DESIGN AND INITIAL TESTS OF A DYNAMIC ENCLOSURE CHAMBER FOR MEASUREMENTS OF VAPOR-PHASE MERCURY FLUXES OVER SOILS

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Abstract. In an effort to establish reliable methodologies for measuring fluxes of mercury (Hg) across the soil-air interface, we have developed a field flux chamber built with FEP Teflon. To evaluate our field flux chamber system, a series of laboratory and field tests were performed. The observations of relatively low chamber blanks and low blank-to-sample ratios for the FEP Teflon chamber suggest its potential in Hg flux investigations. Despite its potential, Hg exchange rate measurements using the field flux chamber method must be made with great caution since it can be subject to contamination problems associated with the selection of chamber materials.

1. Introduction

The transfer of various pollutant chemicals across the biosphere and atmosphere interface is influenced by both anthropogenic and natural processes. It is known that, compared to the generally intense, localized anthropogenic processes, natural processes tend to occur over large areal scale with low flux density. As in the case for many other trace gases of biological origin, the world oceans have been identified to be a major component of the global atmospheric mercury (Hg) budget, with an annual emission rate of approximately 2 Tg yr^{-1} (Fitzgerald, 1989). Terrestrial sources are also suggested to play an important role in the global atmospheric Hg cycling. However, previous estimates of the total terrestrial flux of Hg are highly uncertain due to lack of reliable methodologies and of published data.

Only a small number of experimental techniques have been used for direct exchange rate measurements of atmospheric Hg in terrestrial environments. The pioneering field flux measurements for Hg were conducted using flux chamber techniques (Schroeder *et al.*, 1989; Xiao *et al.*, 1991). Application of a micrometeorological approach, which is generally considered as a more reliable method, has not been attempted

Water, Air, and Soil Pollution **80**: 1059–1068, 1995.

until recently (Kim *et al.*, in press; Lindberg *et al.*, submitted). Previous dynamic flux chamber studies performed in a boreal forest (Xiao *et al.*, 1991) indicate (1) similarly important roles of both emission and deposition processes over daily cycles and (2) seasonal variabilities in exchange patterns (e.g., emission-dominant summer and deposition-dominant winter). By contrast, initial results from micrometeorological studies in a background, temperate forest environment in Tennessee have shown somewhat opposing features characterized by (1) the generally enhanced magnitude of and frequent occurrences of emission (vs deposition) over daily cycles and (2) consistently emission-dominant trend over seasonal cycles (Kim *et al.*, in press). Kim *et al.* concluded that the level of difference in measured fluxes and temporal exchange patterns may still be explainable considering all different environmental and methodological factors involved in different studies.

In the initial stage of our MASE (Mercury Air/Surface Exchange) project, we have been extensively involved in establishing accurate experimental methods of measuring Hg exchange rates, in particular the micrometeorological modified Bowen ratio (MBR) method. The results of our initial application of the MBR approach to Hg flux measurements have been reported elsewhere (Kim *et al.*, 1993, in press; Lindberg *et al.*, submitted). As a part of our extended effort to accurately quantify Hg exchange rates, we have also been involved in development and application of flux chamber measurement techniques. Here we present and discuss some preliminary results of our flux chamber studies obtained during evaluation periods.

2. Materials and methods

The stainless steel chamber of Xiao *et al.* (1988, 1991), which was built on the basis of their studies of chamber material evaluation (between stainless steel and pyrex glass), still suffered from quite substantial chamber blank problems. Noting the good performance of FEP teflon in various trace gas flux chamber studies (e.g., reduced S: Kuster and Goldan, 1987), we selected it as a chamber material. An FEP-Teflon chamber was constructed with an open bottom and deep stretching skirts (dimension of 60x20x20 cm) and was supported by an external Al frame (Figure 1). This chamber was built to facilitate

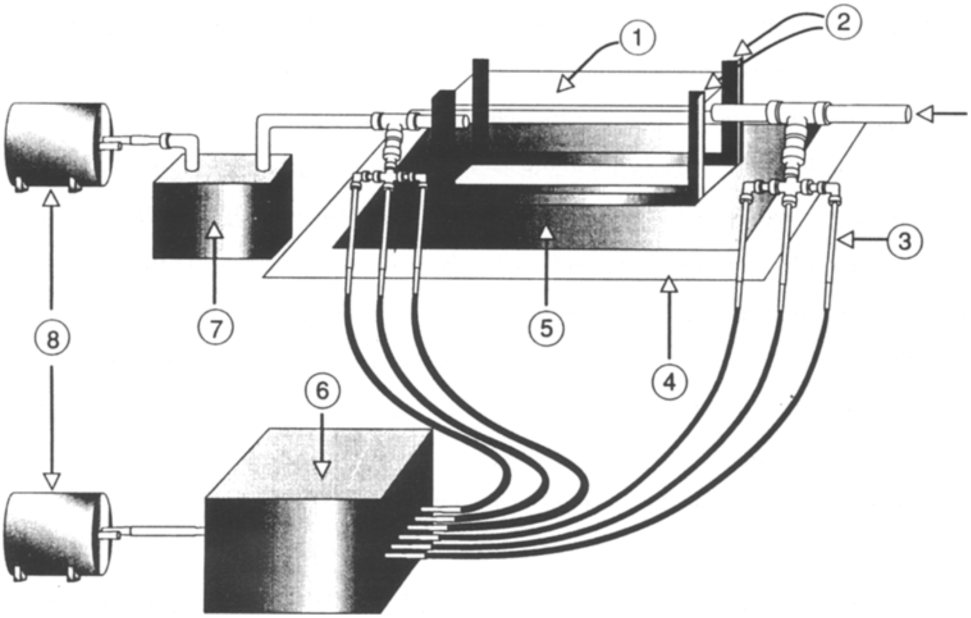

Figure 1. A schematic diagram of flux chamber system: (1) FEP enclosure chamber, (2) external Al-supporting rod, (3) Au-coated sand amalgamation trap, (4) bottom skirt of chamber, (5) frame of Al-supporter, (6) ORNL MFC system for six-replicate sample collection (maximim capacity for each individual MFC unit ~0.5 l min^{-1}), (7) MFC for flushing rate calibration (~15 l min^{-1}), and (8) vacuum pump.

simultaneous collection of three replicate air samples from both inlet and outlet ports to better characterize the true mean concentrations of Hg^o entering and exiting the flux chamber. For each experiment, the air stream at the inlet and outlet port was sampled simultaneously at constant flow rate of about 400 ml min^{-1}. Air samples were drawn for periods of approximately 2 h using a multiple replicate sampling system equipped with six seperate mass flow controllers (MFCs) (Kim and Lindberg, 1994). Flow into and out of the chamber was also maintained at a constant flow rate of 5 l min^{-1} using a high-capacity MFC (corresponding to about 5 min of turnover time for the internal volume of the flux chamber). The traps for Hg collection were made of gold-coated sand absorbers. To achieve a tight seal between chamber and soil surfaces, the four edges of the chamber-skirt were firmly pressed into the soil by lead bricks. The blank levels of our flux chamber were routinely measured by sealing the chamber over a large, clean sheet of FEP Teflon. The measurements of field chamber blanks and bias tests between different sampling methods were performed at the Walker Branch Watershed (WBW) in Oak Ridge, TN during June 1993 through June 1994. A detailed description of the experimental site has been presented by Kim *et al.* (in press). For the quality assurance of our flux chamber measurements, ambient air samples were occasionally collected during the same period using an independent sampling system designed to measure the vertical gradients of Hg at two heights (i.e., 10 and 165 cm). The sampling and analytical procedures used in our gradient measurements are detailed in the companion paper in this volume (see *Lindberg et al.* this volume).

The total amount of vapor-phase Hg collected from each flux chamber measurement was determined using a two-stage gold trap analysis technique (Fitzgerald and Gill, 1979) by cold-vapor atomic fluorescence spectrophotometry (CVAFS). The detection limit for the system, calculated as three times the standard deviation of typical mean blank levels of the Hg-collection traps, is typically found at 1 to 2 pg of Hg. The analytical system was standardized by measuring known volumes of a Hg-saturated atmosphere via an air tight gas syringe using a system of our own design. From our measurements of replicate air samples, we routinely achieved a combined sampling plus analytical precison in the range of 1 to 3 % (expressed in terms of relative standard error, RSE). Statistical outliers from each set of samples collected at the inlet and outlet were eliminated using the statistical method of Skoog *et al.* (1992). Since total gaseous Hg collected by our sampling system is predominantly in elemental form (~98%), the concentration and flux values of Hg in this paper are operationally defined as Hg^O.

The rate at which Hg^O exchanges through the chamber was computed using the following equation:

$$F = \frac{(C_o - C_i)}{A} \times Q$$

where F is Hg^O flux in ng m^{-2} h^{-1}, C_i and C_o are the Hg^o concentrations in ng m^{-3} at the inlet and outlet ports, A is the bottom surface area of chamber in m^3, and Q is the flushing flow rate through chamber in m^3 h^{-1}.

3. Results and discussion

Previous flux chamber studies to measure Hg fluxes over environmental surfaces indicated that the major problem associated with application of this technique was the presence of large chamber blanks which occasionally exceeded the magnitude of sample fluxes (Xiao *et al.*, 1991). To offer insights into the significance of chamber blank problems, the results of blank/soil flux measurements performed by Xiao *et al.* (1991) are summarized in Table I. To facilitate the comparison of chamber blank vs. sample fluxes, chamber blank values expressed in terms of ng min^{-1} of sampling time were converted into units that are comparable to actual sample fluxes (i.e., ng m^{-2} h^{-1}). The mean and 1 SD of chamber blank are 2.13 ± 1.20 ng m^{-2} h^{-1}. The results shown in Table I clearly indicate that chamber blank values are in many cases larger (up to an order of magnitude) than the flux values.

Noting the significance of chamber blank problems as acknowledged by Xiao *et al.* (1991), we began a series of laboratory and field chamber blank measurements as a first step toward the evaluation of our flux chamber system. To check the extent of initial contamination on our chamber system, the flux chamber was tested as delivered (April 10, 1993) without pre-cleaning. Table II shows a summary of seven laboratory and five field blank measurements made during the initial evaluation period. The mean and 1 SD of our laboratory blank fluxes are 0.5 ± 0.3 ng m^{-2} h^{-1} (n = 7), while those of field blank fluxes are 1.0 ± 0.3 ng m^{-2} h^{-1} (n=4). Although our chamber did not go through a complicated chemical cleaning process like that of Xiao *et al.* (1988), the mean chamber blank values derived from both of our laboratory and field tests are approximately two to four times lower than those seen from studies of Xiao *et al.* (1991). From our previous flux measurements using the MBR method (Kim *et al.*, in press), we quantified the mean and 1 SD of the WBW soil emission rates to be 7.5 and 7.0 ng m^{-2} h^{-1} (n=30). Thus, a combined effect of generally low blank values from our flux chamber system and the observations of enhanced emission rates of Hg^{o} from our field study site (relative to the boreal forest site studied by Xiao *et al.*: refer to Kim *et al.*, in press) suggest that more reasonable blank-to-sample ratios may be obtained from our flux chamber measurements at WBW.

TABLE I

Comparison of chamber blanks and blank-to-sample ratio from previous soil-to-air flux measurements of Xiao *et al.* (1991) using stainless steel flux chamber.

Date	Chamber blank* ($ng\ min^{-1}$)	Chamber blank** ($ng\ m^{-2}\ h^{-1}$)	Hg fluxes ($ng\ m^{-2}\ h^{-1}$)	B/S ratio*** (%)
12/17/87	0.0036	1.35	1.4	96
2/9/88	0.0022	0.83	-1.3	63
2/11/88	0.0032	1.20	-1.4	86
4/14/88	0.0099	3.71	-2	186
4/14/88	0.01	3.75	-1.1	341
4/15/88	0.006	2.25	-0.3	750
5/30/88	0.0042	1.58	2.5	63
5/30/88	0.0037	1.39	0.5	278
5/24/89	0.011	4.13	-0.8	516
5/24/89	0.008	3.00	-1	300
6/12/89	0.0042	1.58	0.14	1125
6/12/89	0.0022	0.83	0.17	485
Mean	.0057	2.13		357
1 SD	.0032	1.20		322

* Chamber blanks are presented as originally reported by Xiao *et al.* (1991).
** Chamber blank values of Xiao *et al.* are converted into flux units.
*** Blank-to-sample ratios are expressed in terms of absolute percentage.

To further test the reliability of our flux chamber system, we performed a series of bias tests in which Hg concentrations measured at the inlet and outlet of the chamber system were directly compared with those collected by an independent Hg sampling system. To collect more replicate samples for each sampling system, we modified our typical sampling procedures of each sampling system. For the chamber system, air samples were drawn from both inlet and outlet ports with the bottom of the chamber slightly open to the ambient air. Six replicate samples were collected simultaneously near the chamber inlet using our gradient sampling system for the purpose of comparison. These bias tests between two sampling techniques were performed at both laboratory and

TABLE II

Results of laboratory and field blank flux measurements of Hg^{o} using ORNL FEP flux chamber.

Date	Hg^{o} concentrations Mean ± 1 SE (ng m^{-3}) Inlet	Hg^{o} concentrations Mean ± 1 SE (ng m^{-3}) Outlet	Statistical significance* ($P < x$)	Blank Flux (ng m^{-2} h^{-1})
(1) Flux chamber blanks (Laboratory measurements)				
6/23/93	17.35±0.17	17.78±0.02	0.1	0.7
10/27/93	7.69±0.04	7.61±0.14	ns	-0.2
10/27/93	7.37±0.29	6.95±0.02	0.15	-0.9
11/1/93	6.47±0.13	6.60±0.09	ns	0.3
11/1/93	7.36±0.22	7.16±0.10	ns	-0.4
11/1/93	7.13±0.10	7.20±0.06	ns	0.1
11/1/93	7.52±0.16	7.02±0.03	0.15	-0.7
Mean ± 1 SD of chamber blank fluxes (in absolute terms) = 0.5 ± 0.3 ng m^{-2} h^{-1}				
(2) Flux chamber blanks (Field measurements)				
3/11/93	3.21±0.14	3.68±0.15	0.05	1.4
11/2/93	2.75±0.23	3.20±0.36	ns	1.0
11/2/93	2.36±0.10	2.62±0.15	0.15	0.6
11/12/93	4.17±0.09	4.61±0.07	0.05	1.0
Mean ± 1 SD of chamber blank fluxes (in absolute terms) = 1.0 ± 0.3 ng m^{-2} h^{-1}				

* denotes the probability that two variables are not significantly different

field site. Results from three laboratory bias tests showed that differences between two sampling methods were not statistically significant. (During these tests, Hg^{o} concentrations in lab air generally ranged from 15 to 23 ng m^{-3}.) In contrast to these observations, statistical analysis on our field bias test results showed discernible differences between the two methods (Table III). The initial tests performed on June 15, 1994 (Table III) show that the concentrations of Hg^{o} collected by the chamber system are measurably larger than those measured by the reference sampling system and suggest that the extent of disagreement may decrease with time (probably due to enhanced system flushing with extended operation). The differences between laboratory and field bias tests suggest that our flux chamber system can be more easily subject to contamination under clean conditions (Hg^o concentration from background field site ~1.5 ng m^{-3}) than under high Hg^o levels associated with the laboratory air. In an effort to eliminate the possible contamination of the chamber system, we detached, acid-washed, and oven-dried all Teflon connectors attached to the body of the flux chamber. The effect of acid-washing was quite dramatic as seen from our June 21 tests (Table III). The bias between chamber/gradient system decreased from 40 to 90% (before washing) to approximately ± 5 % (after washing). Similarly, the results of our statistical analysis also show the effect of acid-washing such that differences between two methods become less significant between before and after acid-washing ($P < 0.05$ to $P < 0.10$).

TABLE III

Results of field bias tests between flux chamber and an independent gradient sampling system on June 1994

Date	Time (EST)	Mean Hg^o (ng m^{-3})	Method	N	SE	RSE (%)	Sig ($P < x$)
		(1) Before acid-washing					
6/15/94	0949/1119	2.41	G*	6	0.08	3.1	0.05
6/15/94	0949/1119	4.57	FC**	6	0.11	2.3	
6/15/94	1128/1256	2.19	G	6	0.03	1.6	0.05
6/15/94	1128/1256	2.96	FC	6	0.06	2.1	
		(2) After acid-washing					
6/21/94	1055/1240	5.49	G	4	0.18	3.3	0.10
6/21/94	1055/1240	5.83	FC	5	0.14	2.4	
6/21/94	1247/1419	3.50	G	4	0.11	3.0	0.10
6/21/94	1247/1419	3.33	FC	5	0.03	1.0	

* denotes gradient sampling system.

** denotes flux chamber system.

Despite the potential problems of creating artificial environmental conditions, flux chamber techniques may still be favored over other flux measurement techniques due to: (1) highly senstive measurements of exchange rates; (2) high portability in assessing the spatial variabilities; and (3) allowance of replicate measurements coincident in space and/or time. Its applicability can be further extended to various controlled studies of trace gas behavior (e.g., measurements of Hg^{o} exchange rates under wet/dry conditions or with/without leaf litter). A series of laboratory/field evaluation tests of the field flux chamber shows a great potential of an FEP Teflon flux chamber for its applications to quantification of Hg fluxes over environmental surfaces. However, as indicated by the test results summarized in Table III, our initial tests suggest that measurements of the environmental Hg mobility by Teflon flux chamber must be made with great caution due to the potential for contamination under clean, background conditions.

Acknowledgements

Research sponsored by the Electric Power Research Institute (Project RP3218-02) under contract with ORNL. ORNL is managed by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

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