Determination of Total and Dimethyl Mercury in Raw Landfill Gas with Site Screening for Elemental Mercury at Eight Washington State Landfills for the Washington State Department of Ecology

For

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INTRODUCTION

Elemental mercury and mercury containing species have been identified as important compounds to monitor as they have been classified as persistent bioaccumulative toxins (PBTs). In an effort to reduce human exposure to PBTs in the environment, the state of Washington has targeted mercury as the first compound to be studied under the state's PBT initiative. As part of the effort to understand and quantify anthropogenic sources of mercury, the Washington State Department of Ecology proposed a study of mercury emissions in a variety of the state's landfills. In May and June of 2003, a sampling campaign was conducted at eight landfill sites. Frontier Geosciences prepared the equipment, traveled to the site, collected landfill gas samples and analyzed the samples in the laboratory for total and dimethyl mercury (THg and DMHg). In addition, on-site screening of elemental mercury emissions was performed at each site using field instrumentation. Frontier Geosciences collected an additional 11 DMHg samples for the purposes of method development and evaluation. These additional DMHg results are reported here as well.

METHODS AND SAMPLING DESCRIPTION

Dimethyl Mercury in Landfill Gas (DMHg)

The method used to determine DMHg in the atmosphere is very sensitive and highly selective (Bloom and Fitzgerald, 1988; Carpi et al., 1997; Bloom, 1999 and Lindberg et al., 2001). Appendix B contains the introductory sections of Frontier's current SOP on DMHg in environmental media. Briefly, DMHg was collected by pulling landfill gas through a trap containing a 10 cm long by 0.4 cm diameter adsorbent bed of Carbotrap™ (40/60 mesh, Supelco Inc., Bellefonte, PA) packed between silanized glass wool plugs in a silanized glass tube. Carbotrap™ has been found to have high adsorption capacity for DMHg, while allowing the bulk of mercury, which is generally in the elemental form, to pass through (Bloom and Fitzgerald, 1988). The DMHg content of the Carbotraps™ was determined by thermal-desorption, gas-chromatography, and cold vapor atomic fluorescence spectroscopy (TD –GC-CVAFS). The analytical system was calibrated by purging precise quantities of DMHg in methanol (20 –730 pg) from deionized water onto Carbotraps™ and then thermally desorbing (30 seconds at a 25 to 450 ºC ramp) them directly into the isothermal GC (1 m X 4 mm ID column of 15%OV-3 on Chromasorb WAW-DMCS 80/100 mesh) held at 80 ºC. The output of the GC was passed

through a pyrolytic cracking column held at 700 ºC to convert the organomercury compounds to elemental form. DMHg was identified by retention time and quantified by peak height.

There are no available certified reference materials (CRM) or second source standards for DMHg to assess accuracy. However we have obtained good agreement between two separately calibrated sources of DMHg; the first is a liquid standard in methanol (calibrated against total Hg in 1994 and again in 1999 with equivalent results of 1.49 ng/mL). An additional second source DMHg methanol solution was obtained from a colleague with a concentration of 1.0 ng/mL and was utilized when it became available. Other QA included a 5-point calibration curve, method blanks, continuing calibration verification, continuing calibration blanks, field blanks, trip spikes, field spikes, and matrix spikes.

For each sampling site, the DMHg sample train consisted of a new 1/8" Teflon line inserted into the landfill gas duct port, a water dropout (trace-cleaned glass mini-impinger with a Teflon lined cap) in an ice-water-salt bath, the Carbotrap adsorber, and fixed volume hand pump. The Teflon sample line, water-dropout and Carbotrap were shielded from light during sampling due the potential for DMHg to be photolytically destroyed. A short guard column (as described in SOP FGS-098, OV-3 on Chromasorb WAW-DMCS 80/100 mesh) was also added based on the supposition that it may selectively prevent some higher molecular weight semi-volatile organics (if present) from reaching the Carbotrap. The nominal flow rate was approximately 0.100 liters/min. Since a fixed volume pump was used to determine volume, there was no need to make volume corrections. The traps were then wrapped in foil and kept refrigerated until they were returned (in coolers with ice or blue ice) to the laboratory for analysis. The samples were stored in a refrigerator until the day of analysis.

Total Mercury in Landfill Gas (THg)

The method for total mercury is described in Lindberg et al., 2001 and FGS SOP-009 and SOP-069. This method collects all gas-phase and particulate atmospheric Hg species by trapping on an iodated carbon matrix. Landfill gas is quantitatively metered through a heated iodated carbon trap using a mass flowmeter pump system. The traps are returned to the lab where the iodated carbon is leached of 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 is analyzed using the FGS-069

CVAFS total Hg analysis method (which served as the basis for EPA Method 1631, developed, authored, and validated by Frontier Geosciences).

For each sampling site, the total mercury sample train consisted of a short length of clean ¼" Teflon tubing inserted into the fluegas duct, followed by the iodated carbon trap inserted into a heated probe held at ~ 20 ºF above the temperature of the landfill gas, a silica gel water trap, flow meter and pump. Both before and after sampling the entire system is checked for leaks. The sample flowrate was nominally 0.5 liters/minute generating sample volumes of approximately 30 liters (1 atm and 70 ºF). The volume was corrected by a factor of 0.71 to take in to account the high fraction of methane present. There were no special storage conditions required for the iodated carbon traps other than to keep them out of any atmosphere with highly elevated Hg.

Elemental Mercury (Hg^0)

The Lumex RA915+ method is ideally suited to quantify and screen landfills for elemental mercury. This instrument has been used to quantify Hg^0 in indoor air for the US EPA and also for Hg^0 emission estimates from industrial flue gases.

The Lumex RA-915+ mercury analyzer is based on atomic absorption spectrometry at the 253.7 nm wavelength absorbed by elemental mercury atoms. The Lumex achieves a low detection limit of 2 ng/m^3 by using a multi-path absorption cell with an effective path of approximately 10 meters. Selectivity is achieved primarily by using the Zeeman effect using high frequency modulation of light polarization (ZAAS-HFM). Briefly, the radiation source, a glow discharge mercury lamp, is placed in a permanent magnetic field, whereby the 253.7-nm mercury resonance line is split into three polarized components, π, s+ and s-. The polarized light source is further manipulated by passing it through a polarization modulator at 50 kHz so that each component of the signal can be separated in time. Additional selectivity is achieved by using narrow-band high-reflectivity mirrors to help isolate the 253.7-nm resonance light by suppressing all the non-resonance and stray radiation. Only two components of the original light source, the circularly polarized s+ and s- are detected for quantification. When the polarized light radiation is observed along the magnetic field lines, only the s-component's light radiation is registered, one s-component being settled under the absorption line envelop and the other one being settled outside it (Figure 2). Thus in the absence of mercury vapor in the absorption cell, the intensity of the s+ and s- light will be equal. When elemental mercury atoms are present in the absorption cell, the

greater the mercury concentration, the greater will be the difference in the s+ and s- light as detected by the photo-detector. Because the spectral shift of the s-components is significantly smaller than the width of any molecular absorption bands or scattering spectra, the background absorption caused by interfering components does not affect the analyzer measurement of mercury concentration. Thus in this measurement technique, the analytical signal depends only on the mercury concentration and is independent of the presence of dust, aerosols, and other foreign contaminants in the analytical cell. See figure 1 for a schematic representation of the instrument.

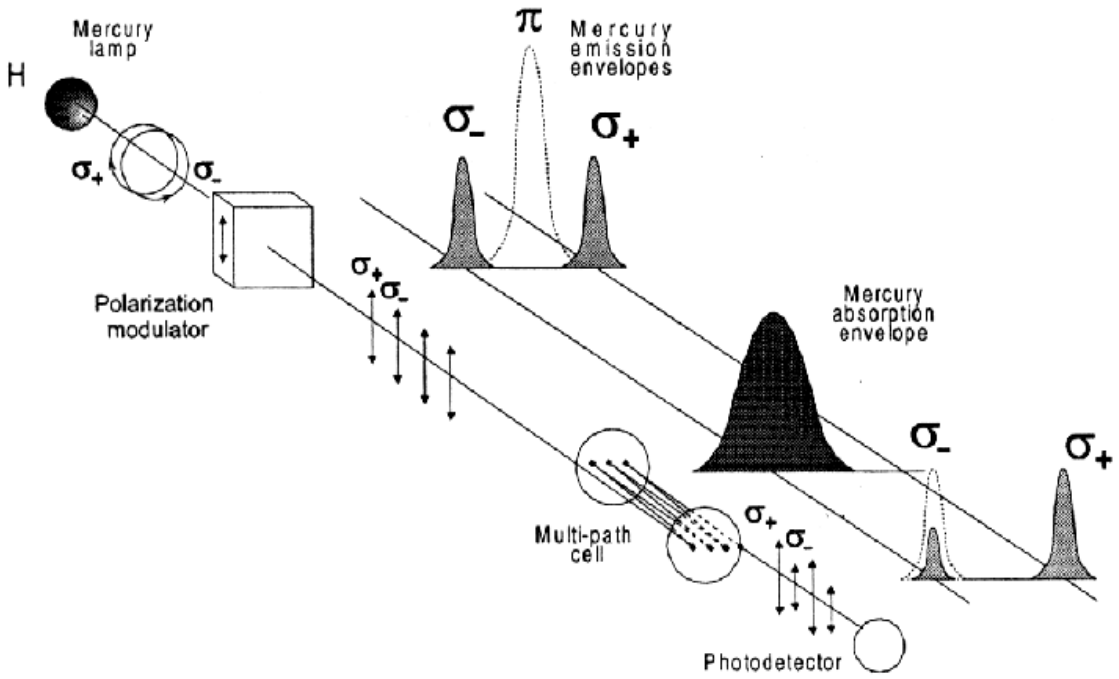

Figure 1: Schematic of Zeeman effect used to detect elemental mercury by the Lumex

SITE DESCRIPTIONS

***** In an effort to maintain confidentiality, site descriptions have been composed in a manner to maintain site anonymity *****

Landfill Site #1:

Two distinct gas streams were present, originating from different areas of the landfill. One gas stream sent to an energy generation facility had a methane content of 36.9%, carbon dioxide content of 30.2% with a flow of 440 scfm. A second gas stream sent to a flare was composed of 25% methane, 23% carbon dioxide, with an average flow of 688 scfm. Samples were collected from both gas steams in order to get a more complete estimate of mercury speciation at the site.

Although it is desirable to collect on the pressure side of gas lines, gas was collected on the vacuum side of the energy gas stream just prior to the compressor. The compressor increased the pipe pressure above the tolerances of our sampling system. The flare gas was collected on the pressure side of the line just after the blower.

For total mercury, duplicate samples were collected at each site for a total of four samples rather than anticipated triplicate samples. From our experience, total mercury sampling is a rigorous method and sample duplicates should provide acceptable reproducibility at both sampling locations. This would thereby allow accurate characterizations of each gas stream without the collection of double the number of samples. Samples were collected with a electric portable flometer unit (PFU) with volumes of 20 L and 30 L were collected from each gas steam.

Dimethyl mercury is more sensitive to matrix effects. Therefore, three samples were collected at the flare gas stream, in addition to the trip spike, field spike and matrix spike. Two flare gas samples were collected at 300 mL and one at 500 mL to help access matrix effects using a fixed volume hand pump. Two additional samples were collected from the energy gas stream: one 300 mL sample was collected using the hand pump and another 1000 mL sample was collected using the PFU.

For elemental mercury screening, numerous spot checks as well as transects of the landfill were performed. The largest single source of elemental mercury on site was associated with the open waste were near-downwind concentrations were observed in the 100 ng/m3 range. Up wind concentrations at the site were low as expected, averaging 2 ng/m3. It should be noted that measurements around the open waste tended fluctuate as a result of a light breeze and the mixing of low-mercury ambient air.

Landfill Site #2:

All gas from this site was combined into one pipeline. Gas content on the day of collection consisted of 32% methane with a flow rate of 703 scfm. All samples were collected on the pressure side of the pipeline just before the flare and after all gas control technology such as water dropouts. For total mercury analysis, three replicates were collected with the PFU using a volume of 30 L. Three dimethyl mercury samples were collected with a hand pump using a volume of 500 mL. To test the ruggedness of the Carbotraps, a fourth sample was collected on a previously used trap. Field QC consisting of a trip spike, field spike, and matrix spike were also

collected. Elemental mercury was performed by taking several transects through the landfill as well as spot checks at various points of interest.

Landfill Site #3:

There was no active or passive control technology for this landfill so gas was collected at in a leachate well where the highest concentrations of methane had been detected. No recent readings for the methane values were available, so an average of last years concentration were used as an approximation and resulted in a value of 3.11%. In addition, no flow rates were available, as the leachate well was open to the atmosphere. Three total mercury samples were collected using the PFU, two at a volume of 30 L and another at 50 L. For dimethyl mercury, three samples were collected with the hand pump using a volume of 600 mL. The field QC collected for dimethyl mercury was a field blank, field spike and matrix spike. Screening for elemental mercury was accomplished by taking several transects through the covered landfill area and open working face, as well as spot checks at various points of interest.

Landfill Site #4:

At this site, gas samples were collected from a passive well that was open up to the ambient air. As there was no way to completely seal up the wellhead during collection, it is highly likely that ambient air was pulled into the well during sample collection. This would result in the values reported for this site being biased low. As all wells on site were passive, there was no flow of methane content data readily available. Three samples were collected for total mercury using the PFU at volumes of 30 L, 30 L and 94 L. Three samples were collected for dimethyl mercury using a hand pump at volumes of 1000 mL, 1000 mL and 1200 mL. Elemental mercury screening for this landfill was performed by taking transects around the perimeter and center of the landfill as well as making spot measurements of points of interest and exposed trash piles that was located on site.

Landfill Site #5:

All gas from this site is collected into a single pipe and sent to a flare facility. Gas samples were collected on the pressure side of the gas lines between the blower and flare. No daily flow or methane concentrations were available on site, however monthly data was provided. From the available 2003 data, the average methane content was 48% and carbon dioxide was 48.9% with an average flow of 409 scfm. Total mercury samples were collected using the PFU at volumes of 30 L, 30 L and 51 L. Three dimethyl mercury samples were collected with a hand pump with

collection volumes of 1000 mL. As part of continuing method research, an additional 1000 mL sample was collected to determine if direct injection of the samples was possible and another 1000mL sample was collected without the guard column in place to determine the response difference as compared to samples collected with the guard column in place. In addition, one last 5000 mL dimethyl sample was collected using the PFU. Screening for elemental mercury performed by making perimeter sweeps as well as transects across the closed and open areas of the landfill in addition to various points of interest.

Landfill Site #6:

Gas at this landfill is sent to both a flare and to an energy generation facility. The gas origination from each line is distinct, however the flare gas is augmented with the richer energy generation gas. The rich methane content is ~50% CH4 and 33.4% CO2 with a flow of 475 scfm, and the flare gas was 29.2% CH4 and 27.5% CO2 with flow of 470 scfm. Samples were collected from the richer content energy generation gas stream at a pipe header on the vacuum side of the line, prior to any gas control systems such as water dropouts. Three total mercury samples were collected at this point using the PFU at volumes of 30 L, 31 L, and 50 L. Three 1 L dimethyl mercury samples were also collected at this point using the hand pump. An additional 1L sample was collected to further investigate direct injection of the sample to the analytical instrument and a large 5 L sample was collected with the PFU to study matrix effects. Field QC collected at this site consisted of a field blank, trip spike and matrix spike.

A second set of samples was collected from the flare gas stream at a point just prior to the flare. One 30 L total mercury sample was collected with the PFU and a 1 L dimethyl mercury sample was collected with a hand pump. Screening for elemental Hg at this site was determined by performing perimeter sweeps of the area as and transects across the middle in addition to spot checks of points of interest.

Landfill Site #7:

Gas at this landfill is combined into one gas stream sent to an energy generation facility that consisted of 55% methane, 37% carbon dioxide, and 1.8% oxygen with an average flow of 900 scfm. All samples were collected from the vacuum side of the combined gas line, at a point prior to the blowers and all gas control technology. In order to reduce the vacuum in the gas line to a workable level, one of the engines was powered down allowing the power plant to scale back the gas demand. Three total mercury samples were collected with the PFU, all at a volume of 30 L.

Three dimethyl mercury sample were collected at a volume of 500 mL and one at 1000 mL using the hand pump. Dimethyl field QC collected for this site was a field blank, a matrix spike with 500 mL gas, and a matrix spike with 1000 mL of gas collected on the trap. Screening for elemental Hg at this site was determined by performing perimeter sweeps of the area as and transects across the middle in addition to spot checks of points of interest.

Landfill Site #8:

Gas at this landfill is combined into one gas stream sent to an energy generation facility. Average gas parameters for this site are approximately 57.5% methane and 38.5% CO2 with an average flow of 2850 scfm. Samples were collected from a combined gas pipeline between the energy generation facility and the blowers and control technology. Three total mercury samples were collected with the PFU at volumes of 30, 31, and 50 L. Three dimethyl mercury samples were collected under normal operating parameters at using the hand pump at volumes of 500 mL, 500 mL and 300 mL. A 500 mL sample was collected without the guard column to help access the benefit of having the guard in place. Field QC collected at the site was a field blank, field spike and three matrix spikes. The matrix spikes were collected at volumes of 1000 mL, 500 mL, and 300 to help determine how increasing gas volumes affect spike recoveries. Screen for elemental mercury was performed at the site by taking perimeter sweeps across the landfill as well as transects through the center. Screening was also performed at the active working face of and at various point of interest.

RESULTS

***** In an effort to maintain confidentiality, sample ID's have been edited to maintain site anonymity *****

The combined results are presented in table 1 below. In addition to total mercury and dimethyl mercury, gas parameters have also been provided. It should be noted that the gas parameters presented in table one are readings during the day of collection. In order to calculate yearly emission, flow data should be gathered and averaged for the entire year. The gathering of yearly averages is beyond the scope of this project. It should also be noted that the mercury measurements made in this study represent only one point in time. In order to have a more accurate estimate of speciation and overall emission rates, additional extended studies should be performed to understand how speciation and emission rates vary with seasonal, day to night, as well as under changing atmospheric conditions.

Atmospheric data has been presented in Appendix A and consists of temperature and dew point, relative humidity, and barometric pressure. This data was gathered from the web (http://www-k12.atmos.washington.edu/k12/grayskies/nw_weather.html) and was downloaded from nearby regional weather station and was not gathered at the point of sample collection. The atmospheric data has been presented only as a general gage of the changing atmospheric conditions during the hours that samples were collected.

Table 1
Combined Results in Landfill Gas for WA Dept. of Ecology

Sample ID	THg (ng/m^3)	DMHg (ng/m^3)	DMHg % of Total	CH_4 Content (%)	CO_2 Content (%)	Average Flow (scfm)	Comments
Site #1 A	16.5	9.5	57.6%	25.0	23.0	688	Flare Stream
Site #1 B	73.8	27.7	37.5%	36.9	30.2	440	Energy Stream
Site #2	1175.6	10.5	0.9%	32.0	20.0	703	
Site #3	-6.7	0.8	-11.6%	3.1	-	-	No CO^2 or Flow available
Site #4	-14.9	1.0	-6.4%	-	-	-	No gas parameters available
Site #5	94.4	7.1	7.5%	48.0	48.9	409	
Site #6 A	334.5	23.2	6.9%	50.0	33.4	475	Energy Stream
Site #6 B	126.9	26.4	20.8%	29.2	27.5	470	Flare Stream
Site #7	8011.9	46.1	0.6%	55.0	37.0	900	
Site #8	252.6	28.8	11.4%	57.5	38.5	2850	

Total Mercury (THg)

The combined total mercury (THg) results from all 8 Washington landfill sites have been presented in table 2 below. B-Trap results indicate that all traps performed exceptionally no sample breakthrough was observed. In all cases where sample concentrations were above 3X the detection limit, field triplicates demonstrated acceptable reproducibility. As all THg samples were collected using a mass flowmeter that has been calibrated to nitrogen, all gas volumes have been corrected based on the major constituents present in landfill gas. By multiplying the constituent percentages by the manufacturer-supplied conversion factors, the true gas volume can be calculated. The conversion factor for methane is 0.7175, carbon dioxide is 0.7382, and the balance gas consisting of both oxygen and nitrogen is 1.0. Therefore, the conversion factor for Site 8 would be: = volume*(0.575*0.7175+0.585*0.7382+0.04*1).

Table 2
Total Mercury (THg) in Landfill Gas for WA Dept. of Ecology
by Iodated Carbon and CVAFS Analysis

Sample ID	Location	A -Trap (ng/trap)	B -Trap (ng/trap)	Net Hg ng/sample	Gas Vol. (liter)	Adjusted Vol. (liter)	THg (ng/m^3)	Quality Assurance Values or Comments
Site1-STM1	Pre-Flare	1.325	-	0.62	31.0	26.9	23.0	Average = 14.4 ng/m^3 (RPD = 80.0%)
Site1-STM2	Pre-Flare	0.878	0.744	0.17	20.0	17.4	10.0	Difference w/in 3X reporting limit
Site1-STM3	Pre-Energy	2.218	0.685	1.51	30.0	24.3	62.3	Average = 59.8 ng/m3 (RPD = 31.0%)
Site1-STM4	Pre-Energy	2.084	-	1.38	20.0	16.2	85.2	Difference w/in 3X reporting limit
Site2-STM1	Pre-Flare	36.17	-	35.47	30.0	25.7	1182	
Site2-STM2	Pre-Flare	35.58	-	34.88	30.0	25.7	1163	Average = 1176 ng/m^3 (RSD = 1.0%)
Site2-STM3	Pre-Flare	36.17	-	35.47	30.0	25.7	1182	
Site3-STM1	Leach Well	0.581	-	-0.12	51.0	-	-2.4	
Site3-STM2	Leach Well	0.447	-	-0.26	30.0	-	-8.6	Average = -6.7 ng/m^3 (RSD = 55.4%)
Site3-STM3	Leach Well	0.432	0.506	-0.27	30.0	-	-9.1	Values below limit of detection
Site4-STM1	Passive Well	0.208	0.443	-0.50	30.0	-	-16.5	
Site4-STM2	Passive Well	0.046	-	-0.66	30.0	-	-21.9	Average = -14.9 ng/m^3 (RSD = 53.6%)
Site4-STM3	Passive Well	0.120	-	-0.58	94.0	-	-6.2	Values below limit of detection
Site5-STM1	Pre-Flare	2.773	-	2.07	30.0	22.1	93.6	
Site5-STM2	Pre-Flare	2.796	0.178	2.09	30.0	22.1	94.7	Average = 69.5 ng/m^3 (RSD = 0.7%)
Site5-STM3	Pre-Flare	4.267	-	3.56	51.0	37.6	94.9	
Site6-STM1	Pre-Energy	8.711	-	8.01	30.0	21.8	366.7	
Site6-STM2	Pre-Energy	7.081	0.590	6.38	31.0	22.6	282.6	Average = 243.4 ng/m^3 (RSD = 13.6%)
Site6-STM3	Pre-Energy	13.59	0.472	12.89	50.0	36.4	354.1	
Site6-STM4	Pre-Flare	3.923	-	3.22	30.0	25.4	126.9	
Site7-STM1	Pre-Energy	185.4	1.206	184.7	30.0	22.4	8233	
Site7-STM2	Pre-Energy	185.4	-	184.7	30.0	22.4	8233	Average = 5991 ng/m^3 (RSD = 4.8%)
Site7-STM3	Pre-Energy	170.5	-	169.8	30.0	22.4	7569	
Site8-STM1	Pre-Energy	7.654	-	6.95	30.0	26.5	261.9	
Site8-STM2	Pre-Energy	7.801	1.515	7.10	31.0	27.4	258.8	Average = 223.4 ng/m^3 (RSD = 5.4%)
Site8-STM3	Pre-Energy	11.19	-	10.49	50.0	44.2	237.1	

The quality assurance summary table for THg has been presented in table 3. All quality assurance measures indicate that digestion and analyses of the iodated carbon traps met all predetermined control limits. The estimated detection limit based on the standard deviation of the digestion blanks was below the expected detection limit of 30 ng/m3. The mercury concentrations reported were wide ranging, indicating that mercury concentrations in landfill gas are significantly affected by site-specific factors. The upper limit concentrations generally agree with previously published values (7190 ng/m3, Lindberg et al. 2001), but as a whole agree better with more recently measured facilities around the country of < 1000 ng/m3 (Lindberg et al., manuscript in preparation).

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Table 3
Quality Assurance for Total Mercury (THg) in Landfill Gas for WA Dept. of Ecology
by Iodated Carbon and CVAFS Analysis

Sample ID	A -Trap (ng/trap)	B -Trap (ng/trap)	Quality Assurance Results
Trap Blanks			
PBIC1	0.041	-	Trap sections digested together
PBIC2	0.026	-	Trap sections digested together
Preparation Blanks			
PB1	0.046 ng/digest	-	
PB2	0.031 ng/digest	-	Average = 0.050 ng/digest
PB3	0.134 ng/digest	-	St. Dev. = 0.062 ng/digest
PB4	-0.013 ng/digest	-	**EMDL = 0.2 ng/digest**
Analytical Duplicates			
Site1-STM4	2.08	-	Average = 1.92
Site1-STM4 AD	1.76	-	17.1% RPD
Site6-STM3	13.59	-	Average = 13.89
Site6-STM3 AD	14.18	-	4.2% RPD
Analytical Spikes			
Site1-STM4 AS +10.0 ng/trap	11.16	-	Net=9.24 ng/L 92.4% Rec
Site1-STM4 ASD +10.0 ng/trap	11.31	-	Net=9.39 ng/L 93.9% Rec 1.6 RPD
Site6-STM3 AS +20.0 ng/trap	35.32	-	Net=21.43 ng/L 107.2% Rec
Site6-STM3 ASD +20.0 ng/trap	35.32	-	Net=21.43 ng/L 107.2% Rec 0.0 RPD

AD = Analytical Duplicate
AS = Analytical Spike
ASD = Analytical Spike Duplicate

Dimethyl Mercury (DMHg)

The combined dimethyl mercury (DMHg) results from all 8 Washington landfill sites have been presented in table 4 below. As the test method for dimethyl mercury is considered a research-based method, a great deal of field QC was collected in order to add confidence to the reported method and improve our overall understanding of factors that affect recoveries.

Table 4
Dimethyl Mercury (DMHg) in Landfill Gas for WA Dept. of Ecology
by Carbotrap and CVAFS Analysis

Sample ID	Location	A-Trap (ng/trap)	B-Trap (ng/trap)	Gas Sample Vol (L)	Adjusted Vol. (liter)	DMHg (ng/m^3)	Comments
Site1-DMHg1	Pre-Flare	0.004	0.000	0.300	-	12.33	
Site1-DMHg2	Pre-Flare	0.002	0.000	0.300	-	7.00	Average = 9.51 ng/m^3 (RSD = 28.2%)
Site1-DMHg3	Pre-Flare	0.005	0.000	0.500	-	9.20	
Site1-DMHg4	Pre-Energy	0.006	0.000	0.300	-	19.67	
Site1-DMHg5	Pre-Energy	0.029	0.000	1.000	0.810	35.69	Average = 24.2 ng/m^3 (RPD = 38.0%)
Site2-DMHg1	Pre-Flare	0.0084	0.0000	0.500	-	16.80	
Site2-DMHg2	Pre-Flare	0.0050	0.0000	0.500	-	10.00	
Site2-DMHg3	Pre-Flare	0.0021	0.0000	0.500	-	4.20	Average = 10.5 ng/m^3 (RSD = 49.1%)
Site2-DMHg4	Pre-Flare	0.0054	0.0001	0.500	-	11.00	
Site3-DMHg1	Leachate Well	-0.0001	0.0001	0.600	-	0.00	
Site3-DMHg2	Leachate Well	0.0003	0.0004	0.600	-	1.17	Average = 0.78 ng/m^3 (RSD = 86.6%)
Site3-DMHg3	Leachate Well	0.0003	0.0004	0.600	-	1.17	Concentrations < 5X MDL
Site4-DMHg1	Passive Well	0.0002	0.0000	1.000	-	0.20	
Site4-DMHg2	Passive Well	0.0009	0.0000	1.000	-	0.90	Average = 0.95 ng/m^3 (RSD = 81.7%)
Site4-DMHg3	Passive Well	0.0012	0.0009	1.200	-	1.75	Concentrations < 5X MDL
Site5-DMHg1	Pre-Flare	0.0072	0.0000	1.000	-	7.20	
Site5-DMHg2	Pre-Flare	0.0064	0.0000	1.000	-	6.40	
Site5-DMHg3	Pre-Flare	0.0072	0.0001	1.000	-	7.30	Average = 7.12 ng/m^3 (RSD = 7.2%)
Site5-DMHg4	Pre-Flare	0.0075	0.0001	1.000	-	7.60	Direct burn to instrument
Site5-DMHg5	Pre-Flare	0.0019	0.0001	1.000	-	2.00	Collected without guard column
Site5-DMHg6	Pre-Flare	0.014	0.0118	5.000	3.682	7.01	Large gas volume
Site6-DMHg1	Pre-Energy	0.0256	0.0003	1.000	-	25.9	Collected without guard column
Site6-DMHg2	Pre-Energy	0.0212	0.0000	1.000	-	21.2	
Site6-DMHg3	Pre-Energy	0.0227	0.0001	1.000	-	22.8	Average = 23.2 ng/m^3 (RSD = 8.5%)
Site6-DMHg4	Pre-Energy	0.0229	0.0000	1.000	-	22.9	
Site6-DMHg5	Pre-Energy	0.0096	0.0321	5.000	3.639	11.5	Large gas volume
Site6-DMHg6	Pre-Flare	0.0264	0.0000	1.000	-	26.4	
Site7-DMHg1	Pre-Energy	0.0221	0.0005	0.500	-	45.2	Collected without guard column
Site7-DMHg2	Pre-Energy	0.0233	0.0003	0.500	-	47.2	Average = 44.1 ng/m^3 (RSD = 9.6%)
Site7-DMHg3	Pre-Energy	0.0228	0.0002	0.500	-	46.0	
Site7-DMHg4	Pre-Energy	0.0375	0.0003	1.000	-	37.8	
Site8-DMHg1	Pre-Energy	0.0077	0.0006	0.500	-	16.60	Collected without guard column
Site8-DMHg2	Pre-Energy	0.0185	0.0024	0.500	-	41.80	Average = 41.7 ng/m^3 (RPD = 0.3%)
Site8-DMHg3	Pre-Energy	0.0067	0.0008	0.500	-	15.00	Statistical outlier, revmoved from ave.
Site8-DMHg4	Pre-Energy	0.0125	0.0000	0.300	-	41.67	

Field spikes are Carbotraps that have been spiked in the lab, sent to the field to collect a landfill gas sample in a normal manner and then returned to the lab for analysis. The field spike should have DMHg present from the landfill gas sampled plus the DMHg spiked onto the trap. Trip

spikes are Carbotraps that have been spiked in the lab, sent to the field and returned to the lab for analysis without opening them. Recent studies of DMHg in landfill gas have found the field spikes to have very low recoveries, while the trip spikes have been normal, with good recoveries. The low recovery of the field spikes from recent studies indicates poor accuracy, which appeared to be due to a matrix interferent that was biasing the DMHg results to the low side. As is often the case, smaller sample volume can minimize the matrix interferent. Significant degradation in sample signal was observed when sample volumes of 1.2 L were used. Although the amount of interferent present at any given site is hard to predict, our target volume for this study was in the 500-1000 mL range. Thus we conclude that when sufficient sample signal is present, the most accurate DMHg concentrations are the ones with the smallest sample volume.

The quality assurance measurements for DMHg are summarized in Table 5 and Appendix A. The analysis system was under very good control as demonstrated by the LCS and 2nd source standard recoveries. In most instances there was good agreement between field replicates. Aside from Site #3 and Site #4 where the concentration were below 5X the reporting limit, only Site #2 displayed greater than expected variability. As all samples were collected in series over the course of several hours, it is possible that the gas speciation was changing throughout the day. For calculation of averages and variability, larger volume and experimental samples have generally been excluded. The generally reproducibility at all other sites suggests that the Carbotrap media is performing consistently and is not likely a significant source of bias. Also, the excellent recovery of field spikes demonstrates that the traps will quantitatively recover a known amount of dimethyl mercury.

The B-trap matrix spike recoveries were all excellent, as well as many of the A-trap matrix spikes. In instances where lower recoveries were present on the A-trap, recoveries were still generally good for the B-trap. This indicates that either an interfering constituent of the landfill gas is being adsorbed onto the A-trap, or else the landfill gas is causing the DMHg spike to migrate down the sampling train. In order to investigate this issue, an additional non-spiked trap (C-trap) was placed at the end of the sampling train. This would help to capture migrating DMHg if this was in fact occurring. As significant portion of DMHg was present on the C –trap, it was evident that migration of the spike along the sampling train was occurring. By summing the DMHg concentrations from all trap sections and accounting for the landfill gas contribution to the signal, the overall spike recovery for the sample train can be calculated. These recoveries have been presented in the comments section of table 4 as “adjusted spike recovery”.

Table 5
Quality Assurance for Dimethyl Mercury (DMHg) in Landfill Gas for WA Dept. of Ecology
by Carbotrap and CVAFS Analysis

Sample ID	DMHg (ng/Trap)	Sample Vol (L)	Recovery	Remarks
2nd Source Standards				
LCS Run #1 (1490 ng/L)	0.139	0.000100	93.3%	
LCS Run #2 (1490 ng/L)	0.148	0.000100	99.3%	
LCS Run #3 (1490 ng/L)	0.151	0.000100	101.3%	
LCS Run #4 (1490 ng/L)	0.152	0.000100	102.0%	
LCS Run #5 (1490 ng/L)	0.145	0.000100	97.3%	
LCS Run #6 (1490 ng/L)	0.151	0.000100	101.3%	
LCS Run #7 (1490 ng/L)	0.147	0.000100	98.7%	
LCS Run #8 (1490 ng/L)	0.146	0.000100	98.0%	
2nd Source Run #4 (1000 ng/L)	0.088	0.000100	88.0%	2nd Source became available
2nd Source Run #5 (1000 ng/L)	0.084	0.000100	84.0%	at run #4
2nd Source Run #6 (1000 ng/L)	0.091	0.000100	91.0%	
2nd Source Run #7 (1000 ng/L)	0.085	0.000100	85.0%	
2nd Source Run #8 (1000 ng/L)	0.084	0.000100	84.0%	
Field Blanks				
Site3-DMHg BLK (A)	0.000	0	-	
Site3-DMHg BLK (B)	0.000	0	-	
Site4-DMHg BLK (A)	0.000	0	-	
Site4-DMHg BLK (B)	0.000	0	-	
Site5-DMHg BLK (A)	0.000	0	-	
Site5-DMHg BLK (B)	0.000	0	-	
Site6-DMHg BLK (A)	0.000	0	-	
Site6-DMHg BLK (B)	0.000	0	-	
Site7-DMHg BLK (A)	0.000	0	-	
Site7-DMHg BLK (B)	0.000	0	-	
030621-S1-DMHg BLK (A)	0.000	0	-	
Site8-DMHg BLK (B)	0.000	0	-	
Trip Spikes				
Site1-DMHg TS (A) +0.183 ng/trap	0.167	0	91.1%	
Site1-DMHg TS (B) +0.183 ng/trap	0.164	0	89.7%	
Site2-DMHg TS (A) +0.183 ng/trap	0.157	0	86.0%	
Site2-DMHg TS (B) +0.183 ng/trap	0.160	0	87.4%	
Site2-DMHg TS (A) +0.183 ng/trap	0.157	0	86.0%	
Site2-DMHg TS (B) +0.183 ng/trap	0.160	0	87.4%	
Field Spikes				
Site1-DMHg FS (A) +0.183 ng/trap	0.155	0.300	84.9%	
Site1-DMHg FS (B) +0.183 ng/trap	0.166	0.300	90.7%	
Site2-DMHg FS (A) +0.183 ng/trap	0.165	0.500	89.9%	
Site2-DMHg FS (B) +0.183 ng/trap	0.143	0.500	77.9%	
Site3-DMHg FS (A) +0.183 ng/trap	0.164	0.600	89.8%	

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Site3-DMHg FS (B) +0.183 ng/trap	0.166	0.600	90.8%	
Site5-DMHg FS (A) +0.183 ng/trap	0.161	1.000	88.1%	
Site5-DMHg FS (B) +0.183 ng/trap	0.150	1.000	82.0%	
Site6-DMHg FS (A) +0.183 ng/trap	0.181	1.000	98.9%	
Site6-DMHg FS (B) +0.183 ng/trap	0.169	1.000	92.6%	
Site8-DMHg FS (A) +0.183 ng/trap	0.183	0.500	99.9%	
Site8-DMHg FS (B) +0.183 ng/trap	0.162	0.500	88.7%	
Site8-DMHg FS (C) +0.183 ng/trap	0.000	0.500	0.0%	No spike on this trap portion
Matrix Spikes				
Site1-DMHg MS (A) +0.183 ng/trap	0.139	0.300	74.2%	
Site1-DMHg MS (B) +0.183 ng/trap	0.169	0.300	92.1%	
Site2-DMHg MS (A) +0.183 ng/trap	0.165	0.500	87.1%	
Site2-DMHg MS (B) +0.183 ng/trap	0.185	0.500	100.9%	
Site3-DMHg MS (A) +0.183 ng/trap	0.175	0.600	95.3%	
Site3-DMHg MS (B) +0.183 ng/trap	0.168	0.600	91.5%	
Site4-DMHg MS (A) +0.183 ng/trap	0.161	1.000	87.3%	
Site4-DMHg MS (B) +0.183 ng/trap	0.164	1.000	89.2%	
Site5-DMHg MS (A) +0.183 ng/trap	0.130	1.000	67.2%	
Site5-DMHg MS (B) +0.183 ng/trap	0.160	1.000	87.3%	
Site6-DMHg MS (A) +0.183 ng/trap	0.091	1.000	38.7%	
Site6-DMHg MS (B) +0.183 ng/trap	0.178	1.000	96.9%	
Site7-DMHg MS1 (A) +0.183 ng/trap	0.141	1.000	53.5%	*Adjusted spiked recovery =
Site7-DMHg MS1 (B) +0.183 ng/trap	0.152	1.000	82.9%	68.2%
Site7-DMHg MS1 (C)	0.000	1.000	-	No spike on this trap portion
Site7-DMHg MS2 (A) +0.183 ng/trap	0.157	0.500	74.0%	*Adjusted spiked recovery =
Site7-DMHg MS2 (B) +0.183 ng/trap	0.157	0.500	85.7%	80.0%
Site7-DMHg MS2 (C)	0.000	0.500	-	No spike on this trap portion
Site8-DMHg MS1 (A) +0.183 ng/trap	0.023	1.000	-1.9%	*Adjusted spiked recovery =
Site8-DMHg MS1 (B) +0.183 ng/trap	0.172	1.000	93.1%	75.2%
Site8-DMHg MS1 (C)	0.108	1.000	-	No spike on this trap portion
Site8-DMHg MS2 (A) +0.183 ng/trap	0.072	0.500	31.8%	*Adjusted spiked recovery =
Site8-DMHg MS2 (B) +0.183 ng/trap	0.180	0.500	97.6%	64.9%
Site8-DMHg MS2 (C)	0.001	0.500	-	No spike on this trap portion
Site8-DMHg MS3 (A) +0.183 ng/trap	0.053	0.300	24.3%	*Adjusted spiked recovery =
Site8-DMHg MS3 (B) +0.183 ng/trap	0.164	0.300	89.3%	89.1%
Site8-DMHg MS3 (C)	0.118	0.300	-	No spike on this trap portion

*Spiked train recovery = (Sum of all sections - Average sample concentrations)/Spike added to A & B sections

Lumex Elemental Mercury Fugitive Emission (Hg^O)

To better characterize Washington landfill gas concentrations, the Lumex RA915+ real-time gaseous Hg^0 analyzer was used to investigate fugitive emissions. At each landfill site, the Lumex was used to perform measurements around the grounds of the landfill as well as targeted sweeps of the various points of interest of each landfill. Unless noted in the individual measurements, all readings were performed at approximately 2 feet above ground. In general, all readings taken in

areas capped or covered areas yielded results in the background-level of 1-2 ng/m^3. Table 6 summarizes all of the measurements that were made with the Lumex. Elevated levels were generally associated with uncovered piles of trash or debris. It should be noted that after the Lumex was removed from its protective case, gradual heating occurred throughout the day. This had the effect of causing the baseline to drift away from a reading a 0 ng/m^3 background. For this reason, as readings tended to drift it was necessary to re-zero the instrument. Therefore gradual increases in concentrations that returned to background levels after the instrument was zeroed are more likely a result of instrument drift rather than actual increases in concentration.

Table 6
Elemental Mercury (Hg^O) in Landfill Gas for WA Dept. of Ecology
by Lumex RA915+ analysis

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #1						
1	10:00	72	108	112	97	Transfer area - Entry area
2	-	83	90	82	85	Transfer area - Drain - 6" off ground
3	-	27	27	56	37	Transfer area - Garbage pile
4	-	463	494	713	557	Transfer area - Center garbage pile
5	-	121	71	156	116	Transfer area - Back of garbage pile
6	-	239	217	199	218	Transfer area - Back of garbage pile
7	-	576	375	327	426	Transfer area - Construction pile
8	-	576	536	683	598	Transfer area - Construction pile
9	-	39	75	69	61	Transfer area - House demo waste
10	-	29	50	6	28	Transfer area - Near upwind
11	-	2	1	4	2	Transfer area - Far upwind
12	10:15	111	59	62	77	Transfer area - Center downwind
1	12:50	28	27	36	30	Transfer area - Refuse Pile - west edge
2	-	22	15	19	19	Transfer area - Refuse Pile - southwest edge
3	-	51	25	100	59	Transfer area - Refuse Pile - southeast edge
4	-	132	72	86	97	Transfer area - Refuse Pile - east edge
5	-	60	59	68	62	Transfer area - Just downwind
6	-	1	2	2	2	Transfer area - Near upwind
7	13:00	0	0	1	0	Transfer area - Far upwind
1	11:30	<2	<2	<2	<2	Tarp Area - south of flare
2	11:45	<3	<3	<3	<3	New Dirt - south of flare
3	-	<2	<2	<2	<2	Grassy area
4	-	2	6	4	4	Short Transect
5A	-	6	7	7	7	Dumpster storage area
5B	-	7	7	8	7	Newish Dumpster
5C	-	0	0	0	0	Repeat of 5C after re-zeroing
6A	-	0	0	0	0	Mid-west road surface
6B	-	-1	-1	2	0	Mid-central road surface

6C	-	1	1	2	1	Mid-east road surface
7	12:30	0	0	1	0	Mid-east road surface
8A	13:25	1	0	0	0	Transect, west of flare - start
8B	-	-1	-1	-2	-1	Mid transect
8C	-	2	2	2	2	End of transect
9	-	<3	<3	<3	<3	In ground panel
10	-	-1	-1	-2	-1	Western boundary
11	-	0	0	1	0	In ground panel
12A	13:47	1	1	1	1	Near treatment station
12B	-	1	0	1	1	Near treatment station
13A	15:36	1	1	1	1	Mid-south tarped area - start (inst. drifted here)
13B	-	0	0	1	0	Mid-south tarped area - mid (inst. drifted here)
13C	-	3	2	3	3	Mid-south tarped area - mid2 (inst. drifted here)
13D	-	2	2	3	2	Mid-south tarped area - end (inst. drifted here)
14A	-	6	7	8	7	Disturbed dirt, measured @ 1" (inst. drifted here)
14B	-	7	7	8	7	Undisturbed dirt, measured @ 1" (inst. drifted here)
14C	-	8	8	8	8	Same spot @ 6" (inst. drifted here)
14D	-	8	9	9	9	Same spot @ 2' (inst. drifted here)
14E	-	1	0	0	0	same spot after re-zeroing
15A	16:03	2	1	1	1	South border heading north @18"
15B	-	1	1	2	1	Mid transect
15C	-	2	2	2	2	End of transect
16A	-	2	1	1	1	Back to south border - start transect
16B	-	3	2	2	2	Mid transect
16C	-	2	2	3	2	End of transect
17A	-	-1	-1	0	-1	North East Corner heading northward - start
17B	-	1	0	0	0	Mid transect
17C	-	0	0	0	0	Mid #2 transect
17D	-	0	0	0	0	End of transect
18A	-	2	1	0	1	East of recycle area heading south - start
18B	-	1	1	-1	0	Mid transect
18C	-	0	0	0	0	End of transect

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #2						
1	10:30	65	-	-	65	Direct LFG sample, mixed w/ ambient air
2	14:00	1	1	0	1	Well KIGW-23
3	-	1	1	0	1	Gravel Road- eastern edge of landfill
4	-	2	-	-	2	Dry culvert near southern corner of landfill
5	-	2	1	1	1	Well, just uphill of culvert
6	-	2	2	2	2	Transect to KIGW-25 from well at #5
7	-	2	1	1	1	Transect from KIGW to E-4
8	-	2	2	1	2	E-4 towards KIGW-10
9	-	-	1	-	1	Around KIGW-10
10	-	0	0	0	0	KIGW-10 halfway to KIGW-2
11	-	0	0	1	0	Rest of way to KIGW-2
12A	14:40	1	1	0	1	KDGW-89
12B	-	0	0	0	0	KDGW-89
13	-	0	0	0	0	Grass
14	-	0	0	0	0	Grass
15	-	0	0	1	0	Culvert near KIGW-3
16	-	1	1	1	1	Between
17	-	-	-	-	-	KIGW-4 - readings not taken at this point
18	-	0	0	1	0	Between
19	-	1	1	1	1	KIGW-26
20	-	5	5	6	5	Culvert near KIGW-26
21	-	2	1	1	1	KSGW-119
22	-	7	7	6	7	Between ditch
23	-	1	3	3	2	KIGW-14
24	-	1	0	1	1	KIGW-13
25	-	1	2	2	2	Between pavement
26A	-	2	3	3	3	Between grass
26B	-	2	2	2	2	KIGW-5
27	-	4	3	2	3	Between
28	-	1	2	2	2	KIGW-6
29	-	0	1	0	0	KDGW-95
30	-	1	0	1	1	Old flares near KDGW-95
31	-	0	0	0	0	Old blowers near old flares
32	-	3	3	2	3	N1
33	-	4	5	5	5	Between
34	-	1	1	1	1	Freshly mowed
35	-	2	0	1	1	KIGW-21
36	-	6	5	6	6	SE of office
37	-	2	4	4	3	KIGW-22 towards office over to newly mowed
38	15:56	3	7	7	6	Across newly mowed section

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #3						
1	-	1	1	0	1	Rail Transfer Facility-start of rail cars
2	-	0	0	0	0	RTF-middle of cars
3	-	0	0	0	0	RTF-new end of cars
4	-	-1	0	0	0	RTF-end of cars
5	-	-2	-5	-3	-3	RTF-6th to last car (empty)
6	-	0	0	0	0	RTF-mid car (empty)
7	-	0	-1	-1	-1	Near start of rail cars (contains ash)
8	8:46	1	2	0	1	Honey Bucket, South end of rail facility
9	-	1	1	1	1	Leachute Pond-South Pond (water only), west side
10	-	1	0	0	0	Leachute Pond-North Pond, west side
11	-	1	1	1	1	Leachute Pond-End of discharge pipe
12	-	0	0	0	0	Sedimentation/Detention Basin, SE corner
13	-	1	1	0	1	Sedimentation/Detention Basin, East side transect
14A	-	3	3	4	3	Retention pond drain-dry, NE corner
14B	-	1	2	1	1	Around retention pond
14C	-	1	1	1	1	Around retention pond
15	-	2	1	1	1	Northside of retention
16	-	0	0	0	0	NW drain-dry
17	9:06	-2	-1	-1	-1	Biofiltration Basin, North
18	9:36	0	0	0	0	Bio Basin South Drain
19	9:50	0	1	0	0	Landfill Cell 1-Leachute drain #1 on NE corner (outy)
20	-	-1	-1	0	-1	LC1-Leachute drain #2 (inney)
21	-	3	3	3	3	LC1-Walking SE across tarp NE corner
22	-	2	2	2	2	LC1-walking SE
23	-	1	1	0	1	LC1-walking SE to road
24	-	0	0	-2	-1	LC1-walking up mound on tarp
25	10:01	0	0	0	0	LC1-walking West on Landfill (not on tarp)
26	-	0	0	0	0	LC1-walking West on Landfill (not on tarp)
27	-	3	2	2	2	LC1-walking West on edge of tarp
28	-	1	0	1	1	Walking SE-not on tarp, 1/2 way up the hill
29	-	1	1	3	2	LC1-walking SE
30	-	3	3	3	3	LC1-walking South
31	10:10	1	1	0	1	LC1-walking South
32	-	1	0	0	0	LC1-walking North to top of Hill
33	-	0	-1	-2	-1	LC1-walking North from top of Hill
34	-	-1	-1	-2	-1	LC1-walking North downhill
35	-	-2	-3	-2	-2	LC1-walking North downhill
36	-	-2	0	0	-1	LC1-walking North downhill
37	-	-2	-1	0	-1	LC1-at gas sample location
38	-	0	0	1	0	LC1-on grass, walking South
39	-	0	0	0	0	LC1-on grass, walking South
40	-	0	0	0	0	LC1-on grass, near ground
41	-	-2	-1	-2	-2	LC1-West side, near ground

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #4						
1A	14:46	0	0	0	0	SE section of landfill - Slight wind to SE
1B	-	2	1	1	1	Heading south
2A	-	0	0	0	0	Passive well in SE section
2B	-	1	2	2	2	Mouth of well
2C	-	2	1	0	1	Hole in top of well pipe
2D	-	-1	-2	-2	-2	Heading south
2E	-	1	1	1	1	Southern edge - instrument zeroed
3A	14:53	1	0	1	1	Well near SE edge
3B	-	5	4	3	4	Mouth of well
3C	-	0	-	-	0	Away from well
4A	-	-2	-2	-1	-2	SE fenceline
4B	-	-2	-2	-2	-2	West transect - Still wind conditions
4C	-	1	1	2	1	West transect
5	-	0	1	0	0	SW area of landfill
6	-	0	-1	0	0	Heading north
7A	-	-2	-3	-2	-2	Passive well in SW section
7B	-	1	1	0	1	Mouth of well
8A	-	-2	-3	-4	-3	Passive Well in mid SW section - rezeroed inst.
8B	-	6	6	5	6	Mouth of well
8C	15:23	2	1	1	1	West area of landfill near fenceline
8D	-	1	0	0	0	Heading north
9A	-	2	3	2	2	Passive well in middle of west section
9B	-	1	-	-	1	Just away from well
10A	-	4	5	5	5	Passive well w/ no screen, samples within pipe
10B	-	0	-	-	0	Just away from well 10A, zeroed inst.
10C	-	7	6	6	6	Re-test of well 10A
10D	-	3	-	-	3	upwin of well 10A
10E	15:22	2	2	2	2	Heading north, wind direction westerly
11A	-	5	9	9	8	Passive well mouth in upper west section
11B	-	1	1	1	1	Just away from well 11A
11C	-	8	-	-	8	Near pipe measurement
12A	-	3	2	2	2	Passive well in NW section
12B	-	-1	-1	0	-1	Heading North
13A	-	0	0	0	0	Passive well in NW section
13B	-	-1	0	0	0	Heading North
14A	15:43	5	5	5	5	Passive well at north edge, rezeroed inst.
14B	-	2	-	-	2	Just away from well 14A
14C	-	7	7	7	7	Resample of well 14A
14D	15:47	4	4	4	4	Heading SE, brisk winds westerly
15A	-	3	3	3	3	Passive well in NE section
15B	-	3	2	3	3	Heading south
16A	-	5	5	5	5	Passive well in min NE section
16B	15:50	3	3	3	3	Heading south

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17A	-	12	11	11	11	Passive Well in upper east
17B	-	2	-	-	2	Just away from well 17A
17C	-	10	10	10	10	Resample of well 17A
17D	15:54	3	2	2	2	Heading south
18A	-	12	12	12	12	Passive Well in mid east
18B	-	4	4	4	4	Heading West
18C	-	5	5	4	5	Continuing west
18D	-	1	1	2	1	Near ground @ 6"
18E	-	12	12	11	12	Upper air @ 4' (tilting instrument)
18F	-	7	5	5	6	Upper air @ 7' (instrument level)
18G	-	6	6	5	6	Lower air @ 1'
18H	-	4	6	6	5	Upper air @ 5'
19	16:05	11	10	10	10	Passive well in east, rezeroed inst.
20	-	10	10	9	10	Passive well in lower east
21A	16:40	0	0	1	0	Leachate area
21B	-	-3	-4	-2	-3	Pipe in leachate area, rezeroed inst.
22A	-	643	383	322	449	Mixed debris, open waste @ 6"
22B	-	1415	2523	3904	2614	Mixed debris, open waste @ 6"
22C	-	2612	3400	3328	3113	Mixed debris, open waste @ 6"
23A	-	-6	-8	-8	-7	Wood waste debris @ 6"
23B	-	-12	-12	-12	-12	Wood waste debris, rezeroed instrument @ 6"
24A	-	0	0	0	0	Concrete waste @ 6"
24B	-	-3	-3	-4	-3	Concrete waste @ 6"
25	-	433	723	847	668	Mixed debris retest @ 6"
26	-	320	260	195	258	Second Mixed debris pile @ 6"
27	-	299	373	460	377	Mixed debris @ metal @ 6", rezeroed inst.
28A	-	36	35	33	35	House Siding <1" (within pile)
28B	-	433	473	490	465	Asphalt shingle waste @ 6", rezeroed inst.
29	-	16	11	9	12	Dumpster (lid mostly closed
30	-	1	0	0	0	Septage Pond @ 6"
31A	-	-1	-2	-2	-2	Leachate pond
31B	-	-3	-2	-1	-2	South edge of leachate pond, wind westerly
31C	-	-1	-1	-1	-1	background air, rezeroed inst.
32	-	3	3	4	3	Septage dumpster

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #5						
0	11:00	0	1	1	1	Upwind from flare - Light breeze
1	-	0	1	0	0	SW corner of new cell - heading east
2	-	0	0	0	0	SW edge of new cell - heading east
3	-	-1	0	0	0	Mid edge of new cell - heading east
4	-	0	0	0	1	Mid edge of new cell - heading east
5	-	2	2	0	1	SE edge of new cell - heading east
6	-	1	-1	0	0	SE corner of new cell
7	-	-1	-1	0	-1	East edge of open cell
8	-	-1	-1	-2	0	East edge of open cell
9	-	1	1	2	1	Just above open cell - SE corner
10A	12:05	1	1	1	0	Just above open cell - NE corner
10B	-	0	-1	-1	7	Bulldozer blade
11	-	23	11	10	16	Mid east open face @ 1'
12	-	12	8	29	12	Center open face @ 1'
13	-	2	10	10	8	Open face - mid south edge @ 1'
14	-	0	11	12	8	Open face - mid south edge
15	-	-	-	-	0	No measurement taken
16	-	-1	0	0	-1	Grass edge of adjacent closed cell
17	-	-2	1	-1	0	West edge of open cell
18	-	0	1	2	0	West edge of open cell
19	-	-1	-2	-1	-1	Wood debris - mid north edge of open cell
20	-	-1	-2	-1	-1	Wood debris - mid north edge of open cell
21	-	0	0	0	-1	West of open cell
22	13:00	-1	-1	-1	0	West of open cell
23	15:00	1	0	0	0	Near leachate pond surface
24	-	-1	0	0	1	West side of leach pond
25	-	2	4	1	2	Easterly transect across closed cell
26	15:20	2	1	2	1	Easterly transect across closed cell
27	-	1	1	1	1	Easterly transect across closed cell
28	-	0	0	1	2	Easterly transect across closed cell - Zeroed instrument
29	-	3	3	3	3	North edge of closed cell on road
30	-	2	3	3	3	North edge of closed cell on road - downwind of flare
31	-	4	4	4	4	North edge of closed cell on road - downwind of flare
32	-	4	4	4	2	Asphalt covered area - downwind of flare
33	-	-1	0	-1	0	Compost pile
34	-	0	0	0	2	Between piles of compost
35	-	3	3	3	4	Fresh wet compost
36	-	5	5	6	4	Walking toward flare (downwind)
37	16:10	1	4	5	4	Green glass recycle
38	-	4	3	4	4	Brown glass recycle
39	-	4	3	3	4	Clear glass recycle
40	-	4	4	4	4	Return to brown glass pile
41	16:20	3	4	5	4	Pile of used tires

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Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #6						
1	12:55	1	2	3	2	Gentle westerly wind, mid-north landfill perimeter
2	-	-4	-5	-5	-5	Heading NW, rezeroed instrument
3	-	-2	-2	-3	-2	Continuing NW, instrument warming to ambient, rezeroed
4	-	-2	-2	-2	-2	Continuing NW
5	-	0	-1	-1	-1	Continuing NW
6A	-	0	1	1	1	Continuing NW, broken up concrete
6B	-	0	0	0	0	Continuing NW, new trash/recycle bins
7	-	-3	-3	-3	-3	Continuing NW, gravel road
8	-	-2	-2	-2	-2	Continuing NW, rezeroed
9	-	0	0	0	0	Continuing NW, drainage ditch
10	13:24	-4	-4	-4	-4	Continuing NW, gravel road
11	-	0	0	0	0	Continuing NW
12	-	-2	-2	-2	-2	Continuing NW, gas well header
13	-	2	1	1	1	Groundwater well at NW corner
14	13:50	0	1	0	0	Midwest edge, Culvert @ end of rip-rap
15	-	-1	-2	-2	-2	Midwest edge, Drainage basin
16	-	0	0	0	0	Heading NE across landfill
17	-	0	0	0	0	Continuing NE
18	-	-1	-1	-1	-1	Continuing NE
19	-	0	0	-1	0	Continuing NE, well 15
20	14:05	-2	-2	-1	-2	Continuing NE, rezeroed
21	-	0	0	0	0	Continuing NE
22	-	0	0	0	0	Heading SE
23	-	-1	-1	-1	-1	Continuing SE
24	-	1	0	0	0	Continuing SE
25	-	-1	-1	0	-1	Continuing SE
26	-	0	0	0	0	Heading N
27	-	0	-1	-1	-1	Continuing N
28	-	0	0	0	0	Heading NE
29	-	5	4	1	3	Small lined cell at east edge, dirt pile
30	-	8	6	14	9	Dirt pile @ 6"
31	-	2	1	0	1	Edge of surface water pond
32	-	0	1	0	0	Edge of surface water pond
33	-	13	12	12	12	Concrete firepit ring @ 6", stagnant air
34	-	3	2	2	2	Pond edge
35	-	2	1	1	1	Open face @ 1"
36	-	1	1	2	1	Top of fill dirt pile
37	-	0	-1	-2	-1	Edge of fill dirt pile
38	-	-1	-1	-1	-1	North edge of active fill area
39	-	0	-1	-1	-1	Gravel and asphalt pile
40	-	6	7	6	6	End of dumping container w/ amimal waste
41	-	7	8	7	7	Other end of container
42	-	2	2	2	2	NE corner of open cell

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43	15:35	2	2	2	2	Heading S
44	-	0	1	-1	0	Concrete pile
45	-	3	3	3	3	Interior of concrete pile @ 4"
46	-	0	1	0	0	Woody debris pile
47	-	3	2	2	2	Top of woody debris pile
48	-	5	9	9	8	Top of woody debris pile, rezeroed
49	-	5	4	12	7	Recheck of dirt pile (site mark #29 & 30)
50	-	14	3	15	11	Recheck of dirt pile @ 4"
51	-	0	1	0	0	SE edge of landfill
52	-	3	2	2	2	Heading SW across landfill
53	-	0	0	0	0	Continuing SW
54	-	0	0	0	0	Continuing SW
55	-	1	0	0	0	Continuing SW
56	-	0	0	0	0	Continuing SW
57	-	1	0	0	0	Continuing SW
58	-	2	1	1	1	SE corner of landfill, drain trench

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #7						
1	11:05	1	1	1	1	Southern edge of landfill
2	-	1	0	0	0	Heading W
3	-	0	0	0	0	Heading W
4	11:13	-1	0	-2	-1	Heading W, rezeroed instrument
5	-	0	0	-1	0	Heading W, gravel ditch @ 1"
6	-	0	0	0	0	Heading W
7	-	0	0	-1	0	Heading W
8	11:20	-2	-2	-3	-2	SE section of landfill
9	-	1	1	0	1	Heading N along western edge of landfill
10	-	0	0	1	0	Continuing north
11	-	0	-1	0	0	Continuing north, gravel ditch
12	-	0	-1	-2	-1	Continuing north
13	11:27	-2	-3	-2	-2	Continuing north, pipe reducer
14	-	-1	-1	-1	-1	Continuing north
15	-	-2	-1	-1	-1	Continuing north
16	11:33	-2	-3	-2	-2	Continuing north
17	-	0	1	0	0	Continuing north, fenceline of old flare
18	-	0	0	0	0	Near old flare
19	-	0	0	0	0	Near old flare
20	-	0	0	0	0	Pipe manifolds in NW section
21	-	0	-2	-3	-2	Gas sample collection point at mid southern edge
22	12:08	-3	-3	-3	-3	Heading N, rezeroed
23	-	0	0	0	0	Heading E in SW section of landfill
24	-	0	0	-1	0	Continuing E
25	-	0	0	-1	0	Continuing E
26	-	1	-4	-4	-2	Continuing E, gravel ditch @ 6"
27	-	0	0	0	0	Heading N in eastern section of lanfill
28	-	-1	0	-1	-1	Continuing N
29	-	-1	-1	-1	-1	Continuing N
30	-	-1	-1	-1	-1	Continuing N
31	-	-1	-2	-1	-1	NE corner of landfill
32	-	-2	-2	-2	-2	Heading W
33	-	-2	-2	-2	-2	Continuing W
34	-	-3	-2	-2	-2	Continuing W
35	-	-2	-1	-2	-2	Continuing W
36	-	-3	-3	-4	-3	Heading S
37	-	-4	-4	-5	-4	Continuing W, rezeroed
38	-	0	0	0	0	Continuing W
39	-	-1	0	1	0	Continuing W, drain culvery @ 6"
40	12:35	0	0	0	0	Continuing W
41	-	0	0	0	0	Continuing W
42	-	0	0	0	0	Heading N
43	-	-1	0	0	0	Continuing N, well heads @ 1'

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44	-	0	-1	-1	-1	Heading W
45	-	-1	0	-2	-1	Continuing W
46	-	0	0	0	0	Heading NW
47	-	0	0	1	0	Heading S over center of landfill
48	-	-1	-1	0	-1	Continuing S
49	-	-1	0	-1	-1	Continuing S
50	-	-1	-1	-1	-1	Continuing S
51	12:54	-3	-3	-2	-3	Heading E over center of landfill
52	-	-2	-2	-2	-2	Continuing E
53	-	-2	-2	-2	-2	Continuing E
54	-	-2	-3	-3	-3	Continuing E
55	13:00	-3	-3	-3	-3	Continuing E, rezeroed instrument
56	-	-1	0	0	0	Continuing E
57	-	0	0	0	0	Continuing E
58	-	-1	-2	-1	-1	Heading SW toward landfill gas collection point
59	-	-1	-2	-3	-2	Continuing SW
60	-	-1	-2	-3	-2	Continuint SW

Note: All measurements are taken at 2 feet above ground unless noted otherwise

Site Mark	Time	Rep 1 (ng/m^3)	Rep 2 (ng/m^3)	Rep 3 (ng/m^3)	Average (ng/m^3)	Remarks
Landfill Grounds - Site #8						
1	12:06	0	-1	0	0	Top center of lanfill, wind from NW
2	12:11	-2	-2	-2	-2	Mid South edge of landfill, rezeroed
3	-	0	0	0	0	Heading SE, following topographical line, rezeroed
4	12:16	0	0	0	0	Continuing SE
5	-	-1	-2	-1	-1	Continuing SE
6	-	-2	-3	-2	-2	Continuing SE
7	-	-4	-4	-4	-4	Continuing SE, rezeroed
8	12:22	0	0	0	0	Continuing SE
9	-	-1	0	-1	-1	Continuing SE
10	-	-2	-2	-3	-2	SE corner of landfill
11	12:29	-2	-2	-3	-2	Heading NE @ 1', rezeroed
12	-	1	1	2	1	Continuing NE
13	-	0	0	-1	0	Continuing NE
14	-	-1	-2	-1	-1	Continuing NE, rezeroed
15	12:36	0	0	0	0	Continuing NE
16	-	0	-1	-1	-1	Continuing NE
17	-	-2	-2	-2	-2	NE corner of landfill
18	-	1	1	0	1	Heading NW, continuing on topographical line
19	-	0	0	0	0	Continuing NW
20	-	0	-2	0	-1	Continuing NW
21	-	-1	-1	0	-1	Continuing NW
22	-	-1	-1	-1	-1	Continuing NW, rezeroed
23	12:48	2	2	2	2	Continuing NW, downwind of working face
24	-	1	0	0	0	Continuing NW, downwind of working face
25	-	4	3	3	3	Continuing NW, downwind of working face
26	-	2	2	2	2	Continuing NW, downwind of working face
27	-	3	3	3	3	Continuing NW, downwind of working face
28	12:54	3	3	4	3	Continuing NW
29	-	2	2	2	2	Continuing NW
30	-	1	2	2	2	Continuing NW
31	13:16	1	1	1	1	Continuing NW
32	-	0	1	0	0	Continuing NW
33	-	0	0	0	0	Continuing NW
34	-	0	-1	-2	-1	Continuing NW @ 1'
35	-	0	-1	-2	-1	Heading N downslope
36	13:34	0	0	0	0	Access road to working face
37	-	0	0	0	0	Dirt covered working face heading N
38	-	2	2	2	2	Dirt covered working face heading E
39	-	1	1	1	1	Dirt covered working face heading E
40	-	2	2	2	2	Dirt covered working face heading E
41	-	4	5	5	5	Dirt covered working face heading E
42	-	3	3	3	3	Dirt covered working face heading E
43	-	4	3	2	3	Mostly covered working face, some visable trash

44	-	4	2	3	3	Mostly covered working face, some visable trash
45	-	2	2	6	3	Mostly covered working face, some visable trash
46	-	2	1	2	2	Mostly covered working face, some visable trash
47	-	1	3	1	2	Mostly covered working face, some visable trash
48	-	3	3	4	3	Mostly covered working face, some visable trash
49	-	2	1	5	3	Mostly covered working face, some visable trash
50	-	2	5	5	4	Border of open trash face
51	-	5	15	29	16	Edge of freshly compacted trash
52	-	11	27	23	20	Freshly compacted trash
53	-	24	80	38	47	Freshly compacted trash
54	-	174	271	430	292	Center of Freshly compacted trash
55	-	1162	1101	315	859	Freshly compacted trash @ 1'
56	-	-2	-3	-4	-3	Dirt covered edge of trash at W edge of working face, rezeroed
57	13:46	2	0	0	1	Dirt covered edge @ 1'
58	-	0	0	0	0	SE of active face, dirt cover
59	-	1	1	2	1	SE of active face, dirt cover
60	-	1	0	3	1	SE of active face, dirt cover
61	-	0	0	0	0	SE of active face, dirt cover
62	13:57	-	-	-	-	Rezeroed instrument
63	-	4	3	3	3	SE of active face, dirt cover
64	-	2	3	3	3	Heading NW, continuing on topographical line
65	-	3	3	3	3	Continuing NW
66	-	3	3	3	3	Continuing NW
67	14:34	-	-	-	-	Rezeroed instrument
68	-	2	2	1	2	Continuing NW
69	-	1	1	1	1	Continuing NW
70	-	1	1	0	1	Continuing NW
71	-	2	2	0	1	Continuing NW @ 1'
72	-	-3	-3	-3	-3	Continuing NW
73	-	2	2	3	2	Heading SW, continuing on topographical line
74	-	0	0	0	0	Continuing SW
75	-	1	1	2	1	Heading NW
76	-	0	1	0	0	Continuing NW
77	-	-2	0	-2	-1	NW section of landfill, rezeroed
78A	14:47	3	5	3	4	Heading SW, rezeroed
78B	14:49	1	1	1	1	Continuing SW
79A	-	7	9	0	5	Heading SE, continuing on topographical line
79B	-	1	-1	-2	-1	Continuing SE @ 8'
80	-	2	2	2	2	Continuing SE
81	-	0	1	1	1	Continuing SE
82	-	1	1	1	1	Continuing SE
83	-	0	1	1	1	Continuing SE
84	-	2	2	1	2	Continuing SE
85	-	0	1	0	0	Continuing SE
86	-	1	1	1	1	Continuing SE
87	-	0	0	0	0	Continuing SE, rezeroed
88	15:06	2	3	2	2	Continuing SE

89	-	1	0	0	0	Heading N uphill
90A	15:19	5	6	4	5	SE top of landfill, still air
90B	-	1	1	1	1	SE top of landfill @ 1'
91	-	5	6	5	5	Heading NW along top
92	-	5	5	5	5	Heading NW along top
93	-	1	3	2	2	Heading NW along top @ 1'
94	-	6	5	6	6	Heading NW along top
95	-	6	5	5	5	Heading NW along top
96	-	6	5	6	6	Heading NW along top, rezeroed
97	15:28	5	5	5	5	Heading NW along top
98	-	4	4	5	4	Heading NW along top
99	-	5	5	6	5	Heading NW along top
100	-	5	5	6	5	Heading NW along top, increasing wind
101	-	6	6	5	6	Heading NW along top
102	-	0	0	0	0	Heading NW along top @ 1'
103	-	4	4	4	4	Heading NW along top
104	-	3	4	6	4	Heading NW along top
105	-	-2	-2	-2	-2	Heading NW along top
106	-	1	3	2	2	Heading NW along top
107	-	-1	-1	-1	-1	Heading NW along top
108	-	-1	0	0	0	Heading NW along top
109	-	0	0	0	0	Heading NW along top
110	-	0	-1	0	0	Heading NW along top
111	-	0	0	-1	0	Heading NW along top

DISCUSSION

A wide range of total mercury concentrations was observed in the Washington landfills included in this study. Levels observed were in the range of 25 to 8000 ng/m^3 and generally agree with concentrations previously reported by Lindberg et al., (2001). Dimethyl mercury can contribute a significant fraction of the mercury species with observed levels of 1-60% of the total mercury content. The strongest relationship ($r^2 = 0.406$) was discovered when comparing the % dimethyl mercury (of total mercury) to % overall methane gas content. This negative relationship suggests that higher levels of elemental mercury may have a slight inhibitory affect on the production of dimethyl mercury. Comparing of DMHg and CH4 concentrations, a slight positive correlation ($r^2 = 0.262$) was determined. This reflects that assumption that as more CH4 is produced by microbial activity, a subsequent increase in DMHg expected. Essentially no correlation was observed ($r^2 = 0.159$ and $r^2 = 0.025$) when comparing the same DMHg parameters to CO2 content. Graphs of these comparisons have been presented in section "C" of the appendix.

In our investigations into the parameters that affect the collection and recovery of dimethyl mercury, it was reinforced that the largest factory affecting recovery is the volume of sample collected. There is somewhat of a balancing act that needs to occur to collect enough gas have sufficient signal to quantify, but not so much gas that the interfering properties of the gas overwhelm the sample. In gas streams where the interferents are in abundant supply, the guard column does seem to play a protective role, and when the guard column is in place where interfering compounds seem to be absent there appears to be no degradation in dimethyl mercury signal.

As the sampling at each landfill was limited to one day per site, caution should be taken in expand the data too much. It is uncertain how seasonality affects emission rates of mercury at each site, as well as daytime/nighttime differences and atmospheric factors such as changes in pressure. In addition as much of the landfill gas is burned either in flare or energy generation facilities, undoubtedly changing the mercury speciation. It is expected that any organomercury compounds would be pyrolized to elemental mercury, however it would be worthwhile to confirm this by testing flare stack emissions and energy generation engine exhaust.

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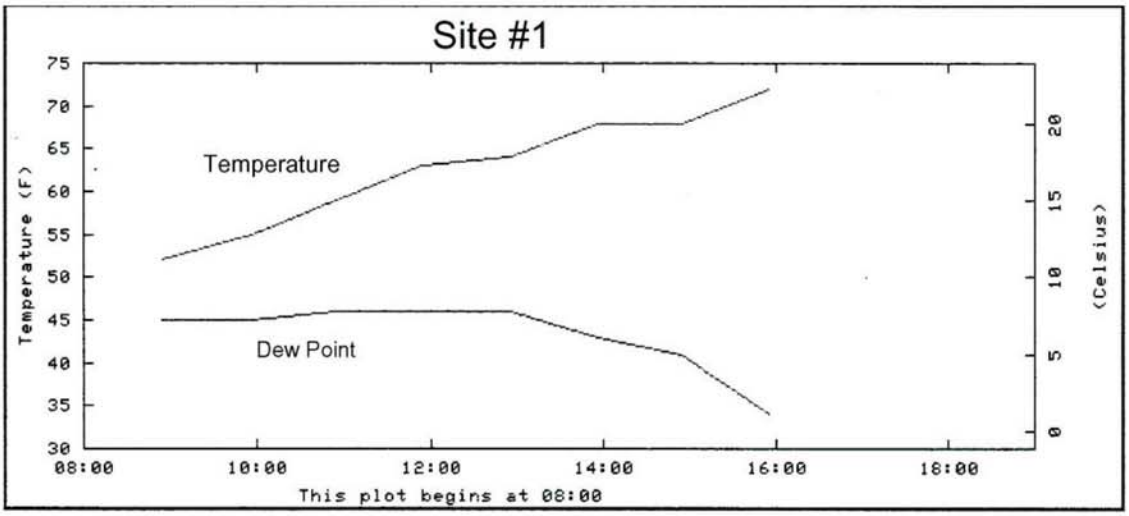
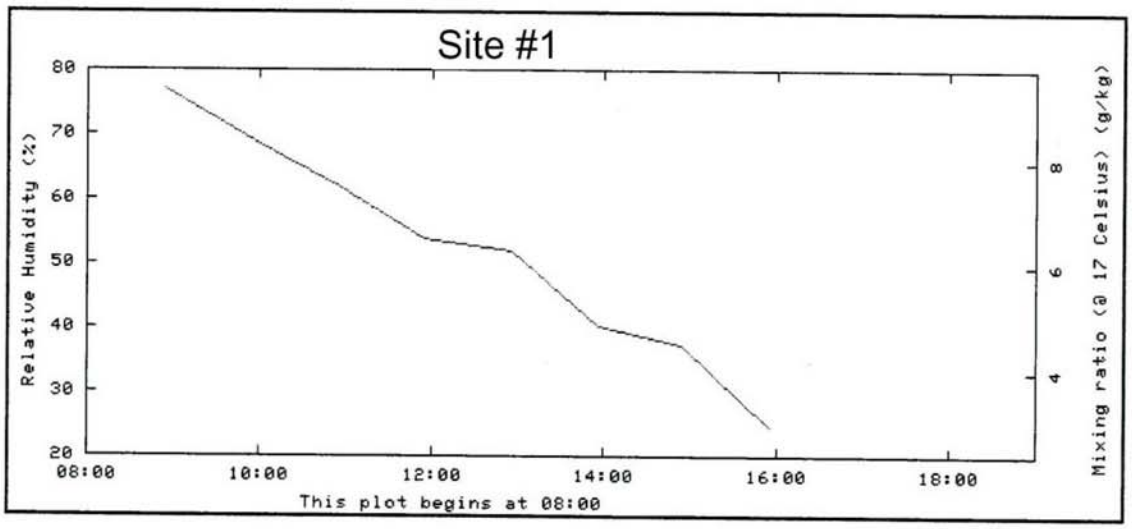
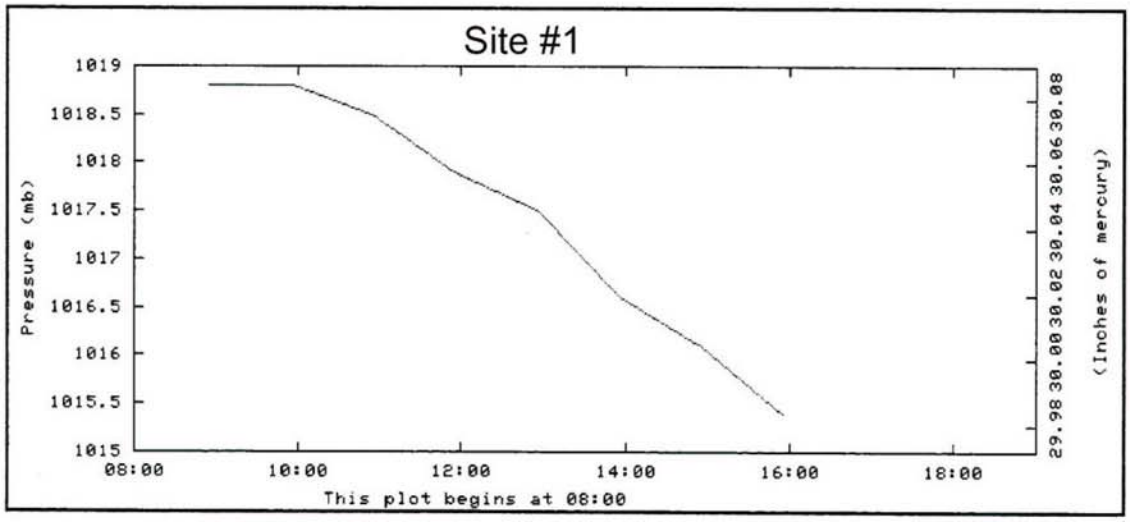
Lindberg S.E., D.Wallschläger, E.M.Prestbo, N.S.Bloom, J.Price and D.Reinhart (2001) Methylated mercury species in municipal waste landfill gas sampled in Florida,USA, Atmospheric Environment, volume 35, pp. 4011-4015.

APPENDIX A - ATMOSPHERIC DATA

Regional data only (Data not collected from sampling point)







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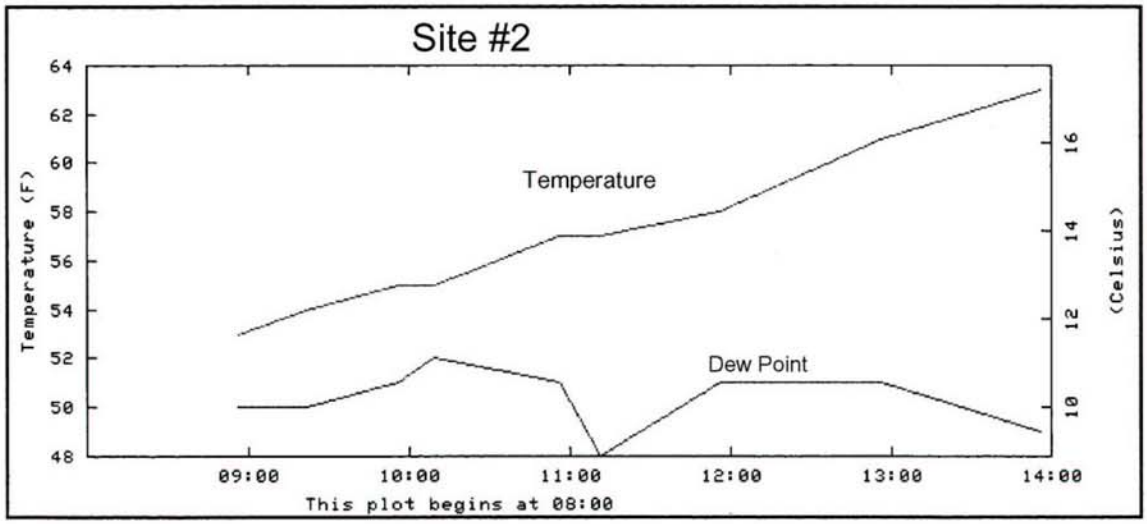

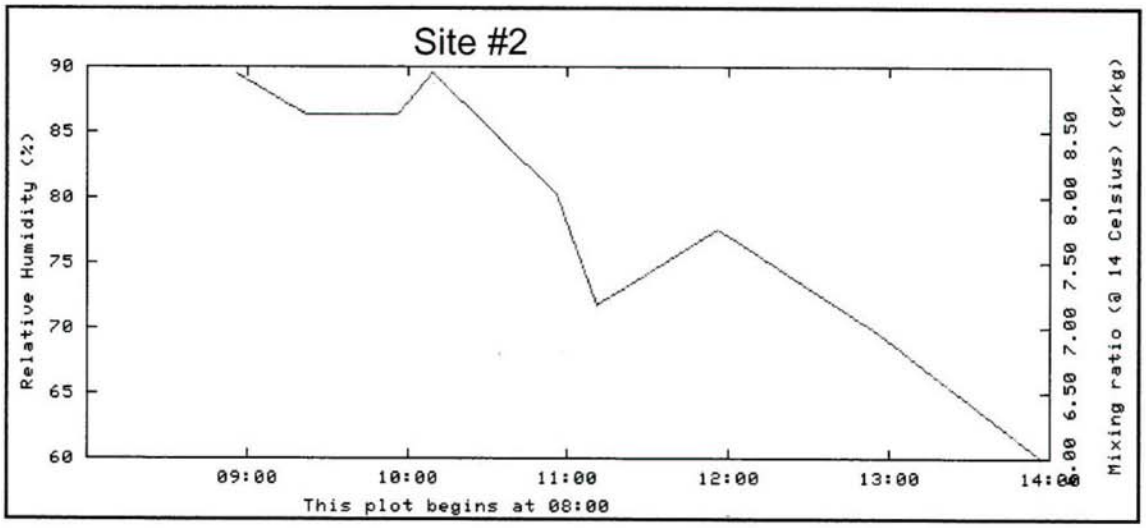

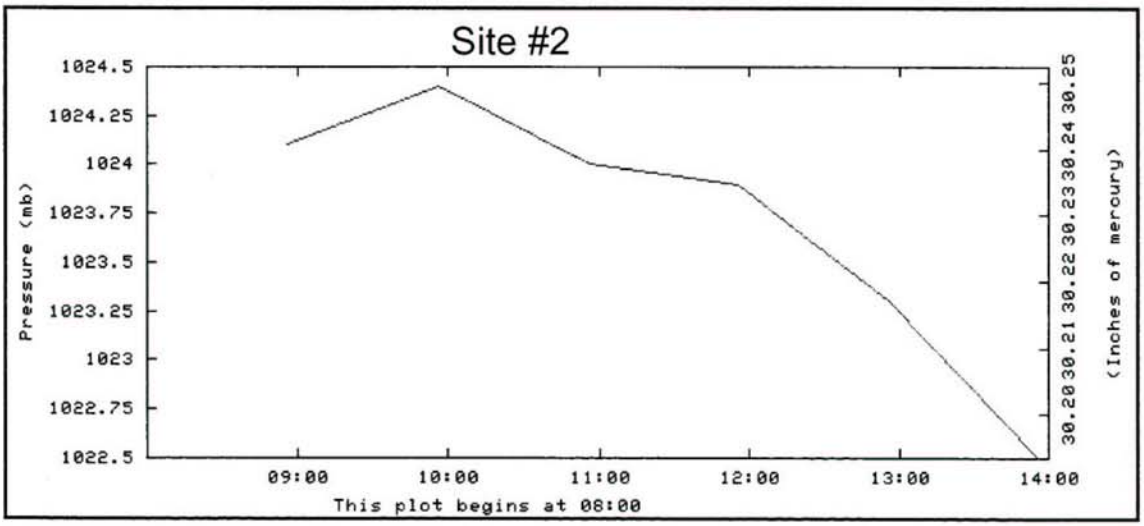

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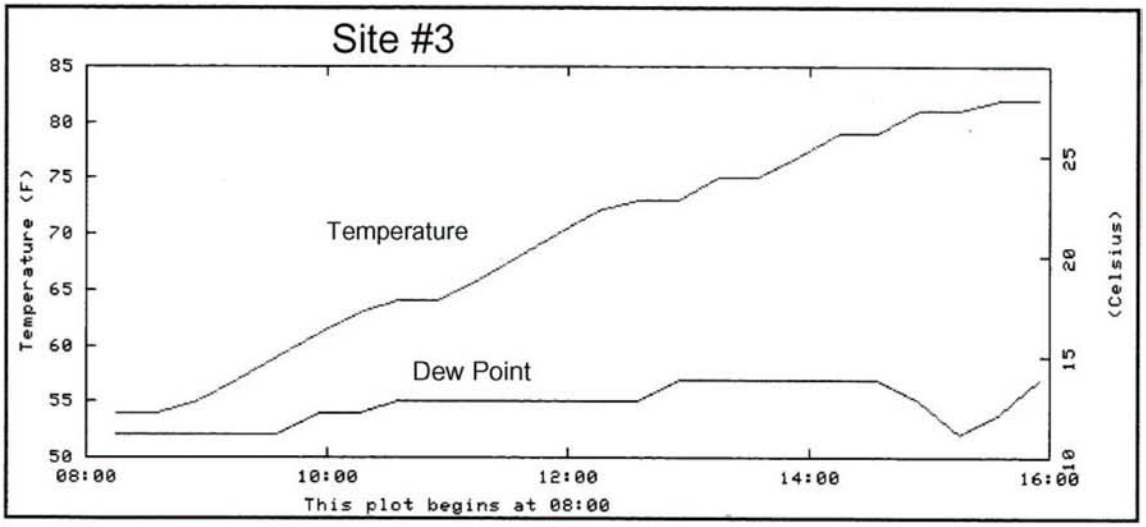

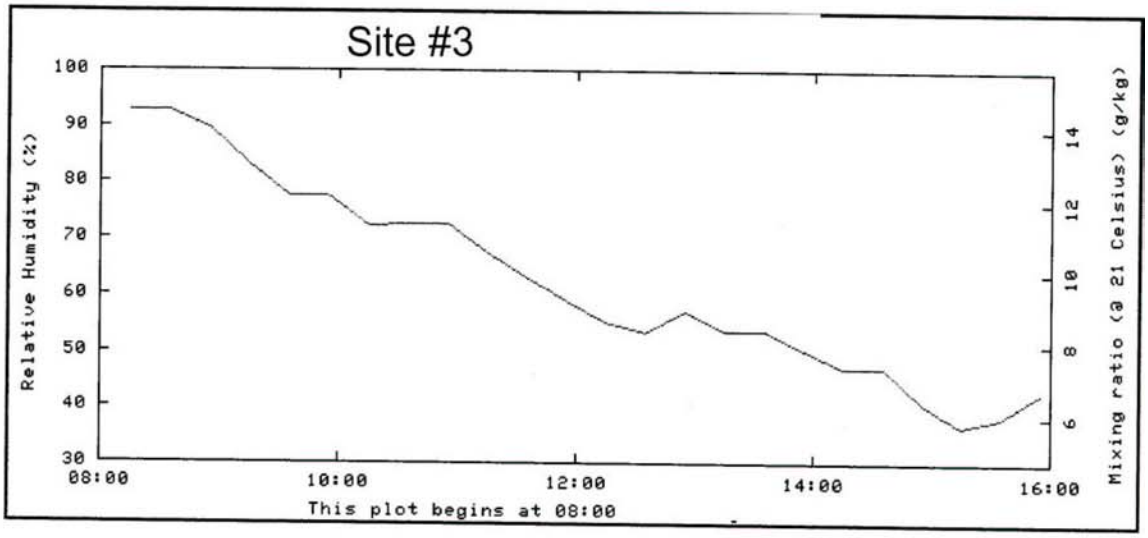

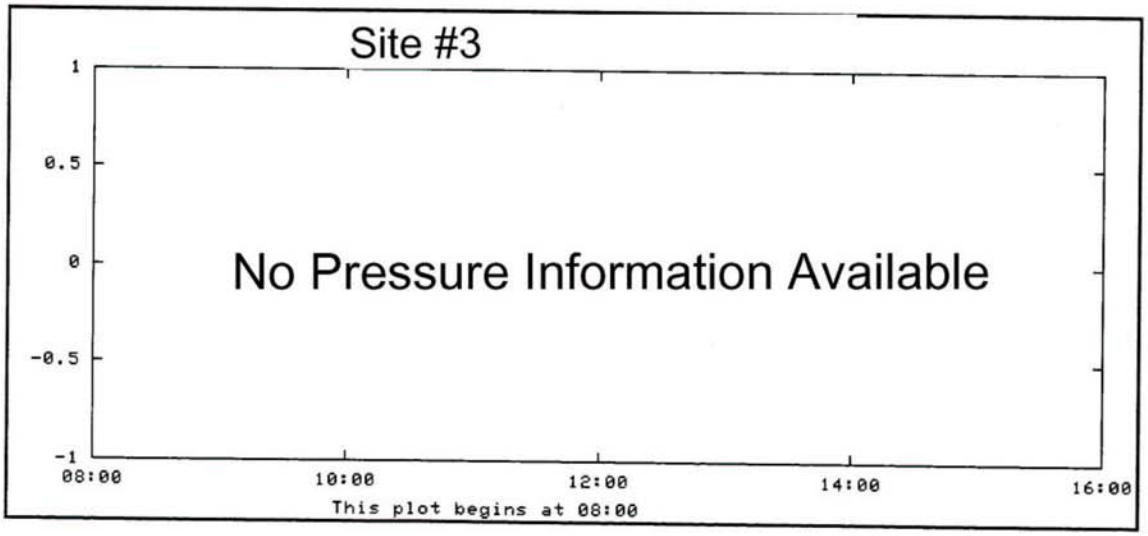

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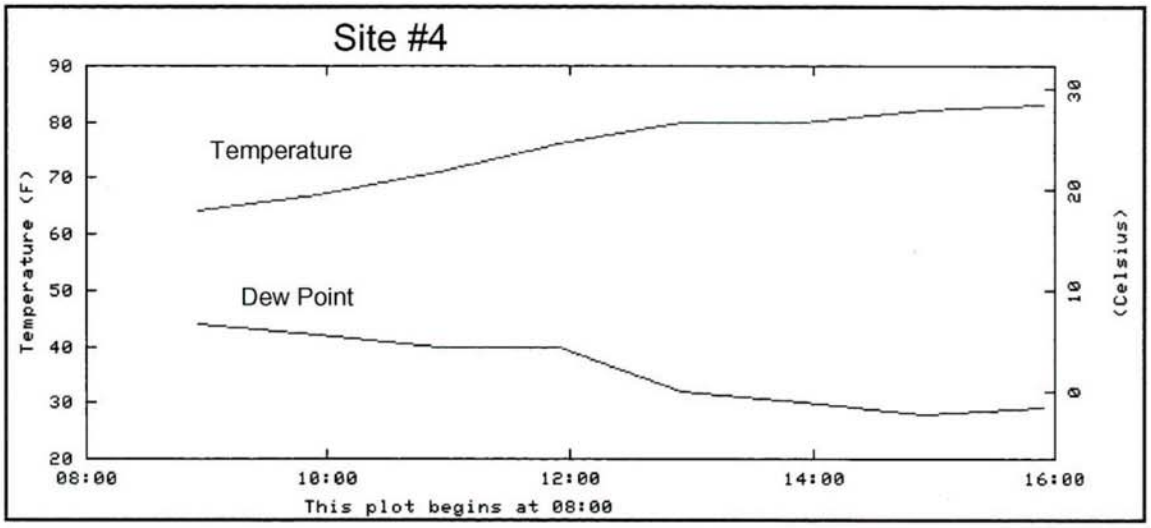

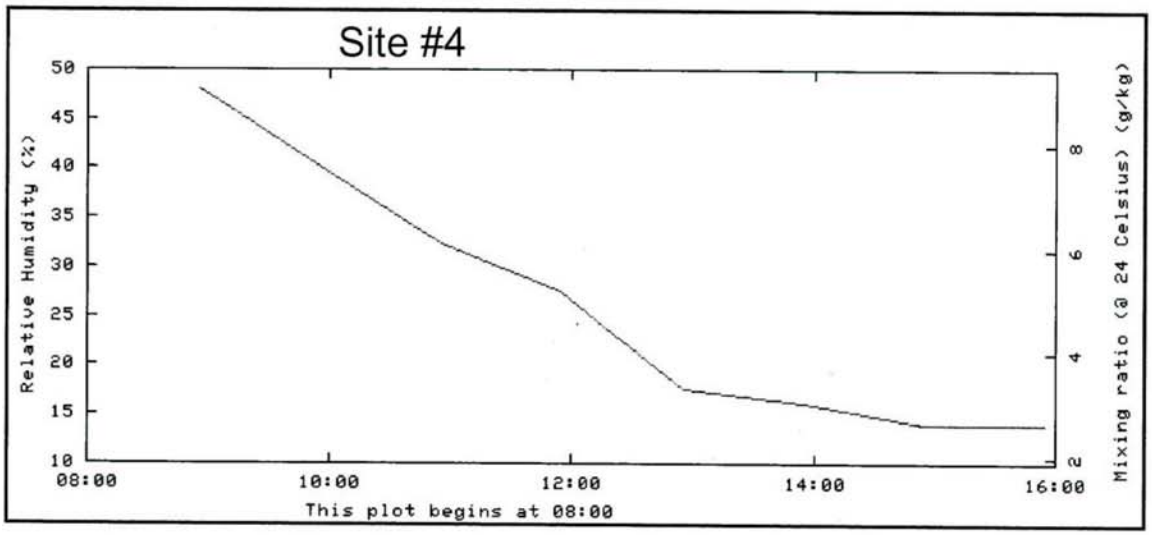

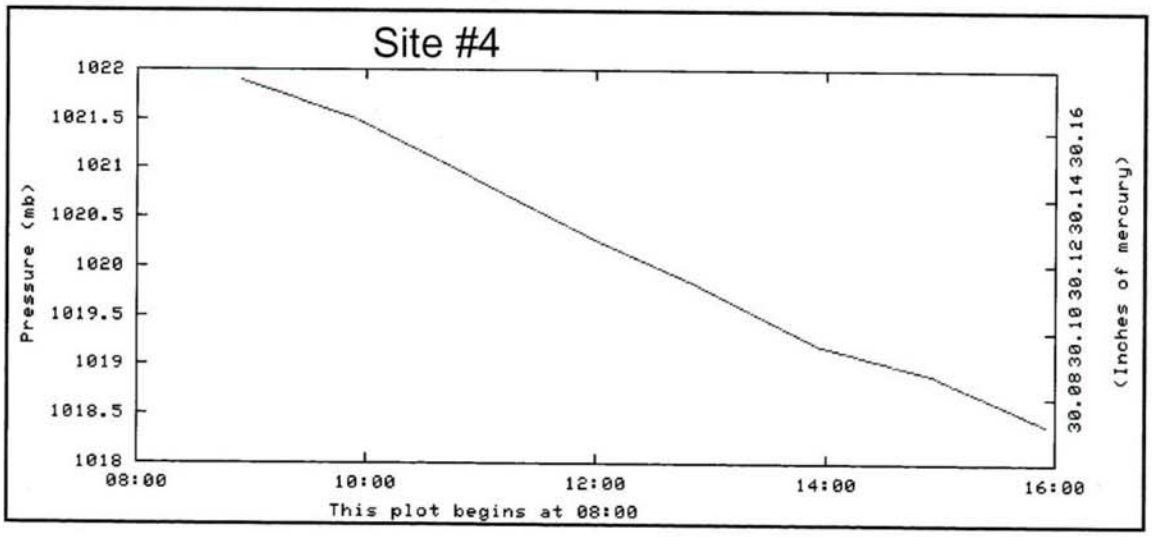

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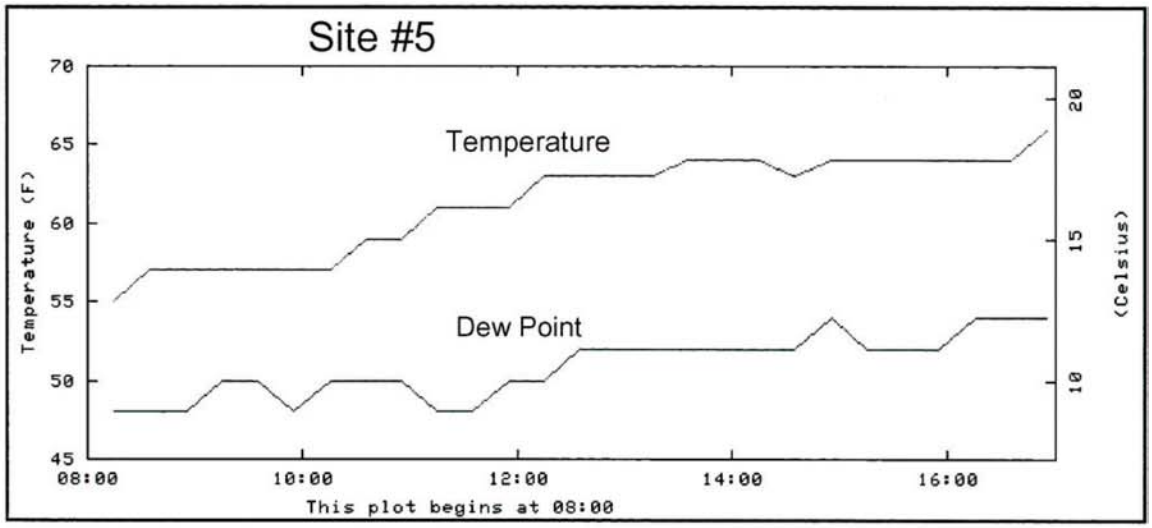
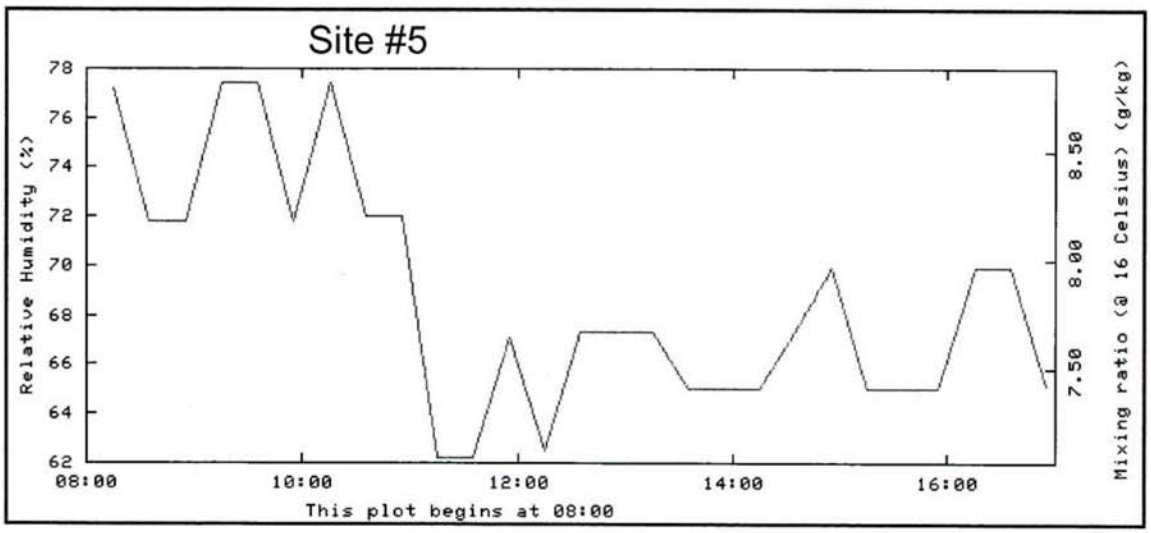
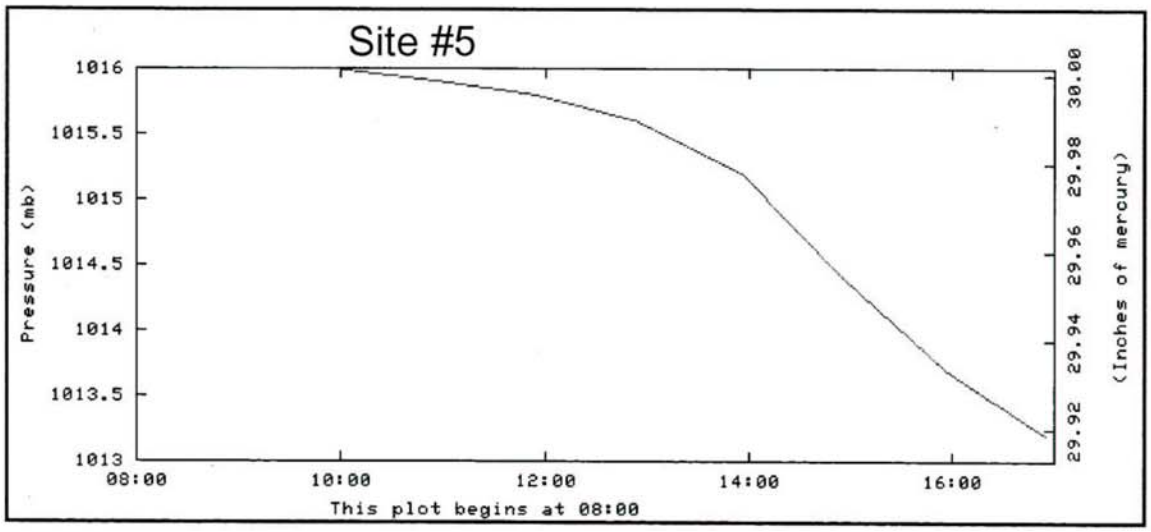
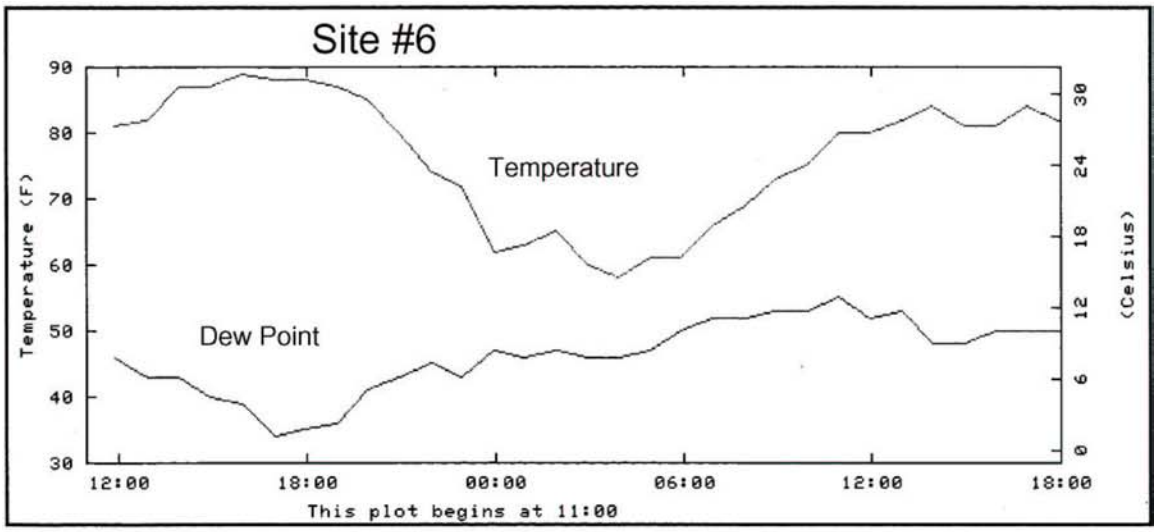
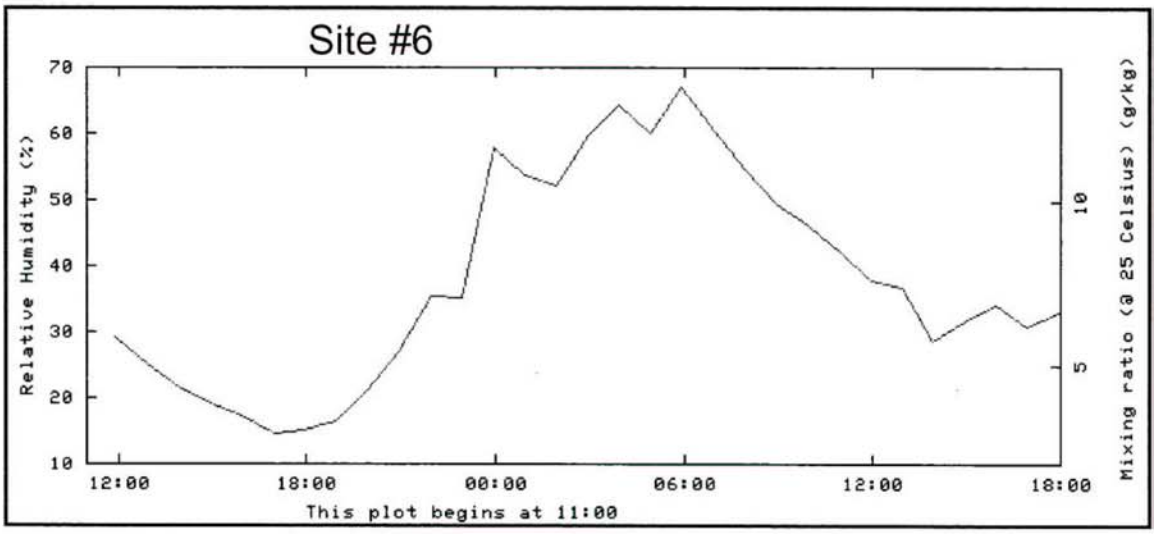
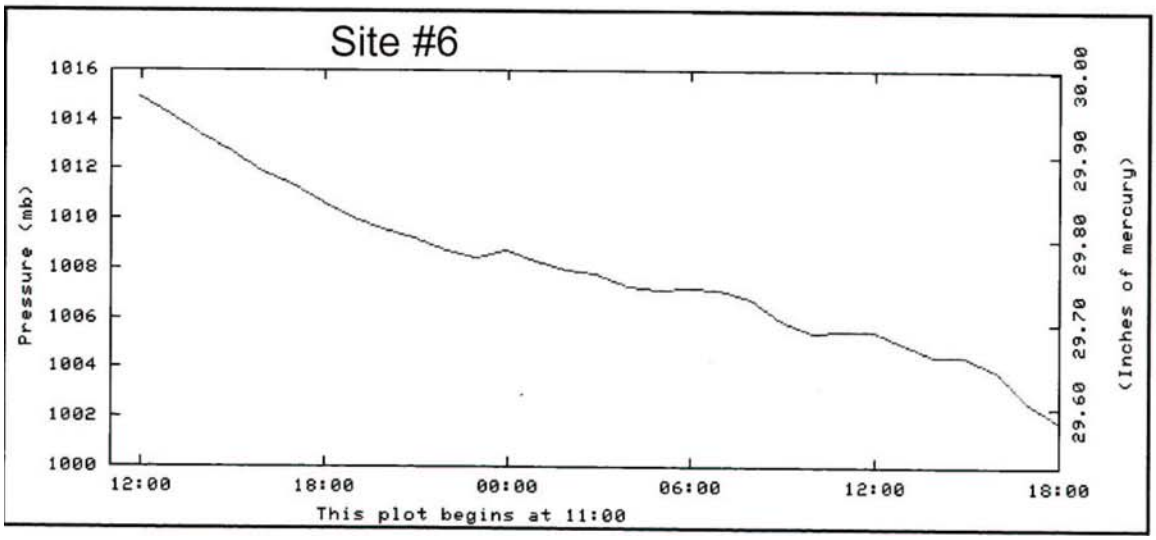

Site #5
Temperature
Dew Point
Temperature (F)
(Celsius)
70
65
60
55
50
45
20
15
10
08:00
10:00
12:00
14:00
16:00
This plot begins at 08:00


Site #5
Relative Humidity (%)
Mixing ratio (@ 16 Celsius) (g/kg)
78
76
74
72
70
68
66
64
62
8.50
8.00
7.50
08:00
10:00
12:00
14:00
16:00
This plot begins at 08:00


Site #5
Pressure (mb)
(Inches of mercury)
1016
1015.5
1015
1014.5
1014
1013.5
1013
30.00
29.98
29.96
29.94
29.92
08:00
10:00
12:00
14:00
16:00
This plot begins at 08:00







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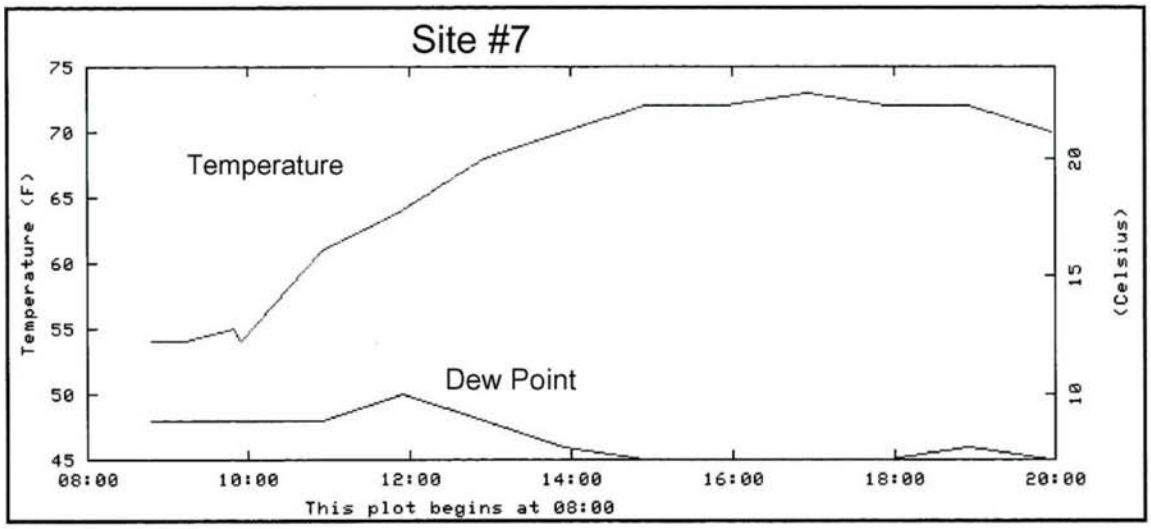

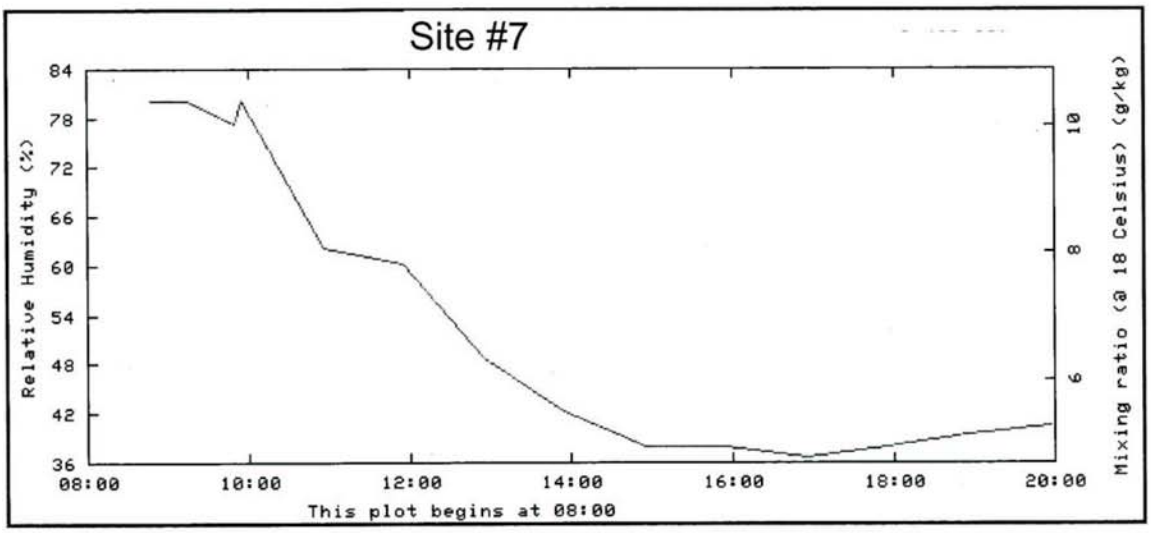

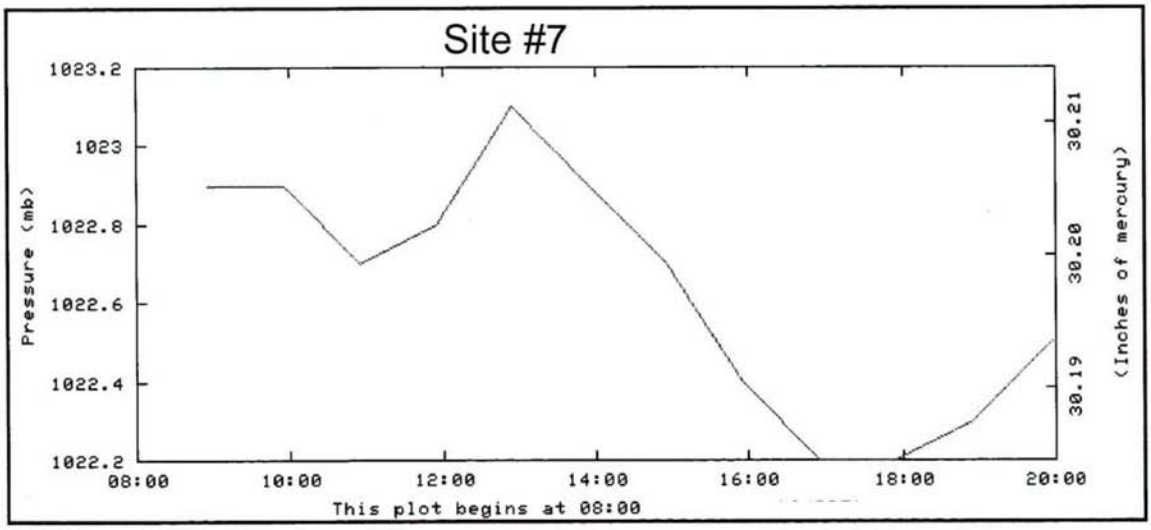

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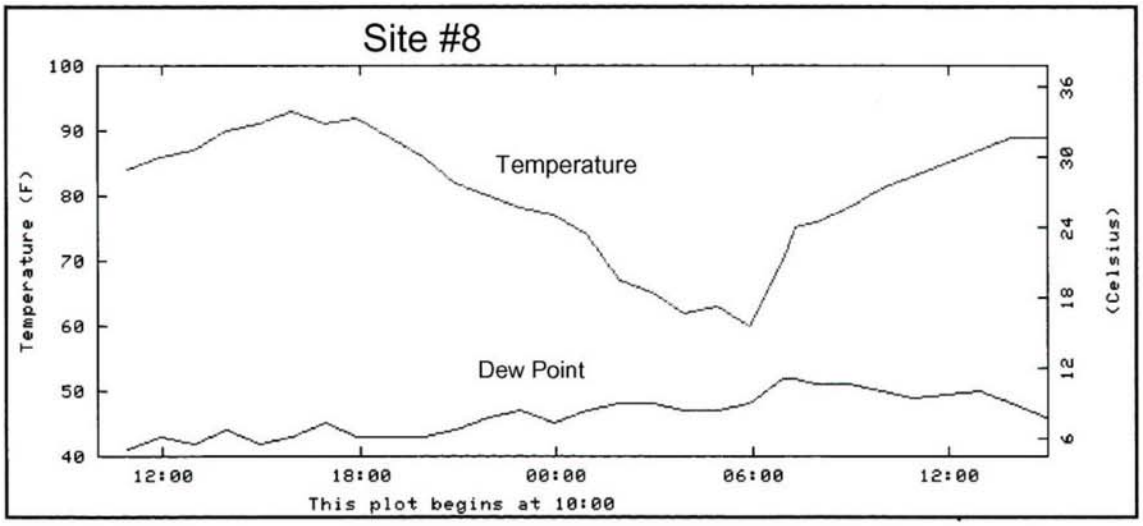

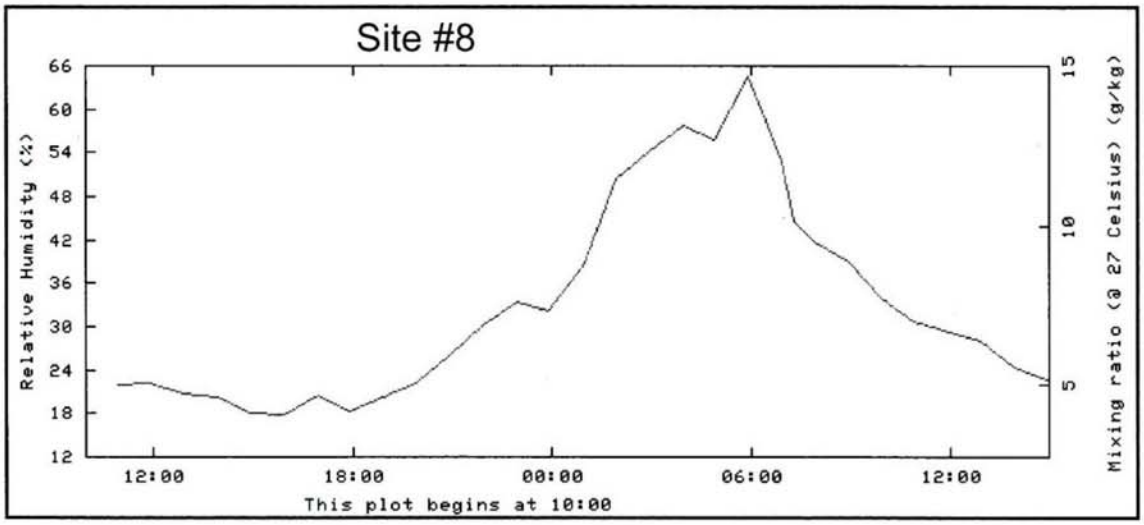

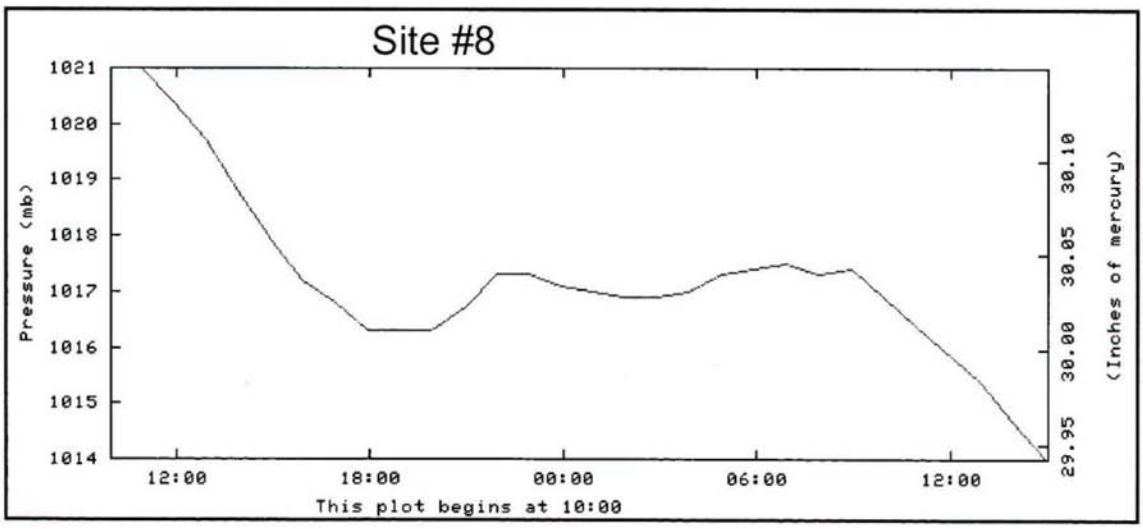

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APPENDIX B

STANDARD OPERATING PROCEDURES

Dimethylmercury in Environmental Media
FGS-098.1

Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, WA 98109

Originated by: Nicolas S Bloom
Revised by: Nicolas S Bloom

February 8, 2000

Effective Date: June 30, 2000

On June 30, 2000, this procedure was reviewed and validated by Michelle L. Gauthier, Laboratory Manager and Beverly H. van Buuren, Quality Assurance Program Director. Signatures are on file.

1.0 Scope and Application

This method is for the determination of dimethyl mercury ($(CH_3)_2Hg$) in all natural media (air, waters, industrial and municipal effluents, sediment and tissue digests) at concentrations as low as 0.001 ng/L. Through the use of smaller aliquots (mL to □L range) contaminated waters and digests of up to 200 ng/L can be directly measured. Because the method has no measurable blanks, detection limits in the range of 0.001- 0.003 ng/L are routinely attainable.

2.0 Summary of Method

Aqueous samples are collected using ultra-clean sample handling protocols (Bloom, 1995) into clean glass or quartz bottles with Teflon™ lined caps. Samples are stored unpreserved in a cool, dark location for less than 48 hours until analysis. The volatile $(CH_3)_2Hg$ is separated from the aqueous matrix by purging onto a Carbotrap™. The trap is then thermally desorbed into an isothermal GC column, for peak separation, and then quantified by cold vapor atomic fluorescence spectrometry (CVAFS). Sediment and tissue samples are first digested with 25% KOH in methanol to release the bound $(CH_3)_2Hg$, and then the digests treated as aqueous samples. Atmospheric samples are collected by vacuum pumping through a "field" Carbotrap™ and the traps analyzed the same way, after refocusing the $(CH_3)_2Hg$ on a second, "analytical" Carbotrap™ .

3.0 Interferences

For best results doing low-level aquatic mercury research, it is important that the laboratory air be low in both particulate and gaseous mercury. Outside air, which is very low in Hg, can be brought directly into the class-100 clean air station intakes. If this is impossible, air coming into the clean air stations can be cleaned for mercury by placing a gold-coated cloth or iodated carbon pre-filter over the intake.

Atomic fluorescence intensity is strongly dependent upon the inertness of the carrier gas. The dual amalgamation technique eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free train.

Aqueous samples must not be preserved, as acidification rapidly degrades the $(CH_3)_2Hg$ content of the sample. If aqueous samples cannot be analyzed within 24-48 hours after collection, they should be purged onto Carbotraps in the field, and treated thereafter as atmospheric samples.

Under no circumstances should ordinary plastic (polyethylene, polypropylene or vinyl) or even Teflon™ containers be used, as they are very diffusive to $(CH_3)_2Hg$ gas. The best containers are made of acid cleaned Borosilicate or quartz glass bottles with Teflon™ caps. It is critical that the bottles have very tightly sealing caps to avoid diffusion of $(CH_3)_2Hg$ through the threads.

No HNO_3 or other oxidizing agents (Cl_2, BrCl, $CrO_4^{=}$, etc.) may be present in the sample, or $(CH_3)_2Hg$ may be destroyed. Particular care must be taken to eliminate the chlorine present in municipal water which feeds the deionized water system, by passing it through an activated carbon bed.

Water vapor can result in positive interferences and poor baselines by condensing on the interior of the fluorescence cell. Careful attention must be paid to the Carbotrap™ drying step to avoid this problem.

To minimize interferences from other atmospheric volatiles, atmospheric samples should be collected for the minimum sample volume consistent with the needed MDLs, and samples should be collected exactly as described in the sampling section.

Carbotrap™ traps should be kept track of by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. Occasionally, due to inadvertent contact with bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and irreproducible results. Suspect traps should be checked with at least two consecutive standard runs before continued use.

When correctly performed, this methodology is virtually interference free, so the method of standard additions is not routinely applied.

(Please contact Frontier Geosciences to obtain the complete SOP)

Digestion for Gas/Air Samples Collected on Iodated Carbon Traps for Total Mercury Analysis
FGS-009.3

Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, WA 98109

Originated by: Nicolas S Bloom and Eric M. Prestbo
Revised by: Jacob Meyer
November 16, 2001

Effective Date: December 31, 2001

On December 27, 2001, this procedure was reviewed and validated by Michelle L. Gauthier, Laboratory Manager and acting Quality Assurance Officer.

1.0 SCOPE AND APPLICATION

1.1. This method is a peer-reviewed, published procedure for the determination of total mercury in air and gas samples collected on dry iodated carbon (IC) traps. All samples must be subjected to an appropriate leaching step, as described herein, prior to analysis by cold vapor atomic fluorescence spectroscopy (CVAFS).

1.2. The typical estimated method detection limit for this method, as derived from the standard deviation of the blank traps, is 0.2 ng Hg/sample trap for a 1-m^3 sample.

2.0 SUMMARY OF METHOD

2.1. Iodated carbon traps with air samples collected on them are subjected to a hot (50-60 $^{\circ}$C) leaching with a 70:30 HNO_3/H_2SO_4 mixture of concentrated acids for 1.5 hours. The leachate is then diluted up with 5% (v/v) BrCl on the day of analysis for total mercury by the CVAFS method (Frontier SOP FGS-069).

3.0 INTERFERENCES

3.1. The carbon granules are not dissolved by this procedure, but experience shows that this strong-acid leach is sufficient to extract all collected mercury that has adsorbed on the surface. It is critical, however, that the final solution contains at least 40% by volume of strong acids to avoid re-adsorption of mercury to the carbon granules.

3.2. Due to the amount of iodine and iodated compounds that leach into the digestates, a maximum aliquot size of 1.0 mL for each digested trap is used for analysis. These compounds have the ability to overwhelm the soda-lime traps on the CVAFS analyzer, which can account for high blanks and the destruction of the gold sample collection traps.

(Please contact Frontier Geosciences to obtain the complete SOP)

Total Mercury Analysis by Cold Vapor - Atomic Fluorescence Spectrometry (CV-AFS)
FGS-069.3

Modified EPA Method 1631E

Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, WA 98109

Originated by: Sarah DuBord, Lucas Hawkins, Dustin Leen, and Amber Steward
Revised by: Amber Steward and Will Hagan
May 15, 2003

Effective Date: May 16, 2003

On May 16, 2003, this procedure was reviewed and validated by Michelle L. Gauthier, Laboratory Manager, and Will Hagan, Quality Assurance Officer.

1.0 SCOPE AND APPLICATION

1.1. This SOP is designed to ensure that reproducible, traceable procedures are followed in the standardization of the total mercury analyzers and in the analysis of samples for total mercury, as well as to establish the bounds wherein data will be considered acceptable.

1.2. This method provides for the determination of total mercury in a wide range of matrices including aqueous, biological, and geological media. In general, using clean handling and reagents, the typical detection limit for the method is less than 0.2 ng/L for aqueous samples and 0.5 ng/g for digested solid samples. A typical detection limit of below 0.5 ng/g can also be achieved for the analysis of Hg(II) in tissues.

2.0 SUMMARY OF METHOD

2.1. Preparation of Total Mercury Standards

2.1.1. Mercury (Hg) standard solutions are prepared using ultra-clean volumetric glassware and gravimetrically calibrated pipettors. To ensure traceability, they must be logged in the Mercury Standard Logbook and assigned a unique identification number.

2.1.2. Any standard, along with its original certification, should be labeled with its receipt date and the receiver's initials. Current, as well as archived certifications, will be kept on file in the QA Office.

2.2. Total Mercury Analyzer Calibration Sequence

2.2.1. The calibration sequence for the determination of total mercury consists of a 5-point calibration curve, an initial calibration verification (ICV) standard, and an initial calibration blank (ICB).

2.2.2. The calibration standard is made from a dilution of a certified stock mercury standard. In most cases, the highest calibration standard limits the range of sample concentrations that are considered valid.

2.2.3. The ICV standard is made from a dilution of a secondary-source stock mercury standard. It verifies the accuracy of the standard used for the calibration curve.

2.2.4. The ICB is used to confirm that the system is low in total mercury and to enable blank correction of the standard curve.

2.3. Total Mercury Analysis

2.3.1. Total mercury analyses are split into two categories: waters and solids. For analysis of aqueous samples, an aliquot of oxidized sample is neutralized with hydroxylamine-hydrochloride (NH_2OH-HCl) and added to a bubbler. For solids, an aliquot of digested sample is directly pipetted into the bubbler.

2.3.2. For the analysis of waters and solids, stannous chloride ($SnCl_2$) is added to reduce the aliquot, and the bubblers are sealed with Keck clips. Blanked gold traps are placed at the end of soda-lime pre-traps. The bubbler is purged with nitrogen (N_2) for 20 minutes. All gas that flows into the bubbler should only leave the system through the soda-lime pre- trap and then gold trap.

2.3.3. The gaseous mercury amalgamates to the gold traps, which are removed and individually placed in the analytical train. The gold trap is heated, thus releasing the mercury into the argon gas stream, which flows into the analyzer.

3.0 INTERFERENCES

3.1. Due to the high levels of acid and halogens (i.e., bromine) in digested solids, it is recommended

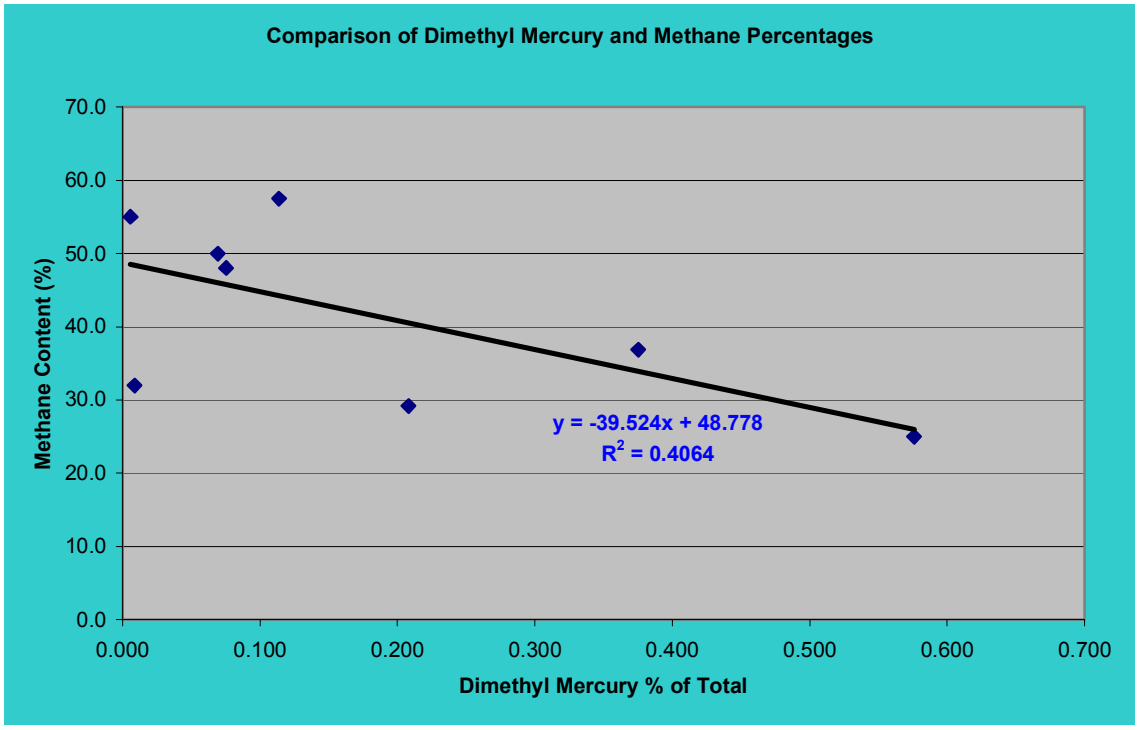
that aliquots of no more then 5.0 mL (1.0 mL if hydrofluoric acid or iodated carbon is present at significant concentrations) of the digestates be analyzed, unless otherwise specified.

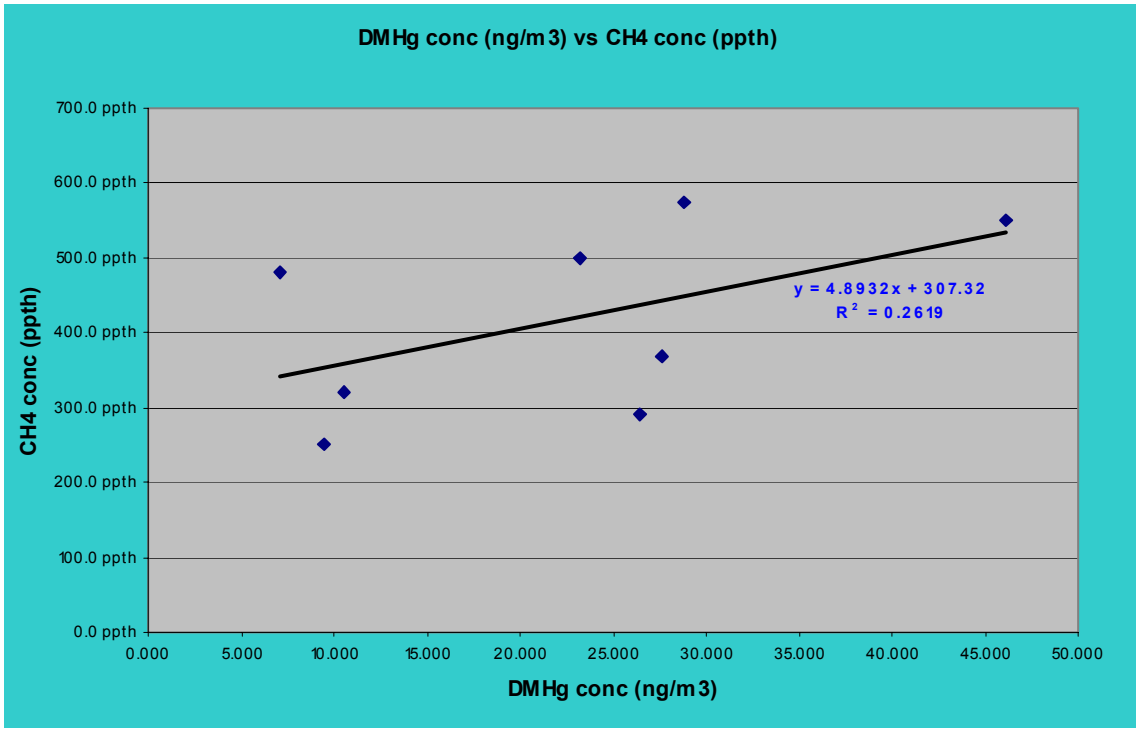
3.2. When running digested solid samples, bubbler water should be changed and purged after a total of 10 mL of digestate has been added to the bubbler. This is done to avoid a build up of acidity and halogens in the bubbler water that can result in low sample recoveries as well as a drop in analyzer sensitivity.

3.3. Water has the potential to create recovery interference. To prevent interference from water, ensure that the soda-lime pre-traps remain dry.

3.4. The presence of high concentrations of silver and/or gold can cause $SnCl_2$ to precipitate out of solution and adhere to the bubbler walls. High concentrations of these metals can sometimes be found in the matrix spike samples from digestion sets that are being shared with the Trace Metals Group. When analyzing digestates where the matrix spike samples have been spiked with silver or gold, the matrix spike samples should not be analyzed for mercury. Instead, an analytical spike/analytical spike duplicate (AS/ASD) should be analyzed. Alternatively, a separate mercury-specific MS/MSD digest can be prepared

APPENDIX C





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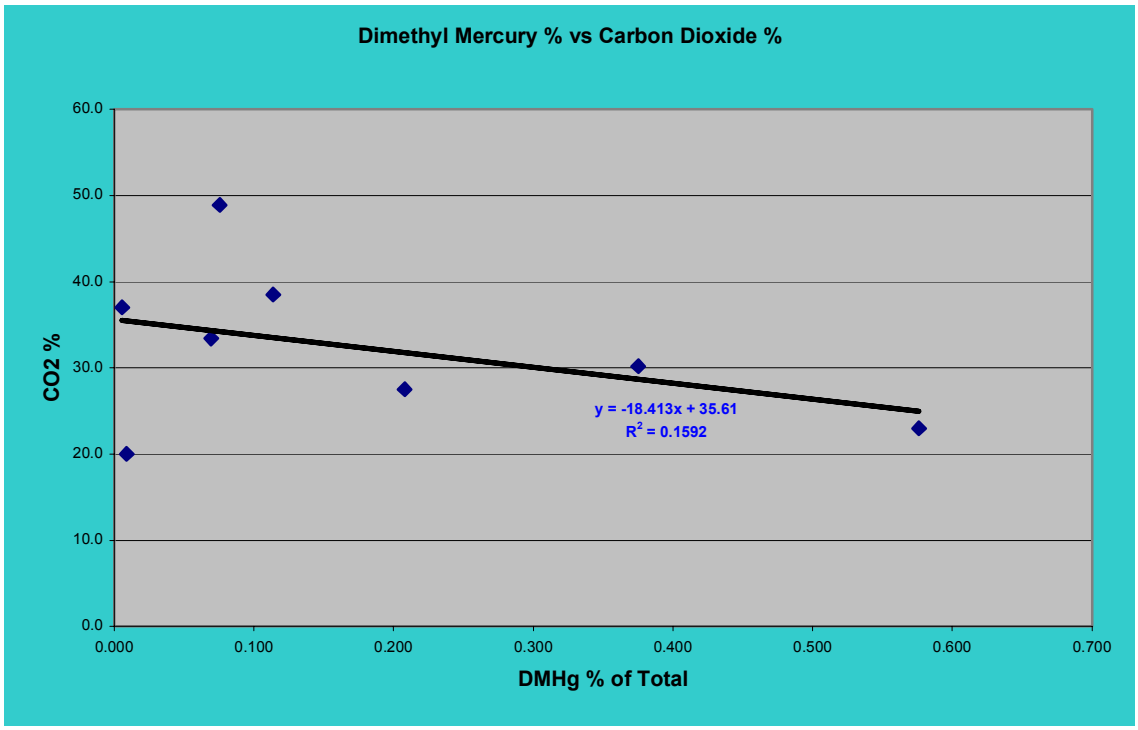
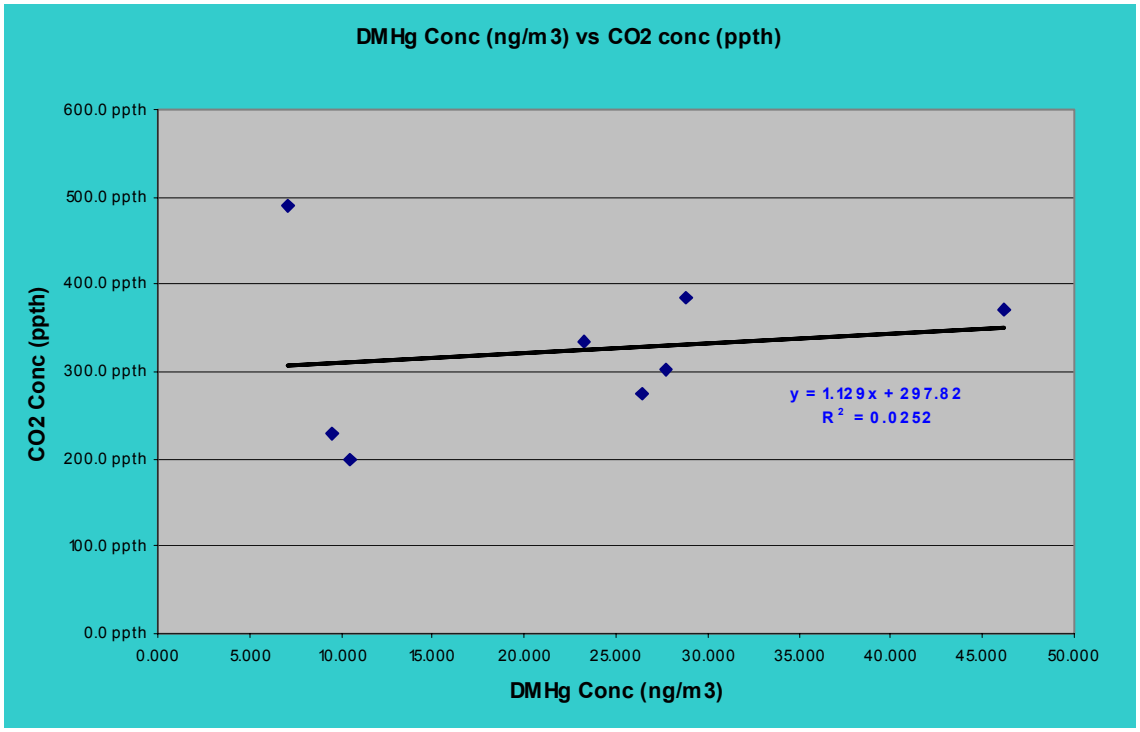

Dimethyl Mercury % vs Carbon Dioxide %
60.0
50.0
40.0
30.0
20.0
10.0
0.0
CO2 %
y = -18.413x + 35.61
R2 = 0.1592
0.000
0.100
0.200
0.300
0.400
0.500
0.600
0.700
DMHg % of Total


DMHg Conc (ng/m3) vs CO2 conc (ppth)
600.0 ppth
500.0 ppth
400.0 ppth
300.0 ppth
200.0 ppth
100.0 ppth
0.0 ppth
CO2 Conc (ppth)
y = 1.129x + 297.82
R2 = 0.0252
0.000
5.000
10.000
15.000
20.000
25.000
30.000
35.000
40.000
45.000
50.000
DMHg Conc (ng/m3)