

# Airborne Emissions of Mercury from Municipal Solid Waste. II: Potential Losses of Airborne Mercury before Landfill

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## ABSTRACT

Waste distribution and compaction at the working face of municipal waste landfills releases mercury vapor ( $\text{Hg}^0$ ) to the atmosphere, as does the flaring of landfill gas. Waste storage and processing before its addition to the landfill also has the potential to release  $\text{Hg}^0$  to the air if it is initially present or formed by chemical reduction of  $\text{Hg}^{\text{II}}$  to  $\text{Hg}^0$  within collected waste. We measured the release of  $\text{Hg}$  vapor to the atmosphere during dumpster and transfer station activities and waste storage before landfilling at a municipal landfill operation in central Florida. We also quantified the potential contribution of specific  $\text{Hg}$ -bearing wastes, including mercury ( $\text{Hg}$ ) thermometers and fluorescent bulbs, and searched for primary  $\text{Hg}$  sources in sorted wastes at three different landfills. Surprisingly large fluxes were estimated for  $\text{Hg}$  losses at transfer facilities ( $\sim 100$  mg/hr) and from dumpsters in the field ( $\sim 30$  mg/hr

for 1,000 dumpsters), suggesting that  $\text{Hg}$  emissions occurring before landfilling may constitute a significant fraction of the total emission from the disposal/landfill cycle and a need for more measurements on these sources. Reducing conditions of landfill burial were obviously not needed to generate strong  $\text{Hg}^0$  signals, indicating that much of the  $\text{Hg}$  was already present in a metallic ( $\text{Hg}^0$ ) form. Attempts to identify specific  $\text{Hg}$  sources in excavated and sorted waste indicated few readily identifiable sources; because of effective mixing and diffusion of  $\text{Hg}^0$ , the entire waste mass acts as a source. Broken fluorescent bulbs and thermometers in dumpsters emitted  $\text{Hg}^0$  at 10 to  $>100$   $\mu\text{g/hr}$  and continued to act as near constant sources for several days.

## INTRODUCTION

Incineration of municipal waste is a major anthropogenic source of mercury ( $\text{Hg}$ ) to the atmosphere,<sup>1–3</sup> making disposal of such wastes in landfills an option for reducing  $\text{Hg}$  emissions associated with the waste. However, this alternative does not eliminate  $\text{Hg}$  emissions. Waste dumping, distribution, and compaction at the landfill working face generates significant releases of  $\text{Hg}$  vapor, and the fugitive emission or flaring of landfill gas acts as another source.<sup>4,5</sup> In an accompanying article,<sup>6</sup> we measured releases from these sources at landfills in Florida and found them to be far lower than what would occur from the incineration of similar amounts of waste, assuming a  $\text{Hg}$  content of 2 mg/kg.<sup>2,7</sup>  $\text{Hg}$  vapor ( $\text{Hg}^0$ ) emission from the working face and via landfill gas may involve the generation of elemental  $\text{Hg}$  ( $\text{Hg}^0$ ) by chemical reduction within the reducing conditions typical of landfilled wastes. In this case, disturbance and compaction that

## IMPLICATIONS

$\text{Hg}$  loss occurs during waste transfer to landfills. Although variable,  $\text{Hg}$  emissions from dumpsters are collectively significant and, when combined with emissions from waste transfer/consolidation practices, approach in magnitude the overall emissions from their associated landfill operations. Efforts to identify specific sources of  $\text{Hg}$  in wastes emitting strong  $\text{Hg}$  vapor signals were generally unsuccessful, suggesting that isolated individual sources may act to cause the ubiquitous contamination of virtually all waste that reaches the landfill working face. This finding reinforces the concept that lowering  $\text{Hg}$  emissions from municipal waste disposal is best achieved by eliminating  $\text{Hg}$  inputs to the waste stream.

occur when fresh waste is applied to the landfill and spread and covered using heavy equipment could “squeeze” Hg<sup>0</sup>-rich gas from interstices in the landfill to generate much of the downwind signal observed at active landfills. However, it is also possible that much of the Hg<sup>0</sup> released at the working face arises from Hg contamination of the fresh waste. In that case, municipal waste would be a potential source of Hg inputs to the atmosphere from the time it is generated until it is landfilled. The objective of this study was to make the first estimates of Hg emissions from waste held in storage (dumpsters) before collection and during processing in transit to the landfill (transfer and compaction). A second objective was to search for primary Hg sources within bulk wastes that generated strong Hg<sup>0</sup> release signals in an effort to confirm that the Hg<sup>0</sup> did indeed come from those materials suspected of being the main sources of Hg in municipal waste.

## EXPERIMENTAL WORK

### Study Sites

This study was conducted at three of the six Florida landfills investigated in the companion article:<sup>6</sup> Volusia, Orange, and Brevard counties. Descriptions of the facilities are found in the companion article.<sup>6</sup>

### Hg Levels in Waste and Dumpster Air

Hg concentration in headspace gas of individual waste storage containers was measured in near real time using a Tekran Model 2537 Mercury Analyzer and a length of 0.65-cm polytetrafluoroethylene (PTFE) tubing inserted into the closed dumpsters. The Tekran instrument supplied air at 1.5 lpm, with a detection limit of ~0.1 ng/m<sup>3</sup>. The dumpster sizes were selected as representative based on conversations with personnel from the local waste disposal contractor. Dumpster contents were sorted in an attempt to correlate Hg signals with potential Hg sources. Limited measurements were also made on waste in place. At Volusia County, a much larger sample of dumpsters was surveyed by following the routes of the commercial waste hauler and measuring headspace Hg concentrations in 188 closed dumpsters with a Lumex RA915+ Mercury Analyzer. The RA915+ sampled air at ~10–15 lpm, with a detection limit of ~10 ng/m<sup>3</sup>. Dumpsters with headspace Hg >20 ng/m<sup>3</sup> were delivered to the landfill site for sorting. The dumpsters surveyed represented ~1.8% of the total commercial waste load of the landfill (thus, ~10,000 dumpsters are serviced by waste haulers using this landfill).

### Hg Sources within Municipal Waste

Waste characterization was accomplished using a field sorting technique.<sup>8,9</sup> Waste was separated into three

types: (1) potential Hg sources, (2) metal cans, and (3) non-Hg source items. The waste was placed onto plastic sheeting in a covered storage area where sorters visually separated the waste into the preselected categories. In addition to sorting wastes from dumpsters that yielded substantial headspace Hg signals, at the Brevard and Orange County landfills we also sorted wastes excavated from a recently filled portion of the landfill where a surface flux of gaseous Hg was evident.

Items sorted from the wastes were placed in covered 0.02-m<sup>3</sup> polypropylene buckets and allowed to equilibrate for 5 min. Headspace Hg in the bucket (sniff tests) was then measured by the procedure used for the dumpsters using the Tekran 2537. Items yielding significant Hg signals (10 ng/m<sup>3</sup> above the bucket blank) were identified and subjected to analysis for surface Hg contamination. Material from the excavated waste was examined under illumination with a long wavelength UV (black light) lamp in an attempt to find evidence of broken fluorescent bulbs in the waste.

“Swipes” of materials that were identified as sources of gaseous Hg in Tekran sniff tests of the waste were used to additionally evaluate those items as potential sources. The items were each wiped (200–400 cm<sup>2</sup> of the surface of each item) with a 100-cm<sup>2</sup> disc of Whatman # 42 filter paper that had been wetted with 1 mL of 5% HNO<sub>3</sub>, following a procedure developed by Florida Department of Environmental Protection (DEP).<sup>10</sup> Samples were analyzed for total Hg by cold vapor atomic absorption spectroscopy after extraction into nitric acid or 5% BrCl/HCl.<sup>11</sup>

Broken fluorescent bulbs have the potential to be important long-term Hg<sup>0</sup> sources. We carried out several studies to quantify this source and evaluate the potential for continuing releases of Hg vapor. These included the following: (1) measuring a time series of Hg headspace and downwind concentrations in and near open and closed dumpsters containing broken bulbs (and thermometers) under different storage conditions; (2) measuring concentrations over bulbs broken in the pit at one transfer station; and (3) measuring concentrations during unloading activities on a working face, including from a bulb-spiked truck. We developed a method using bulb-spiked dumpsters as flux chambers to estimate the magnitude and duration of Hg emissions from broken bulbs in dumpsters. Because some initial readings were over range (>1,000 ng/m<sup>3</sup>), we devised a dilution/mixing system using the Tekran standard additions unit, which allowed us to quantitatively dilute our samples automatically by up to a factor of 30 with zero gas, bringing all of the values within the working range of the Tekran analyzer. We also estimated the Hg emission rates from broken bulbs using sealed dumpsters (flushed at 13 m<sup>3</sup>/hr with ambient [ $<4$

ng/m<sup>3</sup> Hg] air) as dynamic flux chambers and conducting time-series analyses of headspace gas over open dumpsters (in each case, one bulb was broken in a single empty dumpster). In a follow-up to these measurements, we monitored in the Volusia County study the Hg in air of a 6-m<sup>3</sup> dumpster containing a single broken fluorescent bulb using the Tekran 2537 analyzer to continuously measure the airborne Hg over a 4-day period. As part of that study, we also monitored the turnover time of Hg vapor in an open dumpster by enclosing a Hg<sup>0</sup> source within the dumpster for 30 min and then opening the dumpster and continuously monitoring Hg concentration at a point midway between the dumpster opening and the bottom using the Lumex 915+.

## RESULTS AND DISCUSSION

### Waste Characterization and Hg Emissions during Transport, Handling, and Storage

Dumpsters delivered to the Brevard, Orange, and Volusia County sites contained predominantly paper, plastic, glass and metal containers, and a large fraction of "miscellaneous" materials (organic garbage, household items, etc.). Headspace Hg concentrations of dumpsters containing trash ranged from background to ~500 ng/m<sup>3</sup> (Table 1). Dumpster headspace Hg concentrations above our

sorting criteria of 20 ng/m<sup>3</sup> were found in only 2 of 22 containers examined in the Brevard and Orange County studies (Table 1). At Volusia County, a more exhaustive search for Hg-containing dumpsters identified 15 of 188 dumpsters as candidates for sorting (>20 ng/m<sup>3</sup>, see Table 1). Although indicating some level of contamination, the highest headspace Hg levels measured were far below concentrations found when open sources of elemental Hg were present (e.g., broken bulbs or thermometers, >5 µg/m<sup>3</sup>). Suspected Hg sources (electrical and electronic equipment, medical waste, batteries, light bulbs in the dumpsters were isolated for sniff tests; see Table 2), but the only materials that conclusively contained significant elemental Hg were unbroken fluorescent bulbs, dental amalgam capsules, and a metal sink drain with associated hardware. The highest headspace Hg in the sniff tests (~2,000–8,000 ng/m<sup>3</sup>) came from the metal drain trap and hardware (Table 2), which must have received metallic Hg disposal. The dumpster containing this source (D4, Table 1) generated a strong Hg<sup>0</sup> signal when it contained the source (i.e., metal drain pipe and hardware), but also after the source was removed. The dumpster yielding the highest Hg<sup>0</sup> signal (D12, Table 1) did not contain any obvious Hg source. In fact, there was little relationship between the presence of Hg<sup>0</sup> emanating sources and the

**Table 1.** Tagged and sorted dumpsters from Brevard County (BC), Orange County (OC), and Volusia County (VC), FL.

Date	Location	Route Day	Sample No.	Closed Container	Signal at Location <sup>a</sup> (ng/m <sup>3</sup> )	Full <sup>b</sup> (ng/m <sup>3</sup> )	Empty <sup>c</sup> (ng/m <sup>3</sup> )	
11/9/98	BC <sup>d</sup>		Dumpster 8	Yes		28.1	n/a	
10/99	OC <sup>d</sup>		Dumpster 5	Yes		27.6	n/a	
3/19/01	VC	Tue.	D13	Yes	27–36	n/a	12 ± 1	
3/20/01	VC	Wed.	D1	Yes	27–50	18	41 ± 6	
			D2	No	36–67	67 ± 82	n/a	
	VC			D3	No	13–49	69 ± 112	176 ± 29
	VC			D4	No	84–107	364 ± 12	285 ± 53
	VC			D5	Yes	82–101	35 ± 26	34 ± 5
	VC			D6	Yes	54–108	22 ± 42	18 ± 4
	VC			D7	n/a	530–582	111 ± 12	649 ± 23
	VC			D8	Yes	98–114	50 ± 1	541 ± 2
	VC			D9	n/a	39–75	68 ± 18	152 ± 8
	3/21/01	VC	Thurs.	D10	n/a	0–4	3 ± 1	9 ± 1
D11				n/a	0–3	1 ± 1	46 ± 6	
D12				Yes	78–125	390 ± 2	8874 ± 22	
3/22/01	VC	Fri.	D14	Yes	56–82	48 ± 23	280 ± 13	
			D15	Yes	31–71	54 ± 23	117 ± 15	
			D16	Yes	101–157	132 ± 29	1052 ± 120	
			D17	Yes	0	0	12 ± 1	
			D18	Yes	476–500	491 ± 13	78 ± 2	

<sup>a</sup>Signal at Location designates the reading at the dumpster field location before being hauled to the sorting site 1 day later; <sup>b</sup>Full designates the reading at the sorting location before emptying; <sup>c</sup>Empty designates the reading after emptying for sort; <sup>d</sup>Dumpsters at the BC and OC landfills were not measured in the field but after delivery to each site. Only those dumpsters with headspace Hg concentrations >20 ng/m<sup>3</sup> were treated as "contaminated." Because of delivery problems, not all of the tagged dumpsters were sorted (see text).

**Table 2.** Hg measured in sniff and swipe tests of suspected source materials removed from dumpsters and excavated landfill material at Brevard (BC; 1998), Orange (OC; 1999), and Volusia County (VC; 2001) landfills in Florida, as well as in swipe tests conducted at Oak Ridge National Laboratory (2001).

Description	Location	Hg/Area (ng/cm <sup>2</sup> )	Headspace Sniff Test (ng/m <sup>3</sup> )
Empty dental amalgam capsules	VC	14,200	199
Metal cover for drain and pipe	VC	708	7948
Metal sink trap and pipe	VC	260	2250
Counter top (Hg-use lab)	ORNL ESD	43	N/a
Light bulb bottoms, dirt from bucket	BC	11.5	144
Broken lantern battery	BC	8.8	443
Plastic case w/battery and capacitor	BC	6.1	33
Corroded alkaline batteries	BC	3.9	158
Misc. electronic components	BC	3.5	115
Flashlight batteries, Eveready classic	BC	3.3	50
Polaroid camera battery	BC	2.9	16
Remnants of Polaroid camera battery	BC	1.4	16
Wire and plastic covers	BC	1.1	120
Scallop shells	BC	1.0	252
Lava lamp base and cord	OC	0.4	24
Office floor	ORNL ESD	0.23	N/a
Unbroken fluorescent bulb	VC	0.16	218
Plastic bucket	ORNL ESD	0.040	N/a
Outdoor windowsill	ORNL ESD	0.038	N/a

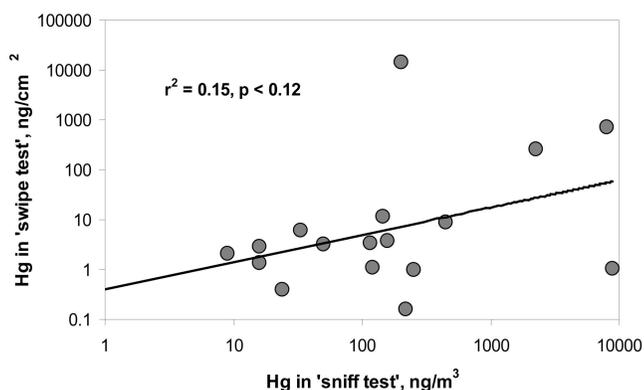
Notes: Mean total Hg ( $N = 2$ ) for blank swipes with  $\text{HNO}_3 = 0.018 \mu\text{g Hg}$ . Recovery of Hg standard (NIST 2711, 24.7 mg; 100% recovery =  $0.154 \mu\text{g Hg}$ ) was  $0.146 \mu\text{g}$  or 95% recovery; ORNL ESD = Oak Ridge National Laboratory Environmental Sciences Division.

magnitude of  $\text{Hg}^0$  signals from individual dumpsters, indicating that historic disposal of  $\text{Hg}^0$  sources in dumpsters plays a dominant role in continuing emissions. This also accounts for the observation that empty dumpsters tended to generate higher  $\text{Hg}^0$  concentrations than dumpsters that contained wastes. In the sniff tests (Table 2), a crushed carbon-zinc lantern battery gave a moderately strong  $\text{Hg}^0$  signal. Interestingly, the result for a sample of scallop shells dumped at the Brevard County landfill in a waste shipment from a seafood processor was similar. That shipment yielded a discernible  $\text{Hg}^0$  signal (and a noticeably strong odor!) downwind of the landfill working face when dumped.

Week-old wastes excavated from the Brevard County working face generated a substantial atmospheric Hg signal when dumped at the sorting station ( $>20 \text{ ng/m}^3$  in

open air). Examination of the Brevard waste with a “black light” to detect fluorescent bulb fragments was unsuccessful because of the ubiquitous presence of highly fluorescent scraps of plastic and paper. We measured the Hg content of soil taken from the excavated mixture and found it to be low ( $<0.1 \mu\text{g/g}$  dry weight). However, several potential Hg sources were identified in the excavated waste, which yielded clearly measurable levels of Hg in headspace gas. We sorted these items into “most likely” and “less likely” Hg sources, and subsequent Hg headspace sampling indicated some success in the sorting. Mean headspace Hg of the most likely source items was  $4,400 \pm 450 \text{ ng/m}^3$  versus  $1,400 \pm 1,800 \text{ ng/m}^3$  for the less likely group. The most likely samples contained 13 crushed and 11 whole batteries and scallop processing waste. The less likely samples contained electrical components, syringes, miscellaneous tools, a telephone, magnetic tape, and a butane lighter. Because it is unlikely that these latter materials originally contained Hg, they may have been contaminated with a diffuse source, such as fluorescent bulb dust, which would be unidentifiable in aged samples. At Orange County, in contrast, no detectable Hg signals (above background) were found in the excavated waste, and no sorted items yielded significant sniff signals.

Most items with elevated  $\text{Hg}^0$  signals for Hg vapor in sniff tests also showed elevated Hg in the swipe tests (Table 2), although the correlation was weak ( $r^2 \sim 0.2$ , Figure 1). The scallop shells were one exception, showing a strong signal in sniff tests but only a faint one in the swipe test, whereas the amalgam capsule exhibited the opposite (moderate sniff and very high swipe). The small variation in Hg concentrations from the swipe tests is curious, because some of these items (e.g., plastic covers and cases) were not primary sources of Hg. We suspect these materials are good absorbers of elemental Hg and accumulate Hg in the subsurface atmosphere of the landfill or while in dumpsters where Hg vapor levels are



**Figure 1.** Linear regression of log [Hg] in swipe tests versus log [Hg] in sniff tests. The slope of the regression is not statistically significant ( $P > 0.05$ ).

elevated. Items separated as potential Hg sources are probably a mix of some primary sources (plumbing, batteries, and their corrosion products), with numerous secondary (re-emission) sources (plastics and scallop shells). Because swipes only remove surface dust and dirt that may contain Hg, results of swipe tests would not be indicative of Hg absorbed or amalgamated by waste surfaces, which appears to dominate as the Hg<sup>0</sup> source in waste. Swipes of uncontaminated surfaces showed lower levels of Hg than landfill waste, and analysis of blank swipes was very low (Table 2). Virtually all of the samples, even laboratory and office surfaces, yielded Hg signals >2 times blank swipe values (0.018 µg Hg). Swipes of two empty dumpsters appeared unrelated to headspace Hg concentrations, measuring 2.2 and 1.1 ng/cm<sup>2</sup>, respectively, for an uncontaminated (9 ng/m<sup>3</sup>) and contaminated (~8,900 ng/m<sup>3</sup>) dumpster.

Many counties use large transfer stations to consolidate wastes for delivery to the landfill working face. At the transfer station, wastes are dumped on a hard surface until the area is nearly filled. The waste is bulldozed into pits and then compacted into waiting trucks. We monitored airborne Hg concentrations in the Volusia County transfer station at ground level ~20 m from the area where an average of 675 metric tons/day of waste was processed. Airborne Hg concentrations were highly variable, averaging ~30 ng/m<sup>3</sup> during inactive periods but rising to 100–200 ng/m<sup>3</sup> when new wastes were dumped on the station floor and additionally to 400–900 ng/m<sup>3</sup> as equipment moved the wastes to the loading pits. Afterwards, Hg dropped rapidly from 200 ng/m<sup>3</sup> to ~30 ng/m<sup>3</sup> within 30 min. The station was well ventilated, with large, open doorways at each end and several large fans exhausting air. Assuming a turnover time of 30 min for air in the building, a “typical” working airborne Hg concentration of 400 ng/m<sup>3</sup>, and a volume of 12,000 m<sup>3</sup> and that Hg concentrations at our monitoring point were representative, we calculate a crude flux estimate of 10,000 µg/hr or ~0.1 g/day for an 8–10-hr day. Whereas the assumptions in this estimate (i.e., ground level concentration of Hg<sup>0</sup> at our monitoring point is representative of the entire building) are untested, results suggest that Hg fluxes from the transfer station, while not trivial, are substantially less than that occurring at a landfill working face.

### The Potential Role of Hg in Consumer Products

Among current consumer household products, Hg thermometers and fluorescent bulbs probably represent the most widely used nontrivial Hg-containing products still entering municipal landfills.<sup>12</sup> Although some states mandate bulb recycling, these programs generally target commercial facilities. We observed both broken and whole fluorescent bulbs in dumpsters, at transfer stations,

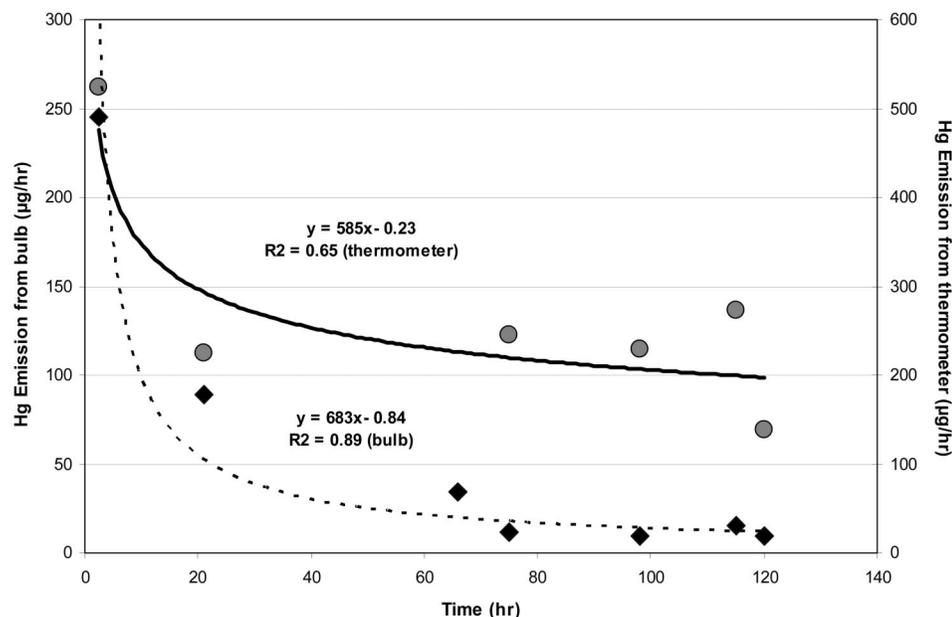
and during unloading of transfer trailers at the working face. The older fluorescent bulbs used in our studies contained as much as 40 mg of Hg per 4-ft tube. However, the industry is in the process of significantly reducing the quantity of Hg in fluorescent bulbs to ~10 mg of Hg. In 1999 the United States replaced between 600 and 800 million fluorescent lamps containing >15 t of Hg, with 85% of these going to landfills.<sup>13</sup> Household fever thermometers also have the potential to generate Hg inputs to the municipal waste stream of 7 t of Hg per year.<sup>12</sup>

In empty dumpsters spiked with broken fluorescent bulbs, headspace Hg concentrations over single broken fluorescent bulbs reached elevated levels, which persisted for at least 1 week in both ventilated and sealed containers. For example, Hg<sup>0</sup> reached levels of 2,400–3,800 ng/m<sup>3</sup> in filtered headspace air within 20 min after breakage of a single bulb in a partially filled dumpster. After 10 min of forced ventilation (and mixing) with ambient air at ~20 m<sup>3</sup>/hr, the Hg concentration actually increased to ~8,200 ng/m<sup>3</sup> in filtered headspace samples, suggesting that there was a strong vertical gradient in Hg above the floor of the dumpster after initial breakage (headspace measurements were taken ~10 cm below the lid, which was ~1.2 m above the floor of the dumpster). Assuming a well-mixed system at this point, there were ~10 µg of gas phase Hg<sup>0</sup> in the dumpster at this time or <0.1% of the potentially available Hg in the bulb. In the field, elevated Hg levels were readily detected 3–10 m downwind of bulb-spiked dumpsters (~700–1,000 ng/m<sup>3</sup>), ~10 m above the floor of the ram pit at the Brevard transfer station during routine activities (~30–90 ng/m<sup>3</sup>), when bulb-containing wastes were dumped (up to 500 ng/m<sup>3</sup>), and downwind of a large cardboard box of broken bulbs in a roll-off container (~300–350 ng/m<sup>3</sup>). Hg<sup>0</sup> is clearly being emitted from broken fluorescent bulbs and lost before landfilling.

In the first bulb study, conducted at the Brevard County landfill, we measured Hg emission rates on seven occasions for ~30-min each over a period of 216 hr after bulb breakage in an empty dumpster kept in the shade (temperatures ranged from 18 to 25 °C). With one end broken, the bulb emitted ~50 µg Hg/hr for the first 16 hr; by 96 hr the flux had decreased to ~10–15 µg/hr, where it remained until 163 hr after initial breakage. At 187 hr, the bulb was crushed, and the resulting flux increased again to ~50 µg/hr but decreased to ~20 µg/hr after another 29 hr. This observation strongly suggests that emissions are related to exposure of bulb debris (phosphor dust) and not just loss of that Hg initially present in the gas phase in the intact bulb. Between flux measurements, the dumpster remained closed and, under these conditions, the bulb lost ~120 µg of Hg during 3.8 hr of active

ventilation of the dumpster. Assuming this average rate, the bulb could have lost ~7 mg of Hg over the 216-hr experiment (~20% of total Hg content).

In the second study, conducted at Orange County, we spiked adjacent trash-filled dumpsters with two broken Hg thermometers and one broken bulb, respectively, and measured Hg emissions for ~120 hr. These spiked dumpsters were exposed to direct sunlight, resulting in much higher fluxes (internal temperatures ranged from 24 to 43 °C). Both dumpsters exhibited initial spikes in flux (~250 µg/hr, measured after 1 hr of ventilation), which declined to relatively stable values ~60 hr after breakage (Figure 2). The initial Hg flux from the bulb was ~5 times greater than seen at Brevard, attributable primarily to the higher temperatures and the fact that the whole bulb was crushed but was only half the flux from the two broken thermometers (~500 µg/hr). By the end of the measurements, the fluxes from the bulb (~10–15 µg/hr, similar to Brevard) were ~10% of those from the thermometers, and the trends suggested an exponential decrease over time to a stable rate between 60 and 120 hr when the measurements were ended. The bulb lost 1.2 mg of Hg during the 30 hr of active ventilation of the dumpster (a mean loss of 40 µg/hr or ~33% higher than in the shaded Brevard dumpsters). The thermometers lost 8.9 mg of Hg during the 30 hr of active ventilation (mean ~300 µg/hr). As before, the dumpsters remained closed (unventilated) between measurements, but if these average emission rates applied to the entire sampling period, the bulb could have lost ~5 mg of Hg in 120 hr of active ventilation, and the thermometers, ~35 mg.



**Figure 2.** Temporal trends in emission of Hg<sup>0</sup> from Hg-containing waste (fluorescent bulb and thermometer were broken in a dumpster, which was monitored as a dynamic flux chamber); both regressions were significant ( $P < 0.05$ ).

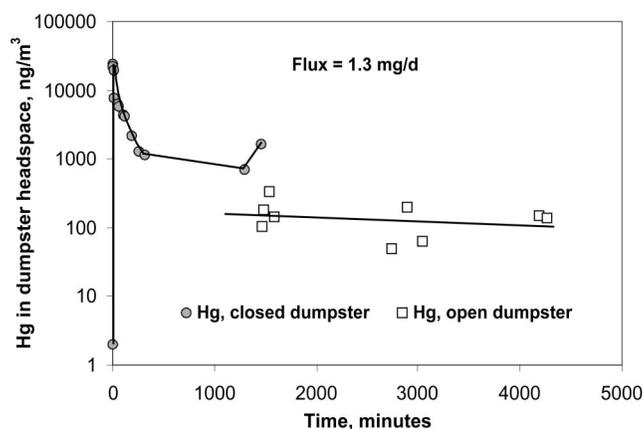
Because these bulbs contained much less Hg (~40 mg) than found in a typical Hg thermometer (~1,500 mg), our data suggest an enhanced mobility (volatility) of Hg from broken bulbs. This difference in the initial fluxes may be attributable simply to the gaseous Hg<sup>0</sup> originally present in the bulb. Bulb Hg would also be dispersed over a larger surface as more and finer particles than Hg from broken thermometers, enhancing the initial volatilization process. This effect appears to persist, however, supporting a generally higher relative mobility of Hg from broken bulbs. Over the course of our measurements, the relative mean Hg emission rates are 10 times higher from the broken bulb than the thermometers (~0.1% hr<sup>-1</sup> versus 0.01% hr<sup>-1</sup>, respectively).

### Cumulative Hg Flux from Dumpsters in a Landfill Service Area

In the Volusia County landfill study, we used a somewhat different approach to quantify emissions from Hg-containing consumer products in dumpsters. To check the method, a single bulb was broken in an empty 6-m<sup>3</sup> dumpster, which was closed for 1 day, then opened to allow Hg vapor to escape to the atmosphere. Very high initial concentrations (>10,000 ng/m<sup>3</sup>) declined to a steady state of ~1,000 ng/m<sup>3</sup> in the closed dumpster, probably reflecting the settling out of Hg-containing phosphor (Figure 3). After the dumpster was opened to the air, the internal concentration rapidly dropped to a new steady-state concentration of 100–150 ng/m<sup>3</sup>. This concentration was sustained for 3 days, with no indication that it would decline rapidly with additional exposure. We estimated the turnover time of air in

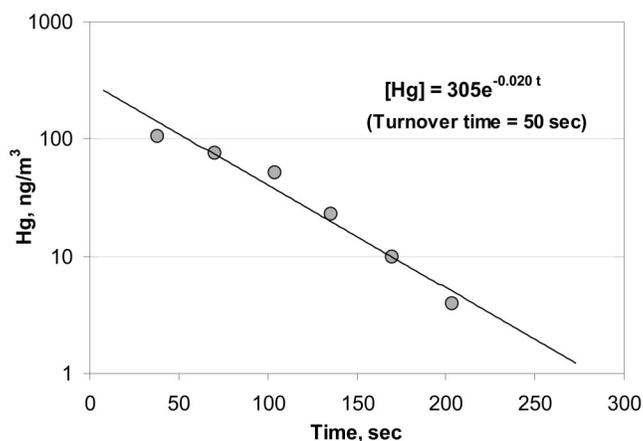
the dumpster by placing a small Hg<sup>0</sup> source in an adjacent clean, closed dumpster for ~30 min. At that time, the dumpster was opened, the source removed, and the airborne gaseous Hg concentration in the dumpster monitored (Figure 4). The first-order decline in Hg<sup>0</sup> corresponded to a turnover time of ~1 min. Using this turnover time, we calculated a mean Hg flux of ~50 µg/hr from the adjacent broken bulb, nicely confirming the fluxes observed in the Orange and Brevard County “dynamic chamber” experiments (Figure 2).

We used this approach to estimate Hg emissions from field dumpsters. Assuming that each dumpster is initially empty, then filled, and emptied again,



**Figure 3.** Hg concentrations in headspace of a dumpster containing a single broken fluorescent lamp vs. time.

the average ( $500 \text{ ng/m}^3$ ) Hg concentration in the headspace of filled and emptied dumpsters (Table 2) would characterize mean headspace concentration in a closed Hg-contaminated dumpster over the course of its use. The steady-state Hg concentration in open dumpsters was estimated at 15% of that value for closed dumpsters (from Figure 3); and because our field survey indicated dumpsters were commonly open, we assumed that all of the dumpsters would be open rather than closed. We calculated an average Hg emission rate for a Hg-contaminated dumpster by multiplying the estimated average headspace Hg concentration by the assumed volume and turnover rate ( $6 \text{ m}^3$ , 1 min) and then scaled that to the number of Hg-contaminated dumpsters in Volusia County ( $\sim 10\%$  of the total 10,000 dumpsters). We estimated a flux of  $\sim 30,000 \mu\text{g Hg/hr}$  to the atmosphere from 1,000 open Hg-contaminated dumpsters at their locations of use. These estimates for undisturbed dumpsters are surprisingly high compared with the airborne flux of Hg from activities at the working face of the Volusia County landfill ( $180,000 \mu\text{g/hr}$ , see below) and constitute an important and previously unquantified source, which is active 24



**Figure 4.** Hg loss from the headspace of an open  $6\text{-m}^3$  dumpster.

hr/day. Because working face emissions are normally negligible after the daily cover is applied, the estimated daily emissions from dumpsters could exceed 25% of those from the working face.

In this study, atmospheric Hg flux from dumpsters was heavily influenced by the presence of a few highly contaminated dumpsters (only the highest 10% of surveyed dumpsters were selected, and the average  $\text{Hg}^0$  signal of those was substantially higher than the median). It is apparent, however, that Hg emission from dumpsters could probably be lowered strikingly if the incidence of highly contaminated dumpsters were reduced through better communication to waste generators of concerns about placing Hg-containing materials in dumpsters. Because a few highly contaminated dumpsters dominate the overall flux from this source, it is important to realize that our estimate represents a single measure that may not be representative of other waste collection routes or even of this route on a different date.

Our data suggest that broken bulbs, thermometers, and other sources of  $\text{Hg}^0$  vapor are capable of emitting significant amounts of  $\text{Hg}^0$  during storage before landfilling. The U.S. Environmental Protection Agency once assumed that only a small percentage of Hg in bulbs was ever emitted to the air (primarily that fraction initially present as gaseous  $\text{Hg}^0$ ). This ignores the possibility of continued airborne losses of Hg in lamp dust, as suggested by our data. These losses probably represent  $\text{Hg}^0$  sorbed to the dust or  $\text{Hg}^{\text{II}}$  in dust later reduced to  $\text{Hg}^0$ . Also, we did not simulate all of the possible conditions during routine handling of bulbs, especially in the home. Bulb debris, if broken, could be scattered over large areas and exposed to different conditions. It is clearly important to assess the long-term stability of the Hg in bulb debris, especially under conditions of elevated temperature and solar radiation, parameters known to elevate Hg emissions from wastes.<sup>14</sup> An earlier study over  $\sim 3$  weeks estimated that even buried bulbs released  $\sim 3\%$  of their total Hg or  $\sim 1,200 \mu\text{g}$ , suggesting that broken bulbs could be a long-term Hg source to the atmosphere under many conditions.<sup>15</sup>

### Revised Estimates of Annual Hg Emissions from Landfills in Florida

Although the estimates of Hg fluxes to the atmosphere from wastes awaiting transport (dumpsters) and wastes in transport (transfer stations) made in this study are very approximate, they do indicate that Hg emissions from wastes before they are landfilled are not inconsequential relative to emissions at the landfill site. It is not unlikely that overall atmospheric emissions from the entire waste generation and landfill disposal cycle may be as much as 20–40% higher than the estimates for losses at landfill sites alone.<sup>6</sup>

## CONCLUSIONS

Hg vapor emissions occur from fresh municipal wastes stored in dumpsters or when processed and compacted at transfer stations. Chemical reduction of the Hg content of these wastes in the reducing atmosphere of a landfill is not needed to generate a strong Hg<sup>0</sup> signal, indicating that a significant fraction of the Hg content of the waste occurs as Hg<sup>0</sup>. Cumulative Hg<sup>0</sup> emissions from waste storage and handling appear to be no larger than emissions from the landfill servicing the waste collection area, but they are large enough to possibly be a substantial fraction (20–40%) of the total emissions of waste generation/disposal cycle.

Overall, it appears that Hg vapor is ubiquitously present in landfilled wastes. Only two strong primary Hg sources were actually found in our study (amalgam capsules and contaminated plumbing). Nevertheless, primary sources must occur at high enough frequencies to produce the levels of contamination and emissions observed in this and our previous study.<sup>4</sup> We speculate that fluorescent light bulbs are potentially important primary sources. Bulbs broken on the working face gave a very distinct signal up to 70-m downwind, yet are difficult to identify in the compacted waste. Regardless of the source, physical mixing and diffusion of Hg vapor throughout wastes in transit and after burial make virtually the entire waste mix a potential source of atmospheric emissions once exposed. This volatile Hg is then emitted to the atmosphere whenever wastes are exposed, including in dumpsters, at transfer stations or bailing facilities, and especially on the landfill working face. Nevertheless, the inability to specifically identify primary Hg sources in wastes, both before and after landfill, despite the presence of a strong Hg<sup>0</sup> signal from such wastes, raises the possibility that some major source of Hg vapor in municipal waste remains unknown.

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