The use of calcium peroxide (CaO_2) as a process applied to arsenic contaminated soil around an abandoned tungsten mine, southern China

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Abstract
To reduce As bio-available and uptake in celery, calcium peroxide (CaO_2) was applied as a stabilizer. In the batch experiments, with the increase of CaO_2 concentration addition, the pH of soil was increased significantly. With the application of CaO_2 at low concentration, the bio-available As was decreased significantly, while application of high concentration of CaO_2 increased As mobility significantly. In the field experiments, CaO_2 application could alleviate As toxicity to celery. The biomass of celery shoots increased significantly while the As concentration in the shoots of celery decreased significantly with CaO_2 application. The optimal dose of CaO_2 application was 750 kg/ha, at this dosage, the celery had the highest biomass and lowest As concentration.

Key Words
Arsenic, calcium peroxide, stabilization, celery.

Introduction
Lianhuashan tungsten mine, one of largest tungsten mines in southern China, had a typical polymetallic sulfide ore, with the main components being wolframite, scheelite, arsenopyrite, pyrite, magnetite, chalcopyrite, quartz, sericite, chlorite and feldspar. Arsenic (As) was found to be the most important contaminant in the tailing and soil samples of the area (Liu *et al.* 2009). As is known to be a very toxic element and a carcinogen to humans (Duker *et al.* 2005; Williams *et al.* 2005). As (III) and As (V) are the most widespread forms in nature and As (III) was both more mobile and toxic (Boyle and Jonasson 1973; Pantsar-Kallio and Manninen 1997). Stabilization is one of the most effective methods to reduce the mobility of heavy metals (Yukselen and Alpaslan 2001). Various combinations such as lime, type F fly ash, silica fumes, iron (II) or (III), silicates and blast furnace slag have been used in the treatment of soils contaminated with As (Akhter *et al.* 1997; Leist *et al.* 2000). Although the leaching of As is significantly reduced by lime application, such a soil treatment is rather disruptive and considered only when the material is disposed of at a landfill. In this research, calcium peroxide (CaO_2) was selected as a stabilizer to reduce As uptake and accumulation in celery.

Methods
In the batch experiments, the soil was collected from a paddy field contaminated with arsenic around Lianhuashan tungsten mine. Air dried soil was passed through a 2 mm diameter sieve, and then calcium peroxide (CaO_2) was added at the concentrations of 0, 10, 20, 50, 100 mmol/kg. After undergoing three cycles of saturation with deionized water and air-drying for 10 d, the pH of these soils was measured by 0.01 *M* $CaCl_2$ at a 1:5 ratio (w/v) using a pH meter and the bio-available As concentrations in these soils were measured by extraction with 0.1 *M* Na_2HPO_4 and 0.1 *M* NaH_2PO_4. The fields near Lianhuashan tungsten mine were selected for the field experiments. Arsenic, concentration in the soil was 935.3 mg/kg and the pH of the soil was 5.71. To reduce As uptake, CaO_2 @ 375, 750 and 1500 kg/ha was applied 15 d before planting, and the soil without CaO_2 application was set as the control. After harvest, the biomass and As concentration were determined.

Results
As shown in Table 1, the pH of control soil was 5.59. With the increasing concentration of CaO_2 added in the soils, the pH increased significantly. At a concentration of 50 mmol/kg CaO_2 , the pH of soil was neutral. Total As concentration in the soil was 837.2 mg/kg, but the bio-available As was only 16.5%. The bio-available As decreased significantly when 10, 20 mmol/kg CaO_2 was added in the soil (12.4, 13.1%, respectively). But when100 mmol/kg CaO_2 were added to the soil, the bio-available As (25.8%) was significantly higher than that of control. In the presence of Ca under highly oxidizing and moderate pH conditions, calcium hydrogen arsenate ($CaHAsO_4$) and calcium arsenate ($Ca_3(AsO_4)_2$) can precipitate and

reduce the mobility of As (Porter *et al.* 2004). But under acid or alkaline pH conditions, As was more mobile (Magalhães 2002).

Table 1. Effects of different CaO_2 concentration treatments on the pH and bio-available As of the soils.

Concentration of CaO_2 treatments （mmol/kg）	pH	Percentage of bio-available As to total As (%)
0	5.59e	16.5b
10	5.88d	12.4c
20	6.19c	13.1c
50	7.12b	18.3b
100	8.39a	25.8a

The different letter in the same column indicates a significant difference at $P<0.05$ according to Duncan's multiple rang test.

CaO_2 application could alleviate As toxicity to celery. The biomass of celery shoots increased significantly while the As concentration in the shoots of celery decreased significantly with CaO_2 application (Figure 1). In comparison with the control, the supply of 375, 750 or 1500 kg/ha CaO_2 lead to an increase in fresh weight of celery shoots of 25%, 56% or 22%, respectively while lead to a decrease in As concentration of celery shoots of 33%, 75% or 53%, respectively. The optimal dose of CaO_2 application was 750 kg/ha, at this dosage, the celery was found with highest biomass and lowest As concentration. CaO_2, a strong oxidizer, could oxidize As (III) into the less toxic As form of As(V) and reduce the mobility of As. Furthermore, the supply of Ca^{2+} could also inhibit As desorption. It has been reported that the amount of soluble As is lower in the presence of Ca when treated with ferric oxides (Dutre and Vandecasteele 1995).

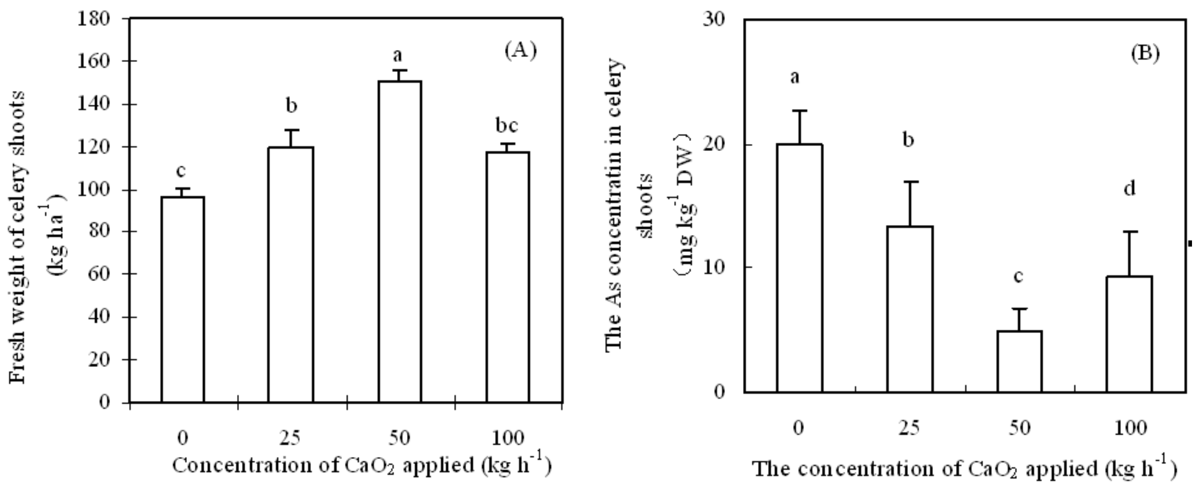

Figure 1. Effects of CaO_2, application on fresh weight (A) and As concentration (B) in celery shoots. (The different letter in the same column indicates a significant difference at $P<0.05$ according to Duncan's multiple rang test).

Conclusion

In present research, CaO_2 was applied to farm lands and used to reduce As accumulated in celery. Results showed that CaO_2 application increased the pH of soil significantly and the bio-available As was reduced with the low CaO_2 concentration application (10, 20 mmol/kg). The bio-available As was increased significantly, for the high concentration of CaO_2 (100 mmol/kg). In the field experiments, CaO_2 application could alleviate As toxicity for celery. The biomass of celery shoots increased significantly while the As concentration in the shoots of celery decreased significantly with CaO_2 application. The optimal dose of CaO_2 application was 750 kg/ha, at this dosage, the celery had the highest biomass and lowest As concentration.

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