Influence of Calcium Carbonate on Cobalt Phytoavailability in Fluvo-aquic Soil

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Abstract. In order to study the efficacy of calcium carbonate for cobalt (Co) fixation, as well as its influence on chemical speciation of Co in fluvo-aquic soil, pakchoies were planted in the soil with different quantities of exogenous Co and calcium carbonate. Co concentrations in the mature plant shoots were analyzed, and the chemical speciation of Co were detected with the Tessier five-step sequential extraction. The results showed that the Co concentration in plants tended to decrease first and then get higher with the concentration of calcium carbonate increasing (0-12g/kg) in soil ($P<0.05$). The proportion of Co in the exchangeable form in the soil followed the similar tendency ($P<0.05$), which might transform from the exchangeable form into the carbonate-associated and organic-associated forms. A regression analysis showed that when the concentrations of calcium carbonate were in the range of 5.0 to 7.5 g/kg, Co concentration in the plant reached to the lowest point, while the proportion of Co in the exchangeable form reached the minimum. In conclusion, to get the optimum effect, the dosage of calcium carbonate should be kept in the range of 5.0 to 7.5 g/kg when it is applied to Co fixation.

1. Introduction

With the rapid development of industrializing and citifying process, the soil heavy metal pollution has been a problem of great concern in recent years [1,2]. Chemical immobilization is a very common soil remediation method, where chemical amendments are used to reduce the ion state content of heavy metals in soil and the migration of heavy metals into crops was inhibited [3,4]. Many studies have shown that calcium carbonate was widely applied as soil amendment and showed a better effect on reducing the bioavailability of common heavy metals in soil, which is cost-effective and gained from environment easily [5]. The mobility, bioavailability and toxicity of heavy metals in soil depend on their specific chemical forms and binding state, so chemical speciation analysis can be an efficient path to research the remediation of polluted soil [6]. The previous studies on the environmental behaviors of heavy metals in soil mainly focused on the common heavy metals such as chromium (Cr), arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg), other heavy metals have a relatively low concern. Cobalt (Co) is an important industrial raw material and strategic resource, which has multiple applications in the industrial production process. However it also has a certain biological toxicity that can cause irreversible harm to human beings throughout the food chain. In this study, pakchoies were planted in the fluvo-aquic soil with different quantities of exogenous Co and calcium carbonate, and the Co accumulation level in the plants was analyzed. The chemical speciation of Co in the soil was also determined, which was designed to provide a theoretical basis for the rational use of the chemical amendments to reduce the bioavailability of heavy metals in soil.

2. Materials and methods

2.1. Materials
Fluvo-aquic soil was collected from the depth of 0-20cm of surface in a schoolyard at the Beijing Institute of Technology. The soil was air-dried at room temperature for approximately two days, while stones and plant material were removed. The soil was then sieved through a 2-mm nylon mesh for subsequent experimentation. $CoCl_2$ (AR) and calcium carbonate (AR) were purchased from *Beijing Chemical Works*. The seeds of pakchoi were purchased from *Dasenlin Flower Market* at the Chinese Academy of Agricultural Sciences in the Haidian District, Beijing, China.

2.2. Phytoavailability experiment
A pot experiment was carried out in a greenhouse at the Beijing Academy of Agriculture and Forestry Sciences in the Haidian District, Beijing, China. Prepared soil was introduced to plastic pots (12cm×Φ10cm) with a mass = 300 g/pot. In total, 15 treatments with various concentrations of exogenous Co and calcium carbonate in soil concluded the experiment phase, which are shown in Table 1. To command the plant growth requirement, N, P and K were added within the soil to reach the following levels: 3.067g/kg, 1.027 g/kg, 0.157 g/kg, respectively [7]. N, P and K were added in the form of urea, NaH_2PO_4 and K_2SO_4 solutions, respectively, while the treatments were conducted in triplicate. The treated soil was incubated in the dark for one week, being irrigated with deionized water to 70% of the water holding capacity, to obtain a stable state. Thenceforth, the pakchois were seeded. Growth period of the plants was 35 days. Plants were regularly watered using distilled water to maintain the moisture content between 60% to 70 % water holding capacity. The plants were kept under the condition of 28℃-14h and 15℃-10h cycles [8]. Ten days after sowing, the seedlings were thinned to three seedlings/pot. Shoots of the plants were sampled and dried at 105 ℃for analysis at the 28th day of growth.

At the same time, to investigate the chemical speciation of Co in the soil, there were 15 treatments with the same levels of exogenous Co and calcium carbonate dosage without planting. The soil was cultivated in the same methods and aged for one week. After sampling, the soil was air-dried and sieved to a 1-mm nylon mesh for Co speciation analysis.

Table 1. Exogenous Co and calcium carbonate for each treatment

number	Exogenous Co	calcium carbonate	number	Exogenous Co	calcium carbonate	number	Exogenous Co	calcium carbonate
1		0	6		0	11		0
2		3g/kg	7		3g/kg	12		3g/kg
3	0	6g/kg	8	20mg/kg	6g/kg	13	40mg/kg	6g/kg
4		9g/kg	9		9g/kg	14		9g/kg
5		12g/kg	10		12g/kg	15		12g/kg

2.3. Analytical procedure
Weights of shoots determined before pre-preparation were used as the biomass. Plant samples were digested with concentrated nitric acid (65%), perchloric acid (70%) and hydrofluoric acid (40%) (8:2:8 v/v) to determine the Co concentration. Tessier five-step sequential extraction was employed to study the Co speciation in the soil samples. Co concentrations were determined with Agilent 7500C Inductively Coupled Plasma Mass Spectrometry (ICP-MS). All the processes were conducted in

triplicate. The data was graphed and statistically analyzed with Origin 9.1 and SPSS Statistical 20.0 software.

3. Results and discussion

3.1. Co accumulation and biomass of pakchois

Co concentration in plants and biomass of plants under different $CoCl_2$ and calcium carbonate treatments are shown in Fig 1 and Fig 2. Co had a higher concentrations in pakchios with the increase of $CoCl_2$ concentration, while the biomass of plants tended to decrease (P<0.05), illustrating that exogenous Co has obvious toxic effects on plants. Co concentration in plants tended to decrease first and then get higher with the concentration of calcium carbonate increasing (0 to 12 g/kg) in soil under different $CoCl_2$ treatments (P<0.05). When the concentration of calcium carbonate were 6g/kg, the decrease rate was 41.3%-55.3% compared with the blank contrast group. The reason for the reduction of the concentration of Coin plants may be that calcium carbonate promoted the formation of $CoCO_3$ precipitate, as well as strengthened the competition of Ca^{2+} and Co^{2+} in terms of plant absorption [9]. However with the continuous increase in calcium carbonate concentration, the Co concentration in the plants increased (P<0.05), which might result from the fact that excessive Ca^{2+} competed with Fe-Mn cation for adsorption site in the soil and Co ions released into the soil and migrated into the plants. The changes of biomass was contrary to Co concentration in plants, it was related to the biological toxicity of Co in the soil.

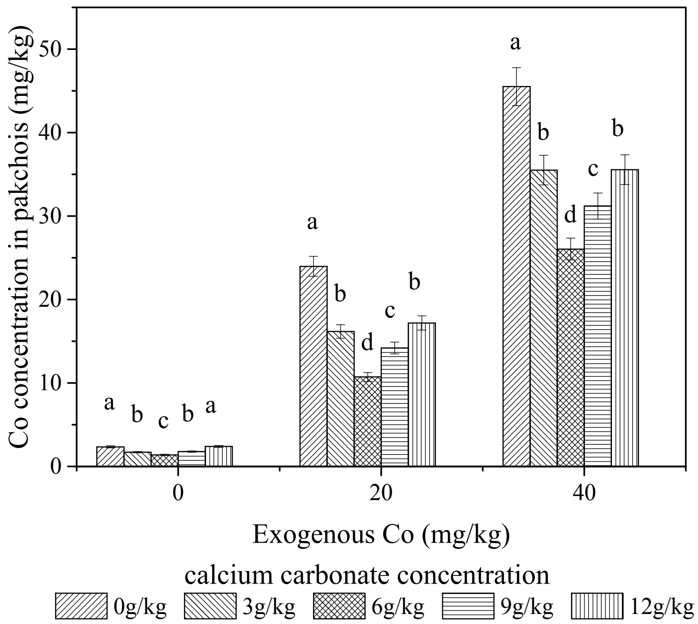

Figure 1. Co concentration in plants under different $CoCl_2$ and calcium carbonate treatments

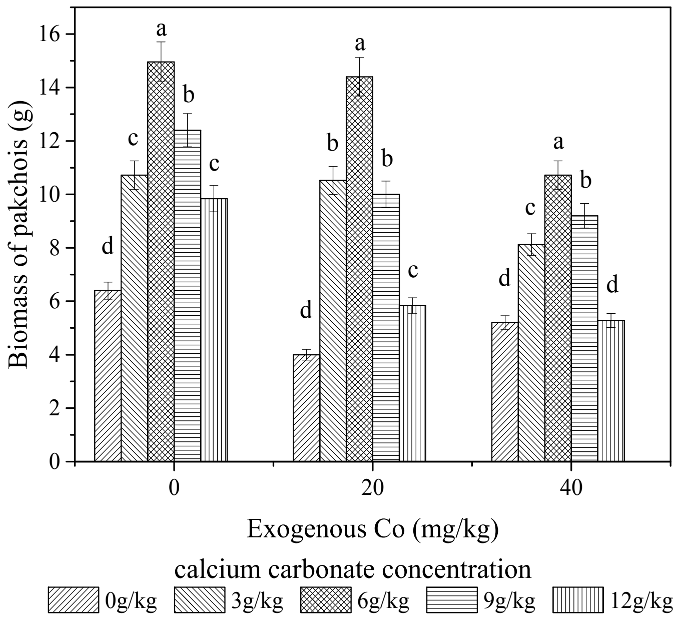

Figure 2. Biomass of plants under different $CoCl_2$ and calcium carbonate treatments

3.2. Chemical speciation of Co in soil

The chemical speciation of Co in soil were indicated by the proportion of Co in each form in the total Co concentration in soil. As can be seen in Fig 3, the proportions of the exchangeable form, carbonate-associated form, Fe-Mn oxides-associated form and organic-associated form were significantly raised with the increase of $CoCl_2$ concentration (P<0.05), illustrating that most exogenous Co accumulated in instable forms had a large environmental risks. With the calcium carbonate concentration rising, the amount of Co in the exchangeable form decreased firstly and then proceeded increase (P<0.05), which had the same tendency with the Co concentration in plants (Fig 1). When the concentrations of calcium carbonate were 6g/kg, the decrease rate of Co in exchangeable form was 28.3%-51.2%. Under this condition, Co in the carbonate-associated form tended to increase (P<0.05), resulting from the increase in CO_3^{2-} concentration in the soil [10]. Co in the organic-associated form tended to increase first and then get lower (P<0.05), while that in the Fe-Mn-associated oxides and residual form were maintained at a stable level.

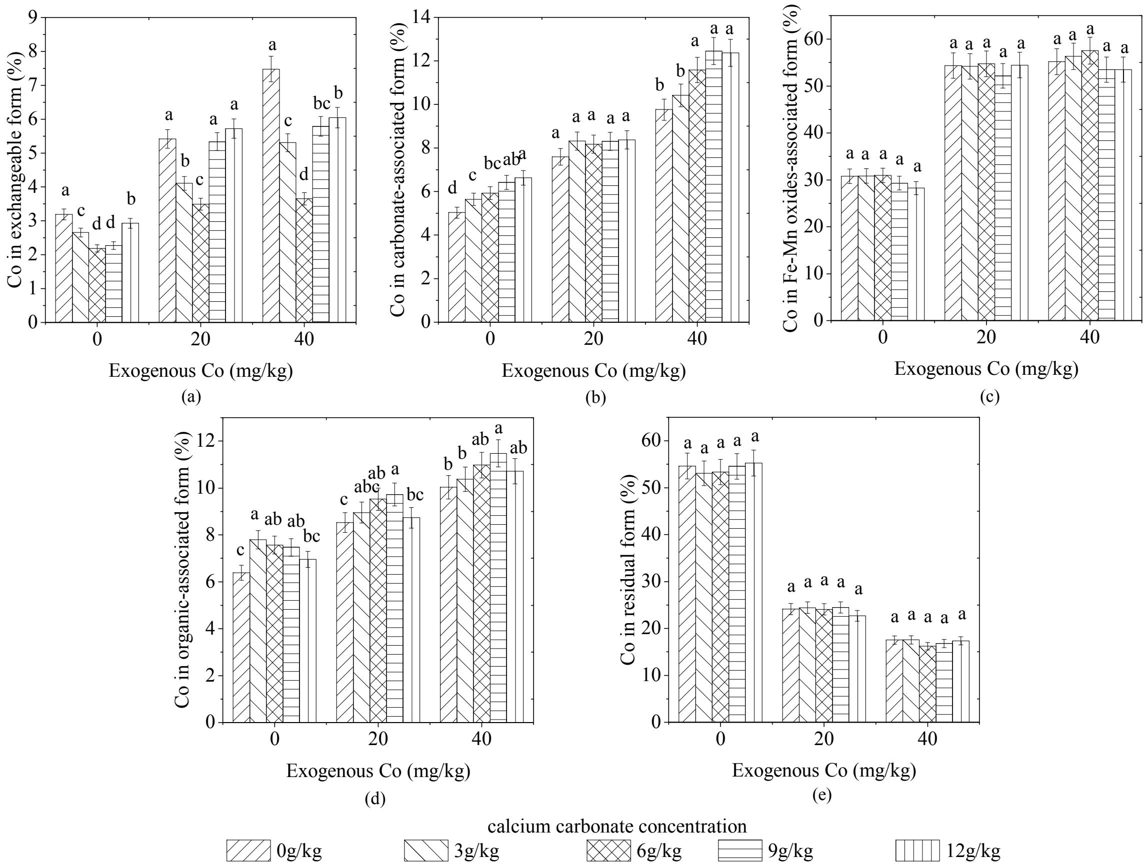

Figure 3. Chemical speciation of Co under different exogenous Co and calcium carbonate treatments (a) Co in exchangeable form; (b) Co in carbonate-associated form; (c) Co in Fe-Mn oxides-associated form; (d) Co in organic-associated form; (e) Co in residual form

3.3. Optimum concentration of calcium carbonate

In order to investigate the optimum concentration of calcium carbonate, a quadratic regression analysis between the biomass of plant, Co concentration in plant, the proportion of Co in exchangeable form in soil and calcium carbonate concentration was conducted, and the results are shown in Table 2. When the concentrations of calcium carbonate were in the range of 5.0 to 7.5 g/kg, the biomass of plan reached to the highest point, while Co concentration in the plant and the proportion of Co in the exchangeable form was the lowest.

Table 2. Results of quadratic regression analysis between calcium carbonate concentration (x, g/kg) and the parameters (y), regression equation: $y=ax^2+bx+c$

Exogenous Co	Parameter	a	b	c	R^2	Extreme point x
0	Biomass	-0.163	2.243	6.215	0.935	6.9
	Plant-Co	0.026	-0.304	2.350	0.984	5.9
	EX-Co	0.0002	-0.003	0.033	0.961	7.5
20mg/kg	Biomass	-0.235	2.928	4.086	0.945	6.2
	Plant-Co	0.242	-3.423	23.913	0.953	7.1
	EX-Co	0.0005	-0.005	0.053	0.751	5.0
40mg/kg	Biomass	-0.141	1.737	4.913	0.963	6.2
	Plant-Co	0.344	-4.932	45.786	0.939	7.2
	EX-Co	0.0007	-0.009	0.074	0.774	6.4

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4. Conclusion

Calcium carbonate has a remarkable influence on the Co concentration in plants as well as its chemical speciation in fluvo-aquic soil. With the calcium carbonate concentration rising, both of Co concentration in plants and Co in exchangeable form in fluvo-aquic soil tended to decrease first and then proceeded increase. In conclusion, calcium carbonate has positive effects on reducing the bioavailability and the environment risk of cobalt in soil. When calcium carbonate was applied, the concentration should be kept in the range of 5.0 to 7.5 g/kg to get the optimum effect.

Acknowledgments

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