Accumulation Status and Sources of Hg in Greenhouse Vegetable Production Systems

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Abstract. Greenhouse vegetable production (GVP) with huge amount of manure, fertilizer and pesticide input can contribute heavy metal enrichment in soils. This research was conducted to explore the accumulation status of Hg in greenhouse soils, reveal the effects of soil properties on Hg enrichment, and find out the pollutant source. Total Hg concentrations in soils increased with utilization ages of vegetable greenhouses in 0-20 cm layers, but the linear relationship was not significant ($F=3.363, P=0.078$), indicating that the shift in land use did not obviously affect Hg accumulation in soils. According to multivariate statistical analysis, it could be concluded that Hg accumulation in soils may be affected by the anthropogenic and geogenic elements. Although Hg contamination did not appear in studied areas according to National Soil Environmental Quality Standard I ($\text{Hg} \leq 0.15 \text{ mg kg}^{-1}$), it must be paid more attention to Hg enrichment due to long-term utilization of greenhouse vegetable production and management technology.

1. Introduction

Nowadays, agricultural soil contamination has been a cause for concern due to food safety issues and the potential human health risk [1, 2]. Heavy metal accumulation, toxicity and persistence in agricultural soils are a widely studied topic in soil and environment sciences because of its high toxicity and pathogenicity [3]. Anthropogenic activities including agricultural practices, mining and smelting and atmosphere deposition have caused soil contamination [4]. The contents of heavy metals and metalloids like Cu, Zn, Cd, Pb, Hg and As in soils have reported to exceed the natural concentrations through agricultural and industrial inputs [4, 5].

Greenhouse vegetable production (GVP) in China has increased rapidly. This type of facility agriculture requires intensive labour and energy input, an enormous amount of fertilizers and pesticides to meet the demand of vegetable yields and economic benefits. All of these agricultural practices could contribute to heavy metal enrichment and contamination in greenhouse soils [6, 7]. Mercury (Hg) is one of the most critical contaminants in the environment due to its toxicity, mobility and ability to be bioaccumulated by organisms. Several physical-chemical properties (e.g. pH, contents of organic matters and clay minerals) govern Hg behaviour in soils [8] and can be used to identify the sources of Hg in soils. Thus, this research was realized with the main objects of: (i) explore the enrichment status of total Hg in greenhouse soils with cultivation years; (ii) find out the potential sources of Hg through multivariate analysis.
2. Materials and Methods

2.1. Study area
The research region is situated in the west of Shenyang City, in northeast China, covering an area of 113.7 km² [9]. The zone is intensively cultivated with greenhouse facilities. Approximately 80 t·hm⁻² of decaying chicken manure, 500 kg·hm⁻² of carbamide or 1000 kg·hm⁻² of ammonium sulphate ((NH₄)₂SO₄), 1000 ~ 1500 kg·hm⁻² of diammonium phosphate ((NH₄)₂HPO₄) are used each year. There are no mining companies and manufacture factories in the study area. Only a national highway traverses through it from east to west. The dominant soil is brown soil with pH 7.14±0.46, TOC 8.16±2.45 g·kg⁻¹, CEC 12.84±0.94 mg·kg⁻¹, the soil bulk density 1.33±0.09 g·cm⁻³.

2.2. Sampling and analysis
Greenhouses of 1, 2, 3, 4, 5, and 6 years were selected, and the adjacent open field served as the control. Surface soil samples (0-20 cm) were collected randomly. All samples were air dried, ground, passed through nylon sieves and store in polyethylene bags for determine total Hg and soil physical-chemical properties (pH, SOM, sand, silt, clay, SiO₂, Al₂O₃ and Fe₂O₃).

Total Hg content was determined by HCl-HNO₃-HClO₄ (3:1:1, v/v) digestion [10] and measured by the atomic absorption spectrophotometer (WFX-120, Beijing Rayleigh Analytical Instrument Corp, China). pH was determined using a combination glass electrode and a conductivity meter in a 1:1 ratio (w/v) of soil: deionised water suspension [11]. Total organic carbon (TOC) was determined according to the dichromate, wet oxidation method described by Walkley and Black [12]. Salt content in soils was determined by gravimetric method. Particle size distribution (texture) of the soil was determined using air-dried samples according to the pipette method [13,14]. Statistical analysis was performed using SPSS 19.0.

3. Results and discussion

3.1. Hg accumulation in greenhouse soils
Total Hg levels of the soils in research greenhouses are shown in Figure 1. Total Hg concentrations in 0-20 cm soils increased with utilization ages of vegetable greenhouses, but the linear relationship was not significant (F=3.363, P=0.078). There was no significant correlation between Hg contents and GVP duration (R²=0.111, P=0.078), indicating that the shift in land use did not obviously affect Hg accumulation in soils. According to the results of one-way ANOVA, Hg contents in soils of 2-year, 4-year and 6-year were significantly higher than those of the open field (P<0.05). Total Hg contents in 4-year greenhouse soils peaked at 0.12 mg·kg⁻¹, which was still lower than National Soil Environmental Quality Standard I (Hg≤0.15 mg·kg⁻¹). Hg pollution did not appear in soils of greenhouses below 6 years in our research; however it must be paid more attention to Hg accumulation due to long-term utilization of greenhouse vegetable production. The utilization of chemical fertilizers, manures, pesticides and compost amendments is considered the main form of heavy metal input into soils [15,16]. Hg concentrations showed higher standard deviation for 1-year, 2-year, 4-year and 5-year greenhouses. Such high deviation can be due to intensification of land use activities, such as irrigation, fertilizer application and pesticide spray, as well as other natural processes (e.g. weathering, erosion), which could alter stabilization of the soil environment.
Figure 1. Total Hg contents in soils under greenhouse cultivation condition. The error bars indicate the standard deviations.

3.2. Principle component analysis

Table 1 Rotated component matrix for total Hg content and the physic-chemical properties of greenhouse vegetable soils

| Component | Total | % of Variance | Cumulative % |
|-----------|-------|---------------|--------------|
| 1         | 3.202 | 35.581        | 35.581       |
| 2         | 2.440 | 27.106        | 62.686       |
| 3         | 1.306 | 14.515        | 77.201       |

Component matrix (rotated)

| Variables | Component |
|-----------|-----------|
|           | 1         | 2         | 3         |
| Hg        | -0.036    | 0.120     | -0.300    |
| pH        | -0.081    | 0.875     | 0.057     |
| SOM       | 0.477     | 0.731     | -0.029    |
| Sand      | -0.950    | -0.254    | 0.031     |
| Silt      | 0.882     | 0.267     | -0.222    |
| Clay      | 0.890     | 0.198     | 0.222     |
| SiO₂      | -0.850    | 0.338     | 0.057     |
| Al₂O₃     | 0.705     | 0.378     | 0.469     |
| Fe₂O₃     | 0.701     | 0.386     | 0.465     |

Principal component analysis (PCA) was carried out to identify the sources of heavy metals in soils of different land uses [17], and used to reduce the high dimensionality of variable space [18]. Factor loadings and variances of the components for total Hg content and the physic-chemical properties of greenhouse soils are given in Table 1. Three factors were obtained which explained approximately 77.20% of all the total variance. According to calculated factor loading coefficients, the first principle component (PC1), which explained 35.58% of the total variance, was composed of sand, silt, clay, SiO₂, Al₂O₃, and Fe₂O₃. Distribution patterns of physic-chemical properties (e.g. SiO₂ and Fe₂O₃,) were generally invariant in soils due to parent material, implying PC1 may derive from natural factors such as weathering bedrocks, soil formation [19]. The second principle component (PC2) explaining 27.10% of the total variance was loaded on pH and SOM. An enormous amount of manure application in facility agriculture has been considered to be SOM accumulation in surface soils in previous studies [20]. pH also shows regular increase or decrease with the utilization of fertilizers [21]. So it can be
concluded that pH and SOM were derived from anthropogenic factors in studied soils. The third principle component (PC3) including Hg explained 14.51% of the total variance. The anthropogenic and geogenic elements can be ascribed to Hg enrichment in surface soils in different land uses [22]. Although Hg input into soils takes place through agrochemicals and manures, correlation between Hg contents and GVP duration ($R^2=0.111$, $P=0.078$) was not significant (Figure 1), suggesting anthropogenic activities are not a primary impact factor.

3.3. Correlation analysis

Table 2 Correlation coefficients among total Hg and soil properties in greenhouse vegetable soils

|          | T-Hg | pH  | SOM  | sand | silt | clay | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ |
|----------|------|-----|------|------|------|------|---------|-------------|------------|
| T-Hg     | 1    |     |      |      |      |      |         |             |            |
| pH       | 0.007| 1   |      |      |      |      |         |             |            |
| SOM      | -0.084| 0.586*| 1    |      |      |      |         |             |            |
| Sand     | 0.169| 0.036|      |      |      |      | 0.628**| 1           |            |
| Silt     | -0.189| -0.150| 0.623**| 0.948**| 1    |      |         |             |            |
| clay     | -0.116| 0.118| 0.536**| 0.910**| 0.731**| 1    |         |             |            |
| SiO$_2$  | -0.043| -0.137| -0.443*| -0.066| 0.015| 0.121| 1       |             |            |
| Al$_2$O$_3$ | -0.049| 0.250| 0.575**| 0.483**| 0.367| 0.558**| -0.350| 1           |            |
| Fe$_2$O$_3$ | -0.053| 0.244| 0.574**| 0.489**| 0.372*| 0.564**| -0.344| 0.793**| 1           |

T-Hg: total Hg contents
Significant levels: * $\alpha=0.05$, and ** $\alpha=0.01$

The Spearman correlation matrix was presented in Table 2. Correlation coefficients showed that some soil physic-chemical properties were strongly correlated. SOM significantly correlated with sand ($r=-0.628**$), silt ($r=0.623**$), clay ($r=0.536**$), Al$_2$O$_3$ ($r=0.575**$) and Fe$_2$O$_3$ ($r=0.574**$), and also correlated with pH ($r=0.586$) and SiO$_2$ ($r=-0.443$) at 0.05 significance level. No significant correlation was observed between total Hg and soil properties. The correlations suggested a close link with toxic metal origin and common geochemical characteristics [18]. Many reports have released that SOM would influence the concentrations of heavy metals, facilitate or limit the mobility of these elements [20]. SOM has been reported to correlate with trace metals [23]. In this study, Hg contents in greenhouse soils were not significantly correlated with SOM, suggesting Hg may not primarily originate from anthropogenic factors. This observation was confirmed principle component analysis (Table 1), and was consistent with the previous literatures by Li J G et al. [24] and Li Y B et al. [25].

4. Conclusion

Total Hg in greenhouse soils had an increase trend with cultivation years (Figure 1), showed higher standard deviation for 1-year, 2-year, 4-year and 5-year greenhouses, and did not significantly correlate with soil physic-chemical properties (pH, SOM, sand, silt, clay, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$) (Table 2). Hg accumulation in greenhouse soils may be ascribed to anthropogenic and natural element (Table 1). This observation was confirmed by correlation analysis. Although Hg contamination did not take place in studied areas according to National Soil Environmental Quality Standard I (Hg≤0.15 mg·kg$^{-1}$), it must be paid more attention to Hg accumulation due to long-term utilization of greenhouse vegetable production and management technology.
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