Accumulation, transfer and environmental risk of soil mercury in a rapidly industrializing region of the Yangtze River Delta, China

Biao Huang[A], Mei Wang[A], Weixia Sun[A] and Yongcun Zhao[A]

[A]Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China, Email bhuang@issas.ac.cn, mwang@issas.ac.cn, wxsun@issas.ac.cn, yczhao@issas.ac.cn

Abstract
Mercury (Hg) accumulation and transfer in soil-plant ecosystems have increased concern. A region at county level under rapid industrialization and intensive agricultural activities in the Yangtze River Delta of China and a factory with Hg-containing wastewater discharge within the region were selected to study the accumulation and transfer of Hg from different sources in soils and crops. The results showed significant Hg accumulations in soils away from factories and enhancement of mobile HCl-extractable Hg concentrations in the soils close to factories due related to soil pH and organic matter. Soil and crop Hg accumulations around the factory were localized and exponentially decreased with distance away from the discharge outlet. Considering the cessation of Hg-containing agrochemicals and limitation of effects of industrial activities on Hg accumulation, more attention should be paid to changing in soil properties and crop rotations because the current risk is mobilization of accumulated soil Hg.

Key words
Soil mercury bioavailability, spatial variability, agricultural and industrial sources, soil-crop ecosystem.

Introduction
With economic and industrial development, increased loading of mercury (Hg) in the environment and the potential public health risk associated with dietary intake have increasingly become a concern. Although the Chinese government has forbidden the use of Hg-containing fertilizer and pesticides since the 1970s, industrial discharges might aggravate the environmental potential threat of soil Hg accumulation and complicate the tracing of environmental Hg sources due to rapid industrialization in recent decades.

Most underlying studies related to Hg accumulation and soil-crop transfer were concentrated on the areas where Hg mainly originated from the atmosphere. However, waste effluent from certain types of factories may also cause Hg accumulation and transfer. With rapid urbanization and industrialization in the Yangtze River Delta, a lot of factories were built up and scattered in agricultural lands. Meanwhile, intensive farming was conducted due to the demands for agricultural products from this urban area. The degree and the extent of Hg accumulation in soil and crops under such complicated situations remain unclear. The specific objectives of this study are: (1) to investigate the distribution of soil Hg in the Zhangjiagang County area, Yangtze River Delta of China; (2) to evaluate and characterize the spatial distribution and transfer of Hg in soil-crops around the factory, a point source of Hg; and (3) to reveal and assess the potential Hg contamination threat to the environment.

Materials and methods
Study area
The study area, Zhangjiagang County, is situated on a flat alluvial plain in the Yangtze River Delta. The main soil types can be divided into two soil orders, Anthrosols (Inceptisols) and Cambosols (Entisols). The rotation of rice and wheat has been the dominant planting system, though historically cotton-wheat was more common on Cambosols. Historically, Hg-containing pesticides had been used for cotton and rice planting in this area. Since the 1980s, Zhangjiagang County has become one of the quickest economically developing areas in the Yangtze River Delta region, and industry mainly flourishes including metallurgical, chemical, electroplating, printing and dyeing, paper-making, etc.

Sample collection and preparation
Within the county, a total of 547 samples of the topsoil (0-20 cm) were collected, of which 386 samples were randomly collected on agricultural land away from the factories throughout the county based on soil types, land use, spatial homogeneity. 161 samples were also collected on agricultural land at ca. 50-100 m from waste discharging factories. An intensive sampling, including soil and crop sampling, was conducted around

the factory with the highest soil T-Hg in order to evaluate the effect of increased Hg in soil on spatial distribution of Hg in soil and crop Hg uptake. Soil basic properties such as soil pH and organic matter (OM), 1 M HCl-extractable Hg (HCl-Hg) and Total Hg (T-Hg) in soils, and Hg in rice and wheat were examined. The Hg fractionation of soils from profile horizons was analyzed for evaluating detailed information on the mobility of Hg in samples.

Results

Distribution of regional soil Hg and soil properties

Soil T-Hg in the Cambosols was greater than that of Anthrosols ($p < 0.05$) (Table 1), which also shows the frequency and spatial distribution patterns of soil T-Hg. Interestingly, two frequency peaks of soil T-Hg are evident with each respective soil order, in particular, Cambosols. Sampling locations also influenced the soil T-Hg concentrations significantly. The average soil T-Hg concentration for sampling sites far away from the factories was significantly higher ($p<0.05$) than that of sites close to the factories(Table 1). But, the highest levels of soil T-Hg appeared in the sites close to the factory, where we sampled intensively.

With soil T-Hg, soil order had a significant effect on HCl-Hg, resulting in a lower soil HCl-Hg in Cambosols than that in Anthrosols. However, without soil T-Hg, the HCl-Hg for sampling sites close to factories was significantly greater than that of the sites away from factories ($p<0.05$).

Table 1. Hg contents in surface soils classified by soil orders and sampling site

	No.	Available Hg (μg/kg)	No.	Total Hg (μg/kg)	SOM (g/kg)	pH
Cambosols	37	35.7a	353	125a	19.40a	7.63b
Anthrosols	16	46.6b	194	167b	25.17b	7.00a
Away from factories	31	32.4a	359	149b	20.98a	7.67b
Close to factories	22	48.1b	188	121a	22.32b	6.91a

Distribution of soil and crop Hg close to factory

In the spatial context, the highest T-Hg and HCl-Hg concentrations were found near the wastewater outlet (about 50 m away from the outlet) and then the T-Hg and HCl-Hg exponentially decreased as distance from the outlet increased.

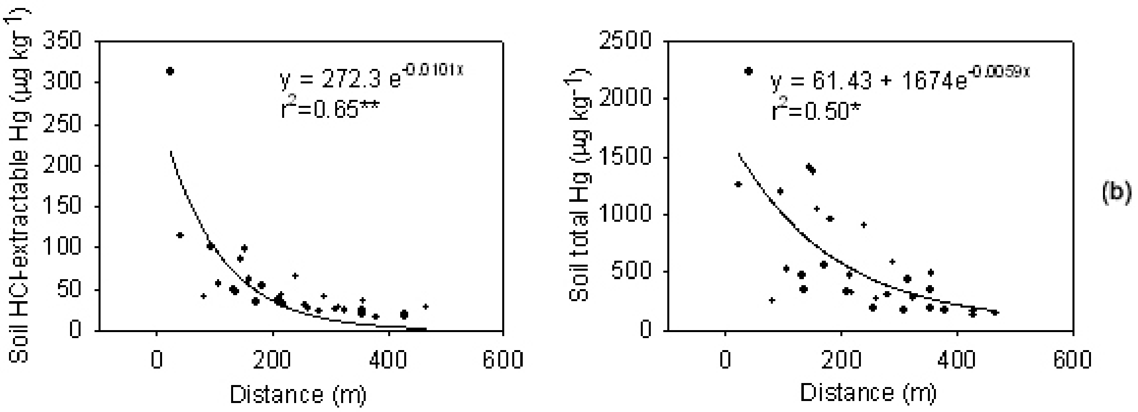

Figure 1. Soil Hg distribution in surface soil around the factory (a) and the soil Hg variability with the distance from the wastewater outlet

In the soil profile near the outlet, the uppermost soil horizon (0-15 cm) had high T-Hg and HCl-Hg concentrations. Total Hg concentrations reached a peak at the 10-15 cm depth (2711 μg/kg), and then rapidly decreased with depth. Lowest T-Hg concentration (94 μg/kg) was below 50 cm in the profile. Likewise, the HCl-Hg concentrations reached a peak at 10-15 cm deep (115 μg/kg) and then decreased with increasing depth. Lowest HCl-Hg concentration (24 μg/kg) was below 50 cm in the profile. The surface soil of the profile nearby the outlet had higher the percentages of mobile and semi-mobile Hg fractions relative T-Hg than those of to profiles away from the outlet. Hg concentrations in rice grain were nearly 5 times higher than those in wheat grain. There were variable trends in distribution between wheat and rice Hg for plants in close proximity to the wastewater outlet. For rice, the high Hg concentrations (above 15 μg/kg) were found within 200 m from the wastewater outlet, and Hg concentrations in rice exponentially decreased with the distance from the outlet. No such a trend was found for uptake of Hg by wheat.

Discussion and conclusions

Regional risk assessment of soil Hg

Compared to the critical value of Chinese Environmental Quality Standards for Soil (CEQS), no soil T-Hg concentrations exceeded the second most stringent critical value (500 μg/kg when pH>6.5) in the Cambosols area, while soil Hg at 6 sampling sites in the acidic Anthrosols area exceeded the critical value of CEQS (300 μg/kg when pH<6.5), among which 5 of 6 sites was located in the sites away from factories and the other one was the site close to the chemical factory, where we did intensive sampling. Because of the historically wide uses of Hg-containing pesticides for cotton and rice planting in the county, it could be inferred that the accumulation of soil Hg probably originated mainly from agricultural activities. As for industrial sources of soil Hg accumulation, the influences might be only localized, which is verified by a lower soil T-Hg at the sites close to factories than the sites away from factories (Table 1) despite a very high level of soil T-Hg that was found close to the factory's wastewater outlet.

Although the Hg-containing pesticides have been prohibited for production and use since the 1970s in China and the risk of Hg accumulation in the county is very limited, it should be noted that the changes of soil properties such as soil pH and OM in the studied area may increase the environmental risk. A stepwise regression of soil HCl-Hg against soil T-Hg, pH, and OM has confirmed that the r^2 (0.38) of the stepwise regression had a significant increase compared to the r^2 (0.27) of the regression between soil HCl-Hg and T-Hg, which indicates that available HCl-Hg could increase with decreasing soil pH and increasing soil OM, even though the soil T-Hg is not changed. Hence, when the soil use conversion is conducted, soil pH and HCl-Hg should be monitored.

Risk assessment of soil Hg accumulation by industrial activities

Exponential decreases of soil Hg with distance from the outlet indicated that the accumulation range was limited spatially. However, the accumulated levels of soil T-Hg and HCl-Hg was so high that some of the rice Hg concentrations were over the critical value of Hg in crops (20 μg Hg/kg) according to the maximum allowable levels of contaminants in foods (MALCF) of China (GB2762-2005). Therefore, effective measurements should be conducted to reduce Hg in the wastewater and control discharges to the surface water.

Risk assessment of crop Hg

The wheat samples did not exceed the MALCF level. However, 2 out of 15 rice samples exceeded the MALCF, indicating some Hg pollution in rice. Concentrations of Hg in rice grain were 5 times as high as wheat grain, suggesting a stronger Hg uptake by rice than wheat, which may be attributed to reduction of soil under water logged conditions during rice growing, which increased the availability of Hg, and, consequently, the uptake by rice or direct Hg uptake from wastewater.

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