

# Activated Limestone

A Sustainable New Remediation Method to Fight Eutrophication

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## Summary

The Baltic Sea suffers from severe eutrophication - a state with massive algal blooms and dead bottom zones. These symptoms are caused by excess phosphorus and nitrogen that have been released by human activities and function as nutrients for algal growth. Unfortunately, nutrient rich bottom sediments often continue to feed eutrophication, although input from land has decreased. This study investigated a new material – activated limestone – that was added to nutrient rich bottom sediment with the ambition to stop nutrient release and thereby reduce eutrophication. Our results show that the activated limestone was very efficient in stopping leakage of phosphorus from eutrophic sediments collected at a fish farm on Åland from which fish feces have contributed to the nutrient load and accumulation in its surrounding waters. The phosphate release from the sediment was completely stopped by addition of 600  $g/m^2$  activated limestone. In addition, the risk of potential side effects, such as greenhouse gas emissions, was measured and found to be low after addition of the activated limestone. Overall, the use of activated limestone can contribute to increasing the sustainability of fish farming, and to diversify the tools needed to curb eutrophication globally.

## 1. Background

## Eutrophication

Eutrophication is occurring across the world and is especially harmful in lakes, coastal areas, estuaries, and inland seas where excess nutrients boost primary production and cause algal blooms, that can be hazardous to aquatic life and a nuisance for human recreation and health. Eutrophication often causes oxygen depletion in large areas, so called "dead zones", that occur when surplus biomass settles on the seafloor and is degraded by microbes in a process that consumes oxygen. The oxygen is supplied by the overlying water, and sometimes by photosynthesizing organisms in the surface sediment. But microbes in sediment can use other chemical agents than oxygen to fuel their metabolism. These include nitrate, manganese, iron, and sulfate (Froelich et al. 1979). Oxygen depleted bottoms, therefore, generate hydrogen sulfide, a toxic gas, that is produced from microbial sulfate reduction. Such anoxic and sulfidic bottoms are wide-spread in the Baltic Sea, that houses the largest anthropogenic dead zone in the world (Diaz and Rosenberg 2008). In these conditions, multicellular life cannot survive. Anoxic sediments also release methane - a greenhouse gas more potent than carbon dioxide - as an end-product of organic matter degradation. In shallow coastal areas, produced methane by microorganisms easily diffuses to the atmosphere where it contributes to global warming (Humborg et al. 2019).

In contrast with oxygenated sediments, anoxic bottoms have an impaired ability to retain phosphate ( $PO_4^{3-}$ , the free ionic and directly bioavailable form of phosphorus). This is a direct effect of oxygen conditions; when oxygen is lacking, formed sulfide can compete with phosphate for binding to iron and manganese (Ingri, Löfvendahl, and Boström 1991; Smolders et al. 2006). Free phosphate can then re-enter the nutrient cycle and be available for primary production. In severe cases, this can generate a feedback loop that supplies itself with phosphate and proliferates when anoxic areas expand, as is the case for the Baltic Sea. This internal loading of phosphate can be the main driver of eutrophication even if nutrient input from land has stopped.

### Remediation

Many techniques to remediate eutrophic ecosystems have therefore focused on stopping this internal cycling of phosphate, preferably by immobilizing it in the sediments using a strong sorbent. The single most utilized sorbent to remediate eutrophic waters is treatment with aluminum. Various forms of aluminum salts have been used for many decades, often successfully, to react with and bind legacy phosphate, primarily in lakes (Huser et al. 2016). A Baltic Sea bay in the Stockholm archipelago was successfully treated with aluminum injection into the sediment, along with land-based efforts to stop external nutrient loading, which together decreased phosphorus and nitrogen concentrations, and, ultimately, plankton biomass (Rydin et al. 2017).

Another method based on phosphate sorption is sediment treatment with Phoslock<sup>™</sup> - a bentonite clay enriched with Lanthanum (a rare earth element) that can form insoluble minerals with phosphate (LaPO<sub>4</sub>) (Zamparas et al. 2015). Phoslock<sup>™</sup> has been used in hundreds of water bodies all over the world, often successfully (Wang et al. 2017).

#### The New Activated Limestone

Sorbents containing calcium are also of interest since insoluble calcium-phosphates such as apatite can be formed in the reaction with phosphate. Our study focused on the new calcium-based sorbent activated limestone (in Swedish aktiverad kalksten (AK)). The AK is a bright gravel-like mineral that is produced by heat treating of so-called marl – a by-product from limestone mining – that is ubiquitous. Our material was collected and heat treated at concrete plants conveniently located on Gotland in the Baltic Sea. The AK has several attractive attributes as a phosphate sorbent for nutrient rich sediments. First, it has a very high sorption capacity for phosphate: 10 g phosphorus/kg<sub>sorbent</sub> (Blomqvist et al. 2023) and recently even a higher capacity has been measured; ca 50 g phosphorus /kg<sub>sorbent</sub> (Björkman, 2023). This can be put into perspective by comparing it with the sorption capacity of Aluminum chloride solution at ca 10 g phosphorus/kg<sub>solution</sub> (Rydin et al. 2016; Schütz, Rydin, and Huser 2017) and Phoslock, also at ca 10 g phosphorus/kg<sub>sorbent</sub> (Haghseresht, Wang, and Do 2009). Second, the AK particles have a high settling velocity which makes it suitable for treating deep areas (100 m) that are often out of bounds for powdered materials or sorbents in solution. The particle size can also be modified to change its velocity to reach different depths without losing material through dissolution. Once on the bottom, the AK will disintegrate to many small microparticles with a high surface area available for phosphate sorption. Finally, for the Baltic Sea, AK produced on Gotland is a potentially cheap and sustainable material due to the vicinity of the gigantic amount of feedstock marl that sits on dumps on the island.

Importantly, the AK has already been applied in the field in a Swedish remediation project in 2022. With the aim to study phosphorus retention by AK under real conditions, 30 tons of the sorbent was spread over 10 hectares by helicopter in the Baltic Sea bay Kyrkviken in Gryts archipelago, Sweden, in September 2022. The application method was quick and efficient, and the results are currently being evaluated. Preliminary findings show that the previous phosphate concentration in the bottom water was reduced by 45% following remediation with AK. A final report from the pilot field study is to be published in 2024 (Björkman, 2023).

On top of the sorbents described here, a rapidly increasing number of materials for in situ (on site) immobilization of various contaminants have been developed and tested in laboratory studies. Unfortunately, there is a disconnect between this developmental engineering and real-world application (Chiang et al. 2012). Therefore, the present study aimed to experiment under field-like conditions using intact samples. We tested the AK on nutrient rich sediment sampled at a fish farm on Åland, with the aim to provide the knowledge needed to conduct future on-site studies in a safe, effective, and sustainable manner.

# 2. Methods

## The Site – Storfjärden Fish Farm

In modern times, traditional capture fisheries have dominated the production of blue food and emptied stocks of fish in the oceans globally. However, aquaculture production is becoming an increasingly important and potentially more sustainable source of blue food. In the year 2000, aquaculture amounted to ca 25% of total fish production. Today, that number is ca 50% of the annual total production of 180 million tonnes fish (FAO. 2022).

Åland aquaculture represents an important part of the export economy of the islands. The contribution to the total nutrient load from the fish farms into the Baltic Sea is small, but local eutrophication effects are seen, and expansion of the aquaculture is thereby limited (Wennström et al. 2011). Hence, there are strong incentives for the producers to reduce their nutrient output and environmental impact. A recent field study performed on 28 Åland fish farms showed that 15 of them had local negative effects that manifested as oxygen deficient and sulfidic sediments. Three fish farms had very poor oxygen conditions at the time of sampling (Naturvatten i Roslagen AB 2023). It is likely that seasonal variations cause more sites to experience hypoxia, meaning that the waters have insufficient oxygen for most animals to survive (defined as < 2 mg/L dissolved O<sub>2</sub>). The sediments were also high in organic matter and constitute local hot spots of nutrient pollution.

## **Sampling of Sediment Cores**

The sampling was done in Storfjärden bay in Eckerö municipality, Åland (WGS 84: N 60.252896 E 19.492400, Figure 1). The locale was chosen after reviewing data collected by the Åland fish farmers organization as part of the recipient control program (Naturvatten i Roslagen AB 2023). According to the monitoring data, the bottoms at the site are rich in organic matter originating from the fish farm, which has resulted in patches of hypoxic and sulfide rich sediments.



*Figure 1.* Map showing the sampling location (red dot) in the Storfjärden bay, Åland, and its location in the Baltic Sea.

A total of 17 sediment cores were collected using a kajak tube corer that was manually lowered to 10 m depth from a boat (Figure 2) 100 m from the fish farm. The fish-farmers kindly escorted us to the site on their working boat and helped retrieving the cores. Water parameters were measured with a multimeter (HACH Hq4Od). The salinity was 6, the temperature was 9°C, pH was 7.8, and the bottom water was well oxygenated (8 mg/L  $O_2$ ) at the time of sampling. The concentration of phosphate (PO<sub>4</sub><sup>3-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) in the bottom water was 3.9 ± 0.03 and 2.0 ± 0.3 µmol/L, respectively. The retrieved sediments had a strong smell of sulfide and were partly black – indicators of so called euxinic conditions (which means that the sediment is hypoxic and sulfidic). Two cores were sampled for water chemistry, using the methods described below.



*Figure 2.* Photos of the sampling with the kajak tube corer from the boat in Storfjärden, and collected sediment cores with intact bottom water overlying the sediment surface.

The sediment cores were transported to Stockholm University where they were put in three separate 100 L incubator buckets in a climate chamber at 9°C temperature which was the temperature measured in the water during field sampling. The buckets contained Baltic Sea surface water collected from Lilla Värtan in Stockholm (N 59.372848 E 18.068803). The bucket water was filtered through a 40  $\mu$ m mesh and treated with addition of artificial seawater to increase the salinity from 2 to 6 before the cores were placed in the incubators. The concentration of PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> in the ambient water was 3.3 and 0.5  $\mu$ mol/L, respectively. Each core was fitted with a magnetic stirrer externally driven by a motor in the middle of each incubator. The magnetic stirrer ensured a gentle turbulence in the water column, and the formation of a diffusive boundary layer (DBL) at the sediment-water interface (SWI), to mimic natural conditions (Broström and Nilsson 1999). The water volume in the core was 1.3 ± 0.05 L.

Out of the 17 cores, a majority hosted visible macrofauna (animals > 1 mm body size) such as sediment dwelling worms (mostly Nereis diversicolor), small clams (Macoma batlhica and Mya arenaria) and a few small amphipods. Two cores were excluded from further experimentation since they contained large individuals of the isopod Saduria entomon and the worm Nereis diversicolor, which resuspended and circulated the sediment and porewater, certainly confounding solute fluxes. The rest of the cores (n=15) were randomly allocated to three treatments (n=5), i.e., one treatment per incubator, according to Table 1. The activated limestone was added to the cores by spreading the material evenly at the water surface after which it settled on the sediment surface immediately. The material had a particle size of 3-6 mm. The cores were left with tops open below the water level of the incubator buckets to allow for water exchange and buffering of pH for three days. The cores were then completely shut with rubber stoppers to stop oxygen from entering the systems, thereby inducing anoxia (0 mg/L  $O_2$ ). Then, release of  $PO_4^{3-}$  from the sediment to the water can be detected. In this manner, the effect of the AK on  $PO_4^{3-}$  release was investigated.



**Figure 3.** Top-view from the opening of the sediment cores showing the activated limestone (600 g/m<sup>2</sup> dose) just after addition (left) and one day after addition when it had dissolved and created white fields on the sediment surface (right).

Treatment	Abbreviation	Activated limestone addition (g/core)	Activated limestone dose (g/m <sup>2</sup> )
Untreated control	CTRL	-	-
Activated limestone, low dose	АК300	1.51	300
Activated limestone, high dose	АК600	3.02	600

#### Table 1.

#### **Sediment Core Incubations**

When the O<sub>2</sub> concentrations in all sediment cores had decreased below 0.2 mg/L, ca two weeks after closing them, several incubations of the sediment cores were done over the course of 8 weeks to determine fluxes of  $PO_4^{3-}$ ,  $NH_4^+$ ,  $O_2$ ,  $CH_4$  (methane), and  $H_2S$  (hydrogen sulfide). The method is based on differences in solute concentrations at the start and end of the incubation. The flux Jx (mmol m<sup>-2</sup> d<sup>-1</sup>) equals ( $C_E - C_S$ )  $\cdot h / t$ , where  $C_E$  and  $C_S$  are end and start concentration in  $\mu$ mol/L, h is the core water column height in m, and t is incubation time in days.

Sampling of solutes in the core water was done from the middle of the column using a syringe with a silicone tubing. Samples for  $PO_4^{3-}$  and  $NH_4^+$  were filtered through a 0.45 µm polyethersulfone (PES) syringe filter into heat-treated (water filled at 60°C for 24 h) PP-tubes, and analyzed using *method* 2 mentioned in the section Chemical Analyses below. All water samples were stored at 4 °C before analysis. Water for CH<sub>4</sub> analysis was transferred without filtering to 12 mL exetainer vials and any biological activity was stopped with addition of 100 µL 7M zinc chloride, to prevent microbial methane production or oxidation while awaiting analysis. Details on all chemical analyses are provided in a separate paragraph, below.

#### Termination

The experiment was terminated 8 weeks after closing the cores. Water was collected for nutrient analysis, as described above, and for  $H_2S$  by siphoning and overflowing core water into winkler flasks that were then fixated with 4 mL zinc acetate. The samples were stored at 4 °C until analysis. A counting of benthic fauna, especially large worms, could not be performed due to the decay of the animals.

The top 2 cm of the sediment surface was sliced. A portion of the wet slice was weighed and dried to establish water content and organic matter content using mass loss on ignition (LOI) at 520 °C for 6 h. The remaining wet slice was transferred to 50 mL PP-tubes and carefully bubbled with nitrogen via 0.40 mm syringe needles to purge oxygen and preserve anoxic conditions. pH was measured, and aliquots were centrifuged at 4000 rpm for 5 minutes before supernatant porewater was analyzed for dissolved  $PO_4^{3-}$  using *method* 1 mentioned in the section Chemical Analyses below.

### **Chemical Analyses**

Watercolumn pH, oxygen, and salinity were measured with a multimeter (HACH Hq4Od). To determine CH<sub>4</sub> concentration in incubation samples, headspace-gas chromatography was done, following the method by Sithersingh and Snow (2012). A headspace was created in the Exetainer vial containing the samples by replacing 2 mL of sample with nitrogen gas using  $\emptyset$  0.4 mm needles pushed through the septum of the lid. After 24 h equilibration at room temperature, 1 mL headspace gas was injected into a Shimadzu 8A gas chromatograph (GC) equipped with a flame ionization detector (FID). We made repeated injections of 1 mL standard gas containing 50 ppm methane (Air Liquide, France), to calibrate the instrument. Additionally, a solubility coefficient for methane in water with salinity of 6 was used to calculate the concentration of CH<sub>4</sub> in the water.

Analysis of dissolved  $PO_4^{3^-}$  was done on filtered water samples (0.45 µm PES) by two methods. The first method (*method 1*) was used to monitor phosphate concentrations in the core water during the experiment, and to analyze dissolved phosphate in the sediment porewater after termination. This method used a mobile spectrophotometer (Spectroquant<sup>®</sup> Move 100, Merck), according to method DIN EN ISO 6878, and had a measuring range of 0.01 – 5.00 mg  $PO_4^{3^-}/L$ . *Method 2* was performed at the SWEDAC accredited Marine Ecological Lab at the Department of Ecology, Environment, and Plant Sciences Stockholm University, by colorimetric analysis on a segmented flow nutrient analyzer system (OI Analytical, Flow Solution IV, Xylem Inc., USA) using the manufacturers method #319528 for  $PO_4^{3^-}$ . Analysis of dissolved NH<sub>4</sub><sup>+</sup> used the same colorimetric analysis with method #319526. *Method 2* had a lower measuring range of 0.5 – 500 µg  $PO_4^{3^-}/L$ . The range for NH<sub>4</sub><sup>+</sup> was 0.5-2500 µg/L. Dissolved hydrogen sulfide was measured by the Marine Ecological Lab using spectrophotometry according to Grasshoff, Ehrhardt, and Kremling (1983) at a range of 0.1 – 2.2 mg/L.

### Statistics

Analysis of variance (ANOVA) and Tukey's post-hoc test were used to establish whether there were significant differences between the treatments. The Tukey test is robust against varying sample sizes that sometimes occurred as a result of sample loss. In case of non-normality, a non-parametric Kruskal-Wallis rank sum test followed by a pairwise Wilcoxon test was done. All statistical analyses were performed in R version 4.2.2 using the package ExpDes.

# 3. Results and future perspectives

In this section we show how the AK reduced phosphate fluxes and affected other important sediment processes. The applicability and steps toward a trial in the field are discussed. The data are presented in the text as the mean value of five treatment replicates ± standard deviation, unless otherwise is stated.

#### Sediment parameters and lab observations



**Figure 4.** One core per treatment (from left: CTRL, AK300, and AK600) showing varying iron sulfide formation as black precipitation. Notice the precipitation on the core liner walls, magnetic stirrer at the top, and the color of the sediment surface.

In untreated control, i.e., natural conditions in the field, the top 2 cm sediment had a water content of 80  $\pm$  0.01 % and porosity ( $\varphi$ ) of 0.9  $\pm$  0.01. Organic matter content was 17  $\pm$  1% dry weight, which is normal for eutrophicated accumulation bottoms, and coherent with existing data collected at Storfjärden (Naturvatten i Roslagen AB 2023). When slicing the sediment (cutting and obtaining different depth segments) at the experiment termination it was clear that most of the solid AK had dissolved, although a few particles of around 5 mm had allocated as deep as 2 cm down into the sediment.

There was a clear visual difference between CTRL and AK cores one month after treatment; the sediment surface, magnetic stirrer and core liner were colored black in the CTRL treatment. In the treatment with activated limestone of low dose (AK300), there was some precipitation but not as pronounced as in CTRL. In AK600, the sediment surface was still brightly colored and very little precipitation had formed (Figure 4). The black precipitate was likely iron sulfide formation, which is limited by iron availability. This interesting observation motivated sampling of the water column for sulfide at the experiment termination, since it was hypothesized that lower iron sulfide formation in AK treatments could lead to release of free sulfide, which it did, see below for more details. As mentioned earlier, iron sulfide is known to decrease the ability of the sediment to bind  $PO_4^{3-}$  which can then be released (Smolders et al. 2006). This effect was detected in untreated CTRL, see below for more details. These observations are typical for anoxic sediments.



#### Nutrient release: phosphate and ammonium

**Figure 5.** Effects of the treatments on sediment-to-water flux (release of free phosphate per  $m^2$  sediment per day). CTRL = untreated sediment; AK300 and AK600 = 300 and 600 g AK/ $m^2$ . Bars show treatment mean and standard deviation. Different alphabetic letters above the bars denote statistically significant differences between treatments (Kruskal-Wallis, p = 0.002, pairwise Wilcoxon test), i.e., all treatment means differed significantly.

Activated limestone treatment decreased the phosphate release from the sediment, measured as release per  $m^2$  over time (flux, Figure 5). The lower dose (300 g/m<sup>2</sup>) decreased flux by 48%, compared with untreated CTRL. The double dose (600 g/m<sup>2</sup>) decreased phosphate release by 100%, i.e., stopped it completely. In summary, the AK material was found to successfully decrease the amount of phosphate released from the sediment.



**Figure 6.** Phosphate concentration in sediment porewater after the experiment termination. Different letters above the bars denote statistically significant differences between treatments (ANOVA, p = 0.003, Tukey's post-hoc test). AK treatments differed from CTRL. n = 4 for AK600.

Simultaneously, sediment porewater phosphate in the top 2 cm increased in the limestone amended sediment (Figure 6). This effect can likely be attributed to the unrealistic changes in pH caused by the AK (see results below); increased alkalinity has been shown to speed up biological degradation of organic matter, which will generate more dissolved phosphate. Generated bicarbonates by AK can also compete with the phosphate anion for binding sites (Smolders et al. 2006). In any case, this did not increase the flux of phosphate from the sediment to the water, which verifies that the dissolved AK in the superficial sediment layer actively sorbed phosphate through the experiment.



**Figure 7.** Effects of the treatments on sediment-to-water flux of ammonium. No statistical differences between treatments were found (ANOVA, p = 0.78).

Ammonium is a dissolved and bioavailable form of nitrogen and a nutrient that together with phosphate drives eutrophication in the Baltic Sea. Ammonium fluxes were measured as an estimation of microbial degradation of organic nitrogen such as proteins and nucleic acids. Figure 7 shows that no effect of the AK was detected regarding release of ammonium.



**Figure 8.** Effects of the treatments on pH in the water overlying the sediment over the first 33 days (left side), and pH in sediment porewater at the experiment termination (right side). Vertical bars show standard deviation of mean. Different letters by the bars indicate significant difference between the groups. pH was found the be statistically different in the water between all treatments at every measurement (ANOVA, p < 0.05, Tukey's post-hoc test), while pH in the sediment porewater was different in the CTRL compared to the AK treatments. n = 4 for AK600 porewater pH.

pH in the water column above untreated sediment (CTRL) decreased from 7,8  $\pm$  0.005 at the experiment start to 7.3  $\pm$  0.04 at day 33. (Figure 8). In contrast, the alkaline AK increased the pH of both the overlying water and sediment porewater. In the highest dose of 600 g m<sup>-2</sup>, pH was 9.2  $\pm$  0.04 after 33 days. pH in the treatment with 300 g m<sup>-2</sup> AK was also affected but not to the same degree as in the higher dose. Porewater pH was measured at the experiment termination and was 7.5  $\pm$  0.25 in CTRL and increased to 8.0  $\pm$  0.22 and 8.2  $\pm$  0.11 in AK300 and AK600.

pH increase in the AK treatments was expected, since the limestone is an alkaline material, releasing hydroxide ions as it dissolves. It is likely that this increase generated more alkalinity, since phosphate and sulfide, which were elevated (more details below), can contribute to porewater alkalinity in anoxic sediments (Lukawska-Matuszewska 2016). It also must be considered that the effect of AK on pH was unnaturally amplified in this experimental setup, where buffering capacity was limited in the 1.3 L core water column, that was not replaced during the experiment. Buffering capacity in the field is many orders of magnitude higher and it is therefore improbable that this pH increase would occur in a field situation. This claim is supported by monitoring data collected in Kyrkviken bay that has been treated with 300 g AK/m<sup>2</sup> without any effect on pH in the bottom water (Björkman, 2023). It is important to point out that several of the effects measured in this study can be linked to changes in pH, since pH is a primary controller that can alter chemical speciation and energy yields of compounds of microbial metabolism. For example, the energy yield for fermentation of, e.g., acetate and lactate in microbial sulfate reduction is at its lowest at neutral pH and increases considerably as pH either increases or decreases (Jin and Kirk 2018).



## Hydrogen sulfide



Since visible precipitation of iron sulfides decreased with the treatment dose, it was hypothesized that these treatments had released higher concentrations of free hydrogen sulfide. This was confirmed by analysis of core water sulfide, although the difference could not be statistically proven (ANOVA, p = 0.09). Hypothetically, this can be an effect of compromised sulfide oxidation by metals, that in turn was precipitated with hydroxide ions in the elevated pH environment. It is also possible that the energy yield of sulfate reduction was increased with the unrealistic increase in pH, as discussed above, and that sulfate reducing microbes proliferated accordingly. Our findings therefore indicate that the AK material had no impact on the amount of sulfide released from the sediment.



### Respiration

**Figure 10.** Total oxygen uptake by benthic microbes and fauna expressed as a negative flux. Different letters above the bars denote statistically significant differences between treatments (ANOVA, p = 0.01, Tukey's post hoc). The AK300 treatment was found to be statistically different from CTRL.

The consumption of oxygen by microbes and benthic fauna (respiration or total oxygen uptake, TOU) was measured during the initial de-oxygenation of the cores before the anoxic incubations were done (Figure 10). The two treatments with AK showed faster oxygen consumption during this phase, and AK300 had significantly higher TOU than untreated control. This indicates that microbes and fauna in the sediment consumed more oxygen, likely due to pH-related increases in microbial metabolic rates, as discussed previously, and pH induced stress to benthic fauna.



#### Methane release from sediment

**Figure 11.** Methane release from the sediments. Statistical analysis showed no difference between the treatments (ANOVA, p = 0.1).

We did not detect any differences in methane release between untreated and treated sediment. Fluxes from the sediment were expected since anoxia mediates microbial methane production. However, measured fluxes were low and more in the range of fluxes from oxygenated Baltic Sea sediments (e.g., Bonaglia et al. (2014), Wikström et al. (2021). Hypothetically, methanogenesis was occurring slowly, or sufficient anaerobic oxidation of methane (AOM) degraded formed methane. Our findings indicate that the AK material did not affect methane release from the sediment.

#### **Future perspectives**

The ability of AK to retain phosphate in the sediment is a promising result that shows the potential of AK for use in remediation of eutrophic waters. A small dose of 600 g/m<sup>2</sup> completely stopped the phosphate release from the sediment. This dose is similar to doses of aluminum chloride that have been injected in eutrophic lake sediments (Schütz, Rydin, and Huser 2017). For 16 lakes remediated with Phoslock<sup>™</sup>, an average dose of ca 300 g/  $m^2$  was applied (Spears et al. 2013). Before such field applications, the pool of available phosphorus in the sediments is determined and the dose is calculated accordingly. Doses will therefore vary depending on the site. The AK increased porewater concentrations of phosphate which is an effect that must be studied further. However, the phosphate was entrapped in the sediment porewater in the AK treatments, possibly to small iron or other mineral hydroxides smaller than 0.45  $\mu$ m in size (thus passing through the filter during phosphate measurement). Porewater phosphate can be mobilized following adverse episodes, such as resuspension caused by storms, or physicochemical alterations following, e.g., climate change. If the increased pH caused the raised porewater phosphate, it is not likely that it would occur in a field situation where buffering capacity against pH changes is high. Furthermore, the partitioning of phosphorus, i.e., how it allocates to bioavailable forms or is trapped by the sorbent or sediment, could change in a longer experiment. A future pilot-scale study must therefore further assess these effects under a long time-period.

To summarize, this study showed that the novel activated limestone trapped phosphate in the sediment effectively, which was the purpose of the amendment, and that the material had no effects on other important sediment processes such as methane formation. There is no universal method to remediate all eutrophic waters due to their ecological and geological variability and complexity. It is, thus, important to continue to develop and test new techniques in the field.

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# About this publication

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