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Magnitude and influence of atmospheric phosphorus deposition on the southern Baltic Sea coast over 23 years: implications for coastal waters

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Abstract

Background: There are various ways for nutrients to enter aquatic ecosystems causing eutrophication. Phosphorus deposition through precipitation can be one pathway, besides point sources, like rivers, and diffuse runoff from land. It is also important to evaluate recent trends and seasonal distribution patterns of phosphorus deposition, as important diffuse source. Therefore, a long-term dataset was analysed including 23 years of daily phosphate bulk depositional rates and 4.5 years of total phosphorus (TP) bulk depositional rates. The study area was at the coastline of the southern Baltic Sea, an area which shows severe eutrophication problems.

Results: The median daily deposition of phosphate was 56 µg m^{-2} day^{-1} (1.8 µmol m^{-2} day^{-1}) at 4222 rain events. The median annual sum of phosphate deposition was 16.7 kg km^{-2} a^{-1}, which is comparable to other European areas. The annual TP deposition depended strongly on methodological aspects, especially the sample volume. The median TP-depositional rates ranged between 19 and 70 kg km^{-2} a^{-1} depending on the calculated compensation for missing values, as not every rain event could be measured for TP. The highest TP-depositional rates were measured during summer (e.g. up to 9 kg TP km^{-2} in August 2016). There was no trend detectable for phosphate- and TP-depositional rates over the sampled period.

Conclusions: Deposition of P is a considerable nutrient flux for coastal waterbodies. Median total annual deposition contributed 3 t (phosphate) to 10 t (TP) per year into the adjacent lagoon system, being therefore close to annual riverine inflows of 10 t phosphate and 20 t TP per year. However, the impact of precipitation is predicted to be higher in lagoon parts with fewer point sources for phosphorus, if equally distributed over the area of interest.

Keywords: Eutrophication, Precipitation, Seasonality, Total phosphorus, Phosphate, Baltic Sea

Background

The Baltic Sea is one of the largest brackish, non-tidal inland seas of the Northern Atlantic. It occupies a basin formed by glacial erosion during the last ice age about 13,000 years ago. The water exchange between the Baltic Sea and the adjacent North Sea is limited. Since the 1900s, the Baltic Sea changed from an oligotrophic sea, although enriched by yellow substances, into a eutrophic marine environment [1]. Phytoplankton growth was stimulated by an excessive nutrient input into the Baltic Sea. This growth led to an excessive organic matter production. Its bacterial remineralization was followed by hypoxia and finally an increased mortality of benthic organisms [1]. Rising applications of mineral fertilizers, increasing populations in urban areas, etc. have caused higher nitrogen (N) and phosphorus (P) loads coming from the catchment areas (e.g. [2, 3]). Since the 1950s, the surplus nitrogen by fertilizers has approximately tripled until the mid-1980s followed by a period of much less increase and even stagnation [4]. Conversely, trends

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for total phosphorus inputs to the Baltic Sea reveal steady statistically significant reduction of 30% over the years from 1995 to 2016 [5].

In the early 1990s, the total annual nitrogen load to the Baltic Sea comprised 1.4 million t of which 69% were waterborne discharges (rivers, point and non-point sources), 10% were caused by N_2 fixation through cyanobacterial blooms, while the rest, 21%, was atmospheric deposition onto the sea surface [6]. During 1980–1993, the total annual input of P to the Baltic Sea was estimated as 59 500 t, of which 69% was derived from riverine load [7]. The remaining 31% of the P input to the Baltic Sea are not explicitly described [8]. Therefore, other sources, such as atmospheric deposition, must be considered in more detail [9].

Atmospheric deposition can supply an important amount of P to ecosystems [10]. The latter author indicated in his review as one of the first to report that atmospheric deposition of P equals weathering of P-rich minerals in soils. However, the amount and relative importance of atmospheric deposition varies widely from place to place, depending on anthropogenic impact in nearby locations. This P deposition fertilizes also remote and oligotrophic systems, like pristine lakes and peatlands and may cause long-term ecological damage [10]. Major sources of atmospheric P include dust from soils and drylands, marine aerosols, primary biological aerosol particles (microorganisms, dispersal units, fragments and excretions) as well as ashes from volcanoes, biomass burning, combustion of oil and coal and finally emissions from phosphate (PO_4-P) manufacture [11]. Estimation of P deposition is important for understanding ecosystem functioning (e.g. [12, 13]) since even small but ongoing P input fluxes partially determine if aquatic primary productivity is ultimately limited by phosphorus or nitrogen.

The importance of P deposition is still discussed, as there are indications that not only N and P, but Fe strongly increases N fixation in oligotrophic oceans [14]. Nonetheless, in some oceanic regions, such as the eastern Mediterranean or the Red Sea, atmospheric flux of phosphorus can sustain up to 50% of new production [15, 16], although its input into aquatic ecosystems has generally been considered as small in relation to other loads [17]. On a global scale, it is assumed that mineral aerosols are the main source for P deposition, with anthropogenic sources contributing only 5–15% of TP and PO_4-P, respectively [18]. Hence, more reliable data are necessary to justify such assumptions, especially in the Baltic Sea where such long-term monitoring programmes for P deposition are rare [19]. Most coastal waterbodies of the southern Baltic Sea are dominated by cyanobacteria [20]. Those cyanobacteria can be highly adapted to low P concentrations [21]. Hence, atmospheric deposition of P, even at low concentrations, may be of ecological significance in sustaining cyanobacterial blooms as well as other biological activities in the Baltic Sea and their coastal waterbodies. There are some publications on P deposition in the Baltic Sea region (e.g. [12, 22]); however, P deposition is considered to be impacted by the close environment [10, 11]. Therefore, averaged values of one sampling site cannot be used for other regions.

In the present study, we report P-depositional rates over 23 years of continuous rain water sampling and chemical analysis at the Biological Station Zingst (University of Rostock) at the southern Baltic Sea coast. The focus was on the seasonal and annual development of P depositions. It was expected to find differences not only between dry and wet years, but also between months (vegetation period vs. winter). A second goal was to find an appropriate calculation method for missing values. Values were sometimes missing due to days with so little rain that the resulting sample could not be analysed for PO_4-P and/or TP.

Materials and methods

Sampling site

Zingst is located at the Darß-Zingst peninsula of the southern Baltic Sea coast (Fig. 1). Precipitation was sampled at the Biological Station Zingst (54.4304°N and 12.6859°E) near the Zingster Strom, which is part of the eutrophic lagoon Darß-Zingster Bodden Chain. The immediate vicinity of the sampling device is covered by 4500 m^2 of grassland. The property is surrounded by holiday flats. However, there is a farm southwest with sometimes open soil and an allotment area in the northwest. The main wind direction is northwest [23]. The peninsula is part of the National Park "Vorpommersche Boddenlandschaft", whereas the mainland in the south is mainly agriculturally used.

Sampling

For 1995 and 1996, precipitation data in mm were obtained from the measuring station of the Federal Environmental Agency in Müggenburg, which is ca. 2.6 km distant from the Biological Station Zingst. Since 1997, precipitation was measured daily at 08:00 CET with a precipitation gauge after Hellmann (opening 200 cm^2) at the Biological Station. Rain water for chemical analyses was sampled in a glass flask mounted by a glass funnel of a similar diameter as the gauge. Rain water was removed every day if precipitation happened. Snow was melted at room temperature prior to phosphorus measurements. Dry deposition, i.e. dust, was not excluded. This sampling

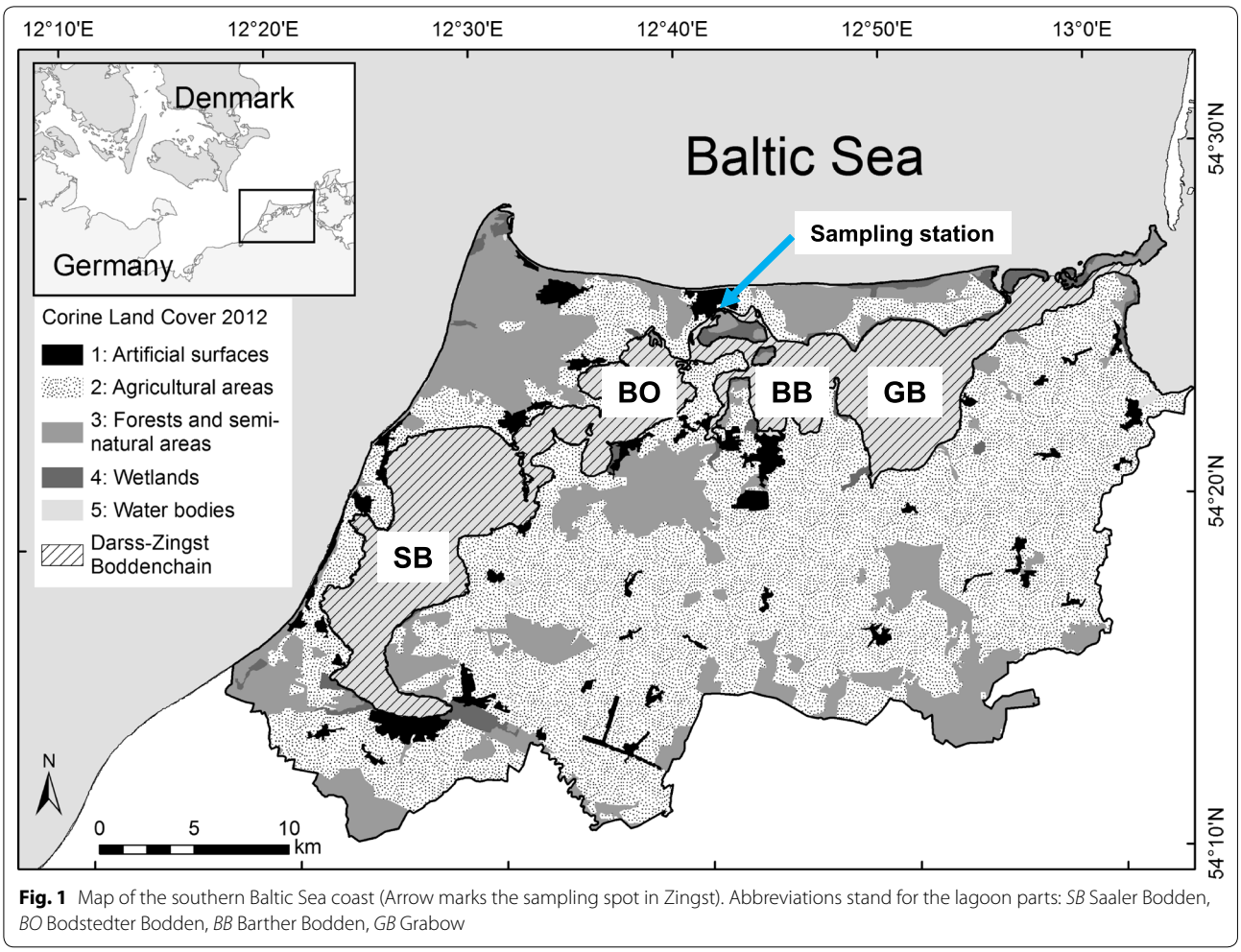

Fig. 1 Map of the southern Baltic Sea coast (Arrow marks the sampling spot in Zingst). Abbreviations stand for the lagoon parts: *SB* Saaler Bodden, *BO* Bodstedter Bodden, *BB* Barther Bodden, *GB* Grabow

design resulted in a combination of wet and dry deposition to a bulk value. The glassware was always kept extra clean by rinsing with deionized water after sampling to avoid contamination of the phosphorus samples.

Samples of at least 10 ml volume were filtered through 0.45 µm cellulose acetate filters and stored frozen for up to 2–3 weeks prior phosphate analysis. Since 2013, additional samples were also taken for total phosphorus (TP) analysis. For that, at least 50 ml rain water was filtered only through a coarse sieve (mesh size ca. 1 mm) to prevent contamination of non-rain associated particles, like insects. Hence, TP measurements were restricted to larger rainfall events of > 2 mm per day.

Chemical analyses

Phosphate was measured as molybdenum blue [24] in a segmented continuous flow analyser (Alpkem RFA 300, since 2011 FlowSys by Alliance Instruments, [25]). Limit of quantification (LOQ) was 0.05 µmol l^{-1}.

Total phosphorus was chemically digested in 15 ml subsamples using an alkaline persulphate solution (16.8 mM final concentration, [26]) in tubes made of perfluoralkoxy-polymere (Teflon® PFA, Fa. AHF, Germany) for 24 h at 90 °C [27]. All samples were neutralized in the presence of a nitrophenol indicator by adding some droplets of ammonia (1 part concentrated ammonia plus 3 parts ultrapure water) followed by a titration with 1 N HCl back to a colourless solution. This solution was filled up to 20 ml by ultrapure water. The neutralized digestate was further analysed for phosphate. LOQ for TP was 0.22 µmol l^{-1}. Up to three blanks (ultra-pure water) and standards of 5 or 10 µmol l^{-1} phosphate standard were measured with each batch of TP samples. Diphenylphosphate (10 µmol l^{-1}) served as a standard for TP.

Data basis

Phosphate values are available from all samples after diurnal precipitation events, i.e. rain periods from 08:00 of 1 day until 08:00 next day, which had a volume > 1 mm

(1 l m^{-2}). Samples of 0.5–1 mm daily precipitation could only be used for chemical analyses, if these samples could be diluted and still have a detectable PO_4-P concentration (> 0.05 µmol l^{-1}). The concentrations resulted only from rain events and a variable number of previous days with dry deposition. Wet samples were not stored for longer than 1 day. Therefore, an artificial conversion of TP to PO_4-P, and vice versa, should be negligible. Nevertheless, the percentage of measured samples increased from 72% in the first decade to 88% in the second decade (Table 1).

Data evaluation and statistics

Numerous precipitations events led to low volume samples which could not be analysed and hence PO_4-P values are missing. The long-term annual phosphate deposition data from 1998 to 2017 (kg P km^{-2} a^{-1}) were calculated with different modes: a) as the sum of direct measurements only. The long-term median of 0.53 µmol P l^{-1} was used for all rain samples which were missed to be analysed (calculation mode b). As comparison, only the long-term median was used for all rain events (calculation mode c). Years of 1995–1997, where precipitation sums were not measured with rain sampling, had to be omitted for (a) (Table 2).

Much more gaps exist for TP measurements, because a substantial sample volume was needed. First, the annual TP deposition was calculated with the available values (see Table 3, calculation a). It was tested, if missing values could be replaced by using the long-term TP concentration (as median, calculation b). Furthermore, it was tested, if a monthly median of the proportion of PO_4-P to TP (in %) worked as more stable approach (calculation mode c). We assumed that this approach can reproduce TP concentration, as they are based on measured PO_4-P values, instead of the same median for all precipitation events.

Replicate samples were averaged with arithmetic means. Averages of different samples (monthly, concentration level classes) were always medians. Monthly or annual precipitation (mm) and deposition are always sums (g P m^{-2} t^{-1}, where appropriate).

Results

Precipitation

The overall median was 605 mm precipitation for this period of 23 years (mean 634 mm, Fig. 2a). These values are comparable to the long-term median of 620 mm

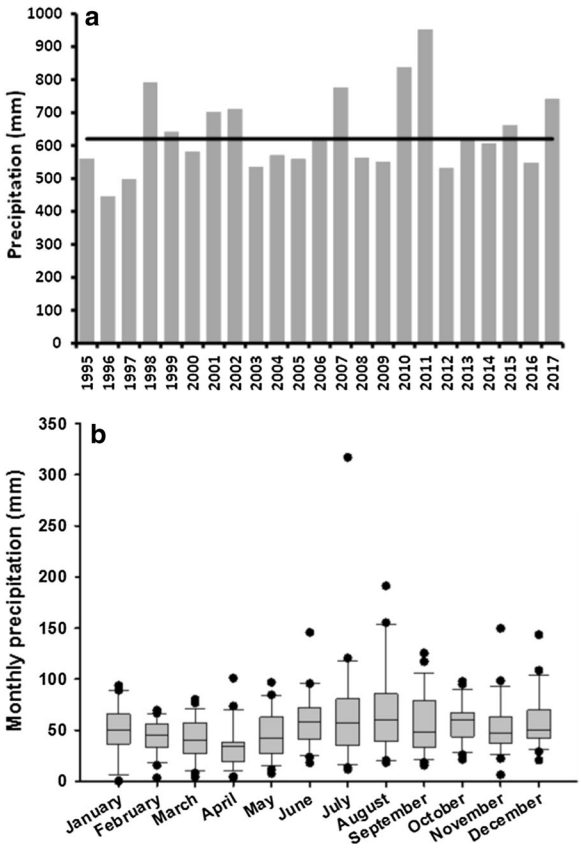

Fig. 2 **a** Annual precipitation between 1995 and 2017 at Zingst and **b** monthly median during that time depicted as Whisker–Box plots. Lines in boxes represent the median, the boxes the interquartile distances (25–75%), and the whisker the 10% and 90% percentiles. Outliers are represented by closed circles

Table 1 Number of precipitation events, precipitation volume (mm day^{-1}) and number of phosphate determinations during 1995–2017, and number of precipitation events during 2013–2017 for total phosphorus (TP) analysis

1995–2017			2013–2017		
Precipitation volume	Precipitation events	Phosphate measurements	Precipitation volume	Precipitation events	TP analysis
< 0.5	1127	31 (3%)	< 2	408	3 (< 1%)
0.5–1	628	139 (22%)	2–5	227	96 (42%)
> 1	2470	2065 (84%)	> 5	177	133 (75%)

(mean 623 mm) measured in Zingst from 1910 to 2017 (Source: German Meteorological Service—DWD, values edited to annual sums, no values in Feb. 1945–Dec. 1946, Dec. 1998). Years with average precipitation were defined as 45–55% percentile around the long-term median (> 100 years, [28]). Years with particularly high precipitation had either above-average precipitation every month (see Fig. 2a; 1998, 2001, 2002) or only 2- to 3 months with twice as much precipitation as the usual average (2007, 2010, 2011, 2017). Contrary, dry years had more months with below-average precipitation (up to 9 months). April was the month with the lowest precipitation (on median), and the highest monthly precipitation rates were recorded in August and October (on median, Fig. 2b).

Calculation of annual PO_4-P-depositional rates

Over the 23 years between 1995 and 2017, 2235 individual PO_4-P concentrations from rain events were measured (Fig. 3a), which covered 26% of all days during this period. The overall median phosphate concentration in rain water was 0.53 µmol l^{-1}, which was used for all rain samples where PO_4-P determination failed. Around 6% of all samples did not contain PO_4-P, i.e. were below determination limit (< 0.05 µmol l^{-1}). About 73% of the samples contained PO_4-P concentrations of up to 1 µmol l^{-1} (31 µg PO_4-P l^{-1}). Higher PO_4-P concentrations of 1–5 µmol l^{-1} occurred in further 13% of all samples. Very high PO_4-P amounts of > 10 µmol l^{-1} were recorded in only 2% of the precipitation samples (Fig. 3a). Three of these high-concentration samples were found after larger precipitation events (> 5 mm). The contribution of samples with PO_4-P concentration > 10 µmol l^{-1} elevated the daily median PO_4-P-depositional rate by 14%. These values remained in the present study, since the occurrence of such events was so low. Moreover, the high daily PO_4-P-depositional rates mostly originated from intensive rain events, which included also the period of dry deposition, i.e. before precipitation. Usually such samples are excluded and attributed to bird droppings, which increase the concentrations dramatically (see "Discussion"). However, the vessels were checked and cleaned daily.

The overall median of PO_4-P deposition amounted to 16.6 kg PO_4-P km^{-2} a^{-1}, if only measured events were considered (see Fig. 4a). Small precipitation events and the preceding dry deposition, for which a concentration estimate was missing, could nevertheless be calculated and the resulting values were included into the annual sum (see description in "Materials and methods", and Table 2). Interestingly, there was a tendency of lower deposition maxima in average years compared to wet and dry years (Table 2). Overall, there was an almost equal distribution pattern for PO_4-P across all months between 0.7 and 1.5 mg PO_4-P m^{-2} $month^{-1}$ (see Fig. 4b).

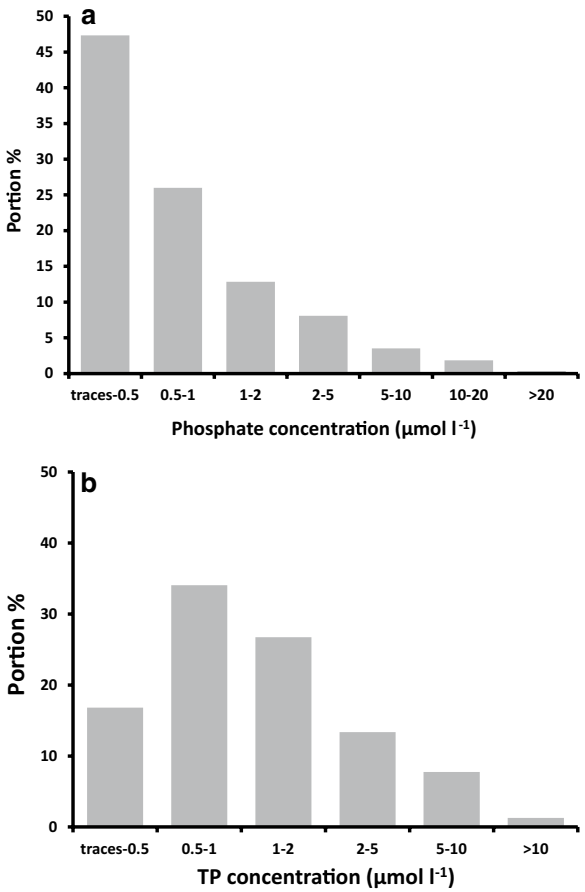

Fig. 3 **a** Phosphate concentrations (µmol l^{-1}) in daily rain water samples between 1995 and 2017 in Zingst. n = 2212. Traces are concentrations below the LOQ = 0.05 µmol l^{-1}. **b** Total phosphorus concentrations (µmol l^{-1}) in daily rain water samples from November 2013 to December 2017 in Zingst. n = 232. Traces are concentrations below the LOQ = 0.22 µmol l^{-1}

Annual PO_4-P deposition did not correlate with annual precipitation (see Additional file 1: Figure S1, Additional file 2: Figure S2). This was unexpected, since bulk deposition was estimated from rain events and the preceding dry deposition.

Calculation of annual TP-depositional rates

The overall median concentration was 0.98 µmol l^{-1} (Fig. 3b), which was almost twice as high compared to the soluble phosphate median value of 0.53 µmol l^{-1}. Traces of TP and concentrations below 0.5 µmol l^{-1} were found in only 17% of all samples (Fig. 3b). Most samples (82%) had TP contents of 1–10 µmol l^{-1}. Higher TP concentrations were rare with only 1% of all samples > 10 µmol l^{-1}, but values > 20 µmol l^{-1} were only observed once.

TP deposition over the years 2013–2017 amounted to 16.7–75.7 kg km^{-2} a^{-1} (Table 3), depending on how to

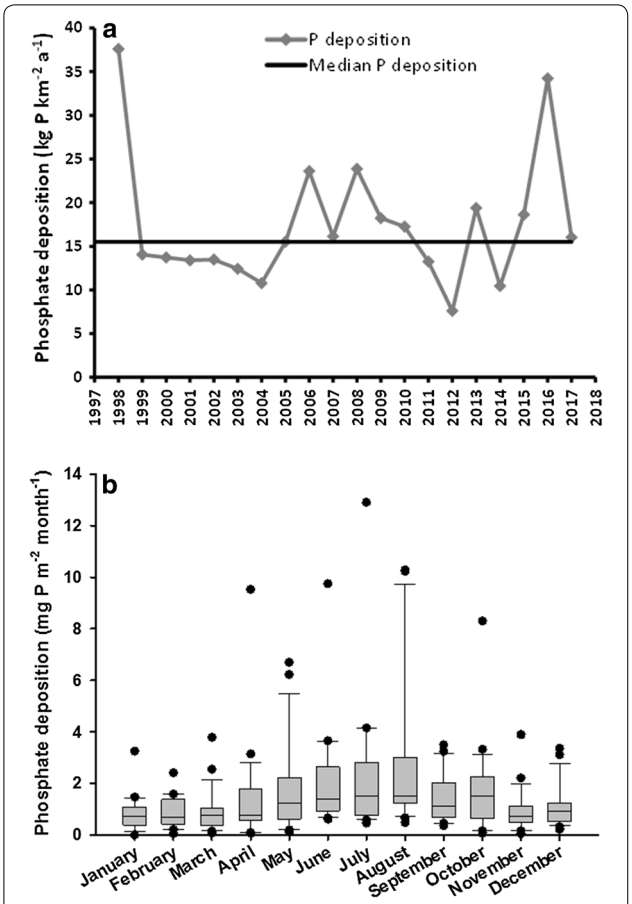

Fig. 4 **a** Annual deposition of phosphate (1998–2017, PO_4-P in kg km^{-2}) and **b** monthly deposition as Whisker–Boxplot (PO_4-P in mg m^{-2}) in rain water (1995 to 2017, if available) at Zingst

compensate for missing TP measurements in our calculations. There were a total of 950 rain events, of which 379 samples could be measured for PO_4-P including 232 samples for TP between autumn 2013 and the end of 2017. Therefore, several mathematical procedures were compared to determine an optimal approximation for missing values. First, it has to be considered that the median share of PO_4-P: TP was 29% (Fig. 5). Only 6% of the samples consisted mainly of PO_4-P (80–100%, Fig. 5b). Contrary, the long-term median of PO_4-P was half the long-term TP median (0.53: 0.98 µmol l^{-1}). This difference is caused by discrepancies between monthly PO_4-P- and TP-depositional rates. The TP concentrations in June, July and August were at least twice the long-term TP median, at only slightly higher PO_4-P concentrations (see Figs. 4b, 6a). These months had also the highest precipitation rates compared to the remaining year (see Fig. 2b, 1995–2017, median). Single individual TP peaks with TP concentrations above 10 µmol l^{-1} were only detected three times (2× in 2016, 1× in 2017). Removing these values as possible contamination altered the annual TP sum between 8 and 20% for 2016, and between 4 and 6% for 2017, depending on the mode of calculation.

Considering only a median TP values for all 950 rain events led to lower calculated depositional rates, as, e.g. PO_4-P deposition alone (see Table 3). Furthermore, the TP-depositional rate was still lower, when median TP values were used for missing values and summed up measured TP values.

The sum of measured TP values plus the use of a monthly median PO_4-P: TP proportion (calculation mode c, Fig. 6b) resulted in TP-depositional rates, which were always higher than PO_4-P-depositional rates. Furthermore, TP deposition during summer months (June–August) contributed between 30 and 75% of the annual deposition depending on mode of calculation. Therefore, calculation mode c) was used in further budget calculations as mode (a) and (b) showed lower annual TP deposition than the annual PO_4-P deposition.

Discussion

Technical considerations

This study did not distinguish between dry and wet deposition, as our rain sampler was always open to the atmosphere. Consequently, PO_4-P deposition and TP deposition were a bulk deposition. The majority of datasets in the review of Tipping et al. [11] are separated in either wet and dry collections, or bulk deposition. Further, the authors stated that wet and dry samples can be pooled to calculate a TP deposition.

Table 2 Annual phosphate deposition from 1998 to 2017 (kg P km^{-2} a^{-1}) estimated (a) as the sum of direct measurements, (b) sum of measured values plus 0.53 µmol P l^{-1} as median for all rain samples, where values are missing and (c) all rain samples with median concentration of 0.53 µmol P l^{-1}

Mode of calculation	Wet years	Average years	Dry years
(a) Sum of all measured values	13–38	10–24	8–34
(b) Sum of measured plus median values	14–39	12–25	13–34
(c) All rain samples with median concentrations	11–16	9–10	9

Years of 1995–1997, where precipitation sums were not measured with rain sampling, were omitted for (a). Average precipitation years were within a ± 10% range of median annual sum

Table 3 Annual TP deposition (kg P km^{-2} a^{-1}) over the years of 2013–2017 estimated (a) as the sum of direct measurements and median concentrations for missing values, (b) as the sum with 0.98 µmol P l^{-1} as median for all rain samples, (c) as the sum of direct measurements and the ratio of PO_4-P:TP as monthly median for missing values and compared with PO_4-P deposition

	2013	2014	2015	2016	2017
PO_4-P deposition (kg km^{-2} a^{-1})	20.3	11.7	19.2	34.9	16.7
Mode of calculation					
(a) Sum of measured TP plus median (annual) TP concentrations	19.1	23.5	23.7	28.6	27.7
(b) All rain samples with median (annual) TP concentrations	18.8	18.5	20.2	16.7	22.6
(c) Sum of measured TP plus PO_4-P:TP portion (monthly median)	27.0	38.9	69.9	75.7	47.9

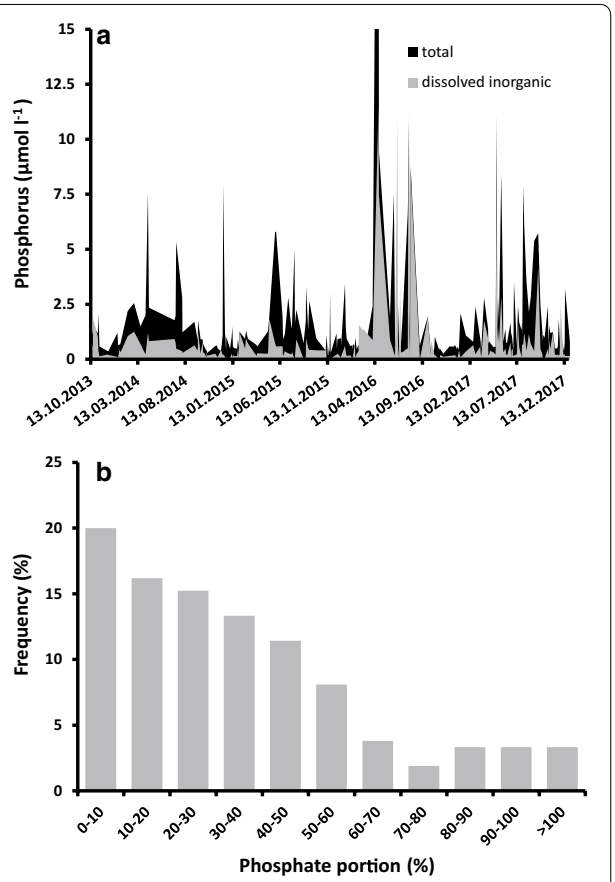

Fig. 5 **a** Total phosphorus and dissolved inorganic phosphorus concentrations (µmol l^{-1}) in rain water between 2013 and 2017 at Zingst. **b** Histogram of simultaneously measured phosphate (µmol l^{-1}) on total phosphorus (µmol l^{-1}) proportions for the same period (n = 210). The *y*-axis was kept at 15 µmol P l^{-1}, as only one TP value was higher (25.04.2016, 39.6 µmol l^{-1})

Only 3% of the PO_4-P analyses were above the determined TP concentration, indicating an overall stable analysis. This result clearly indicates the relevance of TP estimates for a comprehensive P analysis. The ratio of PO_4-P to TP might serve as a moderate way to extrapolate TP deposition into the past, assuming similar dry P-depositional rates.

One major consideration was the possible contamination with bird faeces and insects. Such contaminations can have a high impact on the following P analyses and were also described as possible contamination factor by, e.g. [29]. It cannot be ruled out that some samples were contaminated, which may explain few analyses with extraordinary high P values (see Fig. 4a) or a biased PO_4-P:TP ratio (Fig. 4b). Pollman et al. [30] found out that replicate precision above P concentrations of 2.6 µmol l^{-1} (0.08 mg l^{-1}) was poor. They concluded that P concentrations above this level may be contaminated. TP concentrations were in 16% and PO_4-P in 10% of all cases above this concentration in the current study. On the other side, Tipping et al. [11] stated that simultaneously high NH_4 and K values may indicate a possible contamination. Only 29 of 2235 PO_4-P values with a concentration higher 10 µmol l^{-1} had simultaneously higher NH_4 and NO_3 values (above median of 9 and 36 µmol l^{-1}, respectively, data unpublished). The exclusion of these values would lower the median PO_4-P-depositional rate by 4%, or as stated earlier by 14% if all values above 10 µmol PO_4-P l^{-1} were excluded. However, we cannot conclude further on that topic as true replicates are missing and high concentrations were always repeated upon measurement, i.e. the results were double checked. Future studies should focus on true replicates with a dense sampling grid [31], or analysing isotopic composition to determine origin of P [32].

Nonetheless, the daily check and sampling probably prevented these systematic errors to some extent. Bacterial uptake of PO_4 may be low, but was also described in the review of Newman [10]. Otherwise, a possible bacterial contamination can either reduce PO_4-P by uptake, or liberate PO_4-P by organic matter decomposition. Nonetheless, TP concentrations would be stable within the sampling vessel. A cooling device within a rain sampler would reduce this effect by lowering the bacterial metabolism.

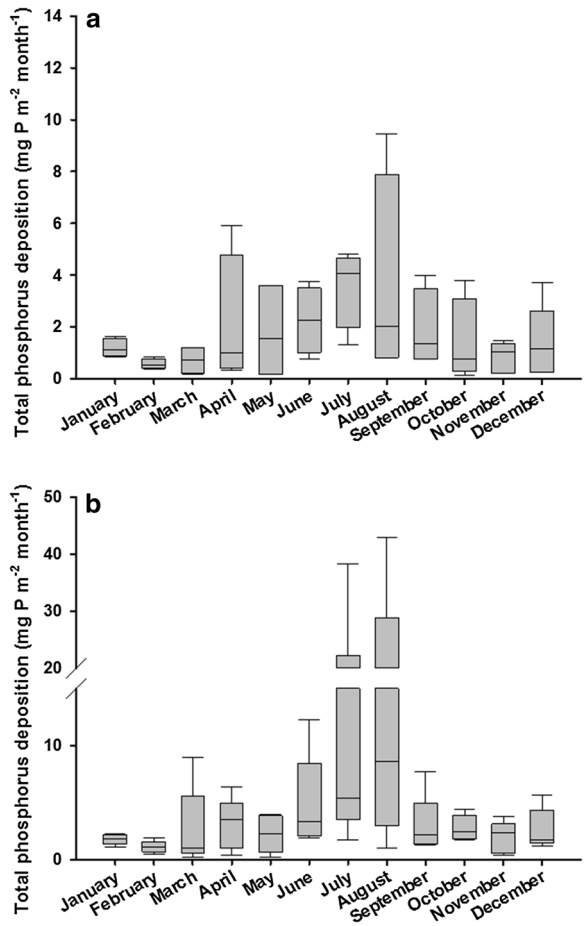

Fig. 6 **a** Deposition of measured total phosphorus (TP in mg m^{-2}) and **b** measured plus calculated TP (in mg m^{-2}) in rain water from 2013 to 2017 at Zingst. Please note the different scaling between **a** and **b** as well as the axis break at **b**. Values for **b** were calculated as the sum of direct measurements and the ratio of PO_4-P:TP as monthly median for missing values

Therefore, a TP determination shall always be considered, even though it does often not represent the readily bioavailable P form. On the other hand, over the course of the seasons organic particles such as pollen are temporarily important as easily biodegradable and hence bioavailable TP source. TP measurements were only possible in precipitation samples > 2 mm per day to get a sufficient volume for the chemical extraction and analysis. Pooling samples is also problematic, since such samples are hard to follow back to the rain events and the preceding weather conditions. Furthermore, bacteria in the rain water samples, and bacterio- and phytoplankton in aquatic systems can produce enzymes (phosphatases) to access bound P forms. It seems unreasonable to focus only on directly bio-available PO_4 forms, as dry deposited P can also be used by terrestrial and aquatic microorganisms.

One major bias with this bulk sampling regime may depend on weather conditions, where a long dry deposition period is followed by so little rain, that the sample could not be measured. This may lead to an underestimation of annual bulk deposition, as the rain gauge was cleaned after each rain event. It remains questionable, if such events should rather be pooled, because our data suggest that some dry deposition events can have considerable amounts of TP.

Depositional rates around the Baltic Sea and worldwide

Dry deposition depends on the surrounding land and may be more important in areas with steady dust deposition, e.g. Sahara dust in the Mediterranean or the Atlantic Ocean. However, burning fossil fuels can also be an important source for atmospheric dry deposition [10]. Behrendt et al. [33] described a drop of dust emissions by 90% from 1985 to 1995 in the eastern part of Germany, where the current research area is located. The authors explained that drop by a reduced industrial and agricultural production, which would subsequently lead to lowered dry depositional rates of P. It is therefore very important to consider the adjacent land use and possible changes over time. However, a trend was not found in the current dataset indicating overall stable conditions.

A difference of P deposition depending on surrounding landscapes was described in another long-term dataset (central part of Lithuania, 1988–1999 site 1, and 1996–2007 site 2, [34]). Highest depositions were found during the 1980s and in agricultural areas. The impact of surrounding land use was also described by several other authors and can be an explanation for the wide range of depositional rates throughout literature. For example, [35] described for a shallow lake in Estonia PO_4-P-depositional rates of around 14.6 kg P km^{-2} a^{-1}. Lower rates were found along the Swedish coastline, where PO_4-P rates ranged from 2.0 to 12.7 kg P km^{-2} a^{-1} and TP depositions of 2.8–15.8 kg P km^{-2} a^{-1} [12]. Those authors found PO_4-P:TP ratios of around 80% contrary to the monthly medians of 25–48% found in this study. One explanation may be the position of sampling points, because our study was conducted within an agricultural catchment, whereas [12] also sampled on islands within the Baltic Sea. Up to 90% of the dry deposition can come from anthropogenic land-based source emissions [36]. Furthermore, it was described that dry deposition can make up a share of 50% of PO_4-P deposition for rural coastal sites in a long-term dataset (Turkey, 1999–2007, [37]). Median deposition fluxes of 13.0 kg PO_4-P km^{-2} a^{-1} and 22.0 kg TP km^{-2} a^{-1} were described for Europe in a review [11]. The PO_4-P median is comparable with our study (16.6 kg PO_4-P km^{-2} a^{-1}), but the described TP median is only 46% of the one in this study. Another

review described that the majority of TP depositions (80%) ranged from 0 to 50 kg TP km^{-2} a^{-1} [10]. The calculated and measured TP values found in this study are within this range. Furthermore, the results of all these studies indicate that the position and surrounding land can have a high impact on bulk depositions. Only the two years 1998 and 2016 showed very high depositional rates for PO_4-P. However, only 1998 was a very humid year (up to 800 mm), and subsequently a high P deposition. The year 2016 was actually dry (550 mm), but with very high depositional rates during July and August It is possible that during 2016 dry deposition was the dominant source for P in our bulk analyses. This result may explain the higher maximum found for either dry or humid years (see Table 3).

Therefore, it is important to consider the origin of rain events, as precipitation rates depend on wind trajectories, i.e. precipitation events coming from the open sea have less P bound, than those from the surrounding land. The most frequent wind direction in our sampling area is west-northwest [23], i.e. the most dry deposition should come from less agricultural used land (Fig. 1). However, there is no information about wind trajectories. Therefore, it cannot be ruled out that our sampling station was influenced by agricultural used land in the south. Nonetheless, our results can be considered as one important and representative source of P for the surrounding coastal waterbodies. The adjacent lagoon system may be influenced over-proportionally by wet P deposition.

Impact onto a coastal lagoon

The Darß-Zingst Bodden chain has only a small connection to the open Baltic and water exchange is mainly driven by wind speed and direction. The TP concentrations within the lagoon systems are mostly stable throughout the year and show no seasonality. We therefore calculated a possible total deposition of PO_4-P and TP in this lagoon system, and compared it to published P stocks within the system (Table 4). State monitoring analysed that 20 t TP are transported per year through point sources (rivers) into the lagoon system [38]. Bulk deposition of TP was of similar size with up to 15 t a^{-1}, depending on the year. This deposition seems to be of considerable size, even if not all of the deposited P is accessible to plankton. The importance of PO_4-P deposition increased in lagoon parts towards the Baltic Sea opening, as TP stocks, and riverine inflow are lower. The acceptable P load per area in a shallow water body like this lagoon is stated to be around 7 kg P km^{-2} to avoid eutrophication [39]. This load is in some years reached considering only PO_4-P depositions (e.g. 2016).

Furthermore, precipitation promotes runoff from land [40] and can contribute along the complete coastline as diffuse nutrient input. There are currently no reliable data on the magnitude of such events. Nonetheless, phytoplankton was described to grow all year round along the land–water contact zone within this ecosystem [41].

Bulk deposition of P by dust and rain fertilizes phytoplankton in the euphotic and entire zone of a water body, in contrast to other patchy distributed P sources, like resuspension from sediment [42], or across the land–water transitional zone [41].

Conclusions

Anthropogenic nutrient inputs need to be reduced within the next few years to decrease human pressure on aquatic ecosystems. It is therefore necessary to evaluate and also re-evaluate known input variables into aquatic systems. P deposition by precipitation can be such an important variable and needs to be considered in management evaluation. A long-term monitoring dataset for bulk P deposition was analysed for monthly and yearly depositional rates at the southern Baltic Sea. The long-term data on precipitation and PO_4-P and, since 2013 also for total P deposition, clearly indicate a significant input of this nutrient from the atmosphere to terrestrial areas and inner coastal waters, but with strong quantitative and seasonal differences which might be partly explained by

Table 4 Comparison of P deposition by precipitation (2013–2017, t a^{-1}) with riverine inflow (1996–2000, t a^{-1}, [43]) and standing stocks of total phosphorus (TP, in t) within the water column of the lagoon system

Lagoon part	Flux PO_4-P deposition	Flux TP deposition	Flux riverine TP inflow	Stock TP lagoon
Total	2.3–6.9	5.3–14.9	13–24	35
Saaler Bodden	1–2.8	2.2–6.1	9.7–17.8	21.1
Bodstedter Bodden	0.3–0.8	0.7–1.8	na	5.1
Barther Bodden	0.2–0.7	0.5–1.5	2.7–9.5	2.6
Grabow	0.5–1.5	1.1–3.1	na	6.1

Precipitation and riverine values represent an annual flux into the system

The TP stock in the lagoon is an estimate out of long-term median within the water column and the size of the water body. Long-term median values of PO_4-P and TP standing stocks were derived from datasets of the State Agency for Nature, Conservation and Geology Mecklenburg–Vorpommern (LUNG, TP 2010–2017) and [44] (PO_4-P, 2000–2014)

specific meteorological conditions. The calculated depositional rates for PO_4-P are within described ranges for Europe, whereas the TP-depositional rates are twice that median. The comparison between other P fluxes into the Darß-Zingst Bodden chain showed that P deposition can contribute a considerable amount of PO_4-P and TP into the system's budget. The impact on such coastal waterbodies is even higher, as water exchange with the open Baltic Sea is low, and P is recycled very efficiently. The theoretical inflow by rivers and bulk P deposition already explained 85% of the P stock within the system. An ecosystem change cannot be expected, as long as these inputs are not reduced further. Erosion control for precipitation-mediated runoff and dust transport by wind need to be considered as management tools on a regional scale, as P-depositional rates differ between regions.

These findings indicate the following two major outcomes:

1. P inputs by bulk deposition are comparable with riverine inflow.
2. Bulk deposition has the potential to fertilize plankton in the photic zone during summer.

Additional files

Additional file 1: Figure S1. Dependence of phosphate (PO_4-P; in µmol l^{-1}) deposition on daily precipitation (in mm) (n = 2235).

Additional file 2: Figure S2. Dependence of total phosphorus (TP, in µmol l^{-1}) deposition on daily precipitation (in mm) (n = 232).

Abbreviations
TP: total phosphorus; PO_4-P: phosphate.

Authors' contributions
RW and VR planned and conducted the sampling and analyses. MB and RS performed the calculations. MB, RS and UK wrote the manuscript with extensive contributions of RW, VR and GN. All authors read and approved the final manuscript.

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Competing interests
The authors declare that they have no competing interests.

Availability of data and materials
The datasets used and analysed during the current study are available from the corresponding author on reasonable request and are currently prepared to be uploaded and made accessible on PANGEA.

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