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Gaseous methyl- and inorganic mercury in landfill gas from landfills in Florida, Minnesota, Delaware, and California ☆

S.E. Lindberg[a,*,1], G. Southworth[a], E.M. Prestbo[b], D. Wallschläger[c], M.A. Bogle[a], J. Price[d]

[a]*Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6038, USA*
[b]*Frontier Geosciences, Seattle, WA, USA*
[c]*Trent University, Peterborough, Canada*
[d]*Florida Department of Environmental Protection, Tallahassee, USA*

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Abstract

Municipal waste landfills contain numerous sources of mercury which could be emitted to the atmosphere. Their generation of methane by anaerobic bacteria suggests that landfills may act as bioreactors for methylated mercury compounds. Since our previous study at a single Florida landfill, gaseous inorganic and methylated mercury species have now been identified and quantified in landfill gas at nine additional municipal landfills in several regions of the US. Total gaseous mercury occurs at concentrations in the $\mu g\,m^{-3}$ range, while methylated compounds occur at concentrations in the $ng\,m^{-3}$ range at all but one of the landfill sites. Dimethylmercury is the predominant methylated species, at concentrations up to $100\,ng\,m^{-3}$, while monomethyl mercury was generally lower. Limited measurements near sites where waste is exposed for processing (e.g. working face, transfer areas) suggest that dimethylmercury is released during these activities as well. Although increasing amounts of landfill gas generated in the US are flared (which should thermally decompose the organic mercury to inorganic mercury), unflared landfill gas is a potentially important anthropogenic source of methylated mercury emissions to the atmosphere.

Keywords: Dimethylmercury; Emissions; Waste; Analytical methods

1. Introduction

Mercury occurs in landfills by the addition of waste products that purposely contain mercury (historically dominated by batteries), but also including fluorescent lights, paint residues, fever thermometers, thermostats and electrical switches (EPA, 1992). Because landfills reduce waste volume by generating methane with anaerobic bacteria, these systems might also be conducive to generating methylated mercury compounds. The toxicity of such species indicates the need to

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*Corresponding author. Tel.: +1 865 574 7857; fax: +1 865 576 8646.
E-mail address: lindbergse@ornl.gov (S.E. Lindberg).
[1]Visiting Scientist, Institute of Ecosystem Studies, New York.

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determine if they are emitted from municipal landfills. During an earlier 1997 study at operating landfills at Martin and Palm Beach Counties in south Florida, we found highly elevated concentrations of total gaseous mercury in many samples of landfill gas (LFG) (Lindberg and Price, 1999). These concentrations ranged from ~30 to 1800 ng m^{-3}, and were higher at the larger Palm Beach facility. Inter-comparisons between charcoal traps (which collect total gaseous mercury, and yielded higher values) and gold traps (for elemental mercury, Hg^0) suggested the possibility of gaseous organic Hg compounds. Measurements of elevated concentrations of monomethyl mercury (MMM) in LFG condensate at these sites affirmed this hypothesis.

The potential for volatile organic Hg species such as dimethylmercury (DMM) to be formed during anaerobic decomposition of municipal solid waste was recently reported in a controlled laboratory study (Earle et al., 2000). In our follow-up study at a third site (Brevard County), we measured total gaseous mercury, Hg^0, and for the first time, gaseous methylated mercury compounds directly in LFG (Lindberg et al., 2001). Again, total gaseous mercury was in the μg m^{-3} range, MMM was found in condensate, but this time we positively identified gaseous methylmercury compounds at ng m^{-3} concentrations. Because of their toxicity, and the lack of known emission sources for airborne methylmercury compounds, it was crucial to repeat our measurements elsewhere. We report here several new measurement campaigns at nine landfills across the US, sampled between 1999 and 2002, including re-sampling of earlier sites, which confirm elevated concentrations of both total gaseous and methylated mercury species in LFG.

2. Sites and methods

2.1. Study sites

Our study was conducted at six landfills in Florida, and one each in Minnesota, Delaware and California over a 4-year period. In November 1998, we sampled the Brevard County Central Disposal Facility (BC) near Orlando, Florida, using the methods below. The Brevard County landfill, an active Class I landfill located in central Brevard County, receives an average of over 900 metric tons per day of waste (further details in Lindberg et al., 2001). LFG is collected from closed areas of the landfill and flared. In October–November 1999, we sampled the landfill in Orange County, Florida, which receives over 1800 metric tons per day of waste from the greater Orlando area; we also re-sampled the Brevard County site. The Orange County landfill contains a large area of closed, unlined cells from which 200+ gas wells extract LFG for fuel at a nearby electric utility, and a large lined cell which has been receiving new waste since 1998. In March 2001, an 8-day study was conducted at the Tomoka Farms Landfill in Volusia County, Florida. Waste deliveries during the study period averaged 750 metric tons per day, approximately 55% of which was commercial waste. The active cell was 14 ha in size, and LFG was collected from a filled 45 ha × 40-m high cell via 33 wells and fed to a diesel-powered co-generation plant.

In April 2002, we sampled LFG from collection systems at three more landfills in eastern Florida. At St. Lucie County, we sampled two gas collection systems, one pumping from a closed landfill segment (operational 1978–1988) and the other pumping from the operational (1988–present) landfill. Daily flow of both systems to a flare was ~10,000 m^3 d^{-1}. We re-sampled LFG from the Martin County landfill, which we sampled previously in 1997. The 1997 study sampled individual LFG vents, since consolidated into a single system feeding a large flare (~20,000 m^3 d^{-1}). We sampled two other LFG systems that we had sampled in 1997 at the Palm Beach County landfill. One of those flared gas (~50,000 m^3 d^{-1}) from the large active class I landfill, while the other flared gas (~7000 m^3 d^{-1}) from a closed (1990) landfill. We also collected limited data on DMM in ambient air near three potential sources where fresh wastes were exposed—the landfill working face (Volusia County), a waste receiving bay at a refuse-derived fuel (RDF) processing plant in Minnesota, and the waste receiving bay at a waste bailing facility (St. Lucie County).

In January of 2003, we sampled the Central Solid Waste Management Center (CSWMC) landfill operated by the Delaware Solid Waste Authority. The CSWMC landfill is located in Kent County near Sandtown, Delaware. The landfill receives general municipal waste at a rate of 360 metric tons per day or 1,01,000 metric tons per year in 2002 (DWSA, 2002). The landfill opened in 1980 and included an in-use area of 41 ha (closed + active). A total of 2,150,000 metric tons of municipal waste have been landfilled as of June 2002. The CSWMC landfill has an active gas collection system that consolidates the gas into a single flare at a rate of ~40,000 m^3 d^{-1}. The methane content of the LFG is approximately 40%. We sampled for mercury speciation at a location between the blower and the flare.

In August of 2001, we sampled the Hamilton Air Force Base Landfill in Marin County, California (a detailed description is in USACE, 2001). The Hamilton Landfill began receiving refuse in the early 1940s and was expanded throughout the 1960s–1970s. The primary waste is commercial wastes and demolition materials, but there were no records to confirm this, or the landfilling methods. The landfill has been inactive since 1974. The waste averages ~5–8 ft thick, and is mostly saturated by groundwater. The volume of the landfill, excluding cover, is ~1.7×10^5 m^3. Hence, landfill 26 is

shallow, small, old, and wet, with a high percentage of non-degradable components compared to typical municipal waste landfills (USACE, 2001). Hamilton Landfill 26 has probably passed its peak in methane, and should exhibit lower methane production compared to a typical municipal waste landfill. We sampled three previously installed gas monitoring probes and four monitoring wells in the landfill by sealing the top and inserting our sampling line 1–2 feet into the well. For elemental mercury, we used a Lumex RA915+ instrument, which provides real-time measurement resolution (1 Hz). The Lumex analyzer is based on Zeeman atomic absorption spectrometry with high-frequency modulation of light polarization of the 253.7 nm wavelength by elemental mercury atoms (Southworth et al., 2004). We used the side-cell absorption path to sample at a low flow rate of 2.0 lpm using an external pump. At every measurement location ($n=7$), the Lumex was checked for accuracy using the internal test-mode feature with an average relative percent difference of 9.3%.

In March 2000, colleagues in Minnesota sampled LFG at the Anoka, County landfill over 2 days (E. Swain, pers. comm.). The landfill was closed in the early 1990s, and contains 5.7 million cubic yards of mostly municipal solid waste. It is an unlined landfill that was operated as an open dump from 1967–1972, when it was permitted as a landfill. The LFG from this site is currently flared. (Note—the LFG at this site was originally sampled in 1993 for total gaseous Hg only, yielding comparable results to those shown below).

2.2. Sampling and analysis of mercury in landfill gas

2.2.1. Total airborne and total gaseous mercury in LFG

Total (inorganic + organic) mercury concentrations in LFG samples were measured using activated, iodated charcoal traps for total airborne mercury (TAM) operated in tandem mode using a primary and backup trap to assess possible breakthrough due to elevated concentrations of reduced sulfur and organic gases present in LFG. Although these traps were operated without an actual prefilter (but including a foam plug), the source of the gas, its high moisture content, and comparisons with measurements of Hg^0 suggest minor concentrations of particulate Hg, and TAM in this case approximates total gaseous mercury (TGM). Samples of LFG were collected at flow rates of $\sim$400 ml min^{-1} from active gas collection systems at each landfill site. Flared sites were sampled between the flame arrestor and the open flame under a slight positive pressure via stainless steel ports, while unflared (co-generation) systems were sampled at a similar point on the positive pressure side. All iodated charcoal traps were heated slightly above LFG temperatures ($\sim$45–55 EC) to eliminate condensation. Total LFG flow rates from the sampled lines were provided by recording flow meters. The traps were returned to the laboratory where the iodated carbon was leached to recover the collected Hg using hot-refluxing HNO_3/H_2SO_4 and then further oxidized by a 0.01 N BrCl solution. The digested and oxidized leachate sample was analyzed by cold vapor fluorescence spectroscopy (CVAFS) (EPA, 1999; Bloom et al., 1995).

2.2.2. Dimethylmercury (DMM) in LFG

The method used to determine DMM in the atmosphere is sensitive and highly selective (Bloom and Fitzgerald, 1988, Carpi et al., 1997, Bloom et al., in press; Lindberg et al., 2001). The sample train consisted of a new 1/8″ Teflon line inserted into the LFG duct port, a water dropout (trace-cleaned Teflon mini-impinger) in an ice-water-salt bath, the Carbotrap™ adsorber, flow meter, and vacuum pump. The sample line, water-dropout and Carbotrap™ were shielded from light because DMM can be photolytically destroyed. At some of the locations, the Carbotrap was contained in a heated probe kept a few degrees above ambient to prevent water from condensing on the Carbotrap. A 5-μm Teflon filter in front of the Carbotrap adsorber eliminated particulate matter co-collection. A short guard column (OV-3 on Chromasorb WAW-DMCS 80/100 mesh) was added behind the filter to prevent higher molecular weight semi-volatile organics (if present) from reaching the Carbotrap. The nominal flow rate was 0.30 l min^{-1} and was measured using a mass flow meter calibrated to 1 atm and 70 °F. Since the mass flow meters were calibrated to dry nitrogen, we used a volume adjustment factor (0.71 × measured volume) to correct for the high fraction of methane and carbon dioxide present. This approach is different from our original studies (Lindberg and Price, 1999; Lindberg et al., 2001) in which we reported all LFG samples on an ''as-collected'' basis.

The typical volume of DMM samples was 5 l, although at one site in Delaware we collected 0.92, 3.6 and 7.1 l samples from the same source in order to evaluate potential matrix interferences. We purged sampled Carbotraps with dry air through a mercury scrubber for 7 min at $\sim$300 ml min^{-1} to preserve the speciation. The traps were then wrapped in foil and refrigerated until shipped (in coolers with ice or blue ice) to the laboratory for analysis. The samples were stored in a refrigerator until the day of analysis.

DMM on Carbotrap™ adsorbers was analyzed by TD-GC-AFS (Bloom and Fitzgerald, 1988). The analytical system was calibrated by purging known amounts of DMM in methanol (MeOH) from DI water onto Carbotraps™ and then thermally desorbing them into the isothermal GC at 80 ± 2 °C. The output of the GC was passed through a pyrolytic cracking column at 700 °C to convert the organomercury compounds to Hg^0, since only atomic Hg is detected by CVAFS. DMM is identified by retention time and quantified by peak

height. Frontier Geosciences obtained good agreement between two separately calibrated sources of DMM, a liquid standard in MeOH (calibrated against total Hg in 1994 and again in 1999 with equivalent results) and a diffusion tube from VICI Metronics Inc. The results of DMM spikes are discussed below.

2.2.3. Monomethyl mercury (MMM) in LFG

MMM in air likely exists as a halide or hydroxide, compounds that are stable and soluble in 0.001 M HCl. The MMM sample train consisted of a 1/8″ Teflon line inserted into the LFG duct port with a series of three mini-impingers with 0.001 M HCl in double deionized water followed by a water dropout (trace-cleaned Teflon mini-impinger), a flow meter and vacuum pump. The sample line, impingers and dropout were shielded from light during sampling to prevent MMM being photolytically destroyed or DMM converted to MMM. The impingers were prepared and connections made at Frontier Geosciences clean facilities. Using the provided 1/8″ o.d. tubing, fittings, and clean gloves the impingers were connected to a flow control valve, mass flowmeter and pump. The flow rate was $0.8\,l\,min^{-1}$ for 20 min, which translates into a sample volume of about 16 l (1 atm and 70 °F). Again, because of the high fraction of methane present, the mass flow volume was correct by a factor of 0.71.

After sampling was complete, the contents of the impingers were combined into a single, trace-metals cleaned glass bottle for storage and shipment to Frontier Geosciences. The samples were kept dark and cold after sampling and during shipment to the laboratory. In the laboratory, additional concentrated HCl (low mercury) was added to the MMM samples to reach 0.4% by volume prior to the distillation step. The analysis method uses distillation, ethylation, Carbotrap preconcentration, thermal desorption, gas-chromatography separation, thermal conversion, and CVAFS detection (Bloom and Von der Geest, 1995). Dissolved MMM was analyzed in LFG condensates collected from wells by the same method described above for MMM in air.

3. Results and discussion

3.1. Hg trends in LFG from landfills in Florida

Our new measurements at operating landfills in six Counties in Florida support our earlier observations that LFG contains appreciable concentrations of gaseous mercury, some in methylated forms. Table 1 summarizes data from these landfills; TGM concentrations at five of the currently operating sites were comparable to those found in coal-fired utility flue gas, which are in the range of $\sim 0.5–10\,\mu g\,m^{-3}$ (e.g. Lindberg, 1980; mercury emission rates from utility boilers exceed those from LFG flares due to the larger gas flows involved). TGM varied widely, with concentrations at operating landfills in Palm Beach (in 2002) and Brevard County ($\sim 10–12\,\mu g\,m^{-3}$) significantly exceeding those at other sites, while concentrations at St. Lucie and Martin Counties were substantially lower ($\sim 200–800\,ng\,m^{-3}$), emphasizing the need to characterize a much larger number of landfills than previously reported.

In April 2002, we re-visited the Palm Beach and Martin County landfills originally sampled in 1997; TGM concentrations in LFG at Palm Beach had increased several-fold over the 5-year period (from $\sim 3000\,ng\,m^{-3}$ in 1997 to $> 10{,}000\,ng\,m^{-3}$ in 2002), while concentrations at Martin County in 2002 were $< 5\%$ of those measured in 1997 (Table 1). Many changes have occurred at both sites in this time (e.g. Martin County established an active LFG collection system to replace the open vent pipes we previously sampled). We found a consistent difference in TGM concentrations at closed vs. operating sites in Florida, with concentrations at the closed landfills much lower than those measured at operating sites, generally by an order of magnitude or more (Table 1). This is consistent with our first study (Lindberg and Price, 1999), and suggests that either the pool of "available" Hg^0 or the ability of Hg(II) to be reduced to Hg^0 in landfills decreases with time after burial.

Our most detailed data (Brevard County) showed that LFG exhibits a consistent level of TGM over the course of a day (Lindberg et al., 2001). Assuming similar behavior at other sites, and using on-site LFG flow data, we can roughly estimate the daily release of TGM via the LFG collection systems. LFG is directed either to flares or co-generation facilities at Brevard County (at a rate of $\sim 32{,}000\,m^3\,d^{-1}$), Volusia County ($\sim 85{,}000\,m^3\,d^{-1}$), Palm Beach ($\sim 48{,}000\,m^3\,d^{-1}$ in 2002), and Orange County ($\sim 141{,}000\,m^3\,d^{-1}$). These data yield an average atmospheric mercury release in LFG of $\sim 0.4\,g\,d^{-1}$ for these four sites, which is several times higher than the maximum of $\sim 0.05\,g\,d^{-1}$ we previously estimated for LFG at typical Florida landfills (Lindberg and Price, 1999).

Our new data indicate that DMM in LFG from all the Florida sites sampled exceeds *total* gaseous Hg in background air ($\sim 1.5\,ng\,m^{-3}$), at several sites by more than an order of magnitude ($\sim 6–80\,ng\,m^{-3}$, Table 1). Both MMM and DMM were identified in the LFG samples, but the primary species appears to be DMM which exhibited similar concentrations at four of the five sites still in operation (means $\sim 40–80\,ng\,m^{-3}$). MMM was also detected in LFG at all three landfills where it was sampled, but concentrations were more variable than DMM ($\sim 2–40\,ng\,m^{-3}$). These organic forms of Hg occur in ambient air at far lower concentrations ($< 0.01\,ng\,m^{-3}$ for DMM and $< 0.001\,ng\,m^{-3}$ for MMM in Seattle, Washington, Prestbo et al., 1996).

Table 1
Summary of Hg concentrations and speciation data measured in landfill gas and condensate collected upstream of landfill gas flair stations at several Florida sites (and dates sampled)

Landfill	Total gaseous Hg (TGM) (ng m^{-3})	Dimethyl Hg (DMM) (ng m^{-3})	Monomethyl Hg (MMM) (ng m^{-3})
Brevard County[a]	10,100±490	44±27	~8[a]
(November 1998)	(14)	(10)	(1)
Brevard County	11,500±560	77±14	39±8
(October 1999)	(6)	(6)	(5)
Orange County	1400±230	66±24	1.7±0.7
(October 1999)	(12)	(12)	(5)
Volusia County	6900±2000	63±3	25±3
(March 2001)	(4)	(3)	(4)
Palm Beach County	66±35	—	—
(closed 1990)	(6)		
(April and June 1997)[b]			
Palm Beach County	2600±56	—	—
(April and June 1997)[b]	(2)		
Palm Beach County	140±140, 28±6[c]	8.7±6.5	—
(closed 1990)	(3 & 4)	(5)	
(April 2002)			
Palm Beach County	10,700±910, 12,000±1300[c]	6.5±3.1	—
(April 2002)	(3 each)	(7)	
Martin County	760±730	—	—
(April 1997)[b]	(7)		
Martin County	10–38, 21[c]	4.5±2.4	—
(closed 1999)	(2 & 1)	(5)	
(April 2002)			
St. Lucie County	31±30, 61±25[c]	15±8	—
(closed 1978–1988)	(3 & 6)	(6)	
(April 2002)			
St. Lucie County	340±37, 170±82[c]	39±14	—
(April 2002)	(3 & 4)	(3)	

The landfills sampled were in current operation and receiving waste unless otherwise noted (e.g. "closed 19"). Values are mean±std. dev. Number of samples analyzed is shown as (*N*). *Note*: For ease of comparison with new data collected outside of Florida, we applied volume adjustment factors (described in Section 2) to account for the large fraction of methane present in the sampled LFG (see Table 2). This results in the values in Table 1 being larger than those we reported previously [a,b] for these same locations since those Hg concentrations were reported on an "as collected" basis. The mean difference between the adjusted and unadjusted values is ~40%.

[a]From Lindberg et al. (2001), MMM represents a single sample analyzed in a 7-h cold condensation trap operated upstream of the carbotraps.

[b]From Lindberg and Price (1999).

[c]The second set in each pair was analyzed in real-time with the Lumex (all other TGM samples collected on charcoal traps for later digestion, see text).

At the Brevard County site, DMM exhibited a trend of increasing concentrations over the day, although TGM remained quite stable (Lindberg et al., 2001). TGM varied by ~15% over 7 h, while DMM increased from a minimum of ~10 to a peak ~100 ng m^{-3} over 3 h. DMM averaged ~0.4% of TGM, but represented nearly 1% of TGM at its peak. This ratio is higher than that reported for ambient air (<0.3%). At the Orange County and Volusia County landfills, MMM and DMM constituted about 1–5% of TGM, and at Volusia all three species exhibited relatively stable concentrations throughout most of the working day (Fig. 1). However, it is clear from Table 1 that there is no simple, direct relationship between the concentrations of DMM and TGM in LFG across the sampled landfills, suggesting that it may not be the availability of inorganic Hg that controls or limits the generation of methylated Hg forms, but other factors.

Because of their volatility, fugitive emissions of methylated Hg compounds may also occur from the working face. In March 2001, DMM was detected in two of four samples of ambient air collected downwind of the Volusia County working face during our routine monitoring of Hg emissions from waste landfilling activities. Those two samples contained 10 and 56 pg m^{-3} DMM, while the remaining two samples were below the ~5 pg m^{-3} method detection limit (MDL). These results must be regarded as semi-quantitative at

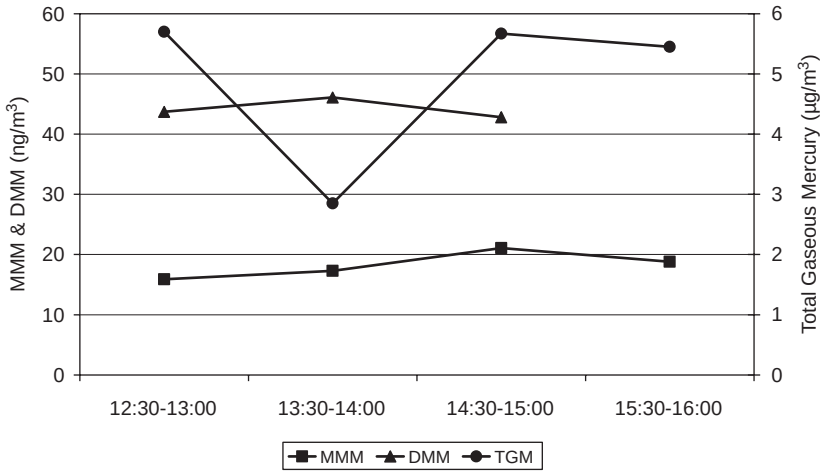

Fig. 1. TGM (see text), MMM and DMM measured in LFG over 1 day at the Volusia County landfill (March 2001, adjusted for the CH_4/CO_2 mixture sampled, see text).

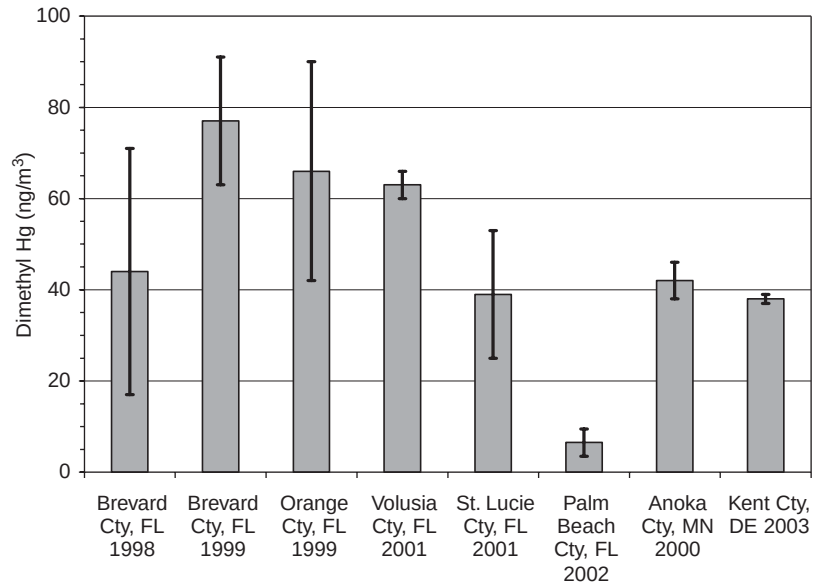

Fig. 2. Mean concentrations of DMM measured in LFG at currently operating municipal landfill sites in Florida, Minnesota, and Delaware (data represent the means $\pm$ SD of 3–12 samples collected over the course of 1–2 working days at each landfill; concentrations adjusted for the CH_4/CO_2 mixture sampled, see text).

best, but are consistent with the presence of high concentrations of DMM in LFG, and with the suggestion that methylated Hg compounds are being formed in landfills. Since emissions of inorganic Hg from the working face exceed those in LFG at several Florida landfills, often by an order of magnitude (Lindberg et al., in press), it is not surprising that DMM is emitted from the working face as well.

These observations led us to measure DMM in ambient air near other waste sites: a waste receiving bay at a RDF processing plant in Minnesota, and a waste receiving bay at the St. Lucie County landfill waste bailing facility. DMM concentrations in ambient air at these sites ranged from undetected at the waste bailing facility, to $\sim$20 pg m^{-3} near the waste receiving bay at the RDF facility. Better quantification of DMM in ambient air requires larger volume samples than the 30–1201 samples used in these exploratory studies (however, see discussion below regarding breakthrough problems). It remains to be seen whether fugitive-source emissions of organomercury compounds could be as significant as those vented in LFG.

3.2. Hg trends in LFG from Northern and Western sites

Since all of our measurements of Hg in LFG were performed in the subtropical climate of Florida, it is important to confirm these results elsewhere. Table 2 summarizes data from LFG sampled in Minnesota, Delaware, and California. Data from colleagues who sampled a landfill in Minnesota support the conclusions drawn from Florida sites, that LFG contains elevated concentrations of gaseous mercury, some in the methylated form. TGM concentrations at the Anoka County, Minnesota site on one winter day were comparable to those found in LFG from Florida (Table 1), falling in the range of ~7–10 $\mu g\,m^{-3}$. This closed landfill continued to generate gas at an average rate of ~35,000 $m^3\,d^{-1}$ in 2000, suggesting an average atmospheric mercury release in LFG of ~0.3 $g\,d^{-1}$, similar to the release rates from the Florida sites. The Anoka site was sampled for DMM 1 day later, also revealing concentrations similar to those seen in the Florida LFG, ranging from 37 to 46 $ng\,m^{-3}$, representing ~0.5% of TGM.

The results for total mercury at the Hamilton Landfill in Marin County, California and the CSWMC Kent County Landfill in Delaware (Table 2) were similar to the Minnesota and Florida data. The concentrations of DMM at the Kent County Landfill were also in the same range as those observed at both the Florida and Minnesota landfills (Fig. 2). For the Hamilton Landfill, however, the DMM concentrations were below the detection limits ($n = 2$). The analysis of the Hamilton Landfill DMM samples was under good control in the laboratory and the trip spike results were well within acceptable limits of 92% and 103% indicating that trap storage and trap quality did not results in DMM losses. The reason for the lack of detectable DMM at the Hamilton Landfill is uncertain, but is likely due to a combination of reasons, including (1) The landfill had been closed for 27 years and thus is expected to be past its peak in methane production, (2) the primary source of waste was commercial and demolition materials, not municipal waste, (3) it is shallow and saturated with water and (4) it has never had an active gas extraction system.

3.3. Tests of possible matrix interferences during collection and analysis of DMM in LFG

The methodology for the measurement of gas phase DMM in ambient air (Bloom and Fitzgerald, 1988) has undergone a recent and rigorous validation study (Bloom et al., in press). This same methodology was applied to LFG with slight modifications, namely much lower sample volume. However, in recognition of the complex nature of the LFG matrix we initiated additional experiments to further evaluate the accuracy of the methodology. Based on tests of the laboratory methods described above (using known standards and the highly selective techniques), we are confident that DMM is present at the $ng\,m^{-3}$ concentrations we report

Table 2
Summary of Hg concentrations and speciation data measured in landfill gas and condensate collected upstream of landfill gas flair stations at sites in Minnesota, Delaware, and California (and dates sampled)

Landfill	Total gaseous Hg (TGM) ($ng\,m^{-3}$)	Dimethyl Hg (DMM) ($ng\,m^{-3}$)	Monomethyl Hg (MMM) ($ng\,m^{-3}$)
Anoka County, MN (closed early 1990s) (March 2000)	8600 ± 1400 (4)	42 ± 4 (4)	—
CSWMC, Kent County, DE[a] (January 2003)	380–440 (2)	38 ± 0.74 (3)	1.3 ± 0.05 (3)
Hamilton Landfill, Marin County, CA (closed 1994) (August 2001)	4700 ± 3700[b] (7)	< 0.03[c] (2)	—

The landfills sampled were in current operation and receiving waste unless otherwise noted (e.g. "closed 19.."). Values are mean ± std. dev. Number of samples analyzed is shown as (*N*). Note that the sampled landfill gas volumes were adjusted to air to account for the large fractions of methane present (since our mass flow meters were calibrated for dry nitrogen, see Section 2).

[a]Central Solid Waste Management Center.

[b]Analyzed in real-time with the Lumex (all other TGM samples collected on charcoal traps for later digestion, see text); statistics based on final value achieved after Lumex reached steady-state concentration at each of seven sampling locations (sampling duration 10–30 mins).

[c]The estimated method detection limit was 0.027 ng/m^3 based on the minimum detectable peak height since the field blanks did not produce a observable chromatography peak.

in LFG. However, we believe that sample volume may influence the accuracy of the method; specifically, lower sample volumes appear to result in more accurate DMM concentrations as outlined below.

Excellent precision has been demonstrated in numerous field campaigns for DMM in LFG, often better than ±10% RPD (Tables 1 and 2) using a constant volume. To determine the influence of volume, we collected field spike samples during our recent LFG field campaigns. Field spikes are Carbotraps that have been spiked with DMM in the lab, sent to the field to collect a LFG sample in a normal manner and then returned to the lab for analysis. The field spike should have DMM present from the LFG sampled plus the known DMM spiked onto the trap. For certain samples, the results were poor, with low recoveries, indicating that the accuracy of the DMM concentrations is less certain than previously thought, based only on the trip spike and precision measurements (trip spikes are Carbotraps that have been spiked in the lab, sent to the field and returned to the lab for analysis unused). The trip spike results have been within acceptable limits throughout our studies (100±8%).

The low recovery of the field spikes suggested poor accuracy, possibly from a matrix interferent that was biasing the DMM results to the low side. As is often the case, smaller sample volume can minimize a matrix interferent. For the field campaign at the CSWMC landfill in Delaware we tested this hypothesis using variable sample volumes. The results in Table 3 support this hypothesis. DMM samples were collected simultaneously at two different volumes of 0.92 and 3.6 l. The 0.92-l samples yielded the highest DMM (by a factor of 2 over the 3.6-l samples), with good precision for both data sets (Table 3). The field spike recoveries also indicate that the lower the sample volume, the better is the recovery on the "A" trap, while the "B" trap recovery (spiked similarly) is good at all sample volumes. The observations of changing concentration and field spike recovery with increasing volume strongly suggest that some previously measured DMM concentrations may be biased low by a factor of 2 or more if only the "A" trap data were reported. Data from the Delaware campaign suggest that the efficiency of the Carbotrap is diminished during sampling, and that DMM is carried downstream from the "A" trap to the "B" trap. The data do not suggest that the DMM is decomposed to Hg^0, nor that a co-eluting compound is released to cause fluorescence quenching. The interferent remains unknown.

Another effort to ensure accuracy of the Carbotrap-based DMM data employed an alternative sampling method. We developed a MeOH impinger to capture DMM in LFG and analyzed the samples in the lab using a direct aqueous purge of small aliquots of the MeOH-based sample onto Carbotraps with analysis as described above; DMM is very soluble and stable in MeOH. The results of the DMM determinations using the MeOH impinger method are summarized in Table 3. The precision between the two DMM determinations by MeOH impinger is quite good (18.2% RPD). Also, the agreement between the two DMM methods is excellent when using the lowest Carbotrap volume results (1.3% RPD, Table 3). Hence, the quality assurance measurements for DMM indicate that the sampling and analysis system was under very good control. Replicate sample results with equal volume sizes agreed well (2.0% and 18.8% RSD), indicating that the properties of the DMM sampling train and LFG are consistent and that any bias is not likely to be due to the trap media or sample gas being out of nominal specifications. During analysis, continuous calibration verification (CCV) standards indicated that the detection system was not significantly biased. The very low DMM field blanks indicated that

Table 3
Summary of DMM concentrations, trip and field spike recoveries for the CSWMC Kent County Landfill in Delaware

Sample method	Sample volume (liters)	Dimethyl Hg (DMM) ($ng\,m^{-3}$)	Field spike recovery A-Trap, B-Trap	Trip spike recovery
Carbotrap™	0.0	—	—	91±3.6% (6)
Carbotrap™	0.92	38±0.74 (3)	42%, 92% (2, 3)	—
Carbotrap™	3.6	19±3.5 (3)	0%, 102% (1, 1)	—
Carbotrap™	7.1	na	0%, 96% (1, 1)	—
Methanol Impingers	11	35 and 42 (2)	—	—

Values are mean±std. dev. Number of samples analyzed is shown as (*N*). The results indicate that lower sample volume returns higher DMM concentrations as supported by excellent trip spike recoveries, but decreasing A-Trap field spike recoveries with increasing sample volume.

the trap media, handling procedures, and analytical technique did not contribute significantly to the reported values. Finally, trip spikes indicated that the laboratory standards, trap media, and trap handling techniques were quantitative and did not create a significant bias. We conclude that the most accurate DMM concentrations will be obtained by collecting the smallest sample volume possible, as we have strived to do here.

3.4. Summary and implications

Our data on total Hg in LFG in several landfills in Florida and Minnesota suggest an average atmospheric Hg release of ~300–400 mg d^{-1} in LFG, higher than our previous estimates of ~50 mg d^{-1} (Lindberg and Price, 1999). Based on the LFG flows noted above, the Brevard, Palm Beach, Volusia, Orange (all Florida), and Anoka County (Minnesota) landfills each generated methylated forms of Hg at rates in the order of 1–10 mg d^{-1}. Although the >1500 °F flares at these sites will ensure that only inorganic Hg is released to the air, the many landfills in the US and around the world which still generate raw LFG without flaring or treatment could be important sources of airborne organic Hg. However, it should be noted from our earlier studies that inorganic mercury fluxes from landfills are dominated not by LFG, but by releases during routine waste handling operations at the working face; direct emissions in LFG are typically <10% of the total Hg release from landfills. Our observations of DMM in ambient air downwind of the working face at Volusia County and in air near waste processing activities such as bailing and transfer, suggest that the methylated species may follow this same trend. Further investigations of landfills as sources of airborne methylmercury are encouraged.

Methylmercury is commonly reported in rain (Bloom and Watras, 1989; Munthe et al., 1995; St. Louis et al., 1995), and some have speculated that the source of methylmercury in coastal rain could be ocean upwelling of DMM (Prestbo et al., 1996; Mason and Sullivan, 1999; Pongratz and Heumann, 1998). However, this may not explain the methylmercury reported in rain from mid-continental sites. To date, waste-related emissions such as those from sewage–sludge-amended soils (Carpi et al., 1997) and LFG are the only measured emission sources of methylated mercury compounds to the atmosphere.

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