

Field Test Measurements at Five Municipal Solid Waste Landfills with Landfill Gas Control Technology

Final Report



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Final Report

Prepared for:
Susan A. Thorneloe
US Environmental Protection Agency
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Prepared by:
ARCADIS G&M, Inc.
4915 Prospectus Drive, Suite F
Durham, North Carolina 27713

Foreword

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This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director
National Risk Management Research Laboratory

Notice

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1. Introduction

The purpose of this field test program is to generate data that may be used to update EPA's factors for quantifying landfill gas emissions from municipal solid waste (MSW) landfills. Because of health and environmental concerns, EPA issued in 1996 New Source Performance Standards (NSPS) and Emission Guidelines (EGs) for new and existing MSW landfills. These regulations are contained in 40 CFR Parts 51, 52, and 60, *Standards of Performance for New Stationary Sources and Guidelines for Control of Existing Sources: Municipal Solid Waste Landfills* (U.S. EPA, 1996, 1991a, 1991b, 1991c). These regulations require that large landfills collect and control landfill gas emissions.

Landfills are listed as a source for residual risk evaluation as part of EPA's Urban Air Toxic Strategy. Landfills are also subject to New Source Review under Title V of the Clean Air Act. The data being used for issuing air permits, developing estimates for emission inventories and environmental or risk assessments, are obtained from EPA's emission factors found in Chapter 2.4 of AP-42 (U.S. EPA, 1997). Factors for evaluating uncontrolled emissions and also combustion by-products are included in AP-42.

Much of the data used in developing the existing set of landfill gas emission factors in AP-42 were collected in support of the NSPS and EGs. Therefore much of this data is at least a decade old. Changes to the design and operation of MSW landfills have occurred that are suspected to influence MSW landfill air emissions. In addition, improvements in quality assurance (QA) and EPA test methods have occurred that enable better detection limits and higher quality data.

Through a Cooperative Research and Development Agreement (CRADA 01/02 CR1 26CFX81 80401F), the U.S. Environmental Protection Agency (EPA) formed a partnership with the Environmental Research and Education Foundation (EREF) to collect comprehensive and up-to-date data at U.S. MSW landfills. Field testing was conducted in two phases. The first phase helped finalize sampling and analytical methods used for the raw landfill gas and combustion by-product emissions. The second phase implemented the agreed upon methods using Category II QA project plan that included on-site auditing of field tests. The field testing began in November 2002 and was completed in June 2005. EPA's Office of Research and Development (ORD) worked in cooperation with industry partners and EPA's Office of Air Quality Planning and Standards (OAQPS) in establishing scope, field sampling and analytical protocols, and site selection. The field testing was conducted by ARCADIS G&M, Inc.

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(ARCADIS), as contractor to the EPA National Risk Management Research laboratory (NRMRL) Air Pollution Prevention and Control Division (APPCD), under several work assignments as part of the Onsite Laboratory Support Contracts (68-C-99-201 and EP-C-04-023).

Testing has been conducted in parallel to this field test program and is providing data that evaluates potential fugitive emissions from landfills. Data has also been collected to help quantify the emission differences between sites with and without leachate recirculation (EPA-600/R-05/072). In addition, guidance has been developed for evaluating the air pathway from older landfills (EPA-600/R-05/123a). The data from this effort, field studies, and data collected from industry and state and local regulatory agencies will be used in updating AP-42. Once updated factors are available, EPA's Landfill Gas Emission Model (LandGEM) will be updated to reflect the newer information (EPA-600/R-05/047). The revised emission factors for estimating uncontrolled emissions and combustion by-products will be provided in a new release of AP-42 including an updated background information document.

The site selection criteria for identifying potential sites for this study included: (1) no enforcement actions associated with the site; (2) the site must be in compliance with applicable EPA regulations (Clean Air Act and Resource Conservation Recovery Act); (3) the site must have state-of-the-art combustion technology in place for landfill gas control; and (4) the combustion technology must be representative of what is typical at U.S. landfills. Because of the potential benefit from utilization of landfill methane, EPA promotes landfill gas-to-energy projects through its Landfill Methane Outreach Program (LMOP). (www.epa.gov/lmop) Updated statistics from LMOP indicate that there are more than 400 landfill gas-to-energy projects in the U.S. (U.S. EPA, 2007). There is also information providing distribution of energy recovery projects in the U.S. (Thorneloe et al., 2000) This information was used in selecting the type and number of combustion technologies to include in this study. Ideally it would be nice to include a wider range of technologies but available funding limited the number to five facilities. The technologies that were included in this evaluation were two enclosed flares, two internal combustion (IC) engines, and one direct gas-fed boiler.

Sites that use leachate recirculation to accelerate waste decomposition were excluded as potential candidate sites. It may be important in future studies to explore how leachate recirculation may affect landfill gas emissions. However, this study did not include sites that use leachate recirculation or other liquid additions to accelerate waste decomposition.

1.1 Objective/Purpose and Intended Use of Project Results

The objective of this project was to collect and provide current data from U.S. MSW landfills with state-of-the-art control technology used for reducing landfill gas (LFG) emissions. Comprehensive testing was conducted of the raw landfill gas and the combustion outlet exhaust. The data will be used to help develop emission factors for use in updating EPA's AP-42 for estimating uncontrolled emissions from MSW landfills and combustion by-product emissions. Pollutants of concern include methane (CH₄), volatile organic compounds (VOCs), persistent bioaccumulative toxics (PBTs) such as mercury (Hg), and hazardous air pollutants (HAPs) such as benzene, vinyl chloride, and methyl ethyl ketone. The data will also be used to supplement AP-42 and to provide QA to data previously supplied by industry and others as part of the AP-42 update.

1.2 Scope of Project

The first phase of the project included two sites in the Northeast (Landfills A and B). Input for Phase I was obtained from EREF and EPA's Office of Air Quality Planning and Standards to identify appropriate sampling and analytical protocols and QA. Input was also obtained to identify pollutants of concern for the raw landfill gas (collected from the header pipe but upstream of gas pretreatment or condensate knockout) and combustion by-product emissions. Prior to initiating Phase 2, a review was conducted to determine changes needed to sampling and analytical protocol and QA. These changes in sampling, analytical protocol and QA are listed in section 3.5. The second phase included three sites located in the mid-west (Landfills C, D and E). Phase 1 testing took place from November 1 through November 5, 2002. Phase 2 testing took place from May 12 to May 16, 2004 for Landfills C and D, and from June 22 to June 23, 2005 at Landfill E.

The pollutants of interest for the raw (untreated) landfill gas included VOCs, non-methane organic compounds (NMOCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hydrogen sulfide (H₂S), carbonyls (acetaldehyde, formaldehyde), and Hg (total, elemental, and organo).

The pollutants of interest for combustion outlet exhaust included carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), NMOCs as total hydrocarbons (THCs), hydrogen chloride (HCl), total Hg, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatics hydrocarbons (PAHs), and toxic heavy metals.

1.3 QA Considerations

This test program was conducted to meet Category II QA requirements. A generic QA program plan (QAPP) was prepared for the field test project. In addition, a site-specific QAPP was prepared for each field test.

This project set out to produce data that qualified to receive the "A" rating with respect to the rating system described in Section 4.4.2 of the Procedures for Preparing Emission Factor Documents (EPA-454/R-95-015). The cited EPA document provides a clear description of the requirements for an "A" data quality rating:

"Tests are performed by using an EPA reference test method, or when not applicable, a sound methodology. Tests are reported in enough detail for adequate validation and raw data are provided that can be used to duplicate the emission results presented in the report."

The Data Quality Objectives (DQOs) were specified in the Generic and Site-Specific QAPPs. The extent to which this program achieved the DQOs was reported in detail in each of the landfill test reports. Overall the DQOs were met except for a few limited cases such as dimethyl mercury for landfills A and B. In addition there were issues with PAH analysis which is discussed in more detail in this report. The issues that were identified in Phase 1 were addressed in Phase 2 so that the DQOs were met as explained in the individual reports. The list of changes made between Phases 1 and 2 is provided in Section 3.5 of this report.

As part of the QA process, an EPA QA representative conducted a Technical Systems Audit (TSA) of the sampling operations during the Landfill C tests. The Audit Report indicated that the sampling operations were in compliance with standard operating procedures (SOPs) and methods.

The following two sections discuss the two groups of measurements that did not produce the results as planned. All other measurements were conducted and produced results as originally planned.

1.3.1 PCDD/PCDF/PCB/PAH Measurements

Method 23 was used to evaluate the concentrations of PAHs and PCBs in the raw LFG for the two sites included in Phase 1 (Landfills A and B).

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In order to achieve the desired low detection limits typically required of these target analytes, the samples had to be greatly concentrated. The process of concentrating the sample extracts produced recovery extracts that were extremely concentrated in some other (not PAHs or PCBs) organic constituents. Those concentrations were sufficiently high to cause instrumental interferences and prevented the extracts from being analyzed to give the required low detection limits of the PAHs and PCBs target analytes. Injection of these organic-rich extracts would have over-ranged and corrupted the analytical instruments, necessitating major instrument repair and cleaning.

In fact, commercial laboratories even declined to attempt to analyze these extracts. The alternative of not concentrating the samples to avoid instrument over-ranging is possible but would produce PAHs and PCBs method detection limits so high as to render the measurements not meaningful. Therefore, during subsequent tests for Landfills C, D and E, these samples were not included in the target list. However, PAHs were analyzed in the combustion outlet exhaust.

1.3.2 Mercury Measurements

Landfills have been found to contain organo-mercury (Lindberg et al, 2005). Because the available organo-mercury measurement and analysis methods are not established EPA standard test methods, questions were raised about their application to landfill gas given the range of constituents of potential interferences. Phase 1 conducted a review of the protocol of these organo-mercury analysis methods and included QA checks to help in the evaluation of the methods. For both Phase 1 sites (Landfills A and B), unsatisfactory spike recoveries were obtained. ARCADIS in working with Frontier Geosciences, the subcontractor laboratory, determined that reducing the sample volume could result in more satisfactory spike recoveries. To help in improving information on the precision of the protocol for organo-mercury, a second analytical laboratory was contracted to compare results for one of the five landfills (i.e., Landfill E). These results were reported in the Landfill E report.

During the course of the test program, after Phase 1 (Landfills A and B) was completed, a review of mercury sampling and analysis was conducted including an audit of Frontier Geosciences laboratory's mercury analysis operations. This resulted in improving the procedures that were used in Phase 2. The conclusion is that organo-mercury sampling and analysis can provide useful results and that refinements in the protocols will improve the methods' applicability, accuracy, and precision.

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Lindberg et al, 2005 reported mercury measurement results from a total of nine landfills. The methodology for sampling and analysis of total, di-methyl, and mono-methyl used in these tests were very similar to the methodologies used at the five landfills included in this report, although sample volumes were slightly different. The range of total mercury in the Lindbergh report is from 10 to 11,500 ng/m³ while the range of total mercury in this report is from 158 to 1330 ng/m³. Overall the concentration of total Hg in the Lindbergh paper is much higher (as much as an order of magnitude in some cases) than the total mercury concentrations included in this report. The range of dimethyl mercury in the Lindbergh paper is from 4.5 to 99.8 ng/m³ while the range of dimethyl mercury in this report is from 6.5 to 77 ng/m³. Overall the concentrations of dimethyl mercury reported in this report and the Lindberg paper are similar. The range of monomethyl mercury in the Lindbergh paper is from ND to 39 ng/m³ while the range of monomethyl mercury in this report is from ND to 8.2 ng/m³. Overall the concentration of monomethyl mercury in the Lindbergh paper is higher than the monomethyl mercury concentrations included in this report.

Prestbo et al. (2003) determined total and dimethyl mercury concentrations in raw LFG and found that dimethyl mercury comprised from 1 to 60 percent of the total mercury in the LFG. Vasuki et al. (2003) measured total and dimethyl mercury concentrations in Delaware LFGD and found that dimethyl mercury comprised about 8 percent of the total LFG mercury. The percent mercury of the Vasuki et al (2003) paper is very comparable with the data reported here for the five landfills tested, however, the percent dimethyl mercury reported by Prestbo et al. (2003) appears to be very high by as much as an order of magnitude. The discrepancy in the percent of dimethyl mercury in LFG will be addressed in a follow-on study.

During the course of the test program, after Phase 1 (Landfills A and B) was completed, ARCADIS' QA staff conducted an in-depth review of the mercury measurement methodologies by conducting an audit of Frontier Geosciences laboratory's mercury analysis operations. The results of that audit were included as a part of the Phase 2 (Landfills C and D) test reports. The findings were that the mercury measurement methods were capable of producing useable results, while the methods were undergoing continuing refinements. Progress has been made steadily to improve the methods' applicability, accuracy, and precision.

2. Landfill Descriptions

The five landfills included in this evaluation were MSW landfills with gas collection and control technology. Two are located in the northeast and three were located in the mid-west. All five are still operational (i.e., accepting waste). Characteristics of these landfills are listed in Table 2-1.

Table 2-1. General Description of Tested Landfills

	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Year that Waste Acceptance Began	1972	1967	1992	1991	1971
Area/Waste Footprint (acres)	56	40	63	31	240
Amount of waste (tons)	2,700,000 in 2003	4,000,000 in 2003	6,400,000 in 2004	2,350,000 in 2004	14,500,000 in 2005
Amount of waste (cubic yards)	---	---	1,580,000 in 2003	421,639	---
Facility estimated LFG extraction rate (standard cubic feet per minute) ^a	1700	1500	600	400	4800
Combustion Control Technology	Internal Combustion Engine	Flare	Internal Combustion Engine	Flare	Boiler
Field Test Dates	11/1/2002 to 11/2/2002	11/4/2002 to 11/5/2002	5/12/2004 to 5/13/2004	5/15/2004 to 5/16/2004	6/22/2005 to 6/23/2005

^a Extraction rate is what was collected, NOT production rate, and it is estimated

2.1 Characteristics of Landfills Selected for Field Tests

2.1.1 Landfill A

Landfill A is located in the Northeast and it began operation in 1972. Available information provided by the landfill site operator indicated that the site had 2,700,000 tons of waste in place in 2003, over an area of 56 acres. The landfill used 3,375 feet of horizontal collectors to collect the LFG. As of 2002, 29 vertical wells were in place to extract landfill gas. The collected gas was piped to two reciprocating internal combustion (RIC) engines. Any excess gas was flared. At this site, one of the two RIC engines was selected for field testing. The engine tested was selected arbitrarily.

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2.1.2 Landfill B

Landfill B was located in the Northeast and began operation in 1967. Based on information provided by the facility operator, the site had 4,000,000 tons of waste in place, over an area of 40 acres in 2003. Approximately 2,500 feet of horizontal collectors were used to collect landfill gas. Operators stated that 49 vertical wells were used to extract landfill gas which is piped to an enclosed flare system.

2.1.3 Landfill C

Landfill C is located in the Midwest and began operation in 1992. Based on information provided by the site operator, Landfill C has approximately 6,400,000 tons of waste in place as of August 2004. Landfill gas is extracted using 54 vertical wells at a rate of 600 standard cubic feet per minute (scfm). The gas was piped to two Caterpillar 3560 engines. Excess gas was combusted in an enclosed flare.

2.1.4 Landfill D

Landfill D is located in the Midwest and began operation in 1991. Based on information provided by the site operator, Landfill D has approximately 2,350,000 tons of waste in place as of August 2004. The waste footprint covers an area of 31 acres. Landfill gas is extracted using 21 vertical wells at a rate of 400 cubic feet per minute. Extracted gas is piped to an enclosed flare.

2.1.5 Landfill E

Landfill E is located in the Midwest and began operation in 1971. As of June 2005, the landfill has 14,500,000 tons of waste in place covering an area of 240 acres. The LFG was extracted with 320 vertical wells and filtered, de-watered, compressed, and piped to the end users. The flow rate of the landfill gas was 4,800 scfm. This site had a number of innovative uses of landfill gas including producing steam for greenhouses, providing fuel for a large industrial boiler (replacing fuel oil), providing fuel for an asphalt plant, and the residual gas was flared. Demand and seasonal factors largely determined the use pattern and the maximum and minimum usage rates.

2.2 Description and Characteristics of Combustion Technology

2.2.1 Enclosed-Ground Flare (Landfills B and D)

2.2.1.1 Landfill B

A Perennial Energy Enclosed Ground Flare Station, rated at a maximum LFG input rate of 1500 scfm, was used to combust landfill gas at landfill B. A burner array and an automatic louver system were designed to control gas and combustion air distribution. Manufacturer information indicated that the flare was designed to obtain a minimum residence time of 0.6 seconds at 1400 °F. The station included a condensate removal device to prevent liquids from contacting the flare burners. The system also included a flame arrestor to prevent flame propagation into the LFG header pipe and collection system. The unit was reported to be able to operate within a 5-to-1 turndown ratio [54.0 to 10.8 million British Thermal Units per hr (MMBtu/hr)]. The manufacturer also reported minimal production of NO_x and effective destruction of hydrocarbons.

2.2.1.2 Landfill D

The enclosed ground flare evaluated at Landfill D was a John Zink Model 72 rated at a maximum LFG input rate of 695 scfm. A condensate removal system prevented liquids from contacting the flare burners. A flame arrestor prevented flame from propagating from the burner array back into the LFG header pipe and collection system. A burner array and an automatic louver system controlled gas and air distribution to achieve effective combustion. The manufacturer claimed that the unit could be operated satisfactorily within a 5-to-1 turndown ratio (from 20.9 to 4.0 MMBtu/hr). The system was designed for a minimum residence time of 0.7 seconds at 1800 °F to combust hydrocarbons with minimal production of NO_x.

2.2.2 IC Engine (Landfills A and C)

2.2.2.1 Landfill A

Landfill A utilized a bank of four Caterpillar (CAT) generator sets for destruction of LFG and generation of electricity. The engines were CAT 3412 four-stroke IC engines, adapted for landfill gas. The CAT 3412 was a spark-ignited (SI) V-12 engine with displacement of 1649 cubic inches. The engine was turbocharged and after-cooled, and had a cylinder bore diameter of 5.4 inches and a stroke of 6.0 inches. Engine #2

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was randomly selected and was tested. The engine was connected to a Caterpillar SR4 Generator that was rated at 470 KW.

2.2.2.2 Landfill C

Landfill C utilized a bank of two Caterpillar generator-sets for destruction of LFG and generation of electricity. The engines were CAT 3516 four-stroke engines, adapted for LFG fuel. The CAT 3516 was a spark-ignition (SI) V-16 engine with 4210 cubic inches displacement. The engine was turbocharged and after-cooled, and had a 6.7-inch diameter cylinder bore and a 7.5-inch stroke. The engine drove a Caterpillar SR4 Generator that was rated at 800KW (at a 0.8 power factor). Engine #1 was randomly selected and tested. The engine did not have pollution control equipment installed.

2.2.3 Boiler (Landfill E)

2.2.3.1 Landfill E

The tested boiler was a Combustion Engineering Model 33-7KT-10, A-Type Package Boiler, rated at 80,000 pounds-per-hour of 250 psi steam. The boiler was fueled by the collected LFG and produced base-load steam for an industrial facility. The boiler was located on the industrial facility's property, located approximately three miles from Landfill E.

3. Test Operations

The testing operations were conducted during spring through late fall (May through early November), when ambient air temperatures were above freezing.

Sample collection and other testing operations typically required seven- to eight-person sampling teams working for two full days. Prior to the sampling crew arriving at the landfills, the host facility operator was asked to install the necessary sampling ports, if these were not already present. In the case of Landfills C and D, excavation of soil was needed to expose the underground raw LFG pipes.

Other than these modifications to allow sampling equipment access, facility modification was not required or observed to have happened immediately prior to these tests.

3.1 Sample Locations

Two kinds of samples were collected - the raw LFG and the exhaust gas from the combustion-based emission control systems.

The raw LFG samples were collected from the LFG header pipe that connects the landfill's network of collection pipes and wells. The sample ports were upstream of the condensate removal unit, blower/compressor, and flow control or distribution equipment. Hence, the collected samples are representative of the raw LFG in its "natural" state.

During Phase 1 testing at Landfill A, a sample of condensate was collected from the LFG pipe leading to the engines. That location was downstream of the condensate removal unit and the condensate sample was not specified in the QAPPs. The sample was judged to be extraneous to the test program and had unclear value. Analysis of that sample was not useful without corresponding analysis of a vapor phase sample collected at the same location. Therefore, that condensate sample was not analyzed and similar samples were not collected during subsequent landfill tests.

For the tested engines and boiler, the exhaust gas samples were collected at their stack as these control devices had distinct stack pipes. The tested enclosed flares did not have distinct stacks as the whole flare unit served as the combustion unit and the stack. For all tests, the sample locations were selected to allow for isokinetic sampling.

3.2 Target Analytes

Through consultation between the CRADA partners and EPA's Office of Air Quality Planning and Standards (OAQPS) and Landfill Methane Outreach Program (LMOP) in the planning phase of the project, target analytes were selected. The list of analytes in the raw landfill gas and combustion outlet was much more comprehensive than that typical for performance tests of LFG control technology.

For organo-mercury compounds, standard EPA test methods were not available. Methods that were developed through Frontier Associates were used. Using these non-promulgated procedures required more effort in terms of quality assurance. Measuring the range of constituents in LFG gas can be quite challenging when compared to measuring other emission sources where there are fewer constituents to analyze.

3.2.1 Raw Landfill Gas

Table 3-1 lists the target analytes for the raw LFG samples that were collected at the gas header pipe. The list of target analytes for the raw LFG matched closely with the constituents listed in AP-42 emission factors for landfills. In addition to these analytes, the test included the "non-AP-42" compounds: carbonyls (formaldehyde and acetaldehyde), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), speciated mercury (monomethyl, dimethyl, elemental, and total). These constituents were of interest because of their status of being on the EPA list of HAPs.

Experience gained during Phase 1 testing revealed that the extracts of the PAH/PCB samples contained excessive amounts of non-PAH organics. In order to make the extracts safe to be injected into the gas chromatograph/mass spectrometer (GC/MS), samples had to be diluted excessively. The high dilution made the method detection levels for the target PAHs too high, resulting in "non-detects" at the high detection limits. The planned analysis method could not produce the desired results at the needed detection levels. Therefore, these measurements were not included in Phase 2 testing.

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Table 3-1. Target Analytes for the Raw Landfill Gas Samples collected at the Gas Header

Target Analytes in AP-42 List of Landfill Gas Constituents		
Methane	Acrylonitrile	t-1,2-Dichloroethene
Ethane	Benzene	Tetrachloroethene
Propane	Bromodichloromethane	Toluene
Butane	Carbon disulfide	Trichloroethylene
Pentane	Carbon tetrachloride	Vinyl chloride
Hexane	Chlorobenzene	Vinylidene chloride
Carbonyl sulfide	Chloroform	Ethanol
Chlorodifluoromethane	Dimethyl sulfide	Methyl ethyl ketone
Chloromethane	Ethyl mercaptan	2-Propanol
Dichlorodifluoromethane	Ethylene dibromide	1,4-Dichlorobenzene
Dichlorofluoromethane	Ethylene dichloride	Ethylbenzene
Ethyl chloride	Methyl chloroform	Xylenes
Fluorotrichloromethane	Methyl isobutyl ketone	
1,3-Butadiene	Methyl mercaptan	Non-methane organic compounds
Acetone	Methylene chloride	Hydrogen sulfide
Acetone	Propylene dichloride	

Target Analytes Not Previously Included in AP-42		
Acetaldehyde	Mercury	Gases
Formaldehyde	Organo-mercury compounds	Carbon dioxide
Polycyclic aromatic hydrocarbon ^a	Elemental	Oxygen
Polychlorinated biphenyls ^a	Total	Moisture

^a These target analytes were part of Phase 1 testing. They were not included in Phase 2 testing because of difficulties experienced by the analytical laboratory to analyze the overly organic-rich sample extracts.

The other analytes, oxygen (O_2), carbon dioxide (CO_2), and moisture, are not pollutants but are of interest as they are useful indicators of the “quality” of the raw LFG. The concentrations of nitrogen (N_2) and O_2 are also indicators of the extent of ambient air infiltration into the LFG collection. Method 25C [for non-methane organic compound (NMOC) determination] specifically recommends that these measurements be made to determine the extent of potential air infiltration. Therefore, while measurements for methane (CH_4), CO_2 , O_2 , and N_2 by Method 3C were not included in the original QAPPs, these measurements were included and performed for all five landfill tests.

There was original interest in determining the concentration of the toxic heavy metals lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), manganese (Mn), and nickel (Ni) in the raw LFG. However, a method suitable for sampling the organics-rich raw LFG and capable of detecting the suspected low concentrations of the toxic metals, does not exist. Therefore measurement of the toxic heavy metals was not planned for the raw LFG.

3.2.2 Control Technology Exit

Table 3-2 lists the target analytes for the control technology exit gas samples. The focus of these analyses was to produce data that allowed for the assessment of the efficacies of the three tested control technologies to destroy the constituents in the raw LFG. They included O_2 , CO_2 , carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2), total hydrocarbons (THCs), hydrogen chloride (HCl), dioxins/furans, PAHs, and the metals Pb, As, Cd, Cr, Mn, Ni and Hg.

Among the specified analytes, NMOC is the only one specified on the AP-42 list. The VOCs analyzed individually for the raw LFG were not individually targeted for the control technology exhaust gases because of the expected very low concentrations there. This assumption turned out to be not true for IC engines.

The gases O_2 and CO_2 were common combustion performance control parameters. CO, NO_x and SO_2 are criteria pollutants, the formation of which is generally associated with combustion processes.

Table 3-2. Target Analytes for the Control Technology Exit Gas

Target Analytes in AP-42 List of Landfill Gas Constituents		
NMOCs		
Target Analytes Not Previously Included in AP-42		
Gases:		Metals:
O ₂	HCl	Pb, As, Cd, Cr, Mn, Ni
CO ₂		Hg (total)
CO	PCDD/PCDF	
NO _x		
SO ₂	PAHs	

The emission reduction performance of hydrocarbons is determined using either Method 25C or 25A. If the NMOC concentration is less than 50 ppm, then Method 25A is recommended for use.

The remaining target analytes include HCl, PCDDs/PCDFs, PAHs, total Hg, and toxic heavy metals (Pb, As, Cd, Cr, Mn, Ni). These analytes are also identified in EPA's list of HAPs.

3.3 Sampling and Analysis Methods

3.3.1 Raw Landfill Gas Sampling Analysis Methods

Table 3-3 lists the sampling, analysis and measurement methods that were followed at the raw LFG header pipe location. The table also included the name of the organizations that performed the procedures. With the exception of the organic mercury methods for mercury analysis, ARCADIS staff performed the field collection of samples and associated data collection. Where multiple organizations are listed, the

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Table 3-3. Testing Methods for Raw LFG

Procedure	Description	Organization Performing Analysis
EPA Method 1	Selection of traverse points	ARCADIS G&M
EPA Method 2	Determination of gas velocity and volumetric flow rate	ARCADIS G&M
EPA Method 3C	Determination of CO ₂ , CH ₄ , nitrogen (N ₂), and O ₂ in raw LFG	Triangle Environmental Services
EPA Method 11	Determination of H ₂ S	Oxford Laboratories (Landfills A, B, C, D) Enthalpy Analytical (Landfill E)
EPA Method 23	Determination of: PCDDs/PCDFs by Method 8290, PAHs by Method 8270 PCBs by Method 1668	ALTA Analytical Perspectives
EPA Method 25C	Determination of raw LFG NMOCs	Triangle Environmental Services
EPA Method 40/TO-15	Determination of VOCs	Research Triangle Park Laboratories
SW-846 Method 0100/TO-11	Determination of carbonyls (formaldehyde, acetaldehyde)	Resolution Analytics
LUMEX instrument	Determination of elemental mercury (Hg ⁰)	ARCADIS G&M
Organic mercury methods	Determination of: monomethylmercury, dimethylmercury, and total mercury.	Frontier Geosciences (Landfills A, B, C, D, E) Studio Geochimica (Landfill E)

letters A, B, C, D, and E in parenthesis following the organization denote the landfill site for which the organization was the performing organization.

Where multiple organizations are listed, the letters A, B, C, D, and E in parenthesis following the organization denotes the landfill site for which the organization was the performing organization.

3.3.2 Control Technology Exit Sampling Analysis Methods

Table 3-4 lists the sampling, analysis and measurement methods that were followed at the control technology exit stack. As before, the table also included the name of the organizations that performed the procedures. ARCADIS staff performed the field collection of samples and associated data at this sampling location.

Table 3-4. Testing Methods for Control Technology Exit Gas

Procedure	Description	Organization Performing Analysis
EPA Method 1	Selection of traverse points	ARCADIS G&M
EPA Method 2	Determination of stack gas velocity and volumetric flow rate	ARCADIS G&M
EPA Method 3A	Determination of O ₂ and CO ₂ for flare stack gas molecular weight calculations	ARCADIS G&M
EPA Method 4	Determination of stack gas moisture	ARCADIS G&M
EPA Method 6C	Determination of SO ₂	ARCADIS G&M
EPA Method 7E	Determination of NO _x	ARCADIS G&M
EPA Method 10	Determination of CO	ARCADIS G&M
EPA Method 23	Determination of: PCDDs/PCDFs by Method 8290, PAHs by Method 8270 PCBs by Method 1668	ALTA Analytical Perspectives
EPA Method 25A	Determination of flare stack gas NMOCs, as THC's when total organic concentration was less than the 50 ppm Method 25C applicability threshold	ARCADIS G&M
EPA Method 26A	Determination of HCl	Resolution Analytics
EPA Method 29	Determination of toxic heavy metals	First Analytical Laboratories
LUMEX instrument	Determination of elemental mercury (Hg ⁰)	ARCADIS G&M

3.4 Field Test Sampling Operations Narrative

As stated earlier, sampling typically required a sample team with seven or more experienced samplers. Prior to the tests, site visits to each landfill were conducted to

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gather necessary information for developing the quality assurance project plans and making arrangements for the field tests. The ARCADIS field chief noted the availability of sample ports and made arrangements with the host facility to have them installed if suitable ports were absent. He confirmed that the necessary staging area was available and that needed electrical utilities were accessible.

Two or more days before the scheduled tests, ARCADIS staff transported its field sampling trailer to the site. The trailer carried the needed sampling instruments, supplies, and emission monitors. Typically, one day of on-site preparation was needed before the scheduled test began.

The actual sample collection required two full days. All measurements and samples were collected in triplicate. The test samples and the required QA samples (field blanks and spike samples) were prepared, recovered, and recorded on sample chain-of-custody forms on site. The samples were transported back to ARCADIS' offices in Durham, North Carolina, by ARCADIS' sampling truck-trailer. The sample custodian, together with the sampling crew chief, made the arrangements to deliver the samples to the subcontracted laboratories for analysis.

3.5 Variation from Test Methods or Planned Activities

The test program for the five landfills spanned over three and a half years. Results from the earlier tests were used to guide the later tests. Some of the originally planned test methods were substituted by other methods and are described in the following sections.

3.5.1 Method Exceptions

Laboratory analytical procedures followed those prescribed by the specified methods, with the following exceptions.

3.5.1.1 Raw Landfill Gas

Alternative method for the raw landfill gas samples included the following:

- Carbonyls were analyzed by EPA TO-11, instead of the originally selected Method 8315. Methods TO-11 and 8315 closely resemble each other.
- PAHs in the raw LFG were to be analyzed by SW-846 Method 8270 - The sample extracts resulting from the raw LFG were found to contain excessive amounts of non-PAH organics. In retrospect, this should have been expected as the LFG is organic-rich (~40%). In order to make the extracts safe for injection into the gas chromatograph mass spectrometer (GC/MS) (i.e., not cause instrument damage), they have to be diluted significantly. The high dilution makes the method detection levels for the target PAHs too high, resulting in “non-detects” at high detection limits. The planned analysis method could not produce PAH concentrations at the needed detection levels. The sample extracts are in storage and may be submitted for analysis if a suitable method is available. These analyses were deleted from the Landfills C, D, and E tests.
- PCBs in the raw LFG were analyzed by EPA Method 1668 (EPA 812/R-97-001) as specified in the QAPP. However, similar to the difficulties experienced for the PAH analysis, in order to make the extracts safe to be injected into the GC, they have to be diluted excessively. The planned analysis method could not produce the desired results at the needed detection levels. These analyses were deleted from the Landfills C, D and E tests.
- NMOCs were analyzed by the GC/MS Method as described in EPA Publication EPA/600-R-98/16.
- VOCs and CH₄ were analyzed by EPA Method TO-15, with GC/MS and with GC/flame ionization detector (FID).
- Method 3C for the analysis of CH₄, CO₂, O₂, and N₂ was added to support the Method 25C analysis, as recommended by Method 25C.
- For Landfills C, D, and E, the sampling procedure for dimethylmercury was altered by reducing the sample size volume on the Carbotrap from 10 L to 0.5 L.

3.5.1.2 Control Device Exit

Alternative method for the control device exit samples included the following:

- Method 25A was to evaluate organic compound concentrations in the combustion outlet because of the low concentrations detected in Phase 1 sites. Method 25C is applicable at concentrations of 50 ppmv or more. However, test results showed that the IC engines exhaust gases contained several hundred ppm of THC's. Therefore, for any future field tests for IC engines, Method 25C should be used to quantify NMOCs rather than Method 25A.
- For Method 23 samples collected at Landfill C, analyses for PAHs were performed by CARB Method 429 as opposed to Method 8270. However, these methods are comparable. CARB Method 429 contains procedures for sampling, sample recovery, clean-up, and analysis. Method 8270 is strictly an analytical method. CARB Method 429 is specific to 19 PAHs, the target analytes of this portion of the specified tests. The 19 PAHs are a subset of the 200+ target analytes listed for Method 8270 for semivolatile organic compounds (SVOCs). Though specific compounds called out for use in instrument performance verifications, internal standard preparation, surrogate standards and continuing calibration verifications/calibration checks are slightly different, both methods require them. CARB Method 429 adds another level of QC with a required recovery standard. Method performance and acceptance criteria for recoveries are better defined in CARB Method 429 and meet or exceed those stated in Method 8270C. As long as any additional compounds reported by the laboratory using CARB Method 429 are included in the calibration standards and acceptable response factors are demonstrated, using CARB Method 429 is essentially equivalent to using SW-846 Method 8270.
- As a result of examining the test results from Landfill A, which showed very low concentrations of PCDDs/PCDFs/PAHs at the exit of an enclosed flare, no Method 23 sampling was conducted at Landfill D, also a site with an enclosed flare. A decision was made to not sample for PCDDs/PCDFs at the exit of the enclosed flare systems because the combustion gas temperature conditions found in the exit of an enclosed flare system were not likely to allow the formation of PCDDs/PCDFs. This also eliminated analysis of PAHs which uses the same sample.

4. Test Results

The following sections present data summaries of the measurements that were planned and conducted. Section 4.1 and its subsections present data related to the raw LFG. Section 4.2 and its subsections present data for the combustion exhaust gases at the exit of the flares, engines, and boiler.

4.1 Raw Landfill Gas

4.1.1 Landfill Gas Flow Rate and Temperature

Table 4-1 presents information regarding the LFG flow rate for each landfill. The LFG flowrate ranged from a low of 400 scfm for Landfill D to over 4000 scfm for Landfill E. Landfill E was a much larger landfill as it was reported to have over 14 million tons of waste in place, while Landfill D had about 2.4 million tons of waste.

The LFG header pipes at all the landfills did not have sufficiently long straight pipe sections to allow ideal EPA Method 2 gas velocity measurements. Velocity measurements were made under non-ideal conditions and were able to provide crude estimates of the LFG flowrates. For the purpose of this study, the estimated LFG flowrates were judged to be sufficiently accurate. For their intended use to estimate pollutant emission rates, the added cost of needed improvement of the landfill gas header piping system, and associated potential schedule delay, were not warranted.

Temperature of the LFG ranged from 54 to 71°F. Landfill E, with the largest volume of LFG, also had the highest measured LFG temperature.

4.1.2 Landfill Gas Constituent Concentrations

The principal focus of this test program was to determine the constituents that were present in the raw LFG. The major constituents consist of CH₄, CO₂, N₂, O₂ and moisture. These constituents were present in percent levels. Other constituents were the various organic compounds which were present in ppm or lower concentrations. Landfill gas also contained mercury including methyl- and dimethylmercury.

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Table 4-1. Raw LFG Flow Rates

Parameter	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Facility flowrate readings (scfm)	1650 – 1700 J	1500 J	550 – 600 J	400 J	4340 J
ARCADIS measured flow rate by pitot probe (scfm)	1580 J	1745 J	700 J	380 -850 J	3860 J
LFG gas temperature (°F)	57	62	56	54	71
Reported amount of waste (ton)	2,700,000 in 2003	4,000,000 in 2003	6,400,000 in 2004	2,350,000 in 2004	14,500,000 in 2005
Header pipe inner diameter (in)	12	11	14	11	16
Straight pipe upstream (No. of pipe diameters)	~8	< 2	> 8	> 8	< 2
Straight Pipe Downstream (No. of pipe diameters)	~4	< 2	> 8	> 8	< 2
Vacuum in header pipe, Inches water column (WC.)	34 - 35	--	21	---	--

J –Estimated value per EPA/G-8 guidance

4.1.2.1 Major Constituents (CH_4 , CO_2 , O_2) by Method 3C and NMOCs by Method 25

Table 4-2 presents the concentrations of the major LFG constituent components and NMOCs. The table provides the range and average for each of the constituent concentrations.

The concentrations CH_4 , CO_2 , O_2 , N_2 , moisture and NMOCs varied over quite a wide range between the landfills. In particular, Landfill D showed unusually high CH_4 content of more than 55 percent. Landfill B showed the lowest methane concentration, at just below 40 percent.

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Table 4-2. Raw LFG Major Constituents

	Constituent		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Method 25C	Methane (% v/v)	Range Average	48.0 – 49.8 48.8	37.7 – 40.6 39.2	54.6 – 57.7 56.0	57.4 – 59.5 58.6	46.7 – 50.9 49.5
	Carbon Dioxide (% v/v)	Range Average	38.1 – 39.4 38.7	29.5 – 31.9 30.7	45.2 – 47.2 46.2	40.2 – 41.7 41.0	33.3 – 36.3 35.3
	NMOC (ppm as hexane)	Range Average	297 – 491 374	314 – 377 355	3650 – 9330 5870	971 -1024 1006	194 – 288 233
Method 3C	Methane (% v/v)	Range Average	43.5 – 45.4 44.5	35.2 – 37.3 36.1	47.4 – 49.1 48.0	54.3 – 55.6 55.1	46.8 – 51.7 49.5
	Carbon Dioxide (% v/v)	Range Average	35.2 – 36.9 36.1	28.2 – 29.9 29.0	35.4 – 36.9 35.9	37.6 – 38.5 38.1	30.2 – 31.9 31.3
	Oxygen (% v/v)	Range Average	1.6 - 1.8 1.7	6.0 - 6.6 6.4	1.4 – 1.9 1.6	0.01 - 0.02 0.02	2.1 - 3.4 2.6
	Nitrogen (% v/v)	Range Average	12.7 – 13.4 13.1	24.4 – 26.2 25.6	13.5 – 18.9 15.9	9.5 – 12.8 11.2	11.9 - 16.4 13.6
Method 23	Moisture (% v/v)	Range Average	11.6 – 12.3 12.0	1.8 – 2.1 2.0	NM	NM	NM

NM – Not measured because moisture data were obtained by Method 23, which were not conducted during these tests.

All values are reported on an as-is basis, without correction for nitrogen-indicated potential air infiltration.

Data on the moisture in the LFG were only available for Landfills A and B because the data is a computed output of the Method 23 sampling procedure. Method 23 samples were collected for PAH and PCB analysis. This procedure was deleted from the test program after experiences with Landfills A and B samples revealed that the analysis could not be done. More explanation of this finding will be presented later in this report. Without Method 23 sampling for Landfills C, D, E, no moisture data were collected.

4.1.2.2 Other Constituents

In addition to the major constituents, the other lower concentration constituents were of interest because of their potential to cause adverse health effects. The following sections summarize the results related to these compounds.

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4.1.2.2.1 VOCs by Method 0040 with TO-15

Table 4-3 presents the average concentrations of the target volatile organic compounds. The concentration data were obtained by summa canister samples collected using Method 40 procedures. Analysis was performed by Method TO-15, with gas chromatography and mass spectrometry (GC/MS). The alkanes (C2 through C6), being present in much higher concentrations, were analyzed by GC flame ionization detection (FID).

Table 4-3. Raw LFG Volatile Organic Compounds

Compound	Unit	Method Detection Limit (NDL) Range ^a		Average Concentration ^b				
				Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
By gas chromatography flame ionization detector (GC/FID)								
Ethane	Part per million by vol (ppmv)	1	1	6.2	4.6	14.3	5.6	14
Propane	ppmv	1	1	8.9	5.9	40.0	30.5	13.0
Butane	ppmv	1	1	4.9	3.3	37.9	ND	3.6
Pentane	ppmv	1	1	3.2	2.6	26.6	2.4	1
Hexane	ppmv	1	1	Not Detected (ND)	ND	28.4	2.5	ND
By TO-15 gas chromatography and mass spectrometer (GC/MS)								
Dichlorodifluoromethane (Freon 12)	Part per billion by vol (ppbv)	0.2	0.3	118	468	1600	1240	232
1,2-Chloro-,1,2,2-Tetrafluoroethane (CFC114)	ppbv	0.2	0.2	8	44	127	110	15.3
Chloromethane	ppbv	0.1	0.2	12	72	1263	232	ND
Vinyl chloride	ppbv	0.2	0.2	97	410	768	1200	63
1,3-Butadiene ((Vinylethylene)	ppbv	0.2	0.3	22	89	642	326	ND
Bromomethane (Methyl Bromide)	ppbv	0.2	0.2	16	46	23	2.8	ND
Chloroethane (Ethyl Chloride)	ppbv	0.2	0.2	770	1880	30400	634	ND
Trichloromonofluoromethane (CFC11)	ppbv	0.2	0.2	51	327	504	116	8.1

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Compound	Unit	Method Detection Limit (NDL) Range ^a		Average Concentration ^b				
				Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
1,1-Dichloroethene	ppbv	0.2	0.2	1.7	8	55	21	ND J
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC113)	ppbv	0.2	0.2	2.0	11	39	19	ND
Carbon Disulfide	ppbv	0.2	0.3	14.4	134	157	93	339
Ethanol	ppbv	0.2	0.2	19.7 J	202	172	394	ND J
Isopropyl Alcohol (2-Propanol)	ppbv	0.2	0.2	114 J	356	1280	6630	2360 J
Methylene chloride (Dichloromethane)	ppbv	0.1	0.2	997	169	5350	1110	3050
Dimethyl sulfide	ppbv	20	20	ND	ND	68	ND	ND
Acetone	ppbv	0.2	0.3	328	1610	11700	12800	15500
t-1,2-dichloroethene	ppbv	0.2	0.3	2.7	9	42	53	ND
Hexane	ppbv	0.2	0.3	2470 J	1950	4940	3980	597 J
Methyl-t-butyl ether (MTBE)	ppbv	0.2	0.3	54.4	177	257	39	ND
1,1-Dichloroethane	ppbv	0.2	0.4	33.4	178	423	591	ND
Vinyl Acetate	ppbv	0.2	0.5	242	686	24	44	111
cis-1,2-Dichloroethene	ppbv	0.2	0.3	74.1	292	1640	1780	163
Cyclohexane	ppbv	0.2	0.3	165	734	3300	2270	ND
Chloroform	ppbv	0.2	0.3	40	190	744	485	ND
Ethyl Acetate	ppbv	0.2	0.3	1830	2310	1420	4600	ND
Carbon Tetrachloride	ppbv	0.2	0.5	0.8	5	ND	38	ND
Tetrahydrofuran (Diethylene Oxide)	ppbv	0.2	0.4	1180	882	1170	2060	ND
1,1,1-Trichloroethane	ppbv	0.2	0.5	4.9	31	ND	ND	ND
2-Butanone (Methyl Ethyl Ketone)	ppbv	0.2	0.3	273	1430	4570	8070	2490
Heptane	ppbv	0.2	0.2	242	918	2860	3580	331
Benzene	ppbv	0.2	0.2	73	251	1630	1200	887
1,2-Dichloroethane	ppbv	0.2	0.3	1.0	5	37	22	ND
Trichloroethylene (Trichloroethene)	ppbv	0.2	0.2	28.0	103	515	418	93.9
1,2-Dichloropropane	ppbv	0.2	0.3	0.8	5	ND	ND	ND
Bromodichloromethane	ppbv	0.2	0.2	2.6	10	ND	ND	ND
1,4-Dioxane (1,4-Diethylene Dioxide)	ppbv	0.2	0.2	1.9	9.4	7	12	ND
cis-1,3-Dichloropropene	ppbv	0.2	0.2	0.2	1.4	ND	4	ND
Toluene (Methyl Benzene)	ppbv	0.2	0.3	1330	6770	23300	30300	7950
4-Methyl-2-pentanone (MIBK)	ppbv	0.2	0.2	1070	886	2170	ND	ND

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Compound	Unit	Method Detection Limit (NDL) Range ^a		Average Concentration ^b				
				Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
t-1,3-Dichloropropene	ppbv	0.2	0.2	0.3	3	33	8	ND
Tetrachloroethylene (Perchloroethylene)	ppbv	0.2	0.3	42.1	176	1690	1020	125
1,1,2-Trichloroethane	ppbv	0.2	0.2	7.6	39	445	ND	ND
Dibromochloromethane	ppbv	0.2	0.2	ND	16	9	16	ND
1,2-Dibromoethane (Ethylene dibromide)	ppbv	0.2	0.2	1.1	7	21	ND	ND
2-Hexanone (Methyl Butyl Ketone)	ppbv	0.2	0.2	557	441	ND	ND	ND
Methyl Mercaptan (Methanethiol)	ppbv	20	20	ND	ND	ND	ND	ND
Ethylbenzene	ppbv	0.2	0.3	575	2800	5890	8120	ND
Chlorobenzene	ppbv	0.2	0.2	195	229 J	833	21	135
m/p-Xylene (Dimethyl Benzene)	ppbv	0.2	0.65	3730 J	3980	9200	13600	9000 J
o-Xylene (Dimethyl Benzene)	ppbv	0.2	0.3	300	1410	3660	5410	3100
Styrene (Vinylbenzene)	ppbv	0.1	0.2	29.5	222	1270	1180	420
Tribromomethane (Bromoform)	ppbv	0.2	0.3	0.4	ND	16	9	ND
1,1,2,2-Tetrachloroethane	ppbv	0.2	0.2	29.9	ND	ND	ND	ND
1-Ethyl-4-methylbenzene (4- Ethyl Toluene) <i>see Note c</i>	ppbv	0.2	0.2	79.3 J	386 J	894 J	976 J	2510
1,3,5-Trimethylbenzene <i>see Note c</i>	ppbv	0.2	0.2	79.3 J	386 J	894 J	976 J	1040
1,2,4-Trimethylbenzene	ppbv	0.2	0.3	193	949	1510	2190	2640
1,4-Dichlorobenzene	ppbv	0.2	0.3	43.4	255	328	686	ND
1,3-Dichlorobenzene	ppbv	0.2	0.3	0.5	2.03	394	650	ND
Benzyl Chloride	ppbv	0.2	0.2	6.3	20	ND	ND	ND
1,2-Dichlorobenzene	ppbv	0.2	0.3	1.9	0.4	ND	31	ND
1,1,2,3,4,4-Hexachloro-1,3- butadiene	ppbv	0.2	0.2	1.2	5	ND	ND	ND
1,2,4-Trichlorobenzene	ppbv	0.2	0.3	1.0	5	ND	ND	ND
Acrylonitrile	ppbv	20	20	ND	ND	ND	ND	ND
Dichlorofluoromethane (Freon 21)	ppbv	20	20	ND	ND	ND	ND	ND
Chlorodifluoromethane (Freon 22)	ppbv	20	20	ND	ND	ND	ND	ND
Ethyl Mercaptan (Ethanediol)	ppbv	20	20	ND	ND	ND	ND	ND
Carbonyl Sulfide (Carbon oxysulfide)	ppbv	20	20	ND	ND	ND	ND	ND

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ND - Constituent not detected at the stated method detection limits

a – Method detection limits provided by analytical laboratory

b – In computing averages, when all measurements are ND, the average is reported as ND. When one or more measurement is above detection, the ND measurement is treated as 50% of the stated MDL. Though not applicable here, the method further specifies that If MDL is not reported, a ND measurement is treated as zero.

c - 1-Ethyl-4-methylbenzene (4-Ethyl Toluene) and 1,3,5-Trimethylbenzene co-eluted from the GC and also have the same quantitation ions, thus making them indistinguishable. Therefore, the reported values represent the combined concentrations of these two compounds.

J – Estimated value per EPA QA/G-8 guidance

4.1.2.2.2 Hydrogen Sulfide (H₂S) by Method 11

Table 4-4 present the concentrations of hydrogen sulfide measured with Method 11.

H₂S concentrations ranged from a low average concentration of 13 ppmv in Landfill A to a high average concentration of 322 ppmv for Landfill E.

Table 4-4. Raw LFG Hydrogen Sulfide

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
(mg/m ³)	Range	10.7 – 26.1	26.4 – 36.1	26.8 – 110.0	32.1 – 185.6	413 – 519
	Average	18.5	32.3	78.3	102.6	458 J
(ppmv)	Range	7.6 – 18.4	18.7 – 25.6	19.0 – 78.0	22.7 – 132	291 – 366
	Average	13.0	22.9	55.5	72.7	322 J

J Estimated value per EPA QA/G-8 guidance

4.1.2.2.3 Carbonyls by Method 0100 & 8315A

Table 4-5 presents the concentrations of formaldehyde and acetaldehyde. Notably, acetaldehyde was uniformly present at a higher concentration than formaldehyde. Formaldehyde was present in the single-digit to low-tens of µg/m³. Acetaldehyde was present at concentration several times higher than formaldehyde.

Table 4-5. Raw LFG Carbonyls

			Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Formaldehyde	($\mu\text{g}/\text{m}^3$)	Range Average	2.3 – 5.0 4.1	3.3 – 4.1 3.6 J	26.9 – 46.6 33.9	16.0 – 39.0 25.0	8.1 – 11.8 9.6
	($\times 10^{-3}$ ppmv)	Range Average	1.8 – 4.1 3.3	2.65 – 3.30 2.90 J	22.7 – 37.3 27.2	12.9 – 31.5 20.1	6.5 – 9.6 7.8
Acetaldehyde	($\mu\text{g}/\text{m}^3$)	Range Average	18.9 – 67.8 45.7	21.9 – 35.0 27.0	114 – 495 242	72 – 534 348	27.9 – 151 92.4
	($\times 10^{-3}$ ppmv)	Range Average	10.3 – 37.0 24.9	12.0 – 19.2 14.8	62.4 – 27.0 132	39 – 293 191	15.3 – 82.8 50.6

4.1.2.2.4 PAHs by Method 0010 with 8270

As discussed previously in Section 3.5.1.1, attempts to analyze the PAH concentrations in the raw LFG were unsuccessful.

4.1.2.2.5 PCBs by Method 0010 with 1668

As discussed previously in Section 3.5.1.1, attempts to analyze the PCB concentrations in the raw LFG were unsuccessful.

4.1.2.2.6 Mercury

Mercury comes in various forms. It can be bound to particulates or in a gaseous form. Gaseous mercury species is either organic or inorganic. Organic mercury or methyl mercury is more toxic and regarded as a priority for determining the potential release from U.S. landfills. Previous testing has identified both methyl and dimethyl mercury in landfills.

Metallic, or elemental mercury, is an inorganic form used in products such as electrical switches, fluorescent bulbs, and thermometers. It is a liquid and can evaporate into the air as a gas. Inorganic mercury compounds take the form of mercury salts. Oxidized mercury (sometimes called ionic or reactive gaseous mercury (RGM)) is found predominantly in water-soluble forms and may be deposited at a range of distances from sources depending on a variety of factors including topographic and meteorological conditions downwind of a source. Once mercury is deposited into bodies of water like lakes or streams, it can be converted to methyl mercury through microbial decomposition in soils and sediments. In this form, it is taken up by tiny aquatic plants and animals. Fish that eat these organisms build up methylmercury in

their bodies. As ever-bigger fish eat smaller ones, the methylmercury is concentrated further up the food chain which is referred to as "bioaccumulation".

Table 4-6 summarizes the results of the mercury measurements which include organo-mercury (i.e., dimethyl and monomethyl), elemental mercury, and total gaseous mercury. Total mercury and organo-mercury were sampled and analyzed by the Organic mercury method. Elemental mercury was measured by the LUMEX instrument. Oxidized mercury was not analyzed directly but can be determined by subtracting elemental and organo-mercury from total mercury.

The dimethyl mercury data for Landfills A and B did not meet data quality objectives and the results were rejected due to low spike recoveries. During the Landfill A and B tests, total sample volumes collected for dimethyl mercury on the Carbotrap were approximately 10 L. The analysis of these samples resulted in poor recovery of spiked dimethyl mercury. According to the researchers of the analytical laboratory, the poor spike recoveries could be attributed to the migration of the spiked material during sampling. The extent of material migration was believed to be highly dependent on sample volume. Therefore spike recoveries in this instance could be improved by reducing the sample volume.

For Landfills C, D, and E, the sampling procedure for dimethyl mercury was altered by reducing the sample size volume on the Carbotrap from 10 L to 0.5 L. The modified procedure resulted in much improved spike recoveries. The details of the mercury measurement methods and method development experiences were included in the Landfill C, and D reports, which are provided in appendices to this document.

Most of the mercury found was in the elemental state. The concentrations of the organic forms of the mercury were about two orders of magnitude lower than the total and elemental mercury concentrations. The results are comparable to those reported by Lindberg et al. in 2005 for twelve landfills, although the total amount of mercury reported in Lindberg et. al. 2005 is as much as one order of magnitude greater than the total mercury reported here. In the Lindberg study, total gaseous Hg ranged from 10 to 12000 ng/m³. Dimethyl mercury ranged from 4.5 to 77 ng/m³ and monomethyl mercury ranged from non-detect to 39 ng/m³.

Total mercury concentration averages ranged from 204 to 1460 ng/m³. Of these amounts, elemental mercury was the highest component, with its averaged values ranging from 58 to 440 ng/m³. Dimethyl mercury was the next most prevalent. After discarding the Landfills A and B data because it did not meet data quality objectives, dimethyl mercury averaged concentrations ranged from 15 to 53 ng/m³ approximately.

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Monomethyl mercury was present at the lowest concentration, ranging from less than 1 to 5.4 ng/m³.

Using the total mercury measurements as the basis, the sum of the elemental, monomethyl and dimethyl mercury species contributed to about 28 to 49 percent of the total mercury measured. It is suspected that the majority of the remaining mercury is in the oxidized form.

Table 4-6. Raw LFG Mercury Compounds

			Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Total	(ng/m ³)	Range Average	601 – 676 632	158 – 234 204	423 – 427 425	723 – 751 740	1330 – 1650 1460 ^a
	(X10 ⁻⁶ ppmv)	Range Average	72.4 – 81.4 76.1	17.7 – 26.2 22.8	50.9 – 51.4 51.2	87.0 – 90.4 89.1	149 – 184 163.5 ^a
Dimethyl	(ng/m ³)	Range Average	R R	R R	6.5 – 20.9 14.8	49.7 – 53.1 51.0	17.4 – 99.8 52.5 ^a
	(X10 ⁻⁶ ppmv)	Range Average	R R	R R	0.7 – 2.2 1.5	5.2 – 5.6 5.3	1.82 – 10.5 5.5 ^a
Monomethyl	(ng/m ³)	Range Average	ND – 1.2 0.4	1.1 – 1.3 1.2	3.1 – 5.4 3.9	2.40 - 2.64 2.47	3.4 – 8.2 5.4 ^a
	(X10 ⁻⁶ ppmv)	Range Average	ND – 0.13 0.04	0.12 – 0.15 0.13	0.35 – 0.60 0.44	0.264 – 0.296 0.278	0.380 – 0.920 0.61
Elemental	(ng/m ³)	Range Average	280 – 325 308	53 – 61 58	90 – 103 99	265 – 290 278	437 – 445 440
	(X10 ⁻⁶ ppmv)	Range Average	33.7 – 39.1 37.1	6.4 - 7.3 7.0	10.8 – 12.4 11.9	31.9 – 34.9 33.5	52.6 – 53.6 53.0

R – Data rejected because spike recovery for these measurements were below acceptable range

ND – Constituent not detected at the detection limit of 0.63 ng/m³

^a - Values are averages of Frontier and Geochimica results

4.1.2.2.7 Metals by Method 29

The standard Method 29 is the reference method to determine trace concentrations of the toxic metals. However, the method was designed for sample streams that are not rich in organic constituents because it uses a strong oxidizer, potassium permanganate solution, to capture the metals. The concern with applying this method to LFG was that the potassium permanganate might react violently with the organic constituents in the LFG. If that happened, the measurement would be invalidated and analysis might also pose safety risk to the sampling personnel. Therefore, it was not included in the test program.

4.2 Control Equipment Stack

The following subsections present the results obtained from measurements made at the control equipment stack.

4.2.1 Gas Flow Rate and Temperature

Table 4-7 presents the exhaust gas flowrates and their temperatures at the stack of the five control devices. The flowrates were obtained by velocity traverse measurements performed according to EPA Method 2. The flowrates reflected the size of the control equipment and ranged from 1310 scfm for the Landfill A engine to more than 28000 scfm for the Landfill E boiler.

The enclosed flares had the highest temperatures, at about 1400 °F. This was consistent with the nature of the process. Flares do not have active heat utilization and removal. The measured temperatures were lower than the expected flame temperatures because of the introduction of dilution air.

The boiler in Landfill E had the lowest exit temperature at about 480 °F. The observed temperature was consistent with typical boiler operations. The two reciprocating IC engines resulted in exhaust temperature around 735 °F for Landfill A's Caterpillar 3412 and 1000 °F for Landfill C's Caterpillar 3516. The Caterpillar 3516 was more than twice the size of the Caterpillar 3412.

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Table 4-7. Control Equipment Exit Stack Flow Rate and Temperature

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Control Technology		Reciprocating IC Engine	Enclosed Flare	Reciprocating IC Engine	Enclosed Ground Flare	Boiler
Unit Model		Caterpillar 3412	Perennial Energy	Caterpillar 3516	John Zink Model 72	Combustion Engineering 33-7KT-10 A Type
Size or Capacity		1649 cu. in displacement, 470KW	10.8 to 54 MMBtu/hr	4210 cu. in displacement, 800KW	4.0 to 20.9 MMBtu/hr	80,000 lb/hr 250 psi steam
LFG Flowrate into Equipment (scfm) ^a		150	1500	300	400	2430
Exit Flowrate (dscfm)	Range	1290 – 1340	19700 – 22000	1890 – 2000	7830 – 8290	26820 – 30400
	Average	1310	20700	1950	8080	28690
Exit Gas Temperature (°F)	Range	732 – 738	1359 – 1419	997 – 1038	1412 – 1446	476 – 488
	Average	735	1389	1016	1437	479

a – This is a crude estimate based on the measured exit flow rate, the measured exit oxygen concentration and the major constituent analysis of the LFG.

4.2.2 Exhaust Gas Constituent Concentrations

The following sections present the concentration and emission rates of the combustion products O₂, CO₂, CO, SO₂, NO_x, THC_s, HCl, dioxin /furans, PAH_s, and toxic heavy metals.

4.2.2.1 CEM Constituents (O₂, CO, CO₂, SO₂, NO_x)

Table 4-8 presents the average concentrations of O₂, CO, CO₂, SO₂, and NO_x found in the control devices' exhaust gases. For the most part, they are unremarkable, except for the very apparent and substantially higher concentrations of CO, THC and NO_x that are produced by the engines. The boiler was by far the most efficient combustion device as it produced the lowest concentrations of CO and THC_s. The flares tended to produce more CO, especially if the more highly diluted flare exhaust gas was accounted for. In addition to producing higher concentrations of CO and THC, the engines also produced significantly higher concentrations of NO_x. The Landfill C engine, in particular, produced about 2700 ppm of NO_x, an alarmingly high level by any measure.

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Table 4-8. Control Equipment Exit O₂, CO, CO₂, SO₂, NO_x

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
O ₂ (% v/v)	Range	7.4 – 7.6	12.5 – 16.1	2.3 – 3.2	13.5 -13.5	7.2 – 7.9
	Average	7.5	14.9	2.7	13.5	7.5
CO ₂ (% v/v)	Range	12.8 – 13.2	2.9 – 4.8	15.6 – 16.5	6.3 – 6.4	12.1 -12.5
	Average	12.9	4.2	16.3	6.4	12.3
Moisture (% v/v)	Range	11.3 – 12.5	5.8 – 7.3	16.2 - 18.3	7.9 – 10.3	11.6 – 14.1
	Average	12.1	6.5	17.0	8.4	12.6
CO (ppmv)	Range	549 – 570	11 – 13	556 – 585	69 -92	ND – 14
	Average	560	10	568	80	9
SO ₂ (ppmv)	Range	29 – 39	3 – 8	–ND	ND	41 – 68
	Average	34	6	ND	ND	55
NO _x (ppmv)	Range	142 – 183	10 – 12	2280 – 3150	7.7 – 9.7	3 – 21
	Average	166	11	2730	8.5	13
Remarks			0.6 sec at 1400 °F			

ND – Constituent not detected at the detection limit of 2.0 ppmv

4.2.2.2 Other Constituents

4.2.2.2.1 THCs by Method 25A

Table 4-9 presents the concentrations of organic materials found in the control device exhaust gases. The measurement was made with a continuous emission monitor, in

Table 4-9. Control Equipment Exit Total Hydrocarbon

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
As Propane, (ppmv)	Range	645 – 786	ND – 6	893 – 994	31.3 – 35.6	ND
	Average	730	4	940	34.1	ND
As Hexane, (ppmv)	Range	323 – 393	ND – 3	447 – 497	15.7 – 17.8	ND
	Average	365	2	470	17.1	ND

ND – Constituent not detected at the detection limit of 1.0 ppmv

accordance with Method 25A. Hydrocarbons concentrations were low for Landfill E's boiler, fluctuating near the bottom of the instruments zero point. They were also very low for Landfill B's flare. Landfill D's flare had a bit more THC in its stack gas, at about 17 ppm hexane. In contrast, both IC engines produced exhaust gases that contained more than 350 ppm of hexane-equivalent hydrocarbons.

The purpose of this measurement was to determine the amount of hydrocarbons in the exhaust gases. Method 25A is suitable for this purpose. Moreover, identification and quantitation of individual organic compounds were not objectives of this test program. For future field tests, when there is a requirement to identify organic constituent species in engine exhausts, we would recommend using EPA Method 40, which is well suited to identify and quantify volatile organic compounds.

This project included measurements for PCDD/PCDFs and PAHs in the stack gases and these data are presented later in this report.

4.2.2.2.2 Dioxin/Furans by Method 23 with 8290

Combustion processes with chlorinated compounds have the potential of producing polychlorinated dioxins and furans (PCDD/PCDF). This is particularly relevant if the combustion is not efficient and if the combustion products are allowed to cool down slowly where they can come into contact with a particle-laden surface.

Sampling for PCDD/PCDFs was performed for all landfills except for Landfill D, which used an enclosed flare. The decision to exclude Landfill D was based on two considerations. Tests at Landfill B where enclosed flare was used resulted in PCDD/PCDF data that were mostly below detection limits. Further, these findings were consistent with the understanding that the flare exit gases could not possibly be cooled to reach temperatures that were favorable to dioxin formation. Given the high cost of sampling and analysis for PCDD/PCDF, it was decided not to conduct PCDD/PCDFs at the second enclosed flare site.

Table 4-10 presents the PCDD/PCDF concentrations. As can be seen, PCDD/PCDFs were mostly below detection limits, except for Landfill E. The boiler in Landfill E is a device that is understood to have the potential to present the conditions that favors PCDD/PCDF formation, which was confirmed.

4.2.2.2.3 PAHs by Method 0010 with 8270

Table 4-11 presents the concentrations of PAHs in the combustion stack gases. Consistent with the THC data presented earlier, the IC engines resulted in the highest

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concentrations of PAHs. In an attempt to provide a means of comparing the control technologies, Table 4-11 included a normalized PAH emission factor expressed as the amount of PAHs emitted per cu. ft. of LFG combusted. As shown, the IC engine at Landfill C was found to emit the highest amount of PAHs at 0.01 mg/cu. ft. LFG. In contrast, the boiler at Landfill E and the flare at Landfill B were both found to emit 0.003 mg/cu. ft. LFG.

4.2.2.2.4 HCl by Method 26A

Table 4-12 presents the HCl concentrations at the control device stacks. They ranged from about 0.9 to 14 ppmv (1.4 to 21 mg/m³).

4.2.2.2.5 Metals by Method 29

Table 4-13 presents the metals found in the control equipment stack. The flares and the engines have low emission rates compared to the boiler. The reason for the generally higher metal emissions from the boiler is not understood.

Table 4-10. Control Equipment Exit Dioxins and Furans Average Concentrations ^a

Concentration (x10 ⁻³ ng/dscm)	Landfill A	Landfill B	Landfill C	Landfill E
Number of Samples Contributing to Average	1	1	3	3
Dioxins				
2,3,7,8-TCDD	ND	ND	ND	0.926
Other TCDD	22.0	11.3	8.2	75.5
1,2,3,7,8-PeCDD	ND	ND	ND	2.6
Other PeCDD	3.4	13.6	3.4	76.6
1,2,3,4,7,8-HxCDD	ND	ND	ND	3.3
1,2,3,6,7,8-HxCDD	ND	ND	ND	6.2
1,2,3,7,8,9-HxCDD	ND	ND	ND	4.5
Other HxCDD	0.2393	4.1	1.2	71.1
1,2,3,4,6,7,8-HpCDD	ND	ND	ND	28.0
Other HpCDD	0	2.4	0	28.5
1,2,3,4,6,7,8,9-OCDD	ND	ND	3.7	43.6
Total CDD	< 33.8	<34.7	ND	341
Furans				
2,3,7,8-TCDF	ND	0.5867	ND	5.8
Other TCDF	46.6	0.0088	0.75	176
1,2,3,7,8-PeCDF	ND	1.1	ND	9.2

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Concentration (x10 ⁻³ ng/dscm)	Landfill A	Landfill B	Landfill C	Landfill E
Number of Samples Contributing to Average	1	1	3	3
Dioxins				
2,3,4,7,8-PeCDF	ND	1.0	ND	12.8
Other PeCDF	3.4	110	0	119
1,2,3,4,7,8-HxCDF	ND	1.1	ND	11.8
1,2,3,6,7,8-HxCDF	ND	0.166	ND	11.6
2,3,4,6,7,8-HxCDF	ND	0.194	ND	11.8
1,2,3,7,8,9-HxCDF	ND	0.218	ND	3.1
Other HxCDF	1.3	34.7	0	59.4
1,2,3,4,6,7,8-HpCDF	ND	0.158	ND	29.6
1,2,3,4,7,8,9-HpCDF	ND	0.215	ND	3.8
Other HpCDF	0	4.6	0	10.8
1,2,3,4,6,7,8,9-OCDF	ND	1.1	ND	11.1
Total CDF	13.9	156	ND	300
Total CDD/CDF	< 47.6	190	ND	640

a – Landfill D was not measured for PCDD/PCDFs.

ND – Constituent not detected.

< - indicates that the concentration of the constituent is less than the listed value. In all cases the number reported is rounded up to the nearest tenth.

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Table 4-11. Control Equipment Exit Averaged PAH Emissions ^a

	Landfill A	Landfill B	Landfill C	Landfill E
Concentration (ng/dscm)	IC Reciprocating Engine	Enclosed Flare	IC Reciprocating Engine	Boiler
Number of Samples Contributing to Average	1	1	3	3
Acenaphthene	521	16.2	555	49.3
Acenaphthylene	731	3.1	1,510	10.2
Anthracene	116	8.3	372	33.6
Benzo(a)anthracene	41	2.5	62.2	302
Benzo(a)pyrene	3.2	1.1	3.1	233
Benzo(b)fluoranthene	22	3.1	45.3	659
Benzo(g,h,i)perylene	15	2.5	6.1	248
Benzo(k)fluoranthene	6.4	1.0	10.8	240
Chrysene	144	2.5	165	512
Dibenzo(a,h)anthracene	3.2	0.3	2.9	63.3
Fluoranthene	154	22.4	361	1400
Fluorene	950	319	707	74.5
Indeno(1,2,3-cd)pyrene	6.6	1.2	8.3	277
Naphthalene	17,900	4,060	43,000	785
Phenanthrene	1,900	12	2,670	1,200
Pyrene	175	18	290	832
2-Methylnaphthalene	7,580	3460	6,700	650
Benzo(e)Pyrene	17	2.5	30.8	355
Perylene	3.1	0.4	1.0	40.3
Total PAH	30,300	7,930	56,500	7,960
Estimated LFG Inlet flow Rate (scfm)	150 J	1500	300	2430
Measured Exit Gas Flow Rate, average (scfm)	1,310	20,700	1,950	28,700
Total Emission Rate, (mg/ft ³ LFG)	0.007	0.003	0.010	0.003

^a – Landfill D was not measured for PAHs.

J Estimated value per EPA QA/G-8 guidance

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Table 4-12. Control Equipment Exit HCl

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
(mg/m ³)	Range	4.1 – 4.4	1.4 – 2.1	13.8 – 20.6	2.0 – 2.2	2.0 – 2.4
	Average	4.3	1.7	18.0	2.2	2.1
(ppmv)	Range	2.7 – 2.8	0.9 – 1.4	9.1 – 14.3	1.3 – 1.3	1.3 – 1.6
	Average	2.7	1.1	12.0	1.3	1.4
(lb/hr)	Range	0.0197 – 0.0213	0.11 – 0.16	0.103 – 0.163	0.06 – 0.06	0.21 – 0.26
	Average	0.0203	0.13	0.136	0.06	0.23

Table 4-13. Control Equipment Exit Metal Emissions

		Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
Estimated LFG Inlet flow Rate	(scfm)	~ 150	1500	300	400	2430
Arsenic	µg/dscm	3.0	0.70	3.13	4.7	2.3
	X 10 ⁻⁶ lb/hr	15	66	22.6	142	221
	X 10 ⁻⁹ lb/scf LFG	1.7	0.7	1.3	5.91	1.5
Cadmium	µg/dscm	0.37	0.18	0.574	0.209	1.2
	X 10 ⁻⁶ lb/hr	1.8	14.5	4.1	6.3	135
	X 10 ⁻⁹ lb/scf LFG	0.2	0.16	0.23	0.26	0.93
Chromium	µg/dscm	8.5	1.7	4.4	4.1	10
	X 10 ⁻⁶ lb/hr	41.4	132	31.6	122	1,200
	X 10 ⁻⁹ lb/scf LFG	0.46	147	1.8	5.1	8.2
Lead	µg/dscm	6.1	0.65	0.52	ND	6.0
	X 10 ⁻⁶ lb/hr	29.5	52	3.7	ND	649
	X 10 ⁻⁹ lb/scf LFG	3.2	0.6	0.21	ND	4.5
Manganese	µg/dscm	13.5	8.3	5.4	7.9	4.0
	X 10 ⁻⁶ lb/hr	66.2	660	38.5	236	439
	X 10 ⁻⁹ lb/scf LFG	7.4	7.3	2.1	9.8	3.0
Mercury	µg/dscm	ND	ND	ND	ND	0.46
	X 10 ⁻⁶ lb/hr	ND	ND	ND	ND	50
	X 10 ⁻⁹ lb/scf LFG	ND	ND	ND	ND	0.23
Nickel	µg/dscm	9.5	1.8	18	4.8	47
	X 10 ⁻⁶ lb/hr	47	140	126	144	5300
	X 10 ⁻⁹ lb/scf LFG	5.2	1.6	7.0	6.0	36.4

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5. Discussions of results

5.1 Comparison with AP-42 Default Values

Table 5-1 provides a comparison of the field test results of the five landfills to existing AP-42 values for landfill gas. The table also identifies the test method and detection limit for each constituent evaluated in the raw landfill gas. Of the forty-four AP-42 values, twenty-nine constituents were found to have average concentrations that are half or lower than their corresponding AP-42 for all five landfills. Twelve of these twenty-nine constituents were present at average concentrations that were no more than one-tenth of the AP-42 values. These twelve compounds are:

1,1,1-trichloroethane; 1,1,2,2-tetrachloroethane; 1,2-dichloroethane; 1,2-dichloropropane; isopropyl alcohol; bromodichloromethane; dichlorodifluoromethane; ethane; ethanol; t-1,2-dichloroethene; trichloroethylene; and vinyl chloride. For acrylonitrile, non-detects were reported for each of the five landfills.

For sixteen constituents, at least one landfill has a concentration greater than the existing AP-42 value. The concentrations that are greater than the existing AP-42 values for at least one of the five landfills are highlighted in the table. These compounds were: acetone, carbon tetrachloride, chlorobenzene, chloroethane, chloroform, chloromethane, dichlorobenzene (1,4; 1,3; and 1,2), ethylbenzene, 1,2-dibromomethane, hexane, hydrogen sulfide, methyl ethyl ketone, pentane, and nonmethane organic compounds. Four compounds were present at average concentrations at least three times their AP-42 default values [i.e., carbon tetrachloride (3.6x), chloroethane (6.7x), chloroform (12x), and 1,2-dibromoethane (10x)].

Twenty six compounds were found to be present in concentrations that are similar to the AP-42 default values, i.e. their averaged concentrations were between 50 to 300% the AP-42 default values. These compounds were: 1,1-dichloroethane; 1,1-dichloroethene; acetone; butane; carbon disulfide; chlorobenzene; chloromethane; 1,4-dichlorobenzene; 1,3-dichlorobenzene; 1,2-dichlorobenzene; methylene chloride; ethylbenzene; trichloromonofluoromethane; hexane; hydrogen sulfide; mercury (total); 2-butanone; 2-hexanone; pentane; tetrachloroethylene; propane; m/p-xylene; o-xylene; benzene; NMOC as Hexane; and toluene.

These data will be of help in providing: (1) QA of industry-supplied data; (2) filling data gaps in the existing sets of LFG emission factors; and (3) updating existing emission factors within AP-42. The inclusion of these data will undergo protocols for AP-42 emission factor development including addressing uncertainty and data quality.

5.2 Control Technology Assessment

Among the three tested control technologies (i.e., enclosed ground flare, IC engine and boiler) the boiler was the one capable of destroying the LFG most effectively, as evidenced by the very low concentrations of organic compounds that exited the boiler stack. However, the boiler does have a higher affinity to form PCDDs and PCDFs than the flares or the engines. A more detailed review of the PCDD/PCDF data may be warranted to assess the potential impacts of the levels of these compounds that were formed.

IC engines do not appear to destroy landfill gas constituents as effectively as boilers or flares. This could be due to tuning or maintenance of the engine. Also, engines are typically operated to minimize NO_x and CO emissions which will result in decreasing NMOC destruction efficiency. In assessing potential impacts from use of IC engines for landfill gas control, pollution prevention tradeoffs can be considered from offsetting power generation at a coal-fired electric utility (EPA-600/R-95-089). Often electricity from IC engines powered on landfill gas is used to help meet peak load energy demands.

Enclosed ground flares are simple devices and are easier to maintain and operate as compared to a boiler or IC engine. They do not have the benefits of IC engines or boilers in offsetting fossil fuel use and providing methane for utilization. However, the two enclosed flares evaluated in this project were found to effectively control hydrocarbons and organic constituents.

5.3 Mercury Measurements

The technology of sampling and analyzing for mercury species is progressing steadily. The current state of technology requires very specific knowledge that does not transfer readily. The development of a method that can be promulgated as an EPA standard procedure would be helpful in future research with mercury emissions.

This notwithstanding, mercury measurement technology appears to be on the cusp of becoming more “main-stream.” Mercury’s inclusion in future research studies should be considered favorably, especially if the per-sample cost will go down because of maturing of the technique and increased competition in the market place. However, the use of independent standards is recommended for primary standard verification, spike recoveries and blanks to provide quality assurance of the results.

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Technical Systems Audits (TSAs) were conducted for the organo-mercury sampling and analysis since this is not a standard EPA test method. One potential source of error in any analysis is due to the standards used to calibrate the instrumentation. Several issues were noted concerning the calibration standards. The first issue was the apparent inability to verify the concentrations of the standards used to calibrate the instrumentation used to measure MMHg and DMHg. The lack of an independent standard to verify the primary standard is a cause of concern because any inaccuracies in the primary standard will be promulgated throughout the analyses. It is recommended that Frontier Geosciences or any other laboratory conducting organo-mercury analyses identify stable standards for use as an independent verification of the primary standard.

A second issue concerned how the calibration standards were stored. No expiration dates were available for either the MMHg and DMHg standard materials. All standards have a limited “shelf life” and should not be used after they have expired. It was not clear if records were kept to prevent use of expired standards. It is recommended that this become part of the standard operating procedures (SOPs) to prevent use of standards that have degraded over time.

A third issue was raised regarding how the standards were stored. The QA officer found the MMHg analytical standard stored in a clear Teflon bottle, un-refrigerated in front of a large window. The work plan had requested that samples and standards be kept refrigerated and away from light.

The QA officer also recommended that standard practice should include retaining an aliquot of spike solution or spiked traps when sending media to a field project.

The QA officer also noted several potential issues associated with the organo-mercury analyses. One area of concern was the instability of the MMHg instrument. The analyst responsible for MMHg analysis indicated that it was common to have to recalibrate and reanalyze samples. One suggestion to improve the robustness of MMHg analysis is the inclusion of analytical spikes. Additionally calibration verification samples should be analyzed frequently to ensure that the calibration is still acceptable, i.e. the instrument has not drifted. Data validation of MMHg analyses must include verification of the initial calibration, spike recoveries and calibration stability. Another area of concern is the practice of forcing the calibration curve through zero. This procedure is not consistent with most EPA-promulgated methods. Retention times during MMHg analysis should be carefully monitored. This is critical given that identification of MMHg is determined by retention times or relative retention times.

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Careful monitoring of retention times must become part of MMHg analysis. The final observation made by the ARCADIS QA officer was that the digestate dilution technique was not acceptably performed. The glassware used to bring the digested samples to volume was not calibrated to Class A or Class B glassware. Furthermore the glassware used was not compared against calibrated glassware. Inaccurate dilution of the digestates is a common source of error in analysis where dilution is required. It is recommended that Frontier Geosciences or any other lab performing these analyses should modify their procedures to ensure accurate dilution of samples. This can be done using calibrated glassware or by using a calibrated balance to determine the dilution gravimetrically.

In addition to the TSA, an internal performance audit was performed by the ARCADIS QA officer. Audit samples for THg, MMHg and DMHg were prepared by Cebam Analytical located in Seattle, Washington. These audit samples were analyzed by Frontier Geosciences as described in the report titled *Determination of Total, Dimethyl, and Monomethyl Mercury in Raw Landfill Gass at Pinconning and Montrose Michigan*. These results are present in Tables 5-3, 5-4, and 5-5. In summary the results met the MQOs for recovery and the RPD between duplicate samples was also acceptable. However, the recovery MQO of 50-150 percent makes it nearly impossible to reasonably close a mass balance around Mercury. The measurement of the MMHg audit samples showed the worst recoveries of the various Hg species, indicating that MMHg analyses are more than likely the least robust of the analyses. Inclusion of the suggestions listed above should increase the accuracy and precession of THg, MMHg, and DMHg analyses. Mercury measurements from landfill gas are still in development, but improvements have been made.

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Table 5-1. Comparison between LFG Constituent Concentrations and AP-42 Default Values

				Concentration (ppmv)							
Method	Compound	CAS Number	Formula Weight	Default Value	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E	Detection Limit	
M-40	1,1,1-Trichloroethane	71-55-6	133.42	0.48	0.005	0.031	ND	ND	ND	0.0003	
M-40	1,1,2,2-Tetrachloroethane	79-34-5	167.85	1.11	0.0290	ND	ND	ND	ND	0.0002	
M-40	1,1-Dichloroethane (Ethylidene Dichloride)	75-34-3	98.96	2.35	0.033	0.178	0.423	0.591	ND	0.0003	
M-40	1,1-dichloroethene	75-35-4	96.94	0.20	0.002	0.008	0.055	0.021	ND	0.0002	
M-40	1,2-Dichloroethane	107-06-2	98.96	0.41	0.001	0.005	0.037	0.022	ND	0.0003	
M-40	1,2-Dichloropropane	78-87-5	112.98	0.18	0.001	0.005	ND	ND	ND	0.0003	
M-40	Isopropyl alcohol (2-Propanol)	67-63-0	60.11	50.10	0.114	0.356	1.280	6.63	2.36	0.0002	
M-40	Acetone	67-64-1	58.08	7.01	0.33	1.61	11.7	12.8	15.5	0.0003	
M-40	Acrylonitrile	107-13-1	53.06	6.33	ND	ND	ND	ND	ND	0.02	
M-40	Bromodichloromethane	75-27-4	163.83	3.13	0.003	0.01	ND	ND	ND	0.0002	
M-40	Butane	106-97-8	58.12	5.03	4.87	3.3	37.9	ND	3.6	1	
M-40	Carbon Disulfide	75-15-0	76.13	0.58	0.014	0.134	0.157	0.093	0.34	0.0002	
M-40	Carbon Tetrachloride	56-23-5	153.84	0.004	0.00083	0.005	ND	0.038	ND	0.0005	
M-40	Ethyl Mercaptan (Ethanediol)	75-08-1	62.13	2.28	ND	ND	ND	ND	ND	0.02	
M-40	Carbonyl Sulfide (Carbon Oxysulfide)	463-58-1	60.07	0.49	ND	ND	ND	ND	ND	0.02	
M-40	Chlorobenzene	108-90-7	112.56	0.25	0.195	0.229	0.833	0.021	0.135	0.0002	
M-40	Chloroethane (Ethyl Chloride)	75-00-3	64.52	1.25	0.77	1.88	30.4	0.63	ND	0.0002	
M-40	Chloroform	67-66-3	119.39	0.03	0.040	0.19	0.744	0.485	ND	0.0003	
M-40	Chloromethane	74-87-3	50.49	1.21	0.012	0.072	1.26	0.232	ND	0.0001	

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Concentration (ppmv)										
Method	Compound	CAS Number	Formula Weight	Default Value	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E	Detection Limit
M-40	1,4-Dichlorobenzene	106-46-7	147.00	0.21	0.043	0.255	0.328	0.686	ND	0.0003
M-40	1,3-Dichlorobenzene	541-73-1	147.00	0.21	0.00047	0.00203	0.394	0.650	ND	0.0002
M-40	1,2-Dichlorobenzene	95-50-1	147.01	0.21	0.0019	0.0004	ND	0.031	ND	0.0003
M-40	Dichlorodifluoromethane (Freon 12)	75-71-8	120.91	15.70	0.118	0.468	1.60	1.24	0.232	0.0003
M-40	Dichlorofluoromethane (Freon 21)	75-43-4	102.92	2.62	ND	ND	ND	ND	ND	0.02
M-40	Methylene Chloride (Dichloromethane)	75-09-2	84.94	14.30	0.997	0.169	5.35	1.11	3.05	0.0001
M-40	Dimethyl Sulfide (Methyl Sulfide)	75-18-3	62.13	7.82	ND	ND	0.68	ND	ND	0.02
M-40	Ethane	74-84-0	30.07	889	6.2	4.6	14.3	5.6	13.5	1
M-40	Ethanol	64-17-5	46.08	27.20	0.020	0.202	0.172	0.394	0.0002	0.0002
M-40	Ethylbenzene	100-41-4	106.16	4.61	0.58	2.80	5.89	8.12	ND	0.0003
M-40	1,2-Dibromoethane (Ethylene dibromide)	106-93-4	187.88	0.001	0.001	0.007	0.021	ND	ND	0.0002
M-40	Trichloromonofluoromethane (Fluorotrichloromethane) (F11)	75-69-4	137.38	0.76	0.051	0.327	0.504	0.116	0.0082	0.0002
M-40	Hexane	110-54-3	86.18	6.57	ND	ND	4.94	3.98	0.597	0.0003
M-11	Hydrogen Sulfide	7783-06-4	34.08	35.50	13.1	22.9	55.5	72.7	322 J	NR
Methods 101A & 324	Mercury (Total)		215.63	253.0E-6	300.E-6	22.8E-6	51.2E-6	89.1E-6	163E-6	6.E-6
M-40	2-Butanone (Methyl Ethyl Ketone)	78-93-3	72.10	7.09	0.27	1.43	4.57	8.07	2.49	0.0003
M-40	2-Hexanone (Methyl Butyl Ketone)	591-78-6	100.16	1.87	0.557	0.441	ND	ND	ND	0.0002

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Method	Compound	CAS Number	Formula Weight	Concentration (ppmv)						Detection Limit
				Default Value	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E	
M-40	Methyl Mercaptan (Methanethiol)	74-93-1	48.11	2.49	ND	ND	ND	ND	ND	0.02
M-40	Pentane	109-66-0	72.15	3.29	3.20	2.60	26.6	2.37	1.30	1
M-40	Tetrachloroethylene (Perchloroethylene)	127-18-4	165.83	3.73	0.042	0.176	1.69	1.02	0.125	0.0003
M-40	Propane	74-98-6	44.09	11.10	8.9	5.9	40.0	30.5	13.0	1
M-40	t-1,2-Dichloroethene	156-60-5	96.94	2.84	0.003	0.009	0.042	0.053	ND	0.0003
M-40	Trichloroethylene (Trichloroethene)	79-01-6	131.38	2.82	0.028	0.103	0.515	0.418	0.094	0.0002
M-40	Vinyl Chloride	75-01-4	62.50	7.34	0.097	0.41	0.768	1.20	0.0634	0.0002
M-40	m/p-Xylene (Dimethyl Benzene)	1330-20-7	106.16	12.10	3.73	3.98	9.21	13.6	9.00	0.00065
M-40	o-Xylene (Dimethyl Benzene)	95-47-6	106.16	12.10	0.30	1.41	3.66	5.41	3.10	0.0003
M-40	Benzene (No-disposal or Unknown)	71-43-2	78.11	1.91	0.073	0.251	1.63	1.20	0.887	0.0002
M-25C	NMOC as Hexane (No-codisposal or Unknown)		86.17	595.00	373	355	5870	1006	233	NR
M-40	Toluene (Methyl Benzene) (No or Unknown)	108-88-3	92.13	39.30	1.33	6.77	23.3	30.3	7.95	0.0003

ND - Constituent not detected at the stated method detection limits

NR – Constituent detection limit not reported by laboratory

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6. Data Quality Assessment

Detailed assessments of this project's performance in terms of quality are included in the individual landfill test reports. With a few exceptions, the project was able to meet the Measurement Quality Objectives (MQOs) established in the QAPPs.

Table 6-1 shows a comprehensive overview of measurements that, for various reasons, did not meet the specified MQOs.

Table 6-1. Summary of Sampling and Analyses Exceptions

		Quality Assurance Observations				
Method	Measurement	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
EPA Method 1	Selection of traverse points	NI	NI	NI	NI	NI
EPA Method 2	Determination of stack gas velocity and volumetric flow rate	NI	NI	NI	NI	NI
EPA Method 3A	Determination of stack gas O ₂ and CO ₂ for stack gas molecular weight calculations	CEM calibration and drift check exceeded criteria slightly.	CEM calibration and drift check exceeded criteria slightly	NI	NI	NI
EPA Method 3C	Determination of CO ₂ , CH ₄ , N ₂ , and O ₂ in raw LFG	NI	NI	NI	NI	NI
EPA Method 4	Determination of stack gas moisture	NI	NI	NI	NI	NI
EPA Method 6C	Determination of stack gas SO ₂	CEM calibration and drift check exceeded criteria slightly.	Drift and system bias checks exceeded criteria	NI	NI	NI
EPA Method 7E	Determination of stack gas NO _x	CEM calibration and drift check exceeded criteria slightly.	Drift check exceeded criteria	NI	1 drift check was at 3.3%	NI
EPA Method 10	Determination of stack gas CO	NI	NI	NI	NI	NI
EPA Method 11	Determination of raw LFG H ₂ S	NI	NI	Exceeded hold time.	Exceeded hold time.	Did not do QAPP-specified spike. However method does not specify spike to be required. Data was flagged.

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Method	Measurement	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
EPA Method 23	Determination of LFG PAHs by Method 8270 PCBs by Method 1668	Extracts too concentrated for analysis. No data was produced	Extracts too concentrated for analysis. No data was produced	Not a specified measurement	Not a specified measurement	Not a specified measurement
EPA Method 23	Determination of stack gas dioxins/furans by Method 8290	1 of 3 samples analyzed. Did not meet 90% completion goal	Exceeded hold time. Detected some targets in blank. Data were notated. 1 of 3 samples analyzed. Did not meet 90% completion goal.	NI	Not a specified measurement	NI
EPA Method 23	Determination of stack gas PAHs by Method 8270	1 of 3 samples analyzed. Did not meet 90% completion goal	Exceeded hold time. Detected some targets in blank. Data were notated. 1 of 3 samples analyzed. Did not meet 90% completion goal.	Detected targets in blank. Data reported and flagged. Recovery of d ₁₂ -perylene was low Relevant data were flagged.	Not a specified measurement	Detected targets in blank. Data reported and flagged.
EPA Method 25A	Determination of flare stack gas NMOCs, as THCs	NI	Drift check exceeded criteria	NI	NI	NI

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Quality Assurance Observations						
Method	Measurement	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
EPA Method 25C	Determination of raw LFG NMOCs	Exceeded hold time. Detected 2 ppmv hexane in field blank.	Exceeded hold time. Detected 8.5 ppmv hexane in field blank.	NI	N ₂ and O ₂ exceeded threshold. Data flagged	Exceeded hold time Detected 3 ppmv hexane in field blank. 1 sample had N ₂ and O ₂ exceeded threshold.
EPA Method 26A	Determination of stack gas HCl	NI	NI	NI	NI	NI
EPA Method 29	Determination of stack gas metals	NI	NI	Nickel CCV at 10.6 and 14.0%	Nickel CCV at 10.6 and 14.0%	Nickel CCV at 10.6 and 12.2%
EPA Method 40/TO-15	Determination of raw LFG VOCs	Detected low concentrations of a few targets in field blank Spike recovery exceeded criteria for ethanol and m/p Xylene. RSD for hexane and isopropyl alcohol exceeded criteria. Affected data were flagged	Detected low concentrations of a few targets in field blank, Spike recovery for chlorobenzene exceeded criteria. RSD for Methylene chloride exceeded criteria. Affected data were flagged	Detected low concentrations of a few targets in field blank. Data were flagged.	Detected low concentrations of a few targets in field blank. Cyclohexane RSD 41.2% Heptane RSD 57.4% Data were flagged.	Detected low concentrations of a few targets in field blank. Ethanol spike recovery 2.4%, m/p-xylene recovery 230% Isopropyl alcohol RSD 56.3% Hexane RSD 40.7%
SW-846 Method 0100/TO-11	Determination of raw LFG carbonyls (formaldehyde, acetaldehyde)	Formaldehyde levels in samples are near the MDL. Results are flagged as estimates “J”	Detected 0.07 µg formaldehyde in field blank	NI	NI	NI

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Quality Assurance Observations						
Method	Measurement	Landfill A	Landfill B	Landfill C	Landfill D	Landfill E
LUMEX instrument	Determination of raw LFG Hg^0	NI	NI	NI	NI	Sampled at compressor exit
Organic mercury methods (Frontier)	Determination of raw LFG monomethyl mercury.	Exceeded 14-day hold time RSD exceeded criteria	Exceeded 14-day hold time RSD exceeded criteria	Exceeded 14-day hold time. 1 of 6 samples was damaged.	NI	Exceeded 14-day hold time
Organic mercury methods (Frontier)	Determination of raw LFG dimethyl mercury	Exceeded 14-day hold time Spike recovery less than 40%. Data rejected.	Exceeded 14-day hold time Spike recovery less than 40%. Data rejected.	NI	NI	Exceeded 14-day hold time
Organic mercury methods (Frontier)	Determination of raw LFG total mercury.	Exceeded 14-day hold time	Exceeded 14-day hold time	Exceeded 14-day hold time	Exceeded 14-day hold time	Exceeded 14-day hold time
Organic mercury methods (Geochimica)	Determination of raw LFG monomethyl mercury.	Not a specified measurement	Not a specified measurement	Not a specified measurement	Not a specified measurement	NI
Organic mercury methods (Geochimica)	Determination of raw LFG dimethyl mercury	Not a specified measurement	Not a specified measurement	Not a specified measurement	Not a specified measurement	NI
Organic mercury methods (Geochimica)	Determination of raw LFG total mercury.	Not a specified measurement	Not a specified measurement	Not a specified measurement	Not a specified measurement	NI

NI – No issues or QA exceptions

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7. Conclusions

The test data collected during this test program provides updated information concerning the constituents in landfill gas and combustion by-products from five MSW landfills. Ideally, it would be preferable to have collected data from a wider range of landfills covering different gas control technology, geographic areas, landfill size and age, and variations in waste composition. The data are considered useful in providing a detailed and comprehensive set of data. It also helps in evaluating how representative data are that have been supplied by industry, state and local regulatory authorities, and others.

The average concentrations of constituents in landfill gas for the five landfills were half or lower of their corresponding AP-42 values. For sixteen constituents, at least one landfill had an average concentration greater than the existing AP-42 value. The details of the sampling at each site are provided in the appendices to this report.

Limitations in the data include lack of data from a wider range of combustion technology. Also, the field test measurements did not include wet or bioreactor landfills. Not clear if there will be an increase in air toxics resulting from increased levels of metals due to leachate recirculation and addition of sewage sludge or other liquid additions. Also, this study did not include turbines since they are not as widely used as boilers, IC engines, and flares. With increasing use of micro-turbines, it would be helpful to have data on combustion by-product emissions to compare to other technologies in use.

With respect to project QA, while a few of the measurements presented some challenges, the project succeeded in producing a comprehensive data set. Therefore, this project met its data quality objective of *“performing tests by using EPA reference test methods, or when not applicable, sound methodology and that tests are reported in enough detail for adequate validation and raw data are provided that can be used to duplicate the emission results presented in the report.”*

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