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# Factors controlling phosphorus release from sediments in coastal archipelago areas

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## Abstract

In coastal archipelago areas of the northern Baltic Sea, significantly higher phosphate concentrations ( $6.0 \pm 4.5 \mu\text{mol/l}$ , mean  $\pm$ SD) were measured in water samples close to the sediment surface compared with those from 1 m above the seafloor ( $1.6 \pm 2.0 \mu\text{mol/l}$ ). The results indicated notable phosphate release from sediments under the bottom water oxygen concentrations of up to  $250 \mu\text{mol/l}$ , especially in areas that had experienced recent temporal fluctuation between oxic and hypoxic/anoxic conditions. No single factor alone was found to control the elevated  $\text{PO}_4\text{-P}$  concentrations in the near-bottom water. In addition to the oxygen in the water, the contents of potentially mobile phosphorus fractions, grain-size, the organic content at the sediment surface, and the water depth were all important factors controlling the internal loading of phosphorus. The complexity of this process needs to be accounted for in assessments of the internal loading of phosphorus and in potential mitigation plans.

Keywords: Baltic Sea, internal loading, sediment, phosphorus fractions, coastal zone, hypoxia

# 1. Introduction

Coastal waters throughout the world are strongly influenced by human activities, and nutrients from terrestrial runoff often cause major problems (Smith, 2003, Diaz and Rosenberg, 2008). In many areas, nutrient enrichment has led to increased biological production (Kennish and Townsend, 2007, Diaz and Rosenberg, 2008) and, as a consequence, to increased accumulation of organic matter in the sediments (Emeis et al., 2000). In addition to the effects of external nutrient sources, recycling of phosphorus (P) through sediments, referred to as internal loading, has considerable impacts on coastal eutrophication (Conley et al., 2002, Rydin et al., 2011, Puttonen et al., 2014). Augmented degradation of organic matter enhances oxygen consumption causing hypoxia in stratified coastal waters (Diaz and Rosenberg, 2008). Oxygen depletion induces dissolution of iron-(oxy)hydroxides resulting in the release of iron-bound P (Mortimer, 1941, Boström et al., 1988, Ingall and Jahnke, 1994). This additional supply of P supports enhanced growth of particularly nitrogen-fixing cyanobacteria (Tyrrell, 1999, Vahtera et al., 2007, Conley et al., 2009, Funkey et al., 2014). Nitrogen fixation results in more nitrogen being introduced into the system, thus also sustaining eutrophication (Westman et al., 2003, Conley et al., 2009).

Phosphorus release from sediments driven by anoxia is widely described in deep, permanently anoxic basins, where hydrodynamic conditions are steady, and sediment accumulation is continuous (e.g. Conley et al., 2002, Funkey et al., 2014). There are few studies of P cycling processes in shallow coastal and archipelago sediments, even though the environmental conditions differ from those in deep marine basins. Internal P cycling in shallow coastal areas is also assumed to play a notable role in eutrophication (Rydin et al., 2011), but the controlling factors may be

different from those in deep areas. In shallow temperate waters, although the halocline can be lacking, a thermal stratification is created during the summer months by the rising temperatures warming up the surface water. Organic matter originated from high primary production, and subsequent degradation of it increases oxygen consumption in the bottom. Oxygen supply from the surface layer and adjacent areas is hindered due to restricted vertical and horizontal water exchange. In coastal stratified waters of high productivity, seasonal hypoxia developed by biochemical processes is a typical phenomenon (Rowe, 2001, Connolly et al., 2010). In contrast to deep anoxic basins, where hydrodynamic conditions are stable, waves and bioturbation make sedimentary conditions fluctuate in coastal areas, and sediment accumulation rates are widely variable (Mattila et al., 2006). Excessive anthropogenic nutrient loading leads to high contents of P in the sediments (Emeis et al., 2000, Rabalais et al., 2007). Further field studies in shallow marine areas are needed to understand the role of various environmental factors and their interactions concerning P cycling between sediments and water.

In the Baltic Sea eutrophication is one of the major environmental concerns, and the current, primary remediation method is reduction in anthropogenic nutrient input (Carstensen et al., 2006, Heisler et al., 2008, HELCOM, 2014). Although external inputs of both nitrogen and P to the Baltic Sea have been considerably reduced during the last two decades, nutrient levels in the water have not markedly decreased, and the Baltic Sea is still highly affected by eutrophication (HELCOM, 2014). The delayed response to the reductions in external nutrient loading can be attributed partly to P remobilization from the sediments, as the release of P from the sediments creates a self-supporting cycle maintaining a high trophic level even decades after reductions in the anthropogenic nutrient input (Eilola et al., 2009).

The aim of this field study was to estimate the intensity and causes of P release during summer months from soft, organic-rich sediments into the water column in a shallow eutrophied coastal area, in the Archipelago Sea region of the northern Baltic Sea. The study assesses the following: the role of oxygen and temperature in the near-bottom water, the total P and potentially mobile P forms, the grain-size distribution and organic content at the sediment surface, and the water depth and exposure to wave action in relation to P concentrations in the near-bottom water.

## 2. Materials and methods

### 2.1. Study area

Our study area, the Archipelago Sea, is located in the part of, in the south-western part of Finland, in the northern Baltic Sea (Fig. 1). It is a shallow brackish-water sub-basin with an average depth of 23 m and salinity between 5 and 7 in the study area. The Archipelago Sea is characterized by a mosaic of thousands of islands and skerries. In the shelter of the numerous islands, accumulation of fine-grained sediments can take place in fairly shallow waters, while deeper areas may experience erosion due to strong bottom currents (Virtasalo et al., 2005).

The water in the Archipelago Sea is thermally stratified during the summer months, and seasonal hypoxia, with declining oxygen concentrations towards late summer, is a common phenomenon (Virtasalo et al., 2005). The area and intensity of hypoxia are increasing because of anthropogenic pressure (Conley et al., 2011). The ecological conditions in the southern and south-western coastal waters of Finland have deteriorated due to human activities (Putkuri et al., 2013). Despite the shallow water depth, an almost continuous accumulation of fine-grained and organic-rich sediment occurs in numerous small basins within the shelter of the islands (Virtasalo

et al., 2005). The accumulation rate in the inner archipelago varies from 0.7–2.3 cm yr<sup>-2</sup> inferred from <sup>137</sup>Cs dating and sediment lamina couplet counting (Nordmyr, 2002, Jokinen et al., 2015). Water mixing is restricted both horizontally and vertically due to the abundance of islands and temporal water stratification. Consequently, much of the nutrients transported from the land and by currents from the Baltic Proper and the Gulf of Finland are used in biological production or trapped in the sediments in the Archipelago Sea, rather than carried further by the currents. For this reason, the Archipelago Sea has been said to act as a filter for nutrients (Mälkki et al., 1979, Jumppanen and Mattila, 1994). The content of P in the sediments is high, and a major part of this can be transformed into a bioavailable form (Virtasalo et al., 2005, Puttonen et al., 2014). Thus, the sediments compose an extensive source of potential P release in the area.

[FIG. 1; 2-column]

## **2.2. Sampling of the sediment and water**

Sediment and water samples were retrieved at 39 sampling stations in the Archipelago Sea in Finland (Fig. 1) during June–September 2010, 2011 and 2012 on board the R/V Geomari and the R/V Muikku. It is not possible to use the water depth alone to estimate the spatial distribution of different sedimentary areas on the seafloor, i.e. the areas of accumulation, transportation, and erosion (Kohonen and Winterhalter, 1999, Virtasalo et al., 2005). Therefore, the sampling stations were selected with an acoustic sub-bottom profiler to ensure that the samples represent seafloor areas where sediment accumulation is present. The water depth at the sampling stations varied between 4–81 m. Sediment samples were collected with a Gemax gravity corer (two cylinders with acrylic liners, the inner diameter 9 cm). The

surface layer, 0–2 cm, was recovered and sealed in a plastic bag for subsequent laboratory analyses. Selected sediment cores were split lengthwise into two halves for a visual inspection of the sediment characteristics in the sediment profile. The sediment surface samples were stored under refrigeration (below +5° C) until the chemical analyses, which were conducted within two weeks of the sampling.

The water samples were collected at the same stations together with the sediment samples, at 1 m above the bottom and in the sediment corer. At each station, a volume of ca. 0.5 l water was collected 1 m above the sediment surface with a Limnos water sampler. Another set of water samples was taken in the sediment corer immediately after recovering the core. These samples with a volume of 0.3-0.5 l were siphoned with a rubber hose above the sediment surface in the corer. The water height in the sampling equipment above the sediment was approximately 15–30 cm, and care was taken to avoid sediment disturbance when recovering the water. Slow lowering of the sediment sampling device allowed a negligible degree of sediment surface disturbance, minimizing secondary turbulence in the water samples. Henceforth, the term 'near-bottom water' will be used for the water samples extracted from the sediment corer.

We examined the differences in oxygen (O<sub>2</sub>) and phosphate (PO<sub>4</sub>-P) concentrations in the near-bottom water and 1 m above the seafloor. The P flux from the sediment to the overlying water was assumed to be observed as an elevated phosphate concentration in the near-bottom water.

The amounts of potentially mobile P forms at the sediment surface were determined and compared with the oxygen and PO<sub>4</sub>-P concentrations in the overlying water.

### **2.2.1. Sediment analyses**

The physical and chemical methods for the sediment analyses are described here only briefly.

Organic matter content was quantified from one gram of dried sediment as weight loss on ignition after 550° C for two hours (LOI, % of dry weight [dw]). The total P content ( $\mu\text{g P g}^{-1} \text{ dw}$ ) was analysed as phosphate after acid hydrolysis at 340° C (Murphy and Riley, 1962). Phosphorus forms were determined following, in principle, the sequential P extraction method proposed by Psenner et al. (1988). The extracted P fractions have been operationally defined but, ideally, each fraction corresponds to a specific binding or solubility form of P within the sediment. Accordingly, the P fractions can be divided roughly into potentially mobile and immobile P pools in the sediment (Lukkari et al., 2007, Rydin et al., 2011, Puttonen et al., 2014).  $\text{NH}_4\text{Cl-P}$ , denoted here as 'loosely bound P' (see Puttonen et al., 2014), BD-P ('Fe-P') and NaOH-nrP ('unreactive P'), which represents the potentially mobile P forms, whereas NaOH-rP, HCl-P and residual P calculated as the difference between total P and the extracted fractions, can be regarded as immobile P fractions. The sediment P contents are expressed as  $\mu\text{g P g}^{-1} \text{ dw}$ . The water content of the sediments was determined by freeze-drying, and the results are reported as a percentage of the wet weight (% ww). Since many of the sediment surfaces were loose and contained a considerable amount of water, the water content values are not used in any analyses (*sensu* Virtasalo et al. 2005). A more detailed description of the physical and chemical methods used for the sediment analyses can be found e.g. in Puttonen et al. (2014).

The grain size distribution was determined by the hydrometric method (Elonen, 1971). To remove the organic matter, the sediment samples were treated prior to the hydrometric analyses with a solution of 30%  $\text{H}_2\text{O}_2$  until the frothing ceased.



Approximately 10 g of dry sediment was weighed out for the analysis, and 200 ml deionized water and 100 ml 0.05 M  $\text{Na}_4\text{P}_2\text{O}_7$  solution was added, then the samples were placed over night on a shaker table to prevent particle flocculation. Grain size distribution is expressed as percentages of sand ( $\text{Ø} > 50 \mu\text{m}$ ), silt (2–50  $\mu\text{m}$ ) and clay ( $< 2 \mu\text{m}$ ). Water content, LOI and P analyses were performed by the Erken Laboratory, Uppsala University, Sweden, which has the P fractionation procedure accredited by the SWEDAC (the Swedish board for accreditation and conformity assessment). Grain-size distributions were analysed at Åbo Akademi University.

We inspected the sediment cores visually to infer the conditions at the sediment surface and in the near past at the sampling station. Each station was classified as oxic, suboxic or anoxic in the same manner as in Virtasalo et al. (2005) (Fig. 2). Oxic stations were identified by a 10–50 mm thick brown oxidized layer at the sediment surface, the homogeneous structure of the sediment profile, traces of abundant bioturbation (Gutiérrez et al., 2000, Smith et al., 2000) and a light brown colour with no or very little black sulfidic sediment below the surface layer. A brown colour is indicative of iron(III)-(oxy)hydroxides. Anoxic stations were identified by the dark grey or black colour of the sediment surface, a characteristic of reduced iron(II) monosulphides (Mortimer, 1941). The profiles displayed pronounced layers, or were completely black, and they had the distinctive smell of  $\text{H}_2\text{S}$ . The stations where the sediment profiles had typical features of both the oxic and anoxic stations were classified as suboxic stations. They were recognized by a thin (2–10 mm), brown oxidized layer at the surface, and black, sulfidic sediment below the oxidized surface layer. Despite the thin, oxic sediment surface, those sediment profiles often contained distinguishable layers as an indicator of diminished bioturbation, which was interpreted as suggesting an oxygen deficiency.

[FIG. 2, 2-column]

### **2.2.2. Water analyses**

The temperature was determined using a thermometer attached to the Limnos water sampler at each sampling station 1 m above the bottom. The PO<sub>4</sub>-P concentrations in the water were determined with a spectrophotometric method in the Erken Laboratory in the samples collected in 2010 and 2011. The oxygen concentrations were determined with a WTW Cellox 325 oxygen sensor, either in the water column or in the sampling equipment immediately after retrieving the samples. The PO<sub>4</sub>-P concentrations in the samples collected in 2012 were determined using a spectrophotometric method and the oxygen concentrations by Winkler titration immediately after sampling in the laboratory of R/V Muikku. The concentrations are expressed as moles per litre (mol l<sup>-1</sup>).

### **2.3. Statistical analyses**

All the analysed variables were tested for normality of error with a One-Sample Kolmogorov-Smirnov test and for homogeneity of variances with Levene's test in IBM SPSS Statistics 21 software prior to statistical tests. When necessary, the data were log-transformed to meet the assumptions of parametric analyses. A paired sample t-test was conducted to compare the PO<sub>4</sub>-P and oxygen concentrations in the water 1 m above the bottom and near-bottom water. A paired sample t-test is a parametric test to compare the means of two groups in matched pairs.

The differences in PO<sub>4</sub>-P and oxygen concentrations in the near-bottom water between the oxic, suboxic, and anoxic stations were explored with a one-way ANOVA, followed by Tukey's post-hoc test. ANOVA is an analysis of variance, and the aim is to find possible differences among the group mean values. F-ratio is the

result of ANOVA;  $F = 1$  designates that the group means do not deviate from the mean of all variables. A large F-ratio means that the differences among the group mean values are larger than would be expected by chance. The degrees of freedom are reported in parentheses after the F-ratio. The post-hoc test compares the mean values of each group pair wise, exploring which groups are significantly different from each other. The P value is the probability of finding the observed values when the null hypothesis is true. We used critical p value 0.05 for rejecting the null hypothesis in all statistical tests (see further in e.g. Grafen and Hails, 2002).

The Principal Component Analysis (PCA) in PRIMER 6 software was applied to explore which variables best explain the similarity of the sampling stations, and to interpret which factors direct the concentrations of oxygen and  $\text{PO}_4\text{-P}$  in the water. Hierarchical clustering with Euclidean distance as the measure of resemblance was applied to examine grouping factors in the data. The variables included in the PCA and cluster analyses were the wave exposure index (simplified wave model, Isæus, 2004), the water depth, LOI, grain size as a percentage of clay, the extracted 'loosely bound P', 'Fe-P', 'unreactive P' fractions, the  $\text{PO}_4\text{-P}$  concentration, the oxygen concentration, and the temperature in the near-bottom water. The wave exposure index depicts the exposure to waves and wind at a given location, and it is widely used for marine habitat classification. The index is derived from SWM developed by Isæus (2004), and it is based on a ten-year average wind speed and the distance over which the wind blows to a given location (fetch). The 25 m resolution wave exposure grid was provided by the Finnish Environment Institute. The variables were normalised by rescaling them to a mean value 0 and a dispersion of 1 before running the PCA in order to eliminate the influence of the differences in scales. The factor

loadings with an absolute value  $> 0.300$  and 80% of the variance explained by the principal components were included in the interpretation of the PCA.

PCA is a multivariate technique to reduce the dimensions in a large set of variables by grouping the original variables into a smaller number of variables, called principal components (PCs). The goal of the PCA is to explore similarity patterns among the variables. Variables that correlate with each other are included in the same PC, and the PCs do not correlate with each other. The values of the factor loadings are the correlation coefficients between the original variables and the components. The plus or minus sign expresses the direction of the variable on the PC axis; a plus sign means a growing value of the variable as the value of the PC axis increases, and a minus sign is the opposite. The eigenvectors show the direction and magnitude of each variable in the PC co-ordinates. A detailed description of PCA can be found e.g. in Abdi and Williams (2010). Hierarchical Clustering is a multivariate technique to find similarity patterns in the set of variables (see further in e.g. Kaufman and Rousseeuw, 2009).

Pearson correlation coefficients ( $r$ ) were calculated to test for correlation between the  $\text{PO}_4\text{-P}$  and oxygen concentrations in the near-bottom water respective to the P forms at the sediment surface.

Mean values ( $\bar{x}$ )  $\pm$  1 standard deviation (SD) were calculated for the results of the measured physical and chemical variables of the sediment and water samples.

### 3. Results

The oxygen concentrations in the near-bottom water varied across all the sampling stations between  $10 - 411 \mu\text{mol l}^{-1}$ , and the measured  $\text{PO}_4\text{-P}$  concentrations were

between 0.42 – 14.3  $\mu\text{mol l}^{-1}$ . The concentrations of  $\text{PO}_4\text{-P}$  were statistically significantly higher in the near-bottom water ( $\bar{x}_{\text{bottom}} = 6.06 \pm 4.49 \mu\text{mol l}^{-1}$ ; mean  $\pm$  SD) than in the water 1 m above the bottom ( $\bar{x}_{1\text{m}} = 1.63 \pm 2.06 \mu\text{mol l}^{-1}$ ;  $t(37) = 7.052$ ;  $p < 0.0001$ ). However, the difference in the oxygen concentrations between near-bottom water and the water 1 m above the bottom was statistically non-significant ( $\bar{x}_{\text{bottom}} = 215 \pm 88 \mu\text{mol l}^{-1}$ ;  $\bar{x}_{1\text{m}} = 217 \pm 80 \mu\text{mol l}^{-1}$ ;  $t(38) = 0.530$ ;  $p > 0.1$ ; Fig. 3).

[FIG. 3; 1.5-column]

Four of the total 39 sediment stations were classified as anoxic, seven stations were classified as oxic, and twenty-eight stations were classified as suboxic. The mean values  $\pm$  1 SD of the measured variables were calculated separately in the three groups of stations (Table 1).

[TABLE 1]

At the oxic stations,  $\text{PO}_4\text{-P}$  concentrations in the near-bottom water varied between 0.42–3.38  $\mu\text{mol l}^{-1}$ , whereas at suboxic stations  $\text{PO}_4\text{-P}$  concentrations were between 0.97–14.29  $\mu\text{mol l}^{-1}$ .  $\text{PO}_4\text{-P}$  concentrations of 7.75–14.08  $\mu\text{mol l}^{-1}$  in the near-bottom water were obtained at the anoxic stations. There was a statistically significant difference in  $\text{PO}_4\text{-P}$  concentration in the near-bottom water among oxic, suboxic, and anoxic stations as determined by the one-way ANOVA ( $F(2,36) = 18.594$ ,  $p < 0.00001$ ). The Tukey's post-hoc test revealed that the  $\text{PO}_4\text{-P}$  concentrations were higher at suboxic ( $\bar{x} = 6.51 \pm 4.08 \mu\text{mol P l}^{-1}$ ,  $p < 0.0001$ ) or anoxic ( $\bar{x} = 11.42 \pm 2.85 \mu\text{mol P l}^{-1}$ ,  $p < 0.0001$ ) stations compared to oxic stations ( $\bar{x} = 1.27 \pm 1.13 \mu\text{mol P l}^{-1}$ ). There was no statistically significant difference between anoxic and suboxic stations (Fig. 4). In addition, the oxygen concentrations in the near-bottom water were statistically significantly different among the groups of oxic, suboxic and anoxic

stations (ANOVA  $F(2,36) = 28.773$ ,  $p < 0.00001$ ). The oxygen concentrations were higher at the oxic stations ( $\bar{x} = 316 \pm 43.3 \mu\text{mol O}_2 \text{ l}^{-1}$ ) than at the suboxic ones ( $\bar{x} = 213 \pm 60.2 \mu\text{mol O}_2 \text{ l}^{-1}$ ;  $p < 0.001$ ), and higher at the suboxic than at the anoxic stations ( $\bar{x} = 48.7 \pm 39.8 \mu\text{mol O}_2 \text{ l}^{-1}$ ,  $p < 0.0001$ ).

[FIG. 4; 1.5-column]

The mean LOI at the sediment surface across all sampling stations was  $11 \pm 3.5\%$  dw, the clay content was  $\bar{x} = 60 \pm 12\%$ , and the water content was  $\bar{x} = 80 \pm 6.6\%$  ww. The total P content varied between 800 and 3100  $\mu\text{g P g}^{-1}$  dw, with a mean value of  $1682 \pm 537 \mu\text{g P g}^{-1}$  dw. The mean 'loosely bound P' content was  $26 \pm 20 \mu\text{g P g}^{-1}$  dw, 'Fe-P' content was  $\bar{x} = 656 \pm 354 \mu\text{g P g}^{-1}$  dw, and 'unreactive P' content was  $\bar{x} = 285 \pm 126 \mu\text{g P g}^{-1}$  dw.

LOI was found to be a strong explanatory variable of the similarity groups created by the Hierarchical Cluster analysis (Fig. 5).

[FIG. 5; 2-column]

In the PCA analysis, the first two principal components (PC's) explained 71.8% of the total variation in the data (Fig. 6). The PC1 explained 48.2% with the highest coefficients for organic matter, 'loosely bound P' and 'unreactive P' fractions at the sediment surface, wave exposure, water depth and temperature in the near-bottom water. The PC2 was composed of 'Fe-P' and grain size at the sediment surface, and concentrations of  $\text{PO}_4\text{-P}$  and oxygen in the near-bottom water (Table 2), explaining 23.6% of the variation. The PC3 was composed of the sediment variables LOI, grain size, and potentially mobile P fractions (Table 2), explaining 9.2% of the variation.

The loadings of all the included factors in each PC were of even levels (absolute values 0.343–0.514).

[FIG. 6; 2-column]

[TABLE 2]

Negative correlations with PO<sub>4</sub>-P were determined for oxygen concentration in the near-bottom water ( $r = - 0.611$ ,  $p < 0.0001$ ) and LOI ( $r = - 0.546$ ,  $p < 0.001$ ) (Fig. 7), and 'unreactive P' ( $r = - 0.480$ ,  $p = 0.002$ , not shown in the figure) at the sediment surface. There was a positive correlation between PO<sub>4</sub>-P in the near-bottom water and the sediment clay content ( $r = 0.489$ ,  $p = 0.002$ ; Fig. 7). The error variances of PO<sub>4</sub>-P concentrations were heterogeneous. No further regression analysis was applicable, since the assumption of homoscedasticity, required for regression analysis, was not met. Correlation between 'Fe-P' at the sediment surface and oxygen concentration in the near-bottom water was statistically non-significant ( $p > 0.05$ ; Fig. 7). Furthermore, the difference in 'Fe-P', as well as LOI, among the oxic, suboxic and anoxic stations was statistically non-significant ( $p > 0.05$ ).

[FIG. 7; 2-column]

## 4. Discussion

The deepest water samples are commonly collected approximately 1 m above the seafloor (e.g. Gunnars and Blomqvist, 1997, Conley et al., 2011). The observed, significantly higher PO<sub>4</sub>-P concentrations in the near-bottom water compared with those 1 m above the bottom, indicate P release from the sediments. Phosphate in the water layers close to the bottom may, to some degree, also originate from the decomposition of organic material in the settling seston. During the study period

(June – September) the  $\text{PO}_4\text{-P}$  concentration in the surface water was typically between  $0.06\text{--}0.65 \mu\text{mol P l}^{-1}$  within the entire study area in 2012. Chlorophyll-*a* concentration in the surface water varied between  $2\text{--}83 \mu\text{g l}^{-1}$ , and 95% of the measurements were between  $2\text{--}20 \mu\text{g l}^{-1}$  (Hertta database, 2014). During this period the thermocline at approximately 15–25 m depth (Virtasalo et al., 2005) prevents vertical mixing of waters and dilution with the surface water, and thus we believe that the sediment was the major source of the elevated  $\text{PO}_4\text{-P}$  concentrations in the near-bottom waters. At our sampling stations (the samples taken in August–September 2012) we observed a thermocline at 12–20 m depth. The strength of the thermocline varied, and the thickness was from 2 to 10 meters. The temperature difference above and below the thermocline was  $5\text{--}9^\circ \text{C}$ . The water quality monitoring data from the study area indicated that in 2012 the thermocline was well developed in late June and became stronger until the surface water temperature started to decrease in September (Hertta database, 2014). Our results imply that measurements of  $\text{PO}_4\text{-P}$  concentrations from 1 m above the bottom reflect poorly the conditions at the sediment-water interface. Although P is evidently leaking from the sediment to the overlying water, the effect is not measurable from 1 m above the sediment surface. Schemes for routine monitoring of the environment (e.g. Ferreira et al., 2007, Hultcrantz and Skjevik, 2011, Ministry of the Environment of Finland, 2014) and also for serious scientific research studies (e.g. Naqvi et al., 2010, Conley et al., 2011) often use measurements from 1 m or more above the sediment surface as the deepest measure points. This is to avoid resuspension and turbidity in the water by the sampling equipment and to protect the equipment from breaking by hitting the sediment surface. However, when the vertical decline of oxygen concentration is steep, due to extensive oxygen consumption by the degradation of organic matter,



oxygen and P concentrations may differ essentially from those in the water close to the sediment surface (Gunnars and Blomqvist, 1997). Thus, the results from most studies may considerably underestimate PO<sub>4</sub>-P concentrations in the near-bottom waters and also the effects of P release from the sediments. Based on our results, we calculated the difference between the PO<sub>4</sub>-P concentrations measured from 1 m above the bottom and from the near-bottom water. If half of the amount of P in the one-meter thick bottom water layer had been released from the sediments, this would mean a release of approximately 245 tonnes of P from the soft, organic-rich sediments in our study area of ca. 6300 km<sup>2</sup>. Water mixing by heavy storms or by a disappearance of the thermocline in the autumn may bring some of the dissolved PO<sub>4</sub>-P to the surface water, where it becomes available for phytoplankton production. Some of it may also be trapped in the Fe-P pool at the sediment surface, as the oxygenated surface waters reach the bottom. However, a vertical decline of P downwards in the sediments suggests P is released from the sediment surface over time (Rydin et al., 2011, Puttonen et al., 2014).

It has been suggested that the term 'suboxic sediment' be abandoned to avoid confusion and inconsistency of the terminology (Canfield and Thamdrup, 2009). Accordingly, the stations with an oxic surface, classified here as 'suboxic', should probably be termed 'oxic'. To be exact, the classification of the sediments would require pore water analysis for chemical zonation within the sediments. We show here, however, that the stations that appeared to be oxic at the surface, but where indications of recent occurrence of hypoxic or anoxic events were observed in the sediment profile, differed from the permanently oxic stations. For this reason we decided to use the term 'suboxic sampling station'.

Clearly elevated  $\text{PO}_4\text{-P}$  concentrations ( $> 6 \mu\text{mol l}^{-1}$ ) were measured at stations with hypoxic bottom water, defined here as dissolved oxygen of  $< 63 \mu\text{mol l}^{-1}$  ( $< 2 \text{ mg O}_2 \text{ l}^{-1}$ ) (Vaquer-Sunyer and Duarte, 2008). This indicates the reduced capacity of the sediment to retain P. It is notable, however, that considerably high concentrations of  $\text{PO}_4\text{-P}$ ,  $> 3 \mu\text{mol l}^{-1}$ , were also observed in the near-bottom water in the oxygen conditions, which were well above the hypoxia level (Fig. 7). At the suboxic stations, the range of the observed  $\text{PO}_4\text{-P}$  concentrations was wide,  $0.97\text{--}14.3 \mu\text{mol l}^{-1}$ , but at the oxic stations, the observed maximum  $\text{PO}_4\text{-P}$  concentration was  $3.0 \mu\text{mol l}^{-1}$ . Hence, our results show that extensive release of P from the sediments occurs not only in the presence of bottom water hypoxia or anoxia, but even when oxygen is present in the near-bottom water and the sediment surface is oxic. The suboxic stations coincided with the near-bottom water oxygen concentrations of  $125\text{--}250 \mu\text{mol O}_2 \text{ l}^{-1}$ . Accordingly, bottom water hypoxia, defined as an oxygen concentration of  $< 63 \mu\text{mol l}^{-1}$ , is not a sufficient indicator to reliably estimate P release from the sediments.

The majority of the sampling stations with an oxic sediment surface layer and oxygen concentration above  $63 \mu\text{mol l}^{-1}$  in the near-bottom water were classified as suboxic. The tolerance of hypoxia may vary among benthic species and communities, but bottom water oxygen concentrations exceeding  $63 \mu\text{mol l}^{-1}$  are often considered 'normoxic' conditions (Diaz and Rosenberg, 1995). Examining the deeper layers of the sediments revealed that many of the stations with normoxic bottom water conditions showed signs of the fact that in the near past oxygen deficiency had been experienced. Suboxic stations were found across the entire water depth range studied. Moreover, the  $\text{PO}_4\text{-P}$  concentrations in the near-bottom water at the suboxic stations were significantly higher than at the stations that appeared permanently

oxic. Classification of the sediment profiles based merely on the visual characteristics is only suggestive. A more exact classification could be done by defining the geochemical and/or metabolic zones in the sediments through chemical analyses. Nevertheless, our approach demonstrates that when signs of oxygen depletion in the near past were observed, the sediments had a reduced capacity to retain P. Thus, seasonal hypoxia induces P release from the sediment, not only during hypoxic/anoxic periods, but also during temporary oxic events. Phosphorus release in shallow basins under oxic conditions has also been reported in previous studies in the Archipelago Sea (Pitkänen et al., 2001, Lehtoranta and Heiskanen, 2003, Suomela et al., 2005). We concluded that the condition of the sediment surface alone is not a good indicator of the sediment's potential for P release, nor is the oxygen concentration in the near-bottom water. In shallow and sheltered locations where the volume of water is small, oxygen may be rapidly exhausted in the near-bottom water by degradation of organic matter, possibly enhancing P release from the sediments. Wind and boat traffic induced waves and currents cause temporal oxic events, which may enhance P binding onto iron-(oxy)hydroxides, but also sediment resuspension, which may cause phosphate release from pore water (Lukkari et al., 2009, Thouvenot-Korppoo et al., 2012). However, it has also been shown that resuspension does not necessarily affect P fluxes between the sediments and water (Almroth et al., 2009). These contradictory findings may suggest that we lack knowledge of the biogeochemical processes that govern the P dynamics between the sediments and water.

The sediment surface or measurements of the oxygen concentrations reflect only transient conditions in the bottom, but the sediment profiles may reveal the conditions at the sediment-water interface in the near past. Phosphorus cycling

between the sediments and water in the archipelago and coastal areas include complex biogeochemical processes that require further studies. Particular attention should be paid to selecting the sediment and water quality monitoring sites in order to obtain, cost-effectively, the essential information about the sediment and water quality, and the spatial and temporal extent of hypoxia.

Organic carbon in the sediment surface layer has been used to estimate P release from sediments (e.g. Kiirikki et al., 2006). Although LOI may overestimate the organic content of sediments rich in clay minerals (Barillé-Boyer et al., 2003), ignition at 550° C for two hours will probably not cause significant loss of structural water from the clay minerals in glacio-lacustrine sediments (Heiri et al., 2001); it can therefore be considered a feasible method for estimating organic matter content in the studied sediments. The detected negative correlation between LOI and PO<sub>4</sub>-P concentration in the near-bottom water showed that, for the studied soft sediments with LOI > 5% dw, organic matter content is a poor indicator of P release, although the most intense P release is expected from them (Malmaeus et al., 2012, Puttonen et al., 2014). The highest PO<sub>4</sub>-P concentrations were found at stations with LOI values < 12% dw, and all PO<sub>4</sub>-P concentrations below 50 µg l<sup>-1</sup> were observed at stations where the sediment LOI was above 12% dw. In other words, in our results the most organic-rich sediments were not the sources of the most intense P release. In the results of the PCA, the most intense internal P loading occurred from sediments with moderate organic matter content, which may suggest that other factors are also involved in governing P release from the sediments. Our results indicate that caution is needed in the use of the content of organic matter as a proxy for P release from sediments.

Our study did not reveal any unambiguous single-variable dependence of the  $\text{PO}_4\text{-P}$  concentration in the near-bottom water. Weak correlations and the heterogeneous spread of  $\text{PO}_4\text{-P}$  concentrations indicate that no particular variable alone could explain the variations in phosphate concentration in the near-bottom water but that the P exchange between the sediment and water is a complex process and the governing factors are interconnected (Caraco et al., 1989, Hupfer and Lewandowski, 2008). Furthermore, the results of the PCA suggest that the interplay of the investigated environmental variables in the system is multifaceted. Apart from the bottom water oxygen, the water depth, as well as the grain size and the contents of organic matter, and the potentially mobile P forms at the sediment surface were important factors explaining the similarity of the samples.

The  $\text{PO}_4\text{-P}$  concentration in the near-bottom water reflects the P release from the sediment to the water. It was included in the PC2, together with the oxygen concentration in the near-bottom water, the grain-size and the Fe-P at the sediment surface. Accordingly, the PC2 can be interpreted and renamed as a component of the internal loading of P. High scores in the PC2 – i.e. high internal P loading – were grouped around the middle of the PC1, whereas low scores in the PC2 formed two main groups, both towards the ends of the PC1 (Fig. 6). Hence, high internal P loading exists together with intermediate values of the variables composing the PC1. Although sediment LOI appeared to be the most prominent variable defining the clusters, the other variables in the PC1, i.e. the sediment P content, the water depth, and the exposure to waves, as well as the temperature in the near-bottom water also impacted the internal loading of P. The low variation of the absolute values of the factor loadings indicates a relatively equal importance among the variables.

Low oxygen concentration in the bottom water may cause depletion in P bound in iron(III)-(oxy)hydroxides in surficial sediments (Rydin, 2000). Iron-bound P is released from sediments when oxygen is depleted in the near-bottom water. Near-bottom water (re)oxygenation results in adsorption of P onto iron-(oxy)hydroxides, (Boström et al., 1988, Conley et al., 2002), which may lead to an increase in the pool of iron-bound P at the sediment surface. Oxygen deficiency may thus be expected to result in low 'Fe-P' content at the sediment surface. In our study, no significant correlation was detected between the 'Fe-P' at the sediment surface and the oxygen concentration in the overlying water, as has been found in deep areas (Mort et al., 2010). However, only four of the sampling stations were anoxic. The 'Fe-P' contents in those were below average, but low 'Fe-P' contents were also found at the oxic and suboxic stations. The content of redox-sensitive P also depends on the quality and composition of the settling matter. Additionally, the duration of oxygen deficiency may influence the fluctuations of iron-bound P in the sediments (Carman and Rahm, 1997), which could be a partial explanation for the relatively high  $\text{PO}_4\text{-P}$  concentrations in the near-bottom water in areas with signs of temporal oxygen deficiency. Furthermore, some transformation may have occurred between the P forms in the sediment samples (Stevens, 1992, Kjeldsen, 1993), causing an increase of the Fe-P pool, due to the contact of the sediment samples to atmospheric oxygen during the recovery of the samples, and possibly also during storage in the plastic bags before the chemical analyses. However, the decline in the 'Fe-P' and 'loosely bound P' pools was assumed to be due to the release of P from the fractions into the overlying water (Rydin, 2000). No transformation of P from the overlying water was possible in the sediment samples, since the overlying water was not included with the sediment surface samples. Although anoxia may cause decline in iron-bound P

at the sediment surface, the content of Fe-P cannot be interpreted as an indication of oxygen conditions.

## 5. Conclusions

Our results showed that control of P release from shallow coastal sediments is more complicated than that of deep areas. No single factor could be defined as decisive although bottom water hypoxia is often considered as the primary factor controlling phosphate fluxes from the sediments (Conley et al., 2009, Mort et al., 2010, Funkey et al., 2014). Most of the other environmental factors studied were found to be equally important as the oxygen concentration in the near-bottom water. Thus, in future research, a wider set of physical and chemical properties of the sediments deserve more attention as possible factors controlling P exchange across the sediment-water interface. Enhanced eutrophication fuelled by increased nutrient input has led to increased accumulation of organic matter and P in the sediments (Emeis et al., 2000, Rabalais et al., 2007), which might have caused changes in P dynamics between sediments and water. Improved understanding of the controlling processes and the role of the internal P loading to eutrophication requires further investigations considering the sediments capacity to retain P. The key challenges are to link more closely the phosphate reflux from sediments with (1) the associated environmental factors and (2) the physical and chemical properties of sediments controlling the efficiency of the adsorption and depositional burial of P.

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