ACCUMULATION AND TRANSLOCATION OF ^{198}HG IN FOUR CROP SPECIES

Liwei Cui,†‡§ Xinbin Feng,*‡ Che-Jen Lin,‡∥# Xinming Wang,† Bo Meng,‡ Xun Wang,‡§ and Heng Wang‡§

†State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China
‡State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China
§University of Chinese Academy of Sciences, Beijing, China
∥Department of Civil Engineering, Lamar University, Beaumont, Texas, USA
#College of Energy and Environment, South China University of Technology, Guangzhou, China

Abstract: The uptake and transport of mercury (Hg) through vegetation play an important role in the biogeochemical cycling of Hg. However, quantitative information regarding Hg translocation in plants is poorly understood. In the present study, Hg uptake, accumulation, and translocation in 4 crops—rice (*Oryza.sativa* L.), wheat (*Triticum* L.), corn (*Zea mays* L.), and oilseed rape (*Brassica campestris* L.)—grown in Hoagland solution were investigated using a stable isotope (^{198}Hg) tracing technique. The distribution of ^{198}Hg in root, stem, and leaf after uptake was quantified, and the release of ^{198}Hg into the air from crop leaf was investigated. It was found that the concentration of Hg accumulated in the root, stem, and leaf of rice increased linearly with the spiked ^{198}Hg concentration. The uptake equilibrium constant was estimated to be 2.35 mol Hg/g dry weight in rice root per mol/L Hg remaining in the Hoagland solution. More than 94% of ^{198}Hg uptake was accumulated in the roots for all 4 crops examined. The translocation to stem and leaf was not significant because of the absence of Hg^{2+} complexes that facilitate Hg transport in plants. The accumulated ^{198}Hg in stem and leaf was not released from the plant at air Hg^0 concentration ranging from 0 ng/m^3 to 10 ng/m^3. Transfer factor data analysis showed that Hg translocation from stems to leaves was more efficient than that from roots to stems. *Environ Toxicol Chem* 2014;33:334–340. © 2013 SETAC

Keywords: Mercury   Stable isotope   Plant uptake   Translocation   Transfer factor

INTRODUCTION

Mercury is a toxic metal that accumulates and is biomagnified in living organisms through the food chain. The toxicity associated with exposure to methylmercury (MeHg) and contamination incidents have been documented worldwide [1–3], with the primary exposure pathway through consumption of fish and rice containing MeHg [4–6]. Mercury in the biosphere comes primarily from atmospheric deposition resulting from both anthropogenic and natural release of Hg into the atmosphere. Therefore, understanding the relative importance of natural emission to the anthropogenic counterpart is critical for assessing the Hg input to water and soils. However, the release of Hg from natural surfaces, including water, soil, and vegetation, has not been well quantified [7,8]. In particular, the role of vegetation in the air–surface exchange of Hg is poorly understood, leading to a large uncertainty in understanding the global biogeochemical cycle of Hg.

Conflicting reports have been made with regard to the role of vegetation as a source or a sink of Hg. Earlier studies have demonstrated that vegetation can release Hg into the air via leaf stomata [9–11]. Several model studies have also suggested that vegetative Hg emission is an important source contributing to regional and global Hg budgets, accounting for up to 75% of total natural release in terrestrial systems [12–14]. Vegetative uptake of Hg from soils has been suggested to be an active process, followed by translocation of Hg into plants and then ultimately release into the atmosphere [15]. Selected plants such as bush bean (*Phaseolus vulgaris* L.), Indian mustard (*Brassica juncea* L.), and hairy vetch (*Viciavillosa* R.) have been used for phytoremediation of Hg-contaminated soils, and the presence of thiosulfatecan enhances the uptake and release [16]. In contrast, several woody plants have been considered as sinks for atmospheric Hg through dry deposition on foliar surfaces. For example, Rocky Mountain juniper (*Juniperus scopulorum*), ponderosa pine *(Pinus ponderosa)*, black locust (*Robinia pseucdoacacia*), young pine tree (*Pinus salius*), sugar maple (*Acer saccharum* Marsh.), yellow birch (*Betula alleghaniensis* Britt.), and American beech (*Fagus grandifolia* Ehrh.) have been shown to absorb Hg^0 from the atmosphere through stomata [17–21]. Dry deposition has been found to be the largest source of Hg in the foliage of Maple (*Acer* spp.), beech (*Fagus* spp.), birch (*Betula* spp.), oak (*Quercus* spp.), and aspen (Populus spp.) trees [22]. Therefore, we must better understand the role of vegetation as a source or a sink for atmospheric Hg.

Limited efforts have been made toward understanding how Hg can be transported in plants and released into the atmosphere. Previous studies have reported that only a small portion (0.17–2.5%) of Hg can be translocated from root to stem in garden pea (*Pisum sativum* L.), spring wheat (*Triticum aestivum* L.), sugar beet (*Beta vulgaris* L.), white clover *(Trifolium repens* L.), and maize (*Zea mays* L.) [23]. No report has shown stem-to-leaf translocation, yet the bidirectional exchange of Hg^0 at the foliar surface has been documented. For example, Hg^0 was released from the foliage of white oak (*Quercus fabri* Hance), red maple (*Acer rubrum* L.), Norway spruce (*Picea abies*), and yellow poplar (*Liriodendron tulipifera* L.) at an air concentration of <2 ng/m^3, and deposition occurred when the plants were exposed to 50 ng/m^3 to 70 ng/m^3 Hg^0 [24]. Although these studies provided initial insights on the uptake and transport of Hg through plants, experimental evidence that plants are capable of mobilizing Hg from soil to air is lacking [25,26]. Recently, advances in isotopic tracer techniques have allowed a systematic investigation of Hg transport in different environmental

compartments [27]. Harris et al. [28] applied multiple stable Hg isotopes for tracing the transport pathways of deposited Hg^{2+} in an isolated ecosystem, and Rutter et al. [29] used ^{198}Hg as a tracer to understand dry deposition to plants and soils under controlled environmental conditions. The stable isotopic tracing technique reliably determines the transport pathways without using radioactive materials that are undesirable and sometimes unfeasible for experimental investigations.

Crops are the most important human-cultivated vegetation. China has nearly 1.6×10^8 hectares of cropland [23]. In combination, wheat, corn, and oilseed rape account for >65% of the planting area. The air–surface exchange over the crop canopy potentially represents an important Hg source/sink in China, which contributes to the greatest amount of anthropogenic Hg emission globally. However, earlier studies of Hg uptake and translocation by plants did not focus on crops. Understanding Hg translocation mediated by crops helps to elucidate the exchange of Hg between atmosphere and vegetation. The objective of the present study is to quantify the uptake, accumulation, translocation, and atmospheric release of Hg by 4 selected crops using stable ^{198}Hg as an isotopic tracer. Hoagland solution (Phyto Technology Laboratories) was used as the growth medium to represent the scenario in which Hg is readily available for uptake under an optimal nutrient condition for plant growth. To our knowledge, this is the first study investigating Hg transport mediated by plants from growth medium to air using stable isotopic tracing techniques.

MATERIALS AND METHODS

Experimental apparatus

An experimental chamber system was constructed to trace the transport of Hg from the growth media via crops to the atmosphere under controlled environmental conditions (Figure 1). The system consisted of a container (0.28 L, borosilicate) holding Hoagland solution spiked with various concentrations of inorganic ^{198}Hg^{2+}, a cylindrical dynamic exchange chamber (12.7 L, borosilicate) isolated from the Hoagland solution for plant growth, and an impinger for capturing ^{198}Hg if released. The upper chamber was designed to allow ambient air to flow through six 6-mm-diameter inlets at the top and an air outlet at the bottom such that air–foliar exchange can take place. A glass isolation plate was placed between the bottom medium container and the chamber. The plate was divided into 2 halves for
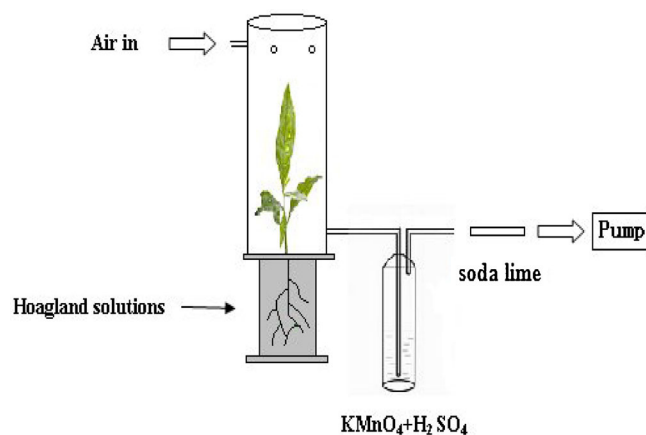

Figure 1. Illustration of the experimental apparatus used for the ^{198}Hg exposure experiment.

allowing placement of the plants through a 1-cm diameter hole. The 2 halves and the opening of the center hole were then sealed using silicone to prevent air exchange between the head space of the medium container and the cylindrical chamber. The outlet of the exchange chamber was connected to a vacuum pump (Gast 1532), drawing the air inside the chamber to an impinger containing 1 wt% KMnO$_4$ and 10 vol% sulfuric acid. The air flow was maintained at 2 L/min, yielding a mean air retention time of 6.35 min in the chamber. Soda lime traps were placed before the pump to remove the humidity and acid gas for protecting the vacuum pump.

Hydroponic experiments

Rice, wheat, corn, and oilseed rape were selected as the model crop species. The crops were germinated in a porous perlite-cultivating medium, which offered suitable conditions for the initial growth. After germination, the seedlings were transferred to soil containing $0.26 \pm 0.10 \, \mu g/g$ Hg and 9.13 wt% organic matter in a greenhouse. The crop plants were watered every 3 d to maintain growth for 50 d to 60 d and then transferred to containers holding 200-mL Hoagland solutions. The Hoagland solutions were spiked with stable ^{198}Hg^{2+} nitrate (94.5% enriched), yielding 0.01 ng/mL to 1 ng/mL ^{198}Hg^{2+} (2–200 ng ^{198}Hg^{2+} in 200 mL Hoagland solution). This concentration range is 2 to 4 orders of magnitude smaller than those used in earlier study that employed HgCl$_2$ for tracing Hg translocation in plants [30]. After spiking with ^{198}Hg^{2+}, the Hoagland solutions were allowed to equilibrate for at least 2 h [31]. The pH of the Hoagland solutions was adjusted to 5.5 to 6.0 with 1 M KOH before each experiment. The experiments for wheat, corn, and oilseed rape were performed at 1 ng/mL of spiked ^{198}Hg^{2+}. For rice, multiple (5) ^{198}Hg^{2+} concentrations ranging from 0.01 ng/mL to 1 ng/mL were tested, because earlier studies suggested that the Hg concentration accumulated in rice is 1 to 2 orders of magnitude higher than Hg concentrations found for other crops [4,32,33].

Triplicate experiments were performed for 3 plants of each crop at each spiked ^{198}Hg concentration. The roots of each crop seedling were thoroughly rinsed 3 times with deionized water before the plant was transferred to the Hoagland solutions. Each plant was allowed to grow for a 72-h period in the experimental chamber, as shown in Figure 1. The temperature was controlled at 25 °C $\pm$ 3 °C for 16 h under light and 18 °C $\pm$ 3 °C for 8 h in the dark. The relative humidity was controlled at 70% to 80% [34]. At the end of the 72-h growth period, the biomass samples of root, stem, and leaf as well as the impinging solution were analyzed to quantify the increase of ^{198}Hg. The transfer factors, defined as the ratio of ^{198}Hg concentration in stem (C_S) to the ^{198}Hg concentration in root (C_R) or as the ratio of ^{198}Hg concentration in leaf (C_L) to the ^{198}Hg concentration in stem (C_S), were calculated to illustrate the relative ease of Hg translocation from root to stem and from stem to leaf in the crop.

Chemical analysis

The collected root, stem and leaf samples were freeze-dried, ground into powder with a grinder (IKA-A11 basic; IKA), and then digested in a solution containing 1:1 vol mixture of HNO$_3$ and H$_2$SO$_4$ at 95 °C using water bath. The ^{198}Hg in the digested samples was determined after BrCl oxidation and SnCl$_2$ reduction. The ^{198}Hg^{2+} collected in the KMnO$_4$ solution was analyzed after SnCl$_2$ reduction. The ^{198}Hg vapor was then preconcentrated in gold traps and then measured by quadrupole inductively coupled plasma mass spectrometry (ICP–MS; Agilent 7700X). The detection limit was 100 pg/L for Hg [27,28,35].

Table 1. Accuracy and precision of isotopic measurements for the Hg standard solution (SRM 3313; $n = 18$)

	$^{200}Hg/^{198}Hg$	$^{201}Hg/^{198}Hg$	$^{202}Hg/^{198}Hg$	$^{202}Hg/^{200}Hg$
Measured ratio	2.303 ± 0.027	1.314 ± 0.010	2.974 ± 0.028	1.291 ± 0.016
Standard ratio	2.305	1.312	2.961	1.285
F (true/measured)	1.000	0.998	0.996	0.995

The data quality of the isotopic Hg measurement was ensured by analyzing blind duplicates and by verifying against a standard reference material (GBW10020). The relative analytical difference between blind duplicates was <10% for all samples. The recovery for plant reference material was in the range of 95% to 97%, and the relative standard deviation (RSD) was <7% ($n = 12$). Analysis of isotopic composition of 1.0 ng/mL National Institute of Standards and Technology Hg standard solution (SRM 3313; $n = 18$) showed that the RSD was between 0.76% and 1.24% and the F (true/measured) ratio was 0.995 to 1.000 (Table 1), comparable to the analytical accuracy reported in an earlier article (0.990–1.003) [27]. Throughout the discussion, the results shown as ^{198}Hg refer to the increased ^{198}Hg caused by the experimental treatment (exposure to spiked ^{198}Hg in Hoagland solution).

The Hg^0 concentration in the laboratory air was measured using a Tekran 2537A Hg vapor analyzer with a 5-min interval. The analytical accuracy of the instrument was controlled via periodic internal recalibration at 25-h intervals. The RSD and detection limit of the instrument were 2% and <0.1 ng/m^3, respectively. The Hg^0 concentration in the laboratory air was found to be 16.16 ng/m^3 ± 6.56 ng/m^3, typical of urban Guiyang, China.

RESULTS AND DISCUSSION

^{198}Hg uptake and translocation in rice

After 72 h of exposure, rice took up 66% to 75% of the spiked ^{198}Hg in the Hoagland solutions (Table 2). This is a relatively small range despite the wide range (0.01–1 ng/mL) of spiked ^{198}Hg concentrations, suggesting that ^{198}Hg uptake by rice was not limited by the concentration range of the exposure experiments. More than 94% of the ^{198}Hg uptake accumulated in roots, and the translocation to stem and leaf was much less significant. This is consistent with earlier findings that <2.5% Hg uptake was translocated to shoots for clover, pea, and sugar beet when the plants were exposed to 200 µg/mL HgCl$_2$ [30]. Increases of ^{198}Hg in both rice stem and rice leaf were detected (Table 2). This is the first direct evidence that the rice plant is capable of moving Hg in the root to the leaf; the only route leading to the increase of ^{198}Hg is through root–stem–leaf transport. Both stem and leaf accumulate ^{198}Hg but at concentrations much lower than those found in root.

The ^{198}Hg concentrations accumulated in root, stem, and leaf after exposure increased linearly with the spiked ^{198}Hg concentrations in Hoagland solutions (Figure 2; $R_{root}^2 = 0.996$, $p < 0.01$; $R_{stem}^2 = 0.934$, $p < 0.01$; $R_{leaf}^2 = 0.852$, $p < 0.05$). The linearity between ^{198}Hg accumulation in root and the spiked concentration in the Hoagland solution was particularly consistent. Using the accumulated ^{198}Hg concentrations in root and the remaining ^{198}Hg concentrations in Hoagland solution, we estimated an uptake equilibrium constant of 2.35 mol Hg/g dry wt per mol/L. The linear trend suggests that a local equilibrium existed between the growth medium and rice root. A similar trend was observed for the white lupin (*Lupinus albus* L.) plant at Hg concentration <100 µM (20 000 ng/mL) in the growth solution [36]. For plants grown in soil, it has been demonstrated that Hg accumulation in rice root also increases with soil Hg content [37–39]. Furthermore, both Hg and MeHg can accumulate and concentrate in rice fruit in Hg mining areas of China [33,40]. Based on our observation that Hg can be translocated from growth medium to leaf, the Hg accumulated in rice fruit may be transported from the Hg in soil.

Comparison of ^{198}Hg uptake among different crop plants

The ^{198}Hg accumulated in the 4 crops after exposure of the plants to 1 ng/mL $^{198}Hg^{2+}$ in Hoagland solution for 72 h (Table 3). Clear differences can be seen in the quantity of Hg uptake and the relative tendency of translocation. The concentration of ^{198}Hg accumulated in corn root was 2 to 3 times greater than the values for the other 3 species. In addition, the tendency of stem-to-leaf transfer for corn is relatively stronger among the 4 crops. Different levels of Hg accumulation in plant root have been reported for tomato, cabbage, clover, sugar beet, pea, wheat and rape when treated with soil and solution having different Hg concentrations [41–43]. The observed uptake differences were likely caused by the specific growth characteristics of each crop plant. Another reason might be the difference in root mass of the 4 crop species. A greater root biomass can lead to a lower Hg concentration as a result of biomass dilution [30]. The biomass of corn root was only 30% to 50% of that of the other crops for similarly sized plants, resulting in a higher accumulated concentration. Nevertheless, the Hg uptake accumulated predominantly in the root zone for all 4 crops.

Plants grown in Hg-contaminated soil often evolve mechanisms to exclude toxic metals from entering the plants via root cells by hindering the movement of Hg [44]. Morphological analysis using x-ray absorption near-edge structure spectroscopy has shown that Hg accumulated in water hyacinth (*Eichhornia*

Table 2. Distribution of ^{198}Hg mass in rice plants ($n = 3$) after 72-h ^{198}Hg exposure

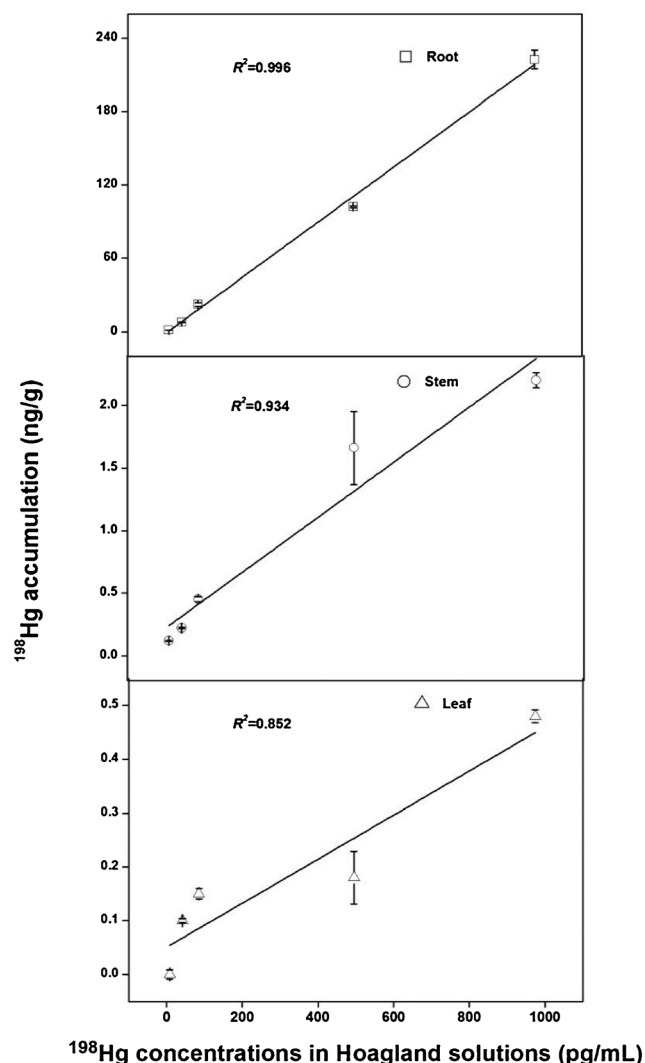| Spiked $^{198}Hg^{2+}$ in solution (ng/mL)	Percentage of $^{198}Hg^{2+}$ translocated to rice plant (%)	Accumulation of ^{198}Hg in root (%)	Accumulation of ^{198}Hg in stem (%)	Accumulation of ^{198}Hg in leaf (%)
0.01	65.33 ± 3.44	94.59 ± 0.21	5.41 ± 0.21	Not detected
0.05	66.16 ± 0.61	96.61 ± 0.04	2.46 ± 0.06	0.94 ± 0.04
0.1	75.19 ± 4.77	97.08 ± 0.07	2.27 ± 0.05	0.65 ± 0.02
0.5	68.79 ± 0.32	98.56 ± 0.26	1.29 ± 0.22	0.15 ± 0.04
1	72.86 ± 2.53	98.75 ± 0.07	1.02 ± 0.06	0.23 ± 0.01

Figure 2. Relationship between the increased [198]Hg concentrations in rice roots, stems, and leaves and [198]Hg concentrations in Hoagland solutions. Error bars represent the standard deviation of 3 replicates.

crassipes), alfalfa (*Medicago sativa* L.), barley and maize roots were dominated by the complexes of phytochelatins (PCs) such as Hg-hPC, Hg-PC$_2$, and Hg-PC$_S$. The phytochelatins can be produced by the roots upon exposure to Hg as detoxification agents [45–48]. The complexes remain predominantly in the root zone, and therefore Hg transport to stem and leaf is hindered [49]. However, the presence of sulfur-containing ligands such as mercaptoethanol or dithiothreitol in soil can greatly increase the accumulation in root and trigger Hg translocation in both woody and grass species, including aspen (*Populus davidiana*), red osier

dogwood (*Cornus stolonifera*) and thale cress (*Arabidopsis thaliana*) [50]. Another chelating agent, ethylenediaminetetra-acetic acid (EDTA), has been shown to increase Hg uptake and translocation in garden cress plants by up to 2.5 times [51]. Because Hoagland solution contains EDTA as a reagent to prevent the oxidation of micronutrients, aqueous speciation calculation was performed using Visual MINTEQ (ver 3.0) to determine whether the spiked [198]Hg^{2+} forms complexes with EDTA under the given water chemistry. The results show that Hg^{2+} speciation was dominated by Hg-chloride complexes (HgCl$_2$, HgCl$_3^-$ and HgCl$_4^-$). The Hg-EDTA complexes constituted only <0.05% of the spiked [198]Hg. This indicates that there was no complex formation facilitating the translocation in our experiment, resulting in the accumulation predominantly in root after Hg uptake.

Hg release from crop plants to air

For all the exposure experiments, there was no detectable [198]Hg in the impinging solution, suggesting no release of Hg from crop leaves to air. During the entire set of experiments, the ambient concentration of Hg was elevated (9.72–18.4 ng/m^3). This level of ambient Hg was similar to the Hg concentration observed in urban Guiyang, where our laboratory is located [52,53], and might have hindered the release of [198]Hg from leaf. It has been proposed that the air–foliar exchange of Hg is bidirectional depending on the the gradient between ambient Hg concentration and a hypothetical compensation point that denotes the interfacial Hg level at the foliar surface [54]. Because ambient air was used as the flushing air in the exchange chamber (Figure 1), we hypothesized that the elevated Hg concentration in the laboratory air could have forced Hg deposition on leaf and supression of the release [55,56].

Based on the [198]Hg translocation results (Table 3), it appeared that corn had the largest Hg accumulation in leaf, giving a greater possibility for Hg release from the plant. To verify that the release can occur, an additional experiment was performed in which corn plants were exposed to 100 ng/mL (100 times of the previous experimental level) [198]Hg^{2+} in Hoagland solution for 72 h. In the experiment, a zero air filter was installed to lower the Hg in the ambient air to <0.2 ng/m^3 before allowing it to enter the exchange chamber. The translocation results are shown in Table 4.

Even with the increased spiked concentration of [198]Hg and reduced air Hg concentration (<0.2 ng/m^3), no [198]Hg was detected in the KMnO$_4$ impinging solution, suggesting that corn leaf did not release Hg to the air. This probably was because of the absence of reduction pathways for the [198]Hg^{2+} translocated from the Hoagland solutions to the corn plants. The Hg^{2+} reduction can occur in transgenic tobacco engineered to express bacterial native mercuric reductase (MerA) that facilitates the transport of ionic Hg to cells and the release of Hg^0 to air [57–59]. The THg concentration in corn leaf decreased slightly after

Table 3. Concentration and distribution of [198]Hg in roots, stems, and leaves of the 4 crops ($n = 3$) after 72-h exposure to 1 ng/mL spiked [198]Hg in Hoagland solutions

Crop species	[198]Hg concentration (ng/g)			Accumulation of [198]Hg (%)		
	Root	Stem	Leaf	Root	Stem	Leaf
Rice	222.50 ± 7.87	2.20 ± 0.05	0.48 ± 0.02	98.75 ± 0.19	1.02 ± 0.06	0.23 ± 0.01
Wheat	219.53 ± 21.73	3.16 ± 0.39	0.21 ± 0.04	99.07 ± 0.14	0.80 ± 0.12	0.12 ± 0.03
Corn	416.24 ± 16.33	2.44 ± 0.61	0.84 ± 0.14	99.45 ± 0.12	0.25 ± 0.05	0.30 ± 0.06
Oilseed rape	137.48 ± 8.16	1.27 ± 0.08	Not detected	98.77 ± 0.10	1.23 ± 0.10	Not detected

Table 4. Total Hg concentration (μg/g) before and after experiment and [198]Hg accumulation and distribution in corn root, stem and leaf after 72-h exposure to 100 ng/mL spiked [198]Hg in Hoagland solutions ($n = 3$)

Crop organs	THg concentration (μg/g)		[198]Hg concentration (μg/g)	Accumulation of [198]Hg (%)
	Before experiment	After experiment		
Root	Not measured	23.23 ± 2.46	23.11 ± 2.45	98.91 ± 0.17
Stem	Not measured	0.28 ± 0.03	0.23 ± 0.02	1.01 ± 0.17
Leaf	0.15 ± 0.01	0.11 ± 0.01	0.016 ± 0.002	0.08 ± 0.01

the exposure experiment. One possible reason is the dilution effect caused by continuous growth of corn leaf during the experiment [23]. The other is that corn leaf released previously deposited Hg to air, because the corn plant was grown in laboratory air that contained elevated level of Hg before the exposure experiment [60]. The results of [198]Hg accumulation in root, stem, and leaf were consistent with those obtained from the experiments using lower exposure concentration in the Hoagland solutions (Table 3). This also confirmed that [198]Hg translocation in corn was mainly hindered by the roots.

Transfer factor

Transfer factor indicates the relative ease of Hg translocation from root through stem to leaf (Table 5) [61,62]. For rice, both transfer factor (C_L/C_S) and transfer factor (C_S/C_R) decreased when [198]Hg^{2+} exposure concentrations were increasing. This suggests that Hg translocation from root to stem and from stem to leaf decreases with the increase of [198]Hg exposure concentration because of the absence of Hg^{2+} complexes that inhibit Hg transport in plants (see above). However, transfer factor (C_L/C_S) was consistently higher than transfer factor (C_S/C_R) for all 4 crops, indicating that Hg translocation form stem to leaf was relatively easier than the translocation from root to stem. This means that the transport barrier for Hg becomes weaker once Hg breaks through the root zone. It has been shown that the introduction of inorganic sulfur compounds such as thiosulfate can greatly increase Hg uptake from soil and translocation to the shoots of red osier dogwood and India mustard (*Brassica juncea*) during phytoremediation through the formation of Hg-S complexes [62,63]. If the release of Hg from plants into the atmosphere is limited by the absence of Hg^{2+} reduction mechanisms in plants, the accumulated Hg in the examined crops is most likely to be retained in the biomass without being re-emitted into the atmosphere.

CONCLUSIONS

Using a stable isotopic ([198]Hg) tracing technique, the uptake and translocation of Hg in rice, wheat, corn, and oilseed rape were assessed quantitatively. A predominant fraction (>94%) of [198]Hg uptake from Hoagland solutions was accumulated in the root zones of the examined crops. The accumulation of [198]Hg in rice root was linearly proportional to the spiked concentration in Hoagland solution. We estimated an uptake equilibrium constant of 2.35 mol Hg/g dry weight in rice root per mol/L of Hg remaining in the Hoagland solution. Far less of the [198]Hg was translocated to stem and leaf because of the absence of Hg^{2+} complexes that facilitate Hg transport in plants. No [198]Hg release into the air from leaf was observed. This indicates that the examined plants are unable to mobilize soil Hg to the atmosphere in the absence of effective chelating agents. Evaluation of translocation factor shows that the transport of Hg from stem to leaf was relatively more efficient compared with the transport from root to stem, suggesting that plants can accumulate a much greater quantity of Hg once the barrier at the roots is broken through. The subsequent release of Hg into the atmosphere is not likely because of a lack of reduction mechanisms that convert translocated Hg^{2+} in the crops examined in the present study.

Table 5. [198]Hg transfer factor of C_S/C_R and C_L/C_S for 4 crops ($n = 3$)

Crop species	[198]Hg^{2+} initial concentration (ng/mL)	Transfer factor	
		C_S/C_R	C_L/C_S
Rice	0.01	0.0950 ± 0.0039	
	0.05	0.0288 ± 0.0007	0.4544 ± 0.0188
	0.1	0.0202 ± 0.0005	0.3255 ± 0.0098
	0.5	0.0162 ± 0.0029	0.1086 ± 0.0165
	1	0.0099 ± 0.0005	0.2192 ± 0.0022
Wheat	1	0.0158 ± 0.0022	0.0495 ± 0.0137
Corn	1	0.0069 ± 0.0015	0.2875 ± 0.1223
	100	0.0100 ± 0.0007	0.0644 ± 0.0072
Oilseed rape	1	0.0094 ± 0.0001	Not detected

$C_S = $ [198]Hg concentration in stem; $C_R = $ [198]Hg concentration in root; $C_L = $ [198]Hg concentration in leaf.

REFERENCES

1. Feng X, Li P, Qiu G, Wang S, Li G, Shang L, Meng B, Jiang H, Bai W, Li Z, Fu X. 2007. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou Province, China. *Environ Sci Technol* 42:326–332.
2. Feng X, Qiu G. 2008. Mercury pollution in Guizhou, southwestern China: An overview. *Sci Total Environ* 400:227–237.
3. Qiu G, Feng X, Wang S, Xiao T. 2006. Mercury contaminations from historic mining to water, soil and vegetation in Lanmuchang, Guizhou, southwestern China. *Sci Total Environ* 368:56–68.
4. Qiu G, Feng X, Li P, Wang S, Li G, Shang L, Fu X. 2008. Methylmercury accumulation in rice (*Oryza sativa* L.) grown at abandoned mercury mines in Guizhou, China. *J Agricult Food Chem* 56:2465–2468.
5. Meng B, Feng X, Qiu G, Cai Y, Wang D, Li P, Shang L, Sommar J. 2010. Distribution patterns of inorganic mercury and methylmercury in tissues of rice (*Oryza sativa* L.) plants and possible bioaccumulation pathways. *J Agricult Food Chem* 58:4951–4958.
6. Feng X, Wang S, Qiu G, Hou Y, Tang S. 2005. Total gaseous mercury emissions from soil in Guiyang, Guizhou, China. *J Geophys Res Atmos* 110. DOI:10.1029/2004JD005643.
7. Gustin MS, Stamenkovic J. 2005. Effect of watering and soil moisture on mercury emissions from soils. *Biogeochemistry* 76:215–232.
8. Feng X, Jiang H, Qiu G, Yan H, Li G, Li Z. 2009. Mercury mass balance study in Wujiangdu and Dongfeng reservoirs, Guizhou, China. *Environ Pollut* 157:2594–2603.
9. Gilmour J, Miller M. 1973. Fate of a mercuric–mercurous chloride fungicide added to turfgrass. *J Environ Qual* 2:145–148.

10. Lindberg S, Hanson P, Meyers T, Kim K-H. 1998. Air/surface exchange of mercury vapor over forests—the need for a reassessment of continental biogenic emissions. *Atmos Environ* 32:895–908.

11. Lindberg S, Jackson D, Huckabee J, Janzen S, Levin M, Lund J. 1979. Atmospheric emission and plant uptake of mercury from agricultural soils near the Almaden mercury mine. *J Environ Qual* 8:572–578.

12. Shetty SK, Lin C-J, Streets DG, Jang C. 2008. Model estimate of mercury emission from natural sources in East Asia. *Atmos Environ* 42:8674–8685.

13. Bash JO, Miller DR, Meyer TH, Bresnahan PA. 2004. Northeast United States and Southeast Canada natural mercury emissions estimated with a surface emission model. *Atmos Environ* 38:5683–5692.

14. Gbor PK, Wen D, Meng F, Yang F, Zhang B, Sloan JJ. 2006. Improved model for mercury emission, transport and deposition. *Atmos Environ* 40:973–983.

15. Bishop K, Lee Y-H, Munthe J, Dambrine E. 1998. Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest. *Biogeochemistry* 40:101–113.

16. Moreno FN, Anderson CW, Stewart RB, Robinson BH, Ghomshei M, Meech JA. 2005. Induced plant uptake and transport of mercury in the presence of sulphur-containing ligands and humic acid. *New Phytol* 166:445–454.

17. Frescholtz T, Sexauer Gustin M. 2004. Soil and foliar mercury emission as a function of soil concentration. *Water Air Soil Poll* 155:223–237.

18. Frescholtz TF, Gustin MS, Schorran DE, Fernandez GC. 2003. Assessing the source of mercury in foliar tissue of quaking aspen. *Environ Toxicol Chem* 22:2114–2119.

19. Graydon JA, Louis VLS, Lindberg SE, Hintelmann H, Krabbenhoft DP. 2006. Investigation of mercury exchange between forest canopy vegetation and the atmosphere using a new dynamic chamber. *Environ Sci Technol* 40:4680–4688.

20. Millhollen AG, Gustin MS, Obrist D. 2006. Foliar mercury accumulation and exchange for three tree species. *Environ Sci Technol* 40:6001–6006.

21. Rea A, Lindberg S, Scherbatskoy T, Keeler GJ. 2002. Mercury accumulation in foliage over time in two northern mixed-hardwood forests. *Water Air Soil Pollut* 133:49–67.

22. Rea AW, Lindberg SE, Keeler GJ. 2001. Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall. *Atmos Environ* 35:3453–3462.

23. Niu Z, Zhang X, Wang Z, Ci Z. 2011. Field controlled experiments of mercury accumulation in crops from air and soil. *Environ Pollut* 159:2684–2689.

24. Hanson PJ, Lindberg SE, Tabberer TA, Owens JG, Kim KH. 1995. Foliar exchange of mercury vapor: Evidence for a compensation point. *Water Air Soil Pollut* 80:373–382.

25. Sun S-Q, Wang D-Y, He M, Li X-Y, Zhang C. 2007. Retention capacities of several bryophytes for Hg(II) with special reference to the elevation and morphology of moss growth. *Environ Monit Assess* 133:399–406.

26. Hintelmann H, Harris R, Heyes A, Hurley JP, Kelly CA, Krabbenhoft DP, Lindberg S, Rudd JWM, Scott KJ, St. Louis VL. 2002. Reactivity and Mobility of New and Old Mercury Deposition in a Boreal Forest Ecosystem during the First Year of the METAALICUS Study. *Environ Sci Technol* 36:5034–5040.

27. Hintelmann H, Ogrinc N. 2002. Determination of stable mercury isotopes by ICP/MS and their application in environmental studies. ACS symposium series. ACS Publications, Washington DC, pp 321–338.

28. Harris RC, Rudd JW, Amyot M, Babiarz CL, Beaty KG, Blanchfield PJ, Bodaly RA, Branfireun BA, Gilmour CC, Graydon JA, Heyes A, Hintelmann H, Hurley JP, Kelly CA, Krabbenhoft DP, Lindberg SE, Mason RP, Paterson MJ, Podemski CL, Robinson A, Sandilands KA, Southworth GR, St Louis VL, Tate MT. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *P Natl Acad Sci USA* 104:16586–16591.

29. Rutter AP, Schauer JJ, Shafer MM, Creswell JE, Olson MR, Robinson M, Collins RM, Parman AM, Katzman TL, Mallek JL. 2011. Dry deposition of gaseous elemental mercury to plants and soils using mercury stable isotopes in a controlled environment. *Atmos Environ* 45:848–855.

30. Greger M, Wang Y, Neuschütz C. 2005. Absence of Hg transpiration by shoot after Hg uptake by roots of six terrestrial plant species. *Environ Poll* 134:201–208.

31. Amyot M, Southworth G, Lindberg S, Hintelmann H, Lalonde J, Ogrinc N, Poulain A, Sandilands K. 2004. Formation and evasion of dissolved gaseous mercury in large enclosures amended with $^{200}HgCl_2$. *Atmos Environ* 38:4279–4289.

32. Jacimovic R, Falnoga I, Liya Q, Faganeli J, Drobne D. 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Sci Total Environ* 304:231–256.

33. Meng B, Feng X, Qiu G, Liang P, Li P, Chen C, Shang L. 2011. The process of methylmercury accumulation in rice (*Oryza sativa* L.). *Environ Sci Technol* 45:2711–2717.

34. Jarecki M, Chong C, Voroney R. 2005. Evaluation of compost leachates for plant growth in hydroponic culture. *J Plant Nutr* 28:651–667.

35. Li Y, Yin Y, Liu G, Tachiev G, Roelant D, Jiang G, Cai Y. 2012. Estimation of the major source and sink of methylmercury in the Florida Everglades. *Environ Sci Technol* 46:5885–5893.

36. Esteban E, Moreno E, Peñalosa J, Cabrero JI, Millán R, Zornoza P. 2008. Short and long-term uptake of Hg in white lupin plants: Kinetics and stress indicators. *Environ Exp Bot* 62:316–322.

37. Yin R, Feng X, Meng B. 2013. Stable mercury isotope variation in rice plants (*Oryza sativa* L.) from the Wanshan mercury mining district, SW China. *Environ Sci Technol* 47:2238–2245.

38. Ericksen J, Gustin M, Schorran D, Johnson D, Lindberg S, Coleman J. 2003. Accumulation of atmospheric mercury in forest foliage. *Atmos Environ* 37:1613–1622.

39. Fay L, Gustin M. 2007. Assessing the influence of different atmospheric and soil mercury concentrations on foliar mercury concentrations in a controlled environment. *Water Air Soil Pollut* 181:373–384.

40. Mitchell R, Burridge J, Mitchell R, Burridge J. 1979. Trace elements in soils and crops. *Philos T Roy Soc B* 288:15–24.

41. Suszcynsky EM, Shann JR. 1995. Phytotoxicity and accumulation of mercury in tobacco subjected to different exposure routes. *Environ Toxicol Chem* 14:61–67.

42. Rasmussen PE, Mierle G, Nriagu JO. 1991. The analysis of vegetation for total mercury. *Water Air Soil Pollut* 56:379–390.

43. Wang J, Feng X, Anderson CW, Zhu W, Yin R, Wang H. 2011. Mercury distribution in the soil–plant–air system at the Wanshan mercury mining district in Guizhou, Southwest China. *Environ Toxicol Chem* 30:2725–2731.

44. Hussein HS, Ruiz ON, Terry N, Daniell H. 2007. Phytoremediation of mercury and organomercurials in chloroplast transgenic plants: Enhanced root uptake, translocation to shoots, and volatilization. *Environ Sci Technol* 41:8439–8446.

45. Krupp E, Mestrot A, Wielgus J, Meharg A, Feldmann J. 2009. The molecular form of mercury in biota: Identification of novel mercury peptide complexes in plants. *Chem Commun* 28:4257–4259.

46. Cobbett CS. 2000. Phytochelatins and their roles in heavy metal detoxification. *Plant Physiol* 123:825–832.

47. Zenk MH. 1996. Heavy metal detoxification in higher plants—A review. *Gene* 179:21–30.

48. Rajan M, Darrow J, Hua M, Barnett B, Mendoza M, Greenfield BK, Andrews JC. 2008. Hg L3 XANES study of mercury methylation in shredded *Eichhornia crassipes*. *Environ Sci Technol* 42:5568–5573.

49. Schwesig D, Krebs O. 2003. The role of ground vegetation in the uptake of mercury and methylmercury in a forest ecosystem. *Plant Soil* 253:445–455.

50. Moreno FN, Anderson CW, Stewart RB, Robinson BH. 2004. Phytoremediation of mercury-contaminated mine tailings by induced plant-mercury accumulation. *Environ Pract* 6:165–175.

51. Smolinska B, Cedzynska K. 2007. EDTA and urease effects on Hg accumulation by *Lepidium sativum*. *Chemosphere* 69:1388–1395.

52. Fu X, Feng X, Qiu G, Shang L, Zhang H. 2011. Speciated atmospheric mercury and its potential source in Guiyang, China. *Atmos Environ* 45:4205–4212.

53. Fu X, Feng X, Wang S, Rothenberg S, Shang L, Li Z, Qiu G. 2009. Temporal and spatial distributions of total gaseous mercury concentrations in ambient air in a mountainous area in southwestern China: Implications for industrial and domestic mercury emissions in remote areas in China. *Sci Total Environ* 407:2306–2314.

54. Ericksen JA, Gustin MS, Schorran DE, Johnson DW, Lindberg SE, Coleman JS. 2003. Accumulation of atmospheric mercury in forest foliage. *Atmos Environ* 37:1613–1622.

55. Pirrone N, Costa P, Pacyna J, Ferrara R. 2001. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmos Environ* 35:2997–3006.

56. Millhollen A, Obrist D, Gustin M. 2006. Mercury accumulation in grass and forb species as a function of atmospheric carbon dioxide concentrations and mercury exposures in air and soil. *Chemosphere* 65:889–897.

57. Patty C, Barnett B, Mooney B, Kahn A, Levy S, Liu Y, Pianetta P, Andrews JC. 2009. Using x-ray microscopy and Hg L3 XANES to study Hg binding in the rhizosphere of spartina cordgrass. *Environ Sci Technol* 43:7397–7402.

58. Haque S, Zeyaullah M, Nabi G, Srivastava P, Ali A. 2010. Transgenic tobacco plant expressing environmental *E. coli* merA gene for enhanced volatilization of ionic mercury. *J Microbiol Biotechnol* 20:917.

59. Carrasco-Gil S, Alvarez-Fernández A, Sobrino-Plata J, Millán R, Carpena-Ruiz RO, Leduc DL, Andrews JC, Abadía J, Hernández LE. 2011. Complexation of Hg with phytochelatins is important for plant Hg tolerance. *Plant Cell Environ* 34:778–791.

60. Stamenkovic J, Gustin MS. 2009. Nonstomatal versus stomatal uptake of atmospheric mercury. *Environ Sci Technol* 43:1367–1372.

61. Meharg AA, HartleyWhitaker J. 2002. Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytol* 154: 29–43.

62. Wang J, Feng X, Anderson CW, Wang H, Zheng L, Hu T. 2012. Implications of mercury speciation in thiosulfate treated plants. *Environ Sci Technol* 46:5361–5368.

63. Kamaluddin M, Zwiazek JJ. 2001. Metabolic inhibition of root water flow in red osier dogwood (*Cornus stolonifera*) seedlings. *J Exp Bot* 52:739–745.