

# Indoor Concentrations of Hg Vapor Following Various Spill Scenarios

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Hg vapor concentrations were measured in an indoor full-scale test environment representative of homes in the rural highlands of Peru, the location of an Hg spill in June 2000. We tested several scenarios of liquid Hg spilled onto a compacted dirt floor in a test room to determine the effect of various parameters, including liquid Hg surface area, temperature, air change rate, and Hg oxidation on room vapor concentrations. The measurements demonstrated that an increase in surface area and/or temperature significantly increased the evaporation rate, whereas oxidation (or age of the Hg) reduced the evaporation rate. We also verified that the Hg vapor analyzers used to test indoor air were capable of detecting very small spills.

Keywords: elemental Hg, Hg vapor, Hg evaporative flux, Hg spills

## Introduction

Elemental Hg has been mined and used in thousands of applications since pre-Roman times. Hg usage peaked in the mid-1960s at 11,000 metric tons and has declined steadily to 2,800 metric tons in 2000 (United Nations Environment Programme [UNEP] 2002) as a result of efforts to limit Hg exposure in the workplace and the environment. The United States Environmental Protection Agency (US EPA) has derived an inhalation reference concentration (RfC) for residential indoor air of  $0.3 \mu\text{g}/\text{m}^3$ . The RfC is based on a lowest observed adverse effects level (LOAEL) of  $0.025 \mu\text{g}/\text{m}^3$  adjusted for 24 h/day and 7-day/week exposures (Agency for Toxic Substances and Disease Registry [ATSDR] 1999).

In spite of greater awareness of the potential health risks of Hg and its reduced use, intentional and unintentional exposure to elemental Hg vapor from spilled Hg is a common occurrence in the United States and other countries. Some members of Hispanic and Caribbean cultures intentionally spill elemental Hg as a folk remedy or during religious practices. Hg is sprinkled in or around a car or crib, burned in a candle, or mixed with bath or cleaning water (Baughman, 2006; Garetano et al., 2006; US EPA, 2002).

Zeitz et al. (2002) reported the types and relative frequencies of 413 Hg spills recorded in 14 American states from 1993 to 1998. The most common locations of Hg spills were schools and universities, homes, and health care facilities. The most common

causes of Hg spills were dropped containers and children playing with Hg.

Beginning in 2000, well-intentioned efforts by natural gas utilities to remove natural gas pressure regulators from customers' homes led to numerous Hg spills. First in Chicago (IL) and then in Detroit (MI), contractors were hired by the utilities to replace pre-1961 regulators that used Hg in an overpressure safety mechanism with non-Hg-containing regulators. Unfortunately, Hg was spilled during removal in more than 1,300 homes in the Chicago area (Hryhorczuk et al., 2006; Hood, 2006) and approximately 60 homes in the Detroit area (Exponent, 2002).

Another large-scale exposure to elemental Hg occurred around the same time in June 2000 in Peru. A truck was carrying flasks of elemental Hg from a gold mine located near Cajamarca in the highlands of northern Peru. During the trip to Lima on June 2, 2000, one of the flasks came loose, and an estimated 151 kg of Hg leaked onto the road as the truck traveled 40 km through three villages. The spill was not reported until the next day. Immediately after the spill, villagers and nearby residents collected the Hg and took it home (Compliance Advisor Ombudsman [CAO], 2000; Gochfeld, 2003). Efforts to recover the spilled Hg began the next day; however, they were not successful until 1 week later when a reward was offered for the return of the spilled Hg (CAO, 2000). Testing of indoor air Hg concentrations began on June 12, 2000, using Jerome 431-X Mercury Vapor Analyzers (Arizona Instrument, Tempe, AZ, USA). More sensitive Lumex RA-915 (OhioLumex, Co., Twinsburg, OH) + Mercury Vapor Analyzers began to be used on June 28, 2000. The results of the indoor air measurements were used to determine the need for remediation (CAO, 2000).

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Assessment of human exposure to Hg vapor in selected homes was later calculated based on the occupants' descriptions of the amount of Hg involved, the nature and duration of their exposure, and estimated air change rates in the homes. Significant uncertainty was introduced into the calculations because of uncertainty in the air change rates, the occupants' abilities to accurately describe their exposure, and the behavior of elemental Hg in the homes. The flux of vapor from a given mass of spilled elemental Hg depends on the temperature of the Hg (dependent on floor and air temperature), the surface area and condition (degree of oxidation) of the Hg exposed to the air, and the room air change rate (Winter, 2003). The surface area of spilled Hg is difficult to reconstruct because it breaks into small beads that spread and can become lodged in cracks and crevices (Baughman, 2006). Calculation of indoor vapor concentrations in the dirt-floored Peruvian homes was further complicated by the common practice of sweeping water across the floor with a broom one or more times a day to maintain the integrity of the floor surface.

Other investigators (Hickson et al., 1993; US EPA, 2005; Winter, 2003) have measured Hg vapor concentrations generated by known amounts of Hg, but none of the previous studies have been done under conditions similar to those in Peru at the time of the spill. The purpose of this study was twofold: to verify that commercially available Hg vapor analyzers can reliably detect small spills and to understand and quantify the parameters that affect vapor concentrations following an indoor spill of elemental Hg. We conducted full-scale experiments involving various Hg spill scenarios and measurement of Hg vapor concentrations under controlled air change rate conditions. The data presented in this article demonstrate the influence of Hg surface area, temperature, and oxidation on indoor vapor concentration and provide a basis for verification of calculated vapor concentrations.



**Figure 1.** Photograph of the exterior view of test room and tent enclosure. Room dimension = 2.9 m long  $\times$  3.5 m wide  $\times$  2.0 m high. The door and window are located on the opposite sides of the shorter walls.

### Experimental Setup

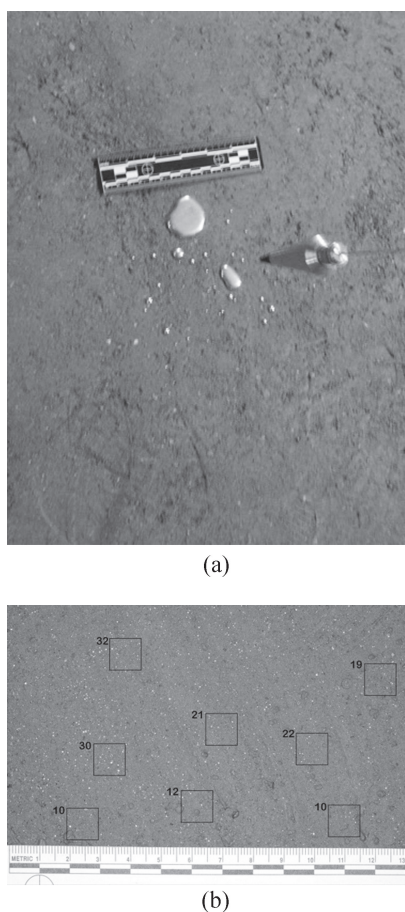
We constructed a 20-m<sup>3</sup> wood-framed room with painted sheetrock and compacted dirt floor to simulate a typical room in a home in the Peruvian highlands near the spill site. The room has one door and one window and was placed within a tent enclosure to provide shielding from ambient wind (Figure 1). A fan was placed within the tent, but outside the room, to provide a constant airflow across the window to maintain an air change rate of 2.2 h<sup>-1</sup> (27-min time constant). The window and door openings were adjusted during the final test to provide an air change rate of 6.7 h<sup>-1</sup> (10-min time constant). The air change rate was determined in accordance with ASTM Standard E741-00 (ASTM, 2006). Sulfur hexafluoride (SF<sub>6</sub>) was injected into the room and allowed to mix. The concentration decay of the SF<sub>6</sub> was recorded as a function of time to determine the air change rate.

Vapor detection experiments were conducted with several Hg spill sizes (Table 1). Reagent-grade elemental Hg purchased

**Table 1.** Summary of experiments

Test ID	Test description	Hg spill description	Test duration	Soil temperature (°C)	Air temperature (°C)	Air change rate (h <sup>-1</sup> )
A	0.034 mL Hg carefully placed on floor	1 Bead (4 mm in diameter)	1 hour	11	17	2.2
B	5 mL (1 teaspoon) Hg carefully placed on floor	2 Large droplets (3.4 and 12 cm lengthwise) 31 Small beads (0.1 to 1 cm in diameter)	1 hour	12	19	2.2
C	Hg beads first sweep with broom	Thousands of small Hg beads (~0.1 mm in diameter)	6 days	11–16	10–22	2.2
D	Hg beads second sweep with broom	Thousands of small Hg beads (~0.1 mm in diameter)	1 day	8–16	7–18	2.2
E	Water (1 L) poured onto dirt floor followed by third sweep with broom	Thousands of small Hg beads (~0.1 mm in diameter)	6 days	8–14	7–19	2.2
F	Water (1 L) poured onto dirt floor followed by fourth sweep with broom	Thousands of small Hg beads (~0.1 mm in diameter)	1 day	9–16	9–21	6.7
G	Water (1 L) poured onto dirt floor followed by fifth sweep with broom	Thousands of small Hg beads (~0.1 mm in diameter)	1 day	10–18	10–24	6.7

from Fisher Scientific (Pittsburgh, PA, USA) was used in the tests. In the first test (Test A), a very small amount of Hg, consisting of one 4-mm bead, was placed on the floor in the center of the room to test the sensitivity of commercially available Hg analyzers. In the second (Test B), 5 mL (68 g, approximately one teaspoon) of Hg was added to the center of the room. The 5-mL quantity formed two large droplets and 31 small beads (Figure 2 [top] before sweeping). We then swept the Hg with a broom, forming thousands of small beads (Figure 2 [bottom] after sweeping). Sweeping was performed with a back-and-forth motion in both a north-south and east-west direction. Several tests (Tests C–G) were performed with the swept Hg scenario. Tests D–G were performed by resweeping the same beads present in Test C. No additional Hg was added. Tests were performed at temperatures representative of the location and season of the Peruvian study area. The range of air temperatures during the tests was 7–24°C. This range was similar to the reported average air temperatures in the study area in early June 2000 (9–24°C, based on measurements at 7:00 AM, 1:00 PM, and 7:00 PM).



**Figure 2.** Photograph of (top) 5 mL (1 teaspoon) of Hg before and (bottom) after sweeping. The object in the before-sweeping photo is a plumb bob that marked the 10-cm sampling point. Roughly 10 to 30 beads are present per cm<sup>2</sup> of floor area, as illustrated in the after-sweeping photo. The bead count is shown on the upper left-hand corner of each 1 cm<sup>2</sup> square.

Hg vapor concentrations were measured with a Jerome 431-X Mercury Vapor Analyzer and a Lumex RA-915+ Mercury Analyzer. Both instruments have been previously tested and compared with other instruments and laboratory methods (NIOSH 6009) in the field and found to provide reliable real-time Hg concentration measurements (Singhvi et al., 2001, 2003). The Jerome analyzer measures the change in electrical resistance of a thin gold film in proportion to the presence of Hg vapor. It has a range of 1–999 µg/m<sup>3</sup> and a practical detection level of 3 µg/m<sup>3</sup>. The Jerome has the benefit of being unaffected by environmental factors such as water vapor and particulates. The Lumex analyzer is a portable absorption spectrometer designed to detect low Hg vapor concentrations. Its low detection limit is achieved through a combination of multi-path optical cells and high-frequency modulation of polarized light used to perform atomic absorption spectrometry. The Lumex, with a range of 0.002–20 µg/m<sup>3</sup>, is more sensitive than the Jerome and is commonly used to quantify Hg vapor exposure (Garetano et al., 2006; Hryhorczuk et al., 2006).

We used the Jerome to make all measurements in our tests except for Test A (Table 1). We used the Lumex in Test A to confirm that it could detect the vapor from a very small spill. The Jerome and the Lumex were both calibrated by the manufacturer prior to use. The concentrations measured in the test room were all within the detection of the instruments used. Air temperatures were measured with a thermocouple near one of the walls approximately 1 m above the floor. Soil temperature was measured with a thermocouple inserted approximately 0.6 cm into the dirt floor.

Hg vapor was generally measured at three different heights above the dirt floor: 0.1 m, 0.75 m, and 1.5 m. (In initial tests only the 0.1-m and 1.5-m elevations were used to record concentrations.) Five sampling locations, the midpoint of the room and four lateral locations (a point halfway from the room midpoint to each of the four walls), were used for each elevation.

## Method

The driving force for the evaporation of Hg is its vapor pressure, which is a function of temperature. Higher temperatures led to higher evaporation rates (Hickson et al., 1993; Winter, 2003). A relevant parameter that incorporates the effect of temperature and directly affects the Hg vapor concentration in the room is the evaporative flux from the liquid Hg surface. Evaporative flux,  $J$  (µg/[cm<sup>2</sup>h]), is defined as the net mass transport of Hg from the liquid phase to the vapor phase per unit of time and liquid-vapor interface surface area,  $A$  (cm<sup>2</sup>). Assuming that there is no loss mechanism of Hg other than air change with the outdoors, the time-dependent well-mixed indoor concentration,  $C_{in}(t)$ , in the room can be determined by:

$$C_{in}(t) = \frac{J \times A}{Q} \left( 1 - \exp \left( -\frac{Q}{V} t \right) \right) + C_{in}(t_0) \exp \left( -\frac{Q}{V} t \right) \quad (1)$$

where  $Q$  is the volumetric air change rate ( $\text{m}^3/\text{h}$ ),  $V$  ( $\text{m}^3$ ) is the room volume, and  $C_{\text{in}}(t_0)$  is the initial indoor concentration.

In analyzing the measurements, we computed a volume-weighted room average concentration as a representative value for the room. Because the five sampling locations were spread out across the room, we took the arithmetic average concentration as the representative value of the concentration at a given height above ground. The concentrations measured 0.1 m above ground,  $C_{0.1\text{m}}$ , represent the concentration from 0 to 0.2 m of the room. The concentrations measured 0.75 m above ground,  $C_{0.75\text{m}}$ , represent the concentration from 0.2 to 1 m of the room. The concentrations measured at 1.5 m above ground,  $C_{1.5\text{m}}$ , represent the concentration from 1 to 2 m of the room. Thus, the room average concentration is approximated by the sum of  $C_{0.1\text{m}}$ ,  $C_{0.75\text{m}}$ , and  $C_{1.5\text{m}}$  weighted by the fraction of room volume that each represents.

$$C_w = 0.1 \times C_{0.1\text{m}} + 0.4 \times C_{0.75\text{m}} + 0.5 \times C_{1.5\text{m}} \quad (2)$$

For the few cases when only  $C_{0.1\text{m}}$  and  $C_{1.5\text{m}}$  were measured, the weighted room average concentration is approximated as follows:

$$C_w = 0.1 \times C_{0.1\text{m}} + 0.9 \times C_{1.5\text{m}} \quad (3)$$

We used the calculated  $C_w$  value as the well-mixed concentration in the room  $C_{\text{in}}(t)$  when calculating the evaporative flux of Hg using Equation (1).

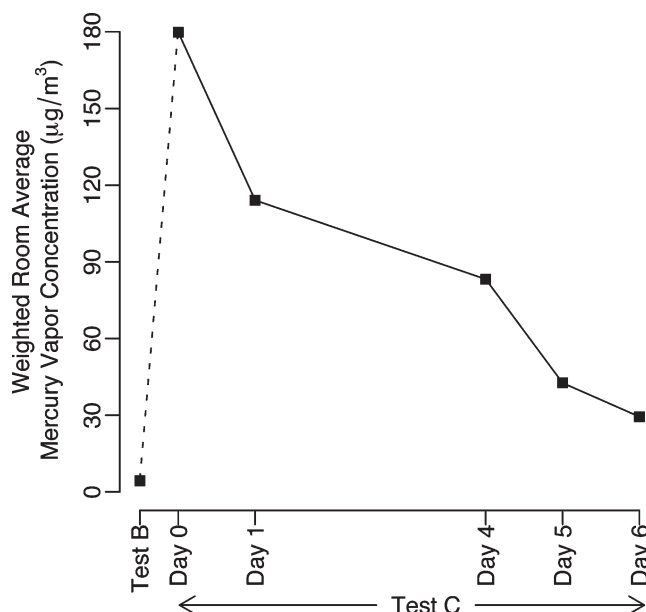
## Results and Discussion

Table 2 summarizes the range of vapor concentrations measured at each sampling height, their respective arithmetic average ( $C_{0.1\text{m}}$ ,  $C_{0.75\text{m}}$ ,  $C_{1.5\text{m}}$ ), as well as the measured soil floor and room air temperature. The coefficient of variance (CV) shows the variability between measurements sampled at the same height above ground. CV is defined as the calculated standard deviation in a sample as a percentage of the calculated mean. The calculated  $C_w$  values are shown in Figures 3 and 4. The calculated evaporative fluxes for Tests C to G are shown in Figures 5 through 7.

### Single-Bead Test (Test A): Analyzer Sensitivity

We used two types of instruments to measure Hg vapor concentrations, a Lumex RA-915+ and a Jerome 431-X analyzer. One bead of Hg measuring 4 mm in diameter was introduced into the room. This amount of Hg corresponds to 0.46 g. The average Hg vapor concentration in the room increased from  $<0.010 \mu\text{g}/\text{m}^3$  to  $0.29 \mu\text{g}/\text{m}^3$  after 0.5 h. We observed a fairly uniform concentration in the room, ranging from a minimum of  $0.26 \mu\text{g}/\text{m}^3$  measured at 1.5 m above ground, to a maximum concentration of  $0.56 \mu\text{g}/\text{m}^3$  measured at 0.1 m above ground.

The Lumex RA-915+ was capable of sensing vapor Hg at any point in the room after a single bead was introduced



**Figure 3.** Graph of weighted room average Hg vapor concentration measured in Tests B and C.

on the ground. The Jerome 431-X was able to detect vapor concentrations only when placed directly above the bead. Based on this comparison, we concluded that the Lumex RA-915+ can reliably detect very minor increases in Hg vapor concentration. The Jerome is also capable of detecting an increase in Hg concentration if placed close to the Hg source.

The Hg vapor concentrations measured in Test A were similar to the upper range of monitored levels in U.S. residential buildings (Garetano et al., 2006). In some cases, elevated Hg concentration measured in the residences was linked to unintentional releases of Hg in the past (e.g., broken thermometers). Carpi and Chen (2001) estimated that up to 10% of U.S. households might have levels of Hg vapor  $>0.3 \mu\text{g}/\text{m}^3$  as a result of past accidents. Our data show that a very small amount of Hg, a single 4-mm bead in this case, in a well-vented room is sufficient to generate such concentrations in the air.

### One-Teaspoon Test (Test B)

#### Measured Hg Vapor Concentration

A vertical concentration gradient was observed when an additional 5 mL of Hg was added to the room. Concentrations measured at 0.5 h after the addition were in the range of  $7.8\text{--}26 \mu\text{g}/\text{m}^3$  and  $1.8\text{--}5.5 \mu\text{g}/\text{m}^3$  at the 0.1 m and 1.5 m height, respectively.

#### Calculated Evaporative Flux

We calculated the surface area of the 5 mL of Hg based on photographs taken in the room (Figure 2). We approximated the surface area of the two largest droplets that are non-spherical by counting squares over a grid and by accounting for a droplet



Table 2. Summary of measured Hg vapor concentrations

Test ID	Time (hours)	Temp. (°C)		Room weighted average concentration $C_w$ ( $\mu\text{g}/\text{m}^3$ )	Concentration measured at 10 cm ( $\mu\text{g}/\text{m}^3$ )			Concentration measured at 0.75 m ( $\mu\text{g}/\text{m}^3$ )			Concentration measured at 1.5 m ( $\mu\text{g}/\text{m}^3$ )		
		Soil	Air		Avg. $C_{0.1\text{m}}$	Range	CV (%)	Avg. $C_{0.75\text{m}}$	Range	CV (%)	Avg. $C_{1.5\text{m}}$	Range	CV (%)
A	0.5	11	17	0.29	0.42	0.30–0.56	16	—	—	—	0.28	0.26–0.32	7
B	0.5	12	19	4.4	14.2	7.8–26	38	—	—	—	3.3	1.8–5.5	33
C	2	14	22	180	511	195–902	53	—	—	—	143	100–169	19
	26	16	—	114	232	138–325	33	—	—	—	101	69–120	19
	98	16	—	83	157	91–261	31	—	—	—	75	56–92	14
	120	14	—	43	60	46–147	43	38	33–55	18	43	36–50	43
	140	11	10	29	32	9–82	67	28	14–49	35	30	20–39	18
	140	11	10	29	32	9–82	67	28	14–49	35	30	20–39	18
D	0.5	11	11	149	158	109–204	20	144	102–167	15	152	147–166	4
	1.5	11	12	96	110	147–166	27	94	62–154	26	95	86–112	9
	2.5	12	13	67	111	62–189	40	59	51–75	13	64	57–69	6
	3.5	12	15	106	176	94–333	43	90	65–119	19	105	97–119	7
	5.5	14	18	125	174	61–304	45	123	103–146	11	118	103–141	9
	7.5	15	18	124	156	108–222	24	123	102–160	18	118	107–137	9
	10	16	18	91	113	45–218	51	93	75–118	15	86	73–98	10
	23.5	8	7	45	56	28–167	74	47	37–73	22	42	38–45	5
	0.5	8	7	68	74	42–174	50	67	52–84	13	67	57–73	9
	1.5	8	8	87	99	80–165	25	86	74–99	10	85	81–90	4
E	2.5	9	11	91	120	81–231	37	91	69–117	20	85	77–92	6
	3.5	9	13	93	151	92–215	28	87	71–103	13	87	78–95	7
	5.5	11	17	110	211	140–389	35	99	87–114	8	98	90–103	5
	7.5	13	19	135	276	186–436	31	121	84–138	13	117	104–125	7
	9.5	14	19	136	212	149–390	33	129	113–179	15	126	114–141	8
	144	8	8	31	52	25–125	61	30	19–49	27	28	22–36	14
	0.5	9	9	48	124	44–260	72	41	30–62	24	38	34–42	6
	1.5	9	11	53	108	54–224	47	46	37–55	11	48	41–55	10
F	2.5	10	14	52	104	39–234	55	51	36–71	21	42	26–62	21
	3.5	11	16	66	163	77–295	43	64	48–83	19	49	34–61	16
	5.5	13	20	102	326	179–601	42	92	52–121	24	66	49–95	22
	7.5	14	21	137	314	187–478	34	132	76–190	24	106	69–133	20
	9.5	16	21	95	227	80–364	47	80	63–116	20	81	69–95	11
	23	9	9	54	79	40–174	60	55	33–75	26	50	38–60	13
	0.5	10	10	46	92	45–193	49	41	34–54	14	41	37–45	6
	1.5	10	13	53	83	40–160	55	46	35–68	25	48	41–57	10
G	2.5	11	15	59	152	31–348	67	49	41–60	11	48	42–56	10
	3.5	12	18	62	179	31–349	52	54	39–76	22	45	38–58	13
	5.5	14	23	95	392	184–667	57	69	48–83	20	57	41–96	40
	7.5	16	24	121	297	170–553	45	131	78–160	27	77	56–98	22
	9.5	18	23	120	200	80–328	45	112	85–155	25	111	95–129	14
	24	12	12	64	112	27–455	121	59	34–111	36	58	41–71	18

thickness of 2 mm. Most (20) of the small Hg beads were 1–2 mm in diameter. The largest bead was 8 mm in diameter but not perfectly spherical. The other beads, 6 mm and less, appeared to be spherical. We assumed all beads to be spherical and that their entire surfaces were subject to evaporation. The total surface

area of the 5-mL Hg spill was calculated at 32 cm<sup>2</sup>. If we assume that  $C_{\text{in}}(t_0) = 0.29 \mu\text{g}/\text{m}^3$  (i.e., the vapor concentration at the start of Test B was equal to the vapor concentration at the end of Test A), Eq. (1) yields a value of  $J = 8.8 \mu\text{g}/(\text{cm}^2\text{h})$  for Test B.

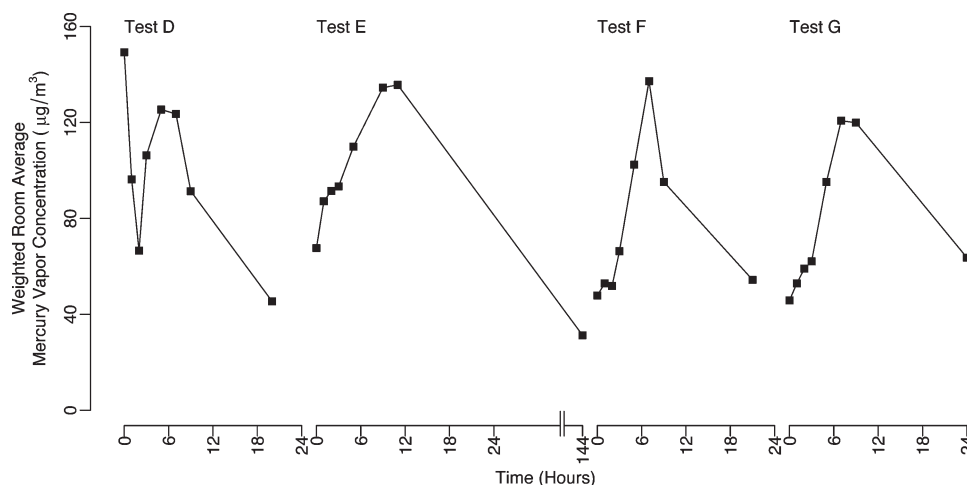


Figure 4. Graph of weighted room average Hg vapor concentration measured in Tests D, E, F, and G.

By visual inspection, small Hg beads in the size range of a few mm or less are fairly spherical. The fraction of the Hg bead surface in contact with the soil appears to be small relative to the part that is exposed to the room air. Some studies have assumed a hemispherical shape when calculating the evaporative flux (Clear and Berman, 1994; US EPA, 2005). In theory, the fraction of exposed surface can be determined as a function of the physical properties of Hg and the characteristics of the flat surface. In practice, however, such careful calculation is unnecessary if one compares and applies the evaporative flux with data similarly normalized. (The reader is reminded that evaporative flux calculated in this article is normalized by the entire spherical surface of the beads.) To obtain a source term in units of mass per time, one should multiply  $J$  with the entire spherical surface of the Hg beads.

#### Swept Bead Tests (Tests C–G)

##### Measured Hg Vapor Concentration

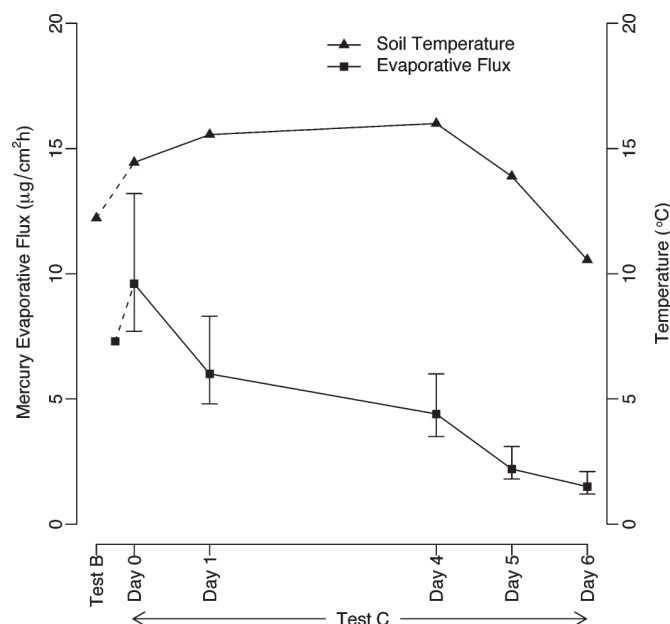
Sweeping caused the Hg vapor concentration in the room to increase (Test C compared with Test B). To obtain measurements around the room as simultaneously as possible, we took only one measurement at each sampling location. The Hg beads in the room were left undistributed for the next 6 days. Measurements were made at roughly the same time in each day (2 PM), except on day 6, when the measurements were taken in the morning (8 AM). We observed a decrease in Hg vapor concentration at a rate that decreased with time. On day 6, the weighted average room concentration ( $C_w = 29 \mu\text{g}/\text{m}^3$ ) was one-sixth of that measured immediately after sweeping ( $C_w = 180 \mu\text{g}/\text{m}^3$ ).

In subsequent single-day tests (Tests D to G),  $C_w$  reached a maximum of 149, 136, 137, and  $121 \mu\text{g}/\text{m}^3$ , respectively (Figure 4). These maximums were consistently lower than the initial maximum ( $180 \mu\text{g}/\text{m}^3$ ) observed in Test C. A similar decreasing trend was also observed when we compared the 12-h average value of  $C_w$  using the seven initial measurements of each test (108, 103, 79,  $79 \mu\text{g}/\text{m}^3$ ).

The Hg vapor concentrations measured in our test room were similar in magnitude to those found in workplaces that handle Hg. Tsuji et al. (2003) reviewed the air Hg levels measured using personal and stationary samplers in an Hg cell chloralkali plant, a dry alkaline battery plant, a heat sensor manufacturing plant, and a thermometer plant. The mean time-weighted average values of 10 selected studies were between 17 and  $107 \mu\text{g}/\text{m}^3$ . One major difference between worker exposures and accidental exposure to a spill is that vapor concentrations in the latter case decrease with time if the Hg is left undisturbed. In our experiment, we found Hg vapor concentrations in the range of  $45$  to  $64 \mu\text{g}/\text{m}^3$  (Tests D, F, and G) after 1 day since the last sweeping occurred. The Hg vapor concentration dropped to approximately  $30 \mu\text{g}/\text{m}^3$  after 1 week (Tests C and E).

##### Calculated Evaporative Flux

After sweeping, thousands of small beads with diameters less than 1 mm were formed on the ground. It is difficult to measure directly the total Hg liquid surface area of thousands of small beads, especially when bead sizes vary. We estimated the total Hg liquid surface area as described in subsequent text, beginning with the total volume of Hg spilled in the room of 5 mL. The total spill volume of 5 mL equals the average volume of each bead times the total number of beads ( $n$ ). The total liquid-vapor interface surface area can be calculated if  $n$  can be quantified. We approximated  $n$  by multiplying the floor area covered by the beads and the observed bead density on the floor. As sweeping was done only in the center of the room, we determined that only an area of  $1.05 \text{ m}^2$  was covered with Hg beads. We analyzed photographs taken during the experiments to determine the number of beads visible within representative  $1 \text{ cm}^2$  areas. The bead count on the floor was estimated at 10 to 30 beads/ $\text{cm}^2$ . Therefore,  $n$  ranged from 105,000 to 315,000. A midpoint estimate within this range is  $20 \text{ beads}/\text{cm}^2 \times 1.05 \text{ m}^2 = 210,000$  beads. In order for 210,000 beads to sum to a total volume of 5 mL, the average bead diameter must equal 0.36 mm. The range of bead diameter is therefore 0.45 to 0.31 mm. Visual inspection



**Figure 5.** Graph of calculated evaporative flux based on measurements from Tests B and C. The vertical bar represents upper and lower bounds on our estimate of liquid Hg surface area.

of the photographs suggests that many Hg beads in the room are roughly in this size range. Next, we made the same assumption used to calculate evaporative flux that the entire spherical surface of a bead is exposed to the room air. As a result, the estimated total Hg liquid surface area ( $A$ ) ranged from 670 to 960  $\text{cm}^2$ , with a midpoint estimate of 840  $\text{cm}^2$ .

We calculated the evaporative flux using Eq. (1) and the total Hg liquid surface area estimated previously. Figure 5 shows that the evaporative flux decreased from 9.6  $\mu\text{g}/(\text{cm}^2\text{h})$  from the start of the experiment to 1.5  $\mu\text{g}/(\text{cm}^2\text{h})$  on day 6. There was no difference in the predicted evaporative flux at the start of the experiment immediately following sweeping (8.4–12  $\mu\text{g}/[\text{cm}^2\text{h}]$ ), and the estimated flux before sweeping (Test B). At the end of

the experiment (day 6), we calculated the evaporative flux to be 1.4–1.9  $\mu\text{g}/(\text{cm}^2\text{h})$ , which is a narrower range. The general downward trend of the flux with time was likely a result of oxidation, as discussed in the Oxidation section later in text.

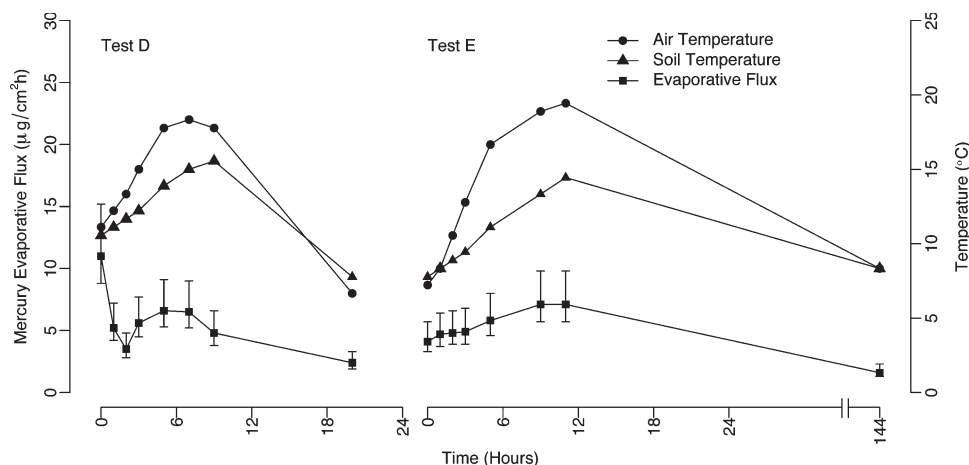
We calculated the evaporative flux for subsequent tests using the same method. The ranges of flux values were comparable in magnitude to those observed daily in the previous test. Tests D and E (Figure 6) were carried out at the same air change rate as Test C, and the calculated fluxes are very similar (1.4–14  $\mu\text{g}/[\text{cm}^2\text{h}]$ ). However, instead of a simple downward trend with time, these hourly measurements reached a peak value between hour 6 and hour 9. This corresponds to roughly 3 to 6 PM local time, when temperatures were higher than morning temperatures.

We calculated a higher evaporative flux in the range of 6.4–28  $\mu\text{g}/(\text{cm}^2\text{h})$  when the air change rate increased from 2.2 to 6.7  $\text{h}^{-1}$  for Tests F and G (Figure 7). In theory, rapid air movement over the liquid Hg surface speeds diffusion, and thus increases the evaporation rate. However, we also noticed that the air temperatures for the last two tests were slightly higher than the previous tests. It is possible that as outdoor air was brought into the room at a higher rate for Tests F and G, warmer air temperature caused Hg to evaporate at a faster rate. In the current study setup, we are not able to discern the impact of warmer air temperature from faster air change rate. Future studies can investigate these relationships with a more controlled experimental setup.

### Factors Affecting Hg Evaporative Flux

#### Temperature.

Figures 6 and 7 illustrate a correlation between soil and air temperature with the calculated evaporative flux. This correlation is to be expected because higher temperatures increase the rate of Hg evaporation. The trend of the evaporative fluxes more closely follows the rise and fall of soil temperature than that of the air temperature. This is illustrated most clearly in Tests F



**Figure 6.** Graph of calculated evaporative flux based on measurements from Tests D and E.

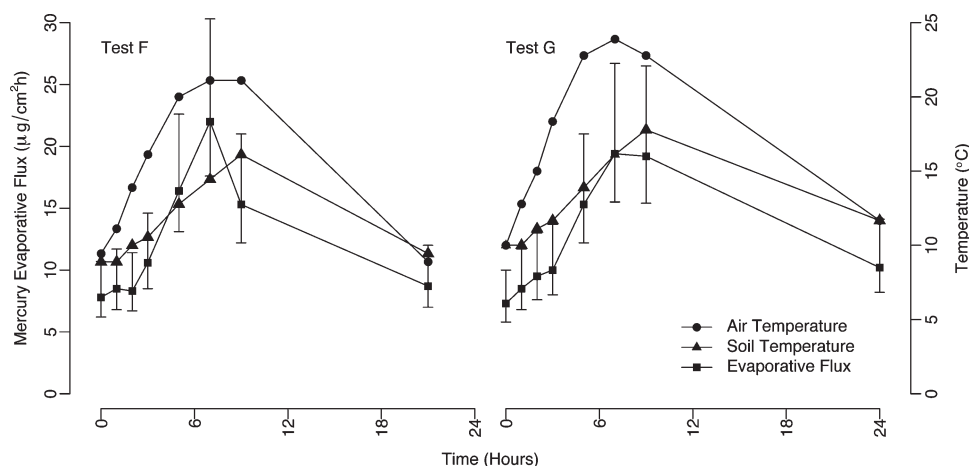


Figure 7. Graph of calculated evaporative flux based on measurements from Tests F and G.

and G (Figure 7) where the evaporative fluxes increased gradually and then increased more rapidly after hour 4. This agrees well with the change in soil temperature but less so with the air temperature, which increased almost linearly with time. Soil temperature is typically cooler than the air temperature, especially if water is added to the floor.

Winter (2003) modeled the temperature dependency of the evaporative flux of Hg (Figure 8). Hg evaporative flux is expected to double as temperature increases from 10 to 20°C, and increase by a factor of 5 as the temperature increases from 10 to 30°C (Figure 8). This temperature dependency explains the relatively high values observed by US EPA (2005). The temperature during our experiments was roughly 15°C, which is lower than the 21°C for Winter (2003) and the 32°C for US EPA (2005). Another key difference between our data and those collected by Winter (2003) and US EPA (2005) is that the lat-

ter studies estimated the evaporative flux by weighting the Hg bead(s) over time. As a result, their estimated evaporative flux is a time-average value. As we will discuss in the next section, Hg evaporative flux tends to decrease over time as a result of oxidation. Therefore, it is expected that the time-average evaporative flux is lower compared with the theoretical flux of a fresh Hg bead. Winter (2003) explained the difference between his model prediction and measurement as a result of oxidation.

During all tests, we observed a vertical gradient of Hg vapor concentration, with higher concentrations near the ground. We also observed a vertical temperature gradient. Namely, the ground was almost always cooler than the indoor air temperature. The vertical temperature gradient influences the level of mixing of the indoor concentration. Because the soil floor can be as much as 10°C cooler than the room air temperature, mixing of the Hg vapor in the room is suppressed by stagnation.

#### Oxidation

A decrease in vapor concentration attributed to oxidation has been reported by others (Hickson et al., 1993; US EPA, 2005; Winter, 2003) although none of these authors discussed the mechanism of oxidation. By itself, liquid Hg does not oxidize, although it is commonly observed to oxidize in air (Mulrooney, 2000) and water. Amyot et al. (2005) found that the rate of oxidation of liquid Hg in water increased with increasing concentrations of oxygen and chloride ion. The oxidation rate decreased over time, which, to the authors, suggested that oxidation products were being formed on the Hg surface that impeded further oxidation. We suggest that the oxidation of liquid elemental Hg in air follows a similar mechanism in the presence of water vapor and impurities.

When the Hg beads were left undisturbed in our tests, the decrease in evaporative flux resembled an exponential decay function:

$$J(t) = J(t_0) \times \exp\left(-\frac{t - t_0}{\tau}\right) \quad (4)$$

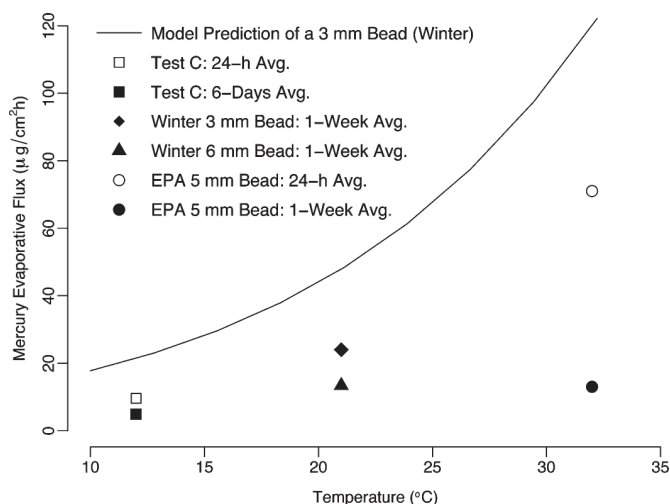


Figure 8. Graph of the comparison of calculated evaporative flux of Test C with model predictions by Winter (2003). The open and solid squares indicate the calculated 1-day and 1-week average evaporative fluxes given  $A = 840 \text{ cm}^2$ . Also plotted are the measured evaporative fluxes by Winter (2003) and US EPA (2005).



The downward trend shown in Figure 5 roughly corresponds to  $\tau = 3.5$  days. The oxidation rate of Hg appears to be a function of temperature. For example, the US EPA (2005) study observed a faster decay in Hg vapor concentration at 30°C with  $\tau = 2.3$  days.

The effect of oxidation is less obvious in the hourly measurements (Test D–G) because the time constant  $\tau$  is on the order of days rather than hours. Instead, temperature dictated the trend of the evaporative flux observed (Figure 6 and 7). The data from Tests E–G also demonstrated that the calculated evaporative flux did not change significantly with each additional sweeping. Disturbances to the beads probably caused new Hg surfaces to be formed, and thus similar Hg concentrations were measured after each sweeping.

We could not independently evaluate the effect of other factors, such as accumulation of dust or dirt (caused by sweeping) on the observed decrease in vapor flux. It is possible that the presence of dust particles could affect the oxidation rate of a fresh Hg surface. Also, we would expect that the surface area contributing to evaporation would be reduced as more dust and dirt accumulates. As a bead becomes completely covered, the overlying dirt would also impede the diffusive flux. In our test that followed sweeping (Tests C–G) some of the smallest beads were likely buried. The observed reduction of Hg vapor flux that we attribute to oxidation, therefore, includes the effects of dust and dirt accumulation on the Hg beads.

## Summary

A set of experiments was carried out to simulate a representative Hg spill in a room that is typical of homes in the rural Peru study area. Hg vapor concentrations were measured as a function of time using two commercially available Hg analyzers, Jerome 431-X and Lumex RA-915+. We found that the Lumex was capable of detecting vapor concentration in the room from a single 4-mm bead of Hg. The Hg vapor concentrations resulted from 5 mL of Hg spilled on the floor were significantly higher. The Jerome was used to monitor the Hg vapor concentrations of the spill and the subsequent changes in concentration when the Hg was swept repeatedly by a broom to form many small beads ~1 mm in diameter. When left undisturbed, we observed a decrease in Hg vapor concentration. However, after each sweeping, Hg vapor concentrations in the room would increase once again.

We analyzed the measured Hg vapor concentrations in terms of various parameters, including Hg surface area, temperature, air change rate, and Hg oxidation. We observed a large increase in Hg vapor concentration relative to its prior value when the 5-mL Hg spill was swept to form many beads. However, the estimated evaporative flux in terms of mass per surface area per unit time remained fairly constant before and after sweeping. Our data showed that higher temperature caused faster evaporation, resulting in an increase in Hg vapor concentrations. In contrast, oxidation of the Hg surface caused the evaporative flux to decay exponentially with time at a rate constant of 3.5 days.

We compared the Hg evaporative flux estimated with values reported by Winter (2003) and US EPA (2005). Our data suggest a lower evaporative flux than the other studies, partly because we conducted our experiment at lower temperatures. When compared with the predicted evaporative flux based on a diffusion model of a spherical droplet (Winter, 2003), measured flux values are always lower. This is because the model predictions did not take oxidation into account. The Hg vapor concentrations measured in our experiments are representative of the spill conditions detailed in this article. When evaluating the Hg vapor concentrations in other conditions, it is important to consider the effects of environmental parameters as well as the characteristics of the spilled Hg.

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