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Environmental Contamination and Toxicology

Mercury Distribution in Farmlands Downstream from an Acetaldehyde Producing Chemical Company in Qingzhen City, Guizhou, People's Republic of China

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Guizhou Organic Chemical Factory (GOCF), a state-owned firm, has been producing acetic acid (AcOH) from acetaldehyde synthesized by the addition reaction of acetylene and water using mercury as a catalyst. The process is basically the same as that used once in Minamata, Japan. In Minamata, the drain of the process is well known to have caused a serious defects of central nervous system in residents through the food-web (Minamata disease). Production of AcOH in the plant was continued from 1971 to 2000 in Shanbeihou, eastern urban of Qingzhen City (Figure. 1, 2). Total loss of mercury into environment announced by GOCF was 134.6 t for the 30 year period. The drain ditch from the acetaldehyde plant runs through paddy fields into the Zhujia River. The name of the river changes to the Dongmenqiao River at Dongmenqiao Bridge where the river branches an irrigation canal 3.5 km downstream from the factory (Figure. 2). Here water is provided into more than 120 ha of farmland. The river and irrigation canal join the Maotiao River which provides raw practical use water into the province's capital city, Guiyang located 20 km east of Qingzhen City (Figure 1). The farmland receiving irrigation from the Zhujia River has been suspected of being mercury polluted as pointed out by Horvat et al. (2003). Therefore, in order to know the extent of the mercury pollution containing waste water in detail, we investigated mercury deposit in the farmland applying 100 m of meshwork.

MATERIALS AND METHODS

The subject field consists mainly of paddy fields, truck farms and some areas of non-farmland lots. It spreads from south (Shanbeihou) to north (Qingshan) surrounding north-east half of Qingzheng City (Figure 2). Irrigation is provided from a drain ditch in Shanbeihou, Qinglong and Xinzhai, from the Dongmenqiao Bridge. The irrigation canal provides water derived from both the Dongmenqiao River and the drain ditch (the Zhujia River). The canal crosses the Maotiao River using a pipeline into Qingshan (Figure 2). The total length of the stream in which the polluted drain flows reaches more than 7 km. In order to take soil samples systematically, we applied a sampling scheme much the same as Juang et al. (2001). The area lower than 1225 m above sea level, which is thought to receive irrigation containing factory waste (Figure. 2), was used as the limit of highest level for the disposing station. On a 100 x 100 m meshwork covering the entire estuary from the factory to Qingshan as shown in Figure 2, 120 samples were taken using a type of drive auger (inner diameter 5 cm) at 10 to 20 cm depth. As a control method, 27 samples from paddy fields, truck farms and non-farmland-lots were taken at 100 m

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Figure 1. Location of the field investigated.

grid in Lanchong Village, located 60 km southwest of Qingzhen City (Figure. 1). Each sample was a mixture of five column of auger core as shown in Figure. 3.

Mercury was detected as total amount using cold vapor atomic absorption spectrometry (CV-AAS) improved by Akagi and Nishimura (1991). Briefly, 0.5 g or less of soil sample was put into a 50 ml volumetric flask, to which 2 ml of a 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℃ for 30 min. After cooling, the digested mixture was diluted up to 50 ml with water, which is used as a sample for mercury analysis by CV-AAS. Mercury in the aliquot of the sample solution was vaporized by reduction in the presence of 0.5 % (w/v) stannous chloride under vigorous bubbling for 30 seconds. The mercury vapor was then sent to the atomic absorption analyzer. This preparation is performed within an automated circulating airflow system (Akagi and Nishimura, 1991, assembled by Sanso Co. Ltd., Tokyo, Japan).
A leaching test of soil samples was performed according to a spread procedure in Japan, that is, 5 g of sample was taken into a 50 ml centrifuge tube with a screw cap to which 50 ml of distilled water was added (pH of the water was adjusted with HCl or NaOH to 5.8-6.3 in advance). The tube was shaken by mechanical shaker for 6 hours and centrifuged at 3000 rpm for 30 minutes. Supernatant was filtered through a 0.45 μm pore size nitro-cellulose membrane filter. Twenty ml of the filtrate was placed into a 30 ml volumetric test tube, incubated at 90℃ for 2 hours after adding 1 ml H_2SO_4, 0.5 ml HNO_3, and 2 ml 10 % $KMnO_4$. The sample was then reduced with the addition of 1 ml of 8 % $HONH_3Cl$ solution, and the amount of mercury was determined by CV-AAS as described above. Each measurement was conducted twice for a soil sample with duplicate determination. To control the quality of measurement, a standard reference material So-2 (CCR-MP, certified value of mercury is 0.082 ± 0.009 μg/g) was used. Our quantification data was 0.0806 ± 0.0014 μg/g (average of 10 times repetition).

RESULTS AND DISCUSSION

A total of 120 soil samples in Qingzhen and 27 samples in the control area were analyzed for mercury concentration and leaching. The basic characteristics of soil, such as moisture content, ignition loss, pH and electric conductivity(EC) were analyzed on randomly selected 27 samples from the Qingzhen area and all samples

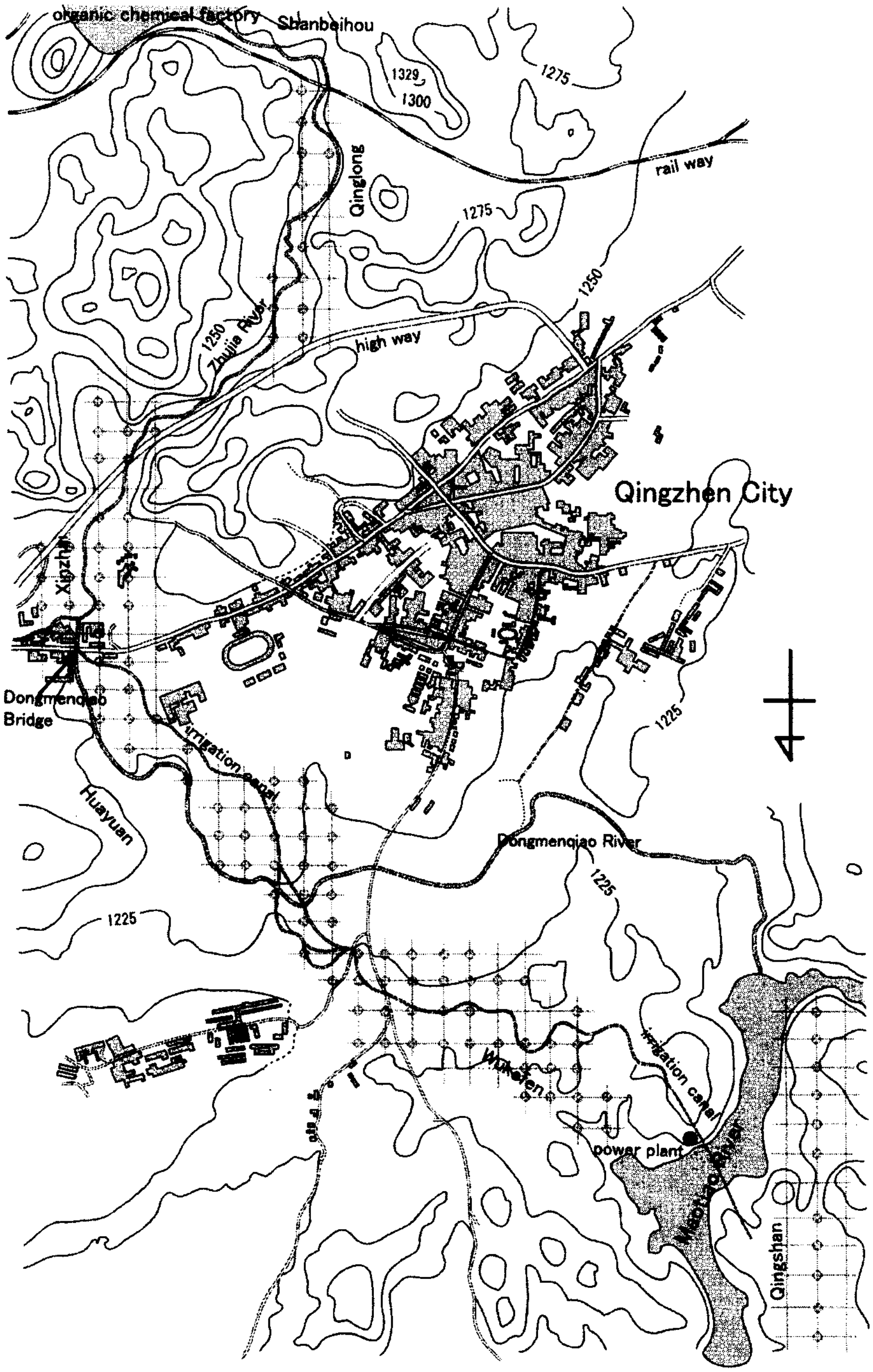

Figure 2. Topography of the investigated field.

from the Lanchong area and listed in Table 1. The EC is employed simply for evaluating total amount of ions in soil samples. Generally, if the EC exceeds 1.0 mS, growth of most vegetables (cucumber etc) is thought to be inhibited by a high concentration of ions in soil (U.S Salinity Lab, 1954). The EC in Qingzhen was 1.02 ± 0.8 on average, whereas that of the control area (Lanchong) was 0.22 ± 0.1 as shown in Table 1. The value of EC in the control area can be evaluated as normal in the viewpoint of plant growth, however, that of Qingzhen was at a sub-hazardous level for plant growth. One of the causes of such a high value of EC in Qingzhen may be due to the irrigation using waste water from GOCF.

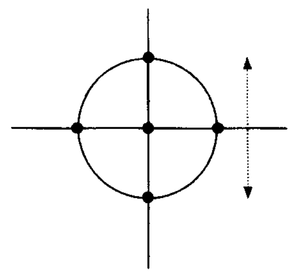

Figure 3. Sample was taken from five points (●) and mixed

Table 1 Characteristics of soil samples

			N	AV	±	SD	(	min.	-	max.	)
ingzhen	moisture rate	(%)	27	31.3	±	5.6	(	22.3	-	41.3	)
	ignition loss	(%)	27	7.8	±	1.8	(	4.2	-	12.1	)
	pH		27	7.7	±	0.4	(	5.9	-	8.1	)
	EC	(mS/cm)	27	1.02	±	0.8	(	0.32	-	3.44	)
Lanchong	moisture rate	(%)	27	25.0	±	3.4	(	20.0	-	35.4	)
(control area)	ignition loss	(%)	27	6.2	±	0.8	(	5.0	-	7.4	)
	pH		27	5.7	±	1.0	(	4.1	-	7.6	)
	EC	(mS/cm)	27	0.22	±	0.1	(	0.08	-	0.56	)

*Qingzhen samples are selected randomly.

Table 2 Average concentration of total mercury in soil and supernatant of leaching

			N	AV	±	SD	(	min.	-	max).	
Qingzhen	T-Hg	(mg/kg dry)	120	15.73	±	42.98	(	0.06	-	321.38	)
	leached-Hg	(μg/L)	120	0.43	±	1.05	(	ND	-	8.28	)
Lanchong	T-Hg	(mg/kg dry)	27	0.11	±	0.05	(	0.05	-	0.22	)
(control area)	leached-Hg	(μg/L)	27	0.13	±	0.12	(	ND	-	0.48	)

The average of total mercury concentration was 15.73 ± 42.98 mg/kg in Qingzhen and 0.11 ± 0.05 mg/kg in the control area as shown in Table 2. Also, the average soluble mercury concentration was 0.43 ± 1.05 and 0.13 ± 0.12 μg/L, respectively. As a reference, the total mercury concentration in some paddy fields located in northern part of Kyushu Island, Japan is 0.197 (Goto et al., 1978), which coincides with the value of the control area. However, the value in Qingzhen obviously indicates mercury pollution of the soil The large value of standard deviation in total mercury on average in Qingzhen is due to the highly variable data among samples as shown below. The distribution of dry weight based total mercury concentration on the meshwork as well as that of leached mercury is shown in Figure 4a and 4b, The

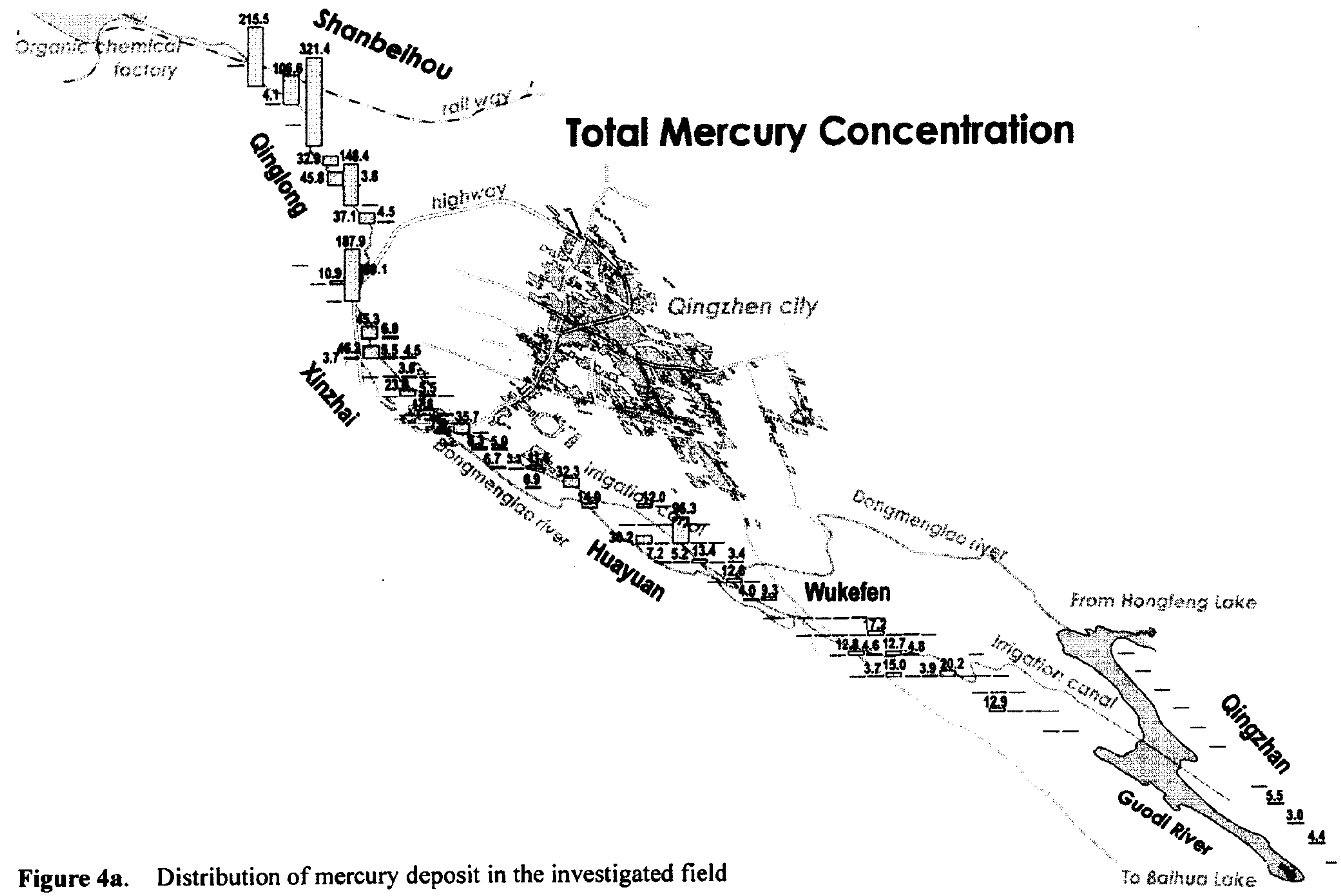

Figure 4a. Distribution of mercury deposit in the investigated field

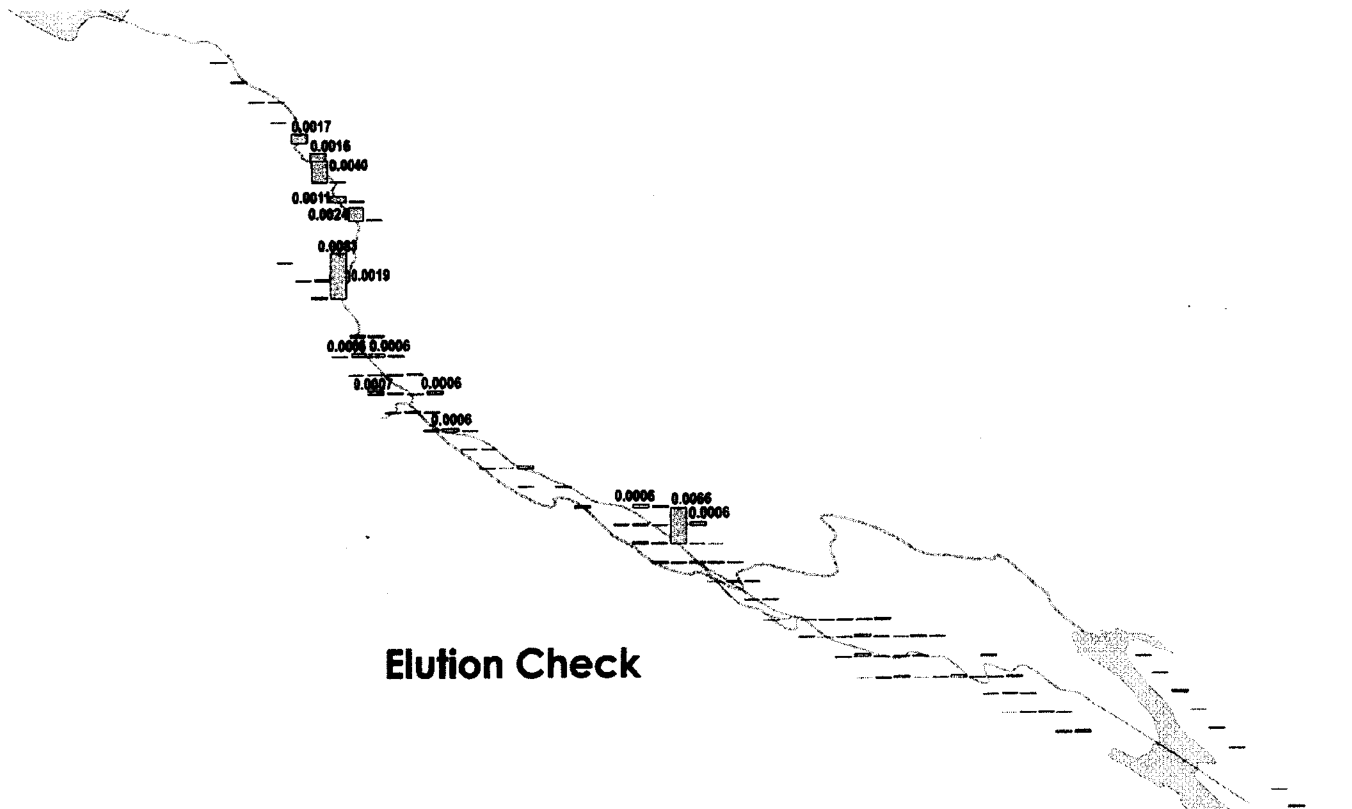

Figure 4b. Elution check of mercury from the soil samples taken in each sampling station shown in Figure 4a.

higher value tends to be found mainly in paddy fields that neighbor streams, but not in truck farms. An extremely high value was found in the ravine of Qinglong where the waste water has been directly introduced into paddy fields before the ditch joins the Zhujia River. The highest concentration was 321.4 mg/kg and five locations exceeding 100 mg/kg were found in Qinglong ravine. After the irrigation canal branched from the river at Dongmenqiao, high values of more than 15 mg/kg (the newly offered regulation value of soil mercury in Japan from 2003) have been found on occasion throughout the irrigation field up to the power plant (see Figure. 2). Stations in the Qingshan area, the detached field irrigated with the drain containing water, were less than 5.5 mg/kg. A total of 22 stations out of 120 exceeded the new Japanese environmental regulation for mercury concentration in soil (15 mg/kg).

In those polluted stations, a significant amount of mercury was also found in soluble form (Figure: 4b). Seven locations in Qinglong leached more than 1μg/L of mercury. The station, which contains a large value of leached mercury, does not necessarily coincide with the distribution of soil mercury. This is particularly true in the Qinglong ravine. Fortunately, however, no mercury was detected from the spring water taken from both Xinzhai and Huayuan, which is used for drinking by thousands of residents in this region (data not shown).

In the present investigation, the distribution of total mercury deposited in the field that received waste water from GOCF was visualized. Since the thickness of the topsoil in the studied field is thought to be less than a meter, the total amount of mercury in the field studied is calculated to be 32 t if the specific gravity of soil is 1.7. This amount of mercury corresponds to 24 % of the total waste for 30 years. Additionally, approximately 80 % of the whole mercury was present in the highly contaminated Qinglong and Xinzhai (25 t).

Methyl mercury deposit distribution is also quite important and is now under analysis. The results indicating methyl mercury contamination will be published elsewhere. The field examined here is currently used to produce crops. Horvat et al. (2003) asserted the mercury pollution of rice in this region. Therefore, the distribution of mercury in the crops grown on the field studied in the present work as well as the vertical distribution of mercury in soil is the next subjects to be investigated.

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