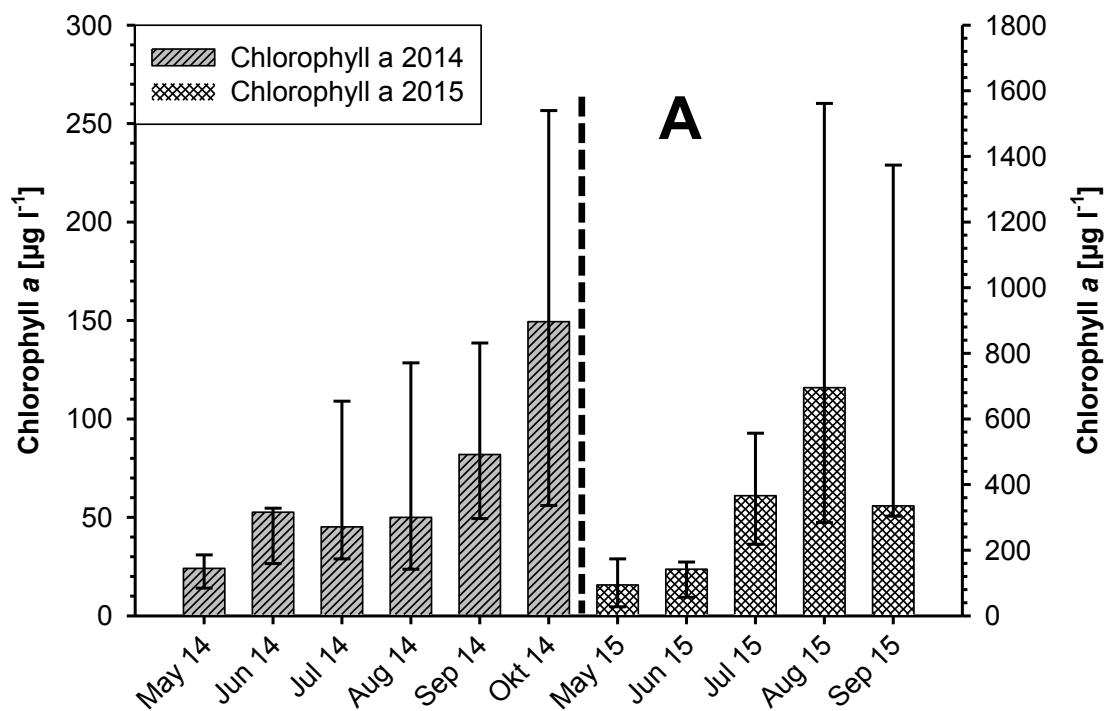


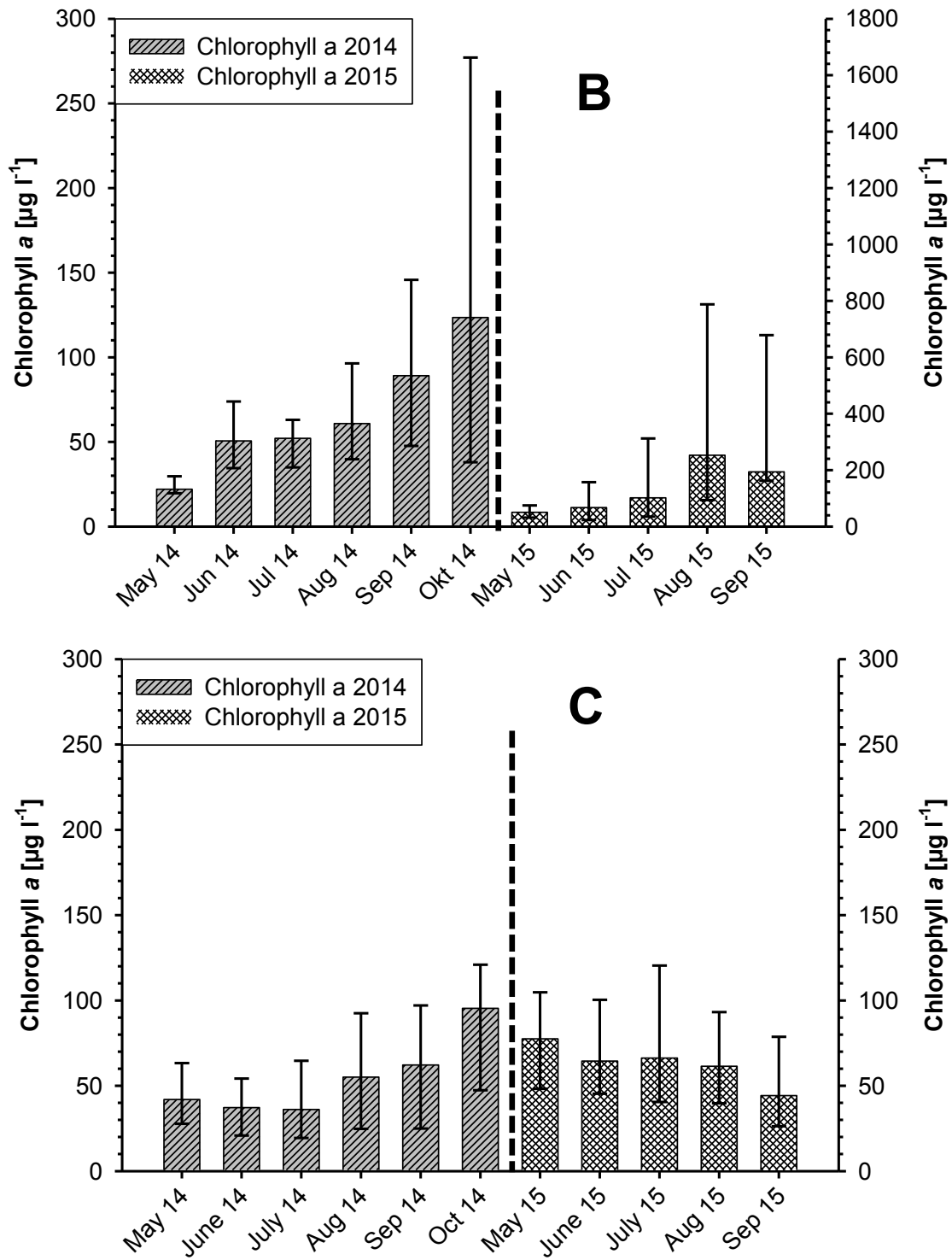
**Figure 20** Oxygen production [% h<sup>-1</sup>] in mesocosms with macrophytes, without macrophytes and the Zingster Strom during 2014. A LDO (Hach-Lange) measured oxygen saturation [%] every 5 min (mesocosms) to 10 min (Zingster Strom).  $O_2$  production in % h<sup>-1</sup> was calculated for every day between 9 am to 3 pm (day) and 8 pm to 3 am (night) Central European Time. Error bars are calculated as standard deviation for the mesocosms ( $n=3$ ). Data set for Zingster Strom: Biological Station Zingst.

*Chlorophyll a development in the water column in 2014 and 2015*

There were no differences in Chl *a* water concentration between macrophyte-free (Figure 21 A) and macrophyte mesocosms (Figure 21 B). The ZS (Figure 21 C) showed the same development only in 2014. Surprisingly were the high differences between minima and maxima found in all treatments. Every replicate of every treatment had at least on mesocosm with high, medium, and low Chl *a* concentrations. It was unexpected that macrophytes showed no regulating effect on the phytoplankton.

The mesocosms in 2015 were not disturbed at all, regarding macrophyte removal. However, macrophytes did not grow in some mesocosms. Therefore, mesocosms without macrophytes were combined regarding the Chl *a* concentration in the water column for 2015 (Figure 21 A). The concentrations were much higher compared to 2014 and the Zingster Strom in 2014 and 2015. The Chl *a* concentration in mesocosms without macrophytes were at least 10 to 15 times higher in August 2015, compared to August 2014. The Chl *a* concentrations in mesocosms with macrophytes were 3 to 8 times higher in August 2015, compared to August 2014. Again, there were mesocosms with high, medium, and low Chl *a* concentrations. This was not expected, because the total macrophyte biomass in macrophyte inhabited mesocosms was comparable between the years (see below).





**Figure 21 Development of chlorophyll a concentrations in mesocosms and the Zingster Strom in 2014 and 2015.** Chlorophyll a concentrations were measured in duplicates. Mesocosms were without macrophytes (A) and with macrophytes (B) (each n=3). (C) are concentrations of the Zingster Strom during the same time (n=202, 2014; n=143, 2015). The dotted line separates both years. Please note the different scaling on the left and right y-axes.

### *Macrophyte biomass development and species composition in 2014 and 2015*

The biomass development of submerged macrophytes showed two germination periods. The biomass consisted to 90 % of *Chara* sp. (Table 8). The macrophyte biomass in permanently sampled mesocosms grew all the time between May and July and September to October. However, the total biomass in macrophyte-free mesocosms ranged only between 3 to 7 g m<sup>-2</sup> per month. The total biomass in undisturbed macrophyte mesocosms was 2.5-times higher at the end (Table 8). In contrast to biomass, the TP concentration in undisturbed macrophyte mesocosms was 10-times higher, compared to permanently sampled mesocosms. The reason for that were low TP concentrations of *Chara* sp. during growth. The TP concentration of freshly germinated *Chara* sp. was only ~30 % of the TP concentration of fully-grown *Chara* sp. in undisturbed mesocosms (data not shown).

**Table 8** **Macrophyte biomass and species composition in undisturbed macrophyte mesocosms and mesocosms that were permanently sampled for macrophytes.** Mesocosms that had to stay macrophyte-free were checked regularly. Macrophytes were separated on genus level, instantly dried after sampling and afterwards ashed. Ash was used for total phosphorus determination (TP). Values are calculated in g dry mass (DM) per m<sup>-2</sup> (n=3) and in mg TP per m<sup>-2</sup> (n=4). All mesocosms were plastic barrels (polypropylene). Barrels were placed 40 cm deep into the ground for temperature control. Mean temperature difference to the Zingster Strom was ±2 °K. Sediment was sampled close to the Zingster Strom. Water samples were pumped from the Zingster Strom once in April 2014 and replaced in May 2015. The total water column was turned over three times per hour by an internal water pump. Mesocosms were open to the top for atmospherically exchange.

	Species and TP composition in 2014			
	Macrophyte mesocosms		Macrophyte-free mesocosms	
	DM [g m <sup>-2</sup> ]	TP [mg m <sup>-2</sup> ]	DM [g m <sup>-2</sup> ]	TP [mg m <sup>-2</sup> ]
<i>Najas</i> sp.	3.5±2.7	2.4±0.1	0.1±0.1	<0.1
<i>Chara</i> sp.	43.8±15.1	62.7±18	16.0±3.4	4.7±0.2
<i>Tolypella</i> sp.	2.4±1.8	1.6±0.1	2.6±2.1	1.7±0.1
<b>Total</b>	49.7	66.7	18.5	6.4

Surprisingly, 5 of the 6 mesocosms were inhabited by a high amount of *Gammarus tigrinus* (Table 9). *G. tigrinus* was found only in small amounts in 2014. The macrophyte biomass was depressed in mesocosms that were densely populated by gammarids (see below). The mean water content of the gammarids was 75.1 ±2.6 %.

**Table 9 Biomass of *Gammarus tigrinus* in all mesocosms in September 2015.** The whole water column and sediment was filtered through a mesh for gammarids. Gammarids were instantly weighed, dried for 24 h at 90 °C and re-weighed. All mesocosms were plastic barrels (polypropylene). Barrels were placed 40 cm deep into the ground for temperature control. Mean temperature difference to the Zingster Strom was  $\pm 2$  °K. Sediment was sampled close to the Zingster Strom. Water samples were pumped from the Zingster Strom once in May 2015. The total water column was turned over three times per hour by an internal water pump. Mesocosms were open to the top for atmospherically exchange. M1 – M6 was the individual label of each mesocosm.

	September 2015					
	M1	M2	M3	M4	M5	M6
<b><i>Gammarus tigrinus</i> biomass DM [g m<sup>-2</sup>]</b>	0.2	3.8	6.2	7.4	2.3	4.9

The initial TP concentration for all mesocosms was around 3.1  $\mu\text{mol l}^{-1}$ . Throughout the year, precipitation added 1 mmol TP per mesocosms (data Biological Station Zingst, unpublished). This accounted up to 8.4  $\mu\text{mol l}^{-1}$  TP per mesocosms and 93 mg TP m<sup>-2</sup>. In contrast to 2015, the precipitation input in 2014 amounted to only 0.2 mmol TP per mesocosm. This accounted up to 1.6  $\mu\text{mol l}^{-1}$  TP per mesocosms and 18.6 mg TP m<sup>-2</sup> in 2014. However, the initial concentration plus precipitation could not explain the found TP values in September 2015 (Table 10).

**Table 10 Phosphorus concentration in water and submerged macrophytes in September 2015.** Macrophyte biomass in dry mass (DM) [ $\text{g m}^{-2}$ ] ( $n=1$ ); total phosphorus (TP) concentrations for water in [ $\mu\text{mol l}^{-1}$ ] and [ $\text{mg m}^{-2}$ ] each ( $n=3$ ); TP concentration in macrophytes [ $\text{mg m}^{-2}$ ] in all mesocosms in September 2015. The P-fluxes into the water column were calculated with initial and final TP concentrations and TP inputs by precipitation throughout the experimental set-up. Macrophytes were separated on genus level, instantly dried after sampling and afterwards ashed. Macrophyte biomass consisted to 95 % of *Chara* sp. and 5 % *Najas* sp. Ash was used for total phosphorus determination (TP). All mesocosms were plastic barrels (polypropylene). Barrels were placed 40 cm deep into the ground for temperature control. Mean temperature difference to the Zingster Strom was  $\pm 2$  °K. Sediment was sampled close to the Zingster Strom. Water samples were pumped from the Zingster Strom once in May 2015. The total water column was turned over three times per hour by an internal water pump. Mesocosms were open to the top for atmospherically exchange. M1 – M6 was the individual label of each mesocosm.

	September 2015					
	M1	M2	M3	M4	M5	M6
<b>TP water</b> [ $\mu\text{mol l}^{-1}$ ]	5.9	10.8	16.4	12.1	15.2	24.0
<b>TP water</b> [ $\text{mg m}^{-2}$ ]	65.8	120.5	183.0	135.0	169.6	267.8
<b>Macrophyte biomass</b> DM [ $\text{g m}^{-2}$ ]	65.6	22.9	-	5.3	14.9	-
<b>TP macrophyte biomass</b> [ $\text{mg m}^{-2}$ ]	130.0 $\pm$ 38	46.0 $\pm$ 13.6	-	10.7 $\pm$ 3.2	30.0 $\pm$ 8.9	-
<b>P balance in the water column</b> [ $\mu\text{mol m}^{-2} \text{d}^{-1}$ ]	-14.3	-1.9	12.4	1.5	9.3	31.6

There were no macrophytes at all in two mesocosms (M3 and M6) (Table 10). The mesocosms M3 and M6 had also high biomasses of gammarids. Macrophytes in mesocosm M4 and M5 already started to decay. Obviously, mesocosms with higher macrophyte biomass showed lower TP concentrations in the water column. The calculated P-fluxes for those mesocosms were negative. That means, that the P input during the year was buffered and lower than expected. Mesocosms without macrophytes had 1.5 to four-times higher TP concentrations, compared to mesocosms with macrophytes. This resulted in positive P balances for the mesocosms M3 – M6. However, M4 and M5 had macrophytes but dense gammarid populations, too.

## 4 Discussion

### 4.1 Methodological discussion

#### *Monitoring effectiveness*

The monitoring programme of the BSZ covers up sampling at high spatial resolution as well as over long time scales. In general, long-term monitoring is a useful tool to detect ecosystem development. Especially the amount and diversity of measured parameters are important for ecosystem analysis (e.g. Dale and Beyeler, 2001; Magurran et al., 2010 and sources cited therein). Comparable data sets are usually obtained by official agencies (e.g. FCC, 1991; Kronvang et al., 2005; LUNG, 2013; Testa et al., 2008). The sheer amount of data may be misinterpreted e.g. by not choosing a representative sampling spot, or using a parameter with less significance (Lindenmayer and Likens, 2009). One major problem is the one-point sampling per Bodden and month of the monitoring programme. This one data point has to be representative for the whole water column of the sampled Bodden part. Further, the water mixing in the DZBC depends on weather and daily wind conditions. One point may be enough for the whole Bodden, because of well-mixed water columns. This was observed by the transect programme of BACOSA (Piepho et al., 2015). However, for the longer time-scale one-point sampling may be insufficient. Due to the changing weather conditions, Bodden water can be pushed back into the Recknitz up to Marlow (~ 20 km away linear distance) or into the Baltic Sea (Schlungbaum et al., 2000). This water body change was also observed in this work by higher Chl *a* and seston concentrations in the RM (Figure A 7 and Figure A 8). Therefore, some water samples may be less significant in terms of representing the actual system status.

The lack of a complete hydrological model for the DZBC is a major problem. Lampe et al. (2013) developed such a model in 2011, but stated that this was a year with unusual high precipitation. The high precipitation reduced the water retention time and increased the water exchange with the Baltic Sea. This evacuation effect of particulate matter was observed by lower seston concentrations in all Bodden during 2011 and 2013 in this work, too. The same effect is already described for the DZBC as “*Ausräumeffekt*” (Schiewer, 2006; Schlungbaum, 1994). Therefore, the model may not be used for years with lower or average precipitation. However, Lampe et al. (2013) stated that the Meiningenstrom separates the inner Bodden (RS, SB and BO) from the

outer Bodden parts (BB, GB and WB) in the DZBC. This was contrary to the results in this work. The stations BO, ZS and BB were always closer related to each other in terms of seston and TP, than the neighbouring stations SB and BO. This may indicate that the water exchange is already reduced between SB and BO, which can explain the high particulate matter in the SB. Also, Schlunbaum et al. (2000) described the low water renewal times for the SB (7 – 8 times a year), compared to the BO (33 times a year). However, a working model can predict possible ecosystem development by analysing abiotic parameters. The BSZ already has an automatic station for atmospheric (light, wind speed, wind direction) and water (pH, salinity, temperature, oxygen saturation) parameters with densely measuring intervals (up to 10 min). In addition, the research vessel *RV Nauplius* has an automatic sensor recording optical density, geographical position, water temperatures and salinity. This can help to set data into a broader context and reduce misinterpretation. This is necessary, because abiotic and biotic water parameter can change in a day in the ZS. Schumann et al. (2012) described in a frequency distribution (n=4001) that Chl *a* changed in 70 % of the time up to  $\pm 10$  % and at least in 20 % of the time between 10 to 20 % in a day. They observed the same tendency for salinity ( $\pm 1$ ; 90 % of the time, n=4018) and pH ( $\pm 0.1$ , 75 % of the time, n=4017). This complete data set shall be put into one model to enable correlation formulas.

#### *Practicability of growth proxies in the DZBC*

The detection of growth was a more challenging work than predicted. It seems that Chl *a* is not the best biomass proxy in the DZBC. One of the reasons is the ongoing cyanobacterial dominance. Cyanobacteria can have more  $\mu\text{g}$  Chl *a* per  $\mu\text{mol}$  TP than other phytoplankton (Scheffer et al., 1997). This can explain the non-predictable range of this ratio in the long-term data set presented in this work. Additionally most cyanobacteria are adapted to low light conditions and can handle high light pulses (Reynolds et al., 2002). This causes higher Chl *a* concentrations *in situ* (Scheffer et al., 1997) and a higher turbidity in the DZBC.

The higher Chl *a* concentration possibly normalised during incubation at sufficient light climate in this work. Another reason is a possible N co-limitation, which reduced the Chl *a* concentration in most experiments (Healey, 1985; Richardson et al., 1969). The missing increase of Chl *a* in the here presented experiments must not necessarily mean, that there was no biomass growth or P limitation (Rouzić and Bertru,

1997). P limited cyanobacteria build up polysaccharides (Ihlenfeldt and Gibson, 1975). However, this can only explain a seston increase by colony growth and not the absence of growth itself. In addition, the negative growth by means of Chl *a* does not mean a deficient incubation procedure. The use of whole community samples can lead to interspecies competition (Rouzic and Bertru, 1997). This means in effect the most affine rather than the most limited species profits by nutrient fertilisation. Especially bacterioplankton competes with phytoplankton for nutrients (Joint et al., 2002; Zubkov et al., 2007). There would be a population limitation rather than a growth limitation independently from the N:P ratio (Theodorou et al., 1991). However, in this work PO<sub>4</sub> was added under light-irradiated conditions. The light irradiation will prefer phytoplankton uptake before bacterioplankton (Tanaka et al., 2006).

An over- or under average zooplankton grazing can be responsible for the Chl *a* reduction as well. If there is an existing daily zooplankton period, it was undersampled at any time during the experiments. Even without daily movement periods, zooplankton was possibly reduced by fish during summer months (Beklioglu and Moss, 1996; Hansson et al., 2004). That can reduce grazing pressure in the water samples due to lowered zooplankton abundance of all experiments during summer presented in this work. Further, it reduces the nutrient release by the microbial loop (Chrzanowski et al., 1995). However, the grazing effect on phytoplankton accounts only up to 1 – 4 % of total primary production in the DZBC (Schnese and Heerkloss, 1978). Therefore, a higher grazing pressure by zooplankton may be ruled out for the low Chl *a* concentrations during summer observed in the presented study.

Another reason for lower Chl *a* concentration during summer can be the missing ultraviolet radiation (UVR). If the turnover rates of nutrients in the DZBC are as high as predicted (Schiewer, 2007), this can be explained by UVR oxidised dissolved organic phosphorus and dissolved organic nitrogen. This would mean a recycling stagnation, as UVR was absent during the incubation (Sereda et al., 2011). This will account for the batch and growth incubator experiments.

However, growth rates in the incubator can be affected by some other factors as well. The sample dilution in the growth cuvettes removed a great part of colloids and may have disrupted nutrient recycling by particulate material (Venrick et al., 1977). However, dilution has some advantages compared to pre-filtration. There is no complete separation and cell damages may occur with a pre-filtration (Venrick et al., 1977). In addition, the same effects, like reduced grazing pressure, are possible as well. Another

reason is fluorescence stimulation. There is a fluorescence depression under nutrient limitation by either low light adapted cyanobacteria (Scheffer et al., 1997), or reduced photosystem II performance (Cullen et al., 1992). In general, the low growth rates during most experiments indicate a systemic co-limitation for other nutrients apart from P (Tanaka et al., 2006; Thingstad and Rassoulzadegan, 1995).

In the experiments, presented in this work, the seston development was contrary to Chl *a* development. The increase of seston does not necessarily indicate higher phytoplankton biomass. It is described for the DZBC by Schumann et al. (1999) that a permanent movement of the water column raises aggregate formation. It is possible that this happened in the batch tanks by permanent air addition through aeration pumps. Therefore, it is possible that the seston filters withheld more particulate matter. Also, a possible co-limitation for other nutrients led to an increase of extracellular polymeric substances (EPS) by algae and bacteria and an increase of seston (Schumann and Rentsch, 2001). However, this may not be present in the shallow parts of the DZBC due to high shear forces (Schumann et al., 1999), but in the here presented experiments.

#### *Interpretability of PO<sub>4</sub> pulses on nutrient limitation*

The use of unlabelled PO<sub>4</sub> as a proxy for phytoplankton demand is a seldom used method. One of the main reasons is the luxury consumption of PO<sub>4</sub> by phytoplankton (Fogg, 1973; Sommer, 1989, 1985). Phytoplankton can take up above-average PO<sub>4</sub> and store it as polyphosphate (e.g. Aubriot et al., 2011; Orchard et al., 2010). This means, uptake rates with PO<sub>4</sub> are much higher, than at ambient concentrations.

Radioactive labelled PO<sub>4</sub> (<sup>32</sup>P e.g. Friebele et al., 1978; Thingstad et al., 1993 & <sup>33</sup>P e.g. Nausch and Nausch, 2006) is used for measurements at ambient concentrations. The uptake rates can e.g. range between 0.7 – 4.2 nmol l<sup>-1</sup> h<sup>-1</sup> in a eutrophic lake (Chróst and Overbeck, 1987), or 0.54 nmol µg<sup>-1</sup> Chl *a* h<sup>-1</sup> in surface waters of the Baltic Sea (median Chl *a* 4.2 µg l<sup>-1</sup> Nausch et al., 2012). In some coastal waters the uptake rates can be up to 390 nmol l<sup>-1</sup> h<sup>-1</sup> (Cotner and Wetzel, 1992). The only measured radioactive uptake rates for the DZBC ranged between 0.08 – 0.2 nmol l<sup>-1</sup> h<sup>-1</sup> in autumn (Müller, 2012). The PO<sub>4</sub> uptake rates with 1.0 – 10 µmol l<sup>-1</sup> h<sup>-1</sup> at both stations were much higher, comparing this work to literature values with radioactive labelled P. Those high uptake rates of PO<sub>4</sub> are comparable to laboratory cultures of *Synechococcus* WH7803 with 17 µmol l<sup>-1</sup> PO<sub>4</sub> in 5 – 10 min (Donald et al., 1997), or 16 µmol l<sup>-1</sup> PO<sub>4</sub>

in 30 min by *Chlorella pyrenoidosa* (Nyholm, 1978). Additionally the uptake kinetic of  $^{33}\text{P}$  uptake in whole communities is comparable to the kinetics found in this work (Friebele et al., 1978). This means the results are quite comparable.

It must be stated that a loss of  $\text{PO}_4$  during the incubation does not necessarily indicate a direct uptake.  $\text{PO}_4$  can attach to EPS and form an extracellular P pool (Cembella et al., 1984; Sanudo-Wilhelmy et al., 2004). EPS act as diffusive boundary layer and trigger a transport limitation (Pasciak and Gavis, 1974). Ploug et al. (1999) showed this for *Phaeocystis* colonies. A direct uptake would be measurable by autoradiography (Friebele et al., 1978). The observed decrease of  $\text{PO}_4$  in the present study was most probably an active uptake instead of adsorption onto seston. The missing uptake in heated samples with no living phytoplankton showed this. This is very important, because phytoplankton accounts only up to 25 % of seston. The uptake rates can be considered as P demand, even though luxury consumption accounted for the high uptake rate. This will also explain the permanent low  $\text{PO}_4$  concentrations of the DZBC.

#### *System reproduction of small mesocosms*

The mesocosms were well suited to reproduce the abiotic development of the DZBC. The reproducibility in terms of biotic parameters was comparable to the ZS during the first year. The temperature regulation through partly burying the mesocosms and atmospheric exchange shall be maintained in further experiments. However, the high atmospheric P deposition in 2015 may have resulted in non-comparable conditions. The main reason was the absent water exchange. The year 2015 can be compared to experiments in which mesocosms were artificial fertilised. A unique addition of  $16 \mu\text{mol l}^{-1} \text{PO}_4$  (final concentration in whole water column) led to a comparable range of Chl *a* between  $50 - 500 \mu\text{g l}^{-1}$  in mesocosms of Bakker et al. (2010) like in the mesocosms of 2015. The additional nutrients can also explain the higher oxygen saturation rates found in this work. Oviatt et al. (1986) described that already a 2-fold increase in P and N could double the oxygen production in the water column. In addition, the absence of fish and most probably macroinvertebrates may have resulted in a different system development compared to the DZBC (e.g. Bucak et al., 2012; Stephen et al., 2004). Some further reasons will be discussed in the following (see chapter 4.2 Submerged macrophytes as system stabiliser in a turbid environment).

#### 4.2 Submerged macrophytes as system stabiliser in a turbid environment

Blindow et al. (2014) described in a review the influence of submerged macrophytes in shallow lakes for the following factors: sediment resuspension, sedimentation, nutrients, zooplankton, benthic invertebrates, and fishes. Macrophytes reduce sediment resuspension, elevate sedimentation rates of phytoplankton and particulate matter, compete with phytoplankton for nutrients and is retreat for zooplankton, macroinvertebrates, and also fish (Blindow et al., 2014).

A patchy distribution of submerged macrophytes was observed in the DZBC (Blindow and Meyer, 2015). Submerged macrophytes covered only 70 % of the shallow areas (< 50cm water depth) in the DZBC. Solitary macrophytes were found up to 1 m water depth. The same results were observed by Schubert (2001) in the DZBC. Mulderij et al. (2007) described that the sedimentation rates above macrophyte colonies decreases further with high patchiness of submerged macrophytes. Further, the transect programme of BACOSA could not indicate any difference in Chl *a* and seston concentration above sole sediment and macrophyte patches (Piepho et al., 2015). There is no reduced turbidity even in the very shallow Kirr bay close the ZS. This bay is to almost 100 % covered with submerged macrophytes (personal observation). The same was observed in the mesocosms experiments presented in this work. There were only two mesocosms with reduced Chl *a* concentration. One was fully grown with macrophytes; one was without macrophytes. These results are contrary to observed effects of submerged macrophytes onto lower turbidity in other shallow lakes (Blindow et al., 2014, 1993). The submerged macrophytes may not buffer resuspension of sediment in this imitated polymictic environment.

There was a direct influence of submerged macrophytes on nutrients in the mesocosms. The calculated P balances were negative for mesocosms with higher macrophyte abundance. This means the mesocosms could actually buffer the high P input by precipitation in 2015. In contrast to 2014, lower turbidity was observed only in mesocosms with submerged macrophytes. The low turbidity with high Chl *a* concentrations (see Appendix Figure A 10, p. A-16) was probably due to high diatom dominance (personal observation). Interestingly, the TP concentrations ( $6 \mu\text{mol l}^{-1}$ ) in these mesocosms were even higher, than the long-term average in every Bodden part of the DZBC (this work). The same circumstances were described by Hosper and Jagtman (1990) and Jeppesen et al. (1990) for Danish lakes with TP concentrations up to  $5 \mu\text{mol l}^{-1}$ . Those lakes were bio-manipulated by reduction of planktivorous fish and

had a low TN concentration (around  $140 \mu\text{mol l}^{-1}$ ). *Chara* sp. can directly compete with phytoplankton for dissolved nutrients (Kufel and Kufel, 2002 and sources cited therein). In the current observations, *Chara* sp. dominated macrophyte biomass with almost 90 % of the total biomass in mesocosms during both years. However, a significant reduction in TP was only observed in mesocosms with dense colonisation of *Chara* sp. in this work. One cause that this competition did not occur in the DZBC was probably due to low *Chara* sp. biomass as observed in the project BACOSA (Piepho et al., 2015). The biomass of *Chara* sp. was up to 25 % of the total submerged macrophyte biomass in the GB. The species *Potamogeton pectinatus* was more abundant. Also, *P. pectinatus* is an indicator species for eutrophication (Melzer, 1999). *P. pectinatus* uses mostly sediment bound P (Howard-Williams and Allanson, 1981). Grazing can release the macrophyte-bound P. Especially water fowl (Nichols and Shaw, 1986 and sources cited therein; Schubert, 2001) and amphipods (Berezina et al., 2005; Orav-Kotta et al., 2009) can feed on submerged macrophytes. *Cygnus olor* (mute swan) was observed to feed on *Chara* sp. up to 30 cm water depth in the DZBC (Schubert, 2001). *Gammarus tigrinus*, a neozoa in the DZBC since mid-1990s (Zettler, 2001), was described to develop high grazing pressure on submerged macrophytes during spring in the Gulf of Riga (Orav-Kotta et al., 2009). Additionally Berezina et al. (2005) observed in the Gulf of Finland that the ideal diet of gammarids consists of a ratio 1:1 algae and animals (e.g. Rotatoria, Nematoda). This feeding behaviour may have had an impact on food webs in the 2015 mesocosms, where a considerable amount of *G. tigrinus* was observed. The missing top-down control by fish can be another cause. This can indicate that the internal nutrient cycle in some mesocosms was heavily influenced by an altered food web. In addition, the food web in the DZBC changed as well during the last 25 years. There are not only neozoa present, but the fish catch quota dropped also after 1990 from  $800 \text{ t a}^{-1}$  to  $150 \text{ t a}^{-1}$  (Winkler, 2004, 2001 and sources cited therein). However, further work is necessary to investigate the effects of altered food webs on eutrophication processes in the DZBC.

Another aspect besides grazing is the low amount of hibernating submerged macrophytes in the DZBC. There were only low macrophyte biomasses during the winter months in the BO and GB (Piepho et al., 2015). *P. pectinatus* can lose 50 % plant tissue bound P in 7 – 15 days during decay (Granéli and Solander, 1988). This means that P bound in macrophyte biomass during summer months is released during wintertime. Additionally, the spring bloom of phytoplankton happens in April, whereas

the highest macrophyte biomass is found in August (Blindow and Meyer, 2015). Phytoplankton can sustain its high biomass and submerged macrophytes will only co-exist.

Consequently, the results of this work and of BACOSA indicate that submerged macrophytes weakly influence the DZBC, because external and internal pressure is too high (light availability, grazing, water level fluctuation). Their influence in the existing system is to some extent a P pump into the water, rather than a P sink. This becomes particularly important, when looking at the P demand of phytoplankton.

### **4.3 Influences on phosphorus dynamics in the water body**

The described high potential P uptake rates show a physiological demand of phytoplankton in the system. The uptake is correlated with Chl *a*, but there is a lower utilisation far from a freshwater inflow. The positions ZS and RS were different, because a potential growth was only realised in the RS most time of the year. The P pulse in the performed experiments was only effective, as long as it raised growth. All three data sets (Chl *a*, seston, Chl *a*:seston) indicated a permanent potential growth at station RS. Phytoplankton was most probably light limited in the DZBC, too. This would allow growth with increasing dilution by seawater in the other Bodden. Nonetheless, phytoplankton at the station ZS did not show such a growth. Further, the Chl *a*:TP ratio of the long-term data showed no clear correlation independent of seasons. This is contrary to annual periodicities in lakes (Kolzau et al., 2014; Sas, 1989a). Deep lakes tend to be P limited during summer, whereas shallow lakes tend to be N- or light limited (Kolzau et al., 2014). This periodicity in nutrient limitation in lakes is contrary to the predicted opinion for the DZBC, where P is the growth-limiting nutrient (Schlungbaum et al., 2000). The sediments probably have a minor role as autochthonous P source. This is indicated by low seston:TP ratio detected in this work. The negative correlation between seston and TP shows that particulate matter composition is low on P. Lampe et al. (2014) stated the same for the DZBC. They observed that seston consists mostly of mineralic components that precipitate fast.

In addition, the water column of the DZBC is even at the deepest point (Meiningestrom, 16 m, LUNG, 2013), in the ZS (Schumann et al., 2012) and in mesocosms without macrophytes (this work) permanently saturated with oxygen. This corresponds with the measured P fluxes from sediment to water column during BACOSA (Bitschofsky & Forster, 2015, submitted). There was only a diffusive

transport of around  $15 \mu\text{mol l}^{-1} \text{m}^{-2} \text{d}^{-1}$   $\text{PO}_4$  from sediment to water. Baader and Schlungbaum (1982) stated a potential transport of up to  $580 \mu\text{mol l}^{-1} \text{m}^{-2} \text{d}^{-1}$  after 42 d of anoxic conditions. This is more than 30-times higher, than fluxes under the most probable oxic conditions. However, the calculated potential would raise the water TP concentration by  $0.3 \mu\text{mol l}^{-1} \text{d}^{-1}$  (2 m water depth). This low TP concentration would not be detectable in the water column. The low P dissolution from the sediments in the DZBC is contrary to other systems. Sediments in the Gotland Basin in the Baltic Sea can release up to  $800 \mu\text{mol P m}^{-2} \text{d}^{-1}$  during hypoxic events (Schneider, 2011). An occasional upwelling transports  $\text{PO}_4$  rich water in the euphotic zone. There, the  $\text{PO}_4$  rich water supports growth of cyanobacteria (Nausch et al., 2009). Nausch et al. (2012) observed another P pathway, where cyanobacteria in the Baltic Sea sink down the water column and take up  $\text{PO}_4$  above the pycnocline. This P pathway seems possible for the DZBC as well, due to the shallowness of the water body. Phytoplankton can sink down onto the sediment and take up released P, even though the rates are low. However, there is a fluffy layer, which influences nutrient dissolution from sediment to water in the DZBC. Felgentreu (2015) showed that natural fluffy layer can take up and release stored  $\text{PO}_4$ . The total fluxes accounted for up to  $65 \mu\text{mol l}^{-1} \text{m}^{-2} \text{d}^{-1}$  into both directions, from high  $\text{PO}_4$  concentrations to fluffy layer and from fluffy layer to low  $\text{PO}_4$  concentrations. However, these results may be interpreted in both directions. The release of diffusively sediment lost  $\text{PO}_4$  may be buffered and re-precipitates into the sediment at high  $\text{O}_2$  levels. Even higher rates at suboxic conditions can be buffered. The regular occurring resuspension of the water body will raise the  $\text{O}_2$  level and  $\text{PO}_4$  precipitates with  $\text{Fe}^{3+}$ . This happens in brackish waters in around 80 min by iron-colloid forming (pH 8, salinity 6) (Gunnars and Blomqvist, 2002). One hundred percent of released  $\text{PO}_4$  may be incorporated into iron-colloids and sink back to the ground (Gunnars and Blomqvist, 2002). The precipitating time may be even faster, at lower released P concentrations. The fluffy layer in the DZBC consists mostly of mineral components (relative frequency distribution, Felgentreu, 2015). Additionally, the biological  $\text{PO}_4$  uptake in aphotic zones of the DZBC is reduced. The experiments on dark and poisoned water samples indicated this within this work. The reduced uptake during unfavourable conditions for phytoplankton may indicate a pathway between bacterio- to later phytoplankton. Heterotrophic nanoflagellates will graze on bacteria (Jürgens et al., 1999) and release stored P. This intermediate step may elevate the turnover time and lower the effectiveness of the microbial loop in the DZBC. It may be more likely, that the

sediment is still an effective nutrient trap (Bitschofsky & Forster, 2015 submitted). There were higher phytoplankton growth rates close to *Phragmites australis* wetlands in unfertilised samples during the whole year (Karstens, Berthold, Buczko, and Schumann, in prep.). This can indicate that rather external diffuse P sources support the permanent high phytoplankton biomass.

#### **4.4 Influencing factors for a possible re-mesotrophication**

The study of long-term monitoring data revealed that the DZBC is still affected by its catchment area. The relationship between precipitation, nutrient and water transport into rivers (Correll et al., 1999a; Correll et al., 1999b) and estuaries (Jordan et al., 2003) is well described. The Patuxent River estuary had a 3.4-times higher discharge from the catchment area in years with 1.7-times higher precipitation. The elevated water discharge doubled the receiving amount of  $\text{PO}_4$  and TP for the estuary mostly through non-point sources (Jordan et al., 2003). The P discharge in 43 rivers and streams in the USA increased 7.4 % per year mostly by non-point sources (Smith et al., 1987). The long-term data set presented here showed the 2-times lower TP concentrations during years with average precipitation. The same decline in TP concentrations like in the DZBC was described for the Bay of Gdansk during the years 2003 to 2005 (Cieszynska et al., 2012) and the coastal area of Mecklenburg-Western Pomerania (LUNG, 2008). The water TP concentration could rise 2- to 3-times in years with high precipitation (see chapter 3.1 Long-term development of phosphorus between 2000 and 2014). After years with high precipitation, the TP concentration remained high, even though the precipitation in the following years was average again. The TP load via the Recknitz River ranged between  $8 - 10 \text{ t a}^{-1}$  in 2003 – 2005, whereas it rose to 14 t in 2011 (Bachor et al., 2007). The riverine P inflows by Recknitz and Barthe were lowered from  $0.068 \text{ g m}^{-2}\text{a}^{-1}$  P (1983 – 1987) to  $0.054 \text{ g m}^{-2}\text{a}^{-1}$  P (1993 – 1997) (Schlungbaum et al., 2000). However, the diffuse P inputs remained stable at  $0.045 \text{ g m}^{-2} \text{ a}^{-1}$  P (Bachor et al., 2016; Schlungbaum et al., 2000). The main cause for that are the very high soil bound P reservoirs in the catchment area (Figure 22). This potential has steadily grown since the 1950ies. P can be released or transported in particulate form during years with high precipitation (Bachor et al., 2016; Jordan et al., 2003; LUNG, 2013). In addition, small point sources still load above-average P concentrations into the water (Bachor et al., 2016). Almost half of all small point sources (catchment area  $<100 \text{ km}^2$ ) failed the water assessment value for  $\text{PO}_4$  in 2014 (Bachor et al., 2016). This is mostly due to

lacking P elimination capacities in small sewage treatment plants. High P potentials are common for agriculturally used land (Hill and Robinson, 2012).

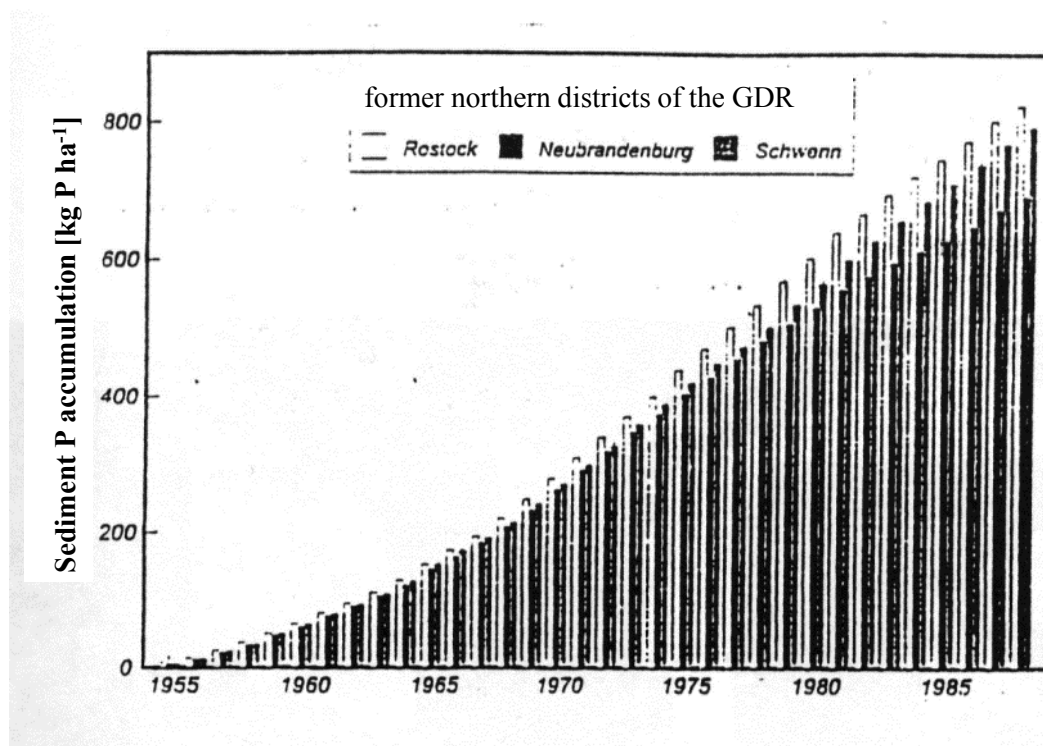
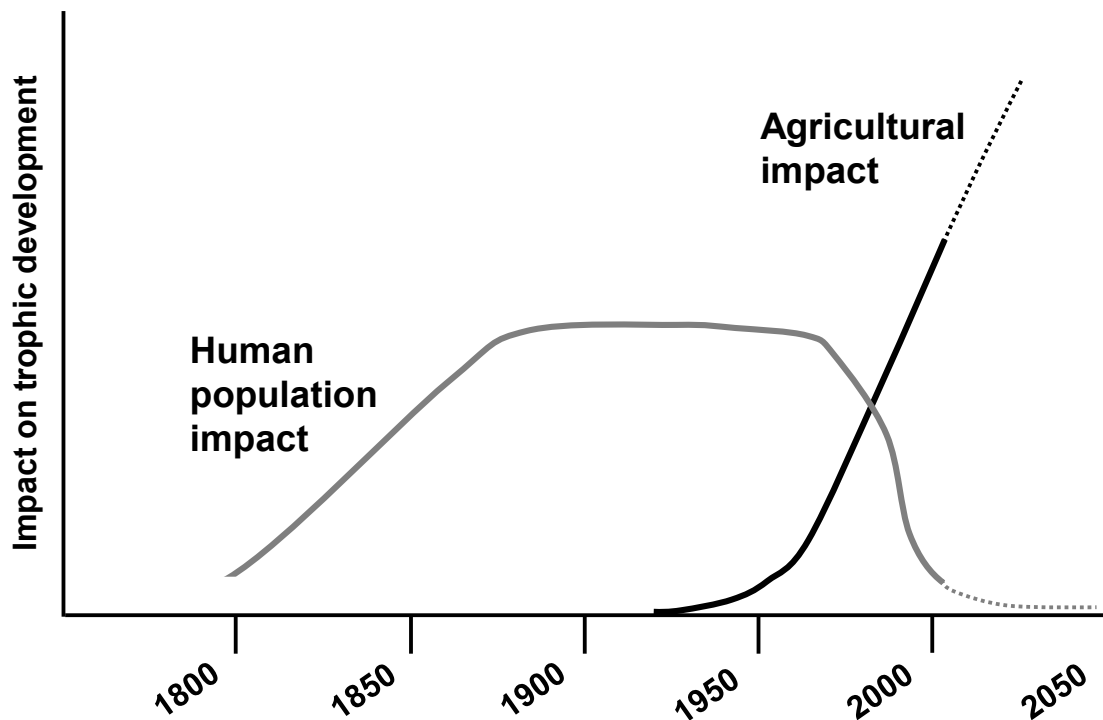


Figure 22 Phosphorus accumulation in soils of the northern districts (former German Democratic Republic) from 1955 to 1990. Modified according to Behrendt (1996) (in Schlungbaum et al., 2000, p. 128).

Another problem regarding the ongoing eutrophication process in the DZBC is that in years with low precipitation the water retention time in the SB is enhanced. A high retention time support a higher phytoplankton biomass, due to lowered dilution (Sas, 1989b). On the other hand, years with high precipitation elevate the P load to the DZBC, which results in higher TP concentrations for some years. In addition, average years produce a sufficient biomass in the SB. This biomass is diluted to other Bodden parts, where phytoplankton more or less sustains itself. The main problem is not a permanent growth of phytoplankton itself, but a permanent growth potential. Those circumstances may negatively affect a re-mesotrophication and “good ecological status” of the DZBC.

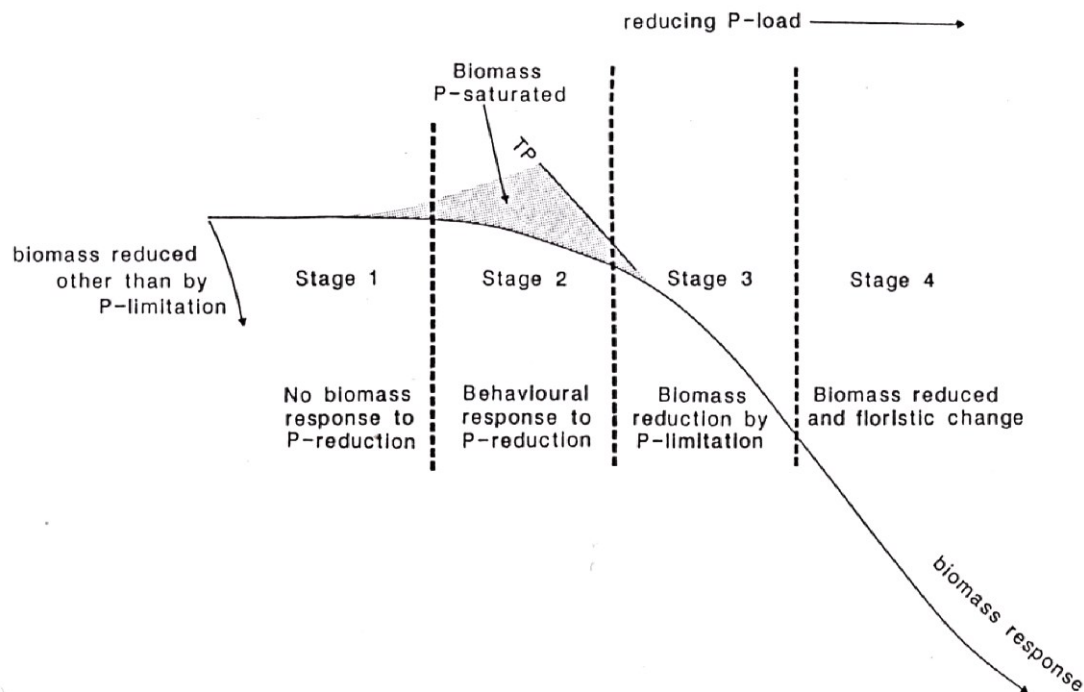
Historical values for P range around  $4.2 \mu\text{mol l}^{-1}$  of organic P in the SB during the 1930ies (Gessner, 1957). First signs of eutrophication were observed in 1932 during a very hot summer (Wundsche 1968 in Schlungbaum et al., 2000, p. 44-a). There was a vegetation decline of charophytes and fish. The sediment was described to turn anoxic. The SB was already dominated by *Sander lucioperca* (zander), an indicator species for

turbid waters, during the 1930ies (Winkler, 2004, 2001 and sources cited therein). *S. lucioperca* can replace *Esox lucius* (northern pike) with increasing eutrophication (Winkler, 2001). *E. lucius* needs less polluted water bodies with lower turbidity (Winkler, 2001). The cause for that is the human population development during 1816 – 1933. The population development reveals an increase of population density of ~25 inhabitants per km<sup>2</sup> (Mecklenburg-Schwerin and Pomerania) to ~58 inhabitants per km<sup>2</sup> (Buchmann, 2009). Around 2.02 million people lived in Mecklenburg-Western Pomerania in 1945 (Buchmann, 2010) and 1.92 million in 1982 (Muth et al., 2010). Around 128 000 inhabitants lived in the catchment area of the DZBC in 1982. This development is crucial to understand the early eutrophication process in the DZBC. Hasler (1947) described that the Lake Zürichsee became dominated by *Oscillatoria rubens* in the 1930ies by the sewage of around 100 000 inhabitants. The same process may have happened in the DZBC. The closing of the Prerow Strom in 1874 (Schlungbaum and Voigt, 2001) and the increasing human population led to a rapid eutrophication process decades before elevated P accumulation in soils occurred. The slowly decreasing impact by humans by treated wastewaters was finally superimposed by industrial fertiliser use (see Figure 23). The high P potential in the catchment area may suppress further re-development. This historical eutrophication process will be investigated further in the project BACOSA II (2016 – 2019).



**Figure 23** Hypothetical impact development of rising human impact by wastewater and agricultural impact by fertilizer use. Course rests upon development of human population and fertilizer use in the catchment area between 1810 and 2014. The rapid end of human impact was because of sewage treatment plants. The dotted line at the agricultural impact are due to ongoing fertilization and nutrient transport by diffuse sources.

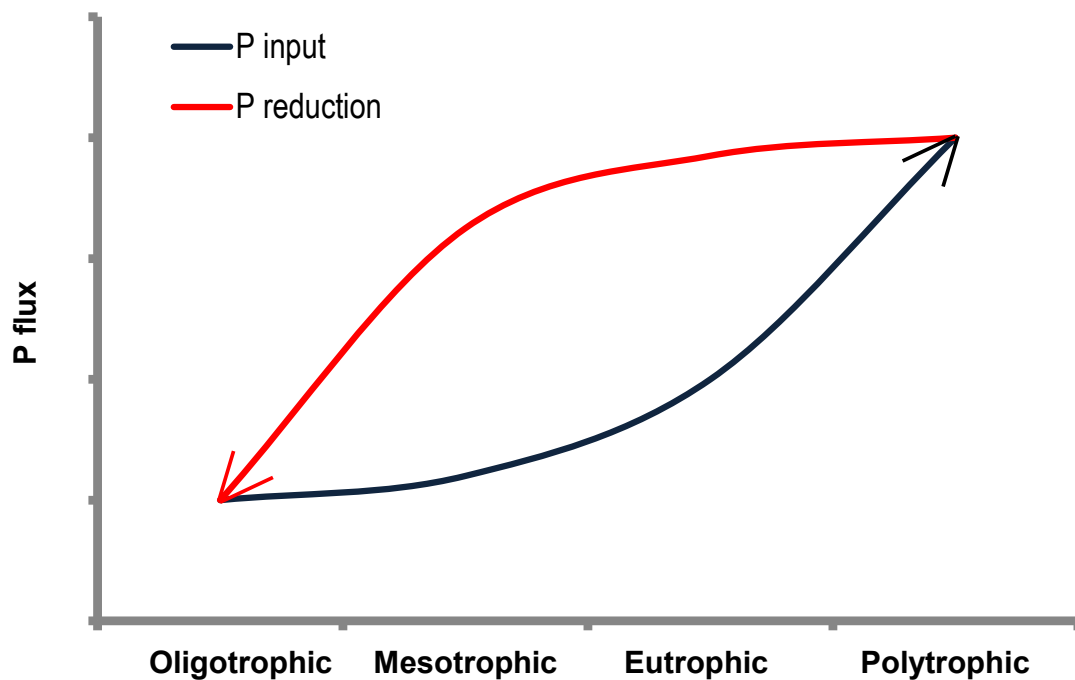
Interestingly, the optical density did not reduce after the nutrient reduction (Schiewer, 2007). A possible explanation is the optical density increase by cyanobacteria (*Oscillatoria* sp.) under nutrient limitation (Ihlenfeldt and Gibson, 1975). The effect can persist even after nutrient pulses. This can be a positive feedback effect by cyanobacteria dominance (Scheffer et al., 1997). This feedback will prevent macrophyte dominance even under moderate TP concentrations. Further, phytoplankton can already be in a compensation process due to the lowered TP concentrations (Figure 24, Sas, 1989b). This was indicated by the variable Chl *a*:TP ratio observed in this work. Phytoplankton had occasionally the same Chl *a* concentration with TP concentration between 0.8 to 4.0  $\mu\text{mol l}^{-1}$  in the GB. If the phytoplankton can sustain its biomass, with at least 0.8  $\mu\text{mol l}^{-1}$ , the P reduction needs to be even lower than that concentration. The question arises, if the phytoplankton can use the whole TP pool. This issue can be solved by fractionating the seston material regarding its P compartments (Hupfer et al., 1995). The fractioning can show the amount of bio-available P in the seston and if phytoplankton can use it.



**Figure 24** Schematic representation of responses by the algal community to reduction of phosphorus inlake concentrations. (Text and Figure in Sas, 1989b; p. 136).

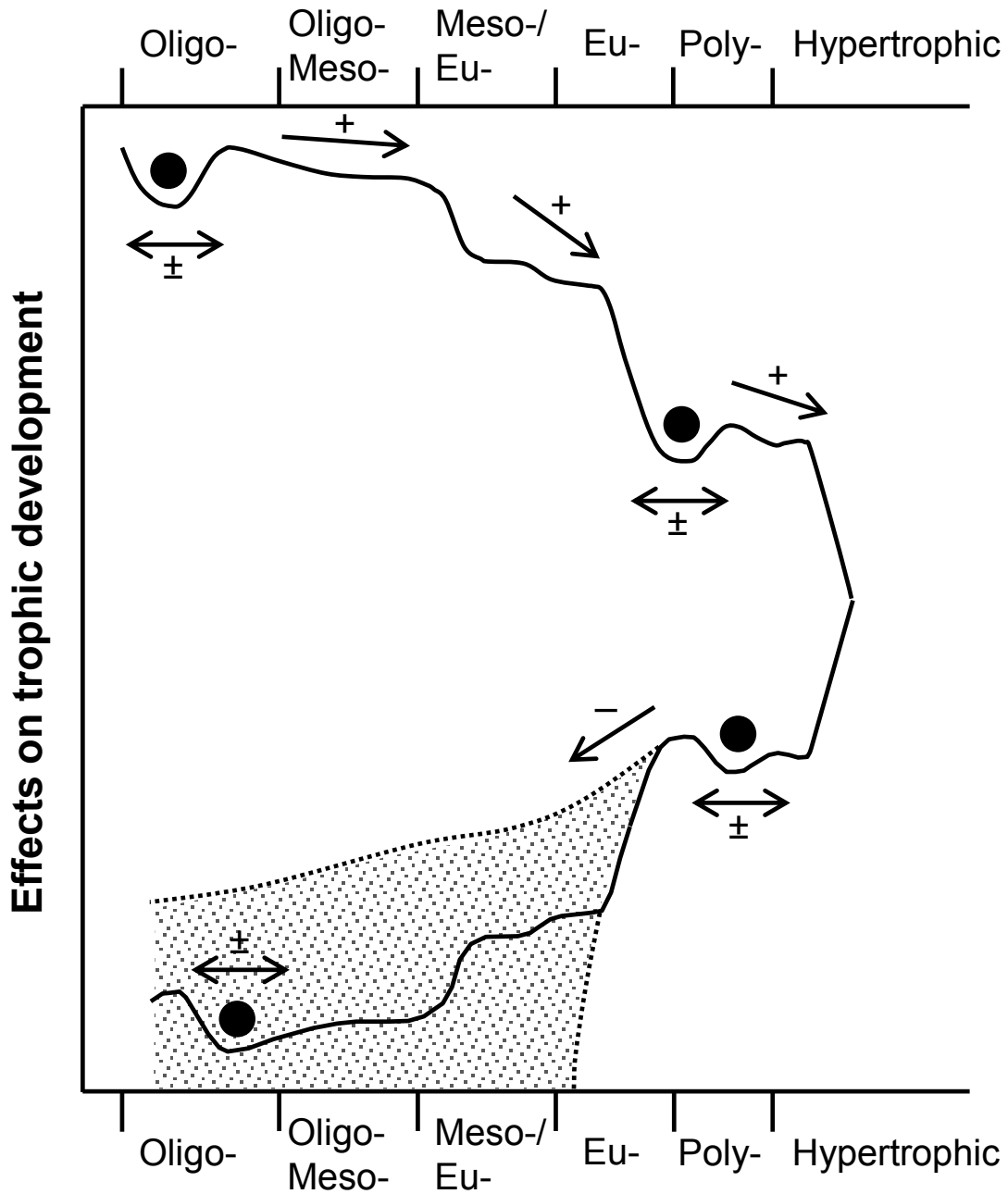
In fact, some mesocosms and field experiments in shallow eutrophic lakes revealed that phytoplankton dominance can be controlled by N reduction (Blindow et al., 2014, 1993; González Sagrario et al., 2005). Macrophytes declined with TN concentrations  $> 140 \mu\text{mol l}^{-1}$  due to shading effects by epiphytes and phytoplankton (González Sagrario et al., 2005).  $\text{NO}_3$  and TN in the ZS can reach winter concentrations up to  $250 \mu\text{mol l}^{-1}$  and  $350 \mu\text{mol l}^{-1}$ , respectively (Schumann et al., 2012). High  $\text{NO}_3$  concentrations lower the P re-solubility from sediments (Jensen and Andersen, 1992). Further, zooplankton grazing increased only after  $\text{NO}_3$  depletion in the DZBC, due to changed food web composition (Heerkloss, 2001). Proposed TN water concentrations ranged from  $70 - >140 \mu\text{mol l}^{-1}$  TN (Blindow et al., 2014; González Sagrario et al., 2005) and  $0.6 - 1.0 \mu\text{mol l}^{-1}$  TP (Blindow et al., 2014; Correll, 1998) to effectively reduce shading effects on macrophytes. In bio-manipulated mesocosms TP values can be higher to achieve a clear water state (Hosper and Jagtman, 1990; Jeppesen et al., 1990). The LUNG and the Institute for Baltic Sea Research (IOW, Warnemünde) calculated a nutrient reduction of 5000 t N and only 62 t P to reach the “good ecological status” in all water bodies in Mecklenburg-Western Pomerania (Bachor et al., 2016). The N:P ratio (mol:mol) for these values are 176:1 and indicate a greater threat by TN than by TP in coastal waters.

However, all these processes can show a hysteresis. This hysteresis is particularly important for aquatic systems (González Sagrario et al., 2005; Morris et al., 2006; Scheffer et al., 1997). The initial amount of P in the catchment area was altered to such an extent that the reduction must be much higher, than the former inputs (Figure 25). The long-term data showed a development that will affect the system for decades.



**Figure 25** Scheme of hysteresis process on trophic levels with phosphorus (P) flux as the input variable. The output variable is the system itself. The initial P flux into the system causing alterations is lower, than the reduction necessary to re-mesotrophicate the system. This is due to the changed output variable because of P enrichment. The reduction has to be higher and longer to alter the system to its former state.

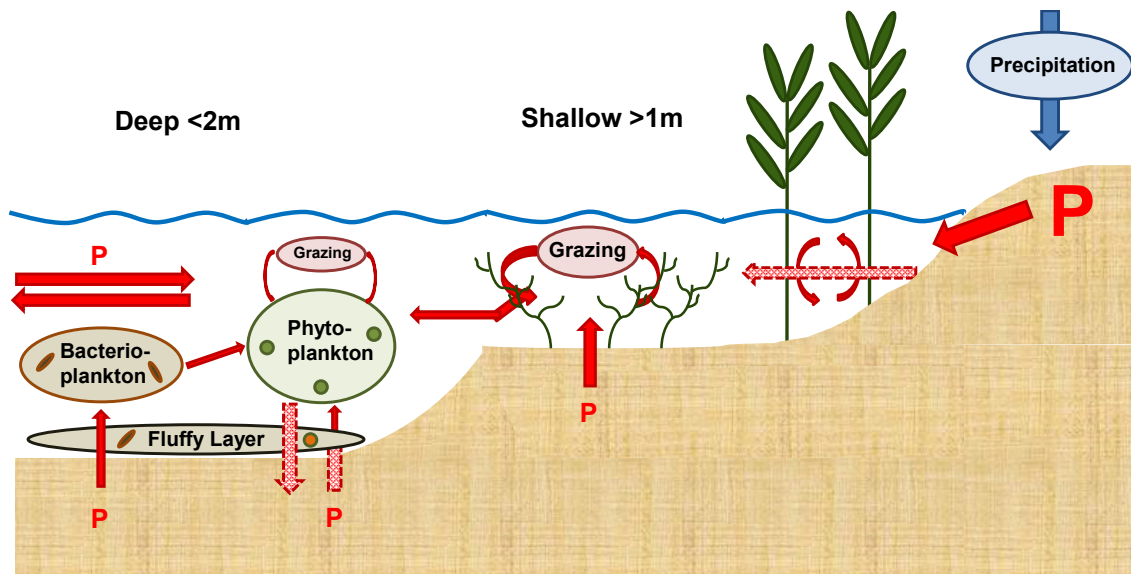
In addition, the way back to a re-mesotrophicated system has different resilience mechanisms that will affect re-mesotrophication (Figure 26). Those effects are hard to predict (González-Alcaraz et al., 2012; Morris et al., 2006). Further, all described re-mesotrophicated or re-oligotrophicated systems have changed in terms of e.g. species composition and food-web structure (Jeppesen et al., 2005; Sas, 1989a).



**Figure 26** Scheme on the trophic development of the Barther Bodden between 1969 and 1990 and the possible re-development including the process of hysteresis. Symbol (+) shows the raising trophic development, symbol (±) show resilience behaviour (positive and negative feedback loops) in a semi-stable state, which can go in both direction, if a threshold is passed, symbol (-) shows effects that lower the trophic level. The dotted area and lines show the possible development due to hysteresis. It is uncertain if the system can re-develop to lower trophic levels, due to unknown feedback loops and the altered output variable (P in system and catchment area); (upper part from oligo- to hypertrophic state after Schiewer, 2007, p. 62.).

#### 4.5 Synthesis and conclusions

Eutrophication is not *a priori* “good” or “bad”. Those are terms of an anthropogenic point of view. Eutrophication was first discussed as chance to elevate C fixation in systems and elevate food webs on higher trophic levels (Hasler, 1947). However, an effect of higher P availability on the global C cycle was not yet observed (Falkowski et al., 2000). It is questionable, if the “good ecological status” can be set fix historical for all aquatic systems. The DZBC has anthropogenic influenced sediment layers up to 1 m (Lampe et al., 2014). Other lagoon systems at the Southern Baltic Sea show lower turbidity and higher macrophyte colonisation, due to an elevated water exchange with the Baltic Sea (Blümel et al., 2002; Schiewer, 2001). The logical consequence would be to re-open the DZBC again to the Baltic Sea. This will recreate the state before human impact. Yet, the Marine strategy framework directive (MSFD) protects the Baltic Sea. Moreover, in cases where the public interest of more than one country is inflicted, following point takes effect: “[...] *Member State refers to action taken for overriding reasons of public interest, the Commission should assess whether any modifications or alterations made to the marine environment as a consequence do not permanently preclude or compromise the achievement of good environmental status in the marine region or subregion concerned or across marine waters of other Member States. The Commission should provide guidance on possible necessary modifications if it considers that the measures envisaged are not sufficient or suitable to ensure coherence of action across the marine region. [...]*” (European Community, 2008). Even though WFD and MSFD are both equal European right, only the MSFD shall be applied, if the Baltic Sea suffers from restoration actions in the DZBC. Until today, the DZBC is a very effective nutrient filter for the Baltic Sea. The concentrations of dissolved nutrients at the opening to the Baltic Sea are less than e.g. at the Warnow river mouth (LUNG, 2013). All actions that will increase the exchange with the Baltic Sea, may negatively affect the eutrophication process in the Baltic Sea itself. It must be considered, that a macrophyte-dominated system may not buffer nutrients to that extent during winter due to a loss of biomass, or inactivity. The present phytoplankton system in the DZBC is very stable and macrophytes do exist as well (see Figure 27 as graphical conclusions). Even the water column is oxygen saturated the whole time regardless of macrophyte colonisation, like observed in the mesocosms in this work and by others (LUNG, 2008; Schumann et al., 2012).



**Figure 27 Graphical conclusions and harmonised hypotheses.** The effect of autochthonous phosphorus (P) sources on the course of eutrophication is lower. The impact of stochastic events, like high precipitation, transport considerable amounts of P into the system and keep it eutrophicated. The impact of submerged macrophytes is low, due to grazing pressure and late growth. Dotted arrows show fluxes of yet unknown magnitude. P flows into and out of the system (left side) may be of equal size. Bacterioplankton is linked to phytoplankton as possible nutrient distributor out of deeper zones. This influences the microbial loop, because of low grazing pressure on the phytoplankton.

The only disadvantage for humans is the high turbidity, due to a loss of utility for recreation (Bartsch, 1970). However, this work stated clearly, that the eutrophication process dates back much longer than just the last few decades. Phytoplankton is most of the time growth limited. P was one of the main causes for the rapid eutrophication in the first place. However, it was replaced by positive feedback loops and co-limitation of N and light (Harpole et al., 2011). The consequences shall be redevelopment of the catchment area before restoration of the DZBC (Bachor et al., 2014; Mikkat, 2014). Such redevelopment measures are e.g. renaturation of the river beds and reforestation in the catchment area. Some of this measures are already planned (Mikkat, 2014). This will result in lower nutrient loads for both, the DZBC and the Baltic Sea. Terrestrial systems will profit from this by higher biodiversity (Smith et al., 1999) and finally this will be beneficial for humans, too.

## 5 Summary

Nowadays, the human induced rapid eutrophication is one of the biggest threats for aquatic systems. The eutrophication process was accelerated by the increased availability of limiting nutrients, like phosphorus (P) and nitrogen (N), which were increasingly utilised as fertilisers for agricultural production. Unlike N, P accumulated in fertilised soils over decades and built up a high potential availability in soils. Already in the mid of the 20<sup>th</sup> century the anthropogenic P input into ecosystems was four times higher, than the natural background. P is transported from fertilised soils into aquatic systems by drainages, groundwater, and erosion. This increased P availability elevated primary production in systems that were P limited. Countermeasures, like the EU-water framework directive, were introduced, which reduced the phosphorus loading by point sources, like rivers. However, not all systems re-developed after the nutrient reduction. One of those aquatic systems is the Darß-Zingst Bodden chain (DZBC), a shallow, polymictic lagoon in the Southern Baltic Sea. P inputs were lowered 25 years ago, but the system remained with a high phytoplankton biomass and turbidity. There are hypotheses, that the autochthonous sources for P, like sediments and microbial turnover, are still too high. However, there is also the possibility that the high phosphorus potential in the catchment area still affects the DZBC. This work analysed for the first time both, the influence of autochthonous and allochthonous P sources on the phytoplankton community.

A 15 year-data set of the Biological Station Zingst was analysed to determine stochastically allochthonous effects in the DZBC. Growth and fertilisation experiments were conducted with samples of the main freshwater inflow and the middle part of the DZBC. A 10  $\mu\text{mol l}^{-1}$  phosphate pulse was used to determine a possible P demand at these sampling areas. A possible competition between recolonising submerged macrophytes and phytoplankton was analysed for two years in mesocosms experiments.

The analysis of the long-term data showed that the DZBC is influenced by the P potential in the catchment area. Particular striking was the 3-times higher total P concentrations in years with high precipitation, compared to years with average precipitation. The total P concentration was highest in Bodden parts close to the main freshwater inflow during years with high precipitation. Simultaneously, the seston concentrations were 3-times lower, whereas the Chlorophyll *a* concentration was doubled.

The phytoplankton growth close to the freshwater inflow was in 90 % of all cases higher with P addition. There was a permanent growth during all seasons and phosphate pulses were taken up in most cases in 1 to 7 hours completely. Phytoplankton in the middle part of the DZBC grew only in 40% of all cases with P addition. Growth only occurred during autumn and winter. Phosphate uptake during summer and winter was reduced by 40 – 90 %.

Submerged macrophytes had no biomass reducing effect on phytoplankton in the mesocosms experiments. There was always one replicate with high, medium, and low Chlorophyll *a* concentration, independently of macrophyte colonisation in 2014. All mesocosms were densely populated with *Gammarus tigrinus* in 2015. The mesocosms with the highest *G. tigrinus* population showed no macrophyte colonisation and up to 8-times higher total P concentration in the water column.

The mesocosm results indicate that food webs can have a considerable effect on the trophic state in the DZBC. The growth experiments showed that the P loading of the DZBC is still high enough to permit permanent growth close to freshwater inflows. Phytoplankton at more distant sites was probably co-limited for other nutrients or light. These results correspond well with the long-term development. The data set analysis revealed that the P potential in soils of the catchment area is still high enough to influence the DZBC in years with high precipitation. These periodic events become important for ecosystem recovery. There will be no ecosystem recovery, as long as the P potential by diffuse sources remains high. Therefore, a redevelopment of the catchment area is favourable before considering restoring actions in the DZBC.

## 6 Literature

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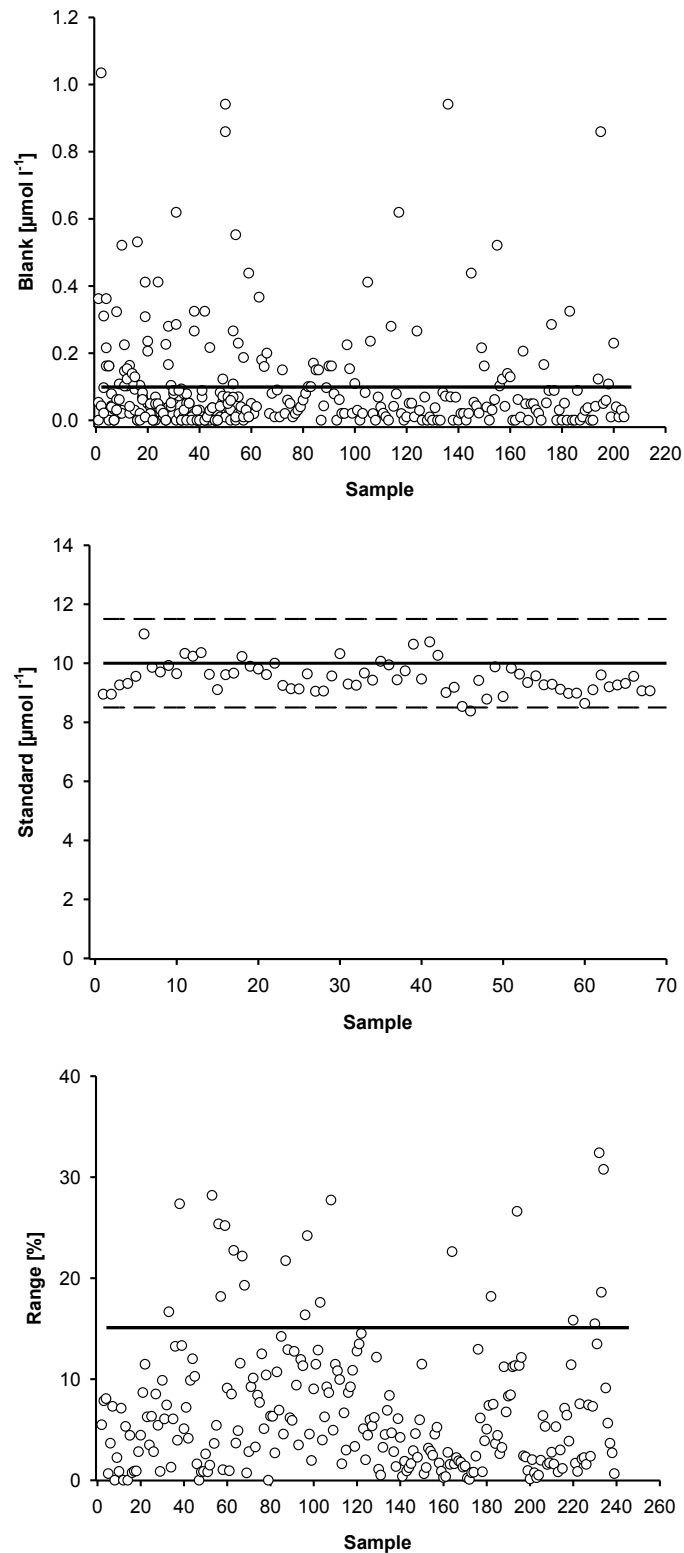
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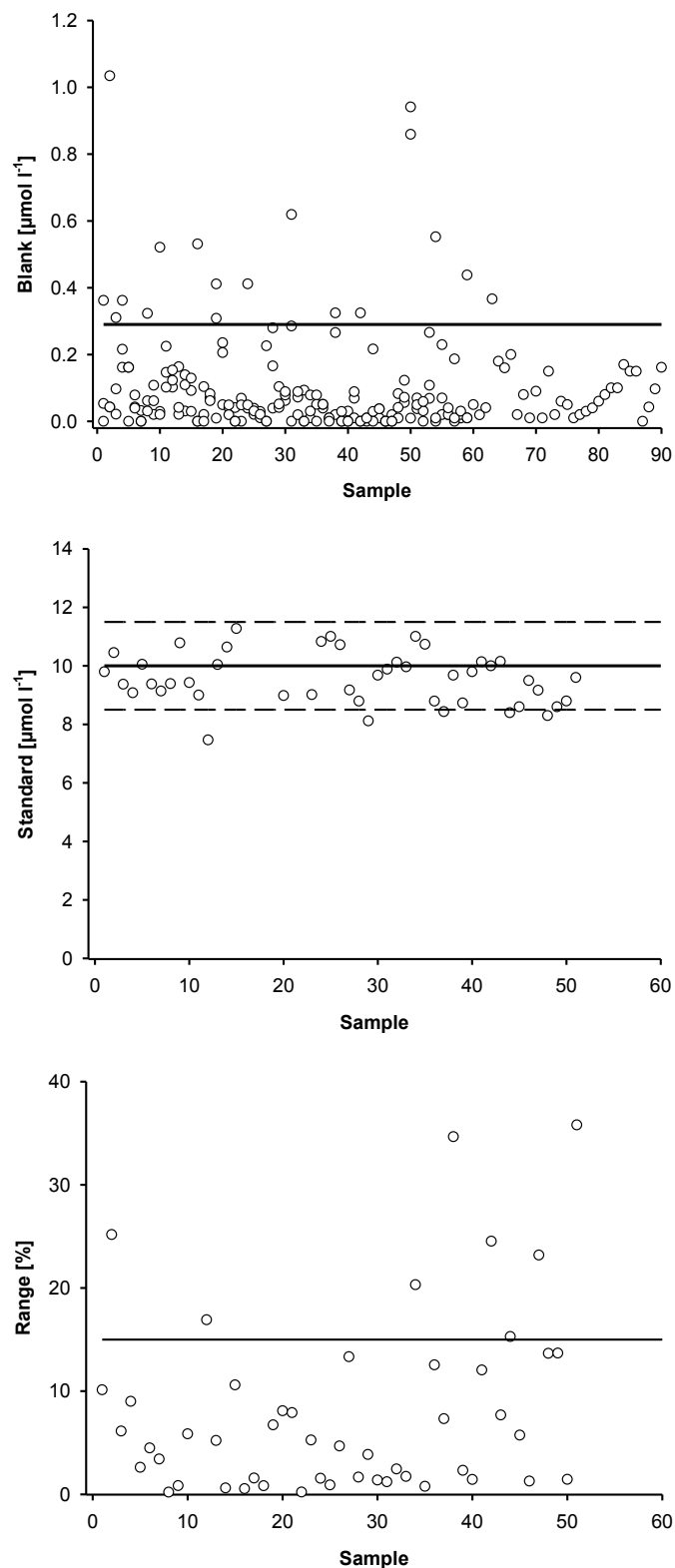
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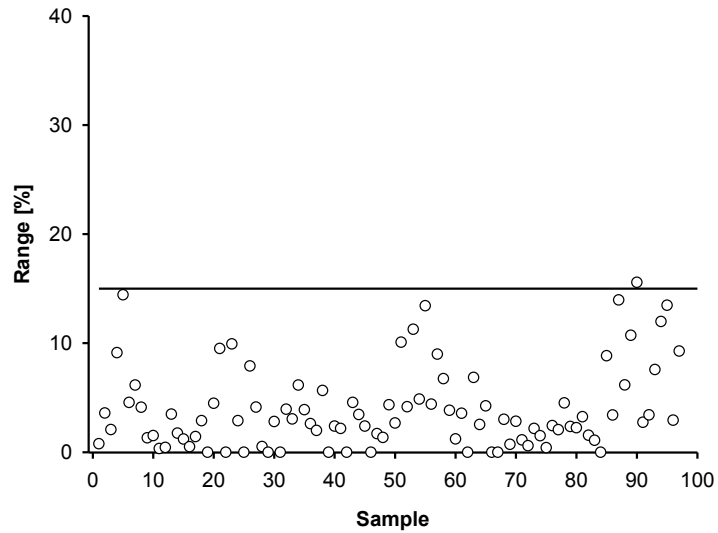
## Appendix



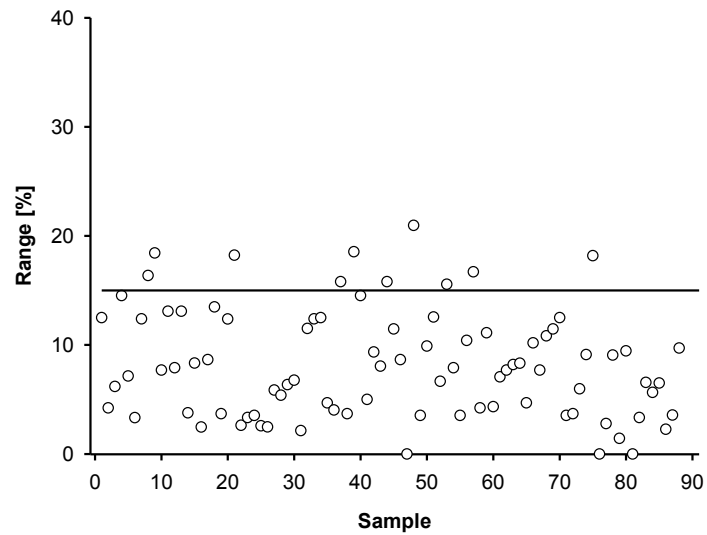
**Figure A 1 Control charts for phosphate analytics for the duration of the experiments.** Blanks ( $n=204$ ) were measured in ultrapure water ( $<0.05 \mu\text{S m}^{-1}$ ); solid line: determination limit of  $0.1 \mu\text{mol l}^{-1}$ . Standards ( $10 \mu\text{mol l}^{-1} \text{PO}_4$ ) for all  $\text{PO}_4$  determinations ( $n=69$ ); dotted line:  $\pm 15\%$  as tolerance limits, solid line: reference values. Range values ( $n=239$ ) as measuring replicates of experimental samples; solid line:  $+15\%$  as tolerance limit.



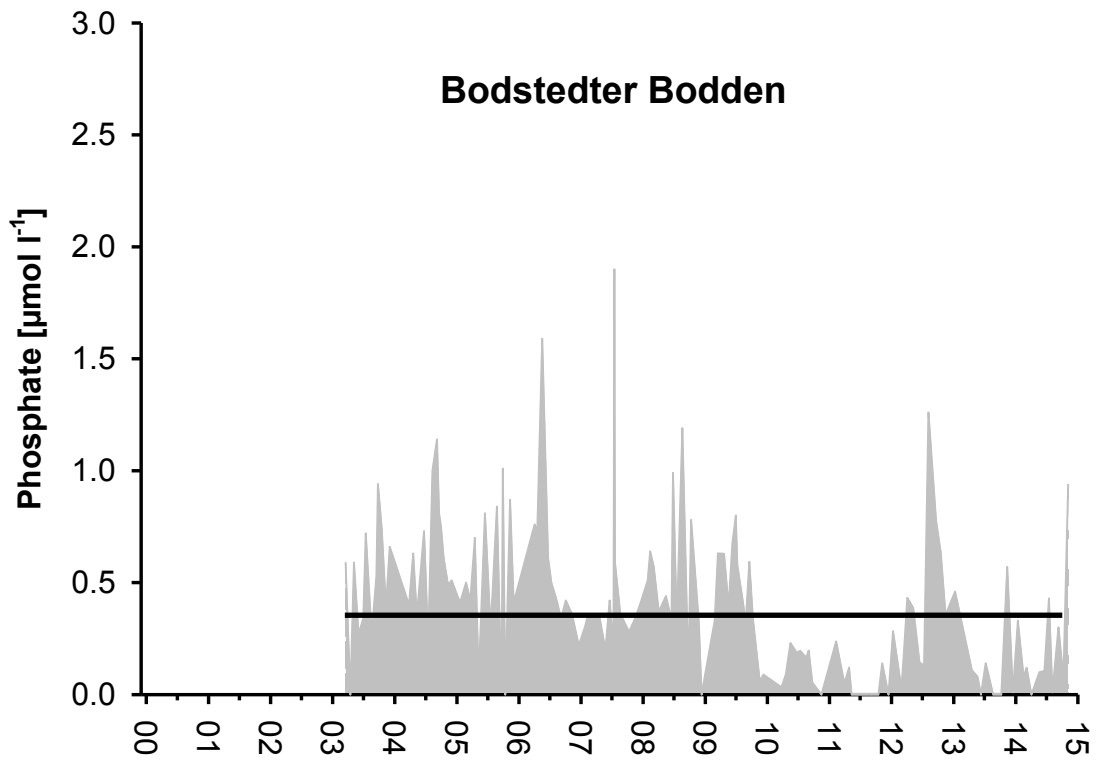
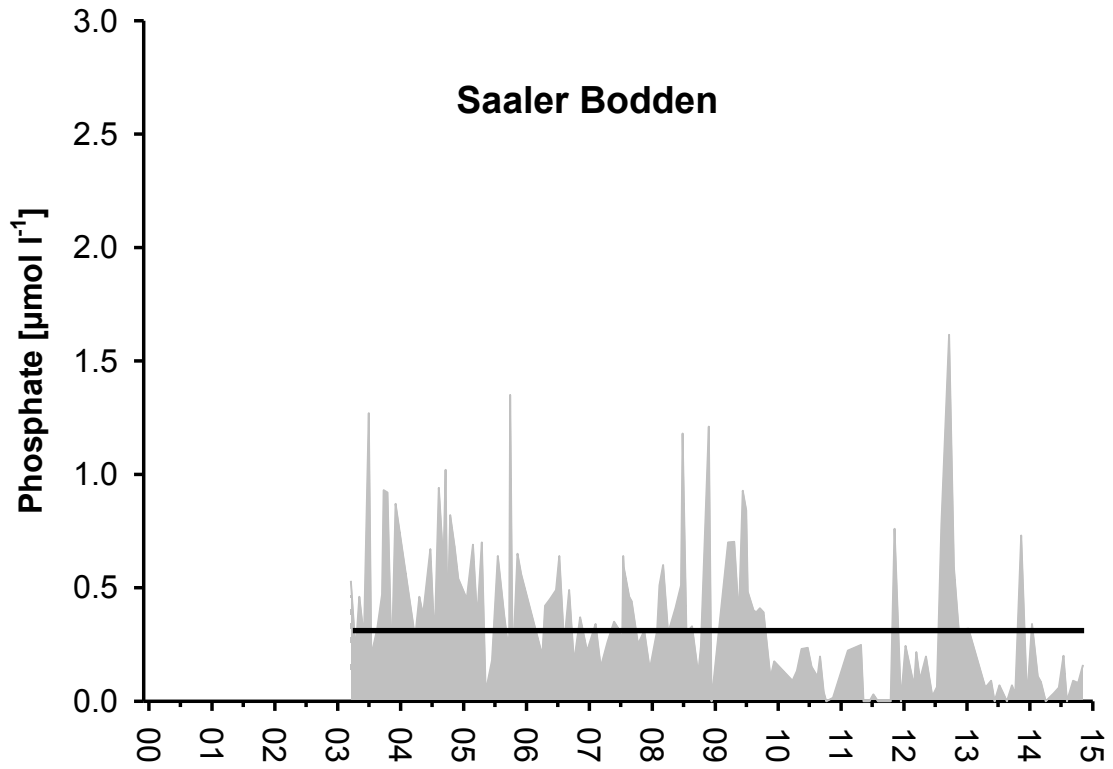
**Figure A 2 Control charts for total phosphorus analytics for the duration of the experiments.** Blank control chart (ultrapure water;  $<0.05 \mu\text{S m}^{-1}$ ;  $n=90$ ) during all TP digestions; solid line: determination limit of  $0.3 \mu\text{mol l}^{-1}$ . Standards ( $10 \mu\text{mol l}^{-1}$  diphenylphosphate or glucose-6-phosphate) during all TP digestions ( $n=51$ ); dotted line:  $\pm 15\%$  as tolerance limits, solid line: reference values. Range values ( $n=51$ ) as measuring replicates of experimental samples; solid line:  $+15\%$  as tolerance limit.



**Figure A 3** Range control chart for Chlorophyll *a* determination for the duration of the experiments. Range values (n=97) as measuring replicates (n=2) of experimental samples; solid line: + 15 % as tolerance limit.



**Figure A 4** Range control chart for seston determination for the duration of the experiments. Range values (n=88) as measuring replicates (n=3) of experimental samples; solid line: + 15 % as tolerance limit.



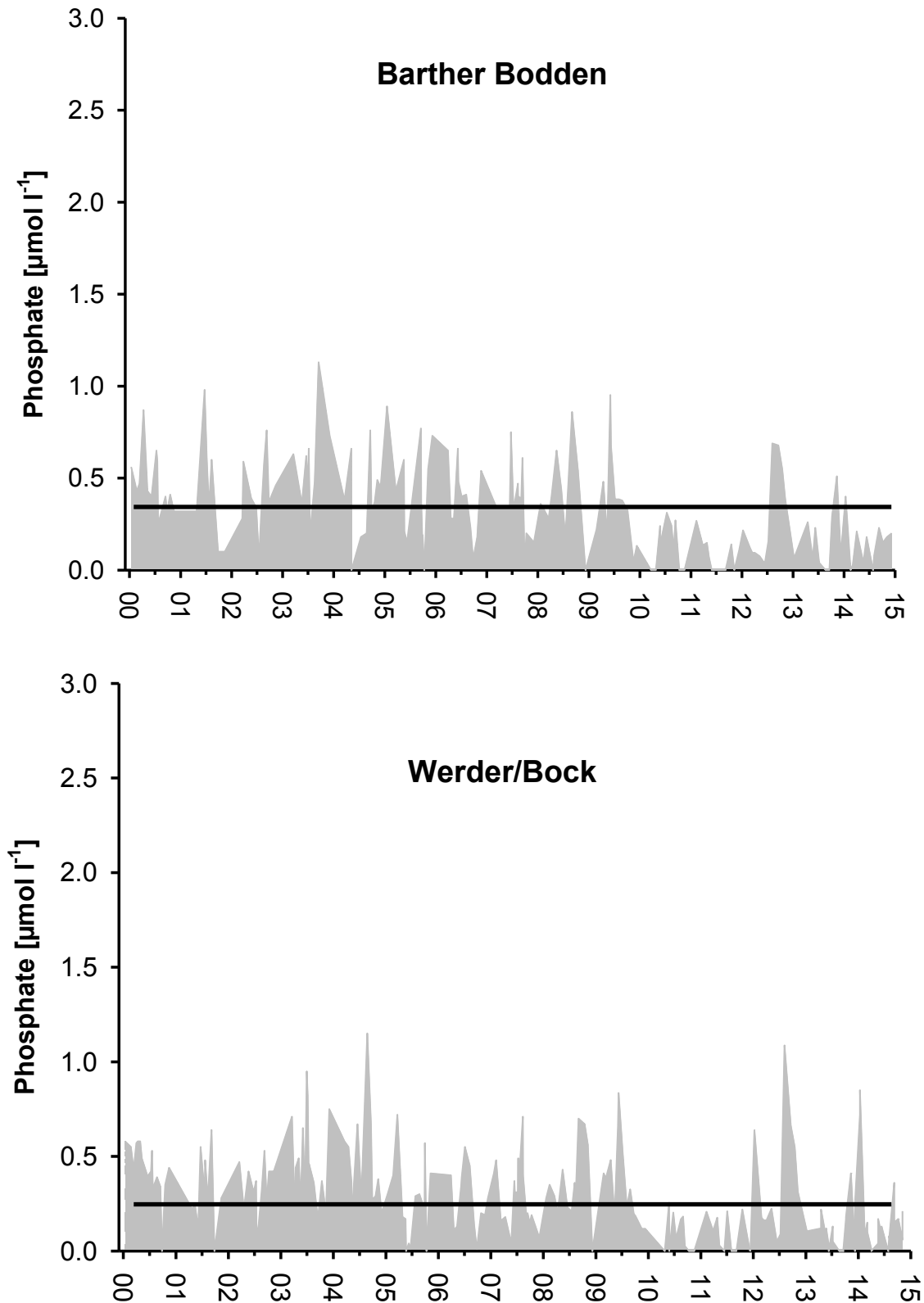
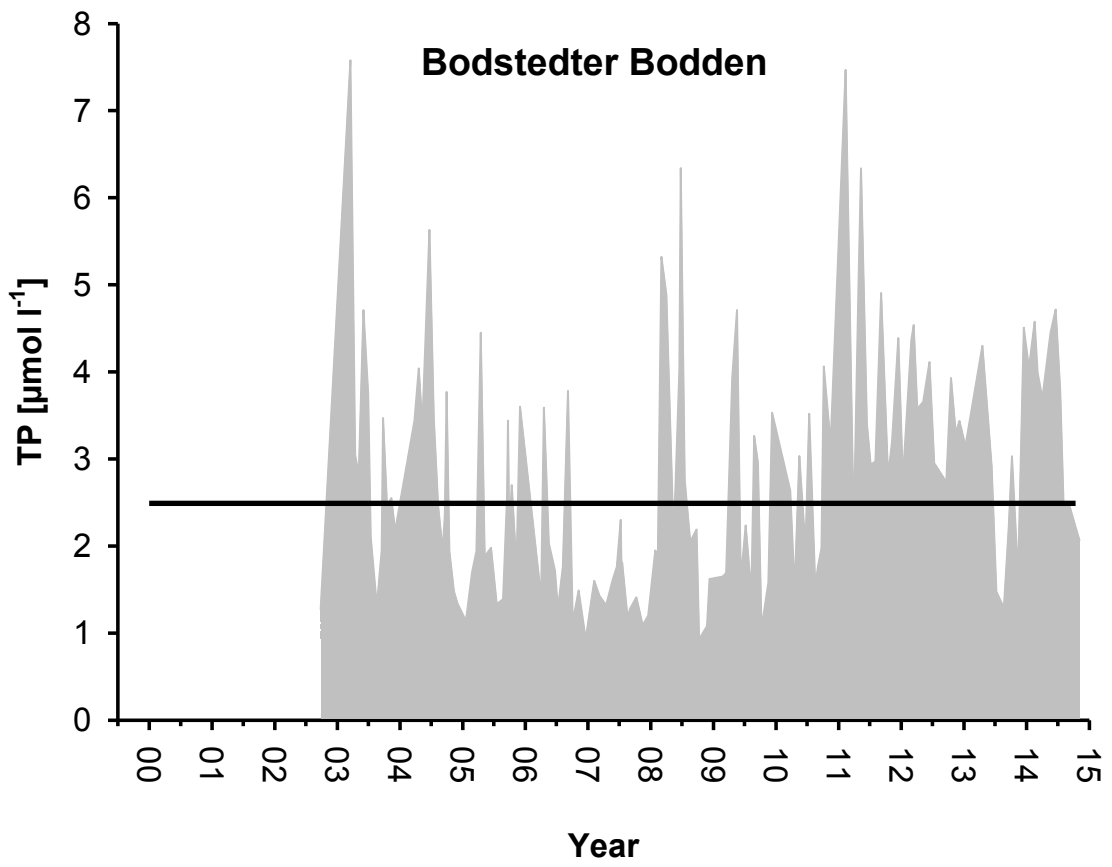
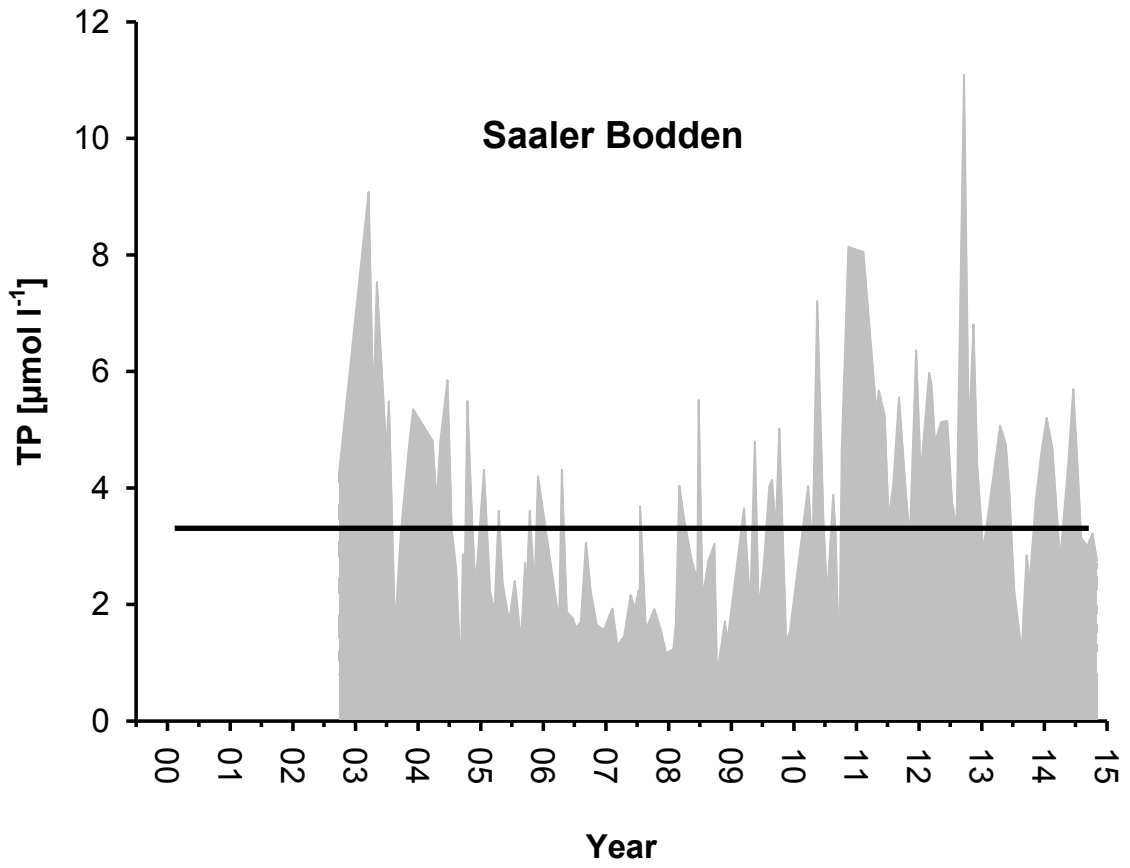
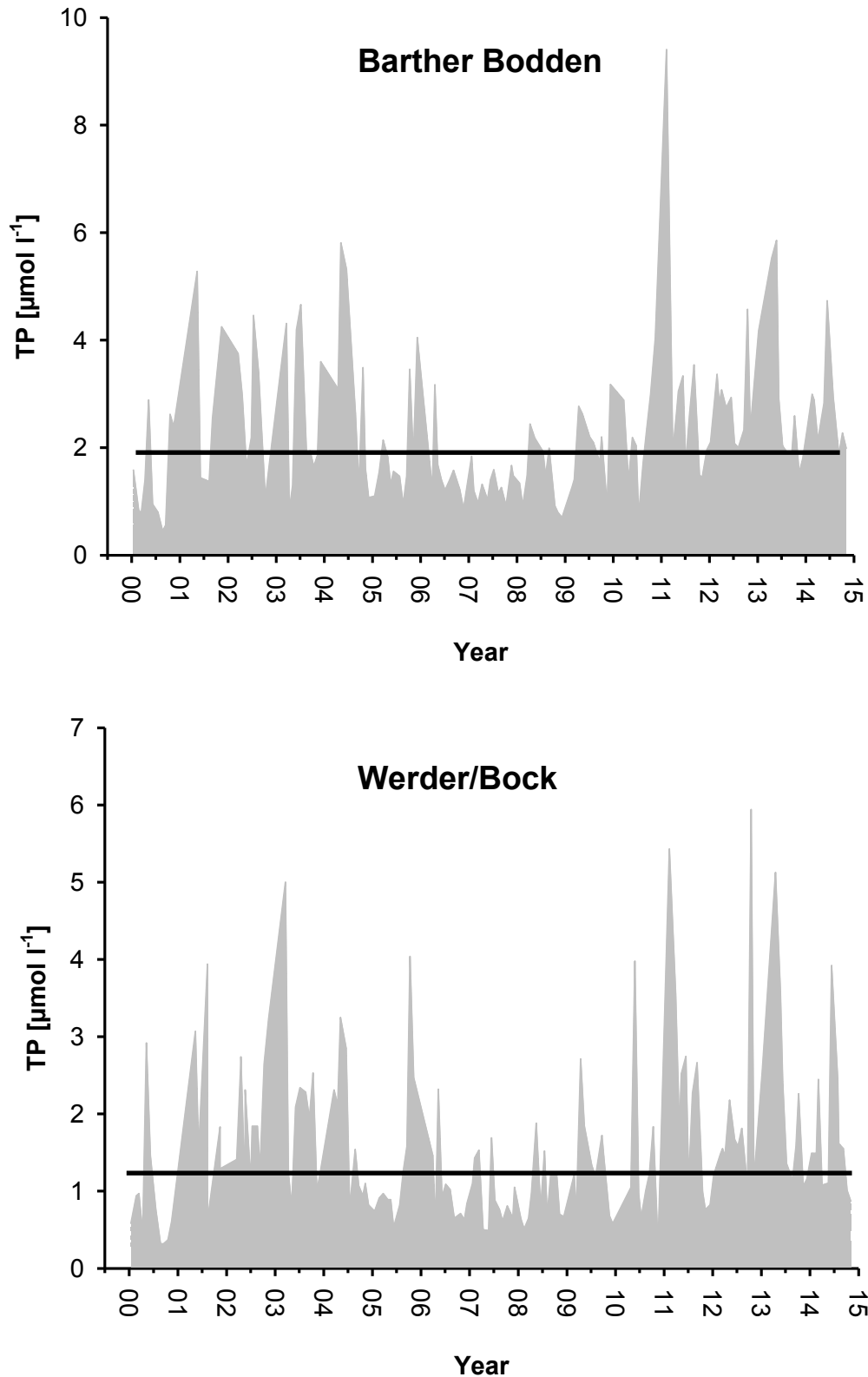
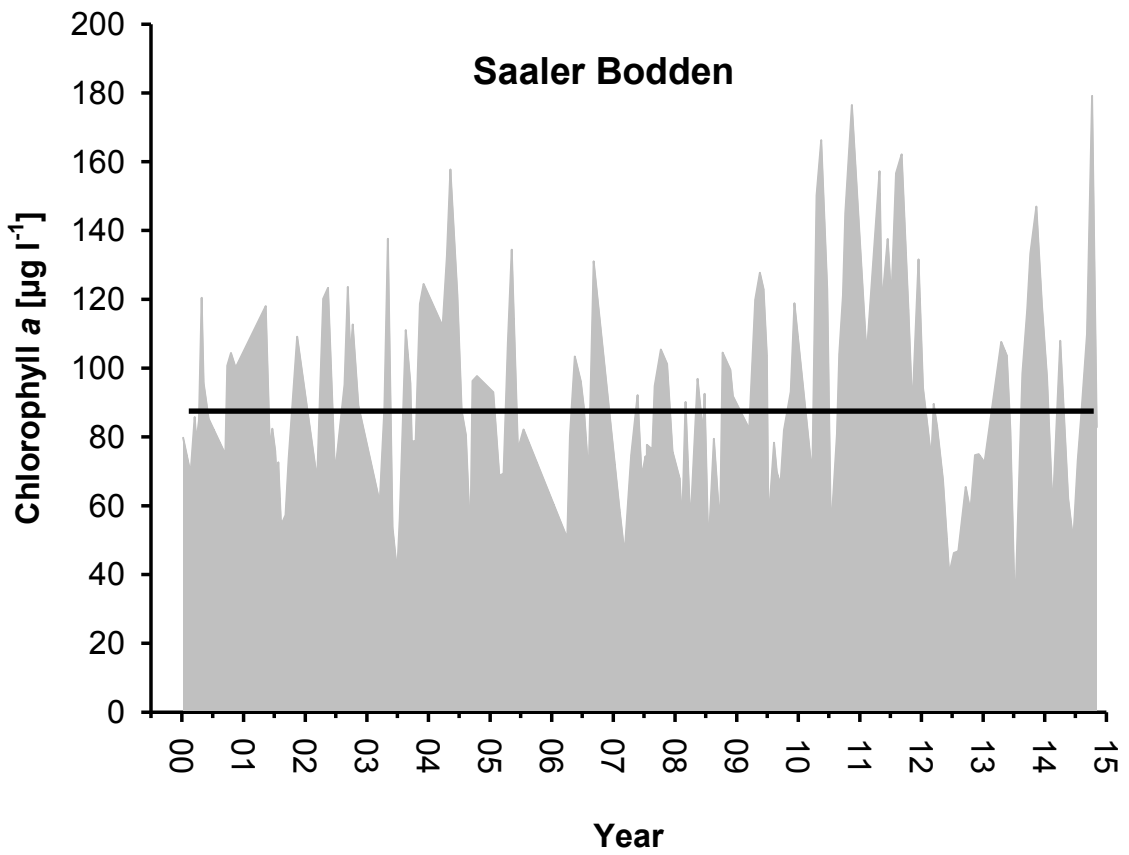
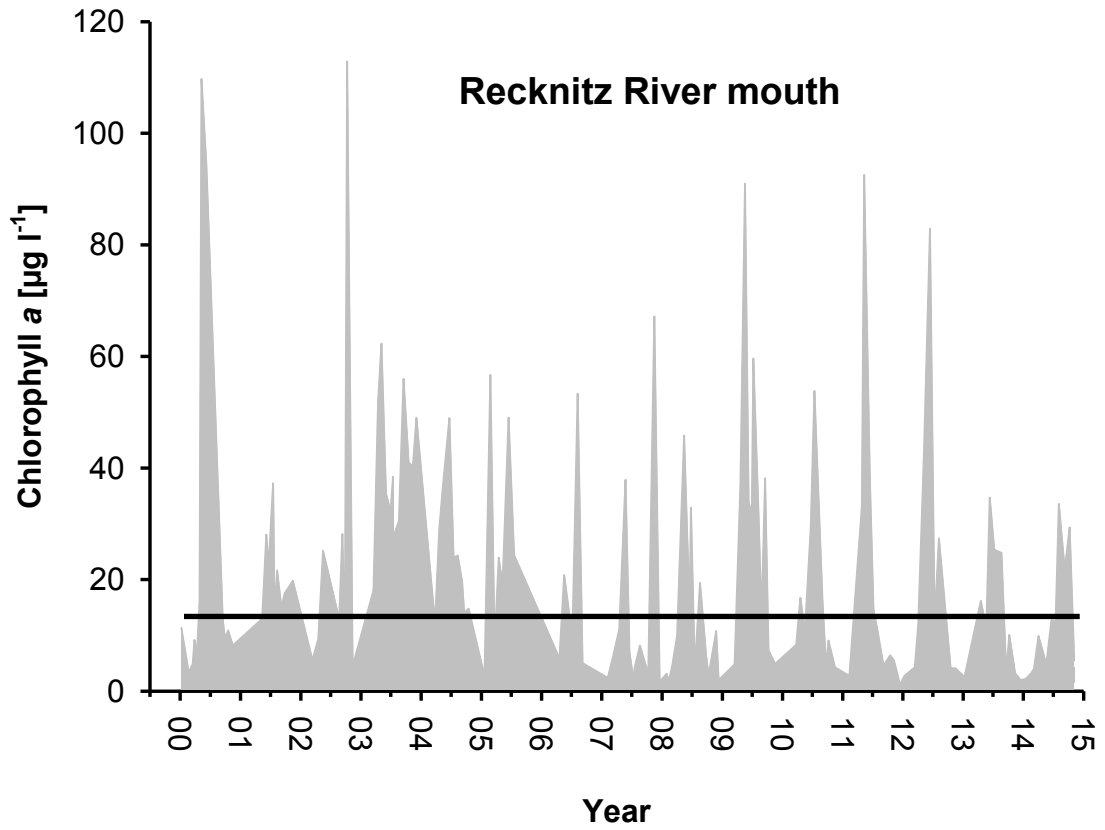


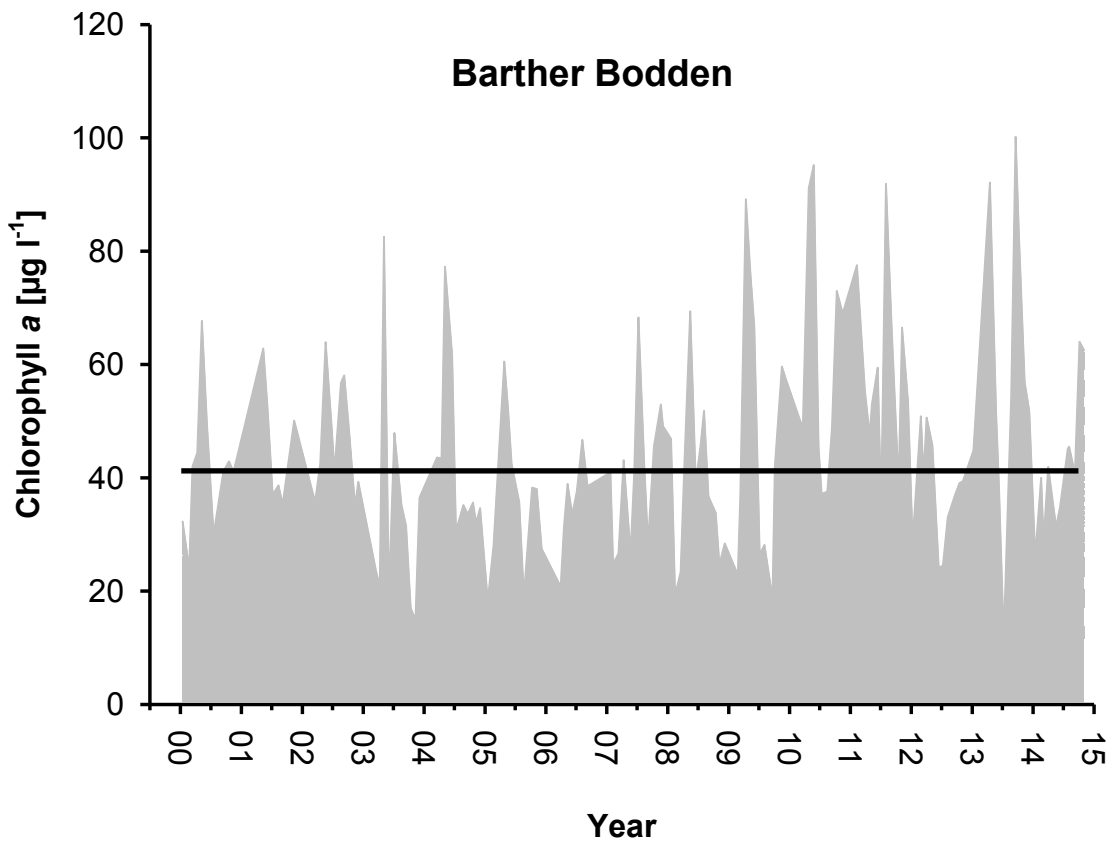
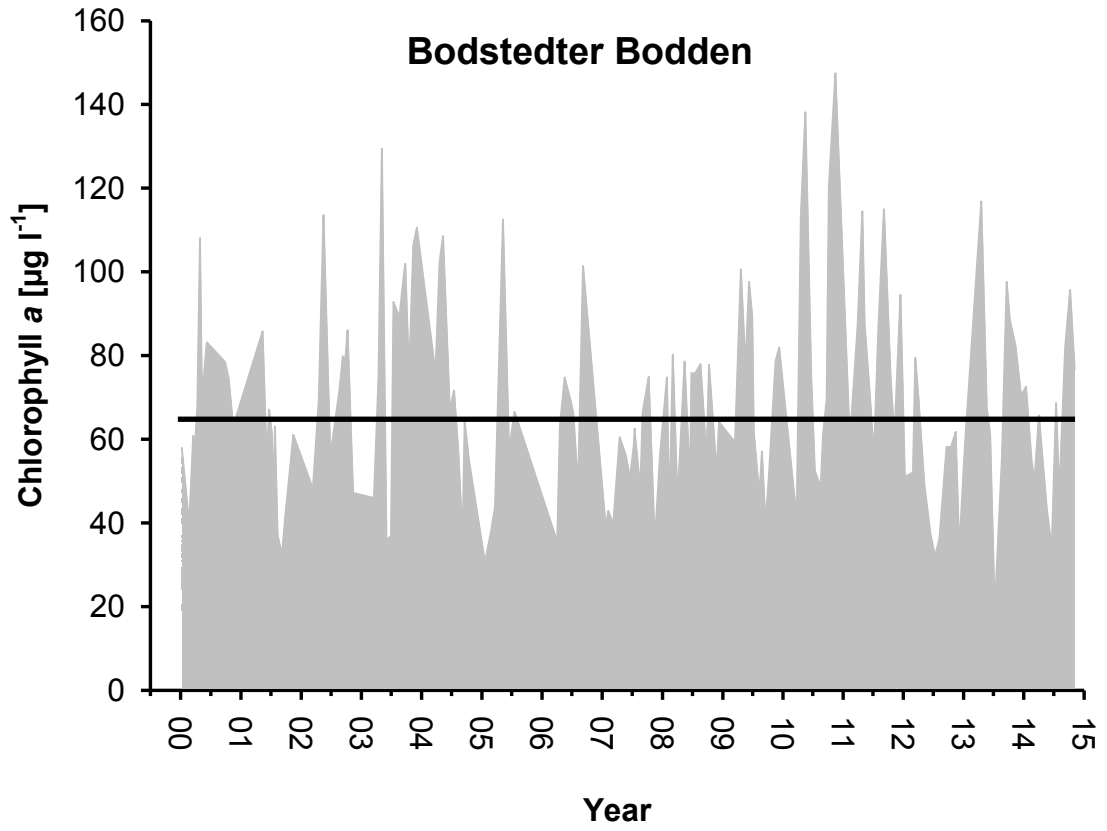
Figure A 5 Long-term development of phosphate ( $\text{PO}_4$ ) [ $\mu\text{mol l}^{-1}$ ] in the Saaler Bodden, Bodstedter Bodden, Barther Bodden and Werder/Bock during 2000 – 2014. From west to east: Saaler Bodden (SB, n=138), Bodstedter Bodden (BO, n=140), Barther Bodden (BB, n=200), Werder/Bock (WB, n=198). Solid black line shows median of all values during the sampling time. Please note the different y-axes scaling for better visualisation of differences. Data set: Biological Station Zingst.

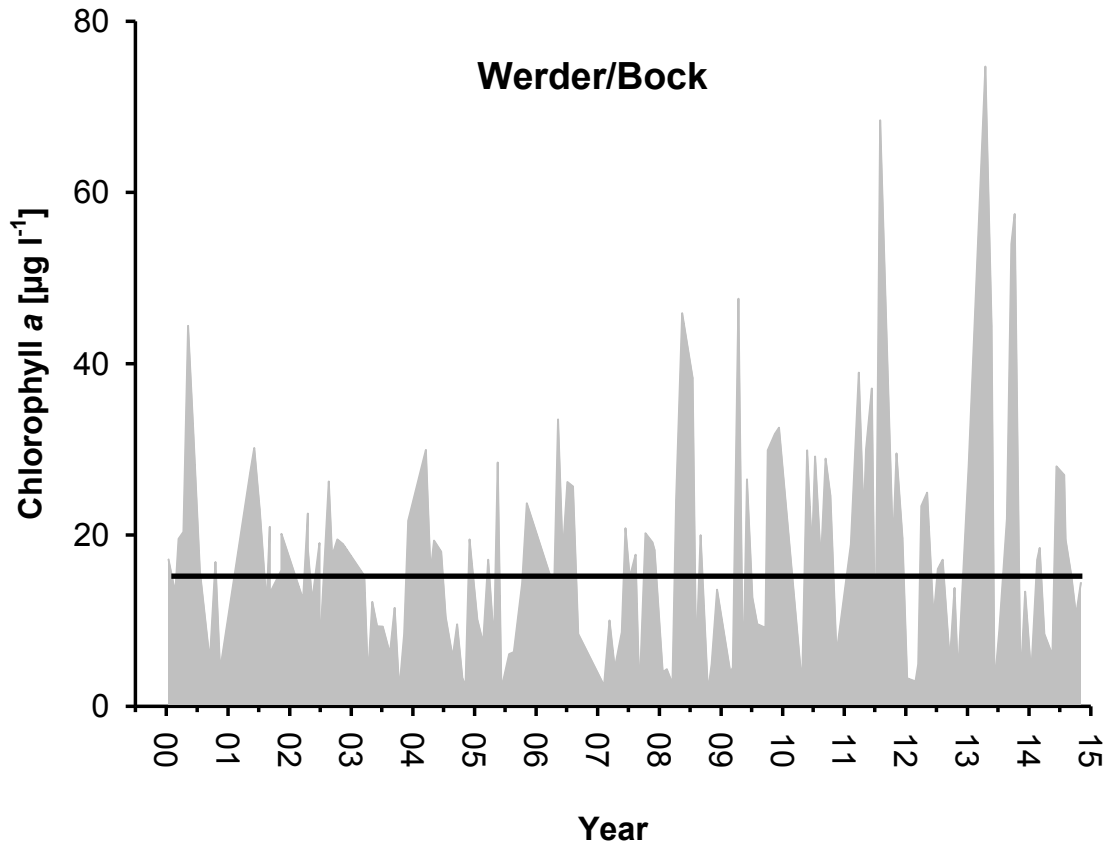




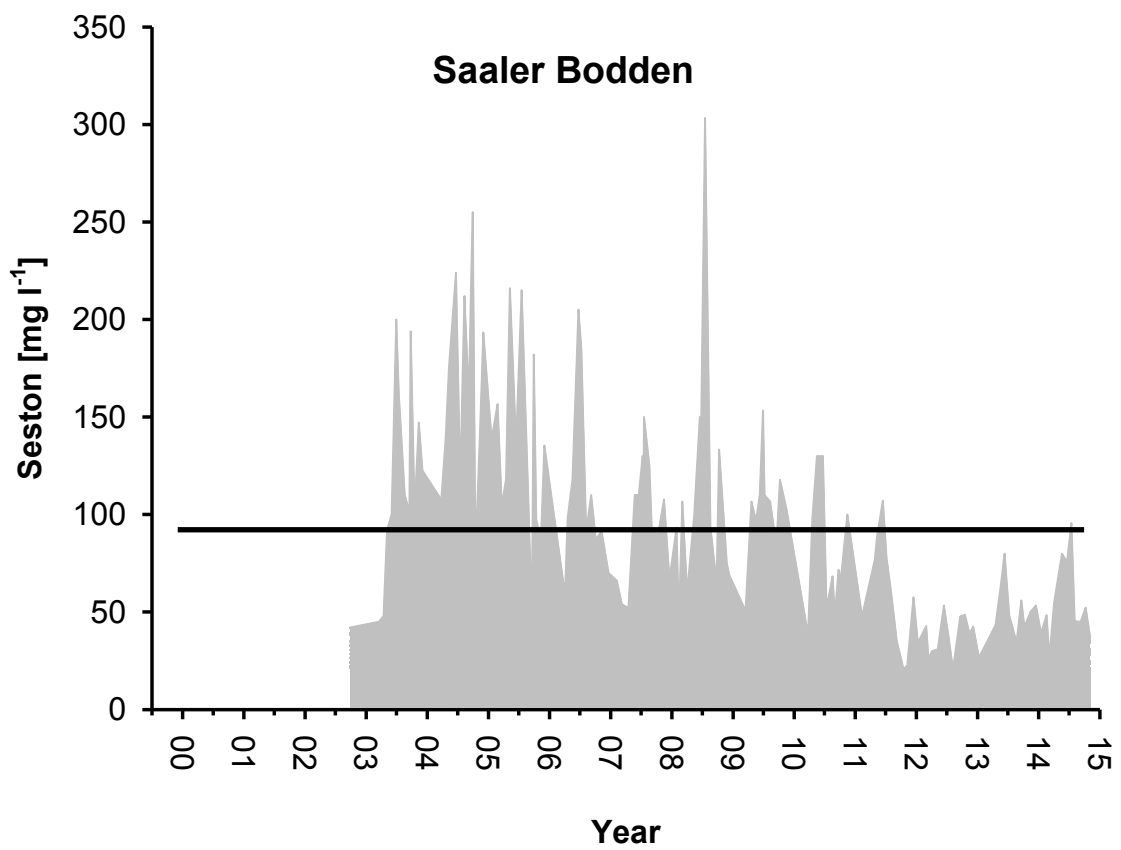
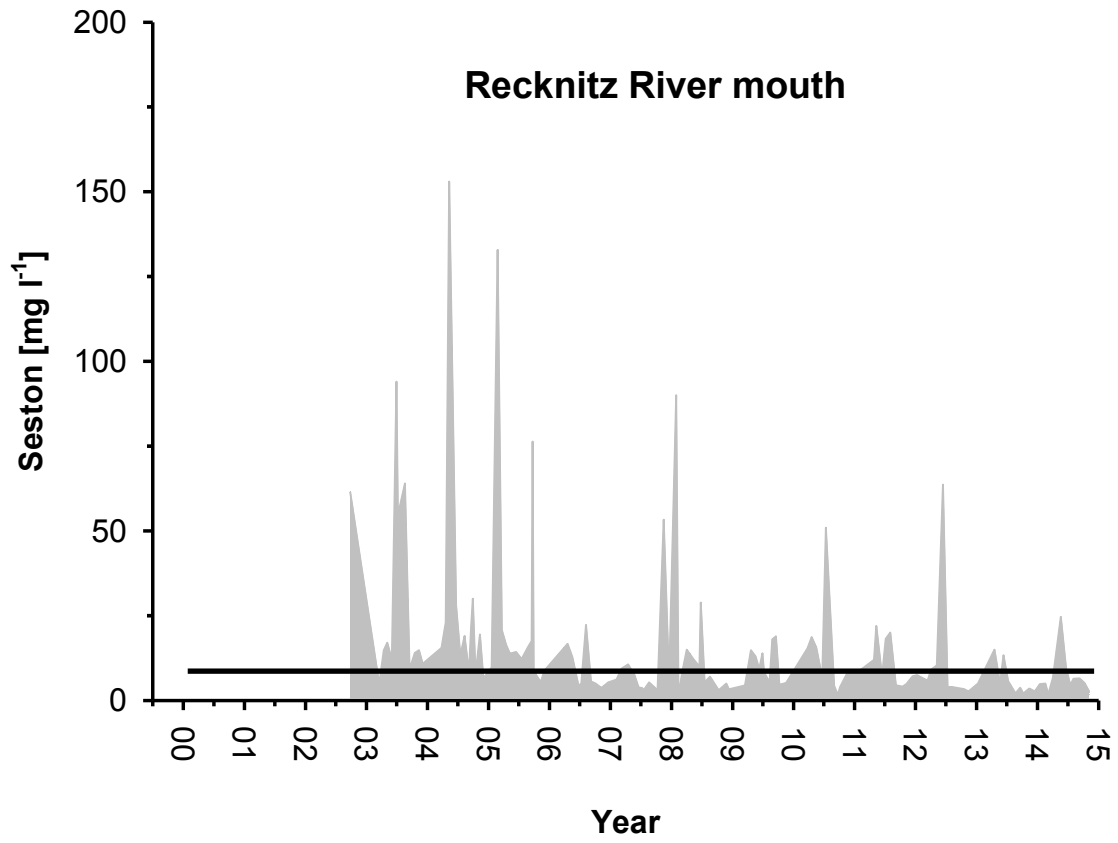
**Figure A 6** Long-term development of total phosphorus (TP) [ $\mu\text{mol l}^{-1}$ ] in the Saaler Bodden, Bodstedter Bodden, Barther Bodden and Werder/Bock during 2000 – 2014. From west to east: Saaler Bodden (SB, n=138), Bodstedter Bodden (BO, n=142), Barther Bodden (BB, n=161), Werder/Bock (WB, n=162). Solid black line shows median of all values during the sampling time. Please note the different y-axes scaling for better visualisation of differences. Data set: Biological Station Zingst.

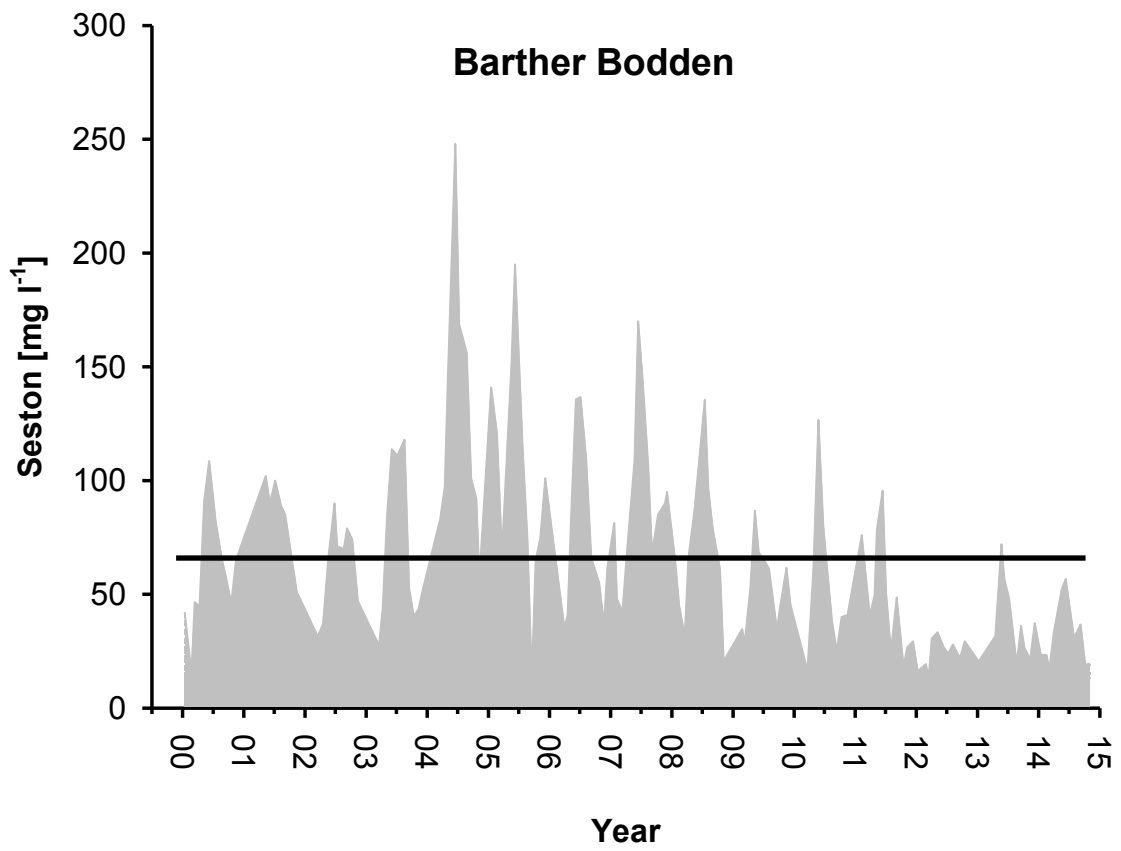
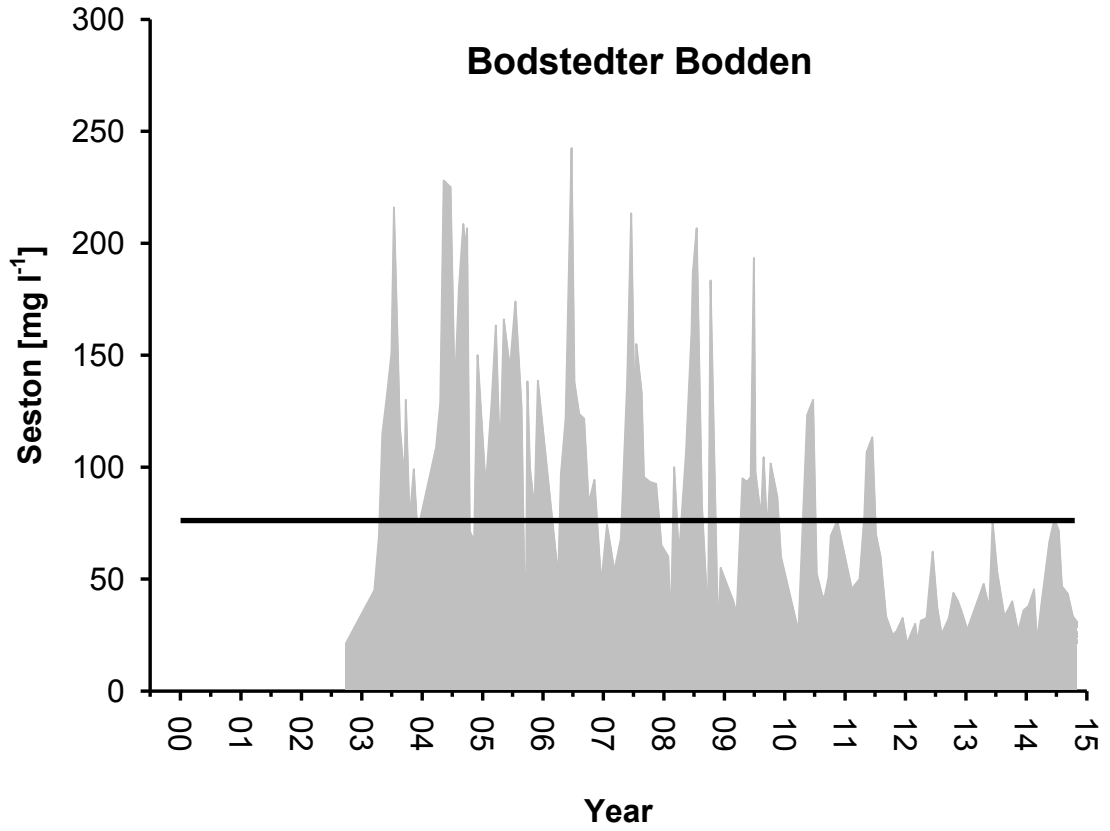


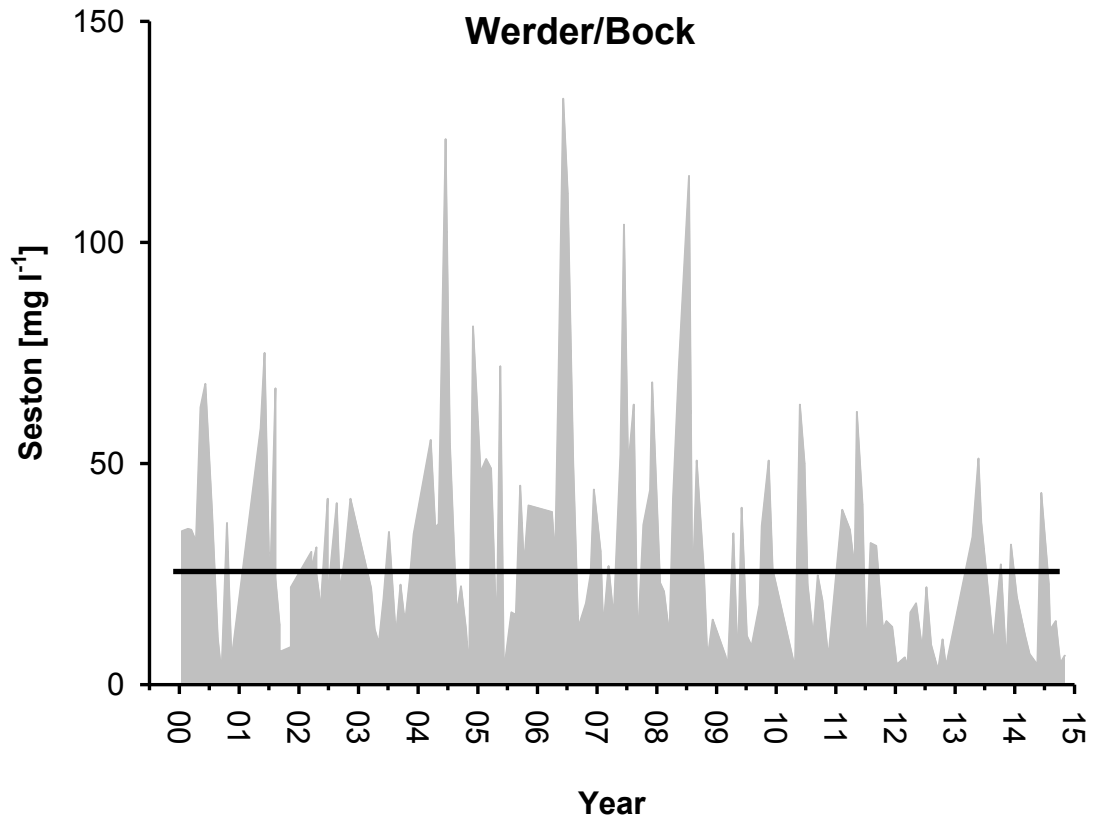




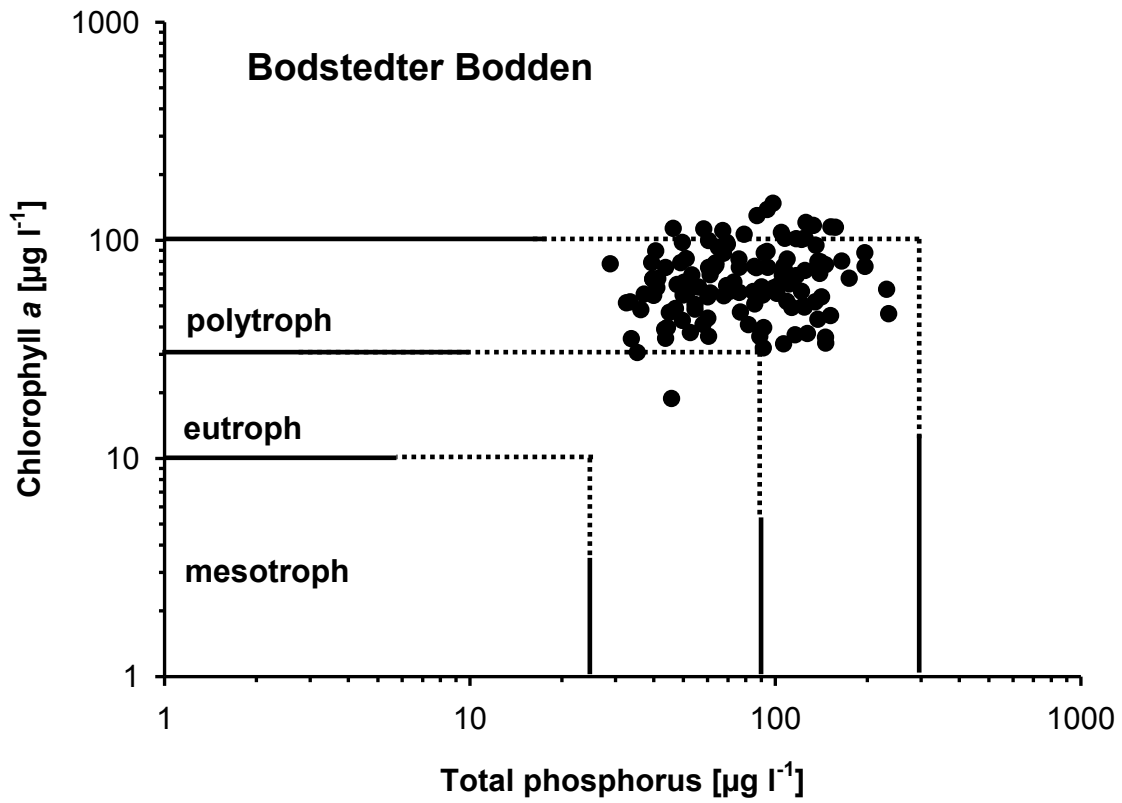
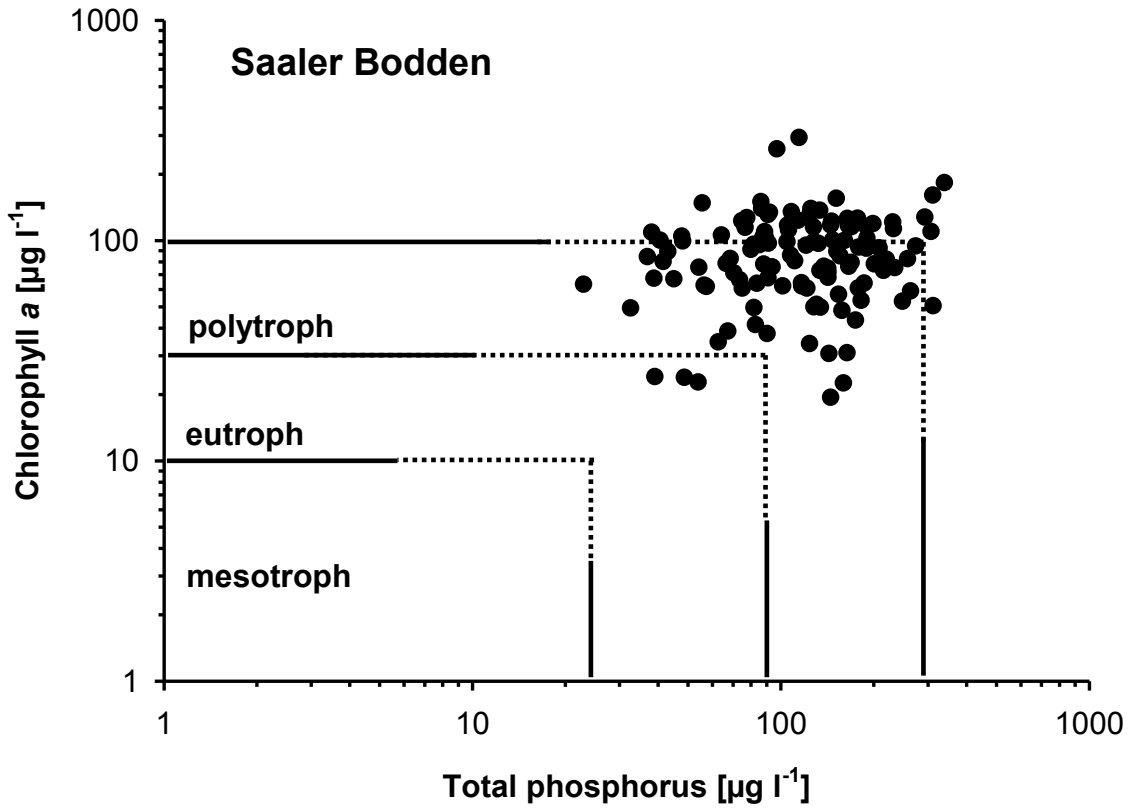
**Figure A 7** Long-term development of Chlorophyll *a* [ $\mu\text{g l}^{-1}$ ] in the Recknitz River mouth, Saaler Bodden, Bodstedter Bodden, Barther Bodden and Werder/Bock during 2000 – 2014. From west to east: Recknitz River mouth (RM,  $n=149$ ), Saaler Bodden (SB,  $n=157$ ), Bodstedter Bodden (BO,  $n=153$ ), Barther Bodden (BB,  $n=159$ ), Werder/Bock (WB,  $n=157$ ). Solid black line shows median of all values during the sampling time. Please note the different y-axes scaling for better visualisation of differences. Data set: Biological Station Zingst.







**Figure A 8** Long-term development of seston [mg l<sup>-1</sup>] in the Recknitz River mouth, Saaler Bodden, Bodstedter Bodden, Barther Bodden and Werder/Bock during 2000 – 2014. From west to east: Recknitz River mouth (RM, n=133), Saaler Bodden (SB, n=140), Bodstedter Bodden (BO, n=143), Barther Bodden (BB, n=163), Werder/Bock (WB, n=161). Solid black line shows median of all values during the sampling time. Please note the different y-axes scaling for better visualisation of differences. Data set: Biological Station Zingst.



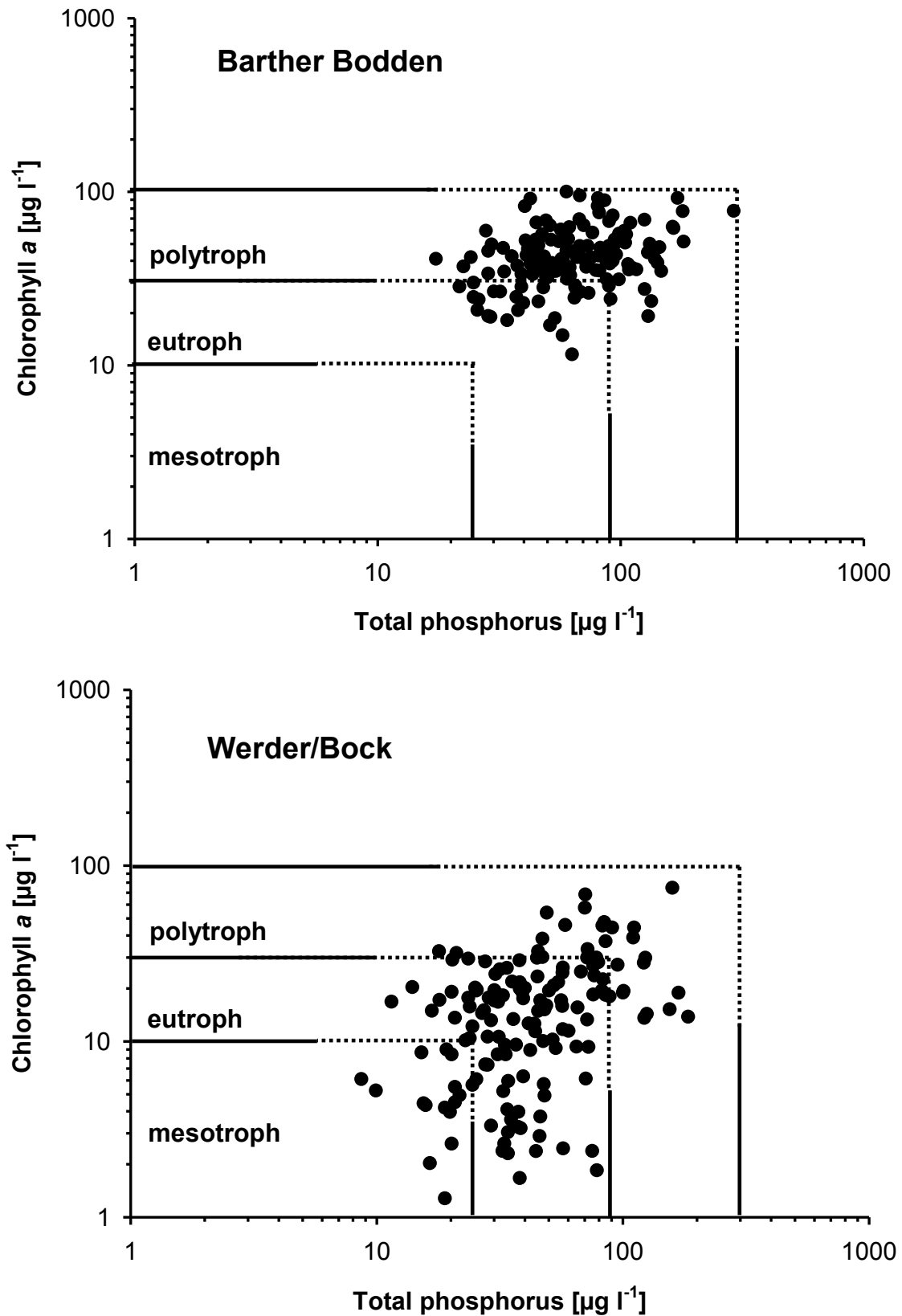


Figure A 9 Chlorophyll *a* concentrations to total phosphorus concentrations ratio in [ $\mu\text{g l}^{-1}$ ] as log-log plot for Saaler Bodden, Bodstedter Bodden, Barther Bodden and Werder/Bock. Scale limit for trophic level after Länderarbeitsgemeinschaft Wasser (LAWA), (1999). Data set: Biological Station Zingst.

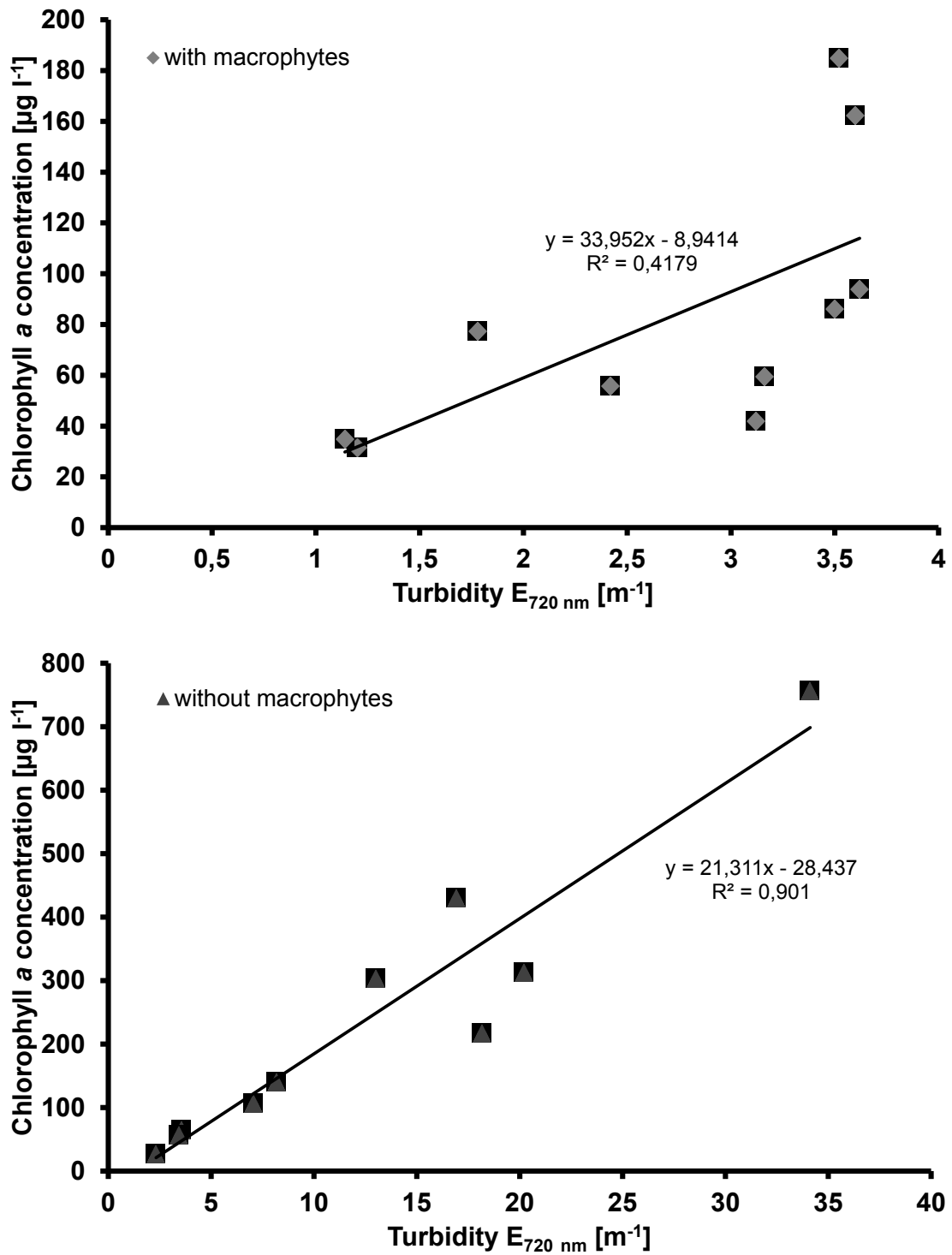


Figure A 10 Relationship of Chlorophyll *a* [ $\mu\text{g l}^{-1}$ ] to turbidity  $E_{720 \text{ nm}}$  [ $\text{m}^{-1}$ ]. Chlorophyll *a* ( $n=2$ ) and turbidity ( $n=1$ ) were measured in mesocosms populated with and without submerged macrophytes.

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**Declaration on oath / Eidesstattliche Erklärung**

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbstständig und ohne fremde Hilfe verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe. Die den benutzten Werken wörtlich und inhaltlich entnommenen Stellen sind als solche kenntlich gemacht.

*I hereby declare, on oath, that this thesis is my own work entirely and has been written without any help from further people. I have not used other than the acknowledged resources and aids and included all the citations correctly, both in word and content.*

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