Effect of cultivation ages on Cu accumulation in Greenhouse Soils in North China

Jun Wang 1, Wenmiao Guo 1, Xin Chen 2, Yi Shi 2,*
1College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China
2State Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110164, China
*Corresponding author. Tel.: +86 024 83970540; fax: +86 024 83970540. E-mail addresses: shiyi@iae.ac.cn (Yi Shi).

Abstract. In this study, we determined the influence of cultivation age on Cu accumulation in greenhouse soils. The concentration of plant available Cu (A-Cu) decreased with depth, and the contents of top soils (0-40 cm) in greenhouses were higher than those of the open field. There was a positive correlation between A-Cu concentrations in soils and cultivation ages (R²=0.572). The contents of total Cu (T-Cu) decreased with depth, and positively correlated with cultivation ages in top soils (0-20cm) (R²=0.446). The long-term usage of manures can cause Cu increase and accumulation in greenhouse soils in comparison to the open field.

1. Introduction
Greenhouse vegetable production in China has increased rapidly to meet the growing demand for vegetables. These artificial facilities are labor- and energy-intensive production systems [1]. Over the last few decades, high-intensive agricultural practices including fertilization and spraying pesticides have caused the accumulation of trace metals in soils. Several trace metal in greenhouse soils have exceeded the natural input [2].

Copper is a trace element, and can be harmful at high concentrations when ingested over an extended period of time. Exposure to excessive Cu has been associated with many diseases in humans. Many studies have shown Cu in agricultural soils originate from anthropogenic inputs [3, 4]. The main organic fertilizers are livestock, cow and pig slurries, which are easily obtained and widely used in urban areas of China. Thus, soils can be contaminated with Cu through the utilization of manures.

In order to avoid human health risk caused by Cu and keep sustainability use of greenhouse soils, it was important to investigate the effects of cultivation age on Cu accumulation in greenhouse soils in North China. The main aims of this study were (i) to reveal the status of Cu in greenhouse soils; (ii) to reveal the relationship between Cu accumulation and cultivation ages.

2. Materials and Methods

2.1 Studied sites
The research was conducted at an important vegetable planting area of 113.7 km², situated in Shenyang suburb, in Northeast China (41°55’N and 122°58’E). This study region has owned numerous agricultural facilities, and become a famous vegetable production base. It has a dry-cold winter and a warm-wet summer. A typical temperature and monsoonal climate prevails in this area.
with the average annual temperature of 8.6℃, the average annual rainfall of 600 mm, and non-frost period of 147-164 days. The most common vegetables in greenhouses are cucumber, tomato and pakchoi. According to the previous investigation, about 100 t·hm⁻² manures (e.g. decaying chicken and dairy manures) are used in greenhouses per year. And other fertilizers used in this area are carbamide (500 kg·hm⁻²) or ammonium sulphate ((NH₄)₂SO₄, 1000 kg·hm⁻²), diammonium phosphate ((NH₄)₂HPO₄, 1000-1500 kg·hm⁻²), and postassium sulphate (K₂SO₄, 1000 kg·hm⁻²) each year.

2.2 Sampling and analysis
Soil samples were collected from greenhouses of 1, 2, 3, 4, 5, and 6 years of consistent cultivation and management. The open vegetable fields were served as the control (CK). The depth of 0-120 cm soils was sampled. Each sample was multi-point mixed.

The tested soils were air dried, passed through nylon sieve, and stored in plastic bottles for Cu analysis. Plant available Cu (A-Cu) was determined by using diethylene-triamine-pentacetic (DTPA) buffered at pH 7.3 [5]. The concentration of total copper (T-Cu) was determined using Aqua Regia (HCl- HNO₃-HClO₄, 3:1:1,v/v) extraction method [6]. The concentrations of Cu were determined using the atomic absorption spectrophotometer (WFX-120, Beijing Rayleigh Analytical Instrument Corp, China).

Statistical analysis was performed using SPSS 19.0. The comparison of Cu contents between treatments was carried out with one way analysis of variance (ANOVA) and a statistical significance of p<0.05.

3. Results

![Graph showing distribution of plant available Cu in greenhouse soil profiles](image-url)

**Figure 1.** Distribution of plant available Cu in profiles of greenhouse soil with different planting years

### 3.1 Distributions of plant available Cu in soil profiles
As shown in Figure 1, the concentration of plant available Cu (A-Cu) decreased with depth, and the contents of top soils (0-40 cm) in greenhouses were higher than those of the open field. The concentration of A-Cu in 0-40 cm soil profiles was higher than those in 40-120 cm soil profiles, and the content of A-Cu in greenhouse soil profiles increased as the number of years under cultivation increased. Compared with that in 60-120 cm soils, DTPA-extraction Cu accumulation in 0-40 cm soils was observed, especially in the top 20 cm of the soil profile. In 60-120 cm soil profiles, A-Cu contents in 4-year greenhouse were lower than those of other greenhouses under utilization years.
3.2 Distributions of total Cu in soil profiles
Total Cu (T-Cu) concentrations in soil profiles decreased with depth, and the contents of T-Cu in top
soils (0-40 cm) were significantly higher than those of the open field (P<0.01) (Figure 2). In 6-year greenhouse, T-Cu content peaked in 0-20 cm soil profiles and was obviously higher than those of other profiles (20-120 cm). After more than 5 years utilization, there was a tendency in accumulation of T-Cu in 80-100 cm soil profiles. In 40-120 cm soil profiles, T-Cu contents in open field soils were significantly lower than those of greenhouses (P<0.01).

3.3 Relationship between Cu contents in soils and different planting years
Figure 3 showed the relationship of Cu accumulation (including plant available Cu and total Cu) with utilization ages of vegetable greenhouses in 0-20 cm layers. For plant available Cu (A-Cu), the A-Cu contents in the greenhouse soils cultivated for 6 years were significantly higher than that from the open field soils (P<0.05). The concentrations of A-Cu in greenhouse soils was positively correlated with cultivation ages (R²=0.572). For total Cu (T-Cu), T-Cu contents increased with the planting years of the vegetable greenhouses, and there was a positive correlation between T-Cu concentrations in soils and cultivation ages (R²=0.446).

4. Discussion
In general, trace metal accumulation in soils due to greenhouse vegetable production can be confirmed when their concentrations in greenhouse soil are higher than those in open-field soil [7]. In this study, the results showed A-Cu and T-Cu both accumulated in greenhouse soils. According to our previous investigation, there are no industrial and mining activities in this area. It is induced that copper may be likely to originate from human inputs through agricultural chemicals (e.g. manures, fertilizers or pesticides), other than the pedogenic weathering of primary minerals [8, 9]. Excessive application of manures plays an important role in heavy metal accumulation, although heavy metal contents in manure are limited. About 100 t hm⁻¹ year⁻¹ chicken and dairy manures were applied, as determined from the investigation. Similar results were found by Yong Chen et al. in west China where overapplication of chicken manures in greenhouses led to significant accumulation of Cu [10]. Furthermore, accumulation in greenhouse soils may be ascribed to discrepant and complicated environmental factors, especially temperature condition, which affects organic matter decomposition. Besides, cultivation ages exerted the most profound influence on Cu accumulation in top soils, which is consistent with the results of previous studies [9, 11]. Cu contents (including A-Cu and T-Cu) increased with the increasing years of greenhouse utilization (Figure 3). It was primarily ascribed to the over-application of manures. Chicken manures containing Cu (e.g. moroxydine hydrochloride, cymoxanil mancozeb) has been proved by several studies [10, 12]. Therefore, the long-term usage of manures can cause Cu accumulation in greenhouse soils [3].

5. Conclusion
Cu was clearly accumulated in greenhouse vegetable production soils. The contents of Cu positively related to cultivation ages. The anthropogenic source including the long-term use of cow and chicken manure contributed to Cu accumulation. The long-term duration of land use shift also caused Cu accumulation.

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