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Mercury in some chemical fertilizers and the effect of calcium superphosphate on mercury uptake by corn seedlings (*Zea mays* L.)

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Abstract

Mercury (Hg) contents in ten chemical fertilizers were determined, and the effect of calcium superphosphate (CSP) on the uptake and translocation of Hg in corn seedlings was investigated by pot experiments. CSP was applied at the levels of 0, 66.7, and 133.4 mg P_2O_5/kg to Hg-treated (2 mg/kg) and untreated soils. CSP had the highest Hg content (5.1 mg/kg), followed by the NPK compound fertilizer 15-5-5 (15% N, 5% P_2O_5, 5% K_2O) (1.2 mg/kg), then by nitrogen fertilizers (except for ammonia sulfate) and potassium fertilizers. Application of CSP did not obviously influence the biomass of corn roots, but it significantly increased the biomass of corn shoots in Hg-treated soil. Application of CSP at the levels of 66.7 and 133.4 mg P_2O_5/kg did not obviously influence the uptake of Hg by corn seedlings on soils without Hg treatment, but it decreased the Hg uptake of corn seedlings significantly on Hg-treated soils. The transfer coefficient of Hg in corn seedlings improved slightly on soils without Hg treatment, but decreased slightly on Hg-treated soils with the application of CSP. These results implied that CSP could ameliorate Hg toxicity to corn seedlings by inhibiting the uptake and the translocation of Hg in plants on Hg-polluted soils.

Key words: Hg uptake; chemical fertilizer; transfer coefficient; calcium superphosphate

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Introduction

Fertilization is one of the most important ways to improve the yields and qualities of crops in agricultural activities. However, fertilization can influence the accumulation and transfer of heavy metals in soil-plant system. Fertilization is a source of soil heavy metals (He et al., 2005). Some heavy metals such as Zn, Cu, As, Cd, and Cr in fertilizers have been determined, and the accumulation of heavy metals in soils resulting from repeated application of metal-enriched fertilizers have also been investigated (Mclaughlin et al., 1996; Wang et al., 1994; Chen, 1996; Chen et al., 2007; Molina et al., 2009). Hg is a global pollutant and a potential neurotoxin. In soils, it can be absorbed by plants and then enter into the food chain (Smolińska and Cedzyńska, 2007). However, little information is available concerning the content of Hg in fertilizers, especially chemical fertilizers. Moreover, fertilization can affect the transfer of heavy metals from soils to plants or to water bodies by alteration the process of metal sorption-desorption and precipitation-dissolution, formation of discrete minerals in soils (Thawornchaisit and Polprasert, 2009), changing the rhizosphere compositions and the growth of plants (Wångstrand et al., 2007). Therefore, fertilization can increase or decrease the contents of heavy metals in plants (Li and Wu, 2008; Wångstrand et al., 2007; McGowen et al., 2001; Jalali and Moharami, 2010). Nowadays, most of those studies focus on the transfer of Cd and Zn in soil-plant systems affected by nitrogen fertilizers and phosphorous fertilizers (Jalali and Moharami, 2010; Xie et al., 2009; Mohamed et al., 2009). A few studies have been carried out to investigate the effect of fertilizers on the uptake and translocation of Hg, one of the most toxic elements, in higher plants. The objective of this study is to determine the content of Hg in some chemical fertilizers and to evaluate the effect of calcium superphosphate on the uptake and translocation of Hg in plant.

1 Materials and methods

1.1 Fertilizer samples

Hg contents in the following fertilizers from the markets of Chongqing, China were determined: urea (46% N), ammonium sulfate (21% N), ammonium dicarbonate (17% N), ammonium chloride (25% N), calcium superphosphate (18% P_2O_5), potassium chloride (60% K_2O, from China), potassium chloride (60% K_2O, from Canada), ammonium phosphate (12% N, 52% P_2O_5), the NPK compound fertilizer 15-5-5 (15% N, 5% P_2O_5, 5% K_2O) and the NPK compound fertilizer 25-10-10 (25% N, 10% P_2O_5, 10% K_2O). Each sample was homogenized before analysis.

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1.2 Pot experiments

The soil, classified as Typic Purpli-Cambosol according to Chinese Soil Taxonomy, was collected from the 0–20 cm layer of a farmland in Beibei, Chongqing, China. The samples were air dried, ground to pass through a 2-mm sieve, and stored in a plastic vessel for chemical analysis and pot experiment. The chemical properties of the soil are described in Table 1.

Pot experiment was conducted in a greenhouse of Southwest University, China. Two kilograms of soils, mixed with 0.44 g urea, 0.22 g potassium chloride, different amounts of calcium superphosphate and Hg, were put into a 1.5 L plastic pot. The calcium superphosphate was added at the level of 0 (P0), 66.7 (P1), 133.4 (P2) mg/kg soil. Hg was added as $HgCl_2$ at the levels of 0 (–Hg) and 2 mg/kg soil (+Hg). Each treatment was arranged randomly with three replicates. Two weeks later, each pot was planted with 3 corn seed (*Zea mays* L.) and irrigated with deionized water throughout the experimental period. After three weeks, corn seedlings were harvested, the root and shoot were separated, washed with tap water and deionized water, then dried at 65°C, finely ground with a stainless grinder, and stored for analysis.

1.3 Laboratory analysis

The determination of Hg in soils and fertilizers was conduced following the methods of Mirlean et al. (2008). Approximately 5.0 g of soil or fertilizer samples were transferred to a 100 mL volumetric flask, 15 mL aqua regia was added and mixed thoroughly, then heated for 2 hr in a water bath at 95°C. The flask was taken out and cooled to the room temperature, and 15 mL of 5% potassium permanganate solution was added slowly. The flask was again placed in the water bath at 95°C for 30 min. After cooling to the room temperature, 6 mL of 24% sodium chloride-hydroxylamine sulfate solution was added, then the suspension was filtered, and the final volume of the filtrate was diluted to 100 mL with Milli-Q water. Hg concentration in solution was determined by cold vapor atomic absorption spectrometry method (SYG-II, Hangzhou, China).

The content of Hg in corn seedlings was determined according to the methods of Shiyab et al. (2009). Approximately 1.0 g corn samples was digested with concentrated HNO_3 and H_2O_2 on a hot plate, and filtered for Hg analysis.

The detection limit was 0.05 g/L. The accuracy of the method was verified by the recovery assay experiments using a certified reference material, GBWO7419, purchased from the Chinese CRM/RM Information Centre. The recovery percentage for Hg in the reference material ranged from 89% to 99%. The precision of the method was determined by analyzing each sample in triplicates.

1.4 Data analysis

All results were expressed as an average value of triplicates. The variance analysis was performed using SPSS software (version 13.0). Differences among treatments were compared by least significant difference (LSD) at $p < 0.05$.

2 Results and discussion

2.1 Hg content in fertilizers

Heavy metals in fertilizers are influenced by their raw materials and manufacturing methods (Chen et al., 2009). As shown in Table 2, the contents of Hg in urea, ammonium bicarbonate, ammonia chloride and two potassium fertilizers were not detected, which are similar to that reported by Li and Wu (2008). Of all the fertilizers determined, calcium superphosphate made from phosphorous rock by acid degradation contained the highest level of Hg. The content of Hg in calcium superphosphate was 5.1 mg/kg, which was 5–10 times higher than the limit of the grade II soil in Environmental Quality Standard for Soils in China (GB 15618-1995), and might cause the accumulation of Hg in soils with low Hg background (Zheng et al., 2008). The content of Hg in the NPK compound fertilizer 15-5-5 was much higher than that in the NPK compound fertilizer 25-10-10. This could also be explained by the source of phosphorous in compound fertilizer (Chen et al., 2009; Wang and Ma, 2004). Calcium superphosphate was the main source of phosphorous for the NPK compound fertilizer 15-5-5, while ammonia phosphate was the main source of phosphorus for the NPK compound fertilizer 25-10-10 (Zhou, 1994). Hg content in the former was much

Table 1 Chemical properties of the tested soil

pH	Organic matter (g/kg)	Available N (mg/kg)	Available P (mg/kg)	Available K (mg/kg)	Cation exchange capacity (cmol/kg)	Total Hg (mg/kg)
6.8	19.3	53.34	20.52	86.35	13.42	0.07

Table 2 Hg content in some chemical fertilizers

Fertilizer	Hg content (mg/kg)	Fertilizer	Hg content (mg/kg)
Urea (*n* = 5)	ND	Potassium chloride (from China, *n* = 5)	ND
Ammonia sulfate (*n* = 4)	0.17 ± 0.06	Ammonium phosphate (*n* = 5)	0.05 ± 0.03
Ammonium bicarbonate (*n* = 3)	ND	NPK compound fertilizer 15-5-5 (*n* = 5)	1.2 ± 0.1
Ammonia chloride (*n* = 3)	ND	NPK compound fertilizer 25-10-10 (*n* = 5)	0.07 ± 0.02
Potassium chloride (from Canada, *n* = 3)	ND	Calcium superphosphate (*n* = 5)	5.1 ± 0.3

ND: not detected.

higher than that in the latter (Table 2).

2.2 Effect of calcium superphosphate on the growth of corn seedling

Biomass can be used as an indicator to evaluate the healthy situation of plants growing on metal-contaminated soils (Wang et al., 2008). Figure 1 shows that 2 mg/kg of Hg treatment slightly affected the biomass of corn root, while decreased the biomass of corn shoot by 8.4%–13.6%. These results coincided with those of Cho and Park (2000), who found that roots of tomato were less sensitive to Hg exposure than shoot.

Application of calcium superphosphate (CSP) increased the biomass of corn shoot, but did not obviously affect the biomass of corn root. The increase of shoot biomass varied with the level of soil Hg. The shoot biomass increased by 6.5%–22.9% in soils without Hg treatment, while increased by 11.4%–30.3% in Hg-treated soil, which indicated that applying CSP to Hg-polluted soils could ameliorate the Hg toxicity to corn seedlings.

2.3 Effect of calcium superphosphate on Hg uptake of corn seedling

The effect of Hg treatment on the content of Hg in corn seedlings is shown in Fig. 2. The contents of Hg in the root and shoot of corn seedlings from the Hg-treated soils ranged from 2.7 to 4.3 mg/kg and from 0.03 to 0.08 mg/kg, respectively, which were accordingly 47.1–57.0 and 1.9–4.1 times, as those of corn seedlings from soils without Hg treatment.

The effect of CSP on Hg content in corn seedlings varied with the level of Hg in soil. Application of CSP did not obviously influence Hg content in corn root, slightly decreased Hg content in the corn seedling shoot on soils without Hg treatment, while significantly decreased Hg content in the root and shoot of corn seedling on Hg-treated soils. Application of CSP at the levels of 66.7 and 133.4 mg P_2O_5/kg to Hg-treated soils caused a reduction of 11.9% and 38.3% for Hg content in corn root, respectively, and a reduction of 38.3% and 59.3% for Hg content in corn shoot, respectively.

To make clear whether the decrease of Hg in corn shoot and root resulted from the dilution effect due to the increase of growth or resulted from the decrease of Hg uptake caused by CSP application, the uptake of Hg by plant was calculated as (Hg content in shoots × weight of shoot) + (Hg content in root × weight of roots). As shown in Fig. 3, application of CSP did not obviously influence the uptake of Hg by corn seedling from soils without Hg treatment, while significantly decreased the uptake of Hg by corn seedling from Hg-treated soils. This implied that a single application of CSP on non-contaminated soil did

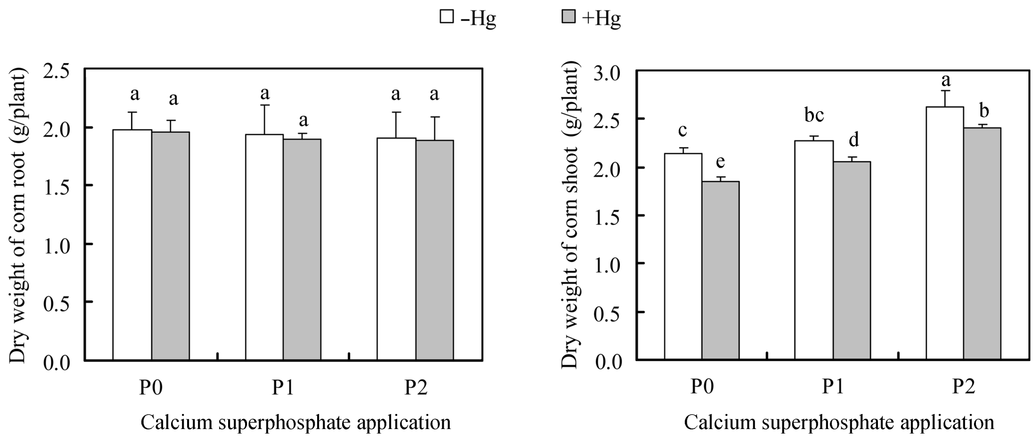

Fig. 1 Effect of calcium superphosphate on biomass of corn seedlings. Values with different letters mean significant differences at the level of 0.05.

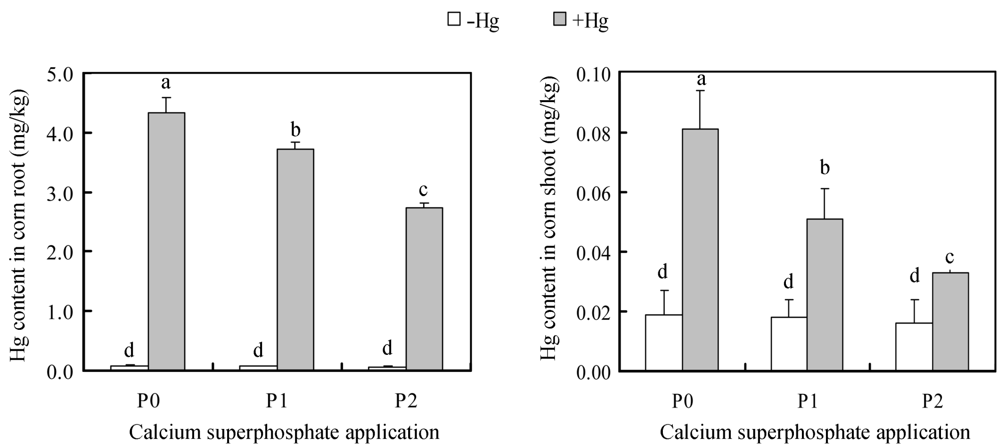

Fig. 2 Effect of calcium superphosphate on Hg content in corn seedlings. Values with different letters mean significant differences at the level of 0.05.

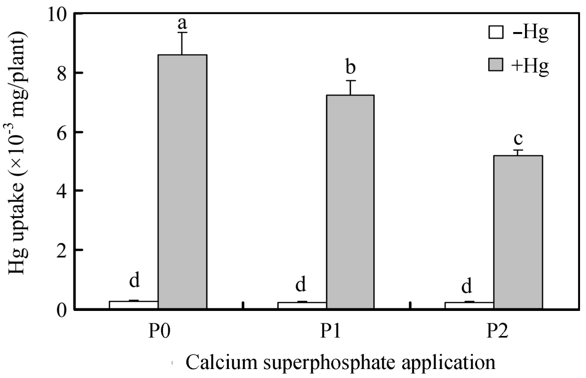

Fig. 3 Effect of calcium superphosphate on Hg uptake by corn seedling. Values with different letters mean significant differences at the level of 0.05.

not increase the accumulation of Hg by plant. The Hg uptake of corn seedlings decreased by 15.9% and 39.6%, respectively, as CSP was applied at the levels of 66.7 and 133.4 mg P_2O_5/kg to Hg-treated soils. This indicated that the decrease of Hg content in corn seedlings on Hg-polluted soils was mainly contributed to the reduction of Hg uptake, which might result from the lower phyto-availability of Hg in soils due to the formation of phosphate precipitation, surface adsorption or complexation when CSP was applied (Cao et al., 2003; Du et al., 2005).

2.4 Effect of calcium superphosphate on Hg translocation in corn seedling

The transfer coefficient, defined as the ratio of Hg content in shoot to that in root, represented the ability of Hg transport from root to shoot. The transfer coefficients of Hg in corn seedling grown in soils without Hg treatment were 12.8–24.4 times higher than those in Hg-treated soil (Table 3), which illustrated that root acted as a barrier to the translocation of Hg from root to shoot, and the absorbed Hg was not readily mobilized and redistributed within plants (Cho and Park, 2000). This might be explained by more Hg bound to the cell walls of roots or less Hg transported through the transpiration stream in plants at higher level of soil Hg (Du et al., 2005).

The change of the transfer coefficient with the increase rate of CSP application also varied with the level of Hg in soil. In soil without Hg treatment, increasing the rate of CSP promoted the growth of corn seedling and led to a higher transpiration stream, thus increased the translocation of Hg to the shoot. In Hg-treated soils, raising the rate of calcium superphosphate caused more phosphate precipitation or absorption of Hg in the root cell wall, therefore decreased the translocation of Hg to the shoot of plant.

Table 3 Effect of calcium superphosphate on transfer coefficients of Hg in corn seedlings

Treatment	–Hg			+Hg		
	P0	P1	P2	P0	P1	P2
Hg transfer coefficient	0.24	0.28	0.29	0.02	0.01	0.01

3 Conclusions

The present study showed that calcium superphosphate contained the highest level of Hg of the fertilizers studied. The Hg content in compound fertilizers depended on their sources of phosphorous. The Hg content in nitrogen fertilizers (except for ammonium sulfate) and potassium fertilizers was not detected. Calcium superphosphate could ameliorate Hg toxicity to corn seedlings by inhibiting the uptake and translocation of Hg from root to shoot.

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