The Distribution of Various Mercury Species in Soil *

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Abstract: According to the mercury species with different solubilities, the analytical procedure involving sequential chemical extraction has been applied to partitioning the mercury species in soils into seven fractions. Soil samples collected from five localities in different areas (the high-mercury area, the man-made mercury-polluted area and the reference area) were analyzed for the seven mercury species. It is found that high mercury contents of soils can be attributed to both man-made pollution and geological processes, but the two kinds of soils show obvious differences in the distribution of their mercury species.

Key words: soil; species of mercury; environmental geochemistry; analytical chemistry

The species of heavy metals in soils can be divided into the following groups: (a) water soluble species, (b) exchangeable species, (c) species combined with carbonate, and Fe and Mn oxides, (d) species combined with humic acid, (e) species combined with easily oxidized and degraded organic matter, (f) species combined with hardly oxidized and degraded organic matter, and (g) residual species existing in mineral lattice.

At present, a lot of work has been made on the mercury speciation analysis of river and lake sediment samples both at home and abroad(Wang Zijian, 1983; Lin Yuhuan et al., 1983; Zhu Jiasen et al., 1992; Pang Shuwei et al., 1981; Zhang Lantian et al., 1985; Rao Lili and Zhang Shen, 1982; Eganhouse et al., 1978; Gambrell et al., 1980), but little work has been done on that of soil samples. There are two kinds of methods to analyze mercury species in soils and sediments. The first one is a chemical method established on the principle that different chemical solutions can extract different Hg species, and the second is a thermodecomposition method developed on the principle that every mercury species can be converted to mercury vapor at a different temperature. Therefore, when a sample is heated successively at higher temperature step by step, mercury will be liberated at each step and concentrated on a gold trap (Azzaria et al., 1991). In this paper, the fisrt method was employed.

Choice of Sample Localities

The authors chose three different areas in Guizhuo Province, namely a high-Hg area, a Hg-polluted area and a reference area. The Danzhai mercury deposit was chosen as the high-Hg area, and three sample localities in the Danzhai Hg mine Fuxingchang (DMF), Yichejian (DMY) and Changbu (DMC), were chosen according to the descending order of Hg contents of soil samples from DMF through DMY to DMC. The mercury-polluted farmland at Dongmenqiao, Qingzheng (DQ) was chosen as the Hg-polluted area and the test farmland of Guizhou

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Institute of Agricultural Sciences (GIAS) was chosen as the reference area. Only one sample locality was chosen each in the Hg-polluted area and reference area. In all the sample localities, soil samples were collected, and Figs. 1 and 2 show the distributions of sample localities. The soil type in the five sample localities is lime soil, and the bedrock consists of limestone or dolomitic limestone. The three sample localities in the Danzhai mercury deposit were chosen, which are far away from anthropegenic activity, and varying degree of Hg mineralization is recognized in this area. At Dongmenqiao, Qingzheng, water for irrigating rice paddies has been contaminated by high-Hg sewage discharged from Guizhou Organic Chemical Plant.

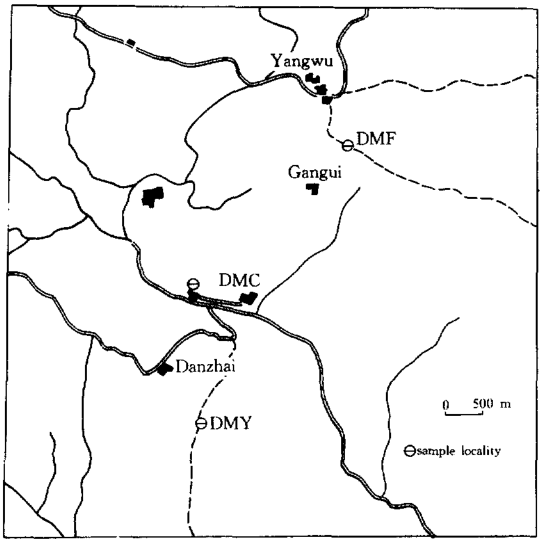

Fig. 1. Map showing the distribution of sample localities in the Danzhai mercury deposit.

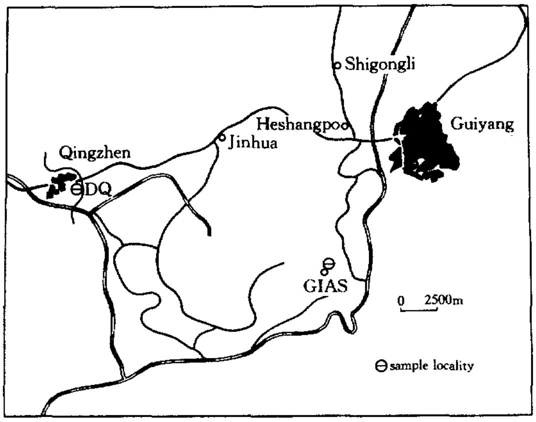

Fig. 2. Map showing the distribution of sample localities at Dongmenqiao, Qingzheng and Guizhou Institute of Agricultural Sciences.

Experimental

Referring to the analytical procedure of mercury species (Lin Yuhuan, et al., 1983) and the total Hg analysis method (Pang Shuwei, et al., 1981), the authors adopted the sequential chemical extraction method to analyze Hg species in soil samples. The procedure is presented in Table 1.

Most of the water-soluble Hg and exchangeable Hg extracted in step 1 and step 2 combined with dissolved organic matter in the solution, and can not be reduced by $SnCl_2$ directly. In this paper, firstly the solution containing Hg was oxidized with brominized solution, and then Hg^{2+} was reduced by $SnCl_2$. Studies by previous researchers (Lin Yuhuan, et al., 1983) showed that step-2 extraction would weakly affect the extraction efficiency of step 3 and can enhance the extract amount of Hg in step 3 by 0.2% or so. The reason may be that the addtion of Cl^- enhances the complexing capabilities of the solution and increases the extract amount of Hg in step 3.

Table 1. The procedure of analysis of mercury species in soil samples

Step	Extracting method	Mercry species
1	0.5 g of soil sample was weighed into a 50 mL hard plastic tube, and 20 mL of deionized water was added in. Vibrate the tube for 30 min at room temperature, and centrifuge it at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Soluble Hg
2	20 mL of 0.5 mol/L $MgCl_2$ (pH = 7) solution was added into the residue above. Vibrate the tube for 30 min at room temperature, and centrifuge it at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Exchangeable Hg
3	0.5g of soil sample was weighed into a 50 mL hard plastic tube, 20 mL of 0.3 mol/L HCl was added in. Vibrate the tube for 30 min at room temperature, and centrifuge it at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Hg combined with carbonaqte and Fe, Mn oxidates
4	20 mL of 1% KOH solution was added into the residue above. Vibrate the tube for 30 min at room temperature. After 12 hrs, centrifuge it at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Hg combined with humic acid
5	20 mL of 3% H_2O_2(pH=2) solution was added into the residue above, heated at 80℃ in a water bath for 4 h, and centrifuged at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Hg combined with easily oxided and degraded organic matter
6	20 mL of 30% H_2O_2 (pH = 2) solution was added into the residue above, heated at 80℃ in a water bath for 4 h, and centrifuged at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Hg combined with hardly oxided and degraded organic matter
7	20 mL of aqua regia was added into the residue above, heated at 85℃ in a water bath for 4 h, and centrifuged at 3500 r.m.p. for 10 min. The aqueous phase was transfered to a 25 mL volumetric flask. Adopt the brominized method to analyse Hg content.	Residual Hg

The analytical procedures for Hg by the brominized method are described as follows. First, 1 mL of extraction solution is added to a 5 mL volumetric flask, 1 mL of 1:1 HCl is added in it, then 0.1 mL of brominized solution is added to homogenize the solution, and the solution is put aside for 5 min, and one drop of 12% $NH_2OH \cdot HCl$ is added. Deionized water is added to the graduation of the volumetric flask, and finally 1 mL of the solution is used for the determination of Hg content.

The aim of step 3 is to dissolve carbonate and Fe, Mn oxide species, but not to dissolve organic species. Before determining the Hg content in the extraction solution, the solution was oxidized by the brominized solution. The content of Hg species combined with carbonate and Fe, Mn oxides is the Hg content of the extract solution by step 3 subtracting that by step 2 and step 1.

The aim of step 4 is to extract Hg combined with humic acid, and 0.1 – 0.5 mol/L of NaOH also can be used to extract this Hg species.

The pH value of 3% and 30% H_2O_2 used in steps 5 and 6 was adjusted to 2 by diluted HNO_3. Studies showed that 30% H_2O_2 solution can extract 95% organic matter, while 3% H_2O_2 can only dissolve easily oxidized organic matter. Therefore, in this study, the authors adopted a double-step analytical procedure, namely, mercury combined with easily oxidized and degraded organic matter was extracted by 3% H_2O_2, and Hg combined with hardly oxidized and degraded organic matter was extracted by 30% H_2O_2.

The aqua regia can dissolve Hg present in mineral lattice at 85℃. The total Hg was also extracted by this method.

The reagents used were prepared as followes:

(1) A stock standard mercury (Ⅱ) solution was prepared by dissolving 0.0135g of mercury (Ⅱ) chloride and 5 mL of 10% H_2SO_4 and 1% $K_2Cr_2O_7$ and was diluted to 100 mL exactly with deionized water. A working standard mercury (Ⅱ) solution(0.5μg/mL) was prepared by diluting the stock standard solution with deionized water.

(2) A brominized solution was prepared by dissloving 2.784 g of $KBrO_3$ and 10 g of KBr in 1000 mL of deionized water.

(3) A 10% $SnCl_2$ solution was prepared by dissolving 10 g of $SnCl_2 \cdot 2H_2O$ in 10 mL of concentrated HCl while heating the solution, and was diluted to 100 mL with deionized water.

(4) A 12% $NH_2OH \cdot HCl$ solution was prepared by dissolving 12 g of $NH_2OH \cdot HCl$ and 12 g of NaCl in 100 mL of deionized water.

All the reagents were of analytical-reagent grade in our study.

The detection limit of our Hg analyzer is below 0.05 ng, while that of soil sample is 0.001μg/g.

Results and Discussion

Table 2 gives the contents of Hg species and total Hg in all the soil samples. In Table 2 the data in the second row at each sample locality represent the content of each Hg species relative to its total amount of the seven species.

From Table 2 it is seen that the contents of water-soluble Hg and exchangeable Hg in all the samples are very low, about 0.0*n*μg/g, while both the Hg species are easily absorbed by plants. It implies that the contents of Hg species which can directly be absorbed by plants in soils are very low in concentration.

Fig. 3 shows the distribution of relative contents of Hg species in all the soil samples. As can be seen from Fig. 3, according to the distribution characteristics of relative contents of Hg species in soils, the soil samples can be divided into three groups. The first group is characterized by the predominance of the Hg combined with hardly oxidized and degraded organic matter. The soil sample collected from Dongmenqiao, Qingzheng, belongs to this group, and the content of Hg combined with hardly oxidized organic matter in the sample is 1.288μg/g, accounting for 67.15% of the sum of all 7 Hg species. The second group features the predominance of residual Hg, and the relative contents of the other species are about *n*% (less than 10%). The soil samples collected from GIAS and DMC belong to the second group. The content of residual Hg in soil from GIAS is 0.213μg/g, accounting for 59.5% of the sum of all 7 Hg species, while the residual Hg content from DMC is 0.741μg/g, coming up to 79.59% of the total Hg in soil. In the third group the content of residual Hg accounts for more than 95%

of the sum of all 7 Hg species. The soil samples collected from DMF and DMY belong to this group, and the contents of the residual Hg in soils from DMF and DMY are 19.246μg/g and 9.940μg/g respectively, accounting for 97.57% and 96.53% of the total Hg, respectively. The relative contents of the other Hg species in soil samples of this group are very low (≤1.1%).

Table 2. The contents of different mercury species in all the soil samples

Sample locality	Unit of Hg content	Mercury species in soil							Sum of all 7 species	Total Hg digested by aqua regia
		Species 1	Species 2	Species 3	Species 4	Species 5	Species 6	Species 7		
DQ	(μg/g)	–	0.023	0.021	0.115	0.150	1.288	0.321	1.918	1.970
	(%)	0	1.20	1.09	6.00	7.82	67.15	16.74	100	
GIAS	(μg/g)	0.020	0.012	0.038	0.023	0.034	0.018	0.213	0.358	0.345
	(%)	5.59	3.35	10.61	6.42	9.50	5.03	59.50	100	
DMC	(μg/g)	0.019	0.065	0.031	0.046	0.029	–	0.741	0.931	0.871
	(%)	2.04	6.98	3.33	4.94	3.11	0	79.59	100	
DMF	(μg/g)	0.036	0.073	0.038	0.220	0.081	0.031	19.246	19.725	19.984
	(%)	0.18	0.37	0.19	1.12	0.41	0.16	97.57	100	
DMY	(μg/g)	0.009	0.066	0.073	0.116	0.087	0.004	9.940	10.295	10.896
	(%)	0.09	0.64	0.71	1.13	0.85	0.04	96.53	100	

"–" undetectable. Species 1: water-soluble Hg; species 2: exchangeable Hg; species 3: Hg combined with carbonate; species 4: Hg combined with humic acid; species 5: Hg combined with easily oxidized organic matter; species 6: Hg combined with hardly oxidized organic matter; species 7: residual Hg

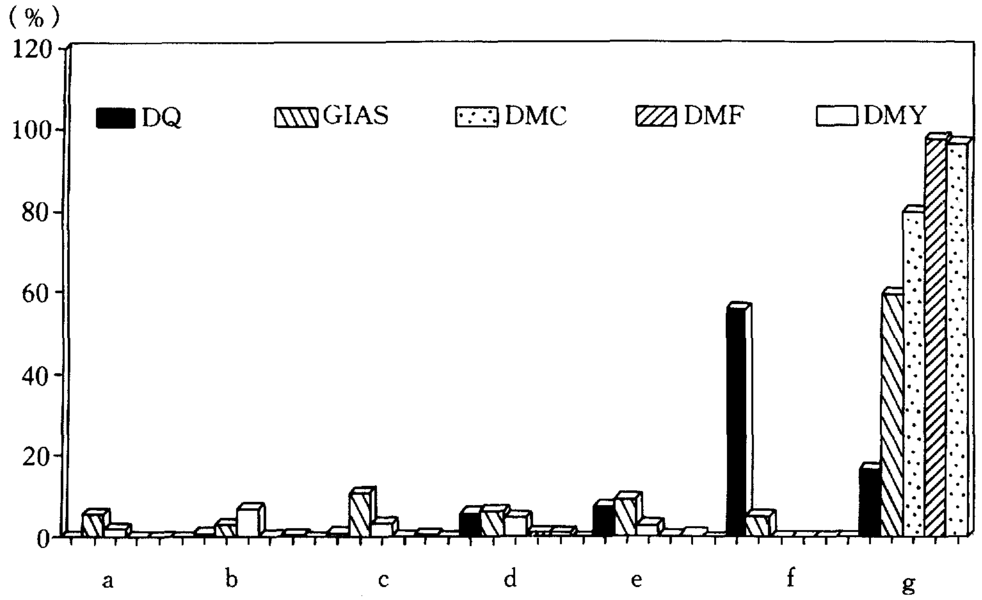

Fig. 3. The diagram showing the distribution of relative contents of all the mercury species in soil samples. a. Water-soluble Hg; b. exchangeable Hg; c. Hg combined with carbonate; d. Hg combined with humic acid; e. Hg combined with easily oxidized organic matter; f. Hg combined with hardly oxidized organic matter; g. residual Hg.

From Table 2 it can be seen that the total Hg content of soil from the reference area (GIAS) is 0.345μg/g, which is higher than the average Hg content of Chinese soil (0.065μg/g). There are at least two reasons for this. The first one is that the background value of Hg in limestone is higher than that of other rocks. The second one is that the farmland of GIAS is contaminated by anthropegenic activities.

The total Hg contents of soil samples from DQ, DMF, DMY and DMC are very high , all higher than that of soil sample from GIAS. The high Hg content of soil from DQ is attributable to artificial pollution, while that of soil samples from DMF, DMY and DMC is ascribed to geological processes, but the two kinds of soils are different in the distribution of mercury species. The dominant Hg species of high-Hg soil due to artificial pollution is the Hg combined with hardly oxidized and degraded organic matter, while that due to geological processes is residual Hg. It is obvious that the potential harm to plants of high-Hg soil due to artificial pollution is greater than that caused by geological processes because the Hg species combined with organic matter, which, however, cannot be absorbed directly by plants, will be released into soil solution more easily than residual Hg species when the environmental condition changes. Comparatively speaking, the residual Hg is inert and hard to absorb by plants.

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