

## Vertical fluxes of volatile mercury over soil surfaces in Guizhou Province, China

Feng Xinbin, Chen Yecai, Zhu Weiguo

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,  
Chinese Academy of Sciences, Guiyang 550002, China

**Abstract**—An instrument that can be used to measure the fluxes of volatile mercury over soil surface in field was set up. From August to October in 1993, the fluxes of volatile mercury over soil surfaces at 5 sites of three different areas (high mercury area, mercury polluted area, and reference area) were measured. The results showed that the measured fluxes over soil surface during daytime were higher than those measured at night, and that the flux of volatile mercury over soil surface has relationship with both the total mercury contents of soil and air temperature.

**Keywords:** mercury; fluxes; flux chamber; Guizhou Province; Danzhai Mercury Mine.

Many researchers abroad (Baeyens, 1991; Fitzgerald, 1991; Vandal, 1991; Schroeder, 1989; Xiao, 1991) have studied fluxes of volatile mercury over sea or lake surfaces in detail. Only a few of researchers (Schroeder, 1989; Xiao, 1991) studied fluxes of volatile mercury over soil surfaces, but they did not get useful results because there were some problems on flux chamber. Since the temporal and spatial variation of volatile mercury over soil surfaces and the factors at work are still unclear. In the present paper, the authors used the technique of flux chamber to study mercury flux over soil surface. This technique allows data to be obtained in natural environment, and gets results more objective. At present, chamber method has been the only available technology for measuring the flux of mercury over water bodies and soil surface in the field (Xiao, 1991).

## 1 Experimental

### 1.1 Sampling method of atmospheric mercury

In this investigation, airborne Hg was collected in gold wire traps, whose collection efficiency is more than 95 % at a flow rate of 1 L/min.

The sampling apparatus of atmospheric mercury is presented in Fig. 1, in which the function of the desiccator tube is to remove water vapor which will decrease the collection efficiency for Hg on the gold traps. Two gold traps in sequence were always used during the field experiments, which ensured that all vapor-phase mercury in the air being sampled. The flow rate is 1L/min, and the sampling time depends on the mercury contents in air.

The principle for choosing the desiccator is that it should efficiently absorb water vapor while not absorb mercury vapor at all. In this investigation, we chose  $\text{CaCl}_2$  as desiccant.

## 1.2 Chamber technology and on-site set up

Xiao *et al.* (Xiao, 1991) and Achroeder *et al.* (Achroeder, 1989) studied the Hg flux over soil surface used a stainless chamber which was used for the measurement of mercury flux over lake surface, but they did not get ideal results. The reasons are that metal will absorb Hg quantitatively and the chamber material does not

allow sunlight to penetrate the soil surface, then the biological activity and photochemical processes could be affected. Seeing that, we chose transparent organic glass material to construct a chamber with a removable bottom plate. Its dimensions is  $80 \times 20 \times 20$  cm (Fig. 2).

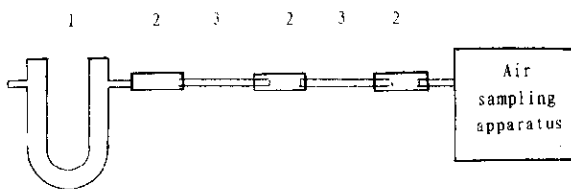


Fig. 1 Schematic diagram of atmospheric Hg sampling

1. U-type desiccant tube filling with  $\text{CaCl}_2$ ; 2. rubber tubing for connection; 3. gold wire traps

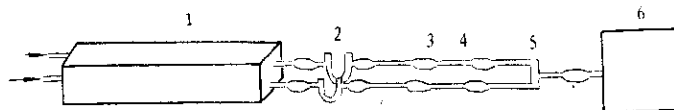


Fig. 2 On-site flux measurement apparatus

1. Flux chamber; 2. U-type desiccant tube filling with  $\text{CaCl}_2$ ; 3. rubber tubing for connection; 4. gold wire traps; 5. three way connector; 6. air sampling apparatus

Ambient air was drawn into the chamber through two inlet ports, while the traps for Hg collection were connected to the outlet ports. The gold traps are intended to collect vapor-phase Hg species in the air stream being sampled. The flow rate is 1 L/min, and the sampling time depends on the mercury contents in the air. In the field, the bottom

plate was removed, and the flux chamber situated on top of soil surface (Fig. 3), the amount of mercury collected on the traps per unit time through the outlet ports of the chamber,  $R_o$  is, given by:

$$R_o = R_i + R_c + R_s, \quad (1)$$

where,  $R_i$  is the rate at which gaseous Hg enters the chamber through the inlet ports,  $R_c$  is the rate at which Hg desorbs from the interior walls of the chamber, and  $R_s$  is the rate at which Hg is emitted from (or deposited to) soil surface.  $R_o$  was measured while the chamber tested directly on the soil surface. To calculate  $R_i$ , the concentration of Hg in the air entering the chamber was de-

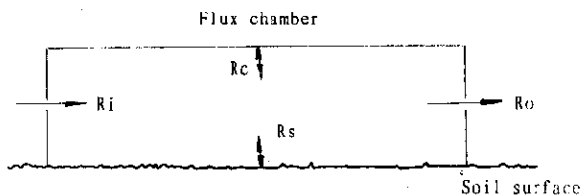


Fig. 3 Schematic diagram of the mass balance approach used when calculating mercury fluxes to and from soil surfaces

terminated experimentally in two separate sets (Fig.1) of measurements spanning the same time period as the chamber blank determinations and the flux measurements.  $R_c$ , the chamber blank, was determined with the removable bottom plate attached to the chamber.  $R_s$  is calculated by retaining Equation(1):

$$R_s = (R_o - R_i) - R_c. \quad (2)$$

It is important to note that  $R_s$  can be assumed to be either a positive value, corresponding to an emission of mercury, or a negative value, corresponding to a deposition of Hg.

### 1.3 Analytical method

Using a two-stage gold trap analysis technique(Fitzgerald, 1979; Feng, 1997), the Hg collected in the individual sampling traps was desorbed by heating at 700°C and transferred to an analytical trap with mercury-free carrier gas. The analytical trap was then heated at the same temperature as the individual sampling traps and the Hg thus released was analyzed by GC-5 type cold vapor atomic adsorption spectrometry (CVAAS) instrument. The detection limit of this method is 0.05 ng. This analytical method have at least two advantages. Firstly, it can eliminate the interference substances which affecting the analysis of mercury. Secondly, it can also enhance the analysis precision through eliminating analysis error caused by the physical difference among individual traps.

## 2 Sampling sites and the speciation of Hg

### 2.1 Sampling sites

The authors chose three different areas in Guizhou Province, namely high Hg-content area, Hg-polluted area and reference area. Danzhai Mercury Mine area was chosen as high Hg-content area, and three sampling sites, Danzhai Hg Mine Fuxingchang (DMF), Yichejian (DMY) and Changbu(DMC), were choosed according to soil Hg contents, the mercury content of soil sample from DMF is the highest, and that from DMC is the lowest. Mercury polluted farmland of Qingzheng Dongmenqiao(QD) was chosen as Hg polluted area and the testing farmland of Guizhou Agricultural Science Institute (GASI) was chosen as reference area. There was only one sampling site at Hg-polluted area and one at reference area.

### 2.2 The speciation of Hg

Using successive chemical leaching method, the contents of different Hg species of all soil samples were determined (Feng, 1996), the results are shown in Table 1.

## 3 Results and discussion

Table 2 summarizes all flux chamber measurements and air concentration determinations for Hg that were carried out at the five sample sites.

**Table 1 The results of different mercury species contents of all soil samples**Unit:  $\mu\text{g/g}$ 

Sampling sites	Different mercury species in soil samples							Total Hg contents
	Species 1	Species 2	Species 3	Species 4	Species 5	Species 6	Species 7	
QD	-	0.023	0.021	0.115	0.150	1.288	0.321	1.918
GASI	0.02	0.012	0.038	0.023	0.034	0.018	0.213	0.358
DMC	0.019	0.065	0.031	0.046	0.029	-	0.741	0.931
DMF	0.036	0.073	0.038	0.220	0.081	0.031	19.246	19.725
DMY	0.009	0.066	0.073	0.116	0.087	0.004	9.940	10.295

Notes: 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 hard oxidized organic matter; species 7: residual Hg

**Table 2 Results of flux chamber measurements of mercury over soil surfaces of five sampling sites**

Sampling date	Sampling time	Sampling site	Hg flux, $\text{ng} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$	Air temp., $^{\circ}\text{C}$	Relative humidity, %	Average Hg conc. in air, $\text{ng} \cdot \text{m}^{-3}$
9 Oct.	12:41—14:21	DMF	$145.38 \pm 45.54$	27.3	48.5	71.43
9 Oct.	20:26—22:43		$30.06 \pm 8.34$	17.0	69.3	16.08
14 Oct.	11:04—12:29		$22.66 \pm 7.00$	16.4	60.0	27.11
10 Oct.	11:45—15:40		29.76	29.5	45.0	77.77
11 Oct.	16:12—17:42	DMC	$12.51 \pm 4.70$	26.7	57.5	43.79
12 Oct.	22:03—23:30		$-18.80 \pm 3.79$	15.9	92.0	57.07
13 Oct.	10:33—12:01		$92.18 \pm 10.61$	26.2	41.0	249.18
13 Oct.	16:36—17:42		$82.55 \pm 28.66$	23.8	50.8	71.27
13 Oct.	21:54—23:20	DMY	$10.05 \pm 0.32$	21.2	54.0	38.01
1 Nov.	13:14—16:24		$16.64 \pm 1.21$	21.9	30.0	25.07
1 Nov.	21:17—23:05		$-2.26 \pm 0.57$	9.0	92.5	10.56
14 Nov.	13:00—14:30		$26.63 \pm 6.63$	23.4	27.5	82.28
14 Nov.	19:17—20:47	QD	2.40	14.7	43.5	33.10

As depicted in Fig. 4, the entire series of Hg flux measurements exhibited a very consistent diurnal pattern, with Hg fluxes being clearly higher during the daytime than that at night. From Table 2, it can be seen that mercury flux is mainly related to air temperature, namely the higher the air temperature, the higher the Hg flux. For example, it was cloudy during daytime on 14 October, and the air temperature was lower than at night of 9 October. The results showed that Hg flux during daytime of 14 October was less than that at night of 9 October. It is obviously that the diurnal pattern of Hg flux over soil surfaces is caused by the variation of air temperature, and that the magnitude of Hg flux soil surfaces is controlled by air temperature.

From Fig. 4, it can be seen that, at similar air temperature, mercury flux sequence from high to low is DMF's, DMY's, QD's, DMC's and GASI's, similar to the Hg contents of soil samples. It suggested that Hg flux also has relationship with Hg content of soil sample, i.e., the higher Hg content of soil sample is, the higher Hg flux over soil surface at the same air temperature.

From Fig. 4, it can also be seen that the Hg flux values at DMC and GASI at night were negative, that means air Hg depositing to the surface of soil. During sampling processes at night, the relative air humidity was very high, 92.5% at GASI and 92% at DMC. This implied that when

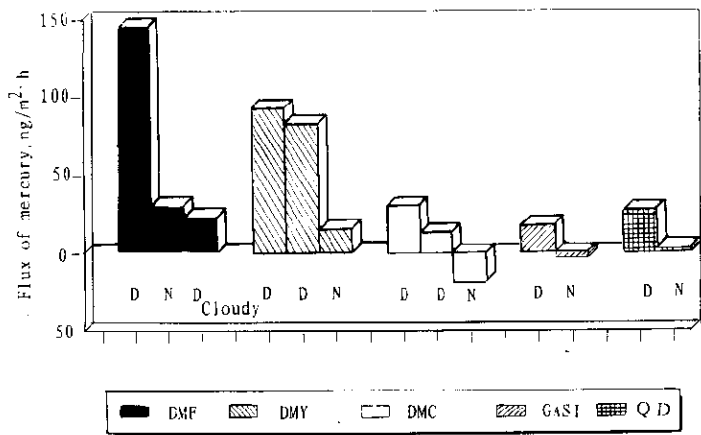


Fig.4 Diurnal variation of mercury flux over soil surfaces of five sampling sites

relative air humidity become very high, airborne Hg will deposit to the surface of soil.

After multivariable progressive regression analyzing between Hg flux and contents of each Hg species, total Hg content in soil samples and air temperature, we can get the regression equation as follows:

$$\ln Y = 52.096 + 0.5\ln C - 14632.356/T,$$

(3)

where,  $r^2=0.8792$ ;  $Y$  is calculated Hg flux;  $C$  is total Hg content of soil sample; and  $T$  is air temperature(K).

From the regression equation, it can be seen that Hg flux only relates to the total Hg content of soil sample, and not relates to the individual Hg species contents of soil samples.

**Acknowledgments**—The authors would like to thank Prof. Xie Hongshen, Prof. Hong Yetang and Prof. Yu Zhichen for their kind instructions.

References

Baeyens W, Leermakers M., Dedeurwaerer H, Lansens P. Water Air and Soil Pollution, 1991; 56:731

Feng Xinbin, Hong Yetang. Environmental Monitoring in China, 1997(In press)

Feng Xinbin, Chen Yecai, Zhu Weiguo. Acta Mineralogica Sinica, 1996; 15(2)

Fitzgerald WF, Mason RP, Vandal GM. Water Air and Soil Pollution, 1991; 56:745

Fitzgerald WF, Gill GA. Anal Chem, 1979; 51:1714

Schroeder WH, Muthe J, Lindqvist O. Water Air and Soil Pollution, 1989; 48:237

Vandal GM, Mason RP, Fitzgerald WF. Water Air and Soil Pollution, 1991; 56:791

Xiao ZF, Munthe J. Schroeder WH, Lindqvist O. Tellus, 1991;43B:267