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ORIGINAL ARTICLE

# Effects of organic mineral fertiliser on heavy metal migration and potential carbon sink in soils in a karst region

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**Abstract** Heavy metal pollution in karst mountainous area of Guizhou has spread due to the long-term exploitation of mineral resources and the improper disposal of environmentally hazardous waste. Heavy metals are characterised by non-degradation, strong toxicity, and constant accumulation, posing a grave threat to karst mountain fragile soil ecosystem. To reduce the harm caused by heavy metal pollution and damage to agricultural products, research was undertaken on the basis of previous work by simulating pot experiments on pak choi cabbage (*Brassica rapa chinensis*) planted in Cd-contaminated soil: different amounts of organic mineral fertilisers (OMF) compared with chemical fertiliser (CF) were used and by detecting the amount of heavy metal in the mature vegetable, a better fertilisation strategy was developed. The results showed that the Cd content in vegetables grown with CF was 23.70 mg/kg, while that of vegetables grown with OMF and bacterial inoculant was the lowest at 15.13 mg/kg. This suggests that the use of OMF and microbes in karst areas not only promotes plant growth but also hinders plant absorption of heavy metal ions in the soil. In addition, through the collection of pot leachate, the detection of water chemistry characteristics, and the calculation of the calcite saturation index, it was found that the OMF method also induces certain carbon sink effects. The results provide a new way in which rationalise the use of OMFs in karst areas to alleviate soil heavy metal pollution and increase soil carbon sequestration.

**Keywords** Karst · Soil pollution · Cd · Organic mineral fertilisers · Carbon sink

## 1 Introduction

China has the largest contiguous karst area in the world. It is mainly distributed in Guizhou, Guangxi, Yunnan, Hunan, and elsewhere (Chen 1986). Among those, Guizhou Province has the largest karst area, and the exposed area of carbonate rock therein is 130,000 $km^2$, accounting for the area of 61.92% of the province (Wang et al. 2003). The soil in Guizhou's karst mountains is barren and the cultivated land resource is poor. Rocky desertification, soil erosion, drought, and other environmental problems impede the long-term development of the local economy (Ruan et al. 2013, 2015; Li et al. 2004); the long-term exploitation of mineral resources in Guizhou makes the local ecological environment extremely fragile and heavy metal pollution are common. Song et al. (2005) detected and analyzed heavy metals in agricultural soils in Guizhou. The results showed that the comprehensive pollution index of farmland soil in Guizhou was 2.81 (intermediate level pollution), which was mainly composed of Cd and Hg pollution; the single pollution index for Cd was 4.05 (heavily polluted). Heavy metal pollution will change the composition, structure, and function of the soil, hinder normal plant growth, and the cultivation of crops can even increase the heavy metal content, which could harm human health. At

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present, commonly used remediation methods include physical repair, chemical repair, and bioremediation, but each method has some drawbacks, such as higher cost and secondary pollution (Chen et al. 2011; Xia and Chen 1997). Therefore, it is necessary to develop a low-cost, convenient way to control soil heavy metal pollution in karst regions. Liu et al. (2004) used organic fertilisers, beneficial microorganisms, and chemical fertilisers on potted plants. The results showed that the contents of Vitamin C in vegetables were significantly higher than those in the control, while the contents of nitrate, lead, and mercury were significantly decreased. Our previous research showed that OMF could partially replace chemical fertilisers for plant growth, soil quality improvement, and carbon sink effect increases (Xiao et al. 2016, 2017). Here, we ascertain whether or not the application of OMF and microorganisms in the Cd-contaminated soil can promote the growth of vegetables and prevent the absorption of heavy metals therein.

## 2 Materials and methods

### 2.1 Configuration of contaminated soil

To collect lime soil samples (from the Puding Karst Ecosystem Observation and Research Station, Chinese Academy of Sciences), the soil was air-dried, passed through a 2 mm square aperture mesh, and prepared as a contaminated soil at a Cd ($CdCl_2$) concentration of 10 mg/kg.

### 2.2 Characteristic of fertilizers

OMF (Xiao et al. 2017), where the N, P, and K contents were 2.3%, 2.3%, and 2.7% respectively was applied at 3000 kg/ha, and the bacterial inoculant (*Bacillus mucilaginosus*, Hebei Institute of Microbiology), was applied 30 kg/ha. According to the N, P, K rating of the organic mineral fertilizers, chemical fertiliser was calculated by conversion of the N, P, and K contents in the CF urea (N = 46.4%), purchased from Bijie Jinhe Chemical Co. Ltd; superphosphate (P = 12%), purchased from Yunnan Xinzheng Phosphorus Chemical Industry Co. Ltd; and potassium chloride (K = 60%), purchased from Sinochem Fertiliser Co. Ltd) (see Table 1).

### 2.3 Pot experiments

To simulate the soil characteristics of the karst area as much as possible, limestone gravel was added to the basin, which the test used six treatments, each with three replicates, making a total of 18 pots (Table 1). We selected 15 full-grain seeds of the vegetables for sowing in each pot (DeGao Vegetable Seed and Seedling Institute). The seeds sprouted after 3 days with attention payed to watering. They were fertilised 20 days later, and then the vegetables were harvested. The biomass was measured and washed with distilled water. The methods of pre-treatment and digestion of plant and soil refer to Liu Lei et al. (2008). The total amount of $Cd^{2+}$ in the solution was determined by Flame Atomic Absorption Spectrometry (AAS, AA900F). Soil pH was measured with reference to the agricultural industry standard NY/T 1377-2007 for soil samples (Multi3420 pH meter).

### 2.4 Statistical analyses

Using MS-Excel®, Origin, and MINTEQ software suites to analyse the experimental data.

## 3 Results and discussion

### 3.1 Analysis of pak choi growth in simulated polluted soil

The results showed that the six groups of pak choi grew well, and the two groups of pak choi with chemical fertiliser addition grew faster,but which had more yellow leaves compared with pak choi grown with OMF. Table 2 shows some biological characteristics of pak choi growth under different treatments.

The results showed that the Cd content of vegetables grown with OMF remained high, the lowest Cd content was 15.13 mg/kg, but this was far lower than that in vegetables grown with CF, the highest Cd content was 23.70 mg/kg (see Figs. 1, 2). The reasons for this behaviour were as follows:

1. The application of OMF can inhibit the activity of heavy metals in soil. Organic matter can change the form of heavy metals, or change the surface properties of adsorbents, thus affecting the adsorption of heavy metals, OMF also contains some clay minerals which can absorb heavy metal ions.
2. The ability of heavy metals to migrate in soil is closely related to the soil pH value, a decrease in pH will lead to an increase in the solubility of heavy metals, under alkaline conditions, heavy metals will precipitate in the form of hydroxides, and phosphate forms also exist, inhibiting their bioavailability (Lou et al. 2005). Tang et al. (2011) experiments show that the application of a variety of fertilizers on the soil pH values have varying degrees of change, and the changes will have different effects on plant growth. In this study, the results

**Table 1** Experimental design of potted plant trials

| Different treatment | Carbonate rock (large) (kg) | Carbonate rock (small) (kg) | Soil (kg) | Bacteria (g) | Organic mineral fertilizer (g) | Carbamide (g) | $KH_2PO_4$ (g) | KCl (g) |
|---|---|---|---|---|---|---|---|---|
| A | 3 | 6 | 2 | 0.234 | 23.4 | – | – | – |
| B | 3 | 6 | 2 | 0.468 | 23.4 | – | – | – |
| C | 3 | 6 | 2 | 0.702 | 23.4 | – | – | – |
| D | 3 | 6 | 2 | – | 23.4 | – | – | – |
| E | 3 | 6 | 2 | 0.234 | – | 1.16 | 4.48 | 1.05 |
| F | 3 | 6 | 2 | – | – | 1.16 | 4.48 | 1.05 |

**Table 2** Biological characteristics of pak choi growth

| Different treatment | Plant height (cm) | Spread angle (cm) | Head diameter (cm) | Maximum leaf(length × width × petiole length)(cm) | Dry weight(g/piant) | Leaves | Water ratio (%) |
|---|---|---|---|---|---|---|---|
| A | 12.85 | 12.67 × 9.30 | 7.47 | 9.0 × 6.0 × 5.0 | 0.95 | 7 | 91.99 |
| B | 11.18 | 14.22 × 10.30 | 7.01 | 7.8 × 5.7 × 5.0 | 0.99 | 7 | 91.27 |
| C | 11.51 | 14.94 × 11.70 | 7.30 | 7.5 × 5.6 × 5.3 | 1.03 | 7 | 91.49 |
| D | 10.96 | 15.60 × 12.42 | 6.97 | 8.4 × 6.2 × 5.8 | 1.00 | 7 | 91.71 |
| E | 12.13 | 18.55 × 12.10 | 8.28 | 9.8 × 7.8 × 5.5 | 1.31 | 7 | 92.02 |
| F | 12.30 | 16.70 × 11.62 | 8.10 | 9.8 × 8.1 × 6.0 | 1.32 | 7 | 92.09 |

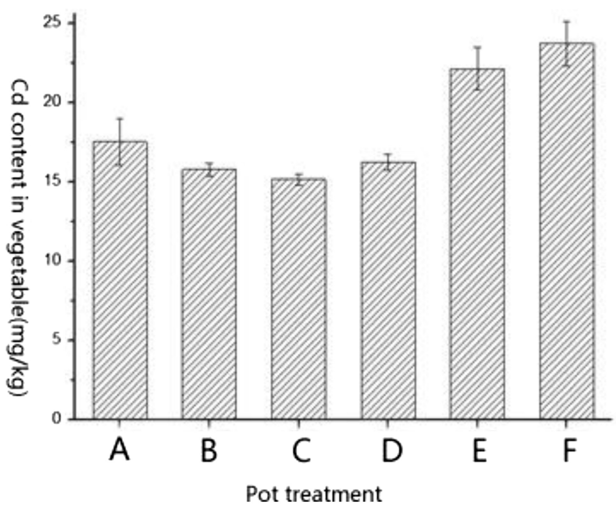


**Fig. 1** The heavy metal content in vegetables

showed that the pH value of CF was low (6.97–7.12), while the pH value of OMF was higher (7.28–7.39). Therefore, the Cd content in Groups E and F were relatively high.

3. Microorganisms can absorb and concentrate heavy metals, so as to accumulate heavy metal ions on the surface or interior of cells. In addition, given an appropriate amount of microorganisms and OMF in the clay minerals, that can interact with each other to promote the adsorption of heavy metal ions, thereby reducing the absorption of Cd ions.

## 3.2 Analysis of water chemical index of leachate of potted pakchoi

During planting, the relevant water chemistry parameters were obtained through assay of the leachate under different treatments (Fig. 3).

The results showed that water–rock interaction occurred during the planting process so that increased the $HCO_3^{--}$ concentration in general (Fig. 3a, b). Carbon sequestration effects can be produced by the microbial enzymes, such as carbonic anhydrase (CA), which can promote $CO_2$ hydration, resulting in the following reaction:

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca^{2+} + 2HCO_3^-$$

The $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$, and $HCO_3^-$ concentrations in the leachate were measured, and the calcite saturation index of the leachate was calculated by MINTEQ software (Fig. 3c). The results showed that, when the calcite saturation index was negative, the reaction system proceeds in the direction of dissolving carbonate, and when the calcite saturation index is positive, the system of carbonate dissolution has reached saturation. The results showed that during the planting process, the calcite saturation index in the leachate changed from negative to positive, forming more

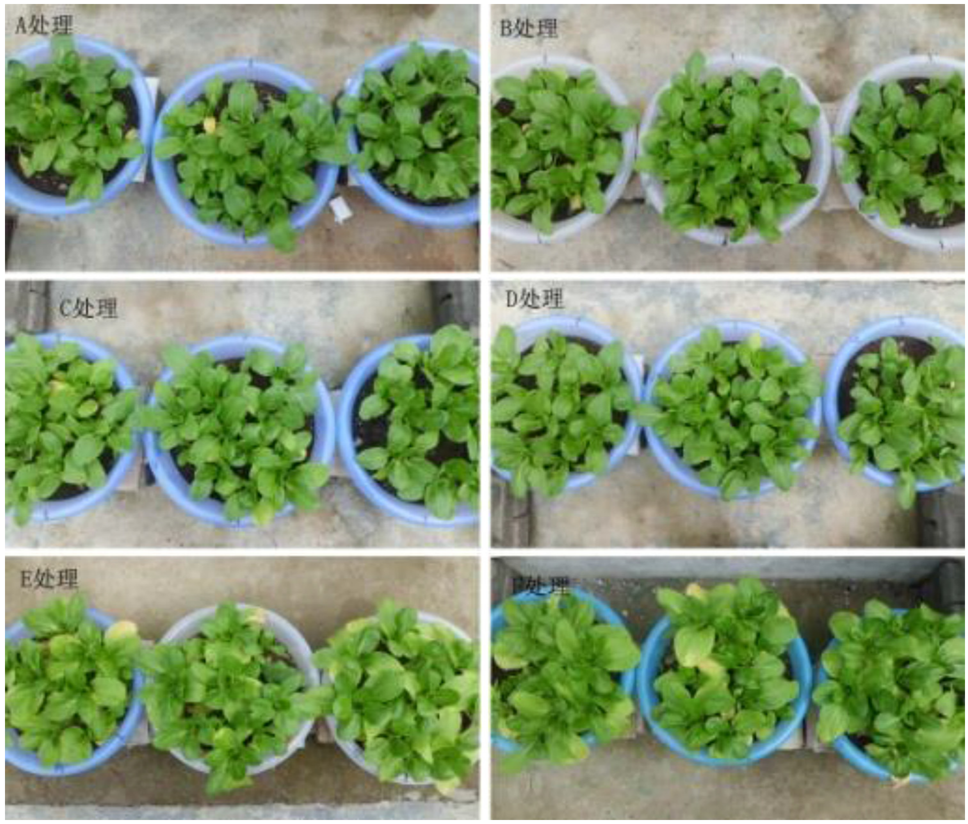


**Fig. 2** Vegetables grow up

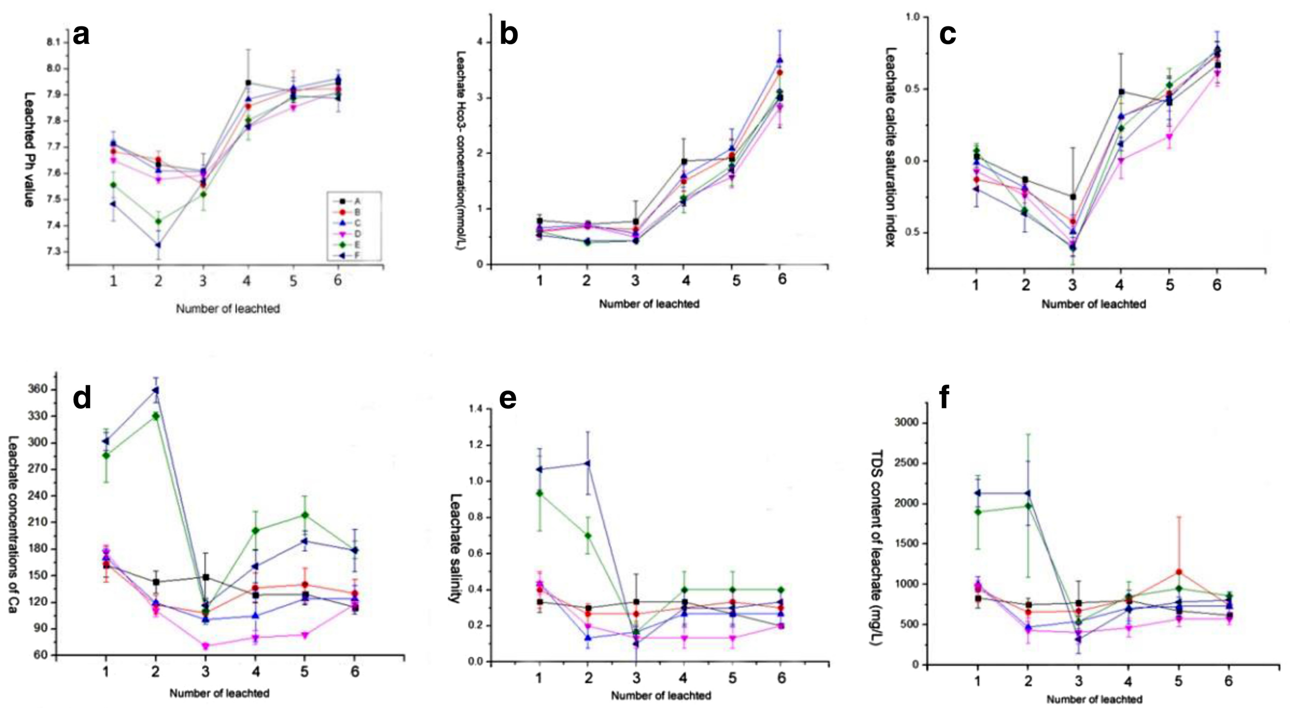


**Fig. 3** Water chemistry of the leachate

bicarbonate ions. For Group E and F treatments, the Ca concentration was very high at the beginning (Fig. 3d) due to the application of CF. In addition, the higher the total dissolved solids concentration in the leachate solution, the greater the amount of impurities and the higher the salt content (Fig. 3e, f) therein.

## 4 Summary

The use of OMF in heavy metal-contaminated soils in karst areas not only promotes the growth of vegetables but also hinders the absorption of heavy metal ions by such soils. OMF can also promote water–rock interactions and increase soil carbon sink effects in karst areas. The long-term use of CF will cause soil compaction and acidification, damages the soil physical and chemical properties, and affects plant growth. The use of OMF to replace some fertilisers in such areas can contribute to the agro-ecological environment and agricultural products safety.

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