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Bioaccumulation of Total and Methyl Mercury by Arthropods

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Abstract Three arthropods, *Locusta migratoria manilensis*, *Acrida chinensis*, and *Paraten-odera sinensis* were selected to study the bioaccumulation of total and methyl mercury. Concentrations of total mercury in the tissues of *Locusta migratoria manilensis* and *Acrida chinensis* were 0.013–0.154 and 0.009–0.138 mg/kg, respectively, while those of methylmercury were 0.001–0.012 and 0.001–0.006 mg/kg, respectively. Concentrations of total mercury in *Locusta migratoria manilensis* and *Acrida chinensis*, which are the primary consumers, are lower than those in their food, while mercury is accumulated more by the secondary consumer, *Paraten-odera sinensis*. For total mercury, the concentrations in *Locusta migratoria manilensis* are inversely proportional to body length and those in *Acrida chinensis* increase first and then decrease with increased body length. For methyl mercury, concentration is proportional to body length for both of these arthropods. Total mercury concentrations vary in different parts of the arthropod body, and increase in the order of: abdomen > thorax > head.

Keywords Arthropod · Mercury · Methylmercury · Food chain

Inorganic mercury may be transformed to more poisonous organic mercury by microorganisms which can result in the poisoning of wild animals and humans through the food chain. Some studies indicate that humans can be exposed to mercury and methylmercury by consuming contaminated fish (Zhang et al. 2005; Horvat et al. 2003; Wang et al. 2002). Recently, mercury accumulation in terrestrial food chains has been investigated. Mercury and methylmercury concentrations in rice from Guizhou Province, China, were 0.569 mg/kg and 0.145 mg/kg, respectively. Therefore, the inhabitants may be exposed to mercury by consuming dietary rice (Horvat et al. 2003). Ecological exposure has been reported in many instances. Wang et al. (2005) reported mercury and methylmercury were accumulated significantly by *Rana chensinensis* in an area impacted by gold mining. Tremblay et al. (1998) observed that the concentrations of mercury and methylmercury in eclosion insects in reservoirs were 0.14–1.50 mg/kg and 0.035–0.80 mg/kg, respectively, and may be transferred to fish via the food chain. Hsu et al. (2006) found that mercury concentrations in snails were 47.1 mg/kg.

Locusta migratoria manilensis and *Acrida chinensis* are primary consumers and representatives of common arthropods in grassland ecosystems. Their preferred foods are *Echinochloa crusgall*, *Phragmites australis*, and *Setaria virdis*. They can be preyed upon by other insectivorous vertebrates and arthropods, such as *Paraten-odera sinensis*. These two species can accumulate mercury which might be transferred to high trophic levels through the food chain and finally poison human receptors. For example, Devkonta et al. (2000) investigated bioaccumulation of mercury in *Locusta migratoria manilensis* in Taifetos Mountain, Germany. So far, little is known about mercury uptake by arthropods in contaminated areas and the contribution of diet to the accumulation. More studies are needed to better understand mercury uptake and biomagnification processes in grassland ecosystems. Therefore, the

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primary objective of this study is to investigate mercury accumulation and transference in the plant–arthropod–predator food chain in a mercury-contaminated area.

Materials and Methods

Huludao City is an important non-ferrous smelting and chemical industry area in northeast China. Wuli River and Cishan River are two main rivers in the city. In the past few decades, water contaminated with heavy metals has been discharged into the Wuli and Cishan Rivers by a chlor-alkali plant and zinc smeltery, respectively. The latter river has also been impacted by the dry deposition of metal-contaminated particulate matter from the zinc smeltery.

In the present study, the grasslands near those two river channels were selected to investigate mercury accumulation in the arthropods. Seven sample sites along the Wuli River were selected: Huafei Bridge, Huagong Bridge, Huaji Bridge, Longwan Bridge, Yuhuang Bridge, the North bridge of Cishan and the sewage treatment plant. Two sample sites along the Cishan river were selected: the South bridge of Cishan and the privately-owned zinc smeltery (Fig. 1).

Locusta migratoria manilensis and *Acrida chinensis* were collected, euthanized with alcohol and preserved in a refrigerator at 4°C until used. Three plants, *Echinochloa Crusgall*, *Phragmites australis*, and *Setaria viridis*, were sampled at the same sites and stored in polythene bags. The leaves of those three species were washed with deionised water to remove mercury attached on the surface, dried at room temperature and preserved in polythene bags after being ground to a homogenous powder. Soil samples were collected, dried at room temperature, and ground to pass through an 80-mesh nylon sieve. Some *Locusta migratoria manilensis*, plants and soil samples were collected from clean grassland sites for experimental controls.

Total mercury in soil and plants was extracted following the method of H_2SO_4-HNO_3-V_2O_5 (Rasmussen et al. 1991). All speciation of Hg in samples were converted to Hg^{2+}, and then Hg^{2+} was reduced to elemental Hg by addition of 20% $SnCl_2$ solution. Cold atomic absorption technique was used to determine the concentrations of total Hg with a F732-V Hg detector with a detection limit of 5×10^{-2} ng/g (Liu et al. 2003; Li et al. 2006). The arthropod samples were digested by the same method and analyzed by a Terkram-2600 with a detection limit of 5×10^{-6} ng/g.

Methylmercury was extracted from the arthropods following the procedure described in Liu et al. (2003) and Jin et al. (1997). A portion of the arthropod samples (1.00–2.00 g) was placed into 100 mL acid-washed beakers followed by addition of 50 mL of 2 M HCl and 1 mL of 1% $CuSO_4$ solution. The solution was filtered after 10 min of shaking. The pH value of filtrate was adjusted to 3–4 by 2 M HCl or 6 M NaOH solution, and then the sample filtered one more time to remove the residues. The filtrate was passed through a sulfhydryl cotton tube which was filled with 0.1 g cotton at a rate of 5 mL/min. Then the methylmercury in the cotton was eluted by 1 mL of 2 M HCl solution, which was repeated two more times with additional 2 mL portions of the solvent. Methylmercury in the elution was extracted with benzene and analyzed by gas chromatography with electron capture detection (GC-ECD) with a detection limit of 1×10^{-4} ng/g.

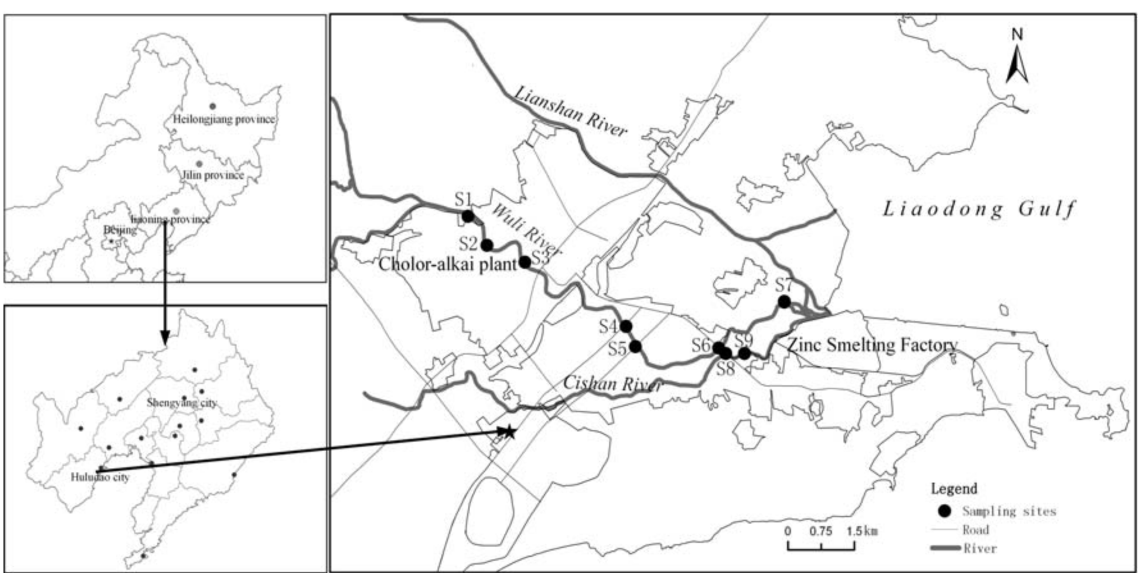

Fig. 1 Map of sampling sites. S1, Huafei bridge; S2, Huagong bridge; S3, Huaji bridge; S4, Longwan bridge; S5, Yuhuang bridge; S6, the North bridge of Cishan; S7, Sewage treatment plant; S8, the South bridge of Cishan; S9, privately owned Zinc smeltery

Precision and accuracy of the analytical method were evaluated by comparing the expected total mercury concentrations in certified reference materials to the measured values. The expected and measured concentrations in plant reference (GBW-07604) were 0.026 ± 0.003 and 0.027 ± 0.001 mg/kg, respectively, in the hair reference (GBW-07601) were 0.36 ± 0.05 and 0.40 ± 0.01 mg/kg, respectively, and in reference material IAEA-443 were 0.17 ± 0.07 and 0.15 ± 0.03 mg/kg, respectively. The average recovery rate of methlymercury was 91.4%.

SPSS 10.0 for Windows and Excel 2003 were used for data analysis. Pearson's correlation coefficients for mercury concentrations in different tissues of the arthropods were calculated by SPSS 10.0 for Windows.

Results and Discussion

Total mercury concentrations of *Locusta migratoria manilensis* and *Acrida chinensis* varied from 0.013 to 0.154 mg/kg (mean, 0.043 mg/kg) and from 0.009 to 0.138 mg/kg (mean, 0.037 mg/kg), respectively. Based on the average concentrations, *Locusta migratoria manilensis* accumulated more mercury than *Acrida chinensis* (Fig. 2). Total mercury concentrations in *Paraten-odera sinensis* (the secondary consumer) were higher than those in *Locusta migratoria manilensis* and *Acrida chinensis* (the primary consumers).

Methylmercury concentrations in *Locusta migratoria manilensis* varied from 0.001 to 0.012 mg/kg (mean, 0.007 mg/kg) and ratios of the methylmercury to total mercury varied from 0.07 to 0.40 mg/kg. For *Acrida chinensis*, methylmercury concentrations varied from 0.001 to 0.006 mg/kg (mean, 0.003 mg/kg) and methylmercury was about 10.5%–29.4% of total mercury (Table 1). The concentrations of both total mercury and methylmercury in

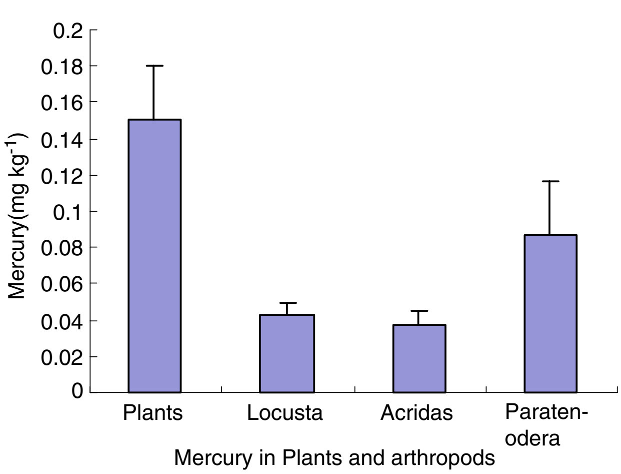

Fig. 2 Mercury contents in plants and arthropods in non-ferrous and chemical industry zones

Locusta migratoria manilensis were higher than those in the controls (0.003 mg/kg), indicating that the arthropods in non-ferrous smelting and chemical industry zones accumulate more mercury. Total mercury and methylmercury concentrations in arthropods were different at the different sites (Table 1). Total mercury concentrations in *Locusta migratoria manilensis* and *Acrida chinensis* increased gradually by site from S1 to S6. In the Cishan River watershed, total mercury concentrations in arthropods in S8 were slightly higher than those in S9. However, there was no obvious spatial pattern for methylmercury.

Figures 3 and 4 illustrate the relationship between total mercury concentration and body length. The accumulation of total mercury by *Locusta migratoria manilensis* decreased with an increase in body length, while for *Acrida chinensis*, the concentrations in tissue increased first and then declined with body length suggesting that mercury assimilation rates might decrease with organism growth for this species. Methylmercury concentrations increased with the growth of arthropods which shows that methylmercury has potential to be accumulated in tissues (Figs. 3 and 4).

Arthropods were dissected into three parts: head, thorax, and abdomen (General Zoology, 1978). Total mercury concentrations were analyzed separately in these three parts and were found to increase in the order of: abdomen > thorax > head (Fig. 5). This result might be attributed to the difference of metabolism processing in different areas of the body.

A significant linear relationship was found between total mercury concentrations in thoraxes and abdomens of *Locusta migratoria manilensis* with different body lengths. No correlations were observed between total mercury concentrations in heads and thoraxes or abdomens possibly due to the inner structure of *Locusta migratoria manilensis* (Table 2). Craw, chewing stomach, and intestine are in the thorax and abdomen, and the high concentrations of total mercury in these two parts suggests that uptake from the diet is the dominant pathway for mercury accumulation in arthropods.

Mercury pollution is heavy in areas with non-ferrous smelting and chemical industry in Huludao city (Wang et al. 2005; Zhao et al. 1997). As discussed above, Wuli River is contaminated due to the discharge of waste water from a chlor-alkali plant. Total mercury concentrations in surface sediments were from 0.254 to 86.303 mg/kg (mean, 13.846 mg/kg). Total mercury concentrations in surface sediments of the Cishan River, which received waste water from a zinc smeltery, varied from 0.077 to 132.521 mg/kg (mean, 28.709 mg/kg). Mercury concentrations in the soil and plants from different sites are shown in Table 3. Total mercury concentrations in plant leaves varied from 0.057 to 0.494 mg/kg (mean, 0.164 mg/kg), which were much higher than those in *Locusta migratoria*

Table 1 Mercury and methylmercury concentrations in arthropods

Sampling sites	Arthropod sample species	n	Total mercury (mg/kg)	n	Methyl-mercury (mg/kg)	Methyl-mercury/ mercury (%)
S1	*Locusta migratoria manilensis*	8	0.020	8	0.008	40.0
	Acrida chinensis	5	0.017	4	0.005	29.4
S2	*Locusta migratoria manilensis*	9	0.040	4	0.008	20.0
	Acrida chinensis	5	0.019	5	0.002	10.5
	Paraten-odera sinensis	4	0.057			
S3	*Locusta migratoria manilensis*	4	0.043	5	0.003	7.0
S4	*Locusta migratoria manilensis*	12	0.033	6	0.006	18.2
	Acrida chinensis	11	0.046	4	0.006	13.0
	Paraten-odera sinensis	4	0.117			
S5	*Locusta migratoria manilensis*	5	0.053	5	0.011	20.8
	Acrida chinensis	5	0.122	4	0.006	4.9
S6	*Locusta migratoria manilensis*	12	0.064	5	0.002	3.1
S7	*Locusta migratoria manilensis*	12	0.039			
	Acrida chinensis	16	0.035	4	0.003	8.7
S8	*Locusta migratoria manilensis*	5	0.037			
	Acrida chinensis	4	0.023	5	0.002	8.7
S9y	*Locusta migratoria manilensis*	5	0.024			
	Acrida chinensis	23	0.022	7	0.002	8.7
Contrasts	*Locusta migratoria manilensis*	9	0.003		–	

"–", out of determination limit

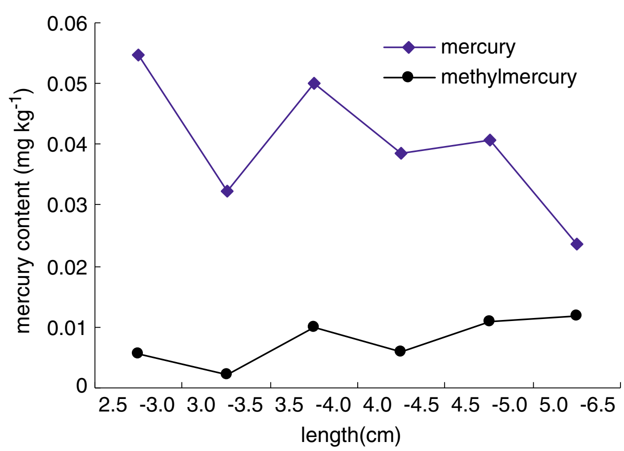

Fig. 3 Relationship between *Locusta migratoria manilensis* body lengths and mercury contents

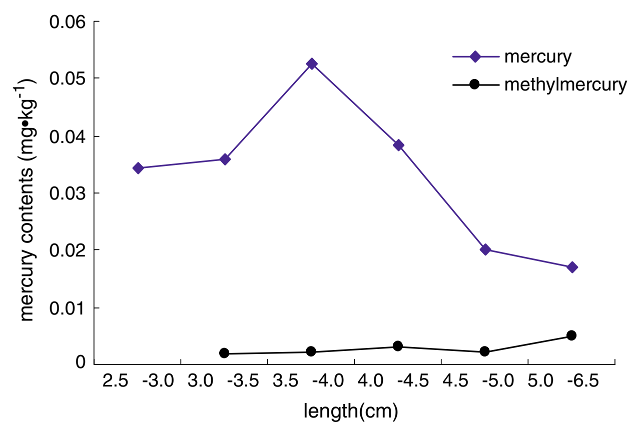

Fig. 4 Relationship between *Acrida chinensis* body lengths and mercury contents

manilensis and *Acrida chinensis* (Fig. 2). Total mercury concentrations in the soil and plants from sites S6, S8, S7, and S9 were higher than elsewhere. Although the mercury concentrations in arthropods also increased at those sites, they were lower than those in plant leaves (Table 3).

Mercury can be accumulated in *Locusta migratoria manilensis* and *Acrida chinensis* (Table 4). In non- or less-contaminated sites, total mercury concentrations in *Locuta migratoria manilensis* and *Acrida chinensis* were higher than those in the plants, demonstrating that mercury can be accumulated in the arthropods.

Devkota et al. (2000) reported that bioaccumulation factors for mercury in arthropods from Taigetos Mountain, Germany were greater than 1.0. Our results are broadly consistent with this observation. In the present study, the only source of mercury at the control sites was dry deposition which resulted in lower total mercury concentrations in plants at those sites. Although total mercury concentrations in *Locusta migratoria manilensis* and *Acrida chinensis* were relatively high in Huludao City, the accumulation factors are less than 1.0 for both species. Total mercury concentrations in arthropods are proportional to

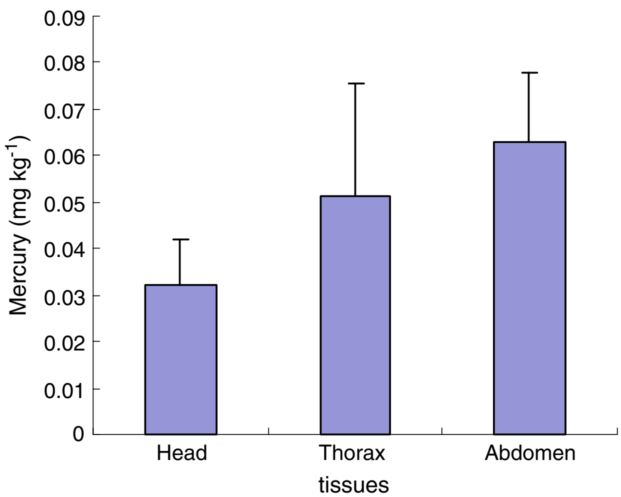

Fig. 5 Mercury contents in different tissues of *Locusta migratoria manilensis*

Table 2 Pearson's correlation coefficients of mercury concentrations in different tissues of *Locusta migratoria manilensis*

Tissues	Head	Thorax	Abdomen
Head	1.000		
Thorax	0.134	1.000	
Abdomen	0.322	0.697*	1.000

* $p < 0.05$

Table 3 Mercury concentrations in soil and plant samples (mg/kg)

	S1	S2	S3	S4	S6	S7	S8	S9
Soil	0.556	2.332	25.404	13.389	18.82	11.867	9.482	12.218
Plant	0.057	0.091	0.184	0.100	0.176	0.073	0.494	0.138

those in plants and decreased with their body lengths within a certain range (Fig. 3 and 4). The mercury accumulation factor for the insectivorous *Paraten-odera sinensis* is more than 1.0, indicating that mercury can also be easily accumulated by this species. Ratios of methylmercury to total mercury in *Locusta migratoria manilensis* and *Acrida chinensis* shows that the concentrations of methylmercury are relatively high at the sites S1 and S2 and lower at the sites S6, S8, S7, and S9 (Table 1). Ratios of methylmercury to total mercury concentrations in arthropods were much higher than those in the soil (Qiu et al. 2006) and sediment (Shi et al. 2005) which demonstrated that methylmercury is bioaccumulated in the organisms. Thus, we conclude that mercury pollution in arthropods is a problem in these combined non-ferrous smelting and chemical industry zones. This is a concern since mercury could advance through food chains via birds and fowls and ultimately poison human populations.

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Revision List

Fortified sample recoveries are reported (No)

Three reference materials were used to control the precision and accuracy. GBW-07604 and GBW-07601 were used to test the total mercury in plants and insects, respectively. IAEA-443 was used to test the methylmercury in insects. The results listed in the "Materials and Methods" part showed that the methods used in the detection were appropriate and the results were reliable.

Considering the matter difference between insects and hair, additional experiments were taken to test the methylmercury recovery. Standard methylmercury solution (CH_3HgCl) was added into the insect samples at the same time when insects were immerged by the 2 M HCl to control the accuracy. Five insect samples were tested and the recovery rate of methlymercury were 88.3%, 89.4%, 91.2%, 93.7%, and 94.5% and the average value was 91.4%.

Table 4 Mercury accumulation factors in different sites

	Plant leaf /soil	*Locusta migratoria manilensis*/plant	*Acrida chinensis*/ plant	*Paraten-odera sinensis*/ *Locusta or Acrida chinensis*
S1	0.126	0.351	0.298	
S2	0.039	0.440	0.528	2.780
S3	0.007	0.330	0.460	
S4	0.007	0.364	0.057	3.000
S6	0.009	0.364	0.057	
S7	0.006	0.534	0.479	
S8	0.052	0.075	0.047	
S9	0.011	0.174	0.159	
Mean	0.013	0.249	0.184	
Contrasts	0.021	1.5		

References

Devkota B, Schmidt GH (2000) Accumulation of heavy metals in food plants and grasshoppers from the Taigetos Mountains, Germany. Agric Ecosyst Environ 78:85–91

Horvat M, Nolde N, Fajon V, Jereb V, Logar M, Lojen S, Jacimovic R, Falnoga I, Qu LY, 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

Hsu MJ, Selvaraj K, Agoramoorthy G (2006) Taiwan's industrial heavy metals pollution threatens terrestrial biota. Environ Pollut 143:327–334

Jin LJ, Guo P, Xu XQ (1997) Effect of selenium on mercury methylation in anaerobic lake sediments. Bull Environ Contam Toxicol 74:980–987

Liu RH, Wang QC, Lu XG, Fang FM, Wang Y (2003) Distribution and speciation of mercury in the peat bog of Xiaoxing'an Mountain, Northeastern China. Environ Pollut 124:36–46

Li ZB, Wang QC, Luo YM (2006) Exposure of the urban population to mercury in Changchun city, Northeast China. Environ Geochem Health 28:61–66

Qiu GL, Feng XB, Wang SF, Shang LH (2006) Total mercury and methylmercury in soils collected from Guizhou Hg-Mined areas (in Chinese). Environ Sci 27:550–555

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

Shi JB, Liang LN, Yuan CG, He H, Jiang GB (2005) Methylmercury and total mercury in sediments collected from the East China Sea. Bull Environ Contam Toxicol 74:980–987

Tremblay A, Cloutier L, Lucotte M (1998) Total mercury and methylmercury fluxes via emerging insects in recently flooded hydroelectric reservoirs and a natural lade. Sci Total Environ 219:209–221

Wang N, Zhu YM, Piao MY, Dong D (2005) Mercury pollution in Rana Chensinensis in Weisha River reach, in the upstream region of Songhua river. Chin Sci Bull 50:2166–2170

Wang QC, Yan BX, Zhang SQ, Zhang L, Li HW, Shao ZG (2005) Distribution characteristics of mercury in the region contaminated by Zinc smelting and chlor-alkali production. Expended Abstract XIII. International conference on heavy metals in environment, June 5–9: pp 492–495

Wang QC, Liu RH, Lu XG, Li ZB (2002) Progress of study on the mercury process in the wetland environment (in Chinese). Adv Earth Sci 17:881–885

Wuhan University, Nanjing University, Beijing Educational University (1978) General Zoology. People's Education Press, Beijing, China

Zhang L, Wang QC, Shao ZG (2005) Mercury contamination of fish in the Di'er Songhua river of China: the present station and evolution law (in Chinese). Ecol Environ 14:190–194

Zhao LD, Yan HF (1997) Mercury pollution of soil and assessment in the Wuli river coast of Huludao city (in Chinese). Chin J Soil Sci 28:68–70