Evaluation of Cadmium Accumulation and its activity in Northeast China

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Abstract. In this study, the concentrations of total Cd and available Cd in different cultivation
greenhouses were investigated to illuminate the effect of greenhouse on Cd accumulation and
its activation under greenhouse vegetable production (GVP). The results revealed that higher
Cd contents (including total Cd and available Cd) accumulated in GVP surface layer (0-20 cm),
and increased with duration years. Total Cd contents and Cd activation rate were positively
correlated with GVP duration (P<0.05). Cd accumulation and activation in soils were mainly
ascribed to anthropogenic input, such as heavy inorganic or organic fertilizer application. For
greenhouse sustainability, much more attention should be paid to Cd contents in soils of 13-yr
greenhouses.

1. Introduction
Greenhouse vegetable production (GVP) is an intensive form of agriculture, which can prolong the
growing season compared with conventional vegetable cultivation [1]. In China, especially Northeast
China, greenhouse vegetable production has rapidly developed. However, due to economic demands
and high crop production, the strategy with heavy-intensive use of agricultural materials (e.g. chemical
fertilizers, manures, irrigation and pesticides) was adopted under greenhouse conditions, which can
cause the accumulation of heavy metals, particularly Cd in GVP soils. The contaminated soils may
elevate the contents of toxic elements in vegetables. The excessive ingestion of these nonessential
elements will cause deleterious effects on human health [2, 3]. During the past decades, the
concentration and accumulation of metals in soils has been studied [4, 5]. However, few studies have
focused on the distribution characteristics of Cd in soils under greenhouse condition in China,
especially in Northeast China. Therefore, the objectives of this research were to (i) investigate the
present accumulation status of Cd, (ii) illustrate the effects of GVP duration on Cd accumulation and
phyto-availability.

2. Materials and Methods
2.1. Area of investigation
The study area (41°55’N, 122°58’E) is situated in Liaoning province, China. It has numerous
agricultural facilities for vegetable cultivation. Fertilizers were utilized each year, such as about 100
t·hm⁻² manures (e.g. decaying chicken and dairy manures), 1000 kg·hm⁻² postassium sulphate (K₂SO₄),
1000-1500 kg·hm⁻² diammonium phosphate ((NH₄)₂HPO₄), 500 kg·hm⁻² carbamide or 1000 kg·hm⁻²
ammonium sulphate ((NH₄)₂SO₄).
2.2. Sampling methods and analysis
This experiment was carried out in 27 sample sites, which comprised four types of greenhouses (vegetable cultivating for 2 years, vegetable cultivating for 4 years, vegetable cultivating for 6 years, and vegetable cultivating for 13 years) and the open vegetable fields (OF). Soil samples were randomly collect in each greenhouse. The sampling depth was 0-120 cm. Each soil sample was multi-point mixed.

Soil samples were air-dried, sieved through 2-mm and 0.149-mm, mixed and stored for total Cd and DTPA-Cd analysis. About 0.2000 g of 0.149 mm soil samples was digested in an HCl-HNO₃-HClO₄ (3:1:1, v/v) mixture, and determined by using inductively coupled plasma spectrometer. Plant available Cd was determined by using diethylene-triamine-pentacetic (DTPA) buffered at pH 7.3 [6].

Data analysis was performed using SPSS 19.0. One-way ANOVA test was used to compare the means among greenhouses under different farming years at $P \leq 0.05$. Stepwise multiple regression analysis was employed to identify the relationships between total Cd contents in top soils and the planting years.

3. Results

3.1. Temporal distribution of total Cd in surface soils
Relationship between total Cd contents in top layers (0-20 cm) and different cultivation years was shown in Figure 1. According to the Kolmogorov-Smirnov test, the concentrations of total Cd were normal distributed. And the percentage of soil samples exceeding the second level criterion of Standard of Soil Environment (GB15618-1995) for Cd was 81.58%. Total Cd in GVP surface soils increased with GVP cultivation and positively correlated with the greenhouse planting years ($R^2=0.8929$, $P<0.01$), which is consistent with the results from Tianjin Municipality in North China [7].

3.2. Distributions of available Cd in soil profiles
Available Cd contents in soils was shown in Figure 2, ranged from 0.01 to 0.13 mg·kg⁻¹ with an average of 0.03 mg·kg⁻¹, and followed normal distributions (K-S, $P>0.05$). Available Cd mainly accumulated in surface layer (0-20 cm) and decreased with depth in the order of 0-20 cm >20-40 cm >40-120 cm. The highest concentrations of of available Cd were found in 0-20 cm soils of 13-year greenhouse. According to One-way ANOVA test, available Cd contents in greenhouse soils (0-20 cm) were significantly higher than those of the open field. The results of analysis of variance showed that the contents of available Cd in 20-40 cm layer of 6-year greenhouse were significantly higher than those of 2-year greenhouse, 4-year greenhouse, 13-year greenhouse, and the open field.

![Figure 1. Accumulation of total Cd in soils under different cultivation years](image_url)

The error bars indicate the standard deviations.

![Figure 2. Distributions of available Cd in soil profiles](image_url)
Figure 2. Distribution of available Cd (DTPA-Cd) in profiles of greenhouse soil with different planting years

3.3. Temporal trend of Cd activation rate in surface soils
Although available Cd is usually used to predict metal phyto-availability, activation rate is more important for its potential toxic to the environment. By including Cd activation rate and GVP cultivation years, empirical model was derived using stepwise multiple linear regression analysis to predict Cd toxic in top layers (0-20 cm) of greenhouse vegetable production in Northeast China (Figure 3). The results showed Cd activation rate in surface soils (0-20 cm) of greenhouses was significantly and positively correlated with GVP cultivation years ($R^2=0.8929$, $P<0.05$), suggesting that Cd activation rate could be explained by GVP planting years.

Figure 3. Temporal trend of Cd activation rate under different cultivation years

4. Discussion
The aim of the present study was to investigate the effects of cultivation years on Cd accumulation and its phytoavailability in soils under semi-artificial environment. Higher values of total Cd and available Cd were observed in greenhouse soils compared to those in the open field soils (Figure 1 and Figure 2). In previous research, the concentrations of heavy metals in greenhouse soils were much higher in this
studied area. Qian X B et al. [8] and Yu P Y et al. [9] have discovered that the concentrations of Hg and As have a significant positive correlation with cultivation ages of greenhouses. It is confirmed that the anthropogenic influence is the key factor increasing the metal contents. In general, trace metal accumulation in greenhouse soils is ascribed to long-term heavy fertilizer application, especially manure [10-12], although Cd, Cu, Pb, and Zn contents in manure are limited [13]. In Jiangsu, China, the mean value of Cu in poultry manures can reach 0.80 mg·kg⁻¹ [14]. In Gansu China, the mean concentration of Cd in pig manure was 0.707 mg·kg⁻¹, and the maximum value of pig manure was 2.927 mg·kg⁻¹ [15]. Moreover, phosphate fertilizer might also result in Cd accumulation in greenhouse soils. This suggestion was supported by Bai et al. [15], who have found that the Cd content was relatively high in complex phosphorous fertilizers, the maximum concentration of Cd was 37.69 mg·kg⁻¹, and the mean concentration of Cd was 2.41 mg·kg⁻¹. Phosphorous fertilizer is widely considered as a ubiquitous source of Cd pollution in agricultural soils [16].

5. Conclusion
Total Cd content and Cd activation rate in greenhouse soils (0-20 cm) both had an increase trend with cultivation ages (Figure 1 and Figure 3), which might mainly ascribed to heavy fertilization under greenhouse vegetable production. Total Cd and available has posed a potential risk to human health in 13-yr greenhouses, which may result in excessive ingestion of Cd via vegetables.

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