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Variations in the amount and composition of phosphorus in settling particles in the northern Baltic Sea archipelagos

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Quantification of the downward flux of phosphorus (P) in the water column is essential for understanding the fates and pathways of different P forms and to establish mass-balances in aquatic systems such as the Baltic Sea. In this study, we investigated the amount and composition of settling P in sediment trap material, as well as the seasonal and spatial variation of the material in four archipelago areas along the Swedish and Finnish coasts of the Baltic Proper. It was found that potentially mobile and immobile forms of P make up roughly equal shares of the total P in settling material, implying that, over time, around half of the settling P will be mobilized in the sediments. We also found substantial temporal and spatial variation in terms of amounts and composition of settling P that may partly be explained by differences in primary production and resuspension.

Introduction

Eutrophication is considered one of the major environmental problems in the coastal and archipelago areas of the northern Baltic Sea. Improving the ecological status of the Baltic Sea is largely associated with reducing the concentrations of phosphorus (P) and nitrogen in the system. Several studies indicate that the reflux of P from the sediments is similar in magnitude to the terrestrial load (Wulff *et al.* 2001, Conley *et al.* 2002, Kohonen *et al.* 2008). Using model simulations, Stigebrandt (2018) estimated that as much as 70% of the total P supply to the Baltic proper comes from deep anoxic bottoms. However, the potential for release of P from the sediments depends on the chemical composition of P and, thus, on the amount of P available in the sediment for mobilization and diffusion to water, or for burial (for example, as organic P or via remineralization of P; Jilbert *et al.* 2011). The internal loading of P from sediments to water is accelerated in anoxic conditions, when iron-bound P is released back to the water (Jensen *et*

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al. 1995, Rydin *et al.* 2011). Other potentially mobile chemical binding and solubility forms of P (operationally defined as “P-fractions”) found in sediments include dissolved and loosely-bound P and organic P compounds originating, for example, from degrading phytoplankton (Hille *et al.* 2005, Ahlgren *et al.* 2006).

Quantification of the downward flux of particulate P in the water column is essential to establish mass balances for P in aquatic systems. Sediments originate as settling particles and the reflux of P from the sediments is clearly dependent on the P forms present in these particles. There are a significant number of studies which quantify the rate of total P sedimentation in the Baltic Sea (Jonsson and Carman 1994, Emeis *et al.* 2000) and the content of different P forms in surface sediments (Carman and Jonsson 1991, Virtasalo *et al.* 2005, Lukkari *et al.* 2009a, b, Puttonen *et al.* 2014, Malmaeus and Karlsson 2016). There are also several studies of total P sedimentation in marine and coastal areas of the Baltic Sea using sediment traps reported in the literature (Blomqvist and Larsson 1994; Kankaanpää *et al.* 1997, Szmytkiewicz and Zalewska 2014). Asmala *et al.* (2017) recently discussed the role of Baltic coastal areas in reducing the P flux from land through sedimentation before it reaches the open sea. However, in this sea area, there are a few studies reporting on the composition of particulate P in settling particles. Hence, our understanding of different P forms in settling particles is limited, as is the local and temporal variability.

Different chemical extraction methods are used to operationally separate various P forms in sediments. The method employed in this study (see Methods section) was introduced by Psenner *et al.* (1984) and modified versions of it were applied in lake sediments as well as marine sediments (e.g., Jensen and Thamdrup 1993, Lukkari *et al.* 2009a, 2009b, Malmaeus *et al.* 2012). Another extraction method developed by Ruttenberg (1992) was used for P speciation in sediment trap material in lakes (e.g., Penn and Auer 1997) and oceans (Faul *et al.* 2005, Lin *et al.* 2012). Both extraction methods were designed to differentiate, for example, iron-bound (i.e., redox sensitive) and organic fractions — part of which may be considered as potentially mobile forms contributing to internal P loading of the systems. They also identified stable P forms that will be permanently buried in the sediment after settling out from the water column, including detrital and authigenic apatite P, and P bound to aluminum oxides (e.g., Psenner *et al.* 1984, Ruttenberg 1992).

The purpose of this study was to investigate the amount and chemical composition of settling particulate P in sediment trap material as well as its seasonal and spatial variation in four archipelago areas along the Swedish and Finnish coasts of the Baltic Proper. More specifically, the aim was to: 1) provide data on the settling rates of suspended particulate matter and total phosphorus (P_{tot}); 2) provide data on the composition of settling material; and 3) illustrate temporal and spatial variability in rates and composition (e.g., increase in organic P deposition as a result of the increase in production).

The results are compared with the P composition of surficial sediments at the same locations, and the possible origin and fate of different P forms are further discussed. We do not attempt to make a comprehensive survey of settling rates in the whole region, but rather illustrate the variability of the fluxes and their patterns in a few case study areas. Nevertheless, we expect the results to be reasonably representative of the region in the topographically fractured archipelagos.

Materials and methods

Site descriptions

The sampling sites are located in the northern part of the Baltic Proper, in the archipelagos of Sweden, Åland and southwestern Finland (Fig. 1). We chose the sites from sea areas where we expected to find accumulation areas in order to study the rates and composition of net sedimentation.

Edöfjärden (hereafter called Edö) is a 17 km^2 coastal area in the central part of the Stockholm archipelago, Sweden. It is relatively sheltered from the sea and connected to the surrounding water areas by several narrow sounds. The topography is variable and most of the area is no

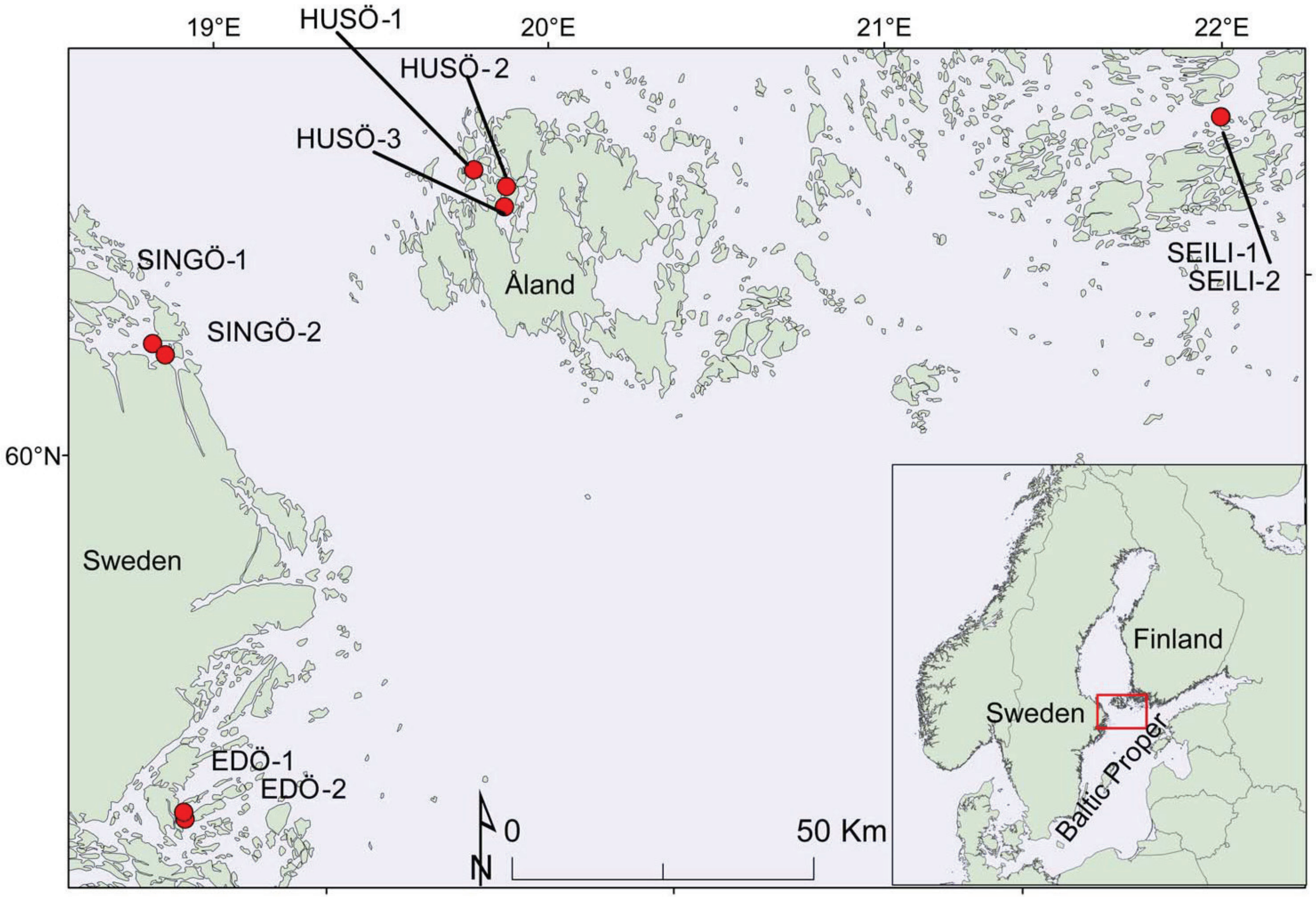

Fig. 1. The locations of the trap sites in the archipelagos of Sweden, Åland and SW Finland. Sites in Edöfjärden: EDÖ-1 and EDÖ-2; sites in Singöfjärden: SINGÖ-1 and SINGÖ-2; sites in the Husö area: HUSÖ-1, HUSÖ-2 and HUSÖ-3; and sites in the Seili area: SEILI-1 and SEILI-2.

deeper than 20 meters although the maximum depth is 31 meters in the south (Edö-1). Accumulation areas occupy around 40% of the bottom (Jonsson *et al.* 2003). The archipelago is influenced by River Norrström and the city of Stockholm annually transporting around 150 tonnes of P.

Singöfjärden (hereafter called Singö) is located along the coast of Uppland and although it is connected to the Åland Sea by only two shallow and narrow sounds to the east, the water exchange to the adjacent areas in the north is relatively effective. The size of the area is 37 km^2 and the maximum depth is 50 meters. In total, 32% of the bottom area consists of accumulation sediments (Jonsson *et al.* 2003). Nutrient loading in the Singö area is influenced by a paper mill some ten kilometers to the west and by local discharge from villages and dwellings.

The Husö study site (hereafter called Husö) is a 77 km^2 semi-enclosed sheltered embayment in the inner part of the Åland main island, Finland. The seafloor is regularly affected by wind-induced waves, as the water depth is, in general, less than 20 meters, reaching in a few depressions down to 30 m. Phosphorus input to the area comes from fish farms, agriculture and domestic waste waters.

The Seili study site (hereafter called Seili) is located at the southernmost part of the Airisto Inlet, SW Finland. The mean water depth in the ca 240 km^2 Airisto sub-basin is only 20 m, but elongated bedrock fractures form deeper channels (50–60 m) on the sea floor, the maximum depth being 90 m. Accumulation of fine grained sediments takes place in shallow areas in the shelter of islands, while in deeper canyons, sediment erosion or non-deposition may prevail due strong bottom currents (Virtasalo *et al.* 2005). Heavy boat traffic to and from the cities of Turku and Naantali causes sea bottom erosion and sediment resuspension (Rytkönen *et al.* 2001). The annual riverine load of P to the study area is around 160 tonnes, with over 60% originating from agriculture.

We used an exposure index to quantify the expected exposure to wave action at each location. The exposure indices were derived from the simplified wave model (SWM; Bekkby *et al.* 2008). The wave exposure index depicts the exposure to waves and wind at a given location, it is based on a ten-year average wind speed and the distance over which the wind blows to a given location (fetch), and it is widely used for marine habitat classification. The Finnish Environment Institute provided the 25 m resolution wave-exposure grid for the Finnish water area, and AquaBiota for the Swedish water area. According to the simplified wave model, all sites are sheltered. However, there are differences between them: Husö-2 is the most sheltered one while the Husö-1 and Singö-1 are more exposed than the rest of the sites.

Sampling

Sediment traps

Overall, we followed the general methods and procedures for sediment trap studies described in Bloesch and Burns (1980) and Blomqvist and Håkanson (1981). Cylindrical sediment traps were used to collect settling material at nine mooring sites; two in the SW Finnish archipelago, three in the Åland archipelago and four on the Swedish coast (Fig. 1). The inner diameter ranged from 4 (Singö traps) to 12 cm (Edö traps) with the trap diameters in Finland and Åland measuring 6 cm; all aspect ratios (height/diameter) were greater than 5 cm, as recommended by Bloesch and Burns (1980). In SW Finland and Åland, a Limnos twin trap system was used (Fig. 2). The traps were moored two to five meters above the sea floor; at the Swedish sites, an additional trap was placed higher in the water column (Table 1). The traps were moored at sites located in areas where continuous sediment accumulation was expected to prevail. Sediment accumulation was confirmed from sediment surface samples taken at the trap mooring sites considering water content > 75% and loss-on-ignition (LOI) > 10% criteria for accumulation areas (Håkanson and Jansson 1983).

The settling material was collected during the open water season in Åland (2011 at Husö), SW Finland (2010 at Seili) and Swedish Singö (2010), and throughout the year in Swedish Edö (2009–2011) (Table 1). The water depth (max. 50 meters) at all sites was less than the depth of the halocline (around 60–70 m in the open waters of the Baltic Sea), but temporal thermoclines are regularly formed at depths separating the upper from the lower traps.

Surface sediments

Surface sediment samples were collected simultaneously with the trap material at the same study sites where the traps were placed (except, at Seili, only at the onset of the study) (Table 1). Sediment sampling was carried out either with a Gemini twin-corer (inner diameter 80 mm), a Willner sampler (inner diameter 56 mm) or a Limnos sediment corer (inner diameter 94 mm). Sediment cores were sectioned into one (Finland) or two (Sweden) centimeter layers. Only the topmost segments from the sediment surface were used in this study.

Analysis

Chemical analyses

The water content was determined in the sediment samples after freeze-drying and expressed as a percentage of wet weight (% ww). The organic content (measurement of LOI) was determined after ignition at 550°C for two hours and expressed as a percentage of dry weight (% dw). Total P (P_{tot}) content in the trap material and the sediments was analyzed as phosphate according to Murphy and Riley (1962) after acid hydrolysis at a high temperature (340 °C).

Phosphorus forms were separated into six fractions following the sequential extraction scheme presented by Psenner *et al.* (1988). These fractions are defined by the extraction method but, theoretically, each fraction (except the residual fraction) corresponds to a specific binding or solubility form of P within the sediment. Generally, NH_4Cl-rP (ammonium chloride-extractable molybdate reactive P) is regarded as loosely-bound and porewater phosphorus; BD-rP as phosphorus associated with reducible iron oxyhydroxides; NaOH-rP (sodium hydroxide-extractable reactive P) as phosphorus bound to aluminum oxides (and non-reducible Fe oxides); NaOH-nrP (sodium hydroxide-extractable non-reactive P) as organic phosphorus forms; and HCl-rP (hydrogen chloride-extractable reactive P) as calcium bound, mainly apatite phosphorus compounds. In this study, residual P is given by subtracting the sum of the above-mentioned extracted phosphorus forms from P_{tot} determined separately from a different subsample. Residual P consists mainly of recalcitrant organic P, but it also contains some inorganic P (Ruttenberg 1992). In the following, the extracted P forms will be denoted as loosely-bound P, P_{Fe}, P_{Al}, P_{Org}, P_{Ca} and P_{res}, respectively. In this study, we regard loosely-bound P, P_{Fe} and P_{Org} as potentially mobile fractions (Rydin *et al.* 2011), since they are normally mobilized with time during sediment diagenesis, and not permanently buried in deeper sediment layers, unlike the rest of the P forms separated (i.e., the immobile or stable P; see Discussion section).

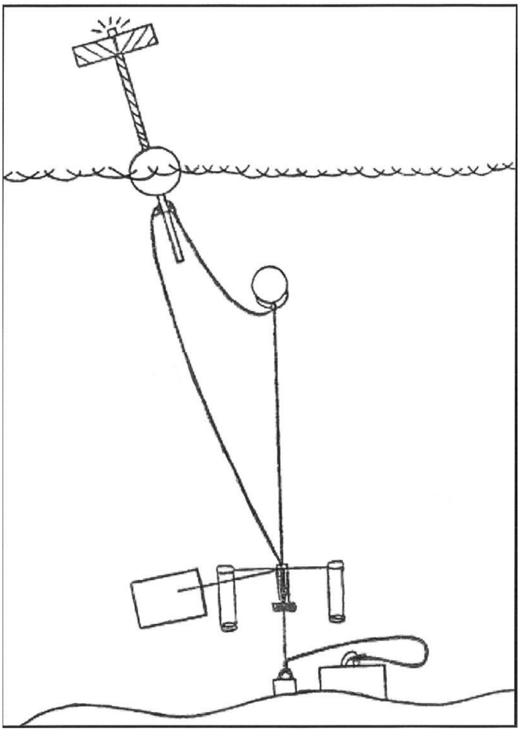

Fig. 2. Illustration of the Limnos trap system used in the Finland and Åland sampling sites. A similar system was used at the Swedish sites but with traps located at two vertical positions.

Table 1. Location and depth of the sediment trap sites and the sampling periods of the settling matter.

Site	Latitude	Longitude	Water depth (m)	Mooring depth (m)	Sampling periods
EDÖ-1 lower	59° 26.48´N	18° 37.06´E	30.4	28.4	10 Dec 2009–19 Apr 2010 19 Apr–29 Jun 2010 29 Jun–24 Aug 2010 24 Aug–14 Nov 2010 14 Nov 2010–19 Apr 2011
EDÖ-1 lower	59° 26.48´N	18° 37.06´E	30.4	10	10 Dec 2009–19 Apr 2010 19 Ap–29 Jun 2010 29 Jun–24 Aug 2010 24 Aug–14 Nov 2010 14 Nov 2010–19 Apr 2011
EDÖ-2 lower	59° 27.1´N	18° 36.97´E	16	14	10 Dec 2009–19 Apr 2010 19 Apr–29 Jun 2010 29 Jun–24 Aug 2010 24 Aug–14 Nov 2010 14 Nov 2010–19 Apr 2011
EDÖ-2 upper	59° 27.1´N	18° 36.97´E	16	10	10 Dec 2009–19 Apr 2010 19 Apr–29 Jun 2010 29 Jun–24 Aug 2010 24 Aug–14 Nov 2010 14 Nov–19 Apr 2011
SINGÖ-1 lower	60° 9.032´N	18° 42.135´E	50	45	27 May–9 Aug 2010
SINGÖ-1 upper	60° 9.032´N	18° 42.135´E	50	5	27 May–9 Aug 2010 9 Aug–8 Nov 2010
SINGÖ-2 lower	60° 7.897´N	18° 44.127´E	19	15	27 May–9 Aug 2010
SINGÖ-2 upper	60° 7.897´N	18° 44.127´E	19	5	27 May–9 Aug 2010
SEILI-1	60° 15.190´N	21° 57.640´E	22	20	6 May–7 Jun 2010 7 Jun–9 Aug 2010 9 Aug–11 Oct 2010 11 Oct–29 Nov 2010
SEILI-2	60° 15.190´N	21° 57.590´E	27.5	25.5	6 May–7 Jun 2010 7 Jun–9 Aug 2010 9 Aug–11 Oct 2010
HUSÖ-1	60° 20.719´N	19° 43.502´E	18	16	12 May–8 Jun 2011 8 Jun–6 Jul 2011 6 Jul–4 Aug 2011 4 Aug–8 Sep 2011 8 Sep–25 Oct 2011
HUSÖ-2	60° 18.833´N	19° 48.848´E	14	12	12 May–8 Jun 2011 8 Jun–6 Jul 2011 6 Jul–4 Aug 2011 4 Aug–8 Sep 2011 8 Sep–25 Oct 2011
HUSÖ-3	60° 17.063´	19° 48.002´E	17	15	12 May–8 Jun 2011 8 Jun–6 Jul 2011 6 Jul–4 Aug 2011 4 Aug–8 Sep 2011 8 Sep–25 Oct 2011

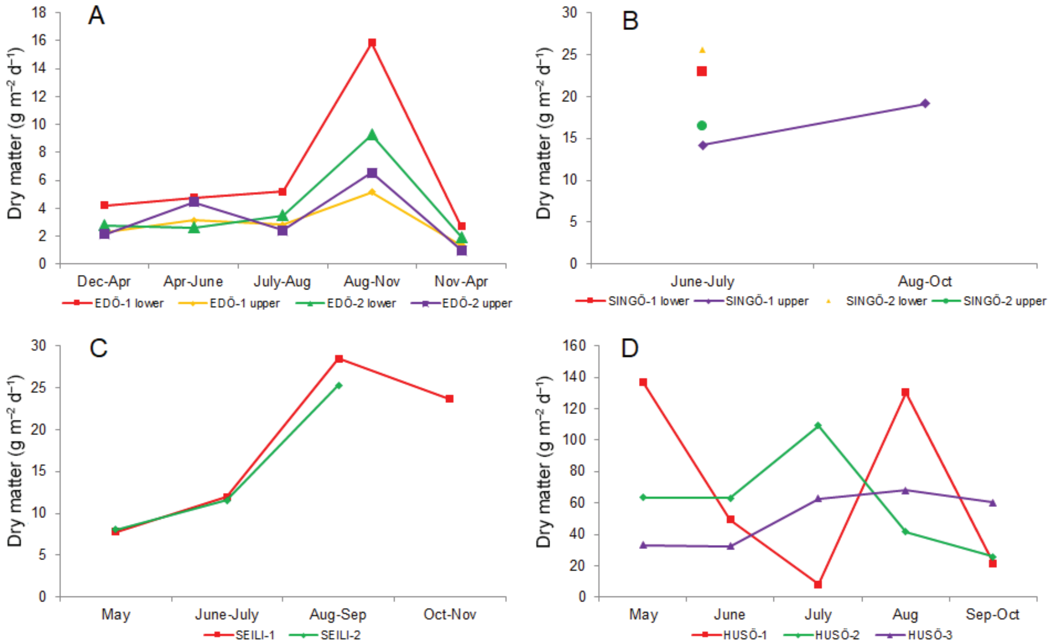

Fig. 3. Seasonal variation of dry matter deposition (g m^{-2} d^{-1}) in the sediment traps in **a**) 2009-2011 at Edö, **b**) 2010 at Singö, **c**) 2010 at Seili and **d**) 2011 at Husö. Note the variation in the scales used and the different timing of sampling periods at different sites (see Table 1).

Calculations and statistical analyses

Sedimentation rates for dry material, total P and six P fractions were calculated by dividing the amounts of material collected in the traps by the cross-sectional area of the trap cylinder and the number of days of deployment. The sedimentation rates are given in (milli-) grams per square meter per day (g m^{-2} d^{-1}). The Pearson correlation method in IBM SPSS Statistics 21 was used to examine correlations between dry matter deposition and P content in the settling material. The Shapiro-Wilk test was used to test for normality and the variables were log-transformed to meet the assumption, if needed. The Kolmogorov-Smirnov test was used to test statistical differences between the concentrations of loosely-bound P in the settling material versus the surface sediment. Due to limited data sets, the latter test could only be run for the Husö site.

Results

Dry matter deposition in the traps varied from 1 to 137 g m^{-2} d^{-1}, with an overall mean of 26 ± 33 g m^{-2} d^{-1} (Fig. 3), while the deposition of P_{tot} varied from 1 to 134 mg P m^{-2} d^{-1}, with an overall mean of 30 ± 35 mg P m^{-2} d^{-1} (Fig. 4). Since winter deposition of dry matter (Nov–Apr) in Edö traps were approximately one-third of the summer deposition, and winter deposition of P_{tot} was approximately one-fifth of the summer deposition, we modified the annual estimates accordingly (we only have full year measurements from the Edö site). Assuming winter conditions during one half of the year and summer conditions in the other half, we estimated that more representative mean values for dry deposition were around 17 g m^{-2} d^{-1} and for P_{tot} deposition around 18 mg m^{-2} d^{-1}. Statistically significant correlations ($p < 0.01$) were observed between the dry matter deposition and the deposition of P_{tot} (Pearson $r = 0.98$) and three of the separated P forms: loosely-bound P ($r = 0.63$), P_{Fe} ($r = 0.89$) and P_{Org} ($r = 0.84$). Deposition rates varied considerably between the sites, with the highest rates observed at the Husö stations. At most stations, the highest dry matter deposition was recorded in mid or late summer. At the Edö and Singö sites, where the traps were deployed

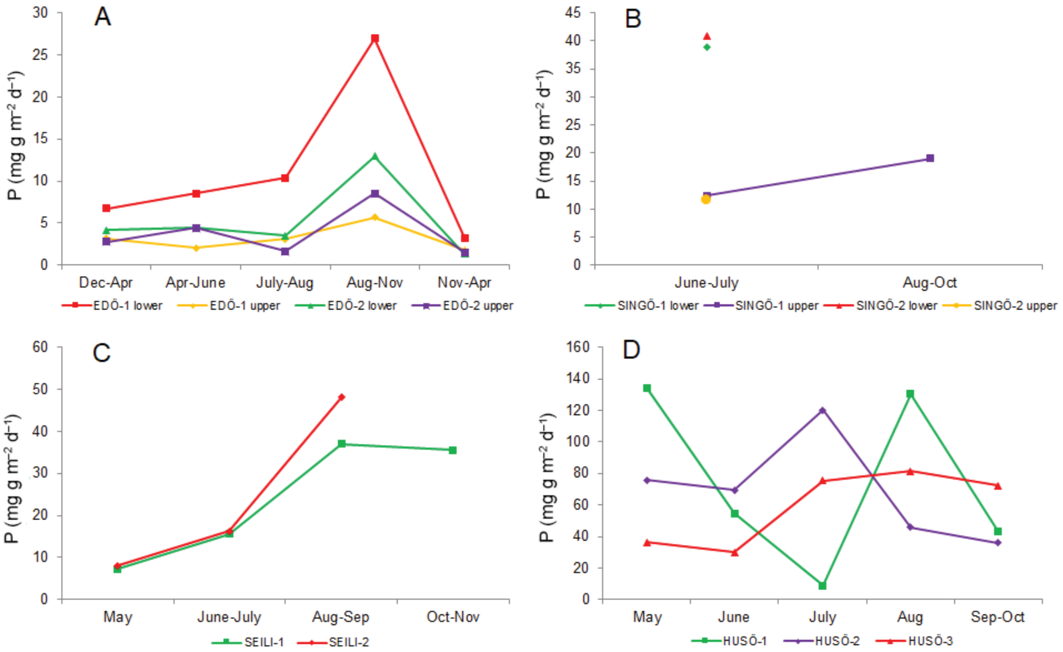

Fig. 4. Seasonal variation of phosphorus deposition (mg m^{-2} d^{-1}) in the sediment traps in **a**) 2009-2011 at Edö, **b**) in 2010 at Singö, **c**) 2010 at Seili and **d**) 2011 at Husö. Note the different scales used.

at two depths, the deposition rates were consistently higher in the lower traps than in the upper traps (Fig. 3).

P_{tot} content in the settling particulate matter was of the same order of magnitude as P_{tot} content in the surface sediments (Table 2). At all sites, except for the Singö site, the deposition of P_{tot} (Fig. 4) followed, in general, the same seasonal and spatial pattern as that of the dry matter, with levels typically three orders of magnitude lower for P_{tot} than for the dry matter.

The phosphorus composition in the settling material varied both temporally and spatially, and no common seasonal trend in the occurrence of various P forms could be observed (Fig. 5). Roughly half of the materials deposited in the traps consisted of potentially mobile fractions (i.e., loosely-bound P, P_{Fe} and P_{Org}) but the variation was large. In the SEILI-1 trap and the lower EDÖ-1 trap, the highest proportion of the potentially mobile P occurred in early spring and, in the HUSÖ-1 trap and upper EDÖ-1 trap, during late fall. The organic P fraction constituted a larger proportion in the upper trap than in the lower trap at the Edö site while the share of the iron-bound P fraction was higher in the lower trap. However, the total deposition of both P forms was larger in the lower trap than in the upper trap. Annual accumulation rates for the settling material and P_{tot} was calculated using the Edö data (Table 3).

Table 2. Total phosphorus in settling particles and at sediment surface (mean values ± SD) at three different sites (upper traps in Edö and Singö excluded). *n* = number of samples.

Site	Settling particles (µg P_{tot} g^{-1} dw)	*n*	Surface sediment (µg P_{tot} g^{-1} dw)	*n*
Husö	1180 ± 250	15	1470 ± 290	18
Seili	1330 ± 320	7	1300	1
Edö	1460 ± 400	10	1180 ± 160	11
Singö	1650	2	4100 ± 2550	13

In general, the composition of the settling material was similar to that of the surface sediment (Table 4), except that the loosely-bound P was consistently higher within the settling particles than on the sediment surface. A statistically significant difference between the trap and the sediment materials was found for the Husö samples (Kolmogorov-Smirnov test, N1 = 18,

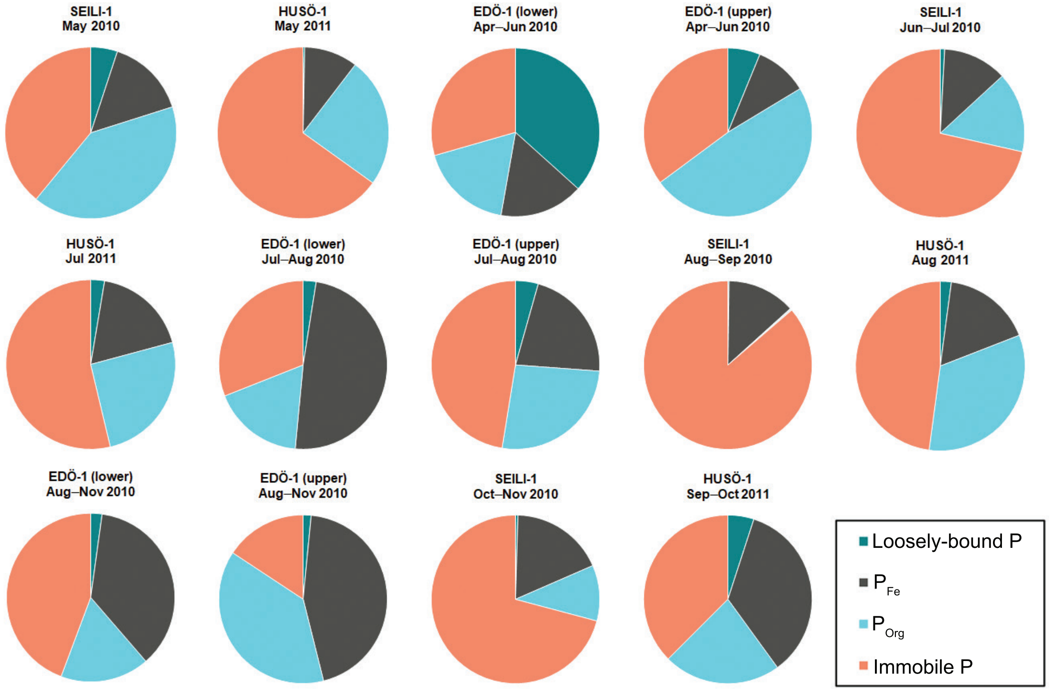

Fig. 5. Seasonal variability in the phosphorus (P) composition (in %) of the material settled into the traps at selected sites.

N2 = 15, D = 0.622, $p = 0.002$). Unfortunately, there were too few samples from the other stations for any statistical analysis. P_{tot} concentrations were, in general, slightly higher in the sediment surface layer compared with the material in the traps, and substantially so at the Singö stations (Table 2).

Discussion

Measured quantities of settling phosphorus

The results of this study showed that the amounts of total phosphorus and different phosphorus forms in the deposited material vary greatly, both temporally and spatially in the studied archipelago areas. Given this variation, we need to be careful in our interpretation of the data. Nevertheless, there are some consistent patterns, for example, similar temporal trends at adjacent stations, indicating that the variability is largely explained by deposition and biogeochemical processes in the system rather than by sampling or analytical imperfections. Between-site variability may be explained by factors such as water depth, wave exposure, and other morphological factors but may also reflect variation in primary production and sediment resuspension in surrounding areas.

The average dry matter deposition was found to be 26 ± 33 g m^{-2} d^{-1}, which is largely consistent with other studies in the area (e.g., Wallin and Håkanson 1992, Blomqvist and

Table 3. Annual accumulation rates for dry material and total phosphorus (P) at Edö during the sampling period 19 Apr 2010–19 Apr 2011 (upper traps excluded).

Site	Sediment accumulation (g m^{-2} yr^{-1})	P accumulation (g P_{tot} m^{-2} yr^{-1})	P % bulk sediment
Edö-1	2350	3.9	0.2
Edö-2	1450	1.8	0.1

Larsson 1994, Jumppanen and Mattila 1994). If converted to annual rates, the P_{tot} sedimentation in the investigated sites ranged between 2 and 27 g P_{tot} m^{-2} yr^{-2}, with both mean and median close to 14 g P_{tot} m^{-2} yr^{-2}. Correcting for lower deposition rates during winter (see Results) we can estimate between 1 and 16 g P_{tot} m^{-2} yr^{-2}, with mean and median around 8.5 g P_{tot} m^{-2} yr^{-2}. These estimates are higher than estimates for P deposition in the open sea, but reasonable as coastal dry matter deposition is typically an order of magnitude higher per area unit than in the open waters of the Baltic Sea (Jonsson and Carman 1994).

A general comparison between trap studies and sediment accumulation studies indicates that trap studies usually measure sedimentation rates at levels of an order of magnitude higher than the latter method. This has been demonstrated by direct comparisons in several studies (e.g., Faas and Carson 1988, Leppänen 1988, Szmytkiewicz and Zalewska 2014). Leppänen (1988) suggested that this may result from the accumulation of the sinking material to a suspension layer floating above the sediment surface where it can possibly escape the sediment sampler and is susceptible to transportation by bottom currents. Also, our P_{tot} sedimentation rates are roughly an order of magnitude higher than P deposition rates determined from sediment dating in Baltic coastal areas by Jonsson *et al.* (2003), Lukkari *et al.* (2009a, 2009b) and Rydin *et al.* (2011). As pointed out by, e.g., Storlazzi *et al.* (2011), the sedimentation rate measured with traps should be interpreted as ‘‘trap collection rate’’ or ‘‘trap accumulation rate’’ recognizing the many factors that affect trapping efficiency in natural environments. Arguably, net sedimentation is better represented by direct measurement at the sediment surface while the actual composition of the settling material may be more readily studied with sediment traps (Kozerski 1994).

We did not use any preservatives in the traps to avoid the mineralization of fresh organic matter. This may underestimate sedimentation due to the degradation and diffusion of dissolved compounds. On the other hand, using preservatives may overestimate sedimentation if actively swimming organisms (plankton and other animals) enter the traps (Lignell *et al.* 1993), which is also supported by results of Heiskanen and Tallberg (1999). Most likely, our estimates slightly underestimate real sedimentation rates due to the degradation of organic matter and should thus be regarded as minimum levels.

On the biogeochemistry of different phosphorus forms

The immobile P forms (i.e., apatite P, P in aluminium oxides and residual P) are, in general,

Table 4. Percentage (%) of mobile phosphorus (P) forms of total phosphorus (P_{tot}) in settling particles and sediment (mean values ± standard deviation) at three different sites (upper traps in Edö and Singö excluded). *n* = number of samples.

P form	Site	Settling particles (% of P_{tot})	*n*	Surface sediment (% of P_{tot})	*n*
Loosely-bound P	Husö	2.6 ± 1.4	15	1.2 ± 0.7	18
	Seili	1.7 ± 1.8	7	0.9	1
	Edö	10.7 ± 15.7	8	0.9 ± 0.4	9
	Singö	8.2	2	2.5 ± 1.3	9
P_{Fe}	Husö	26.9 ± 8.7	15	31.7 ± 8.4	18
	Seili	14.7 ± 2.3	7	32.5	1
	Edö	29.1 ± 12.6	8	16.6 ± 8.3	9
	Singö	46.7	2	53.2 ± 14.7	9
P_{Org}	Husö	29.5 ±10.5	15	18.0 ±3.7	18
	Seili	18.6 ±14.7	7	16.2	1
	Edö	20.7 ±6.2	8	27.7 ±5.2	9
	Singö	9.4	2	13.5 ±7.6	9

considered stable and, once settled to accumulation sediments, they will become permanently buried with time. By contrast, the mobile P forms (i.e., loosely-bound P, P_{Fe} and labile P_{Org}) will be modified in the biogeochemical processes and part of them return to the water column with time. However, part of the mobile P forms will remain in the sediment and be buried, for example, when forming secondary minerals in diagenetic processes (e.g., Ruttenberg 2003, Jilbert *et al.* 2011). A considerable part of P_{Org} will be buried (Jilbert *et al.* 2011) but part of the P in the organic fraction may become bioavailable once the organic material is decomposed or the mineralization-released P can be bound to metal oxide surfaces, if available, changing the form in which P occurs in the suspended particulate material or the sediment. The most easily degradable forms of organic P in algal material can be mineralized within a couple of weeks (Andersen and Jensen 1992) and some P_{Org} deposited in the traps was probably degraded before sampling as it degrades while settling in the water column. However, the water depth in our research area was shallow, which may partly explain why the material settled on the surface of the sediment did not differ considerably from the material in the traps. Other possible explanations for this finding can be due to the resuspension of the surface sediment and settling of mineral material into the traps. The formation of authigenic apatite P has been shown both in sediments and in sediment traps in several coastal sea areas (e.g., Delaney 1998, Faul *et al.* 2005, Ruttenberg 1992). The extraction method used in this study does not separate authigenic apatite P but it has been demonstrated earlier that, in Baltic sediments, formation of this P form is not important (Virtasalo *et al.* 2005, Mort *et al.* 2010) and that most of the potentially mobile P will be returned to the water column (Lukkari *et al.* 2009a, 2009b, Rydin *et al.* 2011, Malmaeus *et al.* 2012, Puttonen *et al.* 2014).

Although the loosely-bound P constitutes only a small part of total P (per dry weight), it is the most bioavailable fraction and presumably consumed quickly. It also includes phosphate released by mineralization of organic P compounds, thus, it is logical that concentrations of loosely-bound P are generally higher in the fluffy trap material containing more newly deposited organic material than on the more consistent sediment surface. In fact, the most easily degradable organic P is mineralized before it reaches the sea floor and, thus, is not included in the pools of the mobile P in the surface sediment although it may represent an important P source. The easily mineralized organic P pool should be quantified in future research. In general, the P_{Fe} fraction is considered stable under oxic conditions and is hence accumulated in the oxic surface sediment (Mortimer 1971, Jensen *et al.* 1995), and released from sediment to water if the sediment becomes anoxic. However, if P-binding sites at the oxide surfaces at the uppermost oxic sediment layer are heavily occupied, some P_{Fe} may be replaced by competing anions (Hingston *et al.* 1967). In such cases, also P_{Fe} released from the deep, reduced sediment layers and diffusing upwards will not be effectively bound to the oxic surface sediment layer.

On average, mobile P forms made up roughly 50% of P_{tot} (in traps as well as in surface sediments, Table 4) although the variation was substantial (Fig. 5). We conclude that, in general, roughly half of the amount of the settling P will be permanently buried in the sediments, while the other half may be mobilized in biogeochemical processes and become available for primary producers. Furthermore, part of the P transformed and mobilized in the biogeochemical processes of the sediment will be incorporated in other P forms buried, for example, into vivianite (Jilbert *et al.* 2011, Jilbert and Slomp 2013). This is consistent with results from previous studies indicating burial efficiency around 50–60% of P_{tot} in accumulation sediments (Lukkari *et al.* 2009a, 2009b, Rydin *et al.* 2011). It should be stressed, however, that part of the mobilized P is transported and deposited again elsewhere and may not reach the productive layer of the water column.

In general, P_{Fe} content was higher in the sediments relative to corresponding trap material, except in Edö, where P_{Fe} content was comparatively low in the sediment surface layer, possibly indicating hypoxic conditions at the sediment surface. For most sites, we conclude that there is an upward migration of phosphate from deeper sediment layers which is trapped by

Fe(III) oxides at the sediment surface (Mortimer 1971, Jensen *et al.* 1995). The P_{tot} concentration in the surface sediments in the Singö site was much higher than in the settling material and we speculate that this might be due to a recent switch from anoxic to oxic conditions (Rydin *et al.* in prep), allowing an efficient entrapment of P by the newly formed Fe oxides.

Interpreting spatial and temporal variation

While the data do not justify any detailed conclusions about the reasons for spatial and temporal variations, it is worth highlighting some of the observed patterns in order to suggest factors that may be of importance for the dynamics of P sedimentation. For example, the high downward P_{tot} flux in Aug–Nov in the Edö traps was associated with a relatively high proportion of P_{Org} in the upper trap, which may indicate a high biological production and deposition of the late summer bloom during this period (Leppänen 1988). In the lower trap, the larger proportion of immobile P may indicate a higher degree of mineralization of organic P compounds and a dominance of resuspended material, which was further supported by the relatively high total sedimentation in the lower trap compared with the upper one.

The lower traps (at Edö and Singö sites), in general, received more dry matter deposition than did the upper traps, indicating a substantial contribution of resuspended material. Total deposition at the shallow Husö sites was substantively higher and more variable than at the other sites, possibly reflecting a higher rate of resuspension due to the shallow water depth and wind-induced waves. According to the weather statistics by the Finnish Meteorological Institute, in 2011, the wind speed exceeded ten m/s in four days in May, once in July, once in August, in three days in September and in two days in October. The higher rate of resuspension is further supported by the relatively high proportion of immobile P in these samples.

We expected a seasonal pattern in particularly P_{Org} deposition, reflecting productivity in the photic zone and subsequent sinking of organic matter. Large proportions of P_{Org} in both Seili traps in May and in the upper Edö trap in Apr–Jun probably reflect an increase in phytoplankton abundance (Fig. 5). At Seili, a high proportion of organic matter (LOI), 23% dw, in the settling material indicates spring bloom, which is also seen as a peak in chlorophyll-*a* concentration in April–May (www.syke.fi/earth-observation). After the first sampling period, the Seili traps received more dry matter deposition, with higher proportions of immobile P and lower LOI values than in May, indicating the input of resuspended sediments from the sea floor.

Overall, the composition of P in the settling material varied between all sites and seasonally, but no common seasonal pattern could be observed. These results indicate that the seasonal variations, as well as the amount and composition of the settling P, can be highly variable and site-dependent in topographically fractured archipelago areas. High seasonal and spatial variation in the deposition of particulate material (e.g., Laakkonen *et al.* 1981, Wallin and Håkanson 1994, Leivuori 2000) as well as the seasonal variation in the composition of the depositing material (Laakkonen *et al.* 1981, Leppänen 1981) have also been reported in previous studies from the Baltic Sea. The seasonal variability in the P composition of the surface sediments (Fig. 6) appears to be more erratic than in the sediment traps, and we are unable find any common temporal pattern. This may be due to the small-scale spatial variation at the sampling sites, and the fact that 2 cm sections (Edö and Singö) collected for fractionation analysis probably contained material of variable ages shielding the impact of the recently deposited material during the sampling season. However, the co-occurring peak values for P_{Fe} and P_{Org} at Husö and Edö may indicate the entrapment of P released from the high P_{Org} input to Fe-oxides (Jensen *et al.* 1995), or just the peak values of the P_{tot} deposition at those times.

It should be stressed that since all study sites were situated in accumulation areas, the resuspended material originates from shallower or more exposed erosion or transportation areas. Indeed, the relatively large contribution by resuspended particles to net sedimentation is consistent with findings from many other studies (Wallin and Håkanson 1992, Blomqvist and

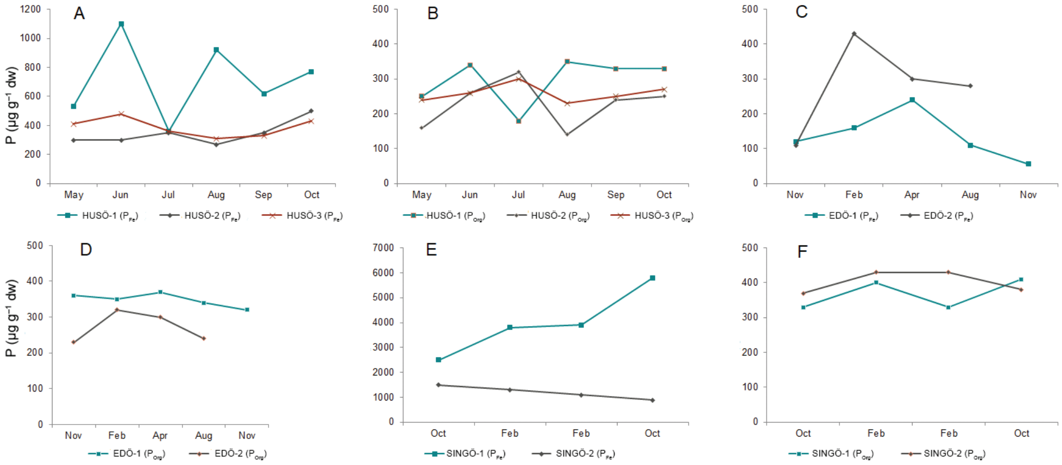

Fig. 6. Seasonal variation in P_{Fe} concentration (μg g^{-1} dw) in surface sediments at **a**) Husö, **c**) Edö and **e**) Singö sites, and respective P_{Org} concentration (μg g^{-1} dw) at **b**) Husö, **d**) Edö and **f**) Singö. Note different scales on y-axes. Husö samples were from 2011, Edö and Singö samples were from 2009–2010.

Larsson 1994, Heiskanen and Tallberg 1999). For example, Wallin and Håkanson (1992) found in a study of 23 coastal areas in the Swedish and Finnish parts of the Baltic Sea that, on average, 56% of the total sedimentation in sediment traps 3 metres below the water surface and 62% of the total sedimentation in sediment traps one m above the bottom originated from resuspended matter.

Conclusion

Various forms of P with differing reactivities are present in settling material and there are substantial temporal and spatial variation in terms of amounts and composition of settling P in the study area. We found that in total, potentially mobile and immobile forms of P contributed roughly equal shares of total P in the settling material. This indicates that after the mineralization of the most easily available P forms, roughly half of the P settling in accumulation sediments will be buried and not contribute to internal loading in the short term. The other half is transformed in biogeochemical processes and part of it remains in the sediment, for example, as secondary minerals, and part can be mobilized and become a source of P to the water column. In order to establish mass-balances for the Baltic Sea and the coastal areas, this kind of estimate is required. Further efforts are needed, however, to more confidently establish the amount and composition of phosphorus in settling particles in different seasons and areas in the Baltic Sea.

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References

Ahlgren J., Reitzel K., Tranvik L., Gogoll A. & Rydin E. 2006. Degradation of organic phosphorus compounds in anoxic Baltic Sea sediments: A 31P-NMR study. *Limnology and Oceanography* 51: 2341–2348.

Andersen F.Ø. & Jensen H.S., 1992. Regeneration of inorganic phosphorus and nitrogen from deposition of seston in a freshwater sediment. *Hydrobiologia* 228: 71-81.

Asmala E., Carstensen J., Conley D.J., Slomp C.P., Stadmark J. & Voss M. 2017. Efficiency of the coastal filter: Nitrogen and phosphorus removal in the Baltic Sea. *Limnology and Oceanography* 62: S222–S238.

Bekkby T., Isachsen P.E., Isæus M. & Bakkestuen V. 2008. GIS Modeling of Wave Exposure at the Seabed: A Depth-attenuated Wave Exposure Model. *Marine Geodesy* 31: 117–127.

Bloesch J. & Burns N.M. 1980. A critical review of sedimentation trap technique. *Schweizerische Zeitschrift für Hydrologie* 41: 15–55.

Blomqvist S. & Håkanson L. 1981. A review on sediment traps in aquatic environments. *Arch. Hydrobiol.* 91: 101–132.

Blomqvist S. & Larsson U. 1994. Detrital Bedrock Elements as Tracers of Settling Resuspended Particulate Matter in a Coastal Area of the Baltic Sea. *Limnology and Oceanography* 39: 880–896.

Carman R. & Jonsson P. 1991. Distribution patterns of different forms of phosphorus in some surficial sediments of the Baltic Sea. *Chemical Geology* 90: 91–106.

Conley D.J., Humborg C., Rahm L., Savchuk O.P. & Wulff, F. 2002. Hypoxia in the Baltic Sea and Basin-Scale Changes in Phosphorus Biogeochemistry. *Environ. Sci. Technol.* 36: 5315–5320.

Delaney M.L. 1998. Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle. *Global Biogeochemical Cycles* 12: 563–572.

Emeis K.C., Struck U., Leipe T., Pollehne F., Kunzendorf H. & Christiansen C. 2000. Changes in the C, N, P burial rates in some Baltic Sea sediments over the last 150 years – relevance to P regeneration rates and the phosphorus cycle. *Marine Geology* 167: 43–59.

Faas R.W. & Carson B. 1988. Short-term deposition and long-term accumulation of lagoonal sediment, Great Sount, New Jersey. *Marine Geology* 82: 97–112.

Faul K.L., Paytan A. & Delaney M.L. 2005. Phosphorus distribution in sinking oceanic particulate matter. *Marine Chemistry* 97: 307–333.

Håkanson L. & Jansson M. 1983. *Principles of lake sedimentology*. Springer-Verlag, Berlin Heidelberg.

Heiskanen A.S. & Tallberg P. 1999. Sedimentation and particulate nutrient dynamics along a coastal gradient from a fjord-like bay to the open sea. *Hydrobiologia* 393: 127–140.

Hille S., Nausch G. & Leipe T. 2005. Sedimentary deposition and reflux of phosphorus (P) in the eastern Gotland Basin and their coupling with P concentrations in the water column. *Oceanologica* 47: 663–679.

Hingston F.J., Atkinson R.J., Posner A.M. & Quirk J.P., 1967: Specific adsorption of anions. Nature 215: 1459–1461.

Jensen H.S. & Thamdrup B. 1993. Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia* 253: 47–59.

Jensen H.S., Mortensen P.B., Andersen F.O., Rasmussen E. & Jensen A. 1995. Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Limnology and Oceanography* 40: 908–917.

Jilbert, T. & Slomp, C.P. 2012. Iron and manganese shuttles control the formation of authigenic phosphorus minerals in the euxinic basins of the Baltic Sea. *Geochim. Cosmochim. Acta* 107: 155–169.

Jilbert, T., Slomp, C.P., Gustafsson, B.G. & Boer, W. 2011. Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles. *Biogeosciences* 8: 1699–1720.

Jonsson P. & Carman R. 1994. Changes in sediment deposition of organic matter and nutrients in the Baltic Sea during the twentieth century. *Mar. Pollut. Bull.* 28: 417–426.

Jonsson P. (Ed.), Persson J. & Holmberg P. 2003. In Swedish: *The seafloor of the archipelagos*. Swedish Environmental Protection Agency Report No: 5212. ISBN 91-620-52512-8.

Jumppanen K. & Mattila J. 1994. *Saaristomeren tilan kehitys ja siihen vaikuttavat tekijät* The development of the state of the Archipelago Sea and environmental factors affecting it (In Finnish, English summary) J. Mattila, ed., Turku, Finland: Lounais-Suomen vesiensuojeluyhdistys Julk 82.

Kankaanpää H., Korhonen M., Suortti A.M. & Heiskanen A.S. 1997. Seasonal sedimentation of organic matter and contaminants in the Gulf of Finland. *Boreal Env. Res*. 2: 257–274.

Kohonen T., Korpinen P., Inkala A. & Engqvist A. 2008. BEVIS II *Report Internal loading of phosphorus. Model modifications to the bottom loads and scenario calculations.* Husö biologiska station, Åbo Akademi. Available at: http://web.abo.fi/fak/mnf/biol/huso/bevis/BEVIS2_report_Kohonen%20et%20al_web.pdf

Kozerski H.P. 1994. Possibilities and limitations of sediment traps to measure sedimentation and resuspension. *Hydrobiologia* 284: 93–100.

Laakkonen, A., Mälkki, P. & Niemi, Å. 1981. Studies on the sinking, degradation and sedimentation of organic matter off Hanko peninsula, entrance to the Gulf of Finland, in 1979 (Progress report). *Meri*, No. 9, 3–42.

Leivuori, M. 2000. *Distribution and accumulation of metals in sediments fo the northern Baltic Sea.* Finnish Institute of Marine Research, No. 2, (PhD dissertation), 43 p.

Leppänen, J.M. 1988. Cycling of organic matter during the vernal growth period in the open northern Baltic Proper. VI. Sinking of particulate material. *Finnish Marine Research* 255:97–118.

Lignell R., Heiskanen A.S., Kuosa H., Gundersen K., Kuuppo-Leinikki P., Pajuniemi R. & Uitto A. 1993. Fate of a phytoplankton spring bloom: sedimentation and carbon flow in the planktonic food web in the northern Baltic. *Mar. Ecol. Prog. Ser.* 94: 239–252.

Lin P., Guo L., Chen M., Tong J. & Lin F. 2012. The distribution and chemical speciation of dissolved and particulate phosphorus in the Bering Sea and the Chukchi–Beaufort Seas. *Deep-Sea Research II* 81-84: 79–94.

Lukkari K., Leivuori M. & Kotilainen A. 2009a. The chemical character and behaviour of phosphorus in poorly oxygenated sediments from open sea to organic rich inner bay in the Baltic Sea. *Biogeochemistry* 96: 25–48.

Lukkari K., Leivuori M., Vallius H. & Kotilainen A. 2009b. The chemical character and burial of phosphorus in shallow coastal sediments in the northeastern Baltic Sea. *Biogeochemistry* 94: 141–162.

Malmaeus M. & Karlsson M. 2016. Comparing the phosphorus regime in soft sediments from two sub-systems of the Baltic Sea with different redox conditions. *Journal of Water Management and Research* 72: 31–40.

Malmaeus J.M., Rydin E., Jonsson P., Lindgren D. & Karlsson O.M. 2012. Estimating the amount of mobile phosphorus in Baltic coastal soft sediments of central Sweden. *Boreal Environment Research* 17: 425–436.

Mort H.P., Slomp C.P., Gustafsson B.G. & Andersen T.J. 2010. Phosphorus recycling and burial in the Baltic Sea sediments with contrasting redox concentrations. *Geochimica et Cosmochimica Acta* 74: 1350–1362.

Mortimer C.H. 1971. Chemical exchanges between sediments and water in the Great Lakes – speculations on probable regulatory mechanisms. *Limnology and Oceanography* 16: 387–404.

Murphy J. & Riley J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31–36.

Penn M.R. & Auer M.T. 1997. Seasonal variability in phosphorus speciation and deposition in a calcareous, eutrophic lake. *Marine Geology* 139: 47–59.

Psenner R., Boström B., Dinka M., Pettersson K. & Puckso R. 1988. Fractionation of suspended matter and sediment. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* 30: 98–103.

Psenner R., Pucsko R. & Sager M. 1984. Die Fraktionierung organischer und anorganischer Phoshorverbindungen von Sedimenten. Versuch einer Definition ökologisch wichtiger Fraktionen. *Arch. Hydrobiol.* Suppl. 70: 111–155.

Puttonen I., Mattila J., Jonsson P., Karlsson O.M., Kohonen T., Kotilainen A., Lukkari K., Malmaeus J.M. & Rydin E. 2014. Distribution and estimated release of sediment phosphorus in the northern Baltic Sea archipelagos. *Estuarine, Coastal and Shelf Science* 145: 9–21.

Ruttenberg K.C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography* 37: 1460–1482.

Ruttenberg K.C. 2003. The Global P Cycle. In: Schlesinger W.H. (ed). *Treatise on Geochemistry*, 8 (Executive Eds. Holland H.D. and Turekian K.K., pp. 682, Elsevier, pp. 585–643.

Rydin E., Malmaeus J.M., Karlsson O.M. & Jonsson P. 2011. Phosphorus release from coastal Baltic Sea sediments as estimated from sediment profiles. *Estuarine, Coastal and Shelf Science* 92: 111–117.

Rytkönen J., Kohonen T. & Virtasalo J. 2001. *Laivaliikenteen aiheuttama eroosio Pohjois-Airistolla.* (In Finnish) (Ship-induced erosion in the northern Airisto). Vesitalous 3/2001, 30–36. Available at: www.vesitalous.fi/wp-content/uploads/2010/04/3-2001.pdf

Stigebrandt A. 2018. On the response of the Baltic proper to changes of the total phosphorus supply. *Ambio* 47: 31–44. doi: 10.1007/s13280-017-0933-7

Storlazzi C.D., Field M.E. & Bothner M.H. 2011. The use (and misuse) of sediment traps in coral reef environments: theory, observations, and suggested protocols. *Coral Reefs* 30: 23–38.

Szmytkiewicz A. & Zalewska T. 2014. Sediment deposition and accumulation rates determined by sediment trap and 210Pb isotope methods in the Outer Puck Bay (Baltic Sea). *Oceanologia* 56: 85–106.

Virtasalo J.J., Kohonen T., Vuorinen I. & Huttula T. 2005. Sea bottom anoxia in the Archipelago Sea, northern Baltic Sea — implications for phosphorus remineralization at the sediment surface. *Marine Geology* 224: 103–122.

Wallin M. & Håkanson L., 1992. Morphometry and sedimentation as regulating factors for nutrient recycling and trophic state in coastal waters. *Hydrobiologia* 235: 33–45.

Wulff F., Rahm L., Hallin A.K. & Sandberg J. 2001. A Nutrient Budget Model of the Baltic Sea. In F. V Wulff, L. A. Rahm, and P. Larsson, eds. *A Systems Analysis of the Baltic Sea*. Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 353–372.