Phosphorus Contents Re-visited After 40 Years in Muddy and Sandy Sediments of a Temperate Lagoon System

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Worldwide, coastal water bodies suffer from anthropogenically elevated nutrient inputs, which led to eutrophication. Sediments in eutrophic systems are assumed to be an important internal nutrient source. The total phosphorus (TP) concentration (mg g^{-1} dry mass) is widely used as a proxy for the sediment nutrient load. 2-D distribution maps of TP concentrations are used for management plans, where areas of high TP values are marked in red. However, the sediment density is lowered at increasing water content, which can lead to different TP stocks per g m^{-2}. The aim of this study was, to do a re-evaluation of TP concentrations and stocks in the model ecosystem of the Darß-Zingst Bodden chain, a typical lagoon system of the southern Baltic Sea. Sediment cores were taken at eight stations along transects from shallow to deeper parts of the lagoon. Samples were analyzed for TP, water and organic content, as well as density. This data set was compared to results from a sediment survey during the time of highest nutrient inputs (40 years ago) at the same sampling stations. TP concentrations from 40 years ago and today were in the same range. The highest TP concentrations (up to 0.6 mg TP g^{-1} dry mass) were found in the deeper basins and lowest concentrations in the shallow areas of the lagoon (down to 0.05 mg TP g^{-1} dry mass). However, normalization over dry bulk density (DBD) reversed some results. The highest TP stocks (up to 5 g TP m^{-2}) were then found in the shallow areas and lowest stocks (down to 0.2 g TP m^{-2}) in the deeper parts of the lagoon. Some stations did not exhibit any differences of TP at all, even after including the DBD. These findings suggest that there seems to be no up-, or downward trend in nutrient concentrations of sediments even after 25 years of reduced external nutrient inputs. Furthermore, TP stocks point to possible diffuse P entry pathways that counteract external nutrient reductions. These findings can have an impact on possible countermeasures for ecosystems rehabilitation, like sediment removal or nutrient reductions in the adjacent land.

Keywords: phosphorus concentration, sediment, brackish lagoon, dry bulk density, Baltic Sea, organic content

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Abbreviations: DBD, dry bulk density; DM, dry mass; DZBC, Darß-Zingst Bodden chain; LOI, loss on ignition; TP, total phosphorus; WC, water content.

INTRODUCTION

Along with the Green Revolution in agriculture in the last 50–75 years in the developed countries, ecosystems worldwide are strongly influenced by high anthropogenic nutrient inputs especially nitrogen (N) and phosphorus (P) (e.g., Smil, 2000; Liu et al., 2008; Schröder et al., 2010; Childers et al., 2011; Lu and Tian, 2017). Even the most optimistic future scenarios point to an overall increased use of P worldwide (Van Vuuren et al., 2010), i.e., overall use will most likely still lead to increased P inputs into aquatic ecosystems, despite of examples of reverse trends by effective reduction of P entering aquatic systems (e.g., Civan et al., 2018). Moreover, Yan et al. (2016) pointed to the fact that P seems to accumulate faster than N in aquatic systems, which means that even reduced P loads can still increase the P background within systems. This accumulated P has short and long-term effects in aquatic ecosystems. In the short term, the primary production within a system increased on a recurring annual basis. On a longer timeframe, P accumulates in sediments, where it can be remobilized occasionally (e.g., Ruttenberg, 2003). Consequently, P is trapped in the biological cycles until it is precipitated in more or less biologically insoluble forms. Such increases of insoluble forms of P in sediments are well described worldwide (e.g., Heathwaite, 1994; Jensen et al., 1995). Elevated P pools are still a burden for restoration, as they can be released massively during suboxia in near-bottom water layers or at a slower rate by diffusion. Such release situations are well described for, e.g., the Baltic proper and sediments of the Baltic coastal zones (Pitkänen et al., 2001). If P is released, it starts to refuel primary production again and the system will remain in its current state (Vahtera et al., 2007). Furthermore, Duarte et al. (2009) described this elevated P background as a main cause, why restoration will not work and ecosystems fail to return to the reference status upon nutrient reduction.

The Baltic Sea is such a highly anthropogenically impacted brackish water body, where the drainage basin ($\sim$1,739,000 km^2, Nilsson, 2006) is around four times larger than the sea ($\sim$412,500 km^2) itself. The nutrient loads into the Baltic Sea increased from the 1950s until peak values around 1980 followed by a decrease continuing up to present (Gustafsson et al., 2012). However, the inputs amounted to 1,056,922 tons of N and 41,163 tons of P in 1995 and 825,825 tons N and 30,949 tons P in 2014 (HELCOM, 2018). Nevertheless, P inputs into water bodies by point sources were reduced during the mid-1980s and are permanently low in German coastal water bodies since then. Therefore, this input reduction of up to 80% (Nausch et al., 2011) could meanwhile have impacted P stocks in sediments of the coastal water bodies. Coastal lagoon systems are of special interest, as they cover 5% of the entire Baltic coastal zone, but account for 10% of the P burial and half of the denitrification of all coastal ecosystems in the Baltic Sea (Asmala et al., 2017). Therefore, such lagoon systems can act as nutrient filter for the open Baltic Sea by trapping nutrients within their system. However, these reduced P inflows take only the reduction of direct river-borne P into account, but Germany's federal state agencies indicated that diffuse P inputs became increasingly important during the last decades (BMUB and BMEL, 2016). In this context, Karstens et al. (2016) showed

the impact of the adjacent land use on the wetland sediments in coastal systems, and Berthold et al. (2018a) described the possible direct export of P from adjacent wetlands into coastal water bodies. These diffuse P input could strongly affect the spatial distribution of P accumulation especially in dependency from coastal distance.

A well-described typical shallow lagoon system of the southern Baltic Sea is the DZBC (e.g., Schiewer, 2007), where a synoptic sediment study was conducted 40 years ago (e.g., Schlungbaum, 1982; Schlungbaum et al., 1994). At that time, sediment samples were taken in every lagoon part in a 500 to 1,000 m sampling grid in shallow and deep areas. Certain P hotspots were shown, often in deeper waters (e.g., Nausch and Schlungbaum, 1984). The sampling coincided with the peak of riverine TP inputs of up to 80 t a^{-1} during 1976 to 1980. Highest TP values were found in the deeper parts between 2 mg P g^{-1} DM in the inner lagoon, and up to 1 mg P g^{-1} DM in the outer lagoon. The LOI ranged between <1 and 40% (Nausch, 1981) depending on the sampling depth. Afterward, TP inputs by rivers were steadily reduced by 75% and are now for the last 20 years constant at 20 t a^{-1} (LUNG, 2013). Interestingly, these P reductions did not reduce turbidity, or phytoplankton biomass within the system, but the light limitation of phytoplankton seems to be so stable that small, light-efficient cyanobacteria (Schiewer, 2007; Albrecht et al., 2017) remain dominant. The original annual periodicity of phytoplankton composition disappeared, leaving the DZBC in a state of permanent high turbidity since the end of the 1980s (Schiewer, 2007). Such results indicate, that other P sources than direct inputs by rivers might explain the permanent high phytoplankton biomass. However, the DZBC is also described to possess a nutrient filter function, as the water exchange rate with the surrounding open Baltic sea is low (0.15 a^{-1} Schiewer, 2007), and the sediments sorption capacity for P is high (0.05–1.1 mg P g^{-1} DM, Schlungbaum, 1982). Furthermore, the particulate matter in this lagoon system has a high TN:TP (15-year median: 36–47:1, mol:mol) ratio, compared to other coastal water bodies of this region (Berthold et al., 2018b). This finding means that sedimented particulate material had a relatively low P status. Moreover, the sedimentation rate in this lagoon system is postulated to be between 1 (Lampe et al., 2013) and 5 mm a^{-1} (Nausch, 1981). Therefore, we hypothesized that the lowered P inputs had already an effect on the first centimeters of the sediment and re-evaluation of sediment P loads might reflect lowered P inputs into the lagoon. Such re-evaluations of sediments are exceptionally important, as the EU-Water Framework Directive and society have to consider the necessary time-spans for reducing anthropogenic impacts in aquatic ecosystems.

As mentioned, P concentrations (in mg g dry mass^{-1} or % of DM) in sediments are assumed to be important indicators for the total P load in an aquatic system and they are often used to create heat maps where hot spots of P- and other element-concentrations are described (e.g., Leipe et al., 2017). This approach could be questionable because sediment density can vary strongly due to the texture and water and organic matter content (Avnimelech et al., 2001; Köster and Meyer-Reil, 2001; Verstraeten and Poesen, 2001; Faas and Wartel, 2006) strongly

affecting P stock in the sediment volume. Moreover, P stocks per m^{-2} seemed to be ecologically much more important, because the exchange at the sediment/water contact zone happens per area.

Due to the potential spatial and temporal differences in P loads of the sediments in the DZBC, sediments were sampled in transects in a right angle from the coastline, i.e., from shallow to the deeper areas across all lagoon basins. These samples were analyzed for bulk density, water and organic matter content and TP concentrations. From theses analyses, P stocks of sediment were calculated per area. All of these data were compared to the historical sample data 40 years ago. With this approach we want to answer the questions (1) if there is a gradient of increasing TP in the sediment from shore to deeper waters – both on a concentration or on a stock basis and (2) if surface TP changed within 40 years in line with decreasing P inputs into the lagoon system and the Baltic Sea.

MATERIALS AND METHODS

Sampling Area

The DZBC is a temperate lagoon system with consecutively connected lagoon basins. The innermost lagoon parts Saaler Bodden (SB) and Bodstedter Bodden (BoB) are oligohaline (salinity 1–4) and highly eutrophic (Schiewer, 2007). The two outer lagoon parts Barther Bodden (BB) and Grabow (GB) are less influenced by riverine nutrient inputs (salinity 5–12) and less turbid (secchi depth up to 100 cm). Sampling spots were chosen for a gradient from shallow areas, proximate to the coastline to deeper parts of the lagoon. Two different spots were chosen per lagoon part. Additionally, samples from the outer southern Baltic coast line were taken as comparison. Those stations were located in Kühlungsborn, Zingst, island of Hiddensee and island of Usedom (**Figure 1**).

Sampling

The sedimentation rate in this lagoon system is postulated to be between 1 (Lampe et al., 2013) and 5 mm a^{-1} (Nausch, 1981). We used the lower sedimentation rate as a conservative approach to test our hypothesis. The time between the first sampling in 1977 and 2017 equals for 4 cm of increased sediment height. P inputs are on a constant low level for more than 27 years (=2.7 cm, LUNG, 2013). We sampled the upper first 1.4 cm (first 5 ml of a syringe), which is half of the sediment increase.

Sediment samples in the DZBC were taken with a sediment corer (10 cm diameter) (Hydrobios) between the water depths of 0.5 and 3.5 m, depending on the sampling site. Geographic coordinates for start and end point of each transect can be found in **Supplementary Table 1**. Sediment samples from the outer coast line were taken by divers, which used hand-held sediment corer with only 5 cm diameter. Six to eight sediment cores were taken along transects per sampling spot from shore to open water. Samples from the outer coast were taken with hand-held sediment tubes (10 cm diameter) by divers starting at water depths of 20 cm up to 5 m water depth. Three sub-samples of the first 1.4 cm were taken with a cylinder, which had a fixed

volume, from the sediment cores. All samples were taken in 2017, except for a transect near Dabitz in the GB, which was already sampled in 2013 and included as an additional station. Additionally, sediment from this transect was separated in the horizons of 0–1, 1–2, and 2–5 cm.

Determination of Dry Bulk Density, Water, and Organic Matter Content

The fixed volume of a cylinder (syringe, 5 ml volume) was used to calculate DBD (g cm^{-3}) after drying. Sub-samples were weighed wet, dried at 105°C for 24 h, and weighed dry again. The difference was used to calculate the WC (%) and DBD. Afterward, the sub-samples were combusted at 550°C for 4 h in a muffle furnace (Heraeus). The sediment ash of the sub-samples were weighed again after cooling down in a desiccator. The difference was used to calculate the organic content as LOI of the sediment. At least, the sub-samples of the sediment ash were pooled again and grinded in a powder mill (5,000 rpm, 2 min, Fritsch). The final grain size was between 1 and 10 μm. The dust was used for subsequent TP analyses.

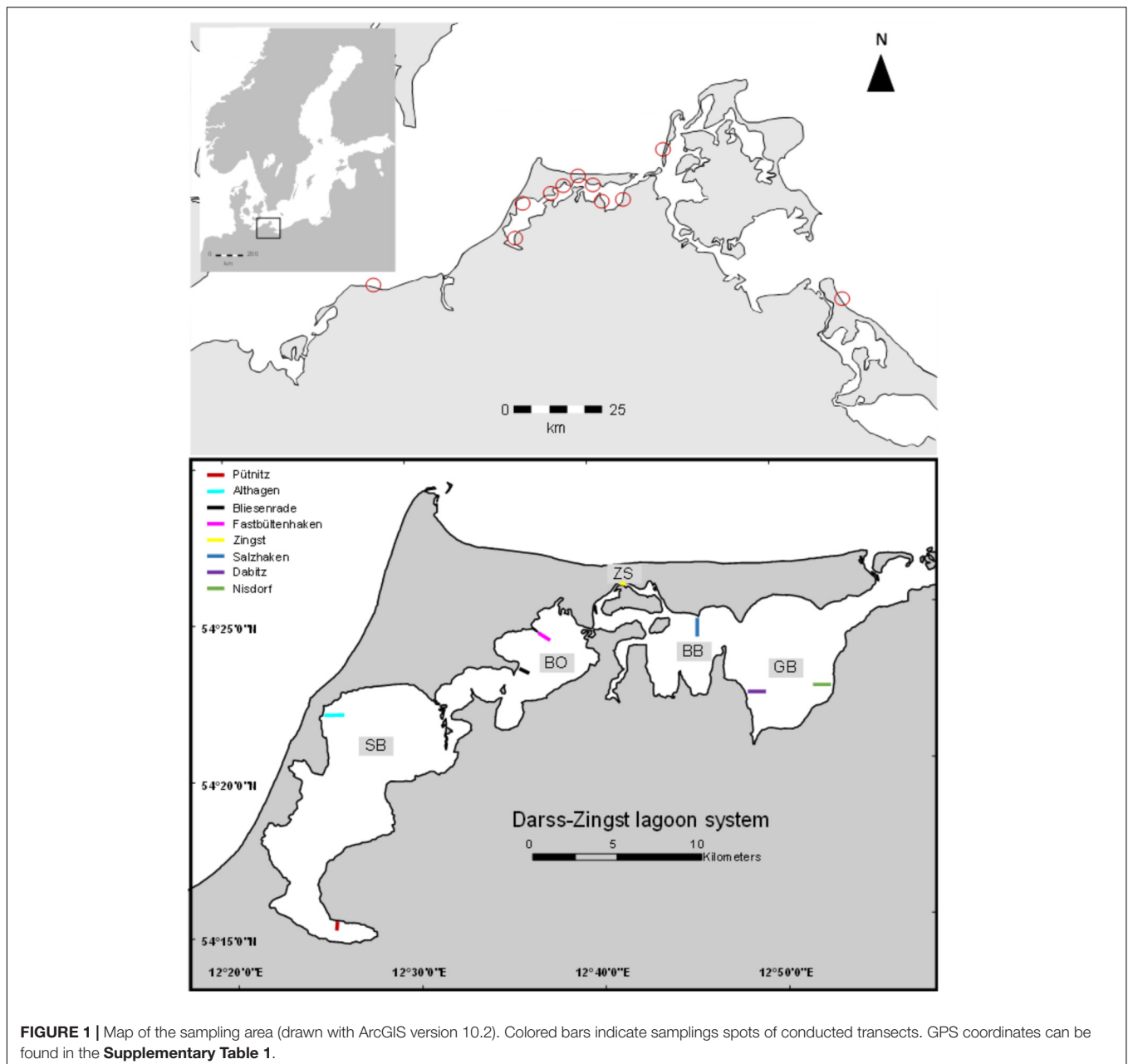## Determination of Total Phosphorus

Ten to 50 mg of sediment ash were weighed in perfluoroalkoxy-polymer (PFA) tubes (AHF Analysentechnik) and suspended in 15 ml of ultrapure, phosphate-free water (power plant Rostock). Subsequently, 1.5 ml of acid persulfate was added, the samples were tightly closed and oxidized at 90°C for 24 h (Berthold et al., 2015). Afterward, the complete sample was neutralized and filtered (GF/F filter, Whatman). TP was determined with molybdenum blue according to Hansen and Koroleff (1999) with a photometer (Hach DR3900, 5 cm cuvette) at 885 nm. All sediment samples were digested and measured in quadruplicates.

The synoptic sediment study from 40 years ago collected amongst other parameters, WC, LOI, and TP concentrations. DBD was only sampled on a random basis and results were averaged for sediments with an LOI of <5% (1.5 g cm^{-3}) and >5% (1.0 g cm^{-3}). These mean DBD values were used to estimate the total P stock (in g P cm^{-2}) in the first cm of the sediments of the lagoon system (Nausch, 1981). Instead, we took the historic values of WC and TP concentrations (only available as range) to re-calculate DBD and areal TP stocks (Equation 1) as such a relationship was missing in the studies from 40 years ago (see the section "Discussion"). The equation for areal TP stocks (g m^{-2}) was calculated out of the TP concentrations (mg P g^{-1} DM sediment) and the relationship of WC (%) to sediment density (**Figure 2A**). The relationship of areal TP stocks to sediment densities are rather widely distributed (**Figure 4**), which affects this approach.

$$\text{Totalphosphorus} \, (g \cdot m^{-2}) \qquad\qquad (1)$$
$$= (3.47 \cdot e^{-0.035 \cdot WC\%}) \cdot TP \, (mg \cdot g^{-1} \, dry \, mass^{-1}) \cdot 10$$

Quality Management and Statistics

Determination (quantification) limit for TP was 0.22 μmol l^{-1} by the blank method in the digestate. Sediment samples

FIGURE 1 | Map of the sampling area (drawn with ArcGIS version 10.2). Colored bars indicate samplings spots of conducted transects. GPS coordinates can be found in the **Supplementary Table 1**.

were prepared to be above that limit and reach at least $2\,\mu\text{mol}\,\text{l}^{-1}$ in the extract. The combined standard deviation was 11.8% for TP determination, which combines the random error of replicate samples and all standard values measured over the whole investigation period. This value describes reproducibility of both (samples and standards, i.e., random error of both).
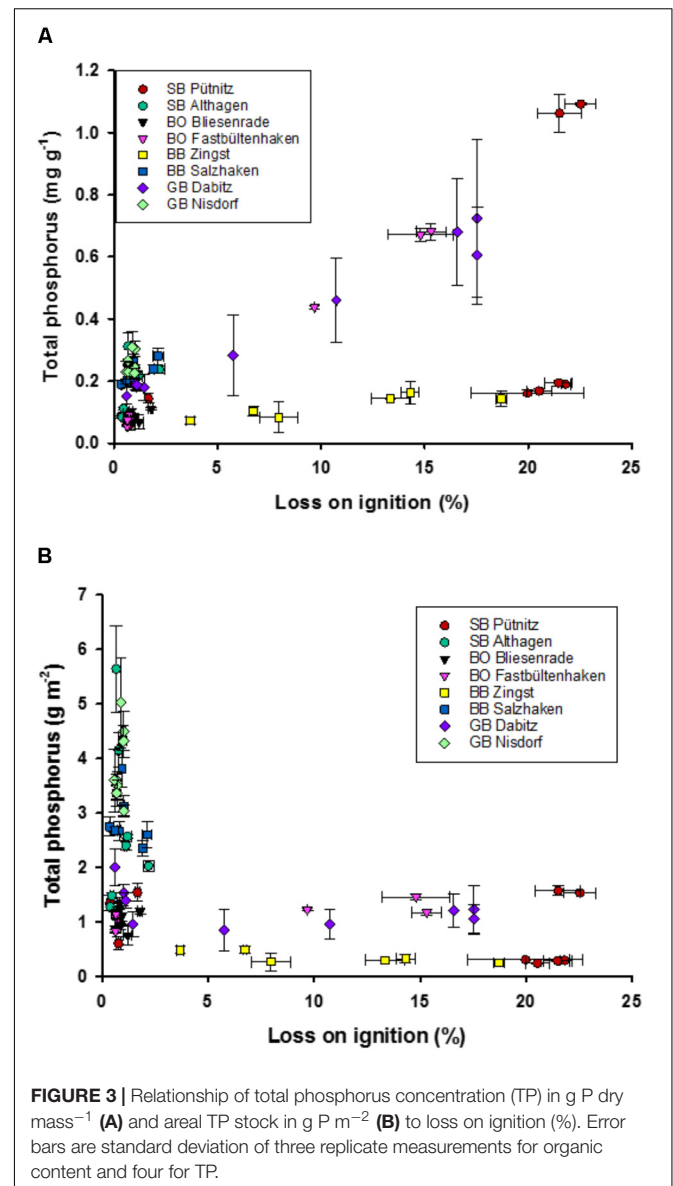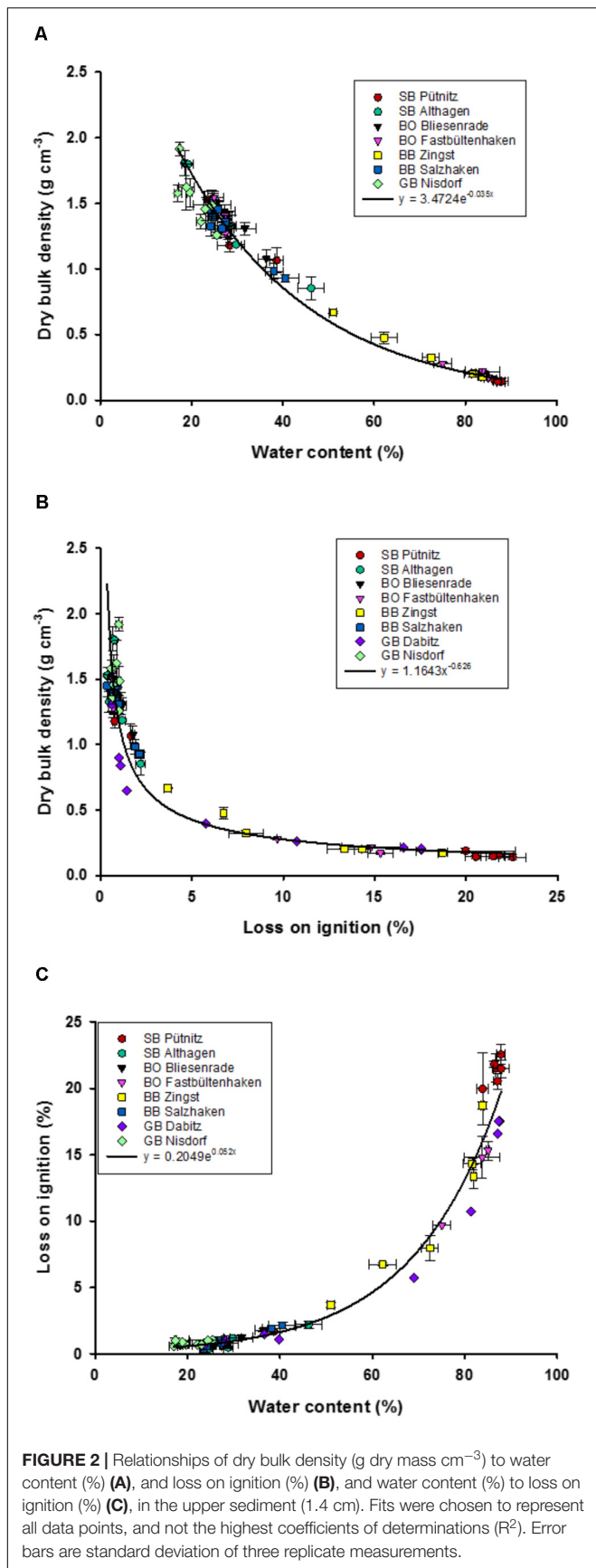
SigmaPlot 13.0 was used for statistical analysis. Shapiro–Wilk tested all data for normal distribution. A Spearman Rank Order test was used for correlations. The principal component analysis (PCA) for the separation of sampling sites was computed for the water depth (in m), the LOI (in %), the DBD (in g cm^{-3}), the total P concentration (in mg TP g^{-1}) and the total P stocks of the first cm (in g TP cm^{-2}) of the sediment samples using STATISTICA 6.0 (StatSoft, Inc., 2001).
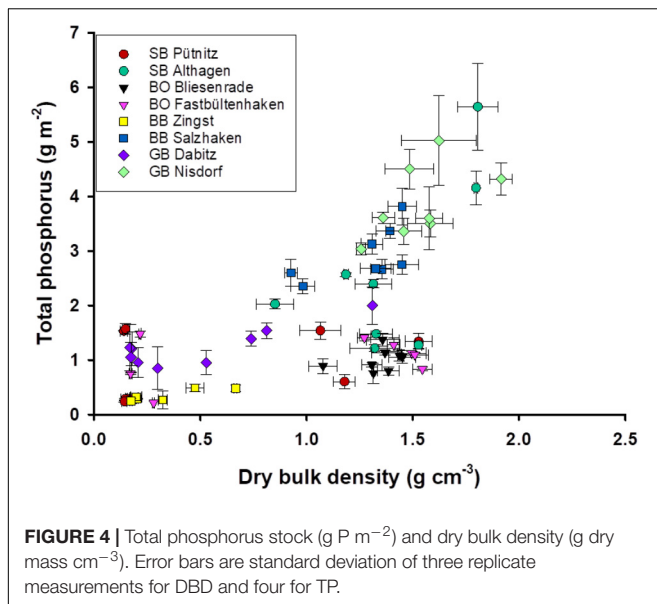
RESULTS

Characteristics and P-Content of Sediment Samples

The water depth of the 64 sediment samples of the eight transects ranged from 0.4 to 4 m. The WC ranged between 17 and 88% and the LOI between 0.036 and 23% LOI (**Figure 2**). Sediment samples from the outer coastline had a WC between 14 and 20%

FIGURE 2 | Relationships of dry bulk density (g dry mass cm^{-3}) to water content (%) **(A)**, and loss on ignition (%) **(B)**, and water content (%) to loss on ignition (%) **(C)**, in the upper sediment (1.4 cm). Fits were chosen to represent all data points, and not the highest coefficients of determinations (R^2). Error bars are standard deviation of three replicate measurements.

FIGURE 3 | Relationship of total phosphorus concentration (TP) in g P dry mass^{-1} **(A)** and areal TP stock in g P m^{-2} **(B)** to loss on ignition (%). Error bars are standard deviation of three replicate measurements for organic content and four for TP.

and a DBD of 1.4 to 1.7 g cm^{-3} (**Supplementary Figure 1**). At least one out of four samples had an LOI higher than 5%, while one third of those samples had a DBD below 1 g cm^{-3} (**Figure 2**). WC and LOI were significantly positively correlated ($r = 0.91$) and both negatively with DBD ($r = -0.84$ and -0.74, respectively). Additionally, the sediment characteristics were different in shallow and deeper waters, since the water depth correlated significantly with WC ($r = 0.52$), LOI ($r = 0.67$), and DBD ($r = -0.48$).

The median of the P concentrations ranged from 0.05 to 1.1 mg TP g dry mass^{-1} and those of the P stocks from 0.24 to 5.6 g P cm^{-2} in the first cm of the sediment. The highest TP concentrations were found at higher LOI (**Figure 3A**). However, there was a huge variability, as some sediments with a high LOI had very low TP concentration per g DM. Low TP concentrations were measured at increasing DBD, i.e., lower WC

FIGURE 4 | Total phosphorus stock (g P m^{-2}) and dry bulk density (g dry mass cm^{-3}). Error bars are standard deviation of three replicate measurements for DBD and four for TP.

and OC. In contrast, TP stocks were very variable at low LOI (**Figure 3B**). Nonetheless, LOI correlated significantly with both, TP concentrations ($r = 0.4$) and areal TP stocks ($r = -0.42$). Most of the samples with a low TP concentration and high WC and LOI originated from the station Zingst and were close to a harbor whereas others were from Pütniz, the innermost lagoon basin.

There was less variation in TP stocks at lower DBDs compared to sampling sites with higher DBD (**Figure 4**). For example, samples from the lagoon part BoB had high areal TP stocks, compared to samples of lower DBD from deeper parts. In contrast, there were also samples with a DBD comparable to BoB (i.e., GB and BB), but those had three- to six-times higher areal TP stocks. Comparable TP stocks of 0.6–2.9 g TP m^{-2} at DBD's from 1.3 to 1.6 were found at the outer coastline (**Supplementary Figure 2**). Interestingly, the stations with very high areal TP stocks were at the southern site of the lagoon, which is at the coast of the main land and receives riverine water. It becomes apparent that even stations in the most eutrophic part of the lagoon, i.e., SB and BoB, have comparably low areal TP stocks. The stations Fastbültenhaken and Bliesenrade, which are in the middle of the lagoon system, had the lowest variations, even though all samples originated from different depths. There were also outliers present in the innermost and outermost lagoon, i.e., Altenhagen and Nisdorf. Areal TP stocks of up to 6 g m^{-2} were found, but at water depths of around 2 m and with low LOI. DBD correlated positively and significantly with the areal TP stocks. Dabitz (GB) was the only transect with low as well as high DBD. At the same depth range the stations at the outer coast only varied in areal TP, but not in DBD (**Supplementary Figure 1**).
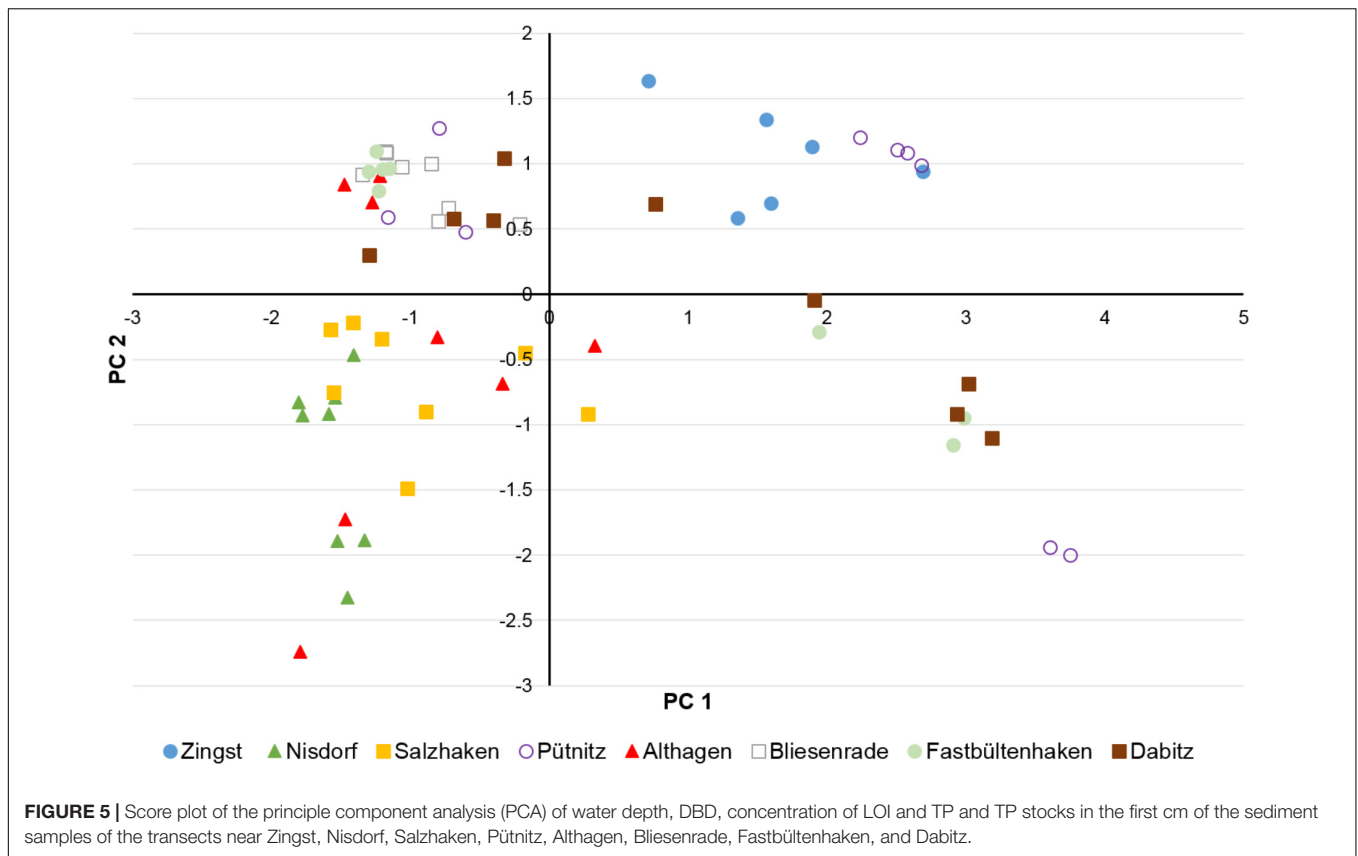
Spatial Separation of Sampling Sites

Water depth, LOI, DBD, TP concentrations and TP stocks were included in the PCA to visualize separation of sampling sites in a two-dimensional plot (**Figure 5**). The first two PCs of the

PCA explained together 82% and the first three PCs 95% of the variance between samples (**Figure 5**). Generally, the stronger the correlation of a factor to a specific PC (**Table 1**) the more the samples are shifted to the outward. Therefore, especially correlations of about ≥ 0.7 are highly important for separation of samples whereas correlations <0.5 are of low importance. Additionally, a negative correlation to a PC shifted samples to the left (PC 1) or downward (PC2) and a positive correlation to the right (PC1) or upward (PC2) (**Figure 5**). According to correlations (>0.9) of factors to PC1 (**Table 1**): the higher the LOI the more the samples are shifted to the right and the higher the DBD the samples are shifted to the left. The water depth had a correlation of 0.672 and the TP concentration of 0.635 to the PC1. That means that the deeper the water and the higher the TP concentrations the more the samples are shifted to the right but due to the lower correlations compared to LOI and DBD the shift is not so strong. The correlation of the TP stock to PC1 is the lowest of all factors and shifted to the opposite direction compared to the TP concentration (Tab. 1). However, TP concentrations and TP stocks were highest positively correlated to PC2 (**Table 1**). That means that samples with higher TP concentrations and/or TP stocks are shifted downward.

It is clearly visible that the sediment samples of Nisdorf (green triangles) and Salzhaken (yellow squares) and in parts those of Althagen (red triangles) are separated from the other sampling transects by shifting downward on the left side of the diagram (**Figure 5**). The shifting of these three transects was mainly caused by highest P stocks (1.2–5.6 g TP m^{-2}) in combination with generally higher DBD (0.85–1.92 g cm^{-3}) and lower LOI (0.36–2.19%) in contrast to the other transects (**Figures 2–5**). For the other transects the TP stocks ranged from 0.24 to 2.0 g TP cm^{-2}, the DBD from 0.14 to 1.53 g cm^{-3} and the LOI from 0.36 to 22.5% (**Figure 5**). The transect Zingst (blue circles) was completely separated from Nisdorf, Salzhaken, and Althagen because the samples of Zingst had low TP stocks (maximum 0.49 g TP cm^{-2}), low DBDs (maximum 0.67 g cm^{-3}) and high LOIs (3.7–18.7%).

Sampling points of the transect Pütnitz (lilac circles) are widely spread at the score plot (**Figure 5**) because TP stocks (0.24–1.57 g TP cm^{-2}), DBD (0.14–1.53 g cm^{-3}), LOI (0.36–22.5%) and TP concentrations (0.06–1.09 mg TP g^{-1}) varied strongly between samples (compare **Figures 2, 4**). Additionally, the six samples from Pütnitz transect with the highest LOI (minimum 20%) had the lowest DBD (maximum 0.19 g cm^{-3}) in contrast to the three samples with lowest LOI (maximum 1.7%) and highest DBD (minimum 1.07 g cm^{-3}). The spreading of the sampling points of the transect Dabitz (brown squares) was caused by the combination of high LOI (minimum 10%) with high TP concentration (minimum 0.46 mg TP g^{-1}) and low DBD (maximum 0.26 g cm^{-3}) in four of the samples whereas in the other five samples the low LOI (maximum 5.8%) was combined with low TP concentrations (maximum 0.28 mg TP g^{-1}) and higher DBD (minimum 0.39 g cm^{-3}). The sampling points of the transect Bliesenrade (gray squares) clustered together because the sediment samples varied less and were very similar to each other (LOI: 0.63–1.78%, DBD: 1.08–1.45 g cm^{-3}, TP

FIGURE 5 | Score plot of the principle component analysis (PCA) of water depth, DBD, concentration of LOI and TP and TP stocks in the first cm of the sediment samples of the transects near Zingst, Nisdorf, Salzhaken, Pütnitz, Althagen, Bliesenrade, Fastbültenhaken, and Dabitz.

concentration: 0.06–0.10 mg TP g^{-1}, TP stocks: 0.75–1.37 g TP cm^{-2}).

There was a general trend of increasing LOI and TP concentrations but decreasing DBD and nearly constant TP stocks with increasing water depth for all samples of all transects (**Supplementary Figure 3**). The nearly constant TP stocks can be attributed to the opposite trends in the different transects because in the transects Zingst, Nisdorf, Althagen, Bliesenrade, and Fastbültenhaken the TP stocks increased but for the transects Salzhaken, Pütnitz, and Dabitz the TP stocks decreased with water depth. Correlations between water depth and the sediment parameters were found for the transect Dabitz. In this transect, the sediment samples were additionally evaluated at three sediments depth at each sampling point. The TP concentrations

in Dabitz ranged between 0.13 and 0.76 mg TP g DM^{-1} with increasing values at deeper waters. Additionally, stations below 1 m water depth had an increasing WC and LOI of up to 87% and 17%, respectively. In contrast, highest TP stocks were found nearshore and were decreasing with distance from land (**Figure 6**), even though the first centimeter was comparably between all stations. The nearshore cores (water depth 0.5–0.7 m) had a TP stock peak in 1–2 cm, even though DBD was highest from 2 to 5 cm sediment depth. This result indicates a P enrichment. Furthermore, combined TP stocks of all horizons were at those nearshore stations at least two times higher, compared to stations below 1 m water depth. The LOI decreased per depth from around 2 to 0.5% at the shallow stations (except at 0.6 m). Samples below 1 m water depth had no clear depth gradient for TP stocks, DBD or OC.
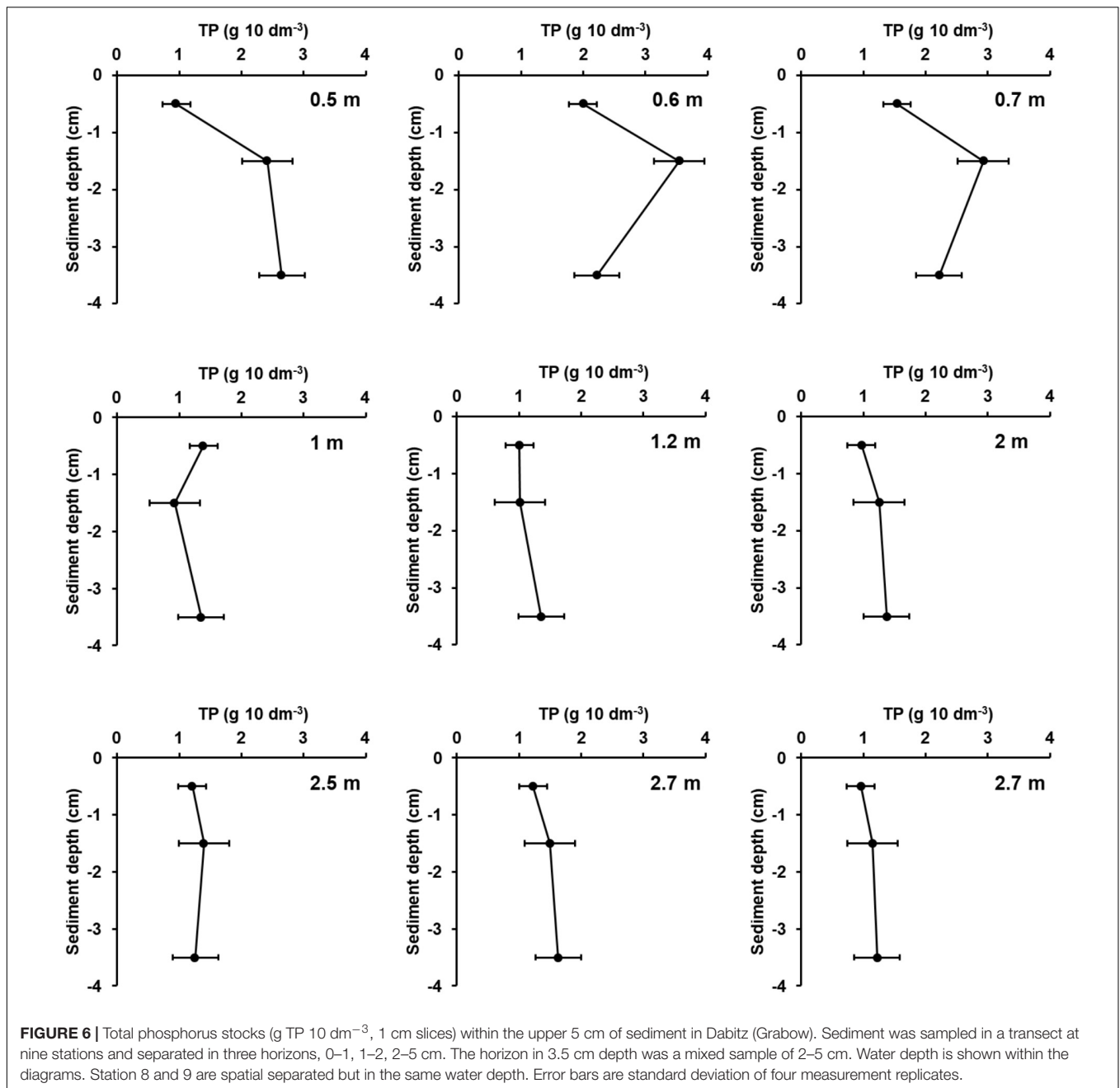
DISCUSSION

Evaluation of P-Content in Sediments

The TP concentration (mg g^{-1}) found in the upper sediments of this study were in a comparable range with other sediments (**Table 2**) of the DZBC (Berghoff et al., 2000), the south-western Baltic Sea (Leipe et al., 2017) and the Gulf of Finland (Lehtoranta and Pitkänen, 2003). However, higher TP concentrations compared to those of our study were detected in sediments of the Archipelago Sea (Conley and Johnstone (1995) and the

TABLE 1 | Correlation of the parameters water depth, organic matter content (OC %), dry bulk density (DBD in g cm^{-3}), total concentration of P (TP in mg g^{-1}) and total P stocks in the first cm (TP in g m^{-2}) with the principle components PC 1 to PC 5.

Parameter	PC 1	PC 2	PC 3	PC 4	PC 5
water depth in m	−0.672	−0.268	0.686	0.072	−0.028
OC in %	0.942	−0.01	−0.141	−0.264	−0.151
DBD in g cm^{-3}	−0.951	−0.172	0.075	0.054	−0.239
TP mg g^{-1}	0.635	−0.634	−0.364	0.222	−0.032
TP g m^{-2} 1 cm^{-1}	−0.534	−0.814	0.048	−0.207	0.087

FIGURE 6 | Total phosphorus stocks (g TP 10 dm^{-3}, 1 cm slices) within the upper 5 cm of sediment in Dabitz (Grabow). Sediment was sampled in a transect at nine stations and separated in three horizons, 0–1, 1–2, 2–5 cm. The horizon in 3.5 cm depth was a mixed sample of 2–5 cm. Water depth is shown within the diagrams. Station 8 and 9 are spatial separated but in the same water depth. Error bars are standard deviation of four measurement replicates.

Landsort Deep (Dijkstra et al., 2016). The LOI (or calculated POC content) found in this study was within the same range as in other studies, but with one of the highest values found in the DZBC. Leipe et al. (2011) found a similar non-linearity between POC and DBD as found in this study. Furthermore, they described that with increasing POC content particles get smaller, whereas mud content <63 μm increases. Simultaneously, WC increases as well, i.e., the amount of water per area increases. Furthermore, the smaller particles have a higher area:volume ratio, compared to bigger particles, which increases P adsorbing capacities (Borggaard, 1983). These results mean, that in areas with fine sediment, like in basins, P concentrations are likely to

be higher per g sediment, but decrease per area (Carman and Jonsson, 1991). However, we did not find a high correlation of LOI to TP concentrations, as described by, e.g., McComb et al. (1998) for the Peel-Harvey estuarine system. This result indicate, that there are possibly other factors influencing the TP concentration besides organic content.

The graphical summary in **Figure 7** points to this additional problem. The share of the solid phase on the wet mass density strongly decreases with increasing WC. Even though the LOI increases from 0.05 to 17% of the solid phase, it only increases from 0.3 to 2% of the complete sediment volume in the WC rich sediments. It seems unreasonable to assume

TABLE 2 | Overview of commonly found sediment parameter in combination with total phosphorus (TP) concentrations.

Water bodies	Location	TP (mg g^{-1} DM)	Org. C (%)	LOI (%)	DBD (g cm^{-3})	Reference
Baltic Sea	Darss-Zingst lagoon	0.05−1.1	0.1−7.4*	0.4−22.5	0.1−1.9	This study
Baltic Sea	South-western Baltic Sea	0−1.5	0−6			Leipe et al., 2017
Baltic Sea	Landsort Deep, Baltic Sea	0.93−2.0	3−6			Dijkstra et al., 2016
Baltic Sea	Grabow in Darss-Zingst lagoon	0.1−0.35		< 1−6.5	0.4 − < 1.6	Bitschofsky, 2016
Baltic Sea	Archipelago Sea, Stockholm Sweden	1.34				Conley and Johnstone, 1995
Baltic Sea	Gulf of Finland, estuary of river Neva	0.7−1.1		9.1−25		Lehtoranta and Pitkänen, 2003
Baltic Sea	Baltic proper	0.9−1.5		2.7−20.7		Carman and Wulff, 1989

LOI, loss on ignition; Org. C, organic carbon; DBD, dry bulk density. The values marked with one asterisk were calculated out of the relationship of POC content (%) to LOI (%) according to Leipe et al. (2010) for Baltic Sea sediments.
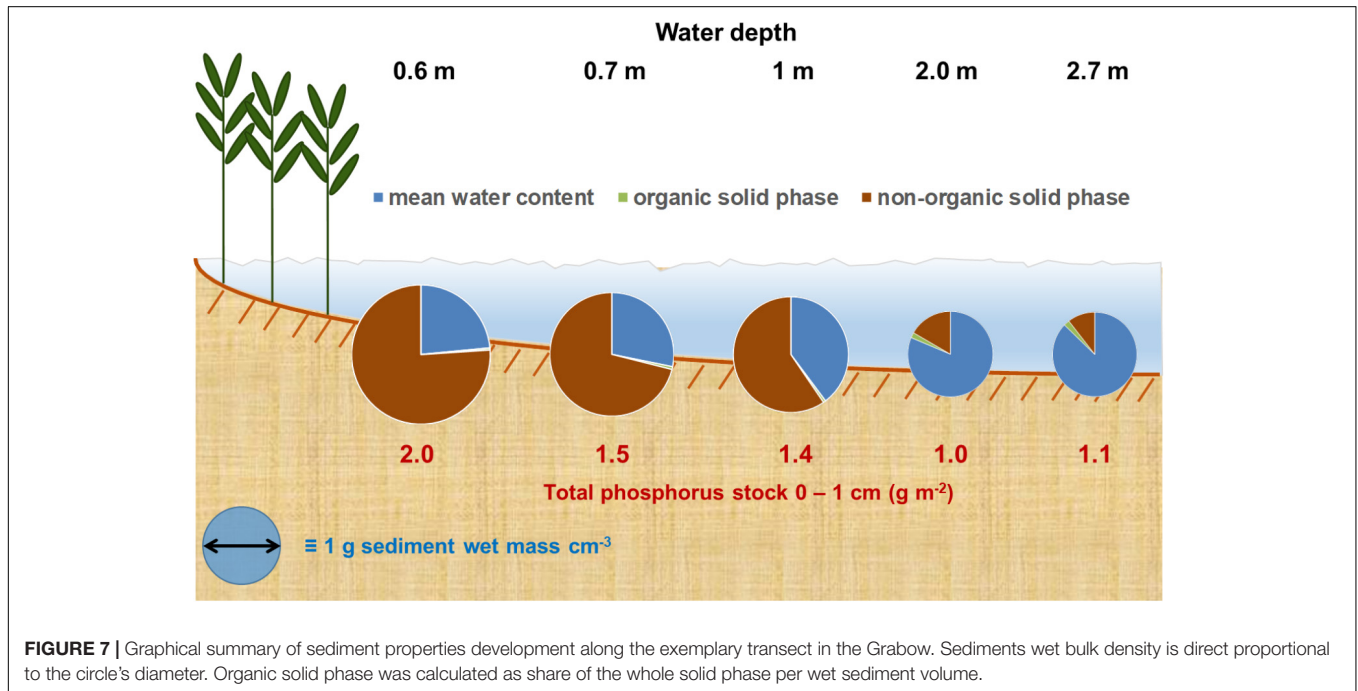

FIGURE 7 | Graphical summary of sediment properties development along the exemplary transect in the Grabow. Sediments wet bulk density is direct proportional to the circle's diameter. Organic solid phase was calculated as share of the whole solid phase per wet sediment volume.

that this small increase represents completely organic bound P. Furthermore, several authors point to the high pore-water concentrations in such apparently LOI rich sediments (e.g., Søndergaard et al., 1992; Kraal et al., 2013; Bitschofsky, 2016), whereas pore-water concentrations in sediments low on LOI have lower or non-determinable pore-water concentrations (e.g., Bitschofsky, 2016). For example, Bitschofsky (2016) determined 3–5 μmol l^{-1} dissolved inorganic phosphate in the pore-water of the DZBC at 2 m water depth. A sediment core with 85% WC would have 80–130 ng PO_4 cm^{-3}. The water evaporates during drying, but P is adsorbed to the solid phase and is determined as TP. However, TP ranged from 90 to 140 ng cm^{-3} in this study and is only slightly higher than the assumed pore-water concentration per sediment volume. This assumption brings up the question how P is actually bound in such water rich sediments. Up-to-date analysis methods like synchrotron-based XAS might be necessary to evaluate this question.

Nonetheless, several locations in the Baltic Sea have areal TP stocks between 1.6 g TP m^{-2} (Lehtoranta, 2003) and 4.9 g TP m^{-2} (Puttonen et al., 2014). Those sites showed high TP stocks even at very low DBD, compared to a maximum of 2 g TP m^{-2} at stations with low DBD in the DZBC. Contrary to these studies, the highest TP stocks were observed in sediments with low LOI and high DBD in this study (up to 6 g m^{-2}, see **Figure 3B**, station Althagen, Nisdorf). Such findings were also described by Carman and Wulff (1989), who found 9.5 g TP m^{-2} in highly dense sediments (WC – 29% LOI 2.7%, 0– 1 cm), but only 1.15 g TP m^{-2} in less dense sediments (WC 91%, LOI 20.7%, 0–1 cm) in the Baltic Proper. This discrepancy highlights the importance of the factor sediment density, as small changes in TP concentrations affect TP stocks due to the non-linear relation (**Figure 3**). Furthermore, these contrary results suggest that knowledge of P loading and cycling within the system is necessary besides the sediment parameter.

Origin of P in Sediments – Location of Sampling Transects

In the PCA Nisdorf, Salzhaken and Althagen clustered together (**Figure 5**), resulting from similar higher TP stocks and DBDs but

lower LOI compared to the other transects. Similarity of these samples is surprising, since these stations are from completely different lagoon parts (**Figure 1**). However, the hinterland of these transects in Nisdorf and Althagen is intensively used for agriculture whereas that of Salzhaken is mainly used as pasture. This agricultural usage and possibly higher TP input could explain similarity of these transects and enriched of P stocks. Heathwaite (1994) described that runoff, transported suspended matter, N, and P loading increased by a factor of 8–9 from heavily grazed pasture areas intro the adjacent land. This increased nutrient inflow was found in the lake sediments as increased allogenic fraction. Generally, P can be transported into the water by agricultural drainage especially during storm events (e.g., Zimmer et al., 2016), by direct soil erosion with soil particles or by submarine groundwater discharge (Knee and Paytan, 2012). However, it has to be pointed out that phosphorus is strongly adsorbed to soil particles especially amorphous Fe-(hydr)oxides (Cornell and Schwertmann, 2004; Fink et al., 2016; Gypser et al., 2017) and only low percentages of P are extractable by water and/or anion exchange resin (e.g., Koch et al., 2018). That means that transport of P in a dissolved form with drainage water or by groundwater discharge might be restricted especially to extreme storm events, to sandy soils with low P sorption capacity or to soils with high P loads (e.g., Tiemeyer et al., 2009; Knee and Paytan, 2012; Zimmer et al., 2016). Therefore, it is assumed that P loading of the shallow sediments in the DZBC resulted mainly from soil erosion by water and transport of P loaded soil particles from adjacent agricultural land. This assumption is supported by the unchanged positive P accumulation in German agricultural used soils (1.8 kg ha^{-1} a^{-1}), as described by van Dijk et al. (2016). A change of P stock in the sediments would be less likely with permanent diffuse P loadings, besides the reduced point sources. However, transport proportions of P adsorbed to soil particles and dissolved P into the sediment cannot be estimated at this point. There is no data available on P specific ground water fluxes or soil erosion in this area.

The effects of usage of the adjacent land on P stocks in sediment is further visible in the separation from the above mentioned transects and the clustering in the PCA (**Figure 5**) of the transects Bliesenrade and Fastbültenhaken. The adjacent land of both transects are without agricultural usage and have comparably low areal TP stock at similar DBDs. The transects Zingst, Pütnitz, and Dabitz are partly separated from the transects of Nisdorf, Salzhaken, and Althagen (**Figure 5**). At theses transects the land is used as harbor area, former airport with close river connection and agricultural used adjacent land. All these land usages might explain an overall increased P stock, as in the other areas. However, it is interesting, that Zingst, Pütnitz, and Dabitz represent a nutrient gradient, i.e., high TP (4 µmol l^{-1}) concentration in the water column in Pütnitz against low TP (2 µmol l^{-1}) in Dabitz (Berthold et al., 2018b). This result might imply that besides the water column as important P source for the sediment, the adjacent land and subsequent run-off is important as well. The transects in Dabitz and Fastbültenhaken exhibited a wide range in the PCA (**Figure 5**) pointing to strong differences between sampling points within both transects. At both stations a sharp increase in LOI and TP concentration but decrease in DBD was observed with increasing water depth (**Supplementary Figure 3**). The transect in Dabitz is located in the western lagoon GB where water exchange with the open Baltic Sea is highest. Fastbültenhaken is in the middle part of the lagoon and is likely subject to changing fresh- and seawater exchange. The clustering of both stations can be a result of different sediment accumulation, due to hydrological conditions. A hydrological model for the DZBC lagoon is missing, therefore no statements are possible regarding underwater currents.

Changes in Sediment P in the Last 40 Years and Ecological Evaluation

The data set from 40 years ago presented a wide range of TP concentrations between 0.05 and 1.5 mg TP g^{-1} DM (Nausch, 1981) (**Table 3**). The LOI ranged between 0.6 and >30% in the whole system, where deeper basins (up to 4 m depth) had not exclusively higher LOI values (possible range 1–30%). This distribution was most likely a result of underwater currents and sediment transports. The percentage of mineral sediments (<5% LOI) of the separate lagoon parts ranged between 60% (GB) and 40% (SB). In the present study had a share of 80% of the sediments were mineral sediments. However, these percentage is not representative as straight sampling transects

TABLE 3 | Total phosphorus (TP) (stock in g P m^{-2} 0–1 cm, and concentration in mg P g dry mass^{-1}) from 40 years ago (40-year BP – before present) compared with today at the same sampling spots.

Location	Sampling depth	TP (mg g^{-1}) 40-year BP	TP (g m^{-2})* 40-year BP	TP (mg g^{-1}) today	TP (g m^{-2}) today
Saaler Bodden	Shallow	0.1−0.2	1.7−2.4	0.05−0.1	1.2−1.5
	Deep	0.8−1.5	1.7−2.0	0.2−1.2	0.3−1.6
Bodstedter Bodden	Shallow	0.1−0.3	1.2−1.8	0.05−0.1	0.8−1.4
	Deep	0.4−0.8	0.8−1.7	0.4−0.7	0.8−1.5
Barther Bodden	Shallow	0.1−0.3	0.6−3.6	0.2	2.7−3.4
	Deep	0.3−0.4	0.9−1.8	0.2−0.3	2.3−2.6
Grabow	Shallow	0.1−0.2	1.4−4.0	0.2−0.3	3.0−5.0
	Deep	0.5−0.8	0.8−1.7	0.5−0.7	1.0−1.2

*Data is derived from Nausch (1981). *Values are assumed from Nausch (1981) with calculated dry bulk densities derived from water content (%) and TP (mg g^{-1} DM, only in ranges). Sampling depth: shallow (<1 m), deep (>2 m).*

were used, rather than a sampling grid. Furthermore, Nausch (1981) sampled 100 sediment cores per lagoon part, whereas the present study had only a maximum of 17 per lagoon part. Generally, the TP concentrations of Nausch (1981) and the present study are comparable for the range and depth distribution (**Table 3**). However, the original data set is only available as a range in tables and figures in the cited publication. DBD cannot be attributed to special samples, only to charts and averages. An uncertainty of the TP stock resulted from the missing exact values for the DBD from the old data sets. Sediment density should always be present within publications, as well as GPS coordinates, or deposited at data bases for future comparisons. This data set will be made accessible via PANGAEA[1]. Methodology of TP extraction was comparable, as the different digestion methods in these studies (HCl) and today (acid persulfate) were equally efficient (Berthold et al., 2015).

Generally, the results suggest that a significant P reduction within 40 years was not verifiable. The TP concentration ranges of the upper sediment layers did not change within the last 40 years. For example, sediment samples of the deeper parts (>1 m) were in the same range as already described by Nausch (1981) (**Table 3**). However, some stations from 2017 had TP concentrations at the lower range compared to 40 years before present. In general, the results found in this study and from 40 years ago are comparable. This similarity of old and new concentrations and stock is somewhat surprising as P inputs were at least reduced by 60 t P a^{-1} (LUNG, 2013). There were around 290 t P bound in the sediments (0–1 cm), if the mean P stocks of the whole system are re-calculate from 1980. The total P stored in the sediments nowadays is 257 t P, if it is assumed that (1) values of this study were representative for most sediments in the system and (2) that sediment characteristics did not change dramatically, i.e., the percentage of mineral to mud sediments remained constant. Some lowered ranges of TP occurred mainly in BoB and SB, which may reflect lower influxes from the Recknitz River. The reduction in TP influxes was largest in the Recknitz decreasing from 50 to 10 t a^{-1} during 1980 through 2010 (LUNG, 2013). No matter if the sediment P load decreased or not, the most important proportion of P in the sediment is the portion of P which normally interacts with the water column.

The interactions between the water column and the sediment depend also on the potential of P being released into or exported from the water column. This potential is higher in suboxic waters regardless of the areal TP. In fact, the State Agency for this region (LUNG, 2013) reported that all inner coastal water bodies of the southern German Baltic coast are oxygen-saturated even above the sediments, i.e., >6 mg O_2 l^{-1}. One pathway for PO_4 in oxic waters is co-precipitation with calcite (Gunduz et al., 2011) or the formation of iron-rich colloids with PO_4 (Gunnars et al., 2002). Such PO_4-colloids are removed by 40% within ca. 40 h in brackish waters (salinity of around 6) (Gunnars et al., 2002). These results suggest that the oxic environment is favoring net P export from the water column into the sediment. Furthermore,

Lampe et al. (2013) described that a wind speed of >8 m/s (5 Bft), or a ground flow velocity of >0.4 m s^{-1} is necessary to induce resuspension events in the inner lagoon part SB. This wind speed happened only 7% of the time in, e.g., 2011 and a TP export via particulate matter into the Baltic Sea amounted only to 3 t a^{-1} (Lampe et al., 2013). However, this export is hard to quantify due to frequent water level changes. A regular occurring resuspension can increase the overall cycling of P between the water column and sediment and might gradually even out the TP concentrations in the growing sediments. Nonetheless, these results indicate that abiotic and biotic particles will be trapped within the lagoon and therefore lead to a TP deposition. Even the deeper basins of other lagoon parts (e.g., station Dabitz, GB) were probably permanently affected by transport of fine material down the slope (Håkanson, 1977), which would explain the absent TP peaks in the sediment horizons (**Figure 6**). This would support the low export rates and the sediment sink function for TP.

There is the possibility that especially high areal TP stocks in shallow areas are subject to frequent TP release events, as they are populated with macrozoobenthos. For example, the burrowing polychaetes *Hediste diversicolor* can reach average population densities of 700 Ind. m^{-2} in the shallow areas (<2 m, max. 7000 Ind. m^{-2}) of the BB and GB. This species was not found below 2 m or in the less saline lagoon parts, i.e., BoB and SB (Arndt, 1989). The burrows of *H. diversicolor* can increase the water-sediment surface by a factor of 3 as well as the nutrient exchange to the overlying water through their ventilation activity (Davey and Watson, 1995). Additionally, *Marenzelleria* spp. established stable populations since the early 1990s (Zettler, 1996) in this lagoon system with 2,000 to 8,000 Ind. m^{-2} in all lagoon parts (Zettler, 1997). *Marenzelleria* can simultaneously shift and increase the PO_4 porewater concentrations in the upper 5 cm sediment depth to the sediment surface by around 5 μmol PO_4 l^{-1} in sandy sediments (Renz and Forster, 2014). Both polychaetes, *Marenzelleria* and *H. diversicolor* have comparable irrigation rates of 12 l m^{-2} d^{-1} at population densities of 3,200 and 800 Ind. m^{-2}, respectively (Hedman et al., 2011). Thus, *Marenzelleria* spp. can replace *H. diversicolor* and expand the bioirrigation activity into the inner lagoon waters. *Chironomidae* occur in high abundances in the SB and BoB with 2,000 to 5,000 Ind. m^{-2} (Arndt, 1994; Zettler, 1997). They appear to be absent in the BB and GB, which means that bioirrigation by these species for deeper lagoon parts can be neglected. Deeper parts of the lagoon may have lower areal TP stocks as well as less P release by animals. The areal P release probably remains lower in deeper parts even if an average diffusive flux of 28.3 $\pm$ 15.2 μmol PO_4 l^{-1} m^{-2} d^{-1} is considered compared to a non-determinable, perhaps lower flux in shallow, unpopulated sediments (Bitschofsky, 2016).

However, these transport fluxes were not commonly monitored, as PO_4 concentrations in the water column were on median 0.1 μmol PO_4 l^{-1}, which is close to the determination limit (0.05 μmol l^{-1}) (Berthold et al., 2018b). One cause can be the luxury consumption of PO_4 by phytoplankton (e.g., Taft et al., 1975). A PO_4 increase would be missed analytically and phytoplankton may still be permanently fertilized. This low, but permanent fertilization might explain the missing ecosystem

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[1]https://doi.pangaea.de/10.1594/PANGAEA.892498

improvement regarding a lower phytoplankton biomass and turbidity within the lagoon (Schiewer, 2007; Berthold et al., 2018b). This possible fertilization effect in the shallow areas is even more concerning, as phytoplankton and submerged macrophytes are not subject to light limitation in these areas, i.e., they can use available nutrients directly for growth and biomass increase, instead of storage. On an area base, TP stocks are much higher here and may fertilize phytoplankton and macrophytes considerably. On the other side, the low PO_4 concentrations within the system could also be caused by the high macrozoobenthos population. One major shift within the system was the aforementioned *Marenzelleria* colonization. The increased water-sediment contact surface in worm burrows could also lower water P concentrations through oxic precipitation and increased remineralization as described earlier. Additionally, a present light limitation (Schiewer, 2007) would always cap phytoplankton biomass, regardless of available P. Therefore, it is reasonable to assume that the P reduction caused only a phytoplankton adaptation to the reduced P availability, like postulated in Sas (1989) for lakes. The reduction of P might have triggered the species composition change (Schiewer, 2007) to small cell cyanobacteria with high volume to surface ratios, which are highly competitive in nutrient uptake (e.g., Friebele et al., 1978). This change could also explain the high TN:TP ratios (36–50) throughout the year found in this lagoon system (Berthold et al., 2018b), as cyanobacteria always show high N:P ratios (Finkel et al., 2010). As conclusion, the net P flux to the sediment might have stayed the same, as seen by the constant TP levels in the sediment, but the decreased P inputs were buffered by a changing species composition and inventory.

Such observations are important for management and restoration actions within eutrophic coastal water bodies. Therefore, future restoration measures shall not predominantly focus on apparently high TP concentrations (mg g^{-1} DM) in the sediment, but rather on diffuse sources in the very shallow areas of coastal water bodies. Those areas can have a greater impact than assumed so far.

CONCLUSION

Analysis of different characteristics of sediment samples, especially TP content, from different transects in the DZBC pointed to the importance of the land use near the transect, affecting the earlier and present day diffuse P input especially in such an almost closed water system such as the DZBC. However, strong differences between sampling points within a transect seem to call for additional effects of P- and/or sediment distribution such as DZBC internal sediment transport or biological sediment mixing by plants and animals. The sampling of sediment cores with parallel analysis of volume percentage of water, DBD and density specific calculation of P stock underlines the importance of sample preparation and area specific P stocks to evaluate ecological relevant P stocks in sediments. Furthermore, it seems reasonable, that the P stocks did not change in 40 years due to a constant P flux into the sediments and increased bioturbation by invasive species.

The phytoplankton composition might have adapted to the lower available P concentrations within the water column and bypassed an ecosystem improvement by, e.g., lower turbidity. Therefore, it can be highlighted that P stock specific evaluation of sediments can draw a different picture of spatial P distribution compared to simple P concentrations in the solid sediment phase. Nevertheless, sediment core analysis have to be extended to separate TP analysis of pore water in the sediment volume and analysis of TP and total concentrations of Al, Ca, Fe, and Mn in the solid phase to get deeper insights into the proportions of dissolved P and adsorbed P as well as in binding partners of P in sediments. This knowledge is urgent necessary to evaluate the potential of P release and its real contribution to eutrophication in shallow lagoon systems and the Baltic Sea. Such enhanced analyses especially of the solid sediment phase from sediment cores from such transects could also contribute to improve the understanding in which diffuse ways P is mainly imported from the adjacent land into the water body. Additionally, a hydrological model seems necessary to determine, where particulate material is transported. This model would help to evaluate, if the lagoon sediment is a permanent P sink, or if particulate matter is transported with a delay into the Baltic Sea.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2018.00305/full#supplementary-material

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