Controlling internal nitrogen and phosphorus loading using Ca-poor soil capping in shallow eutrophic lakes: Long-term effects and mechanisms

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Abstract

Clean soil is a potential capping material for controlling internal nutrient loading and helping the recovery of macrophytes in eutrophic lakes, but the long-term effects and underlying mechanisms of clean soil capping under in-situ conditions remain poorly understood. In this study, a three-year field capping enclosure experiment combining intact sediment core incubation, in-situ porewater sampling, isotherm adsorption experiments and analysis of sediment nitrogen (N) and phosphorus (P) fractions was conducted to assess the long-term performance of clean soil capping on internal loading in Lake Taihu. Our results indicate that clean soil has excellent P adsorption and retention capacity as an ecologically safe capping material and can effectively mitigate NH_4^+-N and SRP (soluble reactive P) fluxes at the sediment-water interface (SWI) and porewater SRP concentration for one year after capping. The mean NH_4^+-N and SRP fluxes of capping sediment were 34.86 $mg \cdot m^{-2} \cdot h^{-1}$ and -1.58 $mg \cdot m^{-2} \cdot h^{-1}$, compared 82.99 $mg \cdot m^{-2} \cdot h^{-1}$ and 6.29 $mg \cdot m^{-2} \cdot h^{-1}$ for control sediment. Clean soil controls internal NH_4^+-N release through cation (mainly Al^{3+}) exchange mechanisms, while for SRP, clean soil can not only react with SRP due to its high Al and Fe content, but also stimulate the migration of active Ca^{2+} to the capping layer, thus precipitating as Ca-bound P (Ca-P). Clean soil capping also contributed to the restoration of macrophytes during the growing season. However, the effect of controlling internal nutrient loading only lasted for one year under in-situ conditions, after which the sediment properties returned to pre-capping conditions. Our results highlight that clean Ca-poor soil is a promising capping material and further research is needed to extend the longevity of this geoengineering technology.

Key words:

Eutrophication; Internal nutrient loading; Capping; Ca-poor clean soil; Sediment-water interface; Shallow lakes

1. Introduction

Eutrophication of lakes arising from excessive nitrogen (N) and phosphorus (P) input leads to harmful algal blooms and retrogressive lake evolution (Bullerjahn et al., 2016). The algae compete for light with submerged vegetation, causing a shift from a macrophyte-dominated lake to algae-dominated. This leads to degradation of the physical and chemical environment beyond the point where self-recovery is possible, with the lake becoming green, turbid and foul-smelling, and potentially threatening drinking water sources (Guo, 2007; Scheffer and Nes, 2007). Geo-engineering solutions typically focus on controlling the input of external nutrients, however even once these are reduced or stopped there can be persistent release of internal N and P loads that may continue to cause eutrophication for years or even decades (Spears et al., 2014; Watson et al., 2016).

Research has shown that both N and P can be limiting nutrients, and hence controlling both is the most effective way to limit eutrophication (Cotner, 2017; Paerl et al., 2016). In-situ capping of lake bed sediment is considered a cost-effective technology for effectively isolating sediment nutrients and preventing or severely reducing their release (Gu et al., 2017; Lurling et al., 2016). Capping materials can include artificially chemically-modified adsorbents such as lanthanum-modified bentonite Phoslock^{TM} (Copetti et al., 2016), iron-modified zeolite (Zhan et al., 2019), and hydrous aluminum oxide (Li et al., 2017). However, depending on the pH of the lake, these can lead to undesired chemical releases, including of toxic trivalent aluminum ions (Al^{3+}) at pH <6, or release of lanthanum (Peterson et al., 1976; Figueiredo et al., 2022). Capping materials that cause conditions to become more alkaline can lead to the conversion of NH_4^+-N into NH_3, which is toxic to biota. Balancing the available active ions in a chemically-modified capping layer with the available nutrients that need locking up (e.g. SRP) is difficult but important because excess

capping material capacity will lead to potential toxicity from the Al/La and NH_3 (Gibbs and Hickey, 2018). Iron-modified capping materials can be effective but they tend to form sediment Fe-P which is easily dissolved and released under seasonal hypoxia (Yang et al., 2020). The use of natural clean soil as a capping material can avoid these potential toxic chemical side effects, reducing both internal nutrient release and sediment resuspension with excellent ecological safety (Pan et al., 2012a; Zhong et al., 2022).

Evaluation of the efficiencies of capping materials for preventing nutrient release are generally conducted under laboratory conditions, and/or with short term small-scale field trials. Both approaches are limited because natural lakes are subject to seasonal and episodic hydrodynamic and temperature fluctuations, which in turn alter the sediment stability and lake biogeochemistry significantly. Longer term field testing is essential to thoroughly test the efficacy of capping approaches to control internal loading.

Shallow lakes are characterized by frequent hydrodynamic disturbances that lead to resuspension and deposition of bed sediments and the deposition of nutrient-rich suspended particular matter (SPM) (Xu et al., 2017). This presents a challenge for using capping layers to control internal release of nutrients because these caps themselves can be remobilized (Liu et al., 2019; Liu et al., 2016). Re-suspension events create fresh sediment-water interfaces that can be highly reactive, leading to a pulse of nutrients being released. At the same time, the material that is removed becomes SPM, mainly comprised of inorganic metal-enriched particles and organic matter, with large reactive surface area for binding any dissolved N and P. These particles, and any nutrients they have scavenged, then settle out of the water column to be re-deposited on top of the newly formed sediment-water interface, ultimately burying it again (Huser et al., 2016; Yu et al., 2017). Lakes that are subject to significant

input of external SPM will have the potential for this particulate material to remove nutrients from the water column into the bed sediment, where they may later become released once buried and conditions change.

The long-term effectiveness of sediment capping under in-situ lake environments is poorly understood (Lin et al., 2019). Hence, in this study, a three-year experimental monitoring approach was adopted, with in-situ control enclosures (uncapped) compared against enclosures where the sediment was capped with clean soil. Nutrient fluxes, porewater nutrient profiles and nutrient fraction transformations were monitored to understand nutrient dynamics and the impact of capping. The aim was to understand the impact of long term in-situ capping with clean soil on nutrient release and hence to provide a reference point for this approach to the management of waterbody eutrophication.

2. Materials and Methods

2.1 Site and material description

The field enclosure experiment was conducted in Shiba Bay (Fig. 1) in the northern part of Lake Taihu, China. Lake Taihu is situated on the Yanqtze delta in a highly industrialized and economically developed area of eastern China. The lake is relatively shallow (~1.5m), impacted by the southeast monsoon, and prone to annual cyanobacterial blooms, severe algal deposition, and water quality problems, which have led to the severe accumulation of internal nutrient loading (Qin et al., 2007).

The clean soil material used for capping was collected on the shore of Shiba Bay at Wuxi City, air dried and passed through a 40 mesh (380 μm) screen before being applied. Table 1 shows its detailed composition, notably, clean soil has a lower Ca content than the native lake sediments.

2.2 Field enclosure experiment design and sampling

Fig.1 shows the location of the field enclosures and the sampling sites within the enclosures. A ~70000 m^2 treatment and a ~50000 m^2 control enclosure were constructed with polyvinyl chloride (PVC), aiming to

prevent material exchange with the external water body. In the treatment enclosure, several sub-enclosures were established, including clean sand, Ca-poor soil, chitosan modified soil capping, etc. For Ca-poor soil capping treatment, pre-processed clean soil for capping was sprayed into one enclosure water body and left to sink to the surface of the sediment, producing a capping layer of 5 cm to 10 cm thickness (Fig. S1). This capping layer depth was based on our previous experimental work to prevent resuspension (Pan et al., 2012a; Pan et al., 2019), which suggested a minimum of 1cm, and the aim to allow macrophyte growth, which requires 5-10cm for establishment and anchoring of roots. The control enclosure without capping was located adjacent to the capping enclosure.

Capping was undertaken in January 2010. In-situ porewater samples were collected 450d, 360d, 150d and 90d prior to capping and both porewater samples and intact sediment cores were collected 60 d and 30 d pre-capping, as well as 30d, 60d, 90d, 180d, 270d, 360d, 480d, 570d and 660d post-capping. The in-situ porewater equilibration sampling devices (Peepers) were placed through the SWI by fixing to bamboo poles (Fig. S1) and left to equilibrate for 15 d before being retrieved. Intact sediment cores were sampled using a gravity core sampler (90 mm diameter, 60 cm length, Rigo Co. Ltd., Japan). All porewater samples and sediment cores were transported to the laboratory within 6 h for subsequent experiments. Incubation experiments on intact sediment cores were used to measure fluxes of NH_4^+-N and SRP at the SWI under in-situ temperature and DO conditions. Details of the sediment core incubations and in-situ peeper experiments are given in the Supplementary material. Additionally, triplicate sediment cores were also collected for the analysis of sediment oxygen demand (SOD) using dissolved oxygen microprobe technology (Presens, Regensburg, Germany). See our previous work for detailed methods (Zhong et al., 2018).

2.3 Sediment sampling and analysis

After the sediment incubation experiments, the top 0-2 cm of the sediment cores were sliced for surface sediment properties analysis. Fresh sediment subsamples were used to analyze the total microbial activity of sediments according to the method described by Schnürer and Rosswall (1982). Then, three surface sediment samples were pooled and homogenized to obtain a representative sample for further analysis. The fresh surface sediment was lyophilized under a vacuum, and ground, then passed through 0.150 mm sieves, and stored at 4 °C until subsequent analysis.

The total nitrogen (TN) content of surface sediment was analyzed by the alkaline potassium persulfate oxidation method (Chinese EPA, 2002). Sediment dissolved inorganic nitrogen (DIN), including NH_4^+-N, NO_3^--N and NO_2^--N was extracted by 2 mol/L KCl and analyzed by UV spectrophotometer (Shannon et al., 2011). Acid microwave digestion was used to determine Al, Fe, Ca, Mn, Ni, Zn, Cu and Cr by ICP-AES (Rukun, 1999). Sediment organic matter content was measured as loss of ignition (LOI) and determined by calcination at 550 °C for 6h. Sediment phosphorus (P) fractions were extracted based on the method reported by Rydin (2000) and were grouped as labile P (NH_4Cl-P), redox-sensitive P (Fe-P), aluminum-bound P (Al-P), organic P (Org-P), other inorganic P (Ca-P) and residual P (Res-P). Sediment total P was calculated as the sum of above fractions. Further details of the extraction process are given in Fig. S2 in the supplementary materials.

2.4 Phosphate adsorption isotherm experiments

Phosphate adsorption isotherms were determined using the method and calculation procedures in Pan et al. (2002; 2013) and Yu et al. (2017). Briefly, 0.5g of the processed surface sediment was added to 40ml of the solution, and mixed in 50ml polyethylene tube. The P concentration gradient of the solutions was set to 0, 0.05, 0.2, 0.5, 1, 2, 5 and 10mg/L. The mixture was incubated for 48h in a constant temperature shaker at 180

rpm and 25 °C. After the incubation, the supernatant was obtained by centrifugation at 5000 rpm and filtered through a GF/C membrane for analysis. Finally, the maximal adsorption capacity (Q_{max}, mg/g) and zero equilibrium P concentration (EPC_0, mg/L) were calculated by the non-linear form of the Langmuir equation to characterize the P adsorption capacity of surface sediments.

2.5 Statistical analysis

One-way analysis of variance (ANOVA) with Tukey's post hoc test was used to identify the significant differences in nutrient fluxes, porewater nutrient concentrations, and sediment properties between control and capping treatment. Pearson's correlation analysis was used to examine the relationships between nutrient fluxes and environmental variables. Significant difference was set at the $p < 0.05$ level. Statistical analysis was performed using SPSS 25.0 (IBM, New York, USA).

3. Results

3.1 Characteristics of clean soil and surface sediment

The physicochemical characteristics of the clean soil and surface sediment are shown in Table. 1 and Fig. 2. The results show that the clean soil is characterized by lower organic matter (LOI), TP and TN and Ca content with slightly higher Al and Fe content than the surface sediment (Table. 1, Fig. 2). This plays a role in systematic differences measured between the capping sediment and uncapped control sediment 30 days post-capping, where the average values of the former are 95% LOI, 46% TP, 52% TN, 31% (Ca), 110% (Al) and 130% (Fe) of those of the latter. Furthermore, lower Mn, Ni, Zn, Cu and Zr contents were measured in the clean soil, indicating its suitability as an ecologically safe capping material. When the Ca-poor soil was introduced into the waterbody, the contents of TP and Ca in the capping sediment increased rapidly within 60d after capping, from 344 $mg \cdot kg^{-1}$and 2.02 $mg \cdot g^{-1}$ to 644 $mg \cdot kg^{-1}$ and 5.13 $mg \cdot g^{-1}$, respectively (Table. 1).

The sediment oxygen demand (SOD) of both capping and control treatment showed significant seasonal variability within one year of capping (Fig. S3). The highest SOD rates appeared in summer (180d) and capping and control treatment only showed significant differences in summer. The total microbial activity of the control sediment showed significant seasonal variation (Fig. S4), and was highest in summer (180d), while the capping sediments did not show significant seasonal variation. Consequently, a significant difference between microbial activity in the capping and control treatments was only found in summer.

3.2 Fraction of N and P in capping and control sediments

The variation of DIN of the surface sediment in control and capping sediments is shown in Fig. 2. Sediment NH_4^+-N content decreased significantly after capping, reaching 57% of control sediment values 30d post-capping, and then increased before further fluctuation. Sediment TN also decreased post capping but then increased to levels similar to the control. No significant difference was observed in NO_3^--N and NO_2^--N between control and capping sediment.

The variation of different P fractions in control and capping sediments were displayed in Fig. 3 and Fig. S5. The dominant surface sediment P fractions were Fe-P, Al-P and Ca-P prior to capping, averaging 27.20%, 24.55% and 22.49% respectively. The capped sediments then evolved such that Al-P, Fe-P and Res-P became the dominant fractions (averaging 31.44%, 21.79% and 15.70% respectively). Furthermore, beyond 30d after capping, the inert P (the sum of Al-P, Ca-P and Res-P) in the capping sediment increased significantly compared with the control sediment, averaging 62.60% of TP (Fig. S5). Sediment Ca-P content increased from 2.00 mg/kg at 30d post-capping to 104.29 mg/kg at 660d post-capping, a 50-fold increase respectively (Fig. 3).

Positive correlations ($p < 0.05$) were found between sediment Ca-P, TP and Ca content, between Fe, Al and Res-P, and also between Al-P and

NH_4^+-N, and NH_4^+-N and TN (Fig. S6). Significant negative correlations ($p < 0.05$) were found between Res-P, Fe and Ca-P content and between Fe, Al and NO_3^--N content, except for between Res-P and Fe, and Fe and Al content in the sediment.

3.3 Phosphate adsorption capacity of capping and control sediments

A Langmuir model was used to fit the equilibrium adsorption data of SRP on the surface sediment and clean capping soil (Pan et al., 2002), results are shown in Fig. 4 and detailed parameters are listed in Table. S1. EPC_0 of the capping sediments was significantly lower than that of the control sediment. Furthermore, the Q_{max} values for the control and capping sediment were 0.2 mg/g to 0.31 mg/g and 0.24 mg/g to 0.35 mg/g, respectively, and the clean soil was 0.36 mg/g. K_p values for retention capacity of solid phase for SRP were 0.03 L/g to 0.54 L/g and 0.43 L/g to 4.27 L/g for the control and capping sediment respectively, and the clean soil was 6.75 L/g. All the above parameters show that the capping sediment was characterized by greater P adsorption and retention capacity than the control sediment, except at the end of the 660-day experiment.

3.4 Nutrients porewater concentrations and fluxes across the SWI

The temporal variation of control and capping sediment porewater nutrient concentrations with sediment depth are shown in Fig. 5. and Fig. 6. For NH_4^+-N, the pre-capping sediments show a good degree of homogeneity, with similar profiles of low overlying water concentrations and then increasing concentrations with depth below the SWI reaching a stable value at about -10cm, with steeper gradients during the warmer sampling periods. Post-capping NH_4^+-N profiles remain largely unchanged in both control and capped systems, which show no significant differences. For SRP, the pre-capping profiles show similar sharp increases in concentration immediately below the SWI and generally peaked at about -2cm to -5cm, with variations reflecting temperatures of sampling periods. Post-capping profiles show clear differences between the control sites and

303 the capped sites. Capping caused burial of previous SRP peaks and then a
304 homogenization of profiles at lower levels of SRP which took a long period
305 (> 1 year) to re-establish diffusive gradients.

306 Fig. 7. shows NH_4^+-N fluxes across the SWI in the control sediment
307 varied from 3.08 ± 1.03 $mg \cdot m^{-2} \cdot h^{-1}$ to 300.68 ± 53.95 $mg \cdot m^{-2} \cdot h^{-1}$, peaking
308 at 180d post-capping in summer. Capped sediments exhibited similar
309 temporal patterns, varying from 4.16 ± 1.31 $mg \cdot m^{-2} \cdot h^{-1}$ to 107.57 ± 40
310 $mg \cdot m^{-2} \cdot h^{-1}$, with a peak at 180d, and second smaller peak (23.82 ± 12.11
311 $mg \cdot m^{-2} \cdot h^{-1}$) at 570d in summer. All measurements showed NH_4^+-N efflux
312 from the sediment to the overlying water. Capping significantly ($p < 0.05$)
313 reduced NH_4^+-N efflux for one year compared to control sediments, but
314 this effect disappeared thereafter.

315 SRP fluxes of control sediment (Fig. 7) show similar temporal trends
316 to NH_4^+-N fluxes, varying from 0.24 ± 0.04 $mg \cdot m^{-2} \cdot h^{-1}$ to 26.97 ± 1.91
317 $mg \cdot m^{-2} \cdot h^{-1}$, with a first peak at 180d post-capping and second smaller peak
318 (9.93 ± 4.10 $mg \cdot m^{-2} \cdot h^{-1}$) at 570d post-capping in summer. SRP fluxes in the
319 capped sediment switched from effluxes to influxes from 90d, reaching a
320 maximum influx of -4.94 ± 2.17 $mg \cdot m^{-2} \cdot h^{-1}$ at 180d post-capping, before
321 then switching back to effluxes, with a peak of 9.05 ± 2.94 $mg \cdot m^{-2} \cdot h^{-1}$ at
322 570d. Fluxes were therefore significantly ($p < 0.05$) different to controls
323 for the first year, but this difference disappeared during the second year.
324 Notably，a significant ($p < 0.05$) positive correlation was obtained between
325 SRP flux and sediment Fe-P content (Fig. S6).

326 **4. Discussion**

327 **4.1 Clean soil capping controls NH_4^+-N and SRP fluxes at the SWI**

328 In this study, Fig. 7 shows that clean soil capping produces an average
329 of 31% reduction of internal NH_4^+-N fluxes from the sediment for one year.
330 Simultaneously, capping caused SRP fluxes to switch from efflux to influx
331 for one year after capping, with the source-sink transition between
332 overlying water and sediment. Overall, clean soil capping effectively

controlled internal NH_4^+-N and SRP release for up to one year, but not thereafter.

The diffusion of N and P from sediment to overlying water mainly depends on the concentration gradient at the SWI. Higher NH_4^+-N fluxes across the SWI consistent with higher porewater NH_4^+-N concentrations were measured in warm seasons (Fig. 7), where the elevated temperature enhanced rates of microbial activity (Fig.S4), increasing the mineralization of organic matter, depleting dissolved oxygen and enhancing anaerobic conditions with sediment depth (Fig. S3) (Ding et al., 2018). A combination of enhanced degradation of organic matter and reduced nitrification caused increased accumulation of NH_4^+-N, leading to steeper pore-water gradients and enhanced efflux (Beutel, 2006; Zhong et al., 2021). Reduced NH_4^+-N effluxes in the capping sediment compared to the control were likely due to the clean soil providing additional cation exchange capacity that led to sorption of NH_4^+-N when diffusing across the capping layer. This ultimately reduced the NH_4^+-N concentration of the overlying water (Leyva-Ramos et al., 2008; Pan et al., 2012b; Zhan et al., 2019).

In parallel, clean soil capping resulted in a reduction in porewater SRP concentration and a switch from SRP effluxes to influxes. This result is attributed to the immobilization of SRP by the clean soil. Prior to capping, SRP was being liberated at depth due to anaerobic conditions, most likely through a combination of release from degrading organic matter and release from iron oxyhydroxides during microbial iron reduction (Tammeorg et al., 2020). Addition of clean soil caused a reduction in SRP generation at depth and led to the sediment becoming a sink for P, thus the SRP concentration of the overlying water was effectively reduced (Pan et al., 2012b, Pan et al., 2019). This is most likely due to oxygenated soil containing abundant iron oxides and other reactive surface sites causing simultaneous retardation of anerobic microbial

activity and sorption of SRP (Hinsinger, 2001; Moore et al., 1994). The increased SRP influx during warmer sampling periods is likely due to enhanced microbial degradation during those periods producing more SRP available to be locked up by the sediment iron oxides (Figs 7, S3), and the lack of accumulation of SRP in the pore-water suggests there are sufficient iron oxides in the sediment to immediately adsorb any SRP produced. This is further supported by the good SRP sorption and retention capacity of the clean soil (Fig. 4; Table. S1). The above processes explain why SRP fluxes were significantly positively correlated with sediment Fe-P content, with smaller SRP influx at higher Fe-P content. Moreover, porewater SRP concentrations of capping sediment within -10 cm reduced to range from 0.0005 $mg \cdot L^{-1}$ to 0.40 $mg \cdot L^{-1}$ compared to 0.04 $mg \cdot L^{-1}$ to 1.84 $mg \cdot L^{-1}$ in control sediment, indicating the presence of a static layer directly below the SWI after the clean soil capping, which has been confirmed to play a key role in controlling internal P desorption and mobilization from the sediment to overlying water across the SWI (Wang et al., 2017).

Temporally, the internal NH_4^+-N and SRP fluxes recovered after one year of capping. Our results suggest a continuous process of transformation from clean soil to native sediment, leading to the return of physicochemical properties towards those of the initial sediment (Table 1). Recovered NH_4^+-N fluxes may attributed to NH_4^+-N being able to transfer across the capping layer unhindered, as any cation capacity to absorb it was used up. Meanwhile, a switch of SRP influxes to effluxes was detected, corresponding with steeper SRP concentration gradient at the SWI (Fig. 6), which supported the internal SRP release (Wen et al., 2020). This was further supported by a weakening of the SRP sorption and retention capacity effect of the clean soil (Fig. 4).

4.2 Underlying mechanisms of clean soil capping to control porewater NH_4^+-N and SRP concentrations

Our results show that clean soil can effectively control porewater SRP

concentration but not NH_4^+-N concentrations (Fig. 5 and Fig. 6). Porewater NH_4^+-N concentration is significantly negatively correlated with the sediment Al ion content (Fig. S6), thus we deduced that cation exchange between the exchangeable cations in the clean soil (Al ion) and NH_4^+-N in porewater is an important mechanism for the adsorptive removal of NH_4^+-N from the porewater and controls its released from the clean soil sediment caps (Alshameri et al., 2014; Lin et al., 2013; Lin et al., 2014). This is supported by the fact that the clean soil has a higher Al and Fe content than the sediment, and that this reduces with time (Table 1). Finally, sediment NH_4^+-N shares the same temporal variation with sediment TN, and is also positively correlated with sediment Al-P content (Fig. S6). This supports the hypothesis that NH_4^+-N is adsorbed by the clean soil. This process could release Al^{3+}, then promoting the reaction of Al^{3+} and SRP in porewater to form Al-P (Fig. 8). Moreover, the aerobic environment caused by clean soil capping could promote sediment microbial activity, particularly nitrifying bacteria, thus NH_4^+-N is decreased in short term (Pan et al., 2019; Zhang et al., 2021). However, the presence of a large amount of organic N in the sediment (Fig. 2) can quickly replenish the porewater NH_4^+-N concentration, which explains why the clean soil capping has limited impact on porewater NH_4^+-N concentrations but can significantly reduce the NH_4^+-N fluxes at the SWI. Vertically, the NH_4^+-N concentration in porewater increased with depth in the sediment and reached a maximum stable value at -10 cm, which is consistent with our previous study (Zhong et al., 2018). The highly anaerobic conditions at depth are conducive to the accumulation of NH_4^+-N (Roberts et al., 2012), while nitrification is inhibited and denitrification was promoted, thus promoting the desorption of NO_2^--N, an intermediate product of denitrification, from the sediment, explaining the negative correlation of sediment NO_2^--N and porewater NH_4^+-N (Zhong et al., 2010a; Zhong et al., 2010b). The possible explanation for the negative correlation

with sediment Res-P content was that capping leads to an increase in pH which promotes the desorption and release of Res-P (Zhou et al., 2019).

Fig. 6 shows that clean soil capping is effective at controlling porewater SRP. This can be attributed to the higher Fe content of the clean soil (Table. 1). Previous studies have confirmed that the ligand exchange of Fe oxide/hydroxide with SRP to form an inner-sphere P-O-Fe link plays an important role in SRP uptake (Ajmal et al., 2018; Cao et al., 2016). Furthermore, since SRP and NH_4^+-N coexist in the porewater, it is possible that the Al^{3+} can be desorbed from the clean soil via cation exchange between Al^{3+} on the clean soil and porewater NH_4^+-N, allowing it to then react with SRP to form Al-P (Fig. 8). Therefore, clean soil capping has a better SRP adsorption capacity to control internal P release due in part to a combination of the high Fe and Al present. This can be further supported by the significant positive correlation between the sediment Fe and Al content and sediment Res-P (Fig. S6), indicating that the presence of Fe and Al can promote the formation of inert P which is consistent with the result that lower SRP concentration was observed in the porewater (Zhan et al., 2019). Notably, sediment Ca content increased from 1.99 mg/g to 5.32 mg/g over the whole experiment (Table. 1), and the migration of Ca could accelerate the chemical precipitation of porewater SRP with Ca^{2+} to form Ca-P, thereby transforming the porewater SRP to sediment inert P (Lin et al., 2011). Therefore, we conclude that the control mechanism of porewater SRP by clean soil capping was likely a combination of SRP adsorption due to the higher Fe and Al content, and the co-precipitation of Ca^{2+} with porewater SRP (Fig. 8). Clean soil capping can effectively reduce SRP concentrations in porewater within one year, which was also confirmed by our previous short-term work (Pan et al., 2019). However, the porewater SRP concentrations recovered gradually after one-year post-capping due to a combination of increased sediment P loading and the weakened P adsorption and retention capacity (Fig. 4) (Wen et al., 2020).

4.3 Variation of P fractions in surface sediments after capping

Sediment P release potential is determined by various P fractions in sediment and their relative abundance (Liu et al., 2022; Rydin, 2000). The upper 2cm of the control and capping sediment contained different P fractions (Fig. 3).

Sediment total P (TP) is the sum of different P fractions. Fig. 3 shows that the TP of capping sediment increased significantly and approached that in the control sediment within the first year after capping, while the TP content of control sediment maintained high values throughout. This is associated with the isotherm parameters determined by the Langmuir equation, the Q_{max} and K_p decrease from 0.36 $mg \cdot g^{-1}$ to 0.32 $mg \cdot g^{-1}$ and 6.75 $L \cdot g^{-1}$ to 0.43 $L \cdot g^{-1}$ within one-year (Table. S1), suggesting the reduced P adsorption and retention capacity of capping sediment, mainly due to the reducing difference in the TP content compared to the control sediment (Lai and Lam, 2009; Wen et al., 2020). The variations of different P fractions in the capping sediment were significant. Previous studies have confirmed that mobile P (the sum of NH_4Cl-P, Fe-P and Org-P) is considered algal-available and hence a potential internal P loading while inert P (the sum of Al-P, Ca-P and Res-P) is considered a pool of permanent burial P which is hard to release (Rydin, 2000). Our results showed that clean soil capping can significantly reduce the mobile P content in the surface sediments (Fig. 3 and Fig. S5). NH_4Cl-P corresponds to immediately algal-available P, which is adsorbed to the surface of sediment particles (Sun et al., 2009). An apparent reduction of NH_4Cl-P in capping sediment was observed, reducing from 3.97 $mg \cdot kg^{-1}$ to 1.43 $mg \cdot kg^{-1}$ compared to the control (Fig. 3), suggesting that clean soil capping can effectively control labile P. This apparent decrease is attributed to the introduction of clean soil characterized by excellent P adsorption capacity that removes labile P by physical adsorption to soil particulates (Zhou et al., 2019). This phenomenon is further supported by reduced porewater

SRP concentration within the clean soil capping layer.

Fe-P is redox-sensitive P, which easily released under anaerobic conditions and transformed to potential algal-available P (Chen et al., 2015). Fig. 3 and Fig. S5 show a decrease of mobile P in the capping sediment mainly originated from Fe-P, accounting for 128.7% of decreased mobile P and 92% of TP. The clean soil characterized by a high Fe that promotes the reaction of Fe^{3+} with SRP to form Fe-P under aerobic conditions during the cold season. And the lack of Ca-P together then results in the increased ratio of mobile P to TP in the early period after capping. Microbial activity and SOD were promoted by increased temperatures (Figs. S3, S4), leading to anaerobic conditions within the sediment during warm seasons, with Fe-P readily released due to the reduction of Fe^{3+} to Fe^{2+} (Wang et al., 2016). Org-P increased slightly early in the experiment but decreased during the warm season accompanied by dissolution of Fe-P in the uncapped sediment, however, the opposite variation was observed in capping sediment. This indicates different P release mechanisms between control and capping sediment, the control sediment being mainly controlled by coupled release of Fe-P and Org-P while the capping sediment is dominated by the traditional Fe-P release process, demonstrating the shift of internal P release processes after capping (Liu et al., 2022; Sun et al., 2022). Notably, there is a negative correlation between sediment Fe and Ca-P content, which gives the likely explanation of competitive adsorption on P by stronger reactive Ca^{2+} and Fe^{3+}, promoting the shift of Fe-P to Ca-P, a similar phenomenon to that reported by Zhou et al. (2019).

Our results show that inert P increased sharply within one year of capping (Fig. 3), which is mainly attributed to the increase of Ca-P and Al-P. This result indicated that capping is beneficial for the formation of inert P fractions in the sediment (Li et al., 2019; Yin et al., 2021), which is further supported by the lower porewater SRP concentration observed in

513 the capping sediment (Fig. 6). Al-P is often analyzed together with Fe-P,
514 and while Al-P is actually more difficult to re-release than Fe-P, our result
515 found that sediment Al-P was positively correlated with sediment NH_4^+-N,
516 implying that the released Al^{3+} is from cation exchange between sediment
517 Al^{3+} and NH_4^+-N in porewater, thus promoting the formation of Al-P
518 (Rönicke et al., 2021; Rydin, 2000). Furthermore, the Al-P content reduced
519 while the Ca-P content increased after 60d post-capping, which may be
520 attributed to the actively competitive adsorption of P by Ca^{2+} over Al^{3+}
521 (Yin et al., 2021). Ca-P is regarded as permanently buried P, and a
522 significant positive correlation was found between sediment Ca-P and Ca
523 content, consistent with our result that Ca-P accounts for 64.07% of the
524 increased TP during the experiment. In this study, Ca-poor soil exhibited a
525 similar excellent internal P control ability to Ca-modified material (Zhou
526 et al., 2019). The underlying mechanism is likely the formation of a Ca^{2+}
527 concentration gradient between the Ca-poor capping layer and native
528 surface sediment, which promotes the migration of active Ca^{2+} to the
529 capping layer and, thus, reacts with SRP to form a precipitate of Ca-P
530 compounds (Fig. 8). The above-mentioned shift in the release mechanism
531 of coupled Fe-P and Org-P to Fe-P suggests the transformation of
532 algae-dominated status to macrophyte-dominated status (Liu et al., 2022),
533 thus the precipitation of Ca and SRP by calcite crusts on the surface of
534 submerged macrophytes might play an important role in increased sediment
535 Ca-P (Blindow, 1992; Sand-Jensen et al., 2021). Furthermore, the reduced
536 sediment Res-P suggests the enhanced alkaline environment, which would
537 allow Ca^{2+} to become the primary SRP-binding reactant over Fe and Al,
538 and also explains the negative correlation of sediment Ca-P and Res-P
539 content (Wu et al., 2022).

540 **4.4 Implication for the development of Ca-poor capping material and**
541 **practical capping geoengineering**

542 In this study, the large-scale field experiment is close to a practical

geoengineering project, and hence understanding the long-term performance is important for decision-making in eutrophication management. The experimental results indicate that clean soil capping could effectively mitigate internal N and P release from sediment simultaneously for one year (Fig.7). Furthermore, clean soil is a natural ecologically-safe material that helps to change the algae-dominated status of a lake to macrophyte-dominated status (Pan et al., 2012a). In this study, the recovery of submerged macrophytes was observed during the growing season. Our results indicate that Ca-poor soil can be used in geoengineering to control internal nutrient loading and provide a better habitat for macrophytes. The dominant macrophytes observed were naturally occurring *P. malaianus* and *P. crispus*, and their recovery was accompanied by reduced Chl-α concentrations (Fig. S7) (Pan et al., 2012b). Previous studies on capping materials have focused on calcium-rich material, such as heat-modified Ca-rich attapulgite (Gan et al., 2009), natural/modified zeolite (Zhan et al., 2019), illite (Gu et al., 2019) and confirmed these have better capacity to control sediment internal P loading and promote the transformation of mobile P to inert P (Hinsinger, 2001). Therefore, use of clean soil characterized by lower Ca content was contrary to the widely accepted view. Interestingly, we found that when Ca-poor soil is introduced into the water body, the Ca-rich water body will automatically supplement the Ca content to the capping layer, thus achieving a similar effect to that of Ca-rich materials. This finding leads us to consider the development of Ca-poor and environment-friendly materials for geoengineering.

The time-limited effectiveness of geoengineering in controlling internal nutrient loading continues to plague the successful application of projects. We found that N and P fluxes accompanied with surface sediment physicochemical properties recovered one-year post-capping (Fig. 7; Table 1). When the clean soil was introduced into the water body, the clean soil

gradually transformed to native sediment under the in-situ lake conditions. For example, the Ca-rich water body will continually supply Ca to the Ca-poor soil, thus causing changes in the P forms and Ca-P shifting process (Fig. 3). In addition, considering the background of persistent external inputs, the external input SPM has high nutrient and organic matter content could continuously deposit upon the capping layer, promoting the return of the physicochemical properties of new born SWI to the pre-capping status (Wen et al., 2020). Furthermore, surface sediment is prone to resuspension under hydrodynamic disturbance, which promotes the potential for deposition of contaminated sediment from uncapped areas to those with capping. Moreover, bioturbation will not only reorganize the sediment vertically to allow the capping material to react with deep sediment (Xu et al., 2017; Yin et al., 2021), but also can accelerate the mixing of the deposited SPM and capping material, promoting the sedimentation process of the capping material. Overall, we found that the change in the color of surface sediment (clean soil) was slow as it transformed from Ca-poor soil to native sediment after capping (Fig. S8). However, the change in the contents of Ca and Ca-P in the surface sediments (clean soil) was rapid (Table 1; Fig. 3). This result suggested that the active migration of substances (such as Ca and P) in the water body rather than sediment disturbance processes and external SPM input dominated the recovery of sediment properties and internal loading.

Clean soil as a natural material can effectively control internal loading of nutrients for only one year and promote macrophyte restoration for a longer period. The results of our long-term enclosure experiment cause us to worry about the long-term effects of other functional geoengineering materials. Future research should focus on the long-term effects of functional materials under field condition and how to use management measures to extend the long-term effects of geoengineering technology.

5. Conclusion

A three-year field enclosure experiment was carried out to investigate the long-term performance and underlying mechanism of clean soil capping on internal nutrient loading mitigation. Clean soil capping can not only reduce internal N and P fluxes and porewater SRP concentration for one year but also promote the restoration of macrophytes in a eutrophic lake. Clean soil characterized with high Al and Fe content can prevent internal NH_4^+-N release through cation exchange, and also has excellent P adsorption and retention capacity. Furthermore, Ca-poor clean soil has performed better in the control of internal P release via not only high cation capacity to react with SRP in the short-term, but also via stimulating the migration of active Ca^{2+} to precipitate with SRP, thus promoting the burial of internal P in long-term. However, under the in-situ conditions of Lake Taihu, the properties of capping sediment will gradually recover to the state of the native sediment, ultimately resulting in weakened effectiveness after one-year post-capping. Our field enclosure experiment demonstrated that the clean Ca-poor soil is a promising capping material to control the internal nutrient loading and help the recovery of macrophytes, and future research efforts should be exerted to extend the longevity of this geoengineering technology.

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Table 1. The physical and chemical properties of clean soil, control and capping sediment treatment during three-year experiment.

Sample	Time	LOI (%)	TP (mg/kg)	Al (mg/g)	Fe (mg/g)	Ca (mg/g)	Mn (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Cr (mg/kg)
Clean soil		3.5	319	61.1	35.6	1.99	557	31	71	13	58
Control	60d pre-capping	3.7	779	55.1	27.3	6.98	902	75	259	98	111
Control	30d pre-capping	3.7	753	54.6	26.6	6.76	875	75	252	96	106
Control	30d post-capping	3.8	748	54.8	27.2	6.56	915	75	255	97	106
Control	60d post-capping	3.9	786	58.5	29.3	6.83	1006	79	264	97	119
Control	90d post-capping	4.2	781	60.1	30.1	7.17	974	79	268	103	122
Control	270d post-capping	4.2	703	53.6	26.7	6.40	835	54	195	83	115
Control	660d post-capping	4.2	647	53.9	26.7	6.78	815	64	220	84	99
Capping	60d pre-capping	4.6	816	59.3	29.1	6.38	938	78	260	101	118
Capping	30d pre-capping	4.6	855	59.8	29.7	6.55	959	78	266	101	122
Capping	30d post-capping	3.6	344	60.3	35.3	2.02	883	33	74	18	60
Capping	60d post-capping	4.0	644	58.7	31.5	5.13	873	60	200	70	99
Capping	90d post-capping	4.3	623	57.6	29.9	4.80	771	61	195	69	94
Capping	270d post-capping	4.5	609	52.5	25.0	5.21	737	61	197	70	90
Capping	660d post-capping	4.7	638	53.4	25.8	5.32	666	57	198	75	91

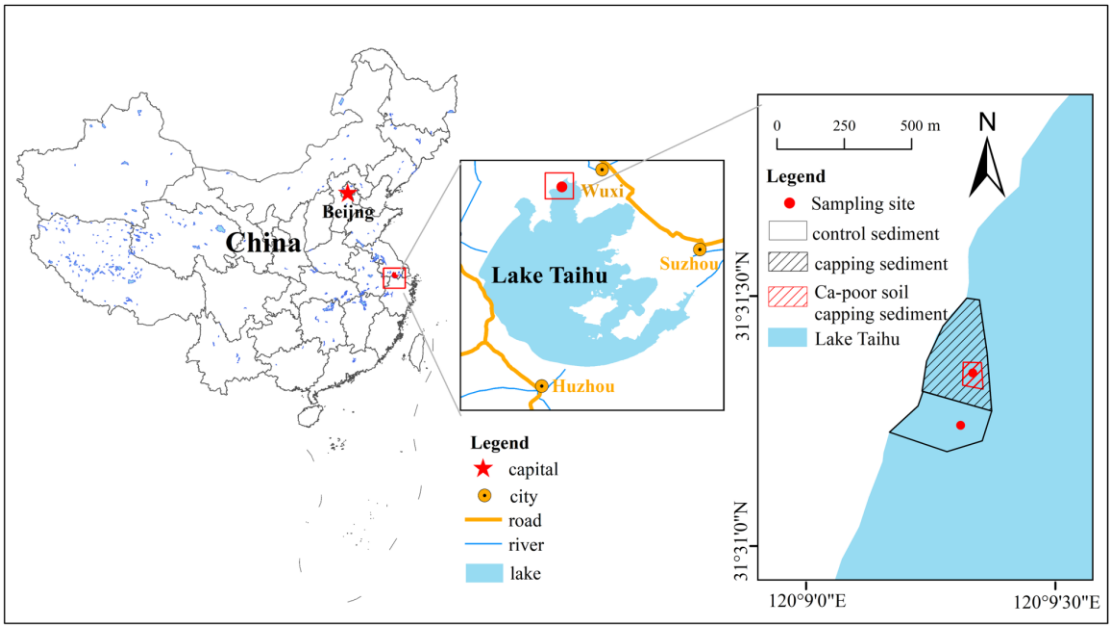


Fig. 1. Location of the field enclosure and the sampling sites in Lake Taihu.

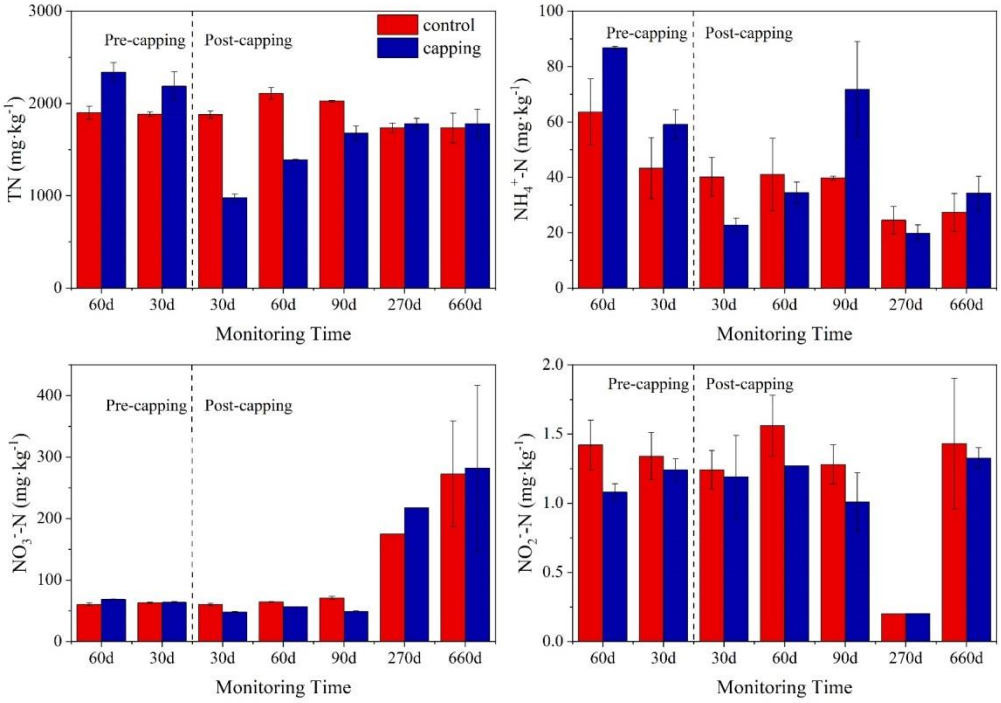
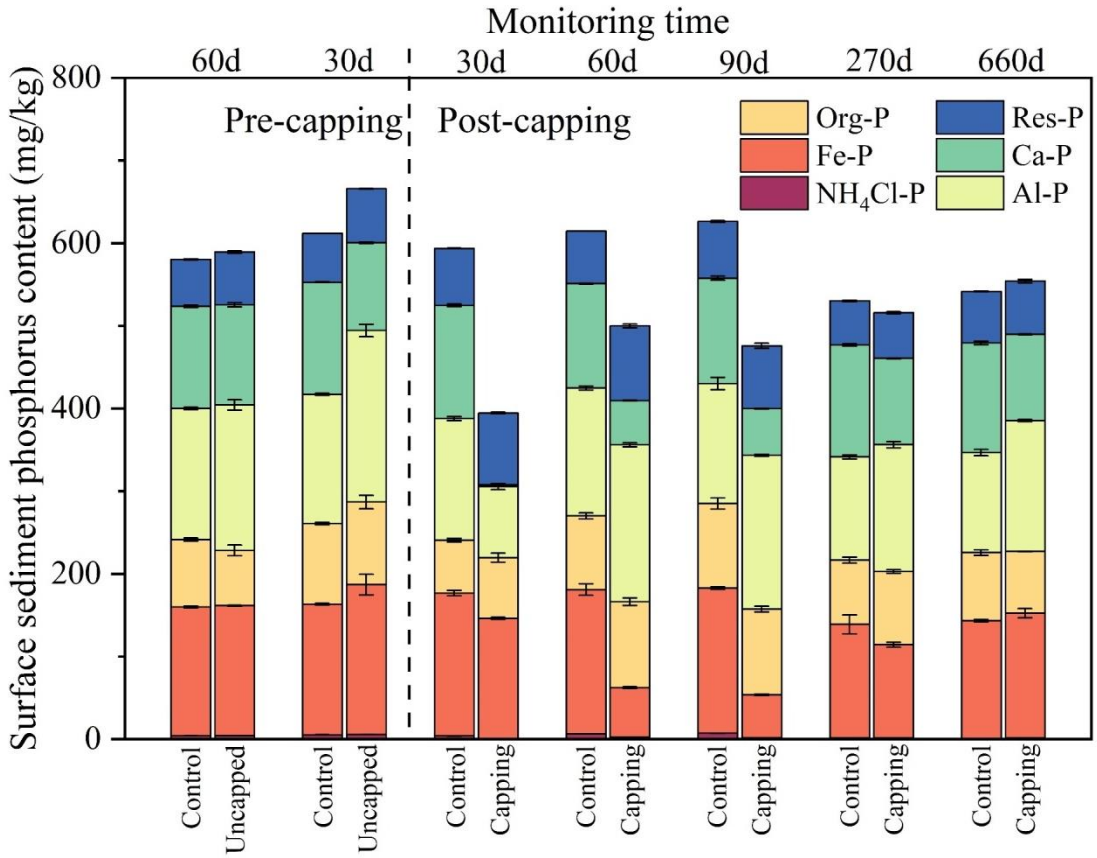


Fig. 2. TN and DIN in control and capping sediment treatment at seven sampling times.



665

666 **Fig. 3.** TP and P fractions in control and capping sediment at seven sampling times.

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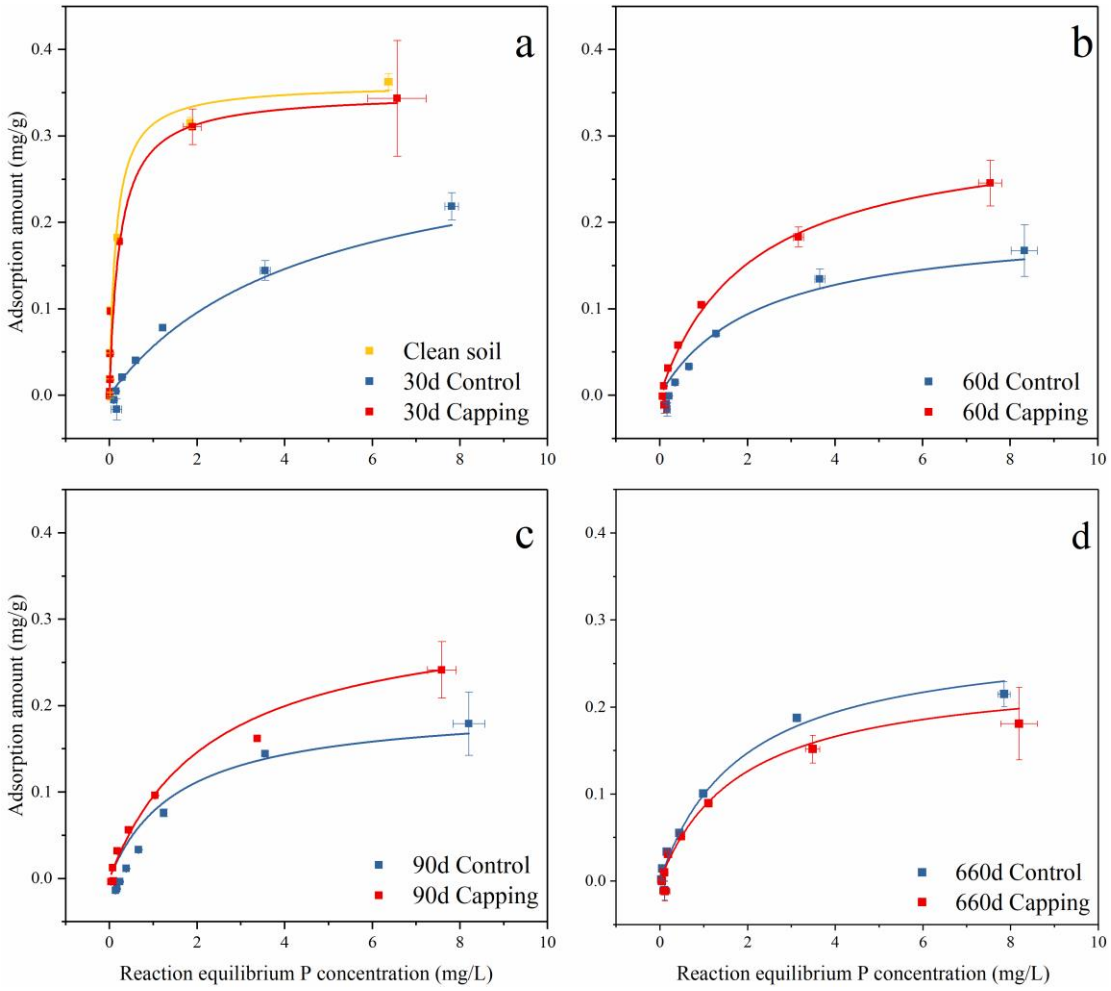
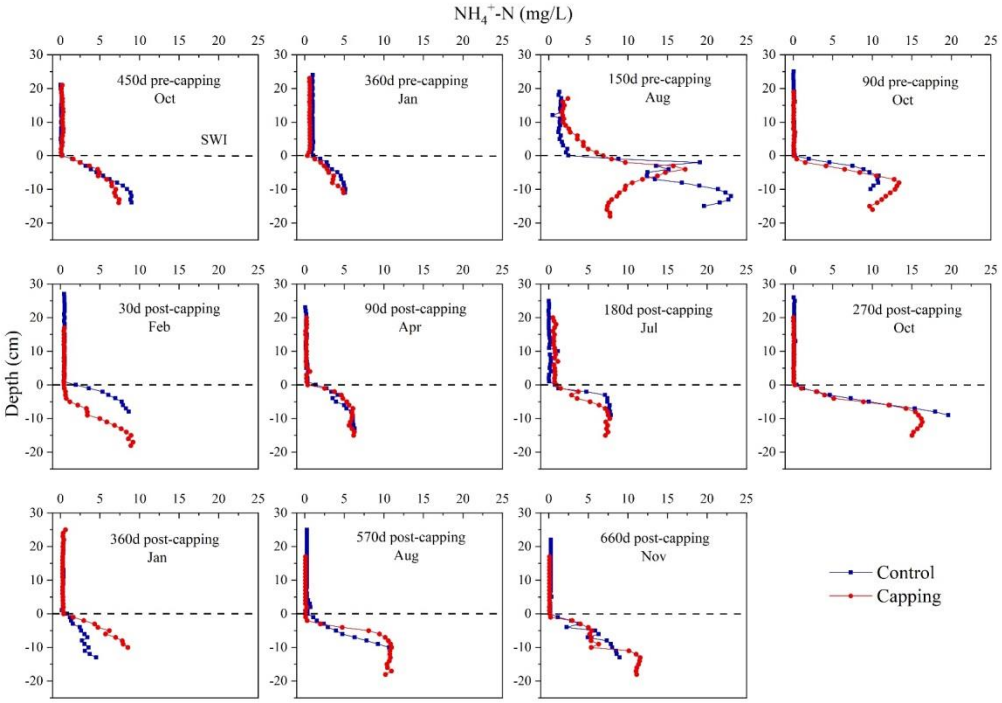


Fig. 4. Phosphorus adsorption isotherm regression for clean soil, control and capping sediment treatment using the non-linear form of the Langmuir equation.



675

676 **Fig. 5.** NH_4^+-N concentration in porewater profiles for control and capping sediment
677 at eleven sampling times.

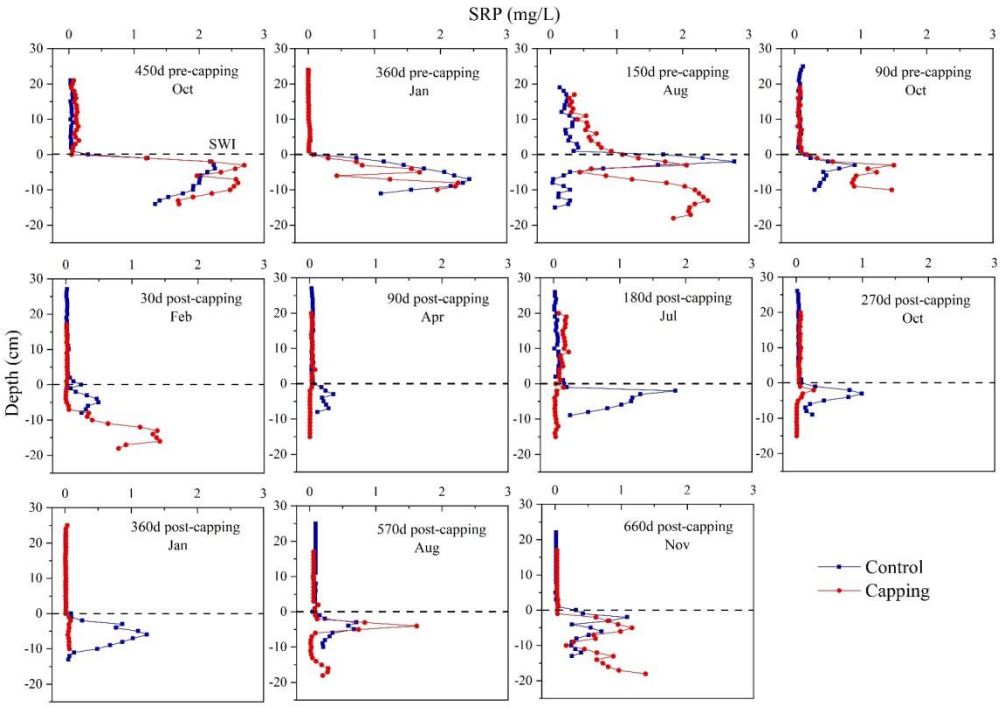


Fig. 6. SRP concentration in porewater profiles for control and capping sediment at eleven sampling times.

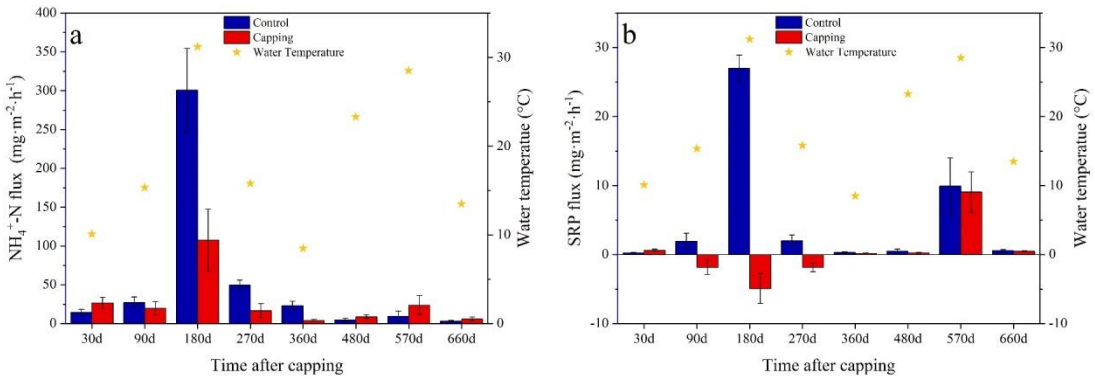


Fig. 7. Diffusive fluxes of NH_4^+-N and SRP across the sediment-water interface for control and capping sediment at eight sampling times.

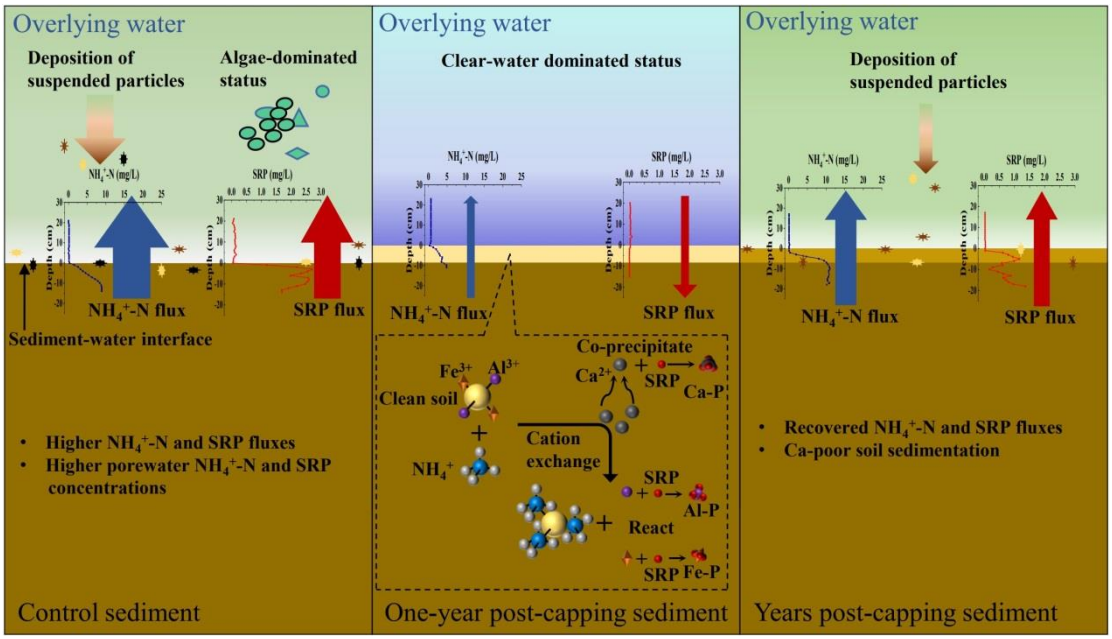


Fig. 8. Schematic representation of Ca-poor soil capping in control sediment internal loading, and the response of overlying water status in temporally.

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