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RESEARCH ARTICLE

Effects on inorganic nitrogen compounds release of contaminated sediment treatment with in situ calcium nitrate injection

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Abstract Notable releases of nitrate, nitrite, and ammonia are often observed in contaminated sediment treatment works implementing in situ calcium nitrate injection. In order to provide extended information for making best decision of employing this in situ sediment remediation technology, in this study the releases of nitrate, nitrite, and ammonia from the sediment after the calcium nitrate addition operation was investigated in column setups designed to simulate the scenarios of a stagnant water (e.g., a pound or small lake) and a tidal-influenced water (e.g., a river mouth), respectively. Comparison with published aquatic toxicity data or authorized criteria was conducted to assess if there is any toxic effect that might be induced. Along with the vigorous N_2 emission due to the denitrification reactions which occurred in the treated sediment, external loaded nitrate, intermediately produced nitrite, and indigenous ammonia in the sediment showed being mobilized and released out. Their promoted release and fast buildup in the overlying water to an excessive level probably cause toxic effects to sensitive freshwater living species. Among them, the potential ecological risk induced by the promoted sediment ammonia release is the greatest, and cautions shall be raised for applying the calcium nitrate injection in ammonia-rich sediments. The caused impacts shall be less violent in a tidal-influenced water body, and comparatively, the continuous and fast accumulation of the released inorganic nitrogen compounds in a stagnant water body might impose severer influences to the ecosystem until being further transferred to less harmful forms.

Keywords Sediment remediation · Calcium nitrate injection · Nitrogen release · Ammonia · Toxic effects · Stagnant water

Introduction

Contaminated sediment is a major problem in water bodies having received pollutants from urban, industrial, agricultural, and other anthropogenic sources. The concentrations of nutrients, toxic chemicals, and toxin-forming microbes are often found much higher in the contaminated sediment than in the overlying water column (Murphy et al. 1999). Remediation of contaminated sediment has gained much attention in the past decade since it has been recognized that substantial improvement in the quality of the overlying water often cannot be achieved if without appropriate contaminated sediment treatment. Among various options for sediment treatment including dredging, capping, and in situ treatment, in situ sediment treatment is becoming attractive in recent years to be used in well-characterized sites to minimize the potential risks and maximize the positive effects.

Several types of chemicals or biological agents have been applied in in situ sediment treatment through directly injecting into the contaminated sediment, such as electron acceptors (e.g., calcium nitrate or ferric salts) (Renholds 1998; Chan et al. 2004), external carbon sources (e.g., methanol, acetate, etc.) (Yuan et al. 2001; Perelo 2010), and bioaugmentation agents (e.g., inoculated microbial organisms) (Tam and Wong 2008), for the purposes of odor control, nutrient inactivation,

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and organic contaminants bioremediation. Calcium nitrate is one of the most used agents injected into the sediment being treated. Its application was well documented as early as 1976 (Ripl 1976) for controlling sediment phosphorus release and degrading organic matters. In the past two decades, in situ injection of calcium nitrate has been applied in a number of field sediment treatment projects and showed effectiveness in phosphorus release suppression (Feibicke 1997; Wauer et al. 2005), odor mitigation (Murphy et al. 1999; Chen et al. 2013), organic contaminants biodegradation (Murphy et al. 1995; Babin et al. 2003), and organo-mercury regulation in contaminated sediments (Todorova et al. 2009; Matthews et al. 2013).

Most of the studies reported so far on the use of calcium nitrate injection for in situ sediment treatment focused on assessing its treatability towards specific pollutants and examining the remediation performance in field. Information addressing the potential risks or problems associated with the operation of this technology is rather few. Some studies indicated that heavy metals speciation might be altered after calcium nitrate injection, resulting in a possible increase in their mobility and hence toxicity (Shao et al. 2009). Besides the potential risk aroused by heavy metal species transformation, nitrate released from the calcium nitrate injected sediment might be of greater concern since remarkable increase in aqueous nitrate concentration was often recorded after the injection operation (Ripl 1976; Feibicke 1997; Yamada et al. 2012). The degree of sediment nitrate release relates not only to the treatment effectiveness of this technology (Fang et al. 2008), but also to whether there is intolerable nitrate toxicity imposed to aquatic living species (Camargo et al. 2005). Additionally, apparent elevation in aqueous nitrite and ammonia concentrations was also often observed soon after calcium nitrate injection operation (Foy 1986; Feibicke 1997; Søndergaard et al. 2000; Yamada et al. 2012). These two nitrogen compounds might be produced through denitrification or reduction of the external added nitrate (Koike and Sørensen 1988). When their concentrations exceed a certain level, they might have toxicity to aquatic living species (Philips et al. 2002; Camargo and Alonso 2006). These observations raise a need of further investigating the technology from the perspective of the releases of inorganic nitrogen compounds (i.e., nitrate, nitrite, and ammonia) from the sediment and the associated potential risks that might be brought by calcium nitrate injection operation.

This study involved a pre-assessment of applying in situ calcium nitrate injection at an urban river (hereafter “the target river”) in Shenzhen, China, for the purpose of sediment odor mitigation, since previous field project has shown very positive results of using this technology to control sediment odors (Babin et al. 2003; Chan et al. 2004). Series of calcium nitrate addition-based sediment treatment experiments were carried out in column and batch setups using samples collected from the target river. The column experiments were designed to simulate two scenarios: (1) a stagnant water body (e.g., a pound or small lake) and (2) a tidal-influenced water body (e.g., a river mouth). For assessing the treatability, the removal of sediment acidic volatile sulfides (AVS) and total organic carbon (TOC) contents was examined in the experiment because they are often used to indicate sediment odor-inducing capacity and organic pollutant contamination. Moreover, the variations of overlying water nitrate, nitrite, and ammonia concentrations in the columns were investigated. Comparison of their concentrations with published aquatic toxicity data or authorized criteria was conducted to assess if there is any toxic effect that might be induced. Gas emission during the calcium nitrate treatment process was monitored for characterizing its effects on inorganic nitrogen compounds release. Upon the purposeful evaluation of inorganic nitrogen compounds release after calcium nitrate addition, extended information could be provided to local authorities for making best decision related to employing the in situ calcium nitrate injection technology for contaminated sediment remediation.

Materials and methods

Sediment and water samples

The sediment samples used in this study were collected at an urban river in Shenzhen, China. This river had been a receptor of industrial and municipal wastewater discharged without appropriate treatment in 1980~1990s. Water quality of this river has been improved in recent years due to the implementation of stringent wastewater discharge regulations. The contaminated sediment, as a sink for accumulated pollutants, is now considered as a limiting factor for river restoration. Odor emission is the most conspicuous problem brought by the contaminated sediment, which is believed to be caused by the decomposition of sediment organic pollutants under anoxic conditions. In anoxic environment, much of organic sulfur or sulfate is transformed to odor-causing sulfides. As often used in field practices (Babin et al. 2003; Chan et al. 2004), the sediment odor-inducing capacity was evaluated in this study by measuring AVS content in the sediment. Higher AVS concentration indicates stronger odor-inducing capacity.

River sediment and water samples were collected within 1 week ahead of starting the experiments. River water was firstly collected by pumping from mid-depth of the river (about 1.5 m) to plastic containers. Then, sediment samples were collected at the same location using a grab sampler at 0–0.5 m depth below the river bed. The collected sediment samples were immediately sealed in polyethylene bags, with squeezing air out to preclude sediment oxidation. Both sediment and water samples were stored in a dark cold room at 4 °C after delivered to the laboratory and until conducting experiments. Prior to carrying out experiment, sediment samples were pretreated by removing litters such as twigs and gravels, and homogenized in N_2 atmosphere.

Column experiment

Two series of sediment remediation experiments were conducted in plexi glass-made columns for evaluating inorganic nitrogen compounds releases associated with calcium nitrate injection operation. There were four columns used in each column experiment: column A, column B, water reference column, and sediment reference column. Columns A and B were treatment columns operated in duplicate. Their setups in column experiments 1 and 2 are illustrated in Fig. 1. At the beginning of the experiment, known amount of calcium nitrate solution was added into quantified wet sediment to achieve a final nitrate concentration of 2,500 mg N L^{-1} wet sediment and followed by moderate mechanical stirring. Subsequently, aliquots of the calcium nitrate-added sediment were moved into the treatment columns to a designed height, and then covered by a thin layer of sediment without adding calcium nitrate. After that, the collected river water was slowly pumped into the column up to a designed height. Finally, the columns were covered with light-resistant canvas and stood in ambient temperature (25–30 °C).

Column experiment 1 was conducted to simulate the scenario of a stagnant water body (e.g., a small lake or a pond). In this paper, stagnant water refers to a water body whose flow velocity over the sediment can be negligible, and its surface flow velocity is small (<0.1 m s^{-1}) under the effects of wind (Sarneel et al. 2014). The depths of overlying water and sediment in column experiment 1 were designed proportionally based on an assumed small lake with 1.5 water depth and 0.5 m sediment depth subject to treatment. In the experiment, except aliquots (about 500 mL) of the overlying water in columns were sampled regularly for chemical analysis, no additional water was drained out or replenished in. Column experiment 2 was carried out to simulate the scenario of a tidal-influenced water body (e.g., a river mouth). In this paper, "tidal-influenced" refers to a water body with a marked characteristic of cyclical fluctuation. The depths of overlying water and sediment in column experiment 2 were set proportionally based on the real average water and sediment depths in the downstream of the target river. The real average levels of slack tide and low tide level are 3.5 and 2.6 m, respectively. The tidal range of slack tide to low tide is 0.9 m, and the average tidal current velocity is 0.5 m s^{-1}. The depth of sediment needing treatment is 0.75 m. The height of the overlying water in columns was usually kept at the line simulating the slack tide level (Fig. 1b). For simulating tidal fluctuation, a daily operation of draining the water to the low tide level line and then replenishing stored river water to the slack tide level line was conducted in column experiment 2. To minimize their effects on sediment resuspension, the flow rates of water draining and replenishing in column experiment 2 were controlled at about 500 mL min^{-1} using peristaltic pump. Little sediment resuspension was observed at this flow rate. Except there was no sediment used in the water reference columns and no calcium nitrate added in the sediment reference columns, all other experimental procedures for the water reference and sediment reference columns were same as those

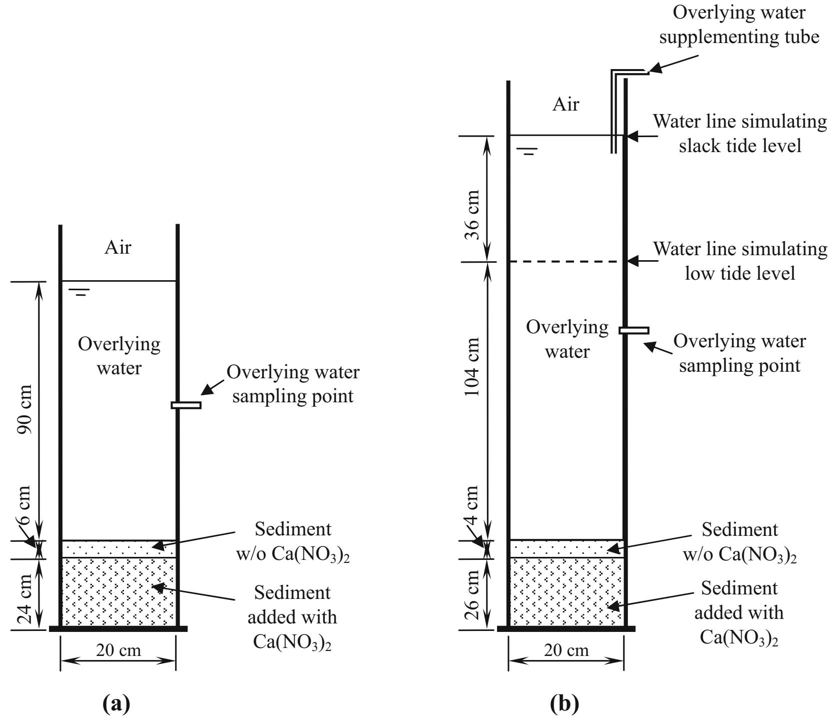

Fig. 1 Diagram illustrating the setups of treatment columns used in **a** column experiment 1 and **b** column experiment 2

for the treatment columns in column experiments 1 and 2. The experimental time was 14 days, typically for a calcium nitrate injection operation period. AVS and TOC contents in the sediment were determined before and at the end of the experiment.

Batch experiments

A series of batch experiments, consisting of a treatment set and a control set, were carried out in 1 L conical beakers in parallel with the column experiment. The variation of sediment ORP and gas generation during the 14-day sediment treatment process were monitored in the batch experiments. At the beginning of the experiment for the treatment set, known amount of calcium nitrate solution was added into quantified wet sediment to achieve the same final nitrate concentration as in the column experiment and followed by moderate mixing. Subsequently, 800 mL of the calcium nitrate-added sediment was moved into each conical beaker, and in turn 200 mL of deionized water was slowly added prior to sealing the beaker by a rubber stopper. A group of beakers were used for monitoring sediment ORP. At every monitoring event, two beakers were opened to stop the experiment, and the ORP value of the sediment inside was measured. Another pair of beakers was used for monitoring gas generation. The released gas was collected in a sampling bag connecting to the beaker head space through a glass tube penetrating the rubber stopper. The collected gas was regularly drawn and gauged using glass syringes. The sampled gas was further subject to the determination of N_2 concentration. Except no calcium nitrate addition, all other experimental procedures for the control set were the same as those for the treatment set.

A supplementary batch experiment using calcium peroxide (CaO_2) to treat the sediment was conducted in 1 L conical beakers. This experiment included a treatment set and a control set. The variation of sediment AVS content, gas generation, and overlying water ammonia concentration were monitored in the 14-day sediment treatment process. At the beginning of the experiment for the treatment set, 200 mL wet sediment was placed into each conical beaker, and then added with quantified CaO_2 powder to achieve a final concentration of 8.78 g kg^{-1} wet sediment, and followed by gentle mixing. After that, 800 mL of deionized water was added into the beaker before sealing the beaker by a rubber stopper. At regular monitoring event, two beakers were opened, and the overlying water and the sediment within them were moved out in sequence and subject to further analyses. The experimental procedure for the gas generation monitoring beakers was the same as in calcium nitrate treatment batch experiment, but no determination of N_2 concentration was conducted. Except no CaO_2 addition, all other experimental procedures for the control set were the same as those for the treatment set.

Another supplementary test was performed to estimate the content of indigenous ammonia in the sediment without any remedial treatment. 100 ml of wet sediment was moved into a 1 L conical beaker before adding 900 mL of deionized water. The sediment and water in the beaker were kept stirred using a magnetic stirring bar for 180 min. Aliquots of the mixture were sampled every 30 min for determining aqueous ammonia concentration after solid liquid separation.

Materials

Calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) used in this study was industrial grade with a purity of >99.0 %. Its solution was prepared by dissolving $Ca(NO_3)_2 \cdot 4H_2O$ in powder form into deionized water. CaO_2 used was reagent grade and directly added into sediment in its powder form. All other chemicals used for chemical analyses were reagent grade.

Analytical methods

The concentrations of nitrate, nitrite, and ammonia in water samples were determined following the methods outlined in Sections 4500-NO_3^- B, 4500-NO_2^- B, and 4500-NH_3 F of the *Standard Method* (APHA 1998), respectively, and expressed as nitrogen (i.e., mg N L^{-1}). AVS and TOC contents in sediment samples were analyzed following a USEPA method (USEPA 1991) and by a TOC analyzer (Shimadzu TOC-L solid module), respectively. Sediment ORP was measured using an ORP meter (YSI 100). The amount of N_2 in gas samples was determined by a gas chromatography analyzer with thermal conductivity detector (GC-TCD, Shimadzu).

Results and discussion

AVS and TOC removal

The mechanism of applying calcium nitrate to mitigate sediment odor lies in supplying an alternate electron acceptor to the contaminated sediment. When adding calcium nitrate, the occurrences of denitrification reactions, conversion of odor-causing sulfides to sulfate, degradation of organic pollutants, and improvement of the reducing conditions in the sediment are expected (Murphy et al. 1995; Babin et al. 2003). The changes of AVS and TOC contents in the sediment before and at the end of the column experiment are shown in Table 1. In both column experiments 1 and 2, over 94 % reductions in sediment AVS content were recorded in all calcium nitrate treatment columns. Comparatively, in sediment reference columns where there was no calcium nitrate addition, the decreases in sediment AVS content can be ignored. The significant removal of AVS observed in the calcium nitrate

Table 1 Changes of AVS and TOC contents in the sediment before and at the end of the column experiment

Experiment	Parameter			
	AVS (mg S kg^{-1} dry sediment)[a]		TOC (% dry weight)[a]	
	Before the experiment	At the end of the experiment (day 14)	Before the experiment	At the end of the experiment (day 14)
Column experiment 1				
Sediment reference	2,884.45±78.05	2,817.69±62.32	3.46±0.10	3.27±0.04
Column A		170.82±14.22		3.12±0.13
Column B		134.27±17.65		2.95±0.06
Column experiment 2				
Sediment reference	2,858.95±92.05	2,747.64±37.37	2.72±0.06	2.65±0.11
Column A		97.48±26.67		2.45±0.12
Column B		78.06±26.18		2.21±0.17

[a] Uncertainties shown in the table are standard deviations with sample size *n*=3

treatment columns announced the effectiveness of oxidizing sulfides in the sediment and suggested the feasibility of injecting calcium nitrate to mitigate sediment odor in the target river. TOC content is an indicator of the degree of organic pollutant contamination in the sediment. The decreases in TOC contents in the calcium nitrate-treated sediments were marginal compared to those of AVS. Only about 9~19 % decreases in sediment TOC were determined in column experiments 1 and 2 (Table 1). Note that the biodegradability of TOC in sediment primarily depends on the characteristics of organic pollutants and the contamination source and history. Wastewater discharged into the target river was much reduced in recent years, the readily decomposed parts of organic pollutants accumulated in the sediment might already be broken down. The residual fractions shall be much more refractory and hard to degrade in a short time after calcium nitrate addition (Chan et al. 2004). Thus, compared to the fast removal of AVS, the breakdown of sediment TOC was neglectable in the 14-day long experiment.

In the parallel batch experiment, the variations of sediment ORP and the amount of gas generated in the treatment process were monitored. After adding calcium nitrate, sediment ORP gradually increased from −340 to −70 mV (Fig. 2a) showing an apparent improvement of the reducing condition in the sediment. Visual observation on the sediment also displayed a progressive change from a blackish to a brownish color after adding calcium nitrate (Supplementary Information, Figs. S2 and S3), suggesting the transformation of sulfides to oxidized forms. Formation and detachment of gas bubbles were observed starting on day 5 and till day 10 after calcium nitrate addition, resulting in a remarkable increase in the amount of gas collected (Fig. 2b). The dominant fraction of the collected gas was determined as N_2. While in other experimental days, the degree of gas release in the calcium nitrate treatment set was similar to that of the control set. Coupling the ORP and gas generation data, it can be seen that the kinetics of transition from reducing condition to more oxidized condition was faster in the first 7 days of the experiment, and in this time span N_2 generation from sediment was becoming more and more intense. These results indicated that the increase of sediment ORP was accompanied by denitrification reactions that are believed to be sulfide-driven autotrophic denitrification and predominantly functioning when using calcium nitrate to treat contaminated sediment (Shao et al. 2011).

Nitrate release

In all water reference and sediment reference columns, overlying water nitrate concentrations ranged between 0.2 and 1.5 mg N L^{-1} (Figs. 3a and 4a), below a proposed safe level (i.e., 2 mg N L^{-1}) (Camargo et al. 2005) for protecting the most sensitive freshwater living species. In contrast, nitrate concentrations in the overlying water of all treatment columns were observed already at a comparatively high level (>12 mg N L^{-1}) at the beginning of the experiment. It is a hardly avoidable consequence of the operation of adding calcium nitrate into the sediment, which would more or less disturb and loosen the sediment and hence facilitate the fast diffusion of nitrate into the overlying water column. In the experiment, overlying water nitrate concentrations in treatment columns of column experiments 1 and 2 ranged in 12 to 60 mg N L^{-1} (Fig. 3a) and 12 to 35 mg N L^{-1} (Fig. 4a), respectively. Aqueous nitrate concentration at this level exceeds a recommended safe level (i.e., 10 mg N L^{-1}) (Camargo et al. 2005) for freshwater living species based on a comprehensive review of nitrate toxicity data. It implies a potential risk of incurring intolerable nitrate toxicity towards sensitive aquatic organisms when calcium nitrate injection operation is implemented towards the sediment.

In column experiment 1, overlying water nitrate concentration in column A kept increasing in a gradual manner to near 23 mg N L^{-1} at the end of the experiment (Fig. 3a), reflecting a steady diffusion of nitrate from the sediment. On the contrary, overlying water nitrate concentration in column B showed a

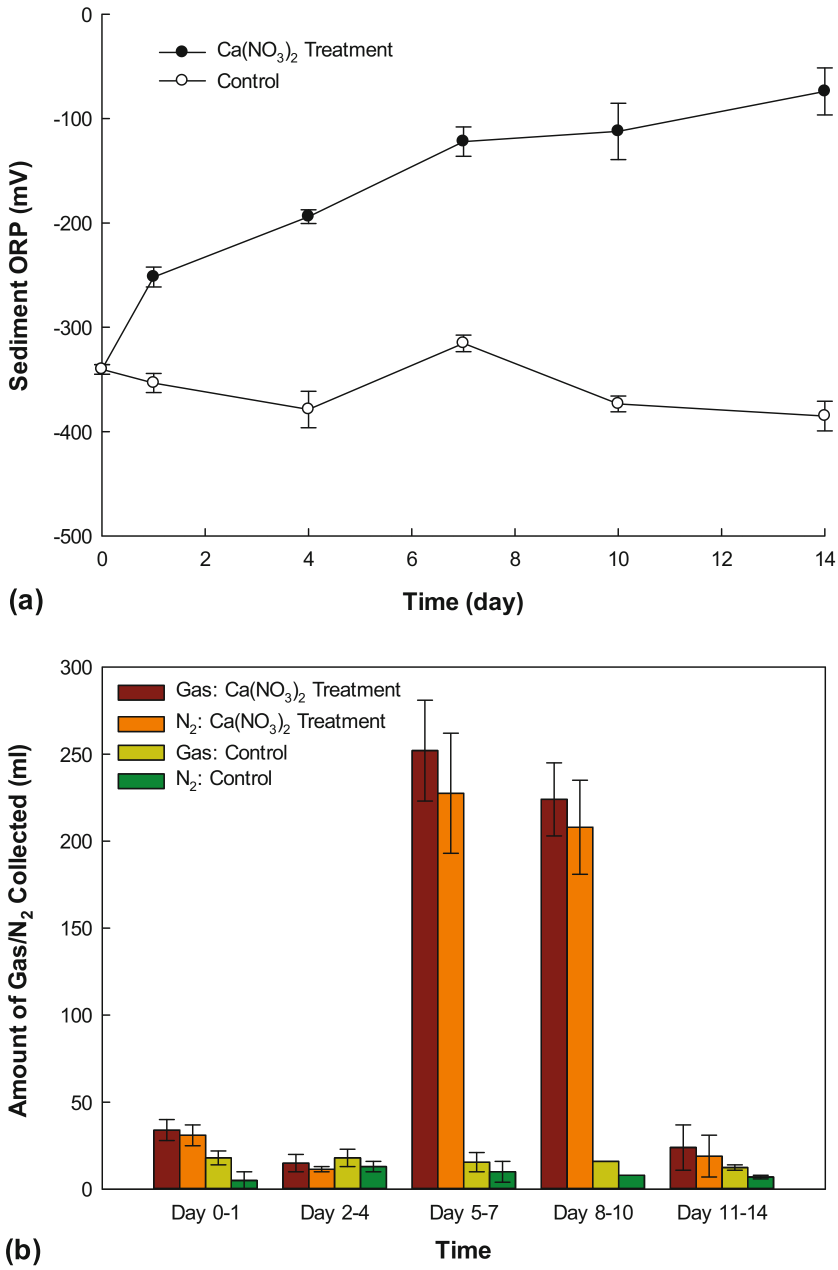

Fig. 2 Changes of **a** sediment ORP and **b** the amount of gas/N_2 collected in the batch experiment of sediment treatment with adding $Ca(NO_3)_2$

significant elevation starting on day 5 and reached near 60 mg N L^{-1} at the end of the experiment. It might be attributed to the vigorous gas release that occurred in the calcium nitrate-treated sediment. As shown in Fig. 2b, vigorous release of N_2, the dominant denitrification product, was recorded during day 5 to day 10 of the treatment process. Fine gas bubbles were visually observed formed in sediment in that time, and eventually agglomerated to form larger ones and finally detached and emitted out from the sediment. The releasing of gas caused local disturbance and resulted in vertical developments of cracks in the sediment (Supplementary Information, Figs. S2 and S3). When the cracks penetrate through sediment pores enclosing calcium nitrate solution, nitrate inside is very likely to be mobilized and finally "blew" out by the emitted N_2 via the cracks. Although not assessed in the experiment, it is recognized that bioturbation by benthic organisms might be able to cause the sediment turnover and hence chemical release (Hedman et al. 2008), though may not be as intense as N_2 emission. Since sediment is a heterogeneous medium, the external added calcium nitrate and the N_2 generated in denitrification reactions cannot evenly distribute in it. The apparent difference in the variations of overlying water nitrate concentrations in columns A and B manifested such heterogeneity. Column experiment 1 was designed to simulate a scenario of a stagnant water body. The relatively high overlying water nitrate concentration experienced in column A

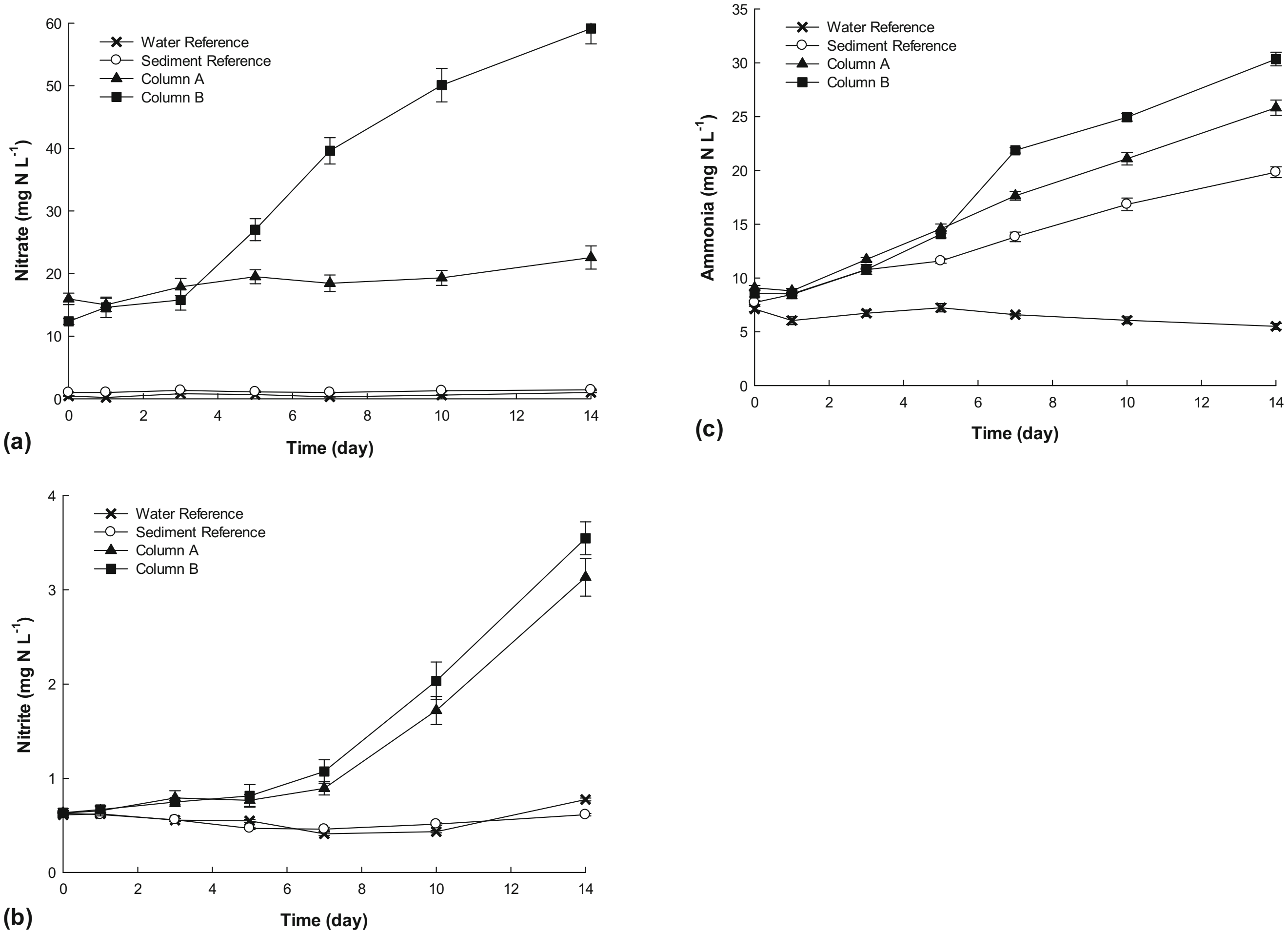

Fig. 3 Changes of the concentrations of **a** nitrate; **b** nitrite; and **c** ammonia in overlying water in the columns of column experiment 1 along with time

raised a concern about nitrate accumulation in the stagnant water body soon after implementing calcium nitrate injection until the excessive nitrate is further denitrified or assimilated by algae and bacteria. Though the toxicity of nitrate in aquatic ecosystems is considered being less than ammonia and nitrite (Camargo and Alonso 2006), the fast buildup of aqueous nitrate to an excessive level is likely to cause short-term damages to sensitive freshwater living species such as invertebrates and amphibians (Camargo et al. 2005; USEPA 2010), and therefore deserves attention.

Column experiment 2 was designed to simulate a scenario of a tidal-influenced water body, and a daily water renewing operation was performed to mimic the tidal fluctuation (see Column experiment). The variations of overlying water nitrate concentrations in columns A and B of column experiment 2 were similar (Fig. 4a), but differed with those in column experiment 1. Overlying water nitrate concentrations experienced an apparent elevation (>24 mg N L^{-1}) during day 5 to day 10, and then decreased to about 12 mg N L^{-1} at the end of the experiment. Similar to column experiment 1, the reason for the notable increase in aqueous nitrate concentration observed on day 5 might be owed to the promoted nitrate release aroused by vigorous N_2 emission. The highest overlying water nitrate concentration was around 35 mg N L^{-1} and much lower than that in column experiment 1. It shall be due to the regular water renewing operation conducted in column experiment 2, by which the overlying water solutes were diluted every day. It suggested that the buildup of aqueous nitrate and associated risks caused by calcium nitrate injection operation in a tidal-influenced water body are less severe compared to in a stagnant water body. To mitigate the possible violation of aqueous nitration concentration against the safe level, besides real-time onsite water quality monitoring, precaution engineering measures such as constructing sheet pile enclosure in the remediation zone at early stage and carrying out calcium nitrate injection in divided periods can be considered to implement during the remediation works.

Nitrite release

As shown in Figs. 3b and 4b, in both column experiments 1 and 2, overlying water nitrite concentrations in treatment columns were apparently higher than those in water reference

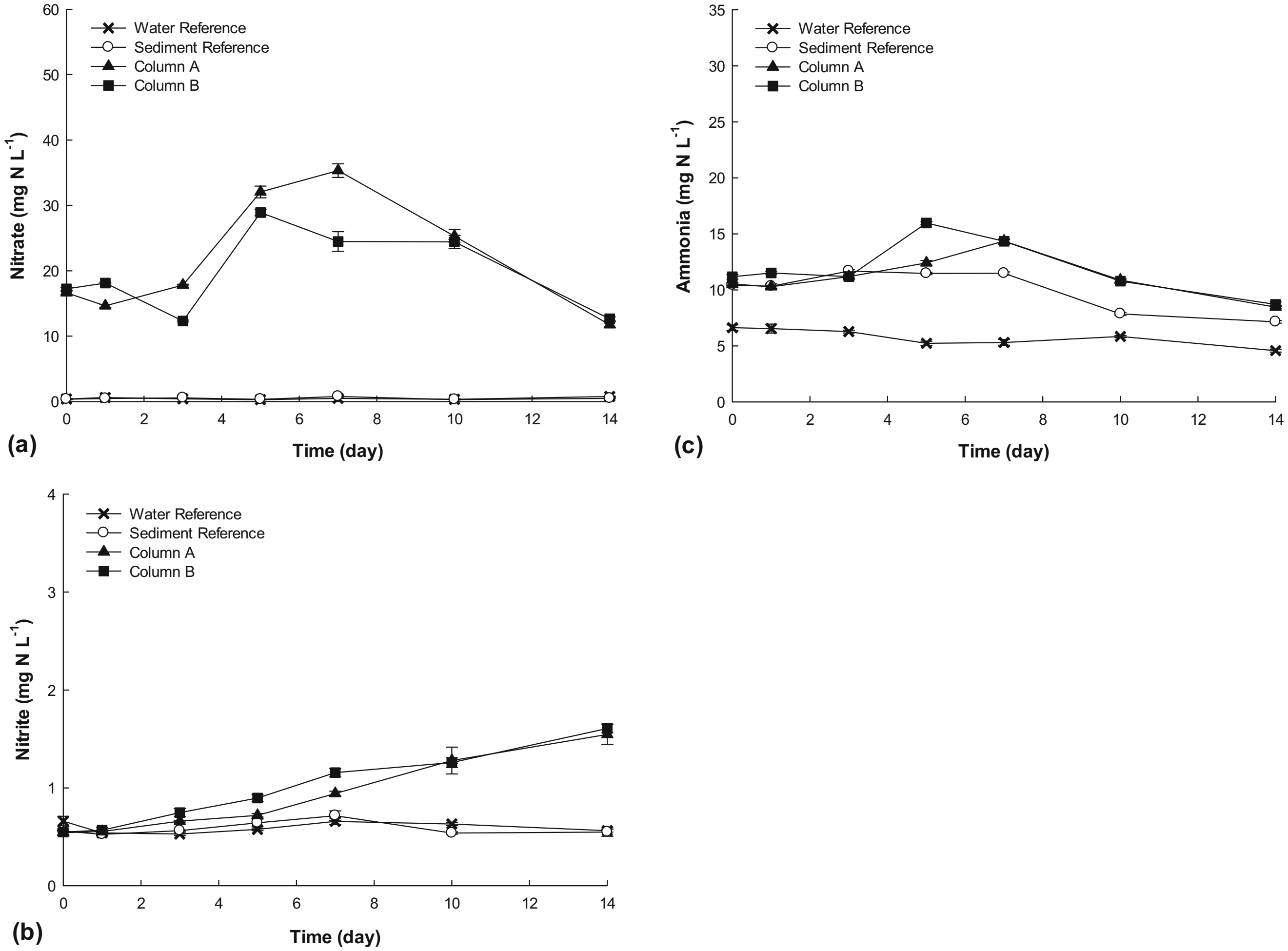

Fig. 4 Changes of the concentrations of **a** nitrate; **b** nitrite; and **c** ammonia in overlying water in the columns of column experiment 2 along with time

and sediment reference columns. It is believed a result of nitrite release from the calcium nitrate-treated sediment to the overlying water column. Nitrite is a common intermediate product of denitrification and nitrate reduction to ammonium in anoxic environments (Koike and Sørensen 1988). Overlying water nitrite concentrations in treatment columns of column experiments 1 and 2 ranged in 0.5 to 3.5 mg N L^{-1} (Fig. 3b) and 0.5 to 1.6 mg N L^{-1} (Fig. 4b), respectively. Aqueous nitrite concentration at this level is similar to what was observed in a previous study examining the adverse consequences caused by using calcium nitrate to immobilize sediment phosphorus (Yamada et al. 2012), and evidenced can cause toxic effects towards sensitive freshwater invertebrates and fishes (Philips et al. 2002; Camargo and Alonso 2006; USEPA 2010). Overlying water nitrite concentrations in the treatment columns of column experiment 1 were apparently higher than those of column experiment 2 in the later stage (day 7 to 14) of the experiment. It reflected the difference in nitrite buildup between water columns simulating a stagnant water body and a tidal-influenced water body, and indicated the risks associated with aqueous nitrite buildup brought by calcium nitrate injection operation are of more caution in a stagnant water body.

Ammonia release

Overlying water ammonia concentrations in the water reference columns of both column experiments 1 and 2 were around 6 mg N L^{-1} throughout the experiment (Figs. 3c and 4c). It exceeded the criteria of surface water quality of China (2 mg N L^{-1}) and the aquatic life ambient water quality for freshwater of the USA (1.9 mg N L^{-1} for chronic toxicity) (USEPA 2013). Such exceedance indicates that wastewater discharged into the target river has not been totally ruled out yet. This is not uncommon for a river experiencing fast urbanization and receiving pollutions from municipal and industrial sources and nonpoint source runoff, in which the potential ecological risk from ammonia exposure is often found the greatest among the chemicals of concern (Chen 2005). Overlying water ammonia concentrations in the sediment reference columns were observed obviously higher than in the water reference columns, implying notable ammonia accumulation in the untreated sediment. It was confirmed in a supplementary test (Supplementary Information, Fig. S4), and the indigenous ammonia content was estimated to be 465 mg N L^{-1} wet sediment. The indigenous sediment ammonia would easily release into the overlying water when encountering disturbance like the stirring operation performed at the beginning of the experiment.

Overlying water ammonia concentrations in the treatment columns were found further higher than those in the sediment reference columns of both column experiments 1 and 2 (Figs. 3c and 4c). Two reasons were considered responsible for this observation. One is due to the promoted indigenous sediment ammonia release caused by the vigorous N_2 emission (similar to the reason for the observed remarkable nitrate release), and the other is the occurrence of dissimilatory nitrate reduction to ammonium (DNRA) in the sulfides bearing sediment as suggested in previous studies (Søndergaard et al. 2000; Yamada et al. 2012). To further distinguish which reason dominated, a supplementary batch experiment was carried out to treat the sediment samples by adding CaO_2, in which there was no calcium nitrate addition and hence DNRA should not occur. CaO_2 has been used to enhance bioremediation of contaminated sediment by releasing oxygen and then improving its reducing condition (Nykänen et al. 2012). The results revealed a good correlation between the variations of the amount of gas collected (O_2 was believed to be the dominant fraction) and the changes of overlying water ammonia concentration (Fig. 5). Coupling the observed correspondence between the variation of gas (N_2 or O_2) emission and the increase pattern of overlying water ammonia concentrations and the fact that there was much amount of ammonia present in the sediment, the promoted release of indigenous ammonia from the sediment led by the vigorous N_2 emission shall be the dominated reason. Nevertheless, the contribution of DNRA to the increased overlying water ammonia concentrations cannot be excluded because this process probably proceeds via a chemolithoautotrophic pathway using sulfides as the electron donor (Brunet and Garcia-Gil 1996; Giblin et al. 2013) which is abundant in the sediment used in the study.

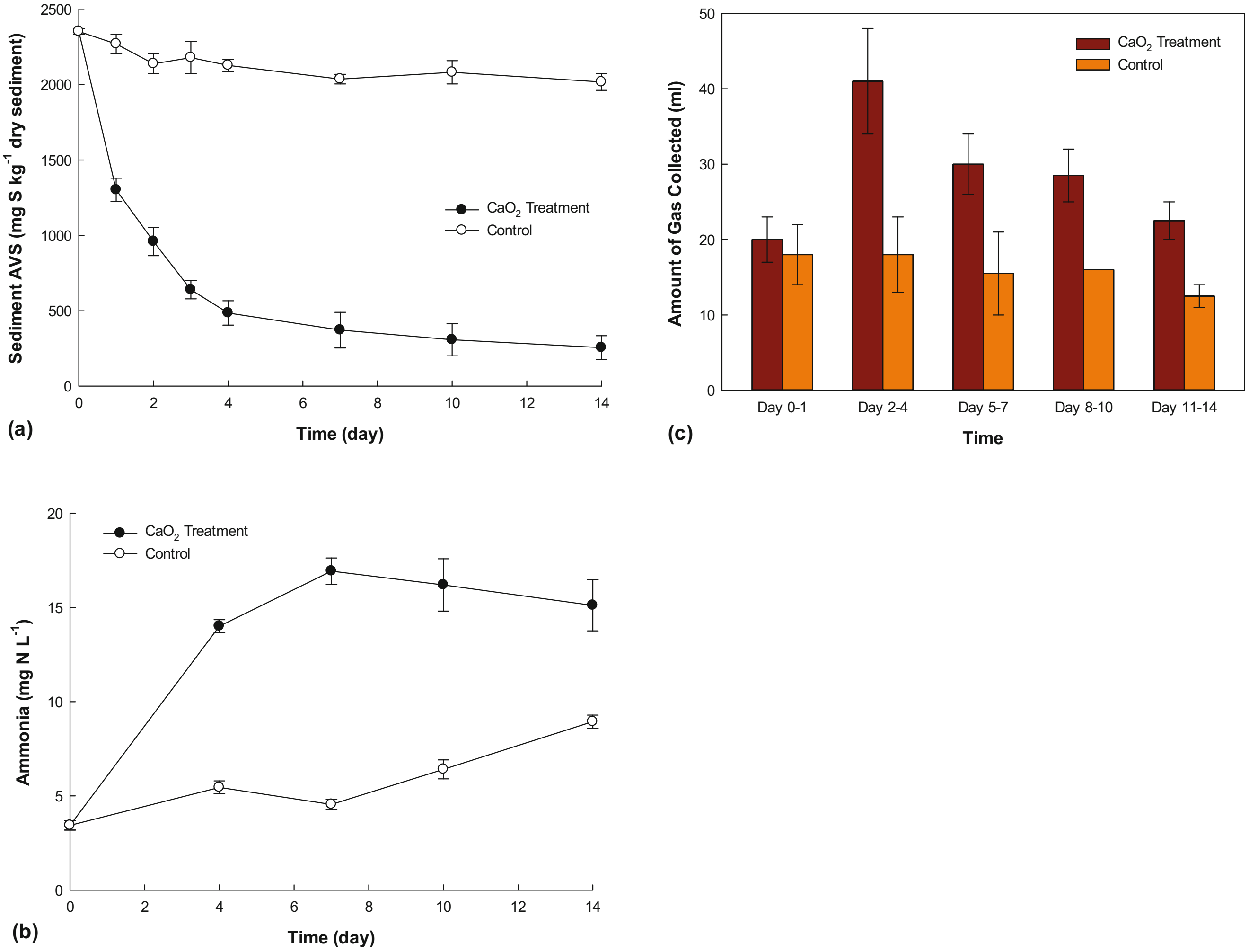

Fig. 5 Changes of **a** sediment AVS concentration; **b** overlying water ammonia concentration; and **c** the amount of gas collected in a batch experiment of sediment treatment with adding CaO_2

In column experiment 1, the continuous buildup of overlying water ammonia was experienced in the treatment columns (Fig. 3c). On day 7 of the experiment, overlying water ammonia concentrations in both columns A and B were already higher than 17 mg N L^{-1}, the acute criterion recommended by USEPA (2013) for protecting freshwater aquatic living species against ammonia toxicity, and then reached up to 30 mg N L^{-1} at the end of the experiment. In column experiment 2, the overlying water ammonia concentrations in the treatment columns reached a highest level on day 5 to 7 and shifted downwards. The peak overlying water ammonia concentration recorded in column experiment 2 was below the acute criterion (17 mg N L^{-1}) of USEPA (2013). It seemly reflected that the impact to freshwater aquatic living species resulted from sediment ammonia release caused by calcium nitrate injection would be less violent in a tidal-influenced water body (simulated in column experiment 2) than in a stagnant water body (simulated in column experiment 1). Despite the difference in their variation pattern, overlying water ammonia concentrations in all the calcium nitrate treatment columns kept above 8 mg N L^{-1} throughout the experiment, suggesting cautions still shall be paid on the promoted ammonia release when applying calcium nitrate injection in a remediation site with ammonia-rich sediment.

Conclusions

Calcium nitrate addition showed effectiveness in oxidizing sulfides and feasibility for mitigating odor of contaminated sediment collected from an urban river. Based on the fact that denitrification reactions are the predominant functioning process when in situ calcium nitrate injection is used to treat contaminated sediment, vigorous N_2 emission from the treated sediment would take place in a short time (about 5 to 10 days) after the addition of calcium nitrate. Along with the gas emission, inorganic nitrogen compounds, including external loaded nitrate, intermediately produced nitrite, and indigenous ammonia present in the treated sediment would be mobilized and “blew” out into the overlying water column, and hence result in their fast buildup in the overlying water. When their aqueous concentrations go up to an excessive level, it probably causes toxic effects to sensitive freshwater living species. Compared to published aquatic toxicity data or authorized criteria, the potential ecological risk induced by the promoted sediment ammonia release into the overlying water is the greatest, and therefore important cautions are raised for applying the calcium nitrate injection technology in a remediation site with ammonia-rich sediment. The caused impacts shall be less violent in a tidal-influenced water body where aqueous solutes would be periodically diluted by tidal fluctuation, and comparatively, the continuous and fast accumulation of released inorganic nitrogen compounds in a stagnant water body might impose severer influences to its ecosystem until these chemicals being further transferred to less harmful forms.

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