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Availability and vertical distribution of Cu, Cd, Ca, and P in soil as influenced by lime and apatite with different dosages: a 7-year field study

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Abstract

It is well known that alkaline amendments could effectively decrease the bioavailability of heavy metals in soils. However, the vertical distribution of heavy metals and the nutrients enriching in amendments are little concerned during long-term field remediation. Thus, the objective of the present study was to investigate the vertical distribution and availability of Cu, Cd, Ca, and P after a 7-year field experiment. In this study, a single application of lime and apatite was conducted with the rates of 1.71–6.84 and 6.84–19.8 tons/ha, respectively. Soil pH and immobilization efficiency of Cu and Cd were both increased with increasing dosages of lime and apatite (0–50 cm). Applications of lime and apatite decreased the mobility of Cu and Cd although soil Cu and Cd in the surface soil were increased due to the input by atmospheric dry and wet deposition. Moreover, concentrations of Cu and Cd in lime- and apatite-amended soils (0–13 cm) were higher than those in the control group. However, applications of lime and apatite decreased the downward eluviations of heavy metals in soils (13–50 cm). For soil nutrients, the Ca concentrations at 0–13 and 13–30 cm were both enhanced with increasing amendment dosages, while only soil P concentration at 0–13 cm was increased in apatite-treated soils and majority of them presented in stable-P. In addition, resin-P was increased with increasing dosages of the apatite, which suggested that high eutrophication risk was induced by excessive P loss. Thus, more attention should be paid to the nutrients (phosphorus) and pollutants enriching in the amendments during in-situ remediation of heavy metal-contaminated soils.

Keywords Heavy metals · Immobilization · Vertical distribution · Lime · Apatite · Dosage

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Introduction

Heavy metals are non-biodegradable pollutants, which can seriously hazard environmental quality and human health, and have attracted much public attention internationally (Zhao et al. 2015). In China, 19.4% of all soil samples are polluted by pollutants, particularly cadmium (Cd) that ranks top (7%) in the list of inorganic pollutants (Ministry of Environmental Protection, P. R. C, Ministry of Land and Resources, P. R. C 2014). Especially the surroundings of mining and industry in which the soils have been seriously contaminated, the quality of farmland soil and the safety of agricultural production are of particular concern (Xu et al. 2017; Zhao et al. 2015). Chemical immobilization among the existing physical, chemical, and biological restoration methods is commonly used in agriculture soils for such large-scale contaminated site due to their low cost (Nejad et al. 2018). In case where vegetation cannot grow due to

metal toxicity, soil acidity, and adverse physical characteristics, immobilization with soil amendments could promote the vegetation cover and make an aesthetical improvement as well as a decrease of wind and water erosion (Friesl-Hanl et al. 2009).

Some studies have reported that lime, apatite, biochar, industrial by-products, etc. are effective to decrease the heavy metal bioavailability (González-Núñez et al. 2017; Mzu et al. 2017) and the sustainable effects of the immobilization are dependent on the type of amendments, application dosage, and frequency. Madejón et al. (2010) reported that vegetation was reestablished and heavy metals bioavailability decreased with the applications of two organic amendments (biosolids compost and leonardite) and one inorganic amendment (sugarlime) in a semiarid contaminated soil, but both organic amendments required repeated applications for the longevity and sustainability of their effectiveness. It is clear that amendment application with high dosages can decrease the mobility of trace metals and prolong the sustainability of heavy metal immobilization efficacy. However, soil may become alkaline and compacted, even low-yield field with excess amount of alkaline amendments applied into the polluted soils (Lahori et al. 2017). Moreover, potentially deleterious trace metals (e.g., Cd, lead, arsenic) and nutrients (e.g., nitrogen (N), phosphorus (P)) enriching in amendments (e.g., biosolids, apatite) may accumulate in top soil and vertically migrate within the soil profile, and even intensify the risk of trace metals transferred in the food chain (Farrell et al. 2010; Mollon et al. 2016; Sukkariyah et al. 2007). Unfortunately, the influence of trace metals and nutrients after long-term field remediation has been of little concern. Therefore, it is essential to evaluate the effects of soil amendments on the vertical distribution of trace metals during long-term stabilization and restoration of soil.

Previous studies mainly concentrated on the investigation and evaluation about vertical distribution of pollutants (Gao et al. 2017; Zhang et al. 2018). However, until now, little is known about the vertical distribution and chemical speciation of heavy metals during long-term immobilization with high dosage of amendments applications in the field condition. Our previous studies have indicated that apatite and lime could effectively decrease soil available copper (Cu) and Cd, and higher dosage of apatite had better immobilization efficiency in a Cu- and Cd-contaminated soil (Cui et al. 2016a; Cui et al. 2017a), but these studies have neglected the heavy metal vertical distribution affected by different application dosages. Consequently, the objectives of the present study were to evaluate the vertical distribution of Cu, Cd, calcium (Ca), P, and soil organic carbon (SOC), and chemical speciation of Cu, Cd, and P after apatite and lime applications with different dosages in the immobilization of heavy metal-contaminated soils from 2010 to 2016.

Materials and methods

Contaminated soil

The Guixi smelter (28°19′30.1″ N, 117°14′28.9″ E) is the largest Cu smelter sites in China, which was established in 1979. During the last 40 years, over 130 hm^2 of farmland around the smelter has been contaminated by the irrigation of discharged wastewater, atmospheric deposition of flue gas, and accumulation of waste residue (Zhou et al. 2018). The field experiment was carried out in a paddy field which was located about 1.0 km (Jiuniugang village) to the west of the smelter. Now, rice and edible vegetables are prohibited to be cultivated near the smelter. The origin soil was incredibly acidic (pH = 4.20), including soil organic carbon (SOC) content, cation exchange capacity (CEC), exchangeable acid, and exchangeable Al of 17 mg/kg, 94, 33, and 25 mmol/kg, respectively. Furthermore, the average concentrations of Cu and Cd and were 662 and 0.52 mg/kg, respectively. Total N and total P in the soil were 1.28 and 0.57 g/kg, respectively.

Field experiment

Experimental design

The experimental field was divided into 21 plots of 3 × 2 m, with a ridge 0.5-m wide between plots. Apatite and lime were mixed with the top soil (0–13 cm, Ap1 horizon) using a harrow on 29 November 2009. The plot treatments consisted of an unamended control, L-lime applied at rate of 1.71 tons/ha of lime (0.1%, w/w), M-lime applied at rate of 3.42 tons/ha of lime (0.2%, w/w), H-lime applied at rate of 6.84 tons/ha of lime (0.4%, w/w), L-apatite applied at rate of 9.89 tons/ha of apatite (0.58%, w/w), M-apatite applied at rate of 19.8 tons/ha of apatite (1.16%, w/w), and H-apatite applied at rate of 39.6 tons/ha of apatite (2.32%, w/w). The experiment was carried out in a completely random plot design with three replicate plots per treatment. Then, the soils were irrigated with tap water (5 × 10^5 L/ha). After a week of equilibrium, a compound fertilizer (N:P$_2$O$_5$:K$_2$O = 15:15:15, 834 kg/ha) was added and ryegrass seeds (50 kg/ha) were sown in each plot. The amendments were applied only once in 2009, and ryegrass and compound fertilizer were applied once each year.

Apatite and lime

Apatite (grain size 0.25 mm, pH 8.4) and lime (grain size 0.16 mm, pH 12.2) were purchased from Hubei Nanzhang Changbai Mineralization Industry Co., Ltd. (Hubei, China) and a local market, respectively. The concentrations of Cu and Cd were 9.54 and 1.18 mg/kg in apatite, respectively, and 1.36 and 0.87 mg/kg in lime, respectively. The contents of CaO in lime and apatite were 25.8% and 13.5%,

respectively. The concentrations of P in lime and apatite were 0.16 g/kg and 109 g/kg, respectively.

Soil sampling

Similar to Ostermann et al. (2014), soil samples were taken at depths of 0–13 (Ap1 horizon), 13–30 (Ap2 horizon), and 30–50 cm (B horizon) from 63 sites (21 plots) using a shovel and then artificially mixed together to form a single replicate sample (three samples per plot) in January 2016. Thereafter, soil samples at the depth of 0–13 cm were air dried at room temperature and passed through a < 2-mm sieve for chemical analysis and moisture content of soil was determined as well.

Analytical methods

Air-dried soil samples were digested with mixed HNO_3-HF-$HClO_4$ (5:10:5 mL) on a hot plate for the determination of total Cu, Cd, and Ca by a flame or graphite furnace atomic absorption spectrophotometer (Hitachi Model Z-2000, Japan). A certified soil reference material (GBW07405, National Research Center for Certified Reference Materials, China) was used to ensure the accuracy of the analytical data and the accuracy ranging from 92.7 to 108%.

The pH of soil and amendments were measured using a pH electrode (E-201-C, Shanghai Truelab Instrument Company, China) in a 1:2.5 (w/v) ratio of soil to distilled water. Soil total N was determined based on the digestion procedure of Kjeldahl (Bremner and Tabatabai 1972). Soil alkali-hydrolyzable N and total P were analyzed by using the method described by Lu (2000). SOC was determined using the method described by Walkley and Black (1934). Soil Olsen-P was analyzed by colorimetry using ammonium molybdate and ascorbic acid (Olsen et al. 1954). Soil-test K was determined by atomic absorption spectroscopy (Pratt 1965). The cation exchange capacity, exchangeable acidity, and exchangeable aluminum (Al) were determined based on the methods described by Pansu and Gautheyrou (2006).

The soil $CaCl_2$ extractability of Cu and Cd was measured in a 1:5 (w/v) ratio of soil to 0.01 mol/L $CaCl_2$ after being shaken for 2 h at room temperature (25 °C). Five chemical fractions of Cu and Cd included exchangeable (EXC), bound to carbonate (CA), Fe–Mn oxides (Fe–Mn), organic matter (OM), and residual fraction (RES) and were measured based on the sequential extraction procedure of Tessier et al. (1979). The modified method of Tiessen and Moir (1993) was used to determine the fractions of soil P including labile resin-P, labile inorganic $NaHCO_3$-P ($NaHCO_3$-Pi) and organic $NaHCO_3$-P ($NaHCO_3$-Po), moderately labile inorganic NaOH-P (NaOH-Pi) and organic NaOH-P (NaOH-Po), stable HCl-P, and residual-P. The detailed experimental description of chemical fractions of Cu and Cd, and soil P can be found in the literature by Cui et al. (2017b).

The mineral phases of soil samples (< 2 mm) were identified by X-ray diffraction (XRD) measurement. The patterns were obtained by a Rigaku X-ray diffractometer with $CuK\alpha$ radiation (40 kV/40 mA). The XRD data was analyzed using MDI Jade 5.0 software (Materials Data Inc., Liverpool, CA).

Data analysis

Data were presented as mean ± standard error and were analyzed by one-way analysis of variance using SPSS version 19.0 for Windows. The multiple comparisons of the means within the treatments were tested by Duncan's multiple range test at the 5% significant level.

Results

Soil chemical characteristics

As shown in Table 1, soil Olsen-P increased from 53.5 mg/kg in the untreated soil to 74.2–143 mg/kg in 0.58–2.32% apatite-treated soils, but little differences were found in the lime-treated soils. Exchangeable acidity was reduced from 42.1 mmol/kg in the untreated soil to 7.86–35.6 and 1.16–24.3 mmol/kg in lime and apatite soils, respectively. Exchangeable Al had the trend similar to exchangeable acidity. In comparison with the control soils, only H-lime, M-apatite, and H-apatite soils had significantly higher available K. However, there were no effects on soil total N, alkali-hydrolyzable N, and cation exchange capacity among all the treatments.

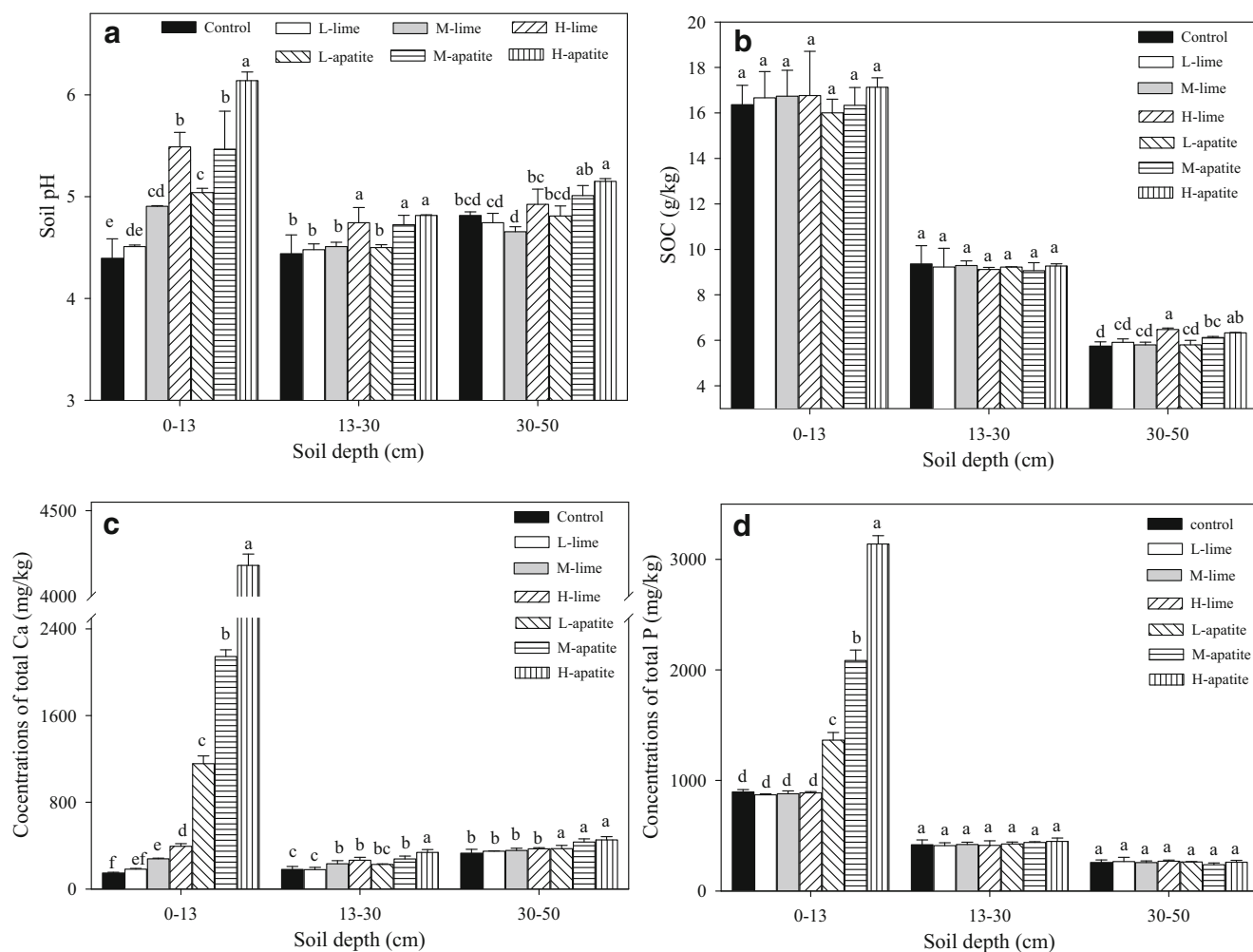### Vertical distribution of soil pH, SOC, Ca, and P

The greatest effect on soil pH was found in the H-apatite due to the higher rate of apatite (2.32%) than that of lime (0.4%), although contents of CaO in lime (25.8%) was higher than that in the apatite (13.5%) (Fig. 1a). For instance, soil pH was 6.12 in the H-apatite after 7 years, which was higher than that in H-lime (pH = 5.49). At a lower soil profile, noticeable differences between the control soils and amended soils were only observed for H-lime, M-apatite, and H-apatite at 13–30 cm and H-apatite at 30–50 cm. Moreover, the effects of lime and apatite on soil pH were mainly restricted to the surface layer, which were dependent on the application rates of lime and apatite and were reduced with increasing soil depth in all treatments. SOC for all soils was characterized by a significant surface enrichment and decreased with increasing soil depth (Fig. 1b). Furthermore, applications of apatite and lime did not change the distribution of SOC at the depths of 0–13 cm and 13–30 cm, which may be due to the fact that shoot and root of ryegrass and *Setaria glauca* were both removed from the plots.

Table 1 Basic chemical characteristics of the soils amended by different dosages of lime and apatite

Treatment	T-N g/kg	A-N mg/kg	O-P mg/kg	A-K mg/kg	CEC mmol/kg	E-acidity mmol/kg	E-Al mmol/kg
Control	16.4 ± 0.85a	125 ± 10a	53.5 ± 5.1d	85.5 ± 4.2b	8.66 ± 0.43a	42.1 ± 1.96a	36.3 ± 2.29a
L-lime	16.7 ± 1.15a	119 ± 13a	47.1 ± 5.8d	87.5 ± 10.6b	8.92 ± 0.36a	35.6 ± 1.96b	28.9 ± 2.73b
M-lime	16.7 ± 1.13a	132 ± 10a	42.1 ± 4.2d	108 ± 7.1ab	9.10 ± 0.50a	28.9 ± 0.33c	20.7 ± 0.85c
H-lime	16.8 ± 1.94a	129 ± 10a	36.8 ± 4d	121 ± 11.7a	9.20 ± 0.22a	7.86 ± 0.65e	4.58 ± 0.21d
L-apatite	16.0 ± 0.60a	116 ± 3a	74.2 ± 6.1c	97.5 ± 7.1ab	9.06 ± 0.14a	24.3 ± 3.6d	18.3 ± 3.51 c
M-apatite	16.3 ± 0.78a	123 ± 8a	114 ± 6b	118 ± 11a	9.16 ± 0.70a	7.17 ± 0.34e	4.39 ± 1.41d
H-apatite	17.1 ± 0.42a	125 ± 16a	143 ± 12a	119 ± 5a	9.45 ± 0.14a	1.16 ± 0. 13f	1.12 ± 0.27d

T-N, total nitrogen in soil; *A-N*, alkali-hydrolyzable nitrogen; *O-P*, Olsen phosphorus; *A-K*, soil available K; *CEC*, cation exchange capacity; *E-acid*, exchangeable acidity; *E-Al*, exchangeable Al. Control = untreated soil, L-lime = 0.1% lime plus soil, M-lime = 0.2% lime plus soil, H-lime = 0.4% lime plus soil, L-apatite = 0.58% apatite plus soil, M-apatite = 1.16% apatite plus soil, H-apatite = 2.32% apatite plus soil

Mean ($n = 3$) and standard error followed by different letters indicated significant differences ($p < 0.05$)

Fig. 1 Vertical distributions of soil pH, SOC, Ca, and P after immobilization for 7 years. Control = untreated soil, L-lime = 0.1% lime plus soil, M-lime = 0.2% lime plus soil, H-lime = 0.4% lime plus soil, L-apatite = 0.58% apatite plus soil, M-apatite = 1.16% apatite plus soil, H-apatite = 2.32% apatite plus soil. Means ($n = 3$) followed by different letters above the columns indicated significant difference at the $p < 0.05$. Error bars are standard error of the mean.

Soil total Ca was mainly concentrated on the surface layer and decreased with the increasing of soil depth in lime- and apatite-treated soils. Here, soil Ca in H-lime and H-apatite soils was increased by 1.67 and 27.3 times at 13–30 cm and by 0.47 and 0.87 times at 30–50 cm than the control soils, respectively (Fig. 1c). At the depth of 30–50 cm, only L-apatite-, M-apatite-, and H-apatite-treated soils significantly increased Ca concentrations by 0.52, 1.33, and 2.51 times, respectively. Similar to soil total Ca, total P was mainly concentrated on the surface layer (Fig. 1d). Especially, total P at 0–13 cm increased from 895 mg/kg in the untreated soil to 1364–3139 mg/kg in 0.58–2.32% in apatite-treated soils. However, no significant differences for P were observed between lime-amended soils and control soils for 0–50-cm layers. In general, concentrations of Ca at 30–50 cm were higher than those at 13–30 cm, which suggested a noticeable leaching effect into the lower horizon (13–30 cm). However, soil P was restricted to the 0–13-cm layer, and no noticeable leaching effect was observed among all treatments.

Vertical distribution of soil total and CaCl$_2$ extractable Cu, Cd

Compared with the control, total Cu and Cd at the depth of 0–13 cm slightly increased with increasing dosages of the lime and apatite, particularly in the H-lime and H-apatite treatments. The highest concentrations of Cu (1071 mg/kg) and Cd (663 μg/kg) at the 13–30-cm layer were found in the control soils and they were higher than those at the 0–13-cm layer (Fig. 2a, b), which suggested that the increases of total Cu and Cd for the lower horizon (13–30 cm) were due to a leaching effect from the top soil (0–13 cm). For the depth of 30–50 cm, the concentrations of Cu and Cd were the lowest than those in the upper soil, and only M-lime, H-lime, and H-apatite decreased total Cu, but no different significance was found for total Cd.

Mean CaCl$_2$-extractable Cu concentrations at the depth of 0–13 cm were decreased with increasing dosages of the lime and apatite compared with the control soils (Fig. 2c, d). A similar trend was found for CaCl$_2$-extractable Cu at the depths of 13–30 and 30–50 cm. However, only H-lime, M-apatite, and H-apatite decreased CaCl$_2$-extractable Cd at the depth of 0–13 cm. As a rule, CaCl$_2$-extractable Cu concentrations decreased with soil depth in all treatments, but no significant decrease for CaCl$_2$-extractable Cd. Moreover, apatite had higher immobilization effect on decreasing CaCl$_2$-extractable Cu and Cd than those of lime except for CaCl$_2$-extractable Cd at the 13–30 cm.

Transformation of Cu and Cd fractions

Five fractions of Cu and Cd at the depth of 0–13 cm were shown in Table 2. For the control soils, Cu preferentially were partitioned into the residual fraction (266 mg/kg, 38.5%) followed by the exchangeable (150 mg/kg, 21.7%) and organic matter fractions (112 mg/kg, 16.2%), while those of the Fe–Mn oxide (96.8 mg/kg, 14%) and carbonate-bound fractions (65.9 mg/kg, 9.59%) were in a low percentage. With increasing dosages of the lime and apatite, the exchangeable Cu decreased remarkably. Specifically, the exchangeable Cu accounted for 5.39% (41.3 mg/kg) and 4.02% (31.7 mg/kg) of the total Cu in H-lime and H-apatite treatments, respectively. On the contrary, the carbonate-bound, Fe–Mn oxide, and organic matter fractions of Cu slightly increased with increasing dosages of the lime and apatite. No significant differences for residual fraction of Cu were observed between amended soils and the control soils.

Cd was mostly concentrated on the bound to exchangeable and residual fractions in the control soils, accounting for 40.3 and 33.9% of the total Cd in the untreated soil, respectively (Table 2). Similar to Cu, the exchangeable Cd decreased markedly with increasing dosages of the lime and apatite, and the carbonate-bound, Fe–Mn oxide, and organic matter fractions of Cd slightly increased. Compared with the control soils, H-lime, M-apatite, and H-apatite increased residual fraction of Cd by 40.9, 60.5, and 70.6 μg/kg, respectively.

Transformation of P fractions

The transformation of soil P (resin-P, NaHCO$_3$-Pi, NaHCO$_3$-Po, NaOH-Pi, NaOH-Po, HCl-P, and residual) in different soils was shown in Table 3. The greatest relative increases of resin-P, NaHCO$_3$-Po, HCl-P, and residual-P were observed in apatite-treated soils, and all followed the order of L-apatite < M-apatite < H-apatite. Since resin-P is freely exchangeable P and can be used as a good indicator of the short-term P loss potential in soil, the increase of resin-P may result in a potential risk of excessive P-induced eutrophication. However, lime application decreased soil resin-P and NaHCO$_3$-Pi, and increased NaOH-P and HCl-P. The percentages of soil labile-P and stable-P in the control soils were 42.1% and 35.8%, respectively. Nevertheless, apatite and lime both decreased the percentages of soil labile-P and moderately labile-P, and increased soil stable-P. In addition, 90.4–94.2% of the increase of soil total P in the apatite-treated soils was transformed into stable-P and only 5.55–8.40% was changed into resin-P. Especially, HCl-P accounted for 66.7–74.4% of the increase of soil total P, which may be due to the fact that HCl-P is considered to be stable-P associated with apatite, other Ca-P compounds, or negatively charged oxides surfaces.

Discussions

Our previous field trial showed that soil pH initially increased after lime and apatite treatment, but later showed a decreasing
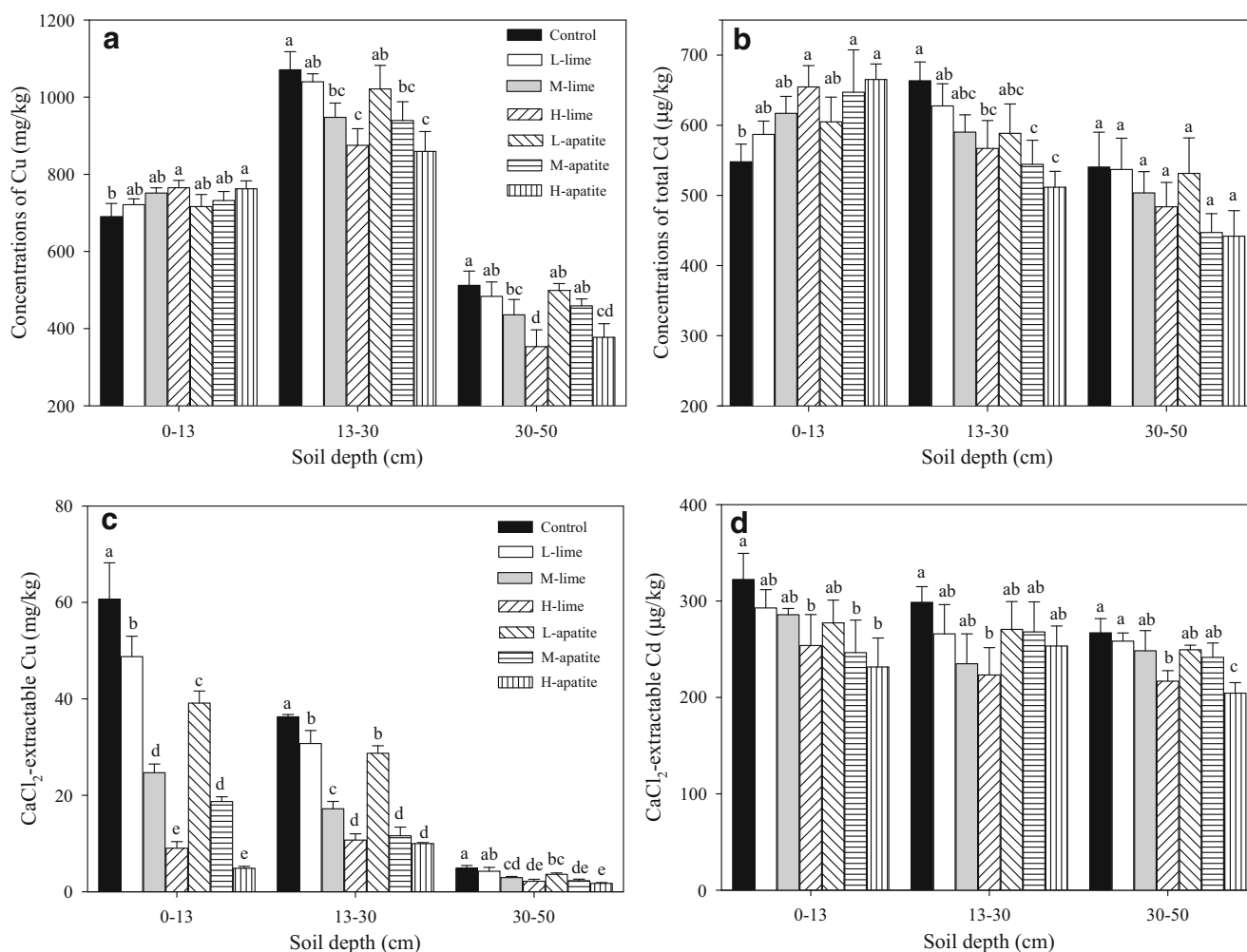
Fig. 2 Vertical distributions of soil total and CaCl$_2$-extractable Cu and Cd after immobilization for 7 years. Control = untreated soil, L-lime = 0.1% lime plus soil, M-lime = 0.2% lime plus soil, H-lime = 0.4% lime plus soil, L-apatite = 0.58% apatite plus soil, M-apatite = 1.16% apatite plus soil, H- apatite = 2.32% apatite plus soil. Means ($n = 3$) followed by different letters above the columns indicated significant difference at the $p < 0.05$. Error bars are standard error of the mean

trend with time due to leaching of alkalinity (Cui et al. 2016b). This present study clearly demonstrated that the effect on soil pH was dependent upon amendment type and rate of application, and application of apatite had better sustainable effect on alleviating acidification. Moreover, soil exchangeable acid and exchangeable Al were decreased due to the input of alkalinity from lime and apatite. However, only apatite-treated soils increased soil Olsen-P because of high P enriching in apatite. After the 7-year field experiment, Cu (690 mg/kg) in the untreated soils of 0–13 cm were higher than Cu (662 mg/kg) in 2009, and it may be resulted from the inputs of Cu by atmospheric dry and wet deposition. For example, Tao et al. (2014) reported that atmospheric inputs of Cu and Cd were 1973 and 15.2 mg/m^2 through dry and wet deposition near the study site. However, total Cu and Cd were slightly increased with increasing the application rates of lime and apatite than the control soils, especially in H-lime- and H-apatite-treated soils. Since the highest inputs of lime and

apatite only increased soil Cu by 5 and 221 μg/kg, and soil Cd by 3.48 and 27.4 μg/kg, respectively, these inputs were of a little positive effect to increase soil total Cu and Cd. The reason may be resulted from the differences in the outputs by surface runoff and leaching downward among the different treatments. Based on previous studies (Cui et al. 2016a and Cui et al. 2016b), we outlined Fig. 3 which clearly suggested that lime and apatite immobilized part of the original and new input Cu and Cd. Firstly, the atmospheric deposition of Cu and Cd in the control soils was identical to that in lime- and apatite-amended soils. Secondly, ryegrass and *Setaria glauca* were both failed to establish in the control due to the adverse soil condition, and they only grew in apatite- and lime-amended soils. However, outputs of the uptake by ryegrass and *Setaria glauca*, and inputs from the applications of amendments had slight influence on the increase of soil total Cu and Cd (Cui et al. 2016a). Thirdly, vegetation cover (ryegrass and *Setaria glauca*) protected the soil surface against

Table 2 Sequentially extracted Cu and Cd in soils amended by different dosages of lime and apatite

	EXC	CA	Fe–Mn	OM	RES	Total
Cu (mg/kg)						
Control	150 ± 13a	65.9 ± 2.9d	96.8 ± 6.5c	112 ± 1.9b	266 ± 27a	690 ± 34b
L-lime	115 ± 9b	81.1 ± 12 cd	109 ± 9.3bc	131 ± 6.2ab	285 ± 33a	721 ± 15ab
M-lime	71.5 ± 6.2d	107 ± 4.9ab	130 ± 5.3ab	149 ± 12a	294 ± 15a	751 ± 14ab
H-lime	41.3 ± 4.6ef	123 ± 4.8a	139 ± 9.2a	147 ± 8.7a	314 ± 37a	765 ± 19a
L-apatite	89.8 ± 3.3c	78.7 ± 0.6 cd	107 ± 8.9bc	118 ± 6.8b	323 ± 32a	716 ± 31ab
M-apatite	54.6 ± 4.2e	89.2 ± 9.5bc	115 ± 9.6abc	141 ± 6.1a	331 ± 22a	732 ± 24ab
H-apatite	30.7 ± 3.7f	103 ± 7.5b	136 ± 19a	149 ± 11a	345 ± 12a	762 ± 21a
Cd (μg/kg)						
Control	221 ± 11a	49.8 ± 5.3c	77.8 ± 6c	13.6 ± 2.5d	186 ± 6b	548 ± 25b
L-lime	189 ± 11b	77.1 ± 9.7b	89.9 ± 8.8bc	16.4 ± 4.6 cd	214 ± 6ab	587 ± 19ab
M-lime	179 ± 4b	82.5 ± 8.9ab	111 ± 8.4ab	21.9 ± 2.1abc	222 ± 19ab	617 ± 24ab
H-lime	176 ± 8b	89.2 ± 4.6ab	133 ± 10a	23.2 ± 1.1ab	233 ± 9a	655 ± 30a
L-apatite	194 ± 19b	73.2 ± 5.9b	99 ± 10bc	12.2 ± 2.8d	227 ± 9ab	605 ± 35ab
M-apatite	178 ± 13b	91 ± 8.9ab	114 ± 19ab	18.1 ± 1.6bcd	246 ± 35a	647 ± 60a
H-apatite	171 ± 4b	98.8 ± 9.1a	121 ± 12ab	25.8 ± 1.8a	248 ± 6a	665 ± 22a

Control = untreated soil, L-lime = 0.1% lime plus soil, M-lime = 0.2% lime plus soil, H-lime = 0.4% lime plus soil, L-apatite = 0.58% apatite plus soil, M-apatite = 1.16% apatite plus soil, H-apatite = 2.32% apatite plus soil

EXC, exchangeable fraction; *CA*, carbonate-bound fraction; *Fe–Mn*, Fe–Mn oxide fraction; *OM*, organic matter fraction; *RES*, residual fraction

Mean ($n = 3$) and standard error followed by different letters indicated significant differences ($p < 0.05$)

wind and water erosion which contributed to reduce the potential for trace element leaching downward and runoff transport (Tordoff et al. 2000). It was strongly supported by the fact that concentrations of Cu and Cd in soil solution in apatite- and lime-treated soils were significantly less than those in the control soils (Cui et al. 2016a). Finally, Fig. 3 indicated that total amount of heavy metals outputted by surface runoff and downward eluviations in apatite- or lime-treated soils was less than that in the control soils after the 7-year field experiment. Consequently, the total Cu and Cd retained in apatite- and lime-amended soils were higher than those in the control soils. Similarly, Bidar et al. (2016) indicated that fly ashes

amendment resulted in a significant enhancement of the metal loadings in the first 25 cm of soil, particularly for Cd, zinc (Zn), mercury (Hg), and Pb. However, Madejón et al. (2009) reported that the addition of different amendments did not increase total trace metals in the soil compared with the control soils after the 3-year field experiment. Tedoldi et al. (2017) noted that metal was typically characterized by a significant surface buildup, and significantly decreased with increasing depth. Unlike these studies, the highest Cu and Cd in the control soils at the 13–30 cm indicated a strong metal leaching effect, which was primarily due to the fact that soil was very acidic in our research. Furthermore, large amounts of

Table 3 Sequentially extracted P fractions (mg/kg) in soils amended by different dosages of lime and apatite

Treatment	Total P	Labile-P			Moderately labile-P		Stable-P	
		Resin-P	NaHCO$_3$-Pi	NaHCO$_3$-Po	NaOH-Pi	NaOH-Po	HCl-P	Residual-P
Control	895 ± 22d	222 ± 13 cd	135 ± 14a	19.4 ± 1.6d	176 ± 9abc	22 ± 1d	92 ± 6e	229 ± 18d
L-lime	870 ± 9d	206 ± 12 cd	99.3 ± 9b	10.6 ± 1.3f	146 ± 13bc	27.2 ± 1.3c	128 ± 5de	253 ± 7d
M-lime	880 ± 25d	186 ± 16de	96.2 ± 2.9b	10.3 ± 0.7f	143 ± 18c	28.7 ± 1.4bc	148 ± 6d	267 ± 12d
H-lime	887 ± 11d	140 ± 13e	102 ± 6b	13.8 ± 1.3e	153 ± 7bc	31.7 ± 1.5b	177 ± 17d	271 ± 27d
L-apatite	1364 ± 70c	248 ± 26bc	146 ± 9a	21.8 ± 0.1c	178 ± 8ab	25.8 ± 0.4c	411 ± 27c	334 ± 35c
M-apatite	2085 ± 95b	275 ± 22b	148 ± 1a	24.4 ± 0.6b	188 ± 12a	25.3 ± 1.2 cd	885 ± 63b	539 ± 39b
H-apatite	3139 ± 76a	338 ± 24a	135 ± 5a	27.8 ± 0.1a	158 ± 11abc	44.3 ± 2.2a	1761 ± 60a	674 ± 22a

Control = untreated soil, L-lime = 0.1% lime plus soil, M-lime = 0.2% lime plus soil, H-lime = 0.4% lime plus soil, L-apatite = 0.58% apatite plus soil, M-apatite = 1.16% apatite plus soil, H-apatite = 2.32% apatite plus soil

Mean ($n = 3$) and standard error followed by different letters indicated significant differences ($p < 0.05$)
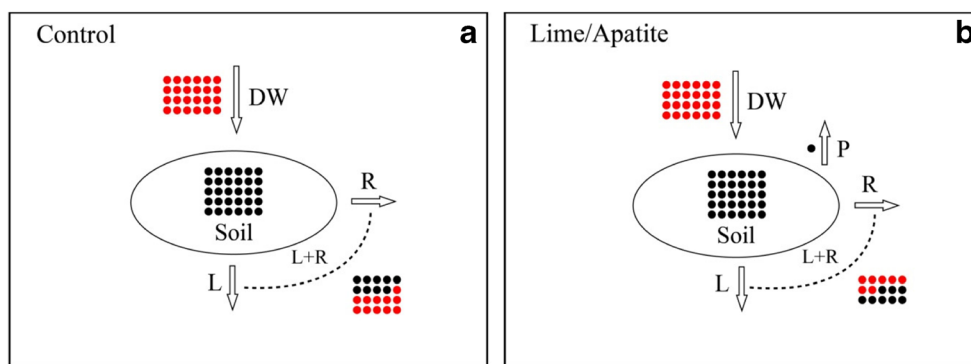
Fig. 3 Migration of Cu and Cd in the control and lime/apatite-treated soil. Control = untreated soil, Lime/Apatite = lime- or apatite-treated soil; DW, metal input by atmospheric dry and wet deposition; R, metal output by runoff; L, metal output by downward eluviations; P, metal output by phytoextraction. The red dots indicate the heavy metals from atmospheric dry and wet deposition. The black dots indicate the heavy metals originally existed in the soil. The dots named "L + R" at bottom right corner refers to the total amount of heavy metals outputted through surface runoff and leaching downward after the 7-year field experiment

heavy metals persistently imported into the field resulted from the smelter activities (exhaust gas, dust), which made it significantly different from the other study sites.
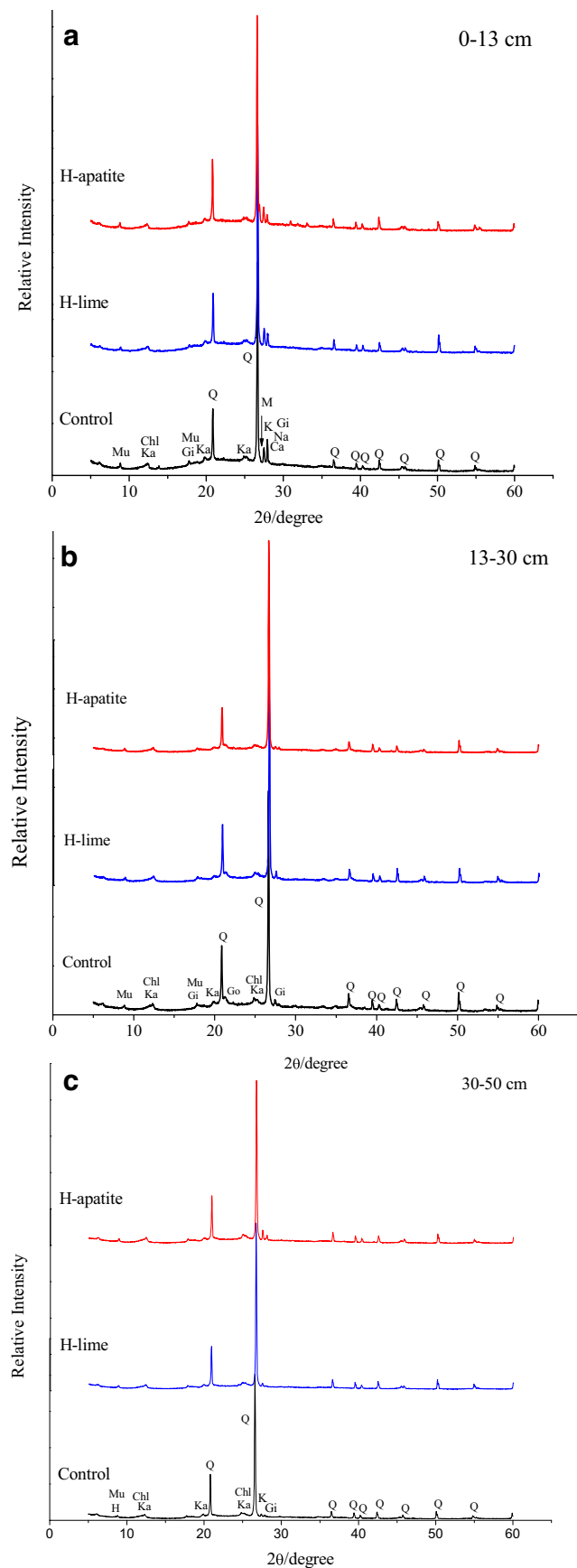
In addition, our study clearly indicated that increasing dosages of lime and apatite could effectively immobilize soil Cu and Cd (0–50 cm) and decrease the leaching of Cu and Cd to the lower layers (13–50 cm), which resulted in a significant difference in total Cu and Cd at the depths of 13–30 and 30–50 cm than the control. As expected, increasing dosages of apatite resulted in the increases of total P and total Ca and promoted the enhancement of soil pH. Therefore, soil pH was positively correlated with soil total P and total Ca (Table S1). Tessier et al. (1979) noted that the exchangeable fraction was considered as easily mobile and available, and the fractions of carbonate-bound, bound to Fe–Mn oxide and to organic matter, were potentially available. Our results indicated that increasing dosages of lime and apatite significantly decreased availability of Cu and Cd by decreasing the exchangeable fractions and transforming them into fractions of bound to carbonate, Fe–Mn oxides, and organic matter. Moreover, $CaCl_2$-extractable Cu and Cd were negatively correlated with soil pH (Table S1). The results were in consistent with facts that increasing soil pH was an effective approach to immobilize heavy metals and it controlled the potential release of the immobilized metals (Guo et al. 2018; Meng et al. 2018). Furthermore, it is deemed that the contents of soil available silicon, amorphous iron oxides, and manganese oxides are significantly different among soil layers, and they have high fixation capacities for heavy metals (Akama 2014; He et al. 2017; Li et al. 2014). Therefore, it is indispensable to evaluate the distribution of soil available silicon, amorphous iron oxides, and manganese oxides in the future study, and to illuminate the heavy metal immobilization mechanism in soil profile.

It is known that the increase of soil pH might result in the formation of the metal precipitation as hydroxides, carbonates, and phosphates (Huang et al. 2018; Sun et al. 2018). Consequently, XRD was used to investigate the new formed metal precipitation after lime and apatite applications. The XRD results indicated that the main mineral phases of the untreated soils (0–13 cm) included quartz, feldspar, chlorite-serpentine, and kaolinite (Fig. 4a). Moreover, there were no any new solid phases found in H-lime- and H-apatite-treated soils than the control. Similar to the 0–13 cm, there were no significant differences of solid phases at 13–30 and 30–50 cm soils treated by apatite and lime compared with those in the control soils (Fig. 4b, c). A significant difference was found that the content of feldspar was lower at 13–30 and 30–50 cm than that at 0–13 cm, and only goethite was found at 13–30 cm. Similarly, Huggett and Cuadros (2010) reported that similar soil mineral composition was found at 0–70 cm, and only a small difference was presented at > 90-cm soil layer. It was possible to speculate the precipitation of amorphous metal phosphate/carbonates, or the new crystalline minerals were ⩽ 2 wt% which could not be detected by XRD (Huang et al. 2016; Mignardi et al. 2012). Besides, metal phosphate/carbonates may be transformed with unknown composition and spectra, or peaks broadening, obscuring the identification of peak position (Hettiarachchi et al. 2001). In addition, the newly formed metal precipitation at 0–13 cm may be leach and uptake by plant root during the 7 years.

In the past years, amendment dosages were ranged from 0.2 to 10% in order to maintain long-term stability of immobilized metals (Khan et al. 2013; Luo et al. 2018; Yuan et al. 2017). However, it is not a desirable method to enhance unrestrainedly application dosages of amendments for high immobilization efficiency, considering the cost, soil alkaline, and compacted, toxicity metal enrichment (Farrell et al. 2010; Lahori et al. 2017; Shi and Schulin 2018). One important reason is that some of these remediation practice lacked risk assessment, and high application dosages could result in more heavy metal inputs and higher remediation cost. For example,

the concentration of Cd was over the class II limit (0.3 mg/kg) mandated by the Chinese National Quality Standards for soil environment (GB 15618-1995) after 10% (*w*/*w*) sewage sludge biochar (Cd 3.69 mg/kg, Cu 222 mg/kg, Zn 1102 mg/kg) application in soils (bulk density = 1.31 g/cm^3) (Khan et al. 2013). Additionally, potential eutrophication risk is always lacked in the amendments enriched with phosphorus and organic matter, although they could stabilize heavy metal as well as to promote the growth of vegetation. Nevertheless, our recent experiment indicated that the phosphate in soil effluent was higher than the V limit (0.4 mg/L) mandated by the Chinese National Quality Standards for Surface Waters (GB 3838-2002) in 1% hydroxyapatite-treated column, which showed a potential eutrophication risk (Cui et al. 2017b). The dosage of H-apatite (2.32%) in the present study is over two times higher than that of hydroxyapatite, and the resin-P (338 mg/kg) is also significantly higher than that in hydroxyapatite-treated soil (84.6 mg/kg) (Cui et al. 2017b). This means that high dosages of apatite application may lead to higher risk of eutrophication induced by excessive P loss. Unfortunately, the optimum dosage of the apatite cannot be figured out in the present study because the evaluation of phosphorus in the runoff was lacked in the present field experiment.

Based on the discussions above, it is concluded that the investigations and risk forecast of the metals and nutrients such as nitrogen, phosphorus, and organic carbon in the runoff and leaching solution are indispensable for future study during the immobilization process. Unfortunately, predicting the long-term potential risk of metal immobilization in the field is a challenging task in a short time. Considering the polluted farmland of over 3.33 million ha (China's 13th Five-Year Plan (2016–2020)) distributed in China, some policies and technical guidelines must be drawn up for the immobilization, which should include the following aspects: (1) seeking for cost-effective amendments for polluted soils; (2) formulating a clear limit standard for contaminants (heavy metals, virus, organic pollutants, and radioactive element) enriching in amendments; (3) limiting the application dosages and frequency of amendments, which should be depended on the soil environmental capacity; (4) monitoring the efficacies and sustainability of these immobilizing materials under field conditions; (5) monitoring the nitrogen, phosphorus, and other nutrients in surface water and soil profile during long-term remediation.

Conclusions

The field study indicated that increasing dosages of the lime and apatite effectively increased soil pH, immobilized Cu, and Cd at soil surface layer and decreased their downward eluviations. SOC and Ca were enriched in top soil, and SOC was significantly decreased with increasing soil depth. But apatite only increased soil P at 0–13 cm than the control, and majority of them presented in stable-P. Moreover, high application dosage of apatite had potential P-induced eutrophication risk compared with lime. It is concluded that high dosages of amendments could effectively immobilize soil heavy metal and decrease their eluviations, but more attention should be paid to the other nutrients enriching in the amendments.

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