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Mercury distribution and bioaccumulation up the soil-plant-grasshopper-spider food chain in Huludao City, China

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Abstract

The purpose of this study is to investigate total mercury (THg) distribution and its bioaccumulation up the soil-plant-grasshopper-spider in the Huludao City, which is polluted seriously by chlor-alkali and zinc smelting industry in Northeast of China. Results indicated that average THg concentrations in soil, plant leaves, grasshopper *Locusta migratoria manilensis* and *Acrida chinensis*, and spider were 0.151, 0.119, 0.167 and 0.134 mg/kg, respectively. THg spatial distribution suggested that most of mercury came from the chlor-alkali plant and the two zinc smelteries. The highest mercury concentration was found in the wings among different grasshoppers' organs. Although spiders are the predatory, THg concentrations in their bodies were not high, and only on the same level as in grasshoppers, which might be due to spiders' special living habits. In the light of the mercury transportation at every stage of the soil-plant-grasshopper-spider food chain, the bioaccumulation factors were 0.03, 0.79–1.11 and 0.80–1.13 respectively. It suggested that mercury biomagnification up terrestrial food chains was not so large and obvious as it was in the aquatic food chain.

Key words: mercury; soil; plant; grasshopper; spider; bioaccumulation; food chain

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Introduction

Mercury, especially methylmercury, is a neurotoxin that affects human and ecological health via bioaccumulation through the food chain in nature. Of all mercury compounds, methylmercury is the most toxic, which usually accumulates in muscles, liver and kidney of fishes, birds, and mammals (Wren et al., 1980; Pedersen et al., 2006; Kenow et al., 2007; Horai et al., 2006), the bowels of frogs (Wang et al., 2005) and the brain of human beings (Hać et al., 2000). The impact of methylmercury on nervous system is to result in body tremors, speech disorders, motor disturbance, learning disabilities and Minamata disease. Numerous studies have documented the toxicity, accumulation, and transformation of mercury in environment. High mercury levels in insects such as blackflies from the aquatic ecosystem had been reported (Harding et al., 2006). However, from a literature survey, it is found that few previous investigations are available only about terrestrial insects (Hsu et al., 2006; Heckel and Keener, 2007). There are insects everywhere in environment; their species and individual amounts are more than the sum of the other terrestrial animals. In summer grasshoppers are the representative insect species in grassland ecosystem, and they account for about 20%–30% biomass of all arthropods (Schmidt, 1986). Grasshoppers feed on grass leaves, they are not only the primary consumers in the food webs, but also provide food and proteins for birds and other entomophagous animals. In summer spiders are one of the main predators of grasshoppers in grassland. Some studies indicated that predatory insects were bioindicators of heavy metal pollution. Spiders are mercury sentinels in streamside and the average THg concentrations was 400 ng/g (Pennuto and Smith, 2006).

Mercury in environment could be taken up increasingly by plants and transferred up the food chain. Research has shown that grasshoppers could absorb mercury from their food, and the concentrations factors related to grasshoppers' ages and were in the range of 0.62–2.04 (Devkota and Schmidt, 2000). Symptoms of mercury poison in grasshoppers appear as eggs mortality increase and nymphal hatching reduces with increasing Hg^{2+} in substrate (Devkota and Schmidt, 1999). Injected with a solution of methylmercury hydroxide, chromosomes of grasshoppers' males were affected heavily: the chromosomes became swollen, the chromatin fibres got disorganized and sometimes parts of chromosomes disintegrated (Klšterská and Ramel, 1978).

Another important aspect is that mercury could be enriched potentially in predators that feed on grasshoppers such as mantis through the biomagnification and the bioaccumulation factors was about 2.0 (Zheng et al., 2008). Although some results on mercury bioaccumulation

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and toxicity to grasshoppers have been published, studies were still weak and a few are available on mercury distribution characteristics which might reflect the mercury poison in grasshoppers. The purpose of this article is to investigate the mercury bioaccumulation up the soil-plant-grasshopper food chain and the mercury distribution characteristics in different organs of two species of grasshoppers, *Locusta migratoria manilensis* and *Acrida chinensis*. It is helpful to understand the mercury biomagnification up the terrestrial food chain.

1 Materials and methods

1.1 Study area

The study area, Huludao City, is located in the Liaoning Province, China and is an important non-ferrous smelting and chemical industry area in Northeast of China. The Wuli River and the Cishan River are two main rivers in the city. In the past several decades, wastewater with heavy metals from a chlor-alkali plant (P1) and two zinc smelteries (P2) was discharged into the two rivers. The chlor-alkali plant, Jinxi chlor-alkali plant, produced caustic soda and chlorine using mercury electrode from 1952 to 1998. A large amount of effluent containing mercury was discharged into Wuli River without any treatment for mercury removal. It is reported that about 265t mercury were discharged into the Wuli River, of which about 90t were precipitated in the sediment and the rest flowed into the Jinzhou Bay (Zhao and Yan, 1997). There are two zinc smelteries in Huludao, one is privately owned, the other, the Huludao zinc smeltery is state-operated which was founded in 1937 and now is the largest in Asia. The two zinc smelteries produced 3.3×10^5 tons zinc using mercury-containing ore every year in total. The water, soil and sediment around zinc smelteries were heavily polluted by mercury from the wastewater and residue. The Cishan River had carried most wastewater from the two zinc smelteries, and also had been impacted by the dry deposition of the metal-contaminated particulate matter from the two zinc smeltery. But, few data were available about air concentrations of mercury in Huludao although it was thought to be high. Zheng (2007) suggested that mercury concentration in the sediments and soils along the Wuli River and the Cishan River were high.

1.2 Sampling, preparation and chemical analysis

In 2007 and 2008, soil, plant and insect samples were collected by hands from 8 grasslands along the Wuli River and the Cishan River, which were Tielu Bridge, Huafei Bridge, Huagong Bridge, Wulihe Bridg, Cishan Mountain. Cishannan Bridge, site behind of the person-owned zinc Smeltery and Daochi, respectively (Fig. 1). Soil samples were dried at room temperature, ground to pass an 80-mesh nylon sieve, and then preserved in polyethylene bags before use. The plant (*Echinochloa crusgalli* (L.) Beauvu) were collected at the same site and stored in polythene bags. The plant leaves, which were the favorite food of grasshoppers, were washed with deionized water repeatedly to remove metals attached on the surface, dried at room temperature and preserved in polythene bags after they were ground into a homogenous powder.

After collection grasshoppers, *L. migratoria manilensis* and *A. chinensis* were euthanized with alcohol and preserved in a refrigerator at 4°C until use. All grasshoppers were washed with deionized water repeatedly to remove mercury attached on the surface. The grasshoppers' surface moisture was sucked dry with filters, and their body length and weight were measured, then grasshoppers were dissected into five parts including head, thorax, abdomen, legs and wings. Each part was weighed, then oven dried to constant weight at 30°C. Spiders were collected simultaneously by hands and were prepared as the same as the procedures mentioned above, but they were not dissected. All biological samples were ground into homogenous powder in a quartz bowl and preserved in polythene bags at 4°C before use.

The soil, plant and insect samples were all digested

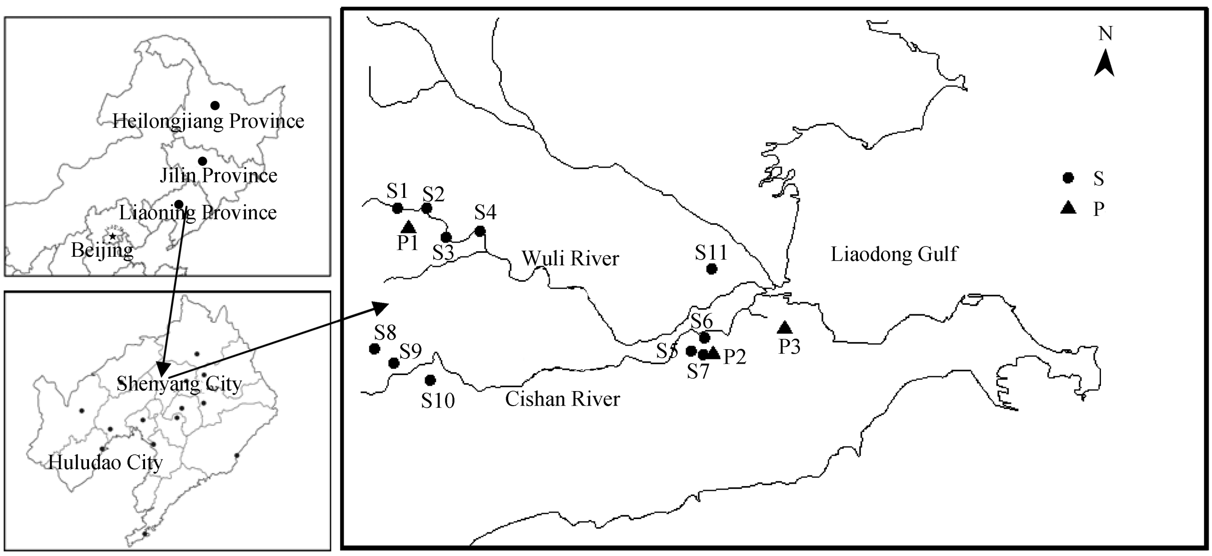

Fig. 1 Sampling sites. S: sample site; P: pollution source.

using the method of H_2SO_4-HNO_3-V_2O_5 (Liu et al., 2003). All speciation of Hg were converted to Hg^{2+} and then Hg^{2+} was reduced to elemental Hg by addition of $SnCl_2$. An F-732V Hg detector was used to determine total Hg in soil and plant and a Tekran-2600 CVAFS (Tekran inc., Canada) with a detection limit of 5×10^{-6} ng/g was used to determine total Hg in biological samples.

1.3 Quality control

Precision and accuracy of the analytical method were evaluated by comparing the expected total Hg concentrations in certified reference materials with the measured values. Simultaneous performance of analytical blanks and standard reference (GBW07601, GBW07604, and GBW07405) confirmed that the accuracy of method was within acceptable limits (Table 1).

Table 1 Results of quality control (mg/kg)

Certified reference	GBW07601	GBW07604	GBW07605
Expected value	0.36 ± 0.05	0.026 ± 0.003	0.29 ± 0.025
Measured value	0.39 ± 0.01	0.027 ± 0.001	0.29 ± 0.012

All of the glass equipments were soaked overnight in 3 mol/L HNO_3, rinsed with copious amounts of distilled deionized water, stored, capped and filled with deionized water prior to use. All solutions were prepared with distilled deionized water in glass bottles and handled with analytical micropipettes. Reagents used were all in excellent pure grades.

2 Results and discussion

2.1 THg concentrations in soil and plant leaves

THg concentrations in the soil samples were in the range of 0.129–28.182 mg/kg, with the average 4.355 mg/kg, which was about 117 times the background value (0.037 mg/kg). It indicated that mercury pollution in Huludao City was serious. It could be concluded that there were two zones with high THg concentrations (Fig. 2). THg concentrations in the sites around the chlor-alkali plant and the zinc smelteries were much higher than those in the other sites. THg concentrations in plant leaves were in the range of 0.001–2.673 mg/kg with the average 0.151 mg/kg. In S7, THg in plant leaves were the highest (Fig. 3).

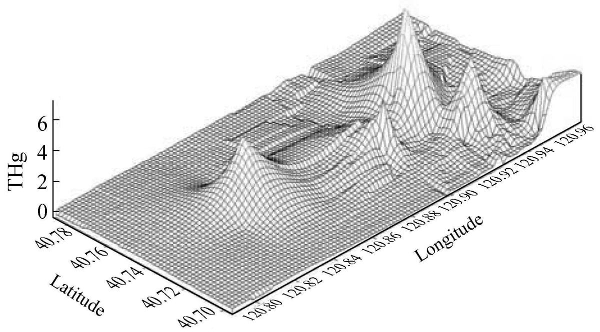

Fig. 2 Total mercury (THg, mg/kg) concentrations in soil.

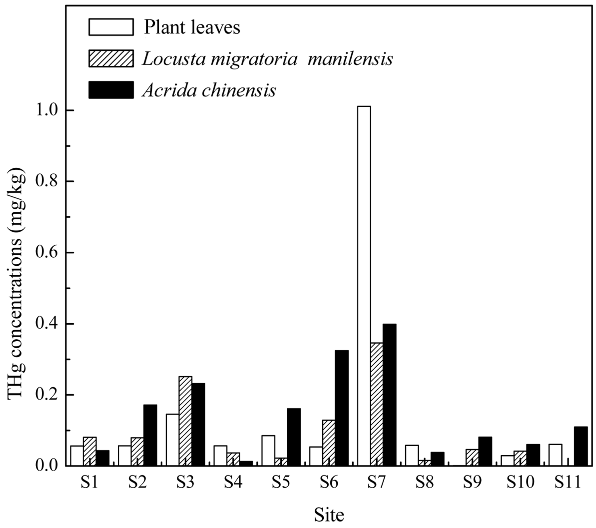

Fig. 3 THg concentrations in plant leaves.

2.2 THg concentrations in grasshoppers and spiders

THg concentrations were in the range of 0.001–0.611 mg/kg, with the average 0.119 mg/kg in *L. migratoria manilensis*, and in the range of 0.008–1.018 mg/kg with the average 0.167 mg/kg in *A. chinensis*, respectively. THg concentrations in grasshoppers varied with sample sites. It was obvious that THg in the sites (S2, S3, S6 and S7) close to pollution sources were comparatively higher than those in the other sites (Fig. 3). The highest THg concentrations in *L. migratoria manilensis* and *A. chinensis* were both found in S7, which located behind of the privately owned smeltery.

THg distribution characteristics in *L. migratoria manilensis* and *A. chinensis* were similar: THg concentrations in wings and head were comparatively high and in other organs were low (Fig. 4). In consideration of weights of different organs, it is suggested that the absolute amount of mercury in abdomen, thorax and heads of grasshoppers accounted for about 75% of the total absolute amount of mercury in sum (Fig. 5). Mercury in wings accounted for 12.27%–12.54% of the total absolute amount of mercury due to its lowest weights although THg concentrations in

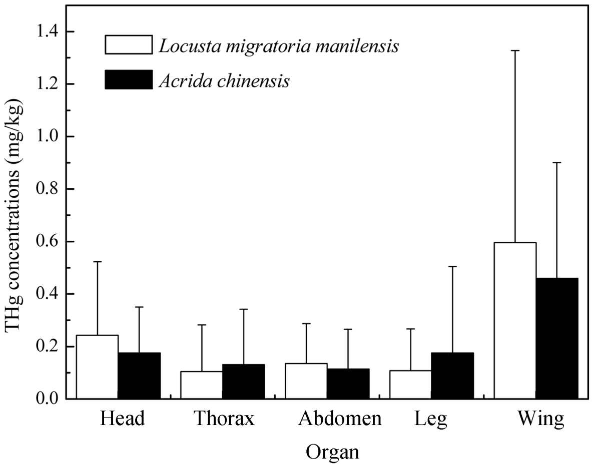

Fig. 4 THg distribution in different organs of grasshoppers.

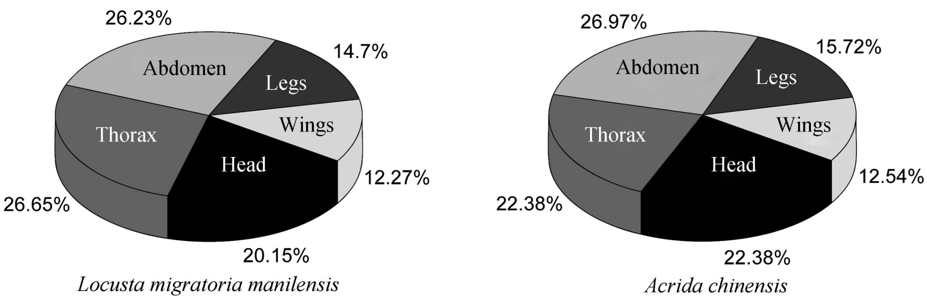

Fig. 5 Proportions of absolute amount of mercury in different organs of grasshoppers.

wings were the highest.

THg concentrations in the spiders were in the range of 0.015–0.412 mg/kg with the average 0.134 mg/kg. Results showed that THg concentrations in spiders collected from the sites around zinc smelteries were comparatively high, among which the highest was found in S11 (Fig. 6).

2.3 Bioaccumulation of THg up the soil-plant-grasshopper-spider food chain

In soil-plant system, THg concentrations in the plant leaves were much lower than that in soil (Table 2). Although it reported that THg in air contributes much to THg concentration in plant leaves, THg concentrations related to THg in soil significantly (r = 0.796, p < 0.01). THg bioaccumulation factor was about 0.05 on average from soil to plant leaves.

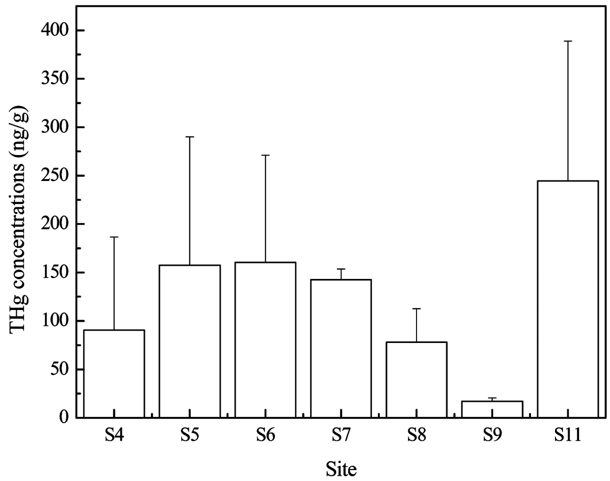

Fig. 6 THg concentrations in spiders.

Significant relations were observed between THg concentrations in the plant leaves and grasshoppers (r = 0.820, p = 0.004 for *L. migratoria manilensis*; r = 0.698, p = 0.017 for *A. chinensis*), which suggested that THg in the grasshoppers came from their food or at least was influenced mostly by plant leaves. For average THg concentrations, THg concentration was 0.79 times the plant leaves for *L. migratoria manilensis*, 1.11 times for *A. chinesis*. In most studied sites, THg concentrations in the grasshoppers were higher than those in the plant leaves, and the bioaccumulation factors in different site except S9 was in the range of 0.26–2.39 for *L. migratoria manilensis* and was in the range of 0.23–6.00 for *A. chinensis*. Although THg concentrations in grasshoppers collected from S7 were relatively higher than those from the other sites, THg bioaccumulation factors here were not the highest; the highest was found in S9, where THg in the plant leaves was much lower than that in other sites.

In the present work, THg concentrations in spiders were 0.134 mg/kg on average, which were much lower than the concentrations reported in literatures (Pennuto and Smith, 2006). The effect of sampling site might contribute to the difference. In this study, we collected biological samples from grassland, not the streamside wetland, where spiders mostly feed on little flying bugs like mosquito with the high potential abilities to enrich mercury from the ambient (Harding et al., 2006).

Compared with other predators, THg in spiders were comparatively low. For example, THg in mantis in Huludao City was 226.5 ng/g (Zheng et al., 2008). There were two possible reasons. One is spiders' living habits

Table 2 THg concentration in soil, plant, grasshopper and spider (unit: mg/kg)

Site	Soil	Plant	Grasshopper		Spider
			Locusta migratoria manilensis	*Acrida chinensis*	
S1	0.814	0.056	0.081	0.044	–
S2	0.694	0.057	0.080	0.172	–
S3	3.211	0.146	0.252	0.232	–
S4	5.056	0.057	0.037	0.013	0.091
S5	0.432	0.085	0.022	0.161	0.158
S6	3.254	0.054	0.129	0.324	0.160
S7	15.857	1.011	0.346	0.399	0.143
S8	–	0.058	0.015	0.039	0.078
S9	0.152	0.001	0.046	0.082	0.017
S10	0.395	0.029	0.042	0.060	–
S11	10.743	0.061	–	0.110	0.244
Mean	4.355	0.151	0.119	0.167	0.134

differing with mantis. Spiders do not eat the outer skins of victim; only convert guts of victim to fluid using their special digestive enzyme for food intake. But mantis eats almost everything of victim. Some researches have indicated that the furs, feathers, nails and shells of animals had commonly high mercury levels (Becker et al., 1994; Mierle et al., 2000; Jones and Holladay, 2006; Mergler et al., 2007). In this study, the wings had the highest THg concentrations among different organs of grasshoppers. This special food intake habit of spiders might enable them to avoid high mercury exposure. The other possible reason is that the food intake amount of spiders is much less than that of mantises. Spiders can survive from hunger for several months after food intake once.

In the light of average THg concentrations in grasshoppers and spiders, bioaccumulation factors were in the range of 0.80–1.13 with the average of 0.96. It suggested that THg concentrations in spiders were at the same levels as that in grasshoppers. THg was not enriched significantly in spiders up the food chain although the bioaccumulation factors varied with the sample sites largely.

THg bioaccumulation factors of each stage up the soil-plant-grasshopper-spiders food chain were 0.03, 0.79–1.11 and 0.80–1.13, respectively. It suggested that THg was not biomagnified obviously up the food chain in grassland in summer. In aquatic system, mercury was highly enriched in some carnivorous fish, THg concentrations in fish were usually thousands of times THg in water. But THg bioaccumulation factors in soil-plant-grasshopper-spider was much lower than those in the aquatic ecosystem, which indicated different fates of mercury in various ecosystems.

3 Conclusions

Mercury pollution in Huludao City was serious. In the light of the spatial distribution characteristics of THg in the soil, there were two mercury sources: the chlor-alkali plant and the two zinc smelteries. THg concentrations in plant leaves, *L. migratoria manilensis*, *A. chinensis* and spider were 0.151, 0.119, 0.167 and 0.134 mg/kg, respectively. Among different organs of grasshoppers, the highest THg concentration was found in their wings. In light of the transportation of mercury up the soil-plant-grasshopper-spider food chain, the bioaccumulation factors were 0.03, 0.79–1.11 and 0.80–1.13 in each stage respectively. It suggested that mercury biomagnification in terrestrial food chains was not as large and obvious as that in aquatic food chain.

Acknowledgments

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