



Transport and retention of phosphorus in soil with addition of Mg-Al layered double hydroxides: Effects of material dosage, flow velocity and pH

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HIGHLIGHTS

- Increasing LDHs dosages, decreasing flow velocity, and increasing pH bring greater irreversible retention for P in LDHs-soil system.
- The change of soil pH and Darcy velocity has little influence on the release of P from soil mixing with LDHs.
- The stability of LDHs in soil increases with greater LDHs dosages, higher pH, and lower velocity.

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ABSTRACT

Mg-Al layered double hydroxides (LDHs) were applied to soils to control phosphorus (P) loss. Column experiments were conducted with soil and LDHs under saturated conditions to investigate the retention and release of P with various LDHs dosages, flow velocity, and pH. The P retention and retardation of P breakthrough in soil with LDHs were enhanced with increasing LDHs dosages and pH as well as with decreasing flow velocity. The retention of P was successfully analyzed using a two kinetic sites model that accounted for irreversible and reversible retentions. Increasing LDHs dosages, decreasing flow velocity, and increasing pH bring greater maximum retained concentration on the solid phases (S_{max1} , i.e. irreversible retention) for P in LDHs-soil system. For reversible retention, the greater release rate from site 2 (k_{2d}) than first-order retention rate coefficient on site 2 (k_2) for most experiments reflects a rapid release process and near equilibrium transport behavior of P in LDHs-soil system. It is worth noting that the change of soil pH (8–5) and Darcy velocity (0.17 – 0.65 cm min^{-1}) has little influence on the release of P from soil mixing with LDHs. The stability of LDHs in soil increases with greater LDHs dosages, higher pH, and lower velocity.

1. Introduction

For several decades, phosphorus (P) fertilizer is usually excessively applied into agricultural soils to increase crop productivity [1,2]. It has potential risk for P transporting to nearby river system by surface runoff during heavy rainfall events shortly after fertilizer application, subsequently promoting water eutrophication [3,4]. It is necessary to develop eco-friendly technologies to promote P retention in soils and to improve the bioavailability of P to plants. The layered double hydroxides (LDHs), known as hydrotalcite-like materials or anionic clays, contain positively charged brucite or brucite-like layers through

isomorphous substitution of divalent cation by trivalent cation. Recently, LDHs were found as promising adsorbents for P from waste water [5–7] due to their permanent positive charge of layers, high anion-exchange capacity, large surface area, and water resistant structure [8]. The P adsorption by LDHs occurs via three different adsorption modes: electrostatic attraction, anion exchange with interlayer anions, and surface complexation [9]. On the other side, the P-loaded LDHs products have been investigated as a slow- and controlled-release P fertilizers [10,11]. The slow release of P from LDHs is potentially obtained by the anion exchange between intercalated HPO_4^{2-} and $\text{HCO}_3^-/\text{CO}_3^{2-}$ from soil solution [10] or part dissolution of LDHs [12].

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It has suggested that phosphate-exchanged Mg-Al LDHs have great P use efficiency in a more sustained way and even brought better plant growth than KH_2PO_4 or P enriched seawater [13]. To date, little research focuses on the direct application of LDHs in agriculture soils with heavy P fertilizer input. According to former researches, the direct application of LDHs to the soils with over-applied P fertilizer through ploughing could potentially immobilize P in soils and reduce P transporting to nearby aquatic systems due to the high adsorption capacity; on the other side, the P immobilized by LDHs could be slowly released for crops during sustained period.

It has been found that the adsorption behaviors of anions on LDHs in aqueous and packed bed column are affected by various physical and chemical properties including solution pH [8,9,14,15], co-existing anions [8], flow rates [14], and LDHs dosage [16]. It suggested that the adsorption behaviors of LDHs in soil are possibly affected by those various soil properties and climatic conditions, and thus the P adsorption on LDHs in soil was probably also affected correspondingly. To date, however, no systematic studies have been conducted to investigate retention and release of P in soil mixing with LDHs under those conditions. In this study, the transport and retention of P were investigated in soil columns with addition of LDHs under different LDHs dosages, pH, and simulated rain flow velocities. Moreover, the influence of variable pH and flow rate on P release behavior was also evaluated. Two kinetic sites model was employed to assess the mechanisms of P retention in LDHs-soil affected by these physicochemical factors. Additionally, the stability of LDHs in soil columns were also investigated under those various conditions. This knowledge can be useful to better assess the environmental application of Mg-Al LDHs on the control of P loss from soil.

2. Materials and methods

2.1. Soil and LDHs

Surface soil (1–20 cm) samples were collected from an agriculture field site with bamboo plant in Shuyang, China and contain 6.4% clay, 52% silt, and 41.6% sand according to the method by Bouyoucos [17]. The soil had a total organic carbon content of $0.14 \pm 0.01\%$ and a neutral pH value of 7.08 ± 0.04 . Soil was digested with microwave and the cation contents of soil were measured by inductively coupled plasma optical emission spectrometer (ICP-OES). For anion contents, the soil was mixed with H_2O then sonicated for 4 h. The supernatant was filtered and measured by ion chromatography. The cation/anion contents were provided in Table S1. Mg/Al-Cl-LDHs (the mole ratio of Mg/Al = 2:1) was prepared by co-precipitation method and detailed information about synthesis of LDHs, X ray diffraction (XRD), and scanning electron microscope (SEM) results was shown in our previous studies [18].

2.2. Transport and retention experiments

Soils were mixed with certain amount of LDHs by shaking over 1 h vertically at 280 rpm. The mixed soil samples were incrementally wet packed with Milli-Q water into stainless steel columns with inner diameter of 3 cm and length of 12 cm. Three-layered polytetrafluoroethylene (PTFE) meshes (100 μm openings) at the column bottom and top were employed to avoid splashing soil from the surface. Before the P leaching experiments, the columns were slowly saturated from the bottom with a 1 mM KCl solution at Darcy velocity of 0.17 cm min^{-1} for 25–30 pore volumes (PVs). In order to establish steady-state flow conditions, the columns were leached with the background solution (i.e. 1 mM KCl) at selected Darcy water velocities before each P transport experiment over 0.5 h. Then P transport experiments were conducted at different LDH dosages (i.e. 0, 0.5, 1, and 2% LDH), Darcy water velocities (i.e. 0.17, 0.32, and 0.65 cm min^{-1}), and pH (i.e. 5, 7, and 8) by injecting a pulse (around 1.9 PVs) of P suspension (around

0.75 g L^{-1}) into the column, followed by elution with the same background solution for another 4.5 PVs. It should be mentioned that 1 mM KCl was adjusted at pH = 5, 7, and 8 with HCl or KOH as the background solution for the experiments related to different pH. The Darcy velocity was fixed around 0.32 cm min^{-1} during P transport experiments except those experiments related to different Darcy velocity.

To further investigate the influence of changed pH and flow velocity on the release of retained P in columns, two release experiments were conducted. The P transport experiment was conducted with 1 mM KCl at pH = 8 as described above then 1 mM KCl at pH = 5 was injected for another 6.4 PVs. The other P transport experiment was employed with 1 mM KCl at Darcy velocity of 0.17 cm min^{-1} then 1 mM KCl solution was injected at Darcy velocity of 0.65 cm min^{-1} for another 6.4 PVs. Effluent solutions were collected using a fraction collector every $\sim 2 \text{ mL}$ and P, Mg, and Al in effluent solution were measured using ICP-OES. After the transport and release experiments, the spatial distribution of P in each column was determined. Soil samples were carefully excavated each 1 cm increment and collected samples were extracted with $\sim 50 \text{ mL}$ Milli-Q water, followed with $\sim 30 \text{ mL}$ H_2SO_4 (3.6 M) then with $\sim 50 \text{ mL}$ Milli-Q water to determine retention profile (RP) of P [18]. It should be mentioned that a control experiment without P injection and the addition of LDHs was conducted in a similar manner to determine background values of P in the soil. The effluent concentrations of P for this control experiment were extremely low and negligible. The Mg concentration above the background value of control experiment in effluent was considered as an indication of Mg from LDHs. A summary of the experimental conditions is provided in Table 1. Several transport experiments were replicated and exhibited similar results.

2.3. Numerical modelling

A one-dimensional form of the convection-dispersion equation that considers kinetic retention at two sites was used to simulate P transport and retention in the saturated soil columns with/without LDHs. Detailed description of the mathematical model, including governing equation was described in research by Jiang et al. [18]. The first kinetic site contained the first-order retention rate coefficients on site 1 (k_1) and the maximum potential concentration of phosphate on site 1 (S_{max1}), which assumes irreversible retention and Langmuirian blocking. The second kinetic site contained the first-order retention rate coefficients (k_2) and the release rate (k_{2d}) from site 2, which assumes reversible retention.

Table 1

Experimental conditions, hydraulic parameters, and mass balance information for all column experiments.

Fig.	LDHs (%)	C_0 (g L^{-1})	Darcy (cm min^{-1})	pH	ϕ	M_{eff} (%)	M_{soil} (%)	M_{total} (%)
1	0	0.72	0.32	6	0.55	84.1	15.7	99.8
	0.5	0.75	0.32	6	0.51	54.4	43.9	98.3
	1.0	0.75	0.31	6	0.47	20.6	76.7	97.3
	2.0	0.75	0.30	6	0.49	1.4	98.3	99.7
2	0.5	0.77	0.17	6	0.49	30.8	63.1	93.9
	0.5	0.75	0.32	6	0.51	54.4	43.9	98.3
	0.5	0.74	0.65	6	0.50	56.1	38.3	94.4
3	0.5	0.73	0.32	5	0.48	52.0	43.0	95.0
	0.5	0.76	0.32	7	0.49	45.3	52.0	97.3
	0.5	0.77	0.31	8	0.48	28.5	63.3	91.7
	0	0.72	0.32	5	0.48	57.9	35.9	93.8
	0	0.68	0.31	8	0.47	49.9	43.2	93.1
	0	0.68	0.31	8	0.47	49.9	43.2	93.1
4 pH change	0.5	0.72	0.33	8-5	0.48	46.2	48.0	94.2
	0.5	0.68	0.17–0.65	6	0.57	38.9	62.2	101.1

Fig. 1: LDHs dosage effect; Fig. 2: flow velocity effect; Fig. 3: pH value effect; C_0 , P input concentration; ϕ , porosity; V, Darcy velocity; M_{eff} , M_{soil} , and M_{total} are mass percentages of P recovered from effluent, soil, and total, respectively.

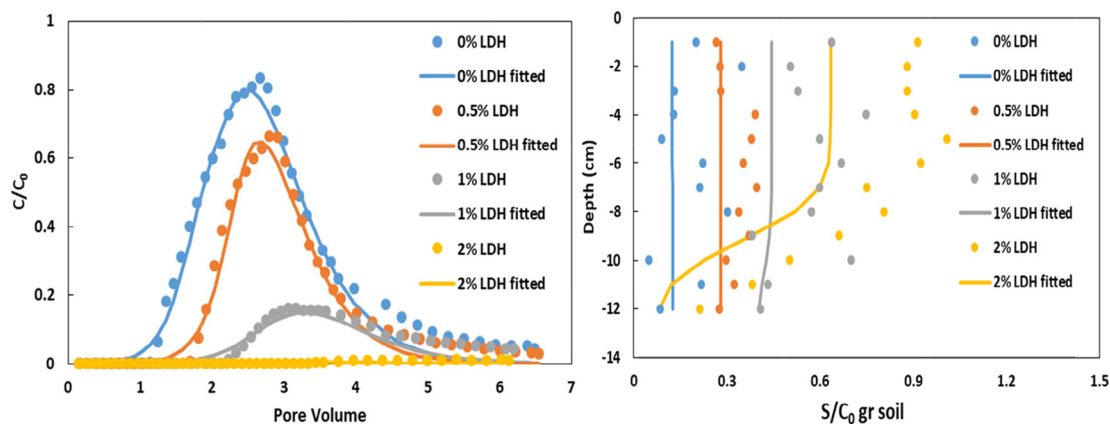


Fig. 1. Measured (symbols) and fitted (lines) breakthrough curves (left) and retention profiles (right) for concentrations of P with addition of different LDHs concentrations (i.e. 0, 0.5, 1, and 2% of mass of total soil), respectively. Fitted curves were obtained using the two-site kinetic retention model. S: the normalized solid-phase concentration, S/C_0 was plotted as a function of distance from the column inlet.

3. Results and discussion

3.1. Effect of LDHs dosages on the transport and retention of P

Fig. 1 presents breakthrough curves (BTCs, left) and retention profiles (RPs, right) for P in soil column with the addition of different LDHs dosages (i.e. 0, 0.5, 1, and 2% LDHs). The BTCs for P are plotted as dimensionless concentrations (C/C_0). The RPs for P are plotted as the normalized solid-phase concentration, S/C_0 as a function of distance from the column inlet. The corresponding mass recoveries of P in the effluent and retained in columns are shown in Table 1. There is a high degree of confidence in the experiment measurements according to the high recovery of 97.3–99.8%. Table 2 summarizes the fitted model parameters and the Pearson's correlation coefficient (R^2) between observed and simulated data. The behavior of P transport and retention in soil column with different LDHs dosages was well described with an $R^2 > 0.94$ using two kinetic retention sites (Table 2). The RPs reflect the amount of irreversible retention (site 1), whereas the tailing portion of the breakthrough curve reflects the reversible site (site 2). In the research of Mansell et al. [19], an irreversible sink with a nonlinear reversible kinetic equation were used to simulate the transport of P through sand soils. The irreversible retention involves the precipitation or chemical immobilization reactions of P and the reversible retention contains the adsorption-desorption process [19].

The BTCs for P were retarded and the amount of transported P decreased with the increasing LDHs dosage in columns (Fig. 1, left).

Accordingly, the peak breakthrough of P occurred later with increasing LDHs dosages (Fig. 1, left). The P effluent mass balance (M_{eff}) strongly decreased 29.7, 63.5, and 82.7% of injected P mass with the addition of 0.5, 1, and 2% LDHs in soil column compared to that in soil column without LDHs, respectively (Table 1). Similarly, the P solid-phase mass balance (M_{soil}) increased from 28.2 to 82.6% as LDHs dosages increased from 0.5 to 2%. More retarded BTCs, lower effluent concentration, and greater retention of P in soil column with increasing LDHs dosages can be explained by the increase in irreversible retention (k_1 and S_{max1}). It occurs due to the increasing adsorption site from LDHs, which increases the time of filling of S_{max1} and brings the retarded BTCs. These observations reflect the increasing anion exchange, electrostatic attraction and surface complexation between phosphate and LDHs as LDHs dosage increases [9]. Similarly, the nitrate leaching was reduced with the addition of LDHs in soils in study of Halajnia et al. [16]. Additionally, similar tailing behavior occurs in all breakthrough curves and plays a relatively small role in comparison to irreversible retention. Values of k_{2d} exhibited an inconsistent trend with LDHs dosages but were always greater than k_2 for all the experiments (Table 2). This reflects a rapid release process that exhibited near equilibrium transport behavior [20].

3.2. Effect of flow velocities on the transport and retention of P

Fig. 2 shows the observed and simulated BTCs and RPs for P in saturated soil column for various Darcy velocities (0.17, 0.32, and 0.65 cm min^{-1}). The total column mass balance (93.9–98.3%) was very

Table 2
Fitted model parameters.

Fig.	LDH (%)	Darcy (cm min^{-1})	pH	k_1 (T^{-1})	S_{max1} (M Ms^{-1})	k_2 (T^{-1})	k_{2d} (T^{-1})	R^2
1	0	0.72	6	3.52E-01	1.25E-01	1.56E-01	4.61E-01	0.962
	0.5	0.75	6	6.92E-01	2.80E-01	1.58E-01	6.02E-01	0.966
	1	0.75	6	6.05E-01	4.45E-01	1.00E+00	1.37E+00	0.940
	2	0.75	6	1.00E+00	6.36E-01	1.16E-01	1.91E-01	0.979
2	0.5	0.17	6	8.18E-01	3.72E-01	1.89E-02	3.25E-02	0.964
	0.5	0.32	6	6.92E-01	2.80E-01	1.58E-01	6.02E-01	0.966
	0.5	0.65	6	9.78E-01	2.65E-01	1.25E-01	3.84E-01	0.965
3	0.5	0.73	5	3.43E-01	3.12E-01	2.13E-01	5.12E-01	0.958
	0.5	0.76	7	8.91E-01	3.43E-01	7.95E-02	1.68E-01	0.953
	0.5	0.77	8	2.59E-01	4.03E-01	1.00E+00	7.17E-01	0.908
	0	0.72	5	6.04E-01	9.77E-02	3.82E-02	1.17E-02	0.946
	0	0.68	8	8.47E-01	2.86E-01	1.26E-01	1.87E-01	0.924

Fig. 1: LDHs dosage effect; Fig. 2: flow velocity effect; Fig. 3: pH value effect; R^2 reflects the correlation of observed and fitted data; k_1 and k_2 , the first-order retention rate coefficients on site 1 and 2, respectively; k_{2d} , the first-order release rate coefficient from site 2; S_{max1} , normalized maximum solid phase concentration of deposited phosphate on site 1.

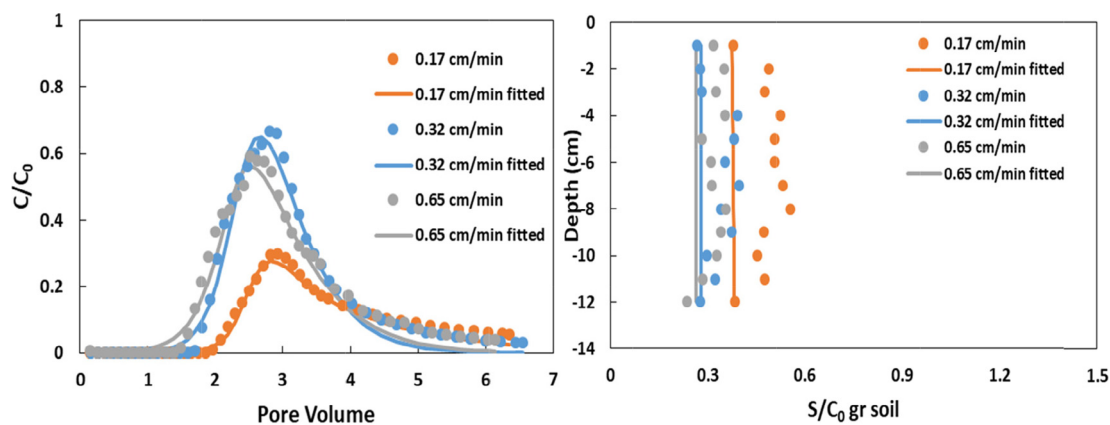


Fig. 2. Measured (symbols) and fitted (lines) breakthrough curves (left) and retention profiles (right) for concentrations of P with different Darcy velocity in soil mixing 0.5% LDHs, respectively. Fitted curves were obtained using the two-site kinetic retention model. S: the normalized solid-phase concentration of P, S/C_0 was plotted as a function of distance from the column inlet.

good (Table 1). Higher effluent concentrations and less retention for P were observed for higher q (flow velocity) in Fig. 2 and Table 1. Macroscopically, when the flow rate increases, the residence time of P in LDHs-soil column decreases, which results in lower retention efficiency [21]. Dadwhal et al. [13] also reported a decrease in breakthrough time with increasing flow rate for the adsorption of arsenic on LDHs. The two-site kinetic retention model provided a good description for both BTCs and RPs of P with different Darcy velocity ($R^2 > 0.96$). The value of S_{max1} decreased with higher Darcy velocity, which brings less retention of P in LDHs-soil column and faster breakthrough time (Fig. 2; Tables 1 and 2). The greater k_{2d} than k_2 for all Darcy velocity (Table 2) reflects a rapid release process and near equilibrium transport behavior [20]. It should be pointed out that the value of S_{max1} was the greatest but the values of k_2 and k_{2d} were extremely the smallest at the Darcy velocity of 0.17 cm min^{-1} in comparison with those at higher velocity (Table 2). It suggested that small velocity could improve the irreversible retention but inhibit the reversible retention of P in LDHs-soil.

3.3. Effect of pH on the transport and retention of P

The results in Fig. 3 demonstrate the effects of pH on transport behaviors for P in soil column with/without 0.5% LDHs. The transport of P in LDHs-soil column was evidently dependent on pH (Fig. 3a). The decreasing P was transported and increasing P was retained under higher pH value (Table 1). The modelling results showed that the value of S_{max1} increased with higher pH, suggesting greater irreversible retention with pH, which is consistent with observed result (Fig. 3a and Table 2). It is worth mentioned that greater adsorption of P occurs on LDHs in more acidic solution, i.e. lower pH [8,15,22]. It was explained that increased protonation in lower pH increased the positively charged sites, thus enlarged the attraction force between sorbent surface and the phosphate anions. Correspondingly, greater negatively charged sites at higher pH enhance the repulsion effect and the amount of adsorption is dropped [22]. However, the P retention in soil mixing with LDHs showed opposite tendency compared to that in solution. To further investigate the role of soil on P adsorption, we compared the P transport experiments from soil column without LDHs at pH = 5 and 8 (Fig. 3c), and found that M_{soil} increased with greater pH value (Table 1). The model results showed that both reversible retention (i.e. k_2 and k_{2d}) and irreversible retention (i.e. k_1 and S_{max1}) are greater under higher pH (i.e. pH = 8) for the transport experiments without addition of LDHs (Table 2). Many researches have shown that calcium-driven sorption and precipitation (e.g. insoluble calcium phosphate) for P increased at higher pH, which reduced transport of P from soil [23–26]. The addition of 0.5% LDHs in soil column decreased k_1 and increased S_{max1} , brought greater irreversible retention and retardation, but did not

change the tendency of P retention in LDHs-soil related to pH. Those results suggested that soil plays an important role for P retention in LDHs-soil system under various pH condition. Additionally, the addition of LDHs increased the soil pH values after the P transport experiments (data not shown). Increased pH was caused by the strong buffering effect of LDHs [27]. The similar results have been demonstrated in aqueous solutions and in soils [11,27–28].

3.4. Change of pH and flow velocity on the release of P

Our previous study has found that the release of P from LDHs-soil column is highly influenced by reduction of ionic strength and ionic exchange [18]. Considering the large difference for transport behavior of P with pH and velocity as above shown, we wonder if the change of pH and velocity has potential to influence the release of P. Fig. 4 presents the observed BTCs and RPs for P when pH changes from 8 to 5 and Darcy velocity changes from 0.17 to 0.65 cm min^{-1} (i.e. from phase 1 to phase 2). No obvious peaks occurred when pH or velocity changed to phase 2 (Fig. 4), suggesting no obvious release for P with the change of pH and velocity. Those results suggested that the retention of P in LDHs-soil system is stable enough and the change of pH and velocity in studied range have little influence on desorption and release of P from LDHs-soil. In the study of Novillo et al. [15], phosphate adsorbed on LDHs in solution can be efficiently desorbed at acid (i.e. pH = 3) and basic pH (i.e. pH = 10) while at neutral pH (i.e. pH = 6) only 7% of phosphate is desorbed. Our studied pH range is between 5 and 8 which are not strong acid or basic pH. On the other hand, the P desorption from LDHs is weaker in soil leaching system than solution batch experiment due to more insufficient contact in soil system. These results also suggested that the conditions affecting P adsorption and desorption behaviors on LDHs-soil are different. The P desorption seems to be more difficult to occur and those conditions such as pH and flow velocity in studied range which could affect P adsorption on LDHs-soil strongly have little influence on the P desorption at least in short-term.

3.5. Stability of Mg/Al-LDHs in soil

For all the P transport experiments with different LDHs dosages, velocity, pH, and change of pH as well as flow velocity, the transported Al concentrations are all extremely low (data not shown), which indicated that there are no transport of LDHs particles for all the experiments. The addition of 0.5% LDHs in soil column caused more transport of Mg in comparison to P transport experiment without LDHs (Fig. 5a). Those additional Mg is probably from the dissolution of LDHs due to the complexity of soil environment and is highly affected by various soil reactions [16,29–31]. Furthermore, the P adsorption on

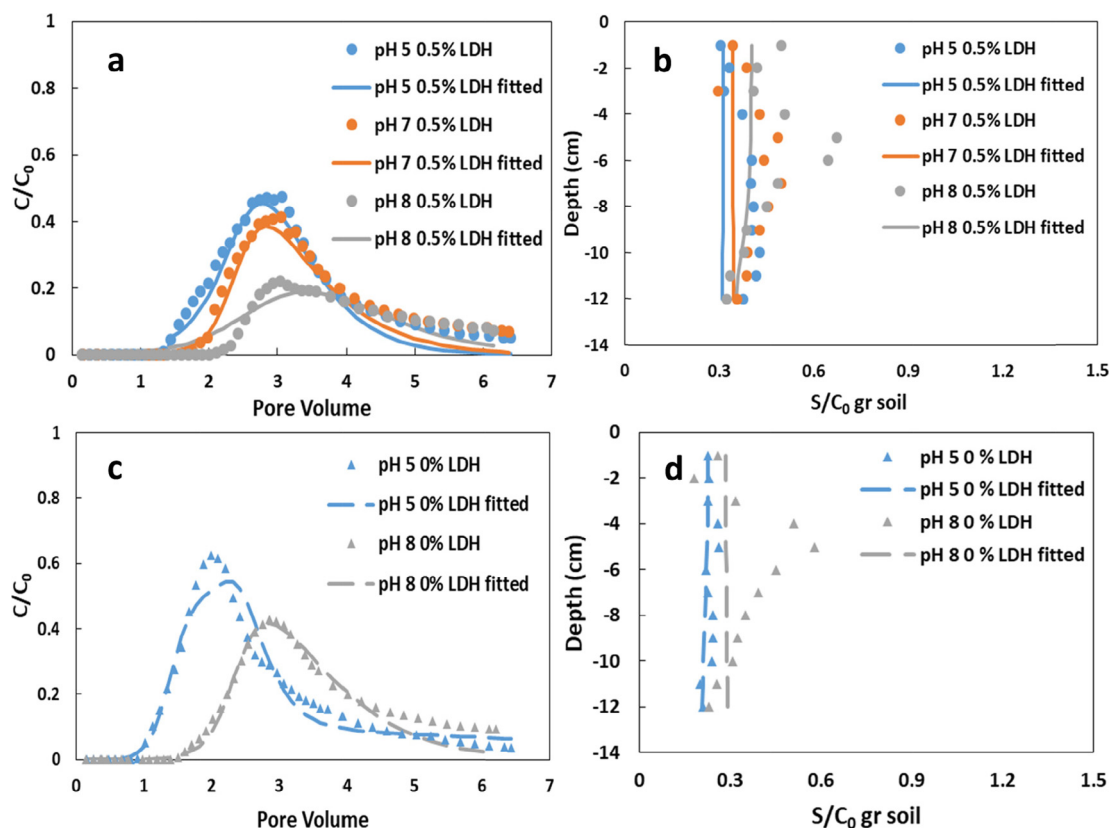


Fig. 3. Measured (symbols) and fitted (lines) breakthrough curves (a,c) and retention profiles (b,d) for concentrations of P with different pH in soil with 0.5% and 0% LDHs, respectively. Fitted curves were obtained using the two-site kinetic retention model. S : the normalized solid-phase concentration of P, S/C_0 was plotted as a function of distance from the column inlet.

LDHs decreased degree of crystallinity of LDHs, which could also increase the solubility of LDHs [16]. However, it is worth noting that the transported Mg from the P transport experiments decreased when the LDHs dosage increases from 0.5 to 2% (Fig. 5a). It seems that more positively charged LDHs increased the electrostatic attraction with soil and the increasing adhesive force has potential to impede the dissolution of LDHs and the Mg transport from soil. The transport of Mg did not reach a steady-state when P transport experiments with the addition of LDHs $\geq 1\%$ finish, which suggested that the dissolution of LDHs still continues when column is washed with background solution again. The transport of Mg with different velocity, pH, and change of those have similar tendency with the transport of P: slower velocity and higher pH

value decreased the transport of Mg. The difference of Mg concentrations transported from soil column with and without LDHs was considered as the indication of LDHs. The transport of Mg from dissolved LDHs from soil column was also impeded under higher pH: 1.47 mg Mg from dissolved LDHs at pH = 5 and 0.34 mg Mg from dissolved LDHs at pH = 8 were transported. Luengo et al. [9] have found that the dissolution kinetic of Mg-Al LDHs in water was very similar in the pH range 5–8. In soil system, greater negatively charged sites at higher pH enhance the attraction force with positively charged LDHs, which could limit the dissolution of LDHs. Additionally, the tendency of transported Mg was similar with the transported P at different Darcy velocity in soil without LDHs (Fig. S1). The transported Mg concentration was greater

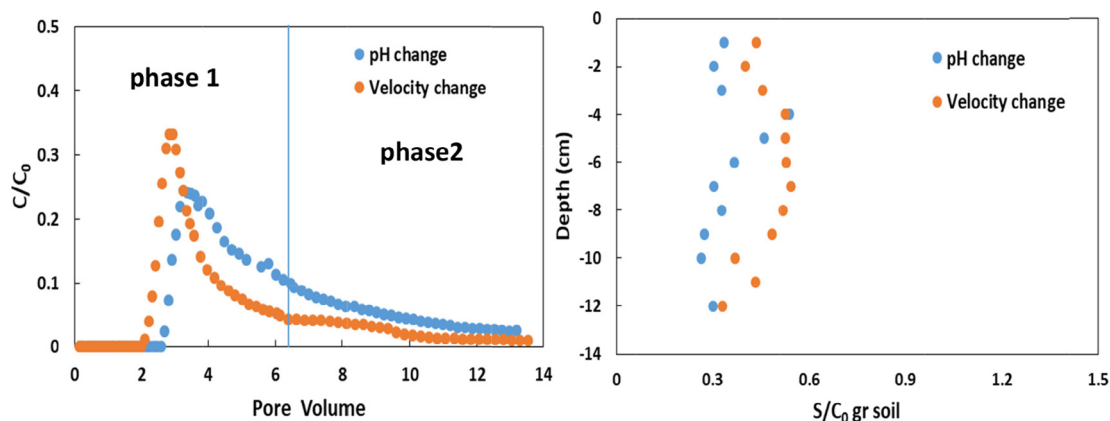


Fig. 4. Measured breakthrough curves (left) and retention profiles (right) for concentrations of P with change of pH (pH = 8 in phase 1 to pH = 5 in phase 2) and Darcy velocity (0.17 cm min^{-1} in phase 1 to 0.65 cm min^{-1} in phase 2) in soil mixing with 0.5% LDHs, respectively. S : the normalized solid-phase concentration, S/C_0 was plotted as a function of distance from the column inlet.

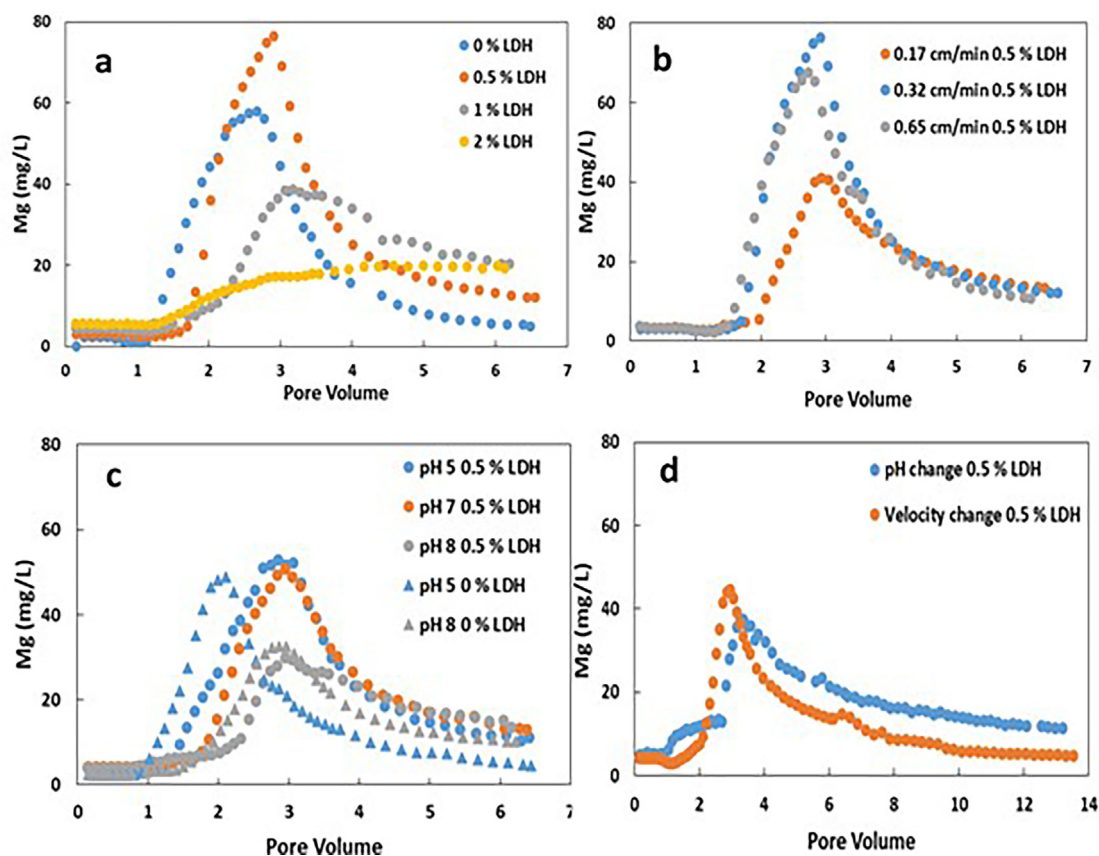


Fig. 5. Measured breakthrough curves for concentrations of Mg with different LDHs concentrations (a), Darcy velocity (b), pH (c), and change of pH as well as velocity (d) in soil column with and without LDHs, respectively.

from soil column in comparison with that from LDHs-soil column at Darcy velocity = 0.17 cm min^{-1} (Fig. S1 and Fig. 5). It seems that the transport of Mg from dissolved LDHs did not occur and the addition of LDHs in soil even impedes the transport of Mg from soil at lower Darcy velocity = 0.17 cm/min .

4. Conclusion

The P loss from agriculture is still a water quality concern in China. The results of this study have significant implication for the land application of LDHs. The retention of P in soil increases with high LDHs dosages, low velocity, and high pH. On the other side, the change of soil pH (i.e. from 8 to 5) and rainfall intensity (i.e. from 0.17 to 0.65 cm min^{-1}) could not affect the release of P from soil mixing with LDHs, suggesting that the slow-release of P from LDHs-soil is also not affected by those factors in short-term. The dissolution of LDHs occurs in soil, however, the great LDHs dosages increase the electrostatic attraction and adhesive force between soil and LDHs and thus could impede the dissolution of LDHs. Additionally, the stability of LDHs increase at higher pH and lower velocity. Those information is important to understand the role of LDHs on the retention and release of P in soil under various environmental factors and evaluate the environmental application of LDHs in soil.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.122154>.

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