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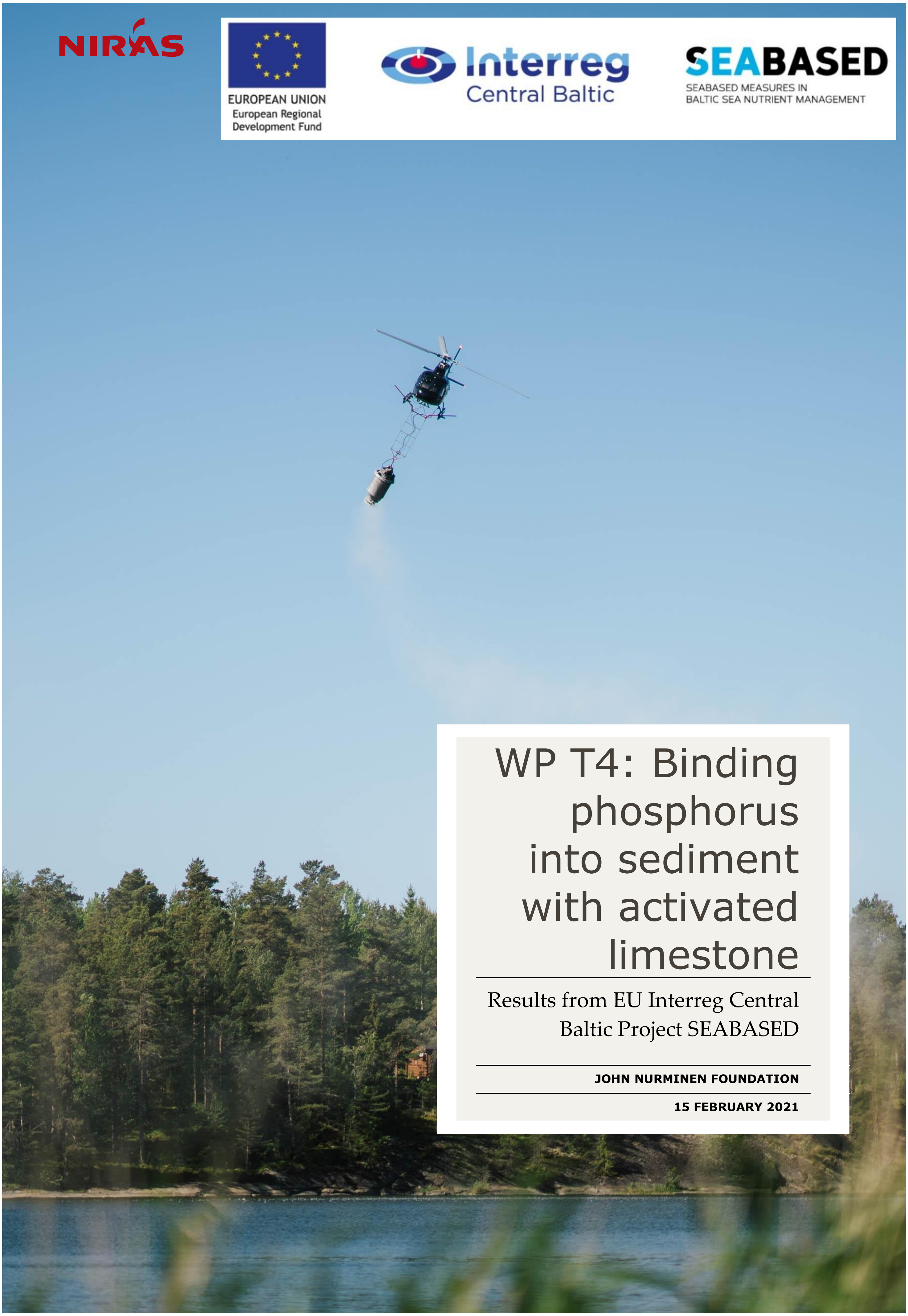
SEABASED
SEABASED MEASURES IN
BALTIC SEA NUTRIENT MANAGEMENT



WP T4: Binding phosphorus into sediment with activated limestone

Results from EU Interreg Central Baltic Project SEABASED

JOHN NURMINEN FOUNDATION

15 FEBRUARY 2021

Preface

The field trials described in this report were carried out within work package T4 of the Interreg Central Baltic SEABASED-project (Seabased Measures in Baltic Sea Nutrient Management), which was led by the John Nurminen Foundation. The planning and execution of the work was a joint effort of the project partners in Finland and Sweden: Stockholm University (SU, responsible partner); the County Administrative Board of Östergötland (CAB Ö); the Centre for Economic Development, Transport and the Environment for Southwest Finland (ELY); and, the John Nurminen Foundation (JNF). NIRAS Sweden was involved in the project, first as a sub-contractor to Stockholm University in the planning, permitting and implementation of the field trials that were carried out in the Stockholm Archipelago, and later as the author of this report on behalf of the John Nurminen Foundation.

The author wishes to thank all project partners for making available measurement data and other relevant information regarding the field trials. Also, the following project members are thanked for fruitful discussions regarding the interpretation of results and/or for providing comments on a draft version of this document which improved the report: Eva Björkman (SU/Levande Hav AB), Sven Blomqvist (SU), Jakob Walve (SU), Kenneth Winroth (CAB Ö), Irma Puttonen (ELY), Janne Suomela (ELY), Pekka Paavilainen (ELY), Miina Mäki (JNF), Marjukka Porvari (JNF) and Jouni Lehtoranta (Finnish Environment Institute, Steering group member of the SEABASED project).

Language review and quality control of the report was carried out by Ian Gloyne-Phillips and David Still at NIRAS United Kingdom.

Summary

This report describes four field trials in small semi-enclosed bays in Sweden and Finland with a new calcium (Ca) based phosphorus (P) binding material (marl sorbent). The marl sorbent was developed (based on previous research) with the intention of restoring the P-binding capacity of bottom sediments in oxygen depleted coastal areas in the Baltic Sea. It is designed to be applied to the water surface above a targeted area. After sinking through the water column, it is expected to form a fine-grained barrier to reduce phosphate (PO_4) flux from sediments to the bottom water. The field trials and development of the marl sorbent were conducted within the Interreg Central Baltic SEABASED-project (Seabased Measures in Baltic Sea Nutrient Management) which was led by the John Nurminen Foundation. Stockholm University was the lead partner for the work in the present report (WP T4 "Binding phosphorus into sediment with activated limestone").

Two of the field studies were whole-bay treatments with the marl sorbent. These were done in Kyrkviken Bay, Östergötland, Sweden (led by The County Board of Östergötland) and Kolkka Bay in the Archipelago Sea near Åbo, Finland (implemented cooperatively by Stockholm University, the Centre for Economic Development, Transport and the Environment for Southwest Finland and John Nurminen Foundation). These bays were selected as they were known to be affected by bottom water oxygen depletion. The aim was to test whether the addition of marl sorbent would lower the PO_4 release from the treated sediment areas and whether this would result in lowered P bioavailability in the water mass of the bays. Environmental monitoring programs were initiated in the bays before the marl sorbent treatment. The sorbent was spread out over the target areas by helicopter – a method which was found to be technically feasible. The target areas were 80 000–90 000 m^2 and the dosage of the marl sorbent varied between 100-130 g/m^2. No persistent clouding of the water or excessive dusting of the adjacent area were noted.

The environmental monitoring results showed no lasting effects of the marl sorbent treatments in either of the bays. The P levels in both surface and bottom waters were unchanged, although there were indications in both bays that PO_4 concentrations in the bottom water changed almost instantaneously after the treatment. However, this effect disappeared within hours to days of treatment. Autonomous monitoring results from Kolkka Bay show that the pH level in the bottom water increased by approximately 0.1 for a period of around two weeks after treatment. An increase in pH of this magnitude has no foreseeable negative environmental consequences.

The other two field trials were carried out in the Stockholm Archipelago, Sweden (led by Stockholm University with NIRAS as a sub-contractor). In the oxygen depleted Djuröfladen Bay, a small fraction of the bottom area in the deepest part of the bay was treated with the marl sorbent (400 g/m^2). Sediment samples were collected after two and nine months from within and outside of the treated area. The aim was to investigate differences between treated and un-treated sediment in terms of P content, pH and other variables. There were no signs of reduced P flux within the treated area compared to the control area. The marl sorbent had, however, caused an increase in pH and Ca-content in the sediment at the treated area. The pH-increase was small and is not considered constitute an ecological risk.

The final field pilot in Farstaviken Bay was undertaken to investigate the reason(s) for the lower than anticipated efficacy of the marl sorbent in the other field trials. In this pilot, different size fractions of the marl sorbent were exposed to oxygen depleted conditions in the deep water of the bay for either 13, 32 or 48 days. The P sorption efficacy of the marl sorbent was determined from the increase in sediment P content that occurred during the exposure periods. It was found that only a small fraction of the marl sorbent (size fractions >1 mm) disintegrated into a fine-grained material while most of the marl sorbent particles remained intact. This was in contrast to expectations as the marl sorbent was designed to disintegrate after some time in water. The fine-grained material had a considerable sorption capacity for P, although much lower than the sorption capacity in laboratory experiments which preceded the field trials. The results from Farstaviken Bay highlight the need for further development of the method to improve efficacy in coastal areas of the Baltic Sea.

In light of the field trial results it is concluded that there were no negative environmental consequences from the marl sorbent application to targeted areas. It has also been shown that the marl sorbent has a preferential affinity to bind P but that the P binding capacity was lower than anticipated based on previous results from the laboratory. The comparatively low binding capacity of the marl sorbent used in the field trials is attributed to sub-optimal conditions during the production stage (heat treatment of the raw material) and further development of large-scale production is required. It is recommended that future developmental work with the marl sorbent should be carried out in parallel with mesocosm-scale experiments to get a good estimate of the P binding efficacy of the manufactured sorbent in natural conditions before further field trials are performed. The importance of adequate monitoring during future potential field trials is stressed. Preferably, field sites with ongoing environmental monitoring and historical time series of physicochemical data should be selected. Additionally, autonomous measurement systems generally provide the most cost-efficient way to obtain measurement data with enough temporal resolution.

Contents

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1 Introduction

Increases in the areas of marine sediments covered by bottom water with little or no dissolved oxygen (DO) (so called "dead zones") pose a major threat to coastal marine areas all over the world (Levin et al. 2009). The main driver for the development of oxygen depleted sediments is increased oxygen consumption brought on by eutrophication. The most apparent effect of oxygen depletion is its impact on faunal assemblages living in or near the bottom, but changes in redox conditions also affect geochemical processes in the sediment and bottom water. For example, low oxygen conditions (hypoxia) or complete depletion of DO (anoxia) in the bottom water is well-known to lower the sediment's capacity to retain phosphorous (P) (McManus et al. 1997). In other words, a greater proportion of deposited P is re-mobilized from the sediment to the water column if the bottom water is hypoxic or anoxic than if it is well oxygenated.

Oxygen depleted sediments are widespread in the Baltic Sea and their lowered P retention capacity has been identified as a major issue associated with eutrophication (Conley et al. 2002; Viktorsson et al. 2013).

This report describes four field trials with a newly developed calcium (Ca)-based sorbent for P. The sorbent was developed to increase the P-binding capacity of oxygen depleted sediment and thereby to counteract the effects of eutrophication. It was designed to be applied to the water surface and thereafter sink down to the sediment surface. Once on the seafloor, the sorbent is designed to form a thin layer in the surficial sediment to trap phosphate from being released into the water column.

The sorbent is produced by heat treatment of marl, which is a by-product of limestone excavation. The raw material originates from the island of Gotland, Sweden and contains over 90% calcium carbonate ($CaCO_3$) by weight. The marl sorbent consists of dry, light grey particles, 0-10 mm in size and the materials' potential to bind P in Baltic Sea sediments was identified by Blomqvist and Rydin (2009). By heat treatment of the marl a minimum P sorption capacity of a lower-end value of 16.8 g P/kg was determined in laboratory studies of the present project. Previous experimental results with marl sorbent that was not heat treated was reported by Blomqvist & Björkman (2014) and briefly by Kononets et al. (2021).

The field trials (pilots) were conducted in Sweden and Finland. Two of the pilots were rather large-scale experiments aimed to lower the concentration of P in the water column of semi-enclosed coastal bays through addition of the marl sorbent to oxygen depleted sediment within the bays. In these trials the marl sorbent was applied by helicopter and potential positive and negative effects of the marl sorbent additions were studied by environmental monitoring programs focusing on measurements in the water column of each bay. These field trials were also performed to test the practical and technical feasibility of spreading the marl sorbent by helicopter and to assess the risk of dusting of adjacent areas by this activity.

Two smaller field trials focusing on changes in sediment parameters due to marl sorbent addition as well as the influence of *in situ* field conditions on the marl sorbent itself were also performed.

1.1 Scope and structure of the report

This report describes the results of the four field trials with the marl sorbent that were carried out within work package (WP) 4 ("Binding phosphorus into sediment") of the SEABASED-project. WP4 also included a developmental phase and laboratory experiments with the marl sorbent. This has been described in previous reports and only certain relevant aspects are reported here.

The following four chapters describe each field trial in chronological order. A summary of the main findings and an outlook is given in the last two chapters.

2 Kyrkviken Bay (field pilot experiment 1)

2.1 Background and aim

Field pilot experiment 1 was the first ever trial with the marl sorbent in the field. The aims of the experiment were to assess and evaluate: 1, the method of application (i.e. spreading); and, 2, the marl sorbent's potential to improve environmental conditions in the water column by reducing the release of P from the sediment. Preparatory work included the initiation of a monitoring program in the bay to be able to detect changes brought on by the marl sorbent.

1. A key aim was to test the feasibility of spreading marl sorbent by helicopter over a relatively large area and to assess potential risks related to this activity. More specifically, the settling of the marl sorbent was documented to see whether the material settled to the seafloor as intended, or if substantial clouding of the surface water occurred. Furthermore, the field trial gave an indication on the level of dusting of adjacent areas that can occur in connection with loading and spreading.

2. Another key aim of the field trial was to improve environmental conditions in Kyrkviken Bay by reducing the recycling of P from the bottom sediment and to document the effect of the marl sorbent addition. This was done by physicochemical monitoring of the water column in the bay, before, during and after the spreading.

2.2 Method

2.2.1 Study site

The semi-enclosed Kyrkviken Bay is located 11 km east of Valdemarsvik in south-eastern Sweden (Figure 2.1). The surrounding area consists mainly of forest and agricultural land. The area is sparsely populated, although the village of Gryt is located a few hundred meters north-east of the bay. The maximum depth of the bay is approximately 8 m according to the sea chart and its total surface area is 0.3 km^2. A narrow strait (Fårströmmen) connects Kyrkviken Bay with another semi-enclosed bay (Gamlebofjärden Bay, with a maximum depth of around 6 m.). In turn, Gamlebofjärden Bay connects with an inner archipelago area of the Baltic proper via a narrow strait. A small stream (Kvarnbäcken) discharges into Kyrkviken Bay. The mean daily water flow in Kvarnbäcken in 2019 was 0.13 m^3/d[*], which corresponds to a total water discharge of 4.2 km^3/yr. Recent bathymetric data show that the mean depth and total volume of Kyrkviken Bay are 4.6 m and 1.4 km^3, respectively. Thus, the water flow from Kvarnbäcken would replace the water volume in Kyrkviken Bay in approximately 120 days. However, due to thermal and salinity stratification the turnover time of the surface and bottom water is unlikely to occur at a similar rate.

No official historical monitoring data were available for Kyrkviken Bay, but low oxygen conditions were known to develop, at least semi-periodically, which is expected given the bay's morphology and location. On this basis, the bay was selected as a suitable pilot site for marl sorbent spreading. The bay's sheltered location in a rural and easily accessible area was also considered as favourable.

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[*] Model data from the Swedish Meteorological and Hydrological Institute (SMHI). Downloaded 2021-01-15: http://vattenweb.smhi.se/modelarea/

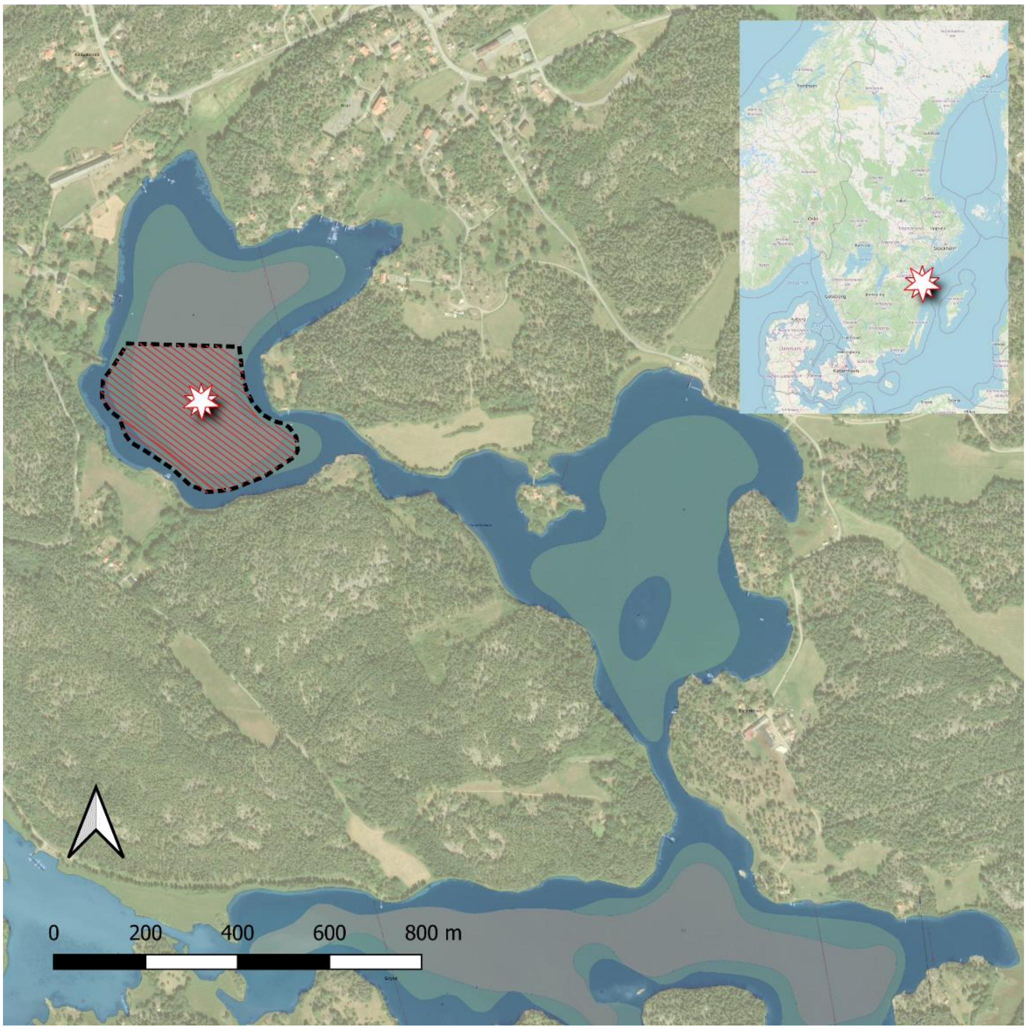


Figure 2.1 The Kyrkviken Bay pilot site. The dashed line shows the targeted area for the marl sorbent. Thin red lines show the logged flight tracks of the helicopter spreading the marl sorbent. The star marks the sampling point.

2.2.2 Field work and spreading of the marl sorbent

The objective was to spread the marl sorbent over the deepest area of the bay where oxygen depleted conditions are most likely to develop. Bathymetric scanning was conducted to define the treatment area. After review of the bathymetric data, a 0.09 km^2 area in the southern (and deepest) part of the bay was selected (Figure 2.1).

A water column measurement program was initiated in June 2018 to verify that low oxygen conditions occurred in the selected treatment area and to gather a time series of data for evaluation of the effects of the marl sorbent addition. The monitoring program included monthly measurements of nutrients (total N, total P, PO_4, NO_2, NO_2+ NO_3), temperature, DO, salinity, pH, alkalinity, total organic carbon (TOC), chlorophyll a and absorbance (420 nm/5 cm) at one sampling site (N 58.17859, E 16.79380, WGS84). All measurements were made in the surface water as well as 0.5–1 m above the bottom (i.e. at two measurement depths per sampling occasion). Positioning was facilitated with a GPS-controlled electric motor, so no anchoring occurred during field work. Water samples were analysed by an accredited laboratory (SYNLAB Analytics & Services Sweden AB) using accredited methods. Measurements of temperature, salinity and DO concentrations were done with a handheld sonde (YSI PRO).

The spreading of marl was conducted on 17 September 2019. This was initially planned to be carried out from a boat but it became clear that spreading by helicopter would be a better option since it would be much faster and more cost-efficient. Also, it became clear that the marl sorbent would likely be more evenly spread over the treatment area by helicopter than by boat. The marl spreading was conducted by a company that specializes in lime-treatment of lakes. Dusting of adjacent areas by the marl sorbent was identified as a potential risk in windy conditions. Therefore, the marl spreading was conducted on a calm day.

A total of 12 000 kg of marl sorbent was applied by helicopter over the selected treatment area which corresponds to 130 g sorbent/m^2. With an estimated binding capacity for P of 16.8 g/kg it was calculated that the sorbent would increase the sediment's capacity of retaining P by 2.2 g/m^2. This is roughly equivalent to the amount of P which is typically rapidly released from accumulation sediments in the Baltic Sea proper during a shift from oxygenated to de-oxygenated conditions in the water column (Conley et al. 2002; Stigebrandt et al. 2014). Thus, immobilization of 2.2 g P/m^2 within sediments in areas with de-oxygenated bottom water could offset the reduced binding capacity of P due to oxygen depletion. The total amount of P which could potentially be immobilized in the sediment was estimated to ~200 kg (16.8 g/kg x 12 000 kg) which is in the same range as the annual P-load from the stream Kvarnbäcken (average value of 311 kg/yr. for the period 2004-2019* above).

Water sampling was conducted before and after spreading on the day of application in order to detect potentially rapid changes in physicochemical variables. Additional water sampling was also carried out eight days after the application of the marl sorbent.

The monitoring program in Kyrkviken Bay is ongoing and is planned to continue until October 2021. This report includes data until October 2020.

2.3 Results and discussion

2.3.1 Observations from the spreading of marl sorbent

The helicopter flew over the area about 20-25 times to ensure that the material was evenly spread (Figure 2.1). Based on visual observations from the helicopter and from the shore, minor dusting of the marl sorbent occurred during the spreading. Due to calm weather, the dust remained confined to a small area directly adjacent to the treatment area and no observable dusting occurred over inhabited areas. Also based on visual observations, clouding of the water due to the marl spread was very limited and passed quickly.

2.3.2 Seasonality of physicochemical variables

The available data indicate that annual variations in water temperature were broadly similar throughout the study period (June 2018 to October 2020) although the highest temperatures were measured during an exceptionally warm summer of 2018. The surface water reached maximum temperatures of 20-25 °C in July–August while the bottom water was generally 10 °C cooler in the same periods (Figure 2.2).

Clear increases in bottom water temperature (Figure 2.2) and DO concentrations (Figure 2.3) occurred in late summer each year (around day 240). These increases were coupled to concurrent decreases in surface water temperature (Figure 2.2), indicating water column mixing. Due to stagnation, bottom water DO concentrations were generally close to zero between day 120–240 (i.e. from May until early September), although very low concentrations were also measured in January and March 2019 and 2020, as well as in early October 2020. Temperature data suggest that mixing could have occurred earlier in 2018 (August) compared to 2019–2020 (September) (Figure 2.2) but PO_4 and DO data suggest mixing in September in all three years (Figure 2.3). After each mixing event the available data suggest that the whole water column remained isothermal until the following spring. The salinity difference between surface and bottom water was generally less than 0.5 units but occasional salinity differences of up to 3.2 units were observed in early spring and autumn due to decreases in salinity in the surface water, presumably due to freshwater inflow from Kvarnbäcken.

Water turnover in autumn led to lowered nutrient concentrations in the deep water and increased concentrations in the surface water (Figure 2.3). This is expected as nutrient levels before mixing occurred were higher in the bottom water than in the surface.

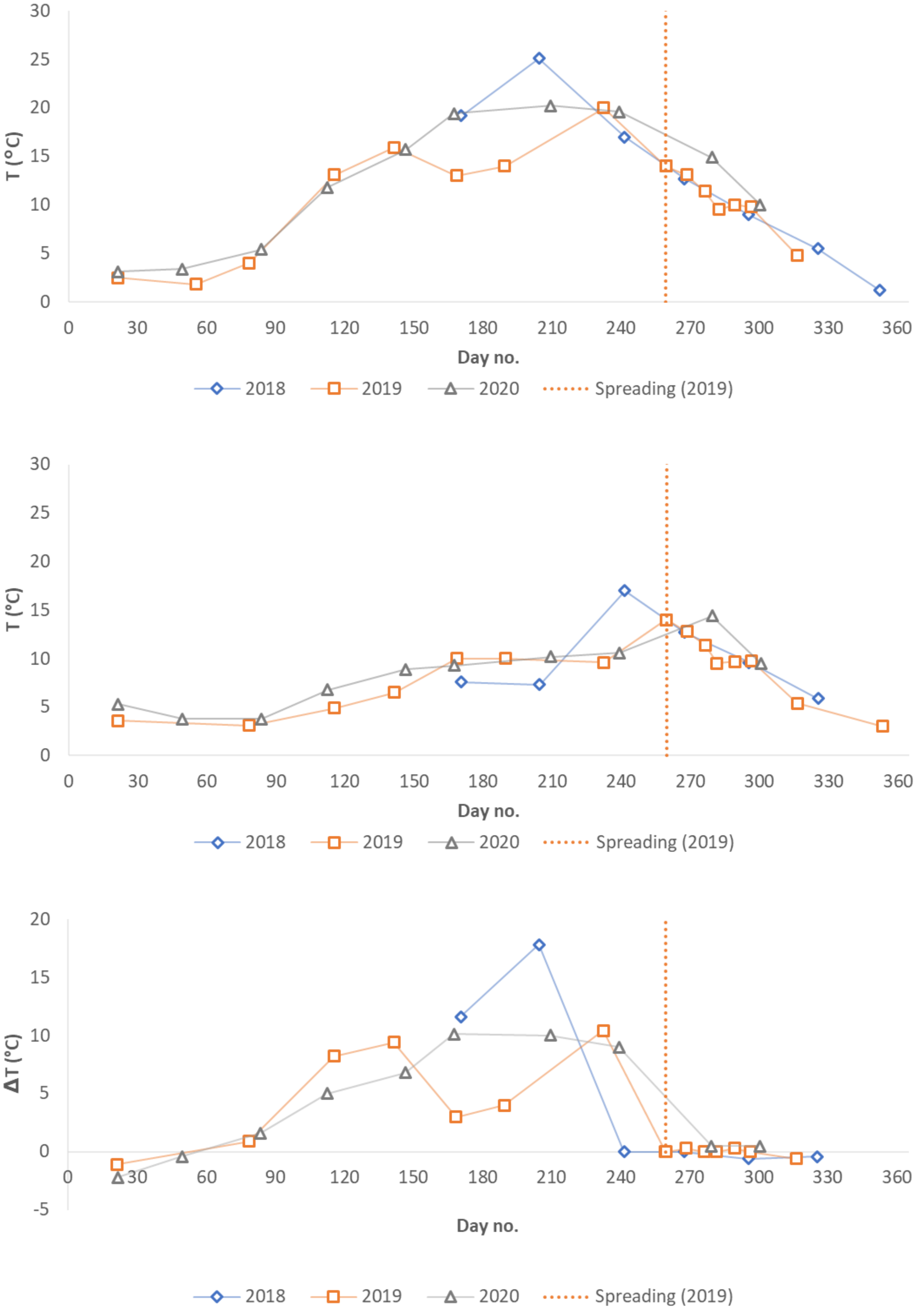


Figure 2.2 Water temperature in surface (top panel) and bottom water (middle panel) in Kyrkviken Bay. Lover panel show temperature difference (surface – bottom water).

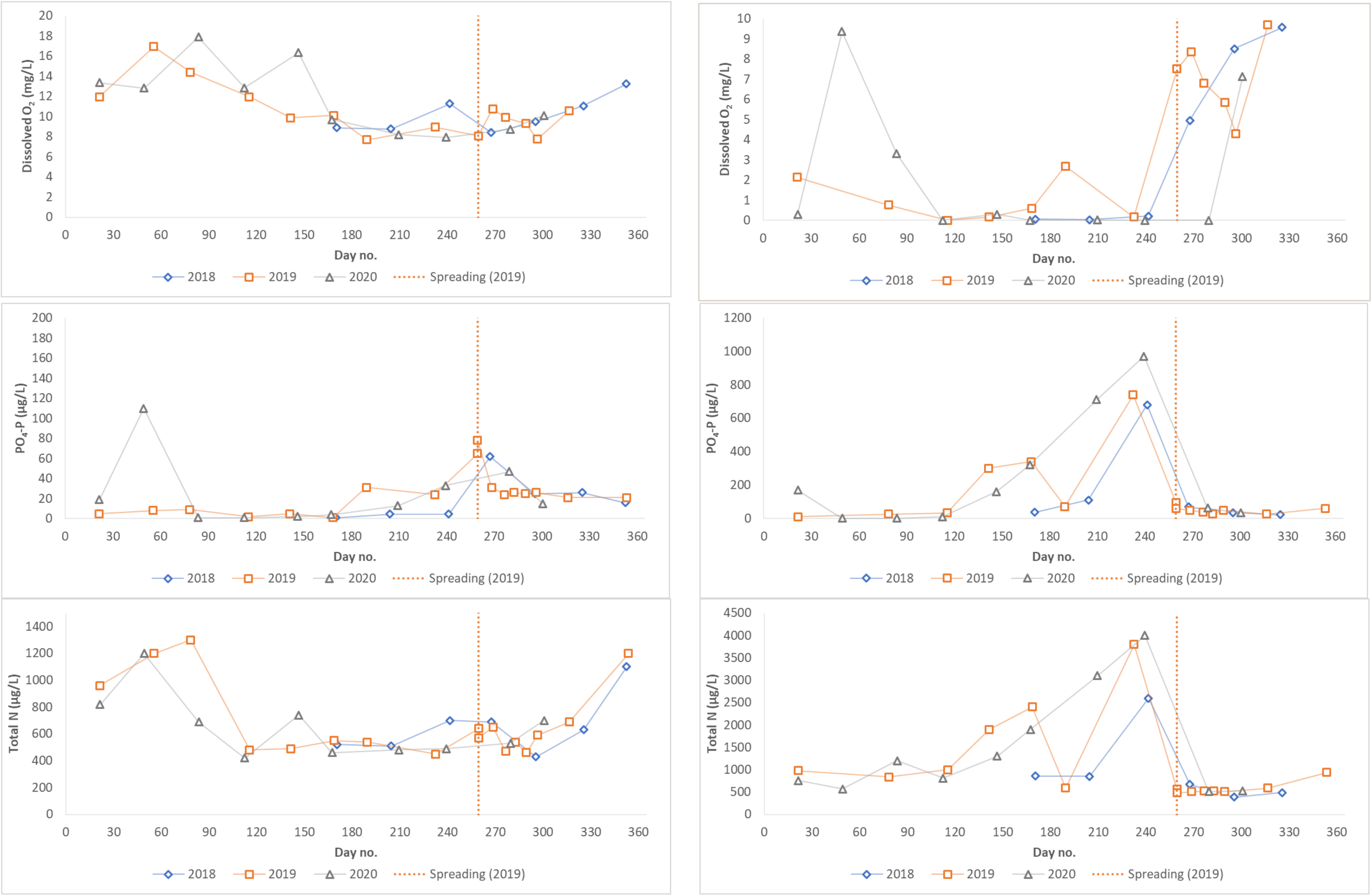


Figure 2.3. Concentrations of dissolved O2, PO4, and total N in the surface (left) and bottom water (right) in Kyrkviken Bay. Note different scales on the y-axes.

2.3.3 Short term effects of marl sorbent addition

In 2019, turnover of the water column had occurred by the time the spreading was performed (Figure 2.2-Figure 2.3) and both temperature and salinity were identical in the surface and bottom water. Also, the surface and bottom water had the same concentration of total P just before the spreading (130 µg/L) although PO_4 constituted a larger fraction of the total P concentration in the bottom water (96 µg/L) than in the surface water (65 µg/L). One hour after the spreading had been completed total P and PO_4 concentrations in the bottom water had decreased by almost 40 µg/L or 28-40% while total P and PO_4 in the surface water as well as total N levels and other variables at both depths remained within the range of analytical uncertainty (Table 2.1). Thus, there is some indication that the marl sorbent addition caused a rapid decline of the PO_4-concentration, plausibly due to sorption of PO_4 by the marl sorbent while it settled through the water column. However, it should be noted that the evidence for this is weak since it is based on unreplicated measurement data.

Table 2.1 Variation in measured water quality parameters before and after marl sorbent application. Combined analytical uncertainty calculated as the root of the squared sums of the uncertainty (in µg/L) related to each value.

	Concentration before spreading	Concentration one hour after spreading	Change	Analytical uncertainty	Combined analytical uncertainty
Surface water	µg/L	µg/L	µg/L	%	µg/L
Total N	640	570	-70	30	254
Total P	130	120	-10	15	23
PO_4	65	78	13	15	13
Deep water					
Total N	570	480	-90	30	219
Total P	130	94	-36	15	24
PO_4	96	58	-38	15	17

2.3.4 Long term effects of marl sorbent addition

After autumn mixing and the marl sorbent treatment in September 2019 the water column remained oxygenated (> 4 mg/L O_2) throughout the remainder of the year (Figure 2.3). Low oxygen conditions developed in the bottom water in winter 2019/2020 (deep water oxygen data is missing from the last measurement campaign in 2019). From late April until early October 2020 (day 112 – 279) oxygen levels in the deep water remained below 0.5 mg/L and the PO_4 concentration progressively increased in the bottom water during this time (Figure 2.3). The rate of increase of PO_4 was similar during periods of anoxia in 2018 and 2019. Thus, the variations in water column PO_4 concentration give no indication of supressed PO_4 release from the sediment due to marl sorbent addition.

2.4 Conclusions

The spreading of the marl sorbent by helicopter went as planned and without excessive dusting outside of the treatment area. This was due to calm winds. Clearly, spreading of marl sorbent in windy conditions should be avoided, especially in the vicinity of inhabited areas and private property (including boats).

The difference in total P and PO_4 shortly before and after the spreading of the marl sorbent give some indication of PO_4 sorption by the sorbent on the time scale of hours. The water monitoring data do not, however, indicate any lasting changes to the variability of physicochemical parameters after the spreading of the marl sorbent. Thus, there is no evidence that the marl sorbent influenced the P retention in the sediment or had any other effect in Kyrkviken Bay. As the annual dynamics in temperature and DO dynamics were rather similar throughout the study period (2018–2020), it was expected that the monitoring program carried out would be sufficient to detect any major effects brought on by the addition of marl sorbent. However, to maximize the probability of detecting changes in future studies with similar experimental designs, it would be beneficial to select a field site where an environmental monitoring program is ongoing and a timeseries of environmental monitoring data is already available. Otherwise, there is a substantial risk that naturally occurring interannual variability complicates the evaluation of results.

3 Djuröfladen Bay (field pilot experiment 2)

3.1 Background and aim

The pilot experiment in Djuröfladen Bay was the first field trial with the marl sorbent in the Stockholm archipelago. The aim was to investigate changes in the sediment by marl sorbent addition by comparing sediment parameters in and outside of a sub-area of the bay that was treated with the marl sorbent.

Our hypothesis was that the addition of marl sorbent would immobilize phosphate in the sediment pore water that would otherwise flux out into the water column. Therefore, the marl sorbent was predicted to increase the concentration of total P and lower the concentration of phosphate in sediment pore water in the treated sediment. Additionally, Ca concentration and pH were expected to increase in the sediment layer in close vicinity of the sorbent.

Another aim of the field trial was to assess whether the spreading of marl would cause clouding of the surface water, which had been identified as a potential risk in the permit application process.

3.2 Method

3.2.1 Study site

Djuröfladen Bay (Figure 3.1) is a small semi-enclosed bay in the Stockholm archipelago, Sweden (Värmdö municipality). The total surface area is about 0.03 km^2 and the maximum water depth is 11 m in the sea chart. There are no streams entering Djuröfladen Bay, but it is connected to the adjacent sea (the water body Breviken) through a shallow (2 m), narrow strait in its southern part. There are two marinas within the bay which is densely occupied with moored boats during the recreational boating season.

There is no ongoing environmental monitoring in Djuröfladen Bay but previous monitoring (1996–1999) revealed seasonally occurring oxygen depleted and sulphidic conditions in the deep water. Measurements by Stockholm University in the summers of 2015, 2017, 2018 and 2019 also showed oxygen depleted conditions each time.

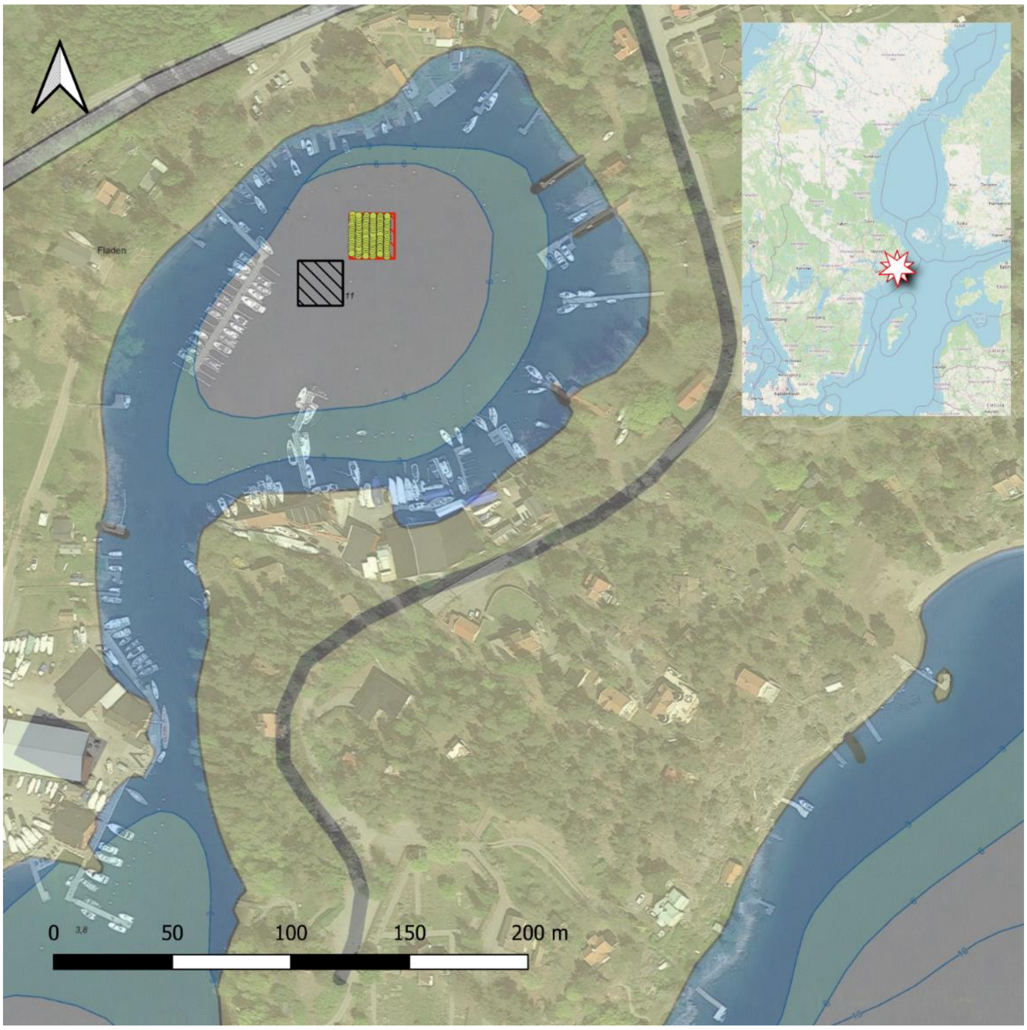


Figure 3.1 Djuröfladen Bay. Red and black hashed squares show the treatment and control plots, respectively. Green markers show positions logged during the spreading of the marl sorbent.

3.2.2 Preparatory work

The experiment included preparatory field investigations in during which physicochemical conditions in the water column were measured at several occasions. In December 2019 surveys of the bathymetry and visual assessments of sediment type within the bay were performed. Using this information, two sub-areas (treatment plot and control plot) were defined. The criteria for selecting these areas were that they had very similar water depth and sediment characteristics. Also, the sediment surface within both plots were flat.

3.2.3 Spreading of the marl sorbent

The marl sorbent was applied to the treatment plot on 16 December 2019 while the control plot remained untreated. The spreading of the sorbent was done from a small boat equipped with a RTK GPS-device, which allowed for very precise positioning (X/Y-error < 1 cm). The GPS-device was connected to a handheld tablet showing the current position and the predefined grid of the treatment plot. The boat was attached by lines to anchors or buoys outside of the treatment plot and positioning of the boat was done by adjustment of the lines.

Spreading of the marl sorbent was done by hand via a 3 m^2 (1 x 3 m) wooden frame mounted on the side of the boat to ensure uniform application (Figure 3.2). In between each addition, the boat was repositioned 1-3 m (depending on direction) until the whole treatment area (16 m x 16 m = 256 m^2) was covered. A total of 108 marl sorbent additions (see Figure 3.1) were performed (18 x 6). A permanently mounted compass was used to aid maintaining the boat’s heading during the spreading.

Figure 3.2 Marl sorbent spreading in Djuröfladen Bay, 16 December 2019.

3.2.4 Sediment sampling

A sediment core sampler, intended for use in soft sediments, was used. It is equipped with an 8.4 mm diameter acrylic tube which collects the sample. The sampler was gently lowered by hand to the bottom. Four vertical and adjustable stainless-steel rods (9 mm diameter, 1 m length) mounted in a square formation outside of the core made first contact with the sediment surface. By going into the sediment, the rods unloaded the corer so that the tip of the core tube was resting a few cm above the sediment surface. Thereafter, the core tube was gently inserted into the sediment to collect the sample. The sampler was then pulled up by hand to the surface where the core sample was carefully removed and immediately sectioned on board the boat. The whole sampling procedure was video documented *in situ* and only cores that were collected without signs of disturbance by the sampling procedure (after review of the video material and by visual inspection on board the boat) were used.

Sediment samplings were performed on 3 February 2020 and 1 October 2020, i.e. approximately 1.5 months and 9.5 months after addition of marl sorbent to the treatment plot. On 3 February a total of eight cores were collected, four from within the treatment area and four from the control area (Figure 3.1). Two cores from each area were sectioned in 2 cm intervals down to 8 cm sediment depth and the individual samples were analyzed for dry content, pH and total concentrations of 15 elements (As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Ni, P, Pb, Si, V, Zn). The remaining two cores from each area were used for determination of pore water concentrations of nutrients and elements (NH4, NOx, SiO2, PO4, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Zn). Pore water extraction was done using Rhizon samplers (Seeberg-Elverfeldt et al. 2005) mounted 1 cm above the sediment surface and at 1 cm intervals down to 6 cm sediment depth. The extraction of pore water was problematic and time consuming due to freezing conditions.

Seven sediment cores were collected on 1 October 2020 (four inside treatment plot and three from the control area). These cores were sectioned in 2 cm intervals down to 10 cm sediment depth (one of the cores down to 12 cm). Each of the sectioned sediment samples was analyzed for dry content, pH and the 15 elements listed above). No pore water analysis was undertaken.

The water depth (recorded by echo sound) at each sampling station and sample types are given in Table 3.1.

Table 3.1 Sediment core samples collected from Djuröfladen Bay.

Core	Treatment (t)/Control (c)	Solid phase analysis(s)/Pore water (p)	Water depth (m)
February 2020			
C5	c	s	10.2
C6	c	s	10.2
M1	t	s	10.0
M2	t	s	10.0
CL4	c	p	10.2
CL5	c	p	10.2
ML1	t	p	10.0
ML2	t	p	9.9
October 2020			
M858	t	s	9.3
M859	t	s	9.3
M860	t	s	9.4
M861	t	s	9.2
C585	c	s	9.4
C862	c	s	9.4
C863	c	s	9.4

3.2.5 Analytical methods

Elements, pH and dry content were analysed by an accredited laboratory (ALS Scandinavia AB). Elements in sediment were determined by ICP-MS after drying (50 °C) and HNO_3-digestion. Some of the samples were also analysed after digestion with lithium metaborate fusion ($LiBO_2$). All analyses were done by accredited methods.

Nutrient samples (NH_4, PO_4, NO_x and DSi) were analysed by an accredited laboratory at the Department of Ecology, Environment and Plant Sciences (Stockholm University) using standard and accredited methods in segmented flow analysis.

3.3 Results and discussion

During application the sorbent particles sank rapidly through the water column, leaving no visually discernible clouding of the surface water. Thus, there were no signs that the sorbent moved outside of the treatment plot.

The sediment cores from the treatment and control plots were visually indistinguishable and there were no visual differences between cores collected in February and October 2020 (Figure 3.3). The sediment was black and had a strong smell of hydrogen sulphide on both occasions. The bottom water on top of the sediment in the cores had a smell of hydrogen sulphide in October but not in February. No sorbent particles were visible in the sediment samples and the sediment appeared rich in organic matter. Loss on ignition was determined in two samples (0-2 cm and 2-4 cm) and ranged between 24.9–25.8 %. Water content of the sediment ranged from 94–92 % in the upper 2 cm to approximately 88–89 % below 6 cm sediment depth (Figure 3.4).

Figure 3.3 Upper section of a typical sediment core from Djuröfladen Bay. Photo from February 2020.

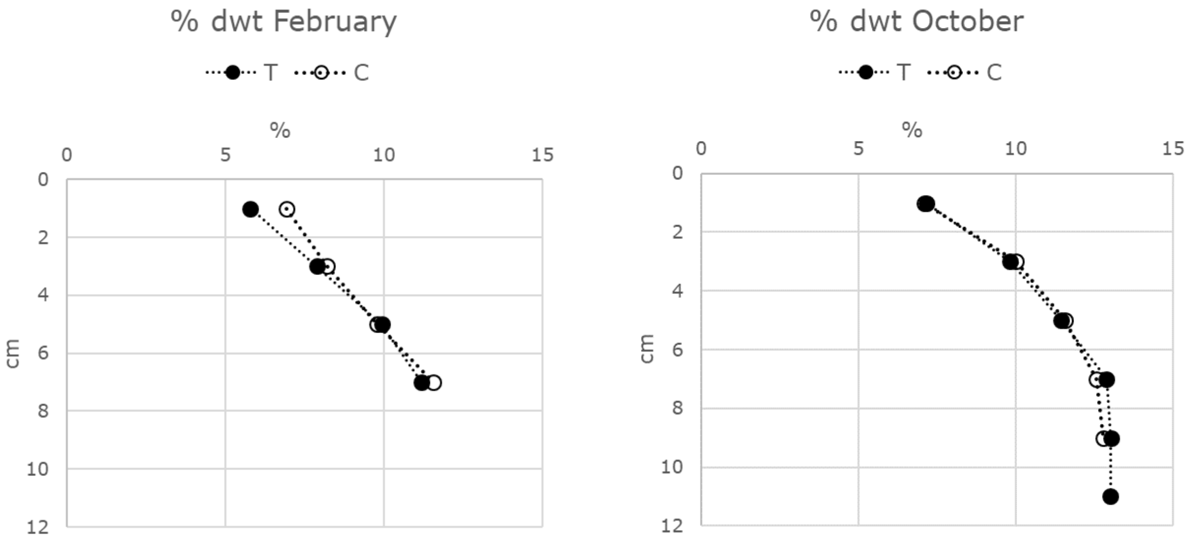


Figure 3.4 Average dry weight concentration in sediment from the treatment and control plot in Djuröfladen Bay in February and October 2020.

Concentrations of elements in the solid phase were in general very similar between the control and treatment plot both in February and October 2020. Sediment surface (0–2 cm) Ca concentrations in the treatment plot were variable (Table 3.2) but both cores in February and three out of four cores in October from the treatment plot had higher Ca concentrations in the surface layer than in the control plot. Profiles of averaged values indicate enrichment of Ca in the surface (0-2 cm) sediment within the treatment plot on both occasions (Figure 3.5). Sediment pH levels were notably different between the treatment and control plots at all sampled depth intervals (Figure 3.5), indicating dissolution of CaO and release of OH ions from the marl sorbent material. Interestingly, surface concentrations of Ca were roughly on average 2 g/kg dwt lower and pH-levels in the 0-6 cm depth interval clearly higher in October than in February in both the control plot and the treatment plot (Table 3.2, Figure 3.4).

Table 3.2 Min, max and average concentrations of Ca and P in the upper 0-2 cm sediment layer of the control (C) and treatment (T) plot in Djuröfladen Bay.

	February 2020		**October 2020**	
	C	**T**	**C**	**T**
Ca	mg/kg dwt	mg/kg dwt	mg/kg dwt	mg/kg dwt
min	33400	55900	20100	16300
max	47400	65300	28800	67800
average	40400	60600	24333	37525
P				
min	1390	1080	1390	1250
max	1430	1180	1550	1620
average	1410	1130	1457	1500

On average, the Ca concentration in the surface sediment from the treatment plot was approximately 50% higher than in the control plot (Table 3.2); however, this was lower than expected given the dosage of marl sorbent that was added to the treatment plot (400 g/m^2). Thus, four of the samples from the treatment plot and three samples from the control plot were re-analysed after digestion with $LiBO_2$. The differences for Ca and P between the alternative digestion methods were within the range of analytical uncertainty.

The Ca concentration of the marl sorbent is approximately 400 g/kg (see Chapter 5) and the added dosage of marl sorbent (0.4 kg/m^2) is therefore equivalent to an addition of 160 g Ca/m^2 (400 g/kg x 0.4 kg/m^2). Assuming that all of the added marl sorbent accumulated in the upper two cm of sediment, the marl sorbent added per m^2 would be mixed in 0.02 m^3 of sediment. The amount of dry matter in the receiving sediment per m^2 treated area can be estimated to approximately 1680 g assuming a wet bulk density of 1200 kg/m^3, which is typical for organic rich accumulation sediments in the Baltic Sea (Endler et al. 2015) and a dry matter content of 7 % (Figure 3.4). The average Ca concentration in the surface sediment of the control plot was approximately 30 g /kg dry weight (Table 3.2), which gives a background content of Ca in the 0-2 cm layer to 50 g/m^2 (30 g/kg dwt x 1.68 kg/m^2). Thus, addition of 160 g Ca/m^2 would be expected to increase the Ca-content in the 0-2 cm depth zone by roughly a factor of 3 (160 g / 50 g).

The P-binding efficacy of the marl sorbent has been determined to be 16.8 g/kg in laboratory studies. Thus, addition of 160 g marl sorbent per m^2 sediment area would be expected to bind 2.7 g P (16.8 g/kg x 0.16 kg). The background P content in surface (0-2 cm) sediments can be estimated to be 2.4 g according to the calculations above and under the assumption of a background P concentration of 1.4 g/kg dwt (Table 3.2). Thus, the addition of marl sorbent would be expected to roughly double the P concentration in the solid phase of the sediment. However, as the average P concentrations in the treatment and control plots were nearly identical (Figure 3.6), there is no indication that the marl sorbent addition influenced the treated sediment's capacity to retain P. On the contrary, the P concentration appeared higher in the surface sediment of the control plot than in the treatment plot in February (Figure 3.6, Table 3.2).

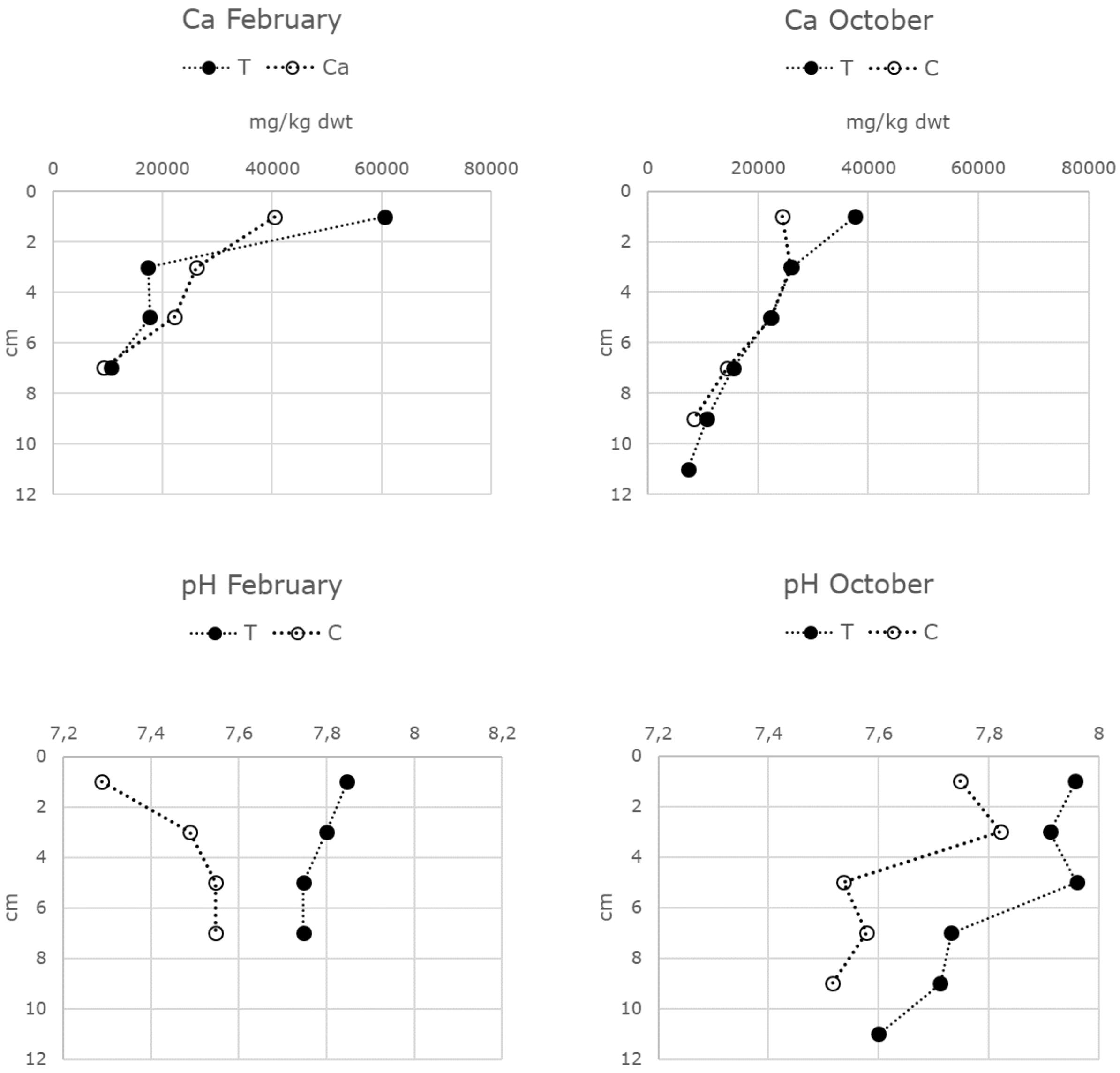


Figure 3.5 Average Ca-concentrations and pH-values (log transformed averaged [H⁺]-values) in sediment from the treatment and control plot in Djuröfladen Bay in February and October 2020.

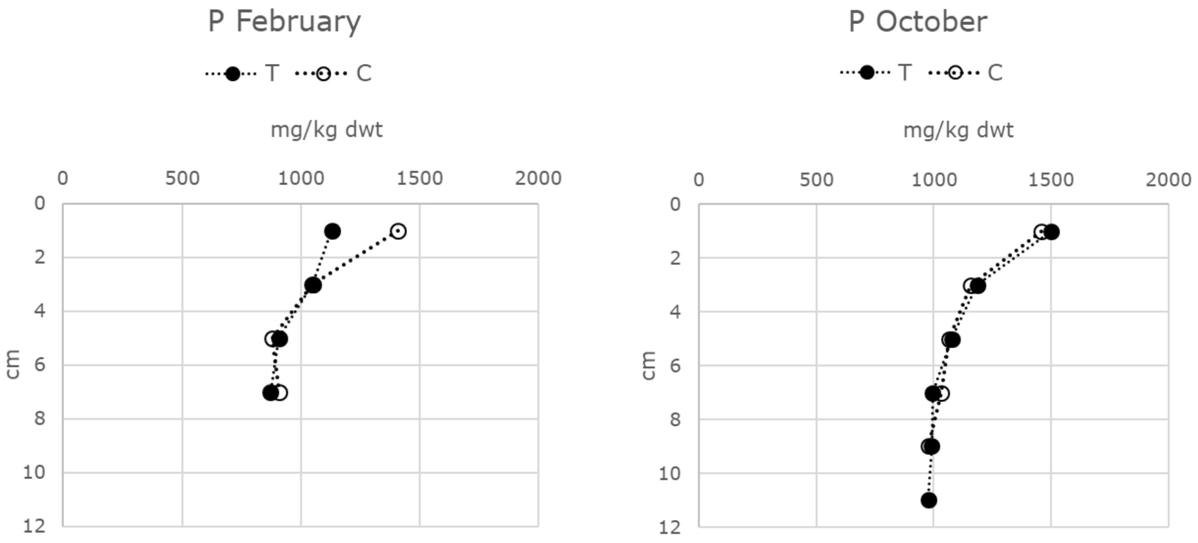
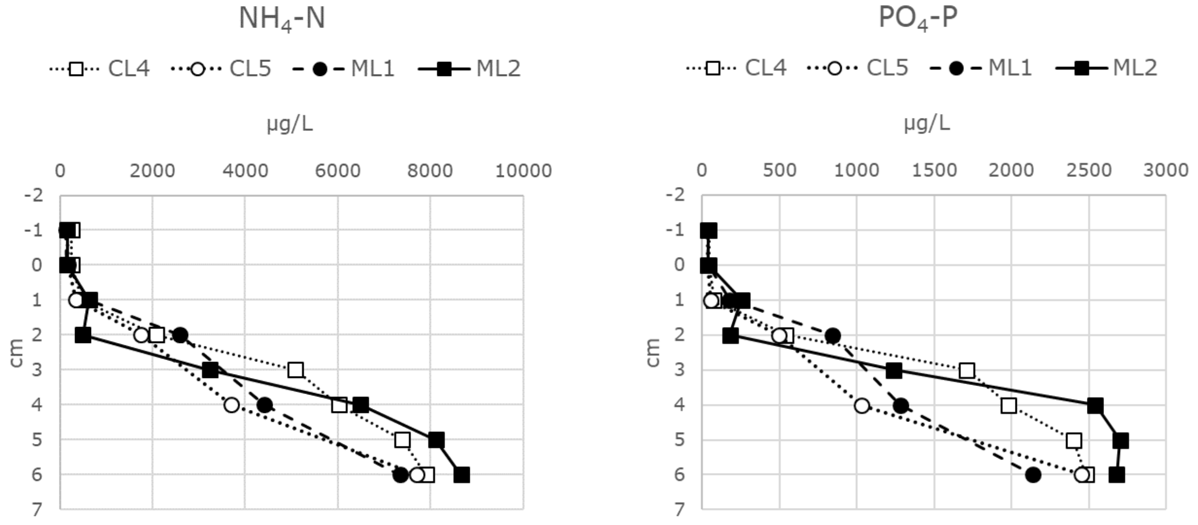
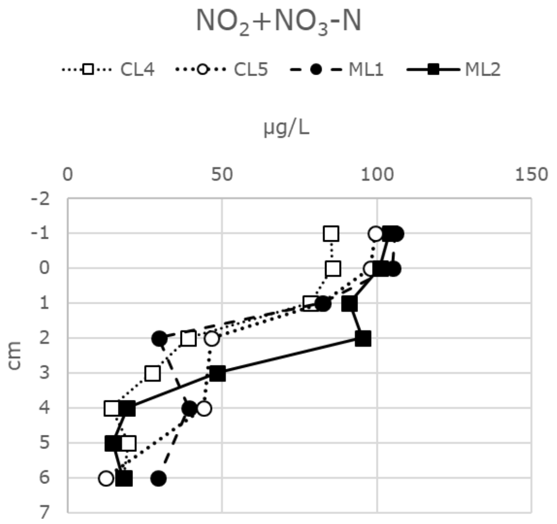
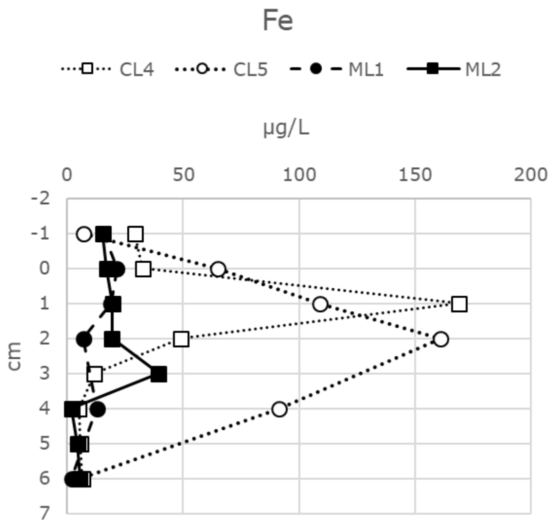


Figure 3.6 Average P-concentrations in sediment from the treatment and control plot in Djuröfladen Bay in February and October 2020.

Low concentrations of NH_4 and PO_4 and presence of NO_2 and NO_3 near the sediment surface indicate that the deep water was oxygenated in February 2020 (Figure 3.7). For most elements, pore water profiles were highly similar between the treatment and control plots. However, Fe and Mn concentrations were much higher around 1-2 cm sediment depth at the control cores (Figure 3.7), likely due to reduction of iron and manganese-oxides above this zone (Mort et al. 2010). P sorption by iron oxides in the surface sediment in cores from the control plot could potentially explain the difference in solid phase P concentrations between treatments (Figure 3.6). The PO_4 concentration at 1 cm depth in the treatment plot was roughly twice as high as the control plot (Figure 3.7), which is another indication of PO_4 sorption. Thus, in February, the P binding capacity in the control plot appeared to be higher than in the treatment plot due to differences in redox conditions within the bay. Pore water or bottom water was not sampled in October but the smell of hydrogen sulphide in the bottom water from both plots suggests oxygen free and sulphidic (so called euxinic) conditions within the whole bay.







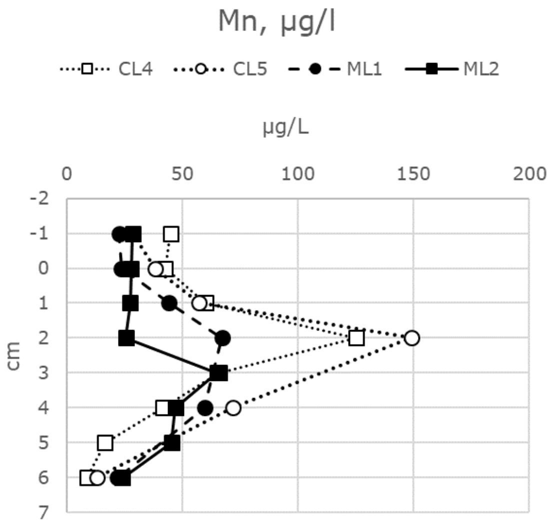


Figure 3.7 Pore water concentrations of NH4-N, PO4-P, NO2+NO3-N, Fe and Mn in sediment cores from the treatment plot and control plot in Djuröfladen Bay. Y = 0 marks the sediment surface.

3.4 Conclusions

Addition of marl sorbent to the sediment increased the Ca content of the upper sediment and increased pH, at least down to 10 cm sediment depth. The increase of Ca was lower than anticipated, based on the dosage and background level of Ca in the sediment. The explanation for this is not fully clear. One potential reason could be that the marl sorbent was lost from the sediment by dissolution or re-suspension (cf. Blomqvist & Larsson 1994). The latter appears highly unlikely based on the high water content of the sediment which is indicative of highly stable conditions. It is also highly unlikely that the marl sorbent went below the sampled sediment depth, i.e. > 12 cm. Test additions of marl sorbent to sediment core samples from the bay suggest that the material is accumulated in the 0-2 cm zone. Loss of marl sorbent by dissolution also appear unlikely based on findings from the follow-up field trial in Farstaviken Bay (Chapter 5).

There were no signs of increased immobilisation of P in sediment treated with the marl sorbent, either in February or October. There are several indications that P retention was higher in the control plot than the treatment plot in February due to natural spatial variability in redox conditions. Thus, in February a potential increase in P sorption efficacy due to the marl sorbent could have been “masked” by the naturally elevated P sorption efficacy within the control plot. In October, environmental conditions were likely similar between the plots which means that effects related to the marl sorption addition were theoretically more easily detected.

4 Kolkka Bay (field pilot experiment 3)

4.1 Aim

The Kolkka Bay field trial was the second "whole-bay" experiment with an overall aim to improve environmental conditions by spreading the marl sorbent to bottom sediments affected by seasonal oxygen depletion. This action was intended to increase P binding in sediment dosed with the marl sorbent. Another important aim was to document the effect of the marl sorbent addition by measurements in the environment.

4.2 Method

4.2.1 Study site

Kolkka Bay is situated near Åbo, Finland, in the Archipelago Sea (Figure 4.1). The bay constitutes the inner part of a shallow sound. The surface area of the bay is 0.5 km^2 and the average and maximum water depths are 3 m and 7.6 m, respectively. The sediment below 6 m water depth consists of silty clay-gyttja with a high organic matter content in the upper part. The water below approximately 6 m depth becomes oxygen depleted in summer. The salinity is around 6 PSU which is the same level reported for neighbouring waters. Kolkka Bay has a small drainage area which mainly consist of forested areas and agricultural land.

Prior to this field pilot there was no ongoing environmental monitoring of the bay.

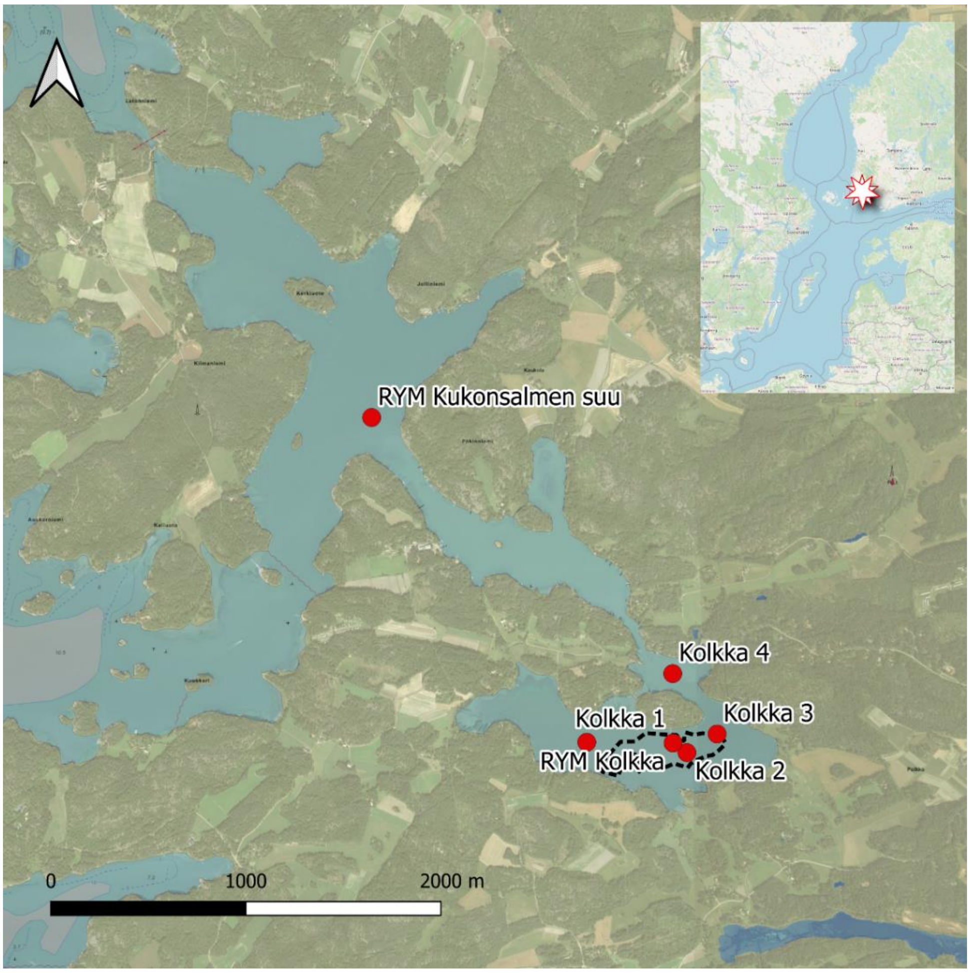


Figure 4.1 The Kolkka Bay pilot site. The dashed line shows the targeted area for the marl sorbent. Red dots indicate sampling stations.

4.2.2 Experimental plan

Using bathymetric data, an 80 000 m^2 area in the central, deepest part of the bay was selected as a suitable treatment area for marl sorbent addition (Figure 4.1). The monitoring program involved water sampling in Kolkka bay as well as at a control station (RYM Kukonsalmen suu) north of the sound connected to Kolkka Bay. The monitoring program started in June 2019 with bi-monthly measurements at one station in the bay (RYM Kolkka) inside of the treatment area and at the control site (RYM Kukonsalmen suu). The measurements in 2019 continued until 10 October 2019. In 2020, measurements were made between May and September with 2–4 measurement campaigns each month. The number of sampling stations was increased to six in 2020 through the addition of three stations within Kolkka Bay (Kolkka 1, 2 and 3) and one station (Kolkka 4) in the sound leading into Kolkka Bay (Figure 4.1). Analyses included inorganic elements and total concentrations of N and P, DO, chlorophyll a, Fe, pH, alkalinity, TOC and absorbance.

An autonomous measurement station was also deployed close to the RYM Kolkka sampling station. The automated measurements included pH, temperature, salinity, turbidity, dissolved organic matter and DO at 6-6.6 m water depth (approximately 1 m above the seafloor). The variables were logged at 15 min to 1 hour intervals between April and December 2020. Temperature, DO and salinity were logged (at 1 hour intervals) between the end of June and beginning of November 2019.

The spreading of marl sorbent was conducted in June 2020. A total of 8000 kg of marl was spread by helicopter over the 80 000 m^2 treatment area. Thus, the dosage was 100 g/m^2, which based on results from adsorption measurements in the laboratory would have the capacity to bind 1.68 g P/m^2 sediment (see section 2.2.2 in chapter 2).

In addition to water monitoring, sediment samples were collected on two occasions before the spreading of the marl sorbent (May and October 2019) and once after (in October 2020). The collected sediment cores were sliced at 2-5 cm intervals down to 10 cm and analysis undertaken for total N, total P, S, Fe, TOC, TC, grain size and crude ash.

4.2.3 Analytical methods

Eurofins Environment Testing collected all samples and analysed the water samples. Sediment samples were analysed by KVVY laboratory. Both laboratories have accreditation to undertake all performed analyses.

4.3 Results and discussion

As described above, the measurement program involves a rather large number of measurement variables and sampling stations. The monitoring is ongoing, and the data being collected will provide valuable information in the future. However, as measurements in 2019 only involved two stations (RYM Kolkka and the control station RYM Kukonsalmen suu) the discussion below is focused on comparisons of data collected before and after the spreading of marl sorbent.

4.3.1 Impact of marl sorbent treatment on P bioavailability

The DO data from the deepest sampling site (RYM Kolkka) show that the bottom water was de-oxygenated in June-July 2019 when the monitoring started (Figure 4.2). After a series of short oxygenation events during summer, the bottom water was oxygenated due to mixing in mid-September 2019 and the bottom water remained oxygenated at least until October when the measurements ended. The data from 2020 show that DO concentration started to decrease rapidly at the end of May 2020 and went to zero in eight days. About ten days after the deep water was de-oxygenated, the marl spreading was conducted (Figure 4.2).

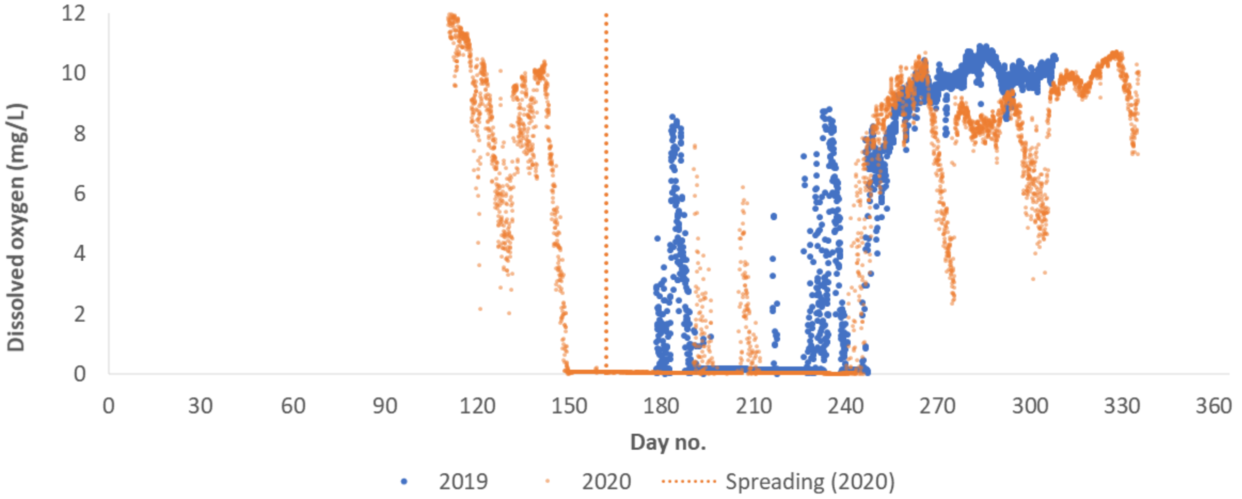


Figure 4.2 Dissolved oxygen concentration in the bottom water of Kolkka Bay. Dashed line indicates the spreading of marl sorbent in June 2020.

PO_4 concentration in the bottom water appeared to be unaffected by the marl sorbent treatment since the build-up of PO_4 continued at a seemingly unchanged rate after treatment (Figure 4.3). A drop in bottom water PO_4 concentration was noted 21 July 2020 (day 202) (Figure 4.3), but this was quite certainly driven by low oxygenation events that occurred twice during the summer of 2020 (Figure 4.2). Later, in autumn (day 240), the deep water was oxygenated (Figure 4.2) and this coincides with a substantial drop in the PO_4 concentration (Figure 4.3).

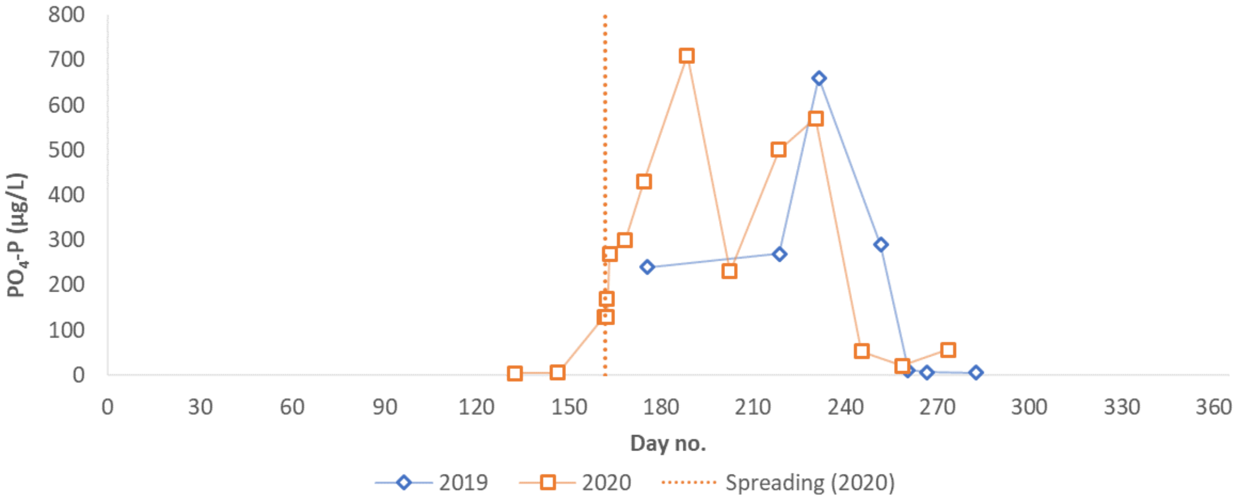


Figure 4.3 Dissolved PO_4 concentration in the bottom water of Kolkka Bay. Dashed line indicates the spreading of marls sorbent in June 2020.

All in all, the high-resolution oxygen data and the variations in PO_4 show very clearly that there is a strong correlation between these two variables. There is no evidence that the marl sorbent addition supressed PO_4 build up in the deep water in Kolkka Bay by P binding in the sediment.

The total P concentration in the surface water of Kolkka Bay (RYM Kolkka) following spreading was generally higher in 2020, or at a similar level to 2019 (Figure 4.4). At the control site (RYM Kukonsalmen suu), surface water total P concentrations were also similar between the two years (Figure 4.5). The chlorophyll a data suggest no major changes between the years although interannual variability is clearly apparent (cf. Figure 4.6,

Figure 4.7). The highest chlorophyll a values were recorded in Kolkka Bay after the spreading of the marl sorbent was completed (Figure 4.6), during a period when chlorophyll a was also high at the control site compared to 2019 (Figure 4.7).

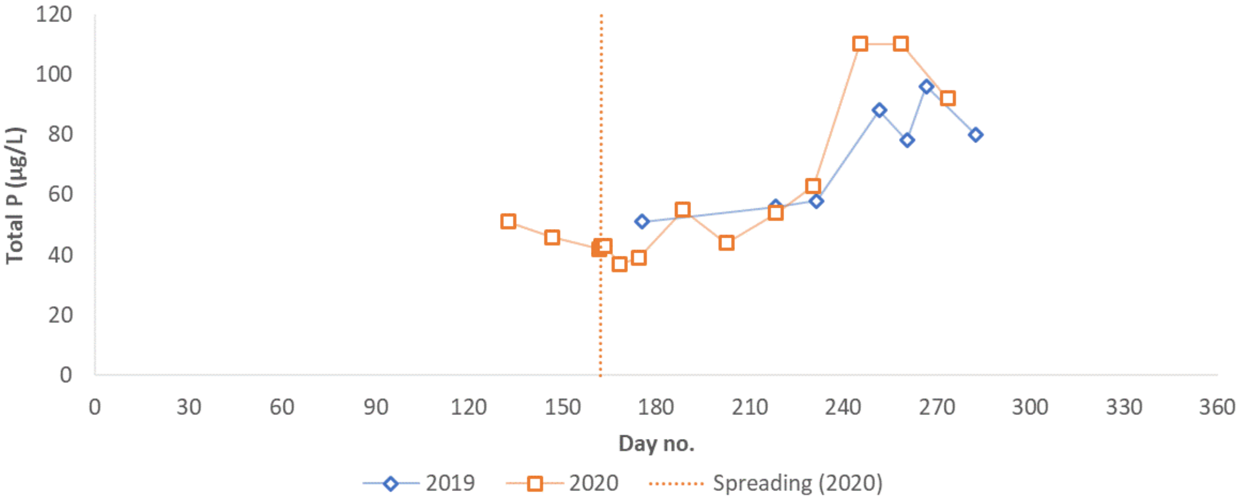


Figure 4.4 Total P concentration in Kolkka Bay surface water (RYM Kolkka). Dashed line indicates the spreading of marls sorbent in June 2020.

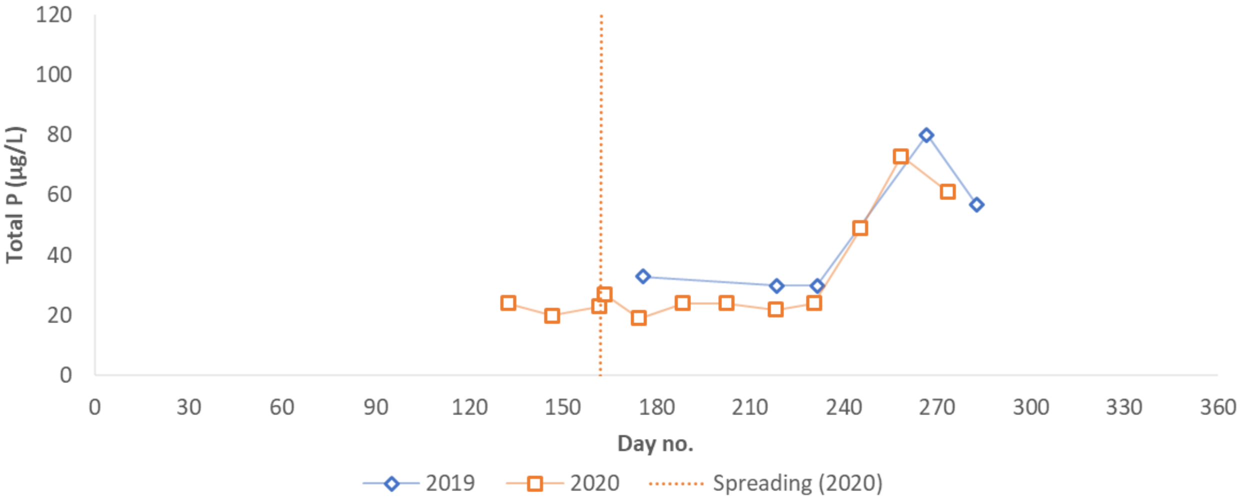


Figure 4.5 Total P concentration in surface water at the control site (RYM Kukonsalmen suu). Dashed line indicates the spreading of marl sorbent in Kolkka Bay in June 2020.

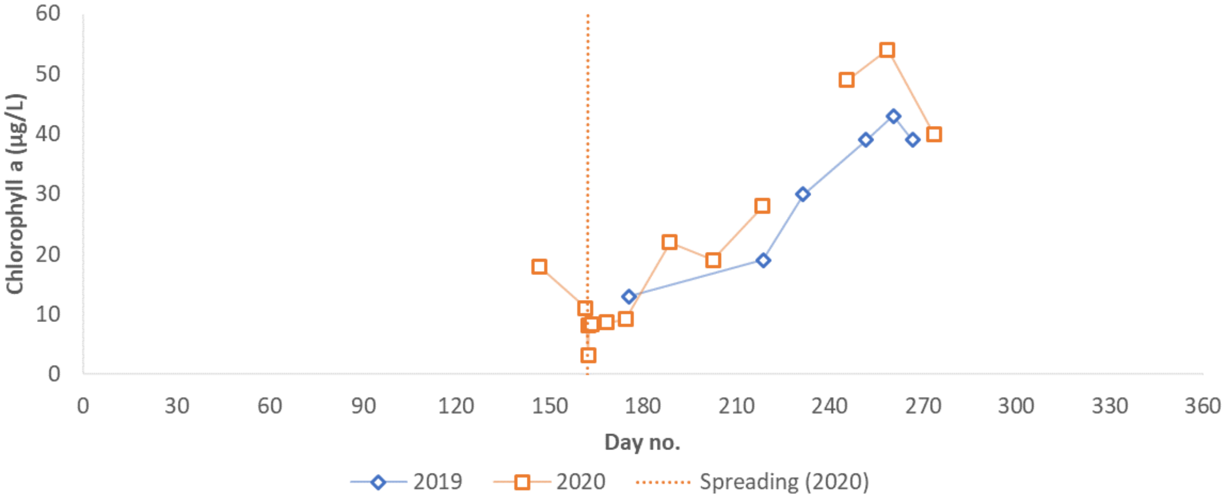


Figure 4.6 Chlorophyll a concentration in Kolkka Bay surface water (RYM Kolkka). Dashed line indicates the spreading of marl sorbent in June 2020

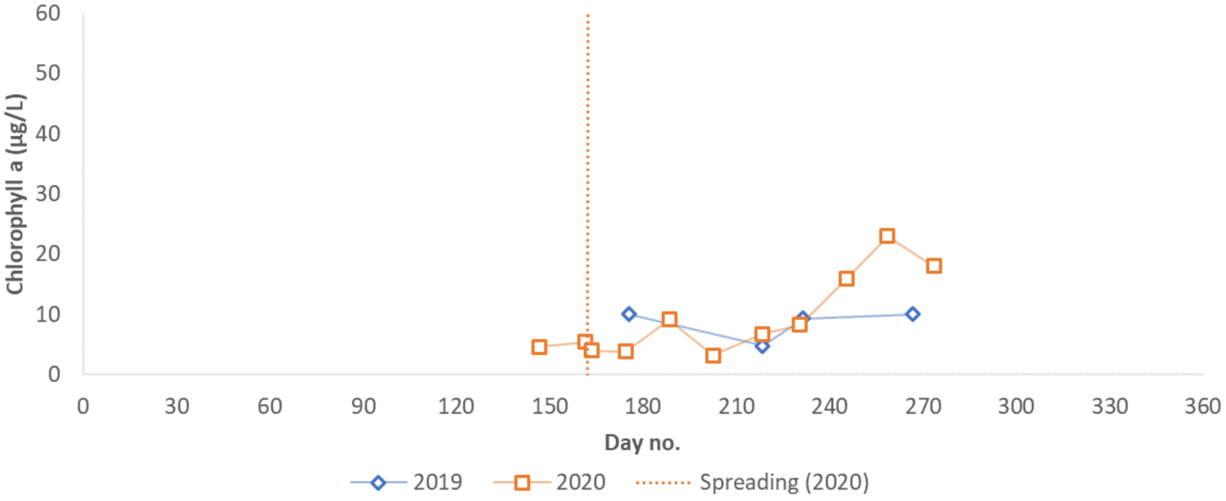


Figure 4.7 Chlorophyll a concentration in surface water at the control site (RYM Kukonsalmen suu). Dashed line indicates the spreading of marl sorbent in Kolkka Bay in June 2020.

In line with observations in the water column, sediment data gave no indication of increased P binding in the treated area. The total P concentration profiles in the sediment were nearly identical in the treatment area before and after the marl sorbent application. They were also nearly identical between the treatment area and control site (Figure 4.8).

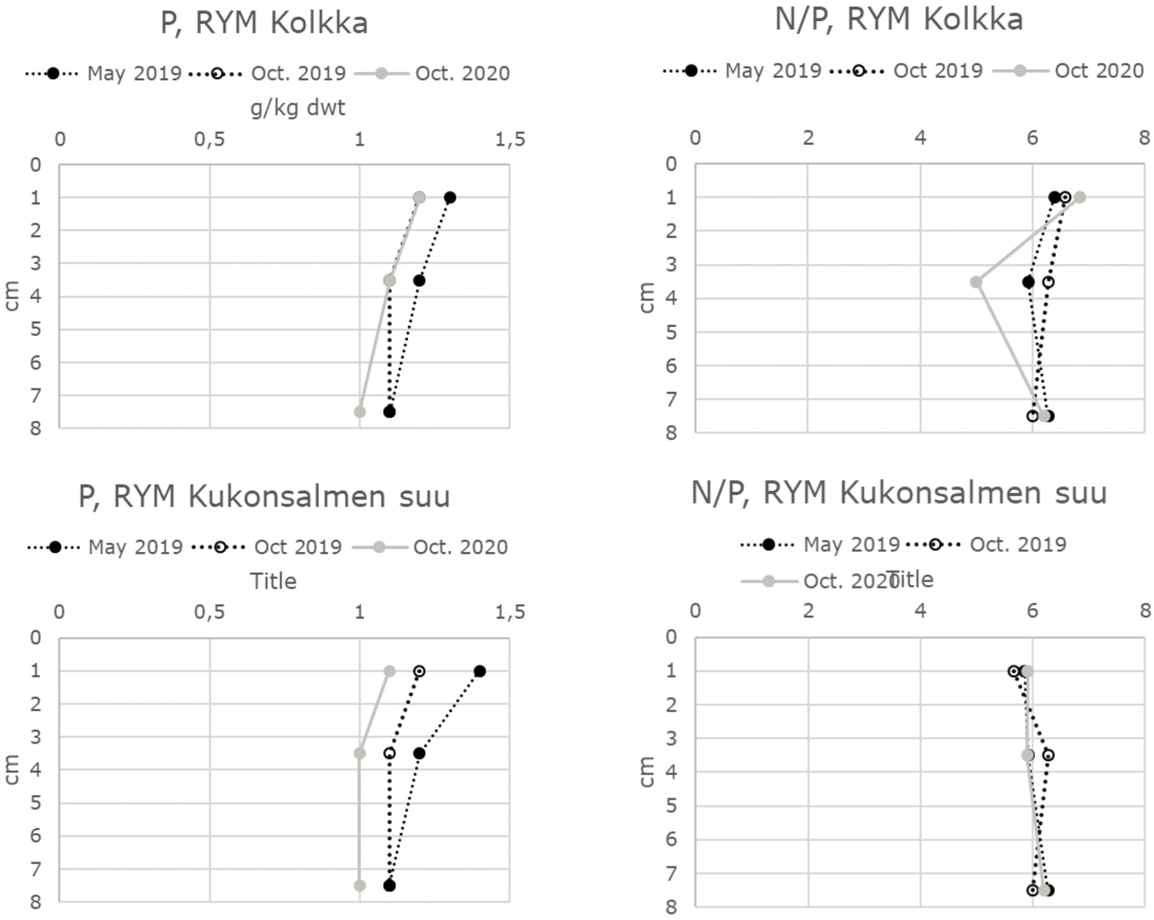


Figure 4.8 Total P concentrations and Total N/Total P ratios in sediment cores from the treatment area in Kolkka Bay and from the control site (RYM Kukonsalmen suu) before and after the spreading of marl sorbent in June 2020.

4.3.2 Short term effects of marl sorbent addition

The intensified sampling and autonomous monitoring in connection with the spreading of marl sorbent in June 2020 reveal a rise in pH in the bottom water (Figure 4.9). The pH increased for approximately 48 h before it levelled off for approximately one week before declining over a period of a few days to pre-application levels. This documented temporary increase in pH by approximately 0.1 units was most likely due to the marl sorbent treatment. No negative consequences can be foreseen by an increase in pH of this magnitude.

Turbidity was not affected by the marl sorbent treatment (Figure 4.10), i.e. there was no measurable water clouding. Likewise, Secchi disc depth measurements gave no indication of any effect related to the spreading of marl sorbent.

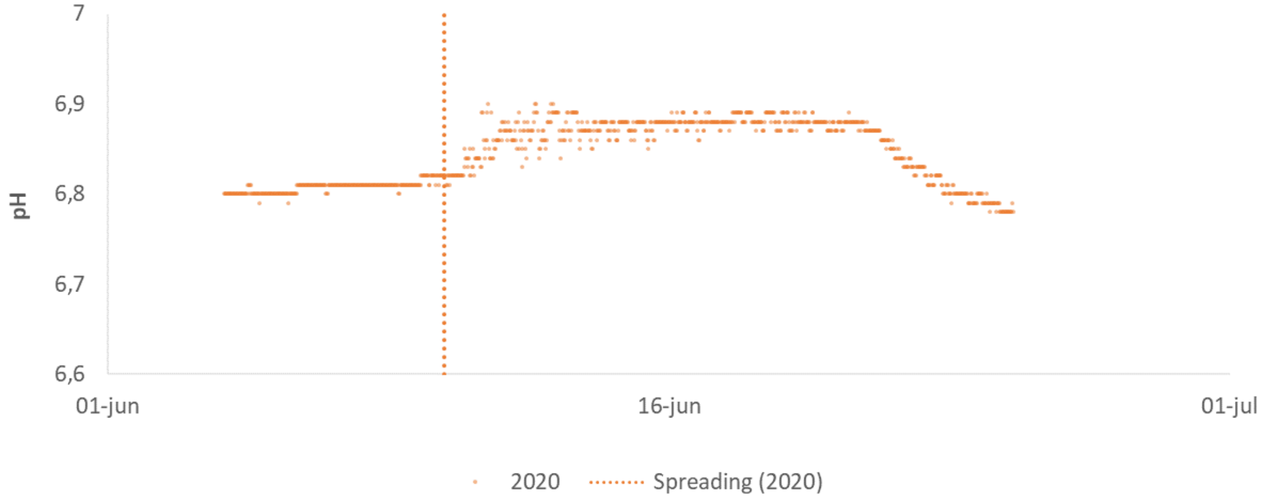


Figure 4.9 pH at 6.6 m depth near the sampling station RYM Kolkka in June 2020. Dashed line indicates the spreading of marl sorbent.

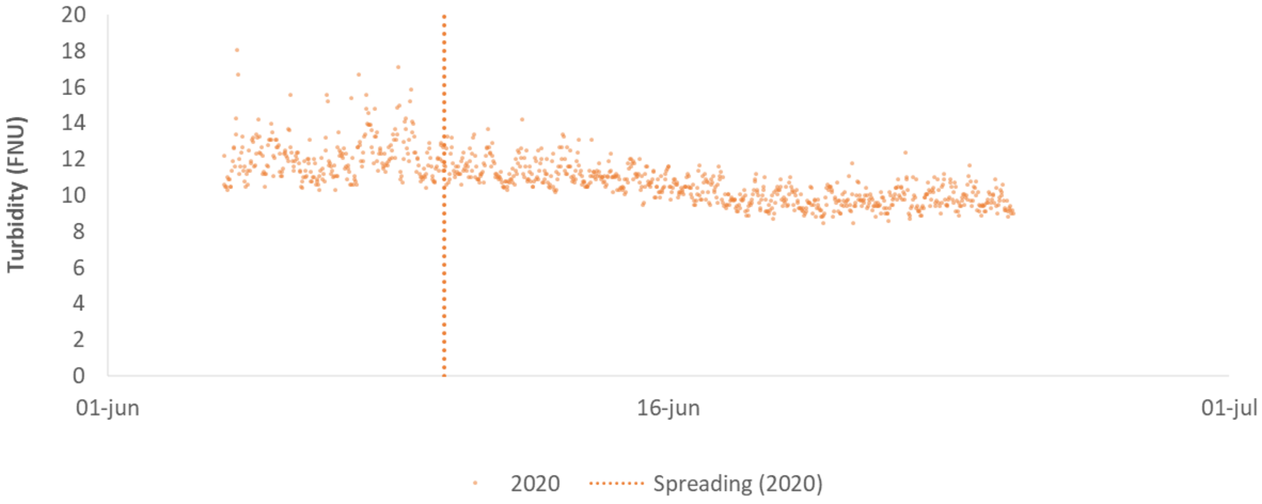


Figure 4.10 Turbidity at 6.6 m depth near the sampling station RYM Kolkka in June 2020. Dashed line indicates the spreading of marl sorbent.

Reductions in bottom water PO_4 and total P concentrations were indicated by measurements that occurred on 11 June, shortly after the spreading of marl sorbent (Figure 4.11). The changes in concentration (16-24%) were within the range of analytical uncertainty, however, and may therefore be coincidental. One day after the spreading, PO_4 and total P concentrations at all sampled depths were either higher or similar to records before the spreading (Figure 4.11). Thus, the spreading may have caused a temporary lowering of P concentrations in the bottom water, but this potential effect did not persist for more than one day.

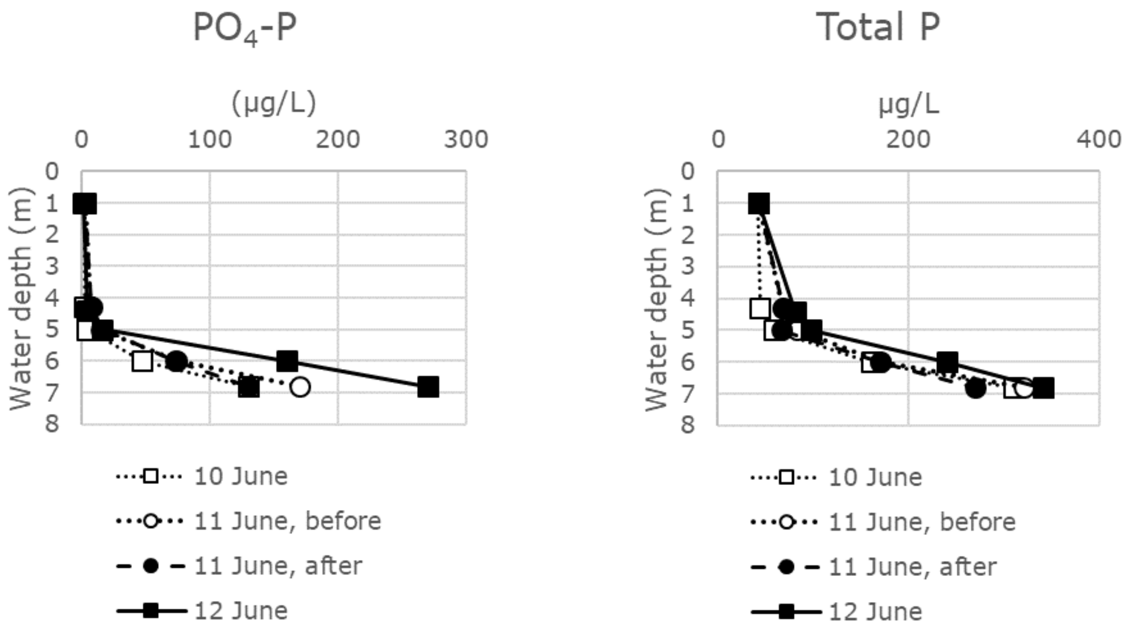


Figure 4.11 Water column concentration of PO4 and total P at RYM Kolkka shortly before and after the spreading of marl sorbent in June 2020.

4.4 Conclusions

There is no evidence that the spreading of marl sorbent influenced P bioavailability in the water column or influenced the P content in bottom sediment of Kolkka Bay. At most, a transient drop in bottom water P concentration may have occurred, but this effect only lasted for approximately one day.

The automated monitoring of pH revealed that the pH in the bottom water increased by approximately 0.1 units (from 6.8 to 6.9) following the addition of marl. This effect lasted for approximately ten days. No negative environmental effects can be foreseen by the recorded variation in pH.

As shown by the automated measurements of turbidity in the bottom water and manual Secchi depth measurements, the marl sorbent treatment did not result in measurable clouding of the water.

The ongoing monitoring program in Kolkka Bay and at the control site (RYM Kukonsalmen suu) is ambitious and extensive both in terms of measurement variables and measurement frequency. Should long-term effects develop by the spreading of marl it is probable that this would be captured by future measurements.

5 Farstaviken Bay (field pilot experiment 4)

5.1 Background and aim

A large scale spreading of the sorbent in Farstaviken Bay was planned to be carried out as part of the SEA-BASED project. However, since the results from Djuröfladen Bay pilot experiment indicated that the efficacy of the sorbent to sequester P was lower than expected (Chapter 3), a controlled *in situ* experiment was carried out to verify that the P-uptake efficacy of the sorbent is indeed lower in field conditions than in the laboratory, and, if this was the case, to investigate potential reasons for this.

The key aims of the experiment were thus to:

- Determine whether various size classes of the sorbent disintegrate into fine particles under *in situ* conditions.
- Determine whether the marl sorbent is dissolved in sea water to any notable extent.
- Determine the P-uptake efficacy of the marl sorbent under *in situ* conditions.

5.2 Method

5.2.1 Study site

Farstaviken Bay is located in the Stockholm archipelago, Sweden (Värmdö municipality). The bay is mostly surrounded by land except for a narrow sound in its western part (Farsta brohål), with a sill depth of 5.5 m (Jonsson et al. 2003). Farstaviken brohål connects Farstaviken Bay with the adjacent water body, Baggensfjärden. Farstaviken Bay has a surface area of 0.6 km^2 and a maximum water of 17 m (Jonsson et al. 2003).

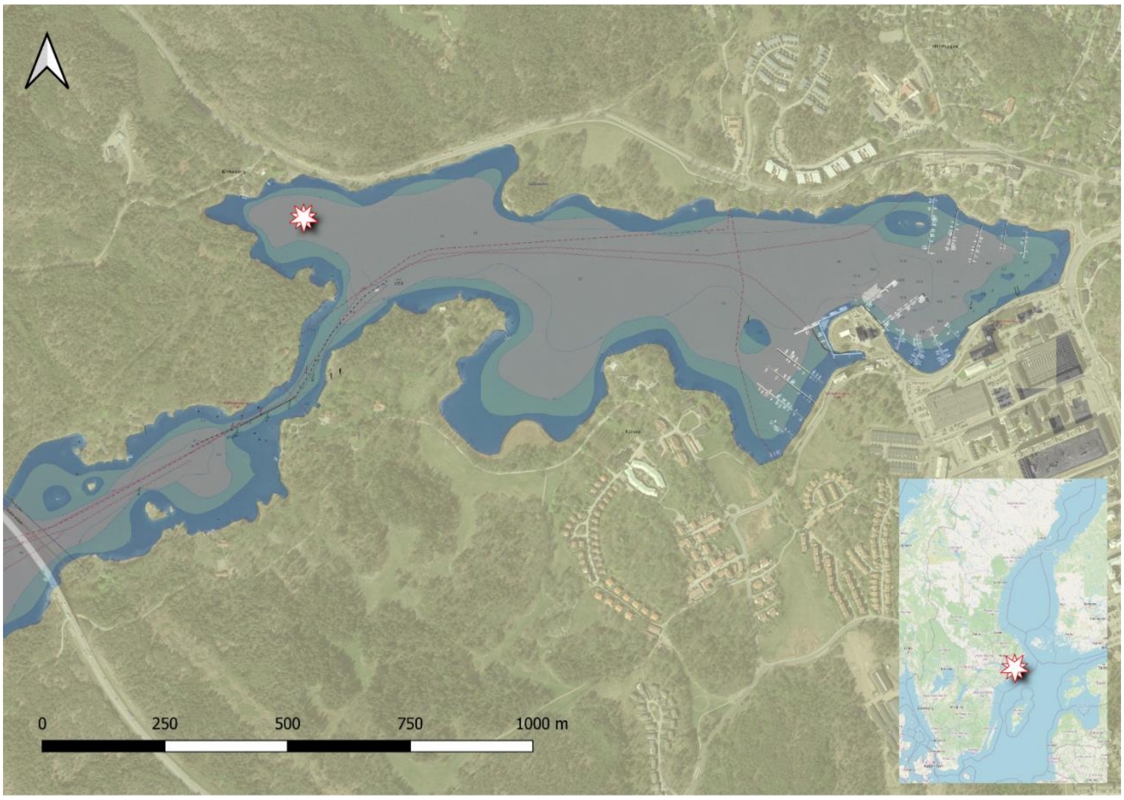


Figure 5.1 Farstaviken Bay with the study area marked with a white star.

Seasonally occurring oxygen depletion in the water column is pronounced in Farstaviken Bay. Environmental monitoring data show that anoxic and sulphidic conditions develop in the deep water annually, at least in the summer months (Figure 5.2). Due to the oxygen depleted conditions, no macroscopic fauna are present below 10 m water depth (Brutemark and Ekeroth 2017, Kling and Brutemark 2018).

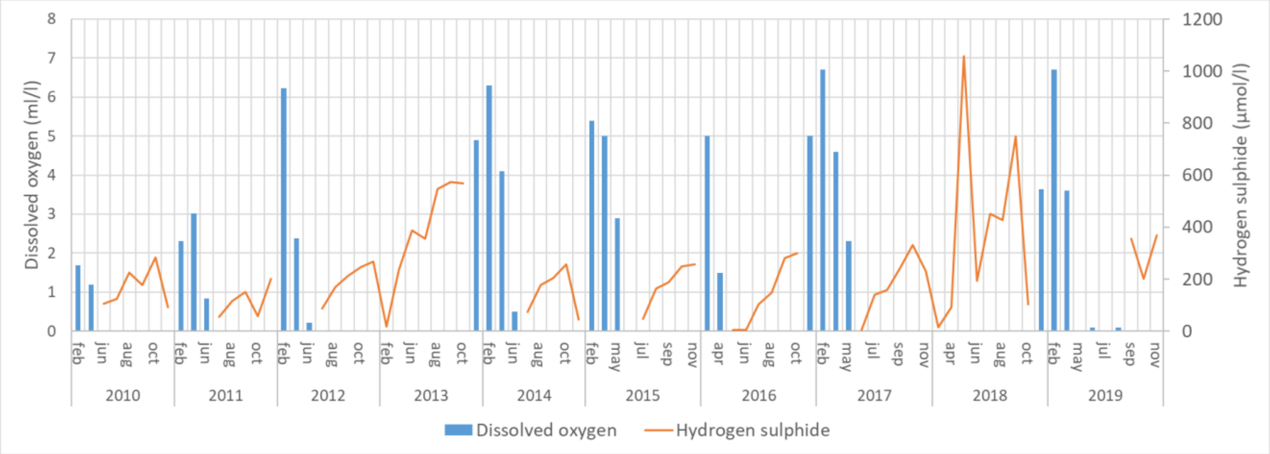


Figure 5.2 Concentrations of dissolved oxygen and hydrogen sulphide at 12 m water depth (4.5 m above the bottom) in Farstaviken Bay. Environmental monitoring data downloaded from Swedish Meteorological and Hydrological Institute (SMHI).

5.2.2 Experimental plan

The objective of the experiment was to expose the marl sorbent to oxygen free and phosphate rich Baltic Sea bottom water and then retrieve the material and measure changes in P-content and other physicochemical variables of the marl sorbent. To achieve this, marl sorbent was placed into a plastic (polypropylene) sample container (125 mL) with a drilled-out hole in the screw cap to allow for water exchange in and out of the bottle (Figure 5.3). Netted mesh fabric was placed under the lid to prevent loss of marl sorbent through the hole in the lid, while still allowing for water exchange. Two mesh sizes were used in the experiment (90 µm and 1 mm). Sets of experimental bottles were attached to metal grids which were lowered to the seafloor at approximately 17 m water depth (Figure 5.3). Each metal grid with fitted experimental bottles was anchored to the bottom and held at constant depth approximately 1 m above the sediment surface using a positively buoyant trawl buoy.

Figure 5.3 Left: Picture of the experimental bottle with 90 µm netted mesh under drilled out lid. The bottom of the bottle is covered by marl sorbent. Right: Deployment of a set of experimental bottles in Farstaviken Bay

The experimental design included two independent variables: size class of the marl and exposure time in *in situ* conditions. Four size classes were tested and three different exposure times (Table 5.1). However, the experimental design was not fully consistent as the netted mesh fabric used in the 32 day exposure trial had a larger mesh size than the 13 and 48 day trials.

Table 5.1 Number of replicates per treatment level in Farstaviken Bay field trial.

Days	Size class 1 (< 1 mm)	Size class 2 (1–4 mm)	Size class 3 (4–9 mm)	Size class 4 (>4 mm)	No sorbent (control)	Mesh size
13 (18/8 – 1/9 2020)	4	4	4	4	4	90 µm
48 (18/8 – 6/10 2020)	4	4	4	4	4	90 µm
32 (3/9 – 6/10 2020)	4	8[†]	4	-	4	1 mm

The following dependent variables were investigated in the experiment:

- Dry weight difference of the marl sorbent before and after exposure to in situ conditions
- P-content difference of the marl sorbent before and after exposure to in situ conditions
- Disintegration (an assessment, based on visual appearance, of the extent to which marl sorbent had broken down into a fine powder after exposure to *in situ* conditions)

In addition, measurements of complementary variables such as physicochemical conditions in the water column and in the water inside the experimental bottles were also carried out.

5.2.3 Field and laboratory work

The experimental bottles used in the experiment were weighed before and after a small amount of marl sorbent (covering the bottom of the bottle, Figure 5.3) was added. The experimental bottles were then attached to the metal grids and lowered to the seafloor as described above. All bottles subject to the same exposure time were attached to the same grid so that each grid was deployed and retrieved once. Control bottles without marl sorbent were also included, to control for any sedimentation of particulate matter in the experimental bottles. The study site was located in the western part of Farstaviken Bay (N 59.3258°, E 18.3595°, WGS84) (Figure 5.3).

5.2.4 Measurements and analytical methods

Water sampling and CTD measurements of the water column were carried out upon recovery of the experimental bottles. Immediately after the experimental exposure time had ended, and upon retrieval, a water sample was taken from each bottle and the contents photographed. These water samples were immediately filtered, stored cold and later analysed for phosphate and other nutrient elements. The experimental bottles and remaining contents were stored cold and transported to Stockholm University within a few hours. Once at the university, measurements of pH were carried out (using a pH electrode) in the remaining water of a subset of the experimental bottles. Most of the water in the experimental bottles was thereafter carefully decanted, without observable loss of particles. Finally, the bottles were placed in an oven (50 °C) and dried until constant weight. The weight difference before and after the experimental exposure time was noted. The content of P and other

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[†] The amount of sorbent in each bottle varied. Four replicates contained approximately 2 g of sorbent and the remaining four replicates contained about 9 g sorbent.

elements in the dried marl sorbent were analysed from a subset of the experimental bottles taken from each of the four size classes of the raw material.

5.3 Results and discussion

5.3.1 *In situ* conditions during the exposure period

The water column was stratified with anoxic conditions below approximately 10 m depth throughout the experimental period (Figure 5.4). Concentrations of PO_4 ranged from less than 10 µg/L in the surface water to around 350 µg/L near the sediment surface. At the deployment depth of the experimental bottles (16 m) the PO_4 concentrations varied between 279–330 µg/L between 6 October and 1 September (Figure 5.4).

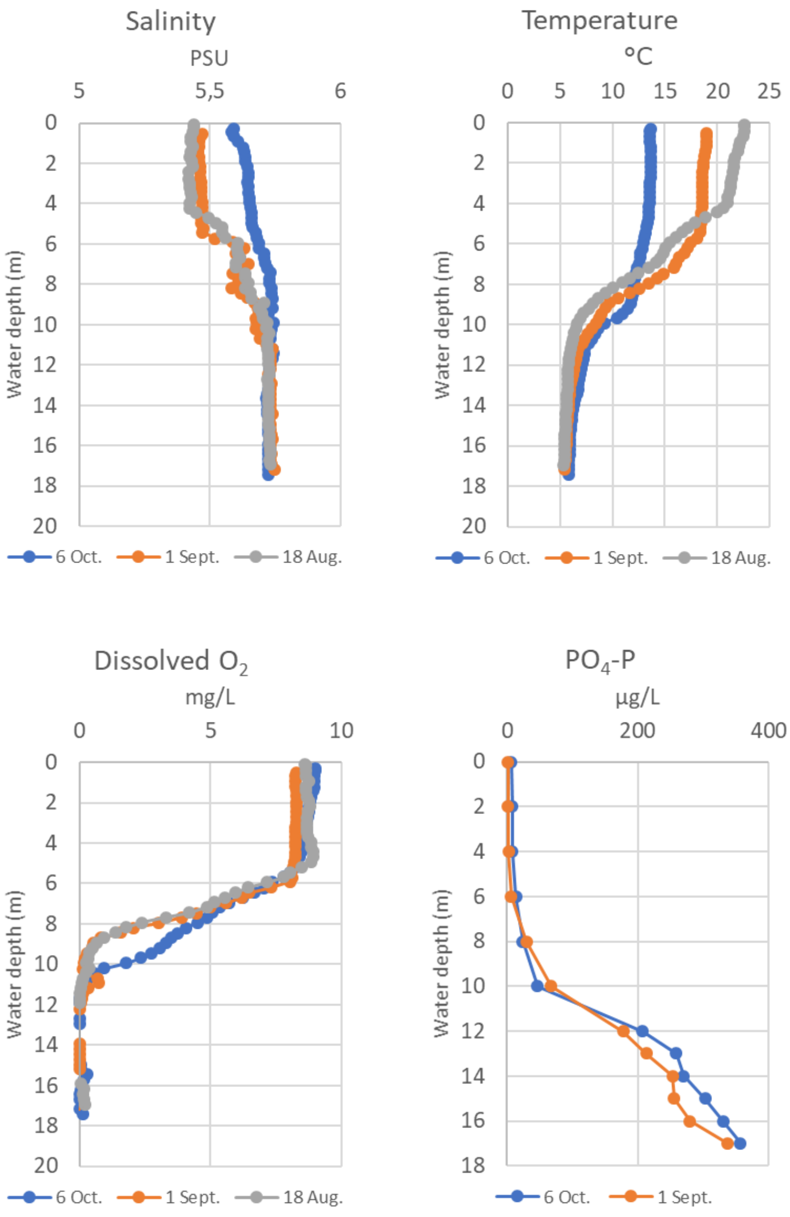


Figure 5.4 Salinity, temperature, dissolved oxygen- and PO_4-concentration at the study site in Farstaviken Bay during the experimental period.

5.3.2 Dissolution and disintegration of the marl sorbent

Irrespective of exposure duration and size fraction of the marl sorbent, the dry weight always increased after the exposure period, although the differences were only of the order of a few percent. This indicates that there was no significant loss of material during the exposure period. The small increase in weight could be due to accumulation of solid $Ca(OH)_2$ (having a higher molecular weight than CaO) by the following reaction:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

For the control bottles the salt corrected weight difference was close to zero which indicates that no significant sedimentation occurred in the experimental bottles.

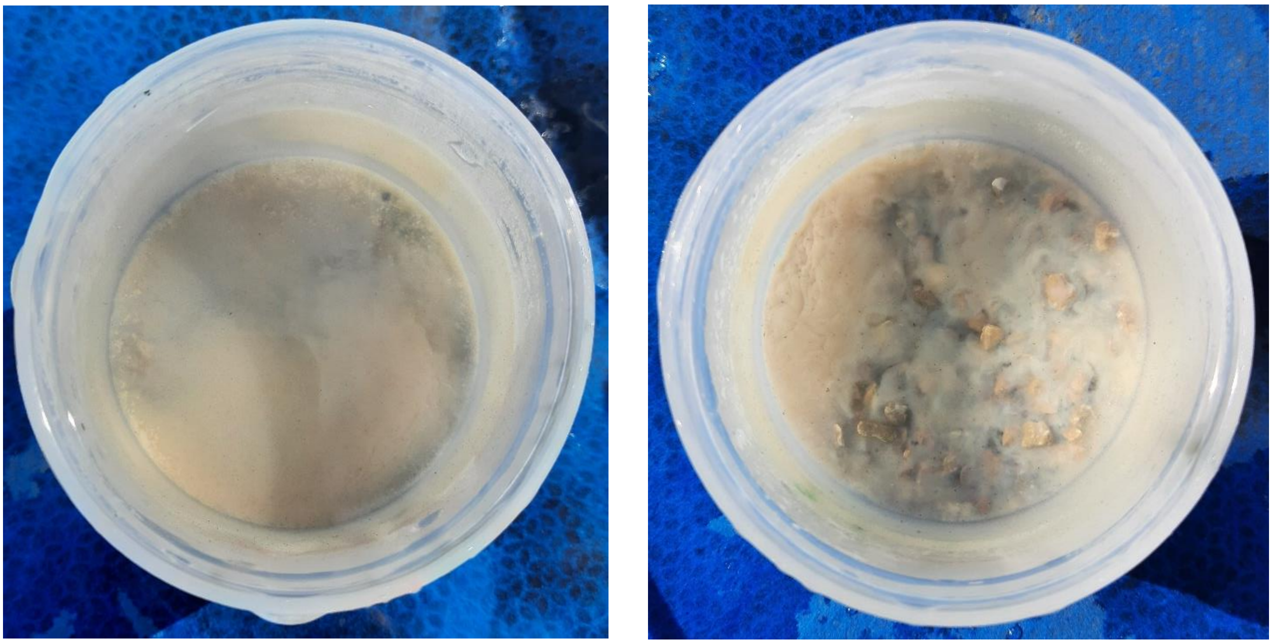
Table 5.2 Weight difference as percentage change following exposure to in situ conditions. Positive values indicate weight gain, negative values weight loss. Average values for each marl sorbent size class and exposure time.

Exposure Time (Days)	Size class 1 (< 1 mm)		Size class 2 (1–4 mm)		Size class 3 (4–9 mm)		Size class 4 (>4 mm)		No sorbent (control)		Mesh size
Salt-corrected	yes	no	yes	no	yes	no	yes	no	yes	no	
13	-	2.9	-	2.5		2.6		2.9		0.3	90 µm
48	2.8	3.5	1.8	2.7	2.2	2.7	2.9	3.6	-0.1	0.4	90 µm
32	0.7	1.6	0.9	2.2	0.5	2.0	-	-	-0.1	0.3	1 mm

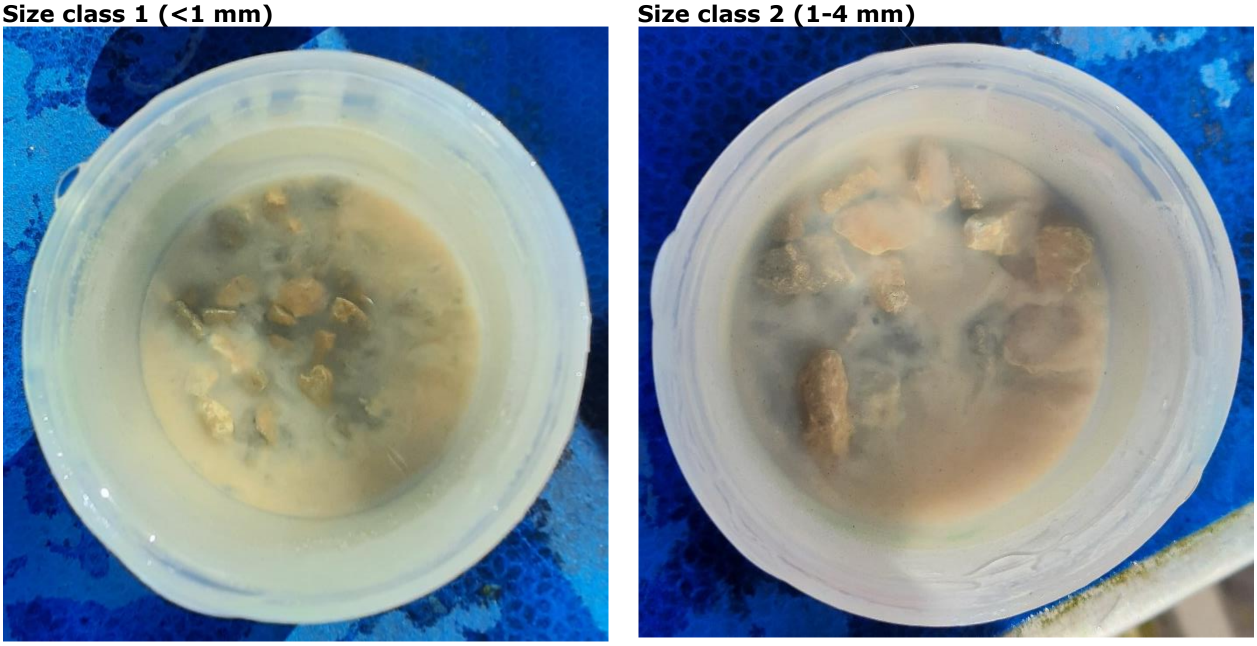
The content of the experimental bottles often had a slimy appearance (Figure 5.5) when recovered. This was likely due to bacterial growth, which could also potentially explain the (small) increases in weight after the exposure periods.

Marl sorbent of larger particle size (classes 2-4) exhibited some disintegration (breakdown) into smaller (<1 mm) particles. There were no clear visual differences in the material related to exposure duration. The sorbent material in 1 mm netted mesh bottles was, however, considerably darker in colour than the material in 90 µm-mesh bottles (Figure 5.6).

After drying of the marl sorbent, the fine-grained material and larger particles for those samples analysed for elemental composition were weighed separately. The results show that the fine-grained matter made up a relative small fraction of the total weight (12–13%, Table 5.3) for size classes 2-4 which is in concordance with visual observations.



Size class 1 (<1 mm) **Size class 2 (1-4 mm)**



Size class 3 (4-9 mm) **Size class 4 (>9 mm)**

Figure 5.5 Photos of the marl sorbent after 13 days of exposure to in situ conditions in Farstaviken Bay.

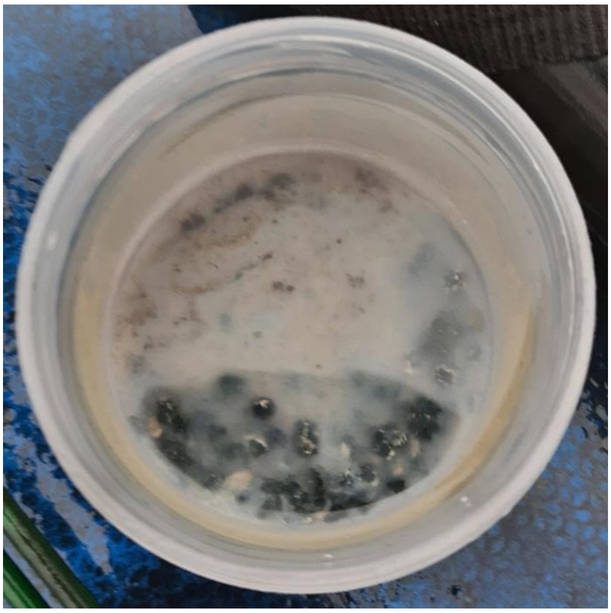


Figure 5.6 Photo of marl sorbent (size class 2) in bottle with 1 mm netted mesh after 32 days of exposure to in situ conditions in Farstaviken Bay.

5.3.3 P-uptake

The concentrations of total P in dry marl sorbent before and after exposure to *in situ* conditions are given in Table 5.3. The P content was clearly elevated after exposure to bottom water in Farstaviken Bay and the enrichment of P was much higher in the fraction of the marl sorbent that had disintegrated after exposure compared to the remaining larger particles. The increase in P concentration in the fine-grained material cannot be explained by the addition of dissolved P in the water of the experimental bottles during evaporation as it was of the same order of magnitude as the enrichment of major elements (Na, Mg) which are present at ~1000-10000 times higher concentration than P in sea water. In other words, the enrichment of P shows that the marl sorbent undoubtably has a preferential affinity for sorption of P. However, the level of enrichment (2-8 times the original P concentration in the sorbent material) is far below the sorption capacity indicated by laboratory studies (Table 5.3). As the fine-grained material only constituted about one tenth of the total sorbent weight, the estimated bulk sorption capacity for the marl sorbent of size classes 2–4 used in the field pilot is closer to that of the larger particles material than the fine grained material.

The dissolved PO_4 concentration was lower in the 90 µm-mesh experimental bottles than in the water column at the deployment depth (Table 5.3). In control bottles (no marl sorbent) PO_4 levels were similar to those in the water column (360–460 µg/L). The difference in PO_4 between treatment and control bottles suggests several things. First, it is another indication that the marl sorbent can take up PO_4 from the surrounding water. It also shows that the water exchange through the netted mesh lid was limited and could not fully compensate for the sorption of PO_4. Finally, the reduced PO_4 levels in experimental bottles shows that P sorption was still ongoing when the exposure period ended after 48 days. Thus, the sorption efficacy over longer timescales may be underestimated by the present results.

Limited water exchange through the netted mesh lid was also indicated by differences in pH between experimental and control bottles. As described above (see 5.2.4), pH measurements were performed in the laboratory a few hours after each set of experimental bottles were retrieved. In the first set of bottles taken up after 13 days of exposure to *in situ* conditions, pH levels in three bottles with marl sorbent varied between 10.6-12.25, while the pH in one of the four control bottles was 7.1. Especially low PO_4 concentrations and high pH values were detected for size class 4 (Table 5.3) and it is probable that the uptake of P by the sorbent in these bottles was rate limited by the PO_4 concentration in the surrounding water. For the other size classes, the PO_4 concentration in the surrounding water was, although lower than in the bottom water, still high enough for P sorption to occur. In laboratory adsorption studies with the marl sorbent, start concentrations of PO_4, typically in the range of 300–3000 µg/L, dropped below the detection limit due to adsorption. Thus, evidently, P sorption must have continued in the laboratory experiments even when the dissolved PO_4 concentrations were close to zero.

Table 5.3 Comparison of P content following in situ exposure to bottom water for varying sorbent size classes. P sorption was calculated by subtracting the P content of the raw material from the P content after the exposure period. The "bulk" sorption shows the average P uptake in the sample, taking in to account the relative proportions of fine-grained material and larger particles. "Sorption capacity (laboratory)" refer to the lower end estimate of the sorption capacity of the most efficient type of marl sorbent tested in the laboratory.

	90 µm mesh, 48 days					**1 mm mesh, 32 days**
	Size class 1 (< 1 mm)	Size class 2 (1–4 mm)	Size class 3 (4–9 mm)	Size class 4 (>9 mm)	No sorbent (control)	Size class 3 (4-9 mm)
Number of pooled samples	1	2	2	2	2	2
Raw material P content (mg P/kg dwt)	84	47	42	34		42
Fine-grained (<1 mm) material P content (mg P/kg dwt)	186	346	351	263		326
P content larger particles (mg P/kg dwt)		70	51	38		54
Weight fine-grained material (g)	26	2.6	3.8	6.0	0	2.4
Weight larger particles (g)		17	24	40	0	18.3
Dissolved PO_4 (µg/L), average concentration for pooled samples	99	139	95	2	408	-
Water column PO_4 (µg/L), 16 m	330	330	330	330		330
P sorption (mg P/kg sorbent)						
Fine-grained material	102	299	309	229		284
Larger particles		23	9	4		12
Bulk	102	59	49	34		43
Sorption capacity (laboratory), 2-4 mm size class	16800					

It is difficult to determine exactly how restricted the water exchange was in the 90 µm netted mesh bottles. However, based on the amount of P taken up by the marl sorbent (Table 5.3), it is clear that the water mass within the bottles must have been exchanged somewhere around the order of *at least* eight times during the course of 48 days. This can be illustrated by using the size class 2-bottles (Table 5.3) as an example. These two bottles contained a total amount of 18 g sorbent, of which 2.6 g had disintegrated into smaller particles. The P content of this fine-grained matter increased by approximately 300 mg/kg and the P content in the rest of the marl sorbent increased by approximately 20 mg/kg. Thus, the total amount of P taken up by the marl sorbent can be estimated to be approximately 1 mg (300 mg/kg x 0.0026 kg + 20 mg/kg x 0.0154 kg). Our measurements in the water column (Figure 5.4) indicate that the PO_4 concentration in the bottom water varied between

330-350 µg/L. The average PO_4 concentration in the control bottles that were taken up after 48 days was within a similar range (358-464 µg/L). Assuming a deep water concentration of 408 µg/L (Table 5.3), the 1 mg of P taken up by the marl sorbent must have originated from more than 2 L of water which is eight times the total volume of the experimental bottles (2 x 125 mL).

5.4 Conclusions

A major advantage in this field pilot was that the marl sorbent could be recovered after being exposed to "typical" environmental conditions in areas where it is intended to be used, i.e., reducing brackish bottom water with high PO_4 concentrations.

It was found that loss of sorbent by dissolution does not occur to any measurable extent. It was also found that only a small proportion of the marl sorbent disintegrated into a fine-grained material as intended, when in contact with water. The proportion of the material which did disintegrate clearly took up PO_4 from the surrounding water, but the uptake capacity was much lower than anticipated.

The fraction of the marl which did not disintegrate into a fine-grained material ("inner core") had a much lower affinity for P than the fine-grained material. The sorption capacity for P of the bulk material can be assumed to be closer to that of the inner core fraction than the fine-grained fraction and thereby several hundred times lower than the material which was used to estimate the P sorption capacity in laboratory studies.

6 Key findings

The main findings from the four field trials described in Chapters 2-5 are as follows:

- The large-scale treatments with the marl sorbent (100–130 g/m^2 sediment area) did not result in measurable lasting changes in P bioavailability in Kyrkviken and Kolkka bays. There are some indications that the marl sorbent treatments induced short term decreases in water column PO_4 concentrations that lasted for timescales of hours.
- Addition of the marl sorbent (400 g/m^2) to reducing bottom sediment in Djuröfladen Bay did not increase the P content in the bottom sediment over a time scale of 2–9 months after treatment.
- Results from Farstaviken Bay show that the marl sorbent clearly has a preferential affinity for sorption of P and that there was no measurable loss of the marl sorbent due to dissolution. The sorption capacity might even be slightly underestimated as the field experiment was relatively short (48 days). Still, the capacity was much lower than anticipated from adsorption studies in the laboratory and this discrepancy explains the lack of expected effects in the other field trials.
- The comparatively low binding efficacy for P in field conditions was partly because only a fraction of the marl sorbent disintegrated into a fine-grained powder in field conditions. This contrasts with the marl sorbent tested in the laboratory which was almost completely pulverized after some time in contact with Baltic Sea water.
- The marl sorbent caused some increases in pH in the bottom water and bottom sediment. The changes in pH were so small, however, that they are very unlikely to cause negative environmental consequences.
- Addition of the marl sorbent by helicopter was successful and appears to be a suitable method to spread the marl sorbent, at least in uninhabited or sparsely populated areas in calm conditions.
- Addition of the marl sorbent to surface waters did not cause clouding in the water column.

7 Outlook

The most likely explanation for the low P binding capacity of the marl sorbent used in the field trials compared to previous laboratory tests is related to the heat treatment used in the preparation of the material. The marl sorbent used in the laboratory tests was produced in very small quantities with the aim of finding the optimal heat treatment conditions for maximised P binding efficacy. Each production batch for the laboratory studies consisted of ~100 g of marl sorbent and the heat treatment procedure required detailed supervision of conditions in the furnace and manual work. However, in order to produce the required amount of marl sorbent for the field trials (~20 metric tonnes), the production had to be scaled-up.

Although great care was taken to reproduce the optimal production conditions in the furnace used for the scaled-up production of marl sorbent (Figure 7.1), there are several indications that the marl sorbent produced for the field trials differed from that produced for the laboratory tests (see Chapter 5). First and foremost, the P binding capacity of the field test sorbent appears to be a fraction of the capacity of the laboratory sorbent. Also, the material used for the field trials only partly disintegrated into a fine powder, unlike the material used in the laboratory sorption tests which was slowly and gradually pulverised when in contact with water.

Figure 7.1 Left: Rotating furnace used for production of marl sorbent for the field trials. Right: Muffle furnace used for production of marl sorbent for the laboratory studies.

The most likely explanation for the difference in P binding observed in field and laboratory conditions thus lies in the production technique as described above. Therefore, further optimisation of large-scale production of the marl sorbent is required and is planned to be carried out within a new project that will start in 2021 (personal communication Eva Björkman, Levande Hav AB).

In retrospect, it would have been optimal to have verified the P sorption capacity of the field trial sorbent in mesocosm and/or laboratory scale experiments before proceeding to the large-scale treatments in Kyrkviken and Kolkka bays. Furthermore, the sorption capacity of marl produced for laboratory experiments should have been verified in conditions resembling those in bottom sediments of oxygen depleted bays in the Baltic. In other words, the leap from laboratory experiments to full scale pilot experiments, with a largely untested batch of sorbent, was too large. Therefore, mesocosm-scaled experiments, such as controlled sediment core incubation studies with manufactured marl sorbents are highly recommended before further large-scale trials are performed.

On the assumption that the production technique can be refined, the P binding efficacy observed from laboratory experiments suggest a capacity to induce large observable changes in P availability and other variables in the field. Thus, the effect of the marl sorbent addition (given an P binding efficacy of 16.8 g/kg) would be relatively easy to detect by the monitoring programs that were initiated.

Still, given the large interannual variability in coastal environments, pilot sites with pre-existing environmental monitoring programs and/or historical time series data are preferable. If case pilot sites with no ongoing environmental monitoring are selected for future pilot tests, environmental monitoring for several years is generally recommended before any treatment with marl sorbent or other manipulations are performed, unless the effect of the manipulation is foreseen to induce drastic effects. As seen in the present work, coastal bays are characterized by rapid shifts and interaction between physicochemical variables. Such shifts may be difficult to detect and interpret without a monitoring program with enough measurement frequency. Autonomous measurement systems, like the one used in Kolkka Bay, likely provide the most cost-efficient way to monitor key variables with enough temporal resolution and are generally recommended for similar future studies.

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