Performance of physical and chemical methods in the co-reduction of internal phosphorus and nitrogen loading from the sediment of a black odorous river

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HIGHLIGHTS

- Dredging, aeration and inactivation were used to control river's internal loading.
- Sediment dredging initially induces a significant NH_4^+ release from sediment.
- Dredging and inactivation can reduce mobile P at various sediment depths with time.
- Clay inactivation performs the best in the co-reduction of N and P in sediment.

GRAPHICAL ABSTRACT
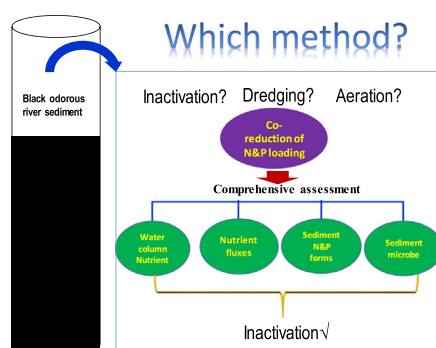
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ABSTRACT

The continuous release of nutrients from sediment is a major barrier to the remediation of black odorous rivers. This study used a long-term laboratory incubation experiment to investigate the effectiveness of sediment dredging, intermittent aeration, and *in situ* inactivation with modified clays to reduce the internal loading of sediment from a seriously polluted river. The results indicated that intermittent aeration and *in situ* inactivation were effective in reducing the TN and NH_4^+ concentrations in the water column. However, sediment dredging did not consistently reduce the TN and NH_4^+ concentrations in the water column. In contrast, the three methods were all effective in controlling the TP and PO_4^{3-} concentrations in the water column. Except for dredging, >30% of NH_4^+ and 40% of PO_4^{3-} fluxes from sediment were reduced when compared with a control sample after 120 days of remediation. Dredging induced a significant release of NH_4^+ from sediment. Dredging and aeration made nearly no change to the amount of extractable nitrogen in the sediment. However, inactivation may increase sediment-extractable ammonium in deep sediment layers with time due to vertical transportation of clay by intensive bioturbation. Dredging is the most effective way to reduce surface mobile phosphorus over time while the transported clays can reduce a large percentage of the mobile phosphorus in deeper sediment. The relative abundance of *Nitrospira* in the surface sediment increased significantly with each remediation measure, creating favorable conditions for the reduction of the ammonium released from sediment. Altogether, the results of this study indicated that clay inactivation is the best method for controlling the internal loading of both phosphorus and nitrogen in seriously polluted river sediment.

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1. Introduction

Black odorous rivers are formed through long-term pollution, which is commonly caused by domestic sewage, industrial wastewaters and agricultural runoff (Liu et al., 2017c), and this phenomenon is serious in China. The sediment of black odorous (visually black with offensive smell) rivers contain high concentrations of nutrients (nitrogen and phosphorus), heavy metals (Hg, As, Cd and etc.) and sometimes organic pollutants (PAH, PCB and etc.) (Xu et al., 2014; He et al., 2018). When sufficient nutrients form in sediment, also called internal loading, they can be released into the overlying water and, under suitable conditions, can cause eutrophication and algal blooms (Yin et al., 2018c). Therefore, developing methods to manage sediment pollutants is critical to remediating black odorous rivers in China.

Methods such as sediment dredging, aeration and *in situ* chemical inactivation have been proposed to remediate polluted river sediment. Dredging has been used extensively in China to restore lakes suffering from eutrophication (Yu et al., 2017). An estimated 100 km^2 of sediment was dredged from Lake Taihu between 2008 and 2018 (Chen et al., 2018). Although reports indicate that dredging has been beneficial to the improvement of the water quality of Lake Taihu (Zhong et al., 2010), some researchers disagree, arguing that dredging can cause such a large disturbance of sediment, it can possibly cause a second wave of pollution (Lürling et al., 2016). In addition, the large amount of land needed to store dredged sediment is another problem. Whether sediment dredging is suitable for the remediation of black odorous rivers is a topic of great controversy (Liu et al., 2015). Hypolimnetic aeration is also considered an effective means of supplying oxygen to the hypolimnion and suppressing benthic phosphorus (P) release in stratified lakes, reservoirs, and borrow pits (Munger et al., 2016; Nygrén et al., 2017). However, some researchers have indicated that hypolimnetic oxygenation has negligible effects on the eutrophic state of lakes (Nygrén et al., 2017). Conversely, in recent years, this method of aeration has been recommended to restore black odorous rivers (Pan et al., 2016).

Beyond the physical methods of sediment dredging and aeration, chemical inactivation using phosphorus and nitrogen (N) binders has been increasingly used for the management of internal nutrients in the sediment of degraded bodies of water (Copetti et al., 2016). P binder can be used to inactivate mobile phosphorus in sediment and change the reactive forms of P into inert P to reduce the potential for release into water (Meis et al., 2013; Reitzel et al., 2013; Hupfer et al., 2016). To date, many solid phase P locking materials have been developed and used to manage internal P loading in sediment. This normally includes lanthanum (La), aluminum (Al) and iron (Fe) based products (Copetti et al., 2016; Lürling et al., 2016). Results indicate that these solid phase P locking materials are an effective way to inhibit P release from sediment and are probably a promising way to control internal P loading in the sediment of black odorous rivers (Copetti et al., 2016; Yin et al., 2018a). Bio-zeolite/zeolite has been used in several polluted rivers to manage the internal loading of nitrogen in sediment (Huang et al., 2011; Zhou et al., 2016) because zeolite has a strong sorption capacity towards ammonium (NH_4^+) (Yin et al., 2018b). Several studies show that using bio-zeolite to inhibit ammonium (NH_4^+) release can also produce an environment for heterotrophic nitrification and aerobic denitrification in river sediment (Huang et al., 2011; Zhou et al., 2016; Yin et al., 2018c). A combination of P locking materials and N binder could probably be used to co-manage the internal loading of nitrogen and phosphorus in the sediment of eutrophic lakes or rivers.

At present, environmental researchers and government managers have not established guidelines or methods for handling the internal loading of river sediment, making the selection of a reasonable method difficult. Therefore, the objective of this study is to assess the feasibility of different measures, such as dredging, aeration and chemical inactivation, for the management of internal loading in sediments. The efficiency of nutrient reduction in overlying water, their fluxes from sediment, and the changes of solid phase N and P forms and microbial community in sediment after remediation were examined in this experiment. The results of this study can provide useful information for the management of sediment internal loading in black odorous rivers.

2. Materials and method

2.1. P sorption material preparation

Raw calcium-rich attapulgite (CAP) was collected from the town of Qiuji, Xuyi County, Jiangsu Province. It was manually ground and sieved into a particle size of 1–2 mm, which was then calcined at 700 °C for 2 h to enhance its P sorption capacity (Yin et al., 2017b). The prepared thermally-treated calcium-rich attapulgite (TCAP) (10.0 g, *e.g.*, 1–2 mm) was added to 25 mL of 2 mol/L aluminum chloride hexahydrate (AlCl·6H$_2$O). The mixture was then placed on a shaker at a constant temperature (25 °C) at 160 rpm for 4 h before being left to stand for 16 h. The Al-impregnated TCAP (Al@TCAP) was then harvested and dried at 90 °C for 24 h, after which it was rinsed with deionized water several times until there was no Cl$^-$ detection. The content of residual Cl$^-$ was tested by the addition 0.1 mol/L AgNO$_3$ solution into the water after washing. There was no remaining Cl$^-$ residue when no white AgCl precipitation existed in the water. Finally, the Al@TCAP was again oven-dried at 60 °C to a constant weight.

2.2. N sorption material preparation

Modified zeolite (Zeo) was produced according to Yin et al. (2018b). In brief, 10 g of zeolite with a particle size of 1–2 mm was added to 25 ml 0.4 mol/L NaCl, and the mixture was rotated in a shaker at 160 rpm for 24 h. The modified zeolite was collected and rinsed several times with deionized water and then dried to a constant weight in an oven at 60 °C.

2.3. Water and sediment sampling and handling

In June 2017, a total of 24 sediment cores (each >40 cm in length) were taken from the estuary of the Nanfei River (31°46′6.89″N; 117°25′35.03″E, Fig. S1) using a core sampler (Ø80 mm × L500 mm). All the cores were transported to a laboratory within 4 h. In addition, >200 L of water was collected at the sampling site, which was an extremely polluted inlet river of Lake Chaohu, and then transported with the sediment cores to the laboratory.

2.4. Experimental design

In the laboratory, the sediment cores were adjusted to 20 cm and filled with 15 cm of lake water overlying the sediment-water interface. For the dredging treatment, the upper 20 cm of sediment was removed in accordance with a simulated dredging depth by Liu et al. (2015) who determined that this was the depth that could remove the most N and P pollution. At the start of the sediment core incubation experiment, the two materials (Al@TCAP + Zeo) were mixed thoroughly by hand and placed evenly on the sediment surface. The amount of Al@TCAP used was calculated by weight based on a ratio of 200:1 to sediment mobile P (0–5 cm) according to Yin et al. (2018a). The Zeo dosage applied to the sediment was calculated based on the N sorption capacity of modified zeolite (around 6 mg N/g, 1–2 mm). However, the theoretical dose of modified zeolite was doubled relative to the content of the sediment's extractable ammonium (0–5 cm) according to the preliminary experiment (data not shown). Four treatments were set up as follows: (1) control—the control was intact sediment cores without any handling, (2) dredging—the upper 20 cm of sediment was removed from the sediment cores, (3) intermittent aeration—the water overlying the sediment cores was oxygenated every two days at an aeration speed of 40 L/min (the aeration device was placed 3 cm above the surface sediment to avoid disturbing the sediment during aeration), (4) Al@TCAP + Zeo—sediment cores were treated with Al@TCAP and modified zeolite.

All the cores were incubated at 20 °C in darkness in a circulating water bath. The water bath consisted of a large container with a water temperature controller and circulator (STIK, ILB-008-02, USA). The circulator was equipped with magnetic stirring bars to ensure complete mixing of the water column. The sediment cores were incubated for 120 days, and each treatment had six replicates. Syringes were used to sample the overlying water (around 50 mL) every 2 to 3 days, which was then filtered using 47-mm Whatman® GF/F filters and used for analysis of total phosphorus (TP), total nitrogen (TN), phosphate (PO_4^{3-}), ammonium (NH_4^+) and nitrate (NO_3^-). An equivalent volume of water was added back into each tube. At day 60 and at the end of the experiment, three sediment cores were extruded from the tubes and sliced at 2 cm intervals to 10 cm. All slices were then freeze-dried and used for P fraction analysis, and the remaining wet sediment was used for N form analysis.

2.5. Chemical analysis

The water parameters, including total phosphorus (TP), total nitrogen (TN), ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}), were determined in the laboratory following the standard analytical methods (Apha, 2012). Sediment water content was measured by weight loss after drying at 105 °C for 24 h, and sediment porosity was calculated from the water content. Loss on ignition (LOI) was determined by heating the dried sediment at 550 °C for 4 h. The calculation method of these parameters can be found in the Supplementary materials. P forms in the control and treated sediments were extracted according to the method proposed by Rydin et al. (2017) and can be found in the Supplementary materials. Phosphorus concentrations in the P fraction and the overlying water samples were analyzed by a spectrophotometer (Shimadzu, UV-2550) using the molybdenum blue method (Murphy and Riley, 1962). Extractable ammonium and nitrate in the sediment were extracted immediately after sampling with 2 M KCl (1:5 of solid:solution by mass). Acid volatile sulfur (AVS) was measured using Hsieh's cold diffusion method with ascorbic acid to prevent interference from Fe (III) (Hsieh et al., 2002).

An HR-Peeper was inserted into the sediment tubes at day 60 and day 120 to obtain the phosphate and ammonium information in pore water across the sediment-water interface. A miniaturized photometrical method utilized an Epoch microtiter plate (BioTek Instruments, Inc., Winooski, VT, USA), which was modified using the molybdenum blue method and Nessler method and used to determine soluble reactive phosphorus (SRP) and NH_4^+ in pore water, respectively (Laskov et al., 2007). A detailed description of the HR-peeper can be found in the Supplementary materials (Xu et al., 2012).

The surface sediment (0–2 cm) was sampled for DNA extraction on days 0, 60 and 120. In addition, the clay contained in the sediment layer (4–6 cm) from the Al@TCAP + Zeo treatment was also tested using an analysis similar to that used for surface sediment (0–2 cm) at day 120. The DNA was extracted with a soil DNA isolation kit (MO BIO Laboratories, Carlsbad, CA, USA), following the manufacturer's instructions and then sequenced in an Illumina® MiSeq® platform (Personal Biotechnology Company, Shanghai, China). Detailed information on DNA extraction and sequencing is provided in the Supplementary material.

2.6. Statistical analysis

Significant differences among treatments were identified through one-way analysis of variance (ANOVA) followed by Tukey's test. Typically, homogeneity of variance for the obtained data was tested and data of the test values >0.05 were adopted for the ANOVA analysis. All statistical analyses were performed using SPSS 19.0 (IBM, New York, USA), and significant levels were reported at $p < 0.05$ and $p < 0.01$.

3. Results

3.1. Sediment and water properties

The water and sediment properties used in the present study are listed in Table S2. The concentrations of TN, TP and NH_4^+ in the water were 8.62, 0.67 and 7.74 mg/L, respectively, all of which exceeded the class five standard of surface water quality in China (GB3838-2002) (China, 2002). The concentration of PO_4^{3-} and NH_4^+ in the water accounted for 89.8% of TP and 68.7% of TN, respectively. Sediment TP and TN was 3514 mg/kg and 3233 mg/kg, respectively, which is 2 to 3 times the average of total phosphorus and nitrogen concentrations in Lake Chaohu. Sediment mobile P was 1215 mg/kg, which was 34.6% of the total phosphorus in the sediment. The amount of Fe-P was 675 mg/kg and contained >50% of the mobile P. The oxidation-reduction potential (ORP) in the sediment was minimal at −230 mV. The sediment was also sulfur-rich and organic with an acid volatile sulfide (AVS) value of 230 mg/kg and contained 12.1% loss on ignition (LOI).

3.2. Variation of nutrient concentrations in overlying water

The nutrient concentrations in the overlying water from the long-term core incubation are presented in Fig. 1. The TN concentrations among the treatments differed widely. In the control, aeration and Al@TCAP treatments, the TN concentrations all generally decreased with the increase of incubation time. The TN concentration in the control increased again after 75 days of incubation and then decreased slowly to the end of the experiment. In contrast, the TN concentration in the dredging treatment increased sharply in the first 10 days of the experiment then decreased slowly to the end of the experiment. Overall, the average TN concentration in the water column of the four treatments decreased as: Al@TCAP + Zeo < Aeration < Control < Dredging. The NH_4^+ concentration in the overlying water from the four treatments all decreased with the increase of the incubation time. The concentration of NH_4^+ in the control was significantly higher than the other three treatments ($p < 0.05$), while there was no significant difference in the NH_4^+ concentration in the water column among the Al@TCAP + Zeo, aeration and dredging treatments. The NO_3^- concentrations in the water columns were similar to that of the TN concentrations. The NO_3^- concentrations for the dredging and aeration treatments increased sharply, reaching a maximum of around 9 mg/L and 7.5 mg/L on the 12th and 25th day respectively. Then, the concentrations decreased consistently. In contrast, The NO_3^- concentration in the water treated with Al@TCAP + Zeo stayed in a relatively low concentration throughout the experiment.

The TP concentration in the control did not fluctuate in an obvious pattern throughout the experiment and generally decreased slowly with the increase of incubation time. In contrast, the TP concentration in the water columns from dredging, aeration and Al@TCAP + Zeo treatments all stayed at a relatively lower concentration than that of TP concentration in the control treatment ($p < 0.05$). The PO_4^{3-} concentration in the control stayed relatively constant for 50 days, then decreased slowly as the incubation time increased. Meanwhile, the PO_4^{3-} concentration for the other three treatments all decreased sharply in the first 10 days, then remained consistent for the next 30 days. However, the concentrations increased again on the 40th day, but remained constant for another 30 days before decreasing slowly to the end of the experiment. The PO_4^{3-} concentrations in the dredging, aeration and Al@TCAP + Zeo treatments were always lower than that of the PO_4^{3-} concentration in the control throughout of the experiment. There was no significant difference in the PO_4^{3-} concentrations among the dredging, aeration and Al@TCAP + Zeo treatments for 40 days ($p > 0.05$). However, the PO_4^{3-} concentration for the dredging treatment was generally higher than that of the PO_4^{3-} concentrations for the aeration and Al@TCAP + Zeo treatments.
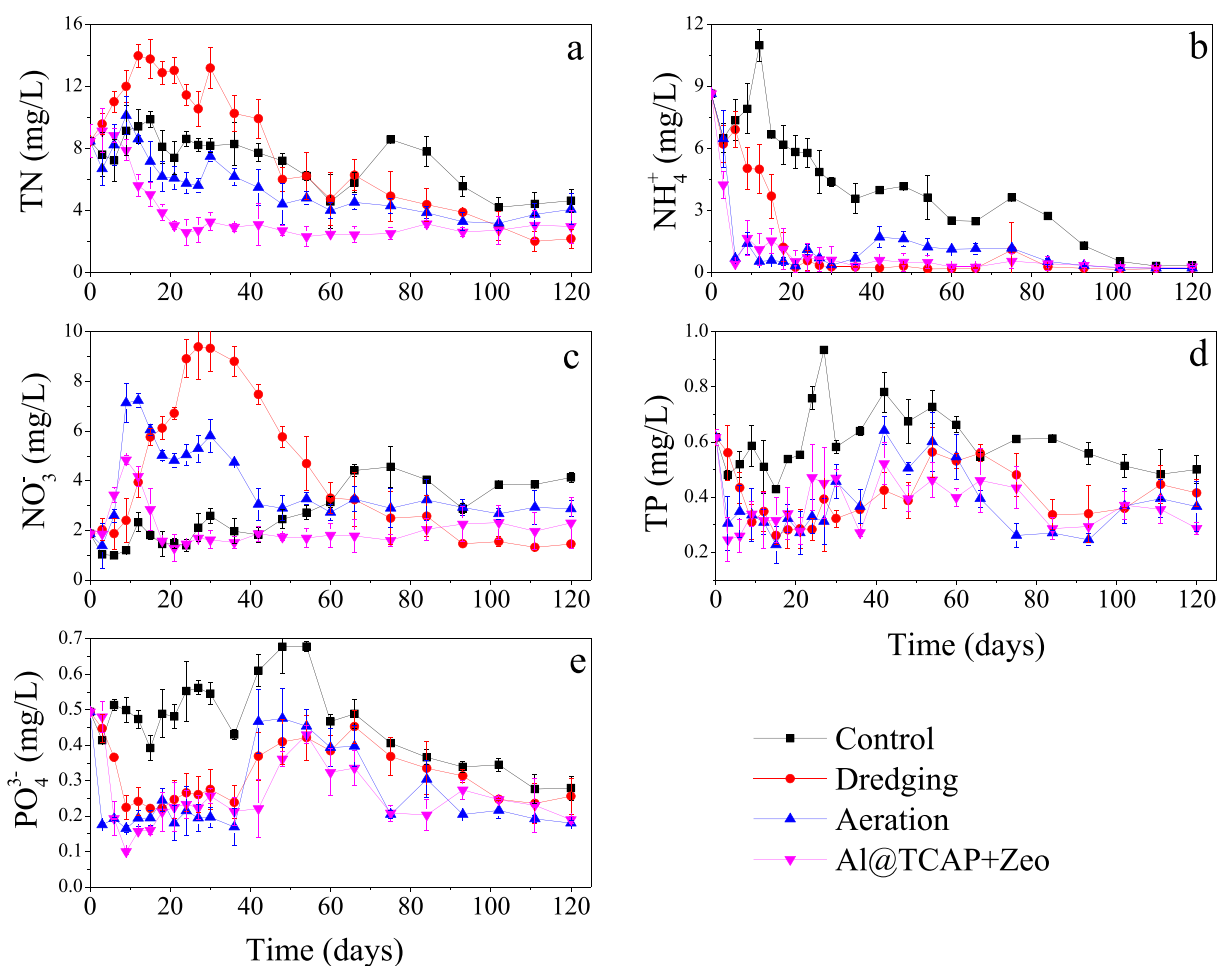
Fig. 1. Concentrations of nutrients in water columns from different treatments (mean ± SD, n = 3).

3.3. PO_4^{3-} and NH_4^+ concentrations in pore water and their fluxes across the sediment-water interface

The concentrations of PO_4^{3-} and NH_4^+ in sediment pore water at day 60 and day 120 are presented in Fig. 2. The results show that these reactive nutrients were distributed differently within sediment. The concentration of PO_4^{3-} in the pore water from the four treatments at the two sampling times generally increased with the increase of sediment depth and peaked at 2 to 4 cm and then either remained constant or decreased slightly at greater sediment depths. The average PO_4^{3-} concentration for the control, dredging, aeration, and Al@TCAP + Zeo treatments were 1.74, 0.94, 1.32 and 0.77 mg/L at day 60 and were 1.50, 1.00, 1.18 and 0.75 mg/L at day 120, respectively. The PO_4^{3-} concentration in sediment pore water from the Al@TCAP + Zeo, dredging and aeration treatments were all significantly lower than that of the PO_4^{3-} concentration found in the control ($p < 0.05$). In comparison, the concentrations of NH_4^+ in sediment pore water from all four treatments increased with the sediment depth. The concentration of NH_4^+ in the sediment pore water from the dredging treatment was significantly higher than that from the control treatment ($p < 0.05$), while the concentration of NH_4^+ in the sediment pore water from the Al@TCAP + Zeo treatment remained the lowest among these treatments.

The calculated PO_4^{3-} and NH_4^+ fluxes across the sediment-water interfaces indicated that various methods can cause different remedial effects (Fig. 2). The value of PO_4^{3-} fluxes from the three treated sediment cores were all significantly lower than the PO_4^{3-} flux in the control

treatment ($p < 0.05$). There was no statistical difference in the PO_4^{3-} flux of the dredging and Al@TCAP + Zeo treatments ($p > 0.05$), but a lower PO_4^{3-} flux was noted in the aeration treatment. The amount of NH_4^+ flux behaved in a pattern similar to the concentration of NH_4^+ in sediment pore water. The NH_4^+ flux found in the dredging treatment was significantly higher than amount of NH_4^+ flux found in the control, aeration and Al@TCAP + Zeo treatments ($p < 0.05$). While NH_4^+ flux in the Al@TCAP + Zeo treatment remained the lowest among these treatments.

3.4. Sediment ammonium and nitrate

The extractable ammonium and nitrate found at increasing sediment depths of the core samples for each treatment are presented in Fig. 3. Except for the Al@TCAP + Zeo treatment, the amount of extractable NH_4^+ increased with the sediment depth at day 60 and 120. However, the amount of extractable NH_4^+ found in the cores used for the Al@TCAP + Zeo treatment increased from the surface sediment and peaked at the 2 to 4 cm section, reaching a maximum concentration of 509 mg/kg and then decreased with increasing sediment depths at day 60. The distribution of extractable NH_4^+ at day 120 was much like the results found at day 60, but the amount of NH_4^+ peaked at 4 to 6 cm in the cores used for the Al@TCAP + Zeo treatment. Meanwhile, intensive bioturbation activity was found in the control, aeration and Al@TCAP + Zeo treatments, and the applied material in the Al@TCAP + Zeo treatment was buried at different sediment depths at different sampling times (2–4 cm at day 60 and 4–6 cm at day 120). Unlike the
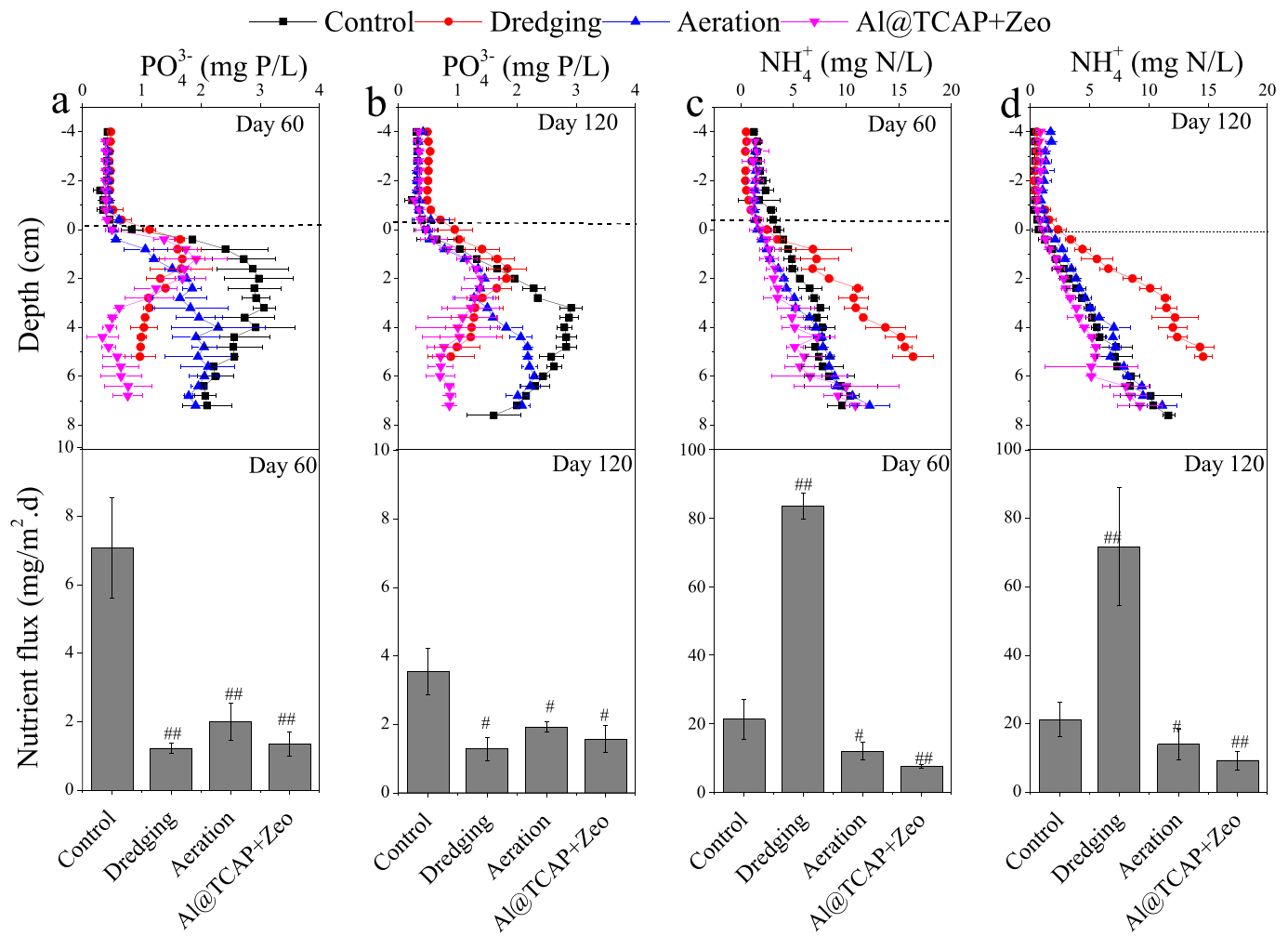
Fig. 2. Phosphate and ammonium concentrations in sediment pore water and their fluxes across sediment-water interface at various sampling times from different treatments (mean ± SD, n = 3). # and ## represent that significant differences are found at $p < 0.05$ and 0.01, respectively, for nutrient fluxes between control and remedial treatment at different sampling times.

amounts of extractable NH_4^+ found in the sediment cores, the levels of extractable NO_3 seen at different depths exhibited no distribution patterns. In addition, we did not find significant differences among the four treatments tested.

3.5. Sediment P forms

The distribution of different P forms at different depths of the sediment core samples for each treatment is presented in Fig. 4. The total phosphorus was in the range of 2143 to 2835 mg/kg among the treatments, but there was no evident distribution pattern of TP seen at different sediment depths among the treatments in this study. While the amounts of mobile P (the sum of Labile-P, Fe-P and Org-P) generally decreased as the sediment depth increased. The amount of mobile P in the surface sediment (0 to 2 cm) in the control treatment was significantly higher than the amount of mobile P found at this depth in the other three treatments ($p < 0.05$). The content of mobile P found in the cores treated with Al@TCAP + Zeo was significantly reduced in the 2 to 4 cm section at day 60 and in the 4 to 6 cm section at day 120 when compared with the control treatment ($p < 0.05$). Except for the dredging treatment, the fraction of Fe-P represented the main part of the TP (>46%) in the surface sediment (0 to 2 cm) of the control, aeration and Al@TCAP + Zeo treatments, while the fraction of Al-P represented the largest part of TP in the surface sediment (0 to 2 cm) in the dredging treatment. However, the fraction of Al-P also represented the

main part of TP from 2 to 10 cm in all of the treatments. The content of mobile P (mostly the fraction of Fe-P) in the surface sediment (0 to 2 cm) of the cores treated with Al@TCAP + Zeo increased again at day 120 when compared with the amount of mobile-P in surface sediment at day 60.

3.6. Sediment microbial community

The relative abundance of bacterial communities in the sediments used in the different treatments at various times is presented in Fig. 5. The results indicated that Proteobacteria account for the main part of the microbial communities found in the sediments used in all the treatments before and after sediment remediation, while the relative abundance of other bacterial communities varied among the treatments at the two sampling times. The abundance of Nitrospirae increased after dredging, aeration and the addition of Al@TCAP + Zeo. However, the abundance of Actinobacteria decreased after these treatments. The relative abundance of Acidobacteria increased in the 4 to 6 cm layer of sediment when compared with that of Acidobacteria in the surface sediment (0 to 2 cm) in the cores treated with Al@TCAP + Zeo at day 120. Interestingly, the abundance of Nitrospirae in the zeolite-containing layer (4 to 6 cm) was a little higher than that of the abundance of Nitrospirae in the surface sediment (0 to 2 cm).
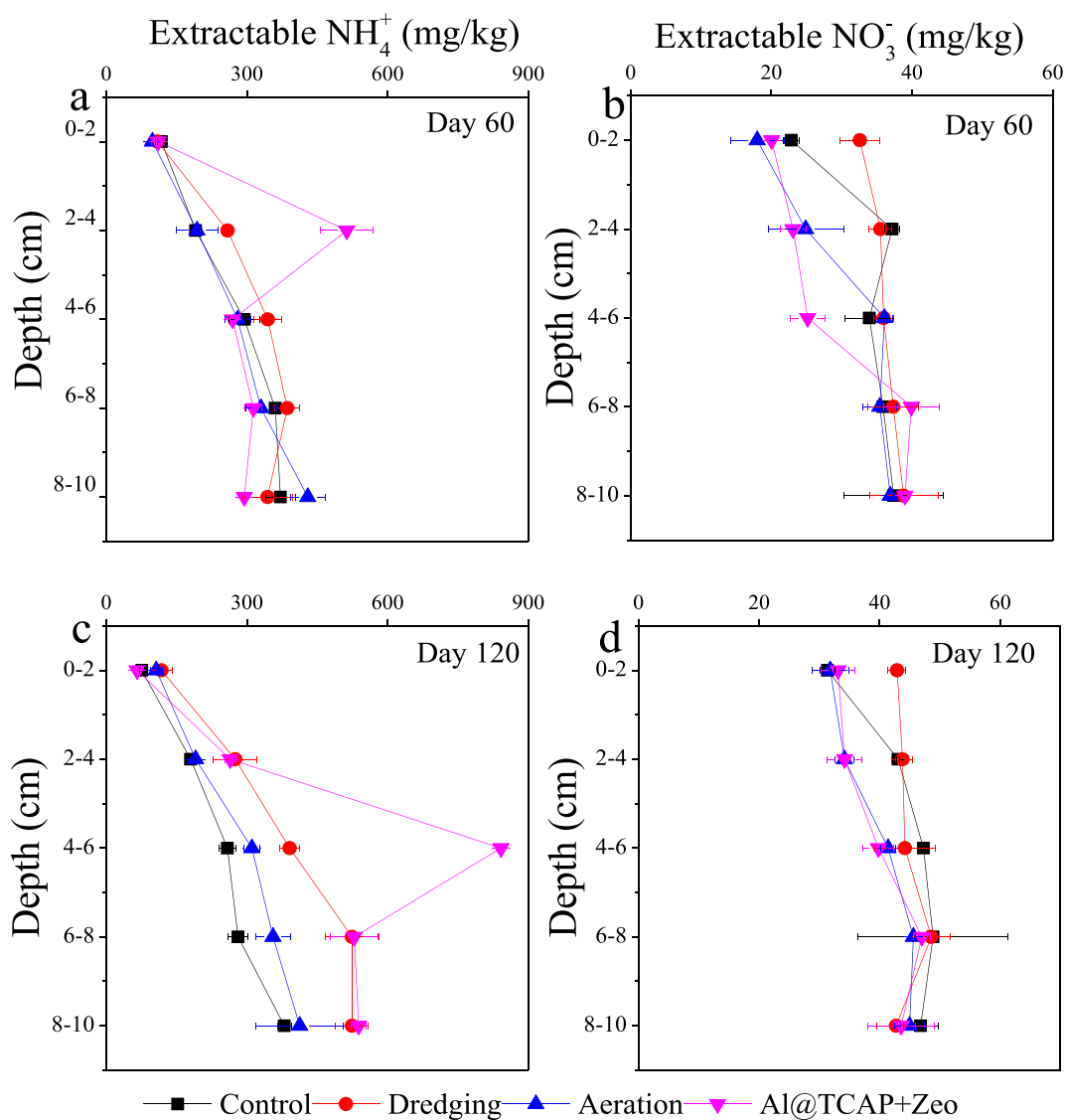
Fig. 3. The vertical distribution of extractable NH_4^+ and NO_3^- in the sediment from different treatments (mean $\pm$ SD, n = 3).

4. Discussion

4.1. Effects of different methods on the quality of overlying water

The improved water quality seen in different methods is based on different theories. For example, intermittent aeration and *in situ* inactivation effectively control the concentrations of TN and NH_4^+ in the water columns during most of the time in this experiment when compared with the control treatment. This is because NH_4^+ in the water can be adsorbed onto zeolite and confined in its structure (Casadellà et al., 2016; Xu et al., 2017). Most of previous studies also indicated that zeolite is a good binder for ammonium removal from aqueous solutions. Huang et al. (2011) found that the use of bio-zeolite could effectively reduce the release of NH_4^+ from polluted river canal sediment. However, whether the adsorbed NH_4^+ can desorb from zeolite and be released back into the water column needs further study. The reduction of the concentration of ammonium from the aeration treatment is caused mostly by the oxygenation of NH_4^+ during aeration. This corresponds with the enhanced nitrate concentration in the water column as indicated in Fig. 1. Unfortunately, the TN concentration in the water column from the dredging treatment increased greatly within 60 days when compared with that of concentrations found in the control. This

abrupt increase of TN resulted from the release of ammonium from the deep sediment layers and the subsequent oxygenation of ammonium to nitrate. This observation is consistent with Liu et al.'s (2017b) study which showed that ammonium is likely to be released from sediment just after the start of dredging. The subsequent decrease of TN concentrations (after day 60) in the water column of the dredged sediment is probably due to the enhanced nitrification activity in the sediment cores.

Aeration, dredging and *in situ* inactivation generally controlled the TP and PO_4^{3-} concentrations in the water columns when compared with the control treatment. Aeration can oxygenate surface sediment and increase the formation of ferric hydroxide to increase the sediment's sorption capacity of phosphate from overlying water. The use of aeration to improve water quality with regards to phosphate is full of controversy. Kuha et al. (2016) showed that although hypolimnetic oxygenation could change the dissolved oxygen regimes in a deep lake in Finland, it did not significantly affect the lake's trophic status. Meanwhile, several researchers showed that hypolimnetic aeration and oxygenation are only temporarily effective in suppressing benthic soluble reactive phosphorus (SRP) release (Inoue et al., 2017; Nygrén et al., 2017). The effects could not be maintained without continuous hypolimnetic aeration/oxygenation operations, and there
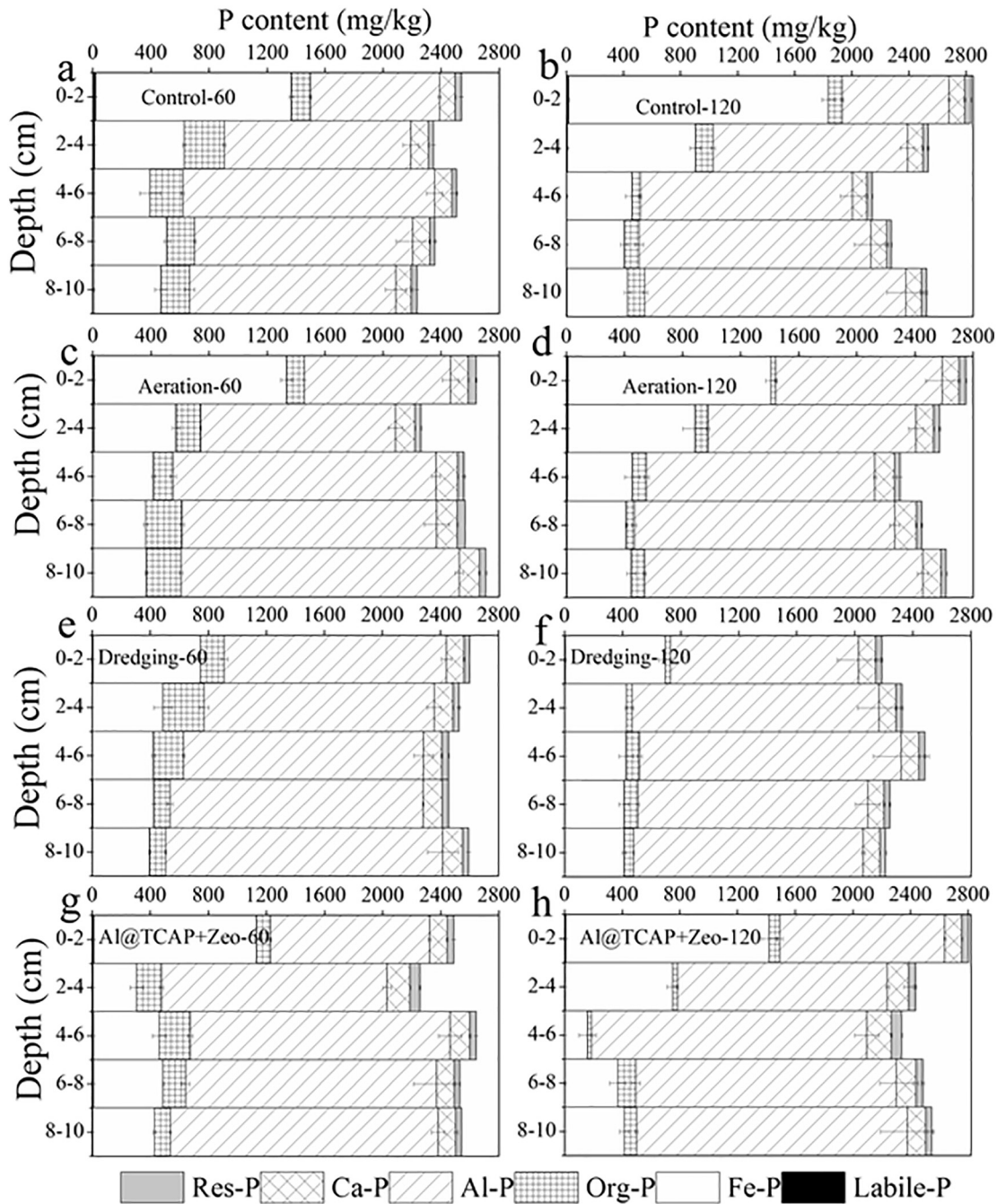
Fig. 4. Content of different P forms estimated at different sediment depths and at various times from different treatments.

would be a dramatic release of accumulated phosphorus at the sediment surface within a few days of discontinuing operations (Nygrén et al., 2017). Several previous studies showed that sediment dredging can improve water quality in water columns (Zhong et al., 2008; Yu et al., 2017; Chen et al., 2018). This is because the renewed sediment-water interface is now favorable for the sorption of phosphate from overlying water. The un-dredged sediment has a relatively larger sorption capacity compared to the upper polluted sediment and can remain saturated for a long period of time. However, factors such as sediment resuspension, external loading and the sedimentation of suspended particulate matter can reduce the efficiency of sediment dredging (Liu et al., 2016). Most importantly, the dredged sediment might require a large area of land for proper handling and disposal. In contrast, *in situ* inactivation is a simple method that has drawn a lot of attention in recent years (Lürling et al., 2016). The results of the present study indicated

that the addition of Al@TCAP + Zeo gave the best performance among the three remediation methods tested in the reduction of phosphate and total phosphorus in the water columns. The active layer formed by Al@TCAP + Zeo contains high amounts of aluminum that can continuously adsorb phosphate from overlying water and promote the formation of phosphate precipitation. However, bioturbation and sediment resuspension can also reduce the efficiency of the applied materials (Yin et al., 2018c).

4.2. Effects of different methods on pore water nutrient concentrations and their fluxes across the sediment-water interface

As indicated in Fig. 2, sediment dredging, aeration and *in situ* inactivation could significantly lower the phosphate concentrations in pore water found at the two sampling times. On average, dredging, aeration
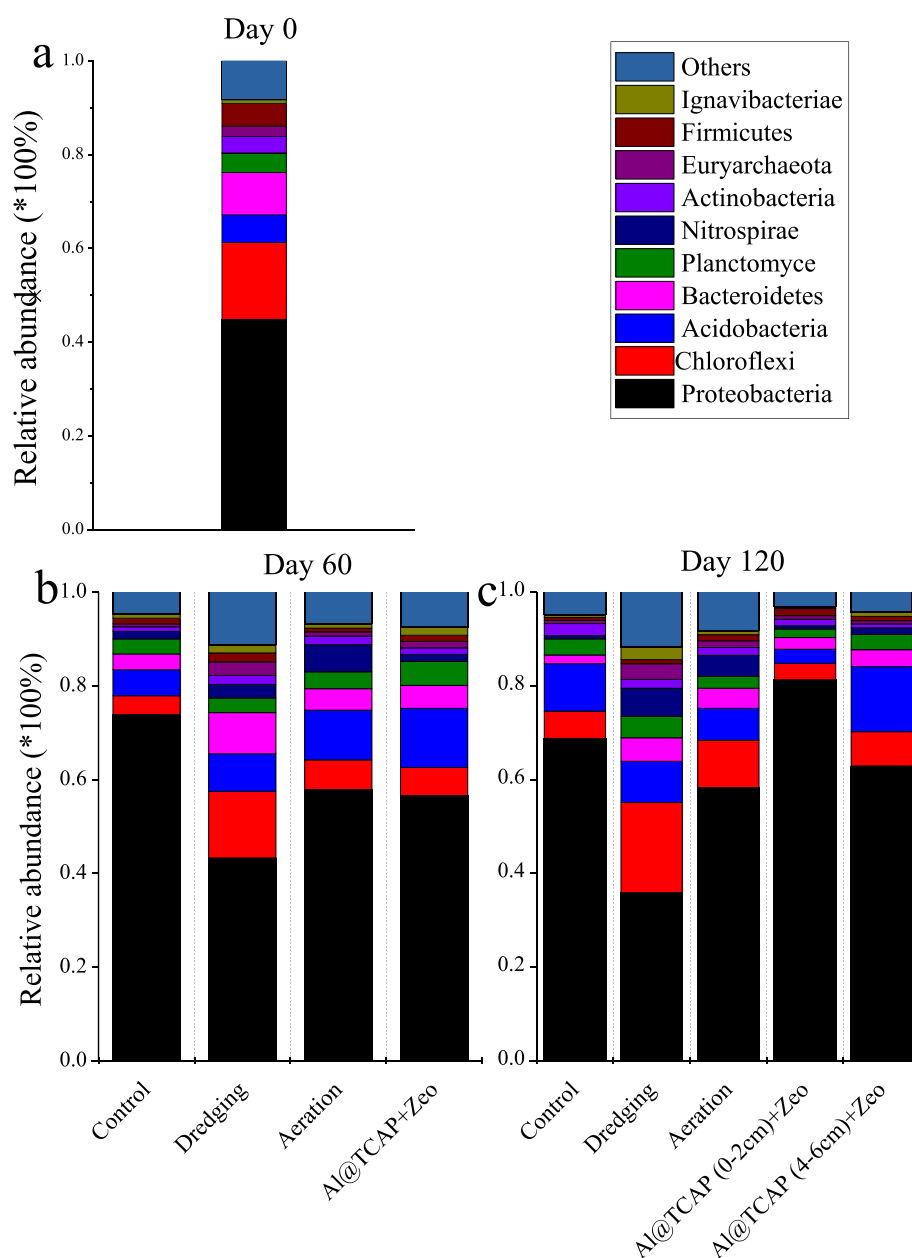
Fig. 5. Bacterial taxa identified in the surface sediments and clay contained sediment from various treatments.

and Al@TCAP + Zeo reduced P concentration in the pore water by 36.0%, 22.9% and 54.0%, respectively, compared to the control at day 120. This corresponds to reductions of the phosphate flux across the sediment-water interface in the three remediated sediments. It was observed that 63.5%, 45.6%, and 55.6% of PO_4^{3-} fluxes were reduced from dredging, aeration and Al@TCAP + Zeo respectively after 120 days' remediation when compared with P flux in the control sediment. Sediment dredging is usually used to remove the most polluted and organic-rich upper sediment layer and is always used in the sediment remediation from eutrophic lakes, rivers and wetland (Kleeberg and Kohl, 1999; Oldenborg and Steinman, 2019). In this study, sediment dredging performed the best among the three restoration measures when attempting to reduce phosphate fluxes in the sediment. These results were consistent with several findings showed that sediment dredging could decrease phosphate concentrations and also the concentration of ferrous ion (Fe^{2+}) in sediment pore water (Yu et al., 2017). Sediment dredging increased the P retention capacity and lowered the P supply ability from the dredged sediment (Yu et al., 2017). The

addition of Al@TCAP + Zeo could induce a comparable P flux reduction as sediment dredging. The application of iron, aluminum and calcium salts has been extensively used in eutrophic lakes for the management of internal P in the sediment (Hupfer et al., 2016). In recent years, a new P binding product, that is lanthanum modified bentonite (the commercial name is Phoslock®) is increasingly used in eutrophic lakes for P control (Lürling et al., 2016). This P binder works by forming a phosphate precipitation to immobilize P in sediment and pore water (Meis et al., 2013). In comparison, aeration was the least successful method to reduce the P fluxes in sediment. Continuous aeration can supply oxygen into the surface sediment and at the same time increase the penetration depth of oxygen in sediment. Liu et al. (2017a) found that with aeration, oxygen penetrates sediment to an average depth of about 1.79 mm. This promotes oxidation of ferrous iron into ferric ion in the sediment, hence increasing the sorption performance of P from pore water (Liu et al., 2017a).

Not all of the three methods used in this study were fully effective at reducing the ammonium concentration and its fluxes across the

sediment-water interface. An average of 34.1% and 56.3% of ammonium flux was reduced through the use of aeration and Al@TCAP + Zeo treatment respectively when compared with the control sample at day 120. However, the ammonium flux observed with the dredging treatment increased 3.38 times when compared with that of the NH_4^+ flux in the control sample. As has been discussed previously, ammonium concentration generally peaked at the deep sediment layers (15 cm to 25 cm or deeper) (Hou et al., 2018). Consequently, sediment dredging enhances the risk of ammonium release (flux) from the deep sediment (Lian et al., 2013). However, researchers also found that the flux of ammonium across sediment-water interface weakened greatly after more than a half year in a laboratory simulated dredged sediment incubation (Liu et al., 2017b). The addition of modified zeolite could be effective in suppressing the ammonium release from sediment by locking the pore water ammonium in its structure. Aeration treatment reduced the ammonium flux due to the oxidation of ammonium in the overlying water.

4.3. Transformation of sediment P and N forms after remediation

The results indicated that the three methods used in this study do not change the amount of extractable ammonium in surface sediment. However, the amount of extractable ammonium produced from the Al@TCAP + Zeo treatment increased greatly in the subsurface sediment over time when compared with the other treatments. This increase resulted from the ammonium in sediment pore water being trapped by the applied zeolite. However, the maximum content of extractable ammonium was not found in surface sediment, but was observed in the 2 to 4 cm layer and the 4 to 6 cm layer at day 60 and day 120, respectively. This vertical movement was caused by bioturbation in the river sediment. Previous field investigations indicated that several benthic organism such as Chironomus larvae or bloodworm and the oligochaete Limnodrilus (red worm) were frequently found in polluted river sediment (Zhang et al., 2018). The high density of these benthic organisms can greatly change the structure of the surface sediment. Normally, the materials were applied to the surface sediment and formed a 1 to 3 mm active layer. Continuous bioturbation would bury the applied material and push it deep into the sediment. This consequently increases the nutrient retention capacity of the material and is the main reason for the increase of the extractable ammonium in subsurface sediment over time. In contrast, no obvious difference of extractable nitrate in sediment was found among these treatments. These results indicated that the three methods could not change sediment nitrate content.

The results of P fractionation indicated that the content of mobile P decreased with the increase of sediment depth in the control. This form of P is regarded as sediment internal P loading and was found to positively correlate with the P flux across the sediment-water interface (Ding et al., 2015; Yin et al., 2017a). As shown in Fig. 4, the content of mobile P in surface sediment (0 to 2 cm) decreased as follows: Dredging < Al@TCAP + Zeo < Aeration ≈ Control over the two sampling times. The mobile P content in the sediment treated with Al@TCAP + Zeo remained the lowest at the 2 to 4 cm sediment layer when compared with the same layer from the other three treatments at day 60. Bioturbation continued to move the applied material into deeper sediment layers over time. It was noted that 63.9% of mobile P was reduced in the 4 to 6 cm sediment layer, which remained the lowest in this layer among the treatments at day 120. Sediment dredging appeared to be the best method to use to reduce internal P loading in the sediment followed by clay inactivation and aeration. In this study these methods all performed better at reducing internal P loading in surface sediment than in deeper sediment. The physical removal of the polluted and organic upper sediment was very effective in the control of internal P loading. In comparison, the addition of Al@TCAP + Zeo into sediment cores chemically changes mobile P into inert P forms such as Al-P and Ca-P. This method is beneficial for the long-term management of internal P in sediment. However, the vertical movement of the applied material should be given consideration when attempting long-term

sediment remediation. A re-occurrence of mobile P in surface sediment was observed at day 120 when compared with the initial application of the materials. Meanwhile, the aeration method seemed to have little effect on the transformation of P forms in surface sediment, which would reduce the content of organic P forms in the sediment through oxygenation.

4.4. Response of sediment microorganisms to different remediation methods

Compared with the control sample, the relative distributions of Nitrospira in the sediment increased when all three remediation methods were used at the two sampling times. Nitrospira are important nitrite-oxidizing bacteria (Ehrich et al., 1995), which play an important role in the bio-oxidation (nitrification) process of ammonium to nitrate (Dionisi et al., 2002; Freitag et al., 2006). This is beneficial for the transformation of ammonium to other forms and reduces its concentrations in the water column. In addition, a recent long-term core incubation experiment also found that sediment dredging can increase the abundance of Nitrospira in surface sediment and reduce the ammonium fluxes across the sediment-water interface (Liu et al., 2017b). Decreases in the abundance of Actinobacteria in surface sediment after these remediation measures indicated that the three methods used in this study promote the formation of good conditions (improved redox potential and reduction of pollutant) in surface sediment, which is beneficial for the improvement of water quality. As reported by Xu et al. (2014), an abundance of Actinobacteria in sediment is closely related to deteriorating conditions in sediment that can stimulate the release of odorous substances such as geosmin and 2-methylisoborneol. The rich abundance of Nitrospira in the 4 to 6 cm sediment layer at day 120 indicated that the addition of zeolite can maintain a high abundance of Nitrospira in the surrounding sediment and consequently reduce the concentration of ammonium in the sediment. These results were consistent with previous studies, which showed that nitrifying and denitrifying bacteria could significantly aggregate on zeolite and thereby inhibit ammonium release from the sediment (Xu et al., 2017; Du et al., 2018). However, bacteria can also assist in remediation of heavily polluted sediment, and this mutualistic symbiotic relationship with the improvement of water quality should be investigated further.

5. Conclusions

In this study, sediment dredging, intermittent aeration and in situ inactivation with modified clays were used to remediate internal loading from a seriously polluted black odorous river. The results of the simulated study indicate that all three methods could effectively lower TP and PO_4^{3-} in the water column. However, sediment dredging was initially not effective in reducing total nitrogen and ammonium in the water column. More than 45% of phosphate fluxes can be reduced by all three methods, while sediment dredging can induce a significant release of NH_4^+ from sediment. This indicates that caution should be taken if dredging is used to remediate river sediment with a high nitrogen content. All treatment measures do not influence surface sediment extractable nitrogen, but sediment extractable ammonium can be increased greatly in deeper sediment layers from the clay inactivation treatment. Among the three measures, sediment dredging is the most effective method with regard to surface mobile phosphorus reduction. In contrast, a large percentage of mobile phosphorus reduction was observed in deeper sediment layers over time from the clay inactivation treatment, which was a result of sediment bioturbation. The content of mobile phosphorus in surface sediment may be renewed over time using the clay inactivation treatment. Meanwhile, aeration seemed to have little effects on sediment P forms. The results of this study, therefore, indicate that clay-based in situ inactivation can simultaneously control the internal loading of phosphorus and nitrogen in the sediment of black odorous rivers. However, periodically dosing for clay

inactivation is necessary if sediment contain a high quantity of benthic organisms. Dredging is a promising method to control sediment internal P, but not N loading. Aeration might only affect the migration of nutrient concentrations in the water column but not in the sediment. Nevertheless, a guideline still needs to be established with regard to the work scope of various methods in the management of black odorous river sediment in the future.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2019.01.326.

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