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Comparison of dredging, lanthanum-modified bentonite, aluminium-modified zeolite, and FeCl$_2$ in controlling internal nutrient loading

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ABSTRACT

The eutrophic Bouvigne pond (Breda, The Netherlands) regularly suffers from cyanobacterial blooms. To improve the water quality, the external nutrient loading and the nutrient release from the pond sediment have to be reduced. An enclosure experiment was performed in the pond between March 9 and July 29, 2020 to compare the efficiency of dredging, addition of the lanthanum-modified bentonite clay Phoslock® (LMB), the aluminum-modified zeolite Aqual-P™ (AMZ) and FeCl$_2$ to mitigate nutrient release from the sediment. The treatments improved water quality. Mean total phosphorus (TP) concentrations in water were 0.091, 0.058, 0.032, 0.031, and 0.030 mg P L^{-1} in controls, dredged, FeCl$_2$, LMB and AMZ treated enclosures, respectively. Mean filterable P (FP) concentrations were 0.056, 0.010, 0.009, 0.005, and 0.005 mg P L^{-1} in controls, dredged, FeCl$_2$, LMB and AMZ treatments, respectively. Total nitrogen (TN) and dissolved inorganic nitrogen (DIN) were similar among treatments; lanthanum was elevated in LMB treatments, Fe and Cl in FeCl$_2$ treatments, and Al and Cl in AMZ treatments. After 112 days, sediment was collected from each enclosure, and subsequent sequential P extraction revealed that the mobile P pool in the sediments had reduced by 71.4%, 60.2%, 38%, and 5.2% in dredged, AMZ, LMB, and FeCl$_2$ treatments compared to the controls. A sediment core incubation laboratory experiment done simultaneously with the enclosure experiment revealed that FP fluxes were positive in controls and cores from the dredged area, while negative in LMB, AMZ and FeCl$_2$ treated cores. Dissolved inorganic nitrogen (DIN) release rate in LMB treated cores was 3.6 times higher than in controls. Overall, the applied in-lake treatments improved water quality in the enclosures. Based on this study, from effectiveness, application, stakeholders engagement, costs and environmental safety, LMB treatment would be the preferred option to reduce the internal nutrient loading of the Bouvigne pond, but additional arguments also have to be considered when preparing a restoration.

1. Introduction

Eutrophication is the most prevalent water quality problem worldwide (Downing, 2014; OECD, 2017; Smith and Schindler, 2009). This nutrient pollution, caused primarily by excessive input of nitrogen (N) and phosphorus (P), often results in an overgrowth of harmful algae, toxic cyanobacteria and other aquatic plants. The negative consequences for aquatic ecosystem health, services and goods delivered by the aquatic ecosystems urged authorities to minimize eutrophication impacts. The European Union Water Framework Directive (WFD; 2000/60/EC) has been implemented to improve the ecological and chemical status of water bodies, and as such the WFD is important in combatting eutrophication. However, diffuse nutrient pollution from primarily agricultural sources confronts water authorities with a 'wicked

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problem' to minimize eutrophication impacts and to realize the WFD goals (Wiering et al., 2020). Likewise, in the Netherlands, nutrient pollution affected 65% of surface water bodies in which the most significant pressures come from diffuse agricultural sources (European-Union, 2019).

Diffuse nutrient pollution and legacy sources in catchments and lake sediments due to past nutrient loads are viewed as the main reason why water quality remains impaired, i.e. not recovering from eutrophication, even when point source nutrient pollution has been managed adequately. Therefore, the importance of in-lake measures is growing in which measures are aimed at reducing the impacts of eutrophication symptoms (Lürling and Mucci, 2020).

There are several in-lake measures that target the internal nutrient pool in the sediment. For instance, sediment dredging is a straightforward but relatively expensive measure to tackle internal nutrient release (Peterson, 1982; Welch and Cooke, 2005). Further, dredging may negatively impact benthic invertebrate communities, cause water column oxygen depletion, release pollutants, or result in the resuspension of sediments increasing turbidity (Knott et al., 2009; Manap and Voulvoulis, 2015; Peterson, 1982). To avoid such environmental impacts, geo-engineering techniques have been introduced that may effectively immobilize nutrients (primarily P) in the sediment (Douglas et al., 2016).

Metal salts based on aluminum (Al) find wide applications in mitigating eutrophication (Cooke et al., 2005). These salts are commonly added to the water where they may adsorb phosphate and/or form $Al(OH)_3$ flocs that entrap cyanobacterial cells. Iron (Fe) salts (Fe^{2+}/Fe^{3+}) are used far less in eutrophication control, despite their common use in wastewater treatment plants as efficient, simple, and cost-effective P-flocculants (Azam et al., 2019; Douglas et al., 2016). The main reason is the redox sensitivity of iron which may impair its phosphate adsorption capacity under low redox conditions that may occur in or near the sediment (Cooke et al., 2005). Nonetheless, several studies have reported that Fe dosing in natural systems controlled internal P-cycling via decreased sediment P-release rates (Azam et al., 2019; Bakker et al., 2016; Boers et al., 1992; Gächter and Müller, 2003; Immers et al., 2015; Kleeberg et al., 2013; Nriagu, 1972; Rothe et al., 2015; Smolders et al., 2001, 1995). In this study, we seek to elaborate on these findings and test the injection of ferrous iron ($FeCl_2$) directly into the sediment. The rationale for using ferrous iron is that under reductive, organic matter rich conditions, such as in sediment, the stable paramagnetic Fe-P mineral vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) may be formed (Rothe et al., 2014). Vivianite may potentially contribute to long-term P burial (Heinrich et al., 2022) but has also gained attention as a potential recovery phase for Fe and P.

As an alternative to liquid metal salts, solid-phase P-sorbents (SPS) have gained interest as they can effectively strip dissolved P from the water column while settling down on the sediment reducing sediment P release (Gibbs et al., 2011; Ross et al., 2008). These SPS are mainly modified clays and zeolites enriched with metals (aluminum, lanthanum (La), iron, or calcium (Ca)) (Gibbs and Hickey, 2018; Gibbs et al., 2011; Haghseresht et al., 2009; Zamparas et al., 2012). One of the most commonly used SPS in lake restoration is the lanthanum-modified bentonite (LMB), known commercially as Phoslock®, which has been used in hundreds of lakes and reservoirs worldwide (Copetti et al., 2016). The lanthanum in the clay matrix of LMB can precipitate with phosphate forming an extremely stable mineral, rhabdophane ($LaPO_4 \cdot nH_2O$). LMB is effective in permanently immobilizing phosphate over a wide pH and temperature range (Kang et al., 2022; Mucci et al., 2018). Another SPS, the aluminum-modified zeolite (AMZ), known commercially as Aqual-P™, may reduce both P and N release from sediments (Gibbs et al., 2011). Although promising and tested under laboratory conditions (Kang et al., 2022) rather little information is available on the performance of Aqual-P under semi-natural conditions.

To get more insight in the efficacy of different in-lake methods to counteract eutrophication by tackling sediment nutrient release, two experiments were conducted, one at field-scale in the form of an enclosure experiment and the other one at lab-scale in the form of a sediment core incubation experiment. The measures tested were 1) dredging, 2) application of LMB, 3) application of AMZ and 4) sediment injection with $FeCl_2$. It was hypothesized that dredging and AMZ addition would reduce both N and P release from sediment, and that LMB addition and $FeCl_2$ injection would reduce only P release from sediment. This was tested by incubating sediment cores for four weeks, taken from a dredged and a non-dredged area in the shallow eutrophic Bouvigne pond. The cores from the non-dredged area remained either untreated (controls) or were amended with AMZ, LMB, or $FeCl_2$. The effects of the treatments on water quality variables in the enclosures were monitored for 112 days to test the hypothesis that all sediment nutrient release abatement measures would improve water quality compared to untreated controls. The hypothesis that the different measures would result in a shift in various sediment P forms was tested by collecting sediment from each enclosure at the end of the experiment and determining the different P fractions via sequential P extraction. For the water manager of the experimental site, the results are used to determine the restoration measures for the eutrophic pond.

2. Methods

2.1. Enclosure site

The enclosure experiment was carried out from the 9th of March until the 29th of July 2020 in Bouvigne pond (51°33′ N, 4°46′ E), Breda, the Netherlands. This period was chosen to ensure the sediments had been treated before they normally start to release nutrients, which in temperate regions in northwestern Europe is around May (Søndergaard et al., 2013). The pond has an open water surface area of 1.43 ha and an average water depth of 1.08 m, ranging from 0.85 m to 1.4 m. The pond is surrounded by a park with gardens that are open to the public. Ongoing diffuse pollution via leaf litter, groundwater, run-off and precipitation was estimated at 0.2 g P m^{-2} year^{-1} (Haasler, 2020). The internal P load was estimated between 0.3 and 0.6 g P m^{-2} year^{-1}, the critical P load based on PCLake from clear water to a turbid state at 1.5 g P m^{-2} year^{-1}, the critical P load from turbid water to clear water at 0.6 g P m^{-2} year^{-1} (Haasler, 2020). Most of the submerged macrophytes present (primarily *Elodea nuttallii*) disappeared during 2013 and did not return on a large scale. Since a major reconstruction of the pond in 2010, cyanobacterial blooms (primarily *Microcystis* sp.) were recorded in 2013, 2014, 2016, 2018 and 2019 (data from Water Authority Brabantse Delta). In April 2020, in the pond itself chlorophyll-*a* (Chl *a*) concentrations were 29.1 μg L^{-1}, transparency was similar to the water depth of 90 cm, total suspended solid was 13.6 mg L^{-1}, pH was 7.65, conductivity was 328 μS cm^{-1}, oxygen saturation was 90%, total phosphorus (TP) 0.06 mg P L^{-1}, filterable P (FP) 12.4 μg P L^{-1}, total nitrogen (TN) 0.33 mg N L^{-1}, ammonium (AN) 0.02 mg N L^{-1}, NO$_2$-N and NO$_3$-N 0.01 mg N L^{-1}. During the course of the experiment the mean surface water temperature was 14.6 (± 0.6) °C in April, 20.0 (± 1.2) °C in May, 20.8 (± 2.4) °C in June and 18.7 (± 1.1) °C in July.

2.2. Enclosure set-up

Before setting up the enclosures, four sediment cores (59.6 cm long, 5.9 cm in diameter) of the upper sediment were collected with a UWITEC core sampler in the middle of Bouvigne pond on October 3rd 2019. These cores were used to determine the mobile P pool, which is important to define the dose of the P binders used in the experiment. The top 9 cm of each sediment core was sliced into 3 cm thick slices using a UWITEC core slicer and subjected to a sequential P extraction method (Psenner, 1988). In short, loosely bound P (H$_2$O-P), redox-sensitive P (Bicarbonate dithionite (BD-P)), organic P in microorganisms, organic P in detritus, P bound in humic compounds (NaOH—NRP, non-reactive

phosphorus), metal oxide-bound P (NaOH-SRP, soluble reactive phosphorus), P bound to carbonates and apatite-P (HCl-P) and residual organic and other refractory P after H_2SO_4 digestion (refractory-P (Ref-P)) were determined. The mobile P that can become available under anoxia or after organic matter degradation was determined by the sum of the H_2O-P, BD-P and the NaOH—NRP fractions (Hupfer et al., 1995). The mobile-P pool varied between 2.11 and 3.78 mg P g^{-1} DW for the first 9 cm of sediment and was on average 3.20 ± 0.47 mg P g^{-1} DW, in which average H_2O-P content was 0.52 ± 0.13 mg P g^{-1} DW, average BD-P was 1.84 ± 0.46 mg P g^{-1} DW, and average NaOH—NRP was 0.84 ± 0.67 mg P g^{-1} DW.

The enclosure experiment consisted of twenty Perspex cylinders (1.05 m in diameter, 1.3 m in height) that were placed in two rows 2–5 m offshore where water depth showed a gradient from ~ 0.8 m to ~1 m (Fig. S1). Using an excavator 1–2 h before placing the enclosures at the shallowest part, approximately 20 cm of upper soft and dark muddy sediment was removed down to the gray sandy substrate. Four enclosures were placed in this dredged area, pushed into the sediment to allow sediment water interaction, and were further labeled as dredging treatment. The other 16 enclosures were placed to the west of the dredged area to which four were treated with LMB (Phoslock®, Water Solutions Limited, Australia), four with AMZ (Aqual-P™, Blue Pacific Minerals, New Zealand), four with $FeCl_2$ (Iron(II) Chloride tetrahydrate, CAS-Nr.: 13,478–10–9, Honeywell) and four left untreated as control. The chemical amendments were assigned randomly to these enclosures (Fig. S1). Approximately 779 L of water was enclosed in each enclosure. The enclosures were placed on March 9th 2020 and allowed to stabilize for a few weeks. On April 8th 2020 (day 0), LMB, AMZ and Fe treatments were applied. The doses of LMB and AMZ were based on the water column TP concentration measured just before the enclosures were placed (~0.08 mg L^{-1}), the mobile P pool in the top 6 cm of the sediment, and a sorption capacity of 11.4 and 8.9 mg P g^{-1} product for LMB and AMZ, respectively (Mucci et al., 2018). A slurry of 563 g LMB or 725 g AMZ was made with water from the corresponding enclosures on site that was added to the water surface and allowed to settle on the sediment. The $FeCl_2$ dose was based on the mobile P in the upper 6 cm of the sediment. A 2 L $FeCl_2$ solution was prepared by dissolving 375 g $FeCl_2$ in HA/Ac buffered water with a pH = 4.2 to prevent quick Fe oxidation as a result of higher pH during the addition and subsequent dilution in each Fe(II) enclosure. The $FeCl_2$ solution was injected directly into the upper ~ 6 cm of the sediment at 10 different spots randomly chosen from a 16 squared grid that was placed on top of each enclosure.

Over four months, all enclosures and the pond were monitored on physicochemical water quality variables biweekly. The initial measurements were taken shortly before the treatment on the 8th of April 2020 (day 0), the last sampling day was on the 29th of July 2020 (day 112). Secchi-disk depth (SD), pH, electrical conductivity (EC), dissolved oxygen concentration and saturation (DO), and temperature (Temp) were measured in situ in the middle of the water column in each enclosure. pH, EC and Temp were measured using a WTW pH/Cond 3320 multimeter. DO was measured using an OxyGuard Handy Polaris 2. A two L whole water column integrated water sample was taken at the center of each enclosure using a sampling tube. Water samples were transported to the laboratory for further analysis of water quality variables. Finally, SD was measured by a 30 cm diameter black/white Secchi-disk.

In the laboratory, turbidity was measured in unfiltered water samples with a Hach 2100 turbidity meter (Hach, Tiel, The Netherlands). The Chl *a* concentrations were determined with a PHYTO-PAM phytoplankton analyzer (Heinz Walz GmbH, Effeltrich, Germany). Total suspended solids concentrations (TSS) were determined after filtration of a known volume of unfiltered water over Whatman GF/C glass fiber filters (Whatman GF/C, VWR International B.V., Amsterdam, The Netherlands) that had been dried at 105 °C. Total nitrogen (TN) and total phosphorus (TP) concentrations were measured using a Skalar SAN+ segmented flow analyzer following Dutch standard protocols

(NNI, 1986; 1990). Filtered (Whatman GF/C) water samples were stored in 50 mL PE bottles at −20 °C upon further analysis.

In filtered water samples, chloride (Cl) concentrations were measured with a Thermo Scientific Orion 720Aplus pH/ISE Meter equipped with a Cl^- ion specific electrode (Thermo Fisher Scientific, Waltham, MA USA). Dissolved inorganic nitrogen (DIN) concentrations consisting of NH_4^+-N, NO_2^--N and NO_3^--N, and filterable phosphorus (FP) were measured using a Skalar SAN$^+$ segmented flow analyzer following the Dutch standards NEN 6663 (NNI, 1986) and NEN-EN-ISO 13,395 (NEN, 1997). In samples taken at days 0, 28, 56 and 84 filterable metals (Al, Fe, Mn, and S) were determined by ICP-OES (Thermo Electron Corporation, Franklin, MA, USA) and La was measured by ICP-MS (Thermo Element 2; Thermo Fisher Scientific). Additionally, sediment from each enclosure and from the pond was collected using a core sampler on July 29th 2020. These sediment cores were sliced into 3 cm slices (0–3 cm, 3–6 cm and 6–9 cm) and each slice was subjected to a sequential P-fractionation analysis (Psenner, 1988). Sediment from two Fe(II)-treated enclosures and one control enclosure was analyzed for vivianite by Mössbauer spectroscopy. The ^{57}Fe Mössbauer absorption spectra were collected at 300 K with a conventional constant-acceleration spectrometer using a ^{57}Co (Rh) source. The velocity calibration was carried out using an α-Fe foil while the fitting of the spectra was performed using the software Mosswin 4.0. The standard vivianite samples are based on two different Fe ion donors: Mohr's salt (S1 Viv.) and $FeCl_2$ (S4 Viv.).

2.3. Core incubation set-up

Twenty sediment cores were taken from the pond on April 8th 2020. Four cores were taken at the dredged area in the pond, whereas the rest of the cores were taken close to the placement of the non-dredged enclosures. In the laboratory, four cores were dosed with LMB, four others with AMZ, four cores were treated with $FeCl_2$ injected in the sediment, while four cores remained untreated (controls) as were the four cores from the dredged area. To test the efficiency of four materials on sediment nutrients release under anoxic conditions, before applying materials to the cores, the overstanding water in each core was bubbled gently with N_2 until oxygen saturation was less than 1%. Subsequently, a water sample was taken from each core (day 0). The doses of LMB, AMZ and $FeCl_2$ were the same as in the enclosures (Section 2.2), 1.827 g dry LMB and 2.354 g dry AMZ were mixed into a slurry with overlying water, respectively, while $FeCl_2$ was injected at one point into the sediment as 20 mL of HA/Ac buffered 0.48 M $FeCl_2$-solution. To prohibit oxygen production by photosynthesis, all cores were incubated at 7 °C in the dark from the 8th of April (day 0) to 6th of May (day 28).

Initially (day 0), and subsequently once every week pH, DO, and EC were measured, and water samples were collected from each core and analyzed on NH_4^+-N, NO_2^--N+NO_3^--N and FP concentrations as well as on filterable metal concentrations (Al, Fe, Mn and La) and S using the same methods as given in Section 2.2. Nutrient fluxes (FP in mg P m^{-2} d^{-1} and DIN in mg N m^{-2} d^{-1}) were calculated based on the differences in FP and DIN concentrations between day 0 and day 28.

2.4. Statistics

Data visualization and statistical analysis were performed using SigmaPlot 14, OriginPro 2021 software (Originlab, Northampton, MA, USA) and IBM SPSS 19.0 (IBM, New York, USA). The time points data of the water quality variables were analyzed by repeated-measures analysis of variance (rmANOVA) and simple effect analysis. Homogeneity of variance for the obtained data was tested and significant levels were reported at $p < 0.05$ (*) and $p < 0.01$ (**). For further intuitive understanding of the linkages between the materials applications and environmental variables, a structural equation model (SEM) was built to develop prediction equations and path analyses and to analyze multivariate hypotheses using SPSS AMOS 26. The experimental data from

control were inputted to compare with the data from the other four treatments. The model parameters, such as Chi-square (χ^2), χ^2/df, root mean square residual (RMR), and goodness fit index (GFI) were used to determine the fit of the model. In this study, the parameters of four SEM models were: (A) dredged: $\chi^2 = 3.13$, χ^2/df = 1.04, RMR <0.0001, GFI = 0.98; B) LMB: $\chi^2 = 5.03$, χ^2/df = 1.68, $p = 0.17$, RMR= 0.001, GFI = 0.97; C) AMZ: $\chi^2 = 2.4$, χ^2/df = 0.8, $p = 0.49$, RMR = 0.001, GFI = 0.99; D) FeCl$_2$: $\chi^2 = 3.23$, df = 3, χ^2/df = 1.08, $p = 0.38$, RMR = 0.001, GFI = 0.98. All these parameters indicated our SEM model was fitting well. In the enclosure experiment, changes in treatments and water quality variables through time were assessed using principal response curves (PRC) (Van den Brink and Braak, 1999). Here, the pond itself and control were taken as the reference, respectively. More specifically, we used the pond itself as one reference and the control group as another reference. All data (except pH) were log-transformed before analysis. The multivariate analysis was performed using the CANOCO software package (version 4.5, Wageningen University, Wageningen, The Netherlands) (Ter Braak and Smilauer, 2002).

3. Results

3.1. Physicochemical water quality variables

Water temperature showed similar courses in the enclosures and in the pond ranging from on average 15.7 °C in spring to 20.2 °C in summer (Fig. 1A). Differences in DO concentration (Fig. 1B) and saturation (Fig. 1C) were more pronounced; DO was also higher in the enclosures than in the pond (Figs. 1B, 1C). The highest values were recorded in June (Figs. 1B, 1C). The rmANOVA's yielded strong evidence that DO concentration and saturation were different between treatments (Table S1), which was supported by the post-hoc comparison (Table S2). In general, DO concentration and saturation were highest in controls and AMZ treatments, and lowest in dredged and FeCl$_2$ treated enclosures (Figs. 1B, 1C). Also, pH differed over time and between treatments and it was a little higher in enclosures than in the pond (Fig. 1D). Compared to the control, the pH in LMB, and AMZ treated enclosures was significantly higher, whereas pH in FeCl$_2$ treated enclosures was lower (Table S1, S2), albeit those differences became most pronounced during the second part of the experiment (Fig. 1D). Likewise, EC differed between treatments (Fig. 1E), where EC in control and LMB treatments
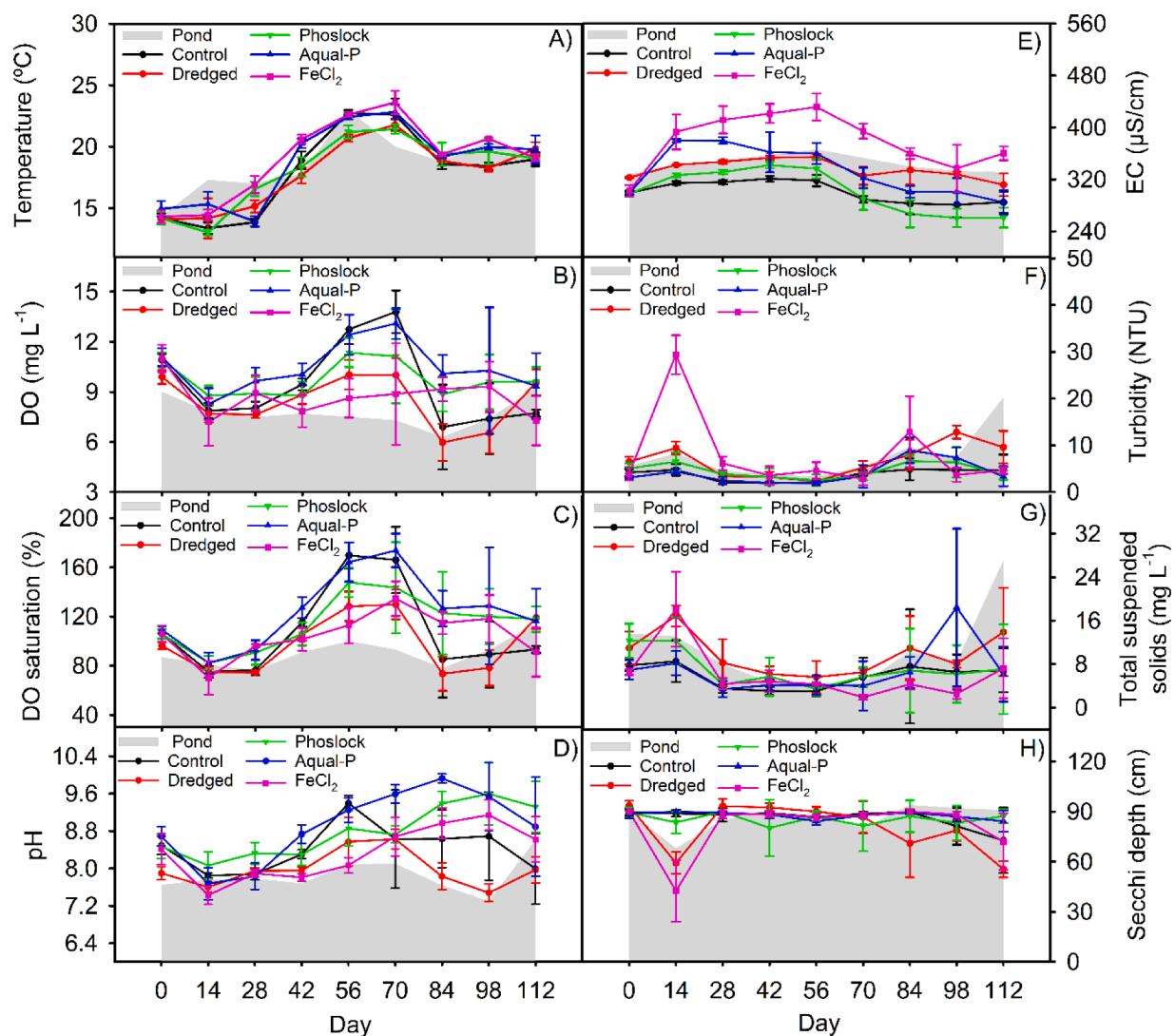

Fig. 1. Course of the environmental variables in non-treated (Control), LMB treated (Phoslock), AMZ treated (Aqual-P), FeCl$_2$ treated (FeCl$_2$), and dredged (Dredged) enclosures during the 112 d experimental period in 2020. A) Temperature (°C); B) dissolved oxygen concentration (DO, mg L^{-1}); C) dissolved oxygen saturation (DO, %); D) pH; E) electric conductivity (EC, µS cm^{-1}); F) Turbidity (NTU); G) Total suspended solids concentration (TSS, mg L^{-1}); H) Secchi disk depth (SD, cm). The gray area represents the measurements done in the pond. Error bars indicate one standard deviation ($n = 4$).

were similar, EC was significantly elevated in dredged and AMZ treatments, and the highest in FeCl₂ treated enclosures (Fig. 1E; Table S1, S2). EC in the latter was also significantly higher than in the pond (Fig. 1E, Table S1). Turbidity was significantly elevated in the first weeks after FeCl₂ addition, but returned to similar levels as in the other enclosures which were comparable to turbidity in the pond (Fig. 1F, Table S1, S2). The course of TSS concentrations was similar in all treatments and comparable to the pond (Fig. 1G). TSS concentrations differed in time, but not among treatments (Table S1, S2). Secchi-depth (SD) showed the opposite pattern to turbidity, the visibility of the water column decreased initially after the addition of LMB, AMZ and FeCl₂ (Fig. 1H). The FeCl₂ treated enclosures had initially the lowest SD, after which the SD of the water column was recovered, SD's were similar to SD in the pond (Fig. 1H).

3.2. Nutrients and chlorophyll-a

TP concentrations showed an increase towards the end of the experiment, particularly in the controls (Fig. 2A). TP concentrations were significantly different between treatments (Table S1) and the LMB, AMZ and FeCl₂ treated enclosures differed significantly from the control (Table S1). Over the entire experimental period, TP concentrations were on average 0.091 mg P L⁻¹ in controls, 0.058 mg P L⁻¹ in dredged enclosures, and 0.032, 0.031, 0.030 mg P L⁻¹ in FeCl₂, LMB and AMZ treatments, respectively (Fig. 2A). Also, FP concentrations were significantly different between treatments (Table S1), and the highest in the controls (Table S2; Fig. 2B). Mean FP concentrations were 0.056, 0.010, 0.009, 0.005, 0.005 mg P L⁻¹ in control, dredged, FeCl₂, AMZ and LMB treated enclosures, respectively. The course of TN concentrations was comparable in all treatments (Fig. 2C). Although a bit higher in dredged enclosures during the first part of the experiment (before June 17th), TN

concentrations were not different between treatments (Table S1 and S2). Likewise, DIN concentrations were similar among treatments (Fig 2D; Table S1 and S2).

The course of total chlorophyll-*a* (Chl *a*) concentrations differed per treatment and over time (Table S1; Fig. 2E). Chl *a* concentrations in the pond and dredged enclosures showed a comparable pattern with lowest values in the middle of the experiment and a stark increase towards the end (Fig. 2E). Median Chl *a* concentrations were 22.6 µg L⁻¹ in the pond, 21.8 µg L⁻¹ in the dredged enclosures, 11.6 µg L⁻¹ in LMB treatments, 11.1 µg L⁻¹ in controls, 8.6 µg L⁻¹ in FeCl₂ treatments and 8.4 µg L⁻¹ in the AMZ treated enclosures (Fig. 2E).

Moreover, the information about filterable metals, S and Cl⁻ concentrations, and macrophytes have been shown in supplementary materials (Fig. S2 and Table S3).

3.3. Relationship between water quality and materials applications

In the pond itself, TP had a strong correlation with turbidity and TSS, whereas TN was negatively correlated with them (Fig. 3A). In controls, TP was positively correlated with FP (Fig. 3B). In dredged enclosures, TP was correlated with FP, whereas DIN had a strongly positive correlation with AN (Fig. 3C). In LMB treated enclosures, Cl⁻ concentrations had a negative relationship with TSS, Chl *a*, TP, while Fe concentrations were positively correlated among N-nutrients (Fig. 3D). In AMZ treatments, TSS and TN were positively correlated, as were Fe and pH, DIN and DO (Fig. 3E). In FeCl₂ treatments, Chl *a* was positively correlated with TSS and TN with FP (Fig. 3E). When combining all data, the PRC curves indicated a clear enclosure effect when the pond was used as reference (Fig. S3A), while there was not a clear pattern when the control was used as reference (Fig. S3B).

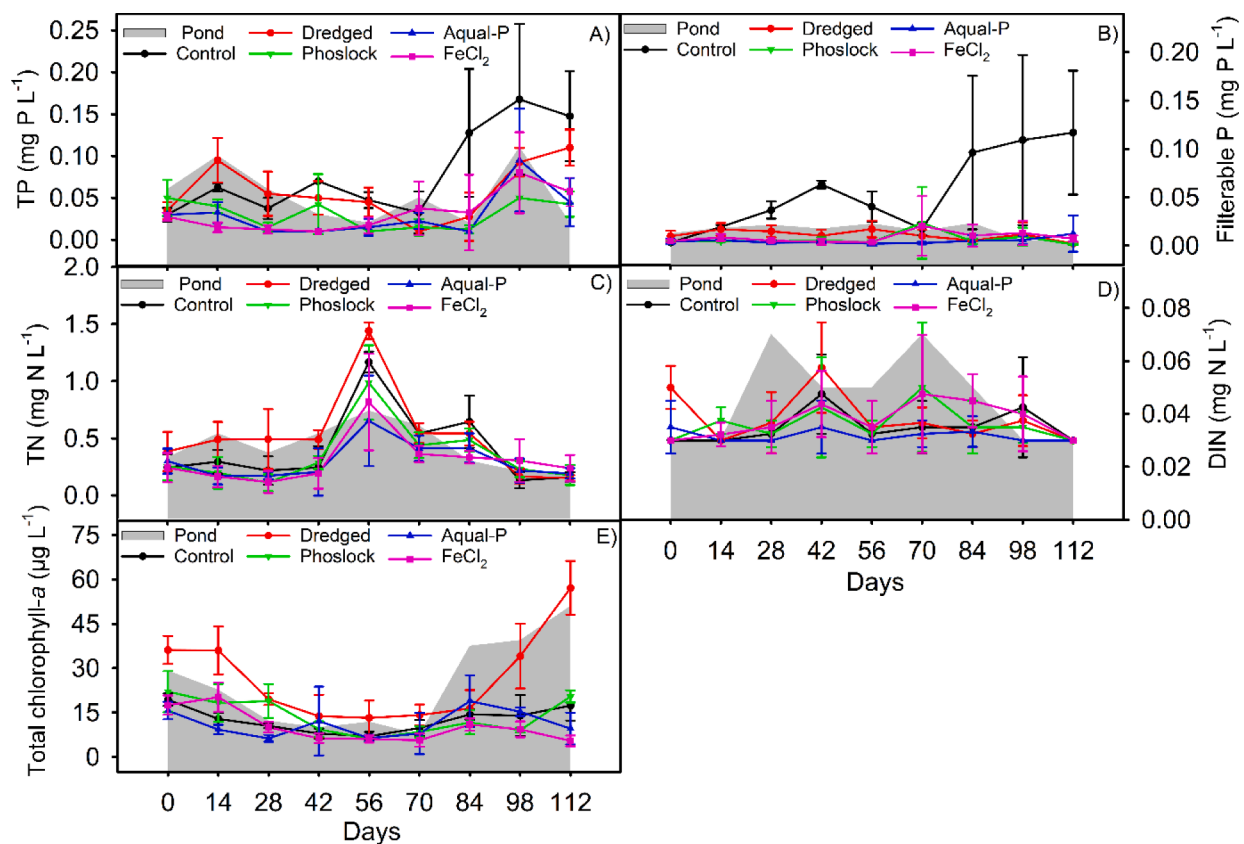SEM analysis was performed to outline the direct or indirect

Fig. 2. Total and filterable nutrients (TP, FP, TN and DIN) and total chlorophyll-*a* in non-treated (Control), LMB treated (Phoslock), AMZ treated (Aqual-P), FeCl₂ treated (FeCl₂), and dredged (Dredged) enclosures during the 112 d experimental period in 2020. A) TP (mg P L⁻¹); B) FP (mg P L⁻¹); C) TN (mg N L⁻¹); D) DIN (mg N L⁻¹); E) total chlorophyll-*a* (µg L⁻¹). The gray area represents the measurements done in the pond. Error bars indicate one standard deviation (*n* = 4).
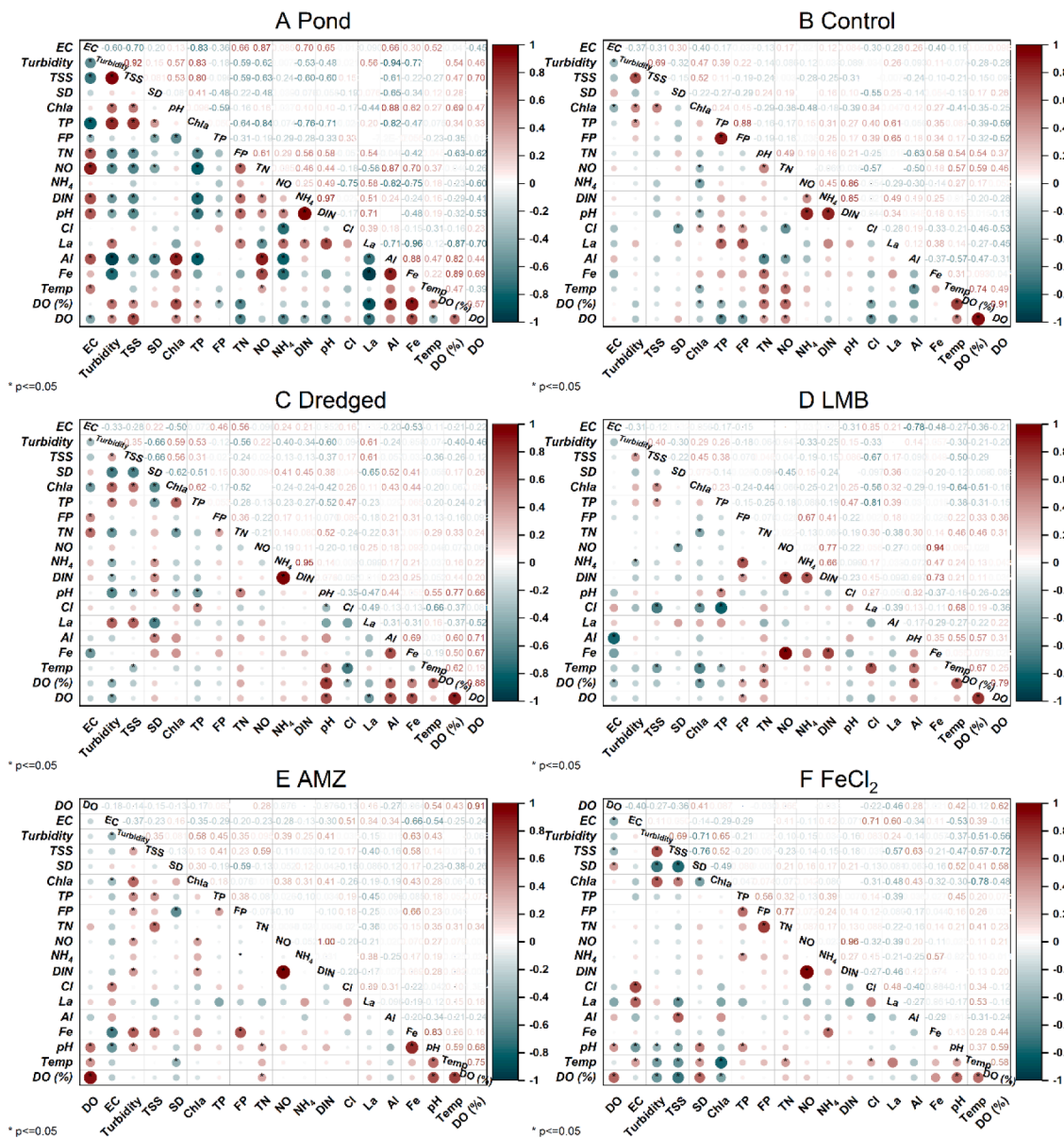
Fig. 3. Heatmap of correlation of physicochemical parameters of water during the 112 days of the experiment. A) Pond; B) Control; C) Dredged; D) Phoslock; E) Aqual-P; F) FeCl₂. The Pearson correlation coefficient varied from −1 to 1.

influence of the addition of materials on selected variables (turbidity, TSS, and Chl a) and on nutrients (TP, TN, and DIN) during the 112 days enclosure experiment. Selected variables were derived from the confirmatory factor analysis (CFA) and exploration factor analysis (EFA) in SPSS, and included turbidity, TSS and Chl a. Dredging had a strong positive impact on selected variables (turbidity, TSS, Chl a) and explained 29% of the variations in turbidity, TSS, and Chl a. TP was positively impacted by selected variables (turbidity, TSS, Chl a) and negatively affected by dredging, they together explained 19% of the variations in TP (Fig. 4A). TN was negatively affected by the selected variables (turbidity, TSS, Chl a) and positively affected by dredging, they together explained 18% of the variations in TN (Fig. 4A). TP was strong negatively affected by LMB, positively affected by the variables (turbidity, TSS, Chl a), LMB and selected variables (turbidity, TSS, Chl a) together explained 28% of variance in TP (Fig. 4B). AMZ had a significant negative relationship with TP, while selected variables (turbidity, TSS, Chl a) had strong negative relationship with TN (Fig. 4C). Selected variables (turbidity, TSS, Chl a) and FeCl₂ also had the positive and negative pathways on TP, respectively, both of them explained 11% of

variance in TP (Fig. 4D).

3.4. Phosphorus fractions in sediment

At the end of the experiment, differences in the P fractions at three different sediment depths (0–3, 3–6 and 6–9 cm) were observed (Fig. 5). In the 0–3 cm layer, sediment TP was highest in the pond (Fig. 5). The sediment TP content in the first 3 cm of the different enclosures were significantly different ($F_{4,15} = 15.5$; $p < 0.001$). The 0–3 cm sediment TP content in control was the highest (383.78 ± 84.62 mg kg^{-1}) and in dredged it was the lowest (98.96 ± 26 mg kg^{-1}). TP content did not show a difference between AMZ and FeCl₂ (Tukey Test, $p = 0.997$). The sediment TP in the sediment depth of 3 to 6 cm among enclosures was significantly different ($F_{4, 15} = 15.5$; $p < 0.001$). Sediment TP content in FeCl₂ (190.18 ± 16.38 mg kg^{-1}) in the sediment depth of 3 to 6 cm was higher than in other enclosures ($p < 0.001$). The sediment TP concentration in the sediment depth of 6–9 cm did not indicate a difference among the treatments ($F_{4, 15} = 15.5$; $p = 0.373$). According to statistical output, mobile-P concentrations differed significantly among enclosure
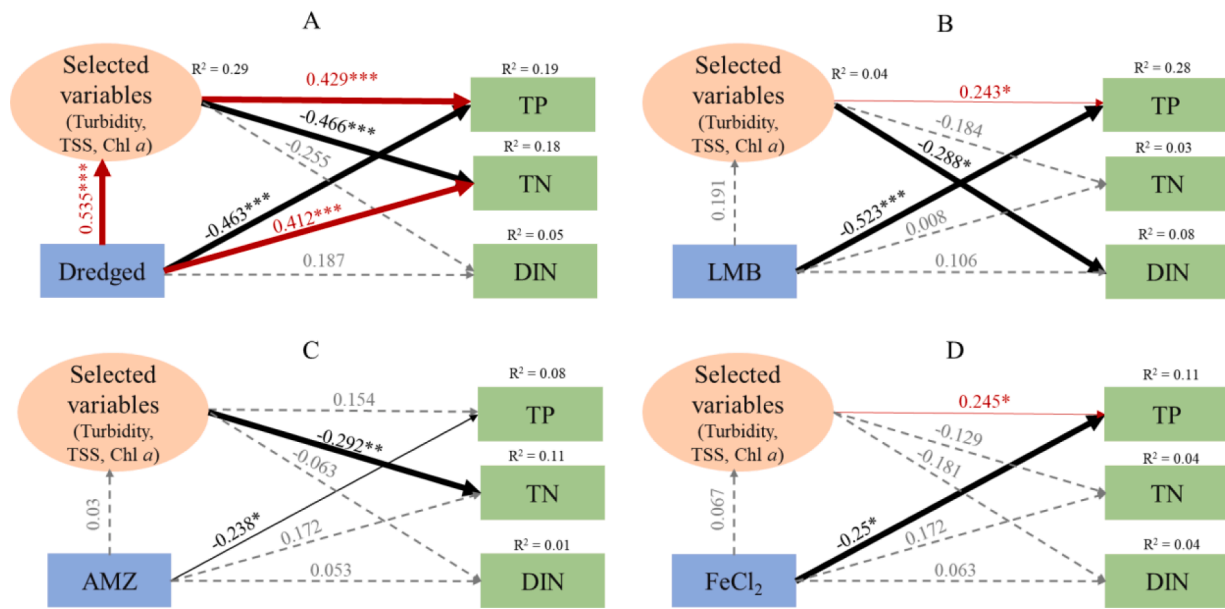
Fig. 4. Structural equation model exploring the relationships among materials, selected variables (turbidity, TSS, Chl a) and water nutrients (TP, TN, DIN). (A) dredged: $\chi^2 = 3.13$, df = 3, $\chi^2/df = 1.04$, $p = 0.37$, GFI = 0.98; B) LMB: $\chi^2 = 5.03$, df = 3, $\chi^2/df = 1.68$, $p = 0.17$, GFI = 0.97; C) AMZ: $\chi^2 = 2.4$, df = 3, $\chi^2/df = 0.8$, $p = 0.49$, GFI = 0.99; D) FeCl$_2$: $\chi^2 = 3.23$, df = 3, $\chi^2/df = 1.08$, $p = 0.38$, GFI = 0.98. Solid and dashed arrows indicate significant ($p < 0.05$) and nonsignificant ($p > 0.05$) relationships, respectively; The black and red lines represent positive and negative pathways, respectively; The arrow thickness is proportional to the strength of the relationship.
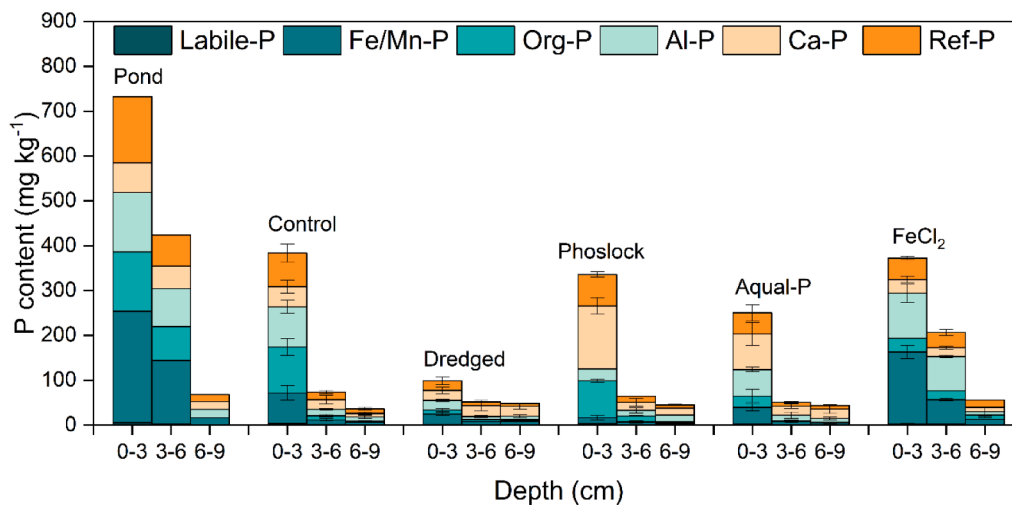

Fig. 5. Characteristics of sediments P fractions (0–3 cm, 3–6 cm and 6–9 cm) in the pond and each enclosure at the end of the experiment. Error bars indicate one standard deviation ($n = 4$).

in all the sediment depth analyzed, 0–3 cm ($F_{4, 15} = 27.4$; $p < 0.001$), 3–6 cm ($F_{4, 15} = 200.5$; $p < 0.001$), 6–9 cm ($F_{4, 15} = 13.3$; $p < 0.001$). In comparison with controls, the content of mobile P in the first 9 cm of sediment was reduced by 71.4%, 60.2%, 38% and 5.2% in dredged, AMZ and LMB and FeCl$_2$, respectively. In the first sediment layer (0–3 cm), mobile P fractions such as organic-P and Fe/Mn-P were dominating the overall sediment P pool in controls and FeCl$_2$, contributing on average 26.6% and 50% to the sediment TP, respectively (Fig. 5). In LMB and AMZ groups, immobile-P fractions comprised most of the sediment P in the 0–3 cm layer, where for instance the Ca-P fraction (a fraction that also includes La-P) contributed on average 41.7% to the sediment TP in LMB treated sediment and 31.7% to the sediment TP in AMZ treatments (Fig. 5).

3.5. Mössbauer spectroscopy

The obtained Mössbauer spectra (Table S4; Fig. S4) did not detect vivianite in response to the FeCl$_2$-injection or in the control sediment (Fig. S4). None of the Mössbauer spectra of the sediment samples present the characteristic doublets of vivianite (Doublet 1: Isomer Shift (IS) = 1.2 ± 0.1 mm s^{-1}, Quadrupole Splitting (QS) = 2.4 ± 0.1 mm s^{-1} and Doublet 2: IS = 1.25 ± 0.1 mm s^{-1}, QS = 3.0 ± 0.1 mm/s (McCammon and Burns, 1980) indicating the absence of this mineral in our samples. Moreover, Fe^{3+} accounts for 65–90% of the total iron (Table S4).

3.6. Sediment core incubation

The pH had increased by 0.5 unit in all treatments on day 7 and then remained stable within pH 7.0 - 7.4 during the subsequent experiment

duration (Fig. S5). Addition of LMB, AMZ or FeCl$_2$ significantly increased EC (Table S5), EC showed the strongest increase in AMZ treatments (Fig. S5). All sediment cores had higher initial DO and DO saturation, from 4.33 ($\pm$3.15) mg L^{-1} in dredged to 7.63 ($\pm$1.23) mg L^{-1} in AMZ and from 39 ($\pm$27.8)% in dredged to 69.5 ($\pm$12.4)% in AMZ. Afterwards, DO concentration decreased due to the N$_2$ bubbling at each sample timepoint (Fig. S5). In the untreated cores (controls) and cores from the dredged area, FP concentrations increased over time. In contrast, in the LMB, AMZ or FeCl$_2$ treated cores, FP reduced to below detection limits (4 µg P L^{-1}) and remained low throughout the experiment (Fig. S5). A rmANOVA revealed a statistically significant difference in FP between the treatments over time (F$_{16, 60}$ = 24.142; $p <$ 0.001). FP concentrations after LMB, AMZ and FeCl$_2$ treatment reduced strongly (Fig. S5). A post-hoc comparison based on FP concentrations revealed two homogeneous groups: 1) controls and dredged; 2) LMB, AMZ and FeCl$_2$ treated cores. The rmANOVAs showed statistically significant differences in NH$_4^+$-N (AN), and NO$_2^-$-N + NO$_3^-$-N concentrations (Table S5). In the end of the experiment, NO$_2^-$-N + NO$_3^-$-N concentrations in all treatments gradually decreased (Fig. S5). AN concentrations gradually increased in control, dredged and LMB treated cores, which was the strongest in the LMB treatments. In contrast, AN concentrations in AMZ and FeCl$_2$ treated cores remained similar during the experiment, but overall AN concentrations in the AMZ treatments were the lowest (Fig. S5). Positive FP fluxes were found in controls and dredged cores, while negative fluxes were measured in LMB, AMZ and FeCl$_2$ treated cores (Fig. 6). DIN release rate in LMB was much higher than in controls, while in AMZ and FeCl$_2$ treated cores the DIN release was inhibited (Fig. 6).

LMB application increased filterable La content within the first 7 days, after that it gradually reduced over time (F$_{4.954, 18.576}$ = 15.713; p = 0.003) (Fig. S5). Based on the calculation, the average filterable La flux during 28 days yielded 0.26 mg La m^{-2} d^{-1}. Filterable Al, Fe, and Mn did not differ among treatments (Table S5). Filterable S concentration seemed to be slightly higher in the cores treated with Aqual-P: A Greenhouse-Geisser corrected rmANOVA followed by a Tukey post hoc test revealed a significant difference between controls and Aqual-P treatments over time (F$_{10.727, 40.228}$ = 2.129; p = 0.003) (Fig. S5).

4. Discussion

This enclosure study tested the hypothesis that the four sediment nutrient release abatement measures (dredging, LMB addition, AMZ addition, and Fe(II) injection in the sediment) would improve water quality compared to untreated controls. Clear differences were observed between treatments and controls where for instance compared to controls water column TP was reduced by $\sim$ 36% in the dredged enclosure and $\sim$ 66% in LMB, AMZ and FeCl$_2$ treated ones.

Nutrient concentrations remained higher in the dredged enclosure than in other treatments and chlorophyll-*a* concentrations were equal to the pond and even higher than in control enclosures. Variable effects of dredging in lake restoration have been attributed to limited and insufficient sediment removal, no external load control (Peterson, 1982), or uncovering of organic matter and nutrient-rich layers (Geurts et al., 2010). Although the excavator used removed $\sim$20 cm of sediment from a site larger than where enclosures were placed and the presence of some remaining sediment cannot be excluded, the course of the phosphate concentrations in each enclosure does not point towards such an effect as a pattern comparable to controls would have occurred (Lürling and Faassen, 2012). The external load was assumed to be equal for all enclosures, while the fresh accumulated nutrient rich layer seems also not to have played a role as the sedimentary P content in the dredged enclosures was strongly reduced compared to non-dredged enclosures (*see* Fig. 5). Despite this strongly reduced P content, TP in the water column was not that strongly reduced as in other treatments and the sediment core incubation revealed the P flux was not reduced at all (*see* Fig. 6), which is opposing findings of others (e.g. (Oldenborg and Steinman, 2019; Yin et al., 2021; Yu et al., 2017)). Possibly a rapid mobilization of releasable P combined with the relatively short duration of the experiment (4 weeks) resulted in a similar P flux as in the controls. The N flux was, however, sharply reduced in line with the removal of nutrient-rich sediment.

In other enclosure studies, dredging strongly improved water quality compared to controls, reduced phytoplankton biomass (Lürling and Faassen, 2012; Zhan et al., 2022) and increased transparency (Lürling et al., 2017; Zhan et al., 2022). The somewhat deviating results in this study may be a result of indirect effects caused by dredging. A short-term response to sediment disturbance due to denitrification and N$_2$O production were stimulated shortly after dredging (Salk et al., 2018). In the dredged enclosures, macrophytes were either absent or present in lower abundance compared to the other enclosures and potentially a large part of the seed bank got removed allowing phytoplankton to take up nutrients. Inasmuch as clear water with submerged macrophytes is the desired state in shallow waters (Scheffer et al., 1993), in the case when a large part of the seed bank has been removed, the introduction of macrophytes after dredging may be considered to improve water quality (Waajen et al., 2016), even if it takes time for these communities to re-establish (Hassett and Steinman. 2022).

While dredging only partly met the expectations of improved water quality, the results of LMB, AMZ and FeCl$_2$ treatments were more in line with expectations. The sediment core incubation experiment revealed a

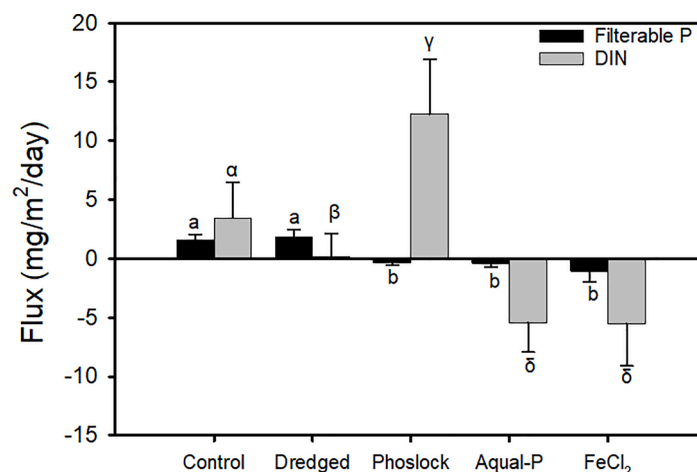**Fig. 6.** Flux of the Filterable P and DIN of Control, Dredged, Phoslock, Aqual-P and FeCl$_2$ during 28 days (mg m^{-2} d^{-1}). Error bars indicate one standard deviation (*n* = 4). Different symbols per column (a, b; α, β, γ, δ) indicate groups that are significantly different.

negative P flux for LMB, AMZ and FeCl$_2$ treated cores, which implies P was effectively removed from the water and kept in the sediment. These findings are in line with previous studies (e.g. de Magalhães et al., 2019; Gibbs et al., 2011; Zeller and Alperin, 2021; Zhan et al., 2021). The active ingredient lanthanum in LMB precipitates with phosphate, forming a stable mineral that is not affected by natural pH and redox fluctuations, unlike other aluminum (Al) or iron (Fe)-based phosphate binders (Copetti et al., 2016; Dithmer et al., 2016). SEM modeling indicated a negative impact of LMB on TP and the sediment core experiment showed a negative P flux. Moreover, the HCl extractable P pool was significantly larger in the LMB amended sediment, which is also the fraction in which most of the La-P is found (Reitzel et al., 2013; Yin et al., 2021).

The sediment core experiment revealed a strongly increased DIN flux in LMB treated cores, which was attributed to NH$_4^+$-N. Similar observations have been made in other studies, where adding LMB increased NH$_4^+$-N concentrations (e.g. Reitzel et al., 2013; Zeller and Alperin, 2021), which might be caused by NH$_4^+$-N leaching from the product (Van Oosterhout and Lürling, 2013) and concentrated in a rather small volume of overstanding water. LMB did not change the bacterial community composition or *Proteobacteria* responsible for N-cycling (Yin et al., 2021). In the enclosures, no increase of DIN or TN in LMB treatments was observed, which is in line with other enclosure studies (Lürling and Faassen, 2012; Zhan et al., 2022). Hence, no impact from the leached NH$_4^+$-N is expected. Filterable lanthanum concentrations were elevated in the LMB treated enclosures and showed a tendency to decline gradually over time, which is in line with other studies of whole lake LMB treatments (Spears et al., 2013; van Oosterhout et al., 2020). LMB has been tested extensively and no harmful effects on aquatic life have been found (Copetti et al., 2016; van Oosterhout et al., 2020).

AMZ, formerly known as Z2G1, was highly effective in hindering the P release in sediment cores collected in Lake Okaro, New Zealand (Gibbs and Özkundakci, 2011), and in Lake Rotorua, New Zealand (Gibbs et al., 2011). AMZ is designed as a sediment capping agent and besides the modification with poly-aluminum chloride, which gives it its P sorption capacity, the zeolite carrier has a natural affinity for NH$_4^+$-N (Gibbs and Hickey, 2018). The sediment core experiment revealed a negative DIN flux indicating the capacity of AMZ to bring DIN to the sediment and prevent release. A reduced NH4$^+$-N release was also observed in sediment cores from Lake Okaro (Gibbs et al., 2011) and in another study, AMZ was estimated to absorb ~4.5 mg NH$_4^+$-N g^{-1} AMZ (Gibbs and Özkundakci, 2011). AMZ resulted in elevated Al and Cl$^-$ concentrations, but these were within an acceptable range and AMZ is not expected to cause toxic effects in aquatic biota (Gibbs and Hickey, 2018).

In contrast to LMB, experiments with FeCl$_2$ are relatively rare. Smolders et al., 2001 found that the addition of FeCl$_2$ strongly decreased the phosphate concentrations in sediment pore water. Likewise, in enclosures, FeCl$_2$ treatment caused very low porewater sulfide and phosphate concentrations, low water column phosphate and low turbidity (Smolders et al., 1995). Phosphate was likely precipitated with oxidized Fe(III) formed in the enclosures, a similar explanation was given for the effectiveness of FeSO$_4$ addition to the inlet water of De Grote Rug reservoir, The Netherlands (Oskam, 1983). Probably the same occurred in our FeCl$_2$ treated enclosures. Despite FeCl$_2$ being injected in the sediment, it diffused out of the sediment causing a reddish turbid water after two weeks and gradually increased filterable Fe concentrations and caused elevated Cl$^-$ concentrations in the overstanding enclosure water.

The formation of ferric iron oxi/hydroxides may explain the low P concentrations in the enclosures. In the sediment core experiment, cores were made anoxic prior to injecting FeCl$_2$ in the sediment and the low oxygen concentrations during the experiment likely prevented oxidation of introduced iron. Nonetheless, P flux was negative implying P was moved from the overstanding water into the sediment. The main reason for injecting an overdose of FeCl$_2$ directly in the sediment was to scavenge sulfide in porewater and therewith facilitate the formation of solid-phase reduced iron-phosphate compounds, such as reduced-iron-oxi/

hydroxide-phosphate complexes and vivianite (Roden and Edmonds, 1997). Vivianite precipitation is favored by high concentrations of ferrous iron in pore water (Rothe et al., 2014). In addition, iron-sulfides may form a protective layer around ferric iron-oxi/hydroxide particles (Davison and Dickson, 1984), but the abundance of ferrous iron may also have favored nitrate-dependent Fe^{2+} oxidation (Weber et al., 2006) that may subsequently have led to production of ferric iron (hydr)oxides such as goethite (Senko et al., 2005) which may adsorb phosphate (Parfitt and Atkinson, 1976) and subsequently settle down to the sediment. The increased reductive labile P pool in FeCl$_2$ amended sediments may point to this process, while the larger pool of NaOH extractable SRP (Al-P) may point to Fe(II)-phosphate minerals such as vivianite (Rothe et al., 2015). Mössbauer spectroscopy did not yield evidence for presence of (detectable amounts of) vivianite. Mössbauer spectroscopy indicated the vast majority of iron being present as Fe^{3+} and thus precipitation of diverse Fe-oxides (Fe(III)(oxyhydr)oxides) is favored. That vivianite was not detected in our study could therefore be due to insufficient Fe^{2+}-availability for authigenic vivianite formation. In addition, the mineral's purity and crystallinity may have played a role as the vivianite crystal structure is highly sensitive to oxidation. An advanced oxidation status makes vivianite amorphous, consequently, hampering its detection and analysis (Grodzicki and Amthauer, 2000; McCammon and Burns, 1980; Rouzies and Millet, 1993; Wilfert et al., 2016). We did, however, not measure the oxygen state in sediment. The direct mineral detection via Mössbauer may also have been not sensitive enough for the sediment samples analysed. Mössbauer spectroscopy has a precision of 3%, yet Fe-P mineral phases only make up a very small fraction of the total sediment matrix. In the sediment of the pond the Fe-concentration was < 1% of the DW (6.5 mg g DW^{-1}).

Consequently, adjustments to improve the sensitivity of the detection methods could be considered. To improve vivianite detection via Mössbauer in sediments, Rothe et al., 2016 suggested high-density heavy-liquid separation during sample processing to enrich possibly formed vivianite in the high-density fraction of the sediment. pH showed considerable variability and could reach maximum values of pH 9.1 and pH 9.5 in dredged and FeCl$_2$ treatments, pH 10 in LMB and controls or even pH 10.3 in AMZ treated enclosures. Such pH may have an effect on P binding and ligand exchange may promote the release of phosphate from iron and aluminum complexes (Boers, 1991). The elevated pH was a result of photosynthetic activity by plants and filamentous algae growing in the enclosures that may indicate a potential risk of using pH-sensitive P binders such as AMZ, aluminum and iron-based products. At pH 10 AMZ desorbed ~39% of its adsorbed P, alum ~71% of its adsorbed P, while LMB did not desorb any of the P precipitated (Kang et al., 2022). Hence, in shallow surface waters in which clear water and submerged macrophytes are the preferred states, sediment P mobilization by photosynthetically driven high pH (Welch and Cooke, 2005) may limit the options of sediment P release to dredging or use of LMB.

A clear enclosure effect was observed causing the controls to deviate from the pond. Enclosing a small volume of water creates some artifacts such as the limitation of external nutrient loading and the exclusion of wind and fish effects, whereas a relatively large wall may support a community of otherwise far less abundant organisms. The experiment provides valuable insights into sediment nutrient release and highlights the promotion of submerged macrophyte growth with reduced turbulence. Stable weather conditions in spring may contribute to macrophyte development, while more turbulent conditions may favor a phytoplankton-dominated state. The presence of cyanobacterial blooms during turbid conditions was a key factor in conducting the enclosure experiment. This enclosure experiment revealed that all four treatments could improve the water quality of the Bouvigne pond. Treating this pond of 14,344 m^2 with LMB as dosed in the enclosures (650 g m^{-2}) would imply a treatment cost of around € 30,000, for AMZ (837 g m^{-2}) it would be ~€40,000, and removing 20 cm from the entire pond by dredging would come to ~€ 130,000. Despite the product price of FeCl$_2$ being a few times less per ton than LMB or AMZ, it is difficult to make an

estimate of treatment cost as $FeCl_2$ injection into the sediment requires specific equipment (Schütz et al., 2017; Wiśniewski et al., 2010). A system analysis of the pond including the results of this study, insight in the external nutrient loading and the required loading reductions for water quality improvement can guide the water manager to an effective set of executable restoration measures. Based on the results and estimated costs, LMB treatment would appear the first choice to reduce the internal loading of the pond. The water manager decided to dredge the pond as part of maintenance and restoration of the water system, including the realization of a desired increase in water depth. After the restoration of the pond, monitoring of water quality development is essential and if the improvement falls short of expectations, the introduction of macrophytes and an additional polishing step with LMB can be considered.

5. Conclusions

- The addition of AMZ, $FeCl_2$ or LMB resulted in a stronger improved water quality than dredging did in an enclosure experiment lasting 112 days.
- A strong enclosure effect was noted promoting clear water and submerged macrophytes in controls, but no macrophytes were observed in dredged enclosures.
- The amount of total P as well as potentially releasable P was strongly reduced by dredging. In LMB amendments the "Ca-P" pool was enlarged reflecting $LaPO_4$ formation, in AMZ treated sediment the "Al-P" (NaOH-SRP) pool was enlarged indicating more metal-oxide adsorbed P, while in $FeCl_2$ treatments the reductive labile P pool was enlarged reflecting more iron-oxi/hydroxide adsorbed P.
- In the sediment core experiment, P fluxes were negative for AMZ, $FeCl_2$ and LMB treatments, but positive for controls and cores from the dredged area. Negative DIN fluxes were found in AMZ and $FeCl_2$ treated cores, while LMB caused a positive DIN flux. The latter was not observed in the enclosures and probably is due to leaching from the product itself.
- AMZ and $FeCl_2$ increased chloride concentrations and therewith conductivity, LMB led to higher filterable lanthanum concentrations, but all at acceptable levels. The $FeCl_2$ injection did not keep the material in the sediment leading to temporarily turbid water (ferric iron oxi/hydroxide complexes).
- In restoring the Bouvigne pond, a combination of dredging followed by a polishing step with LMB treatments and planting of selected macrophytes could be considered as a meaningful follow-up of the intended deepening of the pond in case water quality improvements are insufficient.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120391.

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