Influence of water quality improvement on the remediation of river sediment with addition of calcium nitrate

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Abstracts: In-situ sediment remediation technique was often used to control the release of pollutants from sediment. Adding calcium nitrate to sediment has been applied to control the release of phosphorus from sediments. The lab experiments were carried out to investigate the influence of water quality improvement on the remediation of river sediment with adding calcium nitrate. The results demonstrated that the redox-potential of sediments increased from -282 mV to -130 mV after 28 d of calcium nitrate treatment. The acid volatile sulfide in the sediments significantly decreased by 54.9-57.1% and the total organic carbon decreased by 9.7-10.2%, but significant difference in both of them was not found with the water quality improvement. The lower phosphate concentration in the water column and intracellular phosphate in the sediment with adding calcium treatments was also found, indicating that calcium nitrate is beneficial to control the release of phosphorus from river sediment. The decrease in release of phosphorus might be attributed to the fixation of iron-phosphorus and calcium-phosphorus due to the addition of calcium nitrate. Calcium nitrate added to sediment caused the oxidation of sulfide to sulfate, resulting in higher nitrate and sulfate concentration in the water column and higher

intracellular nitrate and sulfate in the sediment. Water quality improvement only posed significant influence on the intracellular nitrate and sulfate concentration in the sediment.

Keywords: calcium nitrate, sediment, water quality, acid volatile sulfide, phosphorus, total organic carbon.

1. Introduction

For years, rivers have been used as receivers for domestic wastewater effluent, rainwater run-off, agricultural run-off, and industrial wastewater, resulting in severe degradation of water quality (Scholes et al., 2008). Accompanied with the rapid increases in economy and population in China, considerable amount of pollutants have been discharged into the rivers. The continuing pollution development for the water bodies will cause the black and odorous phenomenon when exceeding the water environmental carrying capacity, which mostly occurred in those water bodies with low flow rate or even static. Therefore, water pollution of urban rivers is becoming one of the largest threats to aquatic ecosystem in China.

Large amount of organic pollutants from wastewater is accumulated in the river sediment, and excessive degradation of organic matter will consume too much dissolved oxygen (DO), resulting in the hypoxia of sediment. Lower dissolved oxygen will then cause lower redox potential (ORP), leading to the microbial reduction of sulfate (SO_4^{2-}) to sulfide hydrogen (H_2S) in the sediment (Berner, 1970). A decrease in the ORP of sediment can also cause the reduction of iron (Fe) and manganese (Mn), resulting in the release of phosphorus (P) adsorbed on Fe and Mn oxide-hydroxide particles (Caraco et al., 1989; Schauser et al., 2006). Subsequently, Fe(II) in the water column and sediment will react with H_2S to form iron sulfide (FeS) due to its low solubility product, which was adsorbed on the organic particles, resulting in black color water and layer sediment. Furthermore, toxic substances such ammonia, H_2S and other odor of gaseous sulfur compounds were produced as a result of anaerobic respiration, leading to the odorous phenomenon along the river.

With the increasing concern, the water quality can be improved with the mitigation of external pollution sources and advanced treatment of wastewater. However, the sediments can continuously release pollutants to water column, delaying the recovery of eutrophic environments (Søndergaard et al., 2007). Previous researches indicated that eutrophic ecosystems might be recovered using in situ technologies, e.g., adding nitrate, aluminum, Fe and calcium (Ca) to the sediment (Ripl, 1976; Foy, 1986; Cooke et al., 1993; Kleeberg et al., 2000; Xu et al., 2008). The addition of these compounds to sediments can improve the oxidation conditions of the sediment and accelerate denitrification activity (Shimizu & Nakano, 2009). Ripl (1976) found that the biochemical oxidation for remediation was achieved by injecting calcium nitrate to sediment to control the P release from sediment for limiting the growth of algae in the lake.

Apart from controlling P release from sediment, the nitrate was also used to abate odors caused by sulfate reducing bacterial in wastewater (Jenneman et al., 1986; Jefferson et al., 2002; Jiang et al., 2009). Nitrate is reduced preferentially to SO_4^{2-} under anaerobic conditions. Thus, once nitrate is metabolized, a portion of organic matter is used to reduce SO_4^{2-} to S^{2-} (Jenneman et al., 1986). The acid volatile sulfide (AVS) concept was defined as the sedimentary S (reduced S) that is extracted by 1 mol/L HCl solution, including porewater sulfides and metastable FeS minerals (Berner, 1964). The AVS content in the sediment had a strong correlation with the sediment's color intensity, which could be used to assess the pollution of organically enriched sediment (Wilson and Vopel, 2012). Sulfur-containing odor compounds were also originated from AVS, and to some extent, AVS can be expressed as the source of odor and the potential production of H_2S . Thus, it is a meaningful and urgent task to reduce the AVS content in the sediment and to control the release of sulfur-related odor to the water column.

The P loading was considered to be the key role in eutrophication. The P release from anaerobic sediments often made up the major fraction of total P load in the lakes or rivers, and thus the reduction of an external P load by controlling the influent water quality may be insufficient (Cooker et al., 1993). Consequently, a remediation

planning for the control of P sources should be a priority. With the upgrading of wastewater treatment plant and mitigation of external pollution resource, the improvement of water column in the river will be realized. However, the improvement of polluted sediment will far less than that of water column. Therefore, the influence of water quality improvement on the sediment remediation will be investigated in this study, which is related to the influence of adding calcium nitrate on the AVS and P in the sediment.

2. Material and methods

2.1. Water and sediment sampling

The sediments and water samples used in this study were obtained from Shajing River (22°46'3", 113°49'52") in Shenzhen City, Guangdong Province. It is a tributary of the Maozhou River which flow into the Pearl River Estuary. Three specific sites were chosen to represent the overall water quality. The river flew slowly with 1.5-2.0 m depth, which received pollutants of rainfall runoff and occasionally industrial and urban wastewater from the sides of the river. Water samples were obtained from the middle zone of the river using water sampler made of glasses. Sediment samples were taken from the top 20 cm layer of three sites using piston column sediment sampler (purchased from Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences). The samples were homogenized and sieved to remove the detritus, plant residues, and plastic products. Collected samples were kept cool in a box contained ice cake, and was transferred to the lab immediately, stored at a temperature of approximately 4 °C until further experiments. Water quality characteristics of the sampling station are summarized in Table 1. The pH and ORP of sediment was 7.25 and -282 mV, respectively, accompanying with high AVS concentration of 5136 mg S kg⁻¹ and high TOC content of 90.4 mg kg⁻¹.

Table 1 Characteristics of Shajing River used in this study

	pH	DO	Eh	NH ₄ ⁺ -N	NO ₃ ⁻ -N	TN	PO ₄ ³⁻ -P	COD
Unit		mg L ⁻¹	mV	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹
Mean	7.26	0.26	-68.6	14.63	0.10	18.21	6.16	84.5
Std	0.05	0.04	12.2	1.17	0.02	0.86	1.21	15.0

2.2. Experimental design

Lab experiments were prepared in 1 L wide-mouth jars with screw top lids. Before the experiments, jars were put in sterilizing pot, and remaining 121 °C for 30 min. 250 g sediment and 800 mL water column was used in the jars, and each treatment was performed in triplicate. Four treatments were carried out: a control treatment which received no calcium nitrate (control); the sediments in other three treatments were all added with the same dosage of calcium nitrate at three dilution levels for water columns (100%, 90%, and 75%), which were shown in Table 2. Dilution indicates $[V_{\text{water column}} / (V_{\text{water column}} + V_{\text{pure water}})]$, which presents the improvement of water quality. The application dosage was 1 g calcium nitrate per 1 kg wet sediment based on the result of Chen (2013). To avoid the oxidation of sediment, nitrogen gas was injected to the jars when calcium nitrate solution was mixed with the sediment. The jars were closed during the whole experiments, which were performed at 25 °C in the incubator. Water samples were withdrawn 0, 1, 3, 6, 10, 15, 21, 28 d after the beginning of experiment, while sediment samples were withdrawn at the beginning and end of the experiment process. Nitrogen gas was injected to the flask to drive out oxygen prior to shaking. The diluted slurry was then centrifuged (7000 rpm min⁻¹), and the supernatant were filtrated through a 0.45 µm Millipore filters for measuring the NH₄⁺-N, NO₃⁻-N, PO₄³⁻-P, SO₄²⁻.

Table 2 Experimental design

Treatments	Experimental design
Control	Sediment & 100% water column
Treatment 1	Sediment & Ca(NO ₃) ₂ & 100% water column
Treatment 2	Sediment & Ca(NO ₃) ₂ & 90% water column
Treatment 3	Sediment & Ca(NO ₃) ₂ & 75% water column

2.3. Measurement method and statistical analysis

For determination of the dissolved nutrients, water samples were filtered through 0.45 μm Millipore filters before chemical analysis. The pH and DO concentration in the water column was measured using *Hach HQ40d* Dual Input Multi-parameter Meter. The $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, TN, $\text{PO}_4^{3-}\text{-P}$, SO_4^{2-} were analyzed by colorimetric analysis according to the standard methods described by the American Public Health Association (APHA, 1998), using a spectrophotometer.

The pH and ORP of the sediment was measured with *Hach HQ40d* Dual Input Multi-parameter Meter at a depth of 5 cm from the surface layer before and after the experiments. Dry weight was measured by drying sediment at 105 $^\circ\text{C}$ for 24 h. The intracellular ions in the sediment were extracted from sediments by preparing a 1:4 dilution of sediment sample and deionized water and shaking for 4 h with 200 rpm min^{-1} . Nitrogen gas was injected to conical flask with cover to keep hypoxia condition before shaking in the shaker. The AVS in the sediment was analyzed using the method described by Hsieh et al. (1997). Total organic carbon (TOC) in the sediment was measured with potassium dichromate – titration method (Schumacher, 2002). The fractional composition of TP (different P binding form) in the sediment was studied with the fractionation scheme according to Psenner et al. (1984). This sequential extraction method divides the TP of sediment into pools as shown in Table 3. The amount of P in each fraction is determined as TP described above. The difference between TP and the sum of the extracted pools is the residual P (P_{res}), consisting mainly of organic bound P.

Table 3 Sequential extraction method of different P binding forms in the sediment

Mark	Extraction / Time	Expected P Binding Forms
$\text{NH}_4\text{Cl-P}$	1.0 M NH_4Cl /2 h	Pore water P, Loosely adsorbed to surfaces.
NaOH-P	0.1 M NaOH /16 h	Inorganic P bound to Al
BD-P	0.3 M $\text{Na}_2\text{S}_2\text{O}_4/\text{NaHCO}_3$ /1 h	Redox sensitive P
$\text{H}_2\text{SO}_4\text{-P}$	0.25 M H_2SO_4 / 2 h	Ca bond P
P_{res}		Organic and other refractory P

The average values and standard deviations of three replicate samples were calculated and shown in this study. Statistical analysis (Two-way ANOVA) was performed to evaluate the significant differences between the means in the sediment

by using SPSS Statistics 19.0.

3. Results

3.1. Water parameters of water column

The pH value in the water column for all samples exhibited a transient increasing trend, and then began to decline consistently (Fig. 1a). The pH of the treatments with adding calcium nitrate all had a slightly higher pH values than those with control at 28 d. The mean pH value with the control was 6.82, whereas they were 7.08, 7.08, and 7.06 with treatment 1, 2, and 3, respectively. Neither adding calcium nitrate to sediment nor water quality improvement had obvious influence on the pH in the water column.

The DO values in the water column with control showed no significant variation during the whole experiment, but those with treatments all exhibited a sharply increasing trend during the first several days. The DO values with treatment 1 and 2 reached the highest values (2.03 and 2.64 mg L⁻¹, respectively) at 3 d, while treatment 3 (2.15 mg L⁻¹) at 6 d, and then all decreased to lower level at 10 d, keeping below 0.5 mg L⁻¹ towards the end of the experiment (Fig. 1b). Adding calcium nitrate to sediment only had influence on the DO values to some extent during the first several days, while water quality improvement had no obvious influence on the DO values.

Fig. 1. Variation of pH and DO in the water column (n=3)

The NO₃⁻-N concentration with control showed a slowly increasing trend, while they increased sharply at short-time (1 d) with calcium nitrate treatments, and began

to decrease until 10 d, and then increased again with the time (Fig. 2a). They increased to 8.8, 10.4, and 11.9 mg g⁻¹ at 28 d with the treatment 1, 2, and 3, respectively. Overall, the addition of calcium nitrate increased the NO₃⁻-N concentration in the water column, and the NO₃⁻-N concentration with treatment 2 exhibited the highest value (11.9 mg L⁻¹). The NH₄⁺-N concentration in the water column increased sharply during the initial stage of the experiment, reaching a maximum of nearly 40 mg L⁻¹ at 10 d, and after that, they began to decrease consistently (Fig. 2b). The NH₄⁺-N concentration with calcium nitrate treatments was a little bit higher than those of control at 28 d. The TN concentration had similar trend with NH₄⁺-N, reaching a maximum of 44.0, 47.6, 46.1, 46.1 mg L⁻¹ at 10 d, and after that, they began to decrease consistently (Fig. 2c). However, the TN concentration in the water column with control was slightly lower than those with treatments, and all of them reached the maximum values at 10 d.

Fig. 2. Variation of NO_3^- -N (a), NH_4^+ -N (b), TN (c), PO_4^{3-} -P (d), and SO_4^{2-} (e) in the water column (n=3)

The PO_4^{3-} -P concentration in the water column with control decreased during the initial period (1 d), and then increased consistently with time (Fig. 2d), reaching a maximum value of 2.4 mg L^{-1} at 10 d. After that, they exhibited a slowly declining trend, and decreased to 2.0 mg L^{-1} at 28 d. However, they all exhibited a decreasing trend with the treatment of adding calcium nitrate, and the PO_4^{3-} -P concentrations at 28 d were 1.2, 0.7, and 0.7 mg L^{-1} with treatment 1, 2, and 3, respectively. The SO_4^{2-} concentration in the water column decreased slowly from 98.5 to 79.3 mg L^{-1} with control, while they all exhibited an increasing trend with the treatment of adding calcium nitrate (Fig. 2e), reaching 138.1, 150.8, and 119.2 mg L^{-1} at 28 d with treatment 1, 2, and 3, respectively.

3.2. The intracellular ions in the sediment

The intracellular ions in the sediment are presented in Fig. 3. The intracellular NO_3^- -N concentration in the sediment with control increased from 6.1 to 7.1 mg kg^{-1} , while they significantly increased to 22.9, 18.1, and 19.0 mg kg^{-1} for the treatment 1, 2, and 3, respectively (Fig. 3a). The intracellular NO_3^- -N concentration in the sediment with treatment 1, 2, and 3 had significantly difference with those of control. Treatment 1 had largest influence on the intracellular NO_3^- -N in the sediment, which also had significant difference with those of treatment 1 and 2. The intracellular NH_4^+ -N in the sediment with control decreased from 646.7 to 472.7 mg kg^{-1} , while they reduced to 406.7, 385.3, and 393.0 mg kg^{-1} with treatment 1, 2, and 3 after 28 d,

respectively. The intracellular $\text{NH}_4^+\text{-N}$ in the sediment with control were all higher than those with treatment 1, 2, and 3 (Fig. 3b), and showed significant difference as compared with those with treatment 2 and 3.

Fig. 3. Comparison of intracellular $\text{NH}_4^+\text{-N}$ (a), $\text{NO}_3^-\text{-N}$ (b), $\text{PO}_4^{3-}\text{-P}$ (c), and SO_4^{2-} (d) in the sediment at 28 d after treatment (n=3)

The intracellular $\text{PO}_4^{3-}\text{-P}$ concentration in the sediment with control decreased from 2.44 to 2.00 mg kg^{-1} , while they reduced to 0.36, 0.27, and 0.41 mg kg^{-1} with treatment 1, 2, and 3, respectively. The intracellular $\text{PO}_4^{3-}\text{-P}$ in the sediment with treatment 1, 2, and 3 had significant difference with that of control. The intracellular SO_4^{2-} in the sediment with control increased from 787 to 813 mg kg^{-1} , while they increased to 1012, 1205, and 1201 mg kg^{-1} with treatment 1, 2, and 3, respectively. The intracellular SO_4^{2-} in the sediment with treatment 2 and 3 were significantly different from those with control, but showed no significant difference to that with treatment 1.

3.3. Variation of AVS and TOC in the sediment

Compared to control, the AVS content in the sediment all decreased significantly with the addition of calcium nitrate, and the AVS with treatment 1, 2, and 3 decreased from 5136 to 2205, 2313, and 2223 mg S kg⁻¹, respectively (Fig. 4a). However, no significantly difference was found among three treatments with different water quality. The variation of TOC in the sediment was presented in Fig. 4b. There is no obvious difference on the TOC content in the sediment with control (decreased from 90.4 to 88.1 mg kg⁻¹). The TOC content significantly decreased from 90.4 to 81.2, 81.6, and 81.2 mg kg⁻¹ with treatment 1, 2, and 3. Similarly, water quality had no significant difference on the TOC content in the sediment.

Fig. 4. Comparison of AVS (a) and TOC (b) in the sediment at 28 d after treatment (n=3)

3.4. Phosphorus fraction in the sediment

The distribution of different P binding forms after 28 d of adding calcium nitrate is presented in Fig. 5. The fraction of P binding forms changed, while water quality had no significant influence on them. There was no obvious difference in the NH₄Cl-P in the sediment with control, while they decreased from 62.95 to 5.32, 5.55, and 5.19 mg kg⁻¹ with treatment 1, 2, and 3, respectively. In the original sediment, most proportion of P is NaOH-P and H₂SO₄-P, while BD-P and NH₄Cl-P only account for a small fraction. After adding calcium nitrate, the amount of NH₄Cl-P in the sediment all decreased, while the amount of NaOH-P, H₂SO₄-P, and BD-P all increased. Furthermore, P_{res} exhibited a little decreasing trend with all treatments.

Fig. 5. Comparison of distribution of different P binding forms in the sediment at 28 d after treatment (n=3).

4. Discussion

4.1 Influence of water quality

It was observed that water quality in the water column had certain influence on the intracellular NO_3^- -N in the sediment and the NO_3^- -N concentration in the water column. Compared to treatment 1, higher NO_3^- -N concentration was found in the water column with treatment 2 and 3, indicating the improvement of water quality compared to treatment 1. However, water quality had little influence on the intracellular NH_4^+ -N in the sediment and the NH_4^+ -N and TN concentration in the water column. Furthermore, water quality posed no significant influence on the AVS and TOC in the sediment (Fig. 4). The PO_4^{3-} -P concentrations with treatment 2 and 3 at 28 d presented lower than that with treatment 1 (Fig. 2d). However, water quality had no significant influence on the variation of P fraction in the sediment. Similarly, with the improvement of water quality, lower intracellular PO_4^{3-} -P in the sediment with treatment 2 and 3 was observed compared to treatment 1, but significant difference was not found. It is indicated that variation of water quality had no obvious difference on the intracellular PO_4^{3-} -P in the sediment and the PO_4^{3-} -P concentration in the water column.

In theory, improvement of water quality will increase the diffusive flux at the sediment-water interface, leading to a higher release rate of pollutants from sediment. However, expected results were not found based on the variation of several major pollutants in the water column (Fig. 2). Although the addition of calcium nitrate posed obvious influence on variation of ions in the water column, water quality improvement had no obvious influence on the remediation of river sediment by adding calcium nitrate. Considering shorter incubation time (28 d) in this study, longer time will be required to assess the function of water improvement on remediating river sediment.

4.2 Influence of calcium nitrate

4.2.1. Sulfur

The AVS content in the sediment significantly decreased by 54.9-57.1% and the TOC in the sediment were decreased by 9.7-10.2% (Fig. 4). Janke et al. (2011) also presented that AVS content in the sediment reduced by 99% at 135 d. Yamada et al. (2012) found that the AVS content in the sediment significantly decreased by 99% with treatment of calcium nitrate. However, it was found that the AVS in the sediment was only reduced by 54.9-57.1% with the injection of calcium nitrate (Fig. 4), which exhibited lower content compared with above studies. The first reason might be the difference dosage of calcium nitrate, for the denitrification activity was proportional to the nitrogen concentration (Wang et al., 2007). Secondly, the loss of nitrate due to high water solubility of calcium nitrate into sediment interstitial water could not be directly measured, which might be estimated based on the increase in NO_3^- -N concentration in the water column and intracellular NO_3^- -N in the sediment. Lastly, it is also related with the shorter incubation time (28 d) compared to 145 d in the research of Yamada et al. (2012).

The reduction of AVS content in the sediment was mainly attributed to two reasons. The levels of sulfate reducing bacterial decreased during the prolonged exposure to an oxidizing environment and high N_2O concentration (Mahmood et al., 2007), and thus the microbial reduction of SO_4^{2-} to H_2S were inhibited. The ORP of the sediment with treatment 1, 2, and 3 in this study increased from -282 mV to -130,

127.4, and 128.2 mV, respectively, resulting in inhibition of sulfate reducing bacterial. While the decrease in the ORP of sediment was caused by the buildup of N_2O and NO produced, and the reduction in the amount of organic matter and the production of N_2 during denitrification resulted in an oxidized environment (Jenneman et al., 1986). The second reason is that nitrate acts as an electron acceptor, and the sulfide in the sediment was oxidized to SO_4^{2-} with the existence of nitrate (Ripl, 1976; Jenneman et al., 1986). Jiang et al. (2009) thought that sulfide is oxidized in two steps under anoxic condition with adding nitrate. The first step was the oxidation of sulfide to S and then the further oxidation of elemental sulfur to SO_4^{2-} . The two steps occur sequentially with the second step occurring primarily after sulfide depletion, and the first step is considerably faster than the second one. This inference could be supported by the increase in the SO_4^{2-} concentration of water column (Fig. 2e) and intracellular SO_4^{2-} in the sediment (Fig. 3d). Janke et al. (2011) also stated that oxidation of sulfide increased the SO_4^{2-} concentration and the availability of iron and manganese, previously complexed as FeS and MnS (the predominant forms of AVS), resulting in the reduction of AVS.

The addition of nitrate also caused the oxidation of organic matter (Ripl, 1976; Jenneman et al., 1986). Huang et al. (2010) also illustrated that the TOC in the sediment decreased by 10.5 and 9.5% in reactor with 140 and 70 $\text{g NO}_3^- \text{-N m}^{-2}$, which is in accordance to our results. By the degradation of organic matter, containing N and P compounds are apparently released with a similar ratio (Sinke et al., 1990), contributing to higher N and P concentration in the water column.

During the later stage of experiment, the color of the upper sediment was gradually turned from dark to yellowish orange color. This indicates the presence of oxide-hydroxides of Fe (III) that replaced reduced forms of Fe (II) (Yamada et al., 2012). Furthermore, the formation of calcium phosphate in the sediment due to addition of calcium nitrate might also contribute to the change of surface sediment layer. The color of deeper layer sediment might be also changed as the reaction progress, which could be seen in the research conducted by Yamada et al. (2012). With the variation of sediment color, the release of containing-sulfur odor will be

expected to be reduced significantly due to the addition of calcium nitrate.

4.2.2. Phosphorus

The results demonstrated that the addition of calcium nitrate caused the variation of P fraction in the sediment, leading to a decline in the PO_4^{3-} -P concentration in the water column. The recycling of P from the bottom sediment into the water column can be affected by numerous factors, such as pH, ORP, mineralization, and microbial activities (Boström et al., 1998; Burley et al., 2001) and in various places different factors can be dominant. The P concentration in the water column was directly attributed to the combination of mineralization of organically bound P and desorption/dissolution of redox-sensitively bound P, both of which are the most important P mobilization processes in sediments (Schauer et al., 2006). Mineralization is a temperature controlled process, while desorption/dissolution of redox-sensitively bound P is mainly redox-controlled, mainly bound to iron oxyhydroxides (Schauer et al., 2006). Thus, the variation of P with the addition of nitrate in this study was mainly caused by the latter reason. They also thought that the release potential of P in the sediment can be estimated using profiles of the labile P fractions NH_4Cl -P, BD-P, and NaOH-P. In the Lakes Volvi and Koronia of Greece, the Ca-P (HCl -P) showed the largest contribution to the sedimentary inorganic P-loads (Kaiserli et al., 2002), and the study thought that iron compounds and organic matter seem to play a significant role in regulating the NaOH-P budget. Comparatively, it was found that most P fraction in the river sediment is NaOH-P and H_2SO_4 -P in our study.

It was observed that the PO_4^{3-} -P concentration in the water column with control exhibited an increasing trend. The reason might largely be that the release of P from mineralization of organically bound P is dominant compared to desorption or sedimentation of P in the water column. However, input of calcium nitrate increased the ORP of the sediment, leading to the formation of Fe(III) and SO_4^{2-} . The calcium added and Fe(III) released in the sediment contributed to the increase of H_2SO_4 -P and BD-P in the sediment, but the decrease of NH_4Cl -P (labile fraction P), leading to lower P release rate from sediment. As a resquence, calcium nitrate added to the

sediment resulted in decreasing $\text{PO}_4^{3-}\text{-P}$ concentration in the water column. In our study, the fraction of NaOH-P increased because a reoxidation of Fe(II) occurs in oxygenated water with subsequent co-precipitated with $\text{Fe}(\text{OH})_3$ and adsorption of PO_4^{3-} with Fe(III) (Ripl-1976; Cooker et al., 1993; Gonsiorczyk et al., 2001, Janke, 2011), while the fraction of $\text{H}_2\text{SO}_4\text{-P}$ increased due to the formation of Ca-P compounds. Further, the stability of Fe-P compounds is strongly dependent on changes in the redox state.

4.2.3. Nitrogen

Compared to control, injecting calcium nitrate to river sediment significantly increased the $\text{NO}_3^-\text{-N}$ concentration in the water column and intracellular $\text{NO}_3^-\text{-N}$ in the sediment, which might exert new potential risk for aquatic environment. Our results are shown to be in line with some previous studies (Feibicke et al., 1997; Yamada et al., 2012). Yamada et al. (2012) found that the $\text{NO}_3^-\text{-N}$ concentration in the interstitial water and water column with the treatments were significantly higher than in the controls because of solubility and loss of calcium nitrate $\text{NO}_3^-\text{-N}$ concentration in the water column increased due to the continuous release of nitrate added. The highest $\text{NO}_3^-\text{-N}$ concentration was 285 mg L^{-1} at 85 d, while there was a reduction of approximately 87% in the $\text{NO}_3^-\text{-N}$ concentration after this period towards the end of the experiments, for the nitrate added was denitrified after several weeks and very low level of nitrate were observed. The highest $\text{NO}_3^-\text{-N}$ concentration in the water column in this study (11.9 mg L^{-1}) is rather lower than those of experiments mentioned above, and the reason might be the difference in the dosage of calcium nitrate. Furthermore, our results did not present the submit point and decreasing trend like above, which might be attributed to the shorter incubation time (28 d) compared to 145 d in the above research.

The intracellular $\text{NH}_4^+\text{-N}$ in the sediment reduced after the end of experiment irrespective of treatments, and they all exhibited lower than that of control at 28 d (Fig. 3a). This can explain the result that the $\text{NH}_4^+\text{-N}$ concentration in the water column increased during the initial stage (10 d). Furthermore, the formation of $\text{NH}_4^+\text{-N}$ might be linked to the dissimilatory reduction in anoxic and sulfide-containing environment

(Brunet & Garcia-Gil, 1996). A similar result was also found in the research of Yamada et al. (2012), who found that the $\text{NH}_4^+\text{-N}$ concentrations in the water samples with calcium nitrate treatment were significantly higher than that of control, and the highest $\text{NH}_4^+\text{-N}$ concentration also occurred at 5 d after the addition of calcium nitrate. In our study, the $\text{NH}_4^+\text{-N}$ concentration in the water column decreased after 10 d, which might also be correlated to the continuous ammonia volatilization loss and the transformation of $\text{NH}_4^+\text{-N}$ to N_2 .

According to the results of Yamada et al. (2012), the addition of calcium nitrate significantly increased the TN concentration with nitrate treatment at 0 d. However, the TN differences between control and treatment microcosms were not significant at 145 d. In our study, it was also observed that adding calcium nitrate increased the TN concentration in the water column at 28 d. In our research, gas bubble was also observed during the whole experiments. The result that Foy obtained in his experiments (Foy, 1986) indicated that denitrification to N_2 was the dominant reaction. Gas bubbles indicated the occurrence of intense denitrification process due to the addition of nitrate, which could explain the reduction of TN in the water column.

4.3 Prospect

In previous researches, calcium nitrate solution was injected for remediation of sediment. However, several problems existed during this process. Firstly, it is difficult to accurately inject the calcium nitrate to the estimated position in the sediment due to the fluidity of calcium nitrate solution. Secondly, the release of nitrate to water column is high due to its high water solubility, resulting in high loss of nitrate in the sediment. Wauer et al. (2005) ever produced a new developed compound, consisting of Fe(III) and nitrate, which is able to reduce the release rate and high solubility of nitrate to water, prolonging the availability of nitrate in sediment due to the strong desorbing capacity. In agriculture, coated fertilizer is produced to release nutrients in a controlled and delayed manner according to the requirement of plants for nutrients. Thus, they provide enhanced nutrient use efficiency with higher yields and lower fertilizer leaching and loss. The development of controlled coated urea can reduce

nitrogen loss caused by volatilization and leaching (Liang and Liu, 2006; Ni et al., 2011). Similarly, coated granulated calcium nitrate is expected to reduce the soluble loss of nitrate in sediment and to enhance its remediation efficiency by prolonging its reaction time, which will be further evaluated later. Up to now, few researches paid attention to the potential application of granulated calcium nitrate in sediment remediation (Søndergaard et al., 2000).

5. Conclusions

Injecting calcium nitrate to river sediment improved the ORP of the sediment, resulting in transformation from anoxic to oxidizing sediment environment. The AVS content in the sediment were significantly reduced by 54.9-57.1% due to oxidization of sulfide, and thus higher intracellular SO_4^{2-} content in the sediment and SO_4^{2-} concentration in the water column was observed. The color of the upper sediment was gradually turned to yellowish orange color due to the addition of calcium nitrate, which would contribute to control the containing-sulfur odor. Adding calcium nitrate improved the binding capacity for P in the sediment and reduced the release of P from sediment, leading to lower P concentration in the water column. Adding calcium nitrate to sediment also caused higher NO_3^- -N concentration in the water column and intracellular NO_3^- -N content in the sediment. Water quality improvement had limited influence on the remediation of sediment with calcium nitrate, which only posed significant influence on the intracellular nitrate and sulfate concentration in the sediment.

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