

ABSTRACT

John C. Ihnatolya. Production of Non Methane Organic Compounds During the Decomposition of Refuse and Individual Waste Components and Under Different Operating Conditions. (Under the supervision of Dr. Morton A. Barlaz)

There has been an increased interest in the emissions of non-methane organic compounds (NMOCs) during refuse decomposition. In addition to the New Performance Standards in the Clean Air Act, many state regulatory agencies require estimates of NMOC emissions as part of the landfill permitting process. The objectives of this new project are to measure NMOC yields for specific waste components entering landfills and the effect of alternate oxidation-reduction potentials (O_2 , NO_3 , CH_4) on NMOC production. The experimental design consists of 8 treatments conducted in triplicate 7-l reactors. Four of the 8 treatments consist of shredded residential municipal solid waste (MSW), in which, the residential MSW was decomposed under aerobic conditions for 30 days followed by methanogenic conditions, decomposed under nitrate-reducing conditions, spiked with selected HHW plus methanogenic leachate initially, and decomposed under methanogenic conditions methanogenic leachate. The other four treatments were food waste; a mixture of grass; leaves and branches; a mixture of the dominant paper types present in MSW; and a leachate control. The results are preliminary though day 73. The average NMOC yields for the aerobic, mixed paper, yard waste, MSW, MSW plus HHW, nitrate, food waste and leachate controls were as follows: 2.28×10^{-1} ; 7.44×10^{-3} ; 1.45×10^{-2} ; 6.97×10^{-2} ; 5.84×10^{-2} ; 3.08×10^{-2} ; 2.93×10^{-1} mg-C/dry g; and 6.85×10^{-4} mg-C/mL, respectively.

**PRODUCTION OF NON METHANE ORGANIC COMPOUNDS
DURING THE DECOMPOSITION OF REFUSE AND INDIVIDUAL
WASTE COMPONENTS AND UNDER DIFFERENT OPERATING
CONDITIONS**

by

JOHN CHARLES IHNATOLYA

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Approved by _____
Chairperson of Supervisory Committee

BIOGRAPHY

John C. Ihnatolya, was born on June 23, 1977 in Albany NY. He is the son of Jack and Meg Ihnatolya, and has one brother, Nicholas M. Ihnatolya. He graduated from Colonic Central High School in 1995 and began his college career at Siena College in August 1995. He then transferred to North Carolina State University in August 1998 and graduated in December 2000 with a Bachelor of Science in Environmental Engineering.

In January 2001, John began his research on his Master of Science in Civil (Water Resources and Environmental) Engineering under the direction Dr. Morton A. Barlaz.

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INTRODUCTION

A landfill is a disposal alternative for municipal solid waste (MSW), certain industrial wastes, water and wastewater treatment sludges, and agricultural waste (3). The U.S. Environmental Protection Agency (U.S. EPA) defines MSW to include durable goods (e.g., appliances), nondurable goods (e.g., newspapers), containers and other packaging, food scraps, yard trimmings, and miscellaneous inorganic wastes from residential, commercial, institutional, and industrial sources (13). MSW as defined by the U.S. EPA does not include wastes from construction and demolition debris, automobile bodies, municipal sludges, combustion ash, and industrial process wastes although these wastes are sometimes disposed of in landfills (13).

It has been estimated that 217 million tons of MSW were generated in 1997 (12). According to the U.S. EPA (2), 55.1% or 119.6 million tons of MSW was sent to a landfill while 28% or 60.7 million tons were recovered for recycling and composting, and 16.9% or 36.7 million tons were combusted. Heavy reliance on landfills for MSW disposal is likely to continue for the foreseeable future.

Methane and carbon dioxide are the major endproducts of refuse decomposition and the major constituents of landfill gas. Landfill gas also contains trace amounts of multiple xenobiotic organic chemicals (XOCs), including benzene, toluene, xylene, and chlorinated aliphatics (2,5,6,7,16). The presence of these trace volatile organic compounds (VOCs) is

suspected to originate from the presence of household hazardous waste (HHW) in MSW. Some of the components of MSW that contain VOCs include paint and paint remover (toluene and xylene), motor oil and gasoline (benzene and ethylbenzene), tire sealant (perchloroethene), and glues (trichloroethene) (2,11). The relationship between HHW, VOCs and landfill gas composition has yet to be reported. The presence of VOCs in landfill gas has been represented by an aggregate parameter non-methane organic compounds (NMOCs). Typically NMOCs are a small fraction of the total landfill gas but contain various hazardous air pollutants (HAP), and greenhouse gases (GHG).

On March 1, 1996, the US EPA enacted New Source Performance Standards (NSPS) and Emission Guidelines (EG) to control the amount of NMOCs emitted from both new and existing landfills. This regulation requires that Best Demonstrated Technology (BDT) be used on new and existing MSW landfills emitting 50 tons/yr or more of NMOCs. The NSPS/Emission Guidelines affect new MSW landfills, and existing MSW landfills that have accepted waste since November 8, 1987. Landfills that have a design capacity of 2.75 million tons or more are assumed to generate greater than 50 tons of NMOCs/yr and are thus regulated by the NSPS/EG. Regulated landfills must have: (1) a well-designed and well-operated gas collection system, and (2) a control device capable of reducing NMOCs in the collected gas by 98 weight-percent. Emissions of NMOCs must be estimated for permitting purposes and typical default values are used. These values can be found in the Clean Air Act (CAA) or in the part of the CAA titled the Compilation of Air Pollutant Emission Factors

(AP-42). In the absence of site-specific information, the CAA sets the NMOC emission default concentration at 4,000 ppmv as hexane, however, if a landfill is known to contain only MSW and very little organic commercial/industrial wastes then the default AP-42 value of 595 ppmv as hexane can be used. The objectives of the CAA amendment for landfills were to decrease uncontrolled emissions of methane and NMOCs. By assuming a constant default concentration, total NMOC production will increase as the gas yield increases. However, it is not at all clear that NMOC production should increase in direct proportion to methane production. This contrasts with the concept of an NMOC yield, which would be analogous to an ultimate methane yield (Lo) commonly used in methane production modeling.

Michels and Sullivan (2001) reported that the average NMOC concentration for 146 United States landfills and 1 Puerto Rican landfill was 454 ppmv as hexane. This value is about 10 times lower than the AP-42 default value of 4,000 ppmv as hexane and further emphasizes the importance of being able to predict NMOC production as a function of both waste composition and gas production.

Our current understanding of the sources of NMOCs in landfill gas and the factors that affect their production is incomplete. To illustrate this, Barlaz and Thomas (1999) monitored NMOC production in tests that included (1) fresh residential refuse, (2) a synthetic refuse that did not contain any household hazardous waste, and (3) twenty year old refuse excavated

from a landfill. They found that the NMOC yield for the three samples ranged from 0.6 – 1.0 x 10⁻⁴ gm as C/dry gm. Since NMOC production from fresh refuse was not considerably higher than that of either old refuse or synthetic refuse, this suggests that NMOCs are possibly a product of refuse decomposition. Barlaz and Thomas did observe an initial spike in the NMOC concentration but the NMOC concentration then decreased and remained stable for 150–200 days after the initial spike, suggesting that NMOCs are a natural byproduct of refuse decomposition. If the bulk of NMOCs were VOCs, then NMOC production should have decreased to zero after the initial spike.

The overall objective of this project was to develop a basic understanding of the production of NMOCs during refuse decomposition. Specific objectives were to:

- 1) Measure an ultimate yield (Lo) for NMOCs in individual components of MSW during anaerobic refuse decomposition.
- 2) Evaluate the significance of household hazardous waste (HHW) as a contributor to NMOCs during anaerobic refuse decomposition.
- 3) Identify some of the major components of NMOCs in landfill gas and determine whether volatile carboxylic acids are a major contributor to NMOC concentrations in landfill gas.
- 4) Evaluate the effect of decomposition under nitrate-reducing and aerobic conditions on NMOC production.

2.0 EXPERIMENTAL METHODS

2.1 Experimental Design

A series of seven treatments was used to measure NMOC emissions and all treatments are listed in Table 1. With the exception of the aerobic and nitrate-reducing reactors, all reactors were seeded with leachate to rapidly initiate methane production. Background NMOC emissions from the leachate were measured in a set of control reactors. Treatment 1 consisted of food waste. Treatment 2 consisted of a mixture of grass, leaves, and branches. The mixture ratio was based on EPA's Waste Characterization report (1998). Treatment 3 consisted of residential MSW. To evaluate the effect of HHW on NMOC production, residential MSW was spiked with selected HHW in Treatment 4. The added HHW and the VOCs they contain are presented in Table 2. Treatment 5 consisted of a mixture of the dominant paper types present in MSW (ONP, OCC, OFF, OMG, third class mail). The paper mixture composition was developed from the EPA's Waste Characterization Report (1998). The mixture composition was based on the mass of each of the test paper types that was discarded in 1997 normalized to 100%. Sample calculations for yard waste and mixed paper mixture compositions are presented in Appendix C. Treatments 6 and 7 were designed to stimulate some alternative landfill operating strategies. Treatment 6 consists of residential MSW decomposed under nitrate reducing conditions. Treatment 7 consists of residential MSW decomposed under aerobic conditions for 48 days followed by methanogenic conditions. All treatments were conducted in triplicate.

Table 1 Experimental Design

Treatment	Description
1	Food waste plus leachate (FW)
2	Mixture of leaves, branches, and grass plus leachate (YW)
3	Residential MSW (MSW)
4	Residential MSW spiked with selected HHW plus leachate (HHW)
5	Mixture of the dominant paper types present in MSW (ONP, OCC, OFF, OMG, third class mail) plus leachate (MP)
6	Residential MSW decomposed under nitrate-reducing conditions (DN)
7	Residential MSW decomposed under aerobic conditions for 48 days followed by methanogenic conditions (Aerobic)
8	Leachate Control (Control)

Table 2 Waste Products added to Household Hazardous Waste Reactors

Trade Name	Compounds
Liquid Kutzit Paint Remover	Toluene, Acetone, Methylene Chloride, Methanol
Pennzoil motor Oil	Benzene, Toluene, Ethylbenzene
Nail Polish Remover	Acetone

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 vehicle that collected in residential areas. Refuse was then shredded in a slow speed, high torque shredder to particles that were approximately 1 cm x 2 cm. The protocol for refuse collection and shredding is presented in Appendix A. 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. Food waste represents food scraps from a residential kitchen. It was 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 old refuse was removed and some fresh refuse was added to ensure that an active community of microorganisms was maintained. To add refuse, about 75% of the old refuse was removed after which fresh MSW was added and

mixed with the remaining old MSW. After mixing, more DI water was added to fill the reactor approximately $\frac{3}{4}$ full. The gas from the reactor was analyzed and contained approximately 50/50 CH₄/CO₂ 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 as illustrated in Figure 1.

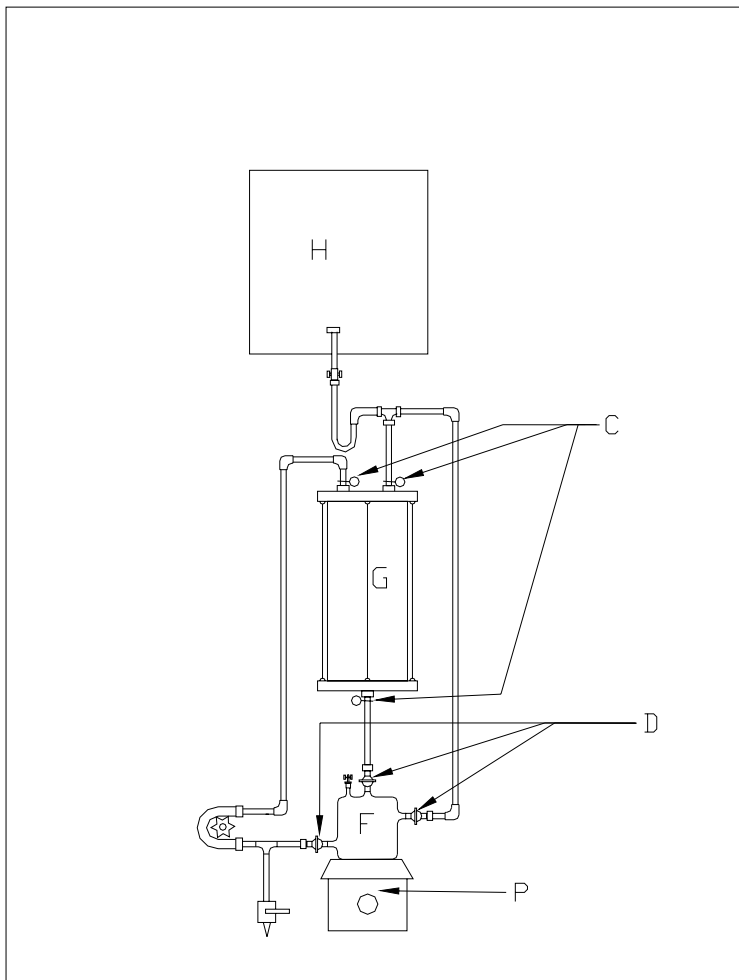


Figure 1. Reactor Design. H, 20-L 2mil tedlar inner with aluminized outer gas bag (P.M.C., Oak Park, IL); G, Reactor; F, leachate collection vessel; P, Magnetic stirrer; C, JN series screwed bonnet needle valves; D, Teflon stopcocks; All other parts will be identified in subsequent drawings.

The reactor and leachate collection vessel were designed with Teflon stopcocks and JN series screwed bonnet needle valves so that each section could be isolated for required maintenance and possible replacement of damaged parts without having to shut down the experiment. The reactors were 8-L and were fabricated from aluminum. The aluminum top and bottom were circular with a diameter of 10". Each top and bottom had a circular

groove cut into it to allow for a 8" diameter teflon coated viton o-ring (Smith Seal, Raleigh, NC). The tops of each reactor also had two 3/8" holes for leachate recycle and gas collection. The bottoms of each reactor had one 3/8" hole for leachate collection. Each hole was sealed with a JN series screwed bonnet needle valve (Raleigh Valve & Fitting, Raleigh, NC). The middle cylindrical section was made from a 8" diameter aluminum pipe and cut to make a reactor with a volume of 8-L. The cylinder length was 11 inches. All surfaces exposed to the MSW were coated with kynar to prevent corrosion (Electro Chemical, Emmaus, PA.). Figure 2 illustrates the 8-L reactor design.

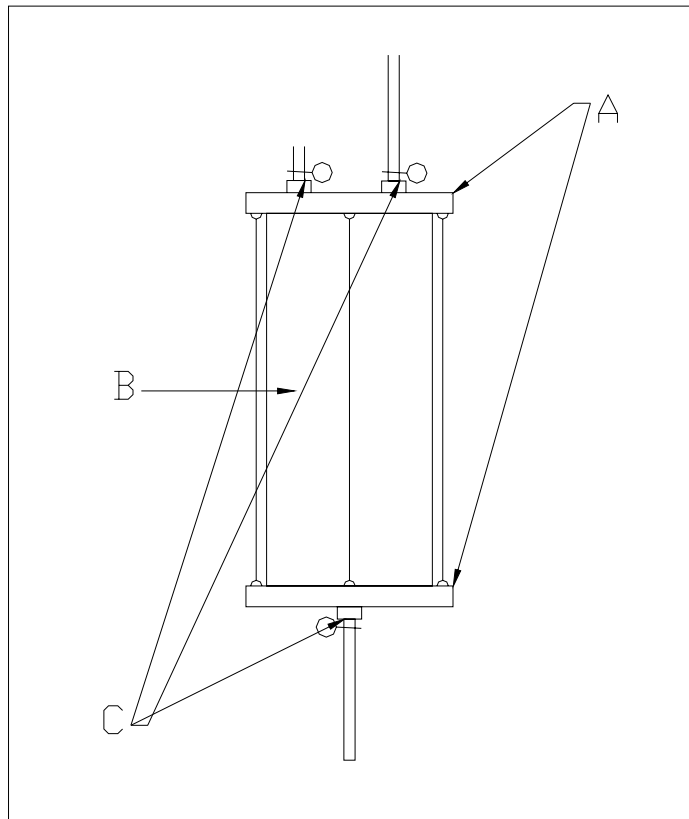


Figure 2. 8-L Reactor Design. A, Aluminum top and bottom; B, 8-L Aluminum Reactor; C, JN series screwed bonnet needle valves

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 is located at the top of the vessel and allows the leachate to drain from the reactor to the collection vessel. The leachate recycle port is located at the bottom front of the vessel to allow the leachate that has been drained into the vessel to be recycled back into the reactor. The gas port is present to alleviate any gas accumulation in the leachate collection vessel and to prevent an airlock during leachate recirculation. The neutralization port is fitted with a 13mm miniert valve (Supelco, Bellefonte, PA) located at the top of the leachate collection vessel and is used to add base when required. Once the leachate is neutralized it was then recycled back to the top of the reactor using a peristaltic pump (Masterflex 7518-00, Cole-Parmer, Vernon Hills, IL) with viton tubing. The leachate collection vessel is illustrated in Figure 3.

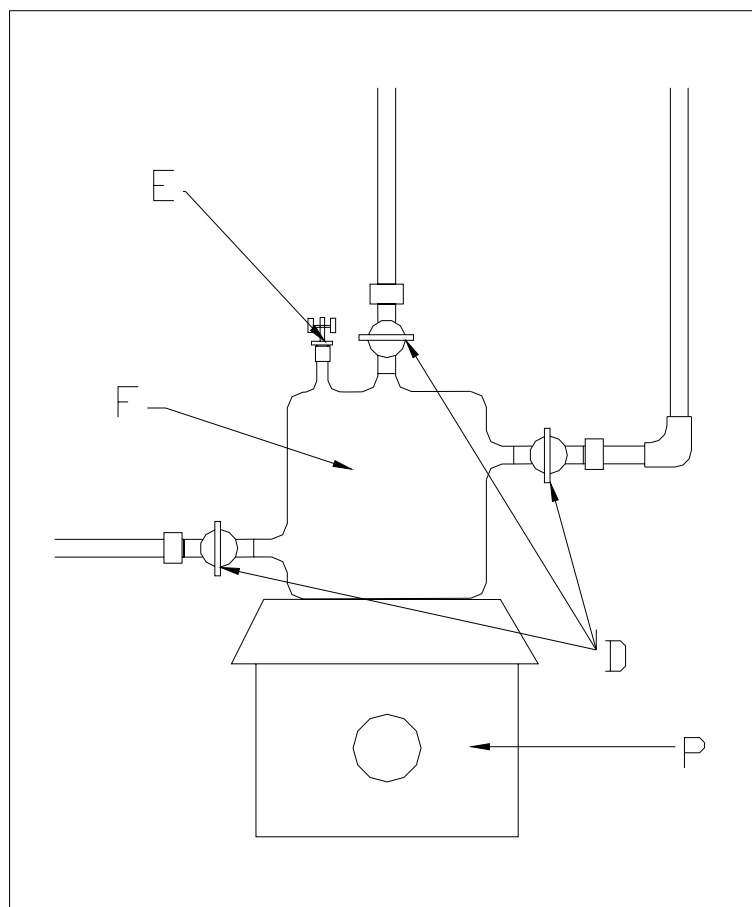


Figure 3. Leachate Collection Vessel. D, Teflon stopcocks; E, 13mm miniert valve; F, Leachate collection vessel; P, magnetic stirrer.

The leachate recirculation system is illustrated in Figure 4 and a detailed parts list is presented in Appendix B, Table 3.

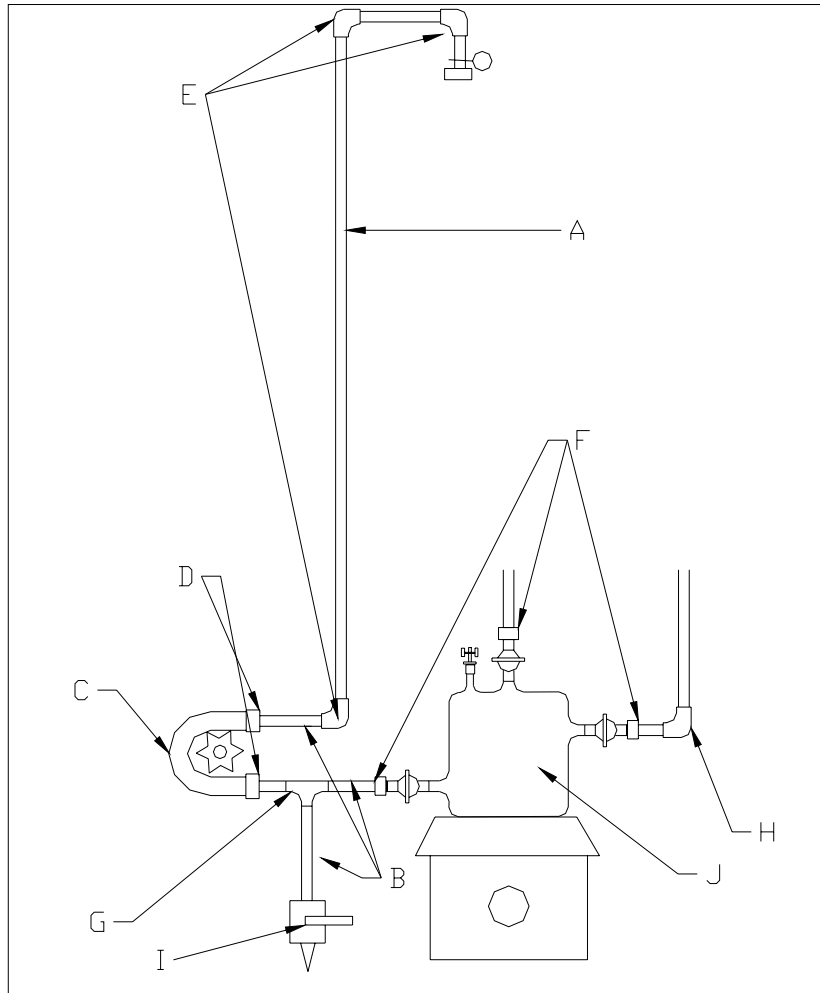


Figure 4. Leachate Recirculation System. A, Kynar tubing; B, Teflon lined tygon tubing; C, Viton tubing; D, Kynar reducing straight connector; E, Female brass elbow; F, brass vibra-timer male straight adapter w/ female brass connector and female brass adapter; G, 1/4" kynar tee; H, Kynar elbow adapter; I, mini brass ball valve

The gas collection system is illustrated in Figure 5 and a detailed parts list is presented in Appendix B, Table 3.

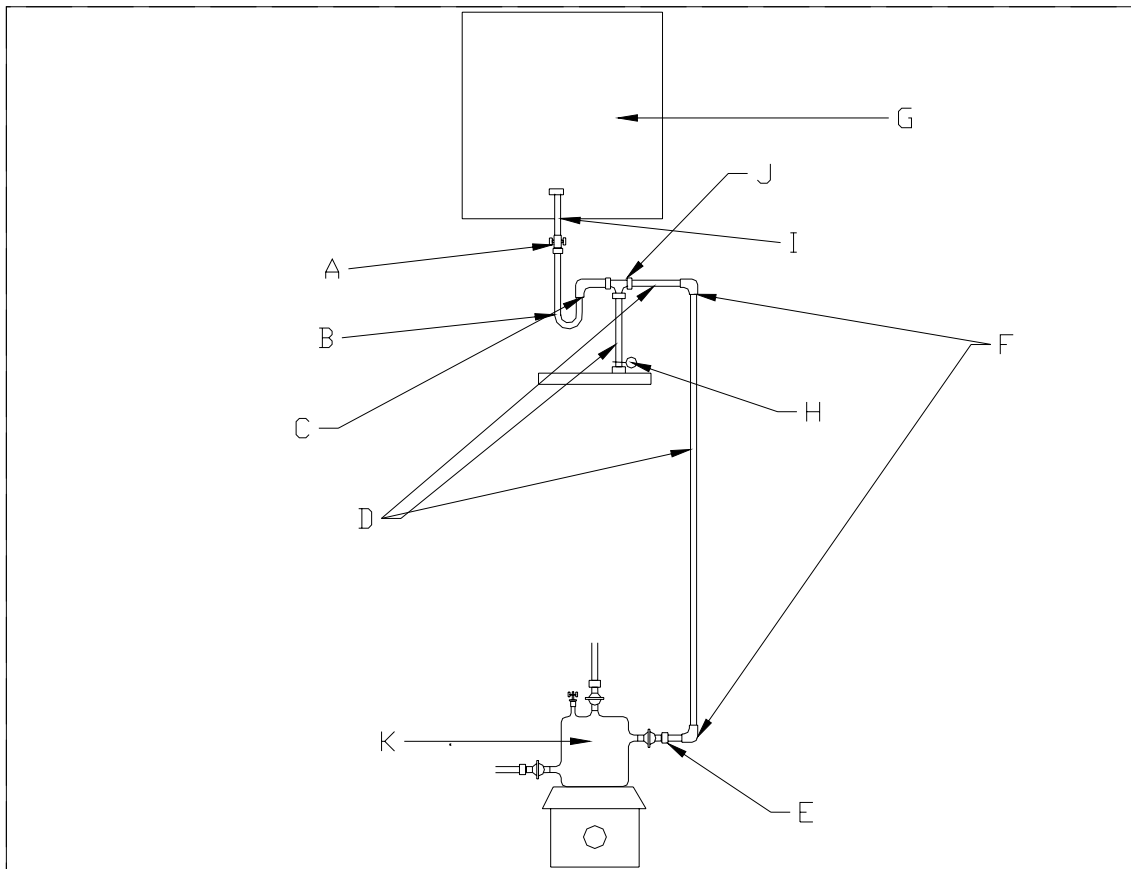


Figure 5. Gas Collection System. A, SGE syringe valve SLLV; B, Teflon lined tygon tubing; C, male luer x barb; D, Kynar tubing; E, Brass vibra-timer male straight adapter w/ kynar elbow adapter; F, Female brass elbow; G, 20-L gas bag; H, JN series screwed bonnet needle valve; I, Kynar tubing w/ ETFE shut-off valve and ETFE female luer adapter; J, Brass Swadgelock male tee; K, Leachate collection vessel

2.3 Reactor Setup

The reactors were filled on April 5, 2002. All reactors had a piece of fiberglass fabric placed on the bottom to cover the leachate drain, followed by a thin layer of gravel. The purpose of the fabric and gravel was to try to prevent the drain from clogging. The reactors were then filled with refuse to approximately 2" from the top. Refuse was added and compacted in 5" lifts. The leachate inoculum was then added to each reactor in varying amounts with no reactor getting less than 1 liter. The contents of each reactor are presented in Table 4. Each reactor in each treatment received the same amount of leachate. Only 500 mL of leachate was added to the leachate controls. Additional leachate was added to any reactor as required to ensure that there was adequate leachate for recirculation. If less than 100 mL of leachate drained into the leachate collection vessel, then another 500 mL was added.

To begin filling a reactor containing MSW, the shredded refuse was mixed in a large bin. The individual components used in the paper and yard waste reactors were weighed and then mixed prior to filling. The food waste reactors were operated in a fed batch mode because the addition of a large amount of food waste would result in an inhibitory acid accumulation and pH decrease. Thus, initially the food waste reactors were filled with 1000 mL of leachate and 360 wet grams of food waste. Prior to food waste addition it was thawed and pureed with a commercial blender. Subsequent food waste additions were made by syringe injection into a mininert valve installed for this purpose. This made it

possible to add substrate without removing the reactor top. A schedule of food waste additions is presented in Table 5. A sub sample of each treatment was taken for initial moisture content measurement and solids analysis.

Table 4 Reactors Contents^a

Treatment	Constituent	Average Moisture %	Wet Weight (gm)	Dry Weight (gm)	Leachate Added (L)	Total Water Volume ^b
Aerobic 1		20.85	1009.10	798.7	1.5	1698.79
Aerobic 2		20.85	972.10	769.42	1.5	1691.50
Aerobic 3		20.85	782.90	619.67	1.5	1654.23
Mixed Paper 1	OCC	0.0		420.10	1.5	1500.00
	ONP	0.0		201.20		
	OMG	0.0		70.40		
	OFF	0.0		150.20		
	Third Class Mail	0.0		153.70		
Mixed Paper 2	OCC	0.0		383.10	1.5	1500.00
	ONP	0.0		183.80		
	OMG	0.0		63.82		
	OFF	0.0		138.25		
	Third Class Mail	0.0		145.60		
Mixed Paper 3	OCC	0.0		398.70	1.5	1500.00
	ONP	0.0		189.50		
	OMG	0.0		66.90		
	OFF	0.0		143.20		
	Third Class Mail	0.0		151.30		
Yard Waste 1	Branches	16.4	200.60	167.74	2	1594.91
	Grass	26.2	400.50	295.79		
	Leaves	7.7	200.60	185.09		
Yard Waste 2	Branches	16.4	146.7	122.67	2	1569.44
	Grass	26.2	292.9	216.32		
	Leaves	7.7	147.1	135.72		
Yard Waste 3	Branches	16.4	189.50	158.45	2	1577.66
	Grass	26.2	301.10	222.38		
	Leaves	7.7	150.40	138.77		

Table 4. (contd.)

Treatment	Constituent	Average Moisture %	Wet Weight (gm)	Dry Weight (gm)	Leachate Added (L)	Total Water Volume ^b
MSW 1		20.85	964.60	763.48	1	1199.67
MSW 2		20.85	1113.70	881.49	1	1230.54
MSW 3		20.85	1259.20	996.66	1	1260.65
MSW with HHW 1		20.85	1001.50	792.69	1	1202.30
MSW with HHW 2		20.85	1002.50	793.48	1	1202.51
MSW with HHW 3		20.85	1000.90	792.21	1	1202.18
MSW under NO ₃ ⁻ reducing Conditions 1		20.85	1211.90	959.22	1	1276.31
MSW under NO ₃ ⁻ reducing Conditions 2		20.85	995.80	788.18	1	1227.04
MSW under NO ₃ ⁻ reducing Conditions 3		20.85	1376.90	1089.82	1	1313.93
Food Waste 1		59.5	495.60	200.74	2	1294.88
Food Waste 2		59.5	499.00	202.12	2	1296.91
Food Waste 3		59.5	493.20	199.77	2	1293.45
Leachate Control 1		na			.5	
Leachate Control 2		na			.5	
Leachate Control 3		na			.5	

a. The percentages of the individual components added to some of the reactors were calculated based on the 1998 Update Waste Characterization Report, as described in Appendix A.

b. The total water is the initial moisture content plus the leachate added to each reactor

Table 5 Food Waste Addition Schedule

Days from Start	Food Waste Added (wet grams)
0	360
20	130
30	130
40	130
50	130
60	130

Once full, a second piece of fiberglass fiber was placed on the top of the refuse except for the food waste reactors. This was done to help evenly distribute recycled leachate over the refuse. Steel rods were placed in pre-drilled holes on the top and bottom plates of the reactors. Dow Corning high vacuum grease (Dow Corning, Midland, Mich.) was then placed on 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 rod. Each reactor was then evacuated to less than 200 mbar and the vacuum monitored for 5 minutes to insure that leaks were not present. After leak checking, 20-L gas bags were placed on each reactor and leachate was added to the leachate collection vessel and recycled to initiate the experiment.

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 finally a DI water container to humidify the air. The DI water container was then attached to an aluminum manifold (McMaster-Carr, Atlanta, Ga.) and then to three flow meters. Each flow meter was attached to a water trap to prevent any leachate that might drain out of the air port from reaching the flow meters.

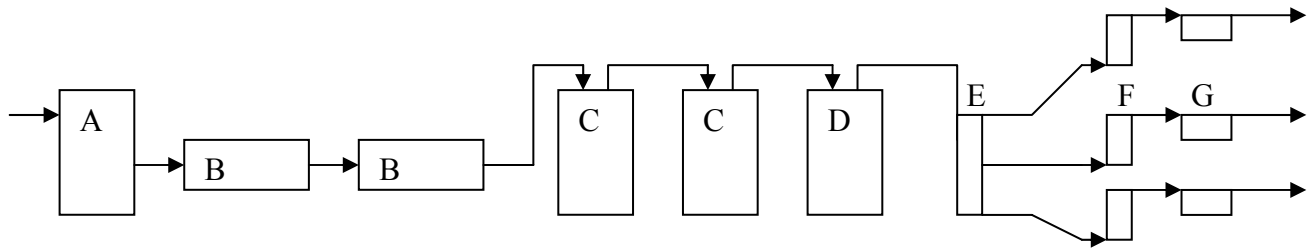


Figure 6. Air flow system for aerobic reactors. A, Regulator attached to lab air system; B, Koby Junior King filters in series; C, 5N KOH traps; D, DI water; E, aluminum manifold; F, flow meter; G, water trap. All tubing used to connect all components was Teflon coated tygon tubing. A detailed parts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

2.4 Reactor Operation and Monitoring

Reactors were monitored for leachate production, pH and COD, and gas production and composition. In addition air flow as monitored in the aerobic reactors. Reactor operating procedures are described in this section. Routine operation of the anaerobic reactors is described first, followed by exceptions for the aerobic, nitrate-reducing, and food waste reactors.

2.4.1 Anaerobic Reactors

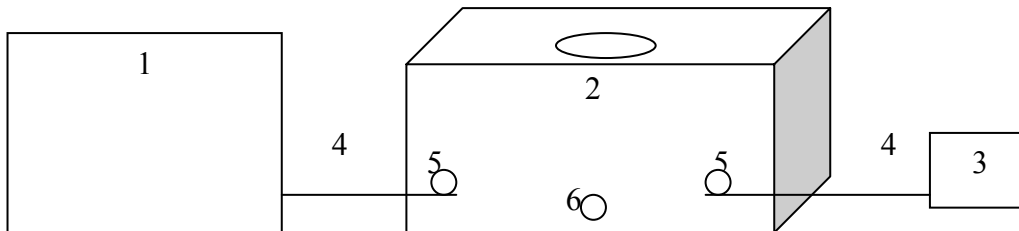
Leachate pH was monitored and maintained in the neutral range, between 6.8 and 7.5, for all reactors. Initially, the pH was measured daily. Once the pH stabilized in the neutral range it was checked weekly. The leachate was stored in the reactor for most of each day. To check the pH and then recycle it, the leachate was allowed to drain into the leachate

collection vessel for a few minutes and then the pH was checked and neutralized, if necessary. 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 was below 6.8 then it was neutralized with 5 M NaOH. Once neutralized, the leachate sub-sample was added back to the leachate collection vessel through the miniert valve and leachate was recirculated back to the reactor. A sample of leachate was taken from each reactor once a week for the first two weeks and then every second week thereafter for a COD measurement.

Gas composition for each reactor was measured once the 20 L aluminum tedlar bag approached its capacity or in some cases more frequently to obtain more data. Gas bags were sampled for NMOCs, VOCs, carboxylic acids and CH₄/CO₂. The procedure for handling a gas bag to accomplish each analysis is described here. First, a sample was removed from the bag by a syringe for analysis of CH₄, CO₂, O₂, and N₂. 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 placing an evacuated 10-L gas bag in the VAC-U-Chamber and then evacuating the chamber at a rate of 2 L/min for 5 minutes. Then, gas was allowed to flow from the large gas bag to the smaller gas bag. This procedure results in the transfer of 2-4 liters of gas to the smaller gas bag for NMOC analysis. This transfer

system is illustrated in Figure 7. NMOC analysis was performed by EPA Method 25C. Triangle Environmental Services (Research Triangle Park, NC), an EPA certified laboratory, conducted this analysis.

Figure 7 NMOC Transfer System



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

After a sample was transferred for NMOC analysis, a sample was preserved for carboxylic acids or volatile fatty acids (VFA) analysis. 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 100 mL/min for 10 minutes. Orbo tubes were

placed directly downstream of the gas bag. They were connected to the gas bag by a luer lock fingertight fitting that was connected to 1/8" OD kynar tubing. The tubing opposite the fingertight fitting was then connected to a 1/8" x 1/4"-28 female-male luer assy (Upchurch Scientific, Oak Harbor, WA.) which allowed one end of the orbo tube to be attached. The other end of the orbo tube was attached to a piece of tygon tubing and then attached to the SKC pump with a flow adjuster. Each bag was sampled in duplicate. VFA analysis is described in the analytical methods section.

Finally, the gas remaining was analyzed by GCD for specified trace organics as described in section 2.6.

The total volume in a gas bag was the sum of the volumes removed for NMOC analysis, VFA analysis, GCD analysis and the residual. The volume removed for NMOC analysis was reported by TES. The volume for VFA analysis was known from the pump flowrate and pump time. The volume for GCD analysis was known from the sample volume specified. The volume remaining was analyzed by a special chamber described in the analytical section.

The final step that occurred after all analyses were completed involved cleaning the gas bag. To accomplish this, each gas bag was flushed with ultra high purity nitrogen and then heated at 60 °C for 30 minutes. After heating the gas bag was evacuated and the procedure was repeated.

2.4.2 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 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 anytime it generated less than 500 mL of leachate. A list of post startup water additions is presented in Table 6.

Table 6 Water Additions for Aerobic Reactors (mL)

Date	Days from Start	Water Addition to Reactor 1	Water Addition to Reactor 2	Water Addition to Reactor 3
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

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, 20 L gas bags were placed on each reactor 5 times a days for 10 minutes to obtain a composite gas sample. This process was conducted daily until a gas bag was full at which point it was processed as described for the anaerobic reactors. In addition, the exit gas flow rate was measured five times a day so that an average gas flow rate could be used for CO₂, NMOC and VOC gas production rate calculations. Finally, the CO₂ concentration was measured twice a day and chromatograms were reviewed to verify the absence of methane production. After 48 days, air additions were discontinued and the reactors were treated as

anaerobic reactors. The procedures for the collection and processing of leachate and gas samples is as described previously.

Airflow rates for the aerobic reactors were measured five times a day at the effluent gas sampling port. To accomplish this a digital bubble flowmeter (model 650, Fisher Scientific, Pittsburgh, PA.) was used. Temperature readings were also recorded once a day to make sure that the aerobic reactors was not overheating, killing the bacteria. This was done through a specially drilled hole in the top of the reactor that was just large enough for a thermometer. The hole was sealed by a stainless steel plug when not open for a temperature reading.

2.4.3 Nitrate-Reducing Reactors

The next set of reactors with unique operating conditions were the nitrate-reducing reactors. 400mg/L of $\text{NO}_3^- \text{N}$ was added every second or third day to maintain nitrate-reducing conditions. The nitrate was added as either KNO_3 or $\text{Mg}(\text{NO}_3)_2$. The reason for adding two different forms of NO_3^- was to prevent the build up of salts in the leachate. The switch occurred once the Mg^{+2} concentration reached between 1000 – 2000 mg/L and the K^+ concentration reached between 5000 – 8000 mg/L based on results published by Kugleman and Chin (1971). Once both salt levels had been reached, the reactors were drained and then flushed once with 500mL of DI water. Once the reactors had been

flushed with DI water, an additional 500 mL of DI water was added and nitrate additions continued. A schedule of nitrate additions and reactor flushing is presented in Table 7. Leachate was monitored for nitrate to ensure that reactors were depleting nitrate and that nitrite was not accumulating. Other aspects of the operation and monitoring the nitrate-reducing reactors were similar to that of the anaerobic reactors.

Table 7 Schedule of Nitrate Additions and Flushings

Days	Nitrate Added (Calculated) (mg NO ₃ -N/L)	Form of Nitrate added
0	0	KNO ₃
0	400	KNO ₃
2	400	Mg(NO ₃) ₂
4	400	Mg(NO ₃) ₂
6	400	Mg(NO ₃) ₂
8	400	Mg(NO ₃) ₂
11	400	Mg(NO ₃) ₂
12	400	Mg(NO ₃) ₂
15	400	KNO ₃
17	400	KNO ₃
19	400	KNO ₃
21	400	Mg(NO ₃) ₂
23	400	Mg(NO ₃) ₂
26	400	Mg(NO ₃) ₂
28	400	Mg(NO ₃) ₂
31	400	KNO ₃
34	400	KNO ₃
38	400	KNO ₃
40	400	KNO ₃

Flushed w/ 500 mL DI

Table 7 (contd.)

Days	Nitrate Added (Calculated) (mg NO ₃ -N/L)	Form of Nitrate added
43	400	KNO ₃
45	400	KNO ₃
47	400	Mg(NO ₃) ₂
49	400	Mg(NO ₃) ₂
51	400	Mg(NO ₃) ₂
53	400	Mg(NO ₃) ₂
55	400	Mg(NO ₃) ₂
57	400	Mg(NO ₃) ₂
58	400	KNO ₃
61	400	KNO ₃
63	400	KNO ₃
65	400	KNO ₃
66	400	KNO ₃

Flushed w/ 500 mL DI

2.4.4 Food Waste Reactors

The food waste reactors were operated in fed batch mode to prevent an accumulation of acidic decomposition intermediates. After the initial amount of food waste was added and the leachate pH stabilized, another batch of food waste was added. Food waste was added approximately every 10 days in 130 g increments. This number was selected so to not cause an acid accumulation. Prior to its addition, food waste was thawed and pureed with a commercial blender. Food waste was added by syringe injection through a mininert valve. This made it possible to add substrate without removing the reactor top. Food waste was

added on days 0, 20, 30, 40, 50 , and 60. After a total of six additions, food waste additions were terminated to allow time to review the available data.

2.6 Analytical Methods

2.6.1 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 as presented in Table 8. A three point standard curve was set up using the gas compositions, given in Table 9. Once the standard curve was established one standard was injected every time the GC was used. If the sample standard was within 5% of the initial curve then the initial standards could be used. If not, then a new standard curve was developed.

Table 8 Settings for GOW-MAC

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

Table 9 Standards Used to Produce GOW-MAC Standard Curve

Standard	% CH₄	% CO₂	% N₂	%O₂
1	10	20	70	0
2	50	40	10	0
3	25	10	1	1

2.6.2 NMOC Analysis

NMOC analysis was performed by EPA Method 25C by Triangle Environmental Services. All samples, including standards were run in triplicate. The GC model and settings used for analysis are presented in Table 10. The NMOC concentration is then reported as milligrams of carbon per cubic meter.

Table 10 Settings for 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

2.6.3 Trace Constituents Analysis

Trace constituents were analyzed by using a Tekmar Autocan Sampler, Model # 14-ACAN-000 and Hewlett Packard G1800A GCD System series gas chromatograph with an electron ionization detector. Settings used for the GCD are presented in Table 11.

Table 11 Settings for GCD

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

2.6.4 Carboxylic Acids Analysis

Carboxylic acids were trapped on orbo tubes and then eluted off with DI water. At the time of this writing, this procedure had not been fully developed.

2.6.5 Nitrate Analysis

Nitrate (NO_3^-) 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 and then a conditioned C18 cartridge (Alltech #20936) and 25 mm syringe filter were placed on the end of the syringe. 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.

2.6.6 COD Analysis

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

2.7 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) by equation 2. The gas volume measurement apparatus consisted of a stainless steel cylinder that was sealed with two ports. One port was connected to a vacuum pump and the other port was connected to a manometer and then to a gas bag. Each port is equipped with a ball valve.

$$V_s = (P_i - P_f) * V_c / P_a \quad (\text{Equation 1})$$

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

2.8 Data Analysis

The methane production rate was calculated by equation 2.

$$\text{mL CH}_4 @\text{STP/day} = (\% \text{CH}_4 \times V_s) / \# \text{ of days} \quad (\text{Equation 2})$$

V_s = Gas volume after correction to STP

% CH_4 = Concentration of methane on a volume basis

of days = Sampling period

For the aerobic reactors the CO_2 production rate was calculated based on Equation 3. The gas volume was calculated from an average gas flow rate multiplied by the time of the sampling period. The gas flow rate was the average of 5 daily measurements.

$$\text{mL CO}_2 @\text{STP/day} = (\% \text{CO}_2 \times V_s) / \# \text{ of days} \quad (\text{Equation 3})$$

V_s = Gas volume after correction to STP

% CO_2 = Concentration of carbon dioxide on a volume basis

of days = Sampling period

V_s was calculated from the average gas production rate multiplied by the time period for the rate calculation.

The NMOC production rate was also calculated for this experiment using the mass concentration given by TES. This calculation is illustrated by equation 4.

$$\text{mg C/day} = (\text{mg C/m}^3) * (1\text{m}^3/1000\text{L}) * V_s / \# \text{ of days} \quad (\text{Equation 4})$$

mg C/m^3 = NMOC mass concentration calculated by TES

V_s = The volume produced by a reactor corrected to STP

of days = Sampling period

The Corrected NMOC yield was calculated using equation 5.

$$\text{mg-C/dry gram} = (M_c * \text{NMOC Yield}_c - (\text{NMOC Yield}_L * \text{mL Leachate})) / \text{dry gram} \quad (\text{Equation 5})$$

mg C/dry gram = Corrected NMOC Yield after factoring in leachate seed

M_c = Dry grams in reactor

NMOC Yield_c = NMOC Yield from reactor

NMOC Yield_L = NMOC Yield from leachate controls (mg C/mL leachate)

mL Leachate = Volume in an individual reactor

3.0 Results

The results of preliminary work to evaluate gas volume measurements and gas sample storage are presented in the first part of this section. This is followed by the results for each set of reactors through day 73.

3.1 Gas Bag Storage

Preliminary tests were performed on two gas bags to test holding time. This was done to evaluate the stability of samples in gas bags as bags generally remained on a reactor for a week or more. To perform this test, two 20-L gas bags were used. Each gas bag was filled with gas from the 30 gallon drum containing refuse used to generate the leachate inoculum. Gas samples were analyzed for NMOCs within 1 day of collection and again after storage in the bags for 7 days. As presented in Table 12, there did not appear to be a trend towards significant NMOC loss on storage.

Table 12 Effect of Sample Storage on NMOC Concentration

Sample	NMOC Concentration (ppm)	% Difference (absolute value)
Sample 1 tested on 11/15/02	587	
Sample 1 tested one week later	619	5.5
Sample 2 tested on 11/15/02	112	
Sample 2 tested one week later	93	17

3.2 Gas Volume Measurement

To verify that the evacuation chamber functioned properly a test was performed to check the volume of gas measured when a known volume of gas was added to a gas bag. This was accomplished by adding 2-L of nitrogen to a gas bag using a 1 L air tight syringe. As presented in Table 13 there was good agreement between the injected and recovered gas volumes.

Table 13 Comparison of Measured and Recovered Gas Volumes

Trial	Recovered Volume (L)	Volume added (L)	% Error
1	1.97	2	1.5
2	1.95	2	2.5
3	1.99	2	0.5
4	1.99	2	0.5

3.3 Aerobic/Anaerobic Reactors

The aerobic reactors were aerated for 44 days after which they were allowed to turn anaerobic. The carbon dioxide production rate for the aerobic period is presented in Figure 8. After about 35 days, the carbon dioxide production rate was nearly zero, which suggests that aerobic decomposition was complete. The results shown in Figure 8 were calculated based on the average effluent gas flow rate, which was measured 5 times a day, and gas composition data that was collected twice daily. The yield was also calculated using the carbon dioxide concentration in the gas bag used to collect a weekly composite sample for NMOC analysis as described in section 2.4.1 and the weekly average gas flow rate calculated from daily averages. The yields based on these methods are compared in Table 14. The difference in yields ranges from 9.5% to 11.7% and reflects the fact that the total volume of gas produced was not all collected, but was rather estimated from gas production rate data.

The NMOC production rate is presented in Figure 9. As illustrated by Figure 9, the NMOC production rate was highest in the first 10 days of the experiment and then decreased. The NMOC yields for these reactors were: 0.266, 0.224, and 0.203 mg NMOC-C/dry g. These yields will be compared to the yields for refuse decomposed under anaerobic conditions in the Discussion.

The temperature in each reactor is displayed in Figure 10. These data illustrate that mesophilic temperatures were maintained throughout the aerobic period. If the temperature was too high ($> 60^{\circ}\text{C}$), then that would inhibit microbial activity. The increase that occurred between day 20 and 22 occurred when a problem occurred with the air flow system. The air supply system clogged and air flow stopped. The continued elevated temperature after day 25 cannot be explained. As planned, sufficient air was provided to eliminate an inhibitory temperature increase. In addition, sufficient air was maintained to maintain greater than 1% O_2 in the effluent stream. The O_2 concentration versus time is illustrated in Figure 11. As illustrated, O_2 consumption decreased with time as decomposition occurred.

The pH is presented in Figure 12. Figure 12 illustrates that the optimal pH for refuse decomposition in each reactor was met. There was a consistent pH decrease in each reactor during the transition from aerobic to anaerobic conditions. One possible explanation is an increase in carboxylic acid concentrations associated with the onset of anaerobic conditions through data are not available to confirm this explanation.

The volume of water added to each reactor is presented in Table 15. Water was added to an aerobic reactor if leachate production was below 500 mL. This strategy was adopted to ensure that the refuse did not become too dry for microbial activity.

On day 67, or 23 days after the air flow was stopped, there was no measurable gas was in the gas bag. However, a sample of gas was analyzed to determine if methane was present. The day 67 methane composition was 7.60%, 8.51%, and 9.47% in 3 aerobic reactors respectively. The methane concentration is expected to increase with time.

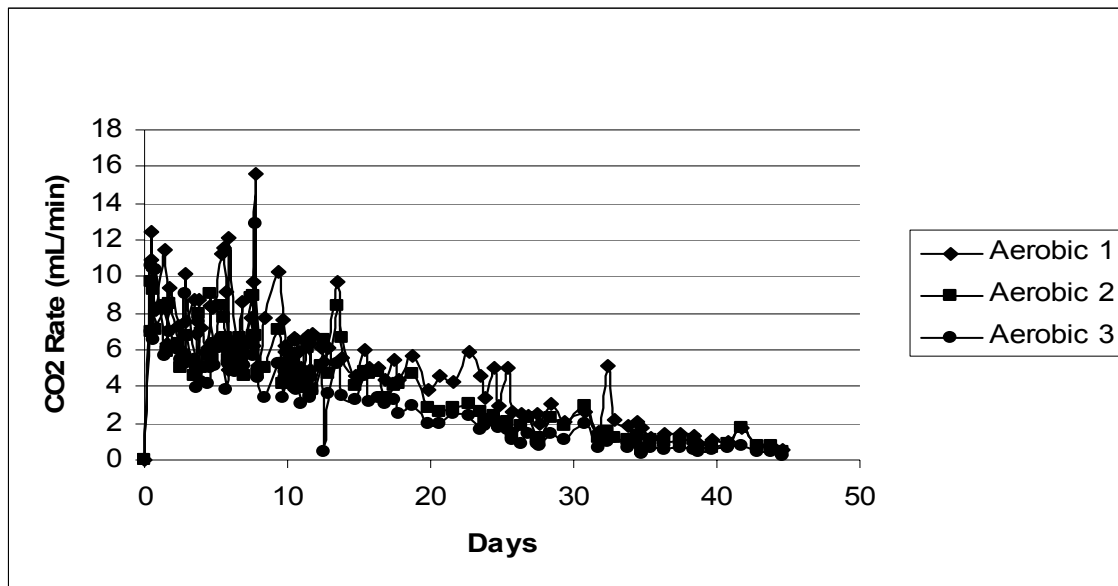


Figure 8. Carbon Dioxide Production Rate for Aerobic Reactors

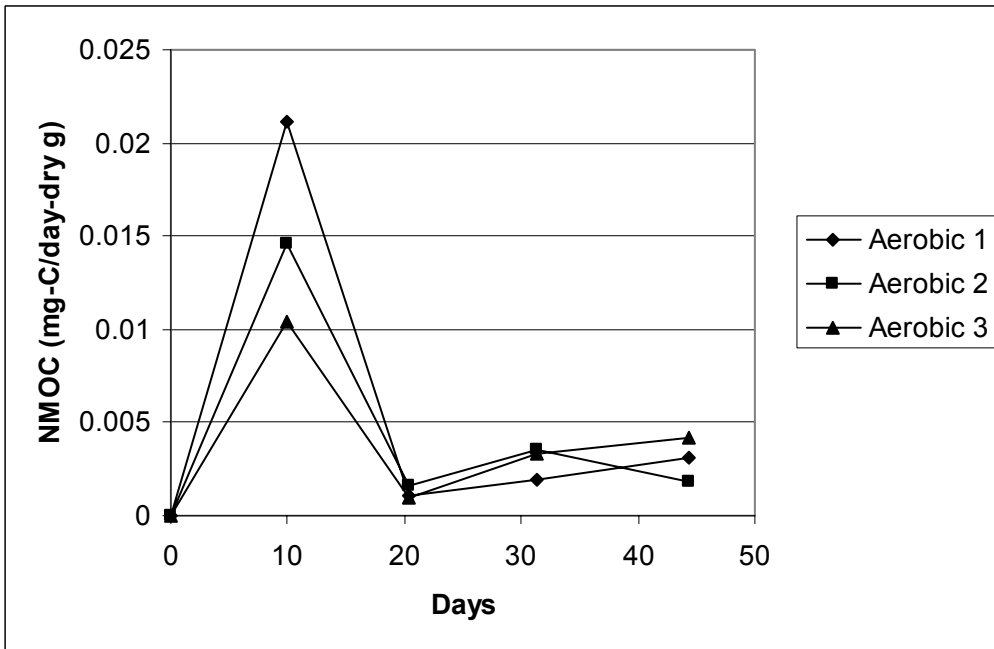


Figure 9. NMOC Production Rate for Aerobic Period

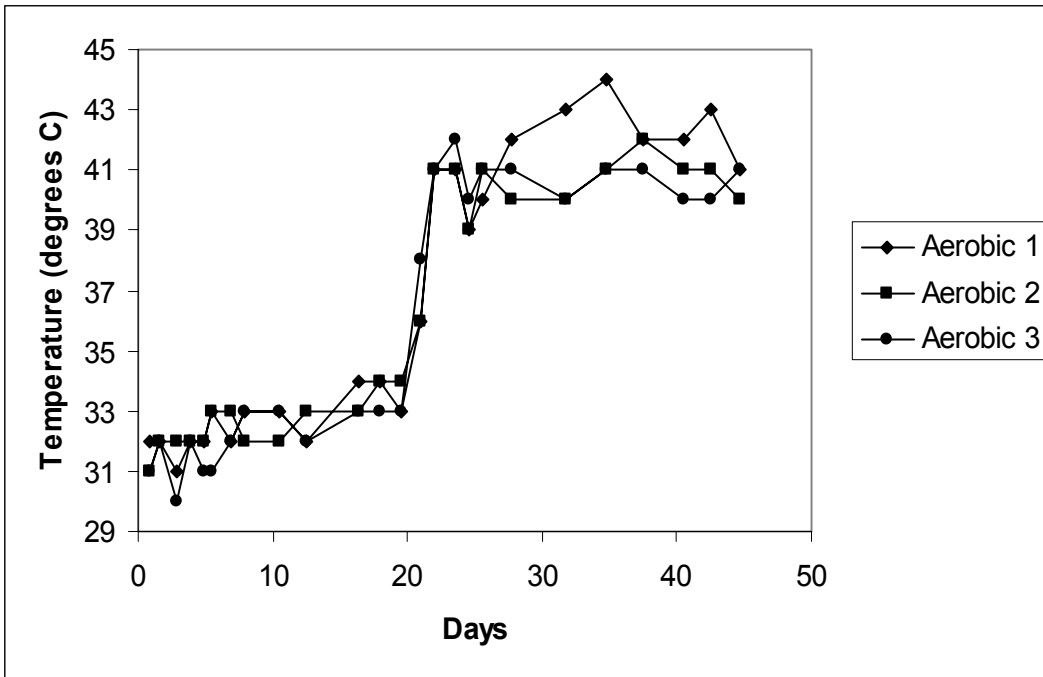


Figure 10. Refuse Temperature in the Aerobic Reactors

Table 14 Comparison of CO₂ Yields from Daily and Composite Measurements^a

Reactor	Daily Measurement	Composite Measurement
1	358.02	316.16
2	282.71	253.64
3	274.23	302.85

a. Data in mL CO₂/dry gm

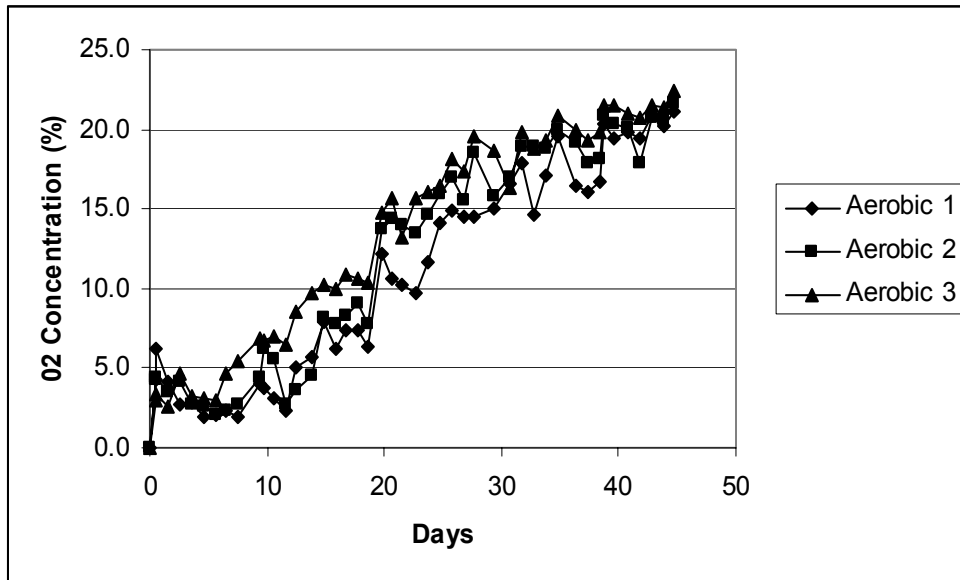


Figure 11. %O₂ in Effluent Gas of Aerobic Reactors during Aerobic Period

Table 15 Water Additions During Operation (mL)

Day	Reactor 1	Reactor 2	Reactor 3
0			
6	100		200
18		400	
44	300	200	100

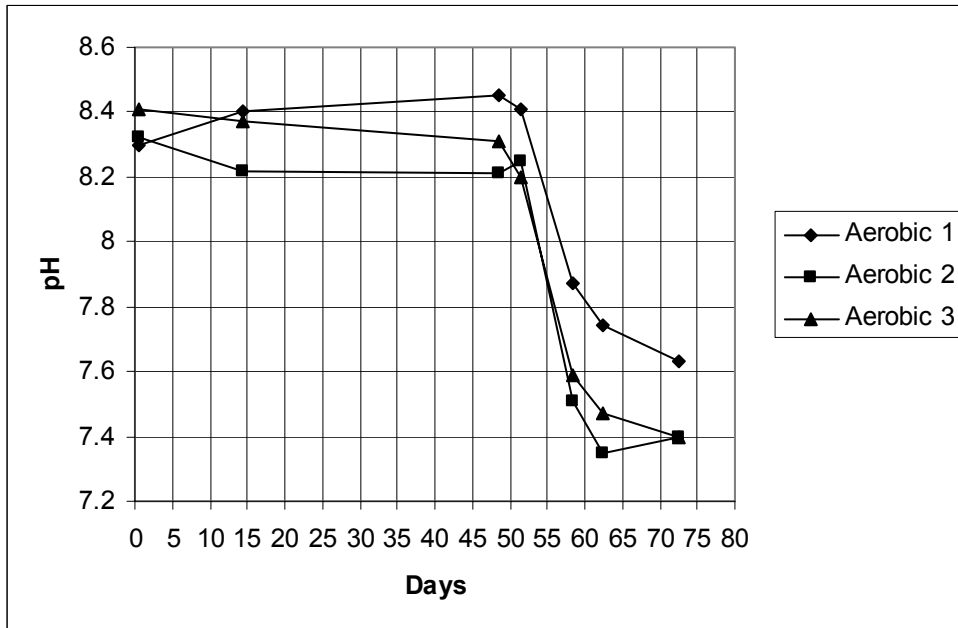


Figure 12. Leachate pH for Aerobic/Anaerobic Reactors

3.4 Nitrate Reducing Reactors

Nitrate was added to the nitrate-reducing reactors every 2-3 days to evaluate refuse decomposition under nitrate-reducing conditions. Figure 13 illustrates the nitrogen production rates, which indicates that nitrate reduction is occurring. The N_2 yields for the three reactors were: 8.72, 9.63, and 12.18 mL N_2 /dry g through day 68.

The purpose of the nitrate-reducing reactors was to get an idea of the effect of nitrate-reducing conditions on NMOC production, however in this experiment methane was also

produced. After 37 days, methane was detected in the gas. After 68 days, the methane yields were: 5.01, 2.32, and 12.57 mL CH₄/dry gm.

Nitrate concentrations are illustrated in Figure 14a – 14c. As illustrated, NO₃ was not completely consumed for the first 30 days. After 30 days, the reactors stabilized and nitrate was completely consumed within 2 days of each nitrate addition.

NMOC production rates are illustrated in Figure 13 though only 1 data point is available, due to the limited amount of data available at the time of this writing for two of the reactors. NMOC yields through day 68 were: 2.02*10⁻², 2.60*10⁻², and 4.39*10⁻² mg NMOC-C/dry gm.

The pH of each of the nitrate-reducing reactors is illustrated in Figure 15.

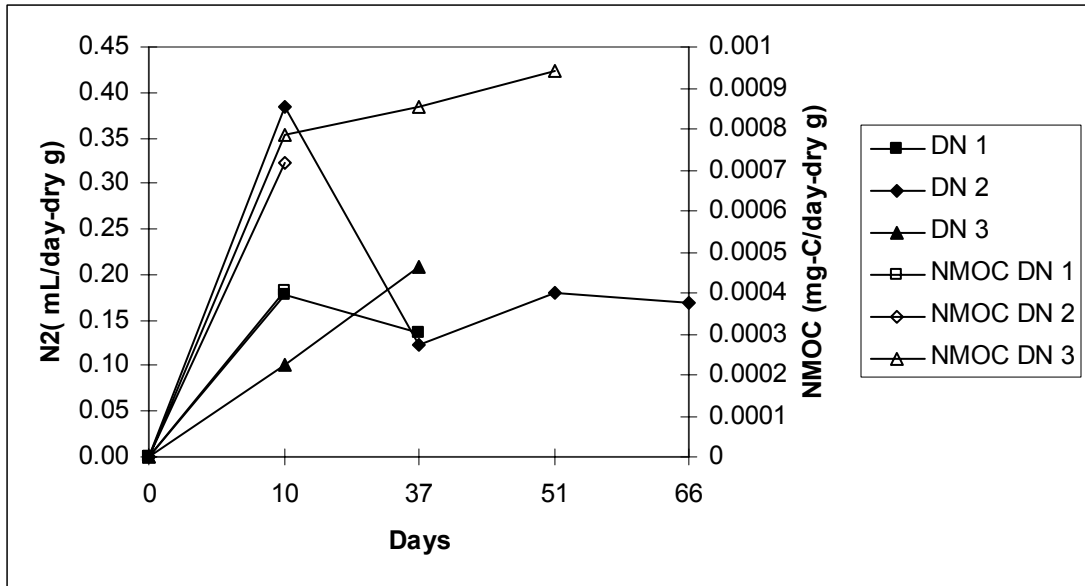


Figure 13. Nitrogen Production and NMOC Production Rates for Nitrate Reducing Reactors

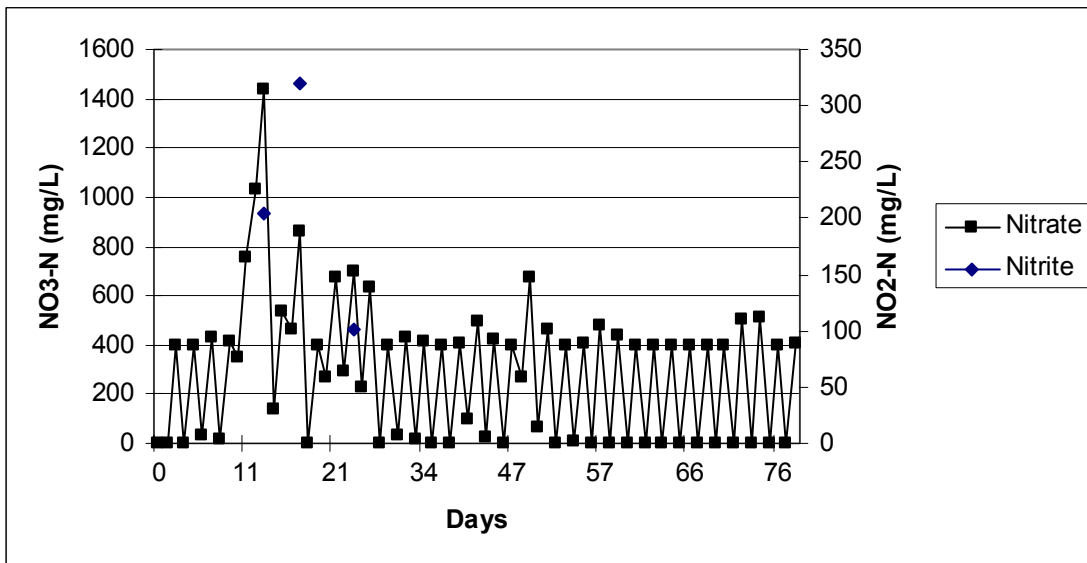


Figure 14a. Nitrate Analysis for Reactor 19

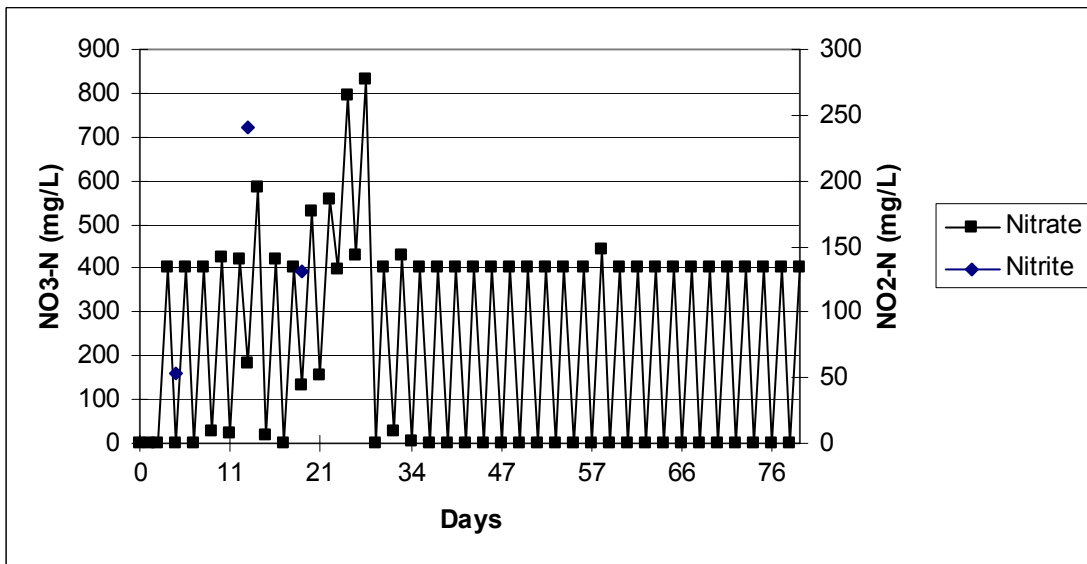


Figure 14b. Nitrate Analysis for Reactor 20

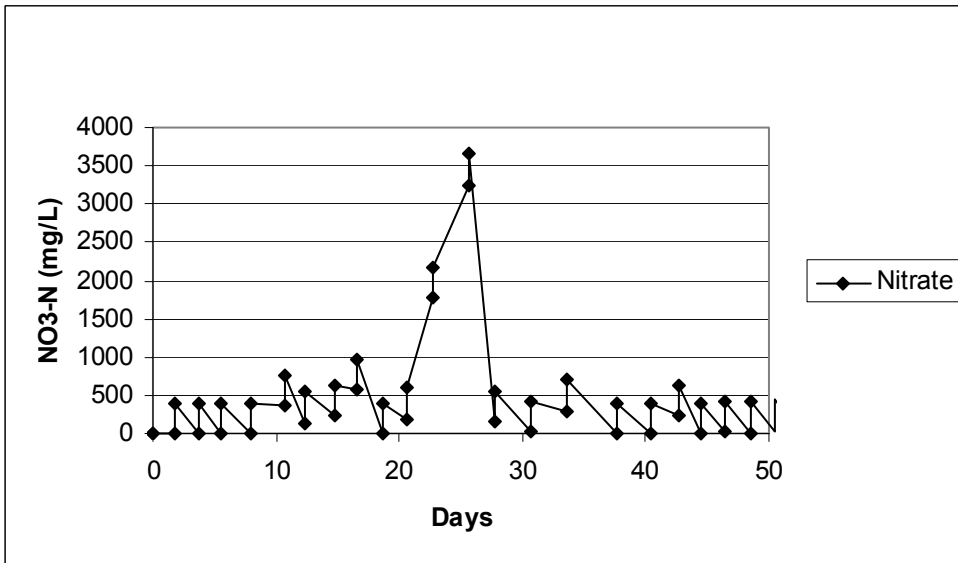


Figure 14c. Nitrate Analysis for Reactor 21

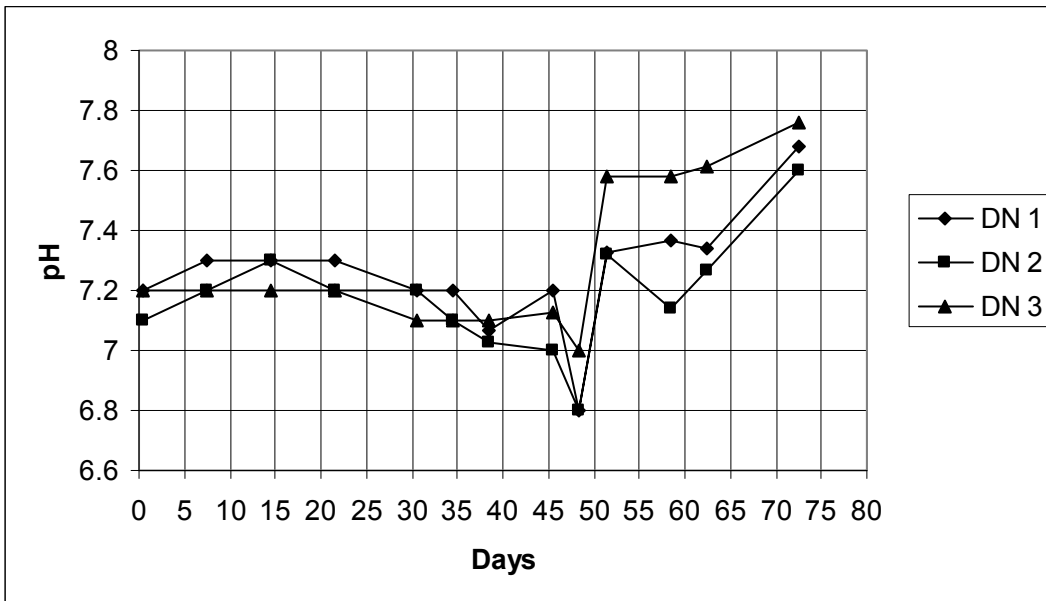


Figure 15. pH Data for MSW under Nitrate-Reducing Conditions

3.5 Anaerobic Reactors

In the following sections results for each anaerobic reactor treatment are presented.

3.5.1 Mixed Paper Reactors

The methane production rates for the mixed paper reactors are presented in Figure 16. As illustrated, methane production rates increased for 25 days and then began to decrease. The methane yield through day 73 is presented in Table 16. Also in Table 16 is a comparison of the yields measured in this research to previous work on pure paper components (Eleazer 1997). This comparison suggests that the yields in this experiment are comparable to previous work at the same stage.

The NMOC production rates are illustrated in Figure 16. The NMOC yields for mixed paper reactors 1-3 through day 73 were $1.25 \cdot 10^{-2}$, $4.59 \cdot 10^{-3}$ and, $5.24 \cdot 10^{-3}$ mg NMOC-C/dry g, respectively.

To illustrate that optimal pH conditions are met for methanogenic activity, Figure 17 displays the pH of each reactor.

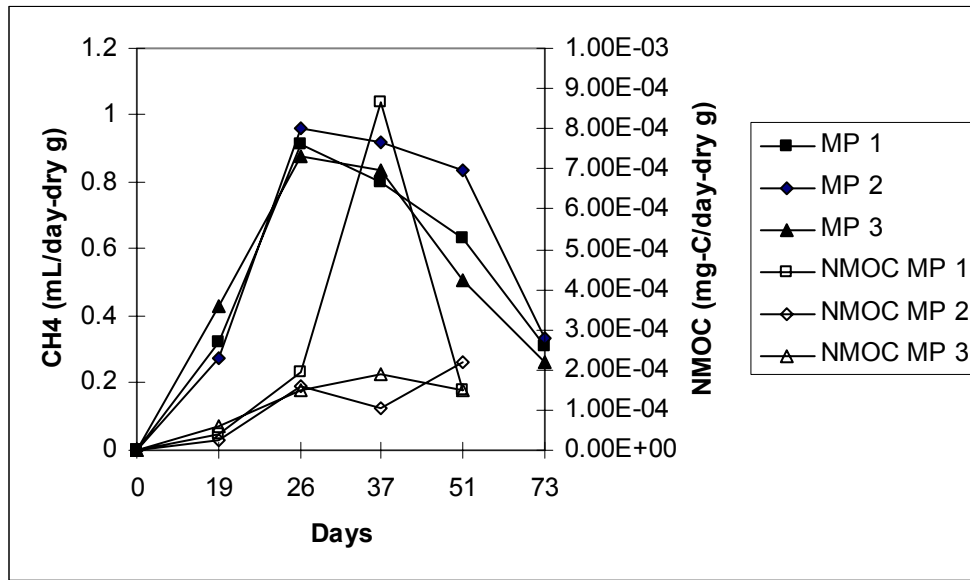


Figure 16. Methane Production and NMOC Production Rates for Mixed Paper Reactors

Table 16 Methane Yields for Mixed Paper Reactors and Ultimate Methane Yield from Eleazer (1997)^a

Reactor Type	Day	CH ₄ yield	Average Ultimate Yield for Eleazer
MP 1	66	35.22	
MP 2	73	41.43	
MP 3	73	36.75	
Eleazer Coated Paper	70	60	84.4
Eleazer ONP	70	15	74.3
Eleazer OCC	70	25	152.75
Eleazer OFF	70	20	217.3

a. Yields presented as mL CH₄/dry g

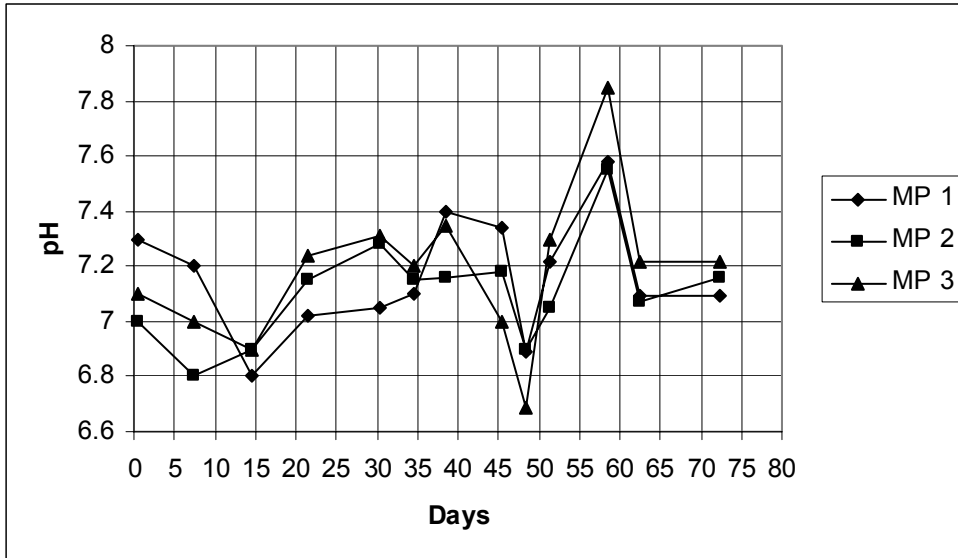


Figure 17. pH Data for Mixed Paper Reactors

3.5.2 Yard Waste Reactors

The methane production rate for the yard waste reactors is presented in Figure 18. The methane yield up to day 73 is presented in Table 17. Also in Table 17 is a comparison to the work done by Eleazer (1997) for individual yard waste components.

The NMOC production rate is illustrated in Figure 18. Figure 18 shows that methane and NMOC production rates follow the same trend. The NMOC yields for the yard waste reactors through day 73 are $1.51 \cdot 10^{-2}$, $1.12 \cdot 10^{-2}$ and, $1.71 \cdot 10^{-2}$ mg NMOC-C/dry g.

To illustrate that optimal pH conditions are met for methanogenic activity, Figure 19 displays the pH of each reactor.

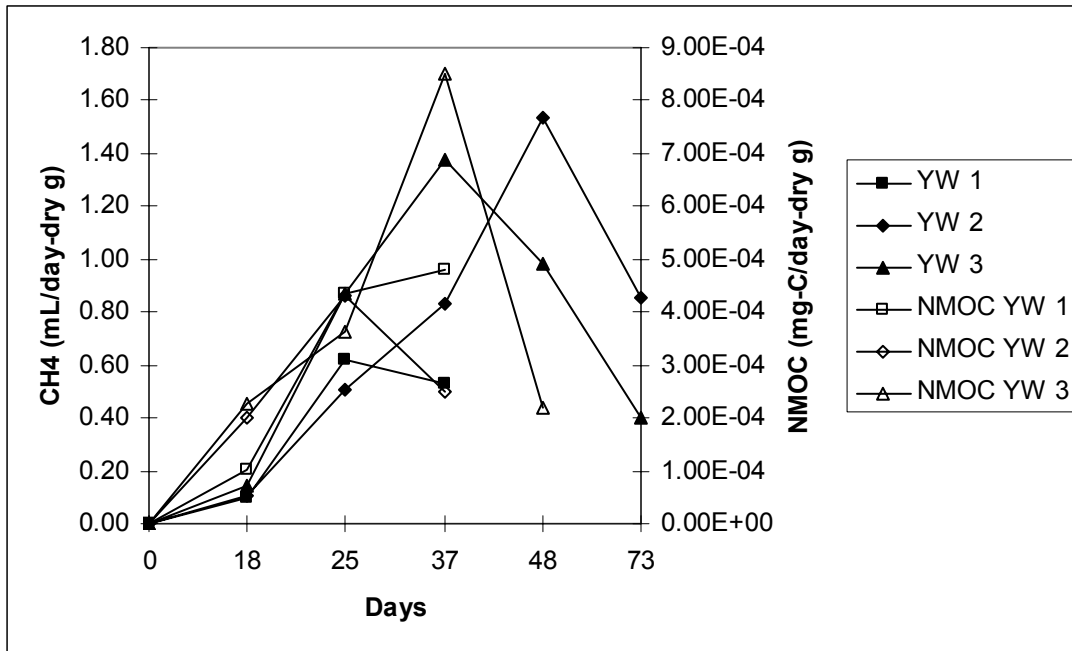


Figure 18. Methane Production and NMOC Production Rates for Yard Waste Reactors

Table 17 Methane Yields for Yard Waste Reactors and Ultimate Methane Yield from Eleazer (1997)^a

Reactor Type	Day	CH ₄ yield	Average Ultimate Yield for Eleazer
YW 1	50	19.9	
YW 2	73	52.13	
YW 3	73	45.54	
Eleazer grass	70	115	144.4
Eleazer branches	70	30	62.6
Eleazer leaves	70	20	30.6

a. Yields presented as mL CH₄/dry g

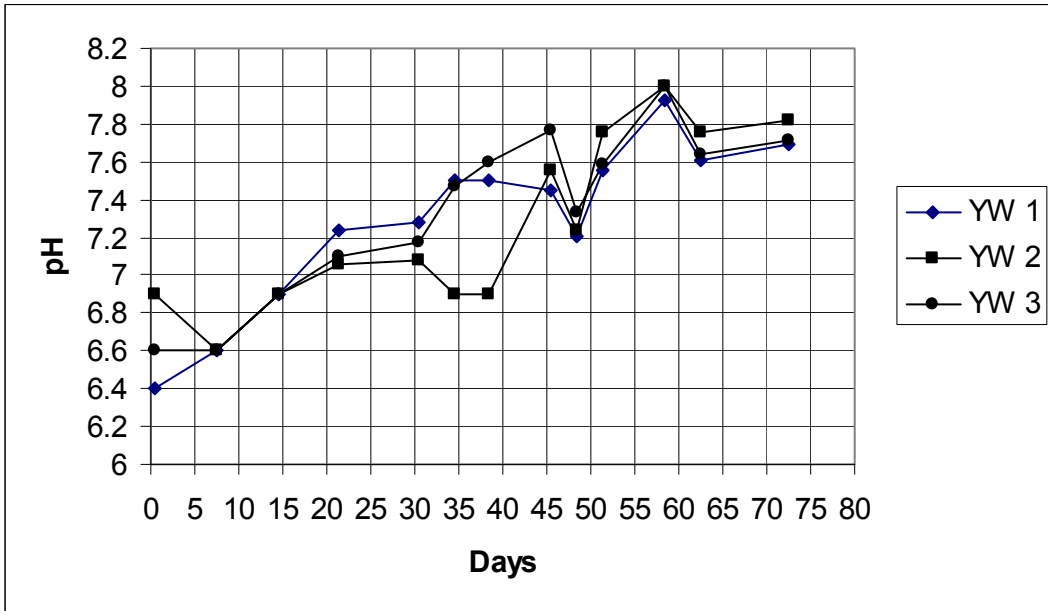


Figure 19. pH Data for Yard Waste Reactors

3.5.3 MSW Reactors

The methane production rate for the MSW reactors is presented in Figure 20. Figure 20 illustrates that refuse decomposition is occurring and methane production is increasing. The methane yield up to day 73 is presented in Table 18. Also in Table 18 is a comparison to the work done by Eleazer (1997). A comparison to methane yield up to 73 days cannot be made since in Eleazer’s work the onset of methane production did not occur until about 100 days. The ultimate yield from Eleazer illustrates that methane yield in this project is 50 – 75% of the yields reported by Eleazer.

The NMOC production rate is illustrated in Figure 20. Figure 20 illustrates that as methane production rate increases NMOC production increases. The NMOC yields for the MSW reactors through 73 days are 8.18×10^{-2} , 7.93×10^{-2} and, 4.85×10^{-2} mg NMOC-C/dry g.

To illustrate that optimal pH conditions were for methanogenic activity, Figure 21 displays the pH of each reactor.

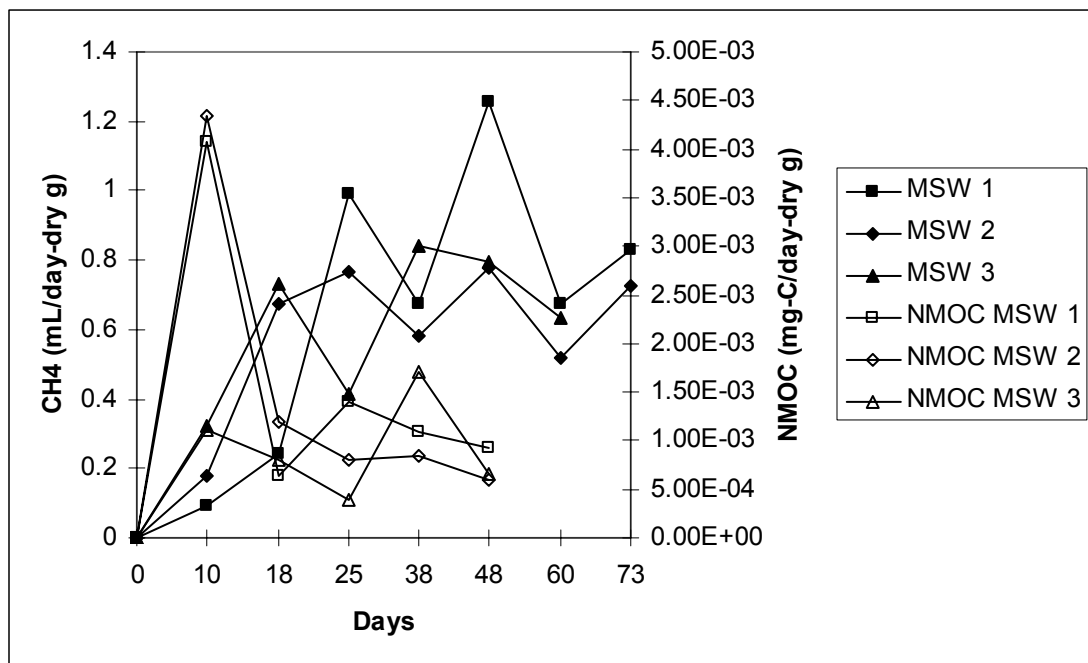


Figure 20. Methane Production and NMOC Production Rates for MSW Reactors

Table 18 Methane Yields for MSW Reactors and Ultimate Methane Yield from Eleazer (1997)^a

Reactor Type	Day	CH ₄ yield	Average Ultimate Yield for Eleazer
MSW 1	68	43.2	
MSW 2	73	48.28	
MSW 3	59	32.02	
Eleazer MSW	70	0.05	76.2

a. Yields presented as mL CH₄/dry g

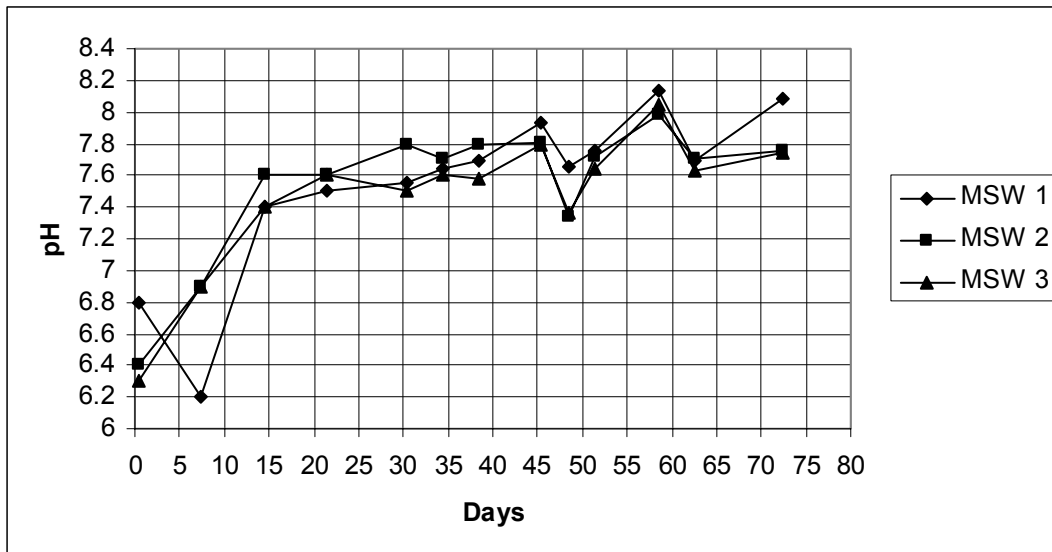


Figure 21. pH Data for MSW Reactors

3.5.4 MSW Plus HHW Reactors

The methane production rate for the MSW plus HHW reactors is presented in Figure 22. The methane production rates are quite low and suggest that they were inhibited through the first 73 days. Gas samples were collected infrequently due to the low gas production. The methane yields in the MSW plus HHW reactors up to day 73 were: 14.55, 3.91, and 3.86 mL CH₄/dry g, respectively.

The NMOC production rate is illustrated in Figure 22. A clear relationship between methane production and NMOC production is not clear from these data. The NMOC yields for the MSW plus HHW were: 6.38×10^{-2} , 2.46×10^{-2} , and 8.84×10^{-2} mg NMOC-C/dry g.

Figure 23 presents the pH of each reactor. The reactor pHs were sub optimal for about the first 40 days of the experiment despite daily leachate neutralization. Apparently, acid consuming bacteria were inhibited which kept the pH depressed. Although HHW concentrations in the leachate were not measured, their concentrations were calculated based on the mass of each component added and the total volume of water in each reactor. The concentrations added to the MSW plus HHW reactors are illustrated in Table 19. Of course, these concentrations assume complete mixing and neglect partitioning to the solid phase.

The concentrations of acetone and methylene chloride appear quite high. Blum and Speece (1991) created a database for chemical toxicity of 100 chemicals for 3 bacterial groups: aerobic heterotrophs, *Nitrosomonas*, and methanogens. The toxicity concentrations reported are concentrations at which 50% of the culture was inhibited compared to the uninhibited controls. The 50% inhibitory concentrations of benzene, toluene, ethylbenzene, methylene chloride and acetone are 1,200, 580, 160, 7.2, and 12,000 mg/L. Table 19 illustrates that the only compound that was above the 50% inhibition concentration is methylene chloride. Finally, no specific studies on motor oil toxicity were identified, though the concentration present could certainly have caused inhibition.

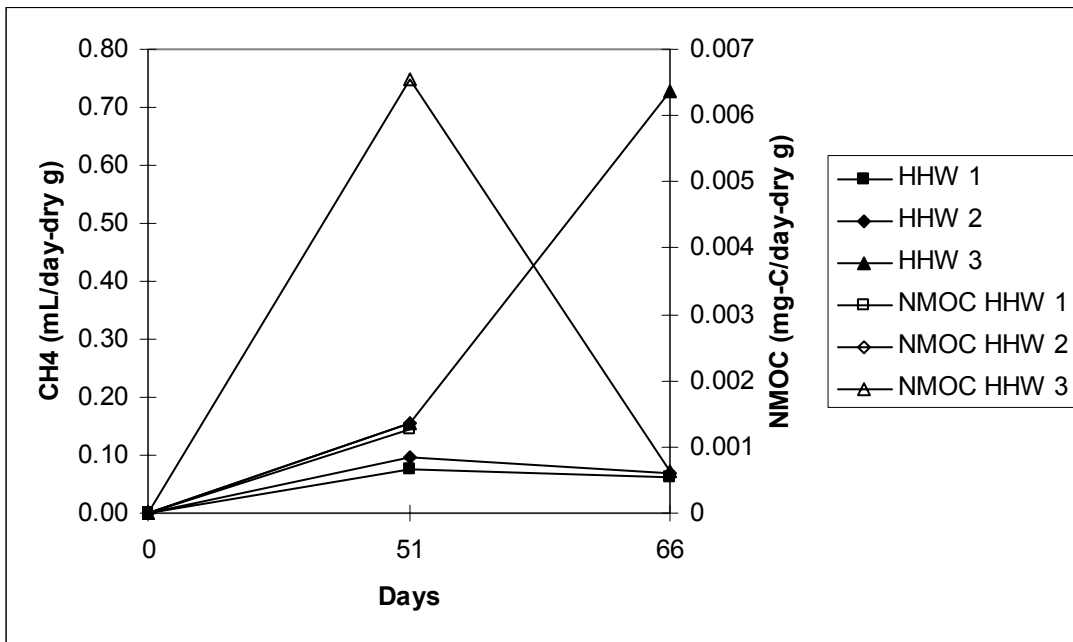


Figure 22. Methane Production and NMOC Production Rates for MSW plus HHW Reactors

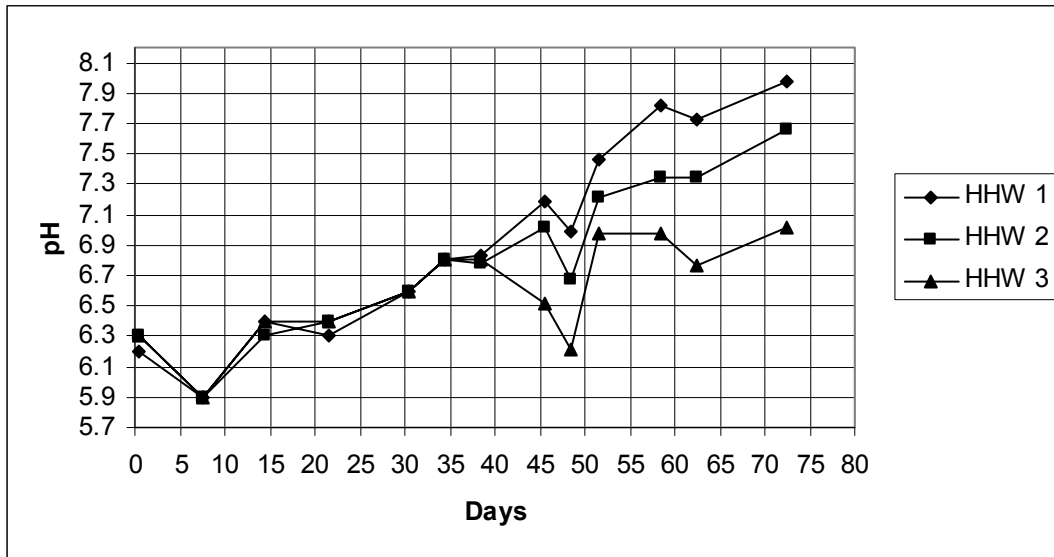


Figure 23. pH Data for MSW plus HHW Reactors

Table 19 Calculated Concentrations of Specific Organic Chemicals in HHW Reactors^a

HHW Component	Concentration (mg/L)
Acetone ^{b,c}	687.5
Methylene Chloride ^c	137.5
Toluene ^{c,d}	143
Benzene ^d	5.5
Ethylbenzene ^d	5.5
Motor oil-other ^d	533.5

- Concentrations were calculated by taking the (2000mg of HHW mixture added* .33*% of HHW component)/(% H₂O in refuse+Leachate added)
- Nail Polish remover was assumed to be 100% acetone
- Paint thinner was assumed to be 25% each of methylene chloride, toluene, acetone
- Motor oil was assumed to be 1% each of benzene, toluene and ethylbenzene. The balance is reported as motor oil-other

3.5.5 Food Waste Reactors

The methane production rate for the food waste reactors is presented in Figure 24. The methane yield up to day 68 is presented in Table 20. Also in Table 20 is a comparison to the work done by Eleazer (1997).

The NMOC production rate is illustrated in Figure 24. Figure 24 illustrates that NMOC production increases and methane production increases. This would be expected given that food waste was added to the reactors in fed batch mode. The food waste additions were done according to the schedule in Table 21. Spikes in gas production were measured after each food waste addition. The NMOC yields for the food waste reactors were: $3.67 \cdot 10^{-1}$, $2.29 \cdot 10^{-1}$, and $2.82 \cdot 10^{-1}$ mg NMOC-C/dry g.

To illustrate that optimal pH conditions are met for methanogenic activity, Figure 25 displays the pH of each reactor. pH data was used to make sure that acidic conditions were neutralized before more food waste was added.

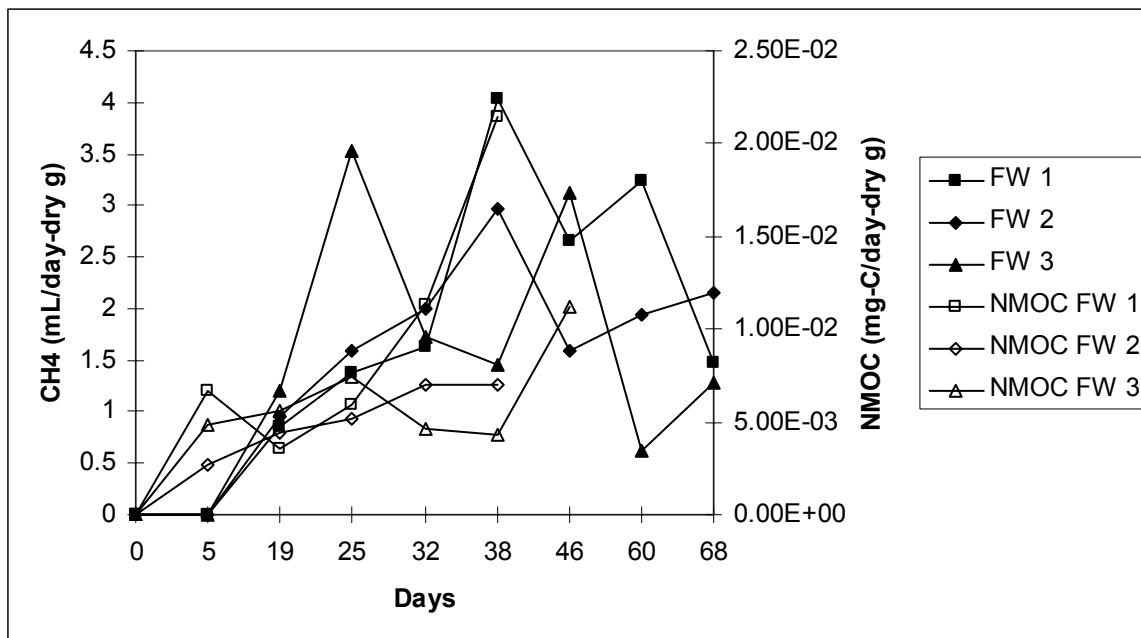


Figure 24. Methane Production and NMOC Production Rates for Food Waste Reactors

Table 20 Methane Yields for Food Waste Reactors and Ultimate Methane Yield from Eleazer (1997)^a

Reactor Type	Day	CH ₄ yield	Average Ultimate Yield for Eleazer
FW 1	67	120.04	
FW 2	68	105.53	
FW 3	68	100.06	
Eleazer Food Waste	70	100	300.7

a. Yields are in mL CH₄/dry g

Table 21 Food Waste Additions

Day	Food Waste Added (wet grams)
0	360
20	130
30	130
40	130
50	130
60	130

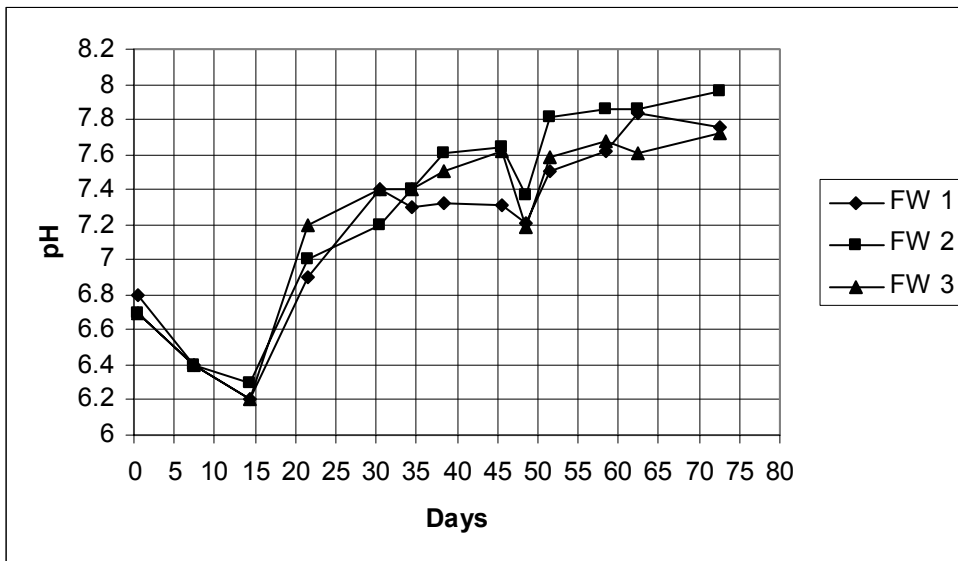


Figure 25. pH Data for Food Waste Reactors

3.5.6 Leachate Controls

The leachate controls were used to measure the background NMOC yield from the leachate seed. Since there was no gas volume present after 52 days, N₂ was pumped through the reactor in order to sparge the NMOCs from the reactor headspace. The NMOC concentration for the leachate controls up to day 52 were 6.49×10^{-4} , 1.15×10^{-3} , and 2.57×10^{-4} mg-C/mL. These NMOC concentrations were then used to correct each NMOC yield for each reactor as described in section 2.8.

Since no methane was present in the sparged gas, the methane yields measured in each reactor did not have to be corrected.

4.0 Discussion

The CO₂, CH₄, and NMOC yields for each reactor are summarized in Table 22 and compared in the first section of this chapter. This is followed by evaluations of inhibition in the HHW reactors and of the relationship between NMOC and CH₄ production.

4.1 Comparison of NMOC Yields Across Treatments

Table 22 illustrates all the carbon dioxide, methane, nitrogen and NMOC yields for the different treatments. Some caution must be used in reviewing the data in Table 22 in that yields are expressed for different time periods in an ongoing experiment. As illustrated in Table 22 the food waste reactors have the highest NMOC yield followed by the aerobic reactors. Interestingly, NMOC yields in the aerobic reactors are over double the yields in the MSW reactors containing the same sample of waste. There are two explanations for this. First, air is being pushed through the refuse and air stripping is occurring. Second, there is a wider array of intermediates produced during aerobic degradation. The mixed paper reactors have the lowest NMOC yields and they also are the purest waste tested with minimal organics other than cellulose, hemicellulose, and lignin.

Table 23 illustrates the NMOC yields at comparable times for the aerobic and anaerobic MSW reactors. As illustrated in Table 23 the NMOC yields for the aerobic reactors are approximately 10 times larger than those of the anaerobic reactors at the same time. There are two explanations for this. First, the greater volume of air may be stripping more organics. Second, about 5 times more carbon was recovered as CO₂ in the aerobic reactors relative to the mass of C recovered as CO₂ + CH₄ in the anaerobic MSW reactors. Table 24 presents the moles of C recovered for the Aerobic and Anaerobic MSW reactors.

To evaluate whether NMOC yields are governed by overall gas production, the NMOC yield were converted to a volume basis (Table 23). When the NMOC yields were

converted to a volume they are approximately 100 to 1000 times lower than the CH₄ yields. Thus, it is apparent that NMOCs must be pushed out as the refuse decomposes. This can be confirmed by comparing methane and NMOC production rates. These figures can be seen in the previous Results section.

Table 22 Summary of Gas Yields for all Reactors

Reactor	Day	CO ₂ Yield (mL CO ₂ @STP/dry g)	CH ₄ yield (mL CH ₄ @STP/dry g)	N ₂ yield (mL N ₂ @STP/dry g)	NMOC Yield ^a	Volume ^c
Aerobic 1	44	316.16	0		0.2630	0.4909
Aerobic 2	44	253.64	0		0.2210	0.4125
Aerobic 3	44	302.85	0		0.2000	0.3733
Leachate Control 1	52		0		0.0006	0.0012
Leachate Control 2	52		0		0.0012	0.0021
Leachate Control 3	52		0		0.0003	0.0005
Mixed Paper 1	66		35.22		0.0125	0.0233
Mixed Paper 2	73		41.43		0.0046	0.0086
Mixed Paper 3	73		36.75		0.0052	0.0098
Yard Waste 1	50		19.90		0.0151	0.0282
Yard Waste 2	73		52.13		0.0112	0.0209
Yard Waste 3	73		45.54		0.0171	0.0319
MSW 1	68		43.15		0.0816	0.1523
MSW 2	73		48.22		0.0792	0.1478
MSW 3	59		31.98		0.0484	0.0903
MSW plus HHW 1	66		17.19		0.0632	0.1180
MSW plus HHW 2	59		3.88		0.0244	0.0455
MSW plus HHW 3	51		3.83		0.0877	0.1637
MSW under Nitrate Conditions 1	68		5.14	8.94	0.0207	0.0386
MSW under Nitrate Conditions 2	59		2.38	9.87	0.0266	0.0497
MSW under Nitrate Conditions 3	66		12.88	12.48	0.0450	0.0840
Food Waste 1	67		120.04		0.3670	0.6851
Food Waste 2	68		105.53		0.2290	0.4275
Food Waste 3	68		100.06		0.2820	0.5264

- a. Data have been corrected for the leachate control (mg NMOC-C/dry g)
- b. Data are reported as mg NMOC-C/mL
- c. Volumes are reported as mL-C/dry g

Table 23 Comparison of NMOC Yields for Aerobic and Anaerobic MSW Reactors

Reactor	Day	NMOC Yield (mg NMOC-C/dry g)
Aerobic 1	44	0.2627
Aerobic 2	44	0.2211
Aerobic 3	44	0.1995
MSW 1	47	0.0816
MSW 2	47	0.0792
MSW 3	47	0.0484

Table 24 Comparison of the Moles of C Decomposed by Aerobic and Anaerobic Reactors^a

Reactor	Moles-C
Aerobic 1	0.0141
Aerobic 2	0.0113
Aerobic 3	0.0135
MSW 1	0.0025
MSW 2	0.0029
MSW 3	0.0022

a. Moles calculated using CH_4 production rate*2/22,400mL/mole for MSW reactors or CO_2 production rate/22,400mL/mole for aerobic reactors

4.2 Inhibition in MSW Plus HHW Reactors

The reactors spiked with HHW were inhibited for the first 50 days. This is thought to be due to the HHW spike since the MSW reactors without the spike had no apparent problems. Figures 20 and 22 found in the Results section illustrate this point. The calculated HHW concentrations added to each reactor were illustrated in Table 19. It is apparent that these concentrations inhibited refuse methanogens given that lag time prior

to the onset of methane production in the HHW reactors. This inhibition is probably due to the high methylene chloride concentration. The methylene chloride concentration is 20 times greater than the 50% toxicity concentrations found in Blum and Speece (1991).

4.3 Relationship Between NMOC and CH₄ Yields

Figure 26 illustrates CH₄ yield versus NMOC yield for all reactors. Figure 26 illustrates reproducibility. Figure 26 also shows that across treatments the substrate is more important than the CH₄ yield as an indicator of NMOC yield.

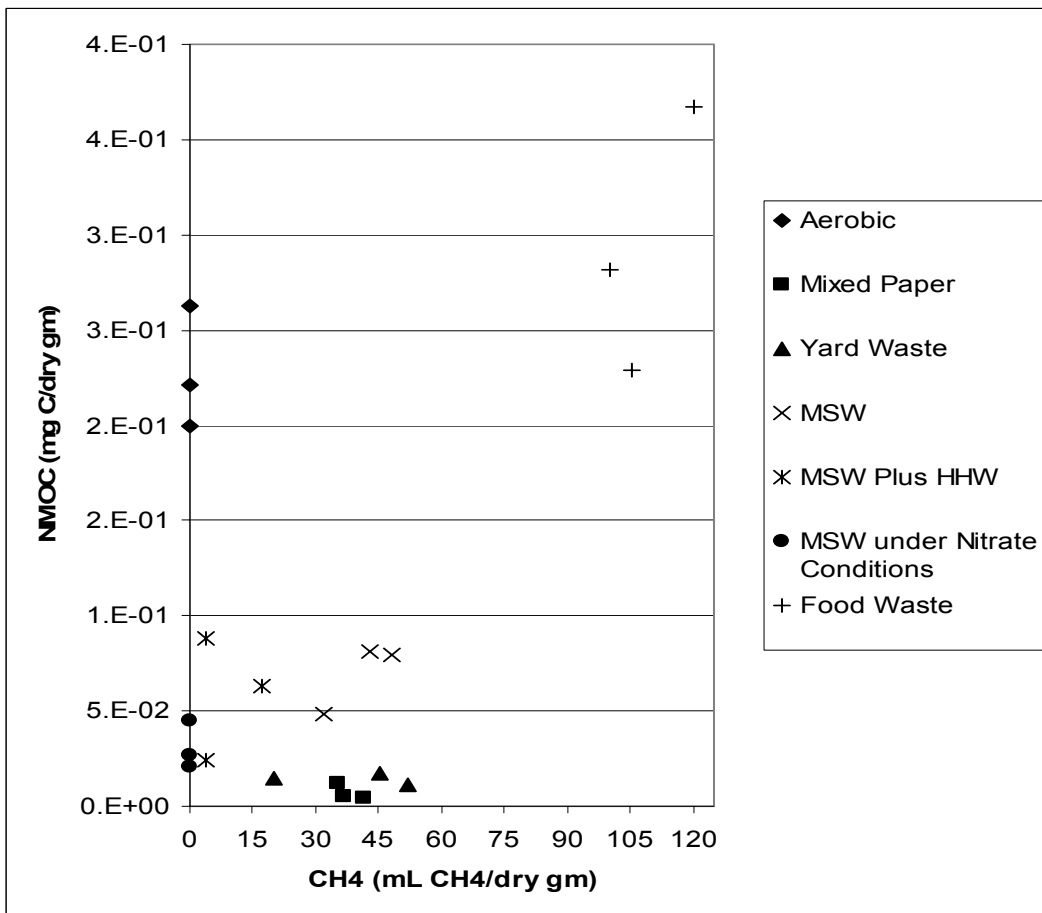


Figure 26. CH₄ Yield versus NMOC Yield for all Reactors

5.0 Conclusions

1. Decomposing refuse under aerobic conditions produces 10 times more NMOCs than under anaerobic conditions after 73 days.
2. NMOCs are being forced out during refuse decomposition.
3. Food waste produces the largest yields of NMOCs and methane.
4. HHW concentrations caused an initial inhibition in refuse degradation.

6.0 References

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7.0 Appendices

7.1 Appendix A

COD Protocol

Sample Digestion

- 1) Dry the potassium acid phthalate overnight at 120°C, then prepare the 5 standards by dissolving the dried potassium acid phthalate in DI water. Store the standard solutions in the refrigerator at 4°C.

Standard Concentration	mg of Potassium Acid Phthalate (per Liter)
100	85
300	255
700	595
1100	935
1500	1275

- 1) Remove leachate samples from the freezer and allow them to thaw. Upon thawing, check the pH of the sample to make sure it is 2.0 ± 0.2 , adjust if necessary, and record both the pH and any adjustments made to the sample. Turn on the COD reactor and preheat it to 150°C.
- 2) Remove the cap on the 0-1500 ppm range COD digestion vial (Hach catalog # 21259-15) and pipet 2.0 mL of leachate sample into the vial. Cap the vial, label the vial with the appropriate information, and record in the lab notebook. Prepare 1 duplicate sample, for a total of 2 replicates, using the same technique. Repeat procedure for all leachate samples. Also repeat the procedure substituting the COD standards for the leachate samples. Prepare 3 blanks by using the same procedure, except substituting 2.0 mL DI water for the leachate.
- 3) Homogenize the liquid in the vial by grasping the vial cap and inverting the vial 8 times. Rinse the outside of the vial with DI water and wipe clean with a Kim-Wipe. Place the vial in the COD reactor. Repeat for all samples. Record the time the samples were placed in the reactor.

- 4) Heat the vials for 2 hours in the reactor. After 2 hours, turn off the reactor and record the time in the lab notebook. Let the samples cool for ~20 minutes.
- 5) Invert the samples ~5 times, while still warm, and place in a test tube rack to allow them to cool to room temperature.

Colorimetric Determination

- 1) Turn on the Spectronic 21 spectrophotometer and allow it to warm up for at least 1 hour. Rotate the wavelength dial to 620 nm.
- 2) Clean the outside of the blank vial with DI water and a Kim-Wipe. Place the vial into the spectrophotometer and cover the vial with the lid. Turn the absorbance adjustment dial until the absorbance reads 0. Repeat the procedure for the other blanks and adjust if needed. Record the absorbance values for the blanks and standards on the lab notebook.
- 3) Clean the outside of the first sample vial with DI water and a Kim-Wipe. Place vial in the spectrophotometer and cover. Record the absorbance; repeat procedure for all samples.

NOTE: If any sample exceeds the absorbance value measured for the 1500 mg/L standard, then dilute the sample and repeat

7.2 Appendix B

Table 3 Parts for Reactor Construction

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) ^a	P-721A	Upchurch Scientific
female Luer adapter, ETFE ^a	P-624	Upchurch Scientific
1/4" O.D. x 1/8" I.D. Kynar tubing ^a	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

b. For making the threaded port on the glass leachate vessels that accepts the Mininert valve

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) *

7.3 Appendix C

Calculations to Develop an Appropriate Paper Mixture for Mixed Paper Reactors

Type of Paper	Thousand Tons Discarded ^b	% of Total ^a
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. Corrected to 100%. Values were then used to get the mixture of paper in each reactor.
- b. Values from 1998 Waste Characterization Report