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Technical note

Methylated mercury species in municipal waste landfill gas sampled in Florida, USA¹

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Abstract

Mercury-bearing material has been placed in municipal landfills from a wide array of sources including fluorescent lights, batteries, electrical switches, thermometers, and general waste. Despite its known volatility, persistence, and toxicity in the environment, the fate of mercury in landfills has not been widely studied. The nature of landfills designed to reduce waste through generation of methane by anaerobic bacteria suggests the possibility that these systems might also serve as bioreactors for the production of methylated mercury compounds. The toxicity of such species mandates the need to determine if they are emitted in municipal landfill gas (LFG). In a previous study, we had measured levels of total gaseous mercury (TGM) in LFG in the $\mu\text{g}/\text{m}^3$ range in two Florida landfills, and elevated levels of monomethyl mercury (MMM) were identified in LFG condensate, suggesting the possible existence of gaseous organic Hg compounds in LFG. In the current study, we measured TGM, Hg^0 , and methylated mercury compounds directly in LFG from another Florida landfill. Again, TGM was in the $\mu\text{g}/\text{m}^3$ range, MMM was found in condensate, and this time we positively identified dimethyl mercury (DMM) in the LFG in the ng/m^3 range. These results identify landfills as a possible anthropogenic source of DMM emissions to air, and may help explain the reports of MMM in continental rainfall. Published by Elsevier Science Ltd.

1. Introduction

As a result of health and environmental concerns associated with elevated levels of mercury observed in the edible tissues of certain species of fish in many of Florida's fresh water bodies, the Florida Department of Environmental Protection (DEP) has been striving to quantify the sources of mercury and their cycling

between the atmosphere and aquatic ecosystems, especially the Everglades. Municipal incinerators are known to be important atmospheric Hg sources, but municipal landfills have not been widely studied. Mercury occurs in important quantities in municipal waste; prior to 1994, mercury levels in waste were estimated to be $\sim 4 \text{ mg}/\text{kg}$, with $> 80\%$ originating from alkaline batteries (EPA, 1992). In addition, inorganic Hg could be transformed into more toxic methylated forms under anaerobic conditions (Compeau and Bartha, 1985), which are common in landfills.

In cooperation with the Florida Department of Environmental Protection we quantified the primary sources of Hg vapor releases to the atmosphere at two municipal landfill operations in south Florida in April, 1997 (Lindberg and Price, 1999). The results of that

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study indicated the need to address several remaining issues including the source of Hg in working face (WF) emissions, the concentration and speciation of Hg in landfill gas, the potential for losses of Hg from MSW prior to land filling, and the overall role of fluorescent bulbs and other possible Hg sources. 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 mercury in the solid waste disposal process. An important goal was to confirm the existence of TGM at highly elevated levels ($\mu\text{g}/\text{m}^3$) in LFG, and in particular, to positively identify the existence and speciation of organic mercury in LFG at another landfill. This note reports results from a single day, including the first positive identification of DMM in municipal LFG in the US. Our follow up to this study, in which MMM, DMM, and TGM were sampled more extensively over one week in LFG at two landfills in central Florida, including a resampling at Brevard County, and a landfill in Minnesota will be described elsewhere (Wallschläger et al., in preparation). Our overall assessment of Hg emissions from all sources at the four Florida landfills we have now studied is being completed (Lindberg et al., in preparation).

2. Methods and site

The study described herein was conducted in November, 1998 at the Brevard County Central Disposal Facility (BC) near Orlando, FL. The BC landfill, an active Class I landfill located in central Brevard County, receives an average of over 900 m tonnes per day of waste. Landfill gas is collected from closed areas of the landfill and flared. In our first study (April, 1997), we collected a limited number of grab samples of LFG from landfills in Martin County (MC) and Palm Beach County (PB), in south FL. Complete Hg emission data from these studies is available elsewhere (Lindberg and Price 1999, Lindberg et al., in preparation).

At BC we expanded our sampling to include multiple replicate samples at two in-line vent ports upstream of the single flare which processed all LFG produced at this site, and extended our sampling to include the complete cycle of daytime operations (throughout the day on 17 November 1998). The LFG flares were sampled between the flame arrester and the open flame under a slight positive pressure via stainless steel ports. Total gaseous mercury ($\text{TGM} = \text{Hg}^0 + \text{HgII} + \text{Hg-organics}$) was collected on activated iodated charcoal traps and analyzed by acid digestion and cold vapor–atomic fluorescence spectrometry (CV–AFS) (Bloom et al., 1995). Samples were collected at flow rates of ~ 400 ml/min, with a backup trap to assess possible breakthrough. All traps were heated slightly above LFG temperatures ($\sim 50^\circ\text{C}$)

to eliminate condensation, and were also preceded by cold traps, since LFG is generally saturated with water vapor. In the earlier study at PB and MC we sampled TGM as above, and also with gold traps, operated in a similar fashion. Total LFG flow rates from all sampled flares at PB were provided by continuous recording flow meters, but only intermittent data were available elsewhere.

Besides using both gold and iodated charcoal traps for collecting TGM, the sampling at BC was also extended to specific methylated Hg species, using Carbotrap adsorbers for DMM and a cooled condensation trap (located upstream of the carbotraps) for MMM in LFG condensate. MMM in the LFG condensates (collected in the cold trap at BC, and collected from wells by local landfill personnel at PB) was analyzed by thermal desorption–gas chromatography–atomic fluorescence spectrometry (TD–GC–AFS) after isolating MMM from the matrix by distillation and conversion to methylethylmercury by aqueous phase ethylation (Bloom and Von der Geest, 1995). The gold traps were analyzed for TGM by cold vapor CVAFS at ORNL.

The method used to determine DMM in LFG is very sensitive and highly selective. More details of this method will be presented elsewhere (Wallschläger and Bloom, in preparation), but briefly, DMM was collected from the LFG behind condensate traps by pulling air through CarbotrapTM adsorbers ($\frac{40}{60}$ mesh, Supelco Inc., Bellefonte, PA) containing a 10 cm long by 0.4 cm diameter adsorbent bed, packed between silanized glass wool plugs in a silanized glass tube. Carbotrap has been found to have high adsorption capacity for DMM, while allowing the bulk of mercury, present as Hg^0 , to pass through (Bloom and Fitzgerald, 1988). In order to stabilize the DMM on the CarbotrapTM sorbent, the traps were immediately purged after sampling with dry nitrogen to remove residual water. DMM on CarbotrapTM adsorbers is analyzed by TD–GC–AFS. The analytical system is calibrated by purging exactly quantifiable amounts of DMM in methanol (1–500 pg) from deionized water onto CarbotrapsTM and then thermally desorbing (45 s at a 25°C to 450°C ramp) them directly into the isothermal GC (1 m \times 4 mm ID column of 15% OV-3 on Chromasorb WAW-DMCS 80/100 mesh) held at $80 \pm 2^\circ\text{C}$. The output of the GC is 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. There are no available certified reference materials (CRM) or second source standards for DMM to assess accuracy. However we have obtained good agreement between two separately calibrated sources of DMM, a liquid standard in methanol (calibrated against total Hg in 1994 and again in 1999 with equivalent results of

1.49 ng/ml) and a diffusion tube from VICI Metronics Inc. (1.961 ng/min at -0.5°C).

3. Results and discussion

During our earlier studies at PB and MC landfills in south Florida, we found highly elevated concentrations of TGM in some LFG samples (Lindberg and Price, 1999). TGM concentrations were highly variable and ranged from ~ 30 to 1840 ng/m^3 ; the average levels were somewhat higher at the larger PB landfill than at MC (means 630 ± 920 and $560 \pm 560\text{ ng/m}^3$, respectively). At these levels of inorganic Hg, the possibility of organic Hg formation was of immediate interest, given the reducing nature of LFG. In support of this hypothesis, MMM was positively identified in LFG condensate collected in wells at PB (range 21–23 ng/l, total $\text{Hg} = 4740 \pm 16\text{ ng/l}$), though MMM could have been formed in the wells after the water was removed from the LFG pipes. We have also observed that TGM concentrations measured with gold traps were consistently lower than those collected in parallel with charcoal traps, which prompted us to suspect the presence of volatile Hg species other than Hg^0 . Hence, because of our limited previous sampling, our major objective in the BC study was to identify any methylated Hg species present, as well as to confirm the existence of such elevated levels of TGM in LFG.

To demonstrate the positive identification of DMM in LFG at BC by TD–GC–AFS and to rule out some possible analytical artifacts, four chromatograms are presented in Fig. 1. The bottom chromatogram (a) shows no DMM signal, but a small signal for elemental Hg^0 , which is typical even for adsorber traps that have been thermally blanked prior to analysis. This signal probably stems from thermal reduction of inorganic Hg contained in the adsorbent material. The next chromatogram up from the bottom (b) was obtained for a DMM calibration standard (3.75 pg Hg). This chromatogram shows the same Hg^0 peak as the blank, proving that there is no decomposition of DMM to Hg^0 during the analysis of standards. The third chromatogram (c) was obtained by generating 125 pg Hg^0 via the CV technique (Bloom and Fitzgerald, 1988) and passing it over a Carbotrap adsorber. This trap was then analyzed by TD–GC–AFS, and no signal for DMM was observed, demonstrating that Hg^0 is not converted to DMM during the analysis of standards. Also, the obtained Hg^0 signal only corresponds to 4 pg Hg, or 3.2% of the total Hg^0 passed over the trap, showing the poor adsorption of Hg^0 on Carbotrap. Finally, the top chromatogram (d) shows the results obtained for one of the LFG samples. In addition to the DMM signal, a small Hg^0 signal above the material blank is also

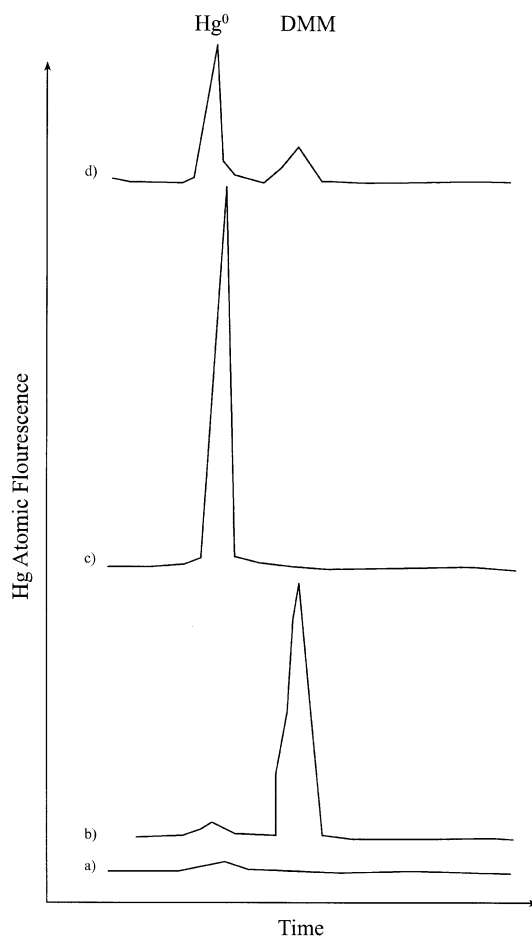


Fig. 1. Thermal desorption–gas chromatography–atomic fluorescence spectrometry (TD–GC–AFS) chromatograms of several sample types: (a) a trap blank, (b) a DMM standard, (c) a Hg^0 standard and (d) a LFG sample from Florida as described in the text.

obtained here, because the concentration of Hg^0 in the studied LFGs is two to three orders of magnitude higher than the DMM concentrations. These results clearly demonstrate that DMM is present in the studied LFG, and also prove that there is no species interconversion between Hg^0 and DMM during the analytical procedure. On the basis of the data presented here, it cannot be ruled out entirely that components of the LFG matrix are capable of methylating Hg^0 or demethylating DMM on the Carbotrap surface between sample collection and analysis. In order to study this question conclusively, one would have to generate an LFG stream containing no volatile Hg species and direct it over a trap pre-spiked with known quantities of Hg^0 or DMM, which is a very complicated (but planned) experiment beyond the scope of this note.

Table 1

Summary of Hg concentrations and speciation measured in landfill gas upstream of the Brevard County landfill flair station on 17 November 1998. Samples ranged from 5–30 min in duration, and were collected over a 7-h period (~1000–1700)

Hg species and sample type	Mean Hg (ng m^{-3})	SD Hg (ng m^{-3})
TGM (charcoal)	7190	330
TGM (backup trap)	4	4
Dimethyl mercury (DMM)	30	18
Ratio (DMM/TGM)	0.4%	0.3
Monomethyl mercury (MMM)	6	— ^a

^a $N = 1$ sample (MMM was analyzed in a single 7-h cold condensation trap operated upstream of the carbotraps, see text for derivation of gas-phase concentration).

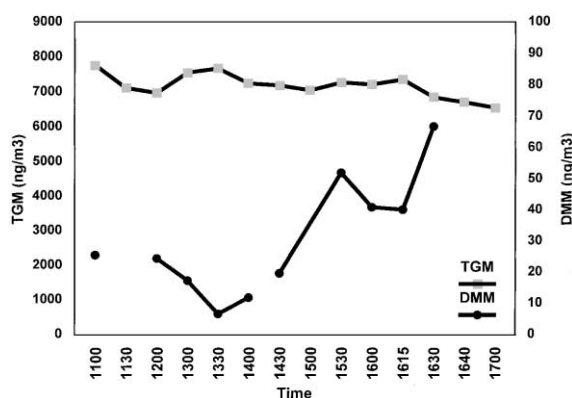


Fig. 2. Total gaseous mercury (TGM) and dimethyl mercury (DMM) measured over 1 day in landfill gas at the Brevard County landfill in Florida. Because of the unique nature of these samples there was only one opportunity for analysis for each trap; due to a varying instrument sensitivity over the period of analysis, we believe that several of the organic Hg results could be low by a factor of ~ 2 (D. Wallschläger, Pers. Comm.).

Our initial data from BC are summarized in Table 1, and show that concentrations of TGM in LFG are clearly in the $\mu\text{g}/\text{m}^3$ range. This is comparable to Hg levels in flue gas and the immediate downwind plume of coal-fired power plants, which are in the range of 1–10 $\mu\text{g}/\text{m}^3$ (e.g. Lindberg, 1980; Prestbo and Bloom, 1995). However, Hg emission rates from utility boilers will exceed those from LFG flares due to the larger gas flows involved (Lindberg and Price, 1999). The BC LFG showed a highly consistent level of TGM over the day (Fig. 2), and the mean concentration of TGM in LFG at this site ($\sim 7200 \pm 300 \text{ ng}/\text{m}^3$) significantly exceeded levels we measured at the MC and PB landfills.

Both DMM in the LFG and MMM in the condensate were identified in the LFG samples taken at BC. The primary species appears to be DMM which exhibited a

mean concentration of $\sim 30 \text{ ng}/\text{m}^3$ (Table 1). MMM was detected in the single LFG condensate sample we collected in a cold trap at a liquid concentration of 330 ng/l ($\sim 0.4 \text{ ml}$ of water was condensed from 381 of LFG). Using Henry's Law, the gas phase concentration was estimated to be $\sim 6 \text{ ng}/\text{m}^3$. The measured DMM and MMM concentrations are several orders of magnitude (> 1000 times) above values reported for these species in background air; e.g., ambient air in Seattle contained $3 \pm 4 \text{ pg}/\text{m}^3$ DMM and $7 \pm 4 \text{ pg}/\text{m}^3$ MMM, or $< 0.5\%$ of TGM (Prestbo et al., 1996). In fact, the DMM concentration in LFG exceeds TGM concentration in background air by more than an order of magnitude. While DMM has been previously identified in LFG and sewage gas (Feldmann and Hirner, 1995), the presence of MMM in LFG (although only identified indirectly in the LFG condensate) has not been previously reported.

Although only a limited number of samples were collected during one day, DMM exhibits a trend of increasing concentrations over the day, while TGM remained quite stable (Fig. 2). TGM varied by $\sim 15\%$ over 7 h, but DMM increased from a minimum of ~ 7 to a peak $\sim 70 \text{ ng}/\text{m}^3$ over 3 h. DMM averaged $\sim 0.4\%$ of TGM, and represented nearly 1% of TGM at its peak (these ratios are higher than those in ambient air measured in Seattle, see above). Unlike at our previously sampled sites where LFG flows were measured directly, there are only limited estimates of total LFG flows at the BC landfill, with rates between ~ 700 and $1300 \text{ m}^3/\text{h}$ having been determined at various times. Using this range, we estimate that the landfill flare releases TGM at a rate of $\sim 3\text{--}6 \text{ mg}/\text{h}$, compared to a maximum of $\sim 2 \text{ mg}/\text{h}$ measured at our other landfill sites (Lindberg and Price, 1999). In addition, we can now state that this landfill generates methylated forms of Hg at a rate of about 10–20 $\mu\text{g}/\text{h}$. The $> 800^\circ\text{C}$ flare will insure that only inorganic Hg is released to the air via the LFG at this particular site. However, any LFG that escapes the collection and flaring process (e.g. Galle et al., 2001) could be an important source of airborne organic Hg. Most landfills around the world generate raw LFG without flaring or other treatment (estimated to be $\sim 50\%$ in the U.S., S. Thorneloe, personal communication), and recent estimates place the global atmospheric emission of LFG at $\sim 40 \text{ Tg yr}^{-1}$ (as CH_4 , Houghton et al., 1996).

Monomethylmercury has been measured in rain from a number of continental sites (Bloom and Watras, 1989; Munthe et al., 1995; St. Louis et al., 1995). Some "natural" sources of methylated Hg in air have been suggested, including wetlands (Wallschläger et al., 1995). Others have speculated that the source of MMM in coastal rain might be oceanic upwelling of a DMM precursor (Mason and Fitzgerald, 1996; Prestbo et al., 1996). However, the upwelling hypothesis has

never been tested, and there are no other known emission sources for the MMM measured in rain from inland continental sites. To our knowledge, sources associated with municipal waste, such as MMM emissions from sludge-amended soils (Carpi et al., 1997) and DMM in LFG (this study) are the only measured anthropogenic emission sources of methylated mercury compounds from terrestrial systems to the mid-continental troposphere.

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