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Airborne Emissions of Mercury from Municipal Solid Waste. I: New Measurements from Six Operating Landfills in Florida

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ABSTRACT

Mercury-bearing material enters municipal landfills from a wide array of sources, including fluorescent lights, batteries, electrical switches, thermometers, and general waste; however, the fate of mercury (Hg) in landfills has not been widely studied. Using automated flux chambers and downwind atmospheric sampling, we quantified the primary pathways of Hg vapor releases to the atmosphere at six municipal landfill operations in Florida. These pathways included landfill gas (LFG) releases from active vent systems, passive emissions from landfill surface covers, and emissions from daily activities at each working face (WF). We spiked the WF at two sites with known Hg sources; these were readily detected downwind, and were used to test our emission modeling approaches. Gaseous elemental mercury (Hg^0) was released to the atmosphere at readily detectable rates from all sources measured; rates ranged from ~1–10 ng m^{-2} hr^{-1} over aged landfill cover, from ~8–20 mg/hr from LFG flares (LFG included Hg^0 at $\mu g/m^3$ concentrations), and from ~200–400 mg/hr at the WF. These fluxes exceed our earlier published estimates. Attempts to identify specific Hg sources in excavated and sorted waste indicated few readily identifiable sources; because of effective mixing and diffusion of Hg^0, the entire waste mass acts as a source. We estimate that atmospheric Hg releases from municipal landfill operations in the state of Florida are on the order of 10–50 kg/yr, substantially larger than our original estimates, but still a small fraction of current overall anthropogenic losses.

IMPLICATIONS

Mercury-bearing material enters municipal landfills from a wide array of sources. We quantified atmospheric Hg vapor releases at landfill operations in Florida. Hg vapor is ubiquitously present and was released to the atmosphere primarily at the WF. We estimate that landfills in Florida release ~10–50 kg Hg/yr, substantially larger than our original estimates. This small fraction of current anthropogenic losses will increase as point sources are regulated. Efforts to reduce Hg releases from landfills should focus on removing Hg-bearing products from MSW before landfilling and encouraging the elimination of Hg in household products.

INTRODUCTION

The Florida Department of Environmental Protection (DEP) is quantifying the sources of mercury (Hg) within the state and its cycling between the atmosphere and aquatic ecosystems, especially the Everglades. While municipal incinerators are known to be important atmospheric sources, municipal landfills have not been widely studied. Hg occurs in important quantities in municipal waste; before 1994, Hg concentrations in waste were estimated to be ~4 mg/kg, with >80% originating from alkaline batteries.[1] Although Hg in waste is decreasing, those early wastes are, of course, still in landfills. The new five-year Research Strategy of the U.S. Environmental Protection Agency (EPA) places emphasis on noncombustion sources of Hg emissions to the environment, including landfill activities.

In cooperation with the Florida DEP we quantified the primary sources of atmospheric Hg releases at two municipal landfills in south Florida in April 1997.[2] These pathways included landfill gas (LFG) releases from passive

and active vent systems, passive emissions from landfill surface covers of different ages, and emissions from daily activities at the working face (WF). Emission rates ranged from ~1 to 20 ng m^{-2} hr^{-1} over aged surface covers (generally comparable to background soils), from ~6 to 2400 ng/hr from LFG vents and flares, and from ~5 to 60 mg/hr at the WF. In general the fluxes increased from older to newer landfills, and from passive to active venting systems. Limited data suggested that methyl- and other organo-Hg compounds may also be emitted from these sites, and this was recently confirmed elsewhere.[3] We estimated that atmospheric Hg releases from municipal landfill operations in the state of Florida were on the order of 10 kg/yr, but this estimate was based on very limited data.

Our results indicated the need to address several issues at a larger number of sites: WF emissions, Hg speciation in LFG, losses of Hg before landfilling, and the role of specific types of waste. The objective of our follow up study "Pathways of Mercury in Solid Waste Disposal" (PaMSWaD) was to reduce the uncertainties in the pathways and mass balance of Hg in the solid waste disposal process. Important goals included quantifying WF fluxes at other landfills, confirming the existence of highly elevated Hg concentrations ($\mu g/m^3$) in LFG, identifying the speciation of organic Hg in LFG, measuring Hg losses during dumpster and transfer station activities and storage, and positively identifying the contribution of Hg-bearing consumer products (e.g., Hg thermometers and fluorescent bulbs). The latter three objectives are reported in companion papers.[4,5] This paper reports more extensive data on WF and LFG emissions collected during sampling campaigns in 1998–2001. Based on these new data, we present revised estimates of statewide landfill emissions for Florida.

APPROACH

Study Sites

Our study was conducted at six Florida landfills over a four-year period. Table 1 presents selected characteristics of these sites including the Martin County (MC) site previously studied in 1997[2] and again in 2002 (LFG only in 2002). In November 1998 we sampled the Brevard County Central Disposal Facility near Orlando, FL. This landfill, an active Class I landfill located in central Brevard County, receives an average of over 1,500 metric tons per day of waste. The south slope was closed in 1989 and the east slope, plus a portion of the north slope, was closed in 1997 per regulatory requirements. Municipal solid waste (MSW) continues to be placed in 3-m lifts over the ~78 hectare footprint of the landfill moving along the north and west slopes. Incoming waste is shredded during wet weather, a unique feature of the Brevard County landfill.

Table 1. Selected Florida landfill characteristics: MSW received daily and cumulative in-place over time; annual landfill gas production.

Site (study yr)	MSW Daily	MSW In-Place (yr)	Landfill Gas (m^3/yr)
Palm Beach (2002)			20,800,000
St. Lucie (2002)			3,650,000
Volusia Co. (2001)	1100	3,600,000 (1990–2000)	31,000,000
Orange Co. (1999)	1800	5,700,000 (1990–1999)	51,500,000
Brevard Co. (1998)	1550	4,100,000 (1990–1998)	11,700,000
Martin Co.			4,850,000[a] (1997)
(1997, 2002)	400 (1997)	1,400,000 (1990–2000)	7,300,000 (2002)

[a]Martin County landfill gas volume estimated based upon MSW in-place using an U.S. EPA landfill gas generation model. Other site volumes are from flowmeter measurement. Units are metric tons unless otherwise indicated. MSW daily mass and LFG volumes are for the indicated study year.

LFG is collected from closed areas of the landfill and flared. In October–November 1999, we sampled the landfill in Orange County that receives over 1,800 metric tons per day of waste from the greater Orlando area. The Orange County site contains a large area of closed, unlined (~54 hectares) and lined (~21 hectares) cells that received MSW between 1985 and 1998, from which 200+ gas wells extract LFG for fuel at a nearby electric utility. There is also a ~26 hectare lined cell which has been receiving waste since 1998. In March 2001, an 8-day study was conducted at the Tomoka Farms Landfill in Volusia County. Waste deliveries during the study period averaged 750 metric tons per day, ~55% of which was commercial waste. The active North Cell is ~14 hectares in size, with waste being placed on a second 6-m lift above an initial 3-m layer of shredded waste. LFG is collected from the closed ~45 hectare by 40-m high South Cell via 66 wells and fed to a diesel powered co-generation plant.

During April 2002, we sampled LFG from collection systems at three landfills in eastern Florida (St. Lucie, Martin, and Palm Beach counties). At St. Lucie County, we sampled two gas collection systems, one collecting gas from a closed landfill segment (operational 1978–1988) and the other from the operational section (1988–present) of the landfill. Daily LFG flow of the combined systems to the flare was ~10,000 m^3/day. We re-sampled LFG from the Martin County landfill that had been previously sampled by us in 1997. The 1997 study sampled individual LFG vents. These had since been consolidated into a single system feeding a large flare (~20,000 m^3/day). We also sampled two other LFG collection systems, previously sampled for total Hg in 1997 by us, at the Palm Beach County landfill. One of the collection systems flared gas (~50,000 m^3/day) from the large active Class I landfill; the other (~7,000 m^3/day) from a closed (1990) landfill.

METHODS

Airborne Hg Analysis and Flux Measurements

The Hg sampling and flux measurement methods applied in this study have all been published in detail.[2,6–8] Briefly, Hg fluxes directly over landfill surfaces were measured using a Teflon dynamic flux chamber (FC) system (60 × 20 × 20 cm).[9] The FC was operated in an automated mode, utilizing a commercially available Tekran Hg analyzer to quantify air concentrations at the inlet and outlet of the FC to yield continuous, near real-time (20-min) fluxes. A Tekran 2537A was operated in 5-min mode to sample two lines via a dual-solenoid switching unit to provide alternating paired samples from the FC inlet and outlet. This system reduced sampling biases resulting from the two alternating gold amalgamation traps used in the Tekran. Additional Tekran analyzers were employed to monitor air concentrations upwind and downwind of the WF at each site as described below. Limited sampling was conducted for reactive gaseous mercury (RGM) and dimethylmercury (DMM) in ambient air near the WF. RGM was sampled manually using quartz denuders[10] and DMM was sampled with carbotraps.[3]

Ambient Hg concentration was measured (5-min samples) with the Tekran Hg analyzer downwind of the landfill WF during routine dumping and compaction of wastes on the WF at the Brevard, Orange, and Volusia County landfills. Monitoring at each landfill site was conducted over a period of 4–5 days with brief periods of downtime for Tekran maintenance, repositioning of monitoring equipment, and power outages. The intake line for the downwind Hg measurements was located ~2 m above the ground and ~ 50–70 m from the edge of the WF operations. On several occasions, we mounted the intake on a mobile platform and used the Hg concentrations from the output of the Tekran to "map" the cross-wind dimensions of the downwind plume under steady winds. On a few occasions, we also mounted the intake on 1–2 sections of ~3-m polyvinyl chloride pipe to determine the height of the downwind plume. Concurrently with the 5-min Hg concentration data, meteorological data were collected from a 3-m tower equipped with a standard meteorological instrument and data logger. Wind speed data for Volusia County were obtained from the meteorological station at the nearby Daytona Beach airport because of a software error in the on-site meteorological system.

When measuring Hg concentrations downwind of a WF, there is always the possibility that vehicle emissions could contribute to the Hg signal because vehicle activity is also proportional to waste delivery rate. Diesel emissions are not considered a major Hg source, but we tested their possible impact by measuring Hg levels in air downwind of several of the waste handling vehicles running in a garage. We sampled 5 m downwind and directly in the exhaust plumes but detected no additional Hg signal above ambient: exhaust = 2.2 ± 0.1 ng/m^3, ambient in garage = 2.5 ± 0.2 ng/m^3. We conclude that the Hg signals we detected downwind of the WF are related to the waste itself and not to vehicle exhaust.

Estimating and Modeling Hg Emissions from the WF

Using the net downwind Hg concentration data (e.g., in a "fence line" approach), Hg emission rates from the landfill WF for the Brevard County and Orange County municipal landfills were modeled using a simple box model described in detail elsewhere[2] as well as with EPA's Industrial Source Complex, Short-Term, version 3 (ISCST3) atmospheric dispersion model.[11] Because they agreed well (as discussed below), we used only our simple box model approach at the Volusia County site. For both models, the WF for each of the landfills was treated as a ground-level area source. Hg emission rates (grams per second) may then be estimated from the downwind concentrations attributable to the source (i.e., landfill WF), whether the atmospheric dispersion parameters are known. Dispersion parameters were computed from the on-site meteorological data.[12] A related mass-balance method for nonintrusive measurements of gas emission rates-based on horizontal fluxes of the gas across upwind and downwind boundaries is described in Denmead.[13] For the ISCST3 modeling exercise, Hg concentration data were selected for hour-long periods when the wind direction was relatively constant, from the center of the landfill WF toward the location of the Tekran. For the Orange County site, the Tekran had to be moved to accommodate a change in wind direction; modeling results were not sensitive to this minor change. Different monitoring periods representing various stability categories were chosen. Emission rates using the box model were estimated for all periods for which up and downwind Hg concentration data were available.

Actual physical dimensions of the WF were used to approximate source geometry. Distances from the centers of the WF sources to the points at which concentrations were measured and modeled were taken as ~70 m. These distances are approximate; results for other distances indicated that a 10% error in distances results in a corresponding error in the emissions rate (ISCST3 model) for the geometries involved. The Orange County landfill WF was treated as a square of 50 m on each side for the box and ISCST3 model (area-source mode); the Volusia site was similar. The shape of the Brevard County landfill WF was roughly described by three adjacent rectangles sharing a common west-east baseline ~60 m long. West-east

dimensions for the Brevard County landfill were ~20 m for each rectangle, south-north dimensions were 30 m for the middle rectangle, and 15 m for the adjacent rectangles on either side (i.e., overall a trapezoid). The WFs remained generally unchanged in location and size throughout our study periods.

For the box model, the height of the box was estimated from dispersion parameters computed from the on-site meteorological data using the methods of Turner.[12] Input data to the ISCST3 and box models included measured hourly average ambient-air Hg concentrations, hourly wind speeds, hourly wind direction, and hourly Pasquill stability categories (a measure of atmospheric turbulence) as determined from the meteorological data. Also input to the box model was a mixing height (i.e., height above ground to which turbulence is sufficient to produce thorough vertical mixing of the atmosphere). This was calculated as 320 times the (3-m) wind speed (in meters per second), roughly consistent with recommendations[11] (for 10-m wind speed). Although we used wind speed data from a 3-m mast, values based on the estimated 10-m wind speed were considered to be unlikely to produce appreciably different results because of the very small pollutant-travel distances considered in this study. The ISCST3 model uses atmospheric dispersion equations for site-specific source configurations and given meteorological conditions to calculate the ambient-air concentration at any specified location;[12] in this case, it was the location of the Tekran. Because the source term in this case is unknown, it was assigned a value of unity, and the calculated concentration represented the ratio, r, of the ambient-air concentration at the Tekran location to the source term. A measured concentration of x times r would then indicate a source term value of x.

Hg in LFG

Inorganic Hg concentrations in LFG samples were measured using activated, iodated charcoal traps (for total gaseous Hg, TGM) and gold traps (for Hg^0), with each type operated in tandem mode using a primary and back-up trap to assess possible breakthrough because of elevated concentrations of reduced S and organic gases present in LFG. We also used the Lumex RA915+ to directly measure Hg vapor in LFG in the 2002 sampling. Measurements of methylated Hg species using carbotraps and water-filled scrubbers will be reported elsewhere.[5] Samples of LFG were collected at flow rates of ~400 mL/min from active gas collection systems with flares at each landfill site. All traps were either heated slightly above LFG temperatures (~45–55 °C) to eliminate condensation or the LFG was passed through a chilled chamber to eliminate condensation on the traps. Total LFG flow rates from the sampled flares were provided by continuous recording mass flow meters. All samples but the gold traps (run at ORNL) were analyzed by cold vapor atomic fluorescence (CVAFS) after preparation and digestion/extraction procedures performed in a commercial laboratory.[14] Details on the sampling methods for gaseous methylated compounds have been previously published.[2,3]

RESULTS AND DISCUSSION

Hg Emissions during Routine Operations on the Landfill WF

Hg Downwind of the Landfill WF. During delivery, dumping and spreading operations on the landfill WF, readily measurable quantities of Hg^0 are lost to the atmosphere;[2] the current study confirms the importance of this pathway, and suggests that our previous estimates of such losses were low considering new data from the larger number of sites included in this study. The concentration of Hg in ambient air downwind of the WF significantly exceeded that measured upwind at the Brevard County (Figure 1), Orange County (Figure 2), and Volusia County landfills. Upwind concentrations of Hg^0 averaged ≤ 2 ng/m^3 and, therefore, were consistent with concentrations reported for global background (1.6–1.8 ng/m^3), indicating no significant upwind sources other than the WF itself. Downwind concentrations of Hg^0 were as much as 80-fold higher than measured upwind at Brevard County (Figure 1) and 10- to 25-fold higher at Orange County (Figure 2). At Volusia County, downwind concentrations were ~ 4–6 times higher than upwind, primarily because of higher wind velocities and greater distance from the WF. Peak concentrations at Brevard County exceeded 150 ng/m^3 on one occasion and 100 ng/m^3 on several occasions. The peak concentration at the Orange County landfill was ~60 ng/m^3. Because our earlier work

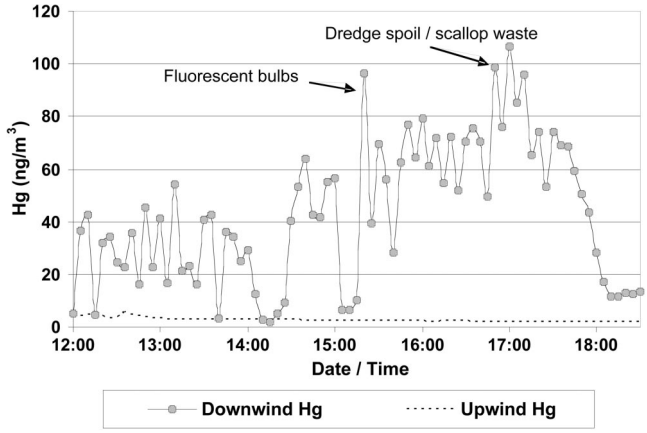

Figure 1. Hg concentration measured upwind and downwind of the Brevard County municipal landfill WF during November 1998. Downwind concentrations are net values (measured downwind minus simultaneous upwind values). Fluorescent bulbs were dumped from a transfer trailer onto the WF at ~15:15 and dredge spoil and scallop processing waste at ~17:00.

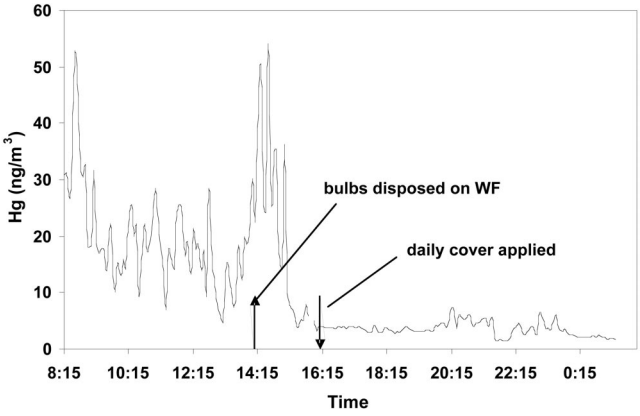

Figure 2. Hg concentrations measured with a Tekran Hg analyzer downwind of the WF at the Orange County municipal landfill during October 1999. Upwind concentrations averaged 1.8 ng/m^3 at this site (not subtracted from downwind values). Fluorescent bulbs were dumped from a roll-off container onto the WF at ~14:00, followed by daily cover at 16:00.

reported only Hg^0, we also performed limited measurements of the speciation of gaseous Hg at the Volusia County site. As expected, the gaseous Hg emitted from the WF is dominated by Hg^0 (~99%), but readily measurable concentrations of reactive gaseous Hg (RGM) and dimethylmercury (DMM) were found; DMM and RGM both fell in the range of 30–50 pg/m^3 (neither were measured upwind). Although this is well above ambient for DMM (see below), RGM in this range would be considered only moderately above background.[15] RGM is an oxidized gaseous Hg-II compound formed during combustion processes, such as incineration of MSW, and is not expected in the "passive" emissions from the WF. RGM is also formed during in-air reactions of Hg^0 under some conditions,[16] but without upwind RGM concentration data, we cannot draw conclusions about its source here. DMM is known to be generated at elevated concentrations within landfills and emitted in LFG,[3] but has not been previously reported in ambient air downwind of landfills.

Downwind Hg^0 concentrations near the Brevard and Orange County WF decreased significantly after the daily soil cover was applied (~4:00–6:00 p.m., Figure 2). Fresh soil cover serves as an effective short-term barrier against gaseous Hg emissions.[2] Concentrations tended to be quite stable at night; the average nighttime downwind Hg was 14 ng/m^3 compared with a daytime average of >40 ng/m^3 at Brevard County. Nighttime Hg^0 downwind of the Orange County landfill approached background (mean = 1.8 ng/m^3) compared with 25 ng/m^3 for the daytime average. At the Volusia County site, however, wet weather prevented the facility from applying temporary overnight cover, and downwind Hg concentrations remained elevated at night (see Table 2).

Table 2. Estimated hourly Hg emissions from the Brevard County and Orange County landfills using a simple box model and EPA's ISCST3 model run in area-source mode for selected sample periods.

Landfill, Date, and Sampling Period	Wind Speed (m/sec)	Pasquill Stability[a] Category	Net Downwind Hg Concentration (ng/m^3)	Box Model Estimated Hg Emissions (mg/hr)	ISCST3 Model Estimated Hg Emissions (mg/hr)
Brevard County, 13:00 to 14:00, November 12, 1998 Hourly averages	2.7	A	31.4	300	320
Brevard County, 15:00 to 16:00, November 16, 1998 Hourly averages	3.1	C	94.4	600	460
Orange County, 12:00 to 13:00, October 27, 1999 Hourly averages	2.4	A	16.8	160	210
Orange County, 11:00 to 12:00, October 26, 1999 Hourly averages	3.3	B	26.6	300	300
Orange County, 15:00 to 16:00, October 26, 1999 Hourly averages	3.8	C	24.8	270	230
Volusia County, Daytime, March 20–21, 2001	6.8–7.3	D	8.9–11.3	150–180	NA
Volusia County, Daytime, March 22, 2001	3.3	C	12.1	230	NA
Volusia County, Night, March 20–21, 2001	3.9–4.7	D	8.0–8.2	75–85	NA

[a]The Pasquill Stability categories are classifications of atmospheric turbulence; the greatest turbulence (least stability) is Category A; the least turbulence (greatest stability) is Category F, which indicates stagnation conditions. This study includes sunny to overcast conditions (Categories A through D). Volusia County landfill emissions were estimated using our box model approach only.

Downwind Hg concentrations at the Brevard and Orange County landfills fluctuated significantly during the day and spikes could often be correlated with the composition of waste delivered to the WF. For example, late afternoon spikes in Hg^0 at Brevard County (Figure 1), observed over several days, occurred during the unloading of scallop processing waste onto the WF. These wastes included significant quantities of shells and what appeared to be dredge spoil; degassing of Hg^0 from reducing sediments is possible, but the "malodorous character" of this waste prevented a more detailed examination of its composition.

To test our ability to track and detect emissions from a "known" Hg source on the WF, dumpsters and waste transfer trailers were spiked with fluorescent bulbs and delivered to the Brevard and Orange County landfills. We added 62 used fluorescent bulbs (4 ft length) to a 100-m^3 transfer trailer at the Brevard transfer station using a hydraulic ram; the load was delivered to the WF the next day where ~50% of the bulbs were broken upon delivery and the rest upon crushing at the WF. At Orange County we added 20 used bulbs to a 20-m^3 roll-off container which was immediately delivered to the WF (~75% of the bulbs were broken when delivered). In both cases, a strong Hg signal was recorded at the downwind monitoring location upon the dumping and breaking of the bulbs on the WF (Figure 2). Although not quantitative, these results illustrate our ability to detect Hg-bearing material in deliveries and support the more quantitative analyses that follow.

Modeled Estimates of Hg Flux. Results of box and ISCT3 model flux estimates are summarized in Table 2. Hg emissions estimated by the two models agreed well for all three daytime stability categories (Figure 3). Daytime Hg^0 emissions from the Brevard County landfill averaged ~1.1×10^{-4} g/sec or ~400 mg/hr for the ISCST3 model versus 440 mg/hr for the box model. Emissions from the Orange County landfill averaged ~0.7×10^{-4} g/sec or 240 mg/hr for both the box and ISCST3 models. Results for Volusia County were similar to the other sites, ranging from 140–230 mg/hr during daytime and 75–85 mg/hr at night (during that period when the normal daily cover was missing as noted above).

Because the ISCST3 model allows a wide variety of conditions to be modeled in one run, it was useful for identifying effects of changes and/or assumptions in the input data for the Brevard and Orange County landfills. Several different source characterizations and assumptions were modeled. We ran the tests for several stability classes treating the WF as either a volume or a point source, as an elevated or a ground-level source, and with or without initial vertical dispersion. These runs showed the expected trends with stability, and that the results were relatively insensitive to the other assumptions, probably because our monitoring was done in the immediate downwind vicinity of the WF. We selected the ISCST3 model results with the least variability across the three stability categories for final comparison with the box model (these were: area source, flat terrain, and initial dispersion, Table 2).

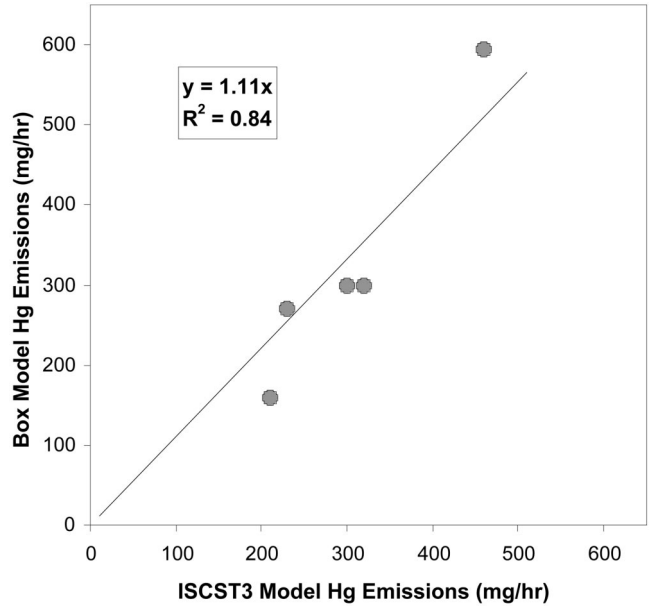

Figure 3. Comparison of Hg emission rate estimates from the WF calculated for both the Brevard and Orange County landfills and using EPA's ISCST3 atmospheric dispersion model and a simple box model. The intercept of the regression line has been forced through zero ($p < 0.05$).

The box model 30-min. fluxes from the WF ranged from 0 to ~350 mg for Brevard County and 0–260 mg for Orange County. The lowest fluxes consistently occurred at night, during periods of little activity, and immediately after the daily cover had been applied. Mean 30-min. nighttime fluxes were more than an order of magnitude lower than daytime (e.g., Brevard County: day = 150 mg, night = 8 mg; Orange County: day = 90 mg, night = 1 mg). As in our previous studies in Florida,[2] the estimated Hg^0 fluxes were significantly correlated with the rate (ton/hr) of waste delivery; e.g., the variance in waste delivery rates at both Brevard and Orange County explains ~70–80% of the variance in measured Hg flux (Figures 4 and 5). Because our estimates of Hg flux were derived independently of waste mass, these significant relationships are both logical and reassuring, and provide further support for our approach. These relationships also suggest that, aside from the unusual "spiked" deliveries, Hg losses from the WF are controlled more by overall waste quantity than "quality."

Assuming emissions occur primarily during normal working hours when the landfills are not covered, and

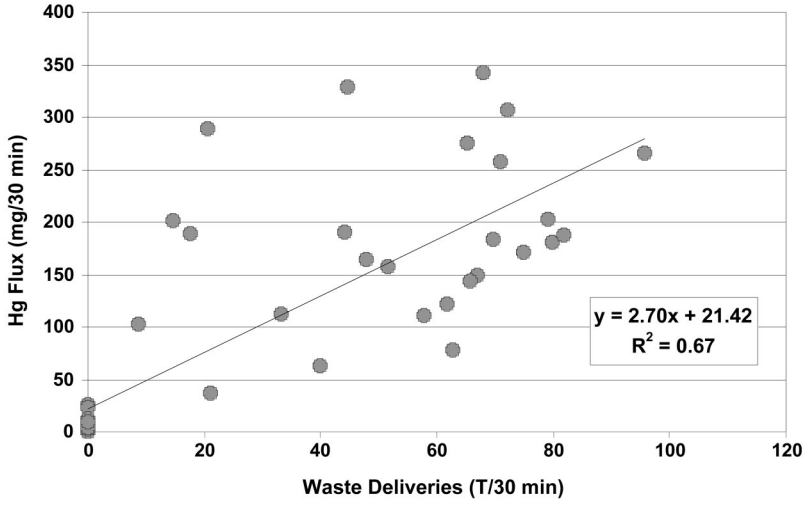

Figure 4. Relationship between the box-modeled 30-min fugitive atmospheric emission of Hg at the Brevard County landfill WF and the recorded delivery of waste (in tons) to the landfill WF during November 1998.

taking the liberty of extrapolating beyond this small data set, the average emission rate for the Orange and Brevard County landfills could be on the order of 1–2 kg/yr. Although the Brevard County landfill has only about half the surface area of the Orange County landfill, it emitted ~1.6 times as much Hg per hour during the period analyzed. We are not aware of any simple explanation for this difference, but many related measurements showed this same trend. For example, total gaseous Hg (TGM) concentrations in LFG at Brevard County averaged ~7 times that measured at Orange County (see LFG discussion below) and were substantially higher than concentrations we have measured at several other Florida landfills.[2] There simply must be more Hg-bearing material delivered to the Brevard landfill. The estimated annual Hg emissions to air from these landfills are significantly higher than those we estimated for smaller landfill operations in south Florida (0.1 kg/yr).[2]

The previously unrecognized but clearly important role of the WF is difficult to quantify directly. Because our modeling approach relies on various assumptions and limited downwind measurements near each diffuse source, it would be reassuring to repeat our studies under more controlled conditions. For example, whether the entire WF could be "contained" in some fashion, we could make more accurate estimates. Though not a practice in Florida, we found waste disposal systems elsewhere that are "contained." Minnesota utilizes MSW for energy production, in so-called refuse-derived fuel (RDF) facilities. Wastes are handled much like on the WF, but the facility is entirely enclosed. We sampled Hg concentrations and speciation in one such building during the waste dumping and compacting process, and our data confirmed our downwind observations at the Florida landfills. Total gaseous Hg concentrations in "ambient" air within the building ranged from 100 to 200 ng/m^3, similar to the downwind measurements reported here; we also detected elevated concentrations of both RGM and dimethylmercury in air within this facility.[17] Air exchange data were not available, and fluxes were not estimated for the RDF facility for direct comparison.

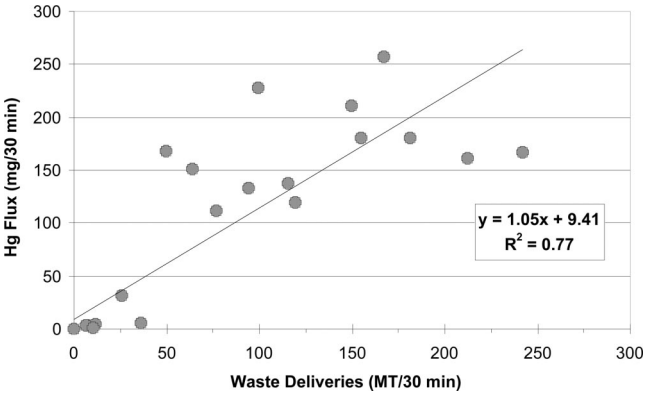

Figure 5. Relationship between the box-modeled 30-min fugitive atmospheric emission of Hg at the Orange County landfill WF and the recorded delivery of waste (in tons) to the landfill WF on October 26, 1999.

Surface Emission of Hg through Landfill Cover

As shown previously,[2,18] Hg emissions through the final, grassed cover of the closed portions of the landfill are small. This was also true at the landfills studied here, where fluxes over finished portions of the landfill were consistently near those for background soils (~1–10 ng m^{-2} hr^{-1}).[9] Several hot spots of methane release were detected with a real-time sensor at Brevard County, and Hg fluxes were measured over the areas of highest methane release (CH_4 concentration >600 ppm in air 5 cm above the ground compared with background concentrations of <5 ppm). Hg did not appear to be released at significantly elevated rates over these areas. The mean daytime flux over one background site at Brevard County was ~9 ng m^{-2} hr^{-1}, while that over the primary hot spot ranged from 2 at night to 11 ng m^{-2} hr^{-1} during the day. Background soil fluxes measured at Orange County on a sunny afternoon at a grass-covered site were ~1.5–2.2 (mean = 1.9 ng m^{-2} hr^{-1}). Flux measurements made over the Orange County WF *cover material* (a mixture of clay and sand with organic substances) averaged ~1.5 ng m^{-2} hr^{-1}. All of these fluxes are well within the range for background soils. Because the methane emission rates

showed no strong diel cycle, the existence of a strong diel cycle for Hg^0 over the hotspot suggests that we are measuring typical Hg^0 fluxes from the surface soil cover, not transport of Hg^0 from the subsurface waste through the cover. Background soil fluxes exhibit marked diel cycles in response to solar radiation and soil temperature.[9]

Hg emissions were also measured with flux chambers placed directly on the WF at the Brevard and Orange County landfills. Fluxes ranged from <1 to 150 ng m^{-2} hr^{-1} at 12 different spots (Table 3). The presence of mulch cover greatly reduced the flux, as expected. Although fluxes were quite variable, the mean flux (70 ± 62 ng m^{-2} hr^{-1}), was well above that for background soils (~1–10 ng m^{-2} hr^{-1}). Emission rates of this order of magnitude across an entire WF would result in a substantial Hg flux downwind. For example, a WF 100-m long by 30-m deep would generate a Hg flux of 200 mg/hr, comparable to the fluxes we estimated at these landfills from our downwind monitoring (Table 2). The three areas in Table 3 with fluxes >100 ng m^{-2} hr^{-1} were excavated (~1 m^3) and sorted. Several potential Hg sources were identified in the waste excavated from the Brevard WF that later demonstrated clearly measurable concentrations of Hg in headspace gas[4] (>100 ng/m^3).

Summary of Recent Measurements of Total Hg Emissions from LFG Vents

In our first landfill study in 1997, we suggested the possibility that methylated Hg species are being generated in LFG-based on findings of elevated concentrations of dissolved methymercury in LFG condensate (up to 23 ng/L) and measurements of total gaseous mercury (TGM) in the emitted gas at concentrations >1000 ng/m^3 at operating landfills in Martin and Palm Beach Counties in south Florida.[2] The nature of landfills to reduce waste through generation of methane by anaerobic bacteria suggests the possibility that these systems might be effective bioreactors for methylated Hg compounds. The possibility of volatile organic Hg species such as DMM being formed during anaerobic decomposition of MSW was reported in a recent controlled laboratory study[19] and DMM was identified in sewage gas in Europe.[20] We recently confirmed our hypothesis with the first measurements of gaseous mono- and di-methylmercury in LFG collected in the U.S. (at Brevard County landfill in 1998).[3] Both species were present at ng/m^3 concentrations that are several orders of magnitude above those reported for ambient air.[21]

Our new measurements from 1999 to 2002 at six operating landfills in north, central, and south Florida (and new sites in the west, midwest, and northeast) will be reported in detail elsewhere.[5] These data support our earlier observations that LFG contains appreciable concentrations of TGM, and that methylated compounds are significantly enriched in these gases[3] (tens of ng/m^3). TGM concentrations at five of the currently operating sites were comparable to those found in coal-fired utility flue gas (in the range of ~1 to 10 μg/m^3);[22] of course, Hg emission rates from utility boilers exceed those from LFG flares because of the larger gas flows involved. We found consistently lower concentrations of TGM at closed versus operating landfills, with one closed site exhibiting TGM as low as tens of ng/m^3, emphasizing the need for more such measurements. Preliminary estimates of emissions of TGM from LFG vents yield an average atmospheric release in LFG of ~0.3 g Hg per day for these sites,[5] well above the maximum of ~0.05 g/day we estimated earlier for Florida landfills.[2]

Table 3. Preliminary fluxes of Hg^0 measured over recently placed waste on the WF of the Brevard County (BC) and Orange County (OC) landfills.

Sample	Surface Appearance	Hg^0 Flux (ng m^{-2} hr^{-1})
BC 1	50/50% waste/mulch	16
BC 2	90% mulch	10
BC 3	100% waste	150
BC 4	100% mulch	3
BC 5	100% waste	120
BC 6	50% waste	80
BC 7	100% waste	120
OC 1	100% waste	59
OC 2	100% waste	4.5
OC 3	100% waste	107
OC 4	100% waste	0.7
OC 5	100% waste	0.6

Fluxes were measured with the ORNL/Tekran flux system.[2] Background soil fluxes in Florida range from ~1 to 10 ng m^{-2} hr^{-1}.

Revised Estimates of Annual Hg Emissions from Landfills in Florida

Using this expanded data set, and applying the methodology we developed previously,[2] we estimated ranges of annualized fluxes from the four landfill sites studied in detail (Brevard, Orange, Volusia, and Martin County). We then scaled our fluxes to Florida's landfills using statewide MSW regulatory inventories.

Consistent with data from our earlier studies,[2,18] Hg emissions through final or intermediate landfill surface covers over the closed portions of these sites (as opposed to daily cover on the active WF) are near those for background soils, as summarized above. For our estimates in this scaling exercise, we ignored these near-background fluxes from closed sections of the landfills. Similarly, still operating portions of the landfill that are covered may also be ignored. The limited data collected on Hg emissions from freshly applied (<1 day) daily cover (mulch) at

Brevard ranged from 3 to 16 ng m^{-2} hr^{-1} (Table 3) are also consistent with our earlier study[2] and only marginally above background. In our earlier study at the Martin site, aged daily cover emission factors were estimated to be less than emissions from LFG by a factor of ~2–3, and were much smaller than emissions from the active WF. Thus, for the purposes of this scaling exercise, fluxes from areas with fresh and aged cover material on the WF were ignored. Annual Hg fluxes in LFG emissions were computed from ranges of measured total gaseous Hg concentrations[2,3] and known or estimated annual LFG flows from site data (Table 1) provided by local staff. The Hg emissions factor (g/t of MSW) was then calculated-based upon MSW mass that was placed at the landfill over the life of the cells of the landfill that were generating LFG, roughly the period 1990–2000 (Table 1). Finally, the Hg emission factor (g/t) for daily waste handling activities at the WF was estimated from the relationship between MSW deliveries to the WF (t/hr) and the downwind Hg fluxes attributable to the WF source using the results of the two models in Table 2.

The two emission factors (LFG and WF) were then applied to estimates of Class I MSW landfilled statewide throughout Florida to estimate ranges of Hg losses from all Florida Class I landfills. LFG emissions factors were applied to Florida MSW placed from 1990–1998. WF emission factors were applied to Florida MSW placed in 1999. These time frames correspond roughly with the age of the MSW at the subject sites from which the emissions factors were estimated. Similar to our earlier study,[2] we scaled up by using ranges of emission factors applied to the quantity of Florida MSW that roughly corresponded in age with that at the study sites, that is, 1999 for WF emissions factors; 1990–1999 for LFG emission factors.

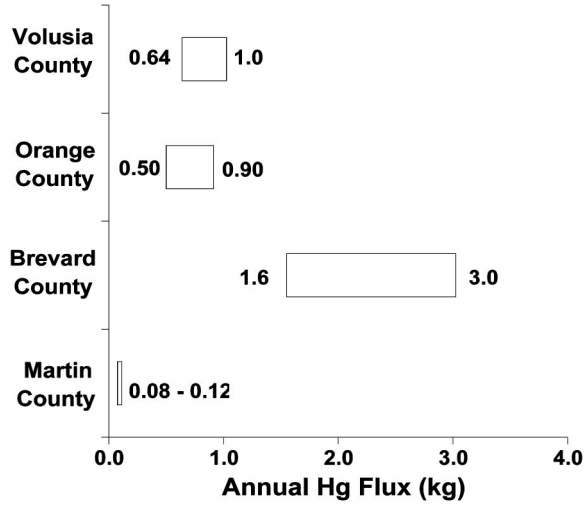

Figure 6. Ranges of annual Hg flux from WF and LFG pathways at four Florida landfills, estimated as described in the text.

Hg emissions from the summed LFG and WF pathways at the four landfill study sites where we have both LFG and WF emission measurements ranged from ~0.1–3 kg/yr (Figure 6). On-site fluxes were dominated by WF emissions. Estimated annual Hg emissions from the WF pathway ranged over two orders of magnitude from ~75 to nearly 3,000 g/yr whereas Hg emission factors ranged from <1 to nearly 7 mg/t of MSW placed annually (Table 4). Hg fluxes from LFG ranged from <1 to ~20% of the total estimated emissions (Martin <1–5%; Brevard 3–5%; Orange 7–9%; Volusia 17–19%). Estimated annual Hg emissions from the LFG pathway alone varied from <1 to nearly 200 g/yr. Hg emission factors varied from <1 to ~54 μg/t of total MSW in place (Table 5).

These data suggest that Hg emissions from Florida landfills have significant variability, ranging over at least two orders of magnitude from site to site. Because the biogeochemical behavior of MSW at the WF and the decomposition processes that occur within solid waste landfills are subject to many variables (age, composition, surface area, and moisture content of the solid waste, and configuration of LFG and leachate collection systems), we may only speculate as to the specific factors controlling the observed variability. For example, while the Brevard, Orange, and Volusia sites are roughly comparable in quantity of MSW in place, the Brevard site showed both the largest WF flux (Figure 6) and largest WF emission factor per ton of MSW placed annually (Table 4). Perhaps Brevard simply receives more Hg in wastes than the other sites. However, there is one other possible explanation for the elevated flux at Brevard: of these three sites, only Brevard shreds some of its MSW before placing it at the WF, and the larger Hg emissions could be a function of the increased surface area of this shredded waste. Such an effect might be expected to be more important for wastes exposed on the WF and less so for buried waste. The observation that the Brevard LFG emission factor of Hg per ton of MSW in place falls between those for the Volusia and Orange sites (Table 5), supports this idea. Certainly different processes influence the decomposition

Table 4. Estimated Hg emissions and estimated emission factors for the landfill working face at selected sites.

Site (Study Year)	MSW (t/hr)	Hg Emissions (mg/hr)	Hg Emission Factor (mg/t)	MSW Placed (t/yr)	Hg Emissions (g/yr)
Volusia (2001)	75	150–230	2.0–3.1	272,000	540–830
Orange (1999)	180	160–300	0.9–1.7	500,000	450–850
Brevard (1998)	90	300–600	3.3–6.6	442,000	1500–2900
Martin (1997)	50	50–70	1.0–1.4	76,000	75–110

Table 5. Estimated Hg emissions and estimated emission factors for landfill gas at selected sites.

Site (study yr)	Hg Concentration (ng/m^3)	Annual Hg Emissions (g)	Hg Emission Factor ($\mu g/t$)
Volusia (2001)	3500–6300	110–200	30–54
Orange (1999)	840–1160	43–60	10–11
Brevard (1998)	6850–8600	80–100	20–24
Martin (1997)	20–1060	<1–5	0.068–3.6

Annual Hg emissions and Hg emission factors calculated from "Landfill Gas" and "MSW In-Place" values, respectively, from Table 1. Concentrations represent the range of values measured directly in landfill gas at each site.

of covered MSW (i.e., the MSW that generates LFG), compared with waste exposed on the WF. Therefore, MSW surface area may have a smaller effect on Hg emissions in LFG. More research is necessary to test this hypothesis.

The input values and resulting annualized emissions from MSW landfilled in all Florida Class I landfills are shown in Table 6. We emphasize that this exercise is not intended to be a statistically significant model of actual Hg emissions from Florida landfills, but the most reasonable "order-of-magnitude" estimate that we can make from our limited site-specific data. Our calculations suggest that all Florida Class I landfills could release nearly 50 kg/yr of Hg to the atmosphere, almost three times the 14 kg/yr estimate from our earlier Florida study.[2] At least 40% of the MSW landfilled in Florida consists of construction and demolition debris (C&D) and yard waste (vegetative matter from landscape maintenance and land clearing operations), as distinct from Class I (putrescible) MSW.[23] C&D and yard waste also contain probable Hg sources (e.g., light switches, lamps, and atmospheric Hg deposited to foliage). The large mass and the existence of probable Hg sources indicate the need for further study of Hg emissions from C&D and yard waste landfills, particularly in light of our earlier[2] limited measurements of Hg emissions at a Class III (C&D and yard waste) landfill in Martin County.

A modeling exercise estimated 1995 U.S. annual Hg emissions at 145 T/yr (±30%) from all anthropogenic source categories.[24] Four combustion sources accounted for ~80% of this total: coal-fired electric utilities (33%), municipal waste combustors (19%), commercial/industrial boilers (18%) and medical waste incinerators (10%). For landfills, emissions from the LFG pathway were estimated to be 70 kg/yr, and WF emissions were not considered. Since our studies indicated that WF emissions account for at least 90% of landfill releases, it appears that the 70 kg/yr estimate for the U.S. could be low by at least an order of magnitude. It is important to note that the potentially important source category of waste collection containers[5] was not considered in the modeling exercise, because of the lack of data.

Table 6. Annualized Hg emissions from working face and landfill gas pathways from Florida Class I MSW landfills estimated from direct measurements at four Florida landfill study sites.

Pathway	Hg Emission Factor (mg/t of MSW)	FL MSW Age	FL MSW Mass (t)	FL Annual Hg Emissions (kg/yr)
WF	0.9–6.6	1999	6,800,000	6.1–45
LFG	6.8E-05–5.4E-02	1990–1999	54,200,000	3.7E-03–2.9
Total				6.1–48

Florida MSW mass has been rounded to the nearest 100,000 t.

A gross approximation (by population) would put Florida's annual Hg contribution from all sources at ~7,500 kg. The estimated maximum values for Hg releases from all Florida landfills (Table 6) would represent <1% of Florida's total anthropogenic releases. In 1995, Hg emissions from municipal waste combustor and medical waste incinerator sources were estimated to account for nearly 30% of total anthropogenic releases. Full implementation of federal and state regulations are expected to reduce emissions from both of these important sources by 90%.[24] With this decline of Hg emissions from these combustion sources, Hg emissions from landfills and related waste collection and storage areas will increase in their relative importance to anthropogenic Hg emissions, with attendant policy ramifications in addressing the issue of overall Hg releases.

CONCLUSIONS

It appears that Hg vapor is ubiquitously present in landfilled wastes. Only two strong primary Hg sources were actually found and identified in our study (amalgam capsules and contaminated plumbing[4]). However, primary sources must occur at high enough frequencies to produce the average waste concentrations of Hg and Hg emissions observed in this and our previous study.[2] We speculate that fluorescent light bulbs are potentially important primary sources.[4] Bulbs broken on the WF 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,[4] and especially on the landfill WF.

A comparison of releases from the WF and in LFG from several Florida landfills confirms our earlier observation that Hg releases from landfills are driven primarily by emissions from the active WF, with LFG Hg emissions contributing at most ~6% of the inorganic Hg releases from Florida landfills (Table 6). However, LFG that is not flared is probably the primary source of organic (methylated) Hg emissions from

landfills.[3,5] Efforts to reduce Hg releases from landfills should initially focus on this pathway by removing Hg-bearing products from MSW before landfilling. Better yet would be encouraging or requiring the reduction or elimination of Hg in common products like fluorescent lamps, thermometers, and batteries. This has been Florida's approach via statutory prohibitions and recycling programs since the early 1990s.

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