

Effects of four different phosphorus-locking materials on sediment and water quality in Xi'an moat

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Abstract To lower phosphorus concentration in Xi'an moat, four different phosphorus-locking materials, namely, calcium nitrate, sponge-iron, fly ash, and silica alumina clay, were selected in this experiment to study their effects on water quality and sediment. Results of the continuous 68-day experiment showed that calcium nitrate was the most effective for controlling phosphorus concentration in overlying and interstitial water, where the efficiency of locking phosphorus was >97 and 90 %, respectively. Meanwhile, the addition of calcium nitrate caused Fe/Al-bound phosphorus (Fe/Al-P) content in sediment declining but Ca-bound phosphorus (Ca-P) and organic phosphorus (OP) content ascending. The phosphorus-locking efficiency of sponge-iron in overlying and interstitial water was >72 and 66 %, respectively. Meanwhile, the total phosphorus (TP), OP, Fe/Al-P, and Ca-P content in sediment increased by 33.8, 7.7, 23.1, and 23.1 %, respectively, implying that under the action of sponge-iron, the locked phosphorus in sediment was mainly inorganic form and the phosphorus-locking efficiency of sponge-iron could be stable and persistent. In addition, the phosphorus-locking efficiency of fly ash was transient and limited, let alone silica alumina clay had almost no capacity for phosphorus-locking efficiency. Therefore, calcium nitrate and sponge-iron were excellent phosphorus-locking agents to repair the seriously polluted water derived from an internal source.

Keywords Urban landscape water · Heavy pollution · Internal phosphorus · Phosphorus control · Calcium nitrate · Sponge-iron

Introduction

Xi'an is the capital of Shaanxi province, which is located in northwestern China and has a population of more than 8 million. The increasing population and changing climatic conditions have made the urban district of the city experience extremely hot weather very often in recent years. The city center is surrounded by Xi'an moat, which has a 14.8-km circumference and is 15–20 m wide and 5–8 m deep. Although the initial function of Xi'an moat was to guard the city against the military offense, the moat has developed to a water landscape for the citizens and a rainwater storage site for the city when the floods come.

Either as a landscape water or rainwater storage, massive pollutants, including nutrients (nitrogen, phosphorus), organic matters, and other hazardous substances, have entered and accumulated at the bottom of the Xi'an moat since 2009 when the transportation made the dredging of moat more and more difficult in urban district. The accumulated substances might be converted into substances that could further damage the ecosystem under special conditions (Ahlgren et al. 2005, Beutel et al. 2008, Chapra & Robertson 1977, Tang et al. 2014, Wang et al. 2009). Increase of nutrients, especially phosphorus, in aquatic ecosystem, is the main reason to cause eutrophication. Thus, serious eutrophication happens often, and the stench emitted by the moat affects its function negatively as a scenic environment.

To date, the moat water has become black because of the occurrence and death of the algae blooms. The moat gives off a stench in its eastern, western, and northern sections in summer, thereby leading to more complains from the nearby

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residents to the administrators. The anthropogenic loadings of phosphorus (P) have a key role in the eutrophication of water (Kopacek et al. 2005, Smith et al. 1999). Consequently, a remediation plan to control P sources must be a priority. However, even when all the external sources are controlled, the internal P loading from sediment into the water column can maintain the eutrophication conditions for decades, thereby delaying the recovery of eutrophic environments (Søndergaard et al. 2007).

To relieve the phosphorus load of water caused by endogenous pollution, three large-scale dredging projects had been carried out between 1998 and 2009. However, the dredging and transportation of bottom mud had several adverse effects on the appearance and traffic of the city because the moat is located in the downtown area and the dredging engineering is time-consuming and costly. In-site phosphorus removal is regarded as a less costly and highly efficient method to lower the phosphorus concentration of water (Hansen et al. 2003, Meis et al. 2013) when the accumulation of sediment is not large enough for dredging, but the phosphorus load has caused huge environmental pressure in water. Thus, a suitable phosphorus removing reagent becomes the key factor of water quality control in moat management.

Common solid-phase phosphorus adsorption materials include sponge-iron (Cheng et al. 2013), zeolite (Westholm 2006), diatomite (Karaca et al. 2006), porous ceramic filter media (Zhang et al. 2015), fly ash (Cheung & Venkitachalam 2000, Li et al. 2006) that can remove the soluble phosphorus in water by adsorption. Adsorption is considered a highly effective and universally applicable method for phosphorus removal from water bodies (Lan et al. 2006) given its advantages of simple equipment, various sources of raw materials, low procurement and operating costs. Researchers have studied the phosphorus removal effects in water but given little attention to the influences on sediment when sponge-iron and fly ash are used as phosphorus adsorbents (Cheng et al. 2013, Li et al. 2015). Others have reported the influences of calcium nitrate on sediment and explored the mechanism of phosphorus removal from sediment (Lin et al. 2015, Yamada et al. 2012). However, a transverse comprehensive comparison to determine the best material for locking phosphorus to control P concentration in water of the Xi'an moat is lacking presently.

In this study, four inexpensive and locally available inorganic materials were selected and applied to the sediment and overlying water from the Xi'an moat. The first purpose of this investigation was to study the influence of the selected materials on

lowering the phosphorus concentration in water. The second purpose of the investigation was to study the variation of the content and form of phosphorus in the sediment. The third and final purpose of this study was to provide a useful reference for the rehabilitation and improvement of water quality in Xi'an moat.

Materials and methods

Sediment and water samples

Sediment and overlying water were collected from the north-western corner of Xi'an moat. Surface sediment samples (0–10 cm depth) were collected with a stainless steel grab sampler. These samples were black, with a slight odor. The samples were homogenized and sieved to remove the large stones and sand particles. Parts of the sieved sediment were freeze-dried and sieved with a standard 100 mesh to remove large particles before measuring the sediment composition. The other parts were used for the phosphorus-locking test. Overlying water samples were collected from 0.5 m below the water surface, whereas, the interstitial water was obtained from the supernatant of sediment centrifuged in a refrigeration centrifuge (5804R). The main indicators of sediment and water samples included the total phosphorus (TP), soluble reactive phosphorus (SRP), organic phosphorus (OP), Fe/Al-bound phosphorus (Fe/Al-P), and Ca-bound phosphorus (Ca-P) content. The corresponding values for the sediment and water samples are shown in Table 1.

Phosphorus-locking materials

Sponge-iron, fly ash, silica alumina clay, and calcium nitrate were used as phosphorus-locking materials in this experiment. Sponge-iron, is a rough, porous, and spongy inorganic product made from iron mineral, which was reduced by carbon under the melting temperature. The iron content of sponge-iron in our experiment was 96.6 %. The density of sponge-iron was 2.62 g/cm³ while the size of sponge-iron was less than 500 μm in this study. The fly ash used in this study was the residue of a coal-fired thermal power plant in the western suburbs of Xi'an. The fly ash consisted of SiO₂ and Al₂O₃ primarily, with a density of 0.78 g/cm³ and a median diameter of 30.2 μm. The silica alumina clay used in this study was obtained from Tianyun Ecological Purification, Ltd. of Zhejiang. The silica alumina clay consisted of SiO₂ and Al₂O₃ primarily, with a density of 1.19 g/cm³ and a median diameter of 11.02 μm.

Table 1 Main indicators of sediment and water samples

Overlying water (mg/L)		Interstitial water (mg/L)		Sediment (mg/g)			
TP	SRP	TP	SRP	TP	OP	Fe/Al-P	Ca-P
0.96	0.8	5.94	4.58	3.6	0.6	0.55	1.45

The calcium nitrate used in this study was a colorless and transparent crystal, with a purity of more than 99 %, as provided by the Tianli Chemical Reagent Co., Ltd. of Tianjin.

Laboratory microcosm experiments

Five columnar glass vessels, with effective volume of 10 L, were used in parallel in this experiment. The vessels were 23 cm in diameter and 38 cm in height with a rubber lid of diameter 10 cm covered on the top. Three glass tubes of 6 mm diameter were installed on the lid, the length of 26 cm tube for sampling of water, the length of 31 cm tube for nitrogen agitation, and the length of 5 cm tube for exhausting only. All the vessels in this experiment were covered with package foil to avoid light during the experiment. First, 2.5 L of fresh sediments (~375 g dry sediment) were filled into the bottom of each vessel. Subsequently, sponge-iron, fly ash, silica alumina clay, and calcium nitrate were added to four respective vessels at a dose of 150 g, and mixed gently later. Another vessel without phosphorus-locking materials was used as the control one. Finally, the overlying water from the moat was added by the siphon method to reach the scale line of 10 L for each vessel. To simulate the dissolved oxygen (DO) of moat water, nitrogen was pumped to adjust the DO concentration of each vessel to less than 1 mg/L at the beginning of the experiment. At the same time, nitrogen had also played the role of mixing during the experiment. All the vessels were maintained at room temperature in static and dark. The sediment and water were sampled continuously and regularly from the glass vessels during the 68 days of operation.

The certain amount of sediments (~11 g dry sediment) were collected from each vessel on days 7, 14, 21, 35, and 68 after phosphorus-locking material application, centrifuged at 7000 rpm for 4 min to obtain the interstitial water, and freeze-dried. The sediment was sieved with a 100 mesh screen after freeze-drying. Meanwhile, 60 mL of the overlying water sample of each vessel was collected near the water-sediment interface on days 1, 2, 3, 8, 13, 18, 23, 28, 38, 48, 58, and 68 after phosphorus-locking material application.

A supplementary experiment using calcium nitrate to treat the sediment was conducted in 500 mL conical beakers. This experiment included a treatment set and a control set. Among the six microcosms, three were set up as controls. The variation of sediment oxidation–reduction potential (ORP) was monitored in the 7-day sediment treatment process. At the beginning of the experiment, 250 mL wet sediment was placed into each conical beaker, then calcium nitrate was added to conical beakers of treatment set at a dose of 15 g, and followed by mixing using nitrogen agitation, and sealed tightly with rubber plug. The sediment ORP was measured at the same time every day, and the procedures were performed in a gaseous nitrogen atmosphere to avoid oxidation of the sediment.

Adsorption isotherm test

The adsorption capacity of phosphorus-locking material was accomplished by the phosphorus adsorption isotherm test (Spears et al. 2013). Briefly, 0.05-g dry weight (d.w.) of each phosphorus-locking material (for sponge-iron, fly ash, and silica alumina clay) was mixed with 100 mL phosphate solution respectively across the following concentration gradient: 0.00, 0.50, 1.00, 5.00, 10.00, 20.00, 50.00, and 100.00 mg/L. The phosphate solution was prepared with KH_2PO_4 in distilled water. The pH of each solution was adjusted to pH 8.2 with HCl or NaOH. The phosphorus-locking materials and phosphate solution were mixed continuously in a water bath shaker at 20 °C for 24 h. After 24 h of contact period, the supernatants were centrifuged 10 min at 3800 rpm and filtered through a 0.45- μm filter later. Then the phosphate concentration of the filter liquors was measured using the Molybdate and L-ascorbic acid colorimetric method.

Chemical analysis

All the analyses, including the sediment, interstitial water, and overlying water from the glass vessels, were performed in Key Laboratory of Ministry of Education. The TP content in sediment was tested by sodium hydroxide melt-Mo-Sb colorimetry. The phosphorous fraction inorganic phosphorus (IP), OP, Fe/Al-P, and Ca-P in sediment were measured by continuous extraction according to the procedure presented in Fig. 1, referring to the standard measurement and test (SMT) procedure of phosphorus forms in the freshwater sediments (Hupfer et al. 1995, Ruban et al. 2001, Ruttenberg 1992). The element composition in sediment was measured with an isotope ratio mass spectrometer (Isoprime 100). The sediment ORP was measured using press ORP meter (YSI 100). The element distribution of phosphorus-locking materials was measured by X-ray fluorescence spectrometry.

The TP and SRP concentrations in overlying water and interstitial water were analyzed with the standard methods proposed by American Public Health (APH) Association, American Water Works (AWW) Association, Water Pollution Control (WPC) Federation, and Water Environment (WE) Federation (Association APH et al. 1915).

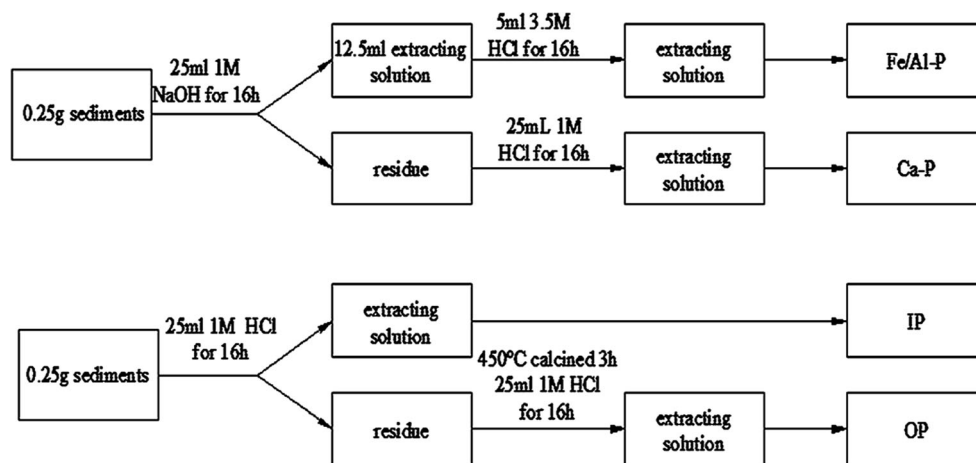
Results

Characteristics of phosphorus-locking materials

Element mass percentage of fly ash and silica alumina clay

The element mass percentage of fly ash and silica alumina clay is shown in Table 2. As seen from Table 2, the main elements of fly ash and silica alumina clay were silicon

Fig. 1 Sequential extraction procedure of phosphorus from sediment



(Si) and aluminum (Al). Si content in fly ash accounted for more than half and reached up to 74 % in silica alumina clay. Al content in fly ash accounted for more than a quarter and only 14.43 % in silica alumina clay.

Adsorption isotherm test of sponge-iron, fly ash, and silica alumina clay

The adsorption isotherms of phosphate for sponge-iron, fly ash, and silica alumina clay are presented in Fig. 2. In general, isotherms by sponge-iron and fly ash showed a rapid rise in the adsorption capacity with an increase in the phosphate solution concentration, followed by a plateau at equilibrium. However, silica alumina clay had minimal adsorption capacity for phosphorus. As seen from Fig. 2a, the phosphate uptake by sponge-iron increased dramatically with the phosphate solution concentration increasing from 0 to 20 mg/L. With further increase of the phosphate solution concentration, the increase of phosphate uptake was less significant. The mean value of the adsorbing capacity was 9.6 mg P/g sponge-iron when the adsorption equilibrium was reached. As seen from Fig. 2b, the isotherm of fly ash was closed to that of sponge-iron, and the adsorbing capacity of fly ash was 10.5 mg P/g when the adsorption equilibrium was reached.

Table 2 Element mass percentage of fly ash and silica alumina clay

Element	Fly ash (%)	Silica alumina clay (%)
Al	26.39 ± 1.21	14.43 ± 0.87
Si	54.54 ± 0.35	74.09 ± 0.13
S	7.51 ± 1.69	6.27 ± 2.82
Fe	8.86 ± 1.32	4.09 ± 1.05

Effects of calcium nitrate on ORP and element content of sediment

The variation of sediment ORP with the addition of calcium nitrate is presented in Fig. 3. After adding calcium nitrate, the sediment ORP increased progressively from the initial -121 mV to -10.7 mV in 7 days, showing an apparent improvement of the reducing condition in the sediment.

The mass percentage of carbon (C) and sulfur (S) in sediment had also changed after the addition of calcium nitrate, which was shown in Table 3. As seen from Table 3, C and S content in sediment added with calcium nitrate decreased by 18.9 and 71.4 %, respectively, compared with the control one after 68 days.

Effects of different phosphorus-locking materials on phosphorus concentrations in water

Phosphorus-locking materials applied in landscape water body would fix phosphorus (P) in overlying water and interstitial water to the sediment via physical adsorption or chemical reaction (Chai et al. 2011). Therefore, the treatment reduced the P concentration in water and ultimately controlled eutrophication. The effects of different phosphorus-locking materials on P concentrations in water are presented as follows:

Effects of different phosphorus-locking materials on P concentrations in overlying water

The P concentration in overlying water plays a key role in the development of eutrophication. Variation of TP and SRP in overlying water during the experiment is presented in Fig. 4.

As seen from Fig. 4, compared with the control, the addition of sponge-iron, fly ash, and calcium nitrate reduced TP and SRP concentrations in overlying water in varying degrees, while the silica alumina clay addition did not lead TP and SRP concentration in overlying water to decrease, instead

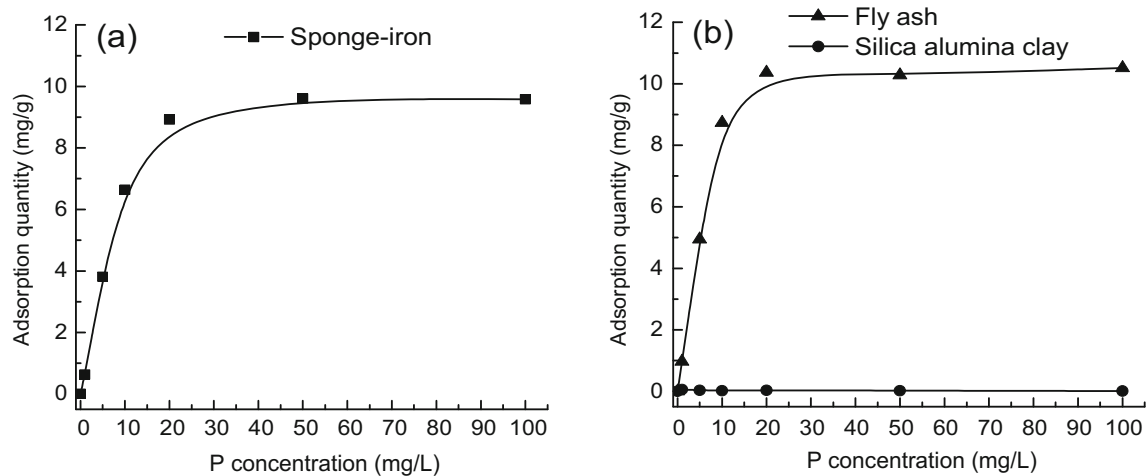


Fig. 2 Adsorption isotherms of P by sponge-iron, fly ash, and silica alumina clay

increased slightly. However, no matter what kinds of phosphorous-locking materials, their impacts on TP and SRP concentration in overlying water were with the same trend.

Although the addition of sponge-iron, fly ash, and calcium nitrate could reduce TP and SRP concentrations in overlying water, the course and magnitude of reducing phosphorus concentration were not equal for each phosphorous-locking material. When calcium nitrate was added, the TP and SRP concentrations in overlying water declined significantly after 2 days, and were always maintained below 0.15 and 0.06 mg/L, respectively, after 7 days. On the 68th day, the TP and SRP concentrations in overlying water were only 2.2 and 0.95 % of the control, respectively, which meant calcium nitrate could lock P in the water. When sponge-iron was added, the TP and SRP concentration in overlying water increased and reached the maximum values of 2.47 and 1.97 mg/L, respectively, on the 4th day. Both parameters were decreased gradually and approached a stable value after 38 days. On the 68th day, the TP and SRP concentrations in overlying water were 27.8 and 21.5 % of the control,

respectively, which implied that sponge-iron could lock most of the P in water. When fly ash was added, the TP and SRP concentration in overlying water were lower than control during the whole experiment. The concentrations increased gradually till the 38th day then decreased to a stable value relatively. On the 68th day, the TP and SRP concentrations in overlying water were 67.4 % of the control, which meant fly ash could lock P to a certain degree. Even worse, phosphorus in overlying water was not locked by silica alumina clay, which increased the TP and SRP concentrations by 8.5 and 13.6 %, respectively. Therefore, the effects of these materials on locking phosphorus in overlying water were clear as follows: calcium nitrate > sponge-iron > fly ash > silica alumina clay.

Effects of different phosphorous-locking materials on P concentrations in interstitial water

The P concentration in interstitial water is critical to the P concentration in overlying water because the P in interstitial water is the bridge between sediment and overlying water. Variation of TP and SRP in interstitial water during the experiment are presented in Fig. 5. As seen from Fig. 5, compared with the control, the addition of sponge-iron, fly ash, and calcium nitrate reduced TP and SRP concentrations in interstitial water in varying degrees, while the silica alumina clay addition had obvious effect on reducing the TP concentration but had little effect on SRP concentration in interstitial water.

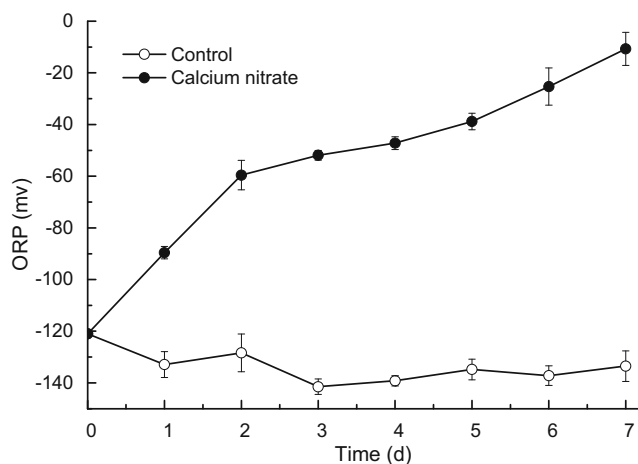


Fig. 3 Change in sediment ORP with the addition of calcium nitrate

Table 3 Effect of calcium nitrate addition on mass percentage of C and S in sediment after 68 days

Element	Mass percentage in sediment (%) on 68th day	
	Control	Calcium nitrate addition
C	10.2 ± 0.23	8.27 ± 0.38
S	1.99 ± 0.11	0.57 ± 0.07

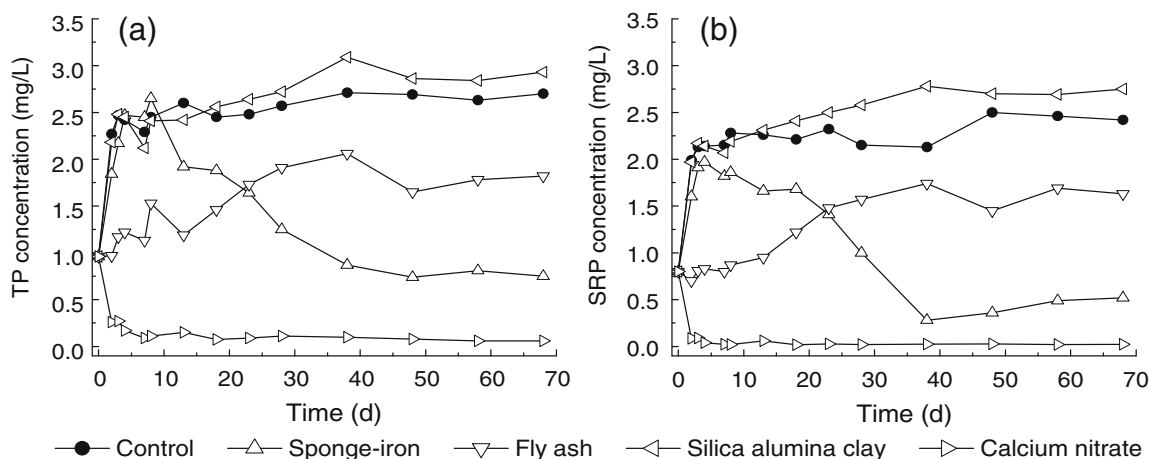


Fig. 4 Time course of P concentration in overlying water. a TP, b SRP

The effects of calcium nitrate addition on TP and SRP concentrations in interstitial water were significant and stable. On the 7th day, the TP and SRP concentrations in interstitial water were respectively 14.3 and 2.3 % of the control, since then both had maintained a low concentration. At the 68th day, the TP and SRP concentrations in interstitial water were 9.9 and 4.5 % of the control, respectively, which meant calcium nitrate had a potent capability to lock P in interstitial water. The effects of sponge-iron addition on TP and SRP concentrations in interstitial water were significant as well, at the 21th day, the TP and SRP concentrations in interstitial water were 16.4 and 9.6 % of the control, respectively, because both had maintained a low concentration. At the 68th day, the TP and SRP concentrations in interstitial water were 23.3 and 22.1 % of the control respectively, which meant sponge-iron could lock most of P in interstitial water. The TP and SRP concentrations in interstitial water after addition of fly ash reduced gradually, and reached a minimum value of 2.21 and 1.74 mg/L at the 21th day. Later, both were increased slowly. At the 68th day, the TP and SRP concentrations in interstitial water were 58.9 and 82.2 % of the

control respectively, which meant fly ash could lock P to a certain degree. After addition of silica alumina clay, at the 68th day, the TP and SRP concentrations in interstitial water were 73.2 and 102.1 % of the control, respectively, which meant silica alumina clay had no locking effect on SRP concentration in interstitial water; worse, a small increase in SRP occurred. Therefore, the effects of four materials on locking phosphorus in interstitial water were clear as follows: calcium nitrate > sponge-iron > fly ash > silica alumina clay.

Effects of different phosphorus-locking materials on P content in sediment

Time course of P content in sediment

Phosphorus in sediment is the most important source of internal pollution and plays a vital role in the eutrophication process of moat water (Golterman 1995). Variations of different P forms in sediment during the experiment are presented in Fig. 6.

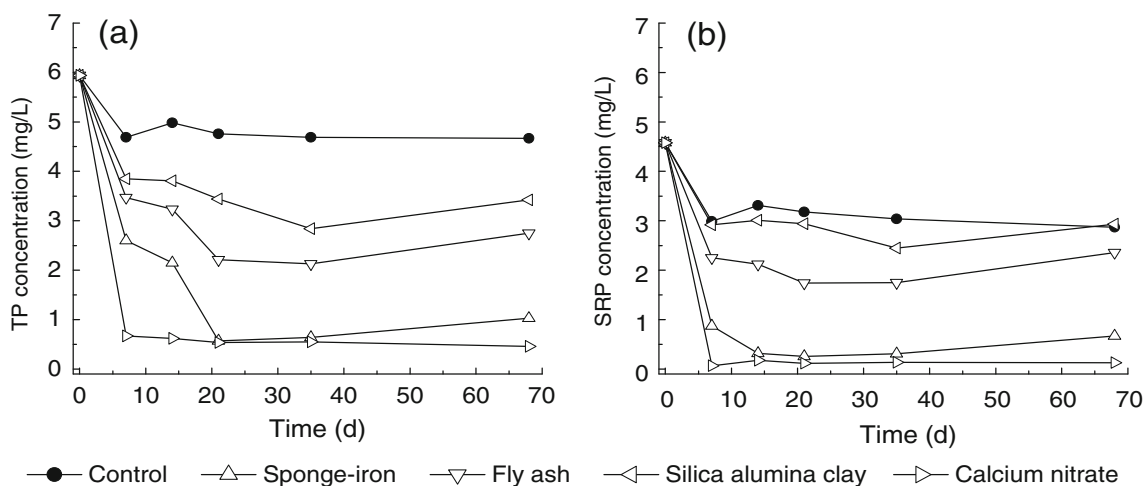


Fig. 5 Time course of P concentration in interstitial water. a TP, b SRP

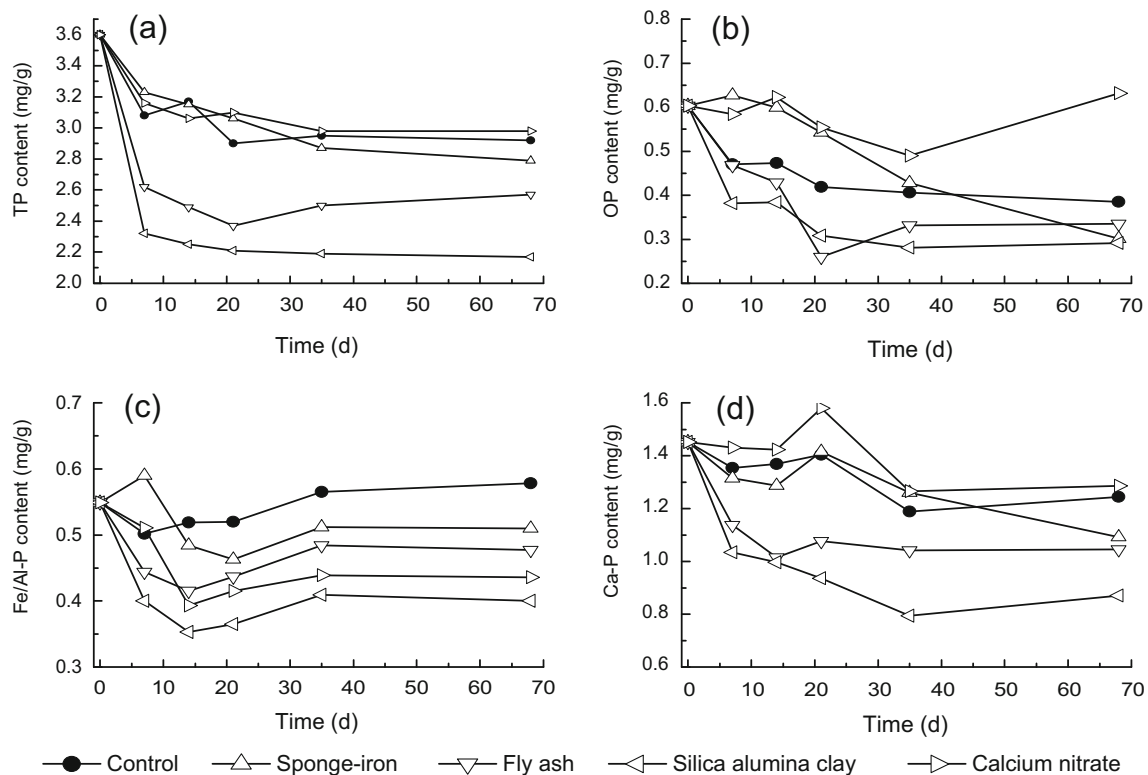


Fig. 6 Time course of P content in sediment. **a** TP, **b** OP, **c** Fe/Al-P, and **d** Ca-P

As shown in Fig. 6a, the TP content in sediment of all vessels decreased at the beginning of the experiment and reached a relatively stable value from the 35th day onward. At the 68th day, the TP content in sediment was 95.5, 88, and 74.3 % of the control when the sediment was added with sponge-iron, fly ash, and silica alumina clay, respectively. Meanwhile, the TP content in sediment with the addition of calcium nitrate was 103 % of the control.

As shown in Fig. 6b, during the whole experiment, the OP content in sediment was significantly higher than that of the control after calcium nitrate was added. The OP content in sediment reached 0.63 mg/g, which was 161.5 % of the control at the end of the experiment. The OP content in sediments after sponge-iron addition was higher than that of the control at the beginning of the experiment. However, the OP content in sediment added with sponge-iron decreased gradually with time. At the end of the experiment, the OP content in sediment was 76.9 % of the control. For the vessel with fly ash addition, the OP content in sediment decreased significantly in the prophase of our experiment then tended to stabilize after 35 days. Similarly, the OP content in sediment was 87.2 % of the control at the end of the experiment. The time course of OP content in sediment added with silica alumina clay was similar to that with fly ash addition; the OP content in sediment was 74.4 % of the control at the end of the experiment.

Fe/Al-P represents a potential bio-available form of phosphorus in sediment (Wang et al. 2009), with a high potential to

be released into the water. Variations of Fe/Al-P content in sediment during the experiment are presented in Fig. 6c. As seen from Fig. 6c, the Fe/Al-P content in sediment with the addition of phosphorus-locking materials showed differences in the prophase of the experiment. However, the apparent concentrations reached a relatively stable value after 35 days and became lower than the control at the end of the experiment. The Fe/Al-P content in sediment added with calcium nitrate had a significant decline in the prophase of our experiment and reached the minimum value of 0.39 mg/g on the 14th day then gradually increased. At the end of the experiment, the Fe/Al-P content in sediment added with calcium nitrate was 0.44 mg/g, which was 75.9 % of the control. The Fe/Al-P content in sediment added with sponge-iron reached the maximum value of 0.59 mg/g on the 7th day and then decreased to the minimum value of 0.46 mg/g on the 21th day. This value eventually became stable after 35 days. The Fe/Al-P content in sediment was 87.9 % of the control at the end of the experiment. The trend of Fe/Al-P content in sediment was similar when fly ash or silica alumina clay was added to the vessels. The Fe/Al-P content in sediment of both treatments first declined then climbed rapidly, although the values were lower apparently than the control after adding fly ash and silica alumina clay. The difference was explained by the Fe/Al-P content in sediment added with fly ash and silica alumina clay, which were 82.8 and 69 % of the control at the end of the experiment, respectively.

Ca-bound phosphorus (Ca-P) is considered refractory (Kaiserli et al. 2002), and its releasing potential is lower relatively. Variation of the Ca-P content in sediment during the experiment is presented in Fig. 6d. As seen from Fig. 6d, the Ca-P content in sediment added with calcium nitrate was higher than that of the control throughout the experiment. The maximum value was reached on the 21st day then decreased gradually. The Ca-P content in sediment was 1.29 mg/g at the end of the experiment, which was 104 % of the control. The time course of the Ca-P content in sediment added with sponge-iron was close to that of the control. The Ca-P content in sediment added with sponge-iron reached a maximum value on the 21st day and then decreased gradually until the minimum value of 1.09 mg/g was reached at the end of the experiment, which was 87.9 % of the control. The Ca-P content in sediment added with sponge-iron reached a maximum value on the 21st day and then decreased gradually until the minimum value of 1.09 mg/g was reached at the end of the experiment, which was 87.9 % of the control. The Ca-P content in sediment added with fly ash and silica alumina clay tended to decrease gradually. The difference was that the Ca-P content in sediment added with fly ash was 84.7 % of the control, whereas that of the treatment with added silica alumina clay was 70.2 % of the control at the end of the experiment.

Time course of the ratio of IP and OP in sediment

TP in sediment mainly consists of IP and OP. One possibility is that OP could be further hydrolyzed and converted into IP eventually, mainly as PO₄³⁻. Thus, OP is a potential bioavailable source of phosphorus. IP has many forms, including Fe/Al-P and Ca-P mainly, and is relatively stable than OP. The ratio of IP and OP in sediment could display the stabilization process of phosphorus when the phosphorus-locking materials are added into the sediment. The time course of the ratio of IP and OP in sediment with addition of four phosphorus-locking materials is presented in Fig. 7.

As seen from Fig. 7, the ratio of IP and OP in the control sediment changed slightly, by varying from 5.2 on the 7th day to 5.6 on the 68th day. The ratio of IP and OP in sediment

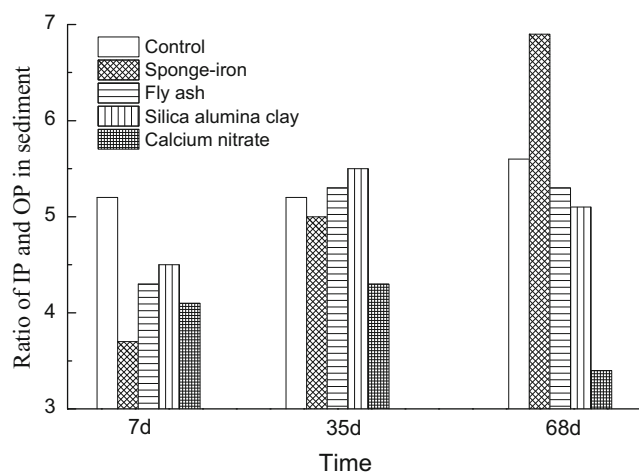


Fig. 7 Time course of the ratio of IP and OP in sediment

added with sponge-iron first decreased sharply and then increased gradually over time, from 3.7 on the 7th day to 6.9 on the 68th day. Both IP and OP in sediment were reduced from the 7th to the 35th day, but OP was reduced continuously, whereas IP in sediment remained stable from the 35th day onward. This trend indicated that not only IP in overlying water and interstitial water was fixed to sediment by sponge-iron via physical adsorption or chemical reaction; OP mineralization was also prompted by sponge-iron. The ratio of IP and OP in sediment added with calcium nitrate was 4.1 and 4.3 at the 7th and 35th day, respectively. This value was reduced to 3.4 at the end of the experiment as the OP in sediment increased. The ratio of IP and OP in sediment after the addition of fly ash increased from 4.3 on the 7th day to 5.3 on the 35th day, then remained stable until the end of the experiment. The ratio of IP and OP in sediment after the addition of silica alumina clay followed a similar trend as the treatment with fly ash.

Discussion

Four different phosphorus-locking materials were applied to water and sediment of the Xi'an moat. As shown in Table 1, the TP content in the sediment was 3.6 mg/g (d.w.) in this experiment. However, according to the Chinese environmental dredging common standard, a lake is considered to be polluted heavily and should be dredged when the TP content in the sediment exceeds 0.5 mg/g (Wang et al. 2009). Therefore, the Xi'an moat is currently highly polluted. Results showed that sponge-iron and calcium nitrate had an excellent effect on locking phosphorus, whereas fly ash and silica alumina clay did not after the continuous operation of 68 days.

In theory, phosphorus in overlying water and interstitial water were fixed into sediment when the phosphorus-locking materials were added, which implied that the TP content in all sediment should be increased. However, the TP content in sediments seemed to decrease mostly in this study, except for the addition of calcium nitrate. The main reason for this phenomenon was the change in the total mass of sediment after the addition of phosphorus-locking materials. As mentioned above, the addition of phosphorus-locking materials was 0.4 g/g dry sediment, but the solubility differed among the phosphorus-locking materials. Sponge-iron, fly ash, and silica alumina clay were insoluble, whereas calcium nitrate had high water solubility. If the increased mass of actual sediment from the addition of insoluble inorganic materials were considered, the mass balance results showed that TP content in sediment was increased by 33.8, 23.2, and 4 % compared with control after the addition of sponge-iron, fly ash, and silica alumina clay, respectively. Correspondingly, the relative OP content in sediment was 7.7, 22.1, and 4.1 % higher than the control,

and the relative Fe/Al-P content in sediment was 23.1, 15.9, and 3.4 % higher than the control. However, the relative Ca-P content in sediment was 23.1 and 18.5 % higher than the control after the addition of sponge-iron and fly ash, whereas that of the treatment with added silica alumina clay decreased by 1.8 % as compared with the control. Given its high water solubility, calcium nitrate addition did not increase the mass of sediment. Therefore, the TP content in sediment after calcium nitrate addition was higher than the control.

Calcium nitrate as a water phosphorus-locking compound was reported in literature. Rippl first tested calcium nitrate and found that the redox condition was improved (Rippl 1976), but the internal phosphorus loading was suppressed in the contaminated sediment. In this study, the ORP of sediment increased progressively (Fig. 3) after calcium nitrate was added. Simultaneously, the sediment changed gradually from blackish to brownish, which may suggest the transformation of sulfides to oxidized sulfur (Liu et al. 2015, Yamada et al. 2012). As expected, gas escaped at the interface of the overlying water and sediment after adding calcium nitrate. The abovementioned phenomenon could be attributed to NO_3^- as an electron acceptor, which may oxidize Fe^{2+} into Fe^{3+} and further enhance the adsorption of iron oxide for phosphorus in sediment (Ottley et al. 1997). In addition, the total carbon and sulfide in sediment were reduced (Table 3) compared with the control. This trend indicated that sulfides and organic carbon in the sediment may be oxidized into sulfate and CO_2 while the added NO_3^- was reduced into nitrogen or nitrogen oxides via a denitrification process by indigenous microorganism. Therefore, calcium nitrate addition could eliminate reasonably the black and poor odor of the sediment. These results were very consistent with previous findings (Cardoso et al. 2006, Liu et al. 2015, Shao et al. 2009). On the other hand, as a nitrogen source, calcium nitrate addition may promote the proliferation of microorganisms in water (Hemond & Lin 2010, Xu et al. 2015, Yamada et al. 2012). It may be explained why the OP content in sediment was higher than the control. In addition, the Ca-P content in sediment added with calcium nitrate was higher than that of the control throughout the experiment. This phenomenon was attributed to the calcium nitrate addition, which provided more calcium ions (Ca^{2+}) in the water and sediment. The excess calcium ions promoted the formation of insoluble calcium phosphate, where different forms of phosphate in interstitial water or overlying water had more opportunities to come into contact and combine with Ca^{2+} . The formation of more calcium phosphate caused the increased of Ca-P content in sediment.

However, the addition of calcium nitrate into aquatic ecosystems increased the nitrate, nitrite, and ammonia

concentrations in bodies of water inevitably. Indubitably, nitrite and ammonia are toxic to living aquatic species when their concentrations exceed a certain level (Liu et al. 2015). However, these toxic effects could be weakened with time or even disappear completely (Yamada et al. 2012). Therefore, the function and degree of pollution need to be known before calcium nitrate is applied to control eutrophication water. Simultaneously, the impact of calcium nitrate on aquatic and benthic organisms should be assessed without delay after its application. However, for seriously eutrophic water, such as in the Xi'an moat, calcium nitrate was a good choice as a phosphorus-locking reagent because the aquatic ecosystems were damaged seriously, and the black water was malodorous.

As a product generated from iron ore, sponge-iron has been used as a biological carrier in biological wastewater treatment because of its good efficiency for phosphorus removal. As a phosphorus-locking material, sponge-iron was first used in this study to fix more phosphorus into sediment. Sponge-iron has a stable locked-in effect and a long cultivation cycle of phosphorus in eutrophic water. The measured results of the isothermal test showed that sponge-iron had a certain adsorption capacity for phosphorus (Fig. 2a). In addition, sponge-iron could clearly promote the conversion of phosphorus in sediment from inorganic to organic form. The ratio of IP and OP in sediment increased from the initial 4.2 to 6.9 in the end, which may be related to biochemical reaction of sponge-iron in water and the sediment environment. When the total iron content in sponge-iron reached up to 96 %, the irons with various valences coexisted in the same system. The micro-electrolysis reaction may occur easily in this system to the lower valence irons, whereas a large number of ferrous irons could be dissolved out into water. Fe^{2+} was further oxidized to Fe^{3+} , and FePO_4 was produced finally when a certain amount of Fe^{3+} and PO_4^{3-} were combined at a higher pH. This reaction increased the Fe/Al-P content in sediment eventually. Simultaneously, the strong synergy and mutual promotion effect of phosphorus fixation may exist between the sponge-iron and the microorganisms. In the reaction, the oxidation of Fe^{2+} was mediated by the microorganism, chemical flocculation, and precipitation dominated by Fe^{3+} . Thus, the mechanism of locking phosphorus in water and sediment depends on the synergism of physical adsorption, biochemical processes, and chemical reactions.

As industrial waste, fly ash, and silica alumina clay have a limited phosphorus-locking effect in water; thus, the content of different forms of phosphorus was low relatively in sediment. Although fly ash and silica alumina clay had similar elements (Table 2), calculated results of the isothermal test showed that silica alumina clay had minimal adsorption capacity for phosphorus. By contrast, fly ash had an adsorbing capacity when the adsorption equilibrium was reached (Fig. 2b). Therefore, silica alumina clay had a minimal effect on the phosphorus concentration in overlying water and interstitial water; this material even had a negative impact

compared with the control. However, the fixation of phosphorus by fly ash in overlying water and interstitial water involved physical adsorption, although the effect was limited.

Conclusions

Four materials were selected and used to control the phosphorus concentration in the Xi'an moat. The effects of these materials were studied in terms of lowering the phosphorus concentration in water and changing the content and form of phosphorus in the sediment. The following conclusions were drawn:

The influence of calcium nitrate was the most obvious with respect to the lower phosphorus concentration in overlying water and interstitial water. At the end of our experiment, the phosphorus-locking efficiency for SRP in overlying water and interstitial water was 99.1 and 95.5 %, respectively. Meanwhile, the addition of calcium nitrate improved the redox conditions and prevented the phosphorus in contaminated sediment from entering the water body. Simultaneously, the additional calcium nitrate oxidizes sulfides and mitigates the release of odor into the atmosphere from the contaminated sediment effectively. In addition, the increase in available nitrogen stimulated the growth of microorganisms in the sediment, which transformed the bio-available Fe/Al-P into OP and eventually led to a drop in the IP/OP ratio. Therefore, the addition of calcium nitrate is a highly effective method to control and repair seriously polluted water by locking in situ phosphorus.

Sponge-iron could fix most phosphorus in the water. The phosphorus-locking efficiency of SRP in overlying water and interstitial water was 78.5 and 77.9 %, respectively. Compared with the control, all four phosphorus forms in sediment increased after sponge-iron addition; the locking efficiency of phosphorus in eutrophic water was stable and persistent. The phosphorus in overlying water and interstitial water was fixed by fly ash via physical adsorption. The fly ash mainly functioned in the early phase and appeared to dissolve phosphorus in later periods; thus, the phosphorus-locking efficiency for SRP in overlying water and interstitial water was only 32.6 and 17.8 %, respectively. Therefore, fly ash had a limited phosphorus-locking efficiency relatively. Silica alumina clay almost had no adsorption capacity for phosphorus and has a negative impact probably on the control of phosphorus in water.

In summary, calcium nitrate and sponge-iron were excellent phosphorus-locking reagents in this experiment. However, harmful effects may occur if excessive amounts of calcium nitrate and sponge-iron were applied in controlling phosphorus of eutrophication water independently. The former may be toxic to sensitive aquatic organisms, whereas

the latter would increase the total mass of sediment. Therefore, a combination of calcium nitrate and sponge-iron should be a better choice for the in-situ restoration of water with high internal phosphorus load. More exploration in this area is needed in the future.

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