Bull. Environ. Contam. Toxicol. (2004) 73:846–852

DOI: 10.1007/s00128-004-0504-z

Bulletin of Environmental Contamination and Toxicology

Distribution of Methylmercury in an Area Polluted by Mercury Containing Wastewater from an Organic Chemical Factory in China

A. Matsuyama,[1] Q. Liya,[2] A. Yasutake,[1] M. Yamaguchi,[1] R. Aramaki,[1] L. Xiaojie,[2] J. Pin,[2] L. Li,[2] L. Mei,[2] A. Yumin,[2] Y. Yasuda[1]

[1] National Institute for Minamata Disease, Hama, Minamata City, Kumamoto 867-0008, Japan
[2] Guizhou Research and Designing Institute of Environmental Science, 70, Xinhua Road, Guiyang 550002, People's Republic of China

Received: 12 May 2004/Accepted: 30 July 2004

Guizhou Organic Chemical Factory (hereafter called the Factory) was established in late 1960 and located near Qingzhen City in Guizhou Province, China. In order to produce acetic acid, it had synthesized acetaldehyde from acetylene using mercury as a catalyst from 1970 to 2000. The factory employed a similar production process to that of the Japanese organic chemical factory of the Chisso Corporation which finally caused Minamata disease, and had been discharging mercury-containing wastewater into the Zhujia River (Figure 1). This river joins the Dongmenqiao River in its lower reaches, and both these rivers have been utilized as a source of irrigation for the paddy fields and the farmland in the region. Therefore, residents in the irrigated region (Qingzhen) are thought to be suffering from mercury pollution. The factory estimates the total discharged mercury into the environment to be about 135 t.

Yasuda et al. (2003) reported the distribution of total mercury contamination in soil samples mostly from paddy fields and farmlands in the vicinity of the Qingzhen area, while applying meshwork (100 m × 100 m) for sampling. However, since the factory employed a production process similar to that of the Chisso Corporation in Minamata, it is possible that the wastewater from the factory contained methylmercury as well as metallic and inorganic mercury as suggested by Horvat et al. (2003). Methylmercury is well known to pose high risks to human health, as documented in Minamata disease patients. In the present study, to determine the level of methylmercury pollution, the soil samples collected in the Qingzhen and Lanchong (control) areas were analyzed using special analytical techniques for methylmercury. The results provided further details regarding mercury pollution in the Qingzhen area.

MATERIALS AND METHODS

The 147 soil samples (120 from the Qingzhen and 27 from the Lanchong area; see Figure 1) used in the present study were from the same lot as used in the previous study by Yasuda et al. (2003).

The methylmercury analysis of soil (or sediment) basically followed the method of Akagi and Nishimura (1991) with some modification.

Correspondence to: A. Matsuyama

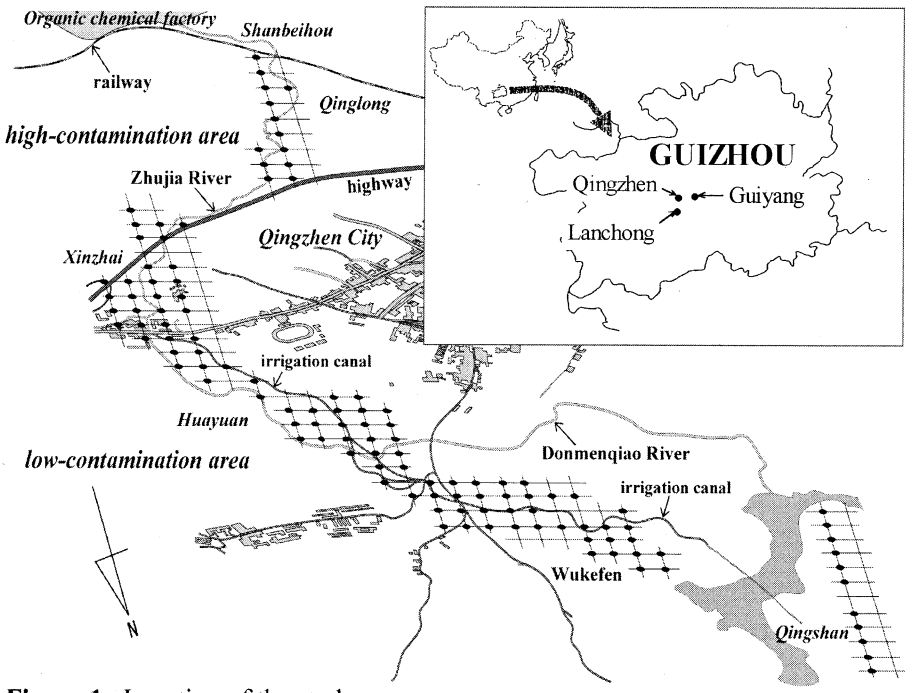

Figure 1. Location of the study area

A known amount of mixed crude soil sample (0.1 to 0.3 g) was dispersed in 10 ml of 1N KOH/ethanol in a 50 ml screw-capped centrifuge tube and sonicated in an ultrasonic bath for 10 min, followed by shaking for 10 min. The treated sample was neutralized with 1N HCl (10 ml) and mixed with 20% NH_2OH-HCl (2 ml) and 20% EDTA-4Na solution (2 ml). Methylmercury in the sample was extracted with purified 0.01% dithizone-toluene solution (5 ml).

For clean-up, an aliquot of dithizone-toluene extract (usually 4 ml) was first passed through a Florisil column (0.5 g Florisil, topped with 0.5 g Na_2SO_4) and washed twice with 1N NaOH (3 ml) to remove excess dithizone from the extract. An aliquot of washed extract (usually 3 ml) was transferred to a 10 ml glass-stoppered test tube and 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 then the aqueous solution was slightly acidified with 1N HCl. The mixture was bubbled with N_2 gas for 5 min to remove sulfide ion as H_2S gas. To the sample solution, Walpole's buffer (2 ml) was added, and the methylmercury in the mixture was re-extracted by adding purified 0.01% dithizone-toluene solution (0.5 ml) and shaking. 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 drops of 1N HCl were added. The toluene solution thus prepared was subjected to an ECD-gas chromatographic measurement.

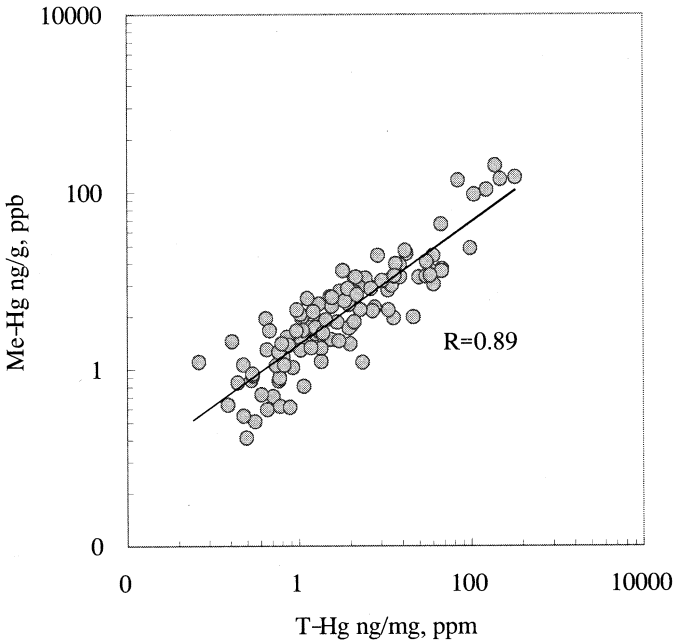

Figure 2. Correlation between total mercury concentration and methylmercury concentration

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

			N	AV	±	SD	(min.-max.)
Qingzhen City							
high-contamination area	**T-Hg**	(mg/Kg dry wt.)	20	61.14	±	93.00	(0.29-328.95)
	Me-Hg	(ng/g dry wt.)	20	45.00	±	65.07	(ND-199.92)
	Me-Hg/T-Hg	(% weighted average)	20	0.14	±	0.19	(0.00-0.91)
low-contamination area	**T-Hg**	(mg/Kg dry wt.)	100	6.95	±	13.24	(0.06-98.27)
	Me-Hg	(ng/g dry wt.)	100	5.82	±	6.70	(ND-43.58)
	Me-Hg/T-Hg	(% weighted average)	100	0.19	±	0.23	(0.00-1.78)
Lanchong	**T-Hg**	(mg/Kg dry wt.)	27	0.11	±	0.05	(0.05-1.78)
(control area)	**Me-Hg**	(ng/g dry wt.)	27	2.29	±	1.70	(ND-6.98)
	Me-Hg/T-Hg	(% weighted average)	27	2.47	±	2.18	(0.00-8.15)

The detection limit of this method is around 0.1 ng/g for methylmercury in soil samples. For the certification of measurement quality, a standard reference material CRM-580 (Commission of the European Communities, certified value of methylmercury is 75.5±3.7 ng/g) was used. Our quantification data were 71.7± 1.3 ng/g (average of 7 repetitions).

RESULTS AND DISCUSSION

Previously, we reported that the 80% of the total mercury in Qingzhen was distributed in the Shanbeihou, Qinglong and Xinzhai areas south of the highway (Yasuda et al., 2003). Accordingly, each of these locations was defined as a 'high-contamination area', while the area north of the highway, Wukefen, Huayuan, Qingshan, and a part of Xinzhai, were defined as a 'low-contamination area' (Figure 1). The results of a methylmercury analysis of 120 soil samples from Qingzhen and 27 from Lanchong (control) are shown in Table 1 along with the results of the total mercury level, as earlier reported. The average methylmercury concentrations from the high- and low-contamination areas were 45.01 and 5.82 ng/g dry wt, respectively. On the other hand, the average concentration in the Lanchong (control) area was 2.23 ng/g dry wt. The average level of the high-contamination areas was shown to be almost 20 times higher than that of the control area. Since the methylmercury concentration of non-polluted paddy fields is 1 to 2 ng/g in Japan (Kanazawa, 1974), the mercury levels in the Lanchong area were thought to be reasonable as a negative standard.

Total mercury levels of soil samples in the previous study (Yasuda et al., 2003) and methylmercury levels in the present study showed a good correlation (r=0.89), as shown in Figure 2. The topographical distribution of methylmercury concentrations on the meshwork is shown in Figure 3 together with that of total mercury. The higher values of methylmercury concentrations tend to be found in high-contamination areas. The maximum value of methylmercury was 199.9 ng/g in Xinzhai which faced the south side of the highway.

Since a geological feature of the Qingzhen area is its original limestone, the thickness of the topsoil in the study area is thought to be less than a meter. Accordingly, the total amount of methylmercury in that area is calculated to be 25.2 kg, if the specific gravity of soil is assumed to be 1.7. Since the total amount of mercury was estimated to be 32 t in the study area (Yasuda et al., 2003), the methylmercury/total mercury ratio is calculated to be 0.08%.

The methylmercury/total mercury ratio in each area is shown in Table 1. Despite a large difference in total mercury levels between high- and low-contamination areas, the methylmercury/total mercury ratios were quite similar in both areas, $0.14 \pm 0.19\%$ and $0.19 \pm 0.23\%$ for low- and high-contamination areas, respectively (Since the values were shown by weighted average, the calculated values include the variations in the differences of mercury concentration at each sampling point. Therefore, the methylmercury/total mercury ratios which were calculated using a weighted average came out higher than the mercury ratio of a total study area (0.08%)). On the other hand, the methylmercury/total mercury ratio control of the area was as high as 2.06%. Although it is difficult to explain the disparity in the ratios between contaminated and control areas, some of the characteristics of soils other than their total mercury concentration might be responsible for it. Hecky et al. (1991) suggested that, the methylmercury concentration in soil or sediment was generally determined by mercury

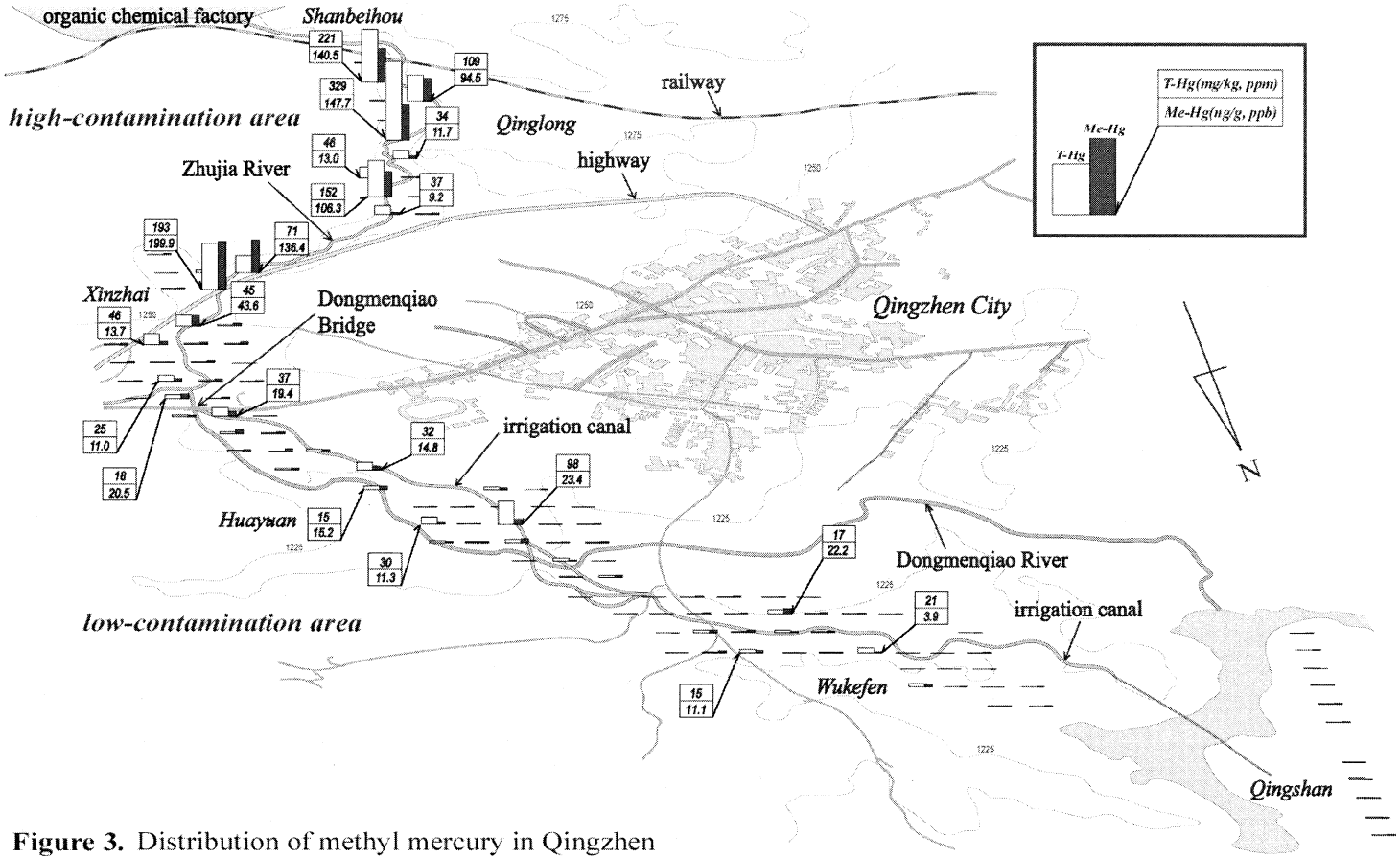

Figure 3. Distribution of methyl mercury in Qingzhen

methylation and demethylation due to environmental factors including microorganisms. Moreover, Ikingura et al. (1998) reported that when sediment artificially polluted by inorganic mercury was incubated in an aquarium, the maximum methylmercury production in the sediment occurred during the first week of incubation. However, the methylmercury level in a state of equilibrium, which was established 3 to 4 weeks after the spike of mercury, was about 10% of the maximum production. In Qingzhen, the factory had been closed 2 years before to end the discharge of mercury-contaminated wastewater. Since a duration of 2 years was thought to be long enough to establish the above equilibrium, the methylmercury/total mercury ratio in both high and low contamination areas would be stable.

In the present study, we showed the topographical distribution of methylmercury concentration in the Qingzhen area. In combination with the previous study of Yasuda et al. (2003), the complete profile of mercury pollution in Qingzhen has been visualized. A drastic chemical change in the mercury pollution level would be impossible there in the near future, since the inter-conversion of chemical forms is thought to be at a stable equilibrium. However, the effects of environmental factors (e.g., organic material, exchangeable ions, species of soil, etc.) responsible for mercury inter-conversion are still unknown. Currently, experiments on the chemical transformation of mercury in soils as well as chemical analysis of the soil samples are in progress using samples from the Qingzhen and Lanchong areas. The results will provide further insights into the behavior of mercury in soil environments.

Acknowledgements. Special thanks go to Yoko Fuchigami for her valuable assistance with some important analyses and manuscript preparation.

REFERENCES

Akagi H, Nishimura H (1991) Speciation of mercury in the environment. In: Suzuki T, Imura N, Clarkson TW (eds) Advances in Mercury Toxicology Plenum Press, New York, p53

Hecky RE, Ramsey DJ, Bodary RA, Strange NE (1991) Increased methylmercury contamination in newly formed freshwater reservoirs. In: Suzuki T, Imura N, Clarkson TW (eds) Advances in Mercury Toxicology, Plenum Press, New York, p33

Horvat M, Nolde N, Fagion V, Jereb V, Logar M, Lojen S, Jacimovic R, Falnoga I, Qu L, Faganeri J, Drobne D (2003) Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. Sci Total Environ 304:231-256

Ikingura JR, Akagi H (1999) Methylmercury production and distribution in aquatic systems. Sci Total Environ 234:109-118

Kanazawa J (1974) The remains of mercury pesticide in paddy field (in Japanese). Nouyakukagaku 2:121-122

Yasuda Y, Matsuyama A, Yasutake A, Yamaguchi M, Aramaki R, Liu X, Jiam P, An Y, Liu L, Li M, Chen W, and Qu L (2004) Mercury Deposit Distribution

in Farmlands Downstream from an Acetaldehyde Producing Chemical Company Located in Qingzhen City, Guizhou, China, which uses Mercury as a Catalyst. Bull Environ Contam Toxicol 72:445-451