

## ABSTRACT

COWIE, STEPHEN JAMES. Emission of non-methane organic compounds (NMOCs) and hazardous air pollutants (HAPs) from decomposing refuse and individual waste components and under different conditions. (Under the direction of Morton A. Barlaz.)

Lab scale reactors were used to measure the emissions of non-methane organic compounds (NMOCs ) and hazardous air pollutants (HAPs) from decomposing refuse. Reactors containing municipal solid waste (MSW) as well as reactors containing individual waste components (paper waste, yard waste, food waste, household hazardous waste) were operated under anaerobic conditions with leachate neutralization and recycle. Decomposition of MSW under aerobic and nitrate-reducing conditions was also studied. NMOC yields ranged from 0.016 mg-C/dry gm (paper) to 0.347 mg-C/dry gm (food). The data suggest that volatilization, or air stripping, is the primary mechanism of NMOC release, although the decomposition process also contributes.

**EMISSION OF NON-METHANE ORGANIC COMPOUNDS  
(NMOCs) AND HAZARDOUS AIR POLLUTANTS (HAPs) FROM  
DECOMPOSING REFUSE AND INDIVIDUAL WASTE  
COMPONENTS AND UNDER DIFFERENT CONDITIONS**

by

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## **Preface**

Sections 2.1-2.7.5 are modified versions of sections that John Ihnatolya wrote as part of his thesis (2002), which dealt with the initial setup and early operation of this research.

## **1.0 INTRODUCTION**

Municipal solid waste (MSW), after the removal of recyclable and compostable material, is typically landfilled in the U.S. Anaerobic conditions dominate waste decomposition in landfills and methane and carbon dioxide are the major decomposition products. In addition, trace amounts of non-methane organic compounds (NMOCs) are also present in landfill gas. These organic compounds include aromatics, aliphatics, chlorinated compounds, alcohols, ketones and terpenes (Allen et al., 1997). Although NMOCs comprise less than 1% of the total volume of gas produced by landfills, the emission of these compounds from landfills can negatively impact the environment. NMOCs include a category of compounds called volatile organic compounds (VOCs) which are precursors for the formation of ozone, a respiratory irritant. Additionally, some NMOCs are known or suspected carcinogens and are classified as hazardous air pollutants (HAPs).

Total NMOC emissions from landfills are regulated under the New Source Performance Standards (NSPS) and Emission Guidelines (EG), which were developed as part of the 1990 Clean Air Act Amendments (CAAA), and enacted on March 1, 1996 (61 Federal Register 9919). The NSPS applies to all landfills constructed after May 30, 1991, while the EG applies to any landfill constructed before this date that has received

waste since November 8, 1987. Under these regulations an annual NMOC emission rate must be estimated for a landfill if its design capacity is greater than 2.5 million Mg or 2.5 million m<sup>3</sup> of refuse. An annual emission rate equal to or greater than 50 Mg per year of NMOCs triggers NSPS/EG control requirements. These requirements include implementation of an active gas collection system, and combustion equipment, such as a flare, boiler or generator, capable of reducing the NMOC content of the gas by at least 98 % by weight.

Estimation of an NMOC emission rate requires an estimate of the gas production rate for the landfill and an NMOC concentration. A computer model known as LandGEM generates the estimate after receiving input for the ultimate methane yield from refuse ( $L_o$ ), the NMOC concentration, and the annual acceptance of refuse. Under the NSPS/EG, an estimate can be made with no site specific testing data. For this rough (Tier I) estimate NSPS/EG requires a default NMOC concentration of 4,000 ppmv as hexane, and an  $L_o$  of 170 m<sup>3</sup> CH<sub>4</sub>/Mg refuse to be used. If the Tier I estimate results in an NMOC emission rate greater than 50 Mg/year, testing can be done at the landfill to obtain site specific data that can be used in place of the default values.

In addition to the NSPS/EG, landfills are affected by the National Emission Standards for Hazardous Air Pollutants (NESHAPs), which were also updated as part of the 1990 CAAA. The NESHAPs are designed to protect humans from exposure to toxic compounds. Under the NESHAPs, 188 compounds are classified as hazardous air pollutants (HAPs). Landfills with potential to emit (PTE) greater than 10 tpy of any given HAP or 25 tpy total HAPs are classified as major sources. HAP emissions are estimated like NMOC emissions, but using the default concentrations for specific HAPs

presented in AP-42—EPA’s Compilation of Air Pollution Emission Factors. Under the NESHAPs, major source landfills are subject to maximum achievable control technology (MACT). Landfills that are not major sources of HAPs are classified as area sources and may be subject to MACT or generally achievable control technology (GACT). NESHAP regulations apply to landfills that are any of the following: 1) major sources of HAPs; 2) co-located with a major source of HAPs; 3) under NSPS/EG regulation, or; 4) a bioreactor with a design capacity greater than 2.5 million Mg or 2.5 million m<sup>3</sup> (68 Federal Register 2227).

The required control technology under NESHAP is the same as that required under the NSPS/EG with the following additions: 1) development and implementation of a startup, shutdown, and malfunction (SSM) plan, 2) more frequent reporting of operating parameters for control devices to ensure they are within an acceptable range, as well as prompt reporting of any deviation of the parameters from the acceptable range, and 3) timely installation and operation of gas collection systems at bioreactor landfills (68 Federal Register 2227).

The recent NSPS/EG and NESHAP regulations have made estimation of NMOC and HAP emissions from landfills very important. However, reliance on current default NMOC concentrations may not be ideal. The default values currently used were not developed with a sound understanding of the sources of NMOCs or the mechanism of their release. For one, the assumption that the NMOC concentration remains constant over the lifetime of a landfill may not be appropriate. Secondly, there is some evidence that the current default NMOC concentrations may be too high. Michels and Sullivan (2000) measured an average NMOC concentration of 454 ppmv as hexane from 146

landfills in the U.S., and 1 in Puerto Rico. The measured HAP concentrations were also lower than the default values listed in AP-42.

Initial research concerning NMOC production during refuse decomposition was performed by Barlaz and Thomas (1999). Comparing fresh residential refuse, a synthetic refuse that did not contain any household hazardous waste, and twenty year old refuse excavated from a landfill, NMOC yields in the range  $0.6 - 1.0 \times 10^{-4}$  grams of NMOC-C/dry gram of refuse were measured. NMOC production from fresh refuse was not considerably higher than that of either old refuse or synthetic refuse. Barlaz and Thomas observed an initial spike in the NMOC concentration, but the NMOC concentration then decreased and remained stable for 150–200 days after the initial spike.

The overall objective of this project was to develop a better understanding of the production of NMOCs during refuse decomposition. Specific objectives were to: 1) measure an ultimate yield for NMOCs from individual components of MSW during anaerobic refuse decomposition, 2) study the relationship between gas production and NMOC release, 3) compare anaerobic, aerobic and nitrate-reducing conditions, 4) identify specific trace organic compounds and determine whether volatile carboxylic acids are a major contributor to NMOC concentrations in landfill gas, 5) quantify emissions of HAPs, and 6) evaluate the contribution of household hazardous waste (HHW) compounds to NMOC emissions.

## **2.0 EXPERIMENTAL METHODS**

### **2.1 Experimental Design**

Seven treatments were used to measure NMOC emissions (Table 1). The first five treatments were designed to study the relative contributions of individual waste components to NMOC emissions. All of these treatments involved traditional anaerobic decomposition. Treatment 1 consisted of food waste. Treatment 2 was a yard waste simulation. According to EPA's Waste Characterization Report (1998), typical yard waste is 25% leaves, 25% branches and 50% grass by wet weight. Therefore, leaves, branches, and grass were added in those relative amounts for Treatment 2. Treatment 3 was a paper mixture. The mixture was prepared by first selecting the major components of paper and then normalizing their concentrations to 100% based on the US EPA's Waste Characterization Report (1998). The paper mixture consisted of 20% newsprint (ONP), 42% old corrugated cardboard (OCC), 15% office paper (OFF), 7% old magazines (OMG) and 16% third class mail. Treatment 4 was residential MSW. Treatment 5 was residential MSW that was spiked with selected household hazardous wastes (HHW). The chemical composition of the HHW material added is shown in Table 2. Sample calculations used to determine the relative amounts of the yard waste and mixed paper components are presented in Appendix A.

Treatments 6 and 7 were designed to simulate alternative landfill operating strategies. In Treatment 6, residential MSW was degraded under nitrate-reducing conditions. Treatment 7 involved aerobic decomposition of residential MSW for a period of 44 days, followed by anaerobic decomposition.

With the exception of the aerobic and nitrate-reducing reactors, all reactors were seeded with methanogenic leachate to rapidly initiate methane production. Background NMOC emissions from the leachate were measured in a set of control reactors. All treatments were tested in triplicate under conditions designed to stimulate refuse decomposition, including incubation in a room at 37°C and leachate neutralization and recirculation.

Table 1. Experimental Design

<b>Treatment</b>	<b>Description</b>
<b>1</b>	Food waste (FW)
<b>2</b>	Yard waste (YW)=25% leaves, 25% branches, 50% grass
<b>3</b>	Mixed paper (MP)= 20% ONP, 42% OCC, 15% OFF, 7% OMG, and 16% third class mail
<b>4</b>	Residential MSW (MSW)
<b>5</b>	Residential MSW spiked with selected HHW plus leachate (HHW)
<b>6</b>	Residential MSW decomposed under nitrate-reducing conditions (DN)
<b>7</b>	Residential MSW decomposed under aerobic conditions for 44 days followed by methanogenic conditions (Aerobic)
<b>8</b>	Leachate Control (Control)

Table 2. Waste Products added to Household Hazardous Waste Reactors

Trade Name	Compounds	
<sup>(a)</sup> <b>Liqued Kutzit Paint Remover</b>	Toluene	25-30%
	Acetone	25-30%
	Methylene Chloride	20-25%
<sup>(b)</sup> <b>Pennzoil Motor Oil</b>	Toluene	6,880 ug/kg
<b>Nail Polish Remover</b>	Acetone	100%

- (a) Supplied in Material Safety Data Sheet (MSDS) for product
- (b) Composition was determined by Chemical & Environmental Technology, Inc. (Cary, NC) using EPA Method 8021

## 2.2 Materials

The residential MSW used in this experiment was obtained from the Holly Springs Transfer Station on April 3, 2002. Refuse was obtained from a residential area collection vehicle. Refuse was then shredded in a slow speed, high torque shredder to a particle size of approximately 1 cm x 2 cm. Each paper type was obtained from the NC State Facilities department and shredded prior to use. The branches and leaves were obtained from the NC State Compost Facility. Freshly cut grass was obtained from a soccer field one day before its use. All yard waste components were kept at 4 °C until use. The food waste represents food scraps from a residential kitchen. The food scraps were collected over a period of several weeks and frozen prior to use.

The leachate added to each reactor was taken from a 30-gallon drum containing MSW that had been decomposing for approximately 1 year prior to use. At three times during the year, some of the old refuse was removed from the drum, and some fresh refuse was added to ensure that an active community of microorganisms was maintained. DI water was added to make leachate. The gas from the reactor was analyzed and contained approximately a 50/50 ratio of CH<sub>4</sub>/CO<sub>2</sub> before its use. In addition, the leachate pH had been 7 or above for approximately ten months.

### **2.3 Reactor Construction**

The reactors consisted of four subsystems: refuse containment, leachate collection, leachate recirculation and gas collection. The reactor setup is illustrated in Figure 1.

#### Refuse Containment

The refuse containment chambers were 8 inch diameter (20.3 cm) aluminum cylinders. The cylinders were fit with circular aluminum tops and bottoms that were 10 inches (25.4 cm) in diameter, and had 8 inch (20.3 cm) diameter grooves cut into them. Teflon coated viton o-rings (Smith Seal, Raleigh, NC) were inserted into the grooves. The tops of each refuse containment chamber also had two 3/8" (0.95 cm) holes—one for leachate recycle, and one for gas collection. The bottoms of each reactor had one 3/8" (0.95 cm) hole for leachate collection. Each hole was sealed with a JN series screwed bonnet needle valve (Raleigh Valve & Fitting, Raleigh, NC). The refuse containment chamber was designed with teflon stopcocks and JN series screwed bonnet needle valves

so that it could be isolated from the rest of the system for maintenance or possible replacement of damaged parts throughout the system. The containment chambers were 11 inches (27.9 cm) in length, forming a volume of 8 liters. All surfaces exposed to refuse were coated with kynar to prevent corrosion (Electro Chemical, Emmaus, PA). Figure 2 illustrates the refuse containment chamber.

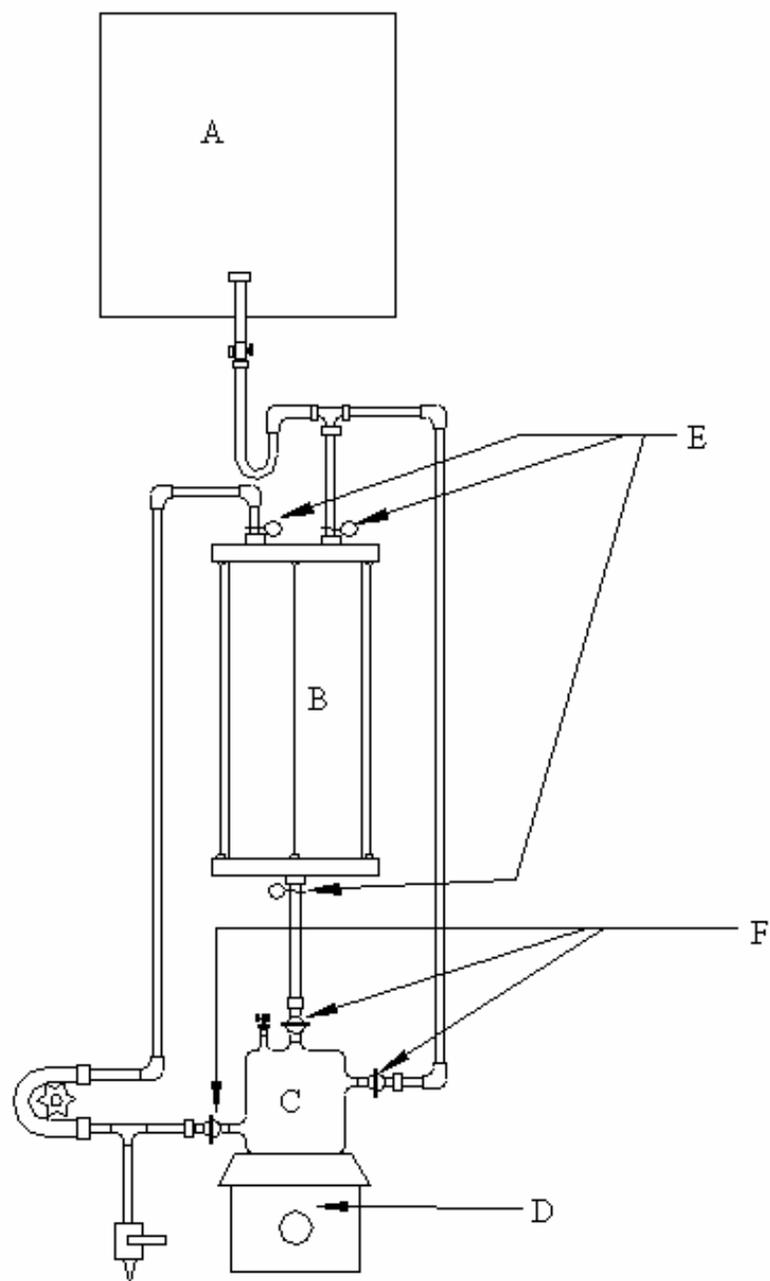


Figure 1. Reactor Design. A, 20-L 2mil tedlar inner with aluminized outer gas bag (P.M.C., Oak Park, IL); B, refuse containment chamber; C, leachate collection vessel; D, magnetic stirrer; E, JN series screwed bonnet needle valves; F, teflon stopcocks; All other parts will be identified in subsequent drawings.

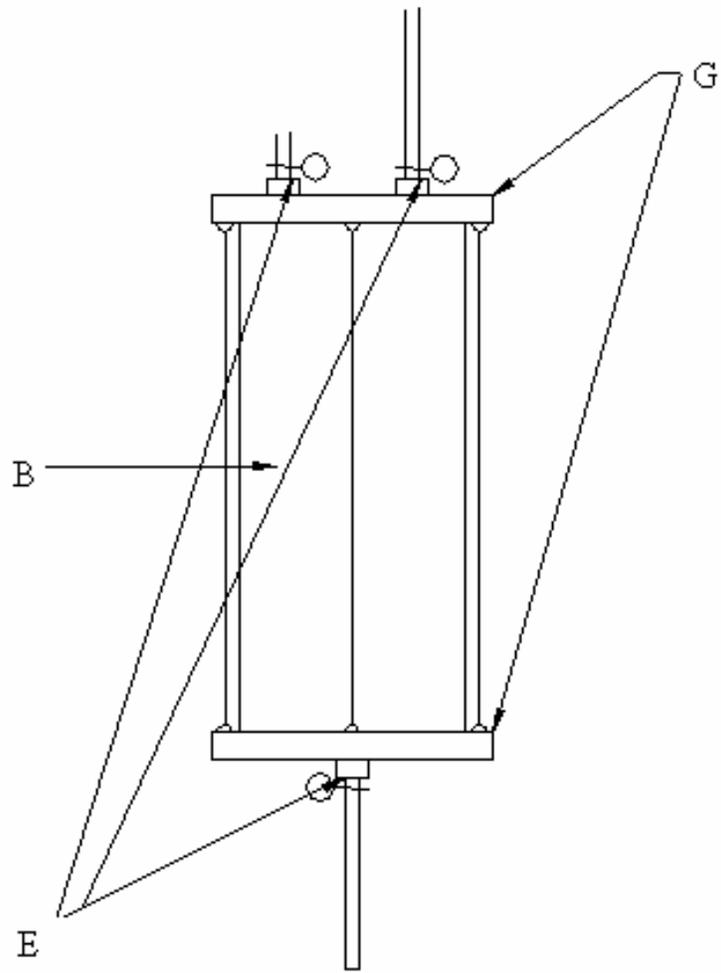


Figure 2. Refuse Containment Chamber. G, aluminum top and bottom

### Leachate Collection

Leachate collection was performed by gravity drainage into a specially fabricated 1.5-L glass leachate collection vessel. The leachate collection vessel includes: a leachate collection port, a leachate recycle port, a gas release port, and a buffer addition port. Each port was equipped with a teflon stopcock. The leachate collection port was located at the top of the vessel and allowed the leachate to drain from the reactor to the collection vessel. The leachate recycle port, located at the bottom front of the vessel, allowed leachate that had been drained into the vessel to be recycled back into the reactor. The gas port was present to alleviate any gas accumulation in the leachate collection vessel and to prevent airlock during leachate recirculation. The neutralization port was fit with a 13mm miniert valve (Supelco, Bellefonte, PA) located at the top of the leachate collection vessel to allow for NaOH addition. The leachate collection vessel is illustrated in Figure 3.

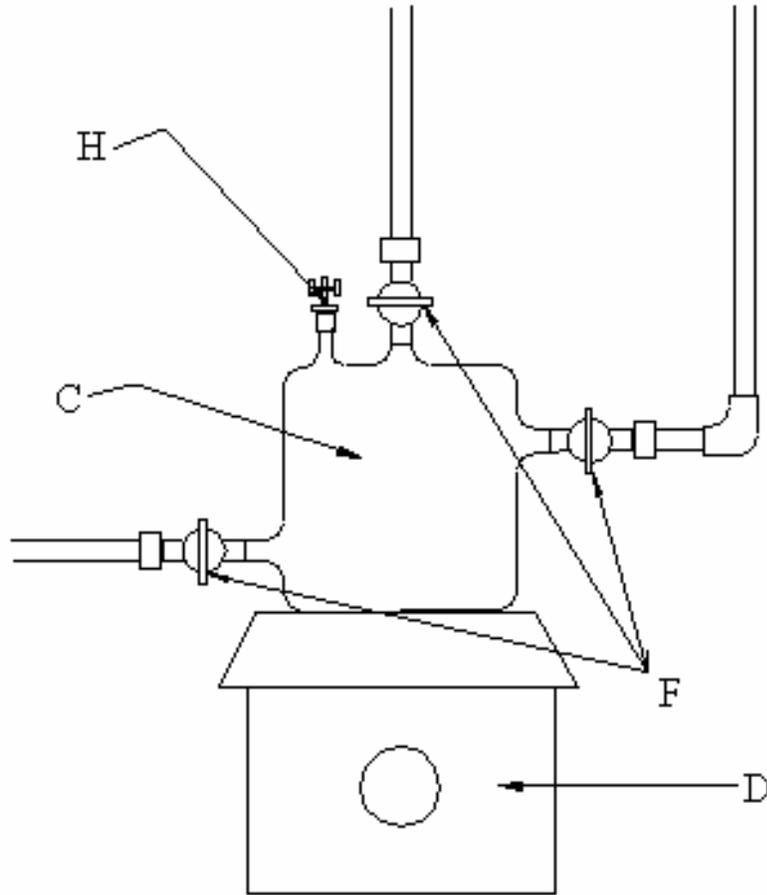


Figure 3. Leachate Collection Vessel. H, 13mm miniert valve.

### Leachate Recirculation

Recirculation of leachate was achieved using a peristaltic pump (Masterflex 7518-00, Cole-Parmer, Vernon Hills, IL). Leachate entered and exited the collection vessel through flexible teflon-lined tygon tubing. The pump operation required compressible viton tubing. Therefore, a piece of viton tubing (approximately 2 feet long) was

connected to the tygon tubing on one end, and stiff kynar tubing on the other. The kynar tubing carried the leachate back into the opening on top of the refuse containment chamber. Kynar tubing was also used to connect the gas port of the collection vessel to the gas port on the lid of the refuse containment chamber. The leachate recirculation system is illustrated in Figure 4 and a detailed parts list is presented in Appendix B.

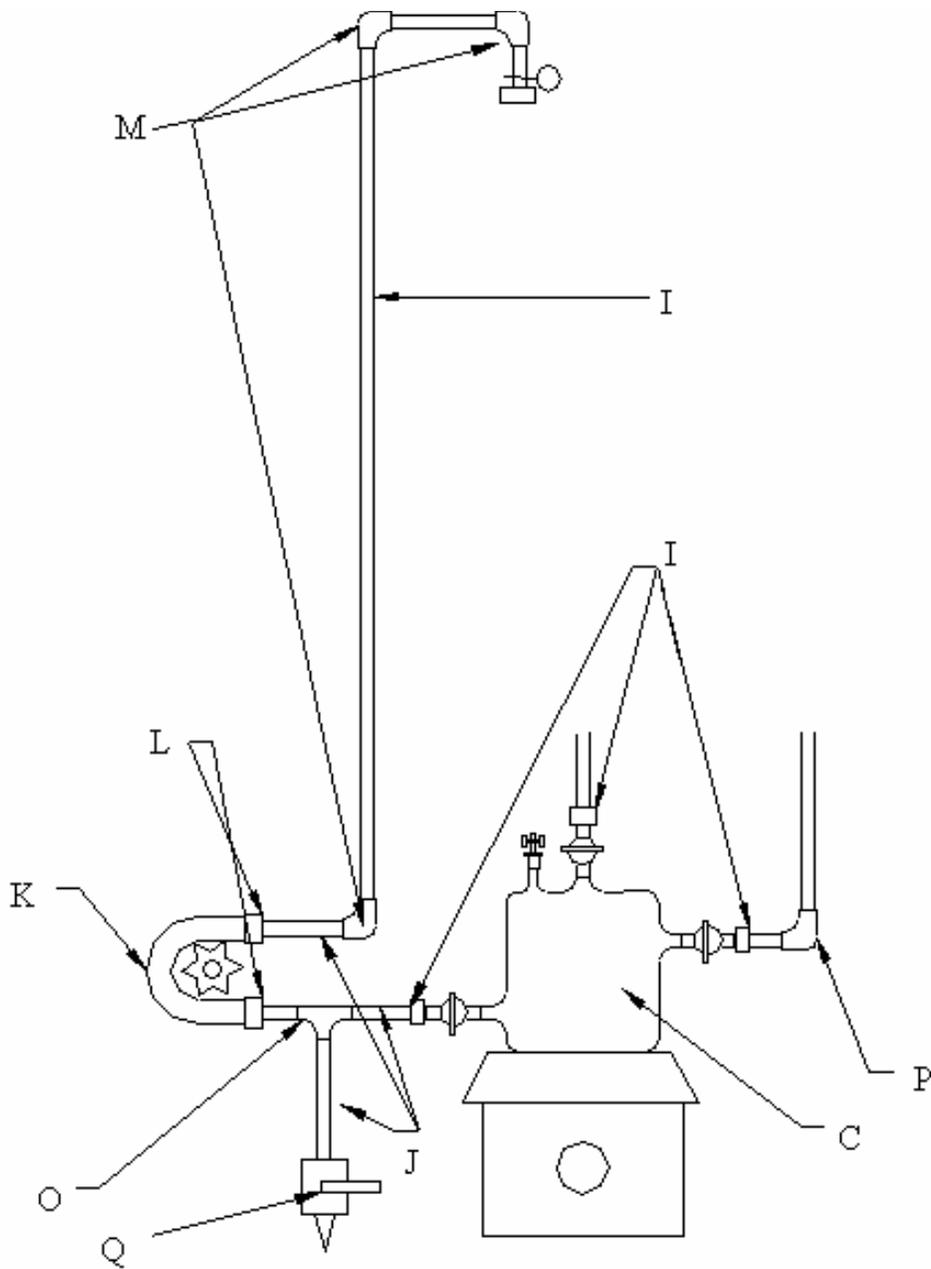


Figure 4. Leachate Recirculation System. I, kynar tubing; J, teflon lined tygon tubing; K, viton tubing; L, kynar reducing straight connector; M, female brass elbow; N, brass vibra-timer male straight adapter w/ female brass connector and female brass adapter; O, ¼" kynar tee; P, kynar elbow adapter; Q, mini brass ball valve

## Gas Collection

Teflon lined tygon tubing was used to connect the kynar tubing of the refuse containment chamber's gas port to the gas-sampling bag. Gas-sampling bags were attached to strings and hung from the ceiling so that they would remain elevated. The gas collection system is illustrated in Figure 5 and a detailed parts list is presented in Appendix B.

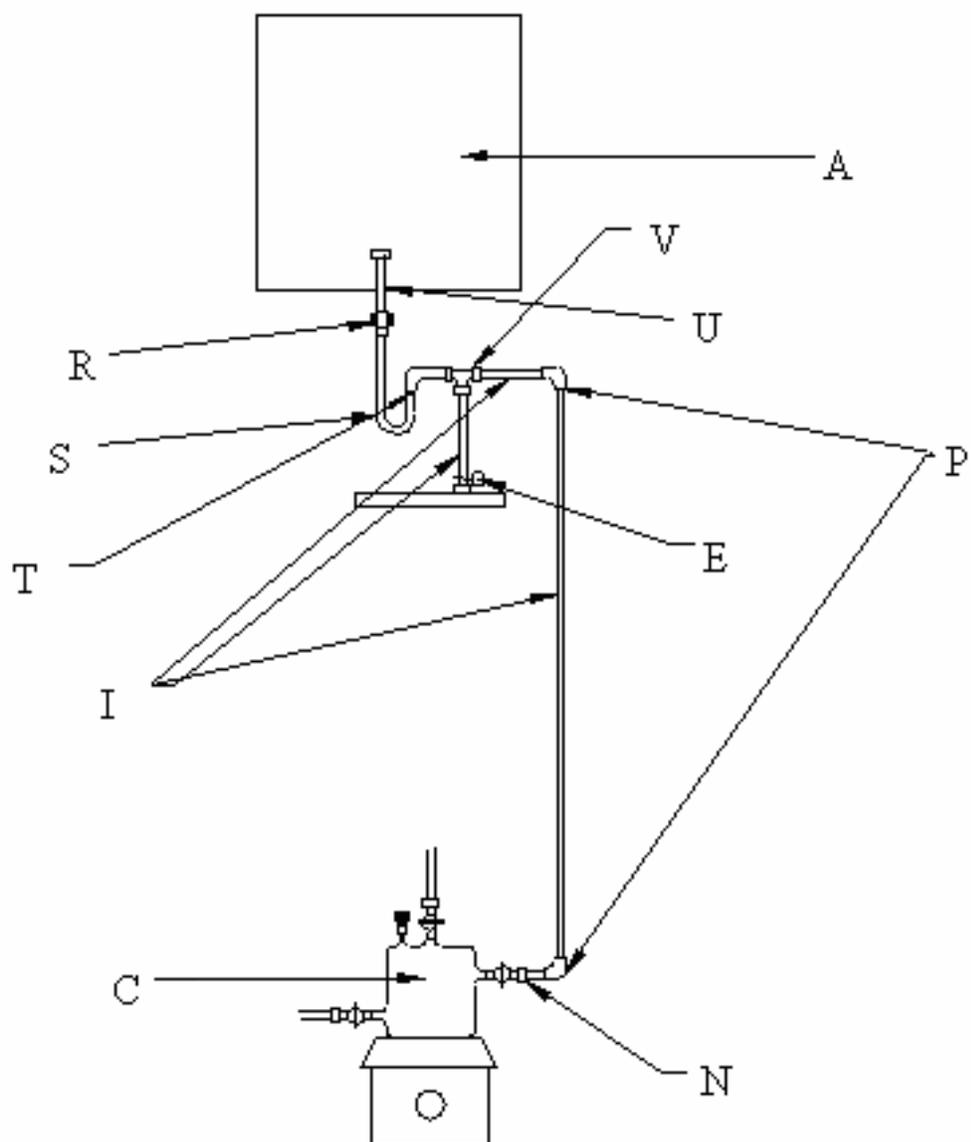


Figure 5. Gas Collection System. R, SGE syringe valve SLLV; S, teflon lined tygon tubing; T, male luer x barb; U, kynar tubing w/ ETFE shut-off valve and ETFE female luer adapter; V, brass Swadgelock male tee.

## Aerobic Reactors

The air supply system for the aerobic reactors is illustrated in Figure 6. The airflow system consisted of a pressure gage attached to the building air system. The pressure gage (McMaster-Carr, Atlanta, Ga.) was then attached to two Koby Junior King filters (Scientific Instrument Services, Ringoes, NJ) in series, to remove VOCs. The air was then routed through two 5 N KOH traps in series and a DI water container to humidify the air. An aluminum manifold (McMaster-Carr, Atlanta, Ga.) was used to split flow three ways. Flow meters were used to monitor and equilibrate the flow rate fed to each reactor. Water traps were installed to prevent any leachate that might drain out of the air port from reaching the flow meters. All tubing used to connect components was teflon coated tygon tubing.

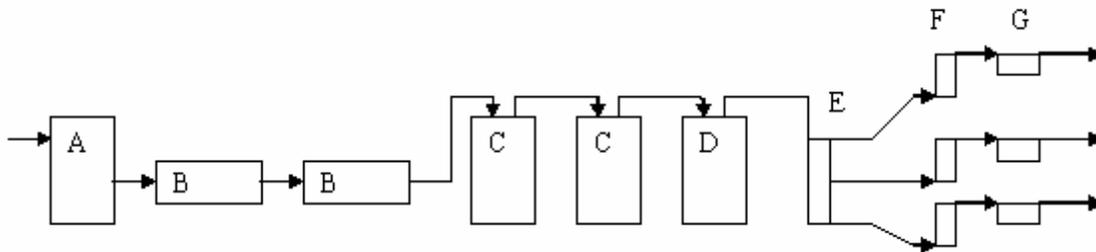


Figure 6. Air flow system for aerobic reactors. A, regulator attached to lab air system; B, Koby Junior King filters in series; C, 5N KOH traps; D, DI water; E, aluminum manifold; F, flow meter; G, water trap. All tubing used to connect all components was teflon coated tygon tubing. A detailed parts list is presented in Appendix B.

## 2.4 Reactor Setup

Refuse was added to all reactors on April 5, 2002. Fiberglass fabric was placed on the bottoms of the refuse containment chambers, followed by a thin layer of gravel. The purpose of the fiberglass fabric and gravel was to allow proper drainage of leachate and to minimize clogging of the drainage hole. Refuse was added and compacted in 5” lifts to a height about 2” from the top. Following refuse addition, fiberglass cloth was placed on top of the refuse to distribute recycled leachate. Steel rods were placed in pre-drilled holes on the top and bottom plates of the refuse containment chambers. A silicone based high vacuum grease (Dow Corning, Midland, MI) was then applied to each teflon coated viton o-ring to provide a good seal. Finally, the reactor covers were tightened on to the reactors by using nuts and the threaded rods. Each reactor was then evacuated to less than 200 mbar of pressure and the vacuum monitored for 5 minutes to ensure that leaks were not present. After leak checking, 20-L gas bags were attached to each reactor and leachate was added to the leachate collection vessels and recycled to initiate the experiment. The amount of leachate added was determined by assessing the volume that drained. If less than 100 mL of leachate drained, an additional 500 mL was added. The contents of each reactor are presented in Table 3, and the masses of HHW components added to each of the HHW treatment reactors are presented in Table 4.

Table 3. Reactor Contents

	Food Waste			Residential MSW			Res. MSW plus HHW			Res. MSW under NO <sub>3</sub>			Res. MSW Aerobic			Leachate Control		
	1	2	3	1	2	3 <sup>(b)</sup>	1	2 <sup>(b)</sup>	3	1	2	3 <sup>(b)</sup>	1	2	3	1	2	3
Wet grams added	1055	1049	1042	964.6	1113.7	1259.2	1001.5	1002.5	1000.9	1211.9	995.8	1376.9	1009.1	972.1	782.9			
% moisture	59.5	59.5	59.5	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8			
Dry grams added <sup>(a)</sup>	427.2	424.8	422	763.5	881.5	996.7	792.7	793.5	792.2	959.2	788.2	1089.8	798.7	769.4	619.7			
Leachate added (L)	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1	0.5	0.5	0.5
Total water volume (L)	2.63	2.62	2.62	1.2	1.23	1.26	1.2	1.2	1.2	1.28	1.23	1.31	1.7	1.69	1.65			
Dry grams out	57.5	54	36.8	363.8	462.7	542.2	459.2	475.9	476.4	502.6	411.4	609	440.2	433.9	388.7			

	Mixed Paper																	
	ONP			OCC			OFF			OMG			Third class mail			TOTAL		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Wet grams added																		
% moisture	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
Dry grams added	201.2	183.8	189.5	420.1	383.1	398.7	150.2	138.3	143.2	70.4	63.8	66.9	153.7	145.6	151.3	995.6	914.6	949.6
Leachate added (L)																1.5	1.5	1.5
Total water volume (L)																1.5	1.5	1.5
Dry grams out																513.4	607.5	633.3

	Yard Waste											
	Leaves			Grass			Branches			TOTAL		
	1	2	3	1	2	3	1	2	3	1 <sup>(b)</sup>	2	3
Wet grams added	200.6	147.1	150.4	400.5	292.9	301.1	200.6	146.7	189.5			
% moisture	7.7	7.7	7.7	26.2	26.2	26.2	16.4	16.4	16.4			
Dry grams added	185.1	135.7	138.8	295.8	216.3	222.4	167.7	122.7	158.5	648.6	474.7	519.7
Leachate added (L)										2	2	2
Total water volume (L)										1.59	1.57	1.58
Dry grams out										468.4	363.6	330.4

- a) Food waste reactors were batch fed according to the schedule shown in Table 5
- b) Reactor leaked and was not considered in the results

Table 4. HHW Addition

<b>Mass added (mg)</b>				
	<b>Product</b>	<b>Acetone</b>	<b>Toluene</b>	<b>Methylene Chloride</b>
Liqued Kutzit Paint Remover	667	183	183	150
Pennzoil Motor Oil	667		4.6 x 10 <sup>-3</sup>	
Nail Polish Remover	667	667		
<b>Total</b>	<b>2001</b>	<b>850</b>	<b>183</b>	<b>150</b>

The food waste treatment reactors initially received only about 370 wet grams of refuse. The initial mass of refuse added was low because these reactors were fed in a batch mode to prevent an inhibitory acid accumulation and pH decrease. Subsequent food waste additions were made through a special hole in the lids of the food waste containment chambers. To accomplish this it was necessary to blend the food waste into a puree. A schedule of food waste additions is presented in Table 5.

Table 5. Food Waste Addition Schedule

<b>Food Waste Added</b>								
	<b>F1</b>			<b>F2</b>			<b>F3</b>	
	<b>Wet grams</b>	<sup>a</sup> <b>Dry grams</b>		<b>Wet grams</b>	<b>Dry grams</b>		<b>Wet grams</b>	<b>Dry grams</b>
<b>Day</b>								
0	368.1	149.1		370.2	149.9		367.3	148.8
20	127.5	51.6		128.8	52.2		125.9	51.0
30	101.5	41.1		100.2	40.6		101.1	40.9
40	148	59.9		150.4	60.9		150.3	60.9
50	154.6	62.6		147.2	59.6		148.7	60.2
60	154.9	62.7		152	61.6		148.5	60.1
<b>Total</b>	<b>1054.6</b>	<b>427.1</b>		<b>1048.8</b>	<b>424.8</b>		<b>1041.8</b>	<b>421.9</b>

a) Percent moisture of food waste was 59.5%

## **2.5 Reactor Operation and Monitoring**

### **2.5.1 Anaerobic Reactors**

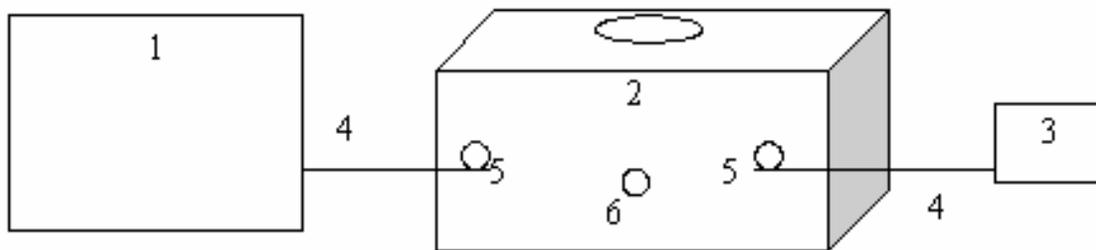
#### Leachate Quality

Leachate pH was monitored and maintained in the neutral range, between 6.8 and 7.5, for all reactors. Initially, the pH was measured daily. Once the pH stabilized in the neutral range, it was checked weekly. The leachate was kept in the refuse containment chamber except during the pH neutralization and recirculation process. During the leachate neutralization process, the leachate was mixed in the leachate collection vessel with a magnetic stir bar. Approximately 10 mL of leachate was sampled using the leachate sampling port. If the leachate pH was below 6.8, 5M NaOH was added through the mininert valve, after which a second sample was collected to verify that the pH was between 7 and 8. Thereafter, leachate samples were returned to the leachate collection vessel by needle and syringe through the mininert valve. Leachate samples were also collected from each reactor bi-weekly for COD analysis.

#### Gas Composition

When a 20-L tedlar gas-sampling bag approached its capacity, gas composition analyses were done. First, a sample was removed from the bag by a syringe for analysis of CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. Next, a sub-sample was taken from the gas bag for NMOC analysis. This sub-sample was transferred from the 20-L gas bag to a smaller (10-L) gas bag by using a VAC-U-Chamber (SKC, Eighty Four, PA). This process consisted of a 30-L plastic airtight chamber, teflon coated tygon tubing and a low flow vacuum pump. The transfer of gas from the larger gas bag to a smaller gas bag was accomplished by

connecting an evacuated 10-L gas bag to tubing inside the VAC-U-Chamber. This tubing extended through the chamber to the outside. To the outside end of the tubing, the full bag was attached. Valves on both of the gas bags were opened allowing flow to occur from one bag to another. The chamber was closed and evacuated at a rate of 2 L/min for approximately 5 minutes. This procedure resulted in the transfer of 2-4 liters of gas to the smaller gas bag for NMOC analysis. The sub-sample of gas was immediately delivered to Triangle Environmental Services (Research Triangle Park, NC), an EPA certified laboratory, where NMOC analysis was done using EPA Method 25C. The transfer system for producing a sub-sample is illustrated in Figure 7.



1. 20-L tedlar gas bag
2. VAC-U-Chamber with 10-L gas bag inside
3. Low Flow Vacuum Pump
4. Teflon lined tygon tubing
5. Quick connect valves used to connect gas bag and pump to Vac-U-Chamber
6. Air release valve

Figure 7. NMOC Transfer System

Samples for determining volatile fatty acid (VFA) composition were also taken from the 20-L bags. Gas was pulled from the gas bag through an orbo tube (Orbo No. 70 Adsorbent orbo tubes 335/165mg) by using an SKC pump (SKC, model 224-PCXR8, Eighty Four, PA) at approximately 100 mL/min for 10 minutes. The exact flow rates and times were measured and recorded. Flow through orbo tubes was established by securing one end of the tube in a luer lock fingertight fitting that was connected to 1/8" (0.32 cm) OD kynar tubing. The kynar tubing was connected to the gas bag with a 1/8" (0.32 cm) X 1/4" (0.64 cm)-28 female-male luer assay (Upchurch Scientific, Oak Harbor, WA.). The other end of the orbo tube was attached to a piece of tygon tubing that connected to the SKC pump. VFA samples were collected in duplicate and frozen prior to analysis. Remaining gas in the 20-L bag was analyzed by GCD for specified trace organic compounds as described in section 2.7.

### Gas Volume

The total volume in a gas bag was calculated as the sum of the volumes removed for NMOC, VFA and GCD analyses, plus the residual volume. The volume removed for NMOC analysis was reported by TES. The volume for VFA analysis was known from the pump flow rate and pump time. The volume for GCD analysis was known from the sample volume specified. The volume remaining was analyzed by a technique described in the analytical methods section.

### 2.5.2 Aerobic Reactors

The aerobic reactors were operated at an air flow rate of 30-50 mL/min. This range was identified in preliminary work as sufficient to insure the presence of at least 1-2% oxygen in the exit gas. Preliminary work also showed that in the absence of supplemental water addition, refuse would dry out. To address this, DI water was added to an aerobic reactor if it generated less than 500 mL of leachate when drained. Water additions were necessary as shown in Table 6.

Table 6. Water Additions for Aerobic Reactors (mL)

<b>Date</b>	<b>Days from Start</b>	<b>Water Addition to Reactor 1</b>	<b>Water Addition to Reactor 2</b>	<b>Water Addition to Reactor 3</b>
4/5/02 11:00 PM	0			
4/12/02 10:00 AM	6	100		200
4/24/02 10:00 AM	18		400	
5/20/02 10:00 AM	44	300	200	100

In addition to drying, overheating was a concern. Therefore, temperature measurements were made daily through holes that had been specially drilled in the aerobic reactors for this purpose.

#### Gas Composition

Gas monitoring for the aerobic reactors was complex because, in contrast to the anaerobic reactors, it was not possible to contain all of the gas passing through the refuse. Instead, the effluent gas flow was connected to a 20-L gas-sampling bag in 10 minute

intervals, 5 times a day. After a period of about 10 days, the bags approached volume capacity. Their contents represented a composite sample from this time period. The composite samples were processed for the same analyses as described for the anaerobic reactors. Effluent gas flow rates were measured and recorded 5 times a day using a digital bubble flow meter (model 650, Fisher Scientific, Pittsburgh, PA.). This flow rate data was used to compute an average flow rate for the entire time over which the composite sample was collected. The CO<sub>2</sub> concentration of the effluent gas was measured daily, and chromatograms were reviewed to verify the absence of methane production. After 44 days, air flow was discontinued and the reactors were operated anaerobically.

### **2.5.3 Nitrate-Reducing Reactors**

Nitrate-reducing conditions were maintained by adding either  $\text{KNO}_3$  or  $\text{Mg}(\text{NO}_3)_2$ , every second or third day, in an amount that resulted in a final concentration of 400 mg/L of  $\text{NO}_3\text{-N}$  in the reactor leachate. The reason for adding two different forms of  $\text{NO}_3^-$  was to prevent the buildup of salts in the leachate. Once the  $\text{Mg}^{+2}$  concentration reached between 1,000 and 2,000 mg/L,  $\text{KNO}_3$  was used. When the  $\text{K}^+$  concentration reached between 5,000 and 8,000 mg/L the leachate was drained and replaced. Results published by Kugleman (1971) suggest that salt concentrations higher than these levels could be inhibitory. Leachate was monitored for nitrate to ensure that nitrate was being depleted and not accumulating. All other aspects of the operation and monitoring of the nitrate-reducing reactors were the same as those for the anaerobic reactors.

## **2.6 Handling of Gas-Sampling Bags**

### **2.6.1 Cleaning**

Since the tedlar gas-sampling bags were reused, it was necessary to clean the bags after the gas sampling process was complete. Used bags were filled about  $\frac{1}{4}$  full with UHP nitrogen and baked at  $60^\circ\text{C}$  for 20 minutes. The bags were then evacuated while the gas was warm. This process was repeated twice.

### **2.6.2 Bag Re-use**

For the first 60 days of the experiment, cleaned gas-sampling bags were re-used indiscriminately. On approximately day 60, it became apparent that the cleaned bags carried over some contamination that was affecting the concentrations of certain organic compounds in subsequent samples. Thereafter, bags were assigned to specific reactors so that no cross-contamination could occur between reactors.

The nature of compound carryover following bag cleaning was analyzed by comparing the concentrations of compounds in a reactor sample to their concentrations in a cleaned bag containing UHP nitrogen. This comparison was done for two MSW reactor samples on day 190 of the experiment. Using the results of these comparisons (shown in Table 7) it was determined that experimental data for some compounds was unusable. Further information concerning the discarding of data is presented with the results.

**Note:**

After the data collection pertaining to this thesis was complete, but prior to additional experimentation, further analysis of bag cleaning was done. Bags were cleaned six times instead of twice, and analyzed to determine whether the additional cleanings could bring the removal of all compounds to an acceptable level. The results of this study are shown in Table 8. Between 80 and 100% removal was measured for all compounds except one measurement of 19% for ethanol, and one measurement of 60% for toluene. The low measurement for toluene is an outlier as 5 other samples resulted in 85-100% removal of toluene. The data for ethanol removal is inconclusive, however, since only two measurements were made. Overall, it was concluded that cleaning bags six times is a satisfactory method for removing residual of organic compounds from gas bags.

Table 7. Results of the Bag Cleaning Effectiveness Analysis

<u>Incomplete Removal</u>	<u>Concentration (ng/L)</u>		<u>Concentration (ng/L)</u>	<u>Concentration (ng/L)</u>
	<u>Original Sample</u>	<u>Residual</u>		
Ethanol	7279	2569	77359	13038
Acetone	3739	7423	9328	3032
2-Propanol	493	178		671
t-Butanol	592	84	734	
2-Butanone	229633	102879	107012	41980
2-Pentanone	12927	4198	12405	2479
Toluene	723	173	935	190
ethylbenzene	4822	1070	3419	498
m&p-xylenes	1870	513	967	182
o-xylene	402	117	190	36
1-methyl-3-ethylbenzene	217	55	230	36
1-methyl-4-ethylbenzene	164	42	71	
1,3,5-trimethylbenzene	202	58	245	48
1-methyl-2-ethylbenzene	107	29	130	22
decane	4471	41	9950	53
1-methyl-4-isopropylbenzene	8589	1717	13386	1742
Limonene	15337	1079	49877	2082
1-methyl-3-propylbenzene	148	41	325	54
1-methyl-4-propylbenzene	51		121	16
1,3-dimethyl-5-ethylbenzene	129	31	299	48
gamma-Terpinene	343	68	353	
1-methyl-2-propylbenzene	84	23	197	32
1,4-dimethyl-2-ethylbenzene	75	29	187	31
n-undecane	2183	37	9604	73
Styrene	89	56		

Complete Removal

<u>Compound</u>	<u>Initial Concentration (ng/L)</u>		<u>Compound</u>	<u>Initial Concentration (ng/L)</u>	
Pentane	8590	3084	2-methylnonane	623	1193
cis-2-Pentene	118	129	3-ethyloctane	71	120
2-methylpentane	253	266	3-methylnonane	433	801
3-methylpentane	82	89	beta-Pinene	5139	1853
hexane	496	466	isobutylcyclohexane	178	323
Ethyl Acetate	182	461	1-decene	67	291
methylcyclopentane	148	199	1-methyl-2-propylcyclohexane	133	468
benzene	36	58	isobutylbenzene	25	89
2-methylhexane	13563	13190	sec-butylbenzene	67	103
3-methylhexane	782	186	butylbenzene	56	125
heptane	587	601	1,2,4-trichlorobenzene	250	692
4-Methyl-2-pentanone	1605	1669	2-methyl-1-butene	116	
1-octene	415	469	1,2-dimethyl-4-ethylbenzene	60	
octane	296	272	trans-2-nonene	44	
trans-2-octene	84	81	2-methyloctane	359	
cis-1,2-dimethylcyclohexane	70	126	cyclohexane	806	
3-methyloctane	75	52	2,5-dimethylhexane	62	
nonane	760	660	methylcyclohexane	51	
1-methylethylbenzene	99	88	2-Methyl-1,3-Butadiene	54	
isopropylcyclohexane	42	34	trans-2-Pentene	115	
Propylcyclohexane	148	243	1,2-dimethyl-3-ethylbenzene		307
alpha-Pinene	3315	6334	2,2,3-trimethylpentane		60
3,3-dimethyloctane	46	55	1-heptene		127
Camphene	107	149	1-Butanol		4336
2,3-dimethyloctane	282	424			

Table 8. Percent Removal After Six Bag Cleanings

Compound	Sample Test Trials <sup>1</sup>					
	1	2	3	4	5	6
Ethanol	N/A <sup>2</sup>	N/A	81	N/A	19	N/A
Acetone	90	91	81	N/A	N/A	N/A
2-Butanone	90	90	92	100	100	N/A
Toluene	88	85	88	100	100	60
Ethylbenzene	100	88	100	N/A	100	100
m&p xylenes	N/A	97	100	N/A	N/A	N/A
o-xylene	N/A	89	100	N/A	N/A	N/A
1-methyl-3-isopropylbenzene	100	100	93	100	86	N/A
1-methyl-4-isopropylbenzene	100	100	94	100	86	N/A
Limonene	100	100	96	N/A	90	N/A

1-The results for each sample test trial are for after 6 cleanings. There were 6 different bag samples used.

2- "N/A" indicates that no data is available for the compound in that sample since it was not present in the original sample.

\*Compounds completely removed are not listed

## 2.7 Analytical Methods

### 2.7.1 Methane and Carbon Dioxide Analysis

Carbon dioxide and methane were analyzed by using a GOW-MAC 580 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a CTR1 column (Alltech, Deerfield, IL). The settings for the GC are presented in Table 9. A three point standard curve was set up using the gas standards given in Table 10. After the initial standard curve was established, one standard was injected every time the GC was used. If the standard injection resulted in peak areas that were within 5% of the initial curve, a new standard curve was not produced. If the peak areas varied from the standard curve by more than 5%, a new standard curve was developed.

Table 9. Settings for GOW-MAC

Description	Setting
Carrier Gas	Helium
Column	CTR1
Attenuation	1
Flow Rates	50 mL/min for Column A and B
Current	150 milliamps
Temperature	75 °C
Temperature	28 °C
Temperature	28 °C

Table 10. Standards Used for Curve

Standard	% CH <sub>4</sub>	% CO <sub>2</sub>	% N <sub>2</sub>	%O <sub>2</sub>
1	10	20	70	0
2	50	40	10	0
3	25	10	1	1

### 2.7.2 Nitrate Analysis

Nitrate (NO<sub>3</sub><sup>-</sup>) samples were frozen immediately after sampling. Prior to analysis they were thawed and filtered. To filter the samples they were placed in a 10 mL plastic disposable syringe connected to a conditioned C18 cartridge (Alltech #20936) and a 25 mm syringe filter. After treatment, samples were analyzed by ion chromatography (IC) using a Dionex AS4A column. A 1.8-nM sodium carbonate/1.7-nM bicarbonate buffer served as the mobile phase.

### 2.7.3 COD Analysis

The COD measurement was accomplished by using a Hach Kit (Hach Co., Loveland, CO). The procedure is described in Appendix C.

### 2.7.4 Gas Volume

A 4-liter evacuation chamber was used to measure gas volume. To calculate the volume of gas in each gas bag, Boyle's law (Equation 1) was used. The volume was then corrected to standard temperature and pressure (273° K and 760 mm Hg). The gas volume measurement apparatus consisted of a stainless steel cylinder that could be sealed at two ports by valves. One port was connected to a vacuum pump and the other port was connected to a manometer and then to a gas bag.

$$V_s = (P_i - P_f) * V_c / P_a \quad (1)$$

$V_s$  = volume of the gas sample

$V_c$  = volume of cylinder

$P_i$  = pressure reading initially of the evacuation chamber

$P_f$  = pressure reading of evacuation chamber after evacuating gas bag

$P_a$  = atmospheric pressure

### 2.7.5 Total NMOC Analysis

Total NMOC analysis was performed by Triangle Environmental Services using EPA Method 25C. All samples, including standards, were analyzed in triplicate. The GC model and settings used for analysis are presented in Table 11. The NMOC concentration was reported as milligrams of carbon per cubic meter.

Table 11. Settings for Total NMOC Analysis

Description	Setting
GC Model	Varian 3400
Column	3.2mm OD Packed, 30cm 680 mesh unibeaded, 60 cm 6080 mesh carbosieve G
Carrier Gas	Helium
Detector	Flame Ionization Detector
Temperature Program	Ramp to 195°C at 30°C/min
Oven Temperature	80°C

### 2.7.6 Analysis of Specific Organic Compounds

The method for identification and quantification of specific organic compounds of analysis is described here, including the type of instrument used and settings, sampling technique, preparation of standard curves, and peak identification and quantification. Furthermore, data is provided to validate the techniques used.

#### A. ANALYTICAL METHODS

##### Instrument

Trace constituents were analyzed using a Tekmar Autocan Sampler, Model # 14-ACAN-000 and Hewlett Packard G1800A GCD System gas chromatograph with an electron ionization detector. Settings used for the GCD are presented in Table 12.

Table 12. Settings for GCD

Description	Setting
GC Model	HP G1800A
Column	Petrocol DH, 100m x 0.25mm ID, 0.50 $\mu$ m film
Carrier Gas	Helium
Detector	Electron Ionization Detector
Oven	35°C (15 min) to 320°C at 2°C/min
Detector Temperature	280°C
Injector Temperature	200°C

### Sampling Procedure

The Autocan sampler was capable of holding up to 16 samples at one time. The gas-sampling bags were connected to the Autocan by PEEK tubing. During GCD analysis, the gas bags were kept inside a wooden box equipped with a small space heater and a latching door. The purpose of the box was to keep the gas samples warm so to prevent any condensation. The temperature in the box was maintained at approximately 40°C. Holes were drilled in the box so that the PEEK tubing could extend from the Autocan sampling ports into the box. The tubing was attached to gas bags with a 1/8" X 1/4"-28 female-male luer assay (Upchurch Scientific, Oak Harbor, WA). The bags were hung from a steel rod that was inserted at the top of the box.

All initial samples were taken at a volume of 200 mL. Chromatograms of the samples were viewed after the initial analysis to determine if further analysis was necessary. For a given sample, if any compound appeared to produce a peak area that would exceed the maximum range of the compound's standard curve, a second sample containing a reduced mass of organic compounds was analyzed. Reduction in the mass of organic compounds was accomplished by sampling a lower volume of gas or preparing

a dilution. The lower volumes used were typically either 50 mL or 25 mL. Dilutions were prepared when the concentration of a given compound was exceptionally high. To prepare a dilution, 940 mL of ultra high purity (UHP) nitrogen was put into a 2-L gas-sampling bag using a 1-L gas tight syringe. Then 50 mL of the original gas was added to the 2-L gas bag. Diluted samples were typically run at a volume of 25 mL.

### Standard Curve Preparation and Analysis

#### 1. Standard Solutions

Standard curves were prepared for 160 compounds. Since no commercially available single standard solution contained all of the compounds of interest for this experiment, five separate solutions were purchased. The compositions of these solutions are listed in Table 13. The PIANO mixture of hydrocarbons was purchased from Supelco (Sigma-Aldrich) Inc. (Bellefonte, PA). The other four standards were purchased from Absolute Standards Inc. (Hamden, CT). For each standard mixture, a gaseous sample was prepared. The procedure for preparation of gaseous standard samples from liquid standards is described in Appendix D.

Table 13. Composition of Standards Used for Quantification of Speciated Organics

<b>PIANO (hydrocarbons)</b>			
1-Pentene	heptane	ethylbenzene	1-decene
2-methyl-1-butene	cis-3-heptene	m&p-xylenes	1-methyl-2-propylcyclohexane
Pentane	trans-2-heptene	3,4-dimethylheptane	isobutylbenzene
2-Methyl-1,3-Butadiene	cis-2-heptene	2-methyloctane	decane
trans-2-Pentene	methylcyclohexane	3-methyloctane	sec-butylbenzene
cis-2-Pentene	2,2-dimethylhexane	ctt-1,2,4-trimethylcyclohexane	1-methyl-3-isopropylbenzene
4-methyl-1-pentene	ethylcyclopentane	1,1,2-trimethylcyclohexane	1-methyl-4-isopropylbenzene
2,3-dimethylbutane	2,5-dimethylhexane	3,3-diethylpentane	1-methyl-2-isopropylbenzene
2-methylpentane	2,2,3-trimethylpentane	o-xylene	1-methyl-3-propylbenzene
3-methylpentane	2,4-dimethylhexane	1,1,2-trimethylcyclohexane	1-methyl-4-propylbenzene
1-hexene	ctc-1,2,4-trimethylcyclopentane	1-nonene	butylbenzene
hexane	ctc-1,2,3-trimethylcyclopentane	isobutylcyclopentane	1,3-dimethyl-5-ethylbenzene
trans-2-hexene	Toluene	trans-3-nonene	1,2-diethylbenzene
2-methyl-2-pentene	2,3-dimethylhexane	cis-3-nonene	1-methyl-2-propylbenzene
cis-2-hexene	2-methylheptane	nonane	1,4-dimethyl-2-ethylbenzene
2,2-dimethylpentane	4-methylheptane	trans-2-nonene	1,2-dimethyl-4-ethylbenzene
methylcyclopentane	3-methylheptane	cis-2-nonene	1,2-dimethyl-3-ethylbenzene
2,4-dimethylpentane	3-ethylhexane	1-methylethylbenzene	n-undecane
2,2,3-trimethylbutane	cct-1,2,4-trimethylcyclopentane	isopropylcyclohexane	1,2,4,5-tetramethylbenzene
benzene	trans-1,4-dimethylcyclohexane	butylcyclopentane	2-methylbutylbenzene
3,3-dimethylpentane	1-octene	3,3-dimethyloctane	pentylbenzene
cyclohexane	1-ethyl-1-methylcyclopentane	propylbenzene	t-1-methyl-2-(4-MP)cyclopentane
2-methylhexane	trans-1,2-dimethylcyclohexane	1-methyl-3-ethylbenzene	1-t-butyl-3,5-dimethylbenzene
2,3-dimethylpentane	octane	1-methyl-4-ethylbenzene	1-t-butyl-4-ethylbenzene
1,1-dimethylcyclopentane	trans-2-octene	2,3-dimethyloctane	Dodecane
3-methylhexane	isopropylcyclopentane	1,3,5-trimethylbenzene	1,3,5-triethylbenzene
cis-1,3-dimethylcyclopentane	cis-2-octene	2-methylnonane	1,2,4-triethylbenzene
trans-1,3-dimethylcyclopentane	cis-1,2-dimethylcyclohexane	1-methyl-2-ethylbenzene	hexylbenzene
3-ethylpentane	propylcyclopentane	3-ethyloctane	tridecane
trans-1,2-dimethylcyclopentane	ccc-1,3,5-trimethylcyclohexane	3-methylnonane	tetradecane
1-heptene	2,5-dimethylheptane	tert-butylbenzene	pentadecane
trans-3-heptene	3,3-dimethylheptane	isobutylcyclohexane	
<b>POLARS</b>			
Ethanol	t-Butanol	Ethyl Acetate	2-Pentanone
2-Propanol	1-Propanol	iso-Butanol	4-Methyl-2-pentanone
Diethyl ether	2-Butanone	1-Butanol	
<b>KETONES</b>			
Acetone	2-Butanone	4-Methyl-2-pentanone	2-Hexanone
<b>CYCLICS</b>			
alpha-Pinene	Camphene	Limonene	gamma-Terpinene
beta-Pinene			
<b>WS-AMP (chlorinateds)</b>			
1,1-dichloroethene	1,2-dichloropropane	Tetrachloroethene	1,4-dichlorobenzene
Methylene chloride	Trichloroethene	Chlorobenzene	1,2-dichlorobenzene
trans-1,2-dichloroethene	1,1,2-trichloroethane	Styrene	1,2,4-trichlorobenzene
1,1,1-trichloroethane			

## 2. Internal Standards

The following compounds were used as internal standards: 1,4-difluorobenzene, chlorobenzene-D5 and 4-bromofluorobenzene. A gas cylinder containing 1ppmv of each of these components in nitrogen was purchased from Spectra Gases Inc. (Alpha, NJ). The cylinder was attached to the GCD with PEEK tubing. 200 mL of internal standard was injected each time a sample was analyzed on the GCD, regardless of the sample volume. The resulting masses of 1,4-difluorobenzene, chlorobenzene-D5 and 4-bromofluorobenzene injected were 652, 669 and 995 ng, respectively.

## 3. Standard Curve Preparations

For each of the five standard mixtures, seven different volumes were analyzed—15, 30, 75, 150, 300, 750, and 1500 mL. To establish a relationship between the mass of a given compound injected and the area of the compound's chromatogram peak, known mass data was plotted against the corresponding peak area data for each compound. To account for variations in the GCD, internal standard data was incorporated into quantities called response ratios and amount ratios. The response ratio is the peak area of the compound of interest, divided by the peak area of the preceding internal standard with the closest retention time. Similarly, the amount ratio is the mass of the compound of interest, divided by the mass of the closest preceding internal standard. Response ratios were plotted against amount ratios and quadratic functions were fit to these plots. The functions made it possible to convert the peak area of any compound to an amount, as long as the response ratio was within the range of values used to establish the function.

The data points for the standard curves tended to show a positively sloped linear relationship for the first 3 or 4 sample volumes as expected. The linear relationship can be expressed with the following equation:

$$AR = mRR + b$$

AR = Amount Ratio  
RR = Response Ratio  
m = slope  
b = y-intercept

In all cases, the standard curve functions were fit only to data points in the range that remained close to linear.

Although the data used for standard curves was nearly linear, quadratic functions were used for an improved fit. The quadratic equations were of the form:

$$AR = aRR^2 + bRR + c$$

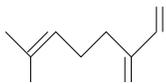
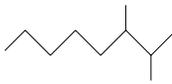
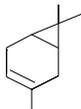
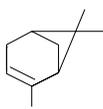
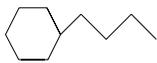
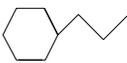
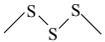
AR = Amount Ratio  
RR = Response Ratio  
a = coefficient of squared term  
b = coefficient of linear term  
c = constant

The validity of both linear and quadratic functions was tested using standard samples. The compound peak areas were converted to amounts using each type of function. Since the actual amounts were already known, it was possible to compare the percent error that resulted from each function. This analysis was done for all of the compounds in the PIANO standard, and at every volume level used to make the functions. The average percent error for the linear fit was 12.8% (sd=20.6) and for the quadratic fit was 4.05% (sd=13.4).

#### 4. Quantification of Compounds for Which no Standards Were Analyzed

Six compounds not present in any of the standards purchased, were consistently identified in gas samples using the computer's library database of compounds. Since no standards were run for the compounds, quantification was done using the standard curves for the most structurally similar compounds for which standards were available. Table 14 lists the compounds that were quantified this way, and the standard compounds used for the quantification. Dimethyl disulfide and dimethyl trisulfide were not quantified since the standard samples did not include any sulfur-containing compounds.

Table 14. Standard Compounds Used to Quantify Compounds for Which No Standards Were Analyzed

Compounds For Which No Standards Were Analyzed	Standard Compound Used To Quantify
Myrcene 	2,3-dimethyloctane 
3-carene 	α-pinene 
3-methylbutane 	2-methyl-1-butene 
Butylcyclohexane 	Propylcyclohexane 
Dimethyl disulfide 	None
Dimethyl trisulfide 	None

## Analysis of Gaseous VFA Concentrations

The process of collecting VFA samples from gas bags using orbo tubes was described in section 2.5.1. The procedure for the analysis of the orbo tubes is presented here.

### 1. VFA Standard Compounds

Standards were purchased for ten volatile fatty acids—acetic, propionic, isobutyric, n-butyric, 2-methylbutyric, isovaleric, valeric, isocaproic, caproic, and heptanoic acid. Of the ten VFAs, acetic acid (ACS grade), and 2-methylbutyric acid (98%) were purchased from Sigma-Aldrich, Inc. (Bellefonte, PA), while propionic acid (99%), iso-butyric acid (99+%), n-butyric acid (99%), iso-valeric acid (99%), valeric acid (99%), iso-caproic acid (99%), n-caproic acid (99+%), and heptanoic acid (98%) were purchased from Acros Organics (New Jersey, USA). All chemicals were used without further purification.

### 2. Extraction

For extraction, orbo tubes were cut at one third of the incoming end. After removing the glass wool plug, the collection adsorbent (335 mg Chromosorb P with 5% Na<sub>2</sub>CO<sub>3</sub>) was collected in 12-mL glass centrifuge tubes. Four mL of de-ionized water was added to the centrifuge tube and mixed completely by a vortex touch mixer. The centrifuge tubes were then shaken horizontally on an Innova 2300 platform shaker (New Brunswick, USA) for 12 hours. The tubes were then centrifuged at 18g for 8 minutes

with an Eppendorf 5810 centrifuge (Eppendorf, Germany) to separate the Chromosorb and aqueous solution.

One mL of aqueous solution was pipetted out, and 78 uL of 1.0N hydrochloric acid was added to neutralize sodium bicarbonate and free VFAs. Seventy-five uL of triethylamine (20 g/L), and 120 uL of 2-bromoacetophenone (0.17 M) were added to derivatize VFAs. <sup>1</sup>One mL of acetone (GC resolve grade, Fisher, USA) was added to the solution. The centrifuge tubes were then capped with a teflon-coated phenolic cap, mixed by vortex mixer and put into a 50 °C water bath for 24 hours.

After 24 hours, 2 mL of ethyl acetate (HPLC grade, Fisher Scientific, USA) was added to the solution to extract all the VFA esters produced. After the ethyl acetate/aqueous solution mixture was shaken for 15 minutes, the ethyl acetate was layer-separated from the aqueous solution. <sup>2</sup>The ethyl acetate layer was collected from the centrifuge tube and the remaining aqueous solution was subjected to another 2 mL of ethyl acetate extraction. The ethyl acetate fraction was again collected and combined with the above ethyl acetate fraction. The collected ethyl acetate fraction was dried under nitrogen. Exactly 2 mL of HPLC grade methanol was added to the VFA ester residue and the solution was transferred to a 2-mL GC vial. Five uL of 2,4,5-trichlorophenoxyacetic acid methyl ester (2000ppm) was added to the extracted VFA samples as an internal standard. Vials were then capped with a crimp top seal.

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<sup>1</sup> Preliminary experimentation showed that a 50:50 ratio of acetone to water was optimal for VFA derivatization

<sup>2</sup> In preliminary experimentation, two extractions with ethyl acetate yielded  $\geq 95\%$  of VFA esters

### 3. GCD Analysis

Extracted VFA samples were analyzed by GCD (Hewlett Packard G1800A). The GCD was equipped with a DB-5 column (30meter, 0.25uM) and electron ionization detector (EID). An automated liquid injector (Hewlett-Packard 6890 series) was used to inject the liquid samples. The injection volume was 2uL. The temperature of the injector and detector were 250 °C and 280 °C, respectively. The initial temperature of the oven, 100 °C, was held for 2 minutes and then increased to 126 °C at 0.5 °C per minute. After holding at 126 °C for 2 minutes, the temperature was increased to 280 °C at a rate of 10 °C per minute. The oven temperature was kept at 280 °C for 2 minutes. The carrier gas, Helium, was set at a flow rate of 1.0mL/minute.

### 4. Peak Identification and Quantification

Compound identification was based on retention time and characteristic ions in the mass spectrum. Selected Ion Monitoring (SIM) was used to lower the detection limit for quantification purposes. Quantification was based on the integrated abundance of the primary ion. Calibration curves with internal standard corrections were used to convert integration areas to masses.

### 5. Recovery Efficiency

Gas samples with known concentrations of VFAs were prepared using the procedure described in Appendix D. The orbo tube trapping process was then carried out, followed by the VFA extraction, derivatization and analytical procedure described above. Percent recoveries were +/- 30% for most of the VFAs, although valeric, caproic,

and isocaproic acids had percent recoveries between 54 and 61%. Correction factors based on the measured percent recoveries were applied to the experimental samples.

## B. METHOD VALIDATION

### 1) Retention Times

Since the retention time of a chromatogram peak for a given compound is used to identify the compound, the retention time must be constant. If retention times varied with the amount of the compound present, identification would be impossible. The independent nature of retention times, with respect to the amount of compound present, was verified using a procedure described in EPA's Method TO-15. For 7 different sample volumes of standard mixes, the retention times of selected compounds were compared. Compounds were selected to represent the range of retention times observed. Random instrumental variation was accounted for by using a quantity called the relative retention time (RRT), which is the ratio of the retention time of a given compound over the retention time of an internal standard. The analysis showed that the relative retention times were not affected by changing the amount of sample (and thus the size of the peaks). The results of this comparison are shown in Table 16.

Table 15. Consistency of Retention Time Analysis

Compound	Relative Retention Times							Ave. RRT
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	
1-pentene	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
2-methyl-1-butene	0.41	0.41	0.41	0.41	0.41	0.41	0.42	0.41
pentane	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
2-methyl-1,3-butadiene	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.43
toluene	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79
2,3-dimethylhexane	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
2-methylheptane	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
2-methyloctane	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
3-methyloctane	0.93	0.93	0.93	0.93	0.94	0.94	0.94	0.94
o-xylene	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95

## 2) Peak Areas

The originally prepared standard curve functions for all of the organic compounds were used, unaltered, throughout the course of the experiment. Due to cost and time limitations standards could not be prepared and analyzed on a regular basis. However, at the end of the experiment, selected standard samples were prepared and analyzed. For these selected compounds, standard curves were reproduced and compared to the original curves. For the comparison, a response ratio within the range of each curve was selected. Each curve was then used to convert that same response ratio to an amount. The differences in the converted amounts were compared. The results of this comparison are

presented in Table 16. The comparison confirmed that the GCD varied by less than 25% for all compounds except ethanol.

Table 16. Consistency of Standard Curves Analysis

Compound	<sup>(a)</sup> Response Ratio	Amount (ng)		% difference
		Original Curve	Post Experiment Curve	
Propylcyclohexane	17	8978	7641	15
alpha-Pinene	27	15087	15412	-2
Camphene	9	8747	7284	17
beta-Pinene	28	15422	15645	-1
Limonene	20	15632	15803	-1
gamma-Terpinene	26	15739	17002	-8
Ethanol	0.35	1721	1020	41
2-Propanol	0.5	625	639	-2
Diethyl ether	0.25	755	758	0
t-Butanol	1.25	1550	1820	-17
2-Butanone	2.8	3492	2645	24
1-Propanol	0.17	1794	1555	13
Ethyl Acetate	2.4	3504	2646	24
iso-Butanol	1.25	3353	2976	11
1-Butanol	0.23	932	881	6
2-Pentanone	3.8	3594	3154	12
4-Methyl-2-pentanone	2.8	3600	2695	25

a- The response ratios were arbitrarily chosen within the range of the standard curves

### 3). Peak Identification

Compounds were identified according to qualifying ions and best retention time (Target Ion Method). The GCD was pre-programmed with information about each compound of interest. For each compound, a target ion was specified along with qualifying ions. Relative responses of the qualifying ions were assigned as a percentage of the target ion that should be expected. Retention time windows were set at +/- 0.5 minutes for all compounds. Each identified compound had a quality value (Q-value) associated with its identification. Q-values ranged from 0-100, 100 being a perfect match. Q-values less than 100 occurred when any of the identifying factors were not

exactly matched to the values of these factors that were programmed into the computer for the given compound. These factors include the compound's retention time, the presence of the target ion, and the presence and relative amounts of qualifying ions. Since some variation in retention time and relative amounts of qualifying ions was considered acceptable, it was not necessary that the Q-value be 100 for a compound identification to be considered correct. The validity of compound identification was not based solely on the Q-value, since it is possible for an identification to be correct even when a low Q-value is reported. This often occurs when peaks are small, making recognition of all the qualifying ions difficult for the GCD. Final decisions concerning the correctness of peak identifications were made only after reviewing each peak and comparing the properties of the peak to those of a standard peak for that compound.

#### 4. GCD Analysis of Extracted VFA's

Prior to analysis, the GCD detector was auto-tuned with Perfluorotributylamine (PFTBA) tuning solution (Agilent, USA). After the auto-tuning, 2 uL of decafluorotriphenylphosphine (DFTPP, 50 mg/L) was injected to check the performance of the detector. The performance met the DFTPP criteria in EPA method 8270C. Additional DFTPP performance checks were conducted after every 10 samples were injected.

### **3.0 RESULTS**

A description of the performance of the reactors in each treatment is presented in this section. Refuse decomposition was characterized by gas production, and leachate pH and COD. In addition, NMOC yields and production rates, as well as identification and quantification of specific organic compounds for each treatment are presented. Methane and NMOC yields for each reactor are summarized in Table 17, yields of speciated organics are presented in Table 19, and VFA concentration data is summarized in Table 20.

#### **3.1 Leachate Control Reactors**

To quantify NMOC emissions associated with the leachate seed, reactors containing leachate only were operated anaerobically for 52 days. No visible gas was produced by the control reactors. After 52 days the reactors were sparged with ultra high purity (UHP) nitrogen to obtain sufficient gas for organic analyses. The collected gas was analyzed for NMOC composition. The average NMOC yield for the control reactors was  $6.85 \times 10^{-4}$  mg NMOC-C/mL of leachate. The NMOC yields for reactors that received a leachate seed were reduced by the leachate NMOC yield presented and the volume of leachate added to each reactor.

Leachate pH and COD data for the control reactors are presented in Figures 8 and 9, respectively. The leachate pH ranged from 7.3 to 8.3 and decreased with time. The COD of the leachate ranged from 1,000 to 1,400 mg/L and remained relatively constant over the 52 days.

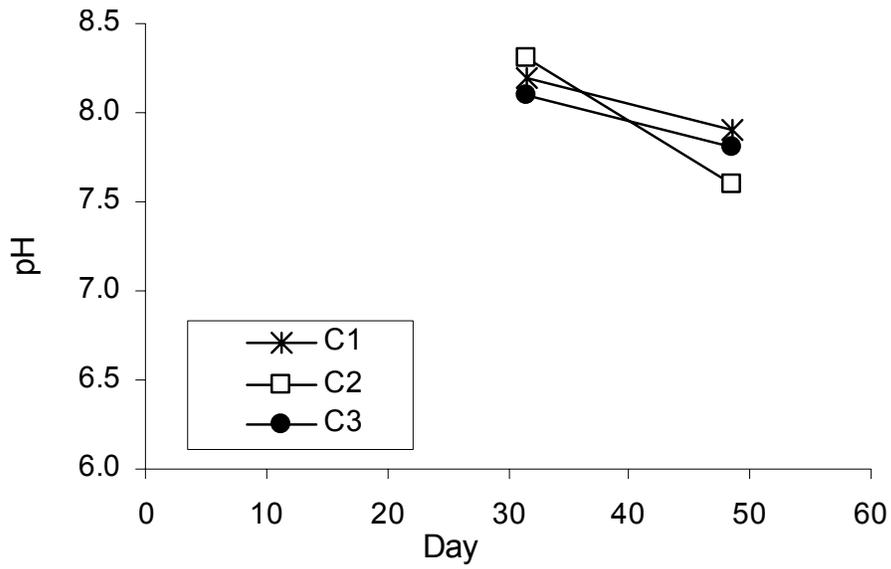


Figure 8. pH in the Control Reactors

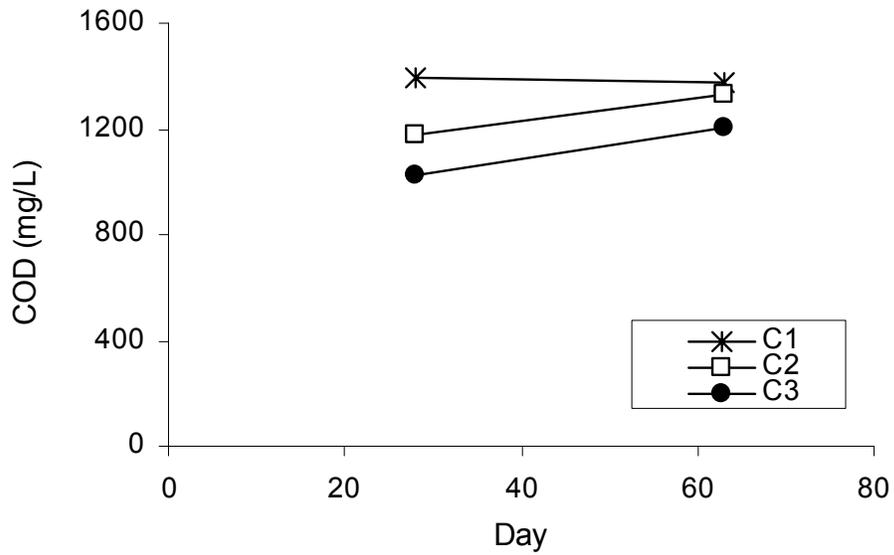


Figure 9. COD in the Control Reactors

Table 17. Summary of NMOC and Gas Yields for All Treatments

Waste	Reactor	NMOC Yield (mg-C/dry gm)	Gas Yield (mL/dry gm)	Type of Gas
Paper	1	0.020	117	CH <sub>4</sub>
	2	0.015	120	CH <sub>4</sub>
	3	0.013	104	CH <sub>4</sub>
	Avg. (s.d.)	<b>0.016 (0.004)</b>	<b>113.7 (8.5)</b>	
Yard	1	0.043	184.000	CH <sub>4</sub>
	2	0.033	128.000	CH <sub>4</sub>
	Avg. (s.d.)	<b>0.038 (0.007)</b>	<b>156.0 (39.6)</b>	
Food	1	0.438	161.000	CH <sub>4</sub>
	2	0.279	147.000	CH <sub>4</sub>
	3	0.324	150.000	CH <sub>4</sub>
	Avg. (s.d.)	<b>0.347 (0.082)</b>	<b>152.7 (7.37)</b>	
MSW	1	0.114	97.000	CH <sub>4</sub>
	2	0.111	98.000	CH <sub>4</sub>
	Avg. (s.d.)	<b>0.113 (0.002)</b>	<b>97.500 (0.71)</b>	
MSW + HHW	1	0.161	120.000	CH <sub>4</sub>
	2	0.183	108.000	CH <sub>4</sub>
	Avg. (s.d.)	<b>0.172 (0.016)</b>	<b>114.0 (8.48)</b>	
MSW Aerobic	1	0.278	316.000	CO <sub>2</sub>
	2	0.221	254.000	CO <sub>2</sub>
	3	0.200	303.000	CO <sub>2</sub>
	Avg. (s.d.)	<b>0.233 (0.040)</b>	<b>291.0 (32.7)</b>	
	1		0.000	CH <sub>4</sub>
	2		0.000	CH <sub>4</sub>
	3		5.970	CH <sub>4</sub>
Avg. (s.d.)		<b>1.990 (3.45)</b>		
MSW NO <sub>3</sub> - Reducing	1	0.046	35.000	N <sub>2</sub>
	2	0.053	47.000	N <sub>2</sub>
	Avg. (s.d.)	<b>0.050 (0.005)</b>	<b>41.000 (8.49)</b>	
			80.000	CH <sub>4</sub>
	Avg. (s.d.)		<b>76.500 (4.95)</b>	CH <sub>4</sub>

### 3.2 Mixed Paper Waste Reactors

The mixed paper waste reactors were operated anaerobically for 497 days. The pH data for the paper waste reactors is presented in Figure 10. The leachate pH was initially close to 7, and decreased slightly during the first 14 days. Some neutralization was required during the first 14 days. Thereafter, the pH stabilized around 7, with the exception of reactor P3, which exhibited some wider fluctuation. The leachate pH was maintained between 6.7 and 7.9 throughout the experiment. The steep pH increase in reactor P3 has been observed in previous studies in well-decomposed refuse (Barlaz et al., 1997).

The chemical oxygen demand (COD) data is presented in Figure 11. The leachate COD increased during the early operation of the reactors, reaching an average maximum of 2,100 mg/L on around day 90. The COD then progressively decreased over the following 275 days. During the final 100 days the COD increased in all reactors. This is surprising as soluble organic matter is typically consumed as decomposition proceeds. However, given the amount of data, the COD concentrations may only represent scatter in P1 and P2, while there appears to be a consistent COD increase in P3. The average COD of the leachate at the time that the reactors were terminated was 1857 mg/L. Both the maximum COD and rate of decrease were highest in reactor P3, though the initial and final CODs for P3 are close to P1 and P2

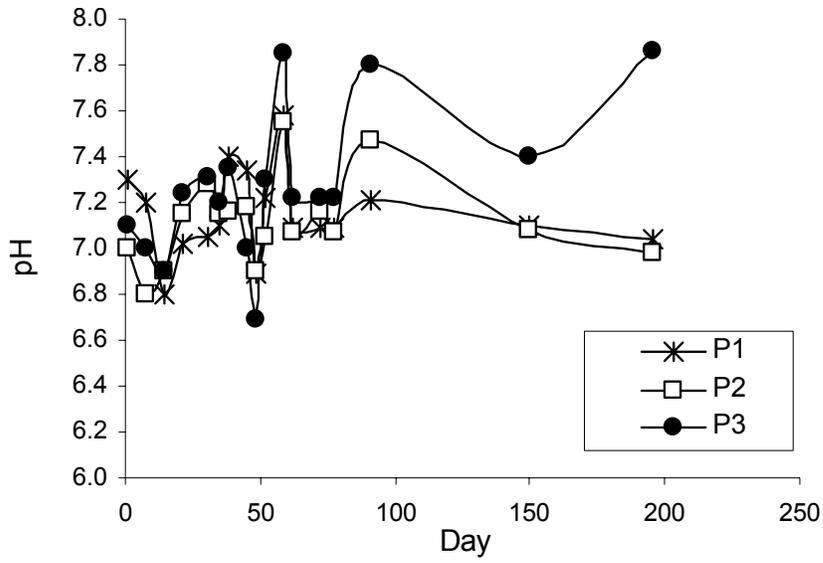


Figure 10. pH in the Waste Paper Reactors

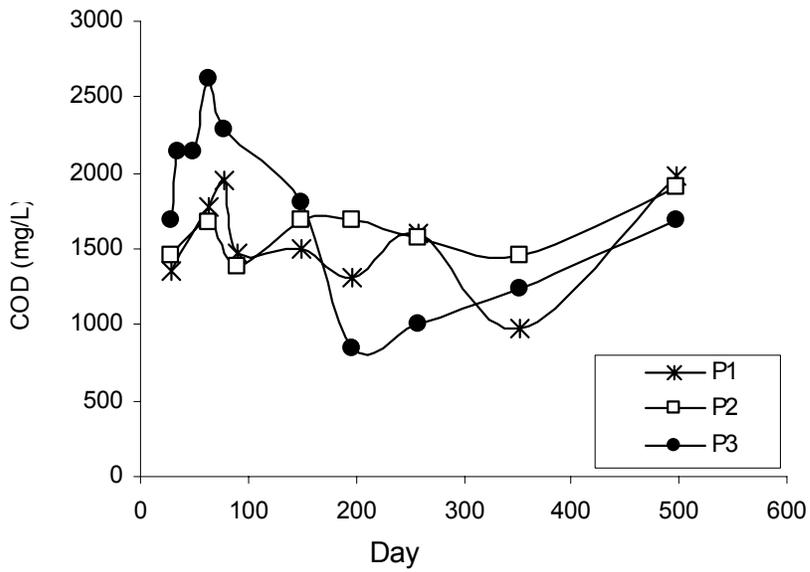


Figure 11. COD in the Waste Paper Reactors

Methane yields and production rates for reactors P1 to P3 are presented in Figures 12 and 13, respectively. The methane yields for reactors P1 to P3 varied from 104 to 120 mL CH<sub>4</sub> /dry gm with an average of 114. Peak methane production rates were measured on days 27, 27 and 37 for P1 to P3, respectively, with peak rates of 0.84 to 0.96 mL CH<sub>4</sub> /day-dry gm). Maximum methane production was sustained for about 20 days, after which it decreased asymptotically. All three reactors were consistent in the trends described.

### Mass Balance

Constituent solid losses are presented in Table 18. Initially the mixed paper was 58.7 % cellulose, 13.4 % hemicellulose and 7.42 % lignin. Losses are reported as the ratio of the cellulose, hemicellulose and lignin removed from a reactor divided by the mass present in the reactor initially. An average of 56% of the cellulose and 52% of the hemicellulose were degraded. The total mass of lignin recovered was, on average, 1.8 times higher than the initial amount present. Generally, it is assumed that lignin is recalcitrant under anaerobic conditions. The data suggesting the increase in the mass of lignin will be evaluated in the Discussion.

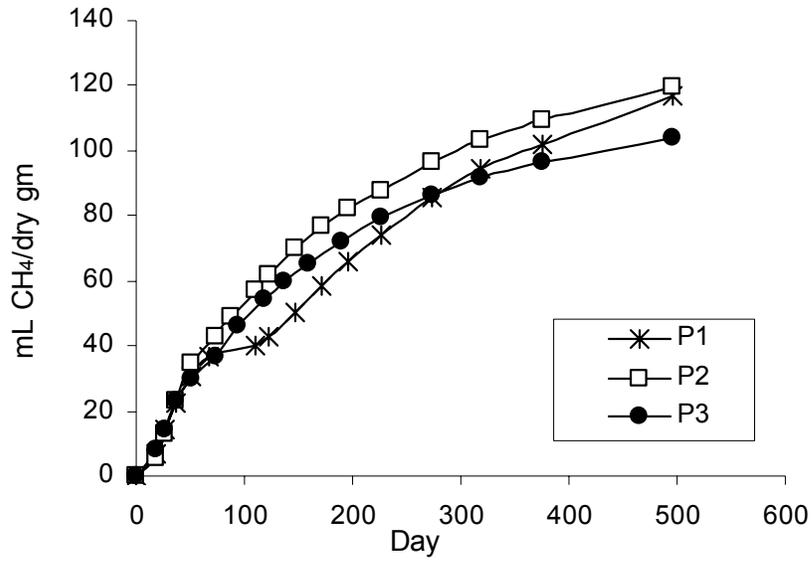


Figure 12. Methane Yields for Paper Waste

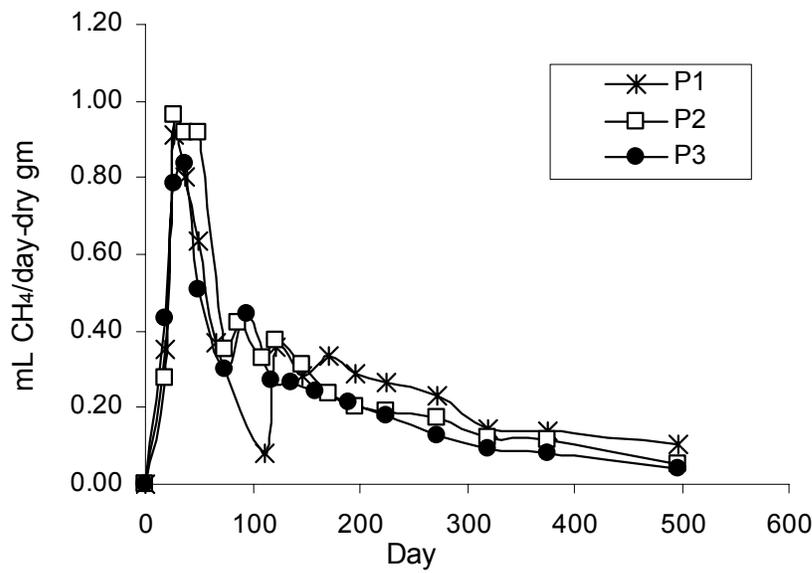


Figure 13. Methane Production Rates for Paper Waste

Table 18. Solids Loss for Paper Waste

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	58.7	13.4	7.4	9.7					
<b>Decomposed</b>									
<b>P1</b>	41.6	9.7	20.8	2.46	0.37	0.38	1.45	81.8	0.88
<b>P2</b>	40.6	11.3	22.4	2.32	0.46	0.56	2.00	85.8	0.87
<b>P3</b>	42.2	10.1	21.5	2.43	0.48	0.50	1.93	84.4	0.87

- a) Cellulose plus hemicellulose divided by lignin
- b) The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- c) The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

#### Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC yields and production rates are presented in Figures 14 and 15, respectively. The total NMOC yields ranged from 0.013 to 0.020 mg NMOC-C/dry gm, with an average of 0.016. Peak NMOC production rates of  $8.67 \times 10^{-4}$  (P1),  $2.39 \times 10^{-4}$  (P2) and  $1.88 \times 10^{-4}$  (P3) mg-NMOC-C/(day-dry gm) occurred on days 38, 51 and 37, respectively. With the exception of one point from reactor P1, near maximum NMOC production was sustained for about 150 days. After 150 days NMOC production asymptotically declined, leveling off near zero for the last 300 days.

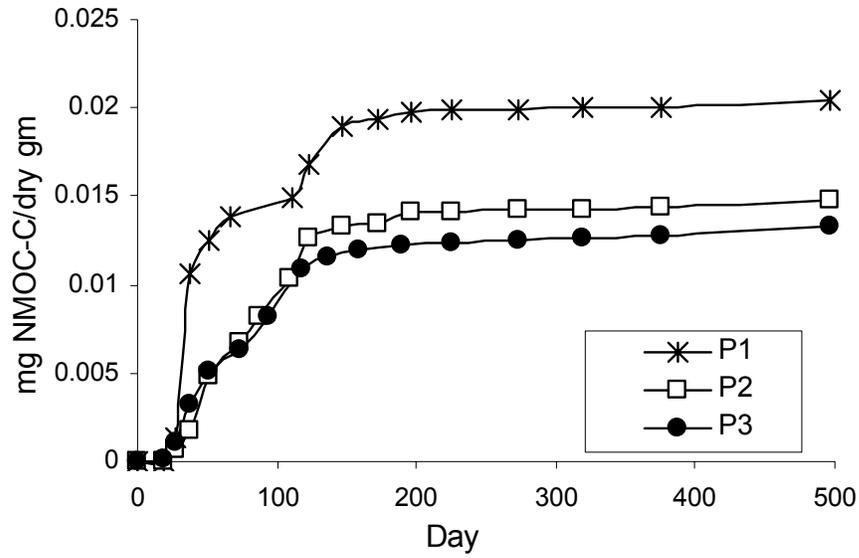


Figure 14. Total NMOC Yields for Paper Waste

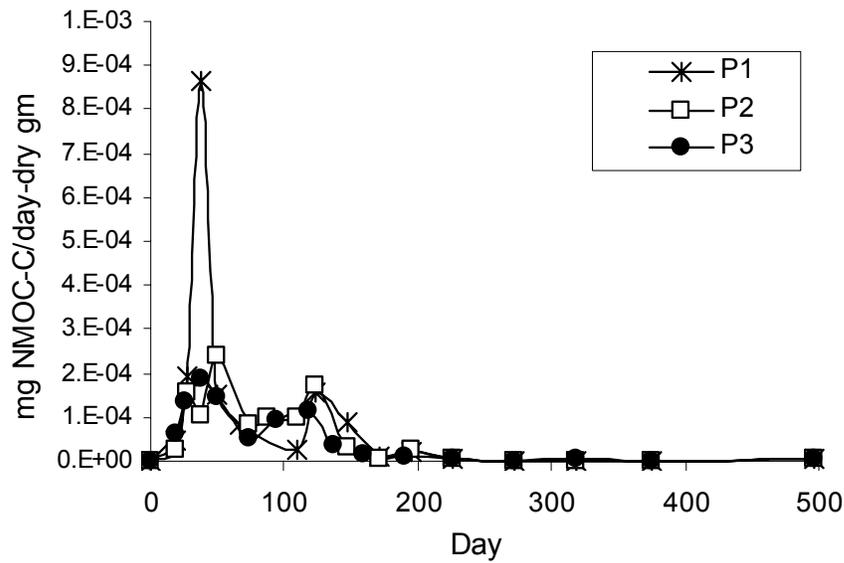


Figure 15. NMOC Production Rates for Paper Waste

The yields of specific trace organic compounds from mixed paper are presented in Table 19. The most abundant category of organics was alcohols. The highest yielding compounds were 1-butanol (907 ng/dry gm) and ethanol (320 ng/dry gm). This result was consistent for all three reactors. Overall, there was good consistency among the reactors with the exception of 2-methylbutane, which was considerably higher in P1 than the other reactors. 2-methylbutane was a compound for which no standard curve was prepared. It was manually identified and integrated with Chemstation software and quantified with the standard curve of another compound (see Table 14).

Volatile fatty acids accounted for 3.4 to 9.0% of the total NMOC concentration for the samples shown in Table 20, which corresponded to the time when leachate COD was highest. In these samples, VFA concentrations were, on average 21 percent higher than the concentration of all other individually quantified organics.

Table 19. Yields of Specific Organic Compounds (ng/dry gm)

	Paper			Yard		Food			MSW		MSW + HHW		MSW aerobic			MSW NO <sub>3</sub> <sup>-</sup>	
	P1	P2	P3	Y1	Y2	F1	F2	F3	M1	M2	MH1	MH2	MA1	MA2	MA3	MN1	MN2
<b>Alkanes</b>																	
pentane	62	32	52	188	192	362	361	331	2176	2619	1723	3445	9179	6981	5564	2081	1184
2-methylbutane <sup>1</sup>	3716						25236	8767		4190			22943	19078	29094		
2,3-dimethylbutane										22	5	4				24	2
2-methylpentane			12						37	46	22	43	52			95	11
3-methylpentane											5	11					
hexane				33	26	16	23	29	109	231	63	362				40	51
methylcyclopentane									32	51	7	46					7
2,4-dimethylpentane												2					
3,3-dimethylpentane									10	23	11	8				11	17
cyclohexane				62	64				43	105	68	134				32	124
2-methylhexane				4758	3454				1233	1386	2703	3821	206			331	183
2,3-dimethylpentane			4						65	156						66	5
3-methylhexane			5						453	577	293	379	427		313	556	323
cis-1,3-dimethylcyclopentane									10	21		7				17	8
trans-1,3-dimethylcyclopentane									42	78		24				59	35
3-ethylpentane									56	86	28	34				68	43
trans-1,2-dimethylcyclopentane									28	28	3	8				31	18
heptane		33	13	56	63		35		525	896	523	601				850	556
methylcyclohexane									105	151	31	69				86	49
2,2-dimethylhexane									41	61	4	34				27	19
ethylcyclopentane									40	59	13	31				37	19
2,5-dimethylhexane		8	34	183	155				62	69	30	31				38	41
2,2,3-trimethylpentane			9	10													
2,4-dimethylhexane			24						78	94	26	55				49	33
cis-1,2,4-trimethylcyclopentane									6	11		3				3	
2,3-dimethylhexane	0	10	21						4	1	9	3				2	4
2-methylheptane											153	50					
4-methylheptane			6						10	42						37	8
3-methylheptane			7							24		24				13	26
3-ethylhexane									10	6		55				9	6
cis-1,2,4-trimethylcyclopentane																	
trans-1,4-dimethylcyclohexane																	
octane	10	16	27	426	363	175	104	92	211	245	318	215	48		485	136	
2,5-dimethylheptane			3						22	19	14	23				4	
3,4-dimethylheptane									179		80						
2-methyloctane									82	103	57	123				118	8
3-methyloctane									43		10	27				14	13
3,3-diethylpentane			2														
nonane				61	48	19			353	373	94	238	227	249	229	106	123
butylcyclohexane <sup>1</sup>									80784	51529	38924	55444				13034	29909
isopropylcyclohexane									19	17		7					
propylcyclohexane									107	94	22	45				19	22
butylcyclopentane												26					
3,3-dimethyloctane				5	6				18	18	5	10				1	1
2,3-dimethyloctane									105	114						18	37
2-methylnonane	10	150	115	82	25				235	2504	115	189	135	207	168	102	157

Table 19 continued

	Paper			Yard		Food			MSW		MSW + HHW		MSW aerobic			MSW NO <sub>3</sub>	
<b>Alkanes cntd.</b>																	
3-ethyloctane									25	23						6	7
3-methylnonane			7	15					159	152	51	114				52	59
isobutylcyclohexane									66	57	11	34				8	20
1-methyl-2-propylcyclohexane										59						11	17
n-undecane	44	68	46	27	34	45	62	38	504	452	544	575	359	441	351	300	418
dodecane			11			33	37	42	16	10							
<b>Total Alkanes</b>	<b>3841</b>	<b>318</b>	<b>396</b>	<b>5905</b>	<b>4428</b>	<b>651</b>	<b>25858</b>	<b>9300</b>	<b>88103</b>	<b>66804</b>	<b>45970</b>	<b>66353</b>	<b>33577</b>	<b>26955</b>	<b>36204</b>	<b>18490</b>	<b>33564</b>
<b>Alkenes</b>																	
1-pentene	14	14		40	98	5	7	15			923	2019				15	6
2-methyl-1-butene	62		94	123	115	784	659	686			60	40				14	25
2-methyl-1,3-butadiene	5	12	15	72	34	438	190	230	51	38	35	48	547	305	319	89	83
trans-2-pentene				107	48		10	10		114							
cis-2-pentene	20	33	38	60	43	423	207	159	40	37	43	8				94	77
4-methyl-1-pentene																	
1-hexene										7	18	6				12	8
2-methyl-2-pentene				100	140						1						
1-heptene									49	1539	22	19				24	42
1-octene	45	136	80	108	67	65	49	34	72	24	47	70	122		192	61	48
trans-2-octene		24	24	24	17	5			13	8	21	19				18	
cis-2-octene		8		8	7						10	4				4	8
1-nonene								8									
trans-2-nonene												11					
<b>Total Alkenes</b>	<b>147</b>	<b>227</b>	<b>250</b>	<b>641</b>	<b>568</b>	<b>1719</b>	<b>1122</b>	<b>1142</b>	<b>226</b>	<b>1767</b>	<b>1181</b>	<b>2244</b>	<b>669</b>	<b>305</b>	<b>511</b>	<b>333</b>	<b>296</b>
<b>Aromatic compounds</b>																	
benzene	10	6	16	24	19				26	11	20	14		81		42	80
toluene <sup>2</sup>	77	97	164	55	85	9	394	8	80	92	53636	68264	197	326	231	574	73
ethylbenzene <sup>2</sup>		13	24	26	93	9	11	4	291	538	481	495	157	252		263	222
m&p-xylenes <sup>2</sup>	6	12		74	385	29	38	5	181	262	231	405	181	463		50	45
o-xylene <sup>2</sup>			11	36	116	16	33	10	51	80	93	116		256		15	14
propylbenzene									26	26	30	32				2	3
1-methyl-3-ethylbenzene <sup>2</sup>			8	16	22		4	6	52	47	50	41				7	12
1-methyl-4-ethylbenzene <sup>2</sup>				3	10				19	23	17	10				6	1
1-methylethylbenzene					4				24	29	73	78		42		18	17
1,3,5-trimethylbenzene <sup>2</sup>									45	39	24	18				7	11
1-methyl-2-ethylbenzene <sup>2</sup>									35		8	3					
sec-butylbenzene									22	19	11	24					
1-methyl-3-isopropylbenzene						22662	21583	29430	435	2027	741	117				335	291
1-methyl-4-isopropylbenzene <sup>3</sup>	15	104	28	140	105	26920	38805	29244	1524	725	685	1512	123	487	569	125	236
1-methyl-4-propylbenzene <sup>3</sup>									14	11	2	2				2	3
butylbenzene									15	12	2	14					8
1,3-dimethyl-5-ethylbenzene <sup>3</sup>				3	5				32	26	5	535				358	1211
1-methyl-2-propylbenzene											16						
<b>Total Aromatics</b>	<b>109</b>	<b>232</b>	<b>252</b>	<b>376</b>	<b>847</b>	<b>49646</b>	<b>60868</b>	<b>58707</b>	<b>2871</b>	<b>3967</b>	<b>56125</b>	<b>71681</b>	<b>658</b>	<b>1907</b>	<b>800</b>	<b>1804</b>	<b>2227</b>

Table 19 continued

	Paper			Yard		Food			MSW		MSW + HHW		MSW aerobic			MSW NO <sub>3</sub> <sup>-</sup>	
<b>Alcohols</b>																	
ethanol <sup>4</sup>	333	284	342	329	335	4730	831	2080	59	159	326	100	10973	9897		675	382
2-propanol <sup>4</sup>								91									285
t-butanol	78	143	168	47	134	94	37	44	18	43	38	45	689	317	507		
1-propanol	146	104	67	273	295	1305	1171	798	86	214			4785				183
iso-butanol											54						
1-butanol	816	1139	766	1251	1058	1780	1615	1093	2170	1835	2454	1105	7355		13467	1301	1404
<b>Total Alcohols</b>	<b>1374</b>	<b>1669</b>	<b>1343</b>	<b>1900</b>	<b>1822</b>	<b>7910</b>	<b>3654</b>	<b>4105</b>	<b>2332</b>	<b>2251</b>	<b>2873</b>	<b>1251</b>	<b>23802</b>	<b>10214</b>	<b>13975</b>	<b>2260</b>	<b>1969</b>
<b>Ketones</b>																	
acetone <sup>4</sup>		26	34	64	67		8	144	18	37	204	50				236	219
2-butanone <sup>4</sup>						1890	3910	1730			935	322			21068	2621	2046
2-pentanone <sup>4</sup>							131	100			618	91				243	128
4-methyl-2-pentanone	20	61	610	276	31	25	24	265	242	716	1227					60	49
2-hexanone			54	720	562				218	349	322	830				59	34
<b>Total Ketones</b>		<b>45</b>	<b>150</b>	<b>1395</b>	<b>905</b>	<b>1921</b>	<b>4074</b>	<b>1998</b>	<b>502</b>	<b>628</b>	<b>2795</b>	<b>2520</b>			<b>21068</b>	<b>3219</b>	<b>2476</b>
<b>Terpenes</b>																	
α-pinene	15	40	14	9746	7339	10667	6783	7457	1617	1119	1451	1149	5235	4635	2332	1054	4141
camphene				1090	958	800	416	1490	45	23	53	28				34	102
β-pinene			3	2765	1870	3631	6544	2396	423	1424	1100	641	1419	1177	1129	471	1312
limonene <sup>3</sup>	32	48	335	1014	1484	225220	78388	104077	6591	4644	9337	16290	8613	25145	10449	5346	7614
γ-terpinene <sup>3</sup>			25	4	53	304	726	7	97	183	253	180				91	207
myrcene <sup>1</sup>				49263	57500	360187	640566	724170	8104		9011	60826				17094	71001
3-carene <sup>1</sup>				67158	67692	277986	468396	718720	60523	40317	230288	100250				45299	60338
<b>Total Terpenes</b>	<b>47</b>	<b>88</b>	<b>377</b>	<b>131040</b>	<b>136897</b>	<b>878794</b>	<b>1201819</b>	<b>1558317</b>	<b>77399</b>	<b>47710</b>	<b>251493</b>	<b>179365</b>	<b>15267</b>	<b>30957</b>	<b>13910</b>	<b>69389</b>	<b>144714</b>
<b>Chlorinated compounds</b>																	
1,1-dichloroethene												91					
methylene chloride											260	524				141	
trans-1,2-dichloroethene																	
trichloroethene					10									842			
tetrachloroethene		74															
chlorobenzene									7								39
styrene <sup>4</sup>				5					2		51	5	155	95		21	8
<b>Total Chlorinateds</b>		<b>74</b>		<b>5</b>	<b>10</b>				<b>9</b>	<b>0</b>	<b>311</b>	<b>620</b>	<b>155</b>	<b>937</b>		<b>162</b>	<b>47</b>
<b>Other</b>																	
diethyl ether																	
ethyl Acetate	89	36	127	215	287	577	453	360	536	804	107	300	25654	13532	5429	165	151

- 1- No standard was analyzed for this compound so it was quantified using the standard curve for the most structurally similar compound, as shown in Table 14.
- 2- Due to incomplete removal during bag cleaning, yields of this compound were reduced by 30% for all samples after the first two—which had new bags.
- 3- Due to incomplete removal during bag cleaning, yields of this compound were reduced by 20% for all samples after the first two—which had clean bags.
- 4- Due to poor removal during bag cleaning, the yield of this compound includes only the first two samples for which new bags were used.

Table 20. Summary of VFA Concentrations (mg-C/m<sup>3</sup>)

	Acetic acid	Propionic acid	Isobutyric acid	n-butyric acid	Z-methylbutyric acid	Isovaleric acid	Valeric acid	Isocaproic acid	Caproic acid	Heptanoic acid	Total VFA Concentration (mg-C/m <sup>3</sup> )	Total Concentration of Individually Quantified Organics (mg-C/m <sup>3</sup> )	Total NMOC Concentration (mg-C/m <sup>3</sup> )
<b>Paper</b>													
P1, day 66	1.9	0.2	0.2	0.7	0.0	0.0	0.0	0.0	0.3	0.0	3.3	2.6	97.0
P2, day 73	2.4	0.2	0.1	0.6	0.0	0.0	0.0	0.1	0.3	0.4	4.3	3.4	99.0
P3, day 73	3.8	0.5	0.3	0.8	0.0	0.0	0.5	0.3	0.3	0.4	6.9	6.3	77.0
<b>Yard</b>													
Y1, day 31	1.5	0.7	0.8	3.0	0.7	0.9	0.6	0.0	0.6	0.0	8.7	74.7	248.0
Y2, day 25	3.2	0.7	1.1	5.1	0.7	0.9	1.2	0.1	0.7	0.7	14.4	65.8	164.0
<b>Food</b>													
F1, day 25	0.0	0.5	0.3	0.8	0.3	0.3	0.3	0.0	0.0	0.0	2.5	478.2	1910.0
F2, day 25	0.0	0.5	0.3	1.3	0.3	0.3	0.3	0.0	0.0	0.0	3.0	111.3	1965.0
F3, day 25	0.0	0.5	0.2	0.6	0.2	0.3	0.5	0.0	0.0	0.0	2.3	63.6	2128.0
<b>MSW</b>													
M1, day 26	2.49	0.76	0.53	4.44	0.65	0.69	1.21	0.13	1.80	0.00	12.7	83.8	671.0
M1, day 25	3.17	0.94	0.53	7.29	0.65	0.69	1.29	0.00	2.49	1.09	18.2	102.0	525.0
<b>MSW + HHW</b>													
MH1, day 52	0.0	0.5	0.4	2.0	0.3	0.3	0.5	0.0	0.0	0.0	4.0	197.7	2707.0
MH1, day 66	0.0	0.4	0.3	1.3	0.2	0.3	0.5	0.0	0.0	0.0	3.0	544.9	653.0
MH2, day 10	0.2	0.6	0.3	1.7	0.3	0.3	0.0	0.0	0.0	0.0	3.4	151.2	3685.0
MH2, day 51	0.0	0.9	0.5	2.3	0.3	0.3	0.0	0.0	0.0	0.0	4.3	208.6	2345.0
<b>MSW Aer.</b>													
MA1, day 20	1.47	0.00	0.00	0.48	0.22	0.00	0.00	0.16	0.00	0.00	2.3	21.6	18.0
MA2, day 20	1.87	0.00	0.00	0.23	0.00	0.00	0.00	0.26	0.30	0.44	3.1	13.0	29.0
MA3, day 20	2.82	0.00	0.00	0.25	0.00	0.00	0.00	0.27	0.32	0.44	4.1	4.2	15.0
<b>MSW NO<sub>3</sub><sup>-</sup> red.</b>													
MN1, day 51	3.83	0.62	0.53	7.35	0.59	0.78	1.40	0.00	1.99	1.28	18.4	182.8	1024.0
MN2, day 37	4.09	1.50	0.32	8.46	0.51	0.59	1.35	0.00	2.88	1.18	20.9	148.6	1351.0

Note: VFA concentrations in the leachate for the samples shown here are presented in Appendix E.

### 3.3 Yard Waste

Yard waste reactors were operated anaerobically for 497 days. One of the triplicate reactors leaked, and therefore results are only presented for two reactors—Y1 and Y2. The pH data for the yard waste reactors is presented in Figure 16. The pH reached a minimum of 6.6 during the first 7 days. By day 30 the pH was close to 7 and the reactors no longer required neutralization. Leachate pH continued to increase in both reactors until about day 100, when the pH stabilized at just over 8.

The COD data for the yard waste reactors is presented in Figure 17. The COD, on average, reached a maximum of 29,600 mg/L within the first 28 days. Over the next 125 days the COD of the leachate decreased sharply and ultimately stabilized at 10,000 to 15,000 mg/L in the yard waste reactors.

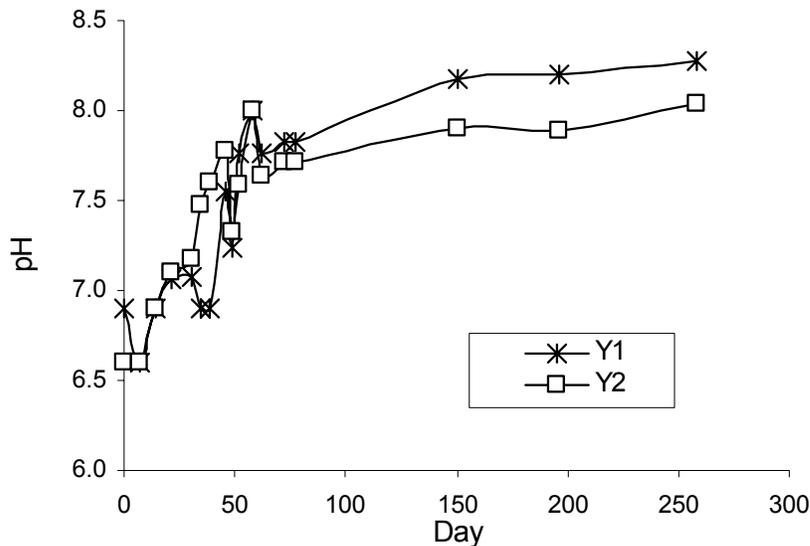


Figure 16. pH in Yard Waste Reactors

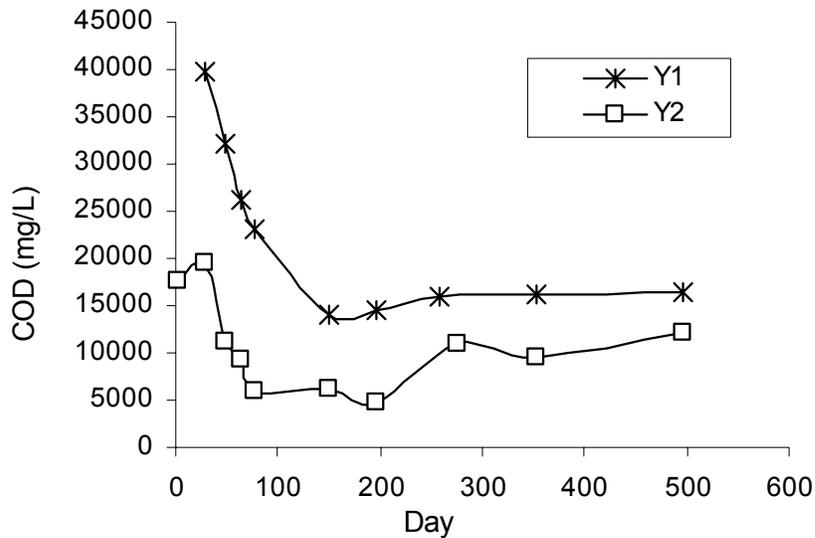


Figure 17. COD in Yard Waste Reactors

The methane yields from reactors Y1 and Y2 were 184 and 128 mL/dry gm, respectively, with an average of 156. (Figure 18). Methane production rates for reactors Y1 and Y2 reached their maximum levels of 1.74 and 1.37 mL/(day-dry gm), respectively, on days 60 and 37, respectively. Methane production rate data is presented in Figure 19. Methane production in both reactors followed the same trend, decreasing asymptotically after reaching the maximum level. However, the production rate curve for reactor Y1 is shifted to the right, since it was initially inhibited, and reached its maximum production rate much later than reactor Y2. Also, reactor Y1 showed a significantly higher maximum production rate and therefore yielded more methane.

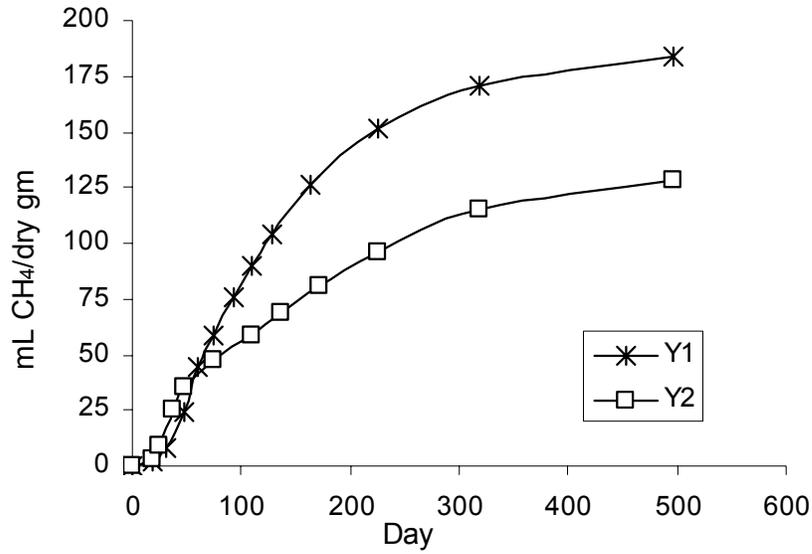


Figure 18. Methane Yields for Yard Waste

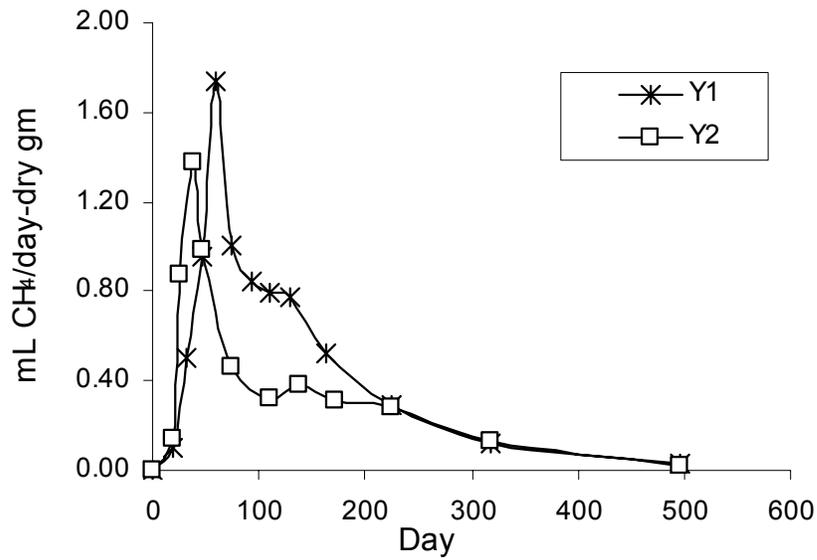


Figure 19. Methane Production Rates for Yard Waste

## Mass Balance

The fresh yard waste was composed of 23.5% cellulose, 11.4% hemicellulose and 24.2% lignin. Solid loss data is presented in Table 21. An average of 61% of the cellulose and 81% of the hemicellulose were degraded. The total recovered mass of lignin, which is generally considered recalcitrant under anaerobic conditions, was 1.30 times higher for reactor Y1 and 1.10 times higher for Y2 compared to the initial mass. The data suggesting the increase in the mass of lignin will be evaluated in the Discussion. The final ratio of cellulose plus hemicellulose to lignin was 0.48 on average.

Table 21. Solids Loss for Yard Waste

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	23.5	11.4	24.2	1.97					
<b>Decomposed</b>									
Y1	11.8	6.5	41.1	0.44	0.38	0.20	1.30	79.2	0.75
Y2	14.7	6.8	40.5	0.53	0.40	0.18	1.10	80.9	0.77

- Cellulose plus hemicellulose divided by lignin
- The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

## Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC yields and production rates are presented in Figures 20 and 21, respectively. The total NMOC yield ranged from 0.033 to 0.043 mg NMOC-C/dry gm, with an average of 0.038. Peak NMOC production rates of  $4.3 \times 10^{-4}$  (Y1) and  $8.51 \times 10^{-4}$  (Y2) were observed.

$10^{-4}$  (Y2) mg-NMOC-C/(day-dry gm) occurred on days 31 and 37 for Y1 and Y2, respectively. Compared to reactor Y2, the maximum production of NMOCs for Y1 was lower, but longer sustained. Only after day 150 did NMOC production dramatically decrease in Y1. In contrast, NMOC production from reactor Y2 decreased asymptotically after peaking. By day 175, NMOC production in both reactors was nearly zero, and remained steady throughout the remainder of the experiment.

The yields of specific trace organic compounds from the yard waste are shown in Table 19. The most abundant category of organics was the terpenes. The highest yielding compounds were  $\alpha$ -pinene (8540 ng/dry gm), camphene (1020 ng/dry gm),  $\beta$ -pinene (2320 ng/dry gm), limonene (1250 ng/dry gm), myrcene (53,400 ng/dry gm), 3-carene (67,400 ng/dry gm), 2-methylhexane (4110 ng/dry gm) and 1-butanol (1150 ng/dry gm). The yard waste reactors were consistent, with no remarkable differences in yields of specific organic compounds. No standard curves were available for myrcene and 3-carene and they were quantified using standard curves of structurally similar compounds (see Table 14). A review of plant material as a source of some specific VOCs is also presented in the Discussion.

Volatile fatty acids accounted for 3.5 to 8.8% of the total NMOC concentration in the samples shown in Table 20, which correspond to the time when leachate COD was highest. On average, the VFA concentrations in these samples are 83.2 percent lower than the concentrations of all other individually quantified organics.

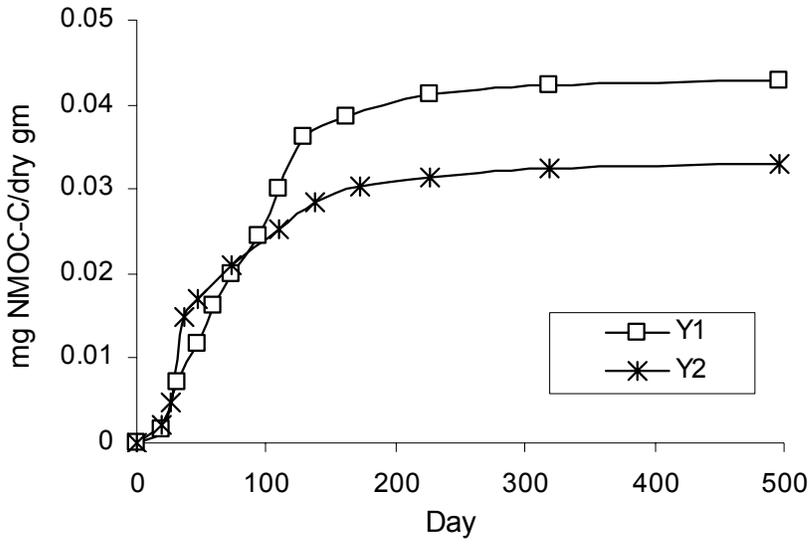


Figure 20. Total NMOC Yields for Yard Waste

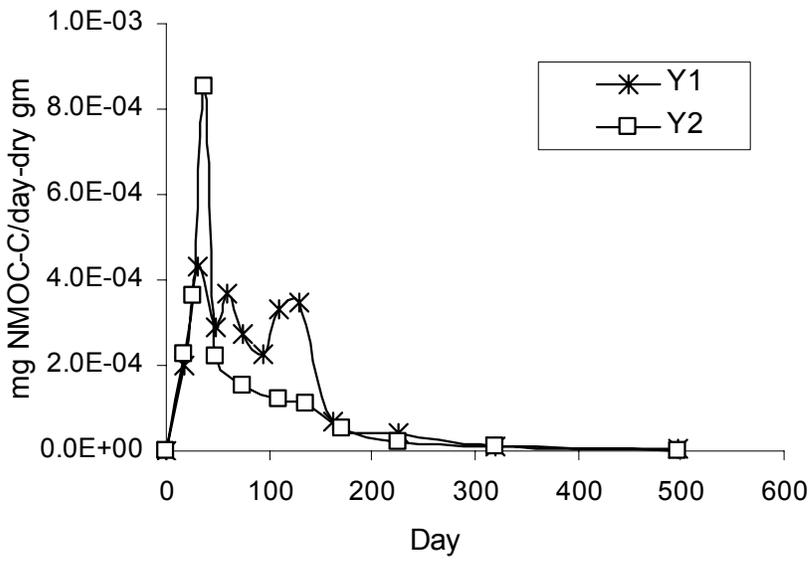


Figure 21. NMOC Production Rates for Yard Waste

### 3.4 Food Waste

The food waste reactors were batch fed and operated anaerobically for 96 days. Leachate pH data for the food waste reactors (F1-F3) is presented in Figure 22. The three reactors behaved very similarly with regards to pH. During the first 14 days the pH reached a minimum of 6.2 as acids accumulated. The pH was actively neutralized during this time, reached 7 by day 20, and continued to increase thereafter even though NaOH addition was stopped. The final pH was between 7.8 and 8.0.

COD data is presented in Figure 23. On day 30, the COD for reactors F1-F3 ranged from 10,000 to 22,000 mg/L. After day 30, the COD decreased until day 70, after which it remained constant at about 2,000 mg/L. The average COD of the leachate at the time the reactors were terminated was 1,784 mg/L.

The food waste reactors were fed in batch mode. When methane production slowed, fresh food waste was added, providing a source of the necessary substrates for methane production. The fresh food waste was 40.8 % cellulose, 6.1 % hemicellulose and 7.40 % lignin. Insufficient solid food waste remained after decomposition to measure the final composition. Therefore, mass balances were not done for the food waste reactors.

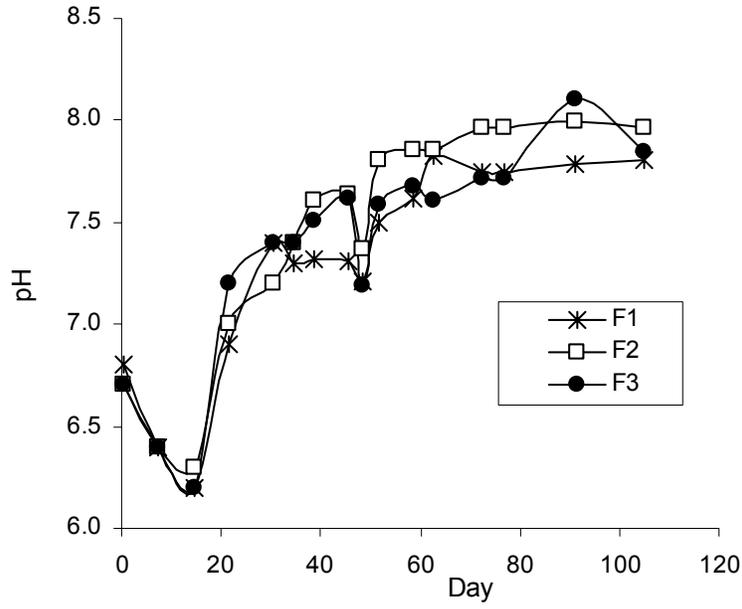


Figure 22. pH in the Food Waste Reactors

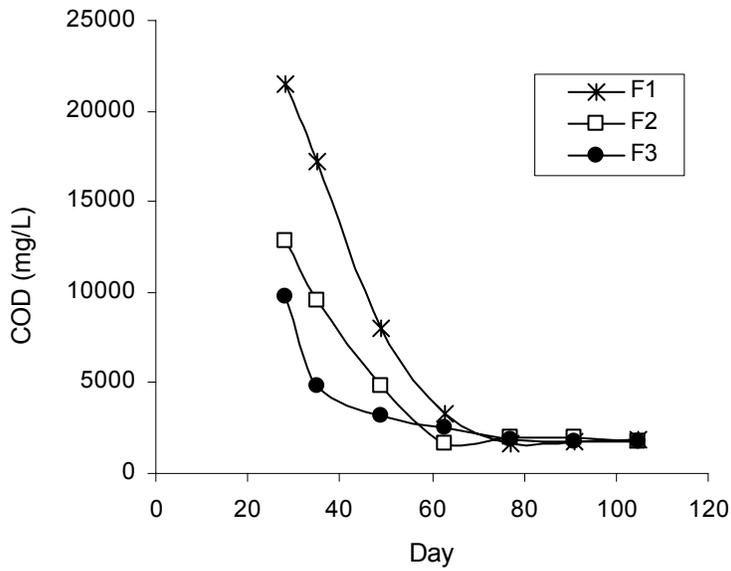


Figure 23. COD in the Food Waste Reactors

Since the food waste was added in batch mode, and all yields and production rates are calculated on a per dry gram basis, only the ultimate yields are reported. The ultimate methane and NMOC yields are summarized in Table 22. Methane yields were 161, 147 and 150 mL/dry gm from reactors F1, F2 and F3, respectively, with an average of 153 mL/dry gm. The total NMOC yields from reactors F1, F2 and F3 were 0.438, 0.279 and 0.324 mg NMOC-C/dry gm, respectively, with an average of 0.347.

Table 22. Methane and NMOC Yields for Food Waste Reactors

	<b>CH<sub>4</sub> Yield (mL/dry gm)</b>	<b>NMOC Yield (mg-C/dry gm)</b>
F1	161	0.438
F2	147	0.279
F3	150	0.324
Ave. (s.d.)	153 (7.37)	0.347 (0.082)

### Production of Specific Trace Organic Compounds

The yields of specific trace organic compounds from the food waste are shown in Table 19. The most abundant category of organics was again the terpenes. The highest yielding compounds were  $\alpha$ -pinene (8300 ng/dry gm),  $\beta$ -pinene (4190 ng/dry gm), limonene (135,900 ng/dry gm), myrcene (575,000 ng/dry gm), 3-carene (488,400 ng/dry gm), ethanol (3170 ng/dry gm) and 2-methylbutane (11,300 ng/dry gm). There was considerable variation in the yields of terpenes from the three reactors. Limonene yields ranged from 78,000 to 225,000 ng/dry gm. There was also a lot of variation in yields of

myrcene, 3-carene and 2-methylbutane—all compounds that were manually identified and integrated, and quantified using the standard curves prepared for similarly structured compounds (see Table 14). A summary of foods as a source of specific organic compounds is also presented in the Discussion.

Volatile fatty acids accounted for .11 to .13% of the total NMOC concentration in the samples shown in Table 20, which correspond to the time when leachate COD was highest. On average, the VFA concentrations in these samples are 85 times lower than the concentrations of all other individually quantified organics. An evaluation of the significance of VFAs for total NMOC yield is presented in the Discussion.

### 3.5 MSW

MSW reactors were operated anaerobically for 319 days. Since one of the three reactors leaked, data is presented for two reactors only—M1 and M2. The leachate pH data for the MSW reactors is presented in Figure 24. The pH was initially between 6.2 and 6.4, but quickly increased, reaching 7 by about day 20. Thereafter, reactor pHs increased gradually, stabilizing at values near 8.

The COD data is presented in Figure 25. The COD trends for the reactors were almost identical. On day 30 the COD was approximately 18,000 mg/L. Over the following 45 days the leachate COD dropped dramatically and stabilized at about 4,000 mg/L. The final leachate COD in reactors M1 and M2 were 5,650 and 4,760 mg/L, respectively.

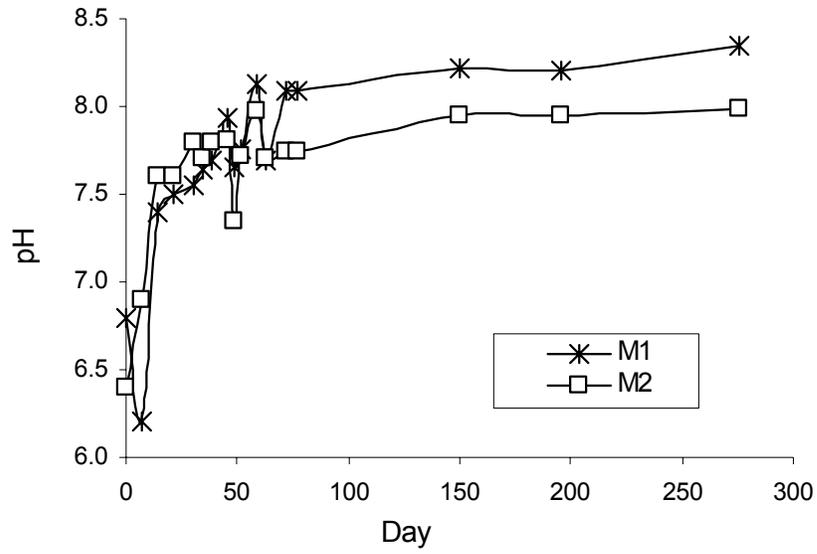


Figure 24. pH in the MSW Reactors

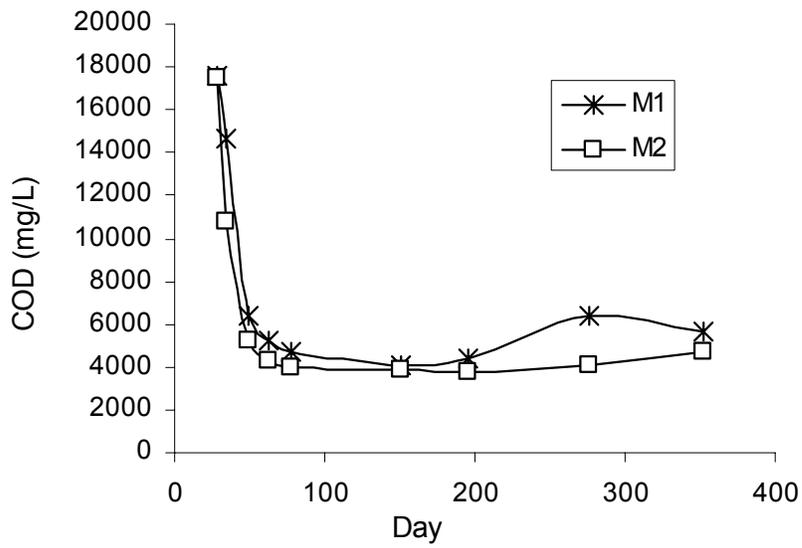


Figure 25. COD in the MSW Reactors

The methane production data for the MSW reactors are presented in Figures 26 (yields) and 27 (rates). Similar to the COD data, the methane production for the two reactors matched very closely. The methane yields for reactors M1 and M2 were 97 and 98 mL/dry gm, respectively. The maximum rate of methane production for reactor M1, occurring on day 48, was 1.26 mL/(day-dry gm), and for reactor M2 it was 0.91 mL/(day-dry gm) on day 87. The general trend was a steady decrease in methane production following the peak level, with one outlier for reactor M2 at about day 200.

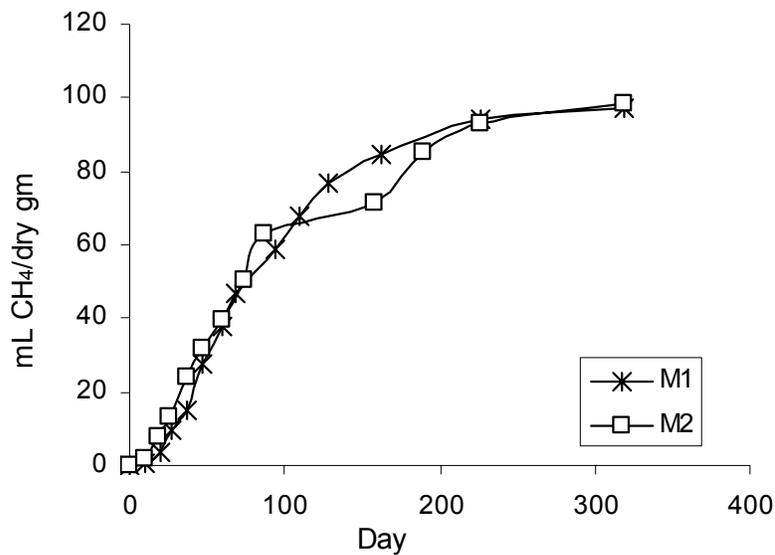


Figure 26. Methane Yields for MSW

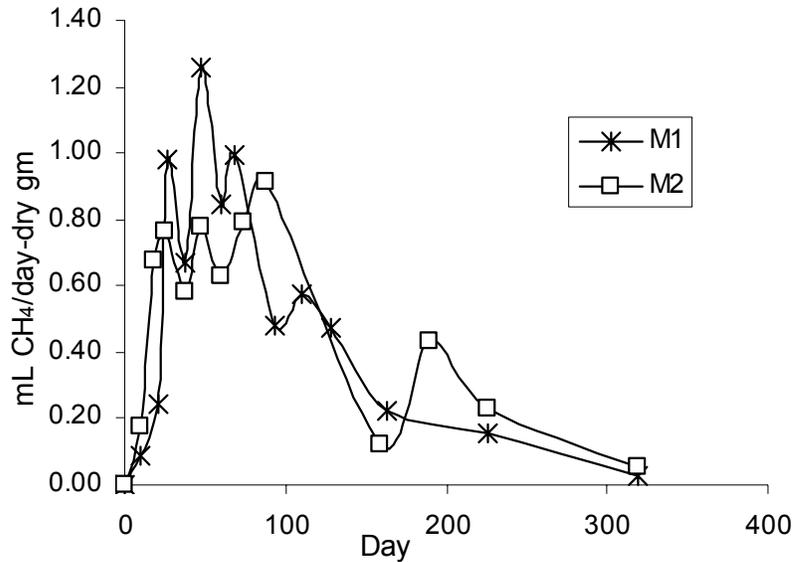


Figure 27. Methane Production Rates for MSW

Mass Balance

Solids loss data is presented in Table 23. The composition of the fresh MSW was 33.5% cellulose, 8.7% hemicellulose and 23.4% lignin. On average, 74% of the cellulose and 58% of the hemicellulose were lost. Sixty one percent of the added lignin was recovered although it is unlikely that 39% of the lignin was degraded, given the recalcitrance of lignin. The behavior of lignin is analyzed in the Discussion. The final ratio of cellulose plus hemicellulose to lignin was 0.95 on average.

Table 23. Solids Loss for MSW

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	39.2	7.9	23.1	2.0				79.4	0.88
<b>Decomposed</b>									
<b>M1</b>	23.6	7.6	30.6	1.02	0.29	0.46	0.63	65.8	0.94
<b>M2</b>	17.2	5.6	26.0	0.88	0.23	0.37	0.59	58.7	0.83

- Cellulose plus hemicellulose divided by lignin
- The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

#### Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC yields and production rates are presented in Figures 28 and 29, respectively. The total NMOC yields ranged from 0.111 to 0.114 mg NMOC-C/dry gm. The peak rates of NMOC production for reactors M1 and M2 were  $4.08 \times 10^{-3}$  and  $4.33 \times 10^{-3}$  mg NMOC-C/(day-dry gm), respectively, and they occurred on day 10. Peak NMOC production was very brief. After peak release occurred, NMOC production showed a steep asymptotic decrease.

The yields of specific trace organic compounds from MSW are shown in Table 19. The most abundant categories of organics were alkanes and terpenes. The highest yielding alkanes were butylcyclohexane, and pentane, and the most predominant terpenes were 3-carene and limonene. The two MSW reactors showed good consistency in the yields of specific organic compounds. Butylcyclohexane and 3-carene were quantified using the standard curves prepared for similarly structured compounds (see Table 14).

Volatile fatty acids accounted for 1.9 to 3.5 % of the total NMOC concentration for the samples shown in Table 20, which correspond to the time when leachate COD was highest. On average, VFA concentrations in these samples are 83.5 percent lower than the concentration of all other individually quantified organics.

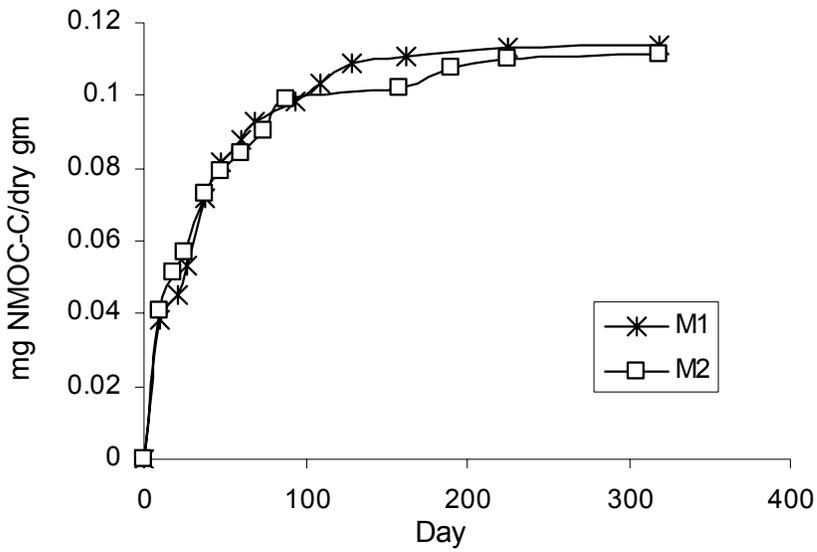


Figure 28. Total NMOC Yields for MSW

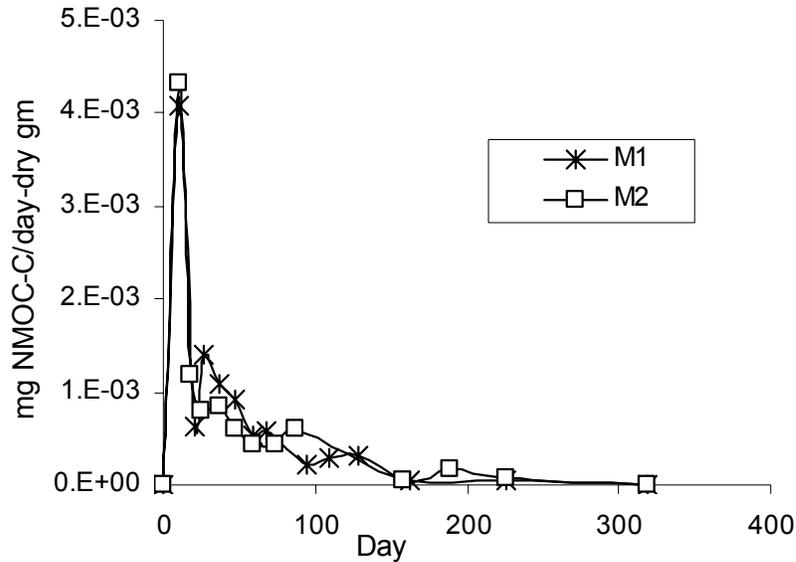


Figure 29. NMOC Production Rates for MSW

### 3.6 MSW with HHW

Reactors were operated anaerobically for 319 days. Data for only two of the three reactors (MH1, MH2) are reported since one reactor leaked. Leachate pH data for the MSW plus HHW reactors is presented in Figure 30. Initially the pH was between 5.9 and 6.3. Daily addition of NaOH brought the pH above 7, for MH1 and MH2 on days 50 and 75, respectively. Once the pH was above 7, NaOH was no longer added. The pH continued to increase to between 8.0 and 8.3.

The COD data is presented in Figure 31. The maximum COD for reactors MH1 and MH2 was 57,000 and 52,000 mg/L, respectively. Reactor MH1 reached its maximum COD on day 35, while the COD of MH2 did not peak until day 77. For both reactors, once COD reached a maximum it steadily decreased over a period of about 100

days, and then remained relatively constant between 2,000 and 8,000 mg/L. The average COD of the leachate at the time the reactors were terminated was 6,100 mg/L.

Methane yields and production rates are presented in Figures 32 and 33, respectively. Both reactors also exhibited a lag period of about 50 days with little methane production. The methane yields from reactors MH1 and MH2 were 120 and 108 mL/dry gm, respectively. The methane production rate curves for the two reactors showed somewhat different trends. Reactor MH1 had a lower maximum production rate than MH2, 0.98 vs. 1.28 mL/(day-dry gm). For reactor MH1, near maximum methane production rates were observed earlier and were longer sustained, compared to MH2. For both reactors methane production decreased asymptotically after peak rates were reached.

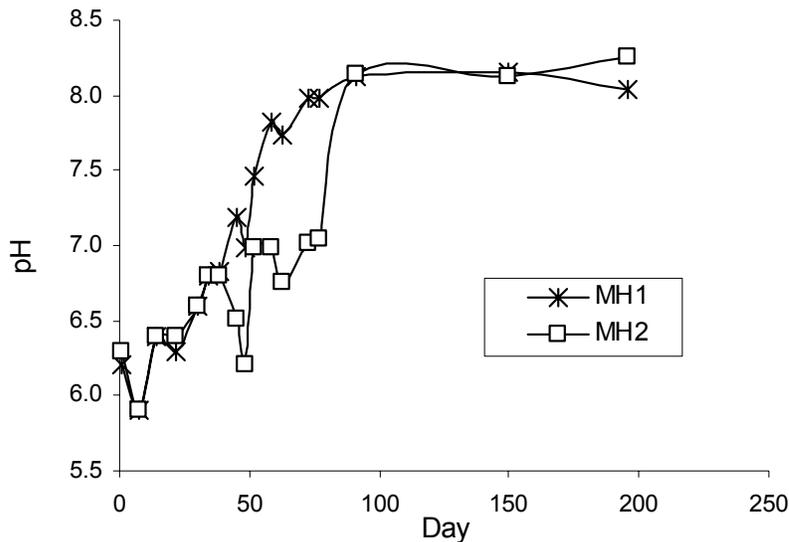


Figure 30. pH in the MSW + HHW Reactors

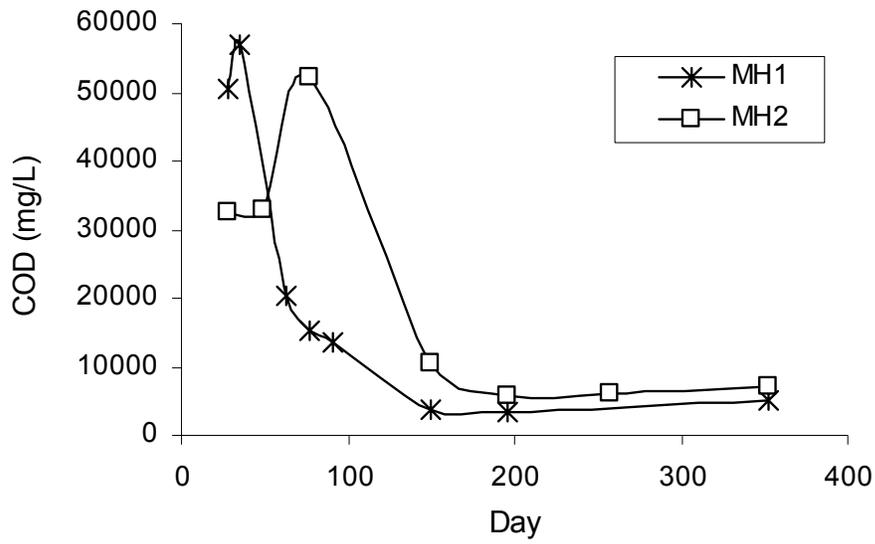


Figure 31. COD in the MSW + HHW Reactors

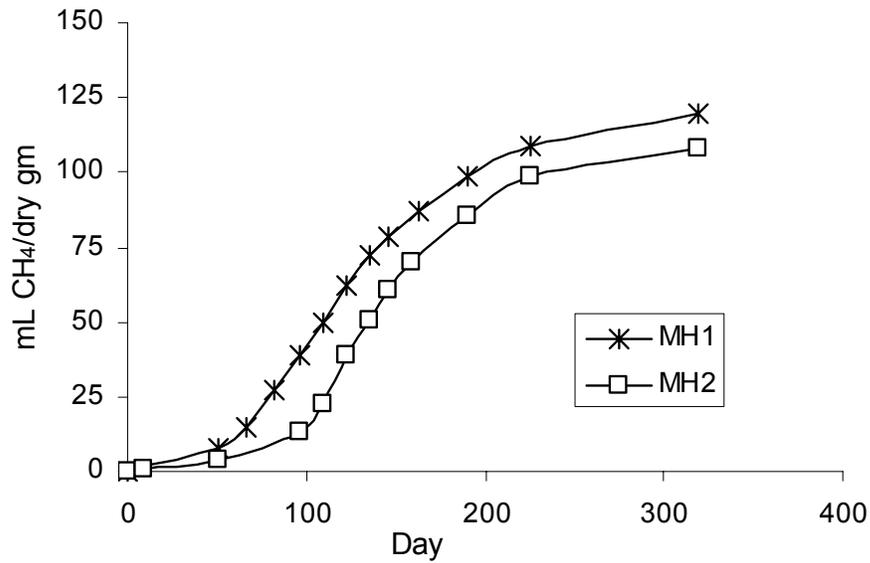


Figure 32. Methane Yields for MSW + HHW

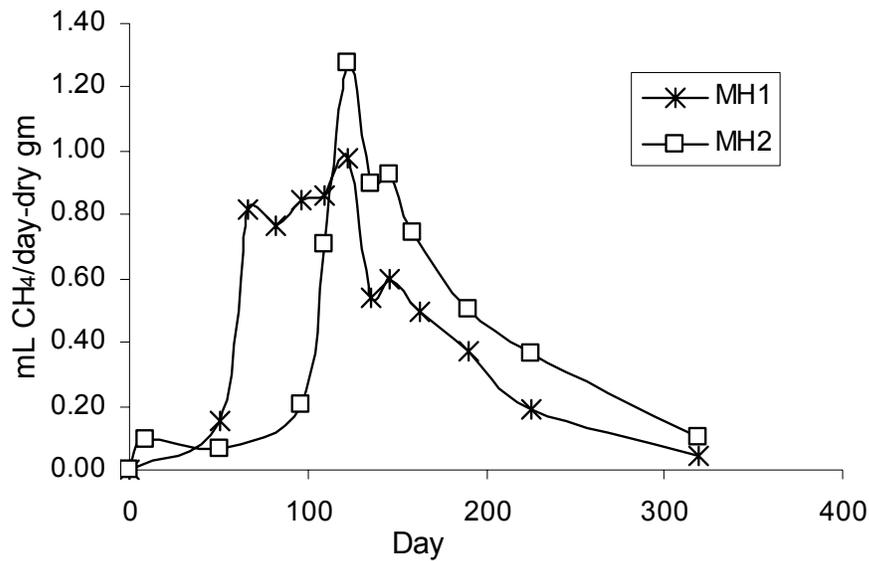


Figure 33. Methane Production Rates for MSW + HHW

### Mass Balance

The composition of the fresh refuse, and the losses of its constituent solids during the experiment are presented in Table 24. The composition of the fresh refuse was 55% cellulose, 7.7% hemicellulose and 20.6% lignin. On average, 70% of the cellulose and 58% of the hemicellulose was degraded. Seventy two percent of the added lignin was recovered, although 28% of the lignin may not have been degraded given the recalcitrance of lignin. The behavior of lignin is analyzed in the Discussion. The final ratio of cellulose plus hemicellulose to lignin was 0.93.

Table 24. Solids Loss for MSW + HHW

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	39.2	7.9	23.1	2.0				79.4	0.88
<b>Decomposed</b>									
<b>MH1</b>	20.4	5.9	26.2	1.00	0.30	0.43	0.65	65.0	0.84
<b>MH2</b>	20.6	5.4	30.1	0.86	0.31	0.40	0.78	61.6	0.56

- a) Cellulose plus hemicellulose divided by lignin
- b) The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- c) The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC yields are presented in Figure 34. The NMOC yields for reactors MH1 and MH2 were 0.161 and 0.183 mg NMOC-C/dry gm, respectively. NMOC production rates are presented in Figure 35. The maximum NMOC production rate in reactor MH2 was much higher than in MH1— $6.51 \times 10^{-3}$  mg NMOC-C/(day-dry gm) compared to  $1.25 \times 10^{-3}$  mg NMOC-C/(day-dry gm). Aside from the initial spike in NMOC production from MH2, the two reactors behaved very similarly. NMOC production generally decreased with time, but for both reactors there were temporary increases around days 120 and 200.

The yields of specific trace organic compounds from the MSW + HHW mixture are shown in Table 19. The most abundant organics were toluene (60,950 ng/dry gm), butylcyclohexane (47,200 ng/dry gm), 3-carene (165,300 ng/dry gm), myrcene (34,900 ng/dry gm) and limonene (12,800 ng/dry gm). The consistency of compound yields between reactors was good with the exception of myrcene, which was much higher in

MH2. Butylcyclohexane, 3-carene and myrcene were quantified using the standard curves of other, similarly structured compounds (see Table 14). The percent recovery of the spiked compounds is presented in the Discussion (section 4.7) along with an analysis of the significance of HHW compounds for total NMOC yields.

Volatile fatty acids accounted for 0.09 to 0.46% of the total NMOC concentration in the samples shown in Table 20, which correspond to the time when leachate COD was highest. On average, the VFA concentrations in these samples are 81 times lower than the concentrations of all other individually quantified organics.

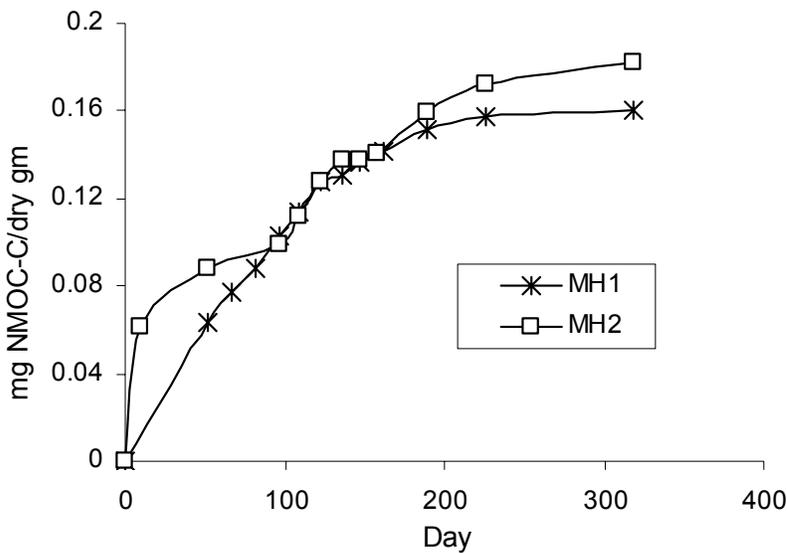


Figure 34. Total NMOC Yields for MSW + HHW

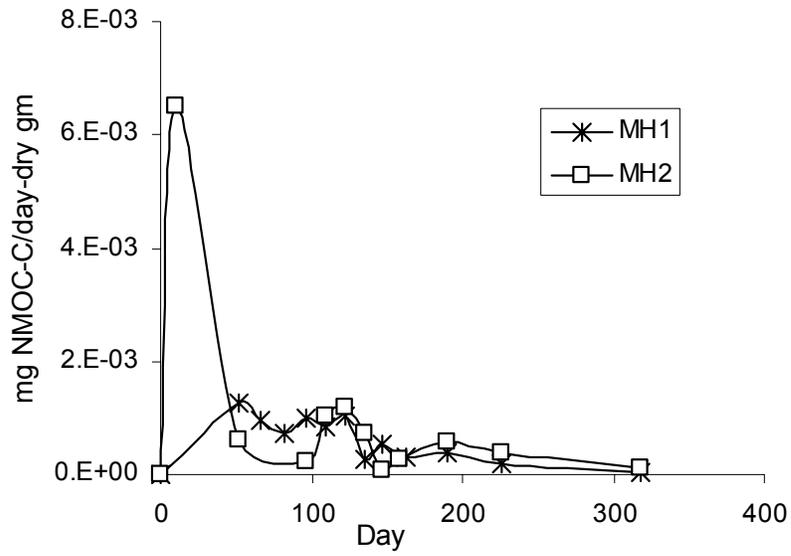


Figure 35. NMOC Production Rates

### 3.7 MSW Aerobic

For the aerobic MSW treatment, reactors were operated aerobically for 44 days, followed by anaerobic operation up to day 148. The average air flow rates for reactors MA1, MA2 and MA3 were 53.1, 47.6 and 45.3 L/day, respectively. The resulting total volume of air that flowed through each reactor was 2.35, 2.12 and 2.02 m<sup>3</sup> for MA1, MA2 and MA3, respectively.

Leachate pH data is presented in Figure 36. No pH data was recorded during the aerobic phase. At day 44, air addition was stopped and the pH ranged from 8.2 to 8.5. During the anaerobic phase, the pH decreased to between 7.5 and 7.7.

Leachate COD data is presented in Figure 37. On day 30 the leachate COD ranged from 3,000 to 4,000 mg/L. The COD increased to maximum values between 6,000 and 7,000 mg/L at about day 65, and then decreased to 4,000 to 5,000 mg/L.

Under aerobic conditions, carbon dioxide (CO<sub>2</sub>) is the end product of refuse decomposition. Carbon dioxide yields and production rates are presented in Figures 38 and 39, respectively. The CO<sub>2</sub> yields for reactors MA1, MA2 and MA3 were 316, 254 and 303 mL/dry gm, respectively, with an average of 291 mL/dry gm. The rate of CO<sub>2</sub> production was highest during the first 10 days. The average CO<sub>2</sub> production rate during the first 10 days was 12.8 mL/(day-dry gm). Production of CO<sub>2</sub> decreased asymptotically with time.

During the anaerobic phase of decomposition, negligible methane was produced, indicating that the refuse had been well decomposed during the aeration. The methane yields for MA1, MA2 and MA3 during the anaerobic phase were 7.36, 1.44 and 0 mL/dry gm, respectively.

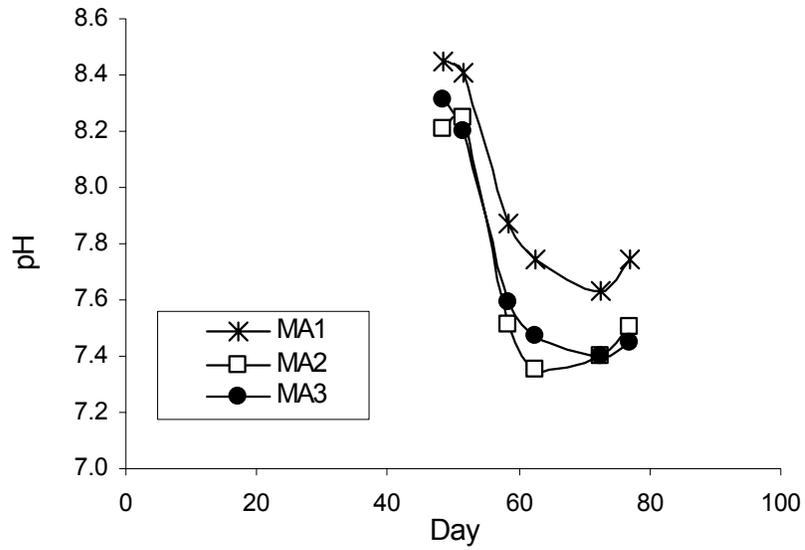


Figure 36. pH in Aerobic MSW Reactors

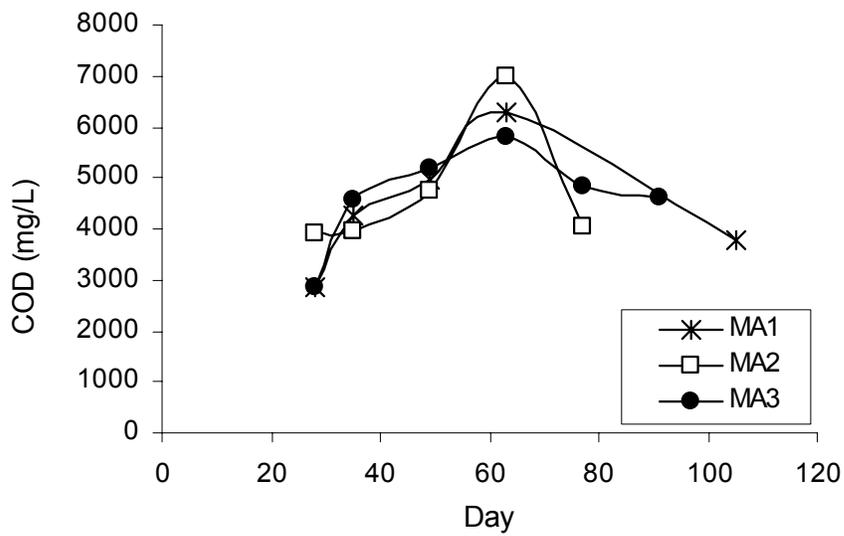


Figure 37. COD in Aerobic MSW Reactors

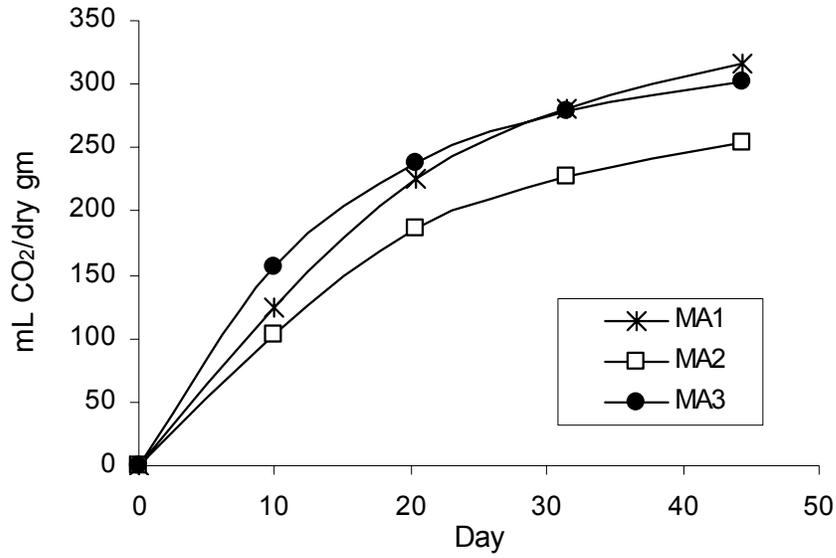


Figure 38. Carbon Dioxide Yields for Aerobically Decomposed MSW

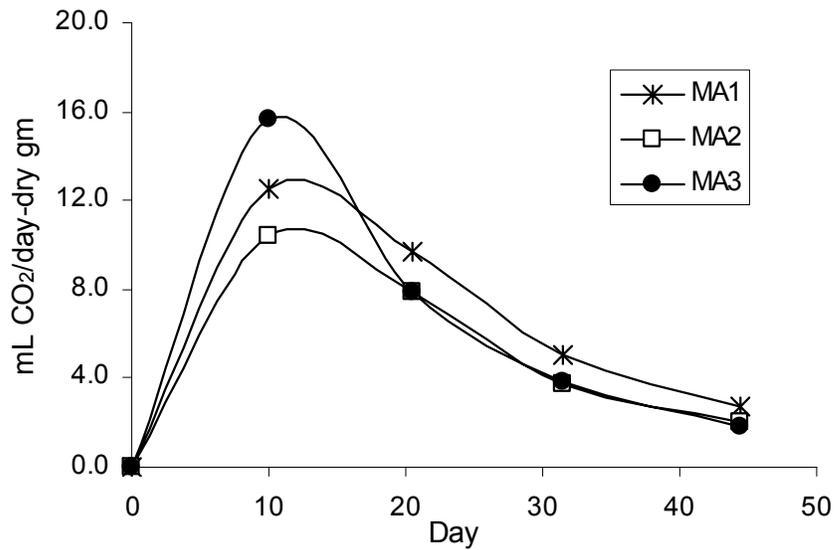


Figure 39. Carbon Dioxide Production Rates for Aerobically Decomposed MSW

## Mass Balance

Constituent solids loss data is presented in Table 25. The initial composition of the MSW was 39.2% cellulose, 7.9% hemicellulose and 23.1% lignin. On average, 91% of the cellulose and 82% of the hemicellulose was degraded. The recovered masses of lignin were 1.02 to 1.61 times higher than the initial masses (see Discussion). The final ratios of cellulose plus hemicellulose to lignin were between 0.10 and 0.33.

Table 25. Solids Loss for Aerobically Decomposed MSW

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	39.2	7.9	23.1	2.0				79.4	0.88
<b>Decomposed</b>									
<b>MA1</b>	4.7	1.9	63.1	0.10	0.07	0.13	1.48	63.0	1.10
<b>MA2</b>	4.8	1.9	67.0	0.10	0.07	0.13	1.61	68.1	1.08
<b>MA3</b>	8.9	3.7	38.2	0.33	0.14	0.29	1.02	53.4	0.95

- Cellulose plus hemicellulose divided by lignin
- The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

### Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC yields are presented in Figure 40. The total NMOC yields from reactors MA1, MA2 and MA3 were 0.278, 0.221 and 0.200 mg NMOC-C/dry gm, respectively. NMOC production rates are presented in Figure 41. Maximum NMOC production rates occurred within the first 10 days and were between  $1.02 \times 10^{-2}$  and  $2.08 \times 10^{-2}$  mg NMOC-C/(day-dry gm). By day 20 NMOC production rates were much lower—around  $1 \times 10^{-3}$  mg NMOC-C/day-dry gm. Towards the end of the aerobic phase, NMOC production increased slightly, but once the reactors were anaerobic almost no NMOC production occurred.

The yields of specific trace organic compounds from the aerobically decomposed MSW are shown in Table 19. The highest yielding compounds were 2-methylbutane (23,700 ng/dry gm), ethyl acetate (14,900 ng/dry gm), limonene (14,700 ng/dry gm), ethanol (6960 ng/dry gm), 1-butanol (6940 ng/dry gm) and  $\alpha$ -pinene (4070 ng/dry gm). For the aerobic reactors there was a lot of variability between reactors in the yields of ethanol, 1-butanol, 2-butanone, limonene and ethylacetate, and no apparent trend (for example one reactor always being much lower or higher).

Volatile fatty acids accounted for 10.7 to 27.3 % of the total NMOC concentration in the samples shown in Table 20, which correspond to the time when leachate COD was highest. The VFA concentrations were 89.3 and 76.1% lower than the concentrations of all other individually quantified organics for MA1 and MA2, respectively. The VFA concentration in MA3 was only 2.4% lower than the concentration of all other individually quantified organics.

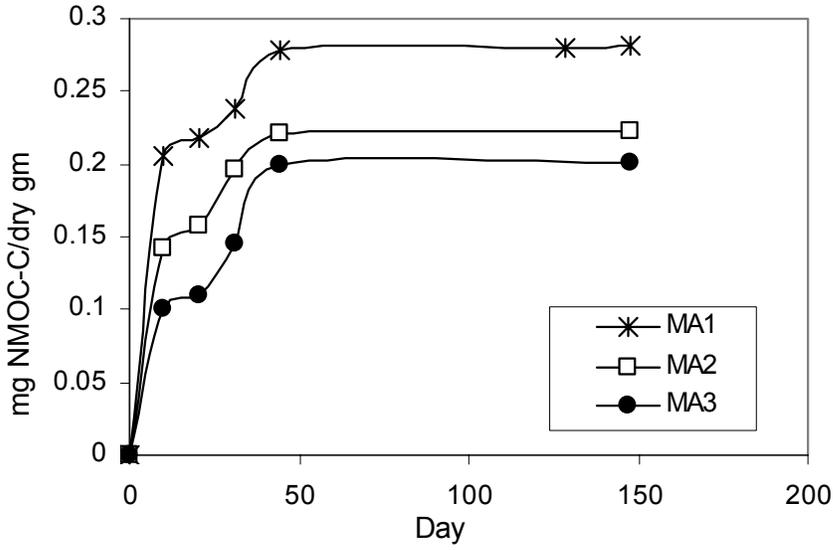


Figure 40. Total NMOC Yields for Aerobically Decomposed MSW

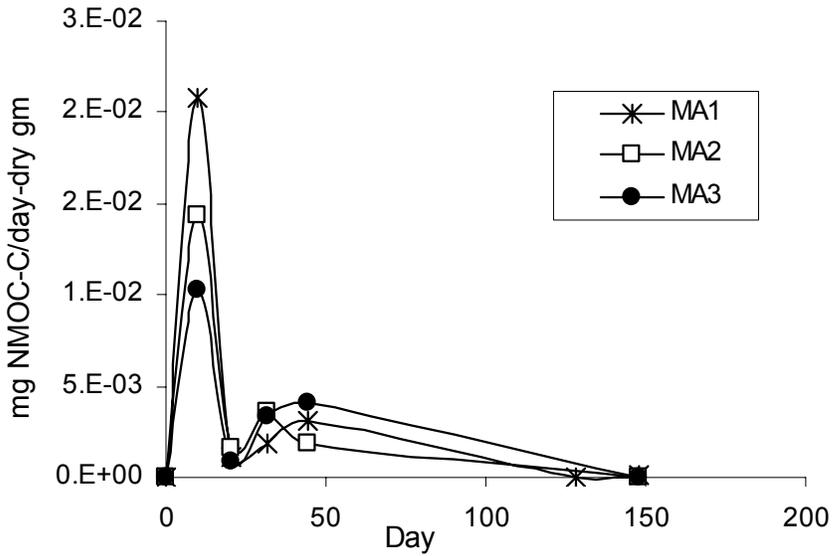


Figure 41. NMOC Production Rates for Aerobically Decomposed MSW

### 3.8 MSW Under Nitrate-Reducing Conditions

Reactors were operated under nitrate-reducing conditions for 319 days. Data is reported for only two of three reactors, MN1 and MN2, since one reactor leaked. The nitrate-reducing environment was maintained through scheduled additions of either  $\text{Mg}(\text{NO}_3)_2$  or  $\text{KNO}_3$  to a leachate  $\text{NO}_3^-$  concentration of 400 mg-N/L. The schedule for nitrate addition was every second day, though at times less frequently due to accumulation of  $\text{NO}_3^-$  in the reactors. The  $\text{NO}_3^-$  concentrations in MN1 and MN2 are presented in Figures 42 and 43, respectively. For the first 100 days, the concentration fluctuated between 400 mg  $\text{NO}_3^-$ -N/L and zero, as added nitrate was consumed. After day 100, nitrate began to accumulate in the reactors. Additions of nitrate were periodically stopped to allow the nitrate to be consumed, but upon resuming additions nitrate again accumulated. The nitrate concentrations in MN1 and MN2 suggest poor mixing of the nitrate. While nitrate is highly soluble in water, the leachate may not have been contacting all of the refuse. For example, during recirculation the leachate could potentially take a preferential flow path and bypass much of the refuse as it settles to the bottom. Evidently this was occurring, since nitrate was accumulating in the leachate at the same time methane was being produced. Furthermore, the magnitude of nitrate accumulation shown in Figures 42 and 43 suggests an error in the nitrate additions. The additions were intended to increase the nitrate concentration of the leachate by 400 mg-N/L. The steep increases shown on the graphs suggest that the nitrate added may have been more highly concentrated than thought, or that the volume of leachate in the reactors was overestimated.

Leachate pH data for the reactors in which MSW was degraded under nitrate-reducing conditions is presented in Figure 44. The leachate pH was initially neutral and remained between 7.0 and 7.3 for the first 70 days except for one measurement of 6.8 from reactor MN2 on day 50. Following day 70, the pH of the leachate increased gradually to between 7.8 and 7.9.

Leachate COD data is presented in Figure 45. The COD of the leachate was highest during the first 28 days. The maximum observed CODs from reactors MN1 and MN2 were 38,000 and 28,000 mg/L, respectively. After day 28 the COD decreased asymptotically in M1. Reactor MN2 exhibited an increase in COD at about day 50, then decreased asymptotically. By day 150 the COD of each reactor was about 1000 mg/L and remained between 600 and 1000 mg/L thereafter.

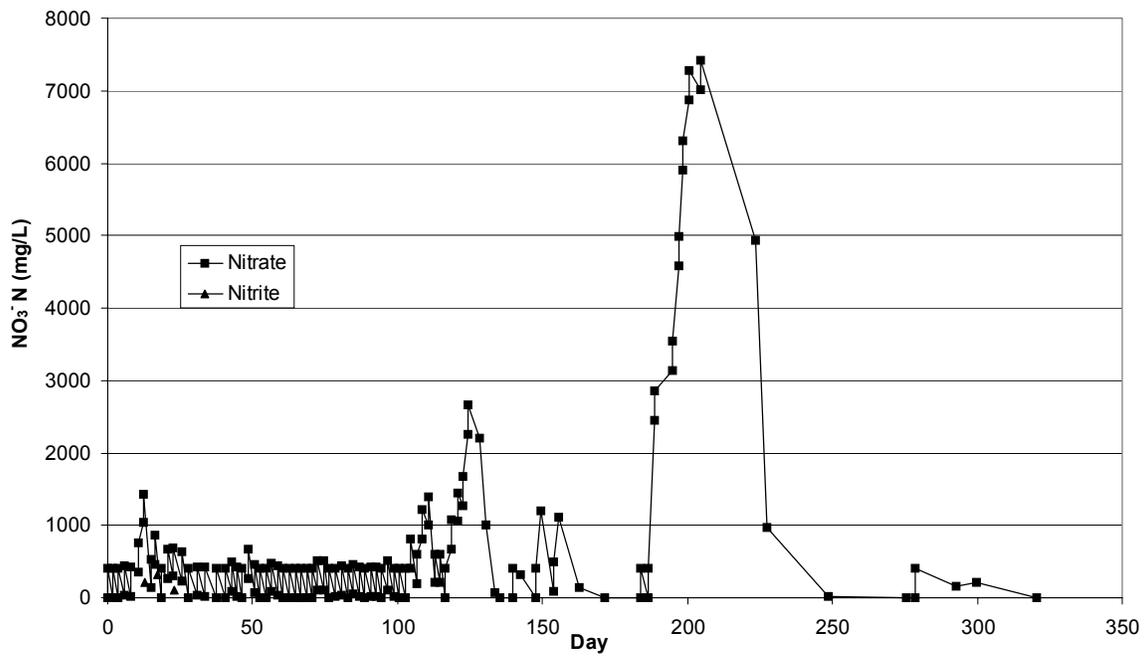


Figure 42. Nitrate Concentration for Reactor MN1

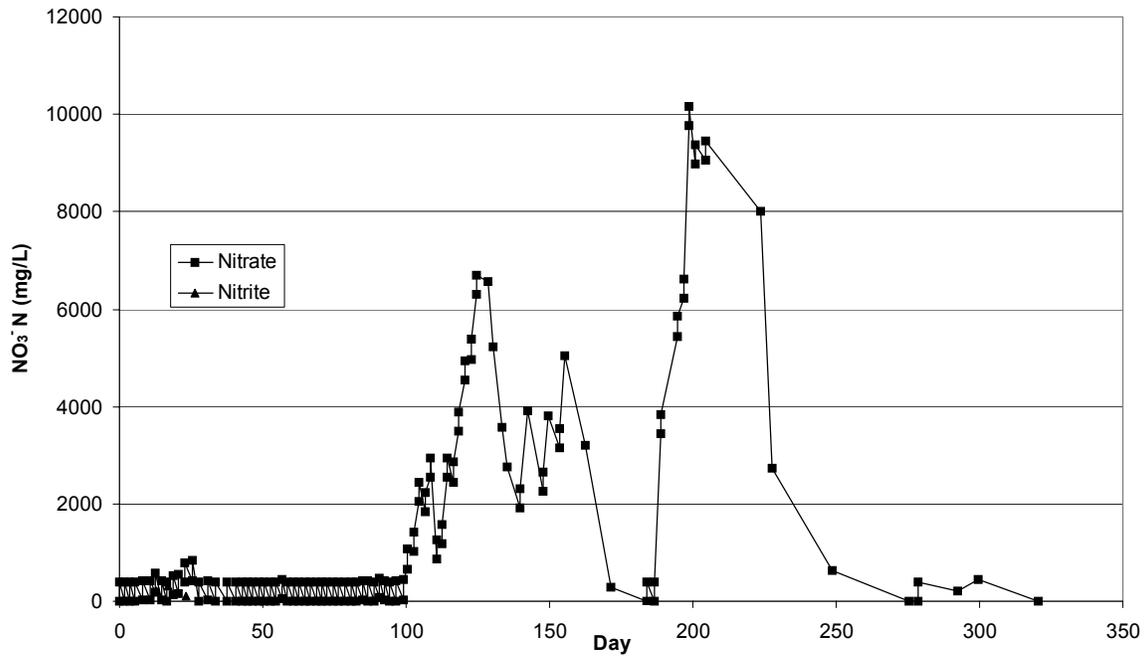


Figure 43. Nitrate Concentration for Reactor MN2

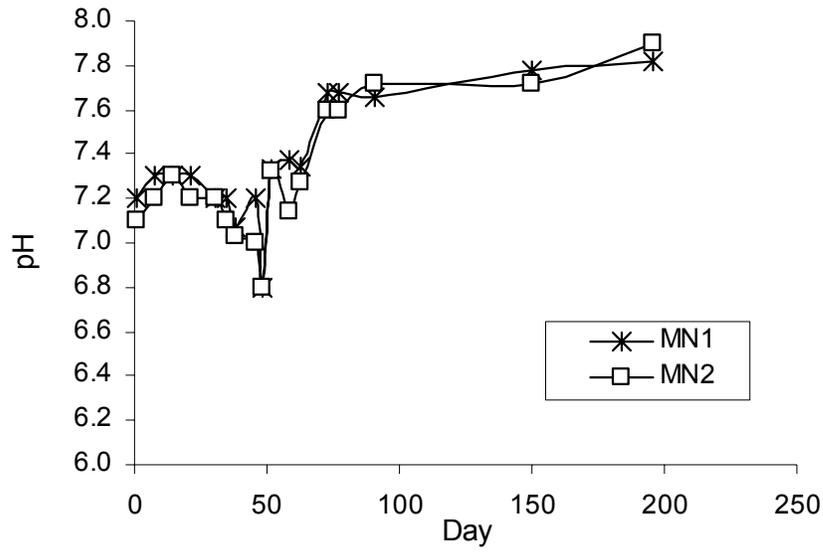


Figure 44. pH in MSW + NO<sub>3</sub><sup>-</sup> Reactors

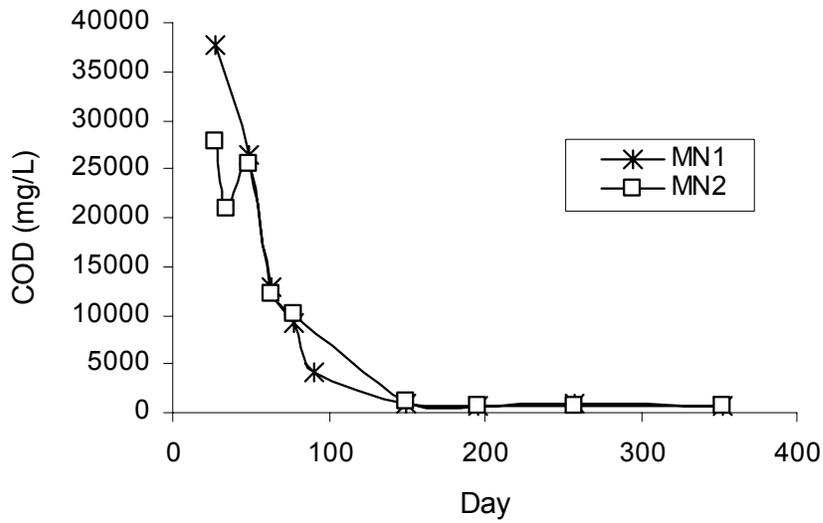


Figure 45. COD in MSW + NO<sub>3</sub><sup>-</sup> Reactors

In the presence of  $\text{NO}_3^-$ , nitrogen gas is produced as a byproduct of microbial decomposition. Nitrogen yields and production rates are presented in Figures 46 and 47, respectively. The  $\text{N}_2$  yields for reactors MN1 and MN2 were 35 and 47 mL/dry gm, respectively. Nitrogen production peaked at about 0.26 mL/(day-dry gm) for both reactors. Peak nitrogen production was sustained for about 50 days between days 80 and 130.

Unexpectedly, methane production occurred as well. Methane yields and production rates are presented in Figures 48 and 49, respectively. The methane yields from MN1 and MN2 were 80.0 and 73.0 mL/dry gm, respectively. Methane production rapidly increased at around day 60, reaching a maximum of approximately 0.66 mL/(day-dry gm), by day 95. Maximum methane production was sustained for about 30 days. From day 120 to 135, methane production decreased dramatically, and from day 135 to 319 the reactors exhibited a linear decrease in methane production. The fact that methane production occurred in the nitrate reactors indicates that there were areas of the reactor not receiving nitrate due to poor mixing of the leachate.

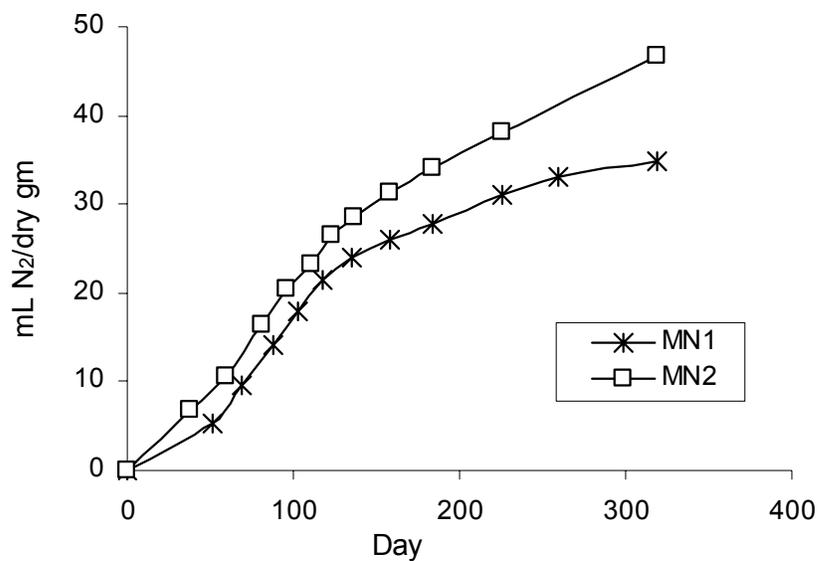


Figure 46. Nitrogen Yields for MSW + NO<sub>3</sub><sup>-</sup>

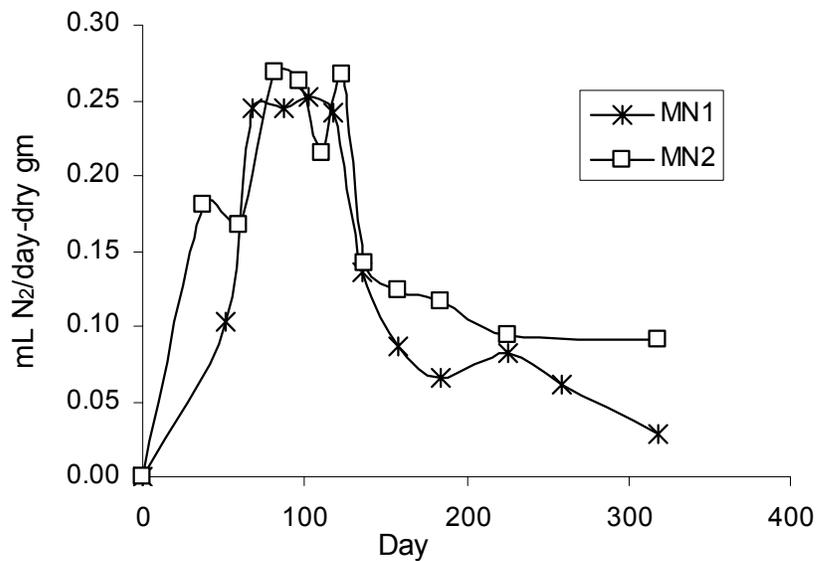


Figure 47. Nitrogen Production Rates for MSW + NO<sub>3</sub><sup>-</sup>

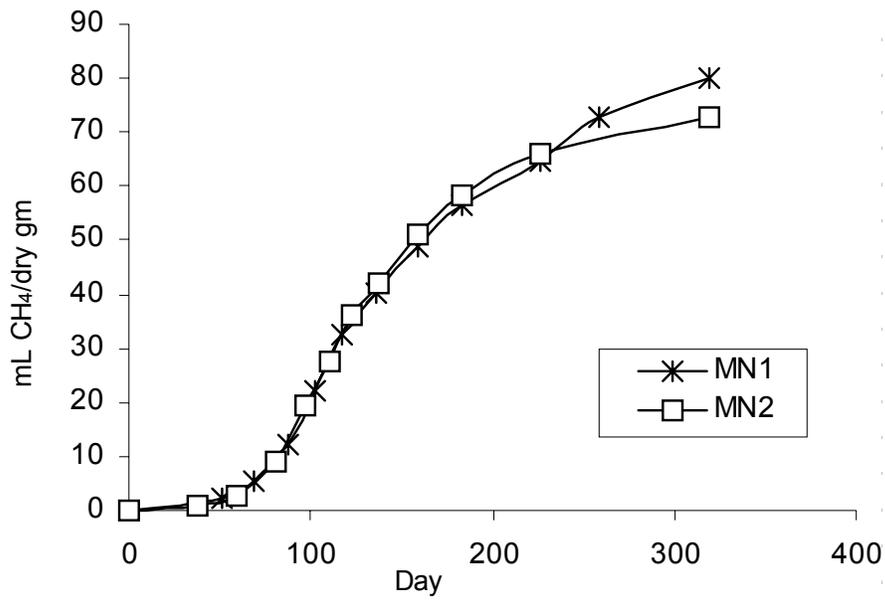


Figure 48. Methane Yields for MSW + NO<sub>3</sub><sup>-</sup>

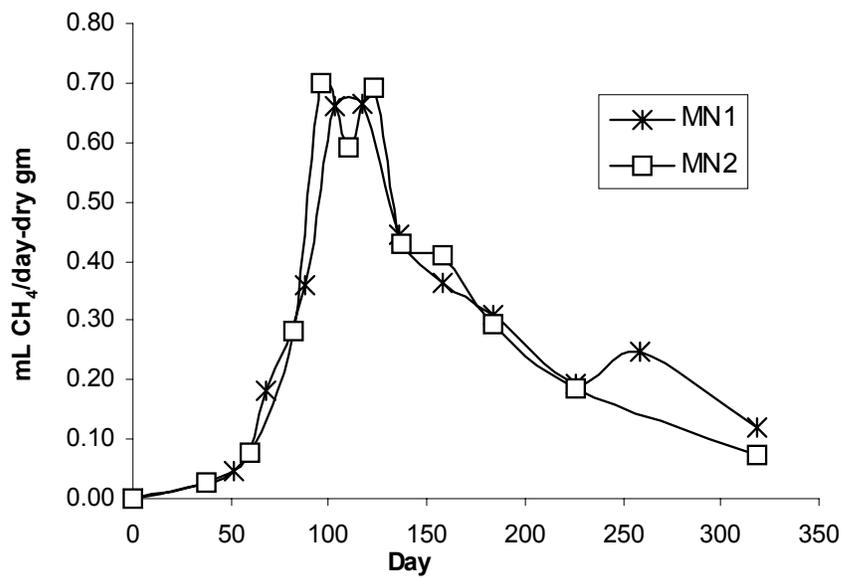


Figure 49. Methane Production Rates for MSW + NO<sub>3</sub><sup>-</sup>

## Mass Balance

Constituent solids loss data is presented in Table 26. The fresh MSW was 39.2% cellulose, 7.9% hemicellulose and 23.1% lignin. On average, 71% of the cellulose and 54% of the hemicellulose was degraded. Ninety three percent of the lignin was recovered. The average final ratio of cellulose plus hemicellulose to lignin was 0.72.

Table 26. Solids Loss for MSW + NO<sub>3</sub><sup>-</sup> Reactors

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	(C+H)/L <sup>a</sup>	MC <sup>b</sup>	MH <sup>b</sup>	ML <sup>b</sup>	Volatile Solids (%)	CHL/VS <sup>c</sup>
<b>Fresh</b>	39.2	7.9	23.1	2.0				79.4	0.88
<b>Decomposed</b>									
<b>MN1</b>	16.8	5.6	40.8	0.55	0.25	0.40	1.01	65.6	0.96
<b>MN2</b>	21.8	7.0	32.8	0.88	0.33	0.52	0.85	69.0	0.89

- Cellulose plus hemicellulose divided by lignin
- The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- The ratio of the sum of the measured cellulose, hemicellulose and lignin concentrations to the measured volatile solids concentration

## Production of Total NMOCs and Specific Trace Organic Compounds

Total NMOC data for reactors MN1 and MN2 are presented in Figures 50 (yields) and 51 (rates). The total NMOC yields for reactors MN1 and MN2 were 0.046 and 0.053 mg NMOC-C/dry gm, respectively. The NMOC production trends for the two reactors were very similar. Peak production of between  $4.0 \times 10^{-4}$  and  $7.5 \times 10^{-4}$  mg NMOC-C/(day-dry gm) occurred around day 50. Between days 50 and 120 NMOC production decreased moderately. At around day 120 the NMOC production dropped dramatically and remained low for the remainder of the experiment.

The yields of specific trace organic compounds from the MSW decomposed under nitrate-reducing conditions are shown in Table 19. The highest yielding compounds were 3-carene (52,800 ng/dry gm), myrcene (44,000 ng/dry gm), butylcyclohexane (21,500 ng/dry gm), limonene (6480 ng/dry gm) and 2-butanone (2330 ng/dry gm). The consistency between reactors for myrcene and butylcyclohexane was poor. Again, these compounds were manually identified and integrated, and quantified using the standard curves of structurally similar compounds (see Table 14).

Volatile fatty acids accounted for 1.5 to 1.8 % of the total NMOC concentration for the samples shown in Table 20, which correspond to the time when leachate COD was highest. On average, VFA concentrations were 87.9 percent lower than the concentration of all other individually quantified organics.

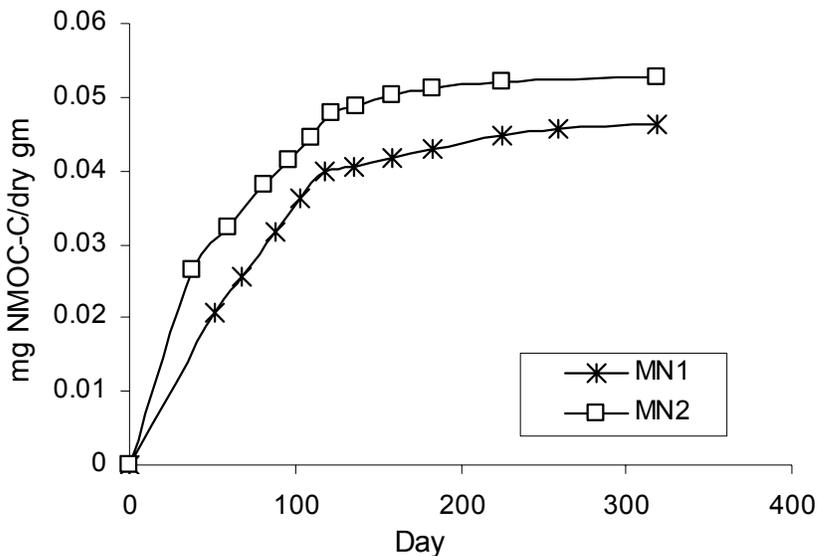


Figure 50. Total NMOC Yields for the MSW + NO<sub>3</sub><sup>-</sup> Reactors

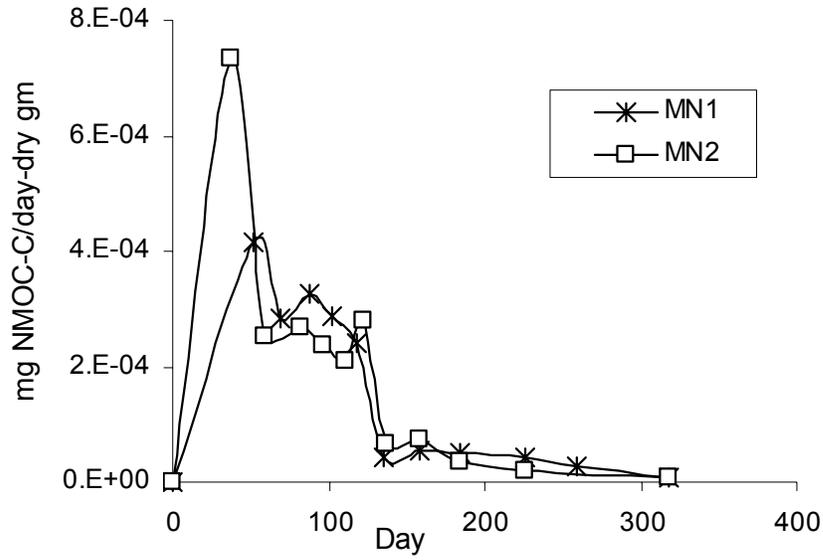


Figure 51. NMO-C Production Rates for the MSW + NO<sub>3</sub><sup>-</sup> Reactors

## **4.0 DISCUSSION**

The primary focus of this section is to relate the data presented in the Results section to the research objectives. To review, these objectives were to: 1) measure an ultimate yield for NMOCs from individual components of MSW during refuse decomposition, 2) study the relationship between gas production and NMOC release, 3) compare anaerobic, aerobic and nitrate-reducing conditions, 4) identify specific trace organic compounds and determine whether volatile carboxylic acids are a major contributor to NMOC concentrations in landfill gas, 5) quantify emissions of HAPs, and 6) evaluate the contribution of household hazardous waste (HHW) compounds to NMOC emissions. Additionally, the appropriateness of the NSPS and AP-42 default NMOC concentrations are analyzed by comparing the laboratory experimental results with regulatory estimates as well as the findings of other studies.

### **4.1 Characterization of Waste Decomposition**

The objective of this section is to compare observations of refuse decomposition in this study to theory and to previous studies.

Refuse decomposition has been described as a four-phase process (Barlaz et al., 1989). Initially there is an aerobic phase during which oxygen and nitrate are quickly consumed. The anaerobic acid phase follows. This phase is characterized by carboxylic acid accumulation. The leachate pH decreases as acids are produced more rapidly than they can be consumed. Also due to carboxylic acid accumulation, leachate COD increases. Gradually methanogenic activity increases and some cellulose and hemicellulose are decomposed. The onset of the third phase occurs when methane

production rapidly increases. During phase 3, methane production reaches its maximum. The pH increases and COD decreases as carboxylic acids are converted to methane. The final phase is a deceleration of methane production. During this final stage of decomposition, the rate of hydrolysis of cellulose and hemicellulose controls the production of methane.

In this study, rapid onset of methane production was desired. To accomplish this, reactors were seeded with methanogenic leachate, operated with leachate neutralization and recycle, and incubated at 37°C. The effect was to minimize the length of the acid accumulation phase.

The waste paper reactor performance is summarized in Figure 52. The paper waste reactors had an initial acid accumulation phase of about 2 weeks before methane production increased. No COD data is available until day 30, but the initial decrease in pH was likely accompanied by a COD maximum during the first 2 weeks. At approximately day 50 a second, brief, period of acid accumulation may have occurred, based on the observed pH decrease. This behavior may be due, in part, to variability in the rate of hydrolysis of the different types of waste paper. Between days 65 and 320, methane production slowly decreased, as did leachate COD. An increase in COD was observed in the leachate at the end of the experiment. This increase was not expected, and may appear exaggerated due to the low variability and frequency of the COD measurements. After day 20, when acid accumulation no longer occurred, carboxylic acids were consumed as quickly as produced and the COD variability may simply be random fluctuation above and below a baseline level. The sustained, moderate level of

methane production suggests that cellulose and hemicellulose hydrolysis occur gradually during paper decomposition.

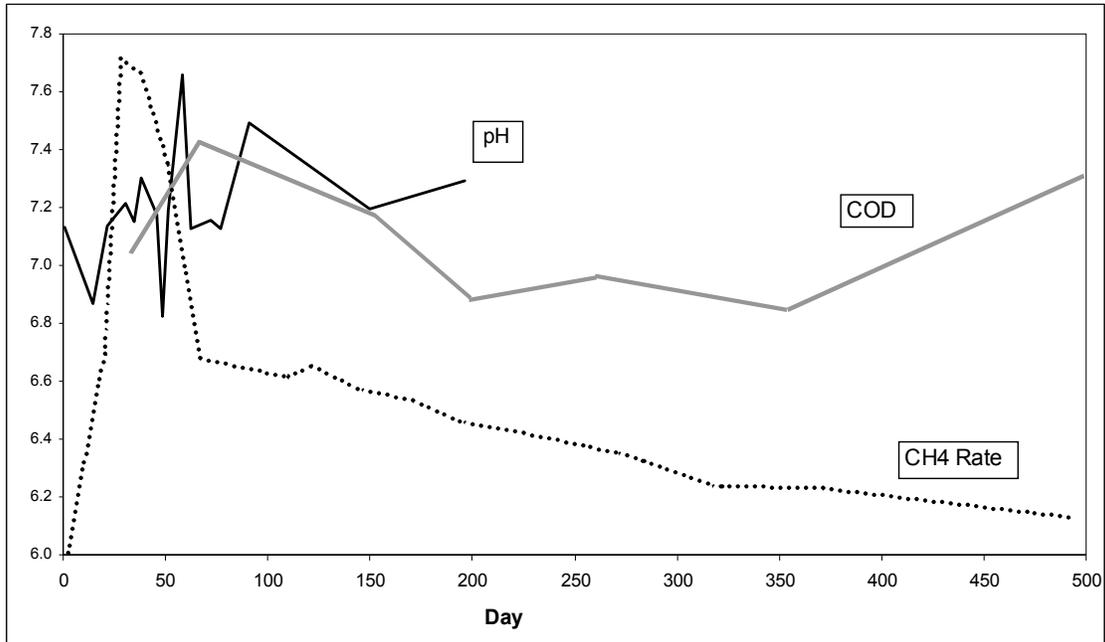


Figure 52. Average pH, COD and Methane Rates for Waste Paper. **Note:** the y-axis is scaled and labeled for pH, the COD and CH<sub>4</sub> curves are only intended to show increasing or decreasing trends.

Methane yields and solids loss data are compared to values reported by Eleazer et al. (1997) in Table 27. A weighted average of Eleazer's data was calculated according to the composition of the mixed paper (Table 1) for comparison. The weighted average methane yield was 145 mL/dry gm, which is close to the yields observed for the paper mixture in this experiment—104-120 mL/dry gm. Solids loss data is similar as well. The weighted average MC (mass of cellulose out divided by mass of cellulose in) from Eleazer et al. is 0.37, which is within the range observed for the mixed paper—0.37 to

0.48. The weighted average of MH (mass of hemicellulose out divided by mass of hemicellulose in) values reported by Eleazer et al. was 0.35, which is also close to the range of the MH for the paper mixture—0.38 to 0.56. The lignin recovery is one area of discrepancy. The ML values greater than 1 observed for the mixed paper treatment suggest an error. Either an analytical error, or a weighing error associated with the mass of refuse added to or removed from each reactor could be responsible for inaccurate lignin recoveries. Since weighing the refuse is a relatively simple procedure, it seems likely that the problem is analytical. Furthermore, it has previously been shown that the testing method used can show variability in lignin concentrations during decomposition even if the lignin is not degraded (Iiyama et al., 1994).

Table 27. Comparison of Decomposition Data for Mixed Paper Reactors to Previous Paper Decomposition Data

Treatment	Yield (mL of CH <sub>4</sub> /dry gm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	MC <sup>a</sup>	MH <sup>a</sup>	ML <sup>a</sup>
P1	117	58.7	13.4	7.4	0.37	0.38	1.45
P2	120	58.7	13.4	7.4	0.46	0.56	2.00
P3	104	58.7	13.4	7.4	0.48	0.50	1.93
<b>Eleazer et al. (1997)</b>							
coated paper	84	42.3	9.4	15.0	0.54	0.58	1.03
old newsprint	74	48.5	9.0	23.9	0.73	0.46	0.99
old corrugated containers	152	57.3	9.9	20.8	0.36	0.38	0.93
office paper	217	87.4	8.4	2.3	0.02	0.09	0.95
<b>weighted avg<sup>b</sup></b>	<b>145</b>	<b>61.4</b>	<b>9.3</b>	<b>15.9</b>	<b>0.37</b>	<b>0.35</b>	<b>0.96</b>

- a) The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- b) Eleazer's data weighted according to the paper mixture used for P1-P3 (7% coated paper, 20% ONP, 42% OCC, 15% OFF, and 16% 3<sup>rd</sup> class mail, which was assumed to be 2/3 OFF and 1/3 coated paper)

Yard waste decomposition data are summarized in Figure 53. The behavior of the yard waste reactors concurs with refuse decomposition theory. A short acid accumulation phase was exhibited for the first 3 weeks. During this time methane production was inhibited and pH decreased to about 6.6. As soon as the pH was neutralized, methane production accelerated rapidly and COD was at its peak. As the COD began to decline so did methane production. During the decelerated methane production phase the pH continued to increase. Increase in pH to between 7.5 and 8.0 has been observed in previous research by Barlaz et al. (1999), and has not been found to inhibit methanogenesis.

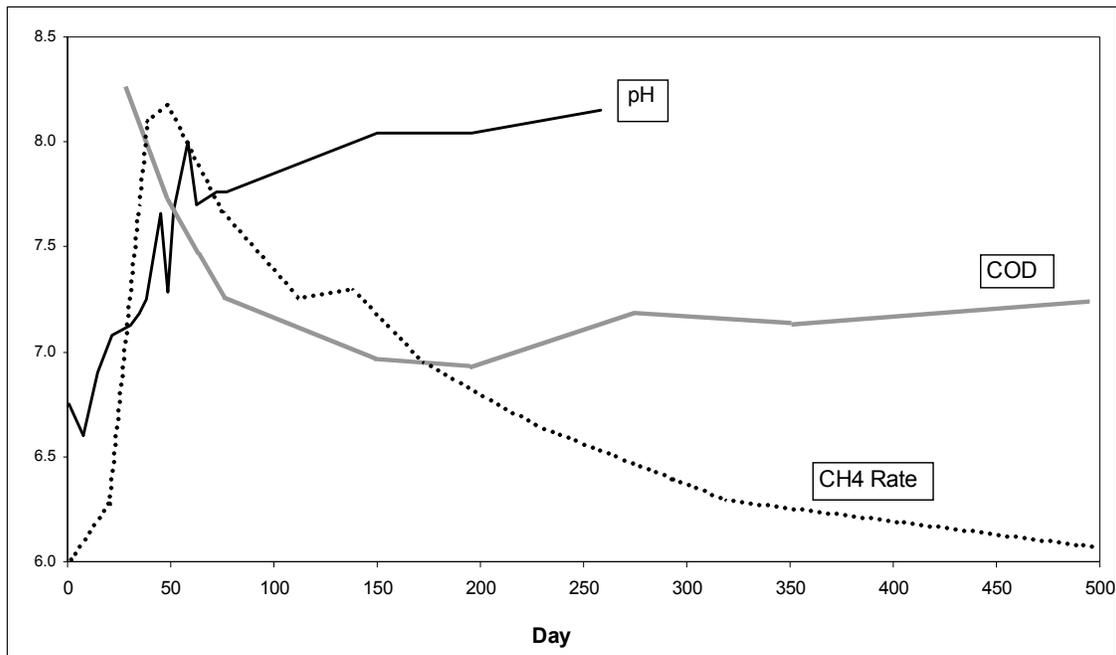


Figure 53. Average pH, COD and Methane Rate for Yard Waste. **Note:** the y-axis is scaled and labeled for pH, the COD and CH<sub>4</sub> curves are only intended to show increasing or decreasing trends.

Eleazer et al. (1997) studied decomposition of individual yard waste components—grass, leaves and branches. The yard waste decomposition data is compared to Eleazer's data in Table 28. A weighted average methane yield (based on a yard waste mixture of 50% grass and 25% each of leaves and branches) from all of the components studied by Eleazer is 92 mL/dry gm, which is considerably lower than the methane yield measured here. The cellulose decomposition was similar for the yard waste mixture and the weighted average of Eleazer's data—61% vs. 67%. The hemicellulose decomposition observed by Eleazer, however, was much lower—47% (weighted average) vs. 81% in this study. Similar to the mixed paper waste reactors, the yard waste mixture showed lignin recoveries greater than 1. Again, the likely explanation is analytical variability.

Table 28. Comparison of Decomposition Data for Yard Waste Reactors to Previous Yard Waste Decomposition Data

Treatment	Yield (mL of CH <sub>4</sub> /dry gm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	MC <sup>a</sup>	MH <sup>a</sup>	ML <sup>a</sup>
Y1	184	23.5	11.4	24.2	0.38	0.20	1.30
Y2	128	23.5	11.4	24.2	0.40	0.18	1.10
<b>Eleazer et al. (1997)</b>							
grass	144	26.5	10.2	28.4	0.19	0.42	0.78
grass-2	128	25.6	14.8	21.6	nm <sup>c</sup>	nm	nm
leaves	31	15.3	10.5	43.8	0.43	0.68	0.9
branches	63	35.4	18.4	32.6	0.52	0.59	0.93
<b>weighted avg<sup>b</sup></b>	<b>91.5</b>	<b>25.7</b>	<b>13.5</b>	<b>31.6</b>	<b>0.33</b>	<b>0.53</b>	<b>0.85</b>

- a) The ratio of the cellulose (MC), hemicellulose (MH) or lignin (ML) recovered from a reactor divided by the mass added originally
- b) Eleazer's data weighted according to the yard waste mixture used for Y1-Y2 (50% grass, 25% leaves and 25% branches)
- c) Not measured

The behavior of the food waste reactors is summarized in Figure 54. Trends in the food waste reactors must be interpreted with caution given the semi-continuous nature of fresh substrate addition. Acid accumulation occurred for about 15 days. During this phase the pH was actively neutralized. On day 30 the COD was at its peak, the pH was about 7.2 and methane production was accelerating. Maximum methane production occurred on approximately day 50, and thereafter declined as the COD declined. A pH decrease occurred on about day 50, followed by a spike in methane production on day 60. The pH drop suggests that a food addition resulted in a particularly high increase of carboxylic acids. These acids were then consumed, producing the methane peak at day 60. According to this theory, a spike in COD should also occur at around day 50, but this

was not observed. After day 60, methane production declined, pH gradually increased and COD remained constant.

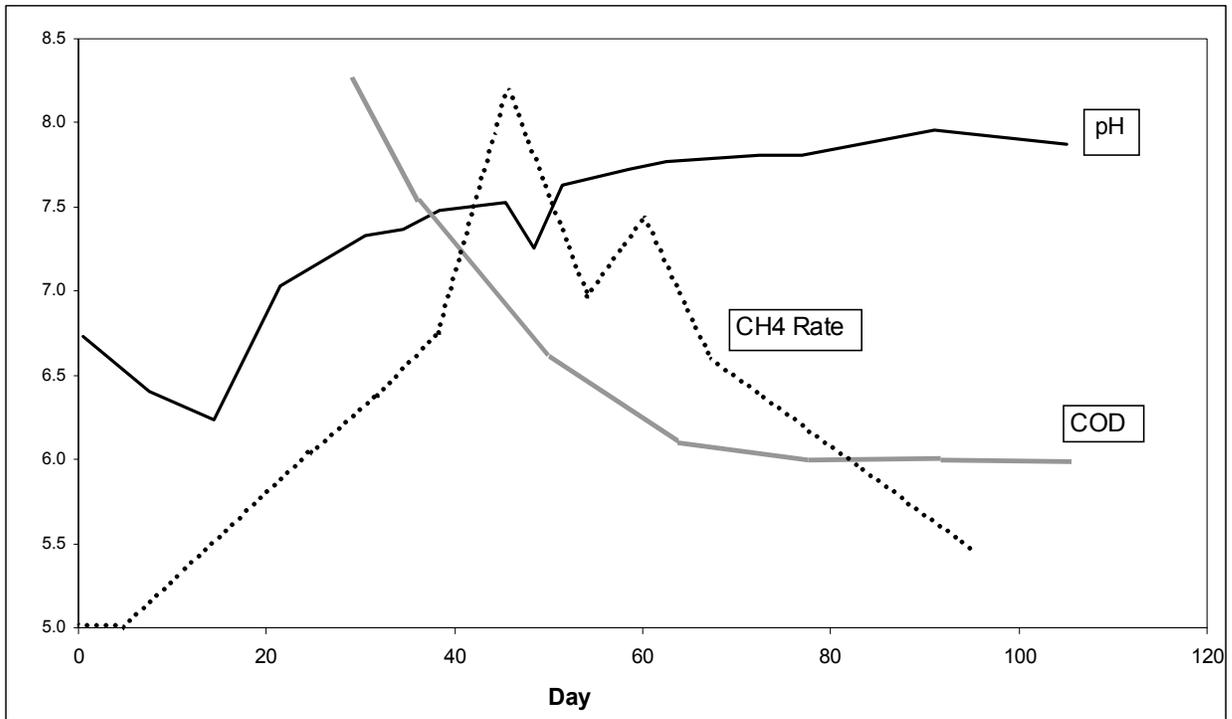


Figure 54. Average pH, COD and Methane Production Rate for Food Waste. **Note:** the y-axis is scaled and labeled for pH, the COD and CH<sub>4</sub> curves are only intended to show increasing or decreasing trends.

No solids loss data is available from the food waste reactors for comparison to the results of food waste decomposition found by Eleazer et al. However, the initial compositions and methane yields are compared in Table 29. The methane yield reported by Eleazer was about twice as high as those from reactors F1-F3. The composition of the food may partially explain this result. The food used by Eleazer had a considerably

higher percentage of cellulose—55 vs. 41%, and slightly higher hemicellulose—7.2 vs. 6.1%. The theoretical methane yield from cellulose is approximately 415 mL/gm, thus an additional 15% cellulose could result in an additional 62 mL of methane per dry gm. However, food is an extremely variable type of refuse, and the bioavailability of the cellulose and hemicellulose can be very different from one type of food waste to another.

Table 29. Comparison of Food Waste Composition and Methane Yields to Previous Food Waste Research

Treatment	Yield (mL CH <sub>4</sub> /dry gm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
F1	161	40.9	6.1	7.4
F2	147	40.9	6.1	7.4
F3	150	40.9	6.1	7.4
<u>Eleazer et al. (1997)</u>				
food	301	55.4	7.2	11.4

The performance of the MSW reactors is summarized in Figure 55. The data match the theory for refuse decomposition. The pH was quickly brought to neutral, reducing the acid phase of decomposition. As a result, methane production was initiated rapidly. Maximum methane production was associated with high leachate COD and neutral pH. Methane production decelerated as the COD also decreased. As methane production decreased, the pH continued to increase to above 8. The increase in pH was not likely responsible for any inhibition of methane production (Eleazer et al., 1997).

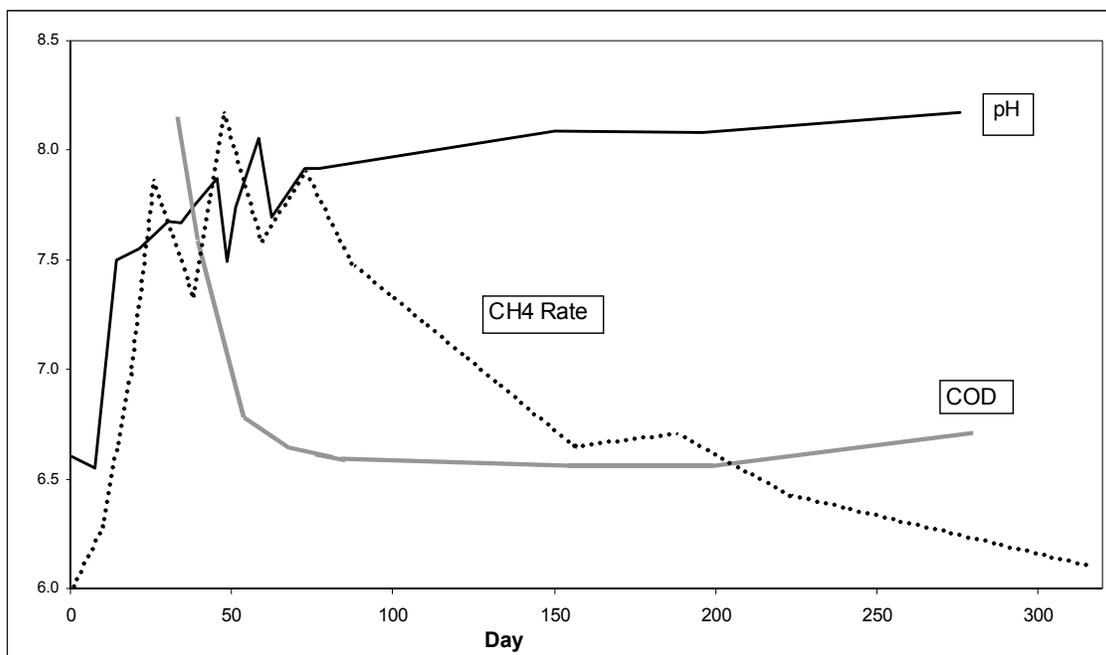


Figure 55. Average pH, COD and Methane Production Rate for MSW. **Note:** the y-axis is scaled and labeled for pH, the COD and CH<sub>4</sub> curves are only intended to show increasing or decreasing trends.

Decomposition data for the MSW + HHW reactors are summarized in Figure 56. These reactors exhibited classic anaerobic decomposition. Methane production was inhibited during the first 50 days, as acids accumulated and the pH remained below 7. During this time the leachate COD was at its maximum. After day 50, the accelerated methane production phase began. The pH increased as the COD sharply declined while methane was rapidly being produced. After peaking, the methane production rate decreased asymptotically as carboxylic acids became limiting, as seen by the low COD at this point.

The early inhibition of methane production may be due to the HHW spike. Approximately 188 mg of toluene, 850 mg of acetone and 150 mg of methylene chloride were spiked (see section 4.7). Each reactor received about 1 liter of leachate seed, and an additional 200 mL of water is estimated to have been present based on the initial moisture content of the refuse. Therefore, the initial concentrations of the spiked compounds were 157, 708 and 125 mg/L, for toluene, acetone and methylene chloride, respectively. These concentrations may have been toxic to acid consuming microorganisms. Data reported by Blum and Speece (1991) suggest that the methylene chloride concentration present in the reactors could be toxic to microorganisms.

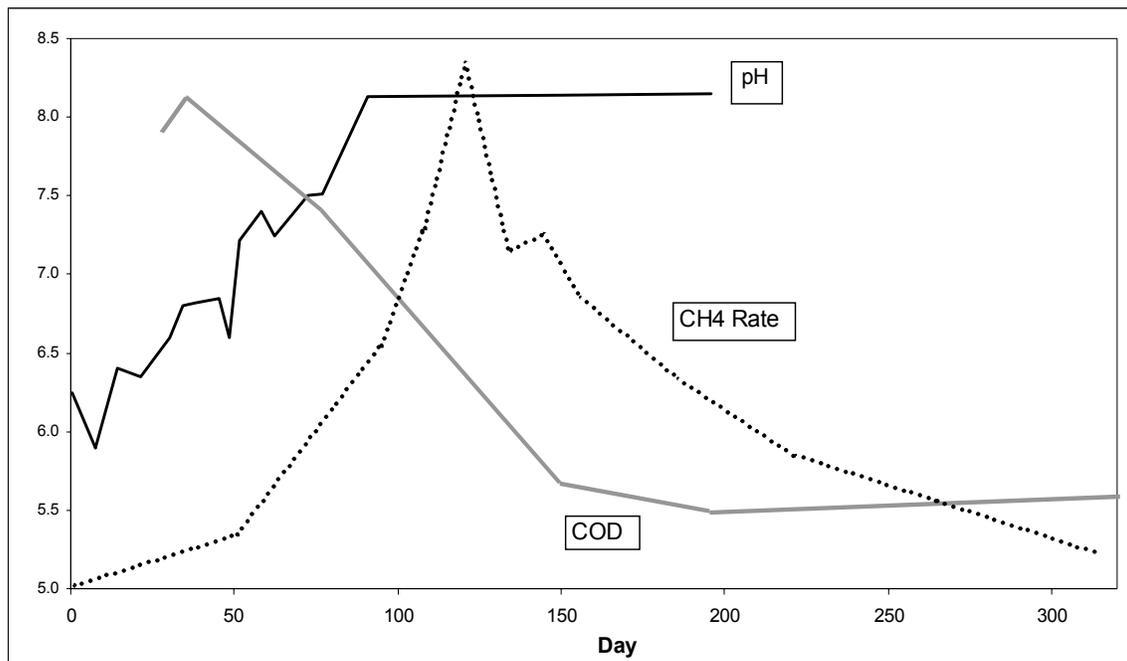


Figure 56. Average pH, COD and Methane Production Rate for MSW + HHW. **Note:** the y-axis is scaled and labeled for pH, the COD and CH<sub>4</sub> curves are only intended to show increasing or decreasing trends.

The decomposition data for the MSW and the MSW + HHW reactors, along with MSW data from previous research, are summarized in Table 30. The MSW from Eleazer et al's study was about 29% cellulose. This percentage is close to the MSW used in reactors M1 and M2, and likewise the methane yields are similar—92 mL/dry gm for Eleazer and 97-98 mL/dry gm for reactors M1-M2. The MSW used in the HHW treatment was much higher in cellulose—55%, and these reactors yielded more methane as well—108 to 120 mL/dry gm. The range of hemicellulose percentages is fairly narrow—7.7 to 9.0%. This data is consistent with the idea that cellulose and hemicellulose account for over 90% of the methane potential of refuse.

The solids loss data differ in that Eleazer et al. observed more decomposition of hemicellulose—78% vs. 54-66%, and less loss of lignin. Lignin is essentially recalcitrant under anaerobic conditions, and recovery close to 100% is expected. As presented in the results, the lignin analysis may not be reliable since recovery ratios greater than 1.0 were observed. The low lignin recoveries here further indicate that the data is unreliable, and suggest a random variation rather than a systematic bias since both excessively high and low values have been reported.

Table 30. Comparison of Decomposition Data for MSW and MSW + HHW to Previous MSW Decomposition Data

Treatment	Yield (mL CH <sub>4</sub> /dry gm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	MC <sup>a</sup>	MH <sup>a</sup>	ML <sup>a</sup>
M1	97	33.5	8.7	23.4	0.34	0.42	0.62
M2	98	33.5	8.7	23.4	0.27	0.34	0.58
MH1	120	55.0	7.7	20.6	0.22	0.46	0.76
MH2	108	55.0	7.7	20.6	0.22	0.42	0.87
<u>Eleazer et al. (1997)</u>							
MSW	92	28.8	9	23.1	0.25	0.22	0.95

- a) The ratio of the mass of cellulose (MC), hemicellulose (MH), or lignin (ML) recovered from a reactor divided by the mass added originally

The aerobic decomposition of refuse does not occur in phases analogous to anaerobic decomposition. Overall, decomposition proceeds much faster under aerobic conditions and there is no lag period. Carbon dioxide production was at its peak in the first few days, and decreased asymptotically thereafter as the most bioavailable compounds were consumed quickly at first and more recalcitrant compounds were later slowly degraded.

For aerobic decomposition, the two most important factors, aside from oxygen supply, are temperature and moisture. Aeration can lead to an increase in temperature as energy is released during the decomposition process. Elevated temperature (>60°C) can be deadly for aerobic bacteria. Aeration can also cause the refuse to dry out, making it unviable for the aerobic bacteria. Temperature and moisture were therefore monitored in the aerobic reactors. To ensure that the refuse was moist, DI water was added to reactors

anytime less than 500 mL of leachate could be generated. The temperature remained between 31 and 44°C, which is within an acceptable range for mesophilic bacteria.

Decomposition under nitrate-reducing conditions is similar to aerobic decomposition in that there is no lag period for nitrogen production. Nitrogen production peaked during the first few days as the most easily degraded compounds were consumed. Unlike in the aerobic treatment, however, supply of the electron acceptor—nitrate—was challenging, and likely became a limiting factor for nitrogen production. The nitrate concentrations in reactors MN1 and MN2—presented in the Results section (Figures 42 and 43) suggest poor mixing of the nitrate (see section 3.8).

Another potential problem that was managed successfully was salt toxicity due to addition of  $\text{KNO}_3$  and  $\text{Mg}(\text{NO}_3)_2$ . To prevent excessive  $\text{K}^+$  and  $\text{Mg}^{+2}$  salts from accumulating, leachate was removed and replaced with 500 mL of DI water when  $\text{K}^+$  concentrations of between 5,000 and 8,000 mg/L and  $\text{Mg}^{+2}$  concentrations of between 1,000 and 2,000 mg/L were reached. These concentrations were reported by Kugleman (1971) to be potentially toxic.

## **4.2 Ultimate NMOC Yields from Waste Components**

The ultimate NMOC yields measured from the individual waste components are presented in Figure 57. The effect of different operating conditions on ultimate NMOC yields is addressed in section 4.4.

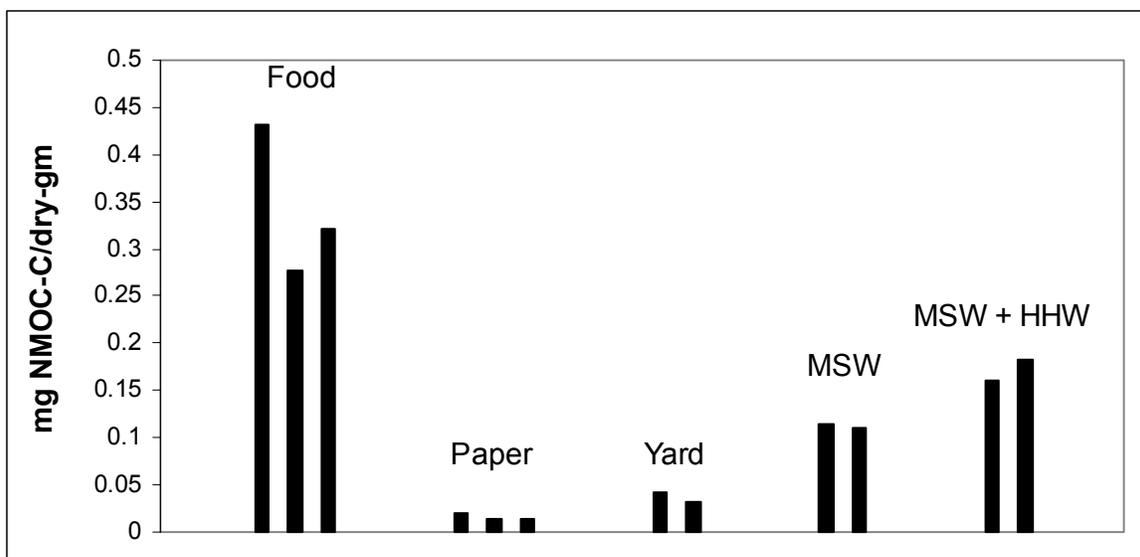


Figure 57. Ultimate NMOC Yields from Individual Waste Components

As expected, the NMOC yield from paper waste was the lowest. The most likely explanation for this is that there is not a wide range of organic compounds present in paper waste. The NMOC yields from yard waste were also relatively low. In contrast, food waste, which is composed of a wide variety of organic compounds, had the highest NMOC yield. MSW contains both inert materials with little or no potential to release organic compounds, such as metals and glass, and materials rich in volatile organics such as food waste and other degradable organics. It is therefore expected that MSW, being a mixture, would emit an intermediate level of NMOCs. The higher release of organics from the MSW + HHW reactors is consistent with the fact that these reactors were intentionally spiked with volatile organic compounds. Further analysis of the significance of HHW is presented in section 4.7.

### 4.3 Relationship Between Gas Production and NMOC Release

The relationship between gas production and NMOC release is not well understood. One mechanism for the emission of organic compounds is volatilization of organics present in the refuse. If this were the dominant mechanism of NMOC release, the majority of the NMOC yield would be expected to occur shortly after the initiation of gas production. Alternatively, the process of release may be associated with microbial decomposition of the waste, in which case NMOCs would be released more gradually as the substrate is degraded. Decomposition could affect NMOC release by freeing volatile organic compounds trapped or bound in the refuse. Another possibility is that the decomposition process could lead to the formation of more volatile compounds from less volatile ones. During anaerobic decomposition, for example, sugars are converted to semi-volatile carboxylic acids by bacteria.

Several comparisons were made between methane and NMOC yields for paper waste, yard waste, MSW and MSW + HHW. The results of these comparisons are summarized in Table 31.

Table 31. Comparisons Between Methane and NMOC Yields at Various Times

	After First Two Samples			At 75% of NMOC Yield			At 50% of Days		
	Day	% Methane	% NMOC	Day	% Methane	% NMOC	Day	% Methane	% NMOC
Paper	27	12.1	6.4	112	47	75	248	71	95.7
Yard	28	5.7	15.5	132	51	75	248	79	95.5
MSW	19	5.7	43	64	40	75	159	80	94.5
MSW + HHW	59	8.1	48	142	50	75	159	69	82

Methane yields were calculated for each reactor for the time at which the reactor had yielded 75% of NMOCs. It was expected that the methane yields would be lower than 75% because NMOC release appears to be characterized by an initial burst. Furthermore, it was expected that the highest methane yields would be seen in the paper and yard wastes since they are not composed of many volatile organic compounds, and therefore NMOC release from these components may depend more on the decomposition process. On the other hand, since MSW is more likely to contain many organics that could quickly evaporate, the MSW and MSW + HHW were expected to have the lowest methane yields at the point of 75% NMOC release. The results, however, were conflicting. For the mixed paper (Figure 58) and yard waste (Figure 59), by the time 75% of the NMOCs were emitted about 50% of the methane had also been produced. For the MSW (Figure 60), at the time that 75% of the NMOC release had occurred, only 40% of the methane had been produced. These results are expected. However, for the MSW + HHW, about 50% of the methane had been produced at the time that 75% of the NMOC release had occurred (Figure 61). The combination of added volatile organics and an early inhibition of gas production would be expected to result in most of the organics being emitted before the majority of gas was produced. Instead, NMOC emissions were more gradual compared to the MSW reactors, suggesting that decomposition may play a significant role in NMOC release, even when a lot volatile organic compounds are inherently present.

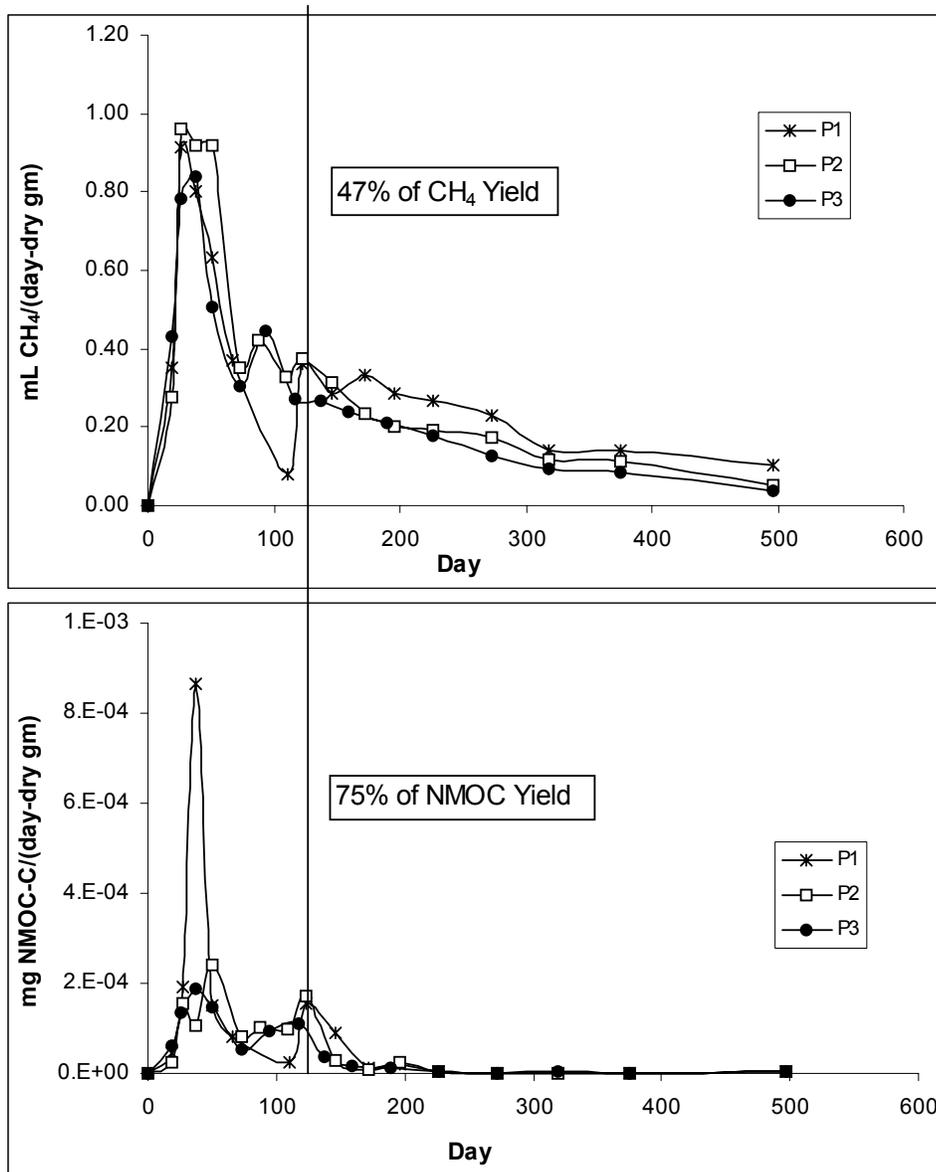


Figure 58. NMOC and CH<sub>4</sub> Production Rates for Mixed Paper  
 Note: The vertical line represents the time of 75% NMOC yield

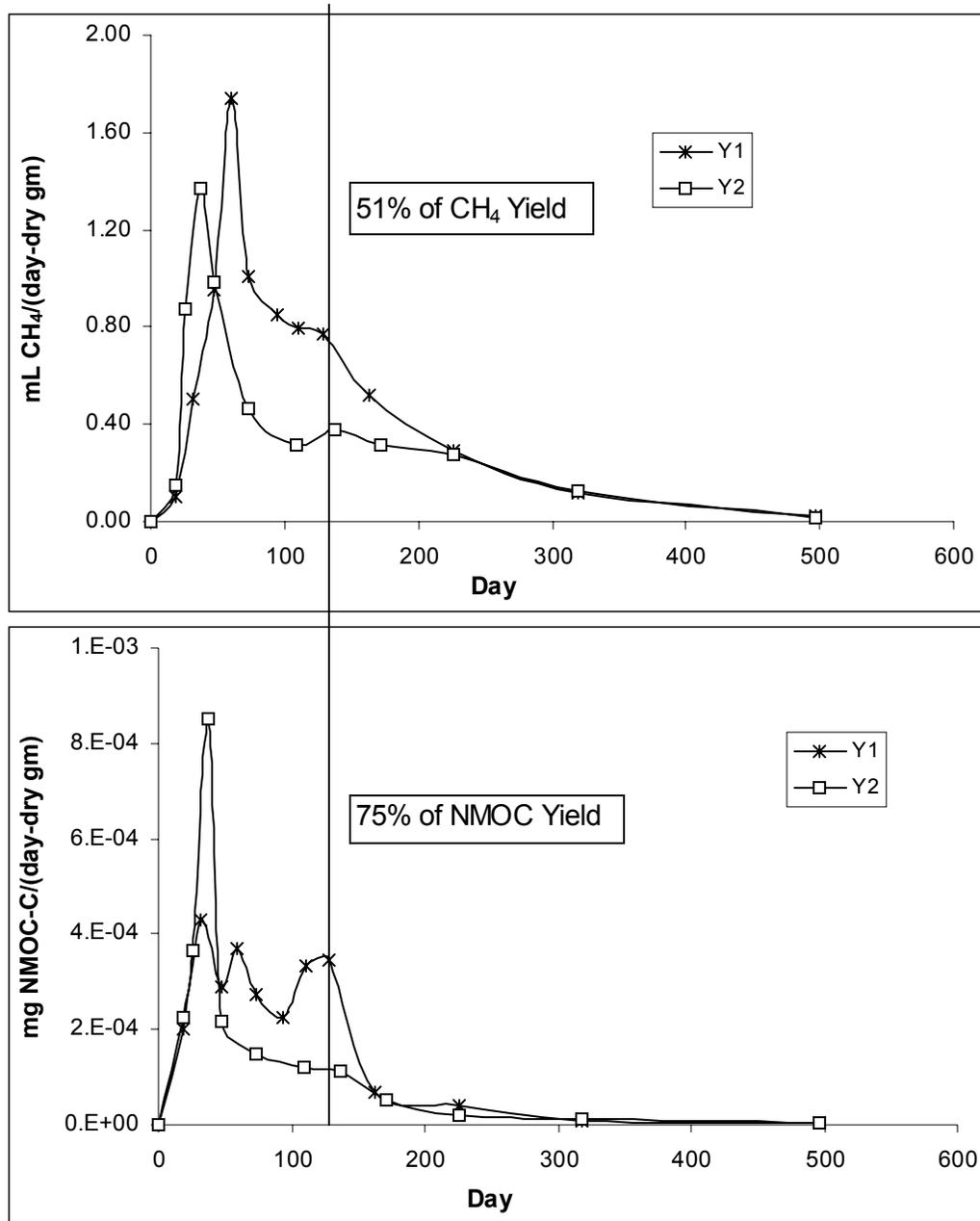


Figure 59. NMOC and Methane Production Rates for Yard Waste  
 Note: The vertical line represents the time of 75% NMOC yield

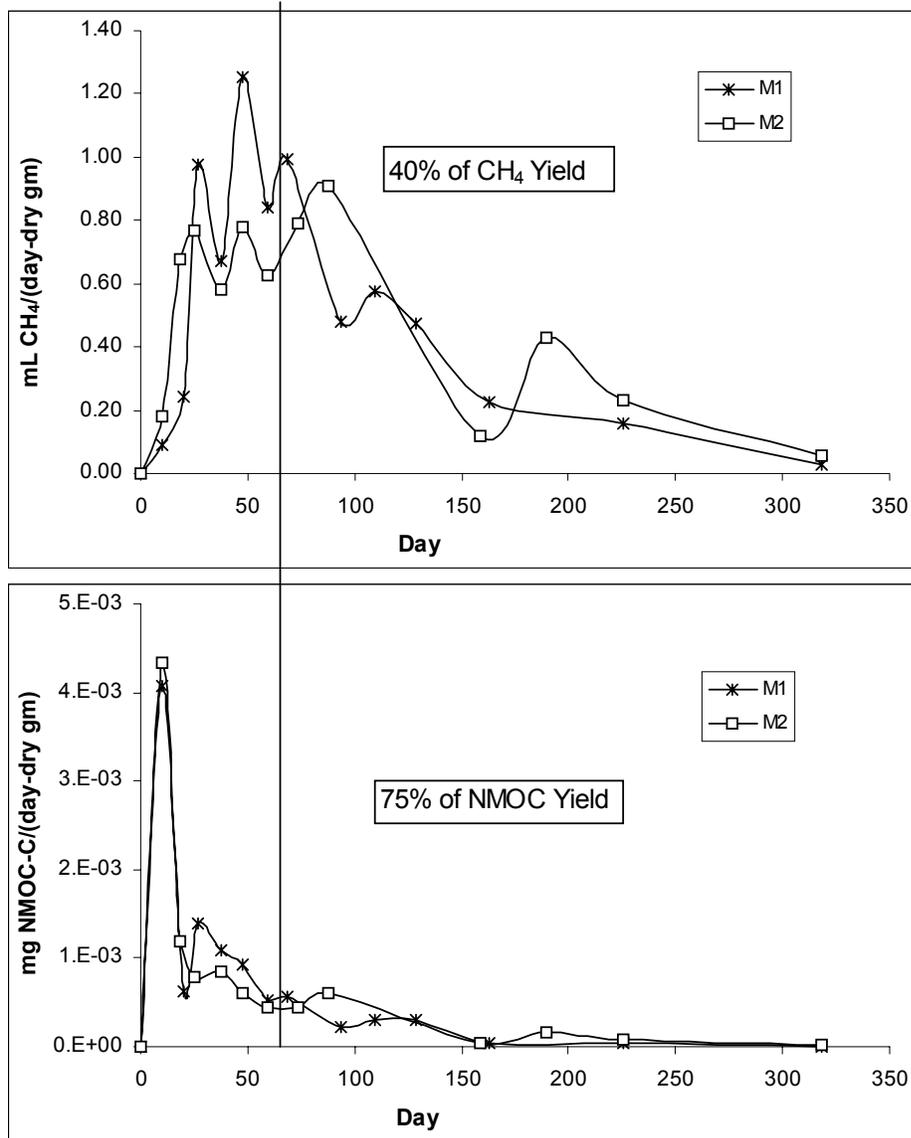


Figure 60. NMOC and Methane Production Rates for MSW

Note: The vertical line represents the time of 75% NMOC yield

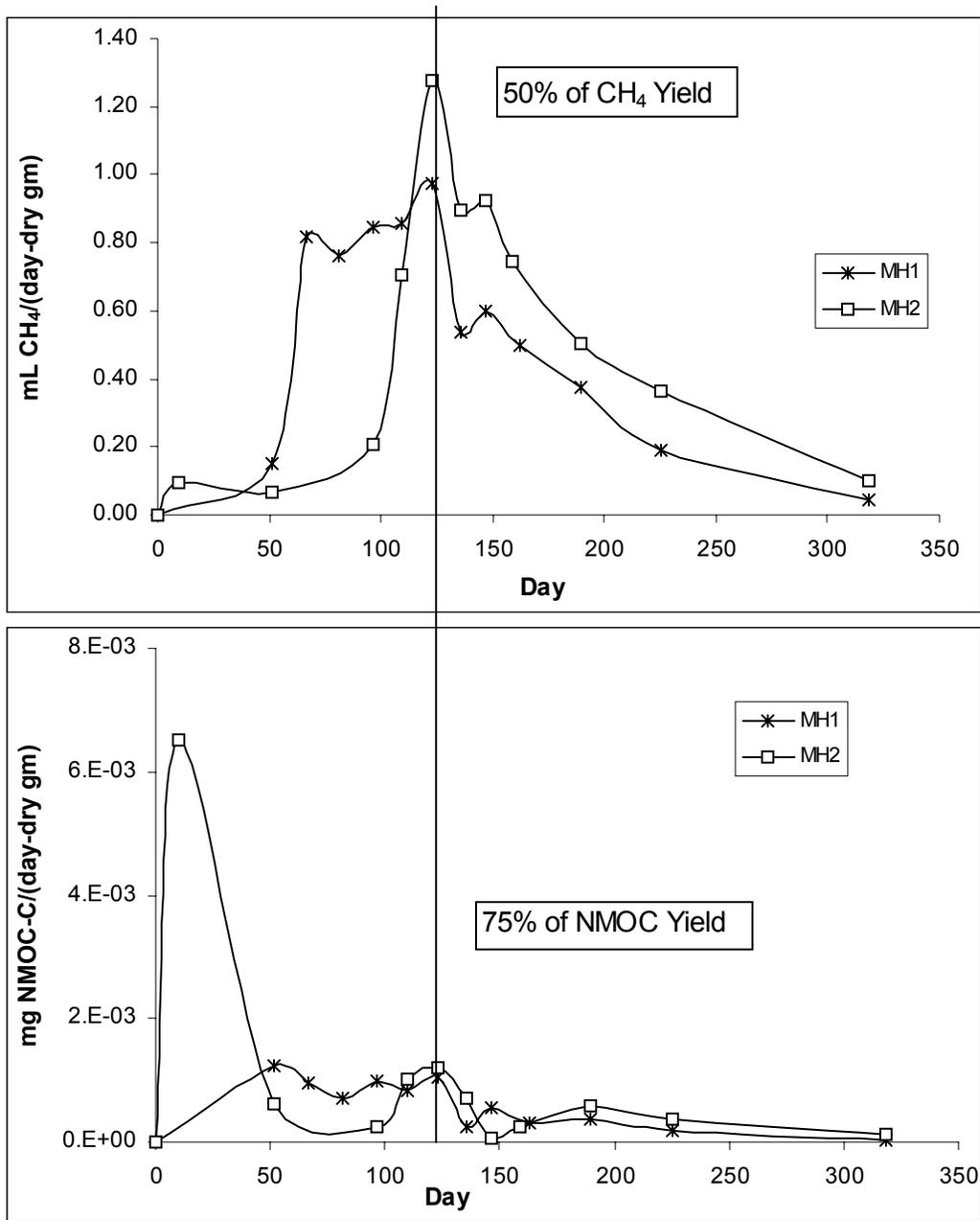


Figure 61. NMOC and Methane Production Rates for MSW + HHW

Note: The vertical line represents the time of 75% NMOC yield

To confirm the observation that NMOC release occurs with an initial burst, methane and NMOC yields were compared after the first two samples (Figure 62). While the time period varies for the components, the gas production is approximately equal since samples were analyzed when the bags filled with gas. As expected the MSW and MSW + HHW reactors showed an initial burst of NMOC production, yielding 43 and 48%, respectively, of the total NMOCs. The percent methane produced by the MSW and MSW + HHW in the first two samplings was 5.7 and 8.1, respectively. For the paper waste, the NMOC and methane yields were 6.4 and 12.1%, respectively; and for the yard waste they were 15.5 and 5.7%, respectively. This data suggests that volatile organic compounds present in the refuse evaporate quickly. Such an occurrence is significant for MSW and MSW + HHW, which have a lot of volatile organics initially present, but not for paper or yard waste.

The same comparison was made for the midway point of operation (by time) for each type of reactor (Figure 63). This figure indicates that by the midway point of operation, the percent of total NMOCs produced from the paper, yard waste, MSW and MSW + HHW were 95.7, 95.5, 94.5 and 82 % respectively. The MSW and MSW + HHW, which showed the initial NMOC burst, were surprisingly lower than the paper and yard waste. This difference was most significant for the MSW + HHW reactors, in which 18% of the total NMOC yield was not yet released.

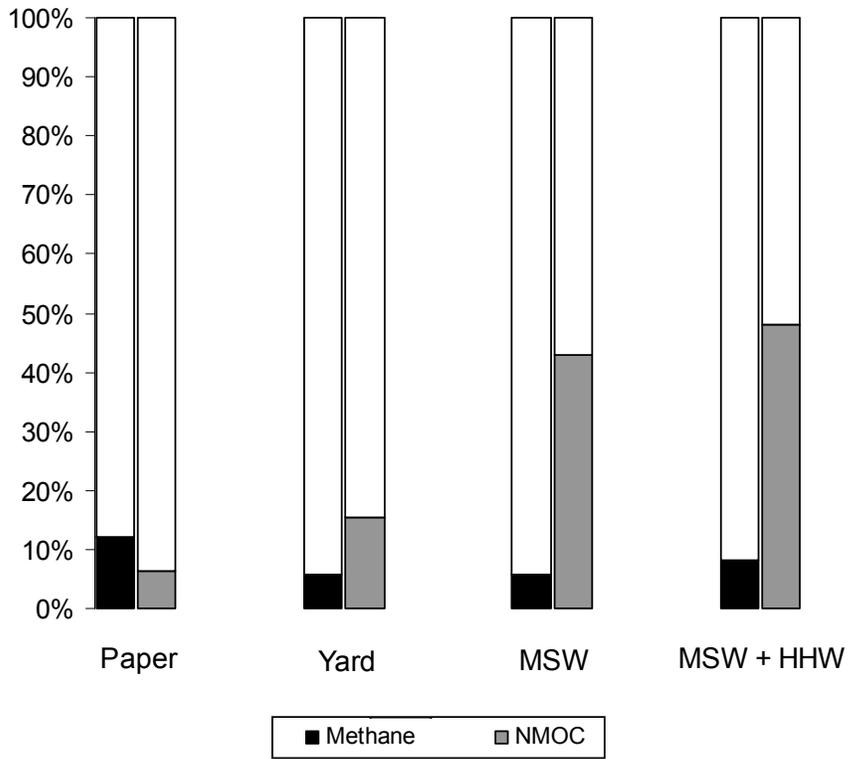


Figure 62. Percentages of NMOC and Methane Released After First Two Samples

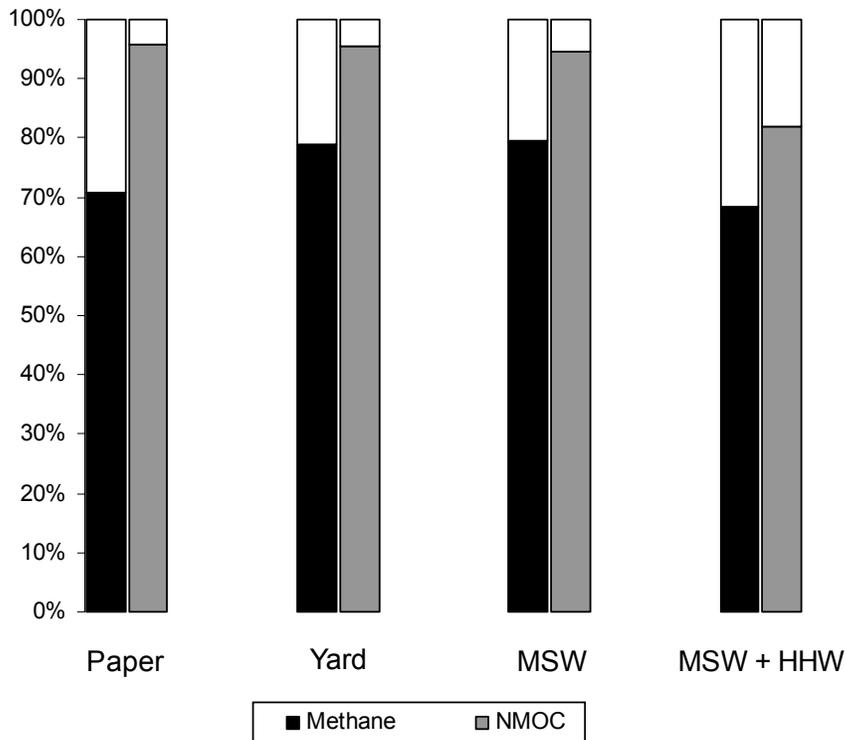
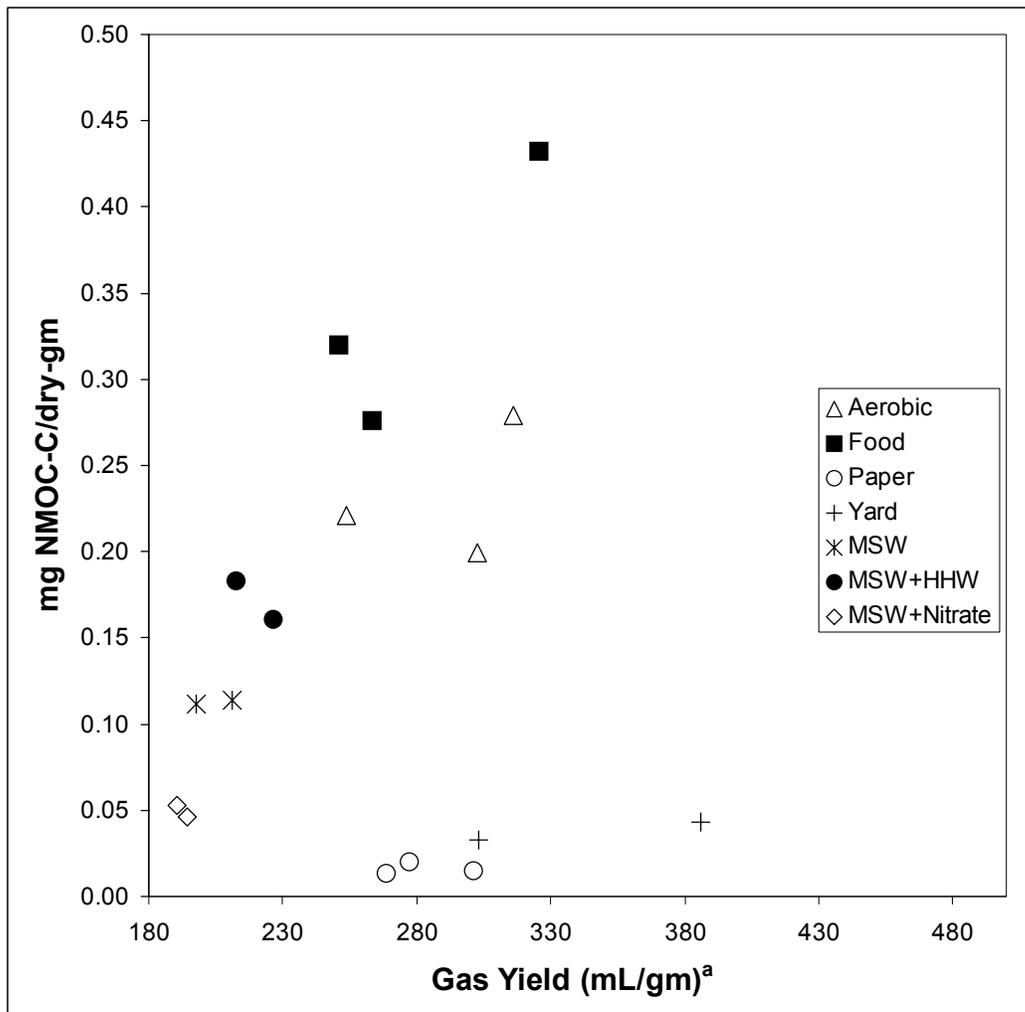


Figure 63. Percentages of NMOC and Methane Released At Midway Point of Operation

Generally, high rates of NMOC release are somewhat correlated with high gas production (Figures 58 through 61). A causative relationship cannot yet be determined, however. It is possible that the timing of high gas production simply coincidentally corresponds to the timing of high NMOC volatilization. Alternatively, the release of NMOCs could be controlled by the decomposition process. The data suggests that microbial decomposition of refuse partly contributes to NMOC release, while some organic compounds are emitted independently of this process. Figure 62 illustrates an initial burst of NMOCs emitted prior to extensive decomposition, while Figure 63 shows that at the midway point of the experimental duration between 5 and 20% of the NMOCs remained to be gradually emitted as the decomposition process proceeded.

Total gas production also correlates positively with NMOC yield, as shown in Figure 64. Two exceptions to this trend are the paper and yard wastes, which yielded relatively large quantities of gas compared to NMOCs. This result suggests that decomposition intermediates are not a major source of NMOCs.

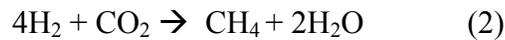


a) For the anaerobic reactors gas yield includes CH<sub>4</sub> and CO<sub>2</sub>, for the aerobic reactors the yield is CO<sub>2</sub> and for the nitrate-reducing reactors the yield includes N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>.

Figure 64. Relationship Between Gas and NMOC Yields

#### 4.4 NMOC Release Under Different Operating Conditions

Three different conditions for decomposition were studied, using MSW as the waste source in all cases. One set of reactors was operated anaerobically as is typical of actual landfills, where refuse is buried under soil and other layers of tightly compacted refuse. Under anaerobic conditions a sequence of biochemical reactions take place that ultimately result in the production of a 50/50 mixture of CO<sub>2</sub> and CH<sub>4</sub>. The final step in this sequence is carried out by a group of microorganisms known as methanogens, and involves a redox reaction in which CO<sub>2</sub> is reduced to CH<sub>4</sub>, as shown in equation 2:



Another, less dominant mechanism of methane formation occurs through the splitting of acetic acid molecules, as shown in Equation 3.

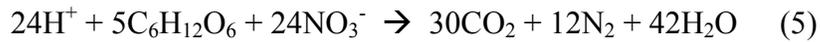


Another set of reactors was operated aerobically. During aerobic decomposition carbon is oxidized and O<sub>2</sub> is reduced as CO<sub>2</sub> gas is produced. An example of a reaction that may be mediated by aerobic bacteria is the following:



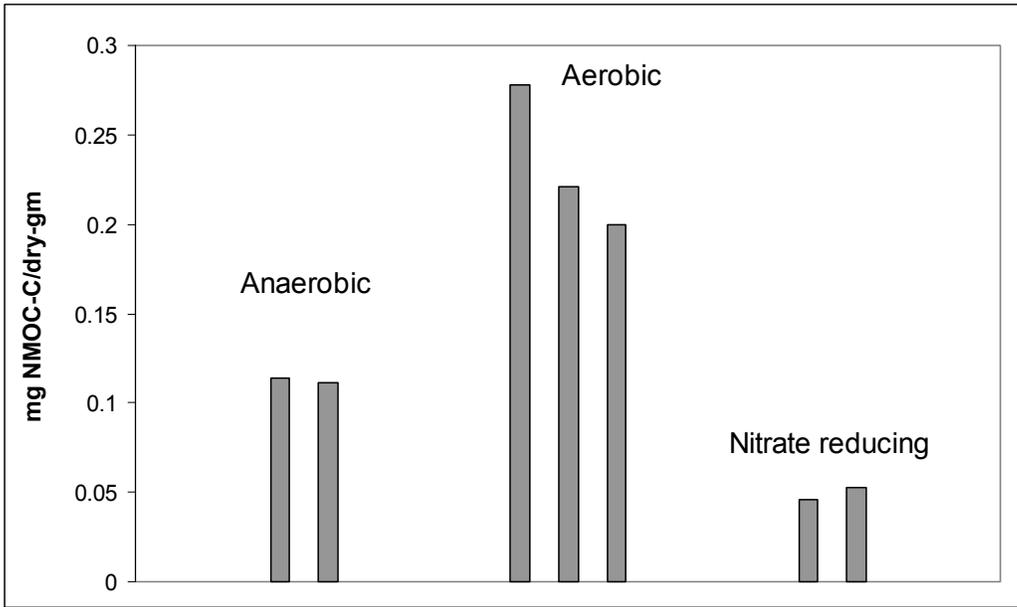
A third set of reactors was operated under nitrate-reducing conditions. In this case, nitrate (NO<sub>3</sub><sup>-</sup>) accepts electrons and is reduced to N<sub>2</sub> gas. For example, in the

absence of oxygen and presence of  $\text{NO}_3^-$ , the glucose in the above reaction would be decomposed as follows:



The total NMOC yields for the three conditions are shown in Figure 65. The aerobic condition yielded the most organic compounds, while anaerobic decomposition resulted in the lowest NMOC release. Emission of organic compounds should decrease as the extent of decomposition of organics increases. Since the decomposition of organic compounds occurs through redox reactions, more decomposition should occur as stronger electron acceptors are used. Table 32 shows the strength of various electron acceptors.

A. NMOC Yields



B. NMOC Yields Normalized for Volume of Gas Flow

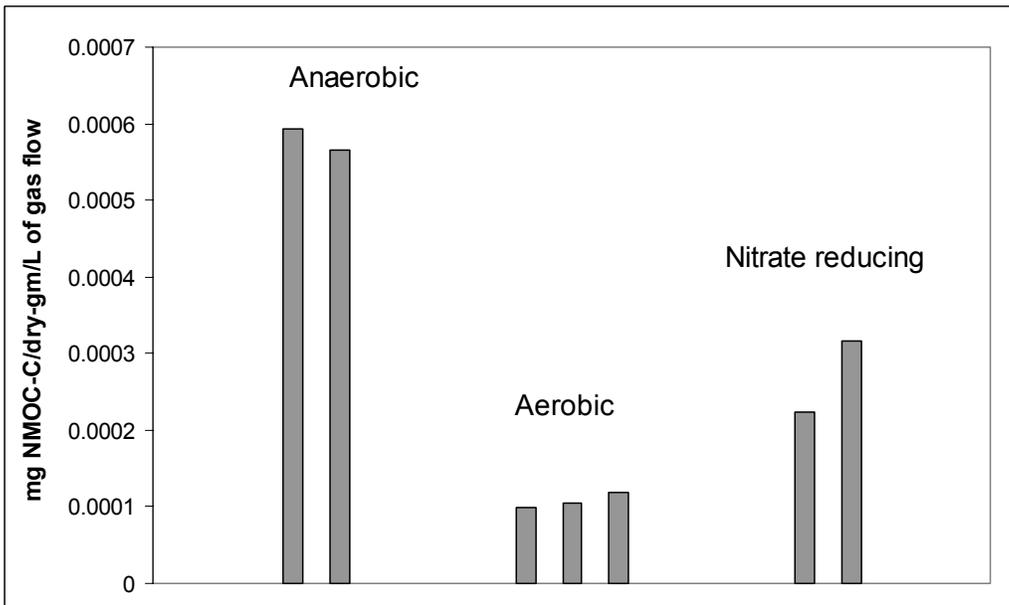


Figure 65. Total NMOC Yields from MSW Under Different Conditions

Table 32. Relative Strength of Electron Acceptors Associated with Treatment Conditions (Bouwer, 1994)

Half Reaction		
<i>Oxidized species</i>	<i>Reduced species</i>	<i>E° (volts)</i>
$O_2 + 4H^+ + 4e^-$	$2H_2O$	0.82
$2NO_3^- + 12H^+ + 10e^-$	$N_2 + 6H_2O$	0.74
$CO_2 + 8H^+ + 8e^-$	$CH_4 + 2H_2O$	-0.24

Based solely on the strength of electron acceptor, the aerobic treatment would be expected to emit the least organics, since oxygen is the strongest electron acceptor and should result in the most decomposition of organic compounds. The anaerobically decomposed refuse would be expected to yield the most organics, since  $CO_2$  is the weakest electron acceptor. The fact that the aerobic treatment produced the most NMOCs is likely due to increased volatilization brought on by the continual flow of air through the system. When the NMOC yields for the three conditions are normalized for gas flow (Figure 65B) the data supports the theory that NMOC decomposition increases as the strength of electron acceptor increases. The role of abiotic air stripping is currently being studied in a follow-up experiment to this research.

The lower NMOC production from the nitrate-reducing reactors, compared to the anaerobic treatment may be explained by the fact that  $NO_3^-$  is a stronger electron acceptor than  $CO_2$ . Another possibility is that volatile carboxylic acids, which are produced during anaerobic decomposition, are a substantial portion of the NMOC yields from the anaerobic systems, but not from the nitrate-reducing ones. However, the available data

on VFA emissions (section 4.5) suggest that VFA compounds are not major contributors to NMOC emissions under nitrate-reducing or anaerobic conditions (Table 20).

## **4.5 Specific Trace Organic Compounds**

### Background

The organic compounds measured in this study can be grouped into 7 categories—alkanes, alkenes, aromatics, alcohols, ketones, terpenes and chlorinated organics. The characteristic chemical structures of each category are illustrated with the examples shown in Figure 66.

Alkanes are hydrocarbons that only have single carbon bonds. This category includes both straight chained hydrocarbons like butane, and cyclic hydrocarbons such as cyclohexane. Alkanes commonly found in landfill gas include pentane, hexane, octane, nonane, decane and undecane (Bjorkqvist et al., 1998; Brooks and Young, 1983; Eklund et al., 1998; Wilkins, 1994; Young and Parker, 1983).

Alkenes contain double bonded carbons. They too, include both straight chained compounds like 1-butene, and cyclic compounds like cyclohexene. Hexene, octane, 2-pentene, nonene, decene and undecene have been detected in landfill gas (Young and Parker, 1983).

Alcohols are distinguished by the presence of an –OH group. Ethanol, 1-propanol and 1-butanol are examples of alcohols that are often found in landfill gas (Allen et al, 1997; Brooks and Young, 1983; Wilkins, 1994; Young and Parker, 1983).

Aromatic compounds have a six-carbon ring. Electrons are shared in a unique way in aromatic compounds. Neither single nor double bonds are formed within the ring, but rather electrons move around the ring continuously. Aromatic compounds emitted from decomposing refuse include benzene, toluene, ethylbenzene and xylenes (Deipser and Stegmann, 1994; Eitzer, 1995; Klafka et al., 1994).

Ketones are characterized by a carbon molecule double bonded to oxygen and a methyl group. Ketones that are often present in landfill gas include acetone, 2-butanone and 2-pentanone (Eitzer, 1995; Eklund et al., 1998; Kim et al., 1995).

Chlorinated organic compounds contain one or more chlorine molecules bonded to carbon. Various chlorinated organic compounds have been detected in landfill gas, including 1,1,1-trichloroethane, dichloromethane, trichloroethene, tetrachloroethene, vinyl chloride, dichlorobenzene and styrene (Deipser and Stegmann, 1994; Kim et al., 1995; Wilkins, 1994; Young and Parker, 1983).

The terpenes, also called mono-terpenes, all contain 10 carbons. The chemical structures of terpenes vary, but often a double ring is formed, like that in camphene (Figure 66). Other terpenes reported to be present in landfill gas include limonene,  $\alpha$ -pinene,  $\beta$ -pinene and  $\gamma$ -terpinene (Allen et al., 1997; Bjorkqvist et al., 1998; Brooks and Young, 1983; Loizidou and Kapetanios, 1992).

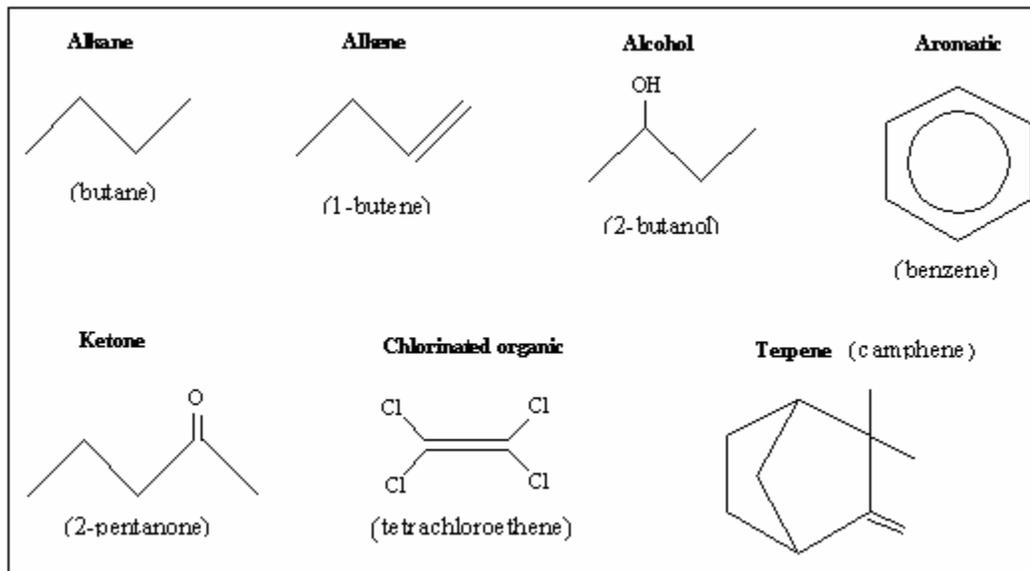


Figure 66. Categories of Organics Released by Decomposing Refuse

Another group of organic compounds that are potentially released from decomposing refuse are the volatile fatty acids (VFAs), also called carboxylic acids. The structure of the simplest carboxylic acid, acetic acid, is shown in Figure 67. VFA compounds are known to be produced as anaerobic decomposition intermediates, but their concentrations in landfill gas are not well documented.

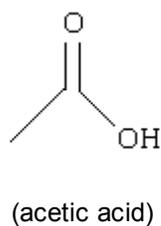


Figure 67. Volatile Fatty Acid Structure

Understanding the sources of the organic compounds that are found in landfill gas remains a challenge. The two sources that probably contribute the most to emissions of organic compounds are household hazardous waste (HHW) products, and vegetative matter. Specific types of compounds originate from each of these sources. Many of the hazardous air pollutants (HAPs) likely come from HHW products in MSW. Although disposal of large amounts of hazardous waste in Subtitle D<sup>3</sup> landfills is not permitted, inevitably some burial of HHW products occurs. Various household products are composed of aromatic and chlorinated organics. For example, paint and paint remover contain toluene and xylenes, gasoline contains benzene and ethylbenzene, and glues contain trichloroethene (Thomas and Barlaz, 1999).

Plants produce VOCs as part of their life process. Annual VOC emissions from land vegetation is estimated to be 1150-1500 Tg<sup>4</sup> (Isidorov and Jdanova, 2002). Although living plants do not contribute to landfill emissions, it should be recognized that plant matter is rich in volatile organic compounds. These compounds, inherently present in the material at the time of burial, could eventually be transported into landfill gas by a number of mechanisms. For example, monoterpenes are produced in specialized plant cells and secreted into storage structures that minimize diffusion (Lerdau et al., 1997). Release of the monoterpenes after plant death could occur if the storage structures are disrupted, which would certainly occur as the material is buried and compacted.

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<sup>3</sup>Subtitle D is a set of federal requirements (Subpart 257 and 258, Title 40, Federal Code of Regulations) for public and private landfills receiving municipal solid waste. It sets out minimum standards for design, operation, location, closure and postclosure. United States Environmental Protection Agency (US EPA) adopted the Subtitle D regulations on October 9, 1991 and most provisions became effective on October 9, 1993.

<sup>4</sup> One Tg = 10<sup>12</sup> grams

Microbial decomposition of the material could also expose reservoirs of VOCs present in the plant material. Isidorov and Jdanova (2002) concluded that microbial decomposition is responsible for monoterpene release from decomposing leaf litter. Drying of plant material has also been suggested as a factor that promotes release of VOCs (De Gouw et al., 1999).

Due to the importance of aroma and flavor in the food industry, many studies have been done to characterize the VOC content in the essential oils of the foods and in the head space above the food. The results of some of these studies are presented in Table 33. The primary types of compounds found in the head space analyses were alcohols, aldehydes and terpenes. The essential oil analyses indicated that citrus peels were highly concentrated with limonene. One study measured a limonene concentration in an orange peel of 2380 mg/kg, while another found limonene to represent as much as 95% of the essential oils in lemon peels (Umano et al., 2002).

In addition to HHW and vegetative matter, hydrolysis of cellulose and hemicellulose under anaerobic conditions could be a significant source of organic compounds. In the early stages of anaerobic decomposition hydrolytic and fermentative bacteria produce short-chain carboxylic acids such as butyric acid and propionic acid, as well as alcohols. These acids and alcohols tend to accumulate during early stages of decomposition before they are converted to acetate and then methane, and they could potentially be contributors to NMOC emissions.

Table 33. Volatile Organic Compounds Identified in Food Sources

	Dekopon peel	Lemon peel	Raspberry	Blackberry	Banana	Celery
<b>Study</b>	Umamo et al., 2002	Lota et al., 2002	Ibanez et al., 1999	Ibanez et al., 1999	Ibanez et al., 1999	Macku and Shibamoto, 1991
<b>Type of analysis</b>	essential oil extraction, GC, GC-MS	essential oil extraction, GC, GC-MS, <sup>13</sup> C NMR	head space gas analysis, HS-PTV-GC	head space gas analysis, HS-PTV-GC	head space gas analysis, HS-PTV-GC	head space gas analysis, SPE, GC
<b>Unit of concentration</b>	mg/kg	GC peak area percent	GC peak area percent	GC peak area percent	GC peak area percent	GC peak area percent
<b>Major components</b>	d-limonene 2380.3	limonene 38.1–95.8	$\alpha$ -pinene 24.1	3-methyl-butanal 1.4	isobutyl-acetate 1.4	d-limonene 61.2
	myrcene 36.5	$\beta$ -pinene 0.1–15.5	$\beta$ -pinene 3.1	hexanal 2.1	isopentyl-acetate 34.4	$\beta$ -pinene 12.7
	bisabolene 30.0	$\gamma$ -terpinene 0–18.0	$\alpha$ -phellandrene 19.9	trans-2-hexanal 7.9	1-pentanol 1.2	$\gamma$ -terpinene 11.0
	sabinene 21.1	linalool 0.1–25.1	linalool 4.7	trans-2-hexen-1-ol 3.9	ethyl-hexanoate 4.7	cis-b-ocimene 3.3
	trans- $\beta$ -ocimene 17.0	linalyl acetate 0–31.2		2-heptanol 11.5	isoamyl-butyrate 4.2	p-cymene 2.6
	valencene 12.8	$\alpha$ -pinene 0.1–1.7		p-cymen-8-ol 37.5	isoamyl-isovalerate 10.3	$\alpha$ -pinene 1.7
	decanal 8.1	p-cymene 0–7.8			hexyl-butyrate 2.7	myrcene 1.6
	$\beta$ -phellandrene 4.5	myrcene 0.7–1.9			butyl-hexanoate 4.0	
	citronellol 4.5	sabinene 0–2.2				
	linalool 4.1	neryl acetate 0–3.9				
		geranial 0–2.9				
<b>% of total*</b>	98.2		51.8	64.3	62.9	94.1

	Brussels sprouts	Cauliflower	Corn Starch	Potato Starch	White Sandwich Bread
<b>Study</b>	Van Langenhove et al., 1991	Van Langenhove et al., 1991	Sayaslan et al., 2000	Sayaslan et al., 2000	Seitz et al., 1998
<b>Type of analysis</b>	head space gas analysis, GC-MS	head space gas analysis, GC-MS	dynamic head space sampling (GC-FTIRD-MSD)	dynamic head space sampling (GC-FTIRD-MSD)	dynamic head space sampling (GC-MS)
<b>Unit of concentration</b>	GC peak area percent	GC peak area percent	peak area ( $\times 10^{-6}$ )	peak area ( $\times 10^{-6}$ )	GC peak area
<b>Major components</b>	dimethyl disulfide 2.8	dimethyl disulfide 13.6	hexanal 138.8	hexanal 45.6	2-methyl-1-propanol 11,100
	dimethyl trisulfide 1.2	dimethyl trisulfide 1.9	methyl-2-hydroxy benzoate 41.0	1-heptanol 19.5	ethanol 9,200
	hexanal 3.6	octanal 13.6	nonanal 19.3	2-octenal 18.4	2,3-butadione 5,700
	nonanal 1.0	hexanal 4.5	2-nonenal 8.0	2-ethyl-1-hexanol 17.3	3/2-methyl-1-butanol 3,400
	1-pentanol 0.9	heptanal 2.6	methylbenzene 7.7	ethylbenzene 14.3	3-methylbutanal 1,400
	but-3-enenitrile 51.6	pentanal 2.1		nonanal 13.6	2-methylpropanal 510
	prop-2-enyl ITC 12.8	nonanal 46.4		2-nonenal 11.2	hexanal 470
	pent-4-enenitrile 12.5	1-octanol 8.0			1-hexanol 400
		1-pentanol 1.3			
<b>% of total*</b>	86.4	94	88.1	41.7	91.4

\*This quantity is the percent of the total identified compounds that are accounted for by the compounds listed

Note: PTV = programmed temperature vaporizer

## Quantification of Individual Organic Compounds

The sum of individually quantified organic compounds is expected to be significantly lower than the total NMOC yield. One reason is that the individual compound yields, in general, are conservative. For example, if a compound produced a response that exceeded the range of the standard curve, and no dilution was prepared that resulted in a response within the range, the mass reported was that of the highest standard. The actual mass of the compound may have been much higher than the highest standard.

Certain compounds<sup>5</sup> were found to persist in sampling bags even after the bags were cleaned. For these compounds, data was used only for the first two samplings when new bags were used. Any production thereafter was not included. Additionally, the list of compounds for which standards were analyzed is not all-inclusive. As a result, some organic compounds may have been present, but not identified or quantified. Furthermore, the sum of individual compound yields does not include VFA compounds, which were analyzed by a different technique and data is currently not available, with the exception of selected samples from the MSW + HHW reactors and the Food Waste reactors.

In several cases, the sum of individually quantified compounds exceeded the NMOC yield (Table 34). The most likely explanation is inaccurate quantification of the compounds for which no standards were analyzed—myrcene, 3-carene, 2-methylbutane and butylcyclohexane. Unlike the other compounds, which were automatically integrated

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<sup>5</sup> These compounds were ethanol, 2-propanol, acetone, 2-butanone, 2-pentanone and styrene. Results of bag cleaning tests are shown in Tables 7 and 8.

and quantified with standard curves, these compounds were manually integrated and then quantified with a standard curve prepared for a different compound. One source of error in this process is the manual integration, which involves some judgment of the correct beginning and end of a peak. This error could be significant, especially in situations where two peaks with close retention times come together. Another source of error is inaccuracy of the standard curve. The magnitude of the quantification errors suggested by the results presented in Table 34, suggest that using a standard curve for structurally similar compounds was not effective. Furthermore, the data for the compounds manual identified and integrated were very inconsistent between reactors of the same type. Such inconsistency rarely occurred with the compounds for which standards were analyzed.

Given the uncertainty in the concentrations of some speciated compounds, the percents of the total NMOC yields attributable to individually quantified compounds were re-calculated, excluding the yields of the compounds for which no standards were analyzed. As a result, in all cases the sum of individual compound yields is well less than the NMOC yield (Table 34). All analyses henceforth concerning specific organic compounds do not include quantities of myrcene, 3-carene, 2-methylbutane or butylcyclohexane.

Table 34. Comparison of Total NMOC Yield and the Sum of Individually Quantified Organics

Treatment	Total NMOC Yield (mg NMOC-C/dry gm)	Sum of Individual Compound Yields (mg NMOC-C/dry gm)		% Accounted For	
		Including All <sup>a</sup>	Only Those with Standard Curves <sup>b</sup>	Including All <sup>a</sup>	Only Those with Standard Curves <sup>b</sup>
<b>Paper Waste</b>					
P1	0.0204	0.0044	0.0013	21	6
P2	0.0148	0.0019	0.0019	13	13
P3	0.0133	0.0021	0.0021	16	16
<b>Yard Waste</b>					
Y1	0.0428	0.1236	0.0210	289	49
Y2	0.0329	0.1275	0.0172	388	52
<b>Food Waste</b>					
F1	0.438	0.828	0.2645	189	60
F2	0.279	1.143	0.1429	410	51
F3	0.324	1.438	0.1595	444	49
<b>MSW</b>					
M1	0.114	0.149	0.0188	130	16
M2	0.111	0.107	0.0232	96	21
<b>MSW + HHW</b>					
MH1	0.161	0.332	0.0727	206	45
MH2	0.183	0.547	0.0953	299	52
<b>MSW Aerobic</b>					
MA1	0.278	0.0705	0.0514	25	18
MA2	0.221	0.0647	0.0488	29	22
MA3	0.200	0.0696	0.0454	35	23
<b>MSW + NO<sub>3</sub><sup>-</sup></b>					
MN1	0.0462	0.0824	0.0163	178	35
MN2	0.0528	0.1614	0.0201	306	38

a) Includes quantities of myrcene, 3-carene, 2-methylbutane and butylcyclohexane which were quantified using the standard curves of other compounds

b) Does not include myrcene, 3-carene, 2-methylbutane or butylcyclohexane

The distributions of different types of organic compounds identified from waste components are shown in Figure 68. Yields of compound categories for all reactors are presented in Table 35.

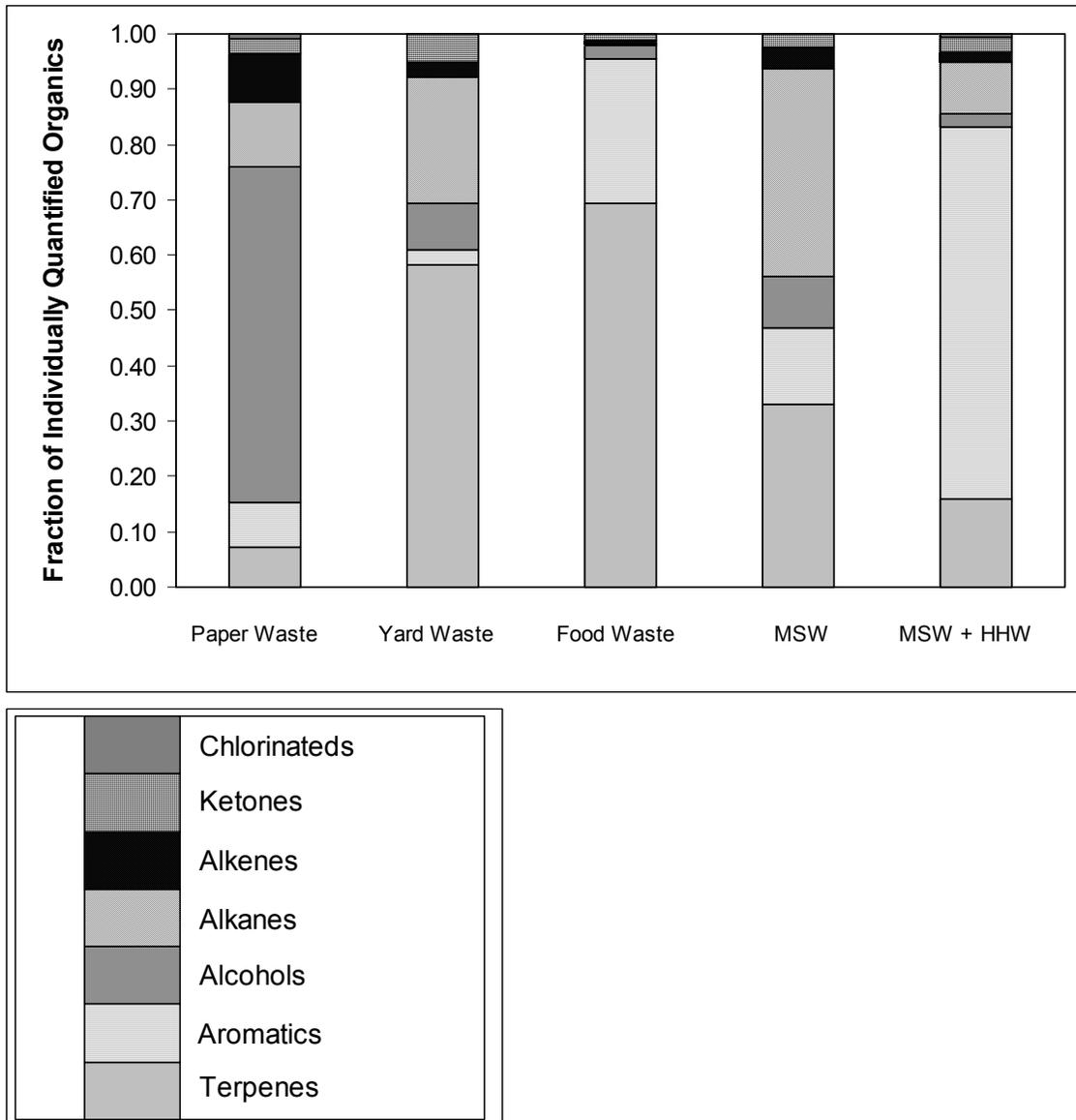


Figure 68. Distributions of Types of Organic Compounds Released from Waste Components<sup>6</sup>

<sup>6</sup> Categorical NMOC data for the Nitrate and Aerobic reactors are presented in section 4.6, where they are compared to the anaerobic MSW.

Table 35. Yields of Compound Categories for All Reactors (ng/dry gm)

	Paper			Yard		Food			MSW		MSW + HHW		MSW aerobic			MSW NO <sub>3</sub> <sup>-</sup>	
	P1	P2	P3	Y1	Y2	F1	F2	F3	M1	M2	MH1	MH2	MA1	MA2	MA3	MN1	MN2
Terpenes	47	88	377	14619	11705	240621	92857	115427	8772	7393	12194	18289	15267	30957	13910	6996	13375
Aromatics	109	232	252	376	847	49646	60868	58707	2871	3967	56125	71681	658	1907	800	1804	2227
Alcohols	1374	1669	1343	1900	1822	7910	3654	4105	2332	2251	2873	1251	23802	10214	13975	2260	1969
Alkanes	125	318	396	5905	4428	651	622	533	7319	11085	7046	10909	10634	7877	7110	5456	3655
Alkenes	147	227	250	641	568	1719	1122	1142	226	1767	1181	2244	669	305	511	333	296
Ketones		45	150	1395	905	1921	4074	1998	502	628	2795	2520			21068	3219	2476
Chlorinateds		74		5	10				9	0	311	620	155	937		162	47
<b>Total</b>	<b>1802</b>	<b>2654</b>	<b>2768</b>	<b>24841</b>	<b>20284</b>	<b>302468</b>	<b>163197</b>	<b>181911</b>	<b>22032</b>	<b>27092</b>	<b>82525</b>	<b>107514</b>	<b>51186</b>	<b>52197</b>	<b>57373</b>	<b>20230</b>	<b>24045</b>

The most abundant organic compounds quantified for the paper waste were ethanol and 1-butanol. Since paper is not inherently composed of many volatile organic compounds, it is logical that ethanol, which is a known fermentation byproduct, would be a dominant contributor to the NMOC yield. The fact that ethanol is a dominant contributor also explains, to some extent, why the individually summed organics account for so little of the total NMOC yield—6-16%. Ethanol was particularly difficult to remove during bag cleaning and as a result only data from the first two samples were used. Ethanol is expected to be highest early in the decomposition process when decomposition intermediates accumulate. Terpenes, aromatics, alkanes and alkenes contributed in roughly equal proportions. The actual amounts of these compounds are all very low, though, since the paper waste reactors yielded the least total NMOCs.

The individually quantified compounds accounted for 49 to 52% of the total for yard waste. Yard waste was particularly high in terpenes. It is likely that a significant amount of the difference in yields is due to un-quantified terpenes, such as myrcene and 3-carene. Significant peaks for those compounds were observed, though accurate quantification was not possible. The dominant presence of the terpenes is not surprising since it is known that plants produce and store monoterpenes (Lerdau et al., 1997).

In the food waste reactors, the individually quantified compounds accounted for 49 to 60% of the total. Again, the difference is likely due in large part to terpenes such as myrcene and 3-carene. Aromatic compounds contributed significantly to the NMOC yield as well. By far the most predominant aromatic compound was 1-methyl-4-isopropylbenzene. The structure of this compound suggests that it was either derived from limonene, or produced by a plant as an intermediate to monoterpene formation

(Figure 69). The apparent similarity of this compound to limonene makes the presence of aromatics more understandable. It would be disconcerting, for example to find benzene, toluene, ethylbenzene or xylenes in large quantities from food waste since these compounds are known or suspected carcinogens.

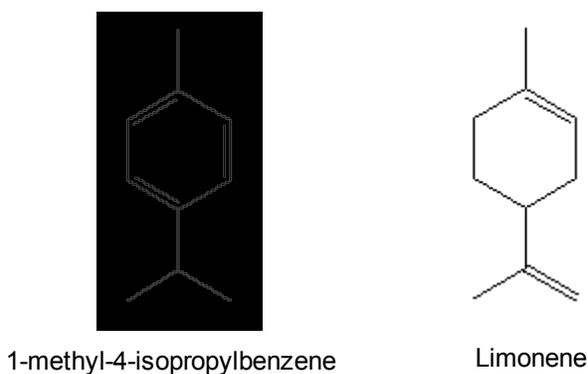


Figure 69. Structures of 1-methyl-4-isopropylbenzene and Limonene

Based on data from selected samples, VFA compounds do not appear to be major contributors to total NMOC yields. The reactor samples for which data is presented represent the highest potential for VFA concentration since these samples were the highest in COD, and high COD is indicative of the presence of decomposition intermediates such as VFAs. The data presented in the Results section (Table 20) indicate that only 0.11 to 0.15% of the total NMOC yield from food waste is due to VFA compounds.

For the MSW, only 16 to 21% of the total NMOC yield was accounted for with the sum of individual yields. Since these values were 96 to 130% when considering the quantification of all compounds, it is likely that one or more of the compounds without standard curves is responsible for much of the difference. Of those compounds, the two most prevalent were butylcyclohexane and 3-carene. The distribution of compound classes for the MSW is logical, considering what is known about the sources of organics. Since MSW is a highly diverse mixture of wastes, the elevated level of alkanes in comparison to paper, yard, and food waste is expected. Alkanes are not anaerobic decomposition intermediates, nor are they inherently present in large amounts in paper, yard or food waste. MSW, however, could contain some household products that contain alkanes, such as motor oil or gasoline. The contributing aromatics are more diverse in the MSW than from the food, which is expected since the waste is much more diverse and some household products (such as paint solvents) are known to contain BTEX compounds. The large contribution of terpenes is also expected. MSW normally contains significant amounts of food waste, which is likely the source of the terpenes.

For the MSW plus HHW, 45 to 52% of the total NMOC yield was identified. Much of the difference is likely due to butylcyclohexane and 3-carene again, as well as acetone, which was spiked but could not be completely quantified because it was a poorly removed compound during bag cleaning. Compared to the unammended MSW, the MSW + HHW had a much increased percentage of aromatics, with all other categories contributing lesser percentages. The elevated level of aromatics is expected since HHW containing toluene was spiked into the reactors. Further analysis of the significance of HHW as a contributor is presented in section 4.7.

Selected samples were analyzed for VFA concentrations (Table 20). The data indicate that the contribution of VFA compounds to the total NMOC yield was only 0.09 to 0.46%.

Between 18 and 23% of the total NMOC yield was accounted for in the aerobically operated MSW reactors. Samples from these reactors produced peaks of 2-methylbutane, which could not be quantified, but the results that include quantification of all compounds indicate that only 25 to 35% of the total NMOC yield is accounted for. Therefore, the difference between the total yield and the sum of individual yields is probably due to conservative decisions regarding peak identification and quantification.

For the MSW decomposed under nitrate-reducing conditions, the compounds without standard curves appear to be significant contributors since the average percent of total NMOCs accounted for is 242 when including all compound quantification and only 36.5 without the compounds for which no standards were analyzed.

An analysis of the specific types of organic compounds released from the aerobic and nitrate-reducing MSW reactors compared to the anaerobic reactors is presented in section 4.6.

#### **4.6 Effect of Operating Condition on Specific Trace Organics Released**

Although the aerobic MSW reactors released twice the total quantity of NMOCs as from the anaerobic MSW treatment (Table 17), the increase was not consistent across all categories of compounds. While alcohols, ketones and terpenes were emitted in higher quantities in the aerobic treatment, the yields of alkanes, alkenes and aromatics were slightly lower from the aerobic system. Figure 70 illustrates the yields of different

compound categories under aerobic, anaerobic and nitrate reducing conditions, and Table 36 summarizes the data with statistical significance testing. Since oxygen is the strongest electron acceptor, aerobic conditions should result in the most decomposition of organic compounds. Therefore, it is likely that air stripping is responsible for increased NMOC emission. In the case of alkanes, alkenes and aromatics this increase in volatility appears to be offset by enhanced degradation. On the other hand, alcohols, ketones and terpenes do not appear to have enhanced degradation under aerobic conditions.

The nitrate-reducing condition resulted in lower emissions of most types of organics compared to the anaerobic treatment. One explanation for this is that  $\text{NO}_3^-$ , being a stronger electron acceptor than  $\text{CO}_2$ , allowed for increased degradation of organic compounds. Exceptions were the terpene compounds and ketones, which were emitted in higher amounts from the nitrate-reducing reactors—probably due to variability in refuse composition.

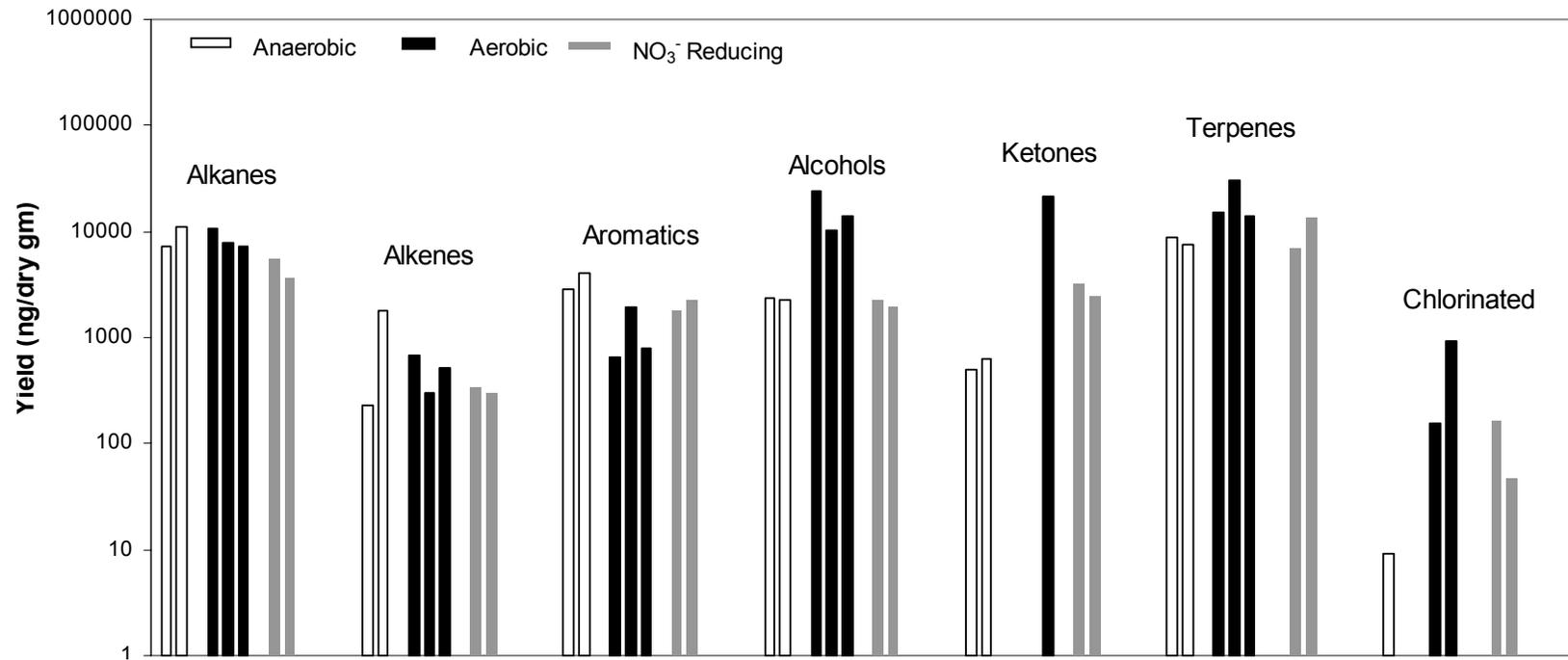


Figure 70. Comparison of the Release of Types of Organics from MSW Decomposed Under Various Conditions

Table 36. Yields of Compound Categories from MSW Decomposed Under Anaerobic, Aerobic and Nitrate-Reducing Conditions

Yields (ng/dry gm)				Probability That the Observed Difference is Due to Chance		
	Anaerobic	Aerobic	NO <sub>3</sub> <sup>-</sup> -reducing	Anaer vs. Aer.	Anaer vs. NO <sub>3</sub> <sup>-</sup> red.	Aer vs. NO <sub>3</sub> <sup>-</sup> red.
<b>Alkanes</b>	7319	10634	5456			
	11085	7877	3655			
		7110				
Ave.	<b>9,202</b>	<b>8,540</b>	<b>4,556</b>	0.40	0.10	0.03
<b>Alkenes</b>	226	669	333			
	1767	305	296			
		511				
Ave.	<b>997</b>	<b>495</b>	<b>315</b>	0.32	0.27	0.11
<b>Aromatics</b>	2871	658	1804			
	3967	1906	2227			
		800				
Ave.	<b>3,419</b>	<b>1,121</b>	<b>2,016</b>	0.04	0.10	0.07
<b>Alcohols</b>	2333	23802	2260			
	2251	10214	1969			
		13975				
Ave.	<b>2,292</b>	<b>15,997</b>	<b>2,115</b>	0.04	0.21	0.04
<b>Ketones</b>	502	0	3219			
	628	0	2476			
		21068				
Ave.	<b>565</b>	<b>7,023</b>	<b>2,848</b>	0.23	0.05	0.31
<b>Terpenes</b>	8772	15267	6996			
	7393	30957	13375			
		13910				
Ave.	<b>8,083</b>	<b>20,045</b>	<b>10,186</b>	0.08	0.31	0.11
<b>Chlorinateds</b>	9	155	162			
	0	937	47			
		0				
Ave.	<b>5</b>	<b>364</b>	<b>105</b>	0.17	0.17	0.23

#### 4.7 Contribution of HHW Compounds to NMOC Yield

The NMOC yields of the MSW and the MSW + HHW reactors are shown in Figure 71. The MSW + HHW treatment resulted in higher yields of NMOCs, which is expected since volatile organics were added. Figure 72 shows the types of compounds that contribute to the total NMOC yield from the MSW and the MSW + HHW treatments. Three categories of organic compounds are elevated in the MSW + HHW reactors compared to the MSW—ketones, aromatic compounds and chlorinated compounds. In the case of the aromatics and chlorinated compounds it is clear that

spiked compounds—toluene and methylene chloride—are responsible for the difference as these compounds are significantly higher in the MSW + HHW reactors. The difference in ketone levels cannot be fully attributed to the spike of acetone, however, since acetone was not measured in significantly higher quantities in the MSW + HHW reactors.

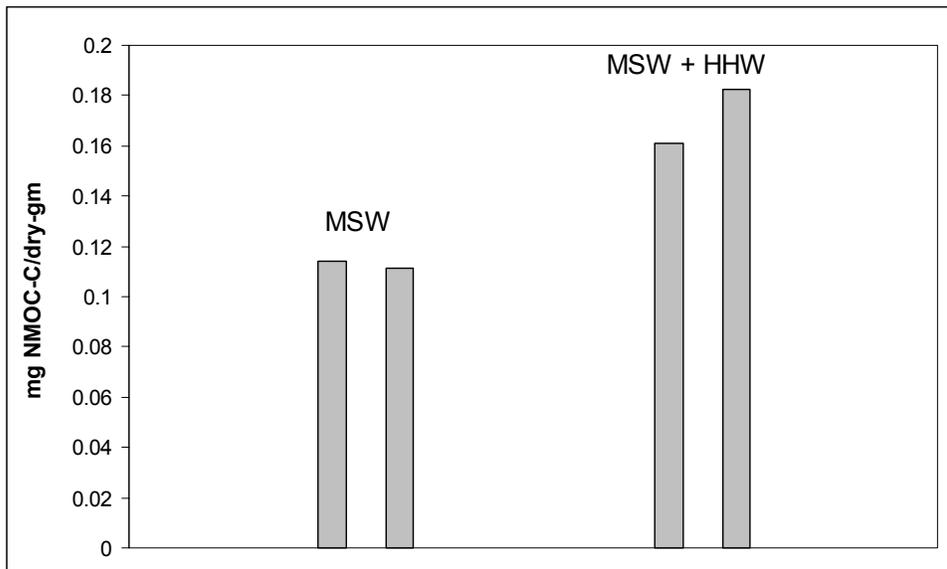


Figure 71. Total NMOC Yields for the MSW and MSW + HHW Reactors

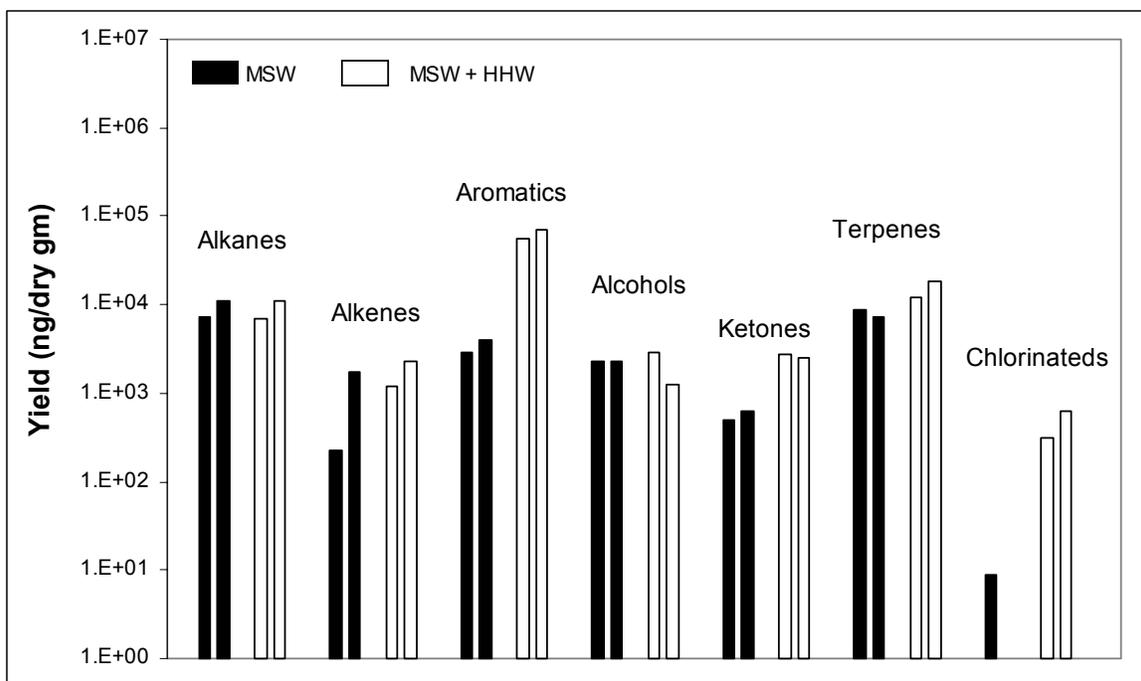


Figure 72. A Comparison of the Types of Compounds Released from the MSW and MSW + HHW Reactors

A more detailed analysis of the recoveries of the added HHW compounds is presented in Table 37. The masses of toluene emitted from reactors MH1 and MH2 were 25 and 32%, respectively, of the masses added in the HHW spike. The percent recoveries of acetone and methylene chloride were very low—less than 1%. Three factors contribute to the low recovery of acetone. First, most of the data for acetone was unusable due to the poor removal of acetone during bag cleaning. The usable data for acetone included the first 50 days.

Second, acetone (<sup>7</sup>K<sub>H</sub>, 30) is much less volatile than toluene (K<sub>H</sub>, 0.15) or methylene chloride (K<sub>H</sub>, 0.40). And, third, acetone is more degradable than toluene or methylene chloride (Sanin et al., 2000).

Table 37. Recoveries of Added HHW Compounds

Compound	Mass Added in HHW (mg)	Final % of HHW Addition Recovered	
		MH1	MH2
Toluene	188 <sup>a</sup>	22.8	29.0
Acetone	850 <sup>b</sup>	na <sup>d</sup>	na
Methylene Chloride	150 <sup>c</sup>	0.140	0.280

- a) Toluene is approx. 27.5% of paint thinner, of which 667 mg were added, and 6,880 ug/kg in motor oil (based on analysis from Chemical & Environmental Technology, Inc), of which 667 mg were added
- b) Acetone is 100% of nail polish remover, of which 667 mg were added, and 27.5% of paint thinner
- c) Methylene chloride is approx. 22.5% of paint thinner
- d) Final data for acetone was not available since acetone was poorly removed during bag cleaning

While the HHW spike increased NMOC emissions compared to the MSW treatment, the increase was not dramatic. The MSW + HHW reactors on average yielded 53% more NMOCs than the MSW. The MSW + HHW reactors were the second highest yielding treatment, but the MSW was the third highest. The high yield is more attributable to the MSW than to the HHW spike. The food waste treatment still yielded much higher amounts of NMOCs than both the MSW and MSW + HHW (Figure 57).

<sup>7</sup> K<sub>H</sub>=Henry's law constant for solubility in water at 298 K (mol/Kg bar)

#### 4.8 Comparison of Laboratory NMOC and HAP Data to Regulatory Estimates

The regulatory default values for NMOCs and HAPs are shown in Table 38. In this section, the observed NMOC and HAP concentrations and yields from this research are compared to what would be expected based on these default values.

Table 38. AP-42 Default Concentrations for Total NMOCs and HAPs

Pollutant Name	AP-42 Default Conc.	NSPS-required Tier I Default Conc.
Total NMOCs (ppmv as hexane)	595	4,000
<b>HAPs (Regulated under NESHAPs)<sup>a</sup> (ppmv)</b>		
Acrylonitrile	6.33	
Benzene	1.91	
Carbon disulfide	0.58	
Carbon tetrachloride	0.004	
Carbonyl sulfide	0.49	
Chlorobenzene	0.25	
Chloroform	0.03	
Ethyl benzene	4.61	
Hexane, n-	6.57	
Hydrogen sulfide	35.5	
Methyl ethyl ketone	7.09	
Methyl isobutyl ketone	1.87	
Toluene	39.3	
Trichloroethylene	2.82	
Vinyl chloride	7.34	
Xylene	12.1	

a) EPA's list of default values for HAPs is incomplete due to lack of available data

#### Previous Research Results

Sullivan and Michels (2000) measured NMOC concentrations in the gas from 146 landfills in the U.S. and 1 in Puerto Rico. The average NMOC concentration was 454 ppmv as hexane, which is 24% less than the AP-42 default for municipal solid waste (MSW) landfills. The lowest measured concentration was 5 ppmv at the Wabash Landfill in Wabash, Indiana. The highest reported concentration was 2283 ppmv, at the Skunk

Creek Landfill in Phoenix, Arizona. The findings of this study are summarized in Table 39.

Table 39. Sullivan and Michels' Landfill NMOC Data

<b>State</b>	<b># of Sites Reporting</b>	<b>Average CNMOC (ppmv-hexane)</b>	<b>Range</b>
Arizona	7	1144	189--2283
California	14	660	89--2115
Colorado	6	956	613--1596
Kentucky	9	373	173--738
Illinois	7	256	71--491
Indiana	7	322	5--816
Missouri	6	311	57--637
North Carolina	10	587	52--2246
Pennsylvania	6	246	51--587
Texas	17	366	61--1009

Sullivan and Michels suggested that higher NMOC concentrations occur in dry climates where gas production tends to be slow. In wet climates, where landfill gas generation is higher, the NMOCs can be diluted. Although the single highest NMOC measurement, as well as the highest average for a state, both came from Arizona—a dry region—there is a lot of variability in the data and the relationship between NMOC concentration and climate remains questionable.

Sullivan and Michels concluded that the existing AP-42 default values need to be replaced with more representative values. The following reasons were offered: 1) AP-42 data was collected in the 1980's when analytical detection limits were not as low as they are today, 2) AP-42 data was collected before regulations came into place restricting

hazardous waste disposal in MSW landfills, and 3) HAP concentrations are assumed to be constant, which does not appear to be true.

Thomas and Barlaz (1999) measured NMOC production from MSW degraded in laboratory reactors. The highest concentration observed was 425 ppmv as hexane. The average total NMOC yield from the MSW was 0.076 mg NMOC-C/dry gram refuse.

Laboratory Results From This Research

The average NMOC concentrations observed for each waste type are presented in Table 40. Of the individual waste components studied, food waste showed the highest concentration of NMOCs with an average of 429 ppmv as hexane, and a maximum concentration of about 1400 ppmv as hexane. While this is considerably higher than the AP-42 default value of 595 ppmv, the concentration was not constant (Figure 73). Generally, NMOC concentrations peaked during the first 50 days after burial and sharply declined thereafter (Figures 73 through 77).

Table 40. Average NMOC Concentrations from Waste Types

Type of Refuse	Average C <sub>NMOC</sub> (ppmv as hexane)
Food Waste	429
MSW	178
MSW + HHW	274
Yard Waste	44
Paper	23

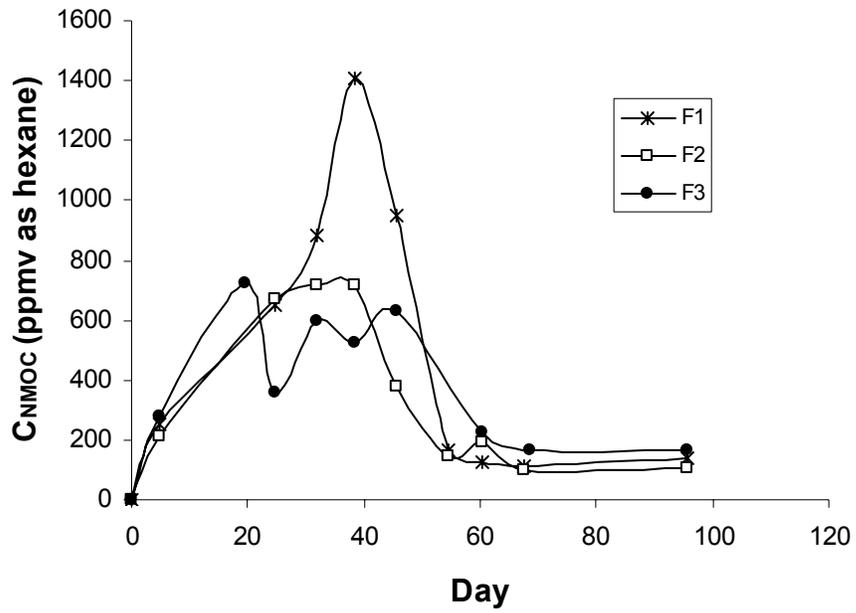


Figure 73. NMOC Concentrations for Food Waste

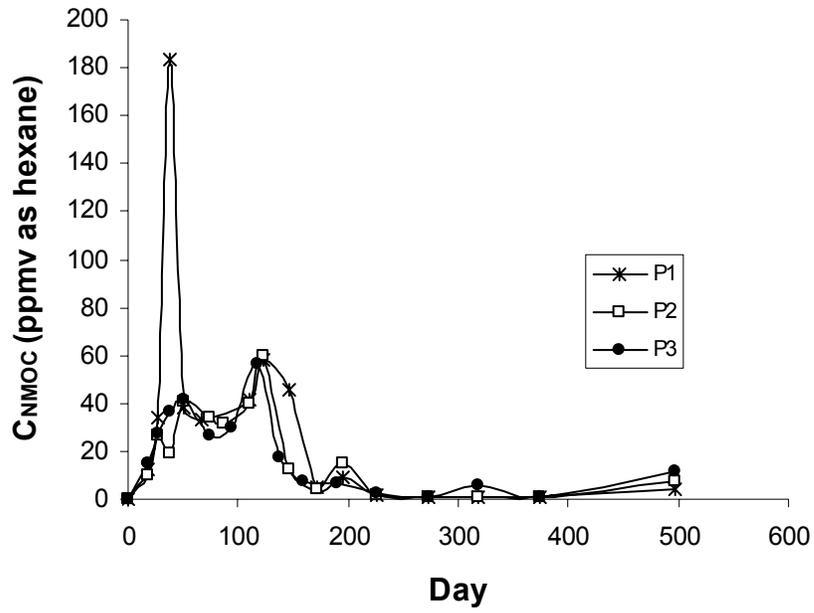


Figure 74. NMOC Concentrations for Paper Waste

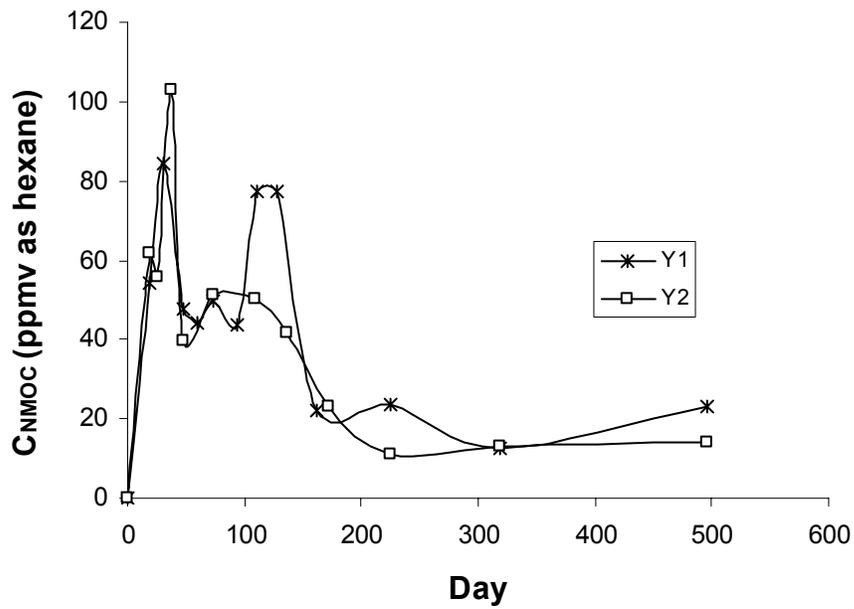


Figure 75. NMOC Concentrations for Yard Waste

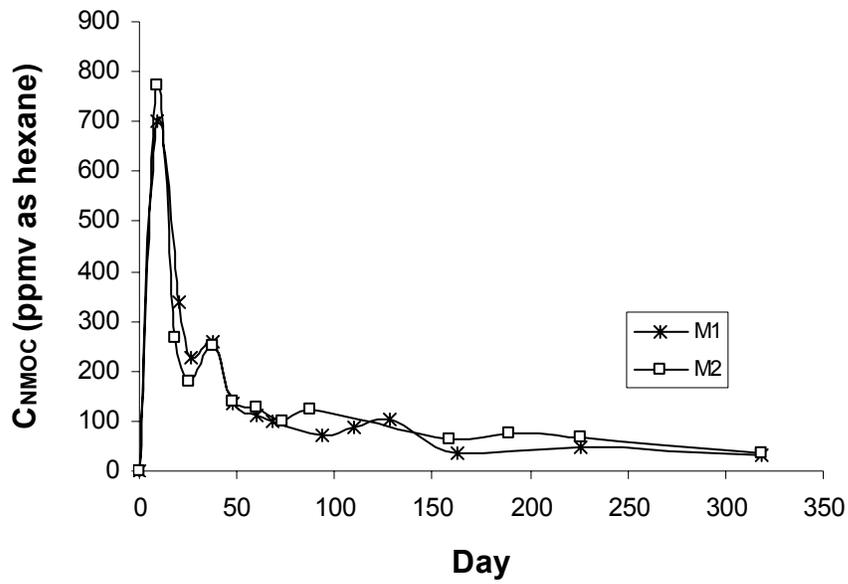


Figure 76. NMOC Concentrations for MSW

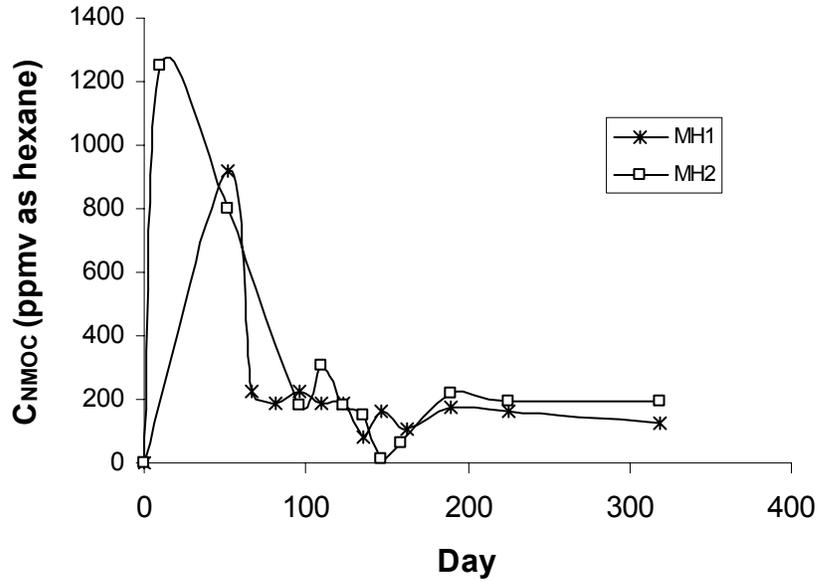


Figure 77. NMOC Concentrations for MSW + HHW

An ultimate NMOC yield for MSW can be predicted based on a default NMOC concentration and an ultimate gas yield ( $L_0$ ). The ultimate NMOC yield calculated using the NSPS required default values is 5.48 mg-C/dry gram refuse, and using the AP-42 default values it is 0.48 mg-C/dry gram refuse. Comparing the measured NMOC yields from individual waste types to the regulatory estimates it is clear that the regulatory estimates are much higher (Table 41).

Table 41. A Comparison of Laboratory Measured NMOC Yields from Waste Types to Regulatory Estimates for MSW (mg-C/dry gm)

	Ultimate NMOC Yield Estimates (mg-C/dry gm)
NSPS Tier 1	5.48
AP-42	0.48
	Measured Ultimate NMOC Yields (mg-C/dry gm)
Food Waste	0.34
MSW Aerobic	0.23
MSW + HHW	0.17
MSW Anaerobic	0.11
MSW Nitrate	0.11
Yard Waste	0.04
Paper Waste	0.02

Of the hazardous air pollutants (HAPs) that have default concentrations listed in AP-42, the following were measured in the laboratory experiment: benzene, toluene, ethyl benzene, xylenes, hexane and trichloroethene. A comparison of the concentrations and yields of these HAPs to the AP-42 estimates is presented in Table 42.

Table 42. Comparison of Concentrations and Yields of Specific HAPs Measured in Lab to AP-42 Predictions

	Food Waste		MSW		MSW + HHW	
	Max. Conc. (ppmv)	Average Yield (ng/dry gram)	Max. Conc. (ppmv)	Average Yield (ng/dry gram)	Max. Conc. (ppmv)	Average Yield (ng/dry gram)
Benzene	nd	nd	0.06	18.4	0.08	17.2
Toluene	0.068	137.1	0.35	86.2	949	60,950
Ethylbenzene	0.038	8.14	1.22	414.5	0.398	488
Xylenes	0.107	43.6	0.429	286.7	0.476	422.3
Trichloroethene	nd	nd	nd	nd	nd	nd
Hexane	0.12	22.9	0.81	170	1.9	212.6
	Yard Waste		Paper			
	Max. Conc. (ppmv)	Average Yield (ng/dry gram)	Max. Conc. (ppmv)	Average Yield (ng/dry gram)		
Benzene	0.09	21.4	0.05	10.8		
Toluene	0.171	70.4	0.343	112.8		
Ethylbenzene	0.225	59.3	0.112	12.5		
Xylenes	0.288	305.8	0.054	9.81		
Trichloroethene	0.27	4.82	nd	nd		
Hexane	0.21	29.2	nd	nd		
AP-42 Default Conc. (ppmv)		AP-42 Predicted Yield (ng/dry gram)				
Benzene	1.91	1,670				
Toluene	39.3	40,540				
Ethylbenzene	4.61	5,480				
Xylenes	12.1	14,390				
Trichloroethene	2.82	4,150				
Hexane	6.57	6,340				

All concentrations and yields of the HAPs are much lower than the AP-42 predictions, with one exception—toluene in the MSW + HHW treatment. The high level of toluene in these reactors is expected since household hazardous waste materials that contain this compound (paint remover, motor oil) were spiked into these reactors at a high level. Concerning HAP emissions, it appears that the presence of the HAP compounds in the waste is a critical factor. For example, food waste, which yielded the highest total amount of NMOCs, was very low in HAP emissions.

## 5.0 CONCLUSIONS

The ultimate yields of NMOCs from different waste components vary substantially. Ultimate yields ranged from 0.02 to 0.34 mg-C/dry gm. The highest yielding waste component was food, while the lowest was paper. All of the yields measured were lower than the values predicted using AP-42. Since lab measurements of ultimate NMOC yields from waste components have not been made prior to this research, additional research would be beneficial to confirm the ultimate yields measured here or to suggest a level of variability or uncertainty.

Production of NMOCs tends to be characterized by an initial “burst” or rapid release, followed by a prolonged period of much lower production. Gas production also occurs with an early period of maximum production followed by an asymptotic decrease. The relationship between gas production and NMOC release remains unclear. There appears to be some correlation between the two since high gas production and high NMOC release generally occur at about the same time, and waste components that yield large amounts of NMOCs also produce a lot of gas.

If NMOC production is controlled to some extent by gas production, the mechanism is still unknown. One hypothesis was that decomposition intermediates could be a significant portion of the NMOCs. Data from this research suggest that this is not the case since VFA's only accounted for 1-2% of the NMOCs in the samples where they were predicted to have the highest contribution. Also, the fact that the NMOC yield was low in the paper waste reactors in spite of relatively high gas production suggests that decomposition intermediates are not significant contributors to NMOC yields. Another possibility is that the flow of gas may facilitate the volatilization of organic compounds

regardless of whether or not the gas was generated by microbial decomposition of the refuse. This possibility is currently being studied with an abiotic air-flow treatment.

Aeration, in this experiment, resulted in considerably higher NMOC release compared to anaerobic decomposition. This result is significant in the context of composting. During composting, the waste (such as food/yard waste) is high in organics and the operating condition is also one that tends to promote release of organics. This combination seems likely to produce considerably higher levels of NMOCs per gram of refuse compared to landfills. It should be noted, however, that the organic compounds that are emitted from food and yard waste tend not to be HAPs. The majority of the compounds measured from these waste components in this experiment were terpenes. The environmental impact of terpenes may need to be studied further.

Lastly, the data suggests that HHW constituents are minor contributors to total NMOC yields. MSW reactors spiked with HHW compounds showed an increase of 52% in NMOC production over MSW without the spike. It is important to note, though, that the majority of HAPs likely originate from HHW in refuse.

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APPENDIX A. Calculations to Develop an Appropriate Paper Mixture for Mixed Paper Reactors

Type of Paper	Thousand Tons Discarded <sup>a</sup>	% of Total <sup>b</sup>
ONP	4,790	20
OMG	1,670	7
OFF	3,470	15
OCC	9,870	42
Standard Mail	3,900	16
Total	23,700	100

a) Values from 1998 US EPA Waste Characterization Report

b) Corrected to 100%. Values were then used to get the mixture of paper in each reactor.

## APPENDIX B. Reactor Parts List

Part Description	Part#	Company
female connector, (3/8" tube X 1/8" female NPT)	B-600-7-2	Raleigh Valve & Fitting
3/8" brass ferrules, 10 sets	B-600-Sets-10	Raleigh Valve & Fitting
female adapter, (3/8" tube X 1/8" female NPT)	B-6-TA-7-2	Raleigh Valve & Fitting
female elbow, (3/8" tube X 1/8" female NPT)	B-600-8-2	Raleigh Valve & Fitting
Parker Vibra-Lok, male straight adapter-- (3/8" OD tube X 1/8" male NPT) w/Viton sleeve	68VLV-6-2	Cross System Components
Viton sleeve for 3/8" Vibra-Lok fittings	60VLV-6	Cross System Components
1/4" Kynar straight connector	53055K116	McMaster-Carr Supply
1/4" Kynar tee	53055K172	McMaster-Carr Supply
Kynar straight adapter (1/4" ID tube X 1/8" male NPT)	53055K211	McMaster-Carr Supply
Kynar elbow adapter (1/4" ID tube X 1/8" male NPT)	53055K181	McMaster-Carr Supply
Kynar elbow adapter (3/16" ID tube X 1/8" male NPT)	53055K202	McMaster-Carr Supply
1/8" brass coupling	50785K91	McMaster-Carr Supply
Kynar reducing straight connector-- (5/16" ID tube X 1/4" ID tube)	53055K132	McMaster-Carr Supply
Male Luer X Barb (1/8" to 3/16" tube ID)	51465K115	McMaster-Carr Supply
7.1-7.9 mm nylon hose clamps	9579K62	McMaster-Carr Supply
FDA-approved Viton tubing (7/16" OD x 5/16" ID)	U-06435-05	Cole-Parmer
FEP-lined Tygon tubing (3/8" OD x 1/4" ID)	U-95711-20	Cole-Parmer
shut-off valve, natural ETFE (no fittings) <sup>a</sup>	P-721A	Upchurch Scientific
female Luer adapter, ETFE <sup>a</sup>	P-624	Upchurch Scientific
1/4" O.D. x 1/8" I.D. Kynar tubing <sup>a</sup>	U-95100-00	Cole-Parmer
stacked filter/regulator	4910K61	McMaster-Carr Supply
replacement filter	4958K81	McMaster-Carr Supply
mounting bracket	4957K62	McMaster-Carr Supply
1/4" brass coupling	50785K91	McMaster-Carr Supply
braid-reinforced PVC tubing	5238K638	McMaster-Carr Supply
hose clamps, 11-20 mm	5416K11	McMaster-Carr Supply
Kynar straight adapter (1/4" ID tube X 1/4" male NPT)	53055K213	McMaster-Carr Supply
Kynar straight adapter (1/4" ID tube X 1/8" male NPT)	53055K211	McMaster-Carr Supply
aluminum manifold (4 outlets)	5469K121	McMaster-Carr Supply
aluminum plug, 1/8" NPT	44705K79	McMaster-Carr Supply
aluminum plug, 1/4" NPT	44705K81	McMaster-Carr Supply
male brass connector (1/4" ID tube X 1/4" male NPT)	B-4-HC-1-4	Raleigh Valve & Fitting
male brass connector (1/4" ID tube X 3/8" male NPT)	B-4-HC-1-6	Raleigh Valve & Fitting
female brass connector (1/4" ID tube X 1/4" female NPT)	B-4-HC-7-4	Raleigh Valve & Fitting
Kynar straight adapter (1/4" ID tube X 1/8" male NPT)	53055K211	McMaster-Carr Supply
mini brass ball valve (1/8" female NPT X 1/8" female NPT)	4912K46	McMaster-Carr Supply
SGE syringe valve SLLV	SG031915	Fisher Scientific
magnetic stir bar, 7/8" x 3/16"	58948-080	VWR Scientific Products
screw-cap vial, 1 dram	28980	NCSU Chemical Supply Room
Mininert valve for 13mm vials	3-3300	Supelco
replacement septa for Mininert valves	9548	Alltech
magnetic stirrer	14-493-120S	Fisher Scientific
8.7 - 10 mm nylon hose clamps	9579K63	McMaster-Carr Supply

a) These parts are used to replace the Luer Locking valve sold by PMC. Purchase bag with Kynar JACO tube fitting (JACOK) instead of Luer Locking Valve (LLV)

## APPENDIX C. COD Analysis Procedure

### *Standards*

Potassium hydrogen phthalate was dried overnight at 120° C. This compound was then used to prepare the 5 standards shown below.

<b>COD (mg/L)</b>	<b>Potassium hydrogen phthalate (mg/L)</b>
100	85
300	255
700	595
1100	935
1500	1275

### *Samples*

Leachate samples were removed from the freezer and allowed to thaw. Upon thawing, the pH of the samples were adjusted to 2.0 +/- 0.2. COD digestion vials in the range 0-1500 ppm were used (Hach catalog # 21259-15). 2.0 mL of leachate sample was pipetted into a vial for each leachate sample. Samples were prepared in duplicate. Vials were also prepared for each of the 5 standard solutions and a blank (DI water). The standards and blank were prepared in triplicate.

After all the vials were inverted 8 times to homogenize the liquid, the vials were placed in a COD reactor and heated for 2 hours at 150° C. Samples were then allowed to cool for about 20 minutes before analysis on a spectrophotometer.

A Spectronic 21 spectrophotometer was turned on and allowed to warm up for at least 1 hour. The wavelength dial was set to 620 nm. With the blank vials, the spectrophotometer was calibrated for zero. Standard samples were placed in the spectrophotometer after being wiped with a Kim-Wipe. Absorbances were recorded and

used to prepare a standard curve. Vials from the leachate samples were placed in the spectrophotometer and their absorbances were recorded. The standard curve function was used to convert the absorbances into COD values in mg/L. If a sample produced an absorbance that was outside the range of the standard curve, an appropriate dilution was made to the leachate and the process was repeated.

#### APPENDIX D. Preparation of Gaseous Standard Samples

The organic standard solutions that were purchased had to be volatilized so that a standard curve for the GCD analysis of gaseous samples could be produced. Figure 78 illustrates the setup used for the preparation of gaseous samples. The goal of the process illustrated in Figure 78 was to generate a tedlar gas sampling bag filled with a known volume of ultra high purity (UHP) nitrogen and a known amount of volatilized standard solution, so to produce a gaseous sample for which the concentrations of all component compounds were known. Typical concentrations of the standard compounds in the gaseous sample were around 30,000 ng/L.

The UHP nitrogen was passed through an adsorbent trap (Supelco Carbotrap 300, P/N 2-0370) that was connected to a flow controller (Dynatherm Model 10). This was achieved by connecting thin polyurethane tubing from the gas cylinder regulator valve to the back of the flow controller. The adsorbent trap served to remove any hydrocarbon contamination. Following the adsorbent trap, rigid PEEK tubing and fittings were used to carry the nitrogen through three VOA vials that were set in series to humidify the nitrogen. The septum of each VOA vial was punctured twice with an 18-gauge needle creating inlet and outlet holes through which the stiff PEEK tubing was forced. The first two vials were partially filled with ultra pure water into which the inlet tubing was submerged so that the nitrogen bubbled through the water. The third vial was left empty and served to trap water droplets.

An empty Target vial was used as a volatilization chamber for the standard solution. A needle was attached to the tubing that carried the nitrogen from the last VOA vial. Flow measurements were taken by attaching a flow meter to the needle. The flow

was adjusted until a flow of 80 mL/min was achieved and shown to be stable. A second needle in the empty target vial was connected to PEEK tubing leading to the gas bag. Both of the needles were forced through the septum of the empty target vial, and the valve to the gas-sampling bag was opened, establishing a nitrogen flow of 80 mL/min into the bag. A known amount of standard solution was injected into the target vial. The target vial was placed in a bath of warm (40° C) water to promote volatilization of the standard solution.

The flow was allowed to continue for 125 minutes so that 10 liters of nitrogen would enter the bag. This time is also sufficient for all of the standard solution to completely volatilize and enter the bag. Complete volatilization was confirmed since no liquid remained in the target vial. The system was leak-checked by squirting water around all of the connection sites and looking for bubbles. No leaks were detected.

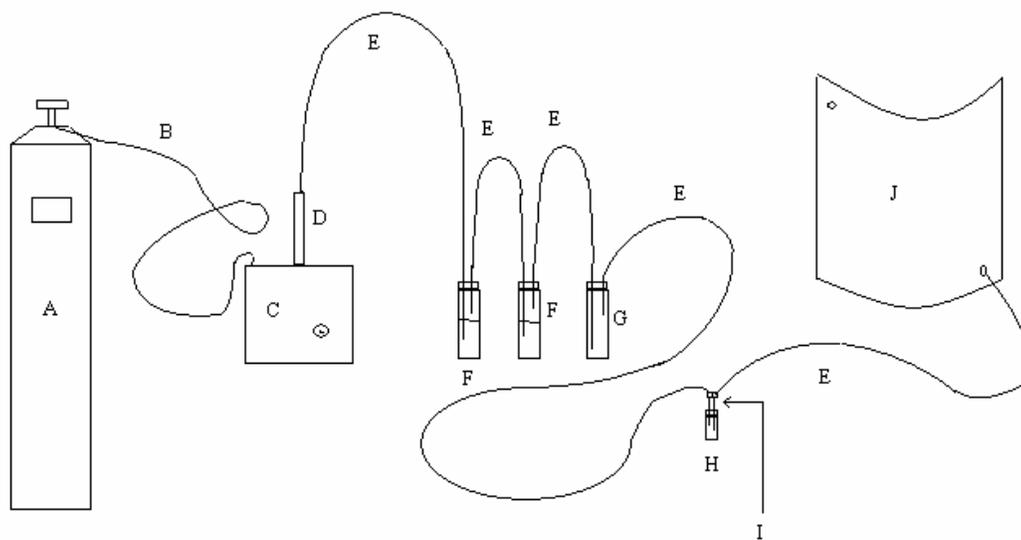


Figure 78. Set-up for Preparation of Gaseous Standard Samples. A, cylinder of UHP nitrogen; B, polyurethane tubing; C, flow controller; D, carbon trap; E, PEEK tubing; F, VOA vials with ultrapure water; G, empty VOA vial; H, target vial containing liquid standard; I, needle; J, tedlar gas-sampling bag.

APPENDIX E. Leachate VFA Concentrations (mg/L)

	Acetic acid	Propionic acid	Isobutyric acid	n-butyric acid	2-methylbutyric acid and Isovaleric acid	Valeric acid	Isocaproic acid	Caproic acid	Heptanoic acid	Total mg/L
<b>Paper</b>										
P1, day 62	1223.9	212.2	120.5	130.1	43.0	0.0	0.0	13.3	6.0	1749.0
P2, day 76	36.6	0.0	0.0	17.9	0.0	2.2	0.0	4.8	0.96	62.5
P3, day 76	0.0	0.0	0.0	12.0	0.0	0.0	0.0	1.1	0.0	13.1
<b>Yard</b>										
Y1, day 27	17142.1	2672.7	2081.3	8924.3	1342.6	616.2	161.8	1402.8	160.4	34504.2
Y2, day 27	6471.7	3013.1	1336.9	560.1	846.5		68.3	118.3	36.5	12451.4
<b>Food</b>										
F1, day 27	17879.8	419.5	1015.8	3621.4	308.2	283.4	0.0	937.7	0.0	24465.8
F2, day 27	8192.3	655.9	405.1	1146.0	222.7	243.2		151.3	75.6	11092.1
F3, day 27	5971.7	1310.3	552.7	92.2	319.3	39.3	20.2	82.2		8387.9
<b>MSW</b>										
M1, day 27	1078.4	1714.0	361.4	224.0	202.3	58.0	8.2	24.9	0.0	3671.2
M1, day 27	122.0	652.0	137.0	0.0	75.0	0.0	0.0	0.0	0.0	986.0
<b>MSW + HHW</b>										
MH1, day 48	11612.9	2791.6	2042.4	10605.3	949.2	708.9	39.4	2647.5	69.0	31466.2
MH1, day 62	6565.0	2672.0	1587.7	409.5	486.3	61.0	21.6	46.4	0.0	11849.5
MH2, day 27	16851.7	3735.1	749.3	11028.7	722.9	1133.0	92.8	1998.9	43.1	36355.5
MH2, day 48	26981.7	1688.5	1497.4	15513.4	496.1	1390.0	0.0	3567.8	108.5	51243.4
<b>MSW Aer.</b>										
MA1, day 27	0	0	0	0	3.29	0	0	0	0.7	4.0
MA2, day 27	0	0	0	0	4.378	4.89	0	2.88	0.91	13.1
MA3, day 27	0	0	2.467	0	2.415	0	0	3.436	0.91	9.2
<b>MSW NO<sub>3</sub><sup>-</sup> red.</b>										
MN1, day 48	14659.7	0.0	1066.5	4215.0	445.4	401.8	55.2	697.6	42.2	21583.4
MN2, day 34	5336.3	622.0	509.7	2925.9	366.8	286.0	63.0	784.6	22.8	10917.1