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Evaluation of heavy metals stability and phosphate mobility in the remediation of sediment by calcium nitrate

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Abstract

The injection of oxidants is one of the useful remediation technology for eliminating hydrogen sulfide (H₂S) and ammonia (NH₃/NH₄⁺) in aquatic sediments. In the current work, the impact of calcium nitrate injection on the release of heavy metals associated with phosphate was evaluated in a column test of sediment with overlying water at a volume ratio of 1: 1 for 131 days. Sulfide was significantly oxidized by calcium nitrate, as its amount was reduced substantially by 85% from the 20th to the 30th day, with a decrease in the oxidation-reduction potential to -68 mV and a simultaneous increase in pH to 9.83. Over 50% of the mobile Zn, Pb and Cu were reprecipitated in the sediment when the phosphate was partially released. It is proposed that the heavy metal immobilization was related to the phosphate content in the pore water due to the precipitation of heavy metals and phosphorus on the surface of Fe hydroxide particles after oxidation. This is supported by chemical

fraction analysis of the heavy metals in the sediment, which indicated increased residual fractions of heavy metals. Our results provide an insight into the remediation of sediment by oxidation with a self-stabilization of heavy metals and phosphate.

Practitioner points

Effective removal of sulfide after calcium nitrate injection was achieved

Metal immobilization was related to the phosphate content in pore water

Over 50% of mobile Zn, Pb and Cu might be reprecipitated in sediment

Oxidizable fraction of heavy metal predominantly transformed to its residual fraction

Keywords

Heavy metal; Nitrate calcium; Iron oxyhydroxide; Phosphorus; Redox immobilization; Sediment

1 Introduction

Black-odorous water bodies, such as highly eutrophic small creeks near industrial zones, have attracted much attention by environmental researchers and governors. The anaerobic sediment in creeks releasing high concentrations of sulfur and ammonia is predominantly responsible for the black-odorous water (He et al., 2017; Yin, Yang, & Kong, 2019). Various technologies have been applied to the solution of the odor problem in creek (Liu, Zhang, Mao, & Yan, 2016). Among these technologies, the injection of calcium nitrate has been identified as an in situ treatment approach to rapidly improve the water quality of creeks since it was introduced by Ripl in 1976 (Ripl, 1976; Wang, Wang, & Zhang, 2018). In the remediation processing, the calcium nitrate (5.2-256 g N/m³) dosed in the system took part in oxidation reactions with pollutants such as organic matter, sulfide, and ammonia in the anaerobic sediment (He et al., 2017; Lin et al., 2015; Liu et al., 2017; McGuire et al., 2002). Meanwhile, the change of chemical properties within the sediment results in the release of heavy metals (Li, Arocena, Zhang, Thring, & Li, 2017). Similar phenomena were found in the mobility of phosphate in the sediments in eutrophic waters, which described the phosphate releasing in the remediation process (Ma, Zhu, Yang, & Li, 2017). Therefore, the mobility of heavy metals and phosphorus is an important issue in the remediation of sediments when considering the application of calcium nitrate (Wu, Qi, & Xia, 2017).

As known, the migration of heavy metal in contaminated sediment is relative to its species (Ali & Khan, 2018; Guan et al., 2016). Different factors such as the oxidation-reduction potential (ORP), sulfur and pH affect the transfer and biogeochemical cycling of heavy metals in the environment (Ali & Khan, 2019; Ali, Khan, & Ilahi, 2019; Li et al., 2017). A low ORP makes iron oxides unstable and reduces the binding of

associated heavy metals, increasing the possibility of sediment-water transfer as the ORP is reduced (Liu et al., 2017). With low ORP values (Eh), however, the binding of cadmium (Cd) and zinc (Zn) was enhanced in the presence of carbonate (Guo, Delaune, & Patrick, 1997) and the binding capacity of As, Cd, Cr and Zn was also enhanced by sulfide and organic matter. Chen et al. (2007) showed that heavy metals coprecipitated with calcium as double hydroxides such as $(\text{Ca}_2\text{Cr}(\text{OH})_7 \cdot 3\text{H}_2\text{O})$, $\text{Ca}_2(\text{OH})_4\text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ which was immobile. In fact, sulfur in sediment is high sensitive to the calcium nitrate. When it is oxidized and removed, sulfur-associated heavy metals would possible release into the overlying water (Jonge, Teuchies, Meire, Blust, & Bervoest, 2012). The percentage of heavy metals associated with reducible fraction and oxidizable fraction was decreased with the treatment of calcium nitrate (Ou, Sun, & Xu, 2013). Therefore, the species changing of heavy metals should be investigated with the soil physical-chemical properties, which may lead to their migration from sediment to water. Moreover, the mobilization of phosphorus was affected by many factors, including Eh, pH, microbial activity and hydrodynamics (Bai, Deng, Cui, & Ouyang, 2007; Kang, Peng, Tian, & Zhang, 2018; Liu et al., 2012; Wang et al., 2013). Boström, Persson, and Broberg (1988) found that the high pH would weaken the P-binding capacity of Al and Fe compounds. Phosphorus release was inhibited by calcium nitrate through changing its status in the sediment. Two possible routes were proposed (Ruban & Demare, 1998; Yamada et al., 2012): (1) Fe(II) is oxidized to amorphous Fe(OOH) after the injection of calcium nitrate, which has larger surface adsorption sites and a stronger adsorption force with phosphorus than Fe(II); and (2) the releasing metal ions form less soluble apatite minerals with dissolved phosphate in the interstitial water. Accordingly, it is proposed that the migration of heavy metals in the remediation of sediment via calcium nitrate has effect on the phosphate releasing. However, the interaction between phosphorus and heavy metals after adding calcium nitrate has not been introduced in available literature. Thus, a synergistic effect of heavy metals and phosphate needs to be taken into account.

The purpose of this investigation was to estimate the impact of remediation on the potential release of heavy metal associated with phosphate after injecting calcium nitrate. Changes in the sulfur and iron contents, the Eh and the pH in the sediment were measured. A further investigation on the coordinated behavior between the phosphorus and heavy metals was conducted. The results provide insight into the oxidation strategy for sediment remediation and the governance of heavy metal pollution and eutrophication in water.

2 Materials and methods

2.1 Sampling and pretreatment

The sediment and overlying water samples were collected from Puhuitang Creek, Shanghai, China. This creek is a branch of the Caohejing River, which cross the Central Business District (CBD) of the city. The geographical coordinates are 31°10'34.7"N, 121°25'34.4"E. This area is in an industrial park with over 20 manufactories. The creek was heavily contaminated by the discharge of wastewater from industry plants nearby. There was a large amount of heavy metals in the sediment. The anaerobic degradation of organic matter in the sediments led to black water and the emission of odor. The overlying water was filtered by a 0.45 µm membrane. The interstitial water was obtained by the centrifugation of wet sediment at 5000 rpm for 20 min (HAREAUS, Primo, Germany). The laboratory sediments were collected from the surface of the bottom creek, with a depth of 10 cm. The sediment was dried at room temperature. Then, plant roots, benthic organisms and other large objects impurities were removed from the dry samples. The samples were sieved with a standard 100 mesh. All solid samples were stored at -4 °C prior to further processing and analysis. The typical concentrations of heavy metals, phosphorus and acid volatile sulfide (AVS) and the pH and Eh values are shown in Table 1, which was close to the average levels of branch creeks in Shanghai (Deng, Zhang, Wang, Chen, & Xu, 2010; Yang, Chen, Liu, Shi, & Meng, 2014; Zhang, Deng, Wang, Chen, & Xu, 2013).

2.2 Experimental procedures

The static method for the simulation study of the stabilization of phosphate and heavy metals in calcium nitrate sediment was used to investigate the behavior of pollutants during the remediation process. The simulated experiment used a cylindrical reaction device with a height of 80 cm and a diameter of 20 cm. The sediment and the overlying water were placed in a cylindrical hard plastic container at a volume ratio of 1: 1 for culture. In addition, the depth of the sediment and the overlying water was 30cm. The container was left open at the top to keep the water in contact with air to simulate natural environmental exchange. To remove the impact of the background in the sediment, a control sample without the addition of calcium nitrate was tested.

Calcium nitrate ($149 \text{ g N} \cdot \text{m}^{-3}$) was added by liquid injection. Considering the infiltration of NO_3^- in the sediment, the injection site was located 5 cm below the sediment and water interface, ensuring an effective depth of 10 cm. To achieve the complete oxidation of total sulfides, the injection was repeated two times on the 1st day and the 26th day during the 131 days of the experiment, with an interval of 25 days between each injection.

All experiments were performed in triplicate. The data are presented as the average values with the standard deviation.

2.3 Chemical analysis of heavy metals

2.3.1 Total metals concentration analysis

The total metals solution of sediments was acquired by digesting 0.1 g of sediment samples with 2.5 mL of a 72% HClO_4 solution, 5 mL of a 65% HNO_3 solution and 2.5 mL of a 40% HF solution in digestion furnace (SH220N, Haineng, China). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to detect the heavy metals concentration in the solution and to analyze the heavy metals in the speciation extraction.

2.3.2 Chemical fraction analysis of heavy metals

The Community Bureau of Reference (BCR) extraction method for metal fractionation is a widely used analysis method. The extractions were carried out by following the method applied in our previous work on creek sediments. After each step of extraction, the sample was washed twice with 10 mL of distilled water (shaking for 15 min, at 25 °C) and centrifuged for 30 min each time. The centrifuge wash was combined with liquid extraction. The association of heavy metals with each chemical fraction was denoted as F1 acid extractable, F2 reducible, F3 oxidizable, and F4 residual. The following steps list the specific speciation extraction in detail (Guevara-Riba, Sahuquillo, Rubio, & Rauret, 2004):

Step 1 (F1) (acid extractable fraction): Approximately 1 g of dry sediment was placed into 100 mL polypropylene centrifuge tube. Then, 40 mL of 0.11 mol L^{-1} acetic acid was added to the tube, followed by shaking in an orbital mechanical shaker for 16 h at a room temperature of 25 °C.

Step 2 (F2) (iron and manganese-reducible fraction): Approximately 40 mL of 0.1 mol L^{-1} hydroxylamine (with a pH adjusted to 2 by the addition of 0.1 mol L^{-1} HCl) was added to the residue from Step 1 in the centrifuge tube.

Step 3 (F3) (oxidizable fraction): Approximately 10 mL of 30% W V^{-1} H_2O_2 was added into the residue from Step 2 in the centrifuge tube. The tube was digested at room temperature for 1 h. Another 10 mL of 30% W V^{-1} H_2O_2 was added. Again, the covered tube was heated to 85 °C and digested for 1 h. After cooling, 50 mL of 1.0 mol L^{-1} ammonium acetate (with a pH adjusted to 2 by the addition of concentrated HNO_3) was added to the residue and the tube was shaken for 16 h at room temperature.

Step 4 (F4) (residual fraction): The residue from Step 3 was digested using a 3:1 mixture of HNO_3 - HF .

For quality control of the extraction data, the amount of heavy metals in each step was summed together and compared to separate the single total metal analysis for each sample. The sum of the fractions was within 10% of the independent total. The discussion on the metal partitioning between fractions was presented in terms of the % of the sample total.

2.4 AVS and simultaneous extract metal measurement

Analyses of the AVS and simultaneous extract metal (SEM) concentrations (mg kg^{-1}) in sediments largely followed the method recommended by United States Environmental Protection Agency (USEPA) (Yang et al., 2014). Typically, 2.0 g of fresh sediment was added into the flask. Then, a round-bottom flask was filled with N_2 for 10 min, and the AVS receiving bottle was prepared. A total of 40 mL of 0.5 mol L^{-1} NaOH was added to the receiving flask as an AVS receiver. The N_2 flow rate was reduced, and the aeration was continued for 10 min. Then 20 mL of 6 mol/L HCl was added into the flask to form H_2S with the sediment. N_2 was continuously added at a flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$, and digestion was carried out for 1 h. In this process, N_2 was used as a purge gas to carry H_2S gas into the N,N-dimethylphenyl-p-diamine (DMPD) solution in the presence of ferric chloride (FeCl_3). The AVS extraction process was conducted for 45 min, with stirring at room temperature to ensure complete H_2S absorption. The H_2S concentration in the DMPD solution was quantified using a UV1000 spectrophotometer. The concentrations of Cu, Pb and Zn during the AVS extraction were operationally defined as the SEM and measured by ICP-AES analysis after filtering with a $0.45 \mu\text{m}$ acetate membrane.

All sample analyses were performed in triplicate. The recovery rates were between 90% and 110%, and the average values are reported.

2.5 Phosphate determination

The total phosphate (TP) in the sediment was extracted by following the Standards, Measurements and Testing (SMT) Program of the European Commission (Medeiros, Cid, & Gómez, 2005). The SMT protocol consists of three extraction procedures that were applied to 0.2 g aliquots of sediment samples:

1. The TP was measured by calcination in a muffle furnace (450°C) for 3 h and then extraction (16 h) using a solution of 20 mL of 3.5 mol L^{-1} HCl,
2. Inorganic phosphorus (IP) was determined by an extraction (16 h) with 20 mL of 1 mol L^{-1} HCl. The residue of this extraction was placed in a porcelain crucible and calcined in a furnace for 3 h at 450°C . Then, the residue was extracted again (16 h) with 20 mL of 1 mol L^{-1} HCl. After centrifugation, the organic phosphorus (OP) in the extract was determined.
3. An extraction (16 h) using 20 mL of 1 mol L^{-1} NaOH was performed, and after centrifugation and separation of the supernatant liquid, the residue was extracted again with 20 mL of 1 mol L^{-1} HCl (16 h). Apatite phosphorus (AP) was determined in the extract. Approximately 4 mL of 3.5 mol L^{-1} HCl was added to one aliquot of 10 mL of the 1 mol L^{-1} NaOH extract and allowed to stand for 16 h to precipitate organic matter. The non-apatite inorganic phosphorus (NAIP) in the supernatant liquid was determined.

The concentration of aqueous phosphate was determined by the spectrophotometric method.

2.6 Statistical analysis

All the analyses were performed in the R environment (version 3.4.4). One-way analysis of variance (ANOVA) was conducted to assess the concentration differences of TP before and after the treatments with a significant level of $p = 0.05$.

3 Results and discussion

3.1 The effect of calcium nitrate on heavy metals and SEM/AVS in sediments

3.1.1 Transformation of heavy metals in sediments

The variations in the concentrations of heavy metals (mg kg^{-1} dry weight) after dosing calcium nitrate within 120 days are shown in [Figure 1](#). The amounts of heavy metals were in the following order: $\text{Cu} > \text{Pb} > \text{Zn}$, with a mean value of Cu 623 mg kg^{-1} , Zn 169 mg kg^{-1} and Pb 248 mg kg^{-1} ([Figure 1](#)).

Although there were no significant changes in the concentrations of heavy metals, the chemical partitioning of heavy metals was altered over time ([Figure 2](#)). The results of ANOVA for the differences of four chemical speciations are provided in Table S1, Table S2 and Table S3. The chemical speciation of Cu was mainly in its oxidizable fraction (F3) and residual fraction (F4) in the original sediment, accounting for 53% and 46% of the total, respectively ([Figure 2](#)). In comparison, the amounts of Cu in the iron and manganese-reducible fraction (F2) and the acid extractable fraction (F1) were very low. After adding calcium nitrate, the amount of F3-Cu gradually decreased to 30% of the total amount of Cu, with the increasing of F1-Cu to 8% and F4-Cu to 61% in 120 days. A similar trend was observed in the case of Pb and Zn ([Figure 2](#)). In 120 days, the proportion of F4-Zn increased from 44% to 51% and that of F1-Zn increased from 36% to 41%, with the reduction of F3-Zn from 15% to 4%. For Pb, the F3-Pb decreased from 30% to 5%, resulting in increases in F4-Pb to 81% and F1-Pb to 16%. This observation implied that the F3 fraction of heavy metals predominantly transformed to its F4 fraction. It is interesting that the F3 fraction decreased in the first 20 days with the simultaneous increase in F4. On the contrary, the increase in F1 happened after 40 days in the remediation. Compared to the relatively stable species of heavy metals in the control sediment (Table S4), the changing of the heavy metal speciation after injecting meant that the heavy metals were stabilized in the initial period with $\text{Ca}(\text{NO}_3)_2$.

The amount of heavy metals had no significant migration from the sediment to the overlying water during the remediation period of calcium nitrate. Similar results were found in the related research (Shao, Zhang, & Fang, 2009). However, the speciation of heavy metals was changed. Shao et al. (2009) reported that heavy

metals Cu, Pb and Zn existed mainly in the oxidizable fraction (F3) while the F3 of heavy metal sharply decreased as remediation process. The F3 fraction reduction was contributed to the oxidation of sulfide affinity to heavy metals. This supposed the releasing of partial heavy metals. In comparison, the F4 fraction of three heavy metals was increased after remediation in current work. This observation suggests that heavy metals in sediment have the tendency to transform to the residue fraction (F4), which is probably relative to anions in sediment such as phosphate.

3.1.2 The change of AVS and SEM/AVS in sediments

The variations of AVS and SEM/AVS after the injection of $\text{Ca}(\text{NO}_3)_2$ are shown in Table 2. The AVS in the sediment decreased rapidly from the initial 6376 mg kg^{-1} to 942 mg kg^{-1} in 26 days at a rate of $209 \text{ mg kg}^{-1} \text{ d}^{-1}$ after the addition of calcium nitrate. Then, the AVS decreased gradually to 238.4 mg kg^{-1} on the 131st day, showing that 85% of the AVS was removed. It appeared that the AVS consumed a large amount of calcium nitrate when converted to SO_4^{2-} , suggesting that S might form heavy metal sulfides in the sediment. The decrease in the F3 fraction of heavy metals was assigned to the reduction of heavy metal sulfides in the reaction with calcium nitrate. In contrast, the increase in SEM/AVS was recorded after 26 days of remediation and reached the highest value of 7.5 on the 131st day (Figure S1), which was consistent with the decrease in the F3 fraction of heavy metals. The F3 fraction in the BCR analysis refers to the heavy metals bound to the sulfide and organic matter. Hence, the reduction in the F3 fraction suggested the simultaneous diminishment of organic matter and sulfide (Figure S2). Generally, the mobilization of heavy metals often occurs when SEM/AVS is more than 1.0, and this leads to an increase in the F1 fraction of heavy metals (McQueen et al., 2016). However, in the current case, the increases of Cu, Zn and Pb in the F1 portion were 10%, 5% and 12% respectively, which were not as much as expected. The BCR results showed that the increases of Cu, Zn and Pb in the F4 fraction were 14%, 7% and 12%, respectively (Figure 2). Thus, the major path of transformation of the heavy metals was changed to the F4 fraction. For instance, the oxidation state changes of Zn and Pb showed a large drop at the beginning of the test; for example, the decreases of Cu, Zn and Pb in the F3 fraction were 17%, 11% and 25%, respectively (Figure 2). Mⁿ shape variation after injection in the first 60 days, with a maximum of 9.83. After 60 days, the pH dropped and remained at 8.35. The huge variation in pH was attributed to both the strong alkalinity of calcium nitrate and the buffering capacity of the sediments, along with the occurrence of chemical reactions.

So far, it has been shown that the AVS concentration decreased as the pH increased and the Eh decreased (Figure S5). According to the redox reaction with NO_3^- as an electron acceptor, the following oxidation of sulfides to sulfate could be expressed as follows:

The generation of SO_4^{2-} was accompanied by a decrease in H^+ , leading to an increase in the pH of the sediment. This is responsible for the observation that the final pH of 8.35 after 131 days of reaction was still higher than the raw pH of 7.5 (Figure 4).

3.4 Effect of substrate alteration on P and heavy metals

3.4.1 The change in Fe and S in the sediment

Because the conversion between Fe(III) and Fe(II) depended largely on the level of the ORP, the value of Fe(III)/Fe(II) was used to determine the ORP in the sediment (Nguyen et al., 2018). In the absence of calcium nitrate, the fluctuations of Fe(III)/Fe(II) were relatively stable (0.034 ~ 0.076) in the sediment (Figure 4). Compared to the control, Fe(III)/Fe(II) significantly increased after the addition of calcium nitrate in the initial 54 days, to the highest value of 0.131 on the 26th and 54th days. Then, it decreased gradually to 0.028 at a rate of 0.0013 d^{-1} at the end of experiment (Figure 4). Fe(II) was easily converted to Fe(III) by the oxidation of calcium nitrate (Li et al., 2018), but the variation range of Fe(III)/Fe(II) was still less than 1 (0.028 ~ 0.131). This was probably due to the strong anaerobic environment. Therefore, the oxidation of calcium nitrate was related to the specific speciation of Fe in the sediment.

Fe and S were changed along with the Eh and the pH. When most Fe and S existed as FeS in the sediment, S^{2-} was converted to SO_4^{2-} and released into water, and Fe(II) was released at the same time (Baldwin & Mitchell, 2012). In the presence of nitrate, the following reaction occurred (Na, Wang, & Park, 2006):

The value of Fe(III)/Fe(II) was in a stable range of fluctuations and was poorly correlated with the reduction of AVS after the addition of calcium nitrate (Figure S6). Therefore, the oxidation of Fe by calcium nitrate did not significantly affect the speciation of FeS in the sediment. The increase of Fe(III)/Fe(II) was restricted when the Fe mainly existed as FeS in the sediment, which indicated that calcium nitrate had no obvious effect on Fe(III)/Fe(II).

3.4.2 Effects of Fe and S on phosphorus

Previous research has shown a correlation between iron, sulfur and phosphorus in sediment (Kraal et al., 2015). Phosphorus was not only bound to Fe(OOH) but also adsorbed on FeS (Martins, Peixoto, Brito, & Nogueira, 2014). Accordingly, the release of phosphorus was suggested after Fe(II) and sulfide oxidation. [Figure 5](#) shows the relationship between Fe, S and the release of phosphorus after the addition of calcium nitrate. The correlation coefficients of AVS and Fe(III)/Fe(II) were 0.494 and 0.077, respectively. The change of Fe(III)/Fe(II) had no obvious effect on the concentration of phosphorus in the interstitial water, while the impact of AVS was quite significant. The relationship between the AVS and the aqueous phosphorus

suggested that the reduction of sulfide was related to the decrease in aqueous phosphorus and implied the precipitation of P after the oxidation of sulfide, which was probably responsible for the increase in the residual fraction of heavy metals.

3.5 Synergistic stability of phosphorus and heavy metals

To estimate the mobility of heavy metal and phosphorus, their concentrations in interstitial water were detected. As the residue fraction of heavy metal increased ([Figure 2](#)), the change of aqueous heavy metal could be described as the following:

where $C_{aq(t)}$ and $C_{aq(0)}$ are the concentrations of aqueous heavy metal in interstitial water with and without the injection of calcium nitrate after t days, respectively. The percentage of aqueous metals indicated the amount of heavy metal release compared to that in the control experiment. It was assumed that when the aqueous heavy metal content was lower, more heavy metals were precipitated.

Heavy metals precipitate under alkaline conditions to form hydroxide (acid extractable fraction), which is unstable. As shown in [Figure 6](#), the metal residue for Cu, Zn and Pb increased as the concentration of TP in the interstitial water decreased. The stability of heavy metal is related to phosphorus by forming heavy metal phosphate (residual fraction). The linear correlation obtained between the three heavy metals (Cu, Zn and Pb) and TP were as follows ([Figure 6](#)):

$$Cu (\%) = -0.6297TP + 64.45, r = -0.820;$$

$$Zn (\%) = -1.079TP + 64.7, r = -0.948;$$

$$Pb (\%) = -0.4200TP + 85.51, r = -0.611.$$

The stronger correlation between the heavy metals and the TP concentration in the interstitial water illustrated the binding of heavy metals and phosphorus ([Figure 6](#)). As the correlation coefficient was lower than -0.8, a good correlation between Zn and P was indicated, while that of Pb was poor ([Figure 6](#)). Therefore, different heavy metals were combined with phosphorus in different forms, which led to differences in their coprecipitation effects.

It was reported that for each common heavy metal, the K_{sp} values of phosphate metals are slightly higher than those of sulfide metals (Banfalvi, 2006). For example, $Pb_3(PO_4)_2 \cdot OH$ reached 62.80 and the phosphates of Cu and Zn reached 53.96 and 49.10, respectively. The K_{sp} values were higher than the corresponding K_{sp} values for the sulfides; the K_{sp} values of CuS , PbS and ZnS were 44, 28 and 23, respectively. These results illustrate that the combination of phosphorus and heavy metals most likely produced heavy metal phosphates in sediments, which promoted the stabilization of heavy metals and phosphorus at the same

time. At a pH of 8.5, HPO_4^{2-} was the predominant species of phosphorus (Liu, Sheng, Dong, & Ma, 2012), which consequently suggested that the effect of Ca-P precipitation on the decrease of TP in the interstitial water was poor with the high solubility of CaHPO_4 (Figure S7). Accordingly, the adsorption of heavy metals with the formation of Ca-P precipitates was not the predominant reason for the increase in the residual fractions of heavy metals. Therefore, it was highly likely that the phosphorus and heavy metals produced heavy metal phosphates in the sediment, which simultaneously stabilized the heavy metals and the phosphorus.

4 Conclusions

The injection of calcium nitrate was used in the remediation of sediment in a simulated column experiment. The heavy metal and phosphorus contents both in sediment and interstitial water were recorded. Under the action of calcium nitrate, sulfide was significantly oxidized by calcium nitrate as its amount was reduced substantially by 85% from the 20th to the 30th day with a linear change of the ORP-pH profiles. Simultaneously, the amount of heavy metals associated with both the acid soluble fraction and the residue fraction increased. Over 50% of the mobile Zn, Pb and Cu was reprecipitated, which seemed to be relative to the loss of phosphorus from interstitial water and contributed to the formation of heavy metal phosphates given the low K_p value. This synergistic relationship of phosphorus and heavy metal in interstitial water occurred significantly in the case of Zn and Pb immobilization.

In practical strategies for sediment remediation, heavy metal contamination is often considered. Although calcium nitrate is recommended by the USEPA to reduce organic matter via the oxidation status of the sediment, the changing of sulfide species by calcium nitrate led to the mobilization of heavy metals to the water body from the sediment. To solve the issue, our results provide a promising approach for the remediation of sediment with the simultaneous use of a phosphate agent to stabilize heavy metals in the form of insoluble phosphate. This extends the application of $\text{Ca}(\text{NO}_3)_2$ in both sediment and soil remediations and avoids secondary contamination.

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Data value statement

The data used to support the findings of this study are available from the corresponding author upon request.

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Table 1 Properties of the water and sediment samples from Puhuitang creek

		<i>Overlying water</i>	<i>Sediment</i>
	<i>pH</i>	7.83	7.25
	<i>Eh</i>	22.9 mV	56 mV
	AVS	nd	6376 mg kg ⁻¹
	<i>Organic matter</i>	nd	107.6 mg kg ⁻¹
	<i>Total phosphorus</i>	3.188 mg L ⁻¹	1665 mg kg ⁻¹
	Cu	nd	625.4 mg kg ⁻¹
	Zn	nd	158.3 mg kg ⁻¹
	Pb	nd	248.36 mg kg ⁻¹
<i>Heavy metals</i>	Fe	nd	7643 mg kg ⁻¹
	Mn	0.685 mg L ⁻¹	130.9 mg kg ⁻¹
	Cd	nd	nd
	Ca	144.7 mg L ⁻¹	4310 mg kg ⁻¹

* nd: Not detected

Table 2 The variations of AVS and SEM/AVS in sediments

Time (day)	AVS(mg kg ⁻¹)		Σ SEM/AVS	
	control	after adding Ca(NO ₃) ₂	control	after adding Ca(NO ₃) ₂
1	5767±81	6144±129	0.02±0.002	0.02±0.002
2	5510±93	4180±115	0.02±0.001	0.03±0.002
12	5293±64	4017±96	0.02±0.001	0.06±0.004
26	5798±85	942.6±56	0.02±0.002	0.25±0.032
33	5535±63	887±47	0.01±0.001	0.32±0.023
47	4641±79	744±54	0.03±0.002	0.66±0.041
61	4834±97	722±32	0.02±0.001	1.23±0.097
75	4873±79	651±25	0.03±0.002	1.5±0.088
89	4711±73	479±33	0.02±0.001	2.87±0.127
103	5091±76	316±23	0.02±0.001	6.57±0.321
131	4989±64	238±31	0.02±0.002	7.45±0.373

*AVS - acid volatile sulfide, SEM/AVS - simultaneous extract metals/ acid volatile sulfide. The values are presented as mean ± SD.

[Figure 1](#) The concentrations of Cu, Pb and Zn in the sediment

[Figure 2](#) Speciation of Cu, Pb and Zn in the sediment (F1- acid extractable fraction, F2- iron and manganese-reducible fraction, F3- oxidizable fraction and F4- residual fraction). The values are presented as mean. The

values of Standard deviations and statistical analysis of four chemical speciation for Cu, Pb and Zn were provided in Table S1, Table S2 and Table S3, respectively.

[Figure 3](#) The TP concentration in the sediment. The arrows represent the time of adding calcium nitrate. Error bars indicate standard deviations. Asterisks indicate TP concentrations significantly different ($p < 0.05$) from untreated controls.

[Figure 4](#) The effect of calcium nitrate on ORP, pH and Fe(III)/Fe(II) in the sediment. The arrows represent the time of adding calcium nitrate.

[Figure 5](#) The correlations among Fe, S and P in interstitial water

[Figure 6](#) The correlations between total phosphorus and heavy metals in interstitial water

Supplementary files

Evaluation of heavy metals stability and phosphate mobility in the remediation of sediment by calcium nitrate

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Fig. S1 Changes of SEM/AVS ratio in the sediment

Fig. S2 Changes of organic matter in the sediment

Fig. S3 Distribution and speciation of phosphorus in the sediment (NAIP: Non-apatite inorganic phosphorus, AP: Apatite phosphorus, OP: Organic phosphorus)

Fig. S4 Changes of total phosphorus concentration in interstitial water

Fig. S5 Correlations between ORP and pH in the sediment

Fig. S6 Changes of correlations between Fe and S in the sediment

Fig. S7 Relationship between concentration of calcium and total concentration of phosphorus in interstitial water

Table S1 The speciation of Cu in the sediment (after adding calcium nitrate) (mg kg⁻¹)

Time(D)	Total	F1	F2	F3	F4
1	567.20±28.36 d	6.81±0.34 f	0.57±0.03 e	298.35±14.92 b	261.48±13.07 f
12	625.52±31.28 bc	10.63±0.53 e	1.25±0.06 a	331.53±16.58 a	282.11±14.11 e
26	627.48±31.37 bc	4.39±0.22 g	0.63±0.03 cd	263.54±13.18 d	358.92±17.95 c
47	680.90±34.04 ab	10.21±0.51 e	0.68±0.03 bc	279.17±13.96 c	390.83±19.54 b
61	690.78±34.54 a	20.72±1.04 d	0.69±0.03 b	255.59±12.78 d	413.78±20.69 a
75	653.90±32.70 b	48.39±2.42 c	0.65±0.03 c	255.02±12.75 d	349.84±17.49 c
89	580±29 cd	66.70±3.34 a	0.58±0.03 de	179.80±8.99 e	332.92±16.65 d
103	610±30.5 c	58.56±2.93 b	0.61±0.03 d	183.00±9.15 e	367.83±18.39 c

*Total- total concentration of heavy metal, F1- acid extractable fraction, F2- iron and manganese-reducible fraction, F3- oxidizable fraction and F4- residual fraction. The values are presented as mean ± SD. Mean values in a column not sharing a letter are significantly different from each other (p < 0.05).

Table S2 The speciation of Zn in the sediment (after adding calcium nitrate) (mg kg⁻¹)

Time(D)	Total	F1	F2	F3	F4
1	165.22 ±8.26 c	59.48 ±2.97 d	8.59 ±0.43 a	24.78 ±1.24 b	72.37 ±3.62 e
12	158.57 ±7.93 c	76.11 ±3.81 a	7.45 ±0.37 b	28.54 ±1.43 a	46.46 ±2.32 g
26	145.41 ±7.27 d	61.07 ±3.05cd	5.09 ±0.25 d	11.63 ±0.58 c	67.62 ±3.38 f
47	142.14 ±7.11 d	58.28 ±2.91 d	2.98 ±0.15 f	7.11 ±0.36 f	73.77 ±3.69 e
61	177.13 ±8.86 b	77.94 ±3.90 a	7.26 ±0.36 b	7.09 ±0.35 f	84.84 ±4.24 d
75	193.59 ±9.68 a	63.88 ±3.19 c	4.26 ±0.21 e	11.62 ±0.58 c	113.83 ±5.69 a
89	175.00 ±8.75 b	68.25 ±3.41 b	4.90 ±0.25 d	8.75 ±0.44 d	93.10 ±4.66 c
103	190.00 ±9.50 a	77.90 ±3.90 a	6.08 ±0.30 c	7.60 ±0.38 e	98.42 ±4.92 b

*Total- total concentration of heavy metal, F1 - acid extractable fraction, F2 - iron and manganese-reducible fraction, F3 - oxidizable fraction and F4- residual fraction. The values are presented as mean ± SD. Mean values in a column not sharing a letter are significantly different from each other (p < 0.05).

Table S3 The speciation of Pb in the sediment (after adding calcium nitrate) (mg kg⁻¹)

Time(D)	Total	F1	F2	F3	F4
1	200.20 ±10.01 d	0.60 ±0.03 h	0.40 ±0.02 e	60.46 ±3.02 a	138.74 ±6.94 d
12	248.92 ±12.45 b	11.95 ±0.60f	3.24 ±0.16 c	52.52 ±2.63 b	181.21 ±9.06 c
26	216.33 ±10.82c	4.76 ±0.24g	1.08 ±0.05 d	25.96 ±1.30 d	184.53 ±9.23 c
47	268.70 ±13.43ab	19.61 ±0.98d	6.45 ±0.32 a	27.94 ±1.40 c	214.69 ±10.73ab
61	254.67 ±12.73b	18.34 ±0.92e	6.62 ±0.33 a	17.83 ±0.89 f	211.89 ±10.59ab
75	260.99 ±13.05ab	37.06 ±1.85a	6.52 ±0.33 a	10.44 ±0.52 h	206.97 ±10.35 b

Time(D)	Total		F1		F2		F3		F4	
89	273.00	±13.65a	27.03	±1.35c	5.19	±0.26 b	19.66	±0.98 e	221.13	±11.06 a
103	257	±12.85b	30.58	±1.53b	5.14	±0.26 b	13.62	±0.68 g	207.66	±10.38 b

* Total - total concentration of heavy metal, F1 - acid extractable fraction, F2 - iron and manganese-reducible fraction, F3 - oxidizable fraction and F4 - residual fraction. The values are presented as mean ± SD. Mean values in a column not sharing a letter are significantly different from each other ($p < 0.05$).

Table S4 The speciation of Cu, Pb and Zn in the sediment (control) (mg kg⁻¹)

	Time (day)	Total		F1		F2		F3		F4	
Cu	1	622.94	±37.38	7.48	±0.45	0.62	±0.04	327.67	±19.66	287.18	±17.23
	26	509.32	±30.56	6.11	±0.37	0.51	±0.03	267.90	±16.07	234.80	±14.09
	75	595.51	±23.82	7.15	±0.29	0.60	±0.02	313.24	±12.53	274.53	±10.98
	103	579.85	±34.79	6.96	±0.42	0.58	±0.03	305.00	±18.30	267.31	±16.04
Pb	1	238.62	±21.37	0.72	±0.06	0.48	±0.04	72.06	±6.45	165.36	±14.81
	26	138.36	±13.82	0.42	±0.04	0.28	±0.03	41.78	±4.17	95.88	±9.58
	75	194.02	±19.52	0.58	±0.06	0.39	±0.04	58.59	±5.90	134.46	±13.53
	103	198.74	±18.35	0.60	±0.06	0.40	±0.04	60.02	±5.54	137.73	±12.72
Zn	1	155.87	±24.99	56.11	±9.00	8.11	±1.30	23.38	±3.75	68.27	±10.95
	26	172.77	±19.37	62.20	±6.97	8.98	±1.01	25.92	±2.91	75.67	±8.48
	75	174.89	±25.00	62.96	±9.00	9.09	±1.30	26.23	±3.75	76.60	±10.95
	103	165.54	±17.28	59.59	±6.22	8.61	±0.90	24.83	±2.59	72.51	±7.57

*Total- total concentration of heavy metal, F1 - acid extractable fraction, F2 - iron and manganese-reducible fraction, F3 - oxidizable fraction and F4 - residual fraction. The values are presented as mean ± SD.

Table S5 The speciation of phosphorus in the sediment (after adding calcium nitrate) (mg kg⁻¹)

Time(D)	Total		NAIP		AP		OP	
0	1556	±25 f	539	±9 e	667	±11 d	350	±6 h
5	2272	±22 a	871	±8 a	754	±7 b	647	±6 a
12	2078	±38 b	891	±16 a	621	±11 e	566	±10 bc
19	1700	±20 e	631	±7 d	637	±7 de	431	±5 f
26	1860	±30 d	627	±10 d	709	±11 c	524	±8 d
33	1762	±22 e	724	±9 b	805	±10 a	233	±3 j
40	1714	±34 e	639	±13 cd	797	±16 a	278	±6 i
54	1733	±23 e	663	±9 c	640	±8 de	430	±6 f
61	2078	±38 b	867	±16 a	710	±13 c	501	±9 de
68	1573	±33 f	619	±13 d	682	±14 cd	272	±6 i
75	1959	±39 c	673	±13 bc	700	±14cd	586	±12 b
82	1727	±27 e	660	±10 cd	668	±10 d	400	±6 g
89	1614	±24 f	660	±10 cd	590	±9 e	364	±5 h

Time(D)	Total		NAIP		AP		OP	
103	1858	±38 d	667	±14 c	676	±14 cd	515	±11 de
117	1799	±29de	620	±10 d	683	±11 cd	496	±8 e
131	1870	±30cd	650	±10 cd	666	±11 d	554	±9 c

* Total - total concentration of phosphorus, NAIP - Non-apatite inorganic phosphorus, AP - Apatite phosphorus, OP - Organic phosphorus). The values are presented as mean ± SD. Mean values in a column not sharing a letter are significantly different from each other ($p < 0.05$).