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Effects of water and organic manure coupling on the immobilization of cadmium by sepiolite

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Abstract

Purpose Natural sepiolite (SP) has proven effective on the in-situ immobilization remediation of Cd-contaminated soils. But the practical remediation effect may largely influenced by water management and the application of organic manure. The effects of chicken manure (CM) on SP-amended soils were investigated under normal and saturated water conditions using a pot experiment with *Brassica campestris* L.

Materials and methods Cd-contaminated paddy soils were amended with CM, SP, and CM + SP with no amendment as control. The amount of sepiolite was 0.5% (*w*/*w*, the same below) either in SP or CM + SP amended soils, while the amount of CM was 0.5, 1.0, and 2.0% in CM and CM + SP-amended soils. The plant metal contents, fresh weight, and soluble sugar content of plant edible parts were measured on harvest. Soil Cd was extracted by diethylenetriaminepentaacetic acid (DTPA) and HCl to estimate the mobility of heavy metal. Soil pH and dissolved organic matter (DOM) of rhizosphere soil were determined. The electronegative charges of soils were also measured using the zeta potential.

Results and discussion The application of CM and increasing soil moisture on SP-amended soil increased plant growth to a greater extent than the application of SP alone. The application of CM along with the increase of soil moisture decreased Cd uptake and translocation in plants grown on SP-amended soil compared to the application of SP alone. Cd content of edible plant parts reached a minimum of 0.24 mg kg^{-1} with the application of 2.0% CM on SP-amended soils under water-saturated conditions, which was approximately 50% lower than the Cd concentration found when applying SP alone.

Conclusions The results of this study suggest that the application of sepiolite on Cd contaminated soil can effectively reduce Cd uptake by *B. campestris* L., and the addition of CM combined with effective water management also appears to further reduce Cd absorption and accumulation.

Keywords Cadmium uptake · Heavy metals · Organic fertilizer · Sepiolite-amended soil · Water conditions

1 Introduction

Cadmium (Cd) is a non-essential and toxic element present in the human food chain and is ultimately indestructible in the soil environment. Farmland soil polluted by Cd poses a serious risk to human health owing to the uptake of the heavy metal by the edible parts of crops and their resultant accumulation in the food chain (Meharg et al. 2013; Tai et al. 2016; Shirvani et al. 2015). Chemical immobilization is a practical in-situ remediation technology that can reduce migration and bioavailability of Cd through chemical interactions among heavy metals, soil particles, and binders Komy et al. 2014, Sun et al. 2016). Numerous soil amendments, i.e., alkaline compounds (Garau et al. 2007; Lee et al. 2013), clay minerals (Xu et al. 2010; Sun et al. 2013; Liang et al. 2014), metal oxides (Komarek et al. 2013; Cui and Wen 2013), organic matters (OM) (Crecchio et al. 2004), and phosphate sulfides (Fayiga and Ma 2006; Cao et al. 2009) have been proposed and evaluated for their ability to immobilize heavy metals in soil environments.

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Natural sepiolite has proven effective in reducing Cd uptake by plants and has advantages upon many other commercially available soil amendments in terms of low-cost, an abundant availability, non-toxic nature (Sun et al. 2017; Li and Xu 2015, 2017; Mohammad, 2017). Furthermore, natural sepiolite reduces the mobility and availability of Cd in soil through two functions. On the one hand, natural sepiolite contains calcite impurities, and therefore, H^+ in soil colloids could exchange with Ca^{2+}, release into the soil solution, and further react with HCO_3^- to form CO_2 and H_2O, which led to the increase of the pH of paddy soil (Yin et al. 2017). On the other hand, natural sepiolite is negatively charged and very effective and extensively used to adsorb metal cations, due to their high cation, exchange capacity, high surface area, and pore volume. However, its actual remediation effect is a function of agricultural management, with soil-water management and the application of organic manures to be the most important parts.

It has been established that water management greatly impacts the bioavailability of Cd in agricultural soils through changes in soil Eh (Fulda et al. 2013). Huang (2004) found that Cd adsorption in maize decreased with the increase of soil moisture from 55 to 85%. Zhang (2016) argued the constant anaerobic condition in water-logged soil indicated a consumption and decomposition of OMs, and the intermediate product organic acids may inhibit the retention of metals in the solid phase and hence to increase the mobile fractions (Tan et al. 2011). It has been demonstrated that Cd content in all parts of rice decreases considerably with increases in the level of soil flooding, which may be due to the reduction of sulfate to sulfide and consequently the formation of insoluble CdS in the flooded soil (Ye et al. 2018). After soil flooding, several reduced organic substances are produced, which are directly or indirectly involved in heavy metal ion adsorption, influencing the surface charge properties of soils and thus affecting the adsorption and desorption of metal ions in water-saturated soils (Davranche and Bollinger 2000).

Dissolved organic matter (DOM) can affect the bioavailability of heavy metals in soil, especially in soils used for vegetable production, where intensive organic fertilization is applied (Kalbitz et al. 2000; Marschner and Kalbitz 2003; Li et al. 2016a,b). However, the impact of DOM on Cd contamination remains controversial. On one hand, DOM reduces the content of heavy metals through complexing, adsorbing, and precipitating (Mohamed et al. 2010; Ren et al. 2016), while on the other hand, DOM may induce metal mobilization through the formation of metal-DOM complexes (Bolan et al. 2003; Salati et al. 2010; Spaccini et al. 2008; Richard et al. 2009). Chicken manures (CM) are common farmland soil additives, as they increase agricultural production by improving the soil structure and fertility status. When CM is added to soil, large amounts of DOM are derived from the CM, which can affect the adsorption/immobilization capacity of clay minerals in soils (Kalbitz et al. 2000; Marschner and Kalbitz 2003).

Previous research has demonstrated that sepiolite (Sun et al. 2015; Liang et al. 2016) was an effective amendment of Cd contaminated farmland. Yet, few studies have focused on the combined effect of CM-DOM and water management on remediation of Cd-polluted vegetable fields using sepiolite. Moreover, there is limited information available on the performance of CM-DOM on sepiolite. Accordingly, the objectives of this study were to investigate the effects of water management and CM application on the remediation of Cd contaminated soils and their combined effect with sepiolite on Cd absorption and accumulation. We hypothesize that metal uptake in vegetables can be reduced by the application of sepiolite and CM together with reasonable water management.

2 Materials and methods

2.1 Physicochemical properties of soil and amendments

Surface soil (0–20 cm) was collected from a cadmium-polluted field in Chenzhou, Hunan, China (112° 43′ 48″ N, 25° 43′ 48″ E). The soil was ground with stainless steel mill to pass through a 20-mesh sieve (< 2 mm) for physical and chemical analyses and 100-mesh sieve (< 0.149 mm) to determine Cd. The OM content of soil measured by the $K_2Cr_2O_7$ oxidation-reduction titration method (Huang et al. 2012) was 34.6 g kg^{-1}. The cation exchange capacity (CEC) analyzed by the $BaCl_2$ compulsive exchange method (Liang et al. 2006) was 25.3 cmol kg^{-1}. Total N, available P, and K were 42.9, 9.3, and 182.7 mg kg^{-1}, respectively. The total Cd concentration in soil, determined by atomic absorption spectrometry after digestion with nitric acid (HNO_3) and 60% perchloric acid ($HClO_4$), was 2.45 mg kg^{-1}. The soil had a pH of 6.21, as measured at a soil-to-water ratio (weight/weight) of 1:2.5 (Honma et al. 2016). The natural sepiolite (SP) used in the pot experiment, containing a small amount of dolomite and talc and other impurities, was purchased from a construction material company in Yixian, Hebei, China (Li and Xu 2017). CM was purchased from a local market in Tianjin, China. The basic physicochemical properties of organic manure are listed in Table 1.

2.2 Experimental setup and water management

The study was performed in a greenhouse in the Agro-Environmental Protection Institute, Tianjin, China. All soil samples were air-dried, sieved (< 5 mm), and homogenized before the pot experiment. Basal fertilizers (150 mg of N kg^{-1} as $CO(NH_2)_2$, 300 mg of P kg^{-1} as KH_2PO_4, and 300 mg of K kg^{-1} as KH_2PO_4) were added to the soil and mixed thoroughly (Xiao et al. 2015). For the treatment, 2.0 kg of contaminated soil was thoroughly mixed with the desired

Table 1 Selected characteristics of chicken manure

	pH	OM (%)	Total N (%)	Total P (%)	Total K (%)	Total S (%)	Total Cd (mg kg^{-1})
CM	6.47	44.1	3.42	0.89	2.04	2.53	4.71

amendments and allowed to equilibrate for a period of 4 weeks (watered daily with deionized water to maintain a 70% water-holding capacity). There were a total of 16 treatment scenarios, including two different amendment conditions (SP and CM) and two water management conditions (Table 2), involving a normal water condition (60% of field water holding capacity (WHC)) and a water-saturated condition (100% of field WHC). Each treatment was replicated three times.

Maintaining soil moisture content: water treatments were conducted using the weighing method (Li et al. 2016a,b). The WHC was determined in accordance with the method recommended by Veronika Hansen et al. (Hansen et al. 2016). Two pots with 2.0 kg soil were weighed and submersed in water for 24 h following a subsequent drainage period of 24 h while preventing evaporation. The recorded weight of the water held in the soil after drainage was taken as WHC.

Seeds of pak choi (*Brassica campestris* L., cultivar Siyueman) were sterilized in 30% H_2O_2 (*w*/*v*) solution for 15 min, followed by thorough washing with deionized water, and then 10 seeds were sown into each prepared pot on 17 April 2017. On the 10th day after germination, seedlings were thinned to four per pot. The soil of each pot was covered by 100 g of plastic beads to minimize water evaporation. One week later, two water treatments were conducted using the weighing method. The pots were watered once daily during the first week and then twice a day during the remaining 4 weeks. Drainage from the pots was prevented during the experiments, and the pots were arranged in random blocks and rotated intermittently to ensure other growth conditions were the same for all pots in the experiment.

2.3 Sample preparation and analysis

All plants of the cultivars were harvested on 23 May 2017. The plants were harvested, washed with tap water, and rinsed three to four times with deionized water, then cut at the rhizome junction, and separated into shoots and roots. Fresh weight and biomass of shoot and root and concentrations of Cd in shoot and root tissue dry matter were subsequently determined. At the time of harvest, rhizosphere soil was collected from a small amount of soil shaken directly from the plant roots. Soil samples were air-dried at room temperature and sieved to < 1 mm and stored in a plastic container for further analysis.

For soluble sugar analysis, 0.2-g sample of fresh weight edible parts was homogenized with deionized water with a ratio of 1:10. The mixture was boiled in a water bath for 10 min and cooled to room temperature. Then, the absorbance was measured at 620 nm using a spectrophotometer (Beijing Purkinje General Instrument TU-1810). The soluble sugar was expressed in terms of mg g^{-1} FW (Bu et al. 2017).

Soil pH was measured with a pH meter (PB-10, Sartorius, Germany) and the solid-to-liquid ratio (m:v) = 1:2.5 (Zhou et al. 2018).

Zeta potentials of soil samples passed through a 300-mesh sieve were measured in $NaNO_3$ solution with a pH range of 3.0 to 7.0, using a micro-electrophoresis meter (JS94H, Powereach, China) (Liang et al. 2017).

The DOM content extracted from the different samples was expressed as the dissolved organic carbon (DOC) content, which was measured using a total organic carbon analyzer (Vario TOC, Elementar Germany element). The DOM was extracted from the soil samples with Milli-Q ultra-pure water (a solid-to-water ratio of 1:5 on a dry weight basis) for 8 h on a horizontal shaker (200 r/min) and at room temperature. The mixture was centrifuged at 4000 rpm for 20 min at room temperature to obtain the supernatant, which was then filtered through a 0.45-mm glass fiber membrane. The supernatant was transferred into a brown reagent bottle to avoid photodecomposition. The remaining OM in the filtrate was considered as DOM. The remaining OM in the filtrate was considered as DOM. The DOC in the DOM was determined with a TOC analyzer, and DOM concentration was expressed as a function of the DOC (Gao et al. 2018).

The bioavailability of Cd in soil was determined by two different extraction solutions, HCl (Liang et al. 2016), and diethylenetriaminepentaacetic acid (DTPA) (Yang et al. 2018, Wang et al. 2016). Soil samples of 5.0 g were dispersed into 25 mL of 0.025-M HCl solutions and 0.05-M DTPA solution and shaken for 60 and 120 min, respectively. Meanwhile, the DTPA solution was used to determine the available Cu and Zn contents in soil.

Dried and powered root and shoot samples (0.2500 ± 0.0005 g) were digested with concentrated HNO_3 (10 mL) using a block digester to conduct the Cd content analysis (Kim et al. 2016). The concentrations of Cd, Cu, and Zn in the digested or extracted solutions were analyzed via inductively coupled plasma mass spectrometry (iCAP Q, Thermo Scientific, USA) or atomic absorption spectrometry (ZEEnit 700P, Analytik Jena Instruments, Germany).

2.4 Quality control

To monitor the quality of chemical analyses and to examine the accuracy of data, quality control measures were adopted according to the geochemical standard references of China for soil (GBW(E)-070009) and tobacco (GBW08514). The mean recoveries of Cd in standard reference materials that were analyzed with the samples during the course of analysis of all samples were 96 and 102%, respectively. All glass and polyethylene bottles were previously soaked overnight in HNO_3 (10%) and rinsed thoroughly with deionized water before use. A blank experiment was set up and used for additional quality assurance.

2.5 Statistical analysis

All the experimental data were presented as means ± SE (n = 3). The criteria for significance were set at $P < 0.05$ (significant). All data analysis was handled using Excel 2010 and SAS 9.2, and all figures were illustrated on Origin 8.5 software.

The ability of *B. campestris* to translocate and take up Cd was assessed using the translocation factor (TF) (Wang et al. 2006) and specific cadmium uptake (SCU) (Li et al. 2016a,b) as follows:

$$\mathrm{TF} = \frac{C_S}{C_R}$$

$$\mathrm{SCU} = \frac{C_S \times B_S + C_R \times B_R}{B_R}$$

where C_S and C_R are the contents of Cd in shoots and roots, respectively; B_S and B_R are the dry weights of shoots and roots of *B. campestris*, respectively.

3 Results and analysis

3.1 Growth responses

Experimental results indicated that *B.campestris* L. grew well in Cd-contaminated soils without obvious symptoms associated with poisoning, suggesting that it is impossible to confirm whether the vegetables are safe to eat from the growth status and apparent phenomenon. Therefore, its potential health risk to human is quite high. The application of SP (0.5%) appeared to alleviate the stress of heavy metals on the plants and slightly increased their fresh weight (Fig. 1). Furthermore, applying CM increased fresh weight by 43.8–87.0 and 3.0–36.8% of non-amended and SP-amended soils under water-saturation, respectively. The application of CM (1.0%) on SP-amended soils significantly increased fresh weigh of edible plant parts compared with other application ratios. In contrast to normal water condition, fresh weight of edible plant parts under water-saturation conditions increased by 38.2, 69.2–134.9, and 53.0–101.2%, for the application of SP alone, CM alone, and the combined effect of SP and CM, respectively. Consequently, fresh weight reached its highest value when amended with 0.5% SP and 1.0% CM, reaching 43.6 g plant^{-1} under water-saturation conditions and 28.5 g plant^{-1} under normal water conditions.

The contents of soluble sugar were expressed in terms of fresh weight (Fig. 1). Experimental results indicated the application of SP alone had little influence on soluble sugar content under normal water conditions and significantly reduced its content under water-saturation conditions, while soluble sugar content increased with the increase of CM content under normal water condition by 8.0~40.3 and 3.6~79.5% for non-amended and SP-amended soils, respectively. By contrast, the application of CM reduced soluble sugar by 39.0~56.2 and 7.4~55.2% for non-amended and SP-amended soils under water-saturation conditions, respectively.

3.2 Micronutrients in soil

Cu and Zn are indispensable micronutrients for the normal growth of various plants. Organic manures can generate organic acids, carbohydrates, phenols, and heterocyclic compounds that contain nitrogen and sulfur, thus impacting the available content of Cu and Zn through complexation and chelating with certain active groups. The application of SP slightly reduced available Cu content under two water conditions (Fig. 2). Available Cu slightly decreased with the increase of CM content on non-amended and SP-amended soils under two water conditions. Gondek and Mierzwa-Hersztek (2016) studied the effect of pig manure (PM) and poultry litter (PL) in doses of 0.5, 1.0, and 2.0% *w/w*. The results indicated that PM and PL increased the mobile forms of Cu extracted from soil with 1-M NH_4NO_3 and higher values of the immobilization index were obtained for a lesser addition of organic materials. Available Cu content determined by DTPA extraction displayed minor differences under normal water conditions and water-saturation conditions. In short, these experimental results suggest the impact of SP, CM, and water conditions on the content of available Cu may be negligible.

Available Zn content slightly increased when SP was applied alone, and the minimum value (2.2 mg kg^{-1}) was much higher than the critical value of 1.2 mg kg^{-1} in soils for normal plant growth. Available Zn increased with the increase of CM content on non-amended and SP-amended soils under different water conditions, besides, combined effect of SP and CM was more effective. According to Gondek and Mierzwa-Hersztek (2016), the application of PM and PL decreased the mobile forms of Zn and higher values of the immobilization index were obtained for a larger addition of organic materials. In this study, no significant differences in available Zn content were observed under different water conditions.

3.3 Accumulation of Cd in shoots and roots

The differences of heavy metal content in plants reflect their potential to be absorbed by plants and the bioavailability of these elements in soils (Li and Xu 2017). As shown in Fig. 3, under normal water conditions, the application of CM and SP

Table 2 Summary of pot experiment treatments

	Amendment	Amount of sepiolite	Amount of chicken manure			
			0	0.5%	1.0%	2.0%
Normal water condition (NM)	Chicken manure	–	CK	C1	C2	C3
	Sepiolite (SP) + chicken manure(CM)	0.5%	SP	SC1	SC2	SC3
Water-saturated condition (WS)	Chicken manure	–	CK	C1	C2	C3
	Sepiolite (SP) + chicken manure(CM)	0.5%	SP	SC1	SC2	SC3

CK, control; C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM; SP, 0.5% SP; SC1, 0.5% SP + 0.5% CM; SC2, 0.5% SP + 1.0% CM; SC3, 0.5% SP + 2.0% CM

alone decreased Cd uptake by 2.52–20.47 and 62.87%, respectively. The application of increasing amount of CM on SP-amended soil significantly increased Cd uptake by root. Cd uptake in shoots was 25.08–38.38% lower than non-amended soils by applying CM alone, 97.60% with SP alone, and 50.09–64.05% with a combined application of SP and CM, respectively. When CM alone was applied, the reduction of Cd uptake by roots slightly increased as the amount of added CM increased. Applying SP alone, Cd content in roots and shoots reached a minimum of 0.91 (fresh samples, the same below) and 0.39 mg kg^{-1}, respectively. Under normal water conditions, the application of CM on SP-amended soils increased Cd uptake by 71.57–81.92% in roots and by 33.19–51.89% in shoots, compared to applying SP alone. However, under water-saturation conditions, SP-amendment decreased Cd content in roots and shoots by 29.7 and 38.6%, respectively. The application of CM alone and combined application of CM and SP resulted in no significant difference of Cd content in roots, under water-saturation conditions. The application of CM on SP-amended soils inhibited shoots' uptake and accumulation of Cd. When applying SP alone, Cd content in roots and shoots reached a minimum of 1.12 and 0.51 mg kg^{-1}, respectively, whereas the application of 2.0% CM on SP-amended soils under water-saturation conditions resulted in a minimum Cd content of 0.24-mg kg^{-1} FW in shoot.

3.4 Translocation factors and specific cadmium uptake

The TFs were 0.69 and 0.51 for non-amended treatment under normal water conditions and water-saturation conditions, respectively (Fig. 4). The application of amendments restrained Cd transport from roots to shoots by approximately 21.58–27.30% applying CM alone, 34.24% with SP alone, and 31.15–51.63% with combined application of SP and CM under normal water conditions. The application of CM alone accelerated the transfer of Cd from root to shoot (except C2) under water-saturation conditions. However, under water-saturation conditions, the application of SP alone and the combined application of SP and CM decreased the TF by 12.60 and 45.25–69.78%, respectively. TF reached a minimum of 0.15 applying 2.0% CM on SP-amended soils.

The application of SP alone dramatically decreased SCU of *B. campestris* under two water conditions, indicating that SP decreased the rate of Cd absorption of root. Moreover, the application of CM decreased SCU by 24.6~35.9 and 49.0~64.5% on non-amended and SP-amended soil under normal water conditions, respectively. However, under water-saturation conditions, the application of CM alone (> 0.5%) significantly increased SCU. The application of SP alone and combined application of CM and SP decreased SCU, but shows no significant difference between the treatments.

3.5 DTPA and HCl extractable Cd contents in soil

The total content of potentially toxic elements (PTE's) in soils is not necessarily related to environmental risks, so a reactive fraction has been introduced which represents the pool of PTE's that plants can uptake (Meers et al. 2007; Peijnenburg et al. 2007). The reactive pool includes precipitates of contaminants, and metal ions reversibly sorbed to the surfaces of clays, soil OM, and amorphous metal oxides are assumed to be readily exchangeable between solid and solution phases (Römkens et al. 2009). The available Cd content extracted by DTPA and HCl could represent chemically reactive metal in soil. The extraction of soil Cd using HCl is the official method adopted in the Agricultural Land Soil Pollution Prevention Law in Japan, and the concentrations of Cd in soil extracted using 0.025-mol L^{-1} HCl were reported to be significantly correlated with the Cd contents in wheat grains (Ibaraki et al. 2005). DTPA-extractable Cd is the most available to plant uptake (Fellet et al. 2014).

Under normal water conditions, DTPA extractable Cd content decreased by 75.51% with the application of SP alone (Fig. 5). The application of CM further reduced DTPA extractable Cd contents by 24.33–34.33% in SP-amended soils, whereas the reduction decreased as the amount of added CM increased. DTPA extractable Cd contents indicated significant differences among different amendment treatments and

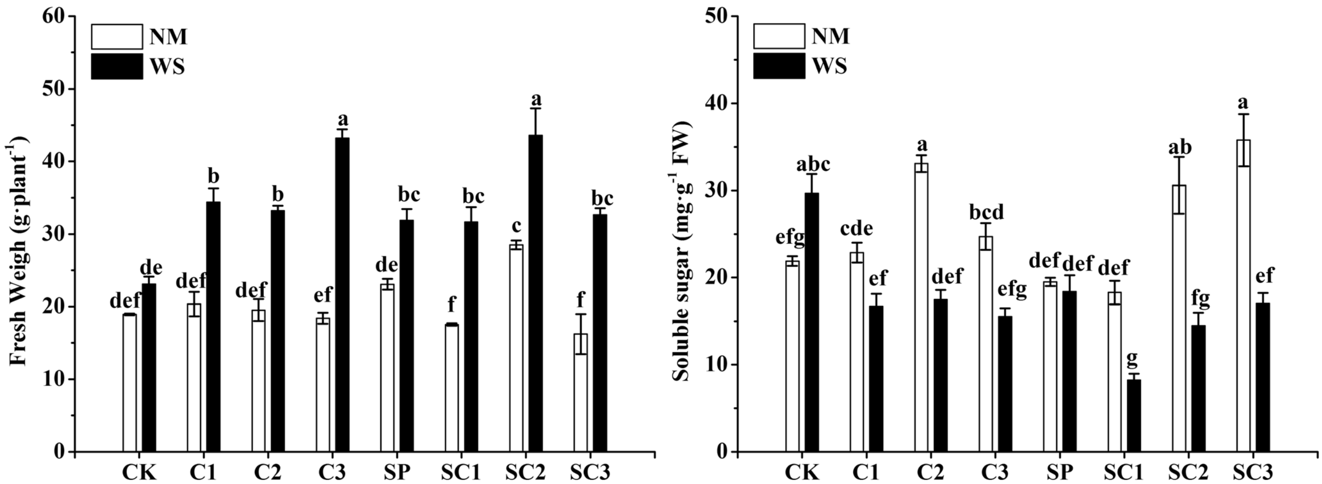

Fig. 1 Fresh weight and soluble sugar of edible plant parts (shoots). NM, normal water condition; WS, water-saturation condition; CK, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM; SP, 0.5% SP; SC1, 0.5% SP + 0.5% CM; SC2, 0.5% SP + 1.0% CM; SC3, 0.5% SP + 2.0% CM. Different letters indicate a significant difference at $P < 0.05$

followed the sequence: CM + SP < SP < CM (except C1). Under water-saturation conditions, DTPA extractable Cd content increased by 79.19 and 12.81~29.62% applying SP and CM alone, respectively. The application of CM slightly increased DTPA extractable Cd contents on SP-amended soils, the acceleration increased as the amount of added CM increased, and followed the sequence: CM < SP < CM + SP. The application of CM and SP resulted in completely different impacts on DTPA extractable Cd contents under different water conditions.

The application of SP alone decreased the HCl-extractable Cd content by 43.33 and 35.09% under normal water conditions and water-saturation conditions, respectively. The application of various amounts of CM on SP-amended soils significantly decreased available Cd content. With an application of 0.5% CM, the Cd content reached a minimum of 0.1990 and 0.2594 mg kg^{-1} under normal water conditions and water-saturation conditions, respectively. Along with increases in soil moisture, available Cd content dramatically increased by 44.23–110.57% from applying CM alone, 19.03% from applying SP alone, and 6.40–37.25% from a combined application of SP and CM. Immobilization of Cd was calculated using the following equation (Park et al. 2011; Gondek and Mierzwa-Hersztek. 2016):

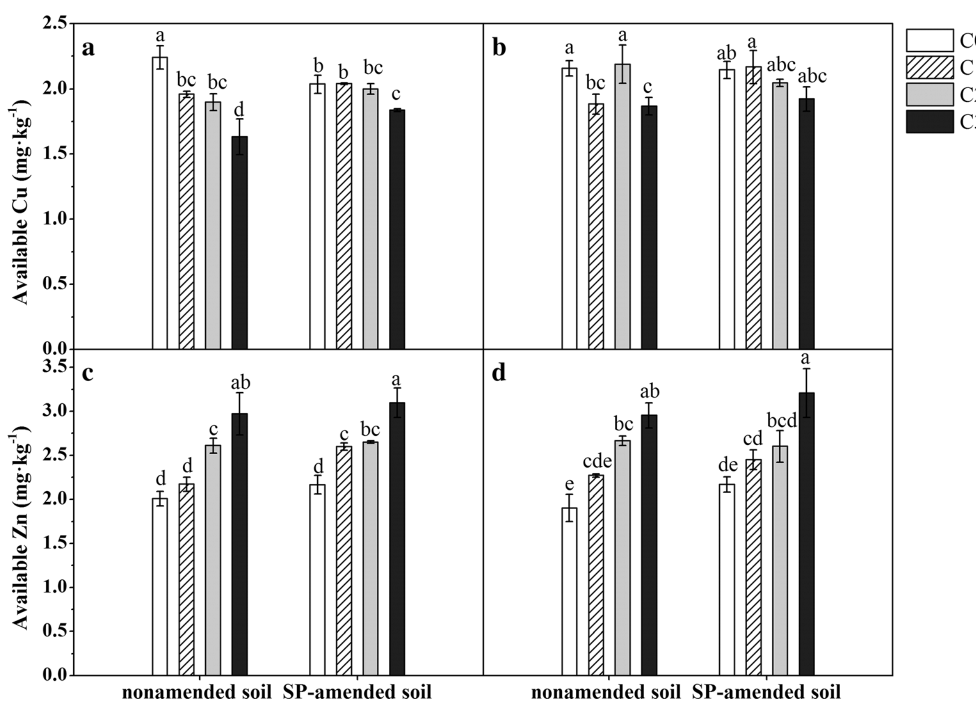

Fig. 2 Available content of Cu and Zn in soil. **a** Available content of Cu under normal water conditions. **b** Available content of Cu under water-saturation conditions. **c** Available content of Zn under normal water conditions; d, available content of Zn under water-saturation conditions; C0, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM. Different letters in the same set indicate a significant difference at $P < 0.05$

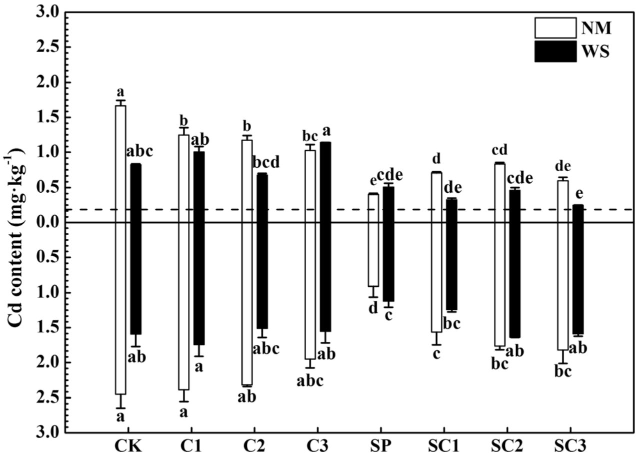

Fig. 3 Cd content of roots (lower part) and shoots (upper part). NM, normal water condition; WS, water-saturation condition; CK, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM; SP, 0.5% SP; SC1, 0.5% SP + 0.5% CM; SC2, 0.5% SP + 1.0% CM; SC3, 0.5% SP + 2.0% CM. Different letters in the same set indicate a significant difference at $P < 0.05$

$$\text{Immobilized metal}(\%) = \frac{(\text{HCl metal for the control} - \text{HCl metal for treated sample}) \times 100}{\text{HCl metal for the control}}$$

The application of SP, depending on soil moisture, reduced the mobility of Cd by 42~43%. The application of CM alone, depending on the amount added, reduced the mobility of Cd from 20 to 45% under normal water condition. But, the application of CM increased Cd in doses of 0.5 and 1.0% under water-saturation condition. The application of CM on SP-amended soil, depending on the amount added, reduced the mobility of Cd from 38 to 54% under normal water condition, from 37 to 43% under water-saturation condition.

3.6 Soil pH, DOM, and zeta potential

Soil pH increased by 21.14 and 18.23% applying SP alone under normal water conditions and water-saturation conditions, respectively (Fig. 6). The application of CM alone slightly increased soil pH under two water conditions. According to Gondek and Mierzwa-Hersztek (2016), the application of PM and PL caused a considerable reduction in soil acidification. The best alkalinization effect was achieved after adding 2% of organic materials. The application of CM on SP-amended soils reduced pH, as the CM was slightly acidic and retarded the effect of SP. Soil pH slightly increased along with an increase in soil moisture for each treatment. Zhang (2016) also found that lime amended soil presented a higher pH value under water-logged condition than that in moist soil.

The application of SP alone decreased DOM by 31.47 and 32.61% under normal water conditions and water-saturation conditions, respectively. Compared to the application of SP alone, the application of CM on SP-amended soils increased DOM by 0.8–467.8 and 9.1–396.5% under normal water conditions and water-saturation conditions, respectively. DOM decreased by 1.07–31.86% along with increased soil moisture in each treatment.

Zeta potential is defined as the electrical potential developed at the solid-liquid interface, which was an important parameter for the adsorbents of heavy metals. As indicated in Fig. 7, CK, C3, SP, and SC1 were selected to show the difference of zeta potential under normal water conditions. Zeta potential of soil samples were negative at pH 3.0–7.0 and showed a decreasing trend with increasing pH levels. Zeta potential of soil particles shifted in the negative direction with the application of SP alone compared to the control experiment, indicating a more negative charge at the solid surface. The negative charge enhanced the sorption of metal cations and reduced their transfer to crops. The addition of 0.5% CM on SP-amended soil increased the quantity of negative charge. However, zeta potential among different CM contents was found to have no significant difference. CK, C2, SP, and SC3 were selected to show the difference of zeta potential under water-saturation conditions. Zeta potential of soil particles shifted in the positive direction with the application of amendments compared with nonamended soil. The results suggested that SP and CM decreased the quantity of negative charge on the surface of colloids and may weaken the sorption of metal on soil particles.

4 Discussion

In this study, sepiolite, CM, and their combination were found to significantly decrease HCl-extractable Cd content in soils and Cd uptake of roots and shoots of pak choi under normal water conditions. Similar results were reported by Sun et al. (2016). According to Gondek and Mierzwa-Hersztek (2016), the application of PM and PL decreased the mobile forms of Cd extracted from soil with 1-M NH_4NO_3 and higher values of the immobilization index were obtained for a larger addition of organic materials. The application of CM alone decreased Cd uptake by roots and shoots and the reduction increased with the increase of CM-DOM, which immobilized Cd with functional groups, such as —COOH, —OH, —C=O, —NH_2, and —SH through specific adsorption, ion exchange, metal complexes, and co-precipitation (Sánchez-Marín et al. 2010). Liu et al. (2014) found that CM inhibited Cd uptake and accumulation in all parts of wheat. The reduction increased as the amount of CM increased (the maximum concentration was less than 1.0%). Applying SP alone decreased available Cd content and plant Cd, which were related both to increases in pH and reactions involving Cd complexation onto SP, Cd diffusion into lattice of clay, and Cd substrate surface retention (Li and Xu 2017). Furthermore, compared with applying SP alone, the content of available Cd extracted by DTPA and HCl had no significant difference with

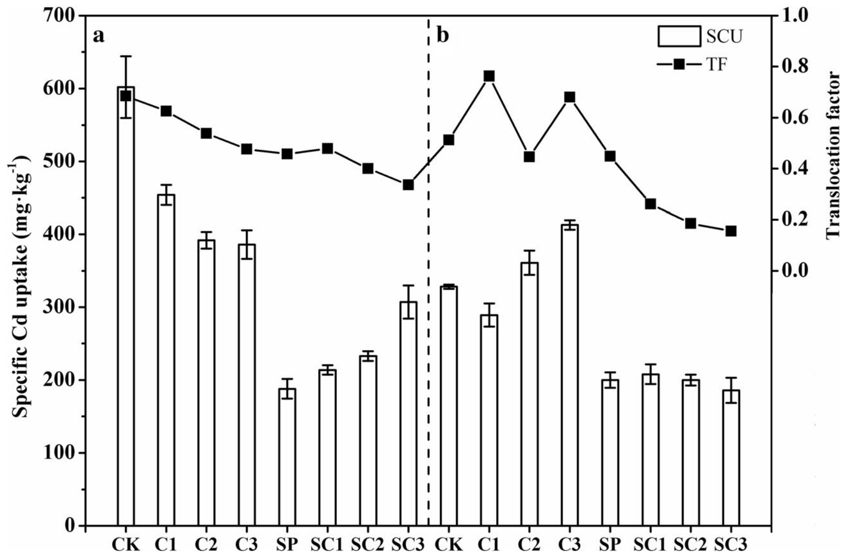

Fig. 4 Specific cadmium uptake and translocation factor. **a** Normal water condition. **b** Water-saturation condition; CK, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM; SP, 0.5% SP; SC1, 0.5% SP + 0.5% CM; SC2, 0.5% SP + 1.0% CM; SC3, 0.5% SP + 2.0% CM. Different letters in the same column indicate a significant difference at $P < 0.05$

applying CM on SP-amended soils. Cd uptake by roots and shoots increased inversely, which may have been caused by mobilization of Cd through the formation of metal-DOM complexes and the increase of low-molecule organic acids.

Except control, the fresh weight of edible plant parts significantly increased under water-saturation conditions compared to normal water conditions. In the control group, compared with normal water condition, the decrease of available Cd extracted by DTPA, Cd uptake by roots, and shoots could be attributed to the formation of insoluble CdS solid phases following soil saturation (Livera et al. 2011; Hofaker et al. 2013). Applying SP alone resulted in an increase in pH in water-saturation conditions compared to normal water conditions, but the content of available Cd determined by DTPA and HCl increased simultaneously, indicating that immobilization mechanisms of heavy metal Cd in soils with SP included two aspects: increasing soil pH and the absorption of Cd, where Cd adsorption by SP plays a larger role than the increase of soil pH. Moreover, when applying SP alone, water-saturation conditions increased Cd uptake in roots and shoots compared to normal water conditions, suggesting that the cause may be higher pore water Cd concentrations associated with water-saturation conditions (Lu et al. 2017). Except applying SP alone, the increase in soil moisture reduced Cd content of roots and shoots, suggesting that this may have been influenced by a “dilution effect” (i.e., the same Cd

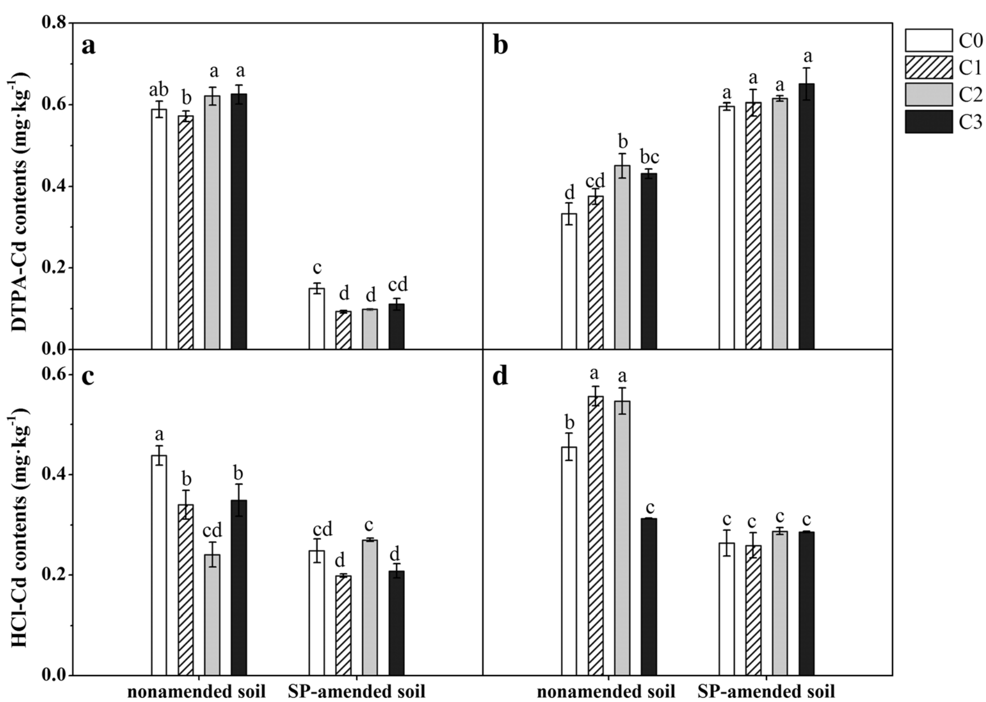

Fig. 5 DTPA and HCl extractable Cd contents. **a** DTPA extractable Cd contents under normal water condition. **b** DTPA extractable Cd contents under water-saturation conditions. **c** HCl extractable Cd contents under normal water conditions. **d** HCl extractable Cd contents under water-saturation conditions; C0, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM. Different letters in the same column indicate a significant difference at $P < 0.05$

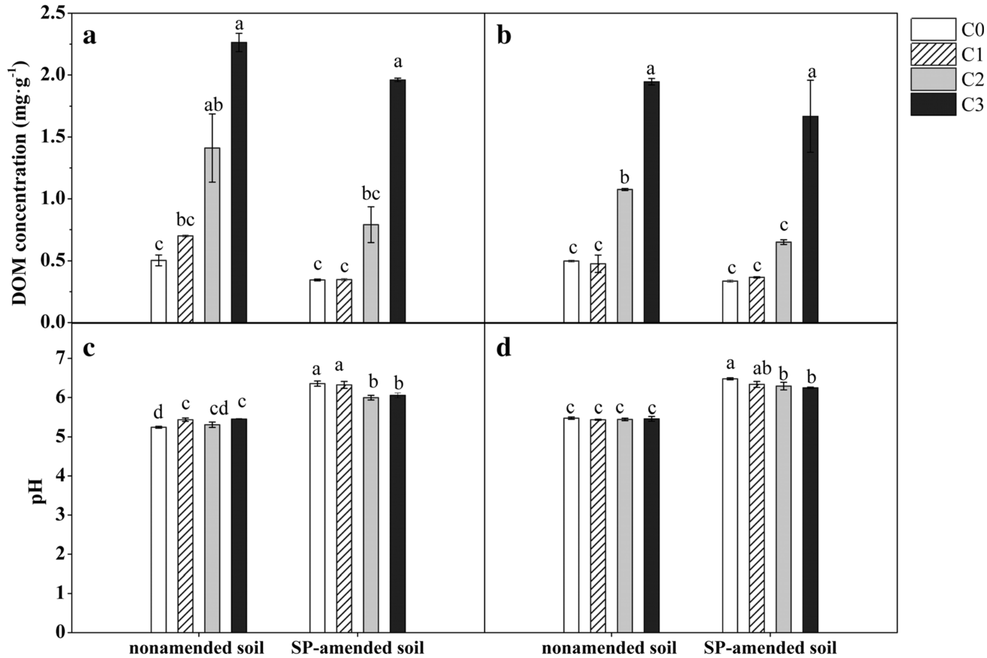

Fig. 6 Soil pH and DOM concentration. **a** DOM concentration under normal water conditions. **b** DOM concentration under water-saturation conditions. **c** Soil pH under normal water conditions. **d** Soil pH under water-saturation conditions; C0, control, C1, 0.5% CM; C2, 1.0% CM; C3, 2.0% CM. Different letters in the same column indicate a significant difference at $P < 0.05$

concentrations and higher biomass) when applying CM alone and combined application with SP.

Available content of Cd determined by DTPA increased with the application of CM on SP-amended soils in water-saturation conditions. Previous studies have shown that the presence of CM-DOM greatly reduces the adsorption capacity of bentonite and zeolite for Cd^{2+}, mainly through the barrier effect (Zhou et al. 2017). Cd content in shoots was the lowest when 2.0% CM was applied to SP-amended soils, but the decrease of Cd uptake in shoots was not caused by dilution effect or the reduction of available Cd content in soil, but the decrease of the TFs from roots to shoots. The increase of CM-DOM following the application of CM resulted in the formation of insoluble organo-metallic complexes and chelates, which were difficult to transport from root to shoot, although they could be absorbed by roots. The results further suggest that the risk of Cd pollution on pak choi with the presence of DOM originating from these organic fertilizers is non-negligible.

5 Conclusions

Results of this study indicated that the application of SP to soil significantly decreases Cd content in roots and shoots of *B. campestris* L. under normal and saturated water conditions. The application of CM and the increase of soil moisture on SP-amended soil increased the growth of plants. The application of CM on SP-amended soil enhanced the reduction of available Cd determined by DTPA under normal water conditions. The application of CM along with the increase of soil moisture of SP-amended soils decreased Cd uptake and translocation compared to the application of SP alone. Therefore, the application of SP could reduce Cd uptake by the plants, and the addition of CM combined with effective water management further reduces Cd absorption and accumulation.

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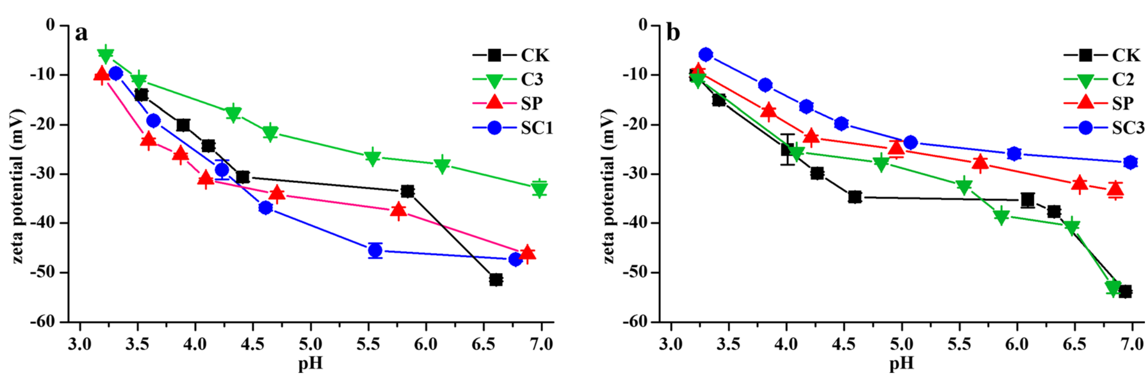

Fig. 7 Zeta potential of soil. **a** Normal water conditions. **b** Water-saturation conditions; CK, control, C2, 1.0% CM; C3, 2.0% CM; SP, 0.5% SP; SC1, 0.5% SP + 0.5% CM; SC3, 0.5% SP + 2.0% CM

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