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Relationships Between Leaching of Methylmercury from the Soil and the Basic Characteristics of Alkali Soil Polluted by Mercury in Guizhou China

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Abstract To determine the relationship between soluble methylmercury and soil characteristics which was contaminated by mercury, several experiments were conducted. As a result, a good correlation was founding between the leached methylmercury level from soil and the EC (electronic conductivity) level of soil. Moreover, to grasp the relationship between soluble methylmercury and soluble anions from soil, several anions (Cl^-, NO^{3-}, SO_4^{2-}) were measured using the ion chromatography method. Although the correlation coefficient was small ($r = 0.40$), only a correlation between the level of SO_4^{2-} and leached methylmercury was recognized.

Keywords Soluble total mercury · Soluble methylmercury · EC · SO_4^{2-}

Farmland in the southern suburb of Qingzhen City in Guizhou Province, China was polluted by irrigation using mercury-containing river water derived from the Guizhou organic chemical factory. Previously we reported that the farmlands around an organic chemical factory in Quinzhen was highly polluted by mercury (Yasuda et al. 2004). On the other hand, Matsuyama et al. (2005, 2006) also reported that although the relationship between the total mercury and methylmercury levels in the soil was very good ($r = 0.89$), there was no correlation between levels of leached total mercury and leached methylmercury from the soil ($r = 0.16$). Furthermore, they reported that although there was a correlation between the total mercury level in the soil and the leached total mercury level from the soil ($r = 0.56$), there was no correlation between the levels of methylmercury and leached methylmercury in the soil($r = 0.36$) (Matsuyama et al. 2005). Thus, the strength of methylmercury leached from soil polluted by mercury is not dominated only by the mercury level in the soil. Therefore, the strength of leached methylmercury was thought to be affected not only by the mercury level in the soil but also by other environmental factors in the soil. Especially, it is known that methylmercury, which caused Minamata disease, is a highly toxic chemical substance fatal to humans. Basically, since groundwater and river water are contaminated over time by the leaching of mercury from the soil, they pose a significant danger to the environment. The result of our survey shows that residents of the Quinzhen area use well water for drinking water. Even if well water contains only a little methylmercury, the leaching of methylmercury from the soil is a serious problem. Based on these facts, the relationships between the leached methylmercury level from the soils and the basic soil characteristics were examined in the present study to evaluate the risk of mercury pollution in this area.

Materials and Methods

In the present study, to investigate the relationship between the basic characteristic data of soils and the characteristics of soils that were contaminated by mercury, we used some data reported by Matsuyama et al. (2005, 2006), including the leached methylmercury level and leached total mercury level. Moreover, in addition to previous analytical data, leached methylmercury levels and leached total mercury levels were measured using 48 soil samples in this present study. These 48 soil samples were chosen from 58 soil samples taken from the farmland on the mercury pollution

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map of Quinzhen already reported by Matsuyama et al. (2006). To select the 48 soil samples in 58 soil samples, a previous Japanese tentative threshold value 3 mg/kg as total mercury level was used (Environment Agency 2002). Therefore, total mercury levels of selected 48 soil samples exceeded 3 mg/kg.

A leaching test of the soil samples was carried out with the official methods used to evaluate the overall environment in Japan (Environment Agency 2004). Our methylmercury analysis of water sample basically followed the method of Akagi and Nishimura (1991) with some modifications. First of all, each 5 g of a soil sample was put into a 50-mL screw-capped centrifuge tube to which 50 mL of distilled water was added. The tube was shaken using a mechanical shaker for 6 h, and centrifuged at 2,500 rpm for 30 min. The supernatant was filtered through a 0.45-μm pore size nitrocellulose membrane filter. The extraction process was repeated more than 3 times, and the filtrates were combined. Then, 100 mL of the filtrate was placed into a 200-mL separator funnel and mixed with 20 N H_2SO_4 (0.5 mL) and 0.5% $KMnO_4$ (0.2 mL). After 5 min, the mixture was neutralized with 10 N NaOH (1 mL), and then mixed with 10% NH_2OH–HCl (0.2 mL) to remove the oxidation effect due to $KMnO_4$. Finally, the methylmercury in the mixture was extracted by the addition of a purified 0.01% dithizone–toluene solution (5 mL). After the cleanup process for the dithizone–toluene extract, the sample solution thus prepared was subjected to ECD-gas chromatographic measurements (Matsuyama et al. 2005). The detection limit of methylmercury using this method on water sample is around 0.1 ng Hg/L. Since there is no reference material for a sample of methylmercury in water, the accuracy and precision of this analytical method have been verified through an interlaboratory comparison (Logar et al. 2002). 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. Organic contents in soils were measured by the Tyurin method (Kononova 1966).

In the cases of ignition losses, to avoid the vaporization of carbonic salt in the soil by heating, the furnace temperature was set at almost 380°C, and soil samples were then heated to 6 h, continuously for pH and electronic conductivity (EC) was measured by electrode methods. Each anion such as Cl^- SO_4^{2-} NO_3^- in the leaching test solution of soil which was made using the official methods was also measured by the ion chromatography method.

Results and Discussion

All data used in this present study were shown in Table 1. Although a correlation is influenced by the number of samples, the correlation coefficient is generally considered to be significant when it is above 0.5 (Ohmura 1985). As a result, only a good correlation between leached methylmercury level from soil and soil characteristics is the EC level of soil ($r = 0.65$, Fig. 1). However, there is no correlation between the EC level and the leached total mercury level ($r = 0.22$, Fig. 2). Then, not only the EC level but also the correlation between the leached total mercury level and other soil characteristics besides the EC shows the same tendency. However, in comparison with the correlation between the EC and the leached methylmercury levels, although the correlation coefficient was lower, a correlation between the leached methylmercury level and the organic material contents in soil was recognized ($r = 0.47$, Fig. 3). Furthermore the correlation between the EC level and the organic materials content in soil was also excellent ($r = 0.72$, Fig. 4). Based on these facts, the reason for such a good correlation was thought to be the influence of soluble anions released from organic materials in soils. It was reported that mercury mobility in soil is easily affected by the strength of ions in the soil. Hahne and Kroontje (1973) and Schuster (1991) reported

Table 1 Analytical data of soil characteristics

			N	AV ± SD	(min−max)
All data*	pH		168	7.61 ± 0.62	(5.90–9.40)
	Ignition loss	%	168	7.43 ± 2.60	(1.31–19.40)
	Organic matter	%	120	4.01 ± 2.03	(1.13–14.20)
	EC	mS/cm	168	0.82 ± 0.55	(0.24–3.68)
Leaching	T–Hg	μg/L	168	0.72 ± 1.34	(0.04–8.28)
Leaching	Me–Hg	ng/L	168	1.71 ± 2.40	(0.09–13.10)

* All data: 100 m mesh and 50 m mesh

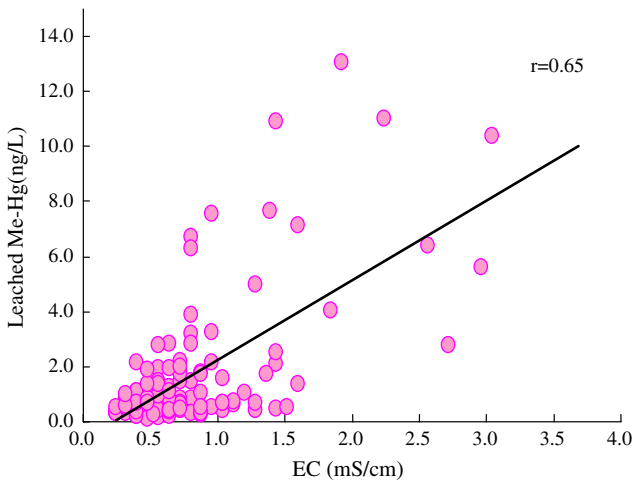

Fig. 1 Correlation between leached methylmercury and EC level in soil

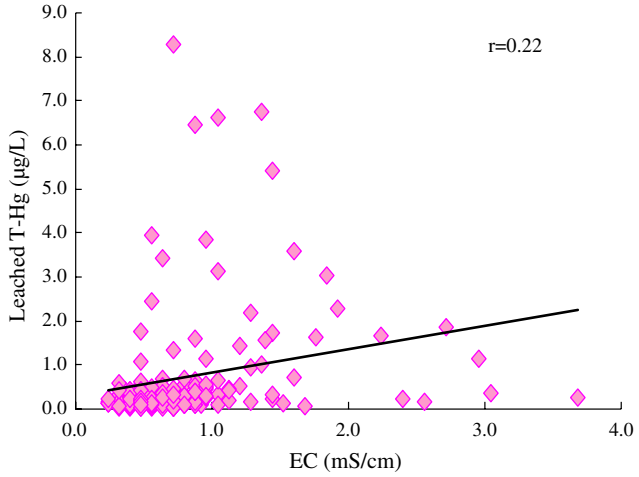

Fig. 2 Correlation between leached total mercury and EC level in soil

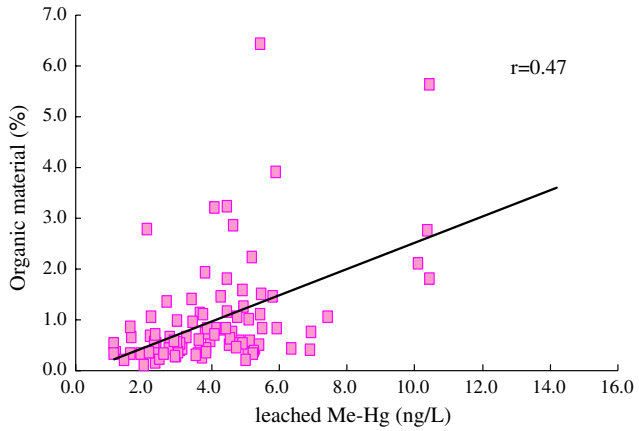

Fig. 3 Correlation between leached methylmercury and organic material in soil

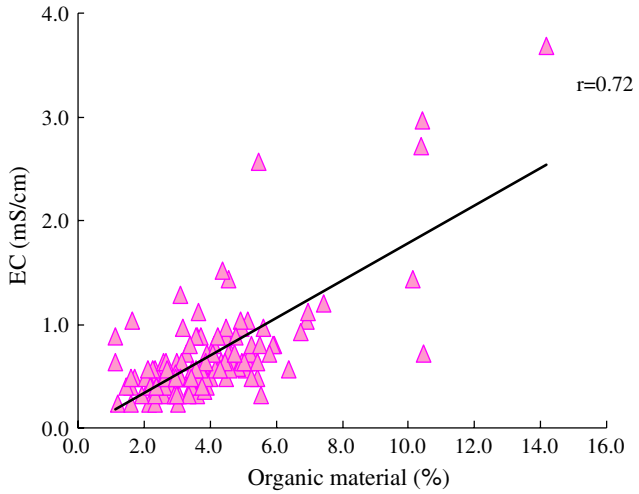

Fig. 4 Correlation between EC level and organic material in soil

Table 2 Correlation between leached methylmercury and soluble anions in soil

	Correlation coefficient (r=)
Cl^-: leached Me–Hg	0.05
$NO3^-$: leached Me–Hg	0.1
SO_4^{2-}: leached Me–Hg	0.4

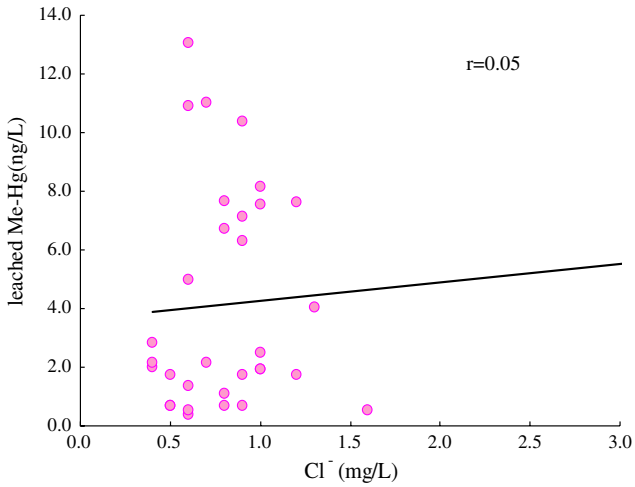

Fig. 5 Correlation between leached methylmercury and soluble Cl^- in soil

that the influence of Cl^- was especially strong. Therefore, in terms of measuring several anion levels in the leaching test solutions of 48 soil samples prepared to measure soluble methylmercury in the present study, the correlation between each anion and each leached methylmercury level was investigated. Such correlations were shown in Table 2. As a result, there was no correlation between the level of Cl^- and that of leached methylmercury ($r = 0.05$, Fig. 5). However, although the correlation coefficient was small ($r = 0.40$), a correlation between the level of SO_4^{2-} and leached methylmercury was recognized. In the present study, although a good relationship was found between the level of EC and leached methylmercury in mercury-contaminated soil, each typical anion level in the leaching test solution showed no correlation with the leached methylmercury level. Therefore, to study further the behavior of soluble methylmercury in mercury-contaminated soil, it is extremely important to examine not only the anion levels but also the cation levels in soil and their relation to the leached methylmercury levels. Furthermore, since the mercury-contaminated soil used in the present study was alkali soil derived from lime stone and clay, we should more fully investigate the behavior of soluble methylmercury in mercury-contaminated soil using not only this type soil but also others such as acid soil to obtain more accurate results.

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