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Characterization of Landfill Gas Composition at the Fresh Kills Municipal Solid-Waste Landfill

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The most common disposal method in the United States for municipal solid waste (MSW) is burial in landfills. Until recently, air emissions from these landfills were not regulated. Under the New Source Performance Standards and Emission Guidelines for MSW landfills, MSW operators are required to determine the nonmethane organic gas generation rate of their landfill through modeling and/or measurements. This paper summarizes speciated nonmethane organic compound (NMOC) measurement data collected during an intensive, short-term field program. Over 250 separate landfill gas samples were collected from emission sources at the Fresh Kills landfill in New York City and analyzed for approximately 150 different analytes. The average total NMOC value for the landfill was 438 ppmv (as hexane) versus the regulatory default value of 4000 ppmv (as hexane). Over 70 individual volatile organic compounds (VOCs) were detected and quantified in the landfill gas samples. The typical gas composition for this landfill was determined as well as estimates of the spatial, temporal, and measurement variability in the gas composition. The data for NMOC show that the gas composition within the landfill is equivalent to the composition of the gas exiting the landfill through passive vents and through the soil cover.

Introduction

The most common disposal method in the United States for municipal solid waste (MSW) is burial in landfills. In 1993, about 62% of MSW was landfilled versus 22% recycled and 15% combusted. Decomposition reactions within the landfills produce large amounts of methane and carbon dioxide, which typically are vented to the atmosphere. The migration of these gases through the landfill also serves to carry out nonmethane organic compounds (NMOCs) that were originally present in the MSW or that were formed during decomposition. Nationwide, MSW landfills are estimated to release about 9.0×10^5 Mg/year of methane and 1.3×10^4 Mg/year of NMOCs (*1*). Until recently, these emissions were not regulated. Under the Clean Air Act, any large landfill (i.e., $> 2.5 \times 10^6$ Mg or 2.5×10^6 m^3 of waste) that emits more than 50 Mg/year of NMOCs is now required to capture and reuse or destroy these gases (*1*).

To comply with the new regulations, MSW operators must determine the NMOC generation rate of their landfill through modeling and/or measurements. Key questions to be answered include the following:

(1) Does the site-specific value for a given landfill vary from the regulatory default values for parameters such as the average total NMOC concentration in the landfill gas? The more potential deviation from the default value, the greater the need for site-specific measurements.

(2) How much variability is there in landfill gas composition from emission source to emission source across a landfill and within a given emission source? Emission sources include passive vents, soil surfaces, and gas collection systems. The expected variability will determine where samples should be collected to characterize the landfill gas composition and how many samples should be collected.

This paper provides information related to both of the above questions. Data are given for a major MSW landfill in the eastern United States where decomposition occurs under optimal moisture conditions for landfill gas generation by microbial decomposition. This study represents the most extensive field measurement program of speciated NMOC composition reported to date and provides information on the variability in gas composition for a large data set.

Objectives

The purpose of the overall study was to measure emission rates of gases from the landfill for input to a human health exposure study. This paper addresses the characterization of the composition of the landfill gas and the variability in the gas composition.

Site Description

The Fresh Kills Landfill is the largest MSW landfill in the United States. In total, the landfill property covers approximately 1200 ha (3000 acre) of Staten Island, a borough of the city of New York. The New York City Department of Sanitation (NYC DOS) operates the landfill and places there approximately 11 800 t/day of municipal solid waste, 6 days a week, throughout the year.

The total area covered by landfilled municipal waste is 426.5 ha, and the mounds of waste extend up to 46 m or more in height. The landfill is divided into four sections, two of which no longer accept waste and two which are open and accept waste from all five boroughs of New York. The landfill currently accepts primarily residential (household) garbage; hazardous waste and medical waste are not currently placed in the landfill. Some organic matter in the garbage, such as leaves and Christmas trees, is segregated and sent to a composting facility. The type of wastes and the composition of the wastes within each of the four sections are believed to be similar. Information about each section is given in Table 1.

Section 1/9 has an active gas collection system which covers the southern $^2/_3$ of this section. The gas collection system is operated by a contractor and produces about 400 000 m^3/day of landfill gas. The landfill gas is routed to a gas processing plant adjacent to section 1/9 where condensate, CO_2, and VOCs are removed and pipeline quality natural gas is produced. The VOCs and condensate are incinerated, and the cleaned gas is sold to a local utility.

Sections 2/8 and 3/4 were undergoing closure at the time of sampling, that is, the summer of 1995. The closure involved retrofitting with (1) passive vents, (2) an impermeable PVC cover, and (3) a series of active gas collection wells. The passive vents in this and the other sections eventually will be plugged, and the gas from the venting system will be

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TABLE 1. Description of Landfill Sections

section	area (h)	years of MSW acceptance	type of cover	other features
3/4	57.2	1955−1992	compacted clay PVC cover	119 passive vents
2/8	58.1	1948−1993	PVC cover geomembrane	102 passive vents
6/7	136	1961−present	compacted soil	None
1/9	176	1948−present	compacted soil	36 passive vents active gas collection wells over $^2/_3$ of the section

TABLE 2. Number and Type of Measurements Performed[a]

	flow rate	VOCs	H_2S	Hg	fixed gases
passive vents	231	95	215	61	202
flux chambers	N/A	93	88	8	93[b]
landfill gas collection system headers	19	12	19	19	19
condensate	0	18	0	0	N/A
extraction wells	34	34	31	31	34
monitoring wells	N/A	9	9	9	9

[a] Totals include samples for temporal variability, duplicate samples, and blank samples. [b] Fixed gas measurements done off-site.

combined with gas from the active gas collection wells. The collected gas will be processed and sold to a local utility. Most of the passive vents had already been installed at the time of the field sampling.

Approach

All four sections of the landfill were sampled to measure the emissions from each major emission source at the landfill, to determine the heterogeneity of the emissions, and to determine the composition of the gas below the surface within the landfill. Emission sources were considered to be the passive vents, soil surfaces, and gas collection system at the facility. The sample matrix is shown in Table 2. A more detailed description of the project objectives, experimental design, sampling and analytical methods, and quality assurance and quality control procedures has been published (*2*). The study took place under summertime conditions.

Passive Vent Sampling. Landfill sections 2/8, 3/4, and 1/9 have numerous passive vents, which are goose-necked pipes open to the ambient air. These vents are used to provide "pathways of least resistance" of the landfill gas near the surface to avoid large gas pockets from building up under the landfill cover. Every vent in these three landfill sections was sampled to determine the flow rate, the concentration of fixed gases (i.e., CH_4, CO_2, and O_2), and the concentration of H_2S. In addition, a subset of these vents was sampled for total NMOC and speciated VOCs. Air flow rates were determined using a 0.10-m diameter vane anemometer. Approximately 10% of the vents did not have flow, so their location was noted, but no concentration data were collected.

Short-term temporal and diurnal variability were evaluated by monitoring five vents over several days. These vents were sampled three times during the program for flow rate, H_2S, and landfill gases. During one of the sampling days, the vents were sampled morning and afternoon to help assess the extent of diurnal variability. Four of these vents were sampled for speciated VOCs using evacuated, stainless steel canisters. VOC samples were collected on three occasions during the program. A duplicate canister was collected at each of the four vents. The duplicate canisters were analyzed in duplicate to allow for a "nested" statistical design.

The H_2S samples were collected from each vent in 1-L Tedlar bags and analyzed in an on-site laboratory. Tedlar bag samples were transported to the laboratory within about 1 h of sampling, and the analysis was completed within 4 h of sample collection. Samples were allowed to equilibrate to the laboratory temperature prior to analysis.

Surface Emission Sampling. The gaseous emissions emanating from the landfill surface were measured using an emission isolation flux chamber (flux chamber). The flux chamber is an enclosure device used to sample gaseous emissions from a defined surface area. It is an accepted standard EPA sampling method (*3*) which has previously been used for measuring VOC emission rates from a variety of solid and liquid sources (*4*). Fixed gases, H_2S, and speciated hydrocarbons were measured in air samples collected from the flux chambers.

The majority of the flux measurements were made on section 6/7, which does not have an impermeable liner, passive vents, or a gas collection system. The gas generated in this section will tend to exit the soil surface, so it was expected to have the highest air emissions from the landfill surface of any of the sections. As a quality control check and to assess short-term temporal variability, four sampling points were sampled three to four times each during the study.

Gas Collection System Sampling. The landfill gas collection system functions over approximately two-thirds of section 1/9. The collected gas is treated at the landfill to remove impurities, and the product gas is sold to a local utility. The collection system is made up of over 250 individual extraction wells manifolded together. All individual wells were manifolded into two well headers designated north or south field. Each of the two headers was 0.46 m in diameter, and combined they carried approximately 350 m^3/min of landfill gas. These two well field headers were sampled six times each during the monitoring program. These data were used to determine the representative landfill gas composition, the mass flow rate, and short-term temporal variability in the landfill gas composition. In addition, 25 individual gas extraction wells were sampled to assess spatial variability of landfill gas composition and concentrations. A small number of condensate samples from the system also were collected.

Analytical Procedures. The analytical procedures for this program are divided into on-site analyses (H_2S, mercury, flow rate measurements, and landfill gases) and off-site analyses (VOC canisters). Details of the analytical methods are presented below.

Samples for fixed gases and H_2S were collected in Tedlar bags and analyzed in the on-site laboratory. A Geo Group landfill gas analyzer was used to measure the concentrations

TABLE 3. Average Landfill Gas Composition (ppmv)[a]

compound	concn (ppmv)	compound	concn (ppmv)
methane	55.63%	*o*-ethyltoluene	3.43
carbon dioxide	37.14%	*p*-diethylbenzene	2.67
oxygen	0.99%	*m*-ethyltoluene	2.49
total NMOC	438.09	*t*-2-pentene	2.37
ethane	222.61	*o*-xylene	2.17
total unidentified VOCs	134.55	*o*-dichlorobenzene	2.17
limonene	35.38	*n*-propylbenzene	2.09
toluene	14.57	styrene	2.02
n-decane and *p*-dichlorobenzene	13.97	1-undecene	2.02
p-isopropyltoluene	13.14	*p*-ethyltoluene	2.01
propane	13.03	1,2,3-trimethylbenzene	1.90
isobutane	8.24	benzyl chloride and *m*-dichlorobenzene	1.88
a-pinene	7.85	1,3,5-trimethylbenzene	1.76
3-methylpentane	7.75	*n*-butylbenzene	1.50
acetone	6.09	*m*-diethylbenzene	1.46
p-xylene + *m*-xylene	5.97	dichlorodifluoromethane	1.27
n-undecane	5.50	chlorobenzene	1.15
1,2,4-trimethylbenzene and *t*-butylbenzene	5.06	dichlorotoluene	1.15
ethylbenzene	4.71	*n*-octane	0.99
1,3-butadiene	3.98	*n*-pentane	0.97
n-butane	3.80	benzene	0.93
isopentane	3.76	*n*-hexane	0.92
n-nonane	3.57	isobutene + 1-butene	0.92

[a] Values are given for all compounds detected above an average concentration of 0.90 ppm or greater in the landfill gas collection system headers.

of methane, carbon dioxide, and oxygen. This instrument uses an infrared measurement technique. The hydrogen sulfide (H_2S) analysis was performed on-site using a Jerome model 631-X analyzer, which uses a gold film technology to measure H_2S. The analyzer contains an internal scrubber so that mercury does not interfere with the analysis.

Samples for speciated VOC analysis were collected in evacuated, Summa polished stainless steel canisters. The VOCs were then analyzed using a gas chromatograph (GC) equipped with dual columns and multiple detectors (GC/MD). The detectors included a flame ionization detector (FID), a photoionization detector (PID), and an electrolytic conductivity detector (ELCD). The system has previously been described (*5*). The FID/PID were used to quantitate the aromatic and aliphatic hydrocarbons. The ELCD was used to quantitate most of the halogenated hydrocarbon species. The speciated VOC sample analysis was performed using cryogenic trapping (flux chamber samples) or fixed loop injection (passive vent and landfill gas collection system samples). The GC/MD system was configured for this program without a Nafion dryer. Condensate samples were analyzed by SW-846, Method 8240.

Results and Discussion

Gas Composition. The samples from the headers of the landfill gas collection system represent integrated samples drawn from over 200 extraction wells at various depths within the landfill and are considered to be the best determination of the average landfill gas composition. These data were averaged to develop the typical gas composition shown in Table 3. Over 70 individual VOC compounds were detected and quantified in these samples. The concentrations of the VOCs were quite constant over the duration of the program with the variability generally less than ±10%.

For the samples collected from the passive vents, about 60 VOCs generally were identified in each sample. These compounds included primarily alkanes (e.g., butane), aromatic compounds (e.g., toluene, xylenes), and chlorinated hydrocarbons (e.g., chlorobenzene). There was relatively little variation in the number and types of compounds detected from sample to sample. Some of the passive vents at the toe areas of the landfill mounds were found to have negative flow; that is, ambient air was being drawn into the vents due to the vacuum produced by gas flow elsewhere in the landfill.

During the course of this project, a total of 74 surface emission flux measurements were made. The sampling locations were selected to address the range of types of surface cover present at the landfill. There were 50 compounds that were present in at least one-half of the flux chamber samples. These compounds included alkanes (e.g., isobutane), aromatics (e.g., toluene, benzene, xylenes), and chlorinated hydrocarbons (e.g., vinyl chloride, 1,1- dichloroethane). There was little variation in the types of compounds detected from sample to sample, but a large variation in the concentrations of compounds from sample to sample. This variation is a result of the large spatial variability in emissions at the surface of the landfill. The emission fluxes were found to be much higher over soil and clay surfaces than over surfaces covered by a PVC liner. The highest emission fluxes were measured over cracks and fissures in the soil or clay.

Liquid condensate samples were collected from the headers of the gas collection system to more fully characterize the composition of gas within the landfill gas collection system. A total of 16 VOCs were detected in one or more of the liquid samples. The compounds detected represent the major compounds detected in the gas samples plus several polar compounds that were not detected in appreciable concentrations in the gas samples: acetone, methylene chloride, 2-butanone (MEK), and methylisobutyl ketone (MIBK). During the monitoring period, between 45 000 and 53 000 L of condensate was collected daily.

The generation of methane and carbon dioxide from MSW has been extensively studied, and a very large body of literature exists regarding the factors that influence gas production and the amount of gas that is produced per category of waste material and per mass of waste. Surprisingly few studies, however, have reported NMOC air emissions from MSW landfills. The average total NMOC value measured at the gas collection plant was 438 ppmv versus the default regulatory value for landfills of 4000 ppmv (both values as hexane). The test results are comparable, however,

TABLE 4. Ratio of Individual VOC to Total VOC Concentration Values (%)

compound	VOC to total NMOC ratio (%)		
	gas collection system	passive vents	flux chamber samples
ethane	37.0	37.3	29.7
total unidentified VOCs	22.4	21.0	30.5
limonene	9.8	4.3	2.2
n-decane and *p*-dichlorobenzene	3.1	2.8	6.1
toluene	2.4	3.4	1.8
a-pinene	2.2	2.4	2.1
propane	2.2	2.7	1.8
n-undecane	1.7	0.8	1.8
1,2,4-trimethylbenzene and *t*-butylbenzene	1.4	1.4	2.3
p-xylene + *m*-xylene	1.3	2.4	2.2
isobutane	0.9	1.0	1.1
n-nonane	0.9	1.5	1.9
o-ethyltoluene	0.9	1.1	1.7
ethylbenzene	0.8	1.2	1.5
p-diethylbenzene	0.7	0.7	1.3
n-butane	0.6	0.7	0.6
m-ethyltoluene	0.6	0.9	0.9
isopentane	0.5	0.3	0.2
n-propylbenzene	0.5	0.7	0.9
acetone	0.5	0.2	0.1
1,2,3-trimethylbenzene	0.5	0.3	0.5
1-undecene	0.4	0.2	0.0
m-diethylbenzene	0.4	0.4	0.6
n-butylbenzene	0.4	0.3	0.6
o-dichlorobenzene	0.4	0.3	0.5
o-xylene	0.4	0.7	0.7
styrene	0.3	0.4	0.4
p-ethyltoluene	0.3	0.4	0.6
3-methylpentane	0.3	0.1	0.0
t-2-pentene	0.3	0.1	0.0
p-isopropyltoluene	0.3	0.1	0.0
benzyl chloride and *m*-dichlorobenzene	0.3	0.3	0.6
1,3,5-trimethylbenzene	0.3	0.4	0.7
isobutylbenzene	0.2	0.2	0.4
naphthalene	0.2	0.1	0.1
n-octane	0.2	0.4	0.2
dichlorodifluoromethane	0.2	0.3	0.4
1,1-dichloroethylene	0.2	0.2	0.0
b-pinene	0.2	0.5	0.7
chlorobenzene	0.2	0.4	0.3
dichlorotoluene	0.2	0.1	0.0
n-pentane	0.2	0.1	0.1
isopropylbenzene	0.2	0.2	0.0
benzene	0.2	0.1	0.1
n-hexane	0.2	0.3	0.1
n-heptane	0.1	0.2	0.1
isobutene + 1-butene	0.1	0.1	0.1
c-1,2-dichloroethylene	0.1	0.2	0.0
methylene chloride	0.1	0.2	0.0
isoheptane + 2,3-dimethylpentane	0.1	0.2	0.1
1,3-butadiene	0.1	0.0	0.0
vinyl chloride	0.0	0.3	0.2
ethanol and acetonitrile	0.0	1.1	0.2

[a] The listing includes all compounds from Table 3 plus any compound comprising 0.2% or more of the VOCs in any of the three sample types.

to the average value of 595 ppmv for landfill gas given in AP-42 (*6*). The U.S. EPA has published one compilation of composition data for landfill gas (*7*). The comparison shows that the Fresh Kills concentrations are at the low end of the range of published valves. The data also tend to be lower than results reported by Allen et al. (*8*) for seven landfills in the U.K. and results compiled by Brosseau and Heitz (*9*). The Fresh Kills data exhibit relatively low NMOC values versus earlier studies, probably due to greater dilution of the NMOC by the dominant landfill gases: methane and carbon dioxide. The moisture content within the landfill is thought to be relatively high (the average rainfall in the area is over 100 cm/year). This would tend to result in rapid degradation of the organic matter and production of relatively large volumes of methane and carbon dioxide versus landfills where the biological activity and gas generation are limited by the available moisture.

Relative Gas Composition as a Function of Emission Source. The flux chamber sampling approach involves dilution of the emitted landfill gas with sweep air, and the amount of dilution varies with the sweep air flow rate. Therefore, no concentration data of undiluted landfill gas were collected from the surface of the landfill. However, the relative composition of the landfill gas can be determined for flux chamber samples by converting the flux values from a mass basis to a molar basis. Table 4 contains the relative composition of VOCs measured in the landfill gas exiting the landfill from the passive vents, from the landfill surface, and to the gas collection plant. The relative fraction of each VOC is given as a function of the total VOC. The landfill gas

TABLE 5. Variability in Measured Concentrations

		variability (%CV)						
sample type	analyte	total	landfill section	spatial	short-term temporal	sampling[a]	analytical	measurement[b]
passive vent	methane	26.2[c]	0.0	25.9	3.6	NC[d]	NC	3.6
	total NMOC	42.7[c]	0.0	41.9	6.8	3.6	2.9	8.3
flux chamber	methane	92.3[e]	NC	82.4	40.8	0.0	7.8	41.5
	total NMOC	179.0[e]	NC	154.9	89.2	6.3	6.3	89.7

[a] Zero value indicates that variability due to this parameter was negligible relative to other parameters (e.g., temporal variability). [b] Measurement variability is equal to [temporal var.^{2} + sampling var.^{2} + analytical var.^{2}]$^{0.5}$. [c] Total variability is equal to [section var.^{2} + spatial var.^{2} + measurement var.^{2}]$^{0.5}$. [d] NC = Not calculated. No value determined due to lack of sufficient measurements to compare landfill sections or due to no duplicate data for methane measured by portable landfill gas analyzer. [e] Total variability is equal to [spatial var.^{2} + measurement var.^{2}]$^{0.5}$.

composition is remarkably consistent among all three measurement locations even though the emission rates for these three sources are quite different, indicating that the composition does not vary significantly as a function of landfill gas flow rate.

Sources of Variability. The measurement program included tests to determine the section, spatial, temporal, sampling, and analytical variability of the data set (the program addressed short-term temporal variability, but not seasonal variability). The variability for each of these factors (the variance component) was calculated using the SAS procedure PROC NESTED. The measured variabilities are summarized in Table 5. The total variability primarily was a function of the spatial variability within a given section of the landfill. The temporal variability exceeded the combined variabilities due to the sampling and analytical methods.

The gas collection system headers were sampled nine times during the program with the exception of VOC samples, which were collected six times. The flow rate and concentrations of the major constituents of the landfill gas (i.e., methane and carbon dioxide) were quite consistent during the program. The flow rate data have a percent coefficient of variation (%CV) of about 8% for both headers, indicating relatively little variation in flow rate during the program. The %CVs averaged 56% for CH_4 concentration and 37% for CO_2 concentration.

The individual extraction wells were sampled to determine the degree of spatial variability in compound concentration and gas composition in the landfill. A total of 25 extraction wells were sampled to make this determination. The average CO_2 and CH_4 concentrations were somewhat lower for the extraction wells than for the landfill gas collection system. This is primarily an artifact of the wells that extract gas from older garbage having very little flow and more air infiltration.

The average VOC concentrations in the extraction wells closely mirrored the values measured in the north and south field headers; however, there was significantly more variability in the concentrations. The %CVs for the individual VOCs usually were in the 70% range, which is a much larger variability than that seen in the north and south field headers.

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