

Spatial and seasonal phosphorus dynamics in a eutrophic estuary of the southern Baltic Sea

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ABSTRACT

Phosphorus (P) is one of the major drivers of eutrophication in aquatic systems. Thus, knowledge of riverine P inputs into the Baltic Sea is essential to evaluate the eutrophication level. In eutrophic estuaries such as the Warnow Estuary, the traditionally monitored parameters of total P (TP) and dissolved molybdate-reactive P (DRP) are not adequate for such an evaluation. Over two years (September 2016 to August 2018), an extended monitoring programme was applied in the Warnow Estuary, determining dissolved non-molybdate-reactive P (DNP), particulate molybdate-reactive P (PRP), and particulate non-molybdate-reactive P (PNP) in addition to TP and DRP. Within the estuary, the concentrations of the P fractions varied on both spatial and seasonal scales. While a gradient in the surface water's PNP was found towards the Baltic Sea, in the bottom water the DRP was distinctive. Particulate P fractions dominated the productive phases (>50% of TP), whereas during regenerative periods dissolved P forms were dominant (>50% of TP). Even though diffusive pore water flux estimates showed a release of dissolved P from the sediment, the calculated TP loads (44 t TP a⁻¹ in 2017) revealed a P retention of 12% within the Warnow Estuary. Although the reduction targets of the Baltic Sea Action Plan are presumably able to reach, further reductions are necessary to achieve the aims (good status according to eutrophication) of the Marine Strategy Framework Directive and the Water Framework Directive in the highly anthropogenically impacted Warnow Estuary.

1. Introduction

The geologically young Baltic Sea is a brackish water body enclosed by nine European countries (HELCOM, 2010). While seawater from the North Sea enters the western Baltic Sea via the narrow and shallow Kattegat, freshwater is contributed to the Baltic Sea by 634 rivers. The annual riverine water input accounts for up to 2% of the Baltic Sea's water volume of 21 760 km³ (HELCOM, 2010). Due to its estuarine character, the Baltic Sea shows both pronounced vertical and lateral salinity gradients with nearly freshwater conditions in the north (Reissmann et al., 2009) and nearly marine conditions in the transition to the North Sea. Along with the stratification-related limitation of vertical water column mixing, water flushing times of 20–30 years (Stigebrandt, 2001) make the Baltic Sea highly sensitive to natural nutrient enrichment (Andersen et al., 2017). The highly populated (85 million people) catchment area of the Baltic Sea (HELCOM 2018^c) shows the highest density in its southern part (HELCOM, 2010).

Eutrophication of the Baltic Sea is mainly caused by anthropogenic inputs of nitrogen (N) and phosphorus (P; OECD, 1982; Hecky and Kilham, 1988) and their levels exceed the natural buffer capacity of the ecosystem, leading to substantial nutrient accumulation. In the beginning of the 20th century, nutrient inputs from human activities increased, which caused a shift in the trophic status of the Baltic Sea from oligotrophic to eutrophic (Gustafsson et al., 2012 and references therein). After reaching maximum loads in the 1980s, numerous measures to reduce the nutrient input were established (Backer et al., 2010). In 2000, the European Water Framework Directive (WFD, 2000/60/EC) declared that many European aquatic ecosystems, including lakes, rivers, and coastal waters, exhibit a high level of eutrophication. Together with the Marine Strategy Framework Directive (MSFD, 2008/56/EC), which generally addresses the oceans, and the Baltic Sea Action Plan (BSAP; HELCOM, 2007; HELCOM, 2013^a) of the Helsinki Commission (HELCOM) the aim is to achieve a good ecological status of the Baltic Sea by 2021. Despite the reduction of nutrient contributions

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from point sources such as sewage plants, the eutrophication level is still high in 97% of the Baltic Sea (HELCOM, 2018^{b, c}; LUNG, 2016; Nausch et al., 2011).

In the Baltic Sea ecosystem, elevated P levels foster summer blooms of N-fixing cyanobacteria especially in the Baltic Proper (Finni et al., 2001), which highlights the special role of P. Approximately 95% of the total P (TP) discharge into the Baltic Sea originates from rivers, in which about 36% of the P originates from agriculture-related diffuse sources, especially those located in the catchment of the southern Baltic Sea (HELCOM, 2010; HELCOM, 2018^a; HELCOM, 2018^c). Consequently, the highest nutrient levels are detected in the coastal waters of the southern Baltic Sea, particularly in Poland and Germany (HELCOM, 2018^c).

Given by the critical trophic status of the Baltic Sea, further reductions of nutrient inputs are necessary in the future to achieve the good ecological status as specified in the WFD and MSFD. The BSAP proposes a maximum allowed input for Germany of about 356 t P a⁻¹ in 2021 (reduction by 170 t P a⁻¹; HELCOM, 2013^{a, b}; Schernewski et al., 2015). New reduction measures require a better understanding of the mobilization and release of P from agricultural soils in the catchment and the composition and biogeochemical cycling of P in the water bodies that finally enter the Baltic Sea (Leinweber et al., 2017). This knowledge could be obtained by an extended P monitoring comprising both dissolved and particulate P fractions in addition to TP (Felgentreu et al., 2018).

The 155 km-long lowland Warnow River in northeastern Germany (Bitschofsky and Nausch, 2019) represents an appropriate model system for such investigations, as its 3024 km² catchment is dominated by agricultural land use. Furthermore, the catchment is among the largest catchments discharging into the German Baltic Sea next to the Oder River.

In previous studies (e.g., Nausch et al., 2011), P was traditionally determined as TP and dissolved inorganic P (DIP). Due to higher levels of particulate P in shallow, eutrophic aquatic systems, the traditional P monitoring is insufficient in such systems. In addition, Jarvie et al. (2002) and Felgentreu et al. (2018) mentioned the problem of confusion caused by the various nomenclatures used partially for one P fraction. As an alternative approach, Felgentreu et al. (2018) suggested an extended

monitoring scheme and introduced a corresponding nomenclature for the different P forms in the water column: dissolved molybdate-reactive P (DRP), comparable to DIP; dissolved non-molybdate-reactive P (DNP), similar to dissolved organic P (DOP); particulate molybdate-reactive P (PRP), equivalent to particulate inorganic P (PIP); and particulate non-molybdate-reactive P (PNP), instead of particulate organic P (POP). In the present study, this improved monitoring approach was applied to the Warnow Estuary connecting the Warnow River with the Baltic Sea (Fig. 1). Special focus is paid to the seasonal changes in P fractions to understand the transformation of one form into another, including the interactions between the water column and sediment as well as the underlying biological processes. Finally, the P load to the Baltic Sea and its seasonal variation is calculated.

2. Study area

The highly anthropogenically impacted Warnow Estuary (Fig. 1) is separated from the Warnow River (comprising a river-like upper course and a lake-like middle course; Bitschofsky and Nausch, 2019) by a weir in the southern part of the city of Rostock (population ca. 207 500 in 2016). The estuary has an area of 12 km², a mean water depth of 4 m (Suppl. 1), and consists of a narrow river-like area (ca. 9 km) as well as a wider area near the river mouth in the north at the *Marina Warnemünde* station (Bachor, 2005). The lake-like area at the north-eastern side of the estuary is not directly involved in water exchange. The average water budget consists of ca. 527 Mio m³ a⁻¹ freshwater and ca. 924 Mio m³ a⁻¹ of intruding Baltic Sea water. Up to 95% of the freshwater is derived from the Warnow River (Bachor, 2005). The flushing time in the estuary is approximately 30 d (Lange, 2018).

According to the salinity structure, the Warnow Estuary can be classified as a partially mixed estuary (Dyer, 1997). The tidal range is less than 20 cm and plays only a minor role in the hydrodynamic processes of the estuary (Winkel, 2003). In addition to vertical salinity stratification in large parts of the estuary, there is also a horizontal salinity gradient from the weir to the river mouth (Suppl. 1; generic salinity profiles from March and August 2017). However, the water column in the northern part of the estuary is nearly totally mixed due to

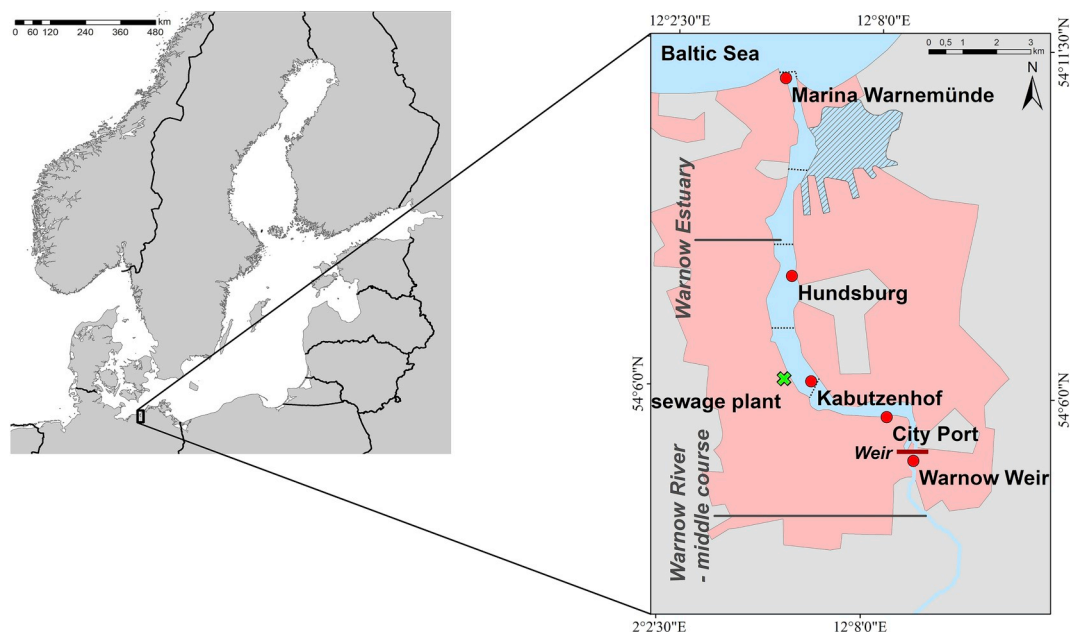


Fig. 1. Study area. Map of Baltic Sea (left) and the study area (right) showing the four sampling stations (red dots) in the Warnow Estuary as well as a site in the middle course of the Warnow River south of the weir (*Warnow Weir*; Bitschofsky and Nausch, 2019); the green cross marks the position of Rostock's sewage plant, and the dotted lines indicate the edges of the five boxes used for budget calculations (chapter 5.3). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

waves and the impact of ferries, cruisers, and containerships. The waves are mainly wind induced and decrease up-estuary.

3. Materials and methods

3.1. Water column sampling

Water column samples were taken monthly at four stations in the estuary (Fig. 1, Suppl. 1) between September 2016 and August 2018. Sampling with the IOW workboat *Klaashahn* usually occurred west of the fairway on two consecutive days. Surface water was sampled with a PE bucket, whereas water close to the bottom was obtained with a Niskin hydrocast (5 l, HydroBios). After rinsing with the water sample, the water was transferred to pre-cleaned HDPE bottles (2 l) and stored in a cooling box until processing in the lab within 6 h.

Oceanographic parameters were measured with two different multi-parameter probes (HQ40d from HACH, HI 9828 from ATP Messtechnik GmbH) from September 2016 to May 2017 and with a CTD including a multi-parameter probe (CTD90M, Sea & Sun Marine Tech) and an oxygen sensor (3835, Aanderaa) from the IOW-MARNET programme from June 2017 onward. Conductivity, water temperature, pressure, and oxygen concentrations were recorded in situ at a frequency of 8 Hz. Salinity and oxygen saturation were calculated from these values. The CTD was lowered as slowly as possible to maximize the spatial resolution of the profile. To maintain the accuracy of the data at a constant high level, the CTD was regularly calibrated in the DakkS-certified IOW calibration lab for the parameters conductivity, water temperature, and pressure.

3.2. Pore water and sediment sampling

Short sediment cores were obtained with a single coring device (patent application DE 10 2012 215 628 A1). Approximately 30 cm-long sediment cores including an about 10 cm-thick supernatant water layer were collected in February, June, August and November 2017.

The pore water was extracted from pre-drilled short core liners with Rhizons (Seeborg-Elverfeldt et al., 2005; Rhizosphere Research Products) with a sampling resolution of 1 cm within the first 10 cm and a resolution of 2 cm below (Häusler et al., 2018). The pore water used for P and iron (Fe) analysis was transferred into acid-cleaned 2 ml reaction tubes and acidified with 20 µl of sub-boiled nitric acid. For the determination of total sulphide, a pore water aliquot was added to 2 ml reaction tubes containing 20 µl of 20% zinc acetate. All samples were stored in a refrigerator (8 °C) until they were analysed.

After extracting the pore water, the cores were sliced with a 1-cm resolution for solid-phase analysis. The sediment samples were freeze-dried (ALPHA 1–4, Christ) and homogenized in an agate ball mill (Pulverisette 5, FRITSCH GmbH).

3.3. Biogeochemical analyses

3.3.1. Phosphorus fractions in the water column

In addition to traditionally monitored total P (TP) and dissolved molybdate-reactive P (DRP), P fractions comprising dissolved non-molybdate-reactive P (DNP), particulate molybdate-reactive P (PRP) and particulate non-molybdate-reactive P (PNP) were analysed. These P fractions were measured colourimetrically with the molybdenum-blue method after Murphy and Riley (1962), whereby TP, DNP and PNP were measured after alkaline digestion following Koroleff (1983).

Due to the acid milieu of the molybdenum blue reaction, not only DIP is detected but also a small but unknown amount of labile organic and colloidal P. Thus, the term DIP would lead to an overestimation of the dissolved inorganic P and to an underestimation of the organic P pools. Consequently, DRP represents the DIP as well as a small amount of DOP and particulate P, DNP consists of the remaining DOP, PRP represents mostly the PIP, and PNP comprises mainly POP (Felgentreu et al., 2018).

3.3.2. Chlorophyll *a* and suspended particulate matter in the water column

Depending on turbidity, water samples of 50–400 ml were filtered (GF/F-filter, Ø = 25 mm, retention range 0.7 µm) for chlorophyll *a* (Chla) determination using vacuum pressure constantly adjusted to 850 hPa, and the samples were then stored frozen at –80 °C for a minimum of 12 h and a maximum of three months until analysis. Chlorophyll *a* was extracted with 96% ethanol at ambient temperature for 3 h and measured with a fluorometer (Turner 110, 10-AU-005) with a determination limit of 0.29 µg l⁻¹ (Wasmund et al., 2006; HELCOM, 2017).

The content of suspended particulate matter (SPM) was determined gravimetrically by weighing dried (min. 12 h at 60 °C) polycarbonate filters (Ø = 25 mm, pore size of 0.8 µm) before filtering 30–500 ml of the water samples. Used filters were dried again (min. 12 h at 60 °C) and the SPM content was calculated from the weight difference before and after filtering.

3.3.3. Dissolved iron and phosphorus in pore water

Dissolved Fe and total dissolved P were measured with an inductively coupled plasma optical emission spectrometer (ICP-OES; iCAP 7400 Duo, Thermo Fisher Scientific) using external matrix-matched calibration adjusted to salinities of 3, 6, and 12 with Atlantic Seawater (OSIL) spiked with Fe and P. Scandium served as an internal standard to compensate for instrument and matrix fluctuations. Precision and trueness were determined with the international reference material SLEW-3 (NRCC) spiked with Fe and P and were 1.9% and <<0.1% for Fe and 7.6% and <<0.1% for P, respectively.

Based on the dissolved P concentrations, the diffusive pore water P fluxes in the first 5 cm were estimated by the numerical rate estimation from concentrations (REC) model (Lettmann et al., 2012), which was successfully applied in the basins of the Baltic Sea by Dellwig et al. (2018) and Häusler et al. (2018). The porosity of the corresponding sediment samples was estimated from dry bulk densities (DBDs) using an average grain density of 2.7075 g cm⁻³. By using temperature and salinity determined in bottom water and porosity, the sedimentary diffusion coefficients of P were calculated after Boudreau (1997) and Schulz (2006).

3.3.4. Total sulphide in pore water

Total sulphide was analysed according to Cline (1996). The samples were homogenized by using an ultrasonic bath (10 min) and a vortexer. Some samples had to be diluted depending on the expected concentrations of total sulphide. A 200 µl volume of diamine (N,N-dimethyl-1,4-phenylen-diaminesulfate) was added to a total sample volume of 2700 µl. Afterwards, the samples were stored for 1 h in the dark for the formation of a coloured complex from sulphide and diamine. Finally, the samples were spectrophotometrically measured at 670 nm.

3.3.5. Solid phase of sediment

After the acid digestion of the freeze-dried and homogenized sediment material using a mixture of concentrated nitric acid, perchloric acid, and hydrofluoric acid (Dellwig et al., 2019), the contents of aluminium (Al), Fe, and P were determined by ICP-OES (iCAP7400 Duo, Thermo Fisher Scientific). Precision and trueness were checked with the SGR-1b (USGS) reference material and were <4.8% and <4.0%, respectively.

4. Results

4.1. Spatial variability of phosphorus and biological parameters in the water column

An overview of the measured parameters is provided in Table 1. The TP concentration generally decreased towards the Baltic Sea in both the surface and bottom water (Tab 1). The median TP values from all stations over the whole sampling period were 2.2 µM at the surface and 1.5

Table 1

Spatial variation of the phosphorus (P) composition and biological parameters as medians over the entire sampling period with the standard error (n = 24) in the Warnow Estuary; data for the Warnow Weir (n = 12) are from [Bitschofsky and Nausch \(2019\)](#); s = surface layer, b = bottom layer; TP = total P, DRP = dissolved molybdate-reactive P, DNP = dissolved non-molybdate-reactive P, PRP = particulate molybdate-reactive P, PNP = particulate non-molybdate-reactive P, Chla = chlorophyll a, SPM = suspended particulate matter.

Station	layer	TP [μM]	DRP [μM]	DNP [μM]	PRP [μM]	PNP [μM]	Chla [$\mu\text{g l}^{-1}$]	SPM [mg l^{-1}]
Warnow Weir	s	2.9 ± 0.7	1.1 ± 0.69	0.3 ± 0.34	0.5 ± 0.29	1.3 ± 0.57	33.9 ± 3.27	4.6 ± 1.00
City Port	s	2.8 ± 0.69	0.8 ± 0.61	0.4 ± 0.31	0.5 ± 0.28	1.3 ± 0.54	32.4 ± 2.84	4.2 ± 1.03
Kabutzenhof	s	2.5 ± 0.79	0.8 ± 0.55	0.4 ± 0.33	0.4 ± 0.24	1.1 ± 0.79	24.5 ± 4.16	4.6 ± 1.12
Hundsburg	s	2.0 ± 0.62	0.6 ± 0.53	0.3 ± 0.33	0.2 ± 0.25	0.7 ± 0.47	10.9 ± 2.47	2.4 ± 0.94
Marina Warnemünde	s	1.0 ± 0.39	0.6 ± 0.37	0.2 ± 0.20	0.1 ± 0.14	0.2 ± 0.26	3.1 ± 1.16	1.3 ± 0.59
City Port	b	3.0 ± 0.96	2.5 ± 0.86	0.3 ± 0.29	0.7 ± 0.42	1.0 ± 0.53	7.0 ± 2.42	3.7 ± 1.28
Kabutzenhof	b	1.8 ± 0.72	1.1 ± 0.60	0.3 ± 0.25	0.2 ± 0.25	0.3 ± 0.54	2.9 ± 2.63	2.2 ± 0.91
Hundsburg	b	1.5 ± 0.61	0.9 ± 0.51	0.3 ± 0.25	0.1 ± 0.20	0.3 ± 0.44	1.9 ± 1.69	1.8 ± 1.5
Marina Warnemünde	b	1.1 ± 0.37	0.6 ± 0.33	0.3 ± 0.20	0.0 ± 0.19	0.2 ± 0.24	2.5 ± 0.84	2.0 ± 1.47

μM close to the bottom. The phosphorus composition at the stations differed between the surface and bottom, and between the individual sites. At the surface, the concentration of particulate P (PRP and PNP) was higher at the southern stations (*City Port* and *Kabutzenhof*), whereas the DRP concentration was higher at these stations close to the bottom than at the northern stations. In the surface water, the concentrations of the dissolved P fractions (DRP and DNP) were nearly the same. The DRP concentrations varied between 0.6 μM (*Marina Warnemünde*) and 0.8 μM (*City Port*), while the DNP concentrations were around 0.3 μM .

The Chla concentration varied between 1.9 and 32.4 $\mu\text{g l}^{-1}$ and was highest in the surface waters at the southern stations. The SPM content ranged from 1.3 to 4.6 mg l^{-1} and showed similar patterns to Chla.

The contributions of the different P fractions to TP are shown in [Fig. 2](#). In the surface layer of the estuary, the amounts of DRP (27–54%) and DNP (12–21%) increased towards the mouth. DNP showed the same behaviour in the bottom layer (6–24%), whereas the variability in DRP was less pronounced (58–52%). While the proportion of PRP clearly decreased in the surface and bottom waters from *City Port* towards

Marina Warnemünde (surface: 17–5%, bottom: 15–4%), this pattern appeared for PNP only in the surface layer (43–20%). In general, the dissolved fractions (DRP and DNP) were dominant close to the bottom at all stations and in the surface water at the northern station (*Hundsburg* and *Marina Warnemünde*). The surface layer of the southern *Kabutzenhof* and *City Port* stations was dominated by particulate P fractions (PRP and PNP). Furthermore, the relative amounts of the P fractions were similar in the surface and bottom layer at *Marina Warnemünde*.

4.2. Seasonal changes of phosphorus and chlorophyll a in the water column

The seasonal P changes ([Suppl. 2](#)) were characterised by dominance of either dissolved P (DRP and DNP) or particulate P fractions (PRP and PNP). Even within the seasonal trend, the dissolved P fractions mostly dominated the bottom waters at each station ([Fig. 3](#)) showing a dominance in 75% of the measurements at *City Port* and 88% at *Marina Warnemünde*. The number of months in which dissolved P was dominant

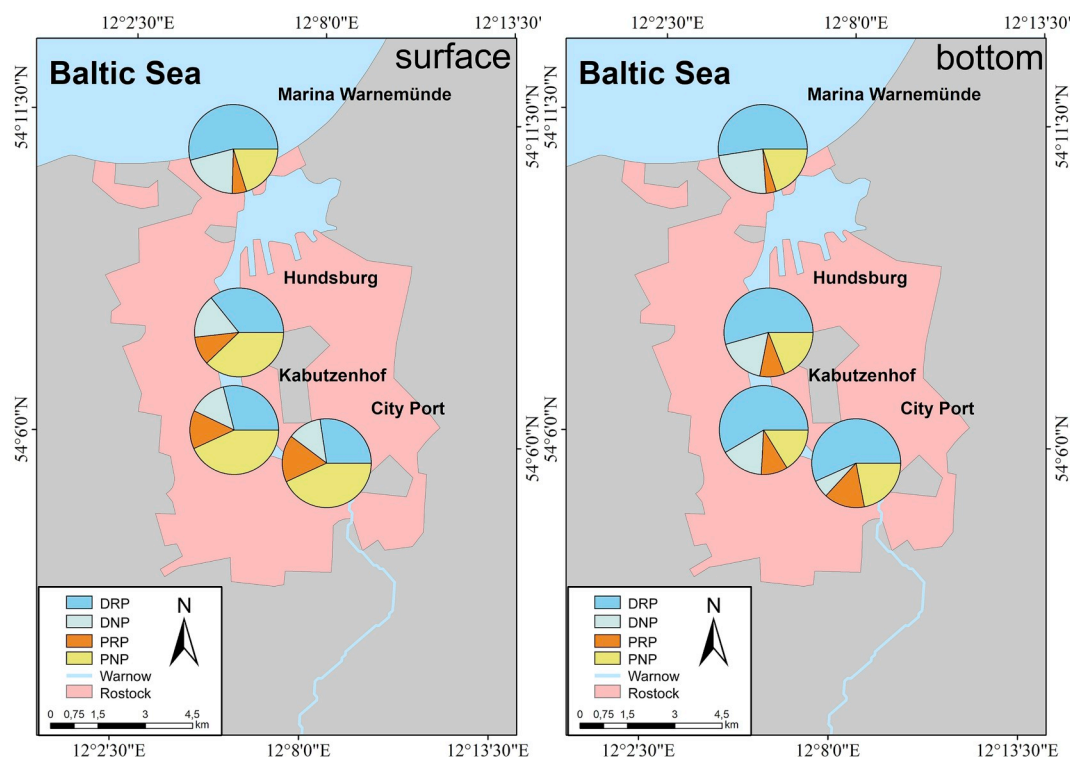


Fig. 2. Proportion of phosphorus fractions. The contributions of different phosphorus (P) fractions to total P (medians over the whole sampling period) in the surface (left) and bottom (right) waters of the Warnow Estuary; DRP = dissolved molybdate-reactive P, DNP = dissolved non-molybdate-reactive P, PRP = particulate molybdate-reactive P, PNP = particulate non-molybdate-reactive P. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

increased towards the Baltic Sea. This trend towards the Baltic Sea was even more pronounced in the surface water as the portion of dissolved P increased from 45% of the measurements at *City Port* to 88% at *Marina Warnemünde*.

During productive phases, particulate P fractions amounted to more than 50% in the surface water (Fig. 3). This occurred from October to December 2016, February to June 2017, and March to July 2018 at *City Port*, in September and November 2016, March to August 2017, and February to July 2018 at the *Kabutzenhof* station, and in September 2016, March to July 2017 and February to July 2018 at *Hundsburg*.

The variability of TP as the sum of the four P forms showed higher concentrations during the summer months in the surface and less pronounced in the bottom layer (Fig. 3). The TP concentrations ranged from 1.3 to 8.4 μM in the surface layer and 1.3–12.6 μM in the bottom layer at *City Port*, 0.8–8.9 μM in the surface layer and 0.2–1.5 μM in the bottom layer at *Kabutzenhof*, 0.3–6.1 μM in the surface layer and 0.2–1.3 μM in the bottom layer at *Hundsburg* and 0.1–2.1 μM in the surface layer and 0.1–1.2 μM in the bottom layer at *Marina Warnemünde*. Thus, the range of the TP concentrations between surface and bottom, and the coupled effects of seasonality decreased towards the Baltic Sea.

In general, the Chla concentration varied between 0.3 and 230 $\mu\text{g l}^{-1}$ (Suppl. 3) in the whole estuary. It showed peaks during periods of particulate P dominance, especially in the surface layer, e.g. 94–230 $\mu\text{g l}^{-1}$ from June to August 2017 at *Kabutzenhof*. Close to the bottom, Chla maxima occurred even when dissolved P dominated (e.g., in June and August 2017 as well as in July 2018 at *City Port*).

4.3. Total dissolved phosphorus, iron, and total sulphide in the pore water

The pore water profiles of total dissolved P, Fe, and total sulphide changed seasonally and spatially (Fig. 4, Suppl. 4) and mostly did not show a steady state. In general, the dissolved P concentrations increased with sediment depth and decreased towards the *Marina Warnemünde* station at the river mouth. The most pronounced seasonal changes were observed for the dissolved P profiles close to the sediment-water interface (first 5 cm), especially at *City Port*. Total sulphide and Fe exhibited tightly related patterns, with strongly decreasing Fe concentrations being associated with elevated sulphide levels and vice versa. At *City Port*, the sulphate reduction zone indicated by increasing sulphide concentrations shifted upwards in the sediment from February to August 2017 and slightly downward in November 2017, whereas nearly the opposite was true for *Kabutzenhof*. Such variations were not observed at *Hundsburg* and *Marina Warnemünde*, where sulphide concentrations generally increased at sediment depths between 5 and 10 cm.

The diffusive pore water fluxes of dissolved P generally decreased towards the Baltic Sea, showing the highest values in the summer months (June and/or August 2017) at each station. An exceptionally high flux of 4036 $\mu\text{mol P m}^{-2} \text{d}^{-1}$ was estimated at *City Port* in August 2017, which was obviously related to the strong gradient of dissolved P in the uppermost pore water samples. The seasonal variability of P fluxes was much less pronounced at *Kabutzenhof* compared to the remaining stations because of the unexpectedly high value determined for February 2017.

4.4. Phosphorus and iron in the surface sediments

The contents of sedimentary P and Fe were normalised to Al to minimise dilution effects especially by quartz and organic matter, which allows comparisons with the lithogenic background and of sandy (e.g. *Marina Warnemünde*) and mud-rich sediments (e.g. *City Port*), respectively. Aluminium was chosen for normalisation as it is hardly affected by biological and early diagenetic processes and serves as an important compound of terrigenous material (Brumsack, 2006). It should be kept in mind, however, that Al normalisation may result in unusually high element ratios, e.g., under conditions of very low lithogenic background sedimentation but enhanced contribution of other components such as

organic matter (Van der Weijden, 2002; Brumsack, 2006).

Similar to the variations in dissolved P and Fe in the pore water, solid-phase P and Fe exhibited pronounced spatial and seasonal variations in the surface sediment (Fig. 5, Suppl. 5). Decreased P/Al and Fe/Al values occurred in most cases during June and August 2017 when the diffusive fluxes of dissolved P were highest. In addition, sedimentary P and Fe contents decreased from *City Port* towards *Marina Warnemünde*.

5. Discussion

5.1. Processes in the Warnow Estuary

Rivers and their estuaries play a key role in P cycling due to intense exchange and transformation processes and their potential ability to retain P during transport towards the coastal ocean (Withers and Jarvie, 2008). Depending on the ecosystem, the transformation of individual P fractions in the water column can occur at very short time scales ranging from several hours (e.g. coral reefs) to one day (Baturin, 2003). On the other hand, storage of phosphate in the sediment, e.g. via adsorption on Fe oxyhydroxides, may last for longer periods if redox conditions are favourable (Jensen and Thamdrup, 1993). During its transport, P undergoes various transformations, including conversion into dissolved and particulate as well as inorganic and organic forms, and further interacts with the sediment (Fig. 6):

The phosphorus, that circulates in the water column originates among others from land via diffuse sources but also from point sources (HELCOM, 2018^c). The main P input into the Warnow Estuary remains the Warnow River itself (Bachor, 2005). In addition to atmospheric inputs, drainage events such as those that occur via inlets of the mixed canalisation system, which may drain into the estuary during extreme rainfall events (H. Stähle, Nordwasser GmbH, personal communication), are defined as diffuse sources in the urban area of the Warnow Estuary. The drainage of the mixed canalisation could be the reason for the elevated DRP concentrations close to the bottom at *City Port* in June and July 2017 (Fig. 3). The one defined point source is the central sewage plant (near *Hundsburg*, Fig. 1), which operates at a high technical standard (P input <6.5 μM ; Nausch et al., 2011).

The presence of all mentioned P fractions at *City Port* showed that P enters the Warnow Estuary both in solution and attached to particles as well as in organic (mainly DNP and PNP) and inorganic (mainly DRP and PRP) forms (Figs. 2 and 3, Suppl. 2). Similar P compositions, Chla concentrations, and SPM contents at *City Port* and *Warnow Weir* (Tab 1, Bitschofsky and Nausch, 2019) indicate that P transport through the weir occurs without substantial transformation.

In the Warnow Estuary, microorganisms presumably take up P in form of DRP, DNP, or PRP, and transform it into PNP comprising particulate organic P (Felgentreu et al., 2018). A hint therefore is the positive correlation of Chla and PNP at the surface (Pearson: 0.895, $p = 0.000$). Phosphorus could be released from the organisms via excretion or in the case of death in the form of either DNP or PRP, which could be transformed back into DRP by mineralisation. In addition, DRP might be transformed into PRP and vice versa by adsorption and desorption on particles (Cade-Menun et al., 2019).

Along with the deepening of the estuary from the weir to the river mouth at *Marina Warnemünde*, both the SPM content and particulate P (Fig. 2) concentrations (Pearson: surface = 0.85, bottom = 0.60, $p = 0.000$) decreased in the surface waters in the same direction (Table 1). This indicates deposition of particulate matter in the shallower areas after entering the estuary due to lower current velocities (Baturin, 2003). The decrease in particulate P and the corresponding increase in dissolved P may result from interactions between the two phases via biological activities and/or physicochemical processes in the water column (Lin et al., 2013).

During oxygen consuming degradation of deposited organic matter in the sediment, PNP is partially transformed into PRP and DNP and further into DRP (Hille, 2005 and references therein). Anoxic conditions

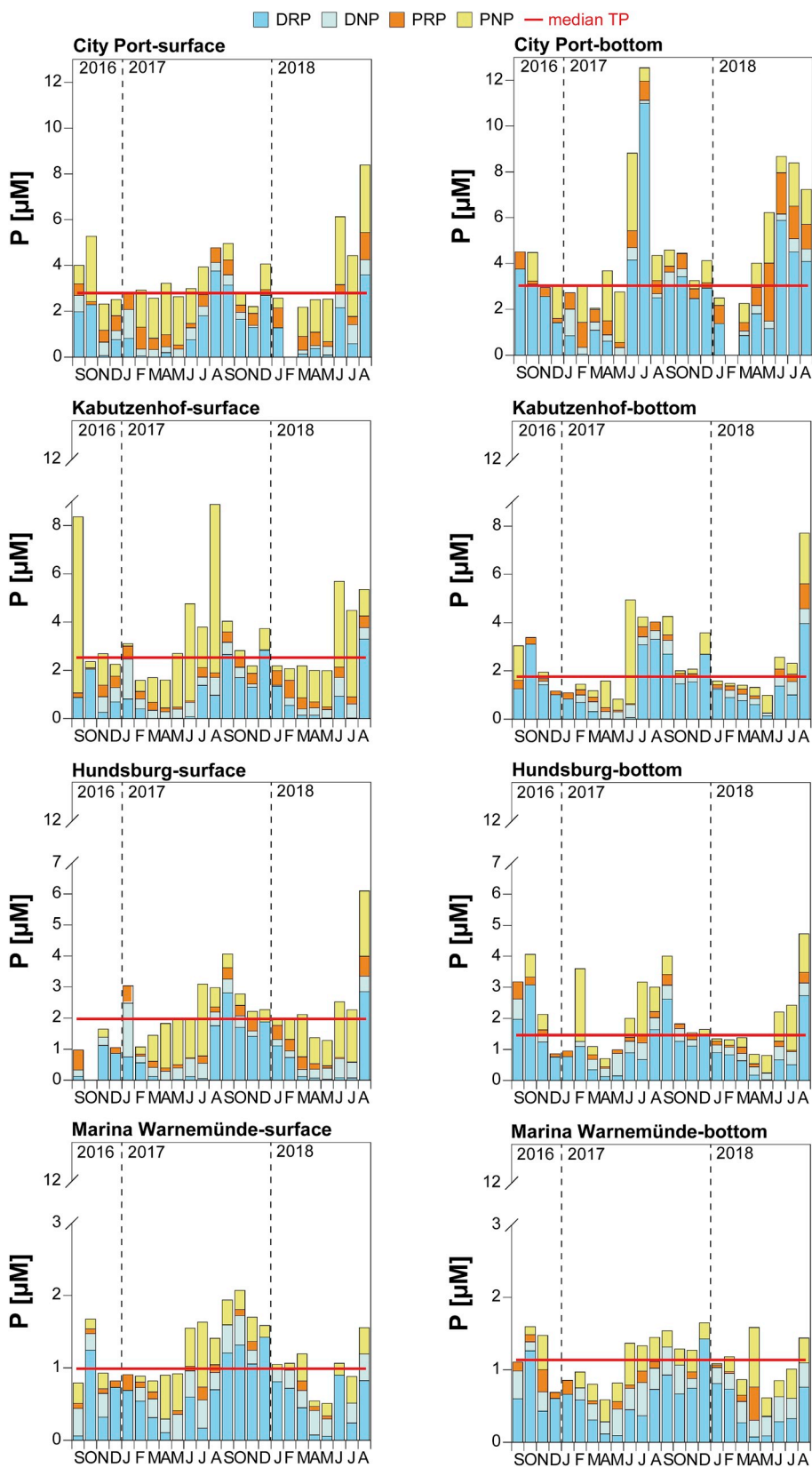


Fig. 3. Seasonal variation in phosphorus fractions. Seasonally changes in phosphorus (P) fractions in the surface and bottom layers; DRP = dissolved molybdate-reactive P, DNP = dissolved non-molybdate-reactive P, PRP = particulate molybdate-reactive P, PNP = particulate non-molybdate-reactive P, red line = median TP over the sampling period. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

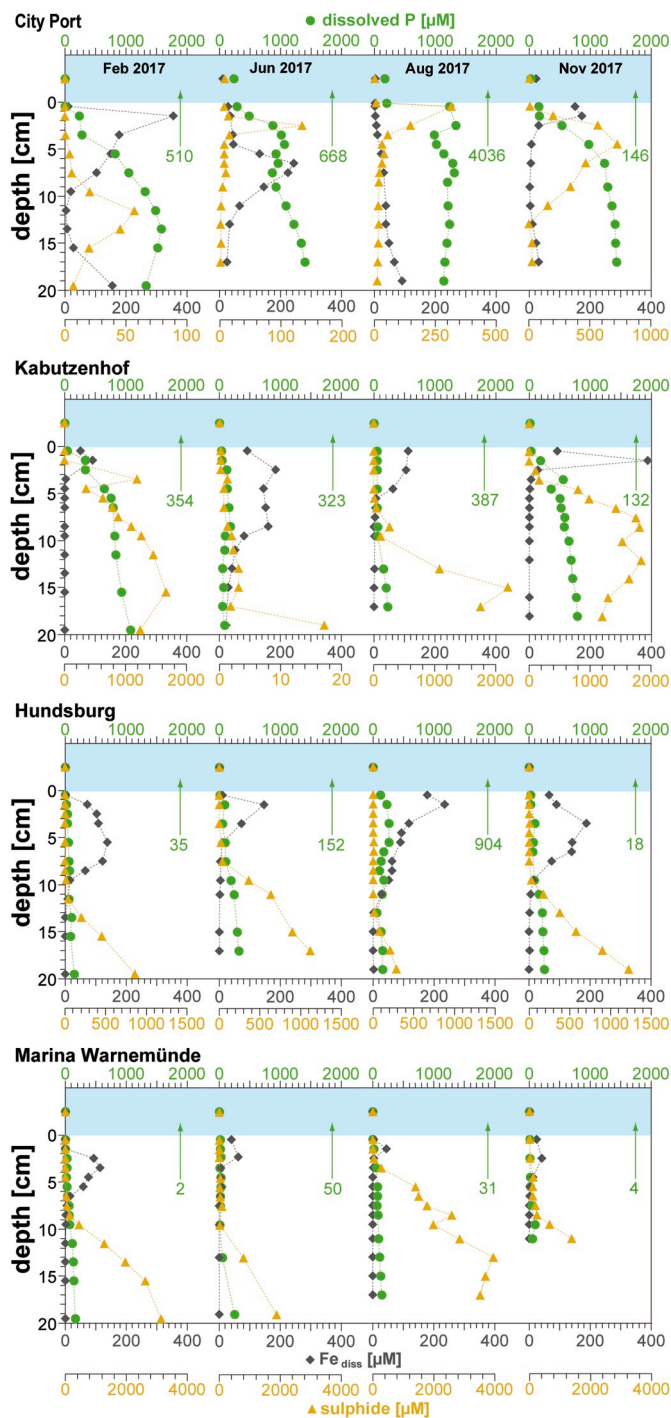


Fig. 4. Pore water profiles. Total dissolved phosphorus (P), dissolved iron (Fe) and total sulphide in the pore water of the *City Port*, *Kabutzenhof*, *Hundsburg*, and *Marina Warnemünde* sampling sites obtained in February, June, August, and November 2017; green numbers with arrows denote diffusive flux estimates of dissolved P in $\mu\text{mol m}^{-2} \text{d}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

also foster the reduction of Fe oxyhydroxides and the release of previously adsorbed phosphate (Einsele, 1936), as shown by the decreases in Fe/Al and P/Al in the surface sediment at all sampling sites (Fig. 5). Accordingly, Fe peaks were often observed in the pore waters close to the sediment-water interface, which indicate dissimilatory Fe reduction and the aforementioned release of P previously bound to Fe oxyhydroxides (e.g. Jensen and Thamdrup, 1993). On the other hand, negligible Fe concentrations within sulphidic pore waters, occurring

even close to sediment-water interface (e.g., August 2017 at *City Port*; Fig. 4), are due to precipitation of solid Fe sulphide phases. Comparing the spatial variation of the sediments in the Warnow Estuary, the sediment at *City Port* is muddy with a high content of organic matter, whereas the sediment at *Marina Warnemünde* is sandy with a lower content of organic matter (Suppl. 5). Thus, the oxygen is more likely consumed at *City Port* due to the higher availability of organic matter and the enhanced degradation, respectively. Due to the higher organic content in this part of the estuary, there are more likely hypoxia and consequently, higher diffusive pore water fluxes of dissolved P than in those at *Marina Warnemünde* (Suppl. 6).

The concentrations of TP decreased in the water column of the Warnow Estuary towards the Baltic Sea, as expected, whereas the TP concentrations remained at nearly the same level along the flow direction of the Warnow River (Bitschofsky and Nausch, 2019). The stations in the middle course of the Warnow River (south of the weir) showed similar patterns in the distribution of the P fractions (Bitschofsky and Nausch, 2019). In contrast, the P composition varied horizontally and vertically within the water column of the adjacent Warnow Estuary (Fig. 2). The differences between each of the P fractions at the surface and close to the bottom decreased towards the Baltic Sea, where the distribution of the P fractions in surface and bottom waters are similar. The reason therefore is possibly a more homogenous water column resulting from mixing by waves and ship traffic in the northern part of the estuary and generally lower P concentrations in the intruding Baltic Sea waters. Compared to the winter TP value of $1.8 \mu\text{M}$ recorded at the surface of a station near *Marina Warnemünde* in 2000 (Bachor, 2005), the median winter TP concentration determined in this study in the surface water at *Marina Warnemünde* (2016/17: $0.7 \mu\text{M}$, 2017/2018: $1.4 \mu\text{M}$) was lower, suggesting a decreasing trend. Moreover, the median (whole study) TP concentration in the surface waters at *Marina Warnemünde* ($1.0 \mu\text{M}$) was nearly half the annual average TP ($1.7 \mu\text{M}$) determined between 2000 and 2010 at a nearby station (LUNG, 2013).

The TP concentration was $0.7 \mu\text{M}$ higher in the surface water than close to the bottom overall. A dilution with the Baltic Sea water plays hereby a minor role as P showed a non-conservative mixing with the salinity (Suppl. 3) in the surface and the bottom water. Another possible reason for this difference could be primary producers, which utilise nutrients in and below internal boundary layers but migrate to the surface for growth (Nausch et al., 2012). During phases of elevated biomass production, P circulates close to the surface of the water column, above the internal boundary layer (Reissmann et al., 2009). In contrast, the DRP concentration and the salinity should be higher close to the bottom due to dissolved P fluxes out of the sediment and the inflowing Baltic Sea water. Indeed, in 68% of the DRP measurements, higher values were observed close to the bottom than in the surface waters, a condition that appeared more often at *City Port* than in *Marina Warnemünde*. In additional 20% of the DRP measurements, the concentration in the surface water was higher than in the bottom water. The remaining 12% of the DRP measurements showed no differences ($\leq 0.1 \mu\text{M}$) between the layers. These observations were independent of seasonality.

5.2. Seasonality of different phosphorus fractions

In surface waters, seasonality of the P fractions was observed, although traditional separation into seasons did not seem to be practical, as biological processes do not respond to meteorological seasons but, rather, depend on temperature, light, and the availability of nutrients.

Although these parameters underlie seasonal trends, the water column begins to warm earlier in the year, and the cool down begins later than has commonly been observed due to climate change. Consequently, the biomass production season is becoming longer. Thus, primary production is higher, and the biomass maximum has shifted into the summer in the Baltic Sea (Kahru et al., 2016).

Along with the extension of spring and autumn blooms, prolongation

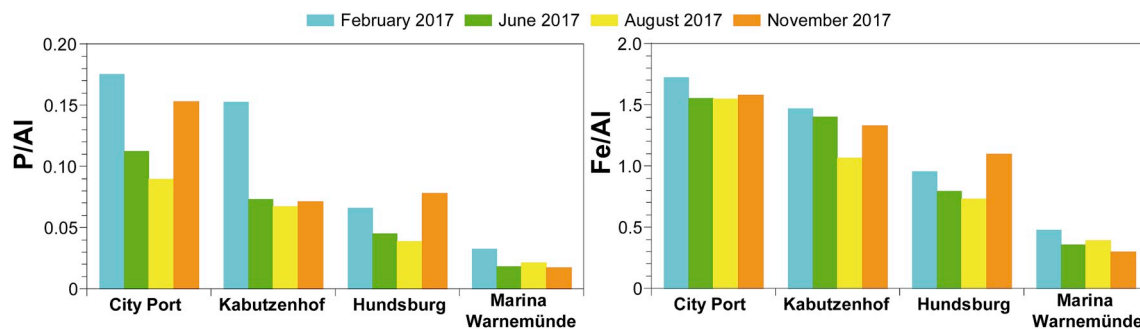


Fig. 5. Changes in sedimentary phosphorus. Aluminium (Al)-normalised contents of phosphorus (P) and iron (Fe) in the surface sediments (0–2 cm) of the four sampling sites in February, June, August, and November 2017. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

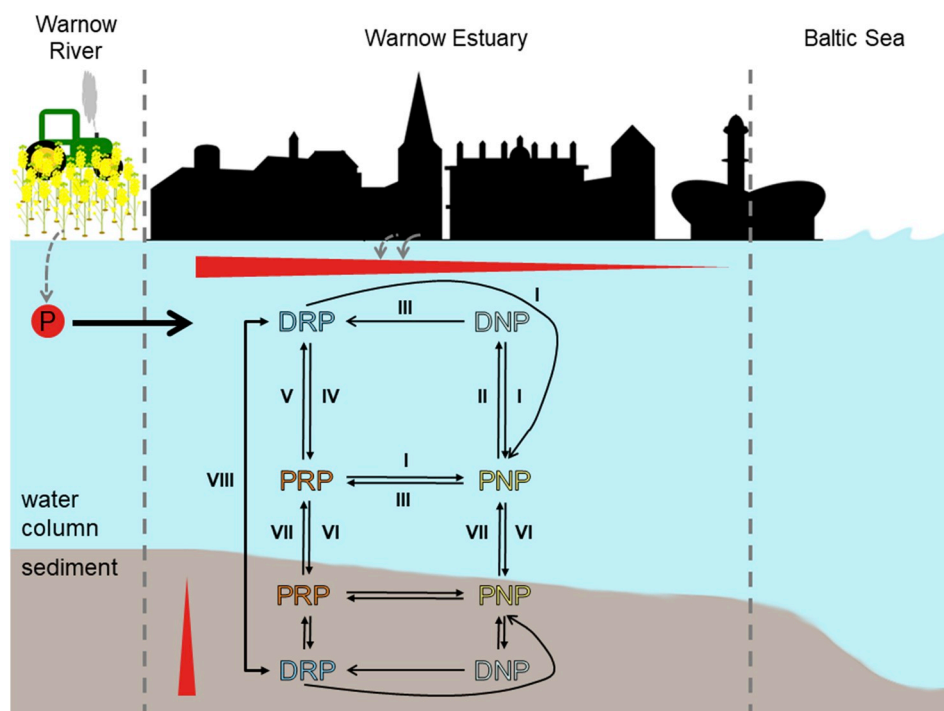


Fig. 6. Estuarine phosphorus cycle. Scheme of the phosphorus (P) cycle in the Warnow Estuary, P in the red circle represents the various P forms, DRP = dissolved molybdate-reactive P, DNP = dissolved non-molybdate-reactive P, PRP = particulate molybdate-reactive P, PNP = particulate non-molybdate-reactive P, grey dotted arrows = diffusive P source, grey arrows = known P input via point sources, thin arrows = transformation processes of P forms, I = uptake by organisms, II = release by organisms, III = mineralisation, IV = adsorption to particles, V = desorption from particles, VI = sedimentation, VII = resuspension, VIII = diffusion of DRP and DNP, red triangles = expected spatial distribution of total P. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of the biomass production season from February to December has also been observed in coastal waters (Wasmund et al., 2019). As a result, the data of the current study were divided into regenerative and productive phases. During the regenerative phase, over 50% of TP consisted of dissolved P (Fig. 3), dominated by DRP, in which particulate and organic bound P is mineralised. In the productive phase, particulate P was dominant, accounting for more than 50% of TP, and a high level of PNP was observed. Additionally, a Chl_a maximum occurred during productive phases at the surface. The positive correlation (Pearson: surface = 0.90, bottom = 0.81; $p = 0.000$) between the organic P dominated PNP and Chl_a (Suppl. 7) indicated that this P fraction mostly comprised fresh biomass. However, this is just an assumption, as data from bioavailability of the different P fractions are not yet available.

Long-term trends in nutrient concentrations are commonly estimated from wintertime monitoring (November–January), as biological processes play a minor role (Nausch et al., 2011 and references therein). The winter average of the DRP concentration in the Warnow Estuary showed a wide range ($1.1 \mu\text{M} \pm 0.7$ at City Port, $0.9 \mu\text{M} \pm 0.5$ at Marina Warnemünde), which indicates an influence of hydrodynamic processes (Bachor, 2005). The winter DRP at Marina Warnemünde ($0.9 \pm 0.5 \mu\text{M}$) during the sampling period (2016–2018) was close to the $0.5 \mu\text{M}$ DRP

concentration measured in 2000 by Bachor (2005) and the $0.7 \mu\text{M}$ DRP concentration measured from 2000 to 2010 by Lung (2013) in Mecklenburg Bay near Rostock.

While the annual average DRP concentrations determined at City Port and Warnow Weir (Bitschofsky and Nausch, 2019) were quite similar ($0.8 \pm 0.6 \mu\text{M}$ in the estuary and $0.7 \pm 0.7 \mu\text{M}$ in the river), the winter averages for the two sites differed ($1.1 \pm 0.7 \mu\text{M}$ in the estuary and $0.2 \pm 0.6 \mu\text{M}$ in the river). The same issue arises for the winter average values when separating P variability into seasons: the development of organisms, especially primary producers, depends on water temperature, light and the availability of nutrients. If there is a change in the seasons in the Baltic Sea (Kahru et al., 2016), the shift could be even more distinct in coastal waters such as the Warnow Estuary (Wasmund et al., 2019) as well as in rivers. For example, under favourable conditions, primary production could begin in late January or late February. Consequently, the DRP concentration in this month would be more influenced by biological processes than during a harsh winter with low temperatures in January and February. The winter average DRP in the river is probably lower because primary production starts earlier than in the estuary.

Phosphorus concentrations in the water column are influenced by

exchange at the sediment-water interface. An upward shift during summer months and a downward shift during winter months were noted in the pore water samples, especially at *City Port* in June 2017 and *Marina Warnemünde* in August 2017 (Fig. 4). The pore water concentrations of dissolved P at the sediment-water interface varied seasonally due to the adsorption of P on Fe oxyhydroxides and its desorption under the extension of reducing conditions, with the latter leading to elevated pore water fluxes of P. This seasonality was also documented in the surface sediments by decreasing P/Al and Fe/Al values during the summer, followed by recovery in fall (Fig. 5).

Mainly during the summer months (June to August), DP was released from the sediment (Fig. 4). This could be visible in the elevated DRP concentrations close to the bottom (Fig. 3). Furthermore, in 2017, there were several heavy rain events from June to August that caused a flooding of the mixed canalisation system flowing into the estuary (H. Stähle, Nordwasser GmbH, personal communication). As quantification of this flooding is not yet possible, the exact effect remains to be determined. Nevertheless, an increase in dissolved P concentrations in the water column, especially in the area of the city port of Rostock, including the *City Port* and *Kabutzenhof* stations, could be a consequence of this flooding.

5.3. Budget calculations and consequences for eutrophication

The knowledge of the retention potential of an aquatic system helps to estimate the eutrophication and, in turn, the potential mesotrophication in such systems. Such estimation needs information on the importance of the individual P sinks and sources in the estuary and finally an in- and output balance. While the contribution via smaller tributaries and the sewage plant play only a minor role (Bachor, 2005), the dominating P source to the estuary represents the Warnow River (Bitschofsky and Nausch, 2019). In addition, sedimentary P reflux may represent an additional source within the estuary. As a first approach, diffusive fluxes of dissolved P were calculated, which however are subject to certain limitations: Besides the potential disturbance of the pore water concentrations gradients during coring, transport and the limited resolution of Rhizon sampling, advection, bioturbation and bioirrigation can affect the elemental fluxes. Advection is generally able to increase nutrient fluxes, which is however less pronounced for P due to the interaction with Fe oxyhydroxides (Huettel et al., 1998). In addition, virtually missing tides and limited resuspension as indicated by the low SPM content in the bottom waters (Table 1, Suppl. 3) argue against strong effects of advection especially in the muddy sediment at *City Port*, where highest P fluxes were calculated. close to the bottom, and pore water is not pressed out of the sediment by advection. Consequently, advection does not increase the real fluxes. The effect of bioturbation and bioirrigation is controversially discussed in the literature. While in some cases, reduced fluxes out of the sediment were observed (Kauppi et al., 2018), other studies showed that, e.g., bioturbation of bivalves or dead end burrows result in higher nutrient fluxes (Chen et al., 2016; Meysman et al., 2006). Thus, the calculated diffusive fluxes of dissolved P in the current study can either be minimum or a maximum values as in the sampled cores bivalves and burrows were found.

To estimate whether the pore water reflux contributes significantly to the P inventory, the Warnow Estuary was subdivided into five boxes with equal surface areas according to the sampling stations (Fig. 1). Based on the pore water fluxes of dissolved P from the short cores, areal fluxes were estimated for four of the five boxes during each season (Suppl. 8). Along with these fluxes and the dissolved P concentrations in the corresponding water volume of the boxes, the inventories of dissolved P were calculated (mean of surface and bottom). The comparison of areal P flux and water column P inventories allowed rough estimation of the time necessary to reach the indicated water column P concentrations solely by pore water reflux. This duration varied from 3 d at *City Port* in February 2017 to a maximum of nearly 9 years at *Marina*

Warnemünde in the same month (Table 2). Compared to the flushing time of about 30 d in the Warnow Estuary (Lange, 2018), the diffusive pore water P flux substantially contributed to the P inventory, especially at *City Port* but also at *Kabutzenhof* and *Hundsburg* in summer. In contrast, at *Marina Warnemünde*, the diffusive pore water P flux played a negligible role.

The function of the Warnow Estuary as a P source or sink was assessed by the P loads entering the Baltic Sea at the river mouth. Phosphorus loads were calculated by multiplying P concentrations with the runoff at the river mouth. The latter mainly depends on river runoff, water exchange with the Baltic Sea, and rainfall. The runoff of the Warnow Estuary was calculated for 2016 using a 3D numerical model (Buer et al., 2018). In 2017, 2018, the net volume flux at the mouth was calculated using the temporal changes in measured water levels near the *Warnow Weir* in the river and in the estuary near *Marina Warnemünde* as well as the runoff of the Warnow River. The monthly average runoff of the Warnow Estuary (median daily runoff) into the Baltic Sea ranged between $2.1 \text{ m}^3 \text{ s}^{-1}$ and $40.6 \text{ m}^3 \text{ s}^{-1}$ between September 2016 and August 2018 (Suppl. 9).

The calculated TP loads varied between 4 kg d^{-1} in September 2016 and 382 kg d^{-1} in August 2017, with the highest value following heavy rain events during the very wet period in summer 2017 (Fig. 7). In contrast to generally higher river TP inputs between September 2016 and July 2017, this maximum TP export (dominated by PNP) to the Baltic Sea was about twice as high as the corresponding import from the river (183 kg d^{-1} ; Bitschofsky and Nausch, 2019; Suppl. 9). A reason therefore could be primary production. Furthermore, internal fertilization resulting from P release from the sediment (LUNG, 2013) or the flooding of the mixed canalisation system could also have led to higher loads.

However, the TP loads showed no clear seasonal trend. They rather depended on precipitation, as the load increased after heavy rain events, as observed e.g. in July and August 2017 (Fig. 7). With respect to the contribution of the different P fractions to the TP load substantial differences were determined. DRP had mostly the highest contribution to the TP, while PRP contributes the least (Table 3, Suppl. 9). Overall, the total dissolved P load was lower into the Baltic Sea than into the estuary during the observation period (September 2016–August 2017, Bitschofsky and Nausch, 2019, Suppl. 9), which indicates that the dissolved P was utilised and/or retained in the estuary.

Precipitation, runoff, and loads depend on each other (Bachor, 2005) as seen, e.g., in October 2017 when elevated precipitation was followed by increasing runoff and TP load in the next month. Consequently, normalisation is necessary to allow comparisons between different years and river systems. The P loads were normalised by multiplication with the quotient of the long term (1981–2010) and the annual mean runoff (method IA1 for systems with no clear trend; Silgram and Schoumans, 2004). The datasets of 2016 and 2018 were extrapolated to one year (Suppl. 9).

The normalised TP loads amounted to 19.1 t a^{-1} in 2016, 43.9 t a^{-1} in 2017 and 15.8 t a^{-1} in 2018 (Table 3) and were characterised by an increasing impact of the P fractions: PRP < PNP < DNP < DRP. In comparison, these differences in P fractions were less pronounced in the

Table 2

Calculated time necessary to reach the indicated water column concentrations of dissolved phosphorus (Suppl. 8) in the four boxes (Fig. 1) according to the given pore water fluxes (Fig. 4).

Box	February 2017	June 2017	August 2017	November 2017
City Port	2.1 d	13.9 d	2.6 d	38.8 d
Kabutzenhof	10.3 d	7.9 d	27.8 d	48.5 d
Hundsburg	151.9 d	33.8 d	12.2 d	422.1 d
Marina Warnemünde	0.4 a	148.7 d	275.5 d	1.2 a
	3219.4 d			2317.9 d
	8.8 a	0.4 a	0.8 a	6.4 a

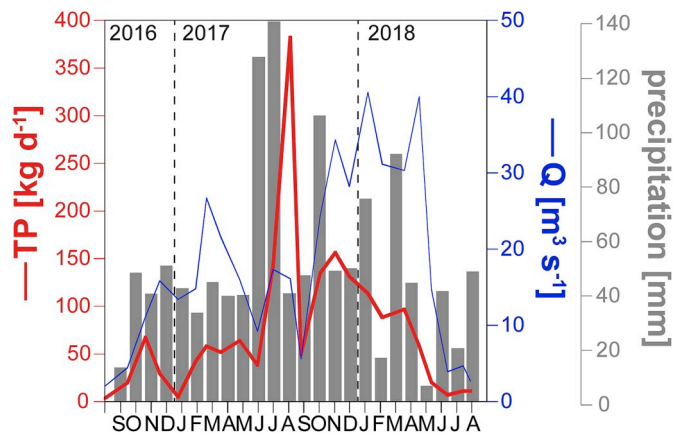


Fig. 7. Phosphorus loads entering the Baltic Sea. Monthly loads of total phosphorus (TP) entering the Baltic Sea together with runoff (Q) and precipitation in Rostock over the sampling period. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

river (Suppl. 9; Bitschofsky and Nausch, 2019), suggesting more intense transformation processes within the estuary.

The highest TP export to the Baltic Sea was consequently found in 2017 and was dominated by DRP (39%) and PNP (47%). In this humid year, the load of dissolved P was approximately 4 t higher than in the very dry year 2018. In the Warnow River, higher output of dissolved P during 2017 was also observed by Bitschofsky and Nausch (2019). However, the particulate P load entering the Baltic Sea from the Warnow Estuary was about 18 t higher in 2017 than in 2018.

The TP load from the Warnow River into the Warnow Estuary was estimated to be 50.1 t a⁻¹ in 2017 (Suppl. 9; Bitschofsky and Nausch, 2019). Consequently, 6.2 t TP a⁻¹ of the introduced TP remained within the estuary, which indicates a retention of about 12%. Although the areal pore water fluxes of dissolved P suggest a contribution to the water column P inventory at least for the *City Port* and *Kabutzenhof*, the efficiency of P deposition obviously exceeds this reflux. Thus, the Warnow Estuary still works as a P sink.

The TP loads of three rivers in northern Germany that discharge into the Baltic Sea (HELCOM database http://nest.su.se/helcom_plc/; Suppl. 10), the Trave (catchment area: 2472 km², TP load: 57 t a⁻¹ in 2017), Ücker (catchment area: 2256 km², TP load: 39.1 t a⁻¹ in 2017) and Peene (largest German catchment area into the Baltic Sea: 5110 km², TP load: 76.5 t a⁻¹ in 2017), were compared to those of the Warnow Estuary in 2017. The catchments of these rivers have a similar agriculture dominated land use as the Warnow System (river and estuary). Considering the error of such estimations and the catchment-load ratios, all river systems are similar to the Warnow system. For example, the TP load and the catchment area of the Peene were about 1.8 times higher than those of the Warnow.

Based on the TP loads from the German rivers discharging into the Baltic Sea, except for the Oder, the reduction target for each of the rivers was calculated according to the German target in the BSAP (Suppl. 10). Thus, the allowed TP load from the Warnow entering the Baltic Sea is 34.1 t a⁻¹, a threshold that was achieved at least in 2014 (HELCOM database; Suppl. 10), 2016 (HELCOM database; Suppl. 10 and Table 3) and 2018 (Table 3). However, the HELCOM database mainly ignores the processes within the estuary by determining the P loads into the Baltic Sea at the regular monitoring station *Warnow Weir*. Consequently, the target could be reached more often in the past, if the estuarine processes were considered.

Nevertheless, the Warnow was not included among the 3% of Baltic Sea coastal waters that have achieved a good status according to eutrophication (HELCOM, 2018^b), so further reduction measures should be implemented in the Warnow area. In contrast, the German Federal

Table 3

Annual runoff-normalised phosphorus (P) loads [t a⁻¹] into the Baltic Sea from 2016 to 2018; TP = total P, DRP = dissolved molybdate-reactive P, DNP = dissolved non-molybdate-reactive P, PRP = particulate molybdate-reactive P, PNP = particulate non-molybdate-reactive P.

Sampling year	TP	DRP	DNP	dissolved P	PRP	PNP	particulate P
2016 ^a	19.1	10.1	6.2	16.3	2.4	1.4	3.8
2017	43.9	16.9	5.8	22.8	2.3	20.5	22.8
2018 ^b	15.8	8.3	4.3	12.6	0.7	2.7	3.4

^a 4 months extrapolated to a year.

^b 8 months extrapolated to a year.

Ministry for Justice and Customer Protection issued a regulation aimed at protecting surface waters (OGewV, 2016 BGBl. I S. 1373) to implement the WFD, wherein benchmarks were set for the different types of water bodies to reach the stated goals. Accordingly, the Warnow Estuary belongs to inner coastal waters with a salinity between 5 and 10 and should not exhibit TP concentrations higher than 0.58 μM. The surface TP concentrations determined in this study only adhered to this benchmark at *Hundsburg* in December 2016 and January 2017 and at *Marina Warnemünde* in April and May 2018. Although the TP reduction target was reached, the TP concentrations mostly exceeded the benchmarks. Related to the benchmark, the reduction target should be revised to about 10 t TP a⁻¹ instead of the currently applied value of 34 t TP a⁻¹ for the Warnow system discharging into the Baltic Sea.

The good ecological status is a multi-parameter tool that also depends on biological parameters. That is why an aquatic system can be classified as “not reached the good ecological status” even if nutrient levels meet the targets. Estuaries react individually due to their own specific hydrodynamics, morphology and nutrient inventories. Hence, water bodies classified as one type according to the WFD could require different target values (Schernewski et al., 2015). Thus, the Warnow Estuary, as a highly anthropogenically influenced aquatic system, may not achieve a good ecological status in the given time framework.

6. Conclusion

The main findings of this study on the behaviour of P in the Warnow Estuary can be summarised as follows:

- Phosphorus circulates in various forms (DRP, DNP, PRP, and PNP) during estuarine transport, including the water column and sediment (Fig. 6). The surface waters are characterised by a gradient of PNP towards the Baltic Sea, whereas DRP dominates in bottom waters.
- The traditional classification into seasons should be revised in respect to climate change. A possible approach is an orientation on the availability of the different P fractions, e.g., a separation into a productive season with dominating particulate P (mainly PNP) and a regenerative season during which dissolved P (mostly DRP) dominates.
- In 2017, the P retention in the Warnow Estuary was approximately 12% (6.2 t TP a⁻¹), thus disclosing the Warnow Estuary as a potential P sink.
- In line with Bachor (2005), the internal P reservoir in the estuarine sediments has to be incorporated in nutrient balances because currently buried P may be released under changing redox conditions.
- Due to the biogeochemical processes in the Warnow Estuary, the entire Warnow system could narrowly achieve the P reduction target of HELCOM's BSAP (2013a, b) by 2021. However, as the good ecological status in the adjoining Baltic Sea coastal waters is not reached, further P input reductions are necessary.

Author contributions statement

All authors were involved in contributing the conception and design of the study; Lisa Rönspiess and Olaf Dellwig analysed the samples, interpreted the data and wrote the manuscript with support of all co-authors. Olaf Dellwig performed flux estimates and sediment analyses; Xaver Lange provided data for budget estimates; Detlef Schulz-Bull, Olaf Dellwig and Günther Nausch supported Lisa Rönspiess during the writing process with ideas for the manuscript design. All authors are involved in manuscript revision, read and approved the submitted version.

Declaration of competing interest

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study, the collection, analysis, or interpretation of the data, in the writing of the manuscript, or in the decision to publish the results.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecss.2019.106532>.

List of abbreviation

Al	aluminum
BSAP	Baltic Sea Action Plan
Chla	chlorophyll <i>a</i>
DIP	dissolved inorganic phosphorus
DNP	dissolved not-molybdate-reactive phosphorus
DOP	dissolved organic phosphorus
DRP	dissolved reactive phosphorus, dissolved molybdate-reactive phosphorus (new)
Fe	iron
HELCOM	Helsinki-Commission
ICP-OES	inductively coupled plasma optical emission spectrometry
MSFD	Marine Strategy Framework Directive
N	nitrogen
P	phosphorus
PIP	particulate inorganic phosphorus
PNP	particulate not-molybdate-reactive phosphorus
POP	particulate organic phosphorus

PRP	particulate molybdate-reactive phosphorus
TP	total phosphorus
SPM	suspended particulate matter
sulphide	total sulphide
WFD	Water Framework Directive

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