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Contrasting distribution and speciation of sedimentary organic phosphorus among different basins of the Baltic Sea

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Abstract

Recycling of phosphorus (P) from deoxygenated sediments perpetuates eutrophic conditions in parts of the Baltic Sea. Sedimentary organic P is a major source of dissolved P to the water column, but also a sink for permanent P burial. The mechanisms behind these two pathways are, however, largely unknown. Using new methods, we determined P in DNA and phospholipids, which are both found in all organisms. We also identified inositol phosphates that are particularly important in eukaryotes. Sediment cores were collected from contrasting basins in the Baltic Sea to study their relative contribution to the total P pool. We found high DNA-P/phospholipid-P ratios in surface sediments from the Bothnian Bay and Bothnian Sea. However, these ratios were low throughout profiles in euxinic Baltic Proper sediments. The elevated ratios present in sediments overlain by oxic bottom waters might indicate the presence of a microbial community stimulated by bioturbation, whereas the low DNA-P/phospholipid-P ratios in Baltic Proper sediments likely indicate an energy-limited microbial community, typical to the "deep biosphere" environment. Inositol-P was almost absent in euxinic Baltic Proper sediments that had a low total P amount compared to those in the other basins. We suggest that variability in the composition of sedimentary microbial communities among the Baltic Sea basins might cause differences in organic P forms that in turn affects its turnover.

During the 20th century, the Baltic Sea became eutrophic in response to massive anthropogenic phosphorus (P) and nitrogen (N) loading that peaked in the 1980s (Gustafsson et al. 2012; Carstensen et al. 2014). Since then, external P loading has been reduced by more than half, and now corresponds to the loads in the 1950s. However, in present day, pronounced eutrophication effects are still evident, including widespread cyanobacterial blooms in summer and a record extent of oxygen (O_2) depleted bottom water areas (i.e., deoxygenation) due to elevated organic matter loading and subsequent mineralization (Savchuk et al. 2008). Hence, the internal P recycling rate, both within the water body and between the sediment and water column, is currently several times greater than the external input (Gustafsson et al. 2012). Deoxygenation can lead to development of "dead zones" characterized by mass mortality of marine life due to lack of O_2 or release of toxic hydrogen sulfide (ΣH_2S) from sediments to the overlying water (Diaz and Rosenberg 2008). Commonly used thresholds (e.g., Breitburg et al. 2018; Algeo and Li 2020) to delineate the degree of deoxygenation are; hypoxia

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($O_2 \leq 63\ \mu mol\ L^{-1}$), anoxia ($O_2 \cong 0\ \mu mol\ L^{-1}$; $\Sigma H_2S = 0\ \mu mol\ L^{-1}$), and euxinia ($\Sigma H_2S > 0\ \mu mol\ L^{-1}$).

Mineralization of organic matter containing organic P forms (org-P) is a primary source of dissolved P in Baltic Sea sediments (Jilbert et al. 2011). During anaerobic degradation, dissolved P release may be enhanced relative to carbon and nitrogen release, due to preferential org-P mineralization (Ingall et al. 1993; Mort et al. 2010). Typically, declining org-P contents with depth in Baltic Sea sediments indicate mineralization of org-P in areas where sediment accumulates, either in coastal zones (Lukkari et al. 2009; Rydin et al. 2011; van Helmond et al. 2020) or offshore (Mort et al. 2010; Malmaeus and Karlsson 2012). In sediments overlain by oxic bottom water, dissolved phosphate can be temporarily trapped by iron (Fe) and manganese (Mn) (oxy)(hydr)oxides (Conley et al. 2002), scavenged by calcium-rich Mn carbonates (Mort et al. 2010), precipitated as Mn(II) phosphates (Hermans et al. 2019, 2021), or stored as polyphosphate (poly-P) in prokaryotic organisms (Hupfer et al. 1995). Deoxygenation, in turn, can mobilize stored phosphate due to reductive dissolution of P bearing Fe and Mn (oxy)(hydr)oxides (Jilbert et al. 2011) and preferential degradation of poly-P (Brock and Schulz-Vogt 2011; Jones et al. 2016), and can then be recycled to the bottom water. This process terminates quickly and cannot be sustained without the presence of poly-P or P bearing Fe and Mn minerals to perpetuate benthic P release (Jones et al. 2016; Jilbert et al. 2021).

Although anaerobic mineralization of org-P continuously sustains sediment pore water with dissolved P that support P release to the water column, a significant proportion of the org-P present in the surface sediment resists degradation and therefore becomes a major sink for permanent P burial (Mort et al. 2010; Hermans et al. 2021). Various forms of org-P differ in resistance to degradation during sediment diagenesis (Ahlgren et al. 2006), depending on organic matter supply and its composition, and bottom water O_2 conditions (Defforey and Paytan 2018). These factors are known to drive changes in the microbial community structure (Hoshino et al. 2020).

To determine the source and fate of the org-P forms found in the surface sediment, its dominant forms should be identified (Defforey and Paytan 2018). Here, we use recently developed methods to identify and quantify P bound as diesters in DNA, phospholipids (lipid-P), and monoester inositol phosphate (inositol-P), as these are the quantitatively most important org-P forms in Baltic Sea sediments (Ahlgren et al. 2006). DNA-P and lipid-P are found in all organisms, with lipid-P being an essential part of cell membranes. Some sulfur oxidizing bacteria in the Baltic Sea, such as the *Sulfurimonas* GD17 subgroup and *Beggiatoaceae* are capable of accumulating high amounts of polyphosphates and store it within their lipid-P membranes (Brock et al. 2012; Möller et al. 2019). Inositol-P is another P-containing compound found in animal and plant cells (Irvine and Schell 2001), and in some prokaryotic organisms (Roberts 2006).

Major environmental factors, such as salinity, trophic status, and bottom water O_2 conditions differ with time and among the major basins in the Baltic Sea; the Bothnian Bay, Bothnian Sea, and Baltic Proper. Differences in the characteristics of these basins' catchment areas likely also influence the origin and composition of organic matter deposited to the seabed.

Unraveling how sedimentary org-P retention is regulated is crucial to better understand eutrophication of the Baltic Sea. By comparing the distribution and speciation of org-P in sediments from different parts of the Baltic Sea and over time, we aim at describing their distribution and identifying the mechanisms regulating their presence in the sediment.

Materials and methods

Study areas (catchment and basin characteristics)

Sediment cores were collected from three major Baltic Sea basins; the Bothnian Bay, Bothnian Sea, and Baltic Proper. In addition, sediment cores from the well-investigated Björnöfjärden (Rydin et al. 2017; Rydin and Kumblad 2019), a small, enclosed bay in the Stockholm Archipelago (Baltic Proper), and the large Lake Mälaren that drains into the Baltic Proper through the city of Stockholm, were also examined (Fig. 1). Characteristics between these basins differ substantially, in terms of, for example, surface area, depth, salinity, trophic status, organic matter deposition, and degree of deoxygenation (Table S1).

Stratification in the Baltic Proper is caused by saline North Sea water inflows and freshwater inputs from major rivers. Vertical mixing between oxygenated surface water and deep water in the Baltic Proper is constrained by a permanent halocline at ~ 60–80 m water depth (Stigebrandt 1987). Therefore, the main O_2 supply to the deeper parts depends on saline seawater inflows through the shallow straits that connect the Baltic Sea with the North Sea. Such events are coined Major Baltic Inflows. Significant saltwater intrusions (Mohrholz et al. 2015) may occur irregularly and temporally oxygenate larger areas in the deepest parts of the sea. The extent of deoxygenation in the Baltic Proper has been high since regular measurements started around 1960 (Almroth-Rosell et al. 2021). The sampling locations in northwestern Baltic Proper are characterized by prominent anoxic/euxinic bottom water conditions (Fig. S1) and sulfidic sediments (Mort et al. 2010). Björnöfjärden, in the coastal zone, has a history of eutrophication as reflected by relatively high total phosphorus (TP) concentrations in the water column primarily due to internal P loading, and is further characterized by seasonal bottom water euxinia (Rydin et al. 2017).

The Gulf of Bothnia, which includes both the Bothnian Sea and Bothnian Bay, is a low saline, oligotrophic, lacustrine environment with low sulfate and ΣH_2S concentrations in its sediments (Egger et al. 2015), where bacterial Fe cycling is the key process (e.g., Reyes et al. 2016) rather than sulfate

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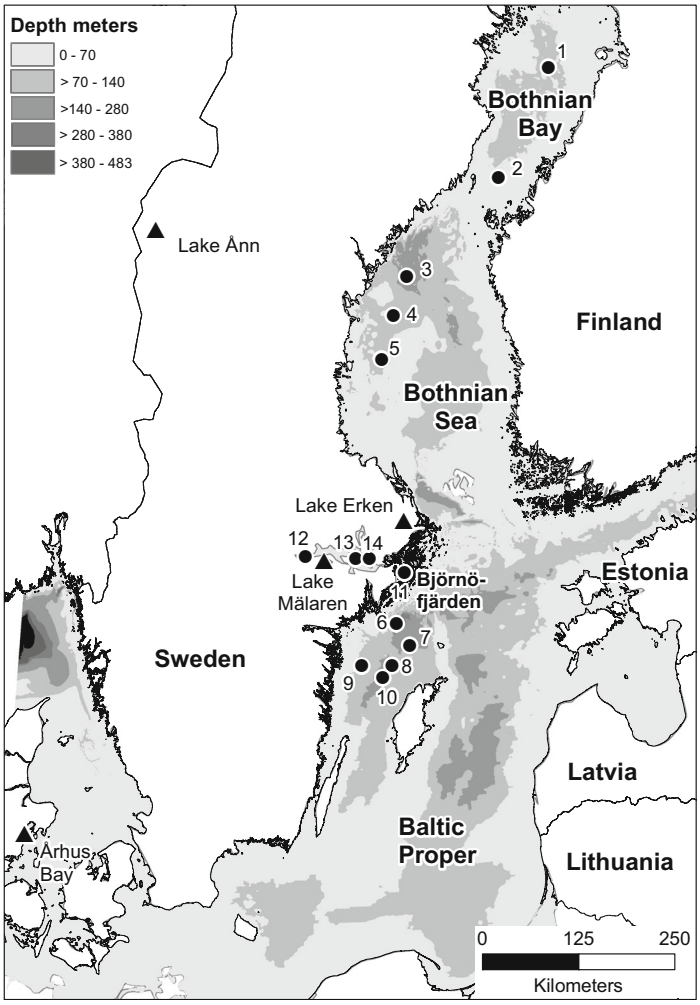

Fig. 1. Bathymetric map of the Baltic Sea. Filled circles represent sediment core sampling sites, and numbers identify the individual cores. Also indicated are Århus Bay, Lake Erken, and Lake Ånn.

reduction. Stratification between surface and deep water is significantly less pronounced compared to the Baltic proper, and O_2 concentrations have been relatively stable over time; above 5 mL L^{-1} (Fig. S1). Surface sediments are generally well-oxidized (Algesten et al. 2006; Malmaeus and Karlsson 2012). Population density in its catchment is low. Rivers entering the Gulf of Bothnia drains a catchment area dominated by boreal forests and marshlands.

Lake Mälaren, the third largest lake of Sweden, is a eutrophic clay-plain boreal freshwater lake. Its catchment area is dominated by forest land, but relatively large areas are used for farming. Population density in its catchment is high, but nutrient loading to the lake has decreased considerably, mainly due to improved wastewater treatment. However, P concentrations in the water column remain high. The O_2 supply from circulation during spring and fall is sufficient to maintain oxic bottom water conditions throughout the year (Fig. S1). Therefore, the sediment surfaces are oxidized except in topographically isolated deep areas. For catchment and morphometric characteristics, O_2 conditions, and water column TP concentrations, *see* Table S1.

Sampling of sediment cores

The sediment cores analyzed in this study were collected using a GEMAX twin-corer during different sampling campaigns. Two cores were taken in the Bothnian Bay, three in the Bothnian Sea, five in the Baltic Proper, and three in Lake Mälaren; all between 2001 and 2006 (except one in 1996) by the Geological Survey of Sweden (SGU; Table S2). One of the five cores from the Baltic Proper was collected from the deepest part of the Baltic Sea, the Landsort Deep. Sediment samples were stored freeze-dried at the SGU sediment archive until further analysis. No water or organic content data are available for these samples. For 8 of the 10 cores from the Baltic Sea, the ^{137}Cs activity peak, representing the Chernobyl accident in 1986, is available, which is located between 3 and 12 cm below the sediment surface (Tables S2, S3). Thus, the different sampling campaigns, as well as different sedimentation rates, make the analyzed sediment layers (0–1 if available, 1–2, 4–5, 9–10, and 19–20 cm) not age compatible.

The Björnöfjärden sediment was retrieved during ice cover in March 2012 using a crust-freeze sampler. The sampler collects a frozen undisturbed sediment core that enabled dating by detailed stratigraphic analysis, so-called varve-counting, representing yearly deposition of matter (Renberg 1981; Renberg and Hansson 2010). The 63-cm long sediment core corresponded to a time record from ~ 1750 to 2010, that is, including pre-eutrophication and eutrophic periods. Sediment from the same core was used for P analyses.

Methods

DNA-P was extracted using extraction buffers containing sodium chloride, ethylenediaminetetraacetic acid (EDTA), Tris–HCl, glass beads, lysozyme, proteinase K, and sodium dodecyl sulfate. Following purification, DNA-P was separated by ultrafiltration. Lipid-P was extracted with a single-phase mixture of chloroform, methanol, and a citrate buffer (pH 4.0). For both methods phosphate was released by potassium persulfate digestion. Then, P concentrations were determined spectrophotometrically (Murphy and Riley 1962). This method has a detection limit of about 3 ng P mL^{-1} with a precision below 10% RSD (Paraskova et al. 2013). The inositol-P identification, consisting of tri- to hexainositols (I-P3, I-P4, I-P5, and I-P6), includes a single extraction step using 0.25 mol L^{-1} NaOH containing 0.050 mol L^{-1} EDTA, shaking, and centrifugation at 10,000 rpm before being placed in an LC autosampler for analysis. Separation was achieved with an ammonium carbonate gradient compatible with electrospray ionization tandem mass spectrometric detection (LC-ESI-MS/MS). An extraction efficiency of about 95% was obtained and the detection limit was between 37–99 ng P g^{-1} sample DW for the different I-P_n with a relative standard deviation generally

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below 10% (Paraskova et al. 2015; Sjöberg et al. 2016). TP contents in the sediments were analyzed as molybdate reactive phosphate (Murphy and Riley 1962) after ignition and acid hydrolysis (Andersen 1976).

Statistics

In the statistical evaluation, the cores from the Bothnian Bay and Bothnian Sea were combined and considered as one location representing the Gulf of Bothnia. These cores were compared to the cores from the Baltic Proper. Regression analysis of the different variables within each basin was performed to investigate covariation. However, the single sediment profile from Björnöfjärden was not statistically analyzed.

Data were analyzed using linear regression models, including Bonferroni correction for multiple comparisons, to identify linear relationships between variables within each sampling site. Bonferroni correction of the significance level was applied, with $n = 18$ (number of pairwise variable combinations times the number of sampling sites). For correlations with TP, the investigated variable was subtracted from TP.

To determine differences between sampling sites, *t*-tests and analysis of variances (ANOVAs) with sediment depth as a blocking factor were used. To evaluate differences in variables between the Baltic Proper and the Gulf of Bothnia with *t*-tests, Bonferroni correction of the significance level was used, with $n = 7$ (n = the number of *t*-tests performed). The effective significance level was $\alpha = 0.05/7 = 0.007$.

Complimentary, to the *t*-test, the nonparametric Kruskal–Wallis test on ranks (with Bonferroni correction) was used to verify that the variability did not mask any differences. For the ANOVAs, the analysis was complemented with analysis of log-scaled data. Zero values were substituted with the lowest non-zero value of the variable in question. One outlier TP value (Core #8, 0–1 cm, 8093 μg P g DW^{-1}; Table S4) was omitted from the statistical analysis. Such a high surface content has been observed at sites where Fe–P temporarily accumulates under hypoxic conditions (Rydin et al. 2021).

Using depth as a blocking factor or not does not change the overall conclusions, nor does the log transformation of the data.

Results

Decline in org-P content with sediment depth

The overall pattern shows a decline with sediment depth below 2 cm in all analyzed org-P forms and TP (Fig. 2). An

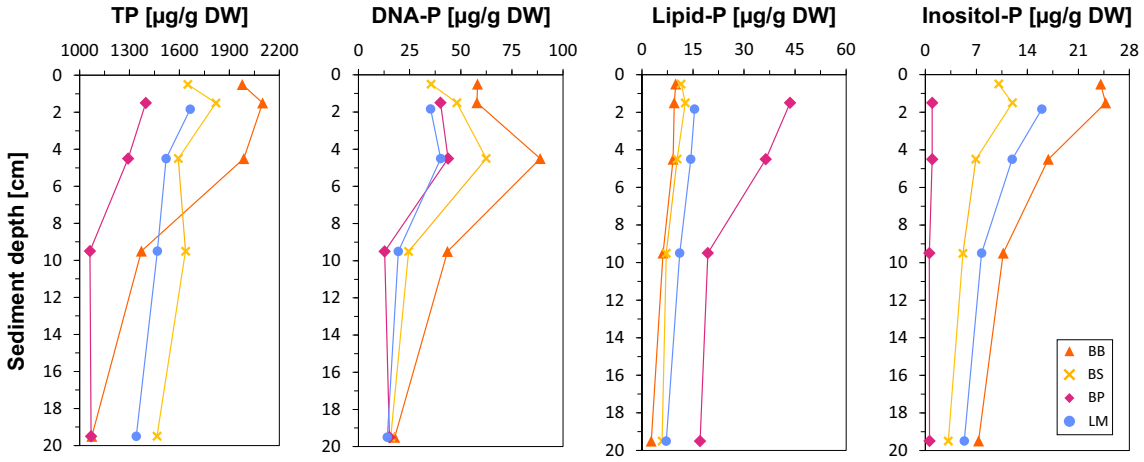

Fig. 2. Average content (μg P g DW^{-1}) of TP and organic P-forms (DNA-P, lipid-P, and inositol-P) in the upper 20 cm of sediment in the Bothnian Bay (BB, $n = 2$), Bothnian Sea (BS, $n = 3$), Baltic Proper (BP, $n = 5$), and Lake Mälaren (LM, $n = 3$).

Table 1. *p* Values for differences between sedimentary P contents in the Baltic Proper ($n = 5$) vs. the Bothnian Bay and Bothnian Sea ($n = 5$). Correlations with *p* values less than $0.05/7 = 0.007$ may be considered as significant according to the Bonferroni correction (bold *p* values).

Variable	Estimate	*p* Value	*p* Value (nonparametric)
DNA-P	−13	0.14	0.018
Inositol-P	−11	0.00000038	**0.0000000040**
Lipid-P	23	0.0000016	**0.00021**
TP	−460	0.00016	**0.00037**
Sum of DNA-P, lipid-P, inositol-P in % of TP	0.0058	0.34	0.69
DNA-P/lipid-P	−4.4	0.0000027	**0.0000000059**
Sum of DNA-P, lipid-P, inositol-P	−0.56	0.96	0.46

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exception to this, is that DNA-P has a pronounced subsurface peak at ~4.5 cm sediment depth before declining with depth (Fig. 2).

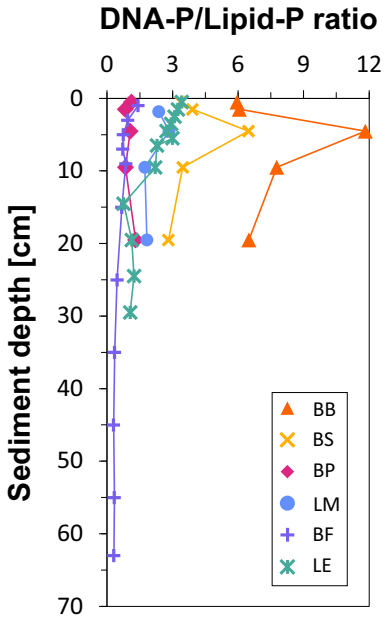

Fig. 3. Average ratio between the DNA-P and lipid-P contents in the upper 20 cm of sediment in the Bothnian Bay (BB, $n = 2$), Bothnian Sea (BS, $n = 3$), Baltic Proper (BP, $n = 5$), Lake Mälaren (LM, $n = 3$), and Björnöfjärden (BF, $n = 1$). This ratio in Lake Erken sediments is also indicated (calculated from Paraskova et al. 2014).

Site specific distribution of org-P

The distribution of DNA-P, lipid-P, and inositol-P varied between the different basins of the Baltic Sea. The Baltic Proper cores had almost no detectable inositol-P, but high lipid-P contents. The cores from the Gulf of Bothnia (i.e., both the Bothnian Bay and the Bothnian Sea), on the other hand, had relatively high inositol-P contents, but low lipid-P contents. There was no significant difference in DNA-P (Fig. 2; Table 1) between the two areas. Hence, the DNA-P/lipid-P ratio was lower in the Baltic Proper cores than in cores from the Bothnian Bay and Bothnian Sea (Fig. 3; Table 1). The difference in DNA-P and lipid-P content with depth in the Gulf of Bothnia resulted in a high DNA-P/lipid-P ratio that peaked at a sediment depth of ~4.5 cm (Fig. 3).

Org-P correlates with TP

The sum of analyzed org-P forms varied from 12 to 279 μg P g DW^{-1} (Fig. 4) and represents on average 5% (min 1%; max 22%) of the TP content (Table S4). In Baltic Proper sediments, TP, lipid-P, and DNA-P contents all correlated (hardly any inositol-P was found), whereas in the Bothnian Bay and Bothnian Sea sediments, the DNA-P contents only correlated to TP and inositol-P (Table 1). No correlations were found among these variables in sediments from Lake Mälaren. Although DNA-P represented only a small fraction of the TP content, these P pools correlated in the Baltic Sea cores (Table 2), especially in the Bothnian Bay, where the DNA-P constituted 7% of the TP contents above the intercept at 917 μg P g DW^{-1} using the equation in Fig. 5a. In the Baltic

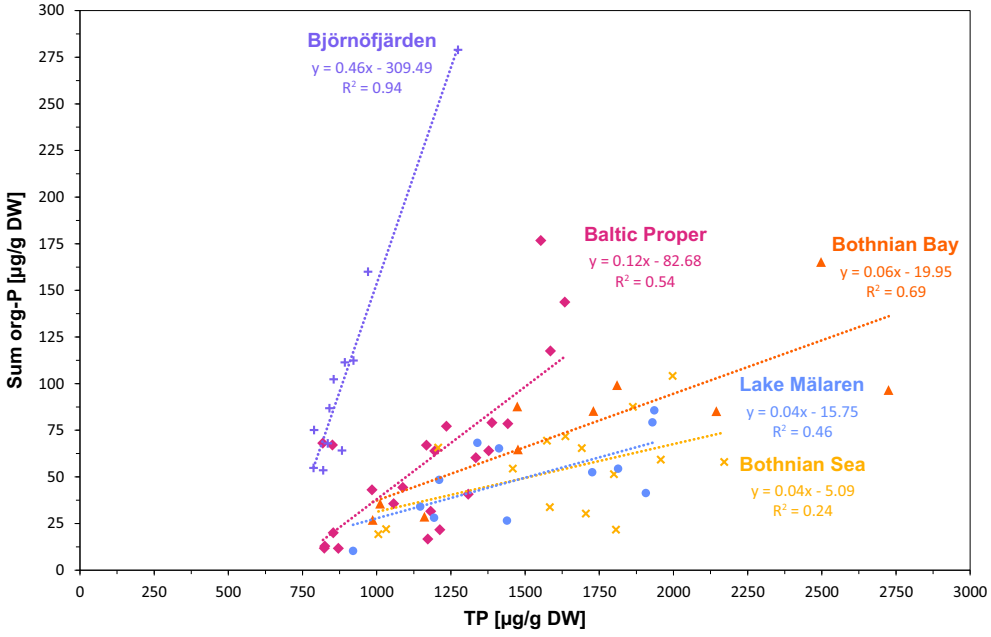

Fig. 4. Correlation between the contents (μg P g DW^{-1}) of extracted org-P (sum of DNA-P, lipid-P, and inositol-P) and TP in the Bothnian Bay, Bothnian Sea, Baltic Proper, Lake Mälaren, and Björnöfjärden.

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Table 2. *p* Values and correlation coefficients for the correlation between variables within the different sampling sites. Correlations with *p* values less than 0.05/18 = 0.0028 may be considered as significant according to the Bonferroni correction (bold *p* values).

Variable 1	Variable 2	Sampling site	*p* Value	Correlation, *r*
DNA-P	Inositol-P	Gulf of Bothnia	**0.0013**	0.6074
DNA-P	Inositol-P	Lake Mälaren	0.092	0.5325
DNA-P	Inositol-P	Baltic proper	**0.00011**	0.7306
DNA-P	Lipid-P	Gulf of Bothnia	0.24	0.2425
DNA-P	Lipid-P	Lake Mälaren	**0.0020**	0.8191
DNA-P	Lipid-P	Baltic proper	**0.00000022**	0.8643
DNA-P	TP-DNA-P	Gulf of Bothnia	**0.00029**	0.6650
DNA-P	TP-DNA-P	Lake Mälaren	0.098	0.5245
DNA-P	TP-DNA-P	Baltic proper	**0.00030**	0.7119
Inositol-P	Lipid-P	Gulf of Bothnia	0.27	0.2278
Inositol-P	Lipid-P	Lake Mälaren	0.45	0.2568
Inositol-P	Lipid-P	Baltic proper	**0.0064**	0.5627
Inositol-P	TP-inositol-P	Gulf of Bothnia	0.043	0.4080
Inositol-P	TP-inositol-P	Lake Mälaren	0.019	0.6896
Inositol-P	TP-inositol-P	Baltic proper	**0.0071**	0.5691
Lipid-P	TP-lipid-P	Gulf of Bothnia	0.14	0.3052
Lipid-P	TP-lipid-P	Lake Mälaren	0.35	0.3096
Lipid-P	TP-lipid-P	Baltic proper	**0.0000015**	0.8437

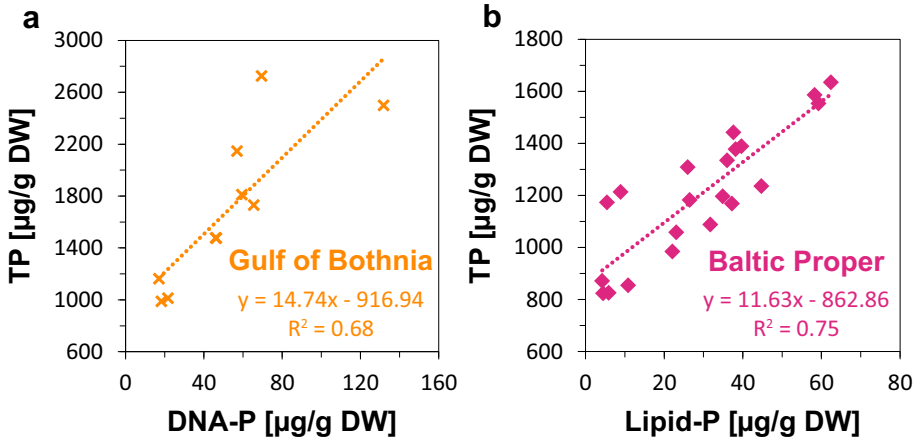

Fig. 5. Correlation between the contents (μg P g DW^{-1}) of TP and DNA-P in the (**a**) Gulf of Bothnia (left), and TP and lipid-P in the (**b**) Baltic Proper (right).

Proper cores, 8% of the TP contents above the intercept at 863 μg P g DW^{-1} was identified as lipid-P (Fig. 5b).

Different inositol-P forms decline with depth

Inositol-P, the sum of the inositol-P species I-P3, I-P4, I-P5, and I-P6, generally declined with sediment depth. The highest contents were found in the Bothnian Bay, in contrast to the Baltic Proper cores where inositol-P was almost absent (Fig. 2). The different forms of inositol-P in the Bothnian Bay cores all decline coherently with depth and their individual contribution was I-P3 < I-P4 < I-P5 < I-P6 (Fig. 6). This contrasts with the Björnöfjärden core, where the elevated inositol-P content in the uppermost sediment layers (Fig. 7) was entirely due to I-P5 (Table S4).

Björnöfjärden sediment age

The surface sediment (0–1 cm) of Björnöfjärden reflects the year before sampling (2011), and showed high contents of DNA-P, I-P5 and lipid-P. Sediment at 3-cm depth, deposited in c. 2008, had just over half (57%) of the content of these forms of org-P found in the surface layer (Fig. 7; Table S4). At 25 cm and below, in sediment deposited before 1970, the org-P content was only a quarter of that in the top layer. This decline with sediment depth was accompanied by a reduction in the

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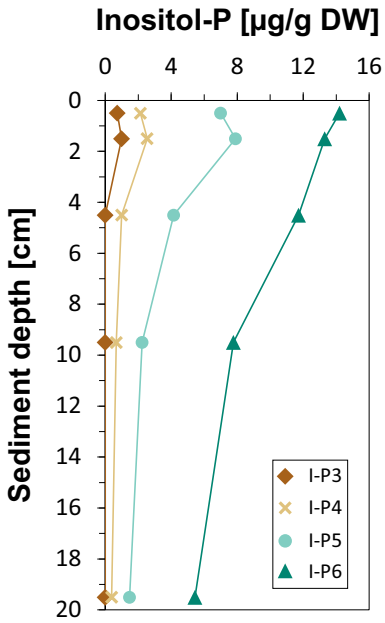

Fig. 6. Average content (μg P g DW^{-1}) of four different Inositol-P forms in the upper 20 cm of sediment in the Bothnian Bay ($n = 2$).

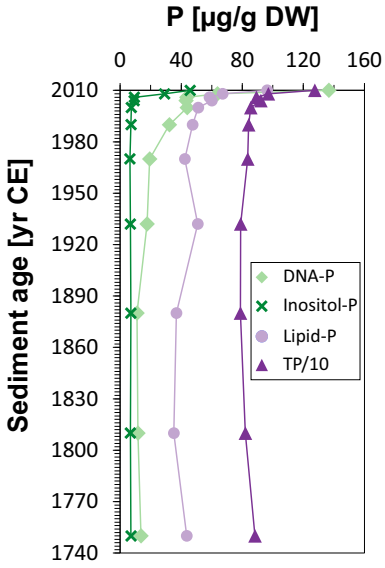

Fig. 7. Contents (μg P g DW^{-1}) of DNA-P, inositol-P, lipid-P, and TP in the upper 63 cm of sediment, representing ~ 250 years, in Björnöfjärden. Minor ticks represent 2-yr intervals.

TP content, about half (46%) of which was due to the decline of the identified org-P forms (equation in Fig. 4). The DNA-P content in layers older than 1970 was only about 10% of that in the surface layer. The lipid-P, on the other hand, declined less with sediment depth (Fig. 7).

The Björnöfjärden core allows an estimate of the contribution of the measured org-P forms to the "permanent" TP burial in sediment deposited 200–250 years ago of about 7%, with lipid-P contributing the most,5%.

Discussion

Mineralization of org-P is a primary source of dissolved P in the sediment (Jilbert et al. 2011). Hence, sedimentary org-P turnover is a central process regulating the trophic status of the Baltic Sea. Yet so far, the composition and origin of org-P in Baltic Sea sediments have rarely been identified with meaningful resolution. This is due to a lack of specific identification procedures, beyond what could be gained from the ^{31}P-NMR method (Carman et al. 2000; Ahlgren et al. 2006). In aquatic environments, most analyses of specific org-P compounds, such as lipid-P and DNA have so far been biomarker studies rather than investigations of the actual sedimentary org-P pool components (Ruttenberg 2014). Our study provides an increased resolution of the targeted org-P compounds and compares the org-P speciation in sediments from different parts of the Baltic Sea and a lake in its catchment.

Inositol-P is lacking in anoxic Baltic proper sediments

The results indicate that the refractory character of inositol-P in the aquatic environment as proposed by McKelvie (2007) and Turner and Weckström (2009), who found preservation of IP6 in anoxic sediment in a brackish bay in Helsinki, seems not to apply under our anoxic/euxinic conditions. This is in agreement with Suzumura and Kamatani (1995). While we cannot entirely rule out that the almost total absence of inositol-P in Baltic Proper surface sediments, reflects a lack of deposition rather than mineralization. However, this seems unlikely considering its presence in other basins of the Baltic Sea. The lack of inositol-P in the Baltic Proper is also in line with the sediment profile from Björnöfjärden, where the inositol-P is present for a few years in the surface layer, but near-absent when exposed to constant euxinic conditions. We suggest that the main reason for the absence of inositol-P in Baltic Proper sediments is that when they turn anoxic/euxinic, iron complexes reductively dissolve and expose the inositol-P to mineralization, for example, enzymatic hydrolysis (De Groot and Golterman 1993; Celi et al. 1999).

The inositol-P contents found in the Bothnian Sea top 20 cm sediments correspond to a P-storage of approximately 0.3 t P km^{-2}, calculated using typical dry matter content (Table S5). If the sediments in the Baltic Proper would have similar inositol-P contents as the Bothnian Sea basin (now lost due to anoxic/euxinic conditions; 6×10^4 km^2), the P-storage in inositol-P forms would have been close to 18,000 t P. This corresponds to the annual external P load of 17,400 t to the Baltic Proper (Savchuk et al. 2008). This estimate indicates that a relatively small difference in sedimentary P content may represent significant amounts of P potentially available for primary production in the water column. Therefore, relatively minor changes in P turnover and burial efficiency in

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different basins of the Baltic Sea may greatly impact its trophic status.

DNA-P and lipid-P

The DNA-P detected in Baltic Proper sediments corresponded well to contents determined by ^{31}P NMR in a sediment core from the same region (Carman et al. 2000). The lipid-P contents reported here are, however, about fivefold higher than those reported by Ahlgren et al. (2006), which could be explained by the hydrophobic character of lipid-P limiting the extraction of these compounds by the NaOH-extract used for the NMR. Carman et al. (2000) detected higher contents of diesters at anoxic sites than at oxic sites in the Baltic Proper. This is in line with the higher lipid-P contents we found in the euxinic Baltic Proper sediments, Björnöfjärden included, compared to the Gulf of Bothnia sites.

Since the lipid-P and DNA-P might derive from both prokaryotes and eukaryotes, we relate it to microbial biomass to gain further insight concerning its origin. The sum of the DNA-P and lipid-P in the Landsort Deep core (core #6, 19–20 cm, 43 μg P g DW^{-1}; Table S4) was divided by the microbial cell abundance of 3.7×10^{10} cells g DW^{-1} previously reported for the Landsort Deep 0.7 m sediment layer by Mhatre et al. (2019). Although microbial turnover is slow in these energy-limited sediments (op. cit), cell abundance in the 19–20 cm layer can be expected to be denser than the 0.7 m layer. The estimated P-content per cell (43 μg P g DW^{-1} divided by 3.7×10^{10} cells g DW^{-1}) was 1.2 fg P which is at the lower end of reported microbial cell P-content (Fagerbakke et al. 1996). This is an estimation, and we are aware that bacteria have, for example, different cell sizes that will influence the calculated P-content per cell. Similarly, with carbon content of 25 fg C cell^{-1} in the Baltic Sea sediment (Jørgensen et al. 2020), and a molar C : N : P ratio of 50 : 10 : 1 (Fagerbakke et al. 1996), this amounts to a cell-specific P content of 1.3 fg ((fg C per cell/C g per mol)/50 × P g per mol, that is, (25/12)/50 × 31 = 1.3 fg P). In parallel to microbial cell numbers, Mhatre et al. (2019) determined N in amino acids representing microbial biomass to 10 μmol amino-acid N g DW^{-1}. The resulting molar N : P ratio using the sum of DNA-P and lipid-P above (43 μg or 1.4 μmol P g DW^{-1}) was 7 : 1, further supporting that both the org-P fractions detected in the euxinic sediments mostly represented microbial biomass.

In the moderately eutrophic Lake Erken, sediment DNA-P and lipid-P content was an order of magnitude higher than in the Baltic Sea basins, but still correlated to bacteria cell decline with sediment depth (Paraskova et al. 2014). The same pattern of bacterial distribution was found in Aarhus Bay, where bacterial abundance was an order of magnitude higher in the bioturbated surface sediment layer (top 8 cm) compared to the sediment below (Petro et al. 2019). The explanation for the higher microbial abundance in surface sediments is that bioturbation supplies both energy and electron acceptors, resulting in a denser and more diverse microbial population (Jochum et al. 2017). The bottom of the bioturbated layer represents the upper boundary of the deep biosphere (Jørgensen et al. 2020), where energy is extremely limited and microbial biomass turnover very slow (Jochum et al. 2017).

In Baltic Proper sediments, limited or absent bioturbation (Hermans et al. 2019) could explain the relatively low DNA-P contents in comparison to the higher contents found in Bothnian Bay and Bothnian Sea sediments, where the elevated DNA-P/lipid-P ratio (Fig. 3) indicates a thriving microbial community. Considering the more eutrophic conditions in the Baltic Proper and Björnöfjärden than in the oligotrophic Gulf of Bothnia, higher DNA-P contents could be expected. Instead, the contents are similar to those in sediments of the oligotrophic mountain Lake Ånn, located at great elevation in the Bothnian Sea catchment (fig. 1, Paraskova et al. 2014). Hence, there is not a simple relationship between sedimentary DNA-P content and productivity.

The relatively high lipid-P content in the Baltic Proper and Björnöfjärden sediments (Figs. 2, 7), might reflect settling of organic matter rich in lipid-P in comparison to DNA-P. However, Lake Mälaren is as productive as the Baltic Proper, but holds relatively low lipid-P contents in the sediment in relation to DNA-P making such a striking difference in settling matter P composition less likely. Although we cannot rule out that the low DNA-P/lipid-P ratio in the Baltic Proper and Björnöfjärden profiles (Fig. 3), reflects a different composition of settling matter, the correspondence to expected microbial P content (*see* above), as wells as the DNA-P/lipid-P ratio pattern with sediment depth, indicate that the DNA-P and lipid-P mainly represent microbial P.

One possible explanation for the relatively low DNA-P/lipid-P ratio observed in euxinic Baltic Proper and Björnöfjärden sediments, could be due to sulfur oxidizing bacteria such as *Sulfurimonas* and *Beggiatoaceae*. *Sulfurimonas* of the subgroup GD17 have been found in Landsort Deep sediments (e.g., Möller et al. 2019) and thrive in euxinic bottom water conditions (< 5 μmol L^{-1} ΣH_2S; Grote et al. 2007). In contrast, *Beggiatoaceae* are well adapted to hypoxic bottom water conditions (Møller et al. 1985), whereas they get outcompeted by other sulfur oxidizing bacteria (e.g., filamentous cable bacteria) under oxic conditions (Hermans et al. 2019). In the Baltic Proper, *Beggiatoaceae* have been found both offshore (Hermans et al. 2019) and in the archipelagos (Rosenberg and Diaz 1993; Dale et al. 2013). Note, however, that the offshore presence of *Beggiatoaceae* documented by Hermans et al. (2019) was observed in June 2016 shortly after two major Baltic inflows when bottom water redox conditions were favorable for *Beggiatoaceae*. Both *Sulfurimonas* GD17 and *Beggiatoaceae* can promote unusually high storage of polyphosphate inclusions within their lipid-P membranes compared to other bacteria (Brock et al. 2012; Möller et al. 2019). Strikingly, *Beggiatoaceae* can reach biomass densities up to 3000 μg cm^{-3} (Jørgensen 1977). This equals to

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3 mm^3 of *Beggiatoaceae* per cm^3 sediment (Jørgensen et al. 2010). Assuming that a *Beggiatoaceae* population of 0.01 mm^3 per cm^3 sediment, it corresponds up to 15 nmol P per cm^3 sediment (Langer 2019). Here, we assume the same sequestering capacity of 15 nmol P per cm^3 sediment for *Sulfurimonas* GD17 due to the lack of available data. This implies that when using this sequestering capacity of 15 nmol P per cm^3 and a sediment density for a fluffy surface layer of 1.03 g cm^{-3} (Faas and Wartel 2006), a fully developed *Sulfurimonas* GD17 or *Beggiatoaceae* community of 3 mm^3 per cm^3 sediment amounts to a P content of maximum 135 μg P g DW^{-1} of which lipid-P make up a significant share. We suggest that the relatively high lipid-P content observed in the surface sediments of the Baltic Proper including the Landsort Deep can be attributed to either *Sulfurimonas* GD17 or *Beggiatoaceae*, or a combination of both. The Landsort Deep was reoxygenated in 1996 when sampling took place (Fig. S1). Such conditions are favorable for *Beggiatoaceae* and they might have outcompeted the *Sulfurimonas* GD17. Therefore, we cannot estimate the relative contribution of these two bacterial genera for the observed lipid-P enrichments. As Björnöfjärden is characterized by seasonally euxinia with some yearly oxic/hypoxic intervals (Rydin and Kumblad 2019), and regular visual observations of the surface sediment revealed the presence of white filamentous *Beggiatoaceae* mats. We suggest that the high lipid-P content observed in the surface sediment from Björnöfjärden is likely due to *Beggiatoaceae* although some *Sulfurimonas* GD17 might have also been present. These surface enrichments in lipid-P for both the Baltic Proper and Björnöfjärden causes a low DNA-P/lipid-P ratio compared to the other basins (Figs. 2, 7). A critical deficiency is, however, that microbially lipid-P is ultimately decomposed under sulfidic conditions (i.e., high pore water ΣH_2S; Brock and Schulz-Vogt 2011). This might explain the decrease in lipid-P with sediment depth in Baltic Proper sediments (Fig. 2). Potentially, either a fully developed *Sulfurimonas* or *Beggiatoaceae* community alone, as well as the ordinary microbial community, could explain the lipid-P contents found in the Landsort Deep and Björnöfjärden cores. However, their relative contribution is unknown as a detailed analysis of the microbial composition would be required to accurately determine this.

Oxic/anoxic org-P turnover

The DNA-P/lipid-P ratio in the Lake Erken sediment profile, calculated from Paraskova et al. (2014), declines to values below 2 at 10 cm sediment depth (Fig. 3). This ratio is similar to those in euxinic sediments in the Baltic Proper and Björnöfjärden. It could reflect the development and turnover of the microbial community and the gradual loss of labile organic matter in the energy-limited "depauperate zone" (Wurzbacher et al. 2017), due to the absence of bioturbating fauna (Jørgensen et al. 2020).

Ahlgren et al. (2006) found that the degradation rates of the different org-P forms in an anoxic core from the Baltic Proper was almost twice as high than those in oxic Lake Erken sediments (Ahlgren et al. 2005). This difference can be explained by the absence of bioturbation that supplies relatively fresh carbon to deeper sediment layers and the resulting lack of energy needed to maintain a thriving microbial community, including the org-P present as microbial biomass, in the top 10 cm of the sediment profile. The microbial community in the anoxic "deep biosphere" environment reaches starvation faster than in the bioturbated sediments, observed as a faster degradation rate of org-P. This phenomenon contributes to lower TP contents in the Baltic Proper and the Björnöfjärden sediment (Fig. 2, 7), compared to the Bothnian Bay and Bothnian Sea (Table 2).

Detected org-P fraction of TP

The close relation between the TP content and detected org-P in the Björnöfjärden core shows that the forms of org-P studied here contributed to 46% (Fig. 4) of the elevated TP contents in the upper sediment layer, and the remainder of the elevated TP content is related to the detected org-P. No elevated contents in Fe or Mn associated with P were detected in surface sediments from the bay (Rydin and Kumblad 2019). Instead, besides the org-P detected, RNA-P, poly-P, and P in free nucleotides are major P pools both in cells of prokaryotes (Mitchell and Moyle 1954), and in eukaryotic phytoplankton (Lin et al. 2016). Such biogenic P-forms can be expected to represent a significant share of the undetected, elevated TP content, in the surface sediment layers in Björnöfjärden.

A similar relation between TP and detected org-P in the open Baltic Proper sediment (Fig. 5a,b) also suggests that changes in the detected org-P pool are paralleled by changes in the larger, undetected P pool. The decline of TP with sediment depth in anoxic sediment from the Stockholm archipelago corresponded to the decline in org-P, estimated through P-fractionation analysis, representing losses of mineralized P through sediment diagenesis and limited inorganic P retention (Rydin et al. 2011).

However, the sum of the detected org-P in the Baltic Sea sediment comprises a smaller share of the TP content, and contributes less, usually around 5–10%, to the decline with sediment depth, compared to Björnöfjärden (Fig. 4). In addition to the DNA-P and lipid-P detected in a Baltic Proper core using ^{31}P-NMR (Ahlgren et al. 2006), monoester P made up a large fraction of TP as the DNA-P and lipid-P together. It was suggested that mainly RNA dissolved during the alkaline extraction was detected as monoesters. Yet, a significant proportion of the org-P present in the sediment remains unidentified.

Only two out of five stations in the Baltic Proper had enough material for org-P analyses of the 0–1 cm layer (Table S4), but none of these stations did show such high contents of detected org-P as the corresponding layer in Björnöfjärden. One explanation for the lower content of the detected org-P in the Baltic Proper compared to the shallow

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Björnöfjärden might be due to the Baltic Proper stations having one order of magnitude greater water depth (Table S2). Part of the easily available organic matter and related P can be expected to be lost during settling (Malmaeus et al. 2019), resulting in lower DNA-P and lipid-P contents in the surface sediment layer compared to Björnöfjärden.

Burial

After the pronounced initial decline of the detected org-P, contents stabilize after up to three decades in Björnöfjärden (Fig. 7), indicating a refractory character to some extent of these compounds. The constant DNA-P/lipid-P ratio with sediment depth suggests that both org-P forms are present in microbial cells. The microbial community in sediment layers deposited during the 19th century (Fig. 7) have a slow turnover that will continue for millennia (Mhatre et al. 2019). However, P in microbial biomass at this depth in the sediment can considered to be permanently buried. The same lipid-P distribution pattern was seen in a shallow bay in Helsinki (Turner and Weckström 2009). Suzumura (2005) divides the lipid-P in a labile and a less reactive fraction. The latter will act as a sediment P sink in marine ecosystems, as indicated by the rather constant contents in deeper sediment layers in Björnöfjärden (Fig. 7).

Implications

If macrofaunal bioturbation ceases due to bottom water O_2 depletion, or by physical disturbance such as bottom trawling (van Denderen et al. 2020; Bradshaw et al. 2021), mineralization of the relatively dense (Jørgensen et al. 2020) but now maladapted aerobic microbial community, can be expected. Microbial phosphatases mobilize P in, for example, lipid-P and DNA-P, with the resulting lipids and DNA acting as carbon sources for the microbial community (Steenbergh et al. 2011), mobilizing P, N, and C. The inefficient "sink switching" (Ruttenberg 2014) in Baltic Proper anoxic sediments recycles mineralized P to the water column, partly explaining the lower sedimentary TP contents found in the Baltic Proper cores (Table 1; Malmaeus and Karlsson 2016). Our data suggest that variability in the composition of sedimentary microbial communities among the Baltic Sea basins might cause differences in org-P forms that in turn affects its turnover. However, to accurately assess the impact of microbial communities on the form in which org-P is recorded in the sediment, it is key to complement future studies on org-P with detailed analysis of the microbial composition and quantification.

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Conflict of Interest

None declared.

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