EARLY-STAGE TESTING OF MINERAL-BASED SORBENT PROTOTYPE SYSTEMS FOR PHOSPHORUS CAPTURE IN EUTROPHIC LAKES OF LATVIA AND ESTONIA

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Abstract. Nutrient enrichment of surface water remains a critical environmental challenge. Mineral-based nutrient capture technologies offer an approach for mitigating phosphorus (P) pollution while enabling nutrient recovery. This study presents an initial assessment of mineral-based sorbent materials for P capture in aquatic systems, integrating site characterization with early-stage comparative testing under real environmental conditions. The research is conducted within three eutrophic water bodies: Dūņezers (LV), Rīdzene pond (LV) and Võnnu lake (EST). Study sites were characterized through integrated field and laboratory investigations, combining *in situ* physicochemical measurements with chemical, optical, and particulate matter analyses, including total phosphorus (TOT-P), chlorophyll a (Chl a), turbidity, and oxygen saturation, to establish baseline pollution levels and spatial variability. The study sites showed differences in eutrophication intensity, with Chl a concentration ranging from 47.5 $mg \cdot m^{-3}$ in Rīdzene to over 200 $mg \cdot m^{-3}$ in Lake Võnnu and intermediate levels of 144 $mg \cdot m^{-3}$ in Dūņezers. TOT-P concentrations were ~0.2 mg $P \cdot L^{-1}$ across sites, while oxygen saturation ranged from typical eutrophic conditions of 94% in Rīdzene to extreme supersaturation reaching 213% in Dūņezers. Based on site conditions, pilot-scale prototype systems incorporating mineral-based sorbent were deployed for P capture. The systems were exposed *in situ* for three months as a preliminary testing phase prior to full prototype implementation. Post-exposure laboratory analyses focused on sorbent material physicochemical properties, P uptake, and the preliminary assessment of reuse potential, including possible application in soil improvement.

Keywords: phosphorus removal, mineral-based sorbents, water treatment, circular economy.

Introduction

Eutrophication is one of the most significant environmental pressures affecting freshwater lakes and is caused by excessive enrichment of water bodies with nutrients, particularly nitrogen and phosphorus (P), which stimulates accelerated growth of algae and phytoplankton [1]. This process is mainly driven by agricultural runoff, wastewater discharges, urbanization, and internal nutrient loading from sediments, while climate related factors such as rising temperatures and altered precipitation may further intensify its effects [1-4]. Among these drivers, P concentrations stimulate excessive phytoplankton growth and accelerate the formation of harmful algal blooms. Since the 1980s, the intensity and frequency of such blooms have increased globally, with many events dominated by cyanobacteria capable of producing toxins that threaten aquatic ecosystems and human health [1; 3]. As algal biomass accumulates and subsequently decomposes, bacterial activity consumes dissolved oxygen, often causing hypoxic or anoxic conditions, especially in deeper water layers during stagnation periods [3; 5; 6]. These oxygen deficient conditions can result in fish mortality and the loss of sensitive aquatic species, while also promoting the release of P from sediments through internal loading, thereby reinforcing eutrophic conditions [6]. At the same time, high algal density increases turbidity, reduces water transparency, limits light availability for submerged vegetation, and contributes to biodiversity loss, unpleasant tastes and odours, and an overall decline in ecosystem health and water quality [1; 3; 5]. Because of its multiple interacting causes and feedbacks, eutrophication is widely regarded as a complex management challenge that requires integrated control of nutrient sources together with in-lake remediation measures [2-5].

P is widely recognized as the dominant limiting nutrient for primary producers in most freshwater ecosystems and is therefore a key factor in the development and control of eutrophication [7; 8]. Because it is often the nutrient in short supply relative to algal demand, P enrichment is one of the main causes of increased phytoplankton biomass and harmful algal blooms in lakes [8]. For this reason, total P is commonly used as a primary indicator of trophic status and as a predictor of phytoplankton biomass, typically expressed as chlorophyll a concentration. In many freshwater systems, chlorophyll a increases rapidly and approximately linearly with rising P concentrations, indicating that P reduction can be an effective restoration strategy [7; 8]. However, once P concentrations become very high, the response may level off, with a reported breakpoint of approximately 100 μg $P \cdot L^{-1}$, above which additional P does

not substantially increase algal biomass. Under such conditions, other limiting factors may become more important, including nitrogen availability and light penetration [8]. Nutrient limitation shifts are often assessed using Redfield molar ratios, with N:P values above 53 indicating P·Limitation and values below 16 indicating nitrogen limitation [8]. From a management perspective, P thresholds are essential for achieving good ecological status under the EU Water Framework Directive, but these limits vary by lake type, for example from about 14 μg $P \cdot L^{-1}$ in deeper, low-alkalinity lakes to around 52 μg $P \cdot L^{-1}$ in shallow, high-alkalinity lakes [8]. Although P load from point sources have been reduced in many regions, continued diffuse agricultural runoff and legacy P remain major challenges for lake restoration.

Lake eutrophication remediation requires a holistic approach in which the reduction of external nutrient inputs is prioritized and complemented by in-lake measures aimed at controlling legacy P stored in sediments [9; 10]. Existing *in situ* remediation methods can generally be divided into physical, chemical, biological, and combined or emerging approaches. Physical methods such as sediment dredging and hypolimnetic aeration can provide rapid reductions in internal P loading and improve oxygen conditions, but they are often costly, technically demanding, and may have only temporary effects if external inputs persist [10]. Chemical methods, including sediment capping with aluminum compounds or lanthanum-modified bentonite, can rapidly reduce P bioavailability, although their effectiveness depends strongly on site-specific conditions such as pH and organic matter content, while incorrect dosing may create ecological risks [9; 10]. Biological approaches such as biomanipulation, constructed wetlands, and phytoremediation are generally considered more environmentally sustainable and cost-effective; however, they usually require longer implementation periods and ongoing management to ensure lasting effects [9]. For this reason, combined strategies are increasingly considered the most effective, while newer options such as geotextile filtration and floating wetlands are being explored as less invasive and potentially more sustainable alternatives for practical P management in eutrophic lakes [10].

Mineral-based sorbents represent a promising in-lake approach for controlling internal P loading and accelerating the recovery of eutrophic water bodies. These P-sorbing products include naturally occurring minerals, industrial by-products, and modified mineral complexes designed to remove dissolved P from the water column and limit its release from sediments [11]. Their effectiveness depends strongly on composition, with calcium-, aluminum-, iron-, and lanthanum-based materials generally showing the highest sorption performance [11; 12]. Among reported materials, wood-derived sand dust and magnesium-based dust materials have demonstrated high adsorption capacities of 63 and 9 mg $P \cdot g^{-1}$ dry weight, respectively, while commercial lanthanum-modified bentonite products such as Phoslock® typically achieve capacities of around 9-10 mg $P \cdot g^{-1}$ [11; 13]. Advanced materials may perform even better, with Fe-Al-Mn tri-metal oxides reaching 1558.1 $mmol \cdot kg^{-1}$ and some layered double hydroxides exceeding 2000 $mmol \cdot kg^{-1}$ [13]. Importantly, efficient sorbents are capable of reducing soluble reactive P concentrations below 5 $\mu g \cdot L^{-1}$, a threshold considered critical for limiting algal primary production [10]. Field applications have also shown practical potential, for example, phosphate concentrations in a reservoir were reduced from 0.98 $mg \cdot L^{-1}$ to 0.16 $mg \cdot L^{-1}$ after treatment with four metric tons of lanthanum-modified bentonite [13]. However, sorbent performance is strongly influenced by environmental conditions such as pH, temperature, and competing ions, which must be considered when selecting materials for site specific P capture applications [12; 13].

Despite the growing evidence on P-sorbing materials, there remains a need for more field-based studies that evaluate their performance under real environmental conditions, where water chemistry, hydrological variability, and site specific eutrophication intensity may affect P capture efficiency.

In this context, the present study assesses the early-stage applicability of mineral-based sorbent prototype systems for phosphorus capture in eutrophic freshwater bodies in Latvia and Estonia. The novelty of the study lies in the pilot-scale in situ testing of sorbent-based phosphorus capture systems directly under real lake conditions, rather than only under controlled laboratory conditions. The research combines site characterization, field deployment of prototype systems, and post-exposure assessment of sorbent material across three water bodies with contrasting eutrophication intensity and hydromorphological conditions. This cross-border comparison provides practical insight into how mineral-based sorbent systems may perform under different environmental settings in municipal water bodies. In addition, the study links phosphorus capture with the preliminary evaluation of spent sorbent

reuse potential, thereby supporting circular nutrient recovery and future development of municipality-oriented water quality management solutions.

Materials and methods

Three pilot water bodies with differing hydromorphological and eutrophication characteristics were selected in Latvia and Estonia in order to compare site conditions and assess the suitability of sorbent-based treatment in contrasting aquatic environments.

Rīdzene lake is a highly modified water body located in the Gauja River basin in Vaive parish, Cēsis municipality, Latvia, with overall ecological potential assessed as medium. It is a shallow, clear-water lake with high hardness and elevated electrical conductivity. The eastern part is flatter, shallower, and densely overgrown with aquatic vegetation, while the western part is deeper and has steeper banks with a narrower littoral vegetation zone. Despite anthropogenic pressure from the nearby settlement, the lake showed relatively high transparency, with a Secchi depth of 2.0 m reported in summer 2020. Strong macrophyte development appears to retain a substantial share of available nutrients and limit phytoplankton growth [14].

Dūņezers lake is a shallow subglacial lake located in Limbaži Municipality, Latvia, and forms part of the Dūņezers Nature Reserve within the Natura 2000 network. The lake has a long and narrow shape and is extremely shallow, with an average depth of about 1.0 m and a maximum depth of 2.0 m, although sediment accumulation has further reduced depth in some areas. It is hydrologically connected to the Donaviņa River, the Raudupīte stream, and several drainage ditches, while the Svētupe River flows out from its northern end. Dūņezers lake is strongly eutrophic and historically characterized by very poor water quality, frequent cyanobacterial blooms, very low water transparency, and extensive overgrowth of reeds and cattails, which cover about 35% of the lake surface [15].

The Võnnu lake system in Estonia consists of two interconnected shallow impounded water bodies formed by damming a stream flowing into the Luutsna River. The upper basin covers about 2.3 ha with a depth of approximately 1.4 m, while the lower basin is about 2.2 ha and only 0.8 m deep. The system is characterized by poor ecological potential, very high nutrient loading, low transparency, and persistent algal blooms dominated by the potentially toxic cyanobacterium *Planktothrix agardhii*. Water transparency is extremely low, with Secchi depth reported at only 0.15 m in the upper basin, and submerged vegetation is absent because of poor light penetration [16].

Water quality at the study sites was characterized during field tests by combining *in situ* measurements with laboratory analyses of collected water samples. The selected parameter set was chosen to describe trophic status, P availability, biological response, and basic physicochemical conditions relevant to P capture. Total P (TOT-P) and orthophosphate phosphorus (PO_4-P) were determined to assess both the overall P load and the readily available dissolved P fraction. Chlorophyll a (Chl a) was used as an indicator of phytoplankton biomass and eutrophication intensity. Turbidity and Secchi depth were used to characterize optical water quality and the effects of algal growth and suspended matter on transparency. Temperature, pH, and oxygen saturation were measured to describe the hydrochemical environment and the intensity of biological processes in the water column. Together, these parameters were used to establish baseline conditions at each study site, compare eutrophication severity among the investigated water bodies, and support the interpretation of mineral-based sorbent prototype performance under natural environmental conditions.

Water samples were collected from each prototype deployment point during field visits. At each site, two prototype locations were monitored, giving two sampling points per water body and six sampling points in total. Samples were collected from the near-surface water layer at approximately 0.20-0.50 m using polyethylene bottles. The samples were transported to the laboratory in cooled conditions and analysed. In situ water temperature, pH, dissolved oxygen saturation and turbidity were measured directly at each sampling point using a calibrated multiparameter water quality probe. Secchi depth was determined using a standard Secchi disk.

Polonite® was used as one of the mineral sorbent materials in the preliminary prototype testing. Polonite® is a commercial reactive filter material produced by thermal modification (900-1000 °C) of opoka, a silica-calcite sedimentary rock [17; 18]. The sorbent is typically used in a granular form with a particle size of 2-6 mm and is characterized by relatively high porosity, specific surface area and

sorption capacity. P capture by Polonite® occurs through a combination of adsorption and chemical precipitation, facilitated by the conversion of calcium carbonate into reactive calcium oxide [17; 19]. When in contact with water, the material increases pH due to the formation of calcium hydroxide, creating conditions favourable for the precipitation of P as poorly soluble calcium-phosphate compounds [17; 20]. Because of these properties, Polonite® has been widely applied as a filter medium for P removal from wastewater and agricultural runoff and was selected in this study as a suitable mineral-based sorbent for early-stage *in situ* testing under eutrophic lake conditions [18; 20].

To quantify P retention by the sorbent material, P accumulation was calculated as the difference between P concentrations in exposed Polonite® samples and in unused material prior to exposure, providing an estimate of net P loading on the sorbent:

$$q = (C_{exposed} - C_{initial})/1000, \quad (1)$$

where q – net amount of P accumulated in Polonite®, mg·g^{-1};
$C_{exposed}$ – P concentration in Polonite® after three months of in situ exposure, mg·g^{-1};
$C_{initial}$ – P concentration in raw Polonite® before exposure, mg·g^{-1}.

For preliminary *in situ* testing, six pilot prototype systems were deployed across the three selected water bodies, with two systems installed at each study site. The placement points were selected according to the potential pollution sources in each lake, and the coordinates were recorded: Dūņezers lake – 57.518605, 24.699165 and 57.520869, 24.702544; Rīdzene lake – 57.261426, 25.429568 and 57.260951, 25.429123; Võnnu lake – 58.285875, 27.048170 and 58.284682, 27.046051. Each pilot unit consisted of filter bags (mesh size ~560 µm) filled with approximately 10 kg mineral-sorbent material intended for P capture under natural environmental conditions.

Following a three-month in situ exposure period during summer, the Polonite® samples were retrieved from the water bodies, dried at 50 °C, and stored at room temperature until delivery to the laboratory. The post-exposure laboratory analysis was carried out to determine the mineral element composition of the material and to assess its potential suitability for further use as a soil-improving material. The analysed parameters included total nitrogen (N), total and plant-available P expressed as P_2O_5 and as P, total and plant-available potassium expressed as K_2O and as K, and pH. Total nitrogen was determined according to LVS EN 13654-1:2003 and LVS EN 13654-1:2003/NAC:2004, total and plant-available P and potassium according to LVS EN 13650:2003, and pH according to LVS EN ISO 10390:2022.

Results and discussion

The measured water quality parameters indicated clear differences in eutrophication intensity among the three study sites. Rīdzene lake showed the least degraded conditions during the summer period, with the lowest chlorophyll a concentration (47.5 mg·m^{-3}), with comparatively low turbidity (4.5-6.7 FNU), the highest Secchi transparency (0.96-1.20 m), and oxygen saturation close to equilibrium (92.6-94.4%), suggesting a more moderate eutrophic status. In contrast, Dūņezers lake and Võnnu lake exhibited markedly stronger eutrophication symptoms. Dūņezers lake was characterized by elevated P concentrations (TOT-P 0.185-0.376 mg P·L^{-1}), high chlorophyll a reaching 144.7 mg·m^{-3}, reduced transparency (0.40-1.00 m), and extreme oxygen supersaturation up to 212.8%, indicating intense photosynthetic activity and strong algal development. The most severe conditions were observed in Võnnu lake, where chlorophyll a exceeded 200 mg·m^{-3} and reached about 247 mg·m^{-3}, turbidity was the highest among the sites (11.5-43.6 FNU), Secchi depth declined to 0.23 m, and total P ranged from 0.17 to 0.706 mg P·L^{-1}. Oxygen saturation in Võnnu lake also remained strongly elevated (137.3-185.0%), confirming intensive primary production. Overall, the results demonstrate a gradient from moderately eutrophic conditions in Rīdzene lake to highly eutrophic or hypertrophic conditions in Dūņezers lake and especially Võnnu lake, providing a suitable contrast for evaluating prototype sorbent performance under different P pressure and algal biomass conditions.

The pilot systems were deployed at locations selected to represent potential P inflow pathways or contrasting hydraulic conditions within each water body. In Dūņezers lake, one prototype was placed close to the Donaviņa river inflow, where elevated P concentrations were expected, while the second was positioned near a ditch inflow potentially carrying stormwater and surface runoff from the built-up

area. In Rīdzene lake, one unit was installed near the livestock watering area as a potential local pollution source, whereas the second was placed in the central part of the pond to represent more open-water conditions and the planned location of the future P capture object. In Võnnu lake, the two prototypes were positioned at the inlet and outlet in order to assess possible changes in P concentration along the flow path through the lake. Preliminary water sampling during maintenance confirmed that all selected locations were exposed to P-rich conditions, with total P concentrations of 0.42-0.43 $mg \cdot L^{-1}$ in Dūņezers lake, 0.24-0.48 $mg \cdot L^{-1}$ in Rīdzene lake, and 0.30-0.32 $mg \cdot L^{-1}$ in Võnnu lake. The highest within-site contrast was observed in Rīdzene lake, suggesting stronger local spatial variability, while Dūņezers and Võnnu lakes showed more uniform P·Levels between the two pilot positions during the sampling campaign. These results indicate that the deployment strategy successfully targeted hydraulically and environmentally relevant zones for early-stage testing of the sorbent systems.

After three months of *in situ* exposure, post-exposure laboratory analysis of the Polonite® material showed that the sorbent remained strongly alkaline at all study sites, with pH values ranging from 9.9 in Dūņezers lake to 10.5 in Võnnu lake. P was detected in all exposed samples, with concentrations averaging approximately 235 mg $P \cdot kg^{-1}$, with the highest values observed in Dūņezers lake, indicating site-specific differences in P retention. Potassium concentrations were relatively high across all samples, ranging from 3418 to 5035 mg K kg^{-1}, with the highest values observed in Võnnu lake. In contrast, total nitrogen content was comparatively low, reaching 251 $mg \cdot kg^{-1}$ in Dūņezers and remaining below 100 $mg \cdot kg^{-1}$ in both Rīdzene and Võnnu lakes.

The highest apparent accumulation was observed in Dūņezers lake (0.0039 $mg \cdot g^{-1}$), whereas lower values were calculated for Võnnu lake and Rīdzene lake, with apparent P accumulation of 0.0028 and 0.0025 $mg \cdot g^{-1}$, respectively. These values are considerably lower than the maximum P sorption capacities reported for mineral-based sorbents under controlled laboratory conditions, which has been shown to reach up to 53 $mg \cdot g^{-1}$ [17; 21]. However, this difference is expected because the present study was conducted during a three-month passive exposure under real *in situ* lake conditions, rather than under controlled laboratory conditions. Under such conditions, sorbent performance may be affected by variable water flow and contact time, as well as by biofilm development, suspended particles, and fluctuating pH and temperature, all of which can influence P retention and adsorption processes [21-24]. Therefore, the obtained values should not be interpreted as maximum sorption capacity, but rather as preliminary field-based evidence of P accumulation during early-stage prototype exposure. Overall, the findings demonstrate that Polonite® can accumulate P under eutrophic lake conditions, although longer exposure periods and improved hydraulic contact are required to assess its full retention potential.

Furthermore, these results suggest preliminary potential for the reuse of spent Polonite® as a soil-improving amendment following P capture in eutrophic water bodies. However, this potential requires further investigation, including agronomic validation, plant-availability testing, potential contaminant analysis, and field-scale applications.

Conclusions

1. The three investigated water bodies showed clear differences in eutrophication intensity, ranging from comparatively moderate conditions in Rīdzene lake to strongly eutrophic conditions in Dūņezers lake and the most severe degradation in Võnnu lake.
2. Water quality characterization confirmed that total P, chlorophyll a, turbidity, Secchi depth, and oxygen saturation were effective indicators for distinguishing site-specific trophic status and for assessing environmental conditions relevant to P capture.
3. Dūņezers and Võnnu lakes were characterized by elevated P concentrations, high phytoplankton biomass, reduced transparency, and strong oxygen supersaturation, indicating intensive algal production and high suitability for testing P-retention measures.
4. The pilot deployment strategy successfully targeted hydraulically and environmentally relevant locations, including inflow zones, runoff-affected areas, and open-water positions, and all selected prototype sites were exposed to P-rich conditions during the monitoring period.
5. The preliminary assessment indicated that mineral-based sorbent systems demonstrate feasibility for application in eutrophic freshwater bodies, but effectiveness remains uncertain and prototype selection should be adapted to local hydrology, P transport pathways, accessibility, and maintenance requirements.

6. Further work is needed to quantify P uptake by the sorbent material, compare the efficiency of the proposed prototype concepts under long-term field conditions, and evaluate the reuse potential of saturated sorbents as soil-improving material.

Acknowledgements

Acknowledgements: This research is supported by "LBTU Doctoral Support and Development Initiative" ERAF project No. 1.1.1.8/1/24/I/002 and Interreg Estonia-Latvia project NutriLoopWorks (EE-LV00163).

Author contributions

Conceptualization, D.G., R.O.-D. and L.G.; methodology, K.K., K.A. and M.U.; validation, K.A.; formal analysis, D.G., R.O.-D. and L.G.; investigation, D.G., K.K., D.G. and M.U.; data curation, K.K., M.U. and K.A.; writing – original draft preparation, D.G.; writing-review and editing, R.O.-D. and L.G.; project administration, R.O.-D.; supervision, K.A. All authors have read and agreed to the published version of the manuscript.

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