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Relationship Between Leached Total Mercury and Leached Methylmercury from Soil Polluted by Mercury in Wastewater from an Organic Chemical Factory in the People's Republic of China

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Farmland in a suburb of Qingzhen City in Guizhou Province, China was polluted by mercury due to irrigation using river water containing mercury. A Guizhou organic chemical factory located upstream of the river had discarded wastewater containing mercury into the river.

Previously we showed that average mercury concentrations of soil samples collected in the Qingzhen area were as high as 150 times those of the control area (Yasuda et al., 2004). Moreover, Matsuyama et al. (2004) reported a good correlation (r=0.89) between methylmercury and total mercury levels in each soil sample, despite the fact that the concentrations varied significantly among the samples. The stable methyl/total mercury ratios were probably due to a state of the development of equilibrium between mercury methylation and demethylation in the soil.

To accurately the estimate hazardousness level of the leaching portion of mercury, particularly methylmercury, the impact of rainfall or flooding must also be considered, since methylmercury is more hazardous to human health than inorganic mercury. Here, we conducted leaching tests of methylmercury from the soil samples to determine in further detail the level of mercury pollution in the Qingzhen area.

MATERIALS AND METHODS

120 soil samples collected from the Qingzhen area in March and November of 2002 were used in the present study, they were same lot as the one used in a previous study (Yasuda et al., 2003; Matsuyama et al., 2004). Leaching tests of the soil samples were carried out according to the official methods established for environmental evaluations in Japan (Ohtsuka et al., 2003).

The methylmercury analysis basically followed the method of Akagi and Nishimura (1991) with some modification described by Ikingura et al. (1999).

Each 5 g of soil sample was put in a 50 ml screw-capped centrifuge tube to which

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Table 1. Average concentration of leached methylmercury and total mercury ratio in soil

			N	AV	±	SD	(	min.	-	max.	)
Soil	**T-Hg**	mg/kg	120	15.56	±	44.34	(	0.06	-	328.95	)
	Me-Hg	ng/g	120	12.62	±	31.03	(	0.17	-	199.92	)
leaching-Hg	**T-Hg**	μg/L	120	0.46	±	1.07	(	0.04	-	8.28	)
	Me-Hg	ng/L	120	0.99	±	1.05	(	0.09	-	6.42	)
	Me-Hg/T-Hg	%	120	0.63	±	0.91	(	0.02	-	4.91	)

50 ml of distilled water was added. pH of the water was adjusted with HCl or NaOH to 5.8-6.3 when necessary. The sample was agitated using a mechanical shaker for 6 hr and centrifuged at 2500 rpm for 30 min. The supernatant was filtered through a 0.45-μm pore nitrocellulose membrane filter. The extraction process was repeated more than 3 times, after which the filtrates were combined. 100 ml of the filtrate was put into a 200 ml separatory funnel, and mixed with 20N H_2SO_4 (0.5 ml) and 0.5% $KMnO_4$ (0.2 ml). After 5 min, the mixture was neutralized with 10N NaOH (1 ml), then mixed with 10% NH_2OH-HCl (0.2 ml). After 20 min, 10% EDTA-4Na (0.2 ml) and purified 0.01% dithizone-toluene solution (5 ml) were added, followed by shaking for 3 min. Methylmercury in the water sample was extracted to the organic phase. After at least 1 hr, the aqueous solution in the lower layer was discarded.

For clean up, a 4 ml aliquot of dithizone-toluene extract was transferred to a 10 ml grass-stoppered test tube. It was washed twice with 1N NaOH (3 ml) to remove excess dithizone, and methylmercury was then back-extracted with 5 ppm Na_2S in 0.1N NaOH-ethanol 1:1 (2 ml). After shaking and centrifuging, the toluene solution in the upper layer was discarded, and the aqueous solution was the slightly acidified with 1N HCl. The mixture was bubbled with N_2 gas for 5 min to remove sulfide ions as H_2S gas. Walpole's buffer (2 ml) was added to the sample solution, and methylmercury in the mixture was re-extracted by shaking using a purified 0.01% dithizone-toluene solution (0.1 ml). After centrifuging, the aqueous layer was discarded and the dithizone toluene layer was washed with 1N NaOH (3 ml). Once the aqueous solution containing excess dithizone at the lower layer was discarded, a few drop of 1N HCl were added. The toluene solution thus prepared was subjected to ECD-gas chromatographic measurement.

The detection limit of methylmercury using the present method on water samples is around 0.1 ng Hg/L. Since to our knowledge there is no reference material on methylmercury in water samples, the accuracy and precision of this analytical method have been verified through an interlaboratory comparison (Logar et al., 2001). The recovery rates of methylmercury added as methylmercury-L-cysteine from the blank solutions (0.5 and 1.0 ng Hg/L) were 0.48 and 1.13 ng Hg/L, respectively.

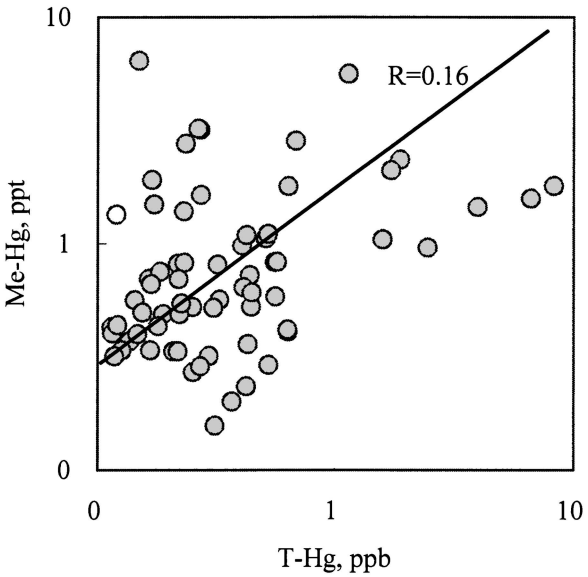

Figure 1. Correlation between leached total mercury concentrations and leached methylmercury concentrations

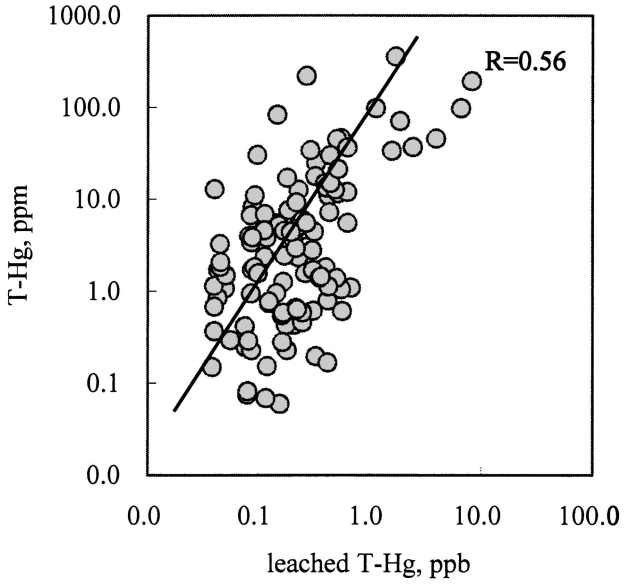

Figure 2. Correlation between leached total mercury concentration from soil and total mercury concentration of soil

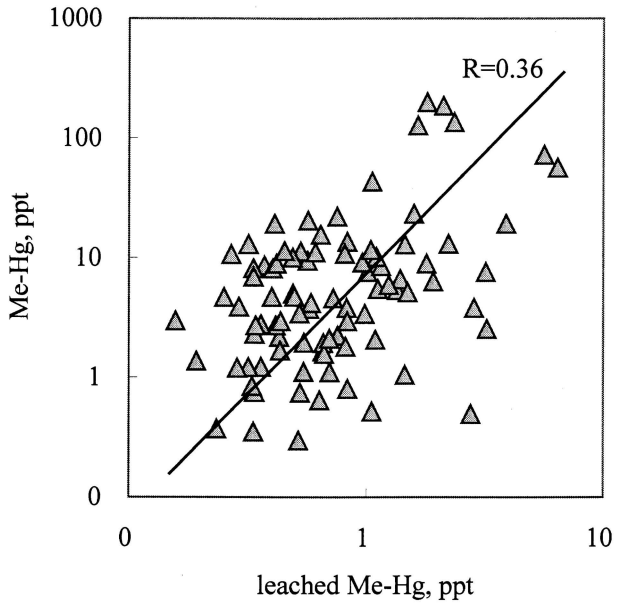

Figure 3. Correlation between leached methylmercury concentration from soil and methylmercury concentration of soil

RESULTS AND DISCUSSION

The analytical data were summarized in Table 1 together with previously reported soil data (Yasuda et al., 2004; Matsuyama et al., 2004). Despite a good correlation (r=0.89) between the total mercury and methylmercury concentrations in soil samples (Matsuyama et al., 2004), the correlation in the leached portion was poor (r=0.16, Figure 1). Moreover, the methylmercury/total mercury ratio in the leached portions varied from 0.02 to 4.91% (0.63±0.91%). These facts suggested that the chemical impacts of soil mercury on leaching are quite different between methyl- and inorganic mercury in the soil samples from different sampling points. On the other hand, the correlation coefficient of total mercury concentrations between the soils and leached portions was r=0.56 (Figure 2). In the case of methylmercury, however, the soil levels and leached portions showed a poor correlation (r=0.36, Figure 3). Since a correlation is considered to be significant when the coefficient is above 0.5 (Ohmura 1985), a considerable portion of the total mercury leached would depend on its soil levels. However, in the case of methylmercury, the contribution of the soil contents to leaching seemed to be low. A topographical distribution of the total mercury and methylmercury leached and that based on the regulation levels in Japan (Ohtsuka et al., 2003) was shown in

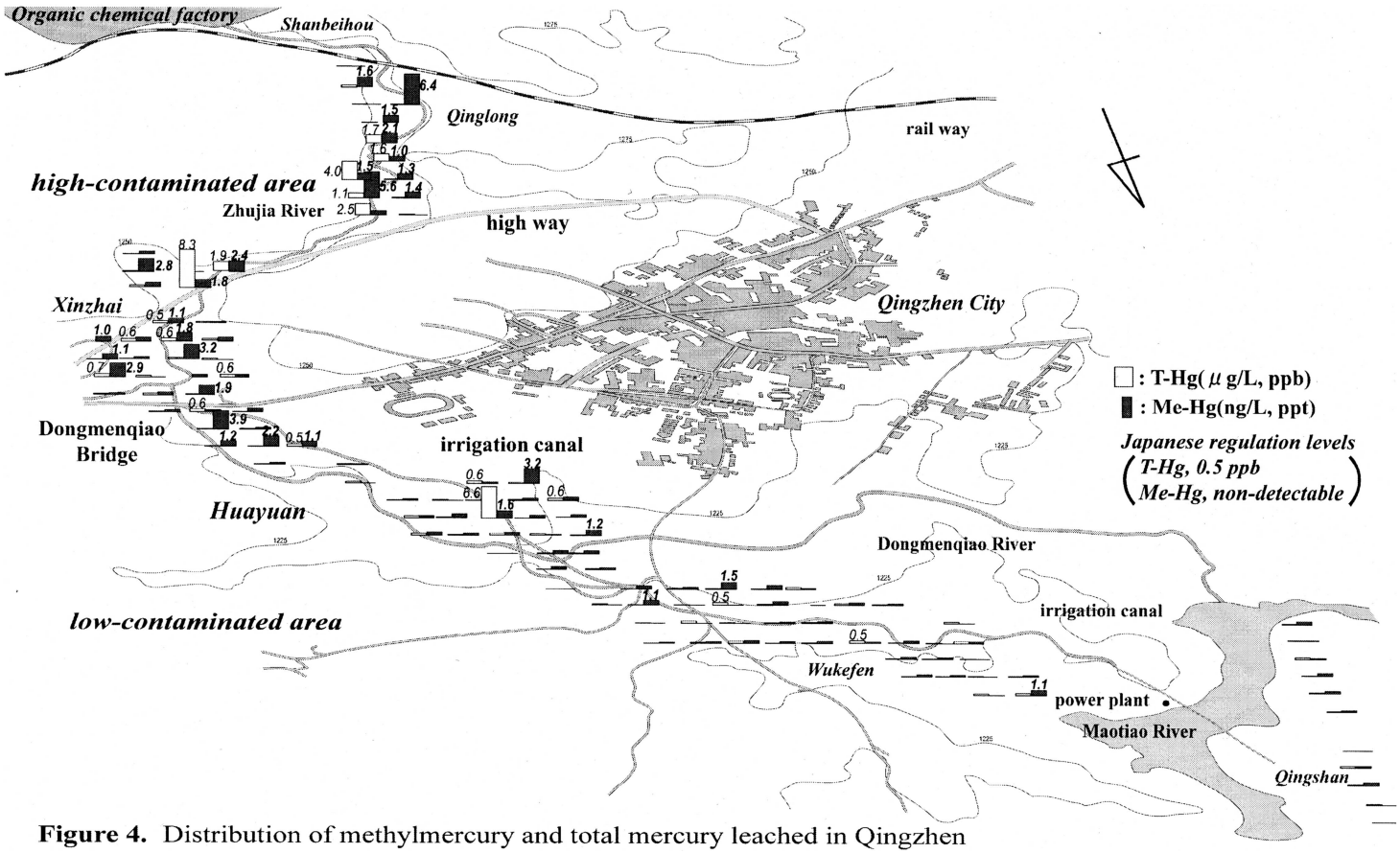

Figure 4. Distribution of methylmercury and total mercury leached in Qingzhen

Figure 4. Since the Japanese regulation on leached methylmercury in soil requires it to be 'non-detectable,' it was provisionally set to 1 ppt in our study. Although the sampling points displaying leached total mercury that exceeded 0.5 ppb were distributed in highly contaminated areas (Shanbeihou, Qinglong, etc.), the leached portions of methylmercury, above 1 ppt were also distributed in areas of low contamination (Xinzhai, Huayuan, and Wukufen, etc.). In other words, the behavior of methylmercury upon leaching from soil might be affected not only by the mercury content detected but also by other factor(s) such as organic materials, pH, EC, etc. in the soil samples.

The chemical behaviors of inorganic mercury in soils were described by Hahne et al. (1973). They showed that the distribution of Hg^{2+} would depend on the solubility of $Hg(OH)_2$ under normal pH conditions in the soils, and that the mobility of mercury in the soils would depend on the accompanying concentrations of Cl^- and the pH levels (1973). However, as mentioned above, no report was found on methylmercury behavior in soils. In the present study, we showed that, despite the good correlation between the total mercury and methylmercury in soil, the correlation between the two mercury species in leached portions were poor. In general, the chemical reactions in soils are complex, and several factors might affect mercury leaching other than those suggested by Hahne et al. (1973) in their study of inorganic mercury leaching.

Among the naturally occurring mercury species, methylmercury is the most hazardous to human health, especially for the developing fetus. Exposure to methylmercury occurs mostly through the consumption of seafood, and the safe exposure level for pregnant women has recently been recommended in the report of the 61st FAO/WHO Joint Expert Committee on Food Additives (2003). Methylmercury exposure is also possible by drinking water from polluted wells. Accordingly, methylmercury leaching from the soil is a very critical issue in a polluted area such as Qingzhen. Although the chemical process of methylmercury leaching is still unknown, the present study will provide a useful understanding of the chemical behavior of methylmercury in soil environments.

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