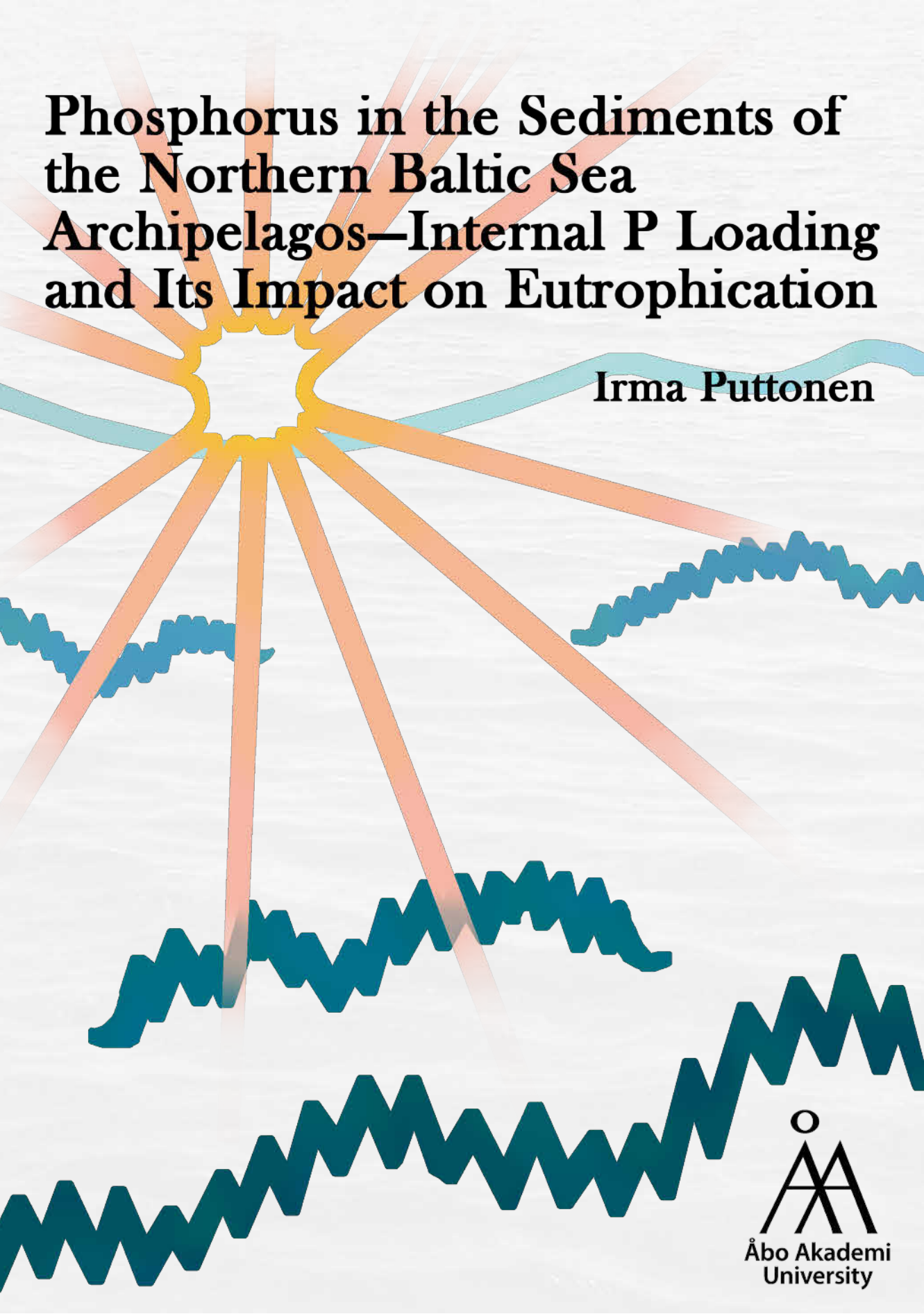


Phosphorus in the Sediments of the Northern Baltic Sea Archipelagos—Internal P Loading and Its Impact on Eutrophication

Irma Puttonen





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Cover art: ©Vilma Itkonen

ISBN (paperback): 978-952-12-3511-5
ISBN (pdf): 978-952-12-3512-2
Electronic version (pdf): <https://www.doria.fi/handle/10024/131068>
Painosalama Oy, Turku 2017

To Otto and Vilma



Frédéric Chopin – Nocturne in E-flat major, op. 9 No. 2, 1830–31 (an excerpt)

Abstract

In the 20th century Eutrophication as a result of anthropogenic enrichment of nutrients has become a global problem in marine coastal waters. In the Baltic Sea, eutrophication is considered the most severe environmental problem, having various harmful consequences in the ecosystems. In the shallow northern coastal and archipelago areas, where the biodiversity is low and many species live close to the limit of their tolerance, the ecosystem is particularly sensitive to environmental stress. Despite reductions of nutrient inflow from the catchment since the 1980's, the water quality has not improved as expected. Phosphorus (P) has accumulated in the seabed sediments due to high input from the catchment, and high levels of P in the water are maintained by P release from the sediments, i.e., the internal P loading. Phosphorus stimulates primary production, particularly intensifying blooms of nitrogen-fixing cyanobacteria.

The release of sedimentary P depends to a considerable degree on P binding in different compounds in the sediments as well as the environmental conditions in the sediments and at the sediment-water interface. The spatial and vertical distribution of different forms of P in the sediments of coastal and archipelago areas in Sweden and Finland were investigated for the first time in the extent of this thesis. The aims were to quantify the pool of potentially mobile P in the sediments of the study area of ca. 20,000 km², to estimate the potential magnitude and spatial distribution of the internal loading of P, and to evaluate the impact of the internal loading of P on coastal eutrophication in relation to the external P input.

This study included analyses of sediment and water samples from 389 sampling stations in the study area. The sediments were analysed for total P, grain size distribution, water content and weight loss on ignition (LOI) to estimate the organic content. Phosphorus was extracted into six fractions applying a sequential P fractionation method. The resulting P fractions characterise the solubility and reactivity of P compounds in the sediment. Acoustic-seismic profiling was used to obtain seabed sediment data for estimations of the coverage of different sediment types in the study area, as well as to obtain a representative sample of sediments over the entire study area.

Temporal variation of P in sinking particles was studied with cylindrical sediment traps placed in the water column. Multivariate statistics were used to investigate possible controls of P release from the sediments. The magnitude of the potential internal P loading was estimated based on the potentially mobile P fractions in the sediments, and the estimates were tested in a water quality model, which has been developed as a tool for Finnish authorities for planning water protection measures.

The pool of potentially mobile P in a two-centimetre thick sediment surface layer was calculated to amount to $31\text{--}37 \times 10^3$ tonnes, which is of the same order of magnitude as the external annual P input to the entire Baltic Sea. The results revealed that while hypoxia, defined as oxygen concentration $< 2 \text{ mg l}^{-1}$, will enhance the internal P loading from the sediments in shallow coastal environments, P release may occur even when the bottom water oxygen concentration is as high as $8 \text{ mg O}_2 \text{ l}^{-1}$. Besides oxygen, contents of potentially mobile P in the sediment, sediment organic content and grain size, exposure to waves, water temperature and depth may affect P cycling between the sediments and the water column. The level of the annual internal P loading was estimated to be $0.31\text{--}0.64 \text{ g P m}^{-2}$ from soft, organic-rich sediments in the study area, amounting to 2,400—5,100 tonnes of P from the study area.

Increasing supply and subsequent degradation of organic matter due to eutrophication leads to spreading of bottom water hypoxia in the Baltic Sea. The water transparency is decreased, toxic and nuisance cyanobacterial blooms are common, benthic communities suffer from hypoxic stress, and long-lasting and severe hypoxia leads to formation of toxic hydrogen sulphide in the sediment, causing mortality of aerobic zoobenthos. The internal loading of P maintains the high productivity and hinders the alleviation of eutrophication that is expected as a result of reductions of the external nutrient loading. The local impact of the internal P loading to the water quality, habitats and food web structure is of fundamental concern. Moreover, the internal P loading will markedly retard the water quality improvement in the entire Baltic Sea scale.

This new information can be used in assessing the effect of nutrient reductions from the catchment to the water quality when planning and implementing water protection measures to achieve a preferable ecological status in the Baltic Sea. The results of the thesis can be exploited even outside the study area, in comparable sedimentary environments.

Keywords: chemical extraction of phosphorus, coastal zone, environment management, hypoxia, marine nutrients, phosphorus cycle, sediment biogeochemistry, water quality

Sammanfattning

Eutrofiering på grund av ökad tillförsel av näringsämnen har blivit ett globalt problem i marina kustvatten under de senaste decennierna. Eutrofieringen har olika skadliga följder på ekosystemen, och anses vara det mest allvarliga miljöproblemet i Östersjön. I de grunda nordliga kust- och skärgårdsområdena, där den biologiska mångfalden är låg och många arter lever nära gränsen för sin tolerans, är ekosystemen särskilt känsliga för miljöstress. Trots en märkbar reduktion av närsaltsbelastningen från avrinningsområde sedan 1980-talet, har vattenkvaliteten i Östersjön inte förbättrats som förutspått. Fosfor har ackumulerats i bottensedimenten, och höga fosfathalter i vattnet bibehålls på grund av den så kallade interna fosforbelastningen, dvs. Då fosfor frigörs från sedimentet. Fosfor stimulerar primärproduktionen, och bidrar till de intensiva blomningarna av kvävefixerande cyanobakterier.

Utsläpp av sedimentär fosfor beror i hög grad på hur fosfor är bundet i olika föreningar i sedimenten, samt hurdana miljöförhållanden i sedimenten och vid gränssnittet mellan sediment och vatten är. Den geografiska och vertikala fördelningen av olika former av fosfor i sediment har nu för första gången undersökts i stor skala i kust- och skärgårdsområden i Sverige och Finland. Målsättningen var att kvantifiera potentiellt mobilt fosfor i sedimenten i det undersökta området som omfattar cirka 20 000 km², och att uppskatta den potentiella mängden och den geografiska fördelningen av den interna fosforbelastningen. Slutligen utvärderades effekterna av den interna fosforbelastningen på vattenkvaliteten i kustområdena i förhållande till den externa fosforbelastningen.

För denna avhandling utfördes analyser av sediment och vattenprover från 389 provtagningsstationer i studieområdet. Sedimenten analyserades för totalfosfor, kornstorlek, vattenhalt och glödförlust (LOI) för att uppskatta mängden organiskt material. Fosfor extraherades i sex fraktioner enligt en sekventiell kemisk fosforfraktioneringsmetod. De olika fosforfraktionerna representerar löslighet och reaktivitet hos fosforföreningarna i sedimenten. Akustisk-seismisk profilering användes för att uppskatta omfattningen av olika sedimenttyper för att kunna göra en representativ provtagning över hela undersökningsområdet.

Den tidsmässiga variationen av fosforfraktionerna i sjunkande partiklar i vattenmassan undersöktes med cylindriska sedimentfällor, som placerades ut i vattnet nära havsbotten. Faktorer som potentiellt reglerar frigörandet av fosfor från sedimentet testades med multivariant statistik. Storleken av den interna fosforbelastningen uppskattades på basis av de potentiellt mobila fosforfraktionerna i sedimenten, och de uppskattade värdena testades i en vattenkvalitetsmodell, som har utvecklats för de finska miljömyndigheterna som ett verktyg för planering av vattenskyddsåtgärder.

Mängden av den potentiellt mobila fosfor i ett två-centimeter tjockt ytskikt av sediment beräknades uppgå till $31\text{--}37 \times 10^3$ ton, vilket är av samma storleksordning som den årliga externa fosforbelastningen till hela Östersjön. Resultaten visade att allvarlig syrebrist, definierad som syrehalt $< 2 \text{ mg l}^{-1}$, ökar den interna fosforbelastningen från sedimenten i grunda kustmiljöer, men också att fosfor kan frigöras även när bottenvattnets syrehalt är t.o.m. $8 \text{ mg O}_2 \text{ l}^{-1}$. Förutom syre kan även fosforhalt och innehåll av organiskt material i sedimentet, sedimentets kornstorlek, exponering för vågor, vattentemperatur och vattendjup påverka fosfors flöde mellan sedimentet och vattnet. Nivån på den årliga interna fosforbelastningen från mjuka sediment med hög halt av organiskt material uppskattades till $0,31\text{--}0,64 \text{ g P m}^{-2}$. Totalmängden beräknat för hela det undersökta området uppgår till $2,400\text{--}5,100$ ton fosfor.

Ökade mängder fosfor och därmed ökad produktion av organiskt material leder till att också nedbrytningen av organiskt material ökar vilket i sin tur förbrukar syre och leder till syrebrist vid Östersjöns botten. Vattnet blir grumligare, giftiga och skadliga blomningar av cyanobakterier är vanliga, syrebrist stressar bottenfaunan, och långvarig och allvarlig syrebrist på sedimentytan leder till bildandet av giftigt svavelväte, som dödar aerobiska bottenjursamhällen. Den interna fosforbelastningen upprätthåller en hög produktivitet och gör att vi inte ser en reducering av eutrofieringen trots att den externa näringsbelastningen har avtagit. Lokalt är den interna fosforbelastningens inverkan på vattenkvaliteten, olika livsmiljöer och näringsvävnars struktur av grundläggande betydelse. Den interna fosforbelastningen fördröjer även markant förbättringen av vattenkvaliteten i hela Östersjön.

Resultaten från avhandlingen kan användas för bedömning av effekter av reducering av näringsbelastning från avrinningsområden. Resultaten är också viktiga vid planering och genomförande av vattenskyddsåtgärder för att uppnå en god ekologisk status i Östersjön. Resultaten från avhandlingen kan användas också utanför det undersökta området i jämförbara havsområden.

Nyckelord: kemisk fosforextraktion, kretslopp av fosfor, kustområden, marina närsalter, miljöförvaltning, sedimentär biogeokemi, syrebrist, vattenkvalitet

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List of original papers

The thesis is based on four papers, which are referred to in the text by their Roman numerals. Irma Puttonen was chiefly responsible for the writing and the data interpretation in **papers I, III and IV**. In **paper II**, IP contributed to the interpretation of the data and the writing of the manuscript.

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- I** Puttonen I., Mattila J., Jonsson P., Karlsson O. M., Kohonen T., Kotilainen A., Lukkari K., Malmaeus M., and Rydin E.: Distribution and estimated release of sediment phosphorus in the northern Baltic Sea archipelagos. *Estuarine, Coastal and Shelf Science* 145 (2014), 9–21.
- II** Malmaeus M., Kohonen T., Puttonen I., Karlsson O.M., Lukkari K., and Mattila J.: Variations in quantity and species of phosphorus in the settling matter in the northern Baltic Sea archipelagos. *Manuscript*, submitted.
- III** Puttonen I., Kohonen T. and Mattila J.: Factors controlling phosphorus release from sediments in coastal archipelago areas. *Marine Pollution Bulletin* 108 (2016), 77–86.
- IV** Puttonen I., Lukkari K., Miettunen E., Ropponen J. and Tuomi, L.: Estimating the internal loading of phosphorus for a water quality model using chemical characterization of sediment phosphorus. *Manuscript*, submitted.

1. Introduction

1.1. *Eutrophication*

The term 'eutrophic' refers to the trophic state of high fertility in an aquatic ecosystem. Accordingly, eutrophication stands for succession or development towards increasing biological production.

Eutrophication can be defined as increased supply of organic matter to the system (Nixon, 1995), and anthropogenic nutrient input is the major cause for marine eutrophication globally (Smith, 2003; Kennish and Townsend, 2007). Increasing eutrophication has decreased the ecological, as well as economic and recreational values of marine coastal areas worldwide in the 20th century (Lotze et al., 2006; Diaz and Rosenberg, 2008; Rabalais et al., 2009).

Eutrophication has a variety of undesired consequences in marine coastal environments (Lotze et al., 2006). Increasing primary production and phytoplankton biomass decrease water transparency, and the light penetration is reduced. Decreasing light energy and increasing epiphyte growth decrease the depth of the occurrence of seagrass and macroalgal populations and shifts the dominance from perennial to annual species (Cloern, 2001). High nutrient concentrations in the water increase the occurrence of harmful and toxic cyanobacterial blooms (Heisler et al., 2008). Enhanced phytoplankton production in the water column increases the supply of settling organic matter to the sea floor, stimulating benthic microbial metabolism and increasing oxygen consumption in the water column and on the seafloor (Cloern, 2001).

Increasing oxygen demand leads to oxygen depletion on the seafloor and in the overlying water. Lack of oxygen causes stress in the benthic fauna, having cascade effects on the whole food web (Diaz and Rosenberg, 2008). Changes in benthic invertebrate communities are reflected to upper trophic levels, as the food source for benthos feeding vertebrates is altered and diminished, e.g., causing changes in fish stocks; some increase, while others decline (Winkler, 2002). Eventually, the changes can be seen in food web structure on all trophic levels (Diaz and Rosenberg, 2008).

Oxygen depletion changes the physiology and behaviour of benthic fauna (Carstensen et al., 2014b). Benthic fauna modifies the substrate by burrowing into the sediment, transports particles and elements, and contributes to organic matter degradation and fluxes of oxygen and nutrients (Covich et al., 1999). Oxygen is transported into the sediment through burrowing holes, and oxic zones are created in the burrows within reduced sediments. Changes in species richness and abundance, biomass and dominance patterns in benthic communities change the ecosystem functioning, thus having indirect implications on sediment biogeochemistry. Weakening or vanishing species may be

replaced by invaders that are more tolerant against disturbance (Mack et al., 2000; Ehrenfeld, 2010). Introduced polychaete *Marenzelleria* spp. is an example of species with high tolerance of hypoxia in the Baltic Sea (Norkko et al., 2012, 2015). The invasion of *Marenzelleria* has been associated with the decline of the native amphipod *Monoporeia affinis* (Carstensen et al., 2014b).

1.2. The Baltic Sea

In the Baltic Sea, eutrophication is considered the most severe environmental problem (HELCOM, 2010). The modern Baltic Sea is a geologically young, semi-enclosed brackish-water sea, connected to the North Sea through narrow Danish straits. The seafloor morphology is mainly of pre-glacial origin but the basin is also scoured and deformed by the most recent glaciations (Voipio, 1981). It is shallow, about 1600 km long, consisting of several sub-basins with unique characteristics and seafloor morphology (Kaskela et al., 2012). It is characterized by gradients: biodiversity, species composition, water temperature and salinity change gradually from the south to the north. Biodiversity is low, and many organisms live close to the limit of their tolerance. These distinctive features make the ecosystem particularly sensitive to environmental stress. The catchment area is ca. 1.7 million km², more than four times the area of the Baltic Sea, with a population of nearly 85 million people (HELCOM, 2015). Seasonal hypoxia (defined as bottom water oxygen concentration < 2 mg l⁻¹) is a common phenomenon in shallow coastal areas of the Baltic Sea, where temperature stratification during summer months prevents vertical water mixing. In deep basins, a vertical salinity gradient sustains water column stratification, allowing development of permanent hypoxia. Large areas of anoxic seabed in the Baltic Sea lack benthic fauna (Carstensen et al., 2014b). Repeated hypoxic events deteriorate ecosystem resilience (Villnäs et al., 2013), and influence the relative regeneration rates of nitrogen (N) and phosphorus (P) (Jilbert et al., 2011).

Eutrophication in the Baltic Sea is caused by anthropogenic nutrient enrichment; during the 20th century the inputs of N to the Baltic Sea have increased three-fold and that of P five-fold (Carstensen et al., 2014b). As the awareness of the harmful consequences of eutrophication has risen, the input of N to the Baltic Sea has been reduced by 16% and that of P by 18% from 1994 to 2010 (HELCOM, 2014). Notwithstanding, the water quality has not improved as expected. Nutrient concentrations have not decreased, and high chlorophyll-a concentrations have still been detected in the surface water as a measure of high primary production (HELCOM, 2014). Phosphorus has accumulated in the sediments due to extensive nutrient loading, and is subsequently recycled back to the water column. The delayed response of nutrient concentrations in the water to the load reductions has been attributed to P release from sediments, so called internal P loading (Lindim et al., 2015).

1.3. The role of phosphorus in the sediments and the water column

The macronutrients nitrogen (N) and phosphorus (P) are vital for the growth, reproduction and metabolism of marine organisms. Nutrients enter the sea from diffuse sources as riverine runoff from land, from point sources, such as wastewater treatment plants, factories and fish farms, and as aerial deposition with rain.

Over long time scales, P can be considered the limiting nutrient of phytoplankton production, because atmospheric N is an endless source for N-fixing species (Tyrrell, 1999). Nitrogen fixation brings more N to the system, turning it towards P limitation (Nausch et al., 2004). Due to bottom water hypoxia, redox conditions at the sediment surface and in the sediment-water interface are altered into a more reductive direction, moving the redox-cline upwards in the sediment. In reducing conditions, iron-bound P is mobilized by reductive dissolution of iron(III) oxy(hydr)oxides (Mortimer, 1941, 1942; Boström et al., 1988). Iron-bound P can also be released from sediments to the water through bacterial sulphate reduction, due to the reaction between hydrogen sulphide and P-bearing Fe oxides (Caraco et al., 1989, 1993). Remineralization of organic P is another important source of bioavailable P in the water (Rydin, 2000; Ahlgren et al., 2006; Jilbert et al., 2011). Organic P is transformed into inorganic form through organic matter degradation. The degree and speed of mineralization depends on the quality of the settling matter and the physico-chemical conditions in the sediment and at the sediment-water interface. Terrestrial organic matter tends to be more refractory than marine sinking P from primary production (Krom and Berner, 1981). Anoxic conditions may also accelerate P release in organic matter degradation (Jilbert et al., 2011).

Phosphorus release from sediments decreases the N:P ratio in the water, supporting blooms of N-fixing cyanobacteria species (Vahtera et al., 2007; Walve and Larsson, 2007; Eilola et al., 2009). Massive cyanobacterial blooms form an oversupply of settling organic matter to the seafloor, bringing more N into the system and thus sustaining high production and eutrophication in the Baltic Sea (Svedén et al., 2016). Decomposition of organic matter increases the oxygen demand at the sediment-water interface, worsening oxygen depletion and sustaining hypoxic conditions. A surplus of settling organic matter to the sediment and bottom water hypoxia increases the fluxes of both P and N to the water (Emeis et al., 2000).

1.4. Objectives and scope

Many of the recent studies on P dynamics in the Baltic Sea between the sediments and water are carried out in the deep anoxic basins (e.g., Mort et al., 2010; Jilbert and Slomp, 2013; Viktorsson et al., 2013; Funkey et al., 2014). There are fewer studies from coastal and archipelago areas (but see: Virtasalo et al., 2005; Virtasalo and Kotilainen, 2008; Rydin et al., 2011; Malmaeus et al., 2012),

where hydrodynamics and sedimentary environments are complex, oxygen conditions unstable and fluctuating, and the composition and functioning of the benthic communities are different from those in deeper and more open sea areas.

Estimates of P release from sediments have been made in previous investigations by calculating from pore water gradients (Mortimer et al., 1999; Lehtoranta and Heiskanen, 2003), in laboratory incubations (Conley, 1997; Thouvenot-Korppoo et al., 2012; Li et al., 2016) or *in situ* P flux measurements (Suomela et al., 2005; Ekeröth et al., 2016; Paytan et al., 2016). Flux measurements give momentary values, but may not quantify P release in a long-time scale. This is the first comprehensive study of the amount and chemical composition of P in the sediments of coastal and archipelago areas in the northern Baltic Sea. The spatial and vertical distributions of different P forms in the sediments of different seabed substrates were investigated in this study. Furthermore, the conditions which would augment P release from the sediments were studied and estimates were made of the total amount of P to be released from the sediments with time.

The objectives of this thesis were:

1) To determine what kinds of sediments act as potential sources of phosphorus release. The sedimentary environments in the study area are heterogeneous and patchy, and small-scale variations of seabed sediment types are common (Kaskela et al., 2012). It is possible to reliably estimate the potential internal P loading and its local variability only when the seabed sediments that act as potential sources of P are identified.

2) To quantify the store of potentially mobile phosphorus in the sediments of the study area. The knowledge of sediment P contents in different kinds of seabed sediments and in different areas forms the basis for the estimates of the potential and actual magnitude of the internal P loading. This is the first comprehensive study on sediment P contents covering large areas and different seabed sediment types in the study area.

3) To identify the location and extent of the most important areas of P release in the studied Baltic Sea archipelagos.

In this hydrologically complex area, the information of local variations of the potential internal P loading is essential for cost-effective implementation of nutrient reductions in the catchment and other measures for amelioration of eutrophication.

4) To estimate the magnitude of the internal P loading and its contribution to the water quality in the archipelagos.

The estimates of the magnitude of the internal P loading in previous studies are based on mass-balance calculations (Håkanson and Eklund, 2007) and environmental modelling (Kiirikki et al., 2006).

It is of prime importance to account for the internal P loading in planning and implementation of the water quality management measures to achieve the goals for the alleviation of eutrophication, which are defined in the HELCOM Baltic Sea Action Plan (HELCOM, 2007; Backer et al., 2010). The results of this study provide enhanced accuracy in the estimates of the magnitude and spatial variability of the internal P loading. The results can also be exploited in other coastal areas with corresponding sedimentary environments.

1.5. Research contribution in this thesis

In **paper I**, the inventory of total and potentially mobile P in the topmost 2 cm of the sediments is presented. The vertical distribution of different P fractions in the sediments was investigated to estimate the amount of depositional burial of P, and to determine the share of the extracted P fractions that is in potentially mobile form, i.e., can be released from the sediments into the water column as bioavailable phosphate. Contents of potentially mobile P at the sediment surface were studied across the study area to find out the size of the potentially mobile P pool in the sediments and to define the areas where the most intense internal P loading can be expected to occur. Besides from the deposited sediments, P release also may occur in the water column from particulate suspended and settling material (Hupfer et al., 1995; Reitzel et al., 2012). The spatial and temporal distributions of phosphorus forms in the settling particles were studied in **paper II** to examine possible seasonal and spatial patterns in the P composition in settling particles. In this study, the phosphate flux from the sediment and settling particulate material, both of them contributing to the phosphate concentration in the bottom water, are counted as the internal loading of P.

Phosphorus dynamics between sediments and water depends on the physico-chemical conditions in the sediments and the overlying water. Hypoxia is known to accelerate P release, but there is also evidence of P release under ‘normoxic’ conditions (Pitkänen et al., 2001; Lehtoranta and Heiskanen, 2003; Suomela et al., 2005). A group of environmental variables were studied as possible driving factors of P release from sediments in **paper III**. Moreover, oxygen and phosphate concentrations in near-bottom water samples taken from the sediment corer, above intact sediment surface, were compared with those taken from 1 meter above the seafloor. The aim of the comparison was to assess how well bottom water monitoring reflects the conditions near the sediment surface. This is important, since monitoring is commonly done from 1 meter or more above the seafloor, and conclusions of bottom water phosphate concentration and the extent of hypoxia are based on those monitoring data. In **paper IV**, the results of the sediment P extraction data were applied to calculate estimates of the internal P loading in a one-year time scale. The estimated values were entered to the water quality model FICOS (the **F**innish **C**oastal – **O**pen **S**ea nutrient load model) as a source of P,

and the modelled total P and dissolved phosphate concentrations were compared with observed values in the study area. The model has been established by the Finnish Environment Institute in the project “Development of Archipelago Sea nutrient load model assembly and its implementation to coastal Gulf of Finland and Bothnian Sea”. It was developed as a tool for the Finnish environmental authorities for planning and implementing the measures to improve and protect the water quality.

2. Materials and methods

2.1. The study area

Sediment and water samples were collected in field studies during 2009–2012 in the archipelago of Svealand in Sweden and the archipelagos of Åland, Archipelago Sea and western Uusimaa in Finland (Fig. 1).

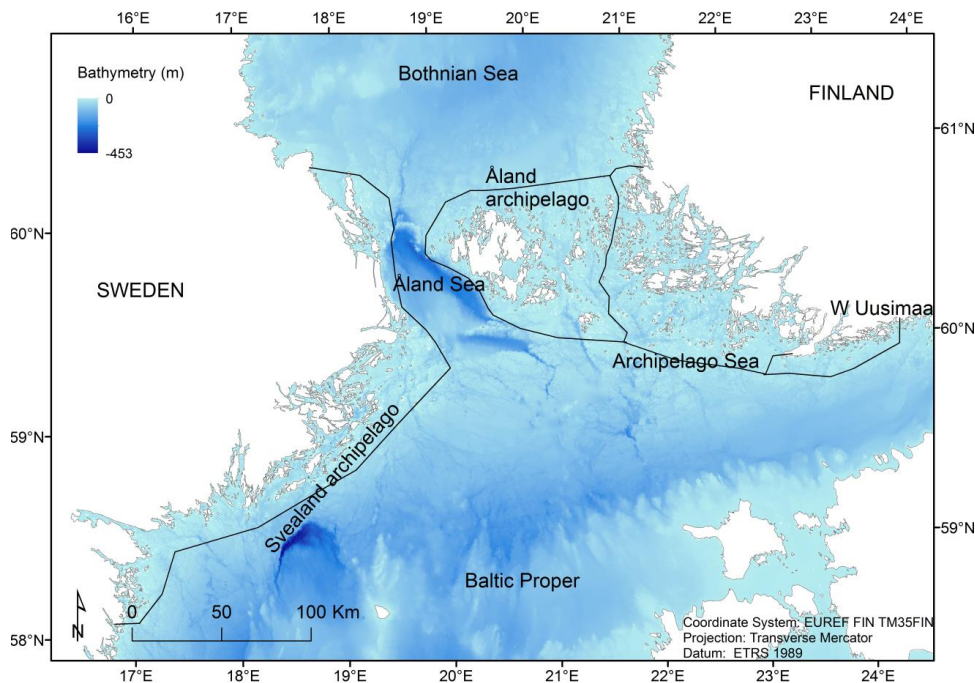


Fig. 1. The archipelagos of Svealand in Sweden and western Uusimaa, Åland and the Archipelago Sea in Finland were included in the study area. The source for the bathymetric data: Baltic Sea Hydrographic Commission, 2013, Baltic Sea Bathymetry Database version 0.9.3. Downloaded from <http://data.bshc.pro/> on 29.6.2016.

The study area covers ca 20,000 km² seafloor in the coastal and archipelago areas of the northern Baltic proper. The archipelago region encloses more than 60,000 islands and skerries altogether, with an average water depth of 23 m and a maximum depth of 294 m in the Åland Sea (Rönnberg and Bonsdorff, 2004). The Åland Sea is located in a fault zone (Winterhalter et al., 1981) separating the Swedish part of the study area from Åland archipelago. The area has undergone several glaciations that have scoured and deformed the crystalline bedrock. The bedrock in the study area consists of Paleoproterozoic crystalline basement rocks (Koistinen et al., 2001). It contains several ancient tectonic lineaments and fracture zones that divide the bedrock into blocks (Härme, 1961; Tuominen et al., 1973; Winterhalter et al., 1981). In the Åland Sea and in Lumparn, in the Åland archipelago, basement rocks are covered by younger sedimentary rocks (Koistinen et al., 2001). The bedrock is partly overlaid by Pleistocene-Holocene glacial and postglacial sediments – older sediments have for the most part been eroded and transported away by repeated glaciations (Winterhalter et al., 1981).

The hydrodynamic conditions and associated sedimentation environments are complex in the coastal and archipelago areas due to heterogeneous and fragmented geomorphology (Kaskela et al., 2012). Water exchange between adjacent basins is restricted. Almost continuous deposition of organic-rich and fine-grained sediment occurs commonly in shallow coastal areas and small basins in the shelter of islands. In contrast, many of the deeper areas in the Archipelago Sea are associated with elongated underwater canyons where strong currents prevent sediment accumulation (Virtasalo et al., 2005). In these eutrophied coastal and archipelago areas organic matter accumulation during the productive season, from March–April to late September, is high. The coastal waters receive nutrients and organic matter also from the catchment, through riverine discharge, as well as from point sources, e.g., fish farms and municipal and industrial wastewater plants. A strong thermocline is created during the summer months, preventing vertical mixing of the water column (**paper III**; Virtasalo et al., 2005). In the Swedish study area, where the water depth reaches more than 100 m in the deepest basins, also halocline may prevent vertical water mixing. Increasing oxygen demand due to organic matter degradation results in bottom water oxygen depletion, as the oxygen-rich surface water cannot reach the bottom layer. The area of hypoxic seafloor areas, as well as the duration of hypoxic periods has increased in the study area during the last century (Conley et al., 2011; Carstensen et al., 2014a).

2.2. Field studies

2.2.1. Acoustic-seismic profiling

Detailed seabed substrate maps were provided by the Geological Survey of Sweden (SGU) for the Svealand archipelago area. In the Finnish archipelago areas the existing and available seabed

substrate maps were not sufficiently detailed to distinguish the variability in local, highly variable sedimentary environments. To study the contents and forms of P in seabed areas, where fine-grained and organic-rich sediment accumulation occurs, as well as in areas of sediment erosion or transportation, the aim was to include sediment samples from different seabed substrates representing the respective seabed areas. Therefore, in the Finnish archipelagos, the final selection of the sampling stations was based on information acquired using the acoustic-seismic equipment of R/V Geomari and R/V Muikku. The data were used to verify the seabed substrate type in order to obtain a representative sample of the sediments, and also to select suitable sampling equipment. The seafloor was investigated with a Side scan sonar (Klein 3000) and sub-bottom profiler system (Pinger 28 kHz and Chirp 4 kHz, Oy Meridata Finland Ltd). With the Side scan sonar an image of seabed surface was obtained with horizontal coverage of ca. 280 metres under the survey line under the vessel. The sub-bottom acoustic profiler system creates a sediment acoustic profile (Fig. 2) penetrating into the seabed sediment directly under the sensor along the survey line. The seismic profiler system ELMA at a frequency of 500 Hz penetrates down to the surface of the bedrock, enabling to detect the upper boundary of a hard bottom, generally bedrock or till. A total length of 380 km of survey lines were collected and post-processed to be used to complement the existing sediment maps.

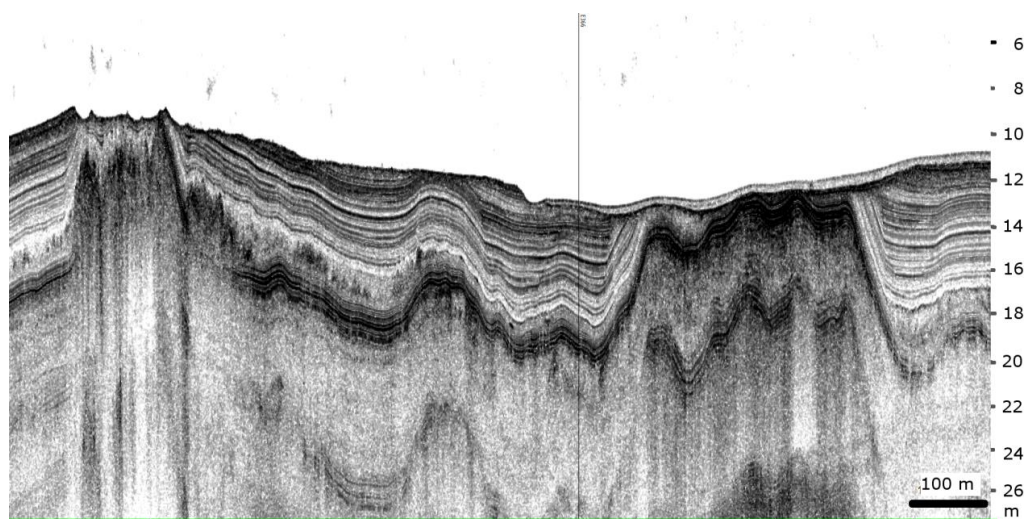


Fig. 2. An example of 28-kHz Pinger profile (Meridata) of seabed substrate. Sediment type and internal structures of the sediments can be identified in the profile. The depth scale gives the depth under the sea surface.

2.2.2. Sample collection

Sediment and water samples and the acoustic-seismic data used in **papers I, II and III** were collected in three research projects in the years 2009-2012:

- 1) *Phosphorus from the seabed and water quality in archipelagos – modeling attempt* (SEABED), funded by the EU Central Baltic INTERREG IVA Programme,
- 2) *Bottom dynamic model for phosphorus in Baltic Sea archipelagos*, funded by the Nordic Council of Ministers
- 3) *Internal loading of phosphorus from bottom sediments to water in the archipelago areas of Åland, SW Finland and W Uusimaa*, funded by the K.H. Renlund's Foundation.

Sediment samples were recovered at 389 sampling stations with different sampling devices. Samples from soft sediments were taken with a gravity corer: Gemini double corer (inner diameter 80 mm), Gemax double corer (90 mm), Niemistö (80 mm), Limnos (94 mm), and Willner corer (56 mm). The length of the sediment cores varied from 18 to 60 cm. Only cores with undisturbed sediment surface were accepted. Sediment cores were sliced in 2 cm sub-samples. Additionally, from randomly selected cores the sediment surface was sliced to 0–1 and 1–2 cm sub-samples. Randomly selected cores were split vertically into two halves for visual inspection of the internal sediment structures and characteristics. From hard seabed substrates surface sediment samples were taken with a Box corer, a van Veen grab sampler or a modified Ponar grab sampler. Sediment surface and a deeper subsample representative of the sediment type at the location were recovered. The thickness of the sediment surface samples recovered from the hard seabed substrates was 1, 2 or 3 cm, depending on the depth of a visually clearly observable change in the colour, internal structure or texture of the sediment. The sediment samples were photographed and the visual characteristics were logged on the research vessel.

Water samples at 1 m above the seafloor were collected with a Limnos water sampler at 100 stations together with the sediment samples. At 39 stations near-bottom water samples were recovered from the sediment corer (**paper III**). Water samples for water quality monitoring are commonly collected at 1 meter or more above the seafloor. Phosphate and oxygen concentrations in the water samples from 1 m above the seafloor were compared with those in the near-bottom water.

Settling material was collected by mooring cylindrical sediment traps at nine sampling stations in the Svealand archipelago, Åland archipelago and Archipelago Sea (**paper II**). Sediment cores of 10–37 cm were collected at the trap mooring locations at the beginning of the study, and sediment surface

samples were taken each time when the traps were emptied, except at the Seili trap locations, where sediment samples were collected only in the beginning of the study. Temporal variation in P composition from early spring to late autumn was studied in the settling particles, and over the winter at one location (**paper II**), and the P composition in the settling material was compared with that at the sediment surface.

2.3. Physical and chemical analyses of the sediment and water samples

An overview of the physical and chemical analyses of the sediment and water samples is given in **Table 1**. A brief introduction to the methods is given in the following. More detailed descriptions can be found in the research papers included in this thesis and in the references therein.

Table 1. The methods of the physical and chemical analyses of the sediment and water samples.

	Variable	Methods	Paper
Sediment	Water content (% wet weight [ww])	Freeze drying	I, II, III, IV
	Organic content (% dry weight [dw])	Loss-on-ignition (LOI), 550° C, 2 hours	I, II, III, IV
	Total P ($\mu\text{g g}^{-1}$ dw)	Acid hydrolysis (Murphy and Riley 1962)	I, II, III, IV
	P fractions ($\mu\text{g g}^{-1}$ dw)	P fractionation scheme (Psenner et al., 1988)	I, II, III, IV
	Grain-size distribution (% clay, $\phi < 0.002$ mm)	SEDEX (Anderson&Delaney), Jensen & Thamdrup	IV
		Hydrometer	I, III
	Seabed sediment type	Laser diffraction, Coulter LS200	II
Water		Visual characterization of the sediments, LOI, water content	I, III
	Water temperature (°C)	Thermometer	III
	Oxygen concentration (mg l^{-1} , mmol l^{-1})	Winkler titration	III
	$\text{PO}_4\text{-P}$ ($\mu\text{g l}^{-1}$)	WTW Cellox 325 oxygen sensor	III, IV
	Total P ($\mu\text{g l}^{-1}$)	Spectrophotometric method Spectrophotometric method	IV
Environmental	Water depth (m)	Echo sounder	I, II, III
	Wave exposure	Simplified wave model	I, II, III

The water content of the sediment samples was determined after freeze-drying, and organic content (measurement of Loss-on-Ignition – LOI,) after ignition at 550°C for two hours. The total P (Tot-P) content in sediments was analysed as phosphate after acid hydrolysis at high temperature (340 °C) according to Murphy and Riley (1962).

The sequential P extraction scheme introduced by Psenner et al. (1988) was used to separate sediment P into six fractions that are defined by the method according to their solubility and reactivity. The method separates P into $\text{NH}_4\text{Cl-rP}$, BD-rP , NaOH-rP , NaOH-nrP , HCl-rP and residual P. The fractions are operationally defined, but ideally, each fraction corresponds to a specific phosphorus containing compound within the sediment. Generally, $\text{NH}_4\text{Cl-rP}$ is regarded as P in pore water and loosely adsorbed P on particle surfaces, BD-rP as P associated with iron hydroxides (Jensen and Thamdrup, 1993), NaOH-rP as P bound to aluminium, NaOH-nrP as organic P forms, and HCl-rP as calcium bound P compounds (Psenner et al., 1988). Residual P was determined by subtracting the extracted and identified P from total P that was analysed from a parallel sample, and it is considered to represent refractory organic P forms. The method allowed distinguishing potentially mobile P in the sediments, i.e., the forms of P that can be released from sediments in particular conditions. The P forms will be termed in this thesis as follows: Total P – Tot-P; $\text{NH}_4\text{Cl-rP}$ – ‘Loosely bound P’; BD-rP – ‘Fe-P’; NaOH-rP – ‘Al-P’; NaOH-nrP – ‘Unreactive P’ (Org-P in **paper II**); HCl-rP – ‘Ca-P’ and residual P – ‘res-P’. The analyses were conducted in Erken Laboratory, Uppsala, Sweden, which has an accreditation for the method by SWEDAC (the Swedish board for accreditation and conformity assessment). The principle of the extraction scheme is given in **paper I**, and a detailed description can be found in Psenner et al. (1988).

Theoretically, the extracted ‘Loosely bound P’, ‘Fe-P’ and ‘Unreactive P’ can be regarded as P forms that can be transformed into bioavailable phosphate to the water column. However, chemical extraction in laboratory conditions overestimates the amount of P that in natural conditions will be subject to recycling between the sediments and water. Typically, the amount of these P fractions declined in the vertical sediment profiles from the sediment surface downwards, stabilizing generally at approximately 6 to 10 cm depth. The amount of the extracted ‘Loosely bound P’, ‘Fe-P’ and ‘Unreactive P’ fractions in the sediments below 10 cm depth were assumed to be the burial amounts of these P fractions, i.e., the share of P that is permanently buried in the sediment in the sediment processes, and accordingly, treated as background contents of P. The content of potentially mobile P at the sediment surface was obtained by subtracting the background content of each of these P fractions from the content of respective P fractions at the sediment surface. However, in some of the sampling stations only sediment surface samples were collected, and thus, the background

content for them could not be determined site-specifically. In those cases, an average value of the above mentioned P fractions in the deep sediments (below 10 cm depth in the sediment) was subtracted as the background P content.

Grain-size distribution was determined by the hydrometer method at Åbo Akademi University, in the laboratory of the Department of Geology and Mineralogy (**paper I** and **paper III**). For the samples in **paper II**, the grain-size analyses were conducted by University of Turku, Department of Quaternary Geology with a laser diffraction method using a Coulter LS200 device.

The seabed substrate types in the sampling stations were classified into two categories: accumulation areas (A) and erosion or transportation areas (E/T). In A-areas the seabed sediments were fine-grained and organic-rich. The A-areas were identified by visual characteristics of the sediments together with LOI value > 10% of dry weight (dw) and water content > 75% of wet weight (ww) at the surface layer, both declining gradually downwards in the sediment profile. A lack of observable abrupt change in the sediment colour, internal structure or texture in the sediment core was interpreted as evidence of almost continuous sediment accumulation in the sediment profiles of the A-areas. Hard seabed substrates with low organic content were identified as E/T-areas. At the sediment surface the value of LOI was generally below 10% dw, and below 5.5% dw in the deeper sediment. The sediment surface was covered by coarse material, and sometimes with a thin transient organic-rich layer on top of it. Sediment accumulation was disrupted, as defined by a bluish colour in the relatively hard, clayey sediment below the surface layer in the sediment samples.

The sampling stations in **paper III** were classified as oxic, suboxic and anoxic, based on visual characteristics at the sediment surface and the sediment profile.

Water temperature (°C) was measured in the field with a thermometer attached to the Limnos water sampler. Oxygen (O₂) concentration (mg l⁻¹) was determined with a WTW Cellox 325 oxygen sensor in the field or by Winkler titration in a laboratory. Phosphate (PO₄-P) concentration (µg l⁻¹) was determined by a spectrophotometric method (**paper III**). The units of O₂ and PO₄-P concentrations were converted into (micro)moles per litre in **paper III**.

In **paper IV**, the sediment samples within the selected study area were used. Additional sediment data were compiled from various existing sources (Virtasalo et al., 2005; Lindgren, 2007; Lukkari et al., 2008), including data on sediment P, water content, loss on ignition (LOI), seabed substrate type, grain-size and sediment surface oxygen status. Water quality monitoring data were obtained from the national database Hertta (Finnish Environment Institute, 2014), comprising concentrations of total phosphorus (Tot-P), dissolved inorganic phosphorus (DIP) and dissolved oxygen (DO). In

addition, an oxygen model that was used for estimations of the oxygen conditions in the study area was provided by the Finnish Environment Institute (Virtanen et al., unpublished).

2.4. Data analyses

Existing sediment maps (Al-Hamdani and Reker, 2007; SGU, 2012; seabed substrate map available by the EMODnet Geology project, <http://www.emodnet-geology.eu> funded by the European Commission Directorate General for Maritime Affairs and Fisheries) were used to obtain information of the coverage of different sediment types in the study area. In the Finnish study area, the new acoustic data and sediment samples were used to complement and refine the maps. Acoustic data were post-processed and interpreted using Oy Meridata Finland Ltd's MDPS software and ESRI ArcGIS™ software. Acoustic surveys provided additional and comprehensive information of seafloor topography, seabed substrate type, sediment thickness and internal structures. The interpreted data, together with sediment samples, were used for complementing existing seabed substrate maps and estimating the coverage of different sediment types in the archipelagos. Additional data from the Åland archipelago sediments were provided by Mikael Wennström at the Åland Government.

In **papers I and IV**, P contents in the sediments were interpolated in ArcGIS software over the entire study area and across different sediment types. The Ordinary Kriging interpolation method was used in the calculations. Estimates of the spatial distribution of sediment P and calculations of the store of potentially mobile P in the sediments of the study area were made in ArcGIS software.

Statistical analyses were applied to study patterns within the data and relationships between the variables. The correlation (Bivariate Pearson correlation coefficient) between sediment P contents and water depth or exposure of the sampling stations to wind and waves was studied in **paper I** and between the sediment P contents and phosphate ($\text{PO}_4\text{-P}$) or oxygen (O_2) concentrations in the overlying water in **paper III**. One-way ANOVA was applied to study differences in P content between different sediment types in **paper I**, and differences in $\text{PO}_4\text{-P}$ and O_2 concentration above oxic, suboxic and anoxic sampling stations in **paper III**. In **paper III**, the differences in $\text{PO}_4\text{-P}$ and O_2 concentrations in water samples 1 m above the seafloor and close to the sediment surface were studied with paired sample t-test.

Principal Component Analysis (PCA) was used to reveal patterns in the data in **papers I and III**. PCA was used to examine which factors can explain the variability in sediment P content in **paper I**, and in **paper III** to find possible explanatory factors of $\text{PO}_4\text{-P}$ concentration in the near-bottom water and the internal P loading. Prior to running the PCA, all variables were logarithmically transformed to

meet the assumption of normality of error, and normalised to mean value of zero and dispersion of ± 1 to exclude the influence of differences in scales. Hierarchical clustering was used to group the samples and examine the grouping factors in the data in **paper III**, to detect possible patterns in the data, and to interpret which of the measured variables best explain the patterns.

2.5. Estimating the potential internal P loading

For the estimations of the magnitude of the internal P loading (**paper IV**), the potential release from the pools of Fe-P and organic P forms were estimated by calculating the decline of these P forms from one-cm thick sediment surface layer to the sediment layer below it, at 1–2 cm depth in the sediment (**paper 1**). Additionally, data on the decline of labile Fe-P and organic P fractions from spring to autumn (Lukkari, 2008; Thouvenot-Korppoo et al., 2012; Puttonen et al., unpublished) were used to define the P release rate from the sediment surface. Three different estimates of the potential internal P loading in the model area according to contrasting bottom water oxygen conditions were calculated. Scenario 1, a moderate oxygen status scenario was assumed to represent the actual net release of P from sediments in present environmental conditions. The scenarios 2 and 3 were assumed to represent the lower and upper limits of the potential internal P loading, respectively, depending on bottom water oxygen conditions (**paper IV**).

The estimates of the potential internal P loading were entered as a source of P into the FICOS water quality model. The simulated DIP values produced by the model were compared with observations of DIP concentrations in the model area (**paper IV**). The model simulations were run to evaluate the sensitivity of the model to the estimates of the potential internal P loading and to assess the accuracy of the estimates of the potential internal P loading across the Finnish Archipelago Sea in 14 sub-basins (Fig. 2.3). The sub-basins were defined by their morphology and hydrology according to EU Water Framework Directive 2000/60/EY, 23.10.2000.

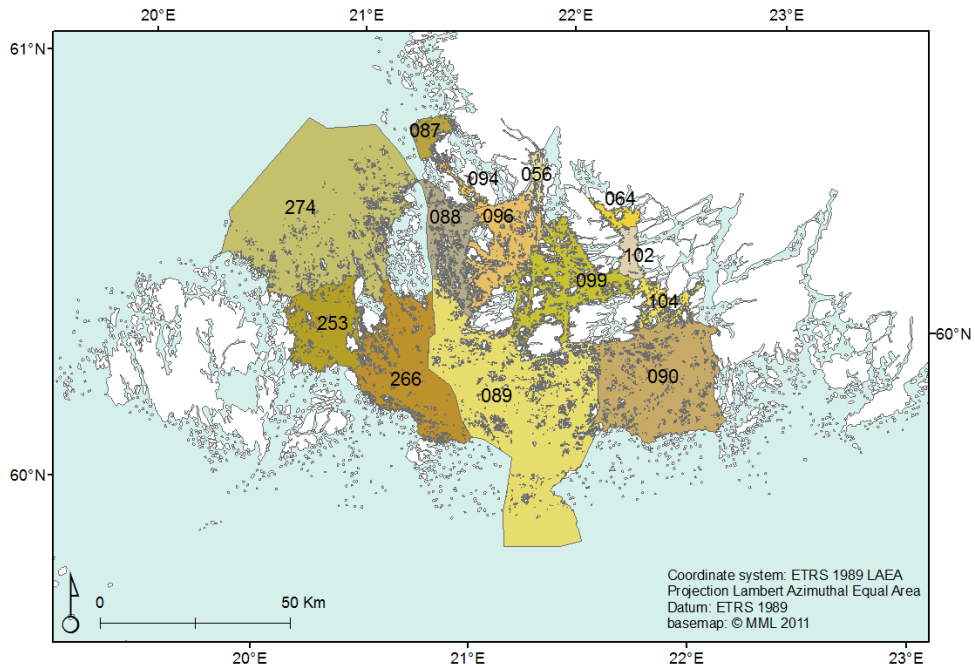


Fig. 3. The sub-basins used for comparison of the DIP concentrations simulated by the FICOS water quality model with observed values, acquired from the national monitoring database Hertta (Finnish Environment Institute, 2014). The number codes identify the sub-basins with respective model simulations in the text and Fig. 7a-c in **paper IV**).

3. Results

3.1. Phosphorus contents in the sediments

The seabed sediment surface layer (0–2 cm) was estimated to contain 126 000 tonnes P in the entire study area of 20,000 km² (**paper I**). The average total P content in accumulation (A) areas was 9.7 g m⁻², and in erosion/transportation (E/T) areas 7.5 g m⁻². The potentially mobile P pool in the two-cm thick sediment surface layer within the entire study area was 31,700–37,300 tonnes, of which 28,000 t were calculated to be stored in soft, organic-rich sediments of accumulation areas (Table 2 in **paper I**).

The phosphorus content was statistically significantly higher in the sediments of the A-areas than those in the E/T-areas (**paper I**). The total P content at the sediment surface varied from 570 to 6,420 µg g⁻¹ dw, the mean value in the A-areas (0–2 cm) was 1,760 ± 810 (± 1 standard deviation) µg P g⁻¹ dw, and in the E/T-areas (0–1/0–2/0–3 cm) 1,000 ± 480 µg P g⁻¹ dw. The extracted 'Fe-P' dominated the potentially mobile P pool in the sediment surface, ranging 5.5–65% of the total extracted P fractions (**paper I**). In the A-areas the mean value of the extracted Fe-P was 36% of the Tot-P and in the E/T-areas it was 20% (Fig. 4).

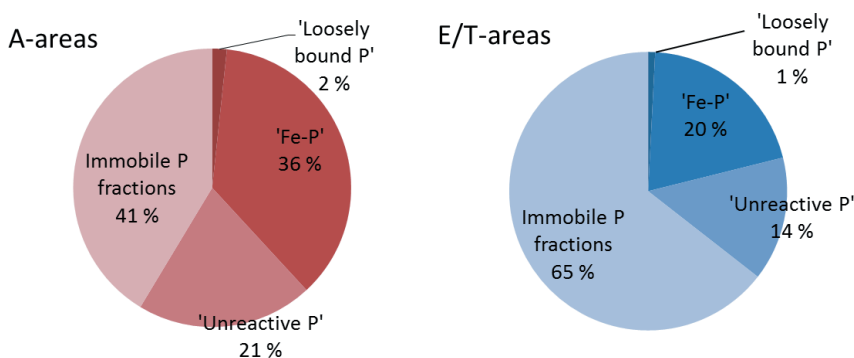


Fig. 4. The average composition of the extracted P fractions at the sediment surface in the accumulation (A) and erosion/ transportation (E/T) areas.

3.2. Spatial and vertical distribution of sediment P

High P contents in the sediments, i.e., the potential areas of intense P release, are located in the Finnish sea areas in the central part of the archipelago between the islands and off the river mouths. In the Swedish sea areas, the highest potentially mobile P contents were observed in the middle part of the Stockholm Archipelago and in sheltered basins in the northern part of the Swedish study area (Figures 7 and 8 in **paper I**).

In accumulation areas, the P content declined gradually from the seabed sediment surface towards deeper layers (**paper I**). The steepest decline occurred from the sediment surface, 0–1 cm or 0–2 cm, to 2–4 cm, and the P content stabilized generally at 6 to 10 cm depth in the sediment. Below 10 cm depth in the sediment, the mean content of 'Fe-P' was $120 \pm 89 \mu\text{g g}^{-1} \text{ dw}$, and that of 'Unreactive P' was $259 \pm 80 \mu\text{g g}^{-1}$. However, the contents of the extracted P fractions below 10 cm depth varied considerably, 'Fe-P' from 21 to $840 \mu\text{g g}^{-1} \text{ dw}$ and 'Unreactive P' from 31 to $450 \mu\text{g g}^{-1} \text{ dw}$.

In the E/T-areas, the decline of P content from the sediment surface was less pronounced than in the sediments in the A-areas. Total P content at the sediment surface in the E/T-areas was $955 \pm 448 \mu\text{g P g}^{-1} \text{ dw}$, and $658 \pm 106 \mu\text{g P g}^{-1} \text{ dw}$ below 10 cm depth. Most of the decline can be accounted for the thin, transient organic-rich layer on top of the sediment.

3.3. Phosphorus in settling particles

The amount and composition of P in the settling matter was highly variable both in space and time (**paper II**). The 'Loosely bound P', 'Fe-P' and 'Unreactive P' fractions together comprised approximately 50% of the Tot-P. Phosphorus content and composition in the settling particles were found to differ from those at the sediment surface. Overall, the content of 'Loosely bound P' was higher in the settling matter than at the sediment surface (**paper II**). However, the variation in the composition of P both in the settling matter and at the seabed sediment surface was large, and no common temporal pattern was observed. The deposition of dry matter, as well as total P were higher in the Åland archipelago than in the rest of the sediment trap mooring stations (**paper II**). There was a positive correlation (Pearson $r = 0.979$; $p < 0.01$) between dry matter and total P deposition among all of the studied sediment trap mooring stations (**paper II**).

3.4. Phosphorus recycling between the sediment and water

Phosphate concentration in the near-bottom water was statistically significantly higher than 1 m above the seafloor. The results in **paper III** show that P release from the sediments to the water column in these coastal and archipelago areas occur not only from anoxic or hypoxic seafloor areas, but also from sediments under 'normoxic' conditions. High $\text{PO}_4\text{-P}$ concentrations in the near-bottom water ($> 100 \mu\text{g P l}^{-1}$) were observed when the oxygen concentration in the near-bottom water was up to $8 \text{ mg O}_2 \text{ l}^{-1}$ (Fig. 5), and the sediment surface appeared oxygenated (**paper III**). The near-bottom water $\text{PO}_4\text{-P}$ concentration was high also at sampling stations where black, sulphidic layers in the sediment profile below the thin, brown, oxic surface layer were identified as signs of past occurrence of hypoxia (Fig. 4 in **paper III**). No single factor alone was found to control the phosphorus cycling between the sediments and water.

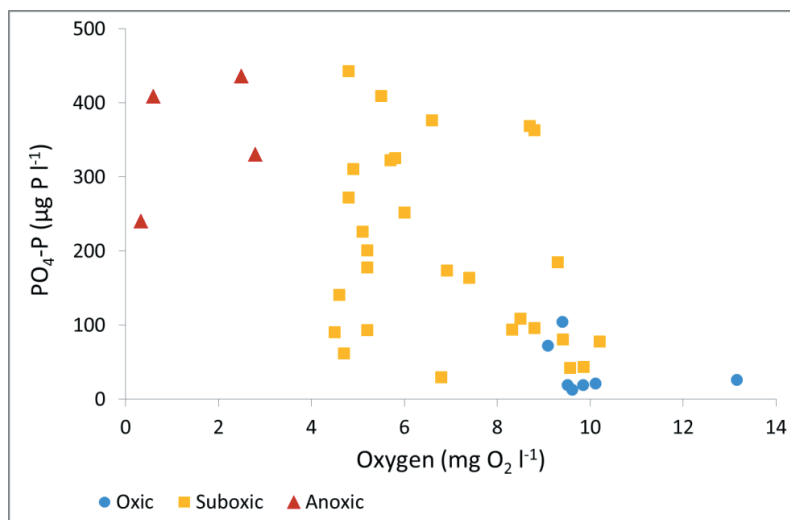


Fig. 5. The relationship between oxygen ($\text{mg O}_2 \text{ l}^{-1}$), and phosphate ($\mu\text{g PO}_4\text{-P l}^{-1}$) concentrations in the near-bottom water at the studied 39 sampling stations in **paper III**. The oxygenation status of the sampling stations is symbolised with dots (oxic stations), squares (suboxic stations with signs of past occurrence of hypoxia, but oxic sediment surface) and triangles (anoxic stations, sediment surface anoxic).

3.5. Estimates of the internal P loading

The P fractionation results were applied in estimates of the magnitude of internal P loading in the Archipelago Sea. The estimated average annual release, according to the three scenarios (**paper IV**), was $0.31\text{--}0.64 \text{ g P m}^{-2}$ from accumulation areas, depending on environmental conditions (Table 3 in **paper IV**). In the present conditions the P release was estimated to be 0.56 g m^{-2} from accumulation areas, resulting in a total net internal P loading of 3,200 tonnes P in the $12,700 \text{ km}^2$ model area. The locations of the most intense P loading from the sediments to the water we found in the organic-rich sediments with high content of 'Fe-P' and/or 'Unreactive-P' fractions (Fig. 8 in **paper I**), coinciding with low oxygen concentration in the bottom water. These occurred in shallow areas in the middle part of the Archipelago Sea in narrow straits and small basins and off the two largest rivers discharging to the study area (Fig. 6 in **paper IV**). The internal P loading was estimated to be low to moderate in the more open outer archipelago.

When the estimated values of P release in present conditions (scenario 1) were entered into the FICOS water quality model, the resulting simulated DIP concentrations in the surface water layer were in general in good accordance with the observed DIP concentrations in most parts of the study area (Fig. 7a in **paper IV**). However, in the sub-basins 99 and 102 in the middle parts of the archipelago, where the estimated internal loading was high, the observed DIP concentrations in the

surface water layers were lower than the simulated ones when the internal loading estimate according to the scenario 1 was used in the model. On the other hand, the observed values were higher than the simulated ones when the lowest internal loading estimate (scenario 2) was used. In the deep water layers, the simulated DIP concentrations were lower than the observed ones in the sub-basins 089, 090 and 102, even when the highest internal P loading estimate according to the scenario 3 was used (Fig 7c in **paper IV**). In the sub-basins 064, 087, 088 and 274, the simulated DIP concentrations in the deep water layers were higher than the observed ones (Fig. 7 in **paper IV**).

4. Discussion

4.1. *Phosphorus contents in the sediments*

A global comparison of the results in **paper I** with other coastal areas revealed that the total P content at the sediment surface in our study area is higher than in most eutrophied coastal or estuarine systems in the world. Corresponding values have been measured in the eutrophied, brackish-water estuary in the Chesapeake Bay (Jordan et al., 2008; Hartzell et al., 2010). However, the Tot-P contents found in the sediments in our study area exceeded sediment surface Tot-P contents in most brackish water coastal areas, for example in the MacKenzie River delta in the Canadian Arctic (788–1,586 $\mu\text{g P g}^{-1}\text{ dw}$), Gulf of Mexico (565–1,043 $\mu\text{g P g}^{-1}\text{ dw}$), Amazon shelf (462–712 $\mu\text{g P g}^{-1}\text{ dw}$; Ruttenberg and Goni, 1997), Delaware River estuary on the eastern coast of the USA (341–1,026 $\text{mg P g}^{-1}\text{ dw}$; Strom and Biggs, 1982), Peel Harvey estuary in Western Australia (169–711 $\mu\text{g P g}^{-1}\text{ dw}$; McComb et al., 1998), and Montego estuary on the western coast of Portugal (460–840 $\mu\text{g P g}^{-1}\text{ dw}$; Coelho et al., 2004). The sediments with high total P content in this study had also higher proportion of potentially mobile P fractions than reported in the above-mentioned studies. Differences in the sediment P contents in different areas of the world can be due to local sedimentary environments, the origin of the settling material, the quantity of P input, sediment and water chemistry, etc., but these results imply that the potential for internal P loading in the study area is pronounced on a global scale. The amount of P stored in only the 2-cm thick sediment surface layer in the study area of ca. 20,000 km^2 is more than three times the annual external P input to the entire Baltic Sea in 2010 (HELCOM, 2015). According to the estimates based on sequential extraction of P, approximately 25–30% of the Tot-P at the sediment surface is in potentially mobile form, and thus can be transformed into bioavailable phosphate with time in particular conditions. Moreover, the cycling of P between the sediments and water is not limited to the topmost 2 cm at the sediment surface. Phosphorus forms can be transformed within the sediment and diffusive transport of P from deeper sediment layers brings potentially mobile P to the sediment surface (Krom and Berner, 1981;

Reed et al., 2011; Egger et al., 2015a). Phosphorus can be released at least from 10 cm depth (Boström et al., 1982), possibly even from 20–25 cm depth in the sediments (Søndergaard et al., 2003).

In the Finnish sea areas, the areas of intense P release with high P contents in the sediments are located in the central part of the archipelago, in narrow straits between the islands and off the river mouths (**paper I and IV**). Those areas are sheltered and shallow, the water circulation is slow and almost continuous sediment accumulation occurs. In the Swedish sea areas, the highest potentially mobile P contents were observed in the middle part of Stockholm archipelago and in the northern part of the Swedish study area (**paper I**). High P contents in the sediments were located in areas where sediment accumulation is rapid due to river discharge and restricted water exchange. Fine-grained, organic-rich sediment with high P content has been accumulated in calm sedimentary environments in the vicinity of point sources of P, including municipal and industrial waste water discharge and fish farms. Yet, nutrients from point sources may be transported and spread into a wider area, and hence the impact of them will be obscured in monitoring, but the impact still exists in the sea. The coastal and archipelago areas receive nutrients also by currents from other sea areas. In the mosaic of islands, the water exchange with adjacent sea areas is restricted due to heterogeneous and patchy topography, which facilitates accumulation of sediments rich in organic matter and nutrients.

The internal P loading is expected to decline, as the P content at the sediment surface is reduced due to reductions in the external P input. However, the sediment surface P contents in this study were at the same level as measured in the Finnish Archipelago Sea in 1991 (Müller, 1997) and 2001 (Virtasalo et al., 2005). The decline of P content in the sediments as a response to the reductions in the external nutrient loading can be a slow process, considering the high potential for the internal P loading that maintains cycling of bioavailable P between the sediment surface and the water column. Furthermore, eutrophication has changed the biogeochemical conditions in the sediments, thus altering the P dynamics within the sediments and at the sediment-water interface. The increasing supply and subsequent degradation of organic matter has resulted in increasing rates of sulphate reduction and methanogenesis. As a consequence, the sulphate-methane transition zone has moved upwards in the Baltic Sea sediments (Egger et al., 2015b, 2016), causing transformation of P in deep sediment layers and upward migration of P, thus impacting the P content at the sediment surface. Although the content of the 'Loosely bound P' 'Fe-P' and 'Unreactive P' fractions below 10-cm depth in the sediments were regarded as a permanent depositional burial amount of those P fractions, diffusive transport of P from the deep sediment layers is likely to occur.

Furthermore, the local variations in the sediment P content and composition in the settling material were large (**paper II**), as well as the variations in the vertical distribution of P fractions in the sediments across the study area (**paper I**). In order to observe possible change in time, systematic monitoring would be required with uniform methods, in the same areas and at the same time of the year.

The vertical profiles of sediment P in the sediments of the A-areas revealed a steep decline of P content from the sediment surface towards deeper layers, which is typical for a eutrophic system (Rydin, 2000). The content of 'Loosely bound P' fraction at the sediment surface was relatively low, only 2% of the Tot-P in average. 'Fe-P' composed the major part of the potentially mobile P forms, i.e., 'Loosely bound P', 'Fe-P' and 'Unreactive P'. Also the content of 'Fe-P' declined downwards from the sediment surface more steeply than those of 'Loosely bound P', or 'Unreactive P' fractions. Furthermore, the variations in the contents of 'Fe-P' were largest of the three 'potentially mobile' P fractions in all investigated depths in the sediments. This suggests that the 'Fe-P'-pool dominates P release and the release from that P form appeared to be influenced by the existing environmental conditions. In contrast, less variation was observed in the downward decline of 'Unreactive P', suggesting relatively steady release of P from this fraction which is primarily labile organic P (**paper I and IV**). Although oxygen depletion may exhaust the 'Fe-P'-pool at the sediment surface, the size of the 'Fe-P' pool is also influenced by the quality of the deposited material, and no conclusions can be drawn of the oxygen conditions based on Fe-P at the sediment surface (**paper III**).

In the sediments of the E/T-areas, the vertical decline of P was less pronounced, and could be mainly attributed to the higher P content in the thin, transient surface layer that was rich in organic matter. While most of the internal P loading was assumed to occur from the sediments in the A-areas, it is possible that a smaller amount of P may be released from the sediment surface of the E/T areas. If the P release occurs from the sediments in the E/T areas, the 'Fe-P' pool is the most likely origin of the release, since organic content in these sediments is low and 'Fe-P' composes the major part of the potentially mobile P in them. Whether they act as a source or a sink of P still needs to be studied.

A certain part of the internal P loading comes from settling particles in the water column already before they are deposited onto the sediment surface (Hupfer et al., 1995; Faul et al., 2005). The composition of P and the existing conditions together determine how much P is released during particle deposition. Although a seasonal pattern in P deposition could be anticipated (Pettersson, 2001), these results indicate that the share of mobile P varied across locations and through time (**paper II**). The study did not reveal the reasons for the variability, but it can be assumed that the quality and origin of the settling material, the time the particles spend in the water column, and the

conditions in the water column, e.g., hydrodynamic conditions, temperature, salinity, oxygen and light availability, may cause variability both in the degree and time of P regeneration (Paytan et al., 2003). For example, fresh organic matter derived from phytoplankton production is more readily degraded than that of terrestrial origin (Ruttenberg and Goni, 1997), since terrestrial material has already been exposed to degradation during transportation. Regardless of the variability, in the scale of the whole study area on average 50% of the Tot-P in the settling particles will be transformed into bioavailable P, while the other half will be permanently buried within the sediments during depositional processes.

4.2. The estimated magnitude of the internal P loading

It should be noted that the internal P loading is not an additional source of P to the sea, but recycling of the P that has already entered into the system during decades due to external nutrient input that has long been exceeding the outflow and permanent burial of P into the sediments. Nevertheless, the internal loading contributes to the concentrations of bioavailable P in the water, thus affecting the level of primary production in the sea.

The seabed sediments in the study area contain a large pool of potentially mobile P. Besides sediment P contents, the physico-chemical conditions in the sediment and the sediment-water interface control the cycling of P and other elements between the sediment and the overlying water.

Many studies emphasize the role of oxygen as the primary control of P release from sediments in the deep, euxinic basins of the Baltic Sea (Conley et al., 2002; Eilola et al., 2009; Mort et al., 2010; Funkey et al., 2014). However, there are studies that show evident P release in 'normoxic' conditions, i.e., with oxygen concentrations well above 2 mg O₂ l⁻¹ in the bottom water (Matthiesen et al., 1998; Pitkänen et al., 2001; Gächter and Müller, 2003; Lehtoranta and Heiskanen, 2003; Suomela et al., 2005; Hupfer and Lewandowski, 2008; Steinberg, 2011). In deep basins, the water column is stratified by a halocline at 60–80 m depth, and oxic surface water reaches the seafloor only during occasional saline water inflows from the North Sea, which bring oxygenated water to the seafloor. In shallow coastal areas and mosaic archipelagos, the environmental conditions are essentially different from those in deep basins. Sediment accumulation rates are higher (Mattila et al., 2006); almost continuous recent sediment accumulation may occur in small inlets and bays as well as in shallow, sheltered basins between the islands (Virtasalo et al., 2005). Episodic and seasonal hypoxia is common, but generally the water column is mixed vertically throughout in the autumn, oxygenating the bottom layer. Oxygen deficiency in the bottom water was found to enhance P release in the study area, but P release occurred also from sediments with clearly oxic surface (**paper III**). According to the findings in this thesis, P dynamics involve more complex

processes than variability in bottom water oxygen concentration; the contents of potentially mobile P at the sediment surface, sediment grain-size and organic content, water depth, temperature, and exposure to waves and wind are factors that affect phosphorus exchange between the sediments and water. While in deep basins in stagnant conditions oxygen may control the P release (e.g., Ingall and Jahnke, 1994; Mort et al., 2010; Jilbert et al., 2011; Funkey et al., 2014), the results in **paper III** indicate that in shallow coastal areas P dynamics between the sediments and water involves complex and interconnected processes. Also the model results would give too low DIP concentrations, if zero internal P loading was used in the simulations in areas of good oxygen concentrations (Fig. 8 in **paper IV**), providing further evidence of P release from the sediments regardless of the oxygen conditions in the bottom water.

The simulated concentrations of dissolved inorganic phosphorus (DIP) and total phosphorus (TP) by the water quality model agreed in general well with the observed concentrations in the surface water layer in most of the sub-basins where the comparisons were made, when the potential internal P loading estimate according to the scenario 1 was used in the model (Fig. 7a in **paper IV**). However, in some areas the lowest simulated values in the surface water layer exceeded the observed ones, even when zero internal P loading was used in the model. According to the monitoring data (Finnish Environment Institute, 2014), P is often exhausted in the surface in the spring and summer, when the productivity is high. Hence, the internal P loading does not explain this discrepancy, but a possible explanation may be found in the functioning of the model, i.e., how the model simulates the nutrients coming from various external sources and from adjacent sea areas, the vertical and horizontal transport of nutrients within the model area and to the surrounding waters, and regeneration of nutrients in the water column. In the middle parts of the archipelago, the simulated DIP concentrations in the deep water layer are lower than the observed ones, suggesting higher than the estimated internal P loading in some areas. However, the simulated DIP concentrations in the surface water layer agree with the observed ones. Since the model simulations in the bottom water layer give an average value of DIP concentration below 10 m depth, the downwards increasing gradient in the DIP concentrations in the deep water layer cannot be displayed in the model. It is also possible that the dissolved phosphate in the bottom water is not completely transported to the surface water layer, but is partly recycled back to the sediment, for example through sorption onto sedimentary iron oxides in the autumn, when the bottom water becomes reoxygenated by mixing of the water column due to autumn storms and extinction of the thermocline due to drop of the temperature.

In the sub-basin 096, 099 and 102 in the middle parts of the archipelago, where the internal P loading was higher than in the outer, more open archipelago area, the observed DIP concentrations fall between the estimates in the scenarios 1 and 2 (**paper IV**). Thus, the comparison of the observed DIP concentrations in the monitoring data with the three estimates of the potential magnitude of the internal P loading in the model simulations (**paper IV**) suggests that the magnitude of the actual annual internal P loading could be between the estimates in the scenarios 1 and 2, i.e., approximately 1,800–3,200 tonnes of P from the Archipelago Sea sediments, or $0.31\text{--}0.56\text{ g P m}^{-2}$ from the sediments of the A-areas. Considering the P contents in the sediments of the studied Swedish coast and western Uusimaa, the internal P loading can be assumed to be of similar order of magnitude in the entire study area, amounting to 2,400–4,400 tonnes of P annually from the sediments of the A-areas (Table 2 in **paper I**) in the study area. However, the content of potentially mobile P forms in the sediments were high across the study area (**paper I**), and in unfavourable conditions the level of the internal P loading could rise up to 0.64 g P m^{-2} from the sediments of the A-areas (**paper IV**). This would correspond to ca. 5,100 tonnes of P from the entire study area of $20,000\text{ km}^2$. For comparison, the external loading of P in the entire Baltic Sea was 38,300 tonnes of P in 2010 (HELCOM, 2015), and internal P loading from $0.30\text{ g P m}^{-2}\text{ yr}^{-1}$ (Jilbert et al., 2011) to $5.58\text{ g P m}^{-2}\text{ yr}^{-1}$ (Conley et al., 2002) has been estimated to occur from deep, anoxic basins of the Baltic Sea.

4.3. The impact of the internal P loading from the sediments in the study area

The estimated internal P loading amounts to at least three times the external P input to the study area, thus, it plays a substantial role in eutrophication and the water quality in the studied coastal and archipelago areas, maintaining high P levels and productivity in the water. Release of P from the sediments provides a direct source of P for benthic primary producers, increasing the occurrence of microalgal production on the seafloor. If the phosphate that is leaking from the sediments reaches the productive surface layer by currents and vertical mixing of the water column, the productivity is increased. Enhanced growth of drifting benthic algal mats may cause changes in the benthic infauna communities, e.g., a decrease in the number of species and an increase in the abundance and biomass, if large amounts of decaying algal mats cover the seafloor (Heip, 1995; Karlson et al., 2002; Vaquer-Sunyer and Duarte, 2008). The decrease in grazers on epiphytes increases the growth of the epiphytes, and the epiphyte growth on seagrass and benthic macroalgae is increased also directly by nutrient enrichment in the water (Neckles et al., 1993). Perennial submerged plants are replaced by fast growing, annual seagrass and macroalgal species, and with increasing nutrient enrichment, by phytoplankton (Duarte, 1995). The changes in benthic vegetation also change habitats on the

seafloor as well as the overall food web structure (McClelland, 1998). Although response of seagrass and macroalgae on increasing nutrient input may be rapid, the recovery of the vegetation communities can be slow (Duarte, 1995).

While P is released even under good oxygen concentrations in the water, the internal P loading will induce phytoplankton production and organic matter supply to the seafloor. The increased supply and subsequent degradation of organic matter due to P enrichment in the water column exacerbates hypoxia. The oxygen concentration in the bottom water declines, the duration of episodic hypoxic events is prolonged and the spatial extent of hypoxia is extended (Diaz and Rosenberg, 2008). In addition to intensifying the internal P loading, hypoxia has diverse severe consequences to the coastal ecosystems, causing stress on benthic communities, including changes in species composition, decline in body mass, disturbance in larval production and dispersion, and overall shift of the energy flow away from consumers towards microbial activity (Baird et al., 2004; Conley et al., 2009a; Carstensen et al., 2014b). Microbially mediated sulphate reduction produces toxic hydrogen sulphide (H_2S) in anoxic conditions and in the presence of sulphate (Hensen et al., 2006), which leads to mortality of benthic invertebrates. Oxygen depletion affects the metabolism of benthic organisms; the role of bacteria may become more important in relation to the internal P loading (Gächter et al., 1988; Sinkko et al., 2013) with the predicted climate change and the spreading of hypoxia (Meier et al., 2011). Hypoxia may also reduce N removal from the system through denitrification and anaerobic ammonium oxidation (Conley et al., 2009b), which can further enhance P release from the sediments.

Benthic fauna modifies the substrate by burrowing into the sediment, transports particles and elements, and contributes to organic matter degradation and fluxes of oxygen and nutrients. Faunal composition and species abundance can affect the benthic nutrient fluxes. Oxygen is transported into the sediment through burrowing holes, and oxic zones are created in the burrows within reduced sediments. Oxygen depletion changes the physiology and behaviour of benthic fauna (Carstensen et al., 2014b). In benthic communities, changes in species richness and abundance, biomass and dominance patterns change the ecosystem functioning. Implications of disturbance include reductions in individual body size, biomass of the benthic community, reproduction rate, disruption in larval dispersion and shortening of lifespan. Redox potential at the sediment surface and functioning of benthic communities cause considerable spatial variation in P fluxes between different areas of the Baltic Sea (Norkko et al., 2015). Benthic infauna may induce either P retention to the sediments (Norkko et al., 2012) or release from them (Ekeröth et al., 2012). Hypoxic disturbance reduces ecosystem resilience, i.e., the capability of the ecosystem to cope with the

disturbance, and is likely to permanently impair the health of the ecosystem and reduce the ecosystem services (Villnäs et al., 2013), including mineralization of the settling organic matter and providing food source to higher trophic levels.

Bioturbation and bioirrigation may improve the P retention capacity of the sediments by transporting oxygen deeper into the sediments (Norkko et al., 2012), but it can also enhance the internal P loading by transporting P bearing particles to the sediment surface (Holdren and Armstrong, 1980; Clavero et al., 1992; Ekeröth et al., 2012; Chen et al., 2016). In addition, exposure of buried sediments to the bottom water by waves, land uplift, landslides, boat traffic, dredging, underwater constructions and other natural or human induced turbation and erosion may augment the internal P loading from the sediments (Søndergaard et al., 2003).

The results in this study show that the internal P loading will maintain high P levels in the water and hinder the alleviation of eutrophication as a result of nutrient reductions from the catchment. The model simulations (**paper IV**) suggest that a share of the phosphate that is released from the sediments to the water will be transported further to other sea areas. Hence, the high P content in these coastal and archipelago sediments and the associated internal P loading are likely to contribute to the phosphate levels in a wider area. Although reductions in the external nutrient input are expected to diminish the store of the potentially mobile P at the sediment surface, the changes in geochemical conditions in the sediments due to eutrophication may retard this process. The high level of internal P loading may lead to declining oxygen concentrations in the bottom water and spreading of the area of hypoxic bottoms, as well as extend the duration of episodic and seasonal hypoxia. Spreading and worsening of hypoxia may disturb ecosystem functioning and deteriorate benthic communities causing irreversible changes in the benthic communities and food web structure.

4.4. Recommendations for further research

Although this study has increased our knowledge of P contents in the sediments and understanding of the contribution of the internal P loading to eutrophication in the study area, plenty still remains to be unravelled. The sequential extraction analysis of P allowed estimations of the amount of potentially mobile P in the sediments and the settling particles (**papers I and II, III and IV**), but it did not provide detailed information of the P compounds in the sediments. The rate of depositional burial of organic P compounds depends on the composition of it. The behaviour of organic P compounds could be studied in more detail with nuclear magnetic resonance spectroscopy (Clark et al., 1998; McDowell and Stewart, 2005; Ahlgren et al., 2006). The processes of the P cycling in the heterogeneous coastal and archipelago areas are complex (**papers II and III**), and further research is

needed to increase our understanding of these processes. For example, sulphate reduction may enhance P release from sediments and increase the availability of dissolved inorganic P (Krom and Berner, 1981; Caraco et al., 1989; Gächter and Müller, 2003). The role of microbes may also be important in P release from sediments (de Montigny and Prairie, 1993). The transformations of P below the sediment surface and diffusive vertical migration of phosphate in the pore water and the impact of these processes on the amount of potentially mobile P at the sediment surface can be affected by the observed changes in the redox zonation in the sediments (Egger et al., 2015a, 2015b), and more research is needed on its impact on the cycling of P between the sediments and water. A complementing approach to study the P cycling could be to focus on the sediments' capacity to retain P and the pathways of permanent depositional burial of P. For example, the role of Fe-Mn nodules as possible sources or sinks of P in the coastal areas of the Baltic Sea deserves more research. The nodules may be locally abundant on top of the Baltic Sea sediments (Zhamoida et al., 1996; Glasby et al., 1997; Marcus et al., 2004; Vallius et al., 2011; Yli-Hemminki et al., 2016), and their role as a temporary store and possible sink or source of P may be important.

The pool of 'unreactive P' in the deep sediments layers formed a major part of the background P content, and it was abundant also at the sediment surface as well as in the settling matter (**papers I, II III and IV**). However, the sequential chemical extraction does not differentiate organic P compounds, and thus, the composition and behaviour of organic P could not be unravelled in this study. Other techniques, e.g., ^{31}P nuclear magnetic resonance spectroscopy can be applied to investigate the compounds of organic P in the sediments (Kolowitz et al., 2001). Additionally, in the water column, dissolved inorganic P (orthophosphate) is commonly considered the readily bioavailable form of P, but also organic P can be partly bioavailable, or regenerated into bioavailable form, which should be considered in monitoring when determining the levels of bioavailable nutrients in the water.

Furthermore, according to the available sediment maps, in the study area approximately 5,400 km², or 37% of the seafloor, are covered with glacial and postglacial clays. They were excluded from the estimates of the potential internal P loading in this thesis (**paper IV**) on account of the low content of 'Unreactive P' and organic matter in them together with good oxygen conditions in E/T-areas (**paper I**). However, high PO₄-P concentrations were observed in oxic bottom water (**paper III**), and increasing precipitation as a consequence of climate change and the still ongoing land uplift augment erosion in the coastal zone. There is little knowledge of the role of eroding old clays as a source or a sink of P.

The turnover time of P was estimated based on a coarse approximation of the sediment accumulation rate (**paper IV**). Although some information of sediment accumulation rates exists (Mattila et al., 2006; Jokinen et al., 2015), more studies are needed, since local variations are large due to heterogeneous sedimentary environments in the archipelago areas.

Eutrophication and hypoxia are known to drastically change the function of the ecosystem, but less is known about the direct impact of sediment P content and P fluxes on benthic communities.

5. Conclusions

The overall high contents of potentially mobile P in the settling particles in the water column (**paper II**) and at the sediment surface (**paper I**) across the entire study area, the estimates of the magnitude of the internal P loading (**paper IV**), as well as the high $\text{PO}_4\text{-P}$ concentrations in the near-bottom water (**paper III**) indicate that the internal P loading in these coastal and archipelago areas has a marked role for the ecological productivity. The local impact of the internal P loading on the water quality, habitats and food web structure is of fundamental concern particularly in shallow sheltered basins and inlets due to sluggish horizontal water circulation and the vulnerability of the habitats. Moreover, the internal P loading from the coastal and archipelago sediments hampers the improvement of the water quality in the entire Baltic Sea scale, as the nutrients are transported further by currents. It is also likely that internal loading of P influences the water quality and primary production in other coastal areas that are impacted by eutrophication. Knowledge of sediment P contents and understanding of local processes of P cycling between the sediments and water are needed for planning and cost-effective implementation of measures for water quality improvement to alleviate eutrophication and achieve the goals for “good ecological status” in the Baltic Sea, set by the EU Water Framework Directive (WFD, 2000), the Baltic Sea Action Plan (HELCOM, 2007) and the EU Marine Strategy Framework Directive (MSFD, 2008).

Acknowledgements

I want to thank my supervisor Docent Johanna Mattila, who has given me just the right amount of scientific supervision and liberty to find my own way of doing this. She also revealed to have developed during these years the wisdom — not of any less importance — to support, encourage or kick me forward, whatever I needed the most at any given time. I also thank my second supervisor Professor Ale Kotilainen for his always encouraging and supportive comments, and the very professional guidance in marine geology.

I wish to thank the pre-evaluators of my thesis, Professor Veli-Pekka Salonen and Assistant Professor Tom Jilbert for giving their time and effort to read my work, as well as for their professional reviews and valuable comments.

I thank Professor Erik Bonsdorff for his attention and interest towards my progress in my way to the doctoral degree.

The amount of the field data collected for this thesis is huge, and during these years I have had plenty of people assisting me with taking the samples. I thank each and every person who has participated to the field work. I also thank Peter Österholm and the Department of Geology and Mineralogy for the guidance and facilities for the hydrometer analyses. I thank all the co-authors in the papers included in this thesis: Mikael, Magnus, Per, Johanna, Ale, Tuula, Emil, Janne, Laura, Elina and Kaarina for co-operation and assistance in writing the papers. I thank specially Kaarina Lukkari, with whom I have so much enjoyed working. I have adopted her as an unofficial, extra supervisor and she has also become a dear friend to me. I also thank Risto Lignell for inspiring discussions and the encouragement he always showed to me. It has been a pleasure to meet partners and colleagues at the Seili Archipelago Research Institute and the ELY Centres of Southwest Finland and Uusimaa.

The field data were collected in co-operation with three projects:

- 1) Phosphorus from the seabed and water quality in archipelagos – modeling attempt (SEABED), financed by EU Central Baltic INTERREG IVA Programme,
- 2) Bottom dynamic model for phosphorus in Baltic Sea archipelagos, financed by the Nordic Council of Ministers, and
- 3) Internal loading of phosphorus from bottom sediments to water in the archipelago areas of Åland, SW Finland and W Uusimaa, financed by K.H. Renlund's Foundation.

I have received additional funding to complete this thesis from the Finnish Society of Sciences and Letters, the Science Foundation for Women, the Waldemar von Frenckell Foundation, Maa- ja vesiteknikan tuki ry., the Åbo Akademi Foundation and the Ministry of the Environment of Finland. I want to thank Professor John Cann in the University of South Australia, who inspired me into the fascinating world of forams and aroused in me the sparkle of becoming a scientist. Tuula Kohonen I thank for introducing me this appealing opportunity to join the group of marine scientists.

All my fellow students and colleagues at the Department of Biosciences deserve great thanks; I want to thank especially Henna and Sonja for your company, Claire, Nolwenn and Jørgen for delighting me by occasionally sharing the office with me. I am in debt to Ben, who helped me to put this thesis together. Huge thanks to Mikael, who has been an irreplaceable help to me with ArcGIS. It has been a pleasure to work with you all: Anna J., Martin, Anna P., Ben, Marie J, Floriaan, Emilia, Kerstin, Christina, Pierre, Lukas, Alexander, Cami, Tiina, Noora, Krister, Eva, Anna T., Marie N, Katri, Tore, Tom, Christoffer, Sami, Kai, Anki, Picke, Henry, as well as Tony and Martin at the Husö Biological Station, and my assistants in the field work: Matias, Juhani, Anna and Jolanda.

Thank you to Elina, my piano teacher, for giving me the pleasure of arts to balance my scientific thinking. I also thank my friends in the running group: Pekka for taking the responsibility of making us move, and for the ever so invigorating company Sini, Anna, Leena, Suvi, Jari, Aki, Jukka, Raine, J-P, Marja-Liisa, Maaret, Katri, Mira, Kati, Essi, and all the others with whom I have had the joy to share the joy of physical exercise. Without my friends I would be lost — I thank each and every one of you for being in my life.

I want to thank my dear family — my father, who has given me wing by introducing me to aviation already when I was a little girl. I thank my sister Eeva and her family, as well as my brother Seppo and his family for being such a part of my life. I am proud and privileged to belong to a family like no other.

I thank Arto for expressing his appreciation to my effort to study, and for sharing the responsibility of parenting two teenagers living in two separate homes.

I thank my partner Affe for listening to my troubles and sharing the joys. I thank him for staying calm and relaxed if I ever was stressed. I thank him for scientific discussions and reading and suggesting changes to my Swedish text. I thank my precious children Otto and Vilma, who have made my life. Words can never describe my love for them, and the importance of it every moment of my life.

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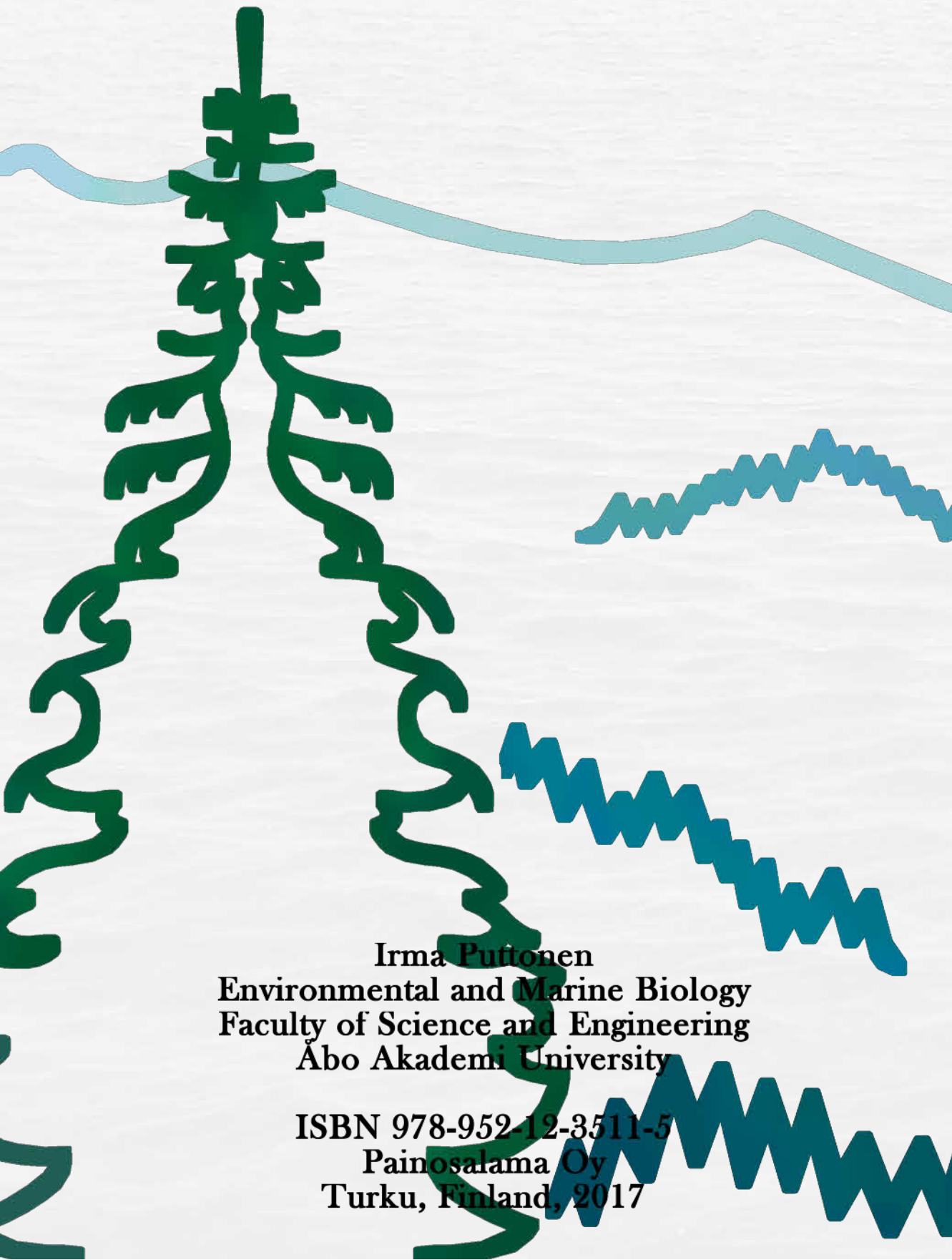
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ISBN 978-952-12-3511-5
Painosalama Oy
Turku, Finland, 2017