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Detailed Pollution Map of an Area Highly Contaminated by Mercury Containing Wastewater from an Organic Chemical Factory in People's Republic of China

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Farmland in the southern suburb of Qingzhen City in Guizhou Province, China was polluted by irrigation with mercury-containing river water derived from the Guizhou Organic Chemical Factory. Previously we reported that mercury accumulated in the soil amounted to 35 tons, including 25 kg of methylmercury (Yasuda et al., 2004; Matsuyama et al., 2004). Especially, the area around the factory such as Shanbeihou, Qinglong and Xinzhai are seriously polluted by mercury, with approximately 80% of the entire mercury in Qingzhen present there (Yasuda et al., 2004). Among the naturally occurring mercury species, methylmercury is the most hazardous chemical form for human health, especially for the developing fetus. Although most mercury in the soil is present in the inorganic form, it may easily change to methylmercury under the influence of environmental factors such as microorganisms, chemical reaction, sunlight etc. (Beijer et al., 1979). In the Qingzhen suburbs, it is necessary to treat the polluted area using suitable remediation technology to avoid the mercury impact on human health and eco-system, especially in the highly contaminated area. In order to implement successful remediation, a detailed mercury pollution map is necessary. However, the mercury pollution in the Qingzhen suburbs has already been diffused widely (Yasuda et al., 2004). Accordingly, we focused on the highly contaminated area which should be treated for remediation in the first step. In the present study, we reported our detailed pollution map of the high contamination area by applying mesh work (50 m × 50 m) including the results of the chemical condition of mercury in the soil.

MATERIALS AND METHODS

The soil samples for analysis were taken from the highly contaminated area in Qingzhen as is defined by the previous study (Yasuda et al., 2004; Matsuyama et al., 2004). Sampling was done in accordance with the previous study (Yasuda et al., 2004), while changing the mesh width from 100 m x 100 m to 50 m x 50 m to obtain 86 soil samples (Figure 1). After removing small stones and small plant roots by hand, soil sample was mixed by the quarter method to obtain homogeneous soil samples. After measuring the moisture content, the samples were analyzed for mercury concentration and its chemical form without drying. The total mercury concentration was determined by cold vapor atomic absorption

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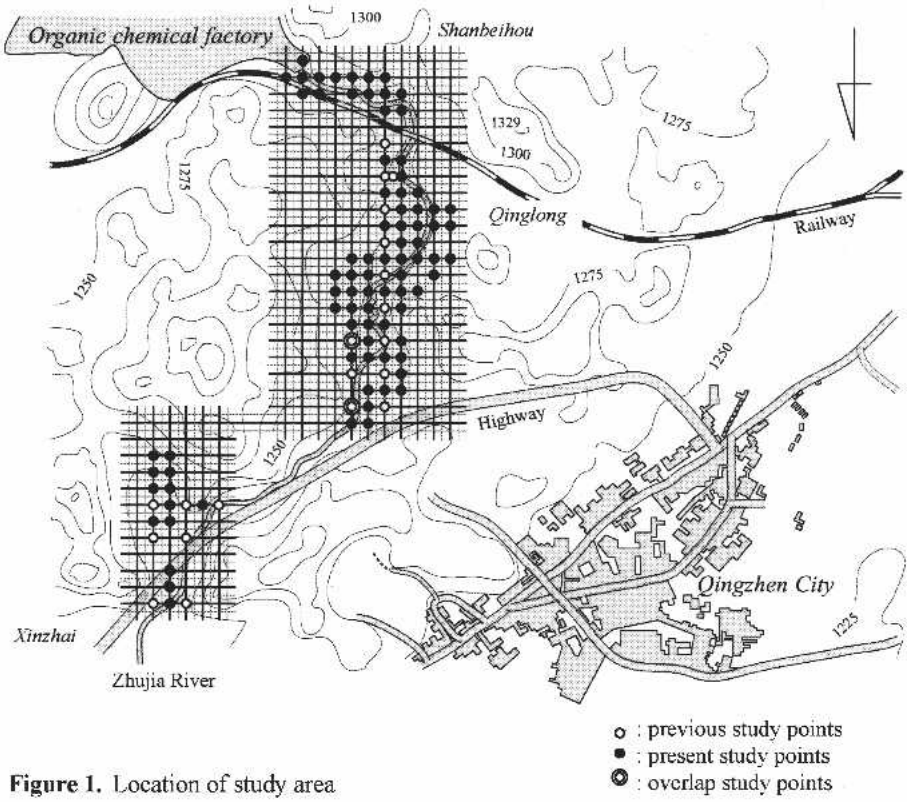

Figure 1. Location of study area

spectrometry (CV-AAS) (Akagi and Nishimura, 1991) as follows. Briefly, 0.5 g or less of soil sample was put into a 50-ml volumetric flask, to which 2 ml of mixture of nitric acid and perchloric acid (1 : 1), 5 ml of sulfuric acid and 1 ml of water were added. The flask was heated at 200 °C for 30 min. After cooling to room temperature, the mixture digested by heating was filled up to 50 ml with distilled water, which was used as the sample for mercury analysis by CV-AAS. The total mercury was measured twice for duplicate determination. To control the quality of measurement, a standard reference material SO-2 (CCR-MP, certified value of total mercury, 0.082 ± 0.009 μg/g) was used. Our qualification data were 0.083 ± 0.001 μg/g (average of 7 repetitions). Methylmercury soil analysis was performed according to the method of Akagi and Nishimura (1991) with some modification as follows. Briefly, about 0.2 g of soil sample was put into a 50-ml centrifuge tube, to which 10 ml of 1N KOH/ethanol was added, and then it was ground with a glass stick, followed by shaking to dissolve methylmercury in the soil sample. Methylmercury in the mixture was then extracted due to addition of purified 0.01% dithizone-toluene solution (5 ml). After the clean-up process for the dithizone-toluene extract, the sample solution thus prepared was subjected to ECD-gas chromatographic measurement (Matsuyama et al., 2004). To control the quality of measurement, a standard reference material CRM-580 (certified methylmercury level of 75.5 ± 3.7 ng/g) was used. Our qualification data were

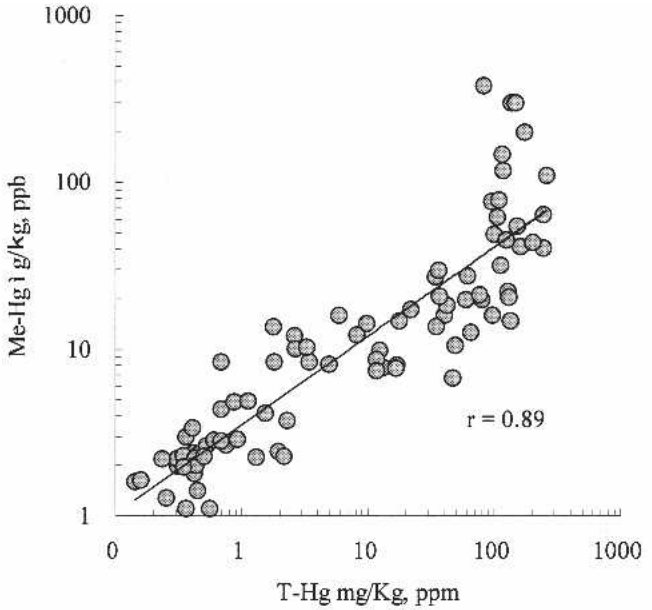

Figure 2. Correlation between total mercury concentration and methylmercury concentration.

Table 1. Comparison of between the previous study and present study about soil characteristics in the high-contaminated area

			N	AV ± SD	(min.-max.)
Present study	Ignition loss	(%)	86	6.87 ± 1.74	(3.25-11.40)
	pH		86	7.29 ± 0.51	(5.90-8.40)
	EC	(mS/cm)	86	0.78 ± 0.56	(0.16-3.04)
	T-Hg	(mg/kg dry wt.)	86	46.97 ± 65.61	(0.14-259.56)
	Me-Hg	(i g/kg dry wt.)	86	31.85 ± 65.57	(1.10-380.25)
	Me-Hg/T-Hg	(% weighted average)	86	0.27 ± 0.29	(0.01-1.24)
	Leached-Hg	(mg/L)	86	0.0010± 0.0014	(ND-0.0068)
Previous study	Ignition loss	(%)	20	6.92 ± 1.70	(3.88-10.10)
	pH		20	7.70 ± 0.48	(6.5-8.3)
	EC	(mS/cm)	20	1.09 ± 1.02	(0.32-3.68)
	T-Hg	(mg/kg dry wt.)	20	61.14 ± 93.00	(0.29-328.95)
	Me-Hg	(i g/kg dry wt.)	20	47.37 ± 65.97	(ND-199.92)
	Me-Hg/T-Hg	(% weighted average)	20	0.15 ± 0.20	(0.02-0.91)
	Leached-Hg	(mg/L)	20	0.0012± 0.0020	(ND-0.0083)

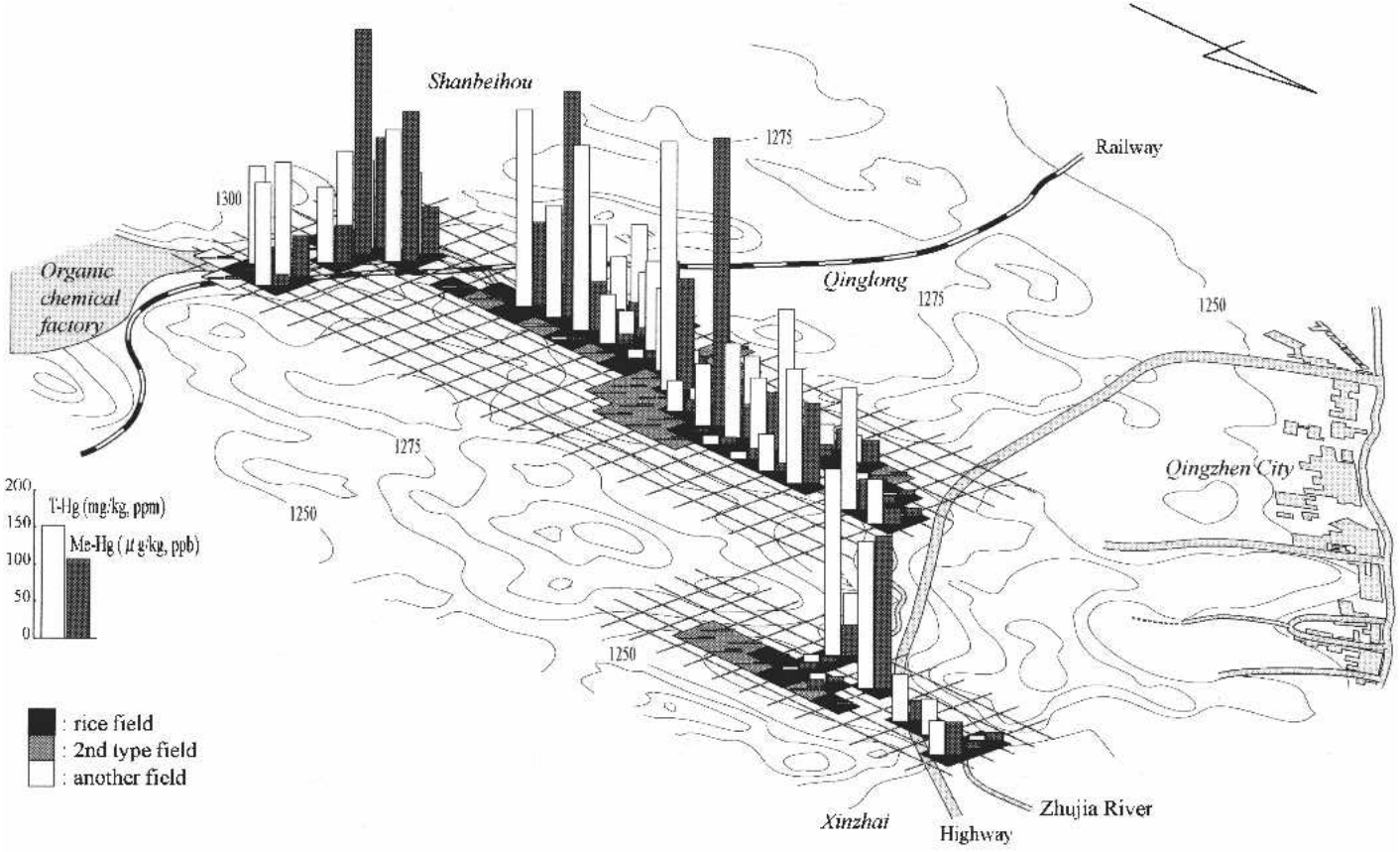

Figure 3. Detailed mercury pollution map of the high contamination area in Qingzhen

71.7 ± 1.3 ng/g (average of 7 repetitions). The leaching test of soil samples was performed according to the Japanese official method (Yasuda et al., 2004). The amounts of organic materials in soils were determined by the Tyurin method (Tyurin, 1936). Electronic conductivity (EC) and pH of soils were measured by the electrode method.

RESULTS AND DISCUSSION

The results of chemical analysis of soils in the high contamination area of Qinzhen are shown in Table 1, in comparison with the previous data (Yasuda et al., 2004; Matsuyama et al., 2004). Mercury concentrations in the present study well fit those in the previous studies (Table 1), except the ratio of the methylmercury concentration to that of the total mercury increased from 0.15% to 0.27%. Since the density of sampling cites increased 4 times from the previous studies, the present results provide a more accurate profile of mercury pollution. The correlation of the total mercury level and the methylmercury level in the soil was shown in Figure 2; the correlation constant was significantly high ($r = 0.89$) and comparable with that of the previous study ($r = 0.89$, Matsuyama et al., 2004). The distribution of mercury deposit obtained in the present study is shown in Figure 3. Obviously, mercury accumulation in the rice field close to the river was much higher than in the fields located at some distance from the stream. One possible reason would be that the river water polluted by mercury had been used for irrigation directly. However, there could be an alternative explanation for the characteristics of mercury distribution. The results of soil analyses in three types of land use shown in Table 2 indicate that a rice has more mercury compared to the other two types of land use. The average total mercury level in the rice field was 69.3 mg/kg, and the average leached total mercury level was 1.4 μg/L. These values are 4.6 and 2.8 times higher than the Japanese regulation for soil mercury (15 mg/kg dry) and leached mercury (0.5 μg/L), respectively. However, the average levels of other types of land use were less than the regulation levels. Although the methylmercury level of the rice field was 16 to 19 times higher than with other land use types, its rate in relation to the total mercury level was lowest (0.16±0.25%) among all types of land use.

Ignition losses and EC in the rice field were higher than in other types or fields (Table 2), suggesting higher organic material contents and accumulated salt in the soil. It has been reported that the mercury methylation in soil are generally correlated with the content and level of organic material in soil (Andersson, 1979). Schuster (1991) reported that the mobility of mercury compounds in soil increased as the concentration of Cl^-, OH^-, F^- etc increased. Therefore, in the case of a rice field, high organic material level and EC values (about 3 times that of the field) would enhance the mobility of mercury, leading to high methylmercury levels. Currently, the rate of methylmercury to total mercury in the rice field is lowest among fields, probably due to the large supply of inorganic mercury by irrigation. However, further methylation of mercury may proceed there in the future. If some treatment will be realized for remediation of the contaminated soil of the Qingzhen suburbs in the near future, the priority of the

treatment plan should be to measure the levels in polluted rice fields.

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