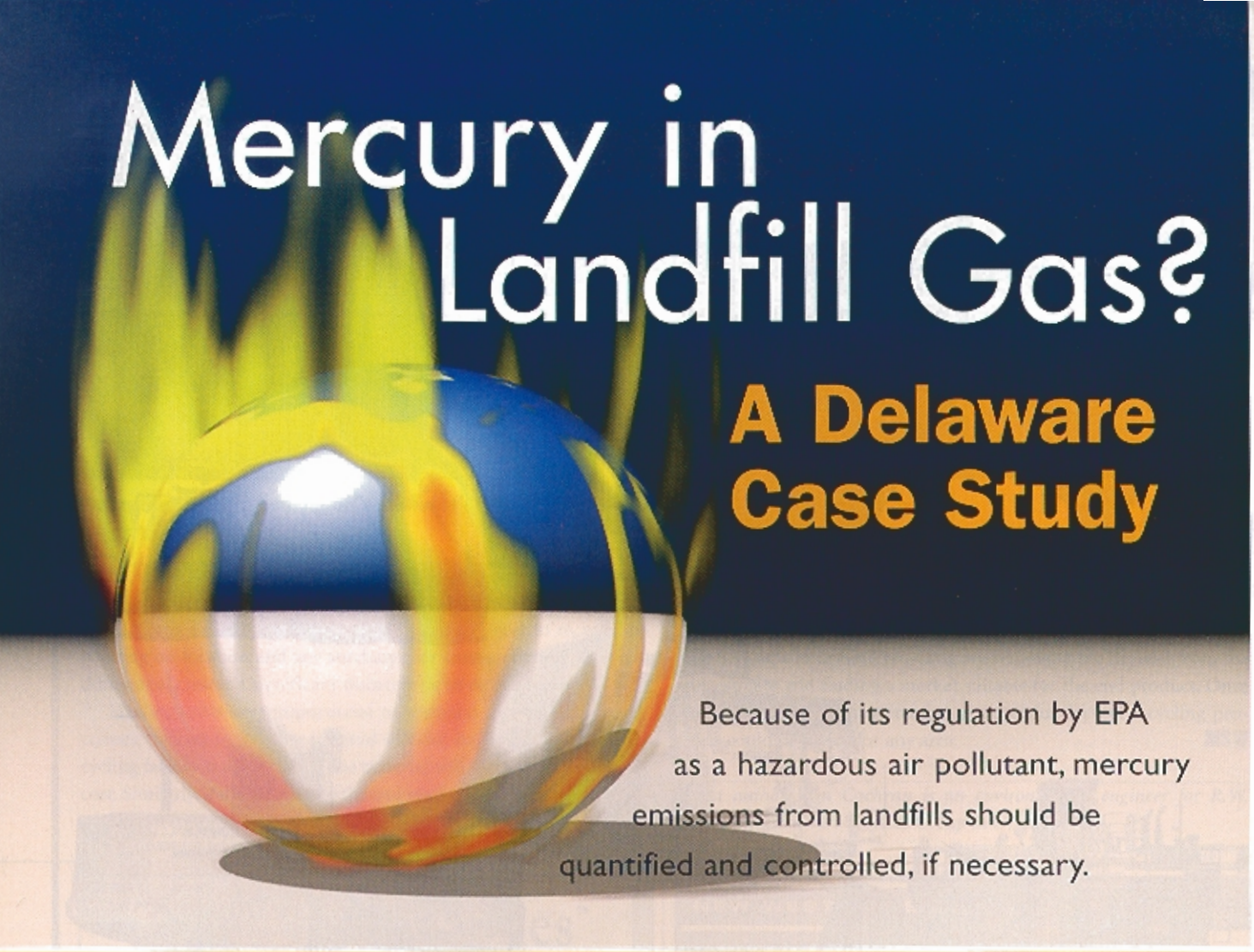
Mercury in Landfill Gas?

A Delaware Case Study



Because of its regulation by EPA as a hazardous air pollutant, mercury emissions from landfills should be quantified and controlled, if necessary.

By N.C. Vasuki, Drew Sammons, Joshua Roth, and Eric Prestbo

Mercury is a highly toxic heavy metal that exists primarily in three forms: elemental mercury, inorganic mercury compounds (e.g., mercuric chloride), and organic mercury compounds (e.g., methyl and dimethyl mercury). People are most likely to be exposed to mercury through the consumption of fish or seafood. Mercury is most likely to be present in fish tissue as methyl mercury, which happens to be the most toxic form of mercury to humans. However, concern over air emissions is not limited to methyl mercury because other forms of mercury can be converted to methyl mercury in the environment through methylation.

In the initial development of emissions factors for constituents of landfill gas (LFG), the United States Environmental Protection Agency published a default total mercury concentration in AP-42 equivalent to 292 parts per trillion (ppt), with no data on individual mercury species. At this concentration, mercury emissions from landfills are extremely low, if not negligible.

In the late 1990s, however, a study conducted by Lindberg et al. at a landfill in Florida suggested that levels of total mercury in LFG might be several times higher than EPA default values, though still much lower than other common landfill trace constituents. This study was also perhaps the first to positively identify the more toxic organic mercury compounds methyl and dimethyl mercury in LFG.

Upon review of the Florida data, the Delaware Solid Waste Authority (DSWA) initiated a study at its Central Solid Waste Management Center (CSWMC) to assess the levels of total, monomethyl, and dimethyl mercury in its LFG stream. The DSWA contracted with Frontier Geosciences Inc. (FGS), the same laboratory used in the Lindberg study, for sample collection and analyses.

The CSWMC is an active MSW landfill in Sandtown, DE, with a total of about 2.5 million tons in place and an acceptance rate of 120,000 tpy. LFG is collected from closed areas of the landfill, with expansion into the active cell by summer of 2003, and combusted in a candlestick flare. Current LFG flows are approximately 750 cubic feet per minute (cfm). SCS Engineers had previously conducted LFG sampling and analyses for other constituents such as methane, hydrogen sulfide, nonmethane organic compounds, and siloxanes. These results have shown the LFG composition to be typical for an MSW landfill.

Sampling Methodology and Analyses

Sampling was conducted in January 2003, with all samples taken from the main gas header pipe to provide a representative composite LFG sample.

Total Mercury

Sampling for total mercury was conducted by passing the LFG through a heated iodated carbon trap, which collects all gas phase and airborne particulate mercury species. The traps then were returned to the laboratory, where the mercury was leached from the carbon and

further oxidized. Analysis was then performed using cold vapor atomic fluorescence spectroscopy (CVAFS) according to FGS Method 069.2, which served as the basis for EPA Method 1631.

Monomethyl Mercury

Monomethyl mercury sampling was conducted by drawing LFG through a series of impingers containing a solution of hydrochloric acid. The sampling train was shielded from sunlight due to the potential for photoelectric degradation of the monomethyl mercury. After sampling, the solutions were refrigerated and delivered to the laboratory. The concentration of monomethyl mercury was determined following FGS Method 70.1 using thermal desorption, separation by gas chromatography, and CVAFS.

Dimethyl Mercury

Sampling of dimethyl mercury was conducted by drawing LFG through a trap containing an adsorbent bed of Carbotrap packed between silanized glass wool plugs within a glass tube. Carbotrap has been found to have a high adsorption capacity for dimethyl mercury while allowing the bulk of mercury, generally in the elemental form, to pass through. The sampling train for dimethyl mercury was also shielded from sunlight to prevent photoelectric degradation of the sample, and the samples were refrigerated until the day of analysis.

For this study, FGS tested the hypothesis that smaller sample volumes would result in higher dimethyl mercury concentrations and better recovery (accuracy). Previous dimethyl mercury studies have shown low recoveries from field spikes, which appeared to be the result of a matrix interferent that would bias the results low. Therefore samples were taken at two volumes: 0.92 and 3.6 lit. The dimethyl mercury concentration was determined using thermal desorption, separation by gas chromatography, and CVAFS.

FGS also attempted an alternative sampling method to evaluate the accuracy of the Carbotrap sampling method. The alternative method used methanol impingers, as dimethyl mercury is highly soluble and stable in methanol. Analyses were performed as previously described.

Results and Discussion

The table below presents a summary of the results of the DSWA laboratory analyses.

Summary of Total and Organic Mercury Species Results

Species		Avg. Concentration (ppt)
Total mercury		50
Monomethyl mercury		0.20
Dimethyl mercury	0.92-lit. sample	4.05
	3.6-lit. sample	2.00
	Methanol impinger	4.10

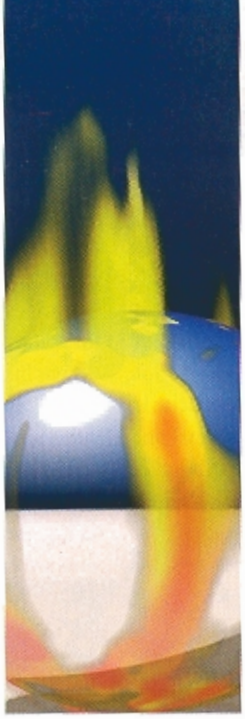
The results of the dimethyl mercury analyses support the FGS hypothesis that smaller sample volumes result in better sample recovery. Furthermore, the precision between these results and the results of the

alternative methanol impinger sampling method was excellent, with 1.3% deviation. Therefore it can be concluded that the more accurate dimethyl mercury concentrations are those with the smaller sample volumes of 0.92 lit., yielding a dimethyl mercury concentration at CSWMC of 4.1 ppt. This is consistent with the dimethyl mercury result of the previous Florida investigation of 3.2 ppt (Lindberg et al.).

The concentrations of total mercury measured at CSWMC were lower than both the AP-42 published value of 292 ppt and the concentration previously reported by Lindberg et al. (875 ppt). The concentrations of monomethyl mercury measured were slightly lower than those reported by Lindberg et al. (0.7 ppt).

Using these results, at an estimated LFG generation rate of 1,000 cfm, the annual emission of total mercury from the CSWMC would be about 0.01 lb./yr. Assuming a total of 5,000 landfills across the US at similar LFG generation rates, this translates to a nationwide annual emission of about 50 lb.

In 1994-95, EPA performed an inventory of estimated mercury emissions from various anthropogenic sources across the US. At that time, the estimated national annual air emission of mercury was about 160 tons. The majority (138 tons) was from combustion sources, such as coal-fired power plants, municipal waste incinerators, and medical waste incinerators. Landfill emissions were estimated to be less than 0.1 ton. The results of the DSWA study suggest that landfill mercury emissions are indeed a small fraction of total annual mercury emissions.



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