Field controlled experiments of mercury accumulation in crops from air and soil

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ABSTRACT

Field open top chambers (OTCs) and soil mercury (Hg) enriched experiments were employed to study the influence of Hg concentrations in air and soil on the Hg accumulation in the organs of maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.). Results showed that Hg concentrations in foliages were correlated significantly ($p < 0.05$) with air Hg concentrations but insignificantly correlated with soil Hg concentrations, indicating that Hg in crop foliages was mainly from air. Hg concentrations in roots were generally correlated with soil Hg concentrations ($p < 0.05$) but insignificantly correlated with air Hg concentrations, indicating that Hg in crop roots was mainly from soil. No significant correlations were found between Hg concentrations in stems and those in air and soil. However, Hg concentrations in upper stems were usually higher than those in bottom stems, implying air Hg might have stronger influence than soil Hg on stem Hg accumulation.

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1. Introduction

Mercury (Hg) is a persistent and toxic heavy metal, and 95% of the atmospheric Hg is in the term of gaseous elemental mercury (GEM) (Fitzgerald et al., 1991). Because of its long atmospheric lifetime (about one year), GEM may spread all over the world through the long-range atmospheric transport (Lindqvist and Rodhe, 1985). Current studies have identified that the strength of known sources of atmospheric Hg is greater than previously realized (Gustin et al., 2000; Engle et al., 2001; Pirroni et al., 2001), and the role of vegetation in Hg biogeochemical cycle has attracted more and more attentions (Veiga et al., 1994; Lindberg, 1996; Lindberg et al., 2004; St. Louis et al., 2001; Obrist, 2007; Friedli et al., 2009), e.g., vegetation as the missing sink in global Hg mass balance (Gustin et al., 2008). A critical question eager for answer in the global Hg cycling is whether the large amount of Hg stored in vegetation originates from the soil or from the atmosphere (Ericksen et al., 2003).

Previous studies have shown that the Hg in tree foliages was mainly originated from air, while the Hg in tree roots was mainly from soil (Barghigiani et al., 1991; Frescholtz et al., 2003; Ericksen et al., 2003; Millhollen et al., 2006a). Roots act as a critical barrier for the transport of soil Hg to the aboveground of trees (Bishop et al., 1998; Rea et al., 2002; Ericksen et al., 2003; Fay and Gustin, 2007).

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However, there are still some controversies on the accumulation of Hg in herbaceous plant organs. Greger et al. (2005) reported that only a small part (0.17–2.5%) of soil Hg was translocated to the shoots for five crop species, whereas Schwesig and Krebs (2003) reported that the percentages of Hg from soil in the foliages of *Deschampsia flexuosa* L and *Calamagrostis villosa* (Chaix ex Vill.) were 30% and 93%, respectively.

Crop is an important component of land vegetation. The area of arable land is 1.4×10^9 ha (FAO, 2009), accounting for 9.5% of global land area. Moreover, crop is closely linked to human and livestock health through daily consumption. So, it is doubtless that the investigation on the role of crop in the biogeochemical cycle of Hg is important. In this paper field open top chambers (OTCs) and soil Hg enriched experiments were conducted to study the correlations of Hg concentrations in crop organs with those in air and soil.

2. Materials and methods

2.1. Site description

The field experimental site is located at a small village (N38.70°, E115.23°) in Wangdu County, Hebei Province, which is in the center of Huabei Plain. This plain is one of the major crop producing areas in China, mainly planted by maize and wheat in rotation. This site has a typical warm and continental monsoon climate. The average annual temperature and rainfall are 12.3 °C and 555.0 mm, respectively. The highest and lowest monthly mean air temperatures are 26.5 °C in July and −4.1 °C in January. The temperature of top soil (10 cm) varies from −4 °C in January to 35 °C in July. This site is far away from cities and factories. The Hg concentrations in soil and air at this site were 25 ± 6 ng g^{−1} and 2 ± 1 ng m^{−3}, respectively. The basic properties of field soil were analyzed based on the methods described by Bao (2000). The soil pH was 7.4 ± 0.2 , alkali-hydrolyzable nitrogen 62.0 ± 15.0 μg g^{−1}, available phosphorus 12.0 ± 4.0 μg g^{−1}, and available potassium 98.0 ± 4.0 μg g^{−1}.

Fig. 1. The structure and equipments of the open top chambers. (gaseous elemental mercury (GEM), liquid elemental mercury (LEM)).

2.2. Experimental crop and management

Summer maize (*Zea mays* L., cv. Xianyu 335) and winter wheat (*Triticum aestivum* L., cv. Shixin 733) were selected as the typical representatives of crops in the both field experiments, i.e. open top chambers (OTCs) and soil Hg enriched experiments. The OTCs experiment was conducted during maize growing season (July to October) and wheat growing season (October to June next year). The soil Hg enriched experiment was conducted simultaneously. The management for the two crops followed local agronomic manners.

2.3. Open top chambers (OTCs) experiment

Field OTCs experiment was employed to study the correlations of Hg concentrations between air and crop organs. Field OTCs can provide more closely ambient conditions than closed-top chambers. The temperature and relative humidity within OTCs were similar to ambient conditions (Heagle et al., 1973). In this study, the OTCs were Heagle-type with the upper part a 23.6° tilted frustum (Fig. 1). The height of the chambers was 2.0 m, bottom diameter 1.5 m and top diameter 1.0 m. The volume of the chambers was about 3.3 m³. The frames of OTCs were made of steel bars with the frustum and side sections covered by 3.0 mm thick polyvinyl chloride plastic film.

The GEM was generated from the evaporation of a small amount of liquid elemental Hg in a glass tube (length of 60.0 cm, diameter of 1.5 cm). The tube was buried into deep soil (60.0 cm) where diurnal variation of temperature was less than 0.5 °C. The temperature was measured by a ZDR-21J temperature recorder (Zeda Co., Ltd, China).

The GEM in the glass tube was carried out by the pure N₂ flow through a Teflon tube (inner diameter of 2.0 mm) into the air flow (2.5 m³ min⁻¹) in pipe (PVC, inner diameter of 7.5 cm) from a centrifugal blower to a chamber for obtaining a GEM mixed air to fill into the chamber from bottom. The PVC pipe in the chamber was perforated equidistantly for GEM mixed air to disperse easily. The GEM mixed air in the chamber was vented from the top of the chamber, and the time for a complete exchange of the air in the chamber was estimated to be about 80 s.

The GEM concentrations of the mixed air into the chambers can be set to certain of values by the carrier gas (N₂) flow rate controlled by an adjustable rotameter. During the experiments the GEM concentrations were monitored for 10 min in the morning, midday and afternoon every day by a RA-915⁺ Zeeman atomic absorption spectrometry Hg analyzer (Lumex Inc., Russia). When a variation of GEM concentration in a chamber was over 10% of the set value, the carrier gas rate was adjusted by rotameter to obtain the desired GEM concentrations.

Four levels of Hg concentrations in mixed air, 2 ± 1, 10 ± 1, 20 ± 2 and 50 ± 2 ng m⁻³ were set for OTCs experiment of maize. The level of Hg concentration of 2 ± 1 ng m⁻³ was set for control check (CK). For OTCs experiment of wheat, the highest concentration of mixed air Hg was set to 70 ± 2 ng m⁻³. Three replicative chambers were set for each concentration level. Total 12 chambers were set for this experiment. The distance between chambers was at least 3.0 m to avoid the mutual shading. The OTCs exposure experiment for maize was from July to October, and then for wheat was from October to next year June.

2.4. Soil Hg enriched experiment

Soil Hg enriched experiment was employed to study the correlations between Hg concentrations in soil and those in crop organs. Mercuric chloride (HgCl₂) is commonly used in the soil Hg enriched experiment (Millhollen et al., 2006a, 2006b; Dunagan et al., 2007; Stamenkovic and Gustin, 2009). Five soil Hg concentrations were set in the soil Hg enriched experiment, including a CK soil treated by the solution without HgCl₂. The field area for each plot was 4 m², and the depth of field soils treated by HgCl₂ solutions was 30 cm. To obtain the soil Hg concentration gradients, five HgCl₂ solutions with the volume of 30 L and the concentration of 0,

10, 20, 30 and 50 mg L⁻¹ were added to the five field soils, respectively, and then the soils were homogenized respectively by thoroughly mixing.

Before the maize was seeded down, the HgCl₂ enriched soils were aged for about 6 months, and then covered by the non-enriched soil (1–2 cm) to establish a buffer layer to minimize the photoreduction and emission of Hg. Zhu et al. (1996) indicated that the fractions of active Hg, alkaline soluble Hg and acid soluble Hg were gradually transformed to residual Hg over time after the soil was enriched by HgCl₂ solution, and residual Hg was dominated the speciation (50–75%) after 6 months. Erickson et al. (2005) reported that there was an immediate Hg release after the soil was enriched by HgCl₂, and then the emission decreased exponentially, finally followed by a relatively steady flux after 62 days. Therefore, in this study, the field soils were aged for 6 months.

When the maize was seeded down, the soil Hg concentrations were measured to be as 25 ± 6 (CK), 158 ± 45, 325 ± 59, 496 ± 63 and 763 ± 133 ng g⁻¹. For wheat case, the Hg concentrations were measured to be as 28 ± 3 (CK), 57 ± 22, 119 ± 26, 243 ± 55 and 552 ± 28 ng g⁻¹. The decrease of Hg concentration is due to the Hg emission to air and the uptake of plant roots from soil.

2.5. Sample collection and measurement

Maize and wheat were sampled at later jointing (LJ) stage, grain filling (GF) stage and dough (D) stage. Crop organs including roots, stems, foliages and seeds were collected, and sheaths were removed from stems and foliages. The collection positions at each stage were consistent. Since the stems of the crops were very long and the quantity of samples to be analyzed was very little, the stems of maize and wheat were divided equally into upper and bottom stems. The foliages of maize were further divided into upper and bottom foliages like stems. For wheat, only upper foliages were collected because the bottom foliages were deciduous.

The samples of plant were collected in plastic self-sealing bags, and then were rinsed by both tap water and ultra pure deionized water in order. The field soils in the soil Hg enriched experiment and chamber soils were sampled both before and at the end of the experiment. Plant samples were dried at 55 °C, and soil samples were air-dried. All the samples were ground, homogenized, and then stored at -4 °C for analysis.

The Hg concentrations in plant and soil samples were measured by RA-915⁺ Hg analyzer attached with PYRO-91 thermal decomposition accessory from Lumex Inc. Some researchers have used this instrument successfully for measuring Hg concentrations in plant and soil samples (Chen et al., 2001; Shuvaeva et al., 2008; Wang et al., 2009). The samples were directly thermally decomposed in atomizer chamber at 750 °C with the aided catalytic action to transform all the form Hg into

Table 1

Root Hg concentrations in maize and wheat at different growth stages in the OTCs experiment (ng g⁻¹).^a

Species	Stages	2 (ng m ⁻³)	10 (ng m ⁻³)	20 (ng m ⁻³)	50/70 (ng m ⁻³)
Maize	LJ	3.3 ± 2.4 (a)	6.0 ± 1.9 (a)	6.1 ± 1.4 (a)	6.2 ± 0.3 (a)
	GF	9.1 ± 2.9 (a)	8.7 ± 2.5 (a)	6.8 ± 1.2 (a)	10.1 ± 3.4 (a)
	D	3.8 ± 1.5 (a)	2.6 ± 1.1 (a)	3.4 ± 1.5 (a)	4.1 ± 1.4 (a)
Wheat	LJ	10.9 ± 1.2 (a)	8.4 ± 2.1 (a)	11.8 ± 4.5 (a)	12.7 ± 2.6 (a)
	GF	9.3 ± 1.9 (a)	8.6 ± 2.7 (a)	10.0 ± 1.4 (a)	11.5 ± 1.7 (a)
	D	5.8 ± 0.7 (a)	11.3 ± 1.4 (b)	10.4 ± 2.2 (ab)	25.0 ± 4.4 (c)

^a In the same row values marked with the same letters in brackets are not significantly different at the 0.05 levels. The air Hg concentration of 50 ng m⁻³ was for maize, and 70 ng m⁻³ for wheat. The growth stage: Later Jointing (LJ), Grain Filling (GF), and Dough (D). The same below.

Fig. 2. The correlations of root Hg concentrations in maize (A) and wheat (B) with soil Hg concentrations at different growth stages. Error bars denote standard error of the mean. (The growth stage: Later Jointing (LJ), Grain Filling (GF), Dough (D), the same below).

Hg^0 , and then Hg^0 was detected by the RA-915⁺ analyzer. Each sample was analyzed for three times to get an average value. The calibration curves were confirmed by soil standards (GBW07404, 590 ng g^{-1}) and peach foliage standards (GBW08501, 40 ng g^{-1}) respectively. The standard samples were also measured for calibration after every ten samples. The detection limit of the instrument was 5 pg of Hg for measuring solid sample. The precisions, obtained from ten replicate determinations of standards, were 3.5% for soil, and 2.8% for peach foliages. The recoveries ranged from 94.2% to 104.9% for soil, and 92.5%–102.0% for peach foliages.

2.6. Data analysis

Correlations between the Hg concentrations in crop organs and those in air and soil were analyzed based on the data from OTCs and soil Hg enriched experiments. The variance analysis of Hg concentrations in the crop organs for the levels of Hg treatments in the two experiments was also performed. Data were presented as mean and standard deviation, and statistical significance was considered at $p < 0.05$.

3. Results

3.1. The correlation of Hg concentration between crop root and soil

The root Hg concentrations in maize and wheat did not show significant correlations with the air Hg concentrations at all stages ($p > 0.05$) in OTCs experiment. Furthermore, the root Hg concentrations in maize did not show significant differences among various air Hg level treatments at all stages ($p > 0.05$), and also no such differences were shown for wheat at LJ and GF stages ($p > 0.05$). However, a pronounced higher Hg concentration in wheat root at

the treatment of 70 ng m^{-3} was observed at D stage ($p < 0.05$) (Table 1).

Fig. 2 shows that significant positive correlations were commonly found between the Hg concentrations in both maize and wheat roots and the Hg concentrations in soil at all growth stages ($R = 0.8990$ – 0.9948 , $p < 0.05$), and an insignificant positive correlation was observed for maize at LJ stage ($R = 0.4934$, $p > 0.05$). Therefore, the results from the two experiments indicated that the Hg accumulated in crop roots was mainly from soil, and air Hg may be able to affect the Hg accumulation in wheat roots at D stage when air Hg concentration reaches certain level (70 ng m^{-3} or higher).

3.2. The influence of air and soil Hg on stem Hg accumulation

For wheat and maize, the Hg concentrations in upper stems were not obviously correlated with both air and soil Hg concentrations at all stages ($p > 0.05$), and the same results were observed for bottom stems.

In OTCs experiment, the Hg concentrations in maize upper stems were not significantly different among the various air Hg level treatments at all the stages ($p > 0.05$), and the same results were observed for maize bottom stems ($p > 0.05$) (Table 2). For wheat, no obvious differences of Hg concentrations in bottom stems were observed at all growth stages ($p > 0.05$), but remarkably higher Hg concentrations in upper stems were observed at

Table 2
Stem Hg concentrations in maize and wheat at different growth stages in the OTCs and soil Hg enriched experiments (ng g^{-1}).^a

Species	Stages	Stems	Air Hg concentrations (ng m^{-3})				Soil Hg concentrations (ng g^{-1})				
			2	10	20	50/70	25/28	158/57	325/119	496/243	763/552
Maize	LJ	Upper	3.0 ± 1.3 (a)	4.8 ± 2.0 (a)	3.3 ± 1.3 (a)	4.9 ± 0.9 (a)	7.6 ± 3.0 (a)	7.4 ± 2.5 (a)	6.7 ± 2.6 (a)	8.5 ± 1.5 (a)	4.9 ± 1.1 (a)
		Bottom	1.6 ± 1.1 (a)	1.7 ± 0.5 (a)	1.7 ± 1.8 (a)	1.9 ± 1.0 (a)	3.6 ± 0.7 (a)	4.5 ± 0.3 (a)	2.8 ± 0.8 (a)	3.7 ± 1.2 (a)	6.9 ± 1.5 (b)
	GF	Upper	2.4 ± 0.4 (a)	3.6 ± 1.0 (a)	4.4 ± 1.5 (a)	3.9 ± 1.3 (a)	3.3 ± 1.4 (a)	4.6 ± 2.0 (a)	5.2 ± 1.2 (a)	3.0 ± 0.7 (a)	4.6 ± 1.4 (a)
		Bottom	3.0 ± 0.9 (a)	2.7 ± 0.6 (a)	2.1 ± 0.5 (a)	3.0 ± 0.6 (a)	1.9 ± 0.2 (a)	1.3 ± 0.5 (a)	1.6 ± 1.0 (a)	1.5 ± 0.8 (a)	2.1 ± 1.1 (a)
	D	Upper	3.3 ± 1.4 (a)	2.1 ± 1.1 (a)	2.4 ± 1.6 (a)	2.1 ± 0.1 (a)	3.4 ± 2.2 (a)	1.8 ± 1.0 (a)	3.6 ± 1.1 (a)	1.4 ± 0.5 (a)	1.5 ± 0.8 (a)
		Bottom	0.2 ± 0.1 (a)	2.1 ± 1.7 (b)	1.3 ± 0.2 (ab)	2.1 ± 0.4 (b)	0.5 ± 0.4 (a)	1.0 ± 0.2 (a)	1.4 ± 1.4 (a)	1.5 ± 0.2 (a)	1.1 ± 0.7 (a)
Wheat	LJ	Upper	2.7 ± 0.5 (ab)	2.6 ± 1.1 (ab)	1.9 ± 0.4 (a)	4.0 ± 1.4 (b)	2.8 ± 1.5 (a)	4.4 ± 0.7 (ab)	4.7 ± 0.9 (ab)	3.4 ± 0.7 (ab)	5.2 ± 1.1 (b)
		Bottom	2.1 ± 0.6 (a)	1.2 ± 0.9 (a)	0.8 ± 0.6 (a)	1.5 ± 1.3 (a)	1.7 ± 0.2 (a)	1.3 ± 1.3 (a)	1.8 ± 0.3 (a)	1.2 ± 1.3 (a)	0.9 ± 0.3 (a)
	GF	Upper	8.5 ± 1.2 (a)	6.6 ± 0.8 (a)	9.5 ± 2.2 (a)	24.7 ± 3.3 (b)	1.5 ± 0.8 (ab)	2.0 ± 0.7 (ab)	1.0 ± 0.4 (a)	0.8 ± 0.5 (a)	2.5 ± 0.8 (b)
		Bottom	2.7 ± 0.7 (a)	2.1 ± 0.7 (a)	2.3 ± 1.0 (a)	2.2 ± 0.7 (a)	1.1 ± 0.5 (a)	0.8 ± 0.5 (a)	1.4 ± 0.3 (a)	1.1 ± 0.3 (a)	0.8 ± 0.5 (a)
	D	Upper	0.9 ± 0.6 (a)	3.0 ± 1.5 (a)	3.3 ± 0.3 (a)	14.8 ± 2.4 (b)	1.3 ± 0.4 (a)	0.9 ± 0.6 (a)	0.8 ± 0.4 (a)	1.3 ± 0.3 (a)	3.1 ± 0.3 (b)
		Bottom	0.9 ± 0.8 (a)	2.0 ± 1.5 (a)	1.6 ± 0.7 (a)	2.6 ± 0.3 (a)	1.0 ± 0.6 (a)	1.5 ± 1.2 (a)	0.7 ± 0.3 (a)	1.1 ± 0.3 (a)	0.8 ± 0.6 (a)

^a Soil Hg concentrations of 25, 158, 325, 496 and 763 ng g^{-1} were for maize, and the concentrations of 28, 57, 119, 243 and 552 ng g^{-1} for wheat. The same below.

Fig. 3. The correlations of foliar Hg concentrations in maize (A) and wheat (B) with air Hg concentrations at different growth stages. Error bars denote standard error of the mean. (Bottom Foliages (BF), Upper Foliages (UF)).

70 ng m⁻³ at both GF and D stages ($p < 0.05$) (Table 2), which suggested that elevated air Hg could enhance the Hg accumulation in wheat upper stems.

In soil Hg enriched experiment, except for the significant differences of maize bottom stems at LJ stage and wheat upper stems at both GF and D stages ($p < 0.05$), most stem Hg concentrations in maize as well as wheat at all the stages were almost consistent under various soil Hg concentrations ($p > 0.05$). So, soil Hg generally had little influence on stem Hg accumulation (Table 2).

Under all treatments, the Hg concentrations in maize upper stems were usually higher than those in maize bottom stems, and the same results were found for wheat (Table 2). These results from the two experiments indicated that compared with soil Hg, air Hg might have stronger influence on crop stem Hg accumulation, especially for upper stems.

3.3. The correlation of Hg concentration between crop foliage and air

Fig. 3 shows that foliar Hg concentrations in both maize and wheat had significant positive correlations with the air Hg concentrations at all the stages ($R = 0.9639–0.9989$, $p < 0.05$). However, no such correlations were observed for soil Hg concentrations. These results suggested that the Hg accumulated in crop foliages was mainly from ambient air.

Although foliar Hg concentrations were not correlated significantly with the soil Hg concentrations ($p > 0.05$), the Hg concentrations in maize bottom foliages under different soil concentrations were obviously different at LJ stage ($p < 0.05$). The same results were found for maize upper foliages at GF stage ($p < 0.05$) and wheat

foliages at both GF stage and D stage ($p < 0.05$) (Table 3). These differences might result from the Hg translocation from roots to foliages, and the uptake by foliages from air Hg emitted from the HgCl₂ enriched soil.

Under all treatments, the Hg concentrations in maize upper foliages were lower than those in bottom foliages at all the growth stages. Foliar Hg concentrations in maize and wheat increased over growth stages in both OTCs experiment (Fig. 3) and soil Hg enriched experiment (Table 3).

3.4. The influence of air and soil Hg on seed Hg accumulation

Seed Hg concentrations in maize and wheat were not significantly correlated with either air Hg concentrations ($p > 0.05$) or soil Hg concentrations ($p > 0.05$). Except for the highest seed Hg concentrations in wheat at 70 ng m⁻³ at GF and D stage ($p < 0.05$), no obvious differences of seed Hg concentrations in wheat were found in soil Hg enriched experiment ($p > 0.05$). The seed Hg concentrations in maize had slight variations under different air Hg concentrations treatments ($p > 0.05$), as well as soil Hg concentrations treatments ($p > 0.05$) (Table 4). So air and soil Hg had little influence on crop seed Hg accumulation in these experiments.

4. Discussion

4.1. The influence of Hg concentrations in air and soil on crop Hg

This study showed that the Hg concentrations in roots increased linearly with the increase of soil Hg concentrations at all the growth stages of the crops, while root Hg concentrations had no obvious

Table 3
Foliar Hg concentrations in maize and wheat at different growth stages in the soil Hg enriched experiment (ng g⁻¹).

Species	Stages	Foliages	25/28	158/57	325/119	496/243	763/552
Maize	LJ	Upper	8.5 ± 3.1 (a)	7.0 ± 1.0 (a)	8.1 ± 1.7 (a)	10.5 ± 1.5 (a)	10.5 ± 1.3 (a)
		Bottom	15.0 ± 2.0 (ab)	16.0 ± 2.0 (abc)	14.3 ± 4.5 (a)	21.0 ± 3.5 (c)	20.3 ± 1.5 (bc)
	GF	Upper	14.0 ± 1.0 (a)	14.0 ± 1.0 (a)	12.3 ± 1.2 (a)	14.0 ± 3.0 (a)	15.7 ± 0.6 (b)
		Bottom	14.3 ± 4.0 (a)	15.0 ± 7.0 (a)	15.7 ± 1.2 (a)	22.7 ± 5.0 (a)	19.3 ± 3.1 (a)
	D	Upper	15.0 ± 1.7 (a)	16.0 ± 1.0 (a)	15.3 ± 1.5 (a)	17.3 ± 1.5 (a)	16.7 ± 0.6 (a)
		Bottom	24.0 ± 1.7 (a)	20.7 ± 3.1 (a)	21.0 ± 3.0 (a)	24.3 ± 2.5 (a)	20.7 ± 1.5 (a)
Wheat	LJ		12.3 ± 0.6 (a)	12.7 ± 1.5 (a)	13.3 ± 1.5 (a)	11.3 ± 1.2 (a)	12.3 ± 0.6 (a)
	GF		24.3 ± 1.5 (a)	26.7 ± 5.1 (a)	28.3 ± 1.5 (ab)	32.7 ± 0.6 (bc)	33.7 ± 1.5 (c)
	D		44.7 ± 3.1 (a)	50.0 ± 3.1 (a)	47.3 ± 2.9 (a)	59.3 ± 4.2 (b)	57.7 ± 2.5 (b)

Table 4Seed Hg concentrations in maize and wheat at different growth stages in the OTCs and soil Hg enriched experiments (ng g⁻¹).

Species	Stages	Air Hg concentrations (ng m ⁻³)				Soil Hg concentrations (ng g ⁻¹)				
		2	10	20	50/70	25/28	158/57	325/119	496/243	763/552
Maize	GF	5.9 ± 0.9 (a)	4.8 ± 0.7 (a)	3.8 ± 1.9 (a)	4.3 ± 1.0 (a)	10.7 ± 1.2 (a)	8.7 ± 1.3 (a)	7.9 ± 2.0 (a)	8.1 ± 2.1 (a)	10.9 ± 1.2 (a)
	D	1.6 ± 0.5 (a)	1.4 ± 0.6 (a)	1.8 ± 1.3 (a)	2.1 ± 0.4 (a)	1.2 ± 0.6 (a)	1.3 ± 1.0 (a)	1.2 ± 0.3 (a)	2.1 ± 0.3 (a)	0.9 ± 0.6 (a)
Wheat	GF	0.8 ± 0.2 (a)	0.6 ± 0.4 (a)	0.7 ± 0.3 (a)	1.6 ± 0.5 (b)	0.9 ± 0.8 (a)	0.5 ± 0.4 (a)	0.1 ± 0.1 (a)	0.7 ± 0.5 (a)	0.7 ± 0.4 (a)
	D	0.7 ± 0.0 (a)	1.1 ± 0.3 (a)	0.6 ± 0.1 (a)	2.7 ± 1.0 (b)	0.8 ± 0.2 (a)	0.4 ± 0.3 (a)	0.4 ± 0.2 (a)	0.7 ± 0.3 (a)	0.6 ± 0.7 (a)

linear relationships with air Hg concentrations, demonstrating that Hg accumulated in crop roots was mainly originated from soil. Many studies showed that the root Hg concentrations of trees were related to the soil Hg concentrations (e.g., Frescholtz et al., 2003; Ericksen et al., 2003; Millhollen et al., 2006a). Millhollen et al. (2006b) showed that higher soil Hg concentrations resulted in higher root Hg concentrations in grass and forb species. No evident influence of air Hg on root Hg accumulation in trees or crops was reported in previous studies. In this study, however, a significantly higher root Hg concentration in wheat exposed to 70 ng m⁻³ was observed at D stage ($p < 0.05$) of the growth, which might result from the translocation of Hg from foliages to roots, accompanied by the translocation of photosynthate, but further research is needed to confirm this process. In addition, no statistical difference ($p > 0.05$) of Hg concentrations for surface soils (3–5 mm) in chambers were found before (27 ± 7 ng g⁻¹) and after (27 ± 4 ng g⁻¹) the fumigation. The GEM fumigation did not change the soil Hg concentrations in chambers, therefore, the significant difference of the root Hg concentration in wheat at D stage may be influenced by air Hg concentration.

Accumulation of Hg in plant stems may result from a combination of atmospheric uptake and translocation from root uptake. In the two experiments, the air Hg concentration (70 ng m⁻³) led to a significant increase of Hg accumulation in wheat upper stems ($p < 0.05$), while soil Hg generally had little influence on Hg accumulation in crop stems. In addition, Hg concentrations in upper stems were usually higher than those in bottom stems. These results suggested that the air Hg played a more important role than soil Hg in the Hg accumulation in crop stems, which was in accordance with the results for trees. Fay and Gustin (2007) showed that trunk Hg concentrations in trees and shrub were influenced by both air and soil Hg concentrations, and the influence of air Hg was stronger.

In this study, significant positive correlations were found between foliar Hg concentrations and air Hg concentrations, while foliar Hg concentrations did not show obvious linear relationships with soil Hg concentrations, which indicates that Hg in crop foliages was mainly taken up from ambient air. These results were consistent with those from previous studies for tree foliages (e.g., Frescholtz et al., 2003; Ericksen et al., 2003; Ericksen and Gustin, 2004; Millhollen et al., 2006a). De Temmerman et al. (2007, 2009) also showed linear correlations ($R^2 = 0.64$ – 0.98) between foliar Hg concentrations and air Hg concentrations in ryegrass and leafy vegetables. Elevated soil Hg concentrations had some influence on the foliar Hg concentrations at some stages ($p < 0.05$), which may be due to the emission from Hg enriched soil and translocation to the foliages from roots. Millhollen et al. (2006b) showed that the high Hg concentrations in leaves in blackeyed susan (*Rudbeckia hirta* L.) were caused by the Hg emission from soil, because the bottom leaves of *R. hirta* were very close to the ground. Foliar Hg concentrations in crop showed the trend of increase over growth stages in this study, and many other studies also reported that foliar Hg concentrations in trees and shrub increased as a function of plant

growth stages (Ericksen et al., 2003; Frescholtz et al., 2003; Millhollen et al., 2006a; Fay and Gustin, 2007).

At the treatment of CK, the Hg concentrations in crop organs increased in the order of seeds < stems < roots < foliages in the two experiments. Ericksen et al. (2003) reported that the Hg concentrations in tree organs increased in the order of stems < branches < roots < leaves. So, the Hg accumulation from air in crop organs was mainly retained in foliages.

4.2. Health implication of crop production with elevated Hg exposure

In this study, the seed Hg concentrations at GF and D stages were lower than the Chinese tolerance limit of Hg for food (20 ng g⁻¹) (CNSA, 1994). However, the foliar Hg concentrations in crop in this study exceed the European Commission (2002) Hg standard for livestock (110 ng g⁻¹, dry weight) at high air Hg exposure and also exceed the Kazakhstan (Ullrich et al., 2007) standard for livestock (100 ng g⁻¹). Therefore, from the OTCs experiment, it can be concluded that crop foliages grown in the area with elevated air Hg concentration (50 ng m⁻³ or higher) may be not suitable for fodders.

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