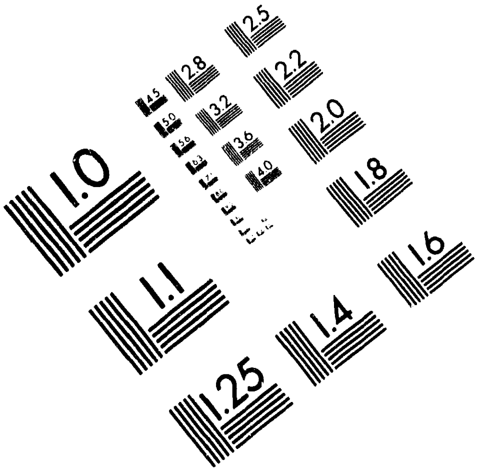

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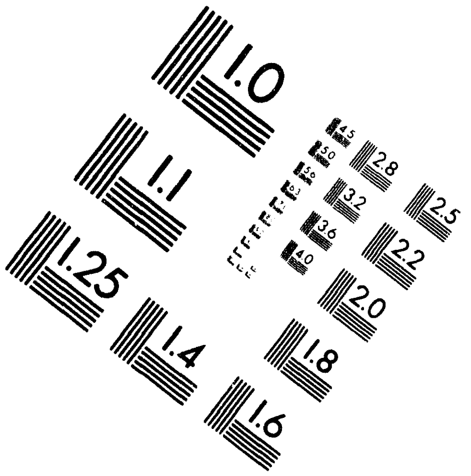

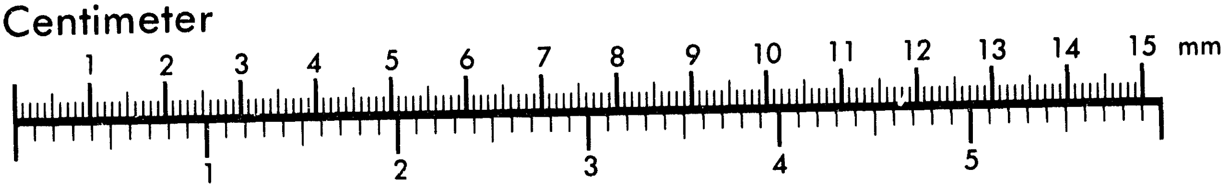

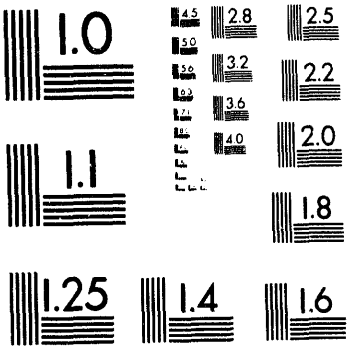

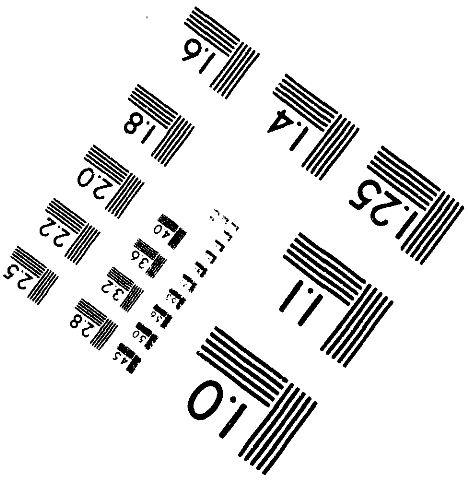

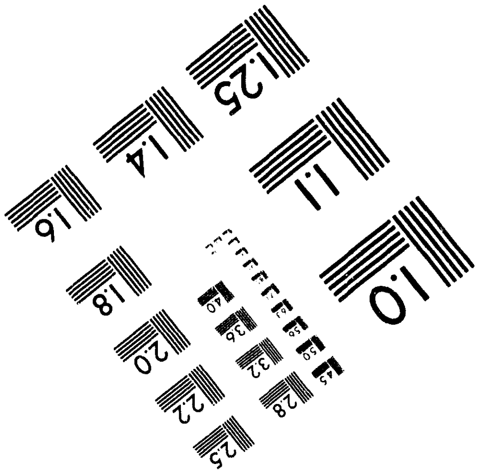

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MICROMETEOROLOGICAL METHODS FOR MEASUREMENTS OF MERCURY EMISSIONS OVER CONTAMINATED SOILS

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For publication in: Proceedings of The First Workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals by The United States Environmental Protection Agency in Durham, North Carolina, May 6-7, 1993

Edited by J. M. Pacyna, E. Voldner, G. J. Keeler and G. Evans

Published by Norwegian Institute for Air Research

Nordmoen, Norway

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Application of Micrometeorological Methods to Measurements of Mercury Emissions over Contaminated Soils

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ABSTRACT

As part of a larger study involving development and application of field and laboratory methods (micrometeorological, dynamic enclosure chamber, and controlled laboratory chamber methods) to measure the air/surface exchange of Hg vapor, we performed a series of preliminary measurements over contaminated soils. From March-April 1993, we used the modified Bowen ratio method to measure emission rates of Hg^o over a floodplain contaminated with mercury near Oak Ridge, TN. The measured fluxes (15 to 160 ng m^{-2} h^{-1}) exceeded those estimated by us and others for natural soils (0.3 to 6 ng m^{-2} h^{-1}) by several orders of magnitude. Using a controlled laboratory chamber, we estimated maximum potential emissions under well mixed summer conditions in the range of 840 to 1470 ng m^{-2} h^{-1}. Fluxes from this site are influenced by turbulence, surface soil temperature, and residence time of air masses over the source area.

INTRODUCTION

The contribution of direct discharges from many industrial processes to the global Hg budget has decreased since 1970. Attention must now be given to the possible significance of Hg emissions from local area sources (e.g., landfills, contaminated soils, and other solid waste sites) as they can continuously release Hg vapor (referred as Hg^o hereafter) to the given locality. Yet there is a paucity of reliable information concerning the role of Hg^o emissions from waste sources and their local impacts.

As part of a more extensive project on the atmosphere/surface exchange of Hg^o (e.g., ref 1), we performed an exploratory study of Hg^o emissions from contaminated soils. The study area is located on the forested floodplain of East Fork Poplar Creek (EFPC), Oak Ridge, TN which was contaminated by Hg from an upstream nuclear weapons plant. These floodplain soils contain up to 3000 µg g^{-1} of Hg predominantly as mercuric sulfide but with a small fraction (~6%) in the elemental form (ref 2). The source strengths of these contaminated forest soils have primarily been assessed using a micrometeorological approach, the modified Bowen Ratio method (MBR: refer to ref 3, 4). A maximum emission rate of Hg^o from these contaminated soils has also been investigated using a laboratory-controlled open gas exchange chamber system. These emission rates from contaminated soils are compared with our preliminary Hg emission data collected from a nearby background site, Walker Branch Watershed (WBW) near Oak Ridge, TN as well as with previously reported data for background forest soils. The objectives of this study are to evaluate the applicability of the MBR method to Hg^o emission measurements from contaminated forest soils, to provide insights into the factors and processes governing the fate of Hg in the contaminated environment, and to help derive reasonable source strengths of contaminated soils through comparisons of different approaches.

METHODS

The modified Bowen Ratio method

The concentration gradients of Hg^o in air over contaminated EFPC forest soils have been measured during early spring (March 29 to April 13, 1993). Six replicate samples of vapor-phase Hg were collected from each of two heights above the soil (25 and 165 cm) using gold amalgamation traps and were analyzed by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) (ref 5, 6). Using these methods with a single-manifold/multiple-mass-flow-controller system developed in our laboratory, we routinely achieve a precision of 1 to 3% in determinations of vapor-phase Hg concentrations in air

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mitted to: The Heavy Metals in the Environment Conference 1993
5/11/93

(in the sub-pptv range) from up to 18 replicate samples (ref 7).

Eddy correlation and vertical gradient data for CO_2 and H_2O vapor were measured concurrently with Hg^o gradient data using eddy correlation with fast response instrumentation (ref 8). The air-surface exchange rates of Hg^o were then inferred from the following relationship

$$F_{Hg^o} = K_w \; \Delta Hg^o$$

where F_{Hg^o} is the flux of mercury, ΔHg^o is the vertical gradient of Hg^o, and K_w is the turbulent transfer coefficient which can be calculated from the ratio of CO_2 (or H_2O) flux and its gradient: $K_w = F_{CO_2}/\Delta CO_2$ ($= F_{H_2O}/\Delta H_2O$). The use of independently determined K_w values, which can serve as a quality check on the overall method, avoids the problematic assumptions of the normal gradient method by which the flux of a trace gas is equated with the flux of heat.

Controlled flow chamber method

Six intact forest floor cores 19 cm in diameter and approximately 10 cm deep were obtained from the EFPC and WBW sites. These cores were collected in February when the soils had a water content between 25-30 percent (v/v) and were maintained in that condition during laboratory observations. The mean Hg concentration in the EFPC surface soils was determined to be 48 µg/g, compared to 0.5 µg/g in the WBW soils. Each core was held intact in a 2500 cm^3 Pyrex dish with an exposed planar surface area of 269 cm^2.

The soil cores were enclosed in a controlled flow chamber (ref 9) for measurements of Hg^o emissions. Mean conditions during measurements were as follows: air temperature 29±1°C, CO_2 concentration 355±15 $\mu l \; l^{-1}$, and relative humidity ≈50 percent. Temperatures of the soil cores at 2 cm were typically 1-2°C below air temperatures. Total air flow through the well stirred chamber was 0.56 $m^3 \; h^{-1}$. Hg^o concentrations of the air entering and leaving the chamber were obtained with triplicate and parallel Hg^o traps each sampled at a flow rate of 210 sccm. For each experiment, Hg^o exchange with the surfaces of the empty chamber were evaluated and subtracted as a blank from the inlet/outlet differential before calculating the rate of Hg^o efflux from the soil cores.

Using the equations for trace gas exchange (ref 9), the total Hg^o efflux was calculated as follows:

$$F_{Hg^o} = [C_o - C_i]/A * Q$$

where F_{Hg^o} is the efflux of Hg^o in ng Hg $m^{-2} \; h^{-1}$, $[C_o - C_i]$ is the outlet/inlet concentration differential corrected for efflux from the empty chamber in ng m^{-3}, A is the area of the soil core in m^2, and Q is the flow rate through the reaction chamber in $m^3 \; h^{-1}$.

RESULTS AND DISCUSSION

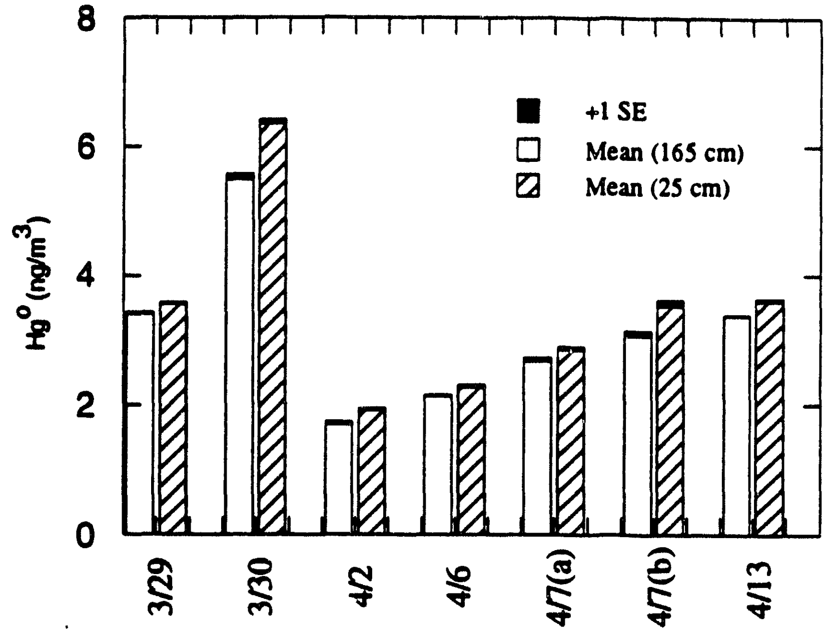
The Hg^o fluxes over contaminated EFPC soils estimated using the MBR method are summarized along with the other results in Table 1. The Hg^o concentration gradient data used for these computations are also presented in Figure 1. The measurements over contaminated soils were characterized by a strong signal of Hg emissions to the atmosphere ranging from 15 to 160 ng $m^{-2} \; h^{-1}$ ($\bar{x}$=44, SE=20, n=7). As expected, the EFPC fluxes are significantly correlated with turbulent transfer coefficient, K_w ($r=0.7$, $P < 0.001$, n=23) and surface soil temperature ($r=0.49$, $P < 0.02$, n=25) (Figure 2). (Note that temperature and K_w data represent 30 min average values (n=23-25), while corresponding Hg^o flux data are approximately 2 hr average values (n=7).) In addition to the possible significance of these parameters, the influence of the retention time of the air masses over the source area is also important. Our sampling site is located near the northwestern edge of the floodplain where it can be influenced by relatively clean air coming from a westerly to northwesterly direction or by high-Hg^o containing air coming

Table 1. Measured Hg^0 emission rates from contaminated and background forest soils.

Method	Study site	Hg^0 emission rate (ng m^{-2} h^{-1})			Reference
		Range	Mean	SE	
MBR	EFPC	15 to 160	44	20	This Study
MBR	WBW	-6* to 6	-0.2*	3	This Study
Lab Open Flow Chamber	EFPC	840 to 1470	1080	110	This Study
Lab Open Flow Chamber	WBW	1 to 37	16	5	This Study
Field Flux Chamber	Sweden	0.1 to 1.4	0.8	0.2	10
Field Flux Chamber	Sweden	-2.0* to 2.5	-0.3*	0.4	11

*All negative values denote deposition of Hg (from air to soil) instead of emission.

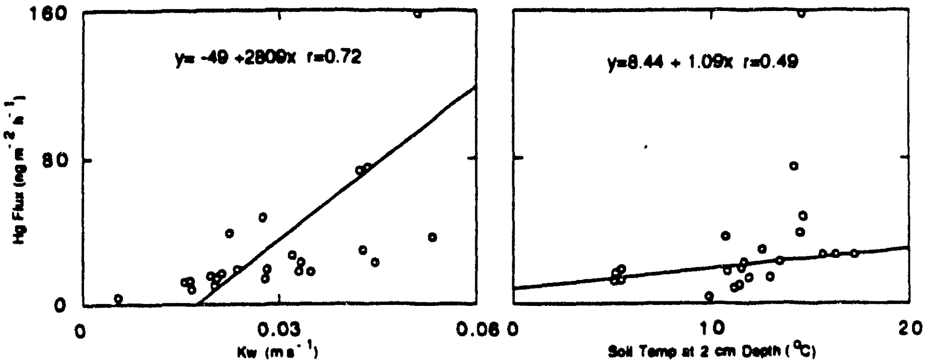
Figure 1. Concentration gradient measurements of Hg^0 over contaminated EFPC soils.



from easterly and southeasterly directions. For a pre-coldfrontal period chracterized by a relatively low wind speed from the southeast, we observed the highest Hg^0 concentration measured (6.4 ng m^{-3}) and a Hg^0 emission of 160 ng m^{-2} h^{-1} (on 3/30). Conversely, the lowest flux of 15 ng m^{-2} h^{-1} and lowest airborne Hg^0 concentration (1.7 ng m^{-3}) were measured when a post-coldfrontal clean westerly air mass with relatively high wind speed was sampled three days later (on 4/2).

As a reference to the Hg^0 emission rates over contaminated soils, the exchange rates of Hg^0 over uncontaminated soils were measured from WBW during late summer 1992. These results are characterized by relatively weak signals of both emission and deposition fluxes (-6 to 6 ng m^{-2} h^{-1}: n=3) and are analogous to those reported for a coniferous forest in Sweden (ref 11). These data support the idea that clean background soils can act as both sources and sinks of Hg^0 to the atmosphere and indicate that the EFPC soils are a significant source of Hg^0 to the local atmosphere.

Figure 2. The measured Hg^0 emission over contaminated soils as a function of turbulent transfer coefficient and surface soil temperature.



Hg^0 flux estimates from EFPC soils obtained using a controlled flow chamber system fell in a relatively narrow range of 840 to 1470 ng m^{-2} h^{-1} with a mean of 1080 ng m^{-2} h^{-1} (n=6). The controlled flow chamber fluxes are much larger in magnitude than those derived using the MBR method because these measurements were conducted under extremely favorable conditions for Hg^0 emission: (1) surface soil temperatures around 28°C relative to 5 to 18°C during the MBR measurements; (2) enhanced turbulent mixing conditions inside the chamber; and (3) disturbed soil structure due to coring and fitting in glass dishes. These Hg^0 flux estimates from our open flow chamber experiments should be considered as an upper bound of Hg^0 emissions. It was observed that surface temperature exhibits a very strong influence on Hg^0 emissions from contaminated sites (ref 12).

SUMMARY AND CONCLUSIONS

The Hg^0 emission rates measured from contaminated EFPC soils using the MBR method during early spring show that: (1) in all cases, the contaminated soils acted as a source of Hg^0 to the atmosphere with source strengths ranging from 17 to 160 ng m^{-2} h^{-1}; and (2) the strengths of Hg^0 emissions can be greatly influenced by the combined effects of surface soil temperature, residence time of air masses over the source area, and turbulence conditions. The Hg^0 fluxes measured in a controlled flow chamber indicate that contaminated soils can exhibit up to an order of magnitude higher emission rates of Hg under conditions of elevated soil temperature, soil structure disturbance, and high turbulence. Hg^0 emissions from contaminated soils exceeded emissions from background soils by one to two orders of magnitude.

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13. Research sponsored by the U.S. Department of Energy and the Electric Power Research Institute under contract with ORNL. ORNL is managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400. Environmental Sciences Division, ORNL.

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