



Research and Development

A Laboratory Study to Investigate
Gaseous Emissions and Solids
Decomposition During Composting of
Municipal Solid Wastes

Prepared for

Office of Prevention, Pesticides, and Toxic Substances
and
Office of Solid Waste

Prepared by

National Risk Management
Research Laboratory
Research Triangle Park, NC 27711

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A Laboratory Study to Investigate Gaseous Emissions and Solids Decomposition During Composting of Municipal Solid Waste

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Abstract

A materials flow analysis was performed for composting municipal solid waste (MSW) and specific biodegradable organic components of MSW. This work is part of an overall U.S. Environmental Protection Agency (EPA) project providing cost, energy, and materials flow information on different methods to reduce, recycle, treat, or dispose of MSW. This information will be used by managers to optimize MSW management. Calculating energy and material flows, emissions, and costs associated with different methods and mixes of methods for handling MSW or for different components of MSW will provide basic information to guide decisionmakers.

Composting is aerobic decomposition of a substrate, in this case MSW or its components. The purpose of this work is to quantify and model energy and material flows into a typical compost facility and material flows out of it. This work required laboratory experiments because material flows in particular were not known for general MSW or its components.

The results indicate that MSW (at 25% inorganics) and its three largest decomposable components (i.e., food wastes, mixed paper, and yard wastes) will lose 47, 66, 35, and 48%, respectively, of their dry weight upon complete composting. This will produce 730, 1,340, 560, and 800 kg of carbon dioxide (CO₂) per dry U.S. ton of MSW, food wastes, mixed paper, and yard wastes, respectively. Corresponding ammonia releases are 0.42, 49, 2.4, and 5.4 kg per dry ton. Volatile organic compound (VOC) releases were quantified for 12 targeted VOCs, and additional VOCs were found but not quantified. The results are modeled for facilities accepting various combinations of MSW components (or MSW of various compositions).

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Acronyms

BTEX	benzene, toluene, ethylbenzene, and xylenes
BVS	volatile solids reduction
COV	coefficient of variation
EPA	U.S. Environmental Protection Agency
FA	fulvic acids
FID	flame ionization detector
FW	food waste
GC	gas chromatograph
HA	humic acids
HHW	household hazardous waste
HPLC	high performance liquid chromatography
HS	humic substances
HW	hazardous waste
HWSM	hot water soluble matter
ISWM	integrated solid waste management
LiPs	lignin peroxidases
LOTV	low odor threshold value
MnPs	manganese-dependent peroxidases
MS	mass spectrometer
MSW	municipal solid waste
MSWCF	municipal solid waste composting facility
MXP	mixed paper waste
NHS	non-humic substances
OCC	old corrugated cardboard
OFP	printed office paper
ONP	old newsprint
PAH	polycyclic aromatic hydrocarbons
RAC	ratio of area counts
SSCF	sewage sludge composting facility
SWM	solid waste management

Acronyms (continued)

TCD	thermal conductivity detector
TCFM	trichlorofluoromethane
TOC	total organic carbon
TLV	threshold limit value
VOC	volatile organic compound
YW	yard waste

Acknowledgments

The research presented here is part of a life cycle inventory project funded by the U.S. Environmental Protection Agency (EPA) through EPA Cooperative Agreement CR 823052 with the Research Triangle Institute. The support of EPA and, in particular, that of the project manager, Susan Thorneloe, is acknowledged, as is the subcontract management and help of Keith Weitz of the Research Triangle Institute.

The carbon dioxide and ammonia capture and quantification methods were checked by an EPA quality assurance and quality control (QA/QC) staff member, Richard Shores, and the recovery numbers given in the paper are from the QA/QC report. The authors would like to acknowledge the assistance of Paul Fritschel, director of the Environmental Engineering Laboratories, and the many laboratory support personnel involved with this project. Total organic carbon and total nitrogen measurements were performed by the Soil and Plant Analysis Laboratory at the University of Wisconsin-Madison, and gas chromatography/mass spectroscopy (GC/MS) analyses were performed at the State of Wisconsin Laboratory of Hygiene and at the Department of Soil Science at the University of Wisconsin-Madison.

Executive Summary

Integrated Solid Waste Management (ISWM) requires making informed decisions to optimize solid waste management (SWM) by minimizing environmental releases, energy and resource use, and costs, while maximizing useful outputs. Judgment is required to balance these factors for a given region. All realistic methods of SWM must be considered, including recycling, combustion, composting, and landfilling. The U.S. Environmental Protection Agency (EPA) initiated research with cofunding from the U.S. Department of Energy (DOE) to develop tools and information for evaluating strategies for ISWM. The research team for this effort was led by the Research Triangle Institute, in cooperation with North Carolina State University, Franklin Associates, Ltd., Roy F. Weston, and the University of Wisconsin in Madison. This document is the report of the research conducted by the University of Wisconsin to develop degradation information for use in a process model for composting. The process model is developed and presented in a separate report.

Composting, as commonly defined for SWM purposes and as used here, is aerobic biological decomposition of solid waste. Factors affecting the rate and completeness of decomposition are manipulated according to local needs and constraints to produce the desired decomposition. These factors include waste selection or exclusion, particle size reduction, mixing, seeding, moisture addition, and aeration. In general, more costly facilities use mechanical methods to prepare the waste and to promote decomposition. Less costly facilities emphasize natural processes, reducing mechanical needs.

Composting occurs in nature as organic materials degrade aerobically. It evolved as a SWM tool when public health and sanitation became municipal functions during the 19th century in some parts of the world. During the 20th century, composting became increasingly understood as research, development, and experience resulted in different facility designs and operating methods to meet local requirements. Composting has been applied most often to municipal solid wastes (MSW), sewage sludge, and agricultural wastes, but increasingly over the last 10 years also to yard wastes. This project focused on MSW and yard waste composting.

Although composting has a long history and has been the subject of much research and development, little is known about the extent of decomposition. There is no information on the

amount of gases produced during decomposition and only general information and theoretical projections of gas composition. Further, there is no such information specific to MSW components such as food waste, paper, and yard waste. Since this information tied to specific components is required for the overall life cycle project, it was considered necessary to perform laboratory work. The dry weight loss of waste fed to composting facilities could have been monitored, but it would have been very difficult to use full-scale facilities to develop this information for different waste components, and it would have been impossible to measure gaseous emissions.

This report begins with project background and a general literature review followed by a chapter on the laboratory methods used to simulate a compost facility, and initial testing of these methods for reasonableness and reproducibility of the results. These methods were used to compost the three major organic components of MSW (i.e., food waste, mixed paper, and yard waste). Although more detailed testing was not done on specific waste sub-components (e.g., different types of paper), the waste components tested are deemed representative of specific degradable sub-components as required for the overall project.

The following report presents the results for major gaseous emissions, solids reduction, and volatile organic compound (VOC) emissions, respectively, for composting food, mixed paper, and yard wastes. The experimental design used involved determining the need for and impact of seed for each waste component, plus composting each component separately and in combination with each of the other two components or with both other components. In addition, a special experiment was performed with a mixture of all three components but at concentrations such that these results, in combination with the results from the individual components and mixtures, could be modeled. The result of this work includes equations relating weight loss and quantitative carbon dioxide, ammonia, and VOC emissions to initial waste composition. The chapter on VOCs also gives qualitative information regarding specific VOCs produced by composting each component and mixtures of components.

The results indicate that MSW (at 25% inorganics) and the three largest decomposable components of MSW (i.e., food wastes, mixed paper, and yard wastes) will lose 47, 66, 35, and 48%, respectively, of their dry weight upon complete composting. This will produce 730, 1,340, 560, and 800 kg of carbon dioxide per dry ton of MSW, food wastes, mixed paper, and yard wastes, respectively. Corresponding ammonia releases are 0.42, 49, 2.4, and 5.4 kg per dry ton. VOC releases were quantified for 12 targeted VOCs, and additional VOCs were found but not quantified.

1.0 Introduction

Integrated Solid Waste Management (ISWM) requires making informed decisions to optimize solid waste management by minimizing environmental releases, energy and resource use, and costs while maximizing useful outputs. Judgment is required to balance these factors for a given region. All realistic methods of managing solid waste must be considered, including recycling, combustion, composting, and landfilling. The U.S. Environmental Protection Agency (EPA) initiated research with cofunding from the U.S. Department of Energy (DOE) to develop tools and information for evaluating strategies for ISWM. The research team for this effort was led by the Research Triangle Institute, in cooperation with North Carolina State University, Franklin Associates, Ltd., Roy F. Weston, and the University of Wisconsin in Madison. This document is the report of the research conducted by the University of Wisconsin to develop degradation information for use in a process model for composting. The process model is developed and presented in a separate report.

Composting, as commonly defined for solid waste management purposes and as used here, is aerobic biological decomposition of solid waste. Factors affecting the rate and completeness of decomposition are manipulated according to local needs and constraints to produce the desired decomposition. These factors include waste selection or exclusion, particle size reduction, mixing, seeding, moisture addition, and aeration. In general, more costly facilities use mechanical methods to prepare the waste and to promote decomposition. Less costly facilities emphasize natural processes, reducing mechanical needs.

Composting occurs in nature as organic materials degrade aerobically. It evolved as a solid waste management tool when public health and sanitation became municipal functions during the 19th century in some parts of the world. During the 20th century, composting has become increasingly understood as research, development, and experience resulted in different facility designs and operating methods to meet local requirements. Composting has been applied most often to municipal solid wastes (MSW), sewage sludge, and agricultural wastes, but increasingly over the past 10 years also to yard wastes. This project focused on MSW and yard waste composting.

The process model of composting requires information on energy and materials flowing into a compost facility, the facility itself, and materials leaving the facility. Further, since a major portion of the materials leaving a compost facility is compost, which is subject to further degradation and leaching when it is applied to land or placed in a landfill, the emissions associated with this additional degradation and leaching are included as well. The model for composting does not include any waste processing, separation, or haul prior to the compost plant. These issues are modeled in other parts of the overall project because they are the same as might be used for recycling, for example. Similarly, haul and landfilling of rejects and haul of compost are excluded from this report but are considered in the overall project.

Although composting has a long history and has been the subject of much research and development, little is known about the extent of decomposition. There is no information on the amount of gases produced during decomposition and only general information and theoretical projections of gas composition. Further, there is no such information specific to MSW components such as food waste, paper, and yard waste. Because this information is required for the overall life cycle project, it became necessary to conduct laboratory analyses. Dry weight loss of waste fed to composting facilities could have been monitored, but it would have been very difficult to use full-scale facilities to develop this information for different waste components and it would have been impossible to measure gaseous emissions.

This report begins with project background and a general literature review followed by a chapter on the laboratory methods used to simulate a compost facility and initial testing of these methods for reasonableness and reproducibility of the results. These methods were used to compost the three major organic components of MSW—food waste, mixed paper, and yard waste. Time and budget constraints did not allow more detailed testing on specific waste subcomponents, such as different types of paper; however, the waste components tested are deemed representative of specific degradable subcomponents as required for the overall project.

The following three chapters present the results for major gaseous emissions, solids reduction, and volatile organic compound (VOC) emissions, respectively, for composting food, mixed paper, and yard wastes. The experimental design used involved determining the need for and impact of seed for each waste component, plus composting each component separately and in combination with each of the other two components or with both other components. A special experiment was performed with a mixture of all three components to further investigate possible interactions between the waste components. The result of this work includes equations relating weight loss and quantitative CO_2 , NH_3 , and VOC emissions to initial waste composition. The chapter on VOCs also gives qualitative information on specific VOCs produced by composting each component and mixtures of components.

Note that care should be taken in using the laboratory data. The data represent emission estimates from three waste components (yard waste, food waste, paper) and thus are not necessarily representative of emissions from the entire waste stream. In particular, variability in the composition of waste entering a compost facility can lead to significant variations in compost products, cost, and emissions.

2.0 Background and Literature Review

Composting in the United States has primarily focused on the treatment of organic substrates such as sewage sludges and agricultural wastes. Composting is also one way of treating and disposing of municipal solid wastes, but it has always had limited success in achieving its ideal purpose, that is to produce a soil amendment. MSW-derived compost in the United States is either stockpiled, landfilled, or used as a landfill cover (Kashmanian and Spencer, 1993). At the same time, higher tipping fees in composting facilities than in landfills (Goldstein and Steuteville, 1994) may render MSW composting a less “popular” option. However, since landfill space is reduced and social and economic reasons focus on recycling practices, MSW composting is gaining more attention. As of November 1995, 17 MSW composting projects were in operation in the United States, while 27 were in various stages of development (Steuteville, 1995). At the same time, MSW composting is studied as a pretreatment solid waste management technique prior to landfilling. The reasoning is that the volume of solid wastes can be reduced to up to 50% (Tchobanoglous et al., 1993) in a relatively short period of time, which increases the active landfill life. Additionally, the concentration of readily organic degradable material in the waste can be reduced significantly during composting, decreasing the organic load emitted from the landfill in both liquid (leachate) and gaseous (biogas) forms (Komilis and Ham, 2000). Thus, the capital and operating costs associated with the design of the relevant landfill elements as well as the overall landfill postclosure monitoring operation are expected to be reduced.

Yard waste composting is now widely practiced in the United States, with approximately 3,260 facilities in operation (U.S. EPA, 1997). The goals are to reduce landfill space utilization and to promote productive use of yard waste as compost.

2.1 Solid Waste Composting

Composting is a method of solid waste management during which the organic portion of the solid waste stream is biologically decomposed under controlled conditions to a state in which it can be handled, stored, and/or applied to the land without adversely affecting the environment (Epstein, 1997). The description of the composting process and wastes to be composted, and the factors that affect it, are subjects covered in several reviews (Gray et al., 1971; de Bertoldi et al., 1983; Diaz et al., 1993) and will not be discussed in detail here.

During composting, oxygen is used as the terminal electron acceptor and the organic matter passes through a thermophilic stage. The main classes of organic compounds in MSW belong to known biochemistry classes and have known structures (Stevenson, 1994). These compounds—referred to herein as nonhumic substances (NHS)—are attacked by several types of mesophilic and thermophilic microorganisms. Bacteria are prevalent in the initial stages of decomposition, while fungi and actinomycetes are prevalent at the final stages (Epstein, 1997).

Some of the organic matter is eventually mineralized to CO₂ and water after passing through several intermediate stages. Another major pathway in composting is the polymerization of a fraction of the initial NHS and probably of the generated microbial tissues to form a group of compounds known under the collective term of humic substances (HS) or humus, which is refractory to biodegradation. Humified organic matter can be applied to soil to enhance plant growth mainly because of its increased water retention potential. The physical structure of the soil is improved and the gradual leaching of nutrients adds to the beneficial effect of humified organic matter. Other effects of humic material on plant growth are discussed by Vaughan and Malcolm (1987).

CO₂ and ammonia (NH₃) gases are the primary metabolic byproducts of the composting process. Carbon dioxide is a well-known greenhouse gas. NH₃ is an intermediate byproduct from protein degradation. Due to thermophilic temperatures normally encountered during composting (>50 °C), nitrification rarely occurs (de Bertoldi et al., 1983), and NH₃ accumulates and volatilizes or is bound to organic matter through biologically mediated processes (Stevenson, 1994). NH₃ is at least partially responsible for odor problems common to composting operations (Diaz, 1987) and can cause human health impacts. Several volatile organic compounds were identified by Eitzer (1995) in U.S. MSW composting facilities, with alkylated benzenes, chlorofluorocarbons, and terpenes being at the highest ambient air concentrations.

Little is known about the yields and production rates of CO₂, NH₃, and VOCs of different solid waste components during composting. Information on these gaseous yields from MSW and yard waste composting facilities is needed to evaluate the contribution of these facilities to the global production of regulated gases. Such knowledge can be used to compare waste management techniques and optimize waste management policies using life cycle analysis tools (U.S. EPA, 1998).

In addition, there is limited information on weight losses and biodegradable carbon fractions of MSW or individual MSW components during composting. Weight loss is a critical factor for composting plant design (Haug, 1993).

Solids loss during composting of organic matter or MSW has been used to study the effect of various parameters affecting the composting process (Regan and Jeris, 1970) and to derive compost maturity indicators (Mathur et al., 1993). Several studies have focused on the use of humic matter measurements to derive compost maturity indicators (de Nobili and Petrussi, 1988; Ciavatta et al., 1993; Riffaldi et al., 1986). Changes in the primary chemical constituents of raw MSW have been suggested as indicators of compost maturity. Inoko et al. (1979) measured the changes of such chemical parameters namely cellulose, hemicellulose, lignin and water-soluble sugars during several stages of composting mixed MSW in actual composting plants in Japan and suggested that, for MSW-derived finished composts, the ratio of carbon in polysaccharides to total carbon should be less than 35%, total N should be above 2% (dry matter basis), and C/N ratio less than 20.

Apart from the effects of various parameters (e.g., pH, C/N ratio, aeration rate) on MSW composting, overall decomposition is expected to be affected by the heterogeneity of the MSW stream and the percentages of each of the different MSW organic components. In one of the

oldest studies, Poincelot and Day, (1960) studied the effect of combining leaves with various organic and inorganic materials on cellulose decomposition. The authors observed that decomposition is enhanced by materials with high contents of readily available nitrogen, such as ammonium salts and sewage sludge. In terms of compost maturity indicators, limited information exists on whether similar characteristics exist among composts derived from different MSW components or from MSW of various compositions.

Compost maturity has been a subject of research for several years, yet there is no universally accepted way of evaluating it (Mathur et al., 1993).

2.2 MSW composting technologies

Mixed MSW or the source-separated organic fraction of MSW are the substrates to the composting facilities. Most operational projects refer to mixed MSW composting with several degrees of pretreatment prior to the actual composting process. Pretreatment usually comprises screening and removal of large items, shredding with hammermills or shear shredders, and occasionally magnetic removal of some items (Gould and Meckert, 1994). There are three basic compost process technologies:

- Windrow turned facilities. The waste is placed in windrows, which are periodically turned using windrow turners or front end loaders until a mature material is produced. Windrows are basically long piles of controlled cross-sectional size to promote air contact and minimize anaerobic conditions. The turning evens decomposition and moisture and spreads organisms. Michel et al. (1993) showed that the turning frequency does not affect composting rates, since aeration concentrations within the pile return to the levels prior to turning within around 3 hours.
- Aerated static pile facilities: This technology is common in sewage sludge composting. Air is pumped from the bottom of the piles through perforated pipes. According to Miller et al. (1982), forced aeration is better than vacuum-induced ventilation in achieving air distribution within the pile and also in cooling a windrow at high temperatures.
- In-vessel (digester) facilities: Several proprietary systems exist, the goal of which is to achieve higher composting rates, since several parameters can be more precisely controlled than with piles or windrows. In-vessel systems are associated with higher capital costs and are almost always used in conjunction with windrow systems to achieve maturation.

According to de Bertoldi et al. (1983), maturation times in composting processes using closed reactors or open windrows do not differ if the processes are carried out correctly. Based on Glaub et al. (1989), the turned windrow process has the least energy requirements (21.4 kWh/ton MSW) compared to aerated static piles (25.2 kWh/ton) and in-vessel systems (30.0 kWh/ton).

2.3 Gaps in Knowledge and Research Objectives

Information is limited on the fate and source of VOCs from municipal solid wastes during composting and the contribution of MSW composting to the production of greenhouse gases. Furthermore, deriving a universally accepted compost maturity indicator is still being researched. Thus, the primary objectives of this work are to

- Provide data and models to estimate CO₂, NH₃, and VOC yields from individual MSW components and MSW of various compositions
- Investigate the sources and fate of VOCs in MSW composting environments
- Investigate solids decomposition and provide potential compost maturity indicators for various organic substrates during composting.

3.0 Methods

To maintain control of the process and to make the necessary measurements, a laboratory procedure was developed that simulates as closely as possible full-scale composting facilities. Composting is an aerobic degradation process in which oxygen is used as the terminal electron acceptor. Heterotrophic bacteria and fungi oxidize the biodegradable carbon fraction of each substrate to obtain energy for metabolic activities and to build new biomass. Nutrient and oxygen concentrations, substrate moisture content, the presence of seed, and temperature levels play critical roles in determining the composting rate (Diaz et al., 1993).

The composting process was simulated based on the following findings and guidelines.

1. Moisture contents ranging from 52% to up to 60% (wet weight) do not limit composting of most organic substrates (Schulze, 1961).
2. A minimum value of 15% (by weight) of oxygen present at the headspace of compost vessels has been found to not limit the composting process (de Bertoldi et al., 1988).
3. Thermophilic temperature ranges (50 to 70 °C) occur frequently in actively composted substrates (Diaz et al., 1993). Schulze (1960), using synthetic garbage as substrate, showed that higher oxygen uptake rates are observed with higher compost temperatures, up to a maximum value of 70 °C. Temperatures higher than 70 °C can significantly hinder decomposition rates (Diaz et al., 1993). In accordance with the Arrhenius temperature dependence rule, biological reaction rates increase with increasing temperatures up to a maximum level (Sawyer and McCarty, 1978), and thermophilic temperatures are expected to result in higher composting rates than mesophilic temperatures.
4. A C/N ratio of 25 to 30 has been suggested for optimum composting (Diaz et al., 1993).
5. Seeding of substrates with microorganisms derived from active MSW composting operations is expected to accelerate the initiation and sustainability of the composting process for some substrates (Gray et al., 1971).

The method developed here was designed to degrade MSW or MSW components aerobically. A closed batch system was used with defined input material to collect and measure all gaseous emissions per unit of substrate. Water, seed, and nutrients were provided at the beginning of the process, based on the above-mentioned guidelines, and excess air was supplied continuously throughout the process. The system is designed to simulate well-operated (i.e.,

minimal anaerobic biological activity) in-vessel MSW composting plants or MSW composting plants of the aerated static pile type with forced aeration.

Mass loadings of CO₂, NH₃, and VOCs were quantified continuously until “full” decomposition was reached, as was indicated by termination of measurable carbon dioxide flow rates. Solids analyses were performed at the beginning and end of the process. The conceptual experimental design is shown in Figure 3-1.

The following sections describe in detail the materials and methods used to develop the laboratory setup.

3.1 Materials and Methods

3.1.1 Substrate Preparation

The decomposable fraction of MSW was simulated by breaking it into three major organic components: mixed paper wastes (MXP), yard wastes (YW), and food wastes (FW). These are the three major organic components of MSW in the United States, accounting for approximately 40%, 19%, and 9% of the overall wet MSW composition, respectively, after recycling (Tchobanoglous et al., 1993). The use of well-defined batches of these three MSW organic components allowed reproducibility of the experiments.

These three organic components were either composted individually or in mixtures. Mixtures were prepared based on a typical U.S. residential MSW composition as achieved after recycling (Tchobanoglous et al., 1993). The three major organic components were normalized to 100% by neglecting inorganic components and smaller organic component fractions. Accordingly, when all three components were tested, the percentages were set at 59.3% mixed paper, 27.4% yard wastes, and 13.3% food wastes, on a wet weight basis, or approximately 80% for mixed paper, 15.4% for yard wastes, and 4.3% for food wastes, on a dry weight basis. The relative weights put in the digesters was kept approximately the same, whether two components were combined or a mixture of all three components was prepared.

Mixed paper wastes (MXP) were prepared by mixing old corrugated cardboard (OCC), printed office paper (OFP), and old newsprint (ONP) at percentages of approximately 45%, 21%, and 34%, respectively, on a wet weight basis. The percentage of each component in the mixture was based on a typical composition for mixed paper in the United States (Tchobanoglous et al., 1993). Other types of paper, present in smaller quantities, were not accounted for.

Cardboard was obtained from a solid waste recycling facility located in Madison, Wisconsin. Newsprint was collected from a newsprint recycling bin, located in a Student Union building at the University of Wisconsin-Madison. Ordinary used office paper (20.3 cm x 27.9 cm sized) was collected from graduate student offices from the Department of Civil and Environmental Engineering at the University of Wisconsin-Madison. All types of paper used in the experiment were shredded with an open top shear shredder (Shred Pax Corporation, Woodale, IL) to approximately 3-cm² to 4-cm² pieces. Shredding was done to promote

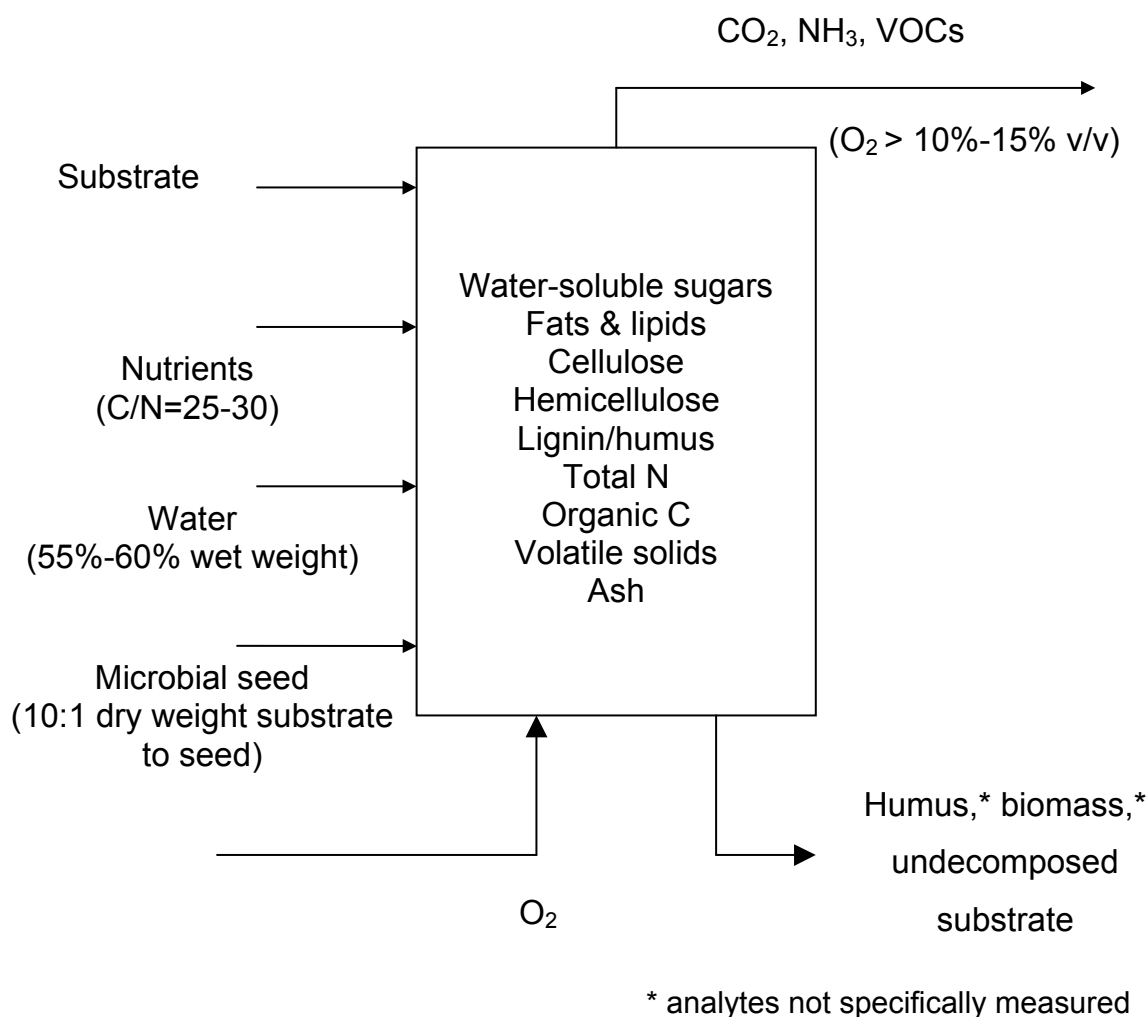


Figure 3-1. Conceptual experimental design.

degradation and so paper would fit in the reactors; it should have no effect on the final extent of degradation. All paper components were collected at the same time and stored in a 4°C room until use.

Yard wastes were prepared by mixing grass clippings and leaves, which are common major constituents of yard waste composting facilities but can also be found in MSW composting as well. The ratio of grass to leaves was arbitrarily set at approximately 1.5:1 on a dry content basis. Grass clippings were collected randomly from a yard waste drop-off area in Madison, Wisconsin, in May 1997 and September 1997. Moisture content analysis and volatile solid content analyses were performed for each grass batch prior to its use in a digester and individual experimental runs were performed on the two batches of grass. There was a difference between them, according to weight loss and CO_2 evolution results. Intermediate

sampling and analyses of volatile solids showed that degradation during storage in the cold room was less than 1% for grass. Leaves were collected once from a local yard. Grass, leaves, and branches were used as is without any shredding. To aid reproducibility, all yard waste components were stored at 4 °C until needed.

Food wastes were simulated using a typical food waste composition, as provided by the In-Sink-Erator company (ISE, 1996). Food wastes were prepared from six common food products: milk, cooked pasta, cooked hamburger, lettuce, raw potatoes, and carrots, mixed in equal wet weight amounts. All food products were obtained from a local grocery store and prepared prior to each run.

Approximately 10% of each of the individual substrates used was sampled using a riffler (Barlaz, 1988) and subjected to moisture content and volatile solids content analyses prior to each experiment. Periodically samples were also analyzed for carbon and nitrogen content. All substrates were weighed to an accuracy of ± 2.5 g. If the overall initial moisture content of a component or mixture was calculated to be less than 55% to 60% by wet weight, water was added using a spray bottle to reach a moisture content of approximately 60%, and the material was mixed. Food wastes and yard wastes had initial moisture contents greater than 60% wet weight, requiring no additional moisture.

Nitrogen was added to all substrates or mixtures for which the initial average C/N ratio was higher than 30. Nitrogen was added in the form of NH_4NO_3 salt that was dissolved in the water used to raise the moisture content. No nitrogen was added to food waste and yard wastes. Both nitrogen forms present in the NH_4NO_3 salt were assumed to be equally available to the microorganisms. A distinct ammonia odor was detected during the spraying of water with the nutrient salts on the substrates while the digesters were open. This volatilized ammonia was a temporary phenomenon and was considered unlikely to have a measurable impact on nitrogen mass balances. No phosphorus or other trace elements were added to the substrates to simulate field conditions; phosphorus is not normally added to MSW or YW prior to field composting. In contrast, nitrogen is often added to MSW during composting in the form of wastewater biosolids.

Overall dry weights of the combined materials used in all runs ranged from 130 g to 1,100 g. Overall wet weights, after addition of moisture, ranged from 1.5 kg to 2.5 kg.

3.1.2 Substrate Seeding

Seeding was considered necessary to start the decomposition process and supply an active microbial population suitable for composting in a reproducible manner. Most of the runs, including individual substrates and mixtures, were seeded with partially composted MSW (not matured), hereafter referred to as seed. Seed was collected from a nearby MSW composting facility located at Portage, WI. Approximately 15 kg of seed (wet weight) was collected in February 1996 from the outlet of a 5-day retention time drum digester that receives raw MSW without any preprocessing. Material leaving the composting vessel is sieved at the exit end of the drum and so was already ground and mixed. The seed was further screened through a 12.7-mm screen to remove larger items such as glass and plastic. It was stored in a 4°C room until the end of the experimental runs. Seeding was provided at a ratio of approximately 1:10 of dry seed to dry substrate.

To evaluate the contribution of seed decomposition to total gaseous emissions of a seeded MSW mixture, seed was composted individually. The volatile solids content of seed, measured immediately after collection from the facility, was $94.8\% \pm 0.19\%$ (dry weight basis). A decrease of the volatile solids content of the seed was observed during storage over a year period. The seed volatile solids content prior to use in all runs reported here had been stabilized to $71.5\% \pm 0.5\%$ (on a dry weight basis).

3.1.3 Reactor Setup and Operation

Experimental runs were done using five custom-made 25-L airtight stainless steel digesters constructed by Hooper Corporation (Madison, WI), as shown in Figure 3-2. All individual materials and their mixtures, after preparation, wetting, and addition of appropriate nutrients, were placed in each digester. All MSW substrates were mixed with #1.5 HyPak aluminum packing material (4.5 cm thickness x 4.5 cm diameter) acquired from Norton Chemicals (Akron, OH). The packing material was uniformly mixed with the substrate to approximately 10% to 15% of the volume occupied by the substrate. The packing material was needed to facilitate air flow, prevent excessive channeling of air at the sides of the digester, and ensure that aerobic conditions were maintained within the substrate. The composting process was simulated in a batch mode.

The five digesters were operated concurrently. Each digester had a removable lid and had one input and one output port. The digesters were kept in a controlled temperature room at a temperature in the thermophilic (55 ± 5 °C) or mesophilic range (32 ± 3 °C), as desired.

Laboratory ambient air was continuously pumped into the digesters using a Barnant oil-less air pump (Barrington, IL, Model No. 400-1901) operating at a positive pressure. The air was first passed through a 200-g activated carbon (Orbo 32, 6-14 mesh) filter to capture ambient air VOCs and then through a 500-mL 5 N KOH solution to capture ambient CO₂. It then passed through 10 L of distilled water, kept at incubator temperature, to humidify the substrate and minimize excessive drying. Air was then directed through a manifold to the individual digesters. Pumped air served as a source of oxygen for the oxidation of substrate as well as the carrier for emitted gases.

A valve and a flowmeter (Barnant Co., Barrington, IL) prior to each digester was used to regulate the airflow to each digester to 150 to 300 mL/min. This flow rate was used to avoid limiting the degradation process by maintaining oxygen concentrations in the exit gas higher than 15% by volume for all runs. A smaller additional VOC filter (Orbo 32) was placed after each flowmeter for each digester. The smaller VOC filters were tested and replenished periodically to check if breakthrough of VOCs from the preceding larger carbon filter occurred.

A 4.5-cm air plenum was created at the bottom of each digester using an aluminum screen supported by aluminum packing material. The air plenum was designed to even the distribution of air in the digester.

After exiting the digesters, the air stream first passed through an activated coconut charcoal trap (Orbo 32, SUPELCO, Bellefonte, PA) to remove VOCs for quantification and to partially remove organic compounds of acidic nature (e.g., acetic acid) that could interfere with

the CO₂ quantification to follow. The coconut charcoal trap (large Orbo-32) consisted of a primary section and a breakthrough section containing 400 mg and 200 mg of activated coconut charcoal (20 to 40 mesh), respectively. The air stream was then bubbled through a 750-mL 5 N KOH solution to capture carbon dioxide and then through a 500-mL 1 N H₂SO₄ solution to capture ammonia. KOH solutions are more efficient than NaOH solutions for capturing CO₂ (Cook et al., 1994). KOH has a water solubility of 107 g/100 mL, compared to NaOH with a water solubility of 50 g/100mL, thus allowing more CO₂ to be trapped as soluble carbonates. An empty sealed jar was kept between the two traps to prevent overflow from the alkaline to the acidic solution. The CO₂ and NH₃ traps were kept outside the incubator at room temperature, while the VOC trap was placed directly after the exit port of a digester at the incubator temperature. The laboratory setup is shown in Figure 3-2.

Concentrations of O₂, CO₂, CH₄, and N₂ were measured occasionally in the exit gas stream, before and after the CO₂ trap. These measurements were made primarily to adjust the air flow rate according to the 15% O₂ content minimum level and were especially important during the first 10 days after initiation of a run, since this was the period of highest O₂ consumption. These measurements also aided in checking when the carbon dioxide trap became saturated if CO₂ was detected in the gas stream after the alkaline trap.

When CO₂ production rates decreased and stabilized at essentially zero, the digester was opened to check whether this rate reduction was due to a moisture limitation. If excessive drying had occurred, moisture was uniformly added to achieve moisture levels of at least 50% wet weight and digester operation was continued. Drying of yard wastes in particular was observed even though moisture was added to the incoming air. This was attributed to the limited production of water due to the low biological activity and to excessive amounts of air supplied for this level of activity. Composting periods varied from 60 days for food wastes to 220 days for mixed paper. The experiment was terminated when carbon dioxide production rates dropped below approximately 0.5 g CO₂ (as C)/dry kg/day and after ensuring that this was not due to a moisture limitation.

Leachate was observed to accumulate at the bottom of the digesters during the process. Analysis of leachate did not take place; however, all leachate was collected and dried at 75°C along with solid matter remaining at the end of an experiment. Though volatilization of low-volatility organic compounds might occur at this temperature, most degradable soluble compounds were expected to have been degraded; therefore, the soluble organic matter remaining was assumed to have been primarily of humic and fulvic acid origin.

Digesters were thoroughly cleaned with soap and hot water at the end of each run.

3.1.4 Gas Composition Analysis

The O₂, CO₂, CH₄, H₂, and N₂ contents of the exit gas stream were measured by withdrawing 0.4 mL gas from a septum connected to the tubing at the outlet port of each digester once or twice per day during the first 10 days of each run. In addition, sampling from a septum placed between the CO₂ and NH₃ traps aided in checking for breakthrough of CO₂ from the alkaline trap. Sampling was done with a 0.5-mL gas-tight Hamilton syringe. Gas samples were injected to a Varian 3300 gas chromatograph equipped with a Molesieve 45/60 4' x 1/8" column,

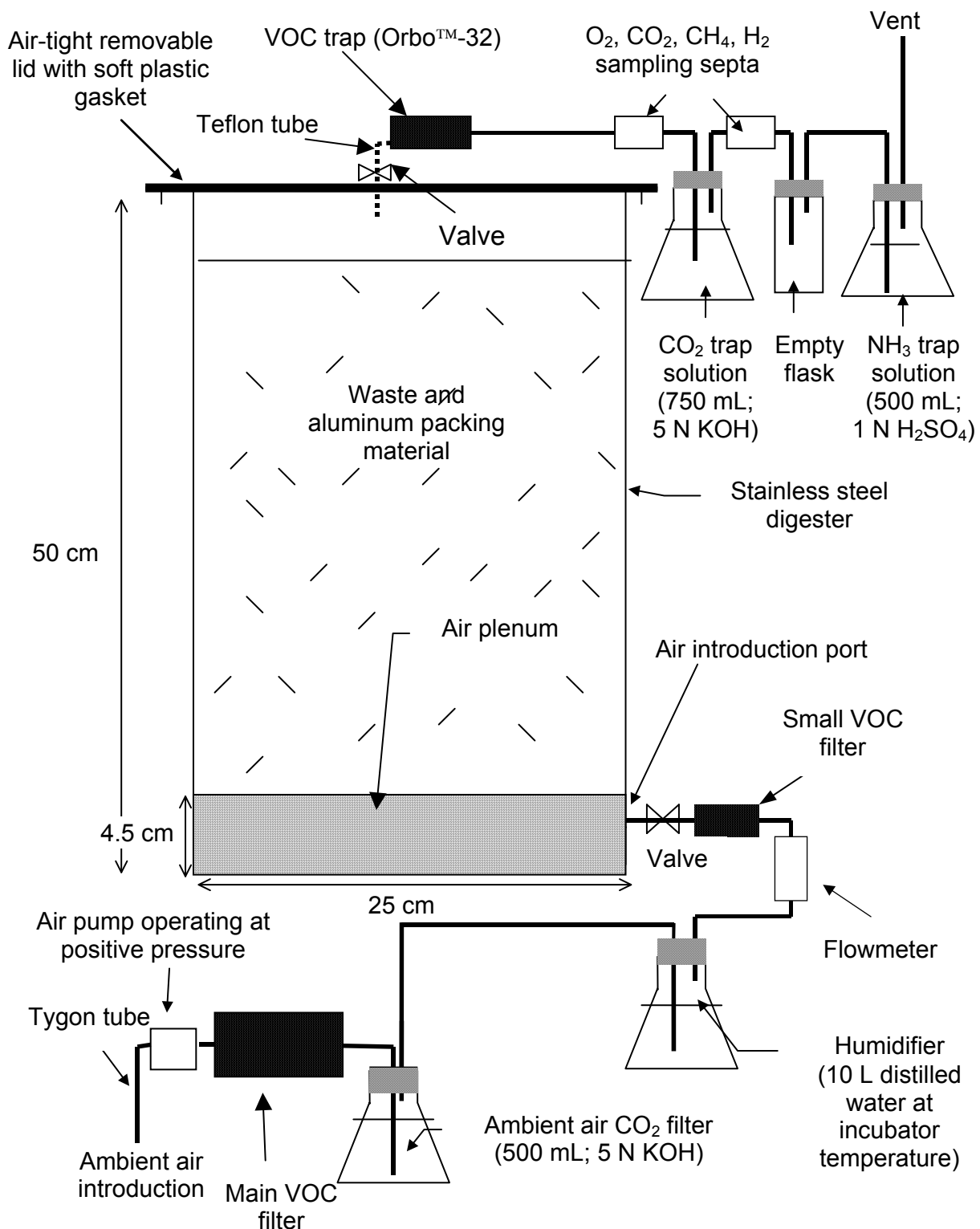


Figure 3-2. Digester setup (not to scale).

a Hayesep N 80/100 6' x 1/8" column, and a thermal conductivity detector (TCD). Column temperature programming was 30 °C for 2 min followed by an increase to 75 °C at a rate of 2 °C/min. Standard mixtures of N₂, H₂, CH₄, and CO₂, provided by Gastech (IL, USA) and Liquid Carbonic Specialty Gases (IL, USA), were used to calibrate the gas chromatograph. In addition, ambient air was used to calibrate nitrogen and oxygen concentrations after correcting for local atmospheric temperature and pressure.

3.1.5 Carbon Dioxide Mass Loadings

The cumulative mass of captured carbon dioxide (expressed as total carbon) was measured periodically by removing 3 mL of the alkaline trap solution, diluting it with 30 mL of deionized water and performing two titrations. The total alkalinity (ALK) (pH 4.3) and phenolphthalein alkalinity (pALK) (pH 8.3) were measured for the same sample using an Orion pH meter. ALK and pALK are given by the formulas $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+]$ and $[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}_2\text{CO}_3] - [\text{H}^+]$, respectively (Stumm and Morgan, 1981). The carbonate species concentration present in the solution due to the dissolution of carbon dioxide is $[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] = \text{Alk} - \text{pAlk}$. The mass of C-CO₂ captured in the solution per unit of dry substrate was calculated using Equation 3-1:

$$\text{C-CO}_{2(t)} = \frac{\frac{(V_{43-83})N_{\text{acid}}}{V_{\text{sample}}} \times 12 \times V_{\text{trap}} - \text{C-CO}_{2\text{control}(t)}}{\text{Dry mass}} \quad (3-1)$$

where

$\text{C-CO}_{2(t)}$	=	g of C-CO ₂ present in the alkaline trap per dry kg of starting material, at time t
V_{43-83}	=	titrant volume (mL) required to decrease the pH of the solution from 8.3 to 4.3
N_{acid}	=	normality of the titrant (eq/L)
V_{sample}	=	amount of alkaline solution to be titrated, mL
V_{trap}	=	recorded volume of alkaline solution at the time a measurement was made, L
12	=	atomic weight of C in g/mol
$\text{C-CO}_{2\text{control}(t)}$	=	amount of C-CO ₂ captured during operation of an empty vessel (control) for the corresponding time t
Dry mass	=	initial dry mass of substrate placed in the digester prior to the initiation of a run, kg

The normality (N_{acid}) of the acid used for titration was standardized at 0.245 N H₂SO₄, based on Sawyer and McCarty (1978).

To check on the accuracy of the CO₂ measurements, 6.907 g of CO₂ were passed through the 5 N KOH trap by bubbling a 10.1% CO₂ molar concentration standard gas (Scott Specialty Gases, IL) for 202.5 minutes at 189.5 actual cm³/min. The mass recovered by the trap was

6.81 g, and the bias was calculated to be 1.4% (U.S. EPA, 1997), as shown in Table 3-1. The EPA audit report is presented in Appendix B.

Due to condensation of moisture in the exit gas stream, the CO₂ trap solution volume was observed to increase during the course of the experiment. For this reason, the exact solution volume (V_{trap}) would be measured each time a CO₂ concentration measurement was performed to accurately calculate the mass of C-CO₂ present in the jar. The alkaline trap was replenished when the C-CO₂ concentration in the solution was higher than approximately 10 g C-CO₂/L. At values less than 8 g C-CO₂, CO₂ losses were negligible, as was shown by the use of backup CO₂ traps during preliminary runs. As the concentration of captured C-CO₂ increased above 10 g/L, CO₂ losses would increase exponentially until the trap would become completely saturated at concentrations of approximately 20 g C-CO₂/L. An equation was developed to describe the C-CO₂ losses as a function of the C-CO₂ mass contained in the trap at any time. The estimated losses were added to the measured C-CO₂ amounts during analysis when the trap was semi-saturated. The coefficient of variation (or precision) of the CO₂ measurements was 0.7% based on triplicate samples collected at the same time.

3.1.6 Ammonia Mass Loadings

A sample of 1.5 mL of the NH₃ trap solution was periodically removed and mixed with 10 mL deionized water. Dissolved ammonia was quantified using the preliminary distillation/titration method based on Clesceri et al., (1989). Solubility of NH₃ in the KOH trap for CO₂ was deemed negligible because of the low solubility and the lack of any uptake once saturation was achieved.

Amines are expected to be captured by the acidic solution. According to Nakasaki et al. (1998), who composted dog food under continuous thermophilic temperatures, total amine concentrations in the ammonia trap were less than 1/1,000 of the ammonia concentration. Therefore, the interference of amines during ammonia quantification can be considered insignificant.

In preliminary testing during the audit by EPA (Appendix B), 3.256 mg of NH₃ were passed through the 1 N H₂SO₄ trap by bubbling a 26.9-ppm standard ammonia concentration gas for 946 min at 187.1 acm³/min. The mass recovered by the trap was 3.073 mg, and the bias was calculated to be 2.4% (U.S. EPA, 1997), as shown in Table 3-1. The coefficient of variation (or precision) of the NH₃ measurements was 4.6%, based on triplicate samples. A methyl orange indicator was added to the acidic trap to indicate the need to replenish a trap by color change (Clesceri et al., 1989).

3.1.7 VOC Identification and Mass Loadings

The VOC activated coconut charcoal traps were removed periodically and a new VOC trap was installed immediately after removal of a trap. The charcoal trap was extracted with 1.5 mL high-purity CS₂ (Aldrich, Milwaukee, WI) in 2-mL vials using a sample agitator (SUPELCO), for 30 min (Eller, 1984). The liquid phase was analyzed using GC/MS, and VOCs were quantified using a gas chromatograph (Varian 3600CX) equipped with a flame ionization

Table 3-1. Summary of Analytical Techniques

	Analyte	Procedure	Precision ^a	Bias ^b	Basic reference
Gas masses	VOCs	Sorption on activated coconut charcoal, carbon disulfide extraction, injection to GC/FID	3.2%	5.4%	Partially based on Eller (1984)
	CO ₂	KOH trap, titration using the total and phenolphthalein alkalinities	0.7% ^c	1.4% ^c	Based on Zibilske (1994) and Stumm and Morgan (1981)
	NH ₃	H ₂ SO ₄ trap, distillation, and HBO ₃ titration	4.6% ^c	2.4% ^c	Clesceri et al., (1989)
Gas concentrations	O ₂ gas concentration	Injection of 0.4 mL gaseous sample to GC/TCD	1.4% ^c	0.5% ^c	Clesceri et al., (1989)
	CO ₂ gas concentration	Injection of 0.4 mL gaseous sample to GC/TCD	9.3% ^c	7.6% ^c	Clesceri et al., (1989)
Solids	Hot water soluble matter ^d	Extraction with 150 mL hot water (60 °C)	18.9%	NM	Partially based on Stevenson (1965) and Nakasaki et al. (1994)
	Fats & lipids ^d	Extraction with 150 mL toluene/ethanol solution	32.7%	NM	Partially based on Stevenson (1965)
	Cellulose ^d	Acid digestion, HPLC	11.8%	4.4%	Pettersen et al. (1984); Barlaz (1988)
	Hemicellulose ^d	Acid digestion, HPLC	8.5%	NM	Pettersen et al. (1984); Barlaz (1988)
	Lignin/humus ^d	Acid digestion insoluble fraction & ashing at 550 °C	17.0%	2.1%	Based on Stevenson (1965) and Effland (1977)
	Total organic carbon	Dichromate oxidation and back titration with FeSO ₄ (Walkley-Black method)	2.9%	NM	Nelson and Sommers (1996)
	Total N	Flow injection analyzer (colorimetric technique)	12.5%	NM	Soils & Plant Analysis Laboratory, University of Wisconsin-Madison
	Volatile matter	Ashing at 550 °C	0.9%	NM	Clesceri et al., (1989)

NM = Not measured.

^a Precision is the coefficient of variation, which is the standard deviation divided by the average based on triplicate samples (solids analyses) and duplicate samples (gas analyses).

^b Bias is the deviation of measurements from accurately prepared standards (%).

^c Based on audit measurement performed by EPA (U.S. EPA, 1997).

^d Precision values are based on averaging from results discussed in this paper.

detector (FID). The GC was equipped with a 60 m x 0.32 mm SPB-5 capillary column. The carrier gas was helium at a flow rate of 2.0 mL/min. The temperature programming was 50 °C for 1 min with an increase to 100 °C at 4 °C/min followed by bake out at 230 °C for 5 minutes. The injector temperature was kept at 180 °C, while the FID temperature was kept at 300 °C. A Varian 8200CX autosampler unit was used to inject 1.5 : L of the CS₂ solution. The GC could not detect concentrations smaller than approximately 300 ppb under the aforementioned conditions.

A standard mixture of 25 VOCs was obtained from SUPELCO in methanol and was used for calibration purposes. Appropriate dilutions were made in CS₂ to achieve desired concentrations, as set during calibration. A four-point calibration was done using the external standard technique; the calibration equation was verified prior to each analysis of a batch of samples. Calibration was repeated using newly prepared standards if, during the verification step, the deviation exceeded 5% for at least one compound.

A solvent injection was made after every five samples to check the presence of residual peaks. If such peaks were present, the last two runs were reinjected. The VOC traps each contained a breakthrough section, which was analyzed to check whether breakthrough occurred.

Between 5 and 10 VOC charcoal traps were used sequentially during each experimental run to characterize the production rate of the studied VOCs over the course of the composting process. The total mass of captured VOCs in each trap was calculated from the volume of the extracting agent and the measured VOC concentrations in the extraction vial.

GC/MS analyses were performed using the same temperature conditions as the GC with a 30 m x 0.25 mm HP-5MS capillary column on a Hewlett Packard (Avondale, PA) 6890 GC equipped with a 5972 A MS (electron impact source and quadrupole analyzer). The carrier gas was helium at a flow rate of 1 mL/min regulated by an automatic flow controller. The injection was made in the splitless mode with a purge-on time of 1.2 min. The injection volume was 1 mL. The scan frequency was 1.5 times/s and the mass range scanned was 50 amu to 550 amu. The identification library contained 75,000 entries and originated from the National Bureau of Standards.

3.1.8 VOC Recovery Tests

A VOC recovery test was performed by spiking 428.5 mg of ethylbenzene (placed in a glass vial) in an empty digester and heating it at 55 °C until no more ethylbenzene was detected in the gaseous emissions. Of the spiked ethylbenzene, 94.2% was recovered in the gaseous phase, while a 15.95% breakthrough of that compound was observed in one of the charcoal traps used during the recovery run. In addition, charcoal traps were spiked directly with 1.2 mg of the combined 25 VOCs present in the standard solution, which was a common level found during the experimental runs involving unspiked MSW components. Spiking was done by adding a known volume of the standard solution directly to the primary section of the Orbo-32 trap, using a 50-: L Hamilton airtight syringe. The CS₂ extraction efficiencies of these compounds were measured approximately 1 day after extraction and ranged from 15% for naphthalene to 87.3% for toluene. These VOC recovery values were used to adjust measured amounts for quantification of VOCs in actual runs. The primary section of a 400-mg charcoal trap can hold

85 to 100 mg of combined toluene, ethylbenzene, m-xylene, and o-xylene before a breakthrough would occur.

No chemical byproducts were observed after storage of spiked traps in a freezer for up to 2 months. It was noticed, however, that 1 day or more after extraction with CS₂, toluene would increase by approximately 80% to 100% at all concentration levels. This twofold increase of toluene was also observed in standard solutions prepared in CS₂, which contained no charcoal. No such increase was observed in the original VOC standards that were supplied in methanol by SUPELCO. No corresponding change of any of the other 25 VOCs was observed. This increase of toluene is probably attributed to a breakdown of some of the other chemical compounds present in the mixture or interactions of the compounds with the CS₂. It is noted that all samples were analyzed for VOCs within 12 hours of extraction, so this increase for toluene would be unimportant.

3.1.9 Control Run

A control run was performed using an empty digester with Al Packing (one of the five digesters) that was operated for a period of 48 days concurrently with digesters containing MSW and under the same conditions as runs with substrates. During that time, a total of 0.64 g CO₂ (as C) was captured in the alkaline trap, partly because of breakthrough from the ambient air CO₂ filtration trap installed prior to the digesters. From this amount, approximately 0.12 g CO₂ (as C) were a result of the preparation process during which atmospheric air CO₂ was rapidly dissolved despite efforts to minimize air contact. The CO₂ amount found in the control run was subtracted from the total carbon dioxide emitted during actual runs. It is noted that typical runs would emit approximately 100±15 g CO₂ (as C) making the CO₂ mass emitted from the control run relatively insignificant. No significant ammonia was detected during the control run.

The combined mass of 2 of 12 targeted VOCs (toluene and ethylbenzene) identified in the control run was 23.6 mg, which was very small compared to the amounts of these VOCs emitted from digesters with substrates. This amount was subtracted from the corresponding masses of these two VOCs emitted during the runs. To further check cross air contamination, two Orbo-32 traps were placed in sequence after the ambient air large carbon filter for a period of 80 days. This was similar to the setup shown in Figure 3-1, without the digester. Negligible VOCs were measured, indicating that the primary filtration system functioned efficiently. The small amounts of VOCs found in the control run were therefore a result of their original presence in the digester, rather than ambient air cross contamination, probably due to residues remaining even after cleaning from a previous run.

The breakthrough sections of the small Orbo-32 filters placed prior to the digesters were always analyzed during the runs. No detectable levels of VOCs were ever measured in these sections. If there had been, the filter tube would have been replaced immediately with a new one before continuation of the run.

3.1.10 Solids Measurements

Solids were sampled at the initiation and at the end of each run. Initial solid matter was sampled using a riffler, which removed approximately 10% of the starting material that had been collected; the sample was stored in the cold room.

At the end of each run, most of the solid material and any leachate remaining in the digester was collected, mixed, and dried at 75 °C until constant weight. Small amounts of residual solids remained on the sides of the digester or attached in the packing material as these materials were not easy to remove completely. The amount of each material at the end of a run would vary according to the mineralization extent and initial weight of material put in the digester. Food waste runs had approximately 30 g of dry material remaining in the digester, which was the smallest amount of finished material from all runs. All runs containing mixed paper had the largest amounts of dry material remaining at the end of a run.

All of the dried materials were ground using a Wiley knife mill with a 2-mm screen. The ground samples either of a starting material or of a finished material from a specific run were each randomly divided and placed in three mason jars and stored in a freezer until analysis. Samples from each mason jar were randomly collected after tumbling the jar. Prior to analysis, the ground solids were dried again to constant weight at 75 °C.

A 0.1-g to 1-g sample was used for analysis of total organic carbon (TOC) using a dichromate oxidation followed by titration (Nelson and Sommers, 1996). The detection limit was 0.05 mg C/mg sample. Total nitrogen analysis was performed using a flow injection analyzer (QuickChem 8000, Lachat, Milwaukee, WI) and the QuickChem method 13-107-06-2-D. The detection limit for total nitrogen was 0.01 mg N/mg sample. Volatile matter was measured by ignition at 550 °C (Clesceri et al., 1989) using duplicate samples, while moisture content was measured by drying to constant weight at 75 °C.

A sequential extraction technique was used to quantify five major classes of solid organic matter: hot water soluble matter (HWSM), fats/lipids, cellulose, hemicellulose, and lignin/humus. A similar sequential extraction technique was suggested by Stevenson (1965) for soil organic matter and was followed by Nakasaki et al. (1994) for MSW. A precisely weighed ground and dried solid sample, close to 1 g, was placed in a Gooch crucible with a 1-: m filter at the bottom. This was extracted under vacuum using 150 mL of 60°C to 65°C distilled water by adding the water slowly with occasional manual stirring. It was observed that 150 mL of water would produce a clear filtrate for all of the substrates. Crucibles were then dried at 75°C to constant weight and weighed. The dry weight HWSM was recorded as the weight difference between crucible weights prior to and after extraction. According to Tenney and Walksman, (1929), HWSM contains starches, pectins, tannins, and uric acid; according to Inoko et al. (1979), it also contains amino acids, pigments, and some water-soluble proteins.

A second extraction of the same sample under vacuum was performed, using 150 mL 2:1 toluene:ethanol solution. The extracted substances were measured by the dry weight difference prior to and after extraction. The fraction extracted by the toluene:ethanol solution contained fats, lipids, waxes, oils, resins, and some tannins (Tenney and Walksman, 1929; Stevenson,

1965; Effland, 1977) and is referred to as fats/lipids. The compounds present in the HWSM group and the fats/lipids group were not individually identified during this experiment.

Cellulose and hemicellulose in the residue were measured by acid hydrolysis followed by high performance liquid chromatography (HPLC) analysis, based on Pettersen et al. (1984). A Beckman System Gold HPLC unit was used, equipped with an AMINEX HPX-87H 300 x 7.8 mm ion exchange column kept at 30°C. The mobile phase was a 0.01 N H₂SO₄ at a flow of 0.60 mL/min. Detection of monosaccharides was done with a Beckman 156 refractive index detector. Cellulose was quantified as D-glucose, while hemicellulose was quantified as combined D-xylose, D-mannose, L-arabinose, and D-galactose. Although small amounts of D-glucose may originate from certain types of hemicelluloses (Laver and Wilson, 1993), it is common practice to measure hemicellulose only as the sum of the sugars mentioned above (Laver and Wilson, 1993; Michel et al., 1993). Standards for the five monosaccharides were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI), and injections were done using the external standard technique. For calculations of bias, cellulose and lignin standards were used. High purified cellulose fibers (Type 100) were obtained from Sigma Chemical Co. (St. Louis, MO), while a standard 32.8% lignin content (dry weight) wood was obtained from the Forest Products Laboratory (Madison, WI).

The acid-insoluble fraction contains ash and lignin/humus (Effland, 1977). Ashing of the acid-insoluble fraction was applied to determine the lignin/humus fraction. Lignin/humus is expected to contain lignin, humic compounds (e.g., humic acids and humin), and acid-insoluble proteins (Tenney and Walksman, 1929; Inoko et al., 1979). Fulvic acids are expected to be solubilized during the 72% acid extraction step, since they are soluble in all pH ranges. It is also noted that 3% to 5% of hardwood lignin is acid-soluble, while negligible softwood lignin dissolves (Effland, 1977). In addition, degradation of lignin may result in some additional lignin dissolved during the acid digestion step (Effland, 1977). Therefore, some caution should be applied in interpreting lignin/humus fractions, especially from composted substrates. The sequential solids analytical procedure followed is shown in Figure 3-3.

The accuracy of the solids chemical composition results was checked against the volatile solids content. The sum of the five analyzed organic classes expressed on a dry weight basis should be approximately equal to the volatile solids content expressed on a dry weight basis. Based on results presented in this paper, the average ratio of the sum of the dry weights of the five chemical components divided over the volatile solids content (dry weight) was 95.0% with a coefficient of variation of 10.9%. Ratios in the range of 70% to 75% were observed for composted yard wastes indicating that a class of organic compounds was probably not identified with the techniques used. This class is speculated to be the fulvic acids, since these compounds are soluble in all pH ranges and would therefore be diluted in the acid hydrolysis step during cellulose determination.

The HPLC method used did not measure these types of compounds. Humic acids are soluble only under alkaline pHs and humin is insoluble in all pH ranges; therefore, they are both expected to be part of only the acid-insoluble fraction.

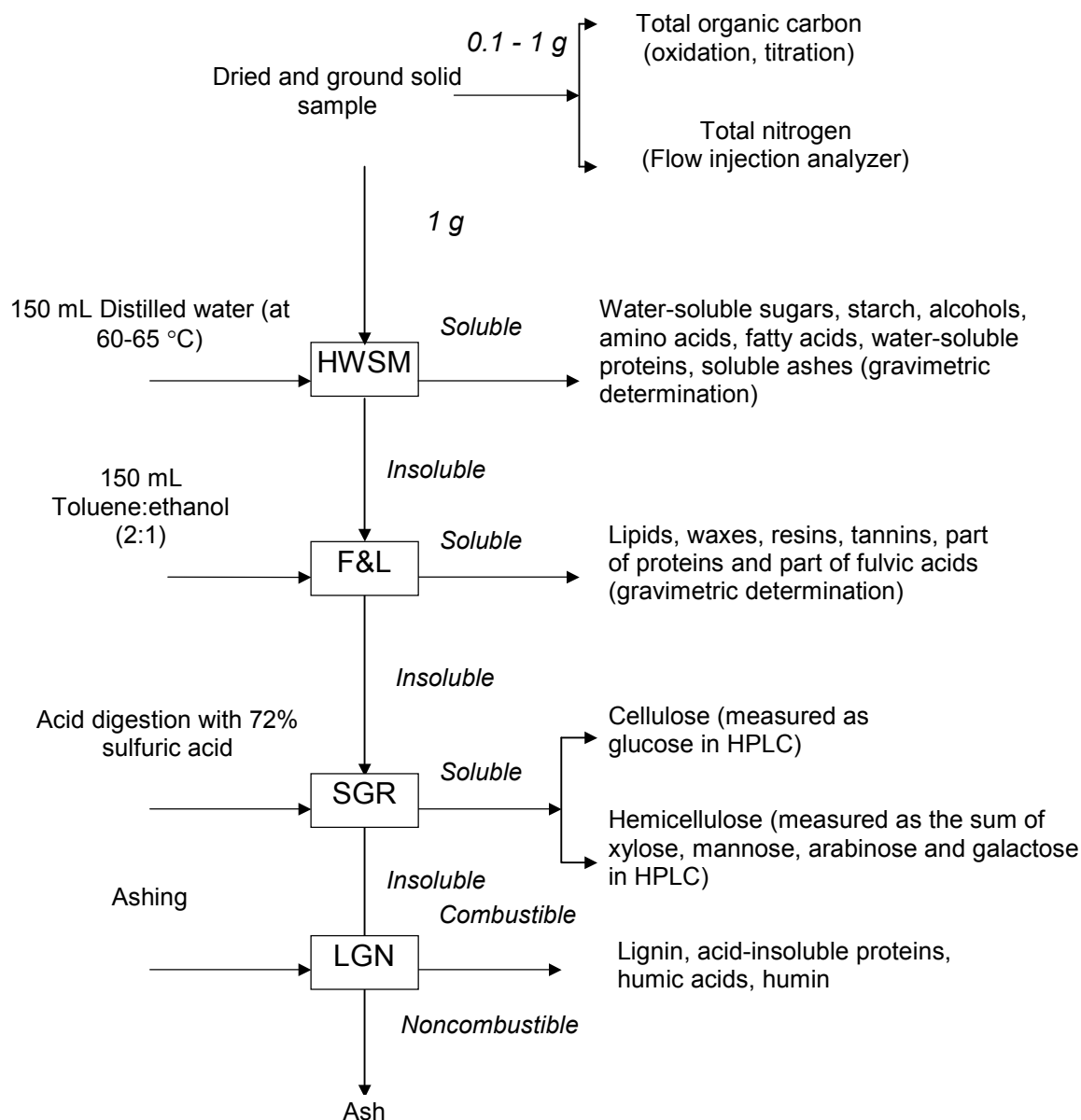


Figure 3-3. Sequential procedure for analysis of solid substrates (HWSM: hot water soluble matter; F&L: fats and lipids; SGR: polysaccharides; LGN: lignin/humus).

3.1.11 Dry Weight Reduction Calculations

The average dry weight of a component or mixture initially placed in a digester was calculated by measuring the wet weights and moisture contents of the individual substances contained in a component or mixture. At the end of a run, due to the incomplete recovery of the solids remaining in the digester, the final dry weight was calculated based on the fact that ash remains constant during a run. This technique requires measurement of only the volatile solids content of sampled solids as opposed to measurement of the dry weight of all the solids in the digester. This technique is also useful for dry weight calculations during the course of a run. By knowing the initial dry weight and the average initial volatile solids content of materials placed in a digester, the dry weight remaining in the digester at any time t is given by Equation 3-2:

$$DW_t = \frac{(1 - VS_0) \cdot DW_0}{1 - VS_t} \quad (3-2)$$

where

- DW_t = dry weight (in g) in the digester at time t
- VS_t = volatile solids content (dry weight) of the solids in the digester at time t
- DW_0 = initial dry weight of solids placed in the digester prior to the initiation of a run
- VS_0 = initial average volatile solids content of the MSW components placed in the digester before initiation of a run.

3.1.12 Precision and Bias

Table 3-1 summarizes the analytical techniques discussed in this report and includes the average precision and average bias values recorded for all measurements. Precision is the coefficient of variation¹ from replicate samples, while bias refers to the deviation of measurements from accurately prepared standards. Bias is interchangeably used with the term recovery efficiency.

No bias measurements were made for the HWSM group, fats and lipids, and hemicelluloses because no surrogate compounds were available for each of these groups.

3.2 Initial Testing of Laboratory Setup and Methods

Ten runs were done to verify the technique and to determine the reproducibility of the measurements. Runs made at thermophilic temperatures were two yard waste runs (YW and YW_{ns}), the first being seeded and the second unseeded; one unseeded yard waste run (YW_h) prepared from a grass clippings batch with a higher VS content than the grass used in the YW and YW_{ns} runs; a run with seeded mixed paper (MXP); one unseeded food waste (FW_{ns}) and one seeded food waste run (FW); and a run with seed only. In addition, two replicate runs with seeded mixed paper (MXP_j and MXP_o) and a run containing yard wastes (YW_{meso}), prepared

¹Coefficient of variation (COV) is defined as the standard deviation divided by the mean.

from the same grass batch as the YW and YW_{ns} runs, were performed at mesophilic temperatures.

Figure 3-4 presents the solids composition over time for the two mixed paper replicate runs performed at mesophilic temperatures. Fats and lipids profiles are not shown in Figure 3-4 due to overlapping with the hemicellulose profile curves. Figure 3-5 shows the cumulative percentage of initial organic carbon of a substrate emitted as carbon dioxide (as C) for 8 runs. Figure 3-6 shows the cumulative percentage of initial nitrogen of a substrate emitted as NH₃ (as N) from 7 runs. Runs MXP_j and MXP_o are not shown in the above figures, because the CO₂ and NH₃ measurement techniques were still under development when those runs were performed. No ammonia or solids measurements were performed for the YW_{meso} run. Table 3-2 presents the gaseous yields of the runs as well as solids decomposition results.

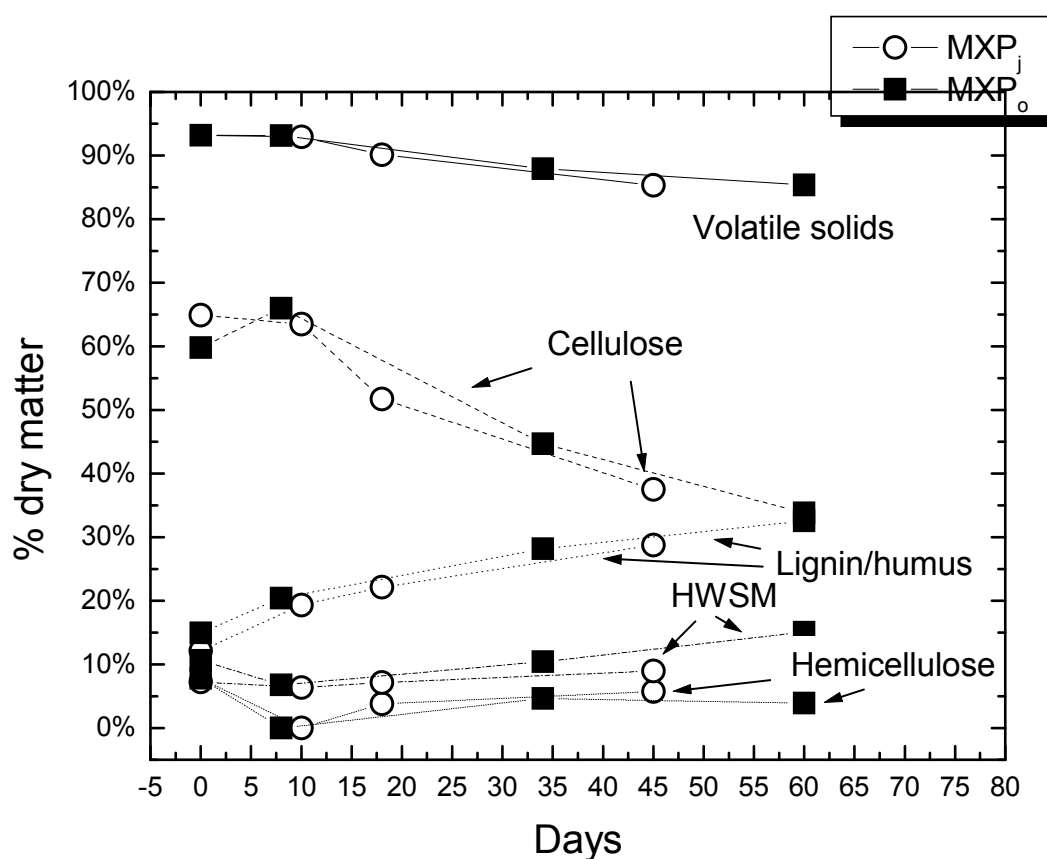


Figure 3-4. Solids decomposition profiles for replicate mixed paper runs MXP_j and MXP_o.

Based on Figure 3-4, volatile solids, cellulose, hemicellulose, and lignin/ humus measurements were reproducible. A zero fats and lipids content was recorded for all samples of the MXP_o run, while the fats and lipids contents for the MXP_j run ranged from 1.1% to 5.3% dw. The difference is attributed to the fact that the toluene:ethanol extraction preceded the hot water extraction for the MXP_j run only. Because no fats and lipids were recorded for the MXP_o.

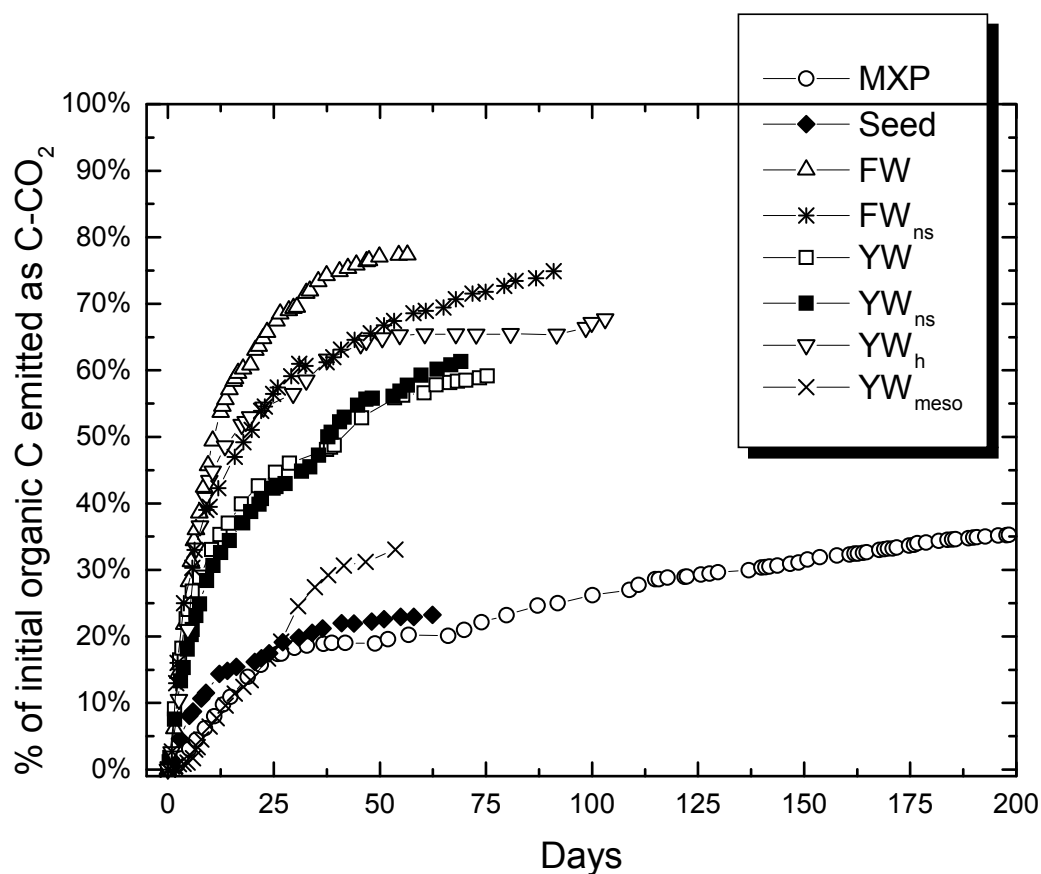


Figure 3-5. Cumulative percentage of total organic carbon emitted as C-CO₂ from different substrates during composting (temperature for the MXP run only was gradually increased from mesophilic to thermophilic during the first 30 days).

samples, the slightly increased HWSM content of the MXP₀ run compared to the MXP_j run is attributed to the fact that substances measured as fats/lipids in the MXP_j run were also removed during the water extraction of the MXP₀ run.

Assuming an additive contribution of seed to the emissions of the FW and YW runs (as calculated based on the run with seed only shown in Table 3-2), seed contributes less than 5% to the total CO₂ and NH₃ emissions for both of these runs. Runs MXP_j and MXP₀ are replicates run 3 months apart. Considering the seed contribution to the final state of decomposition negligible, the YW and FW runs with and without seed are replicates as well. (Results of statistically designed experimental runs to determine the effects of seed are presented and discussed in the next chapter.) The coefficients of variation for the CO₂ yields from the replicate food waste and yard waste runs are 0.8% and 1.6% respectively. The coefficients of variation for the NH₃ yields from the replicate food waste and yard waste runs are 11.9% and 3.1% respectively.

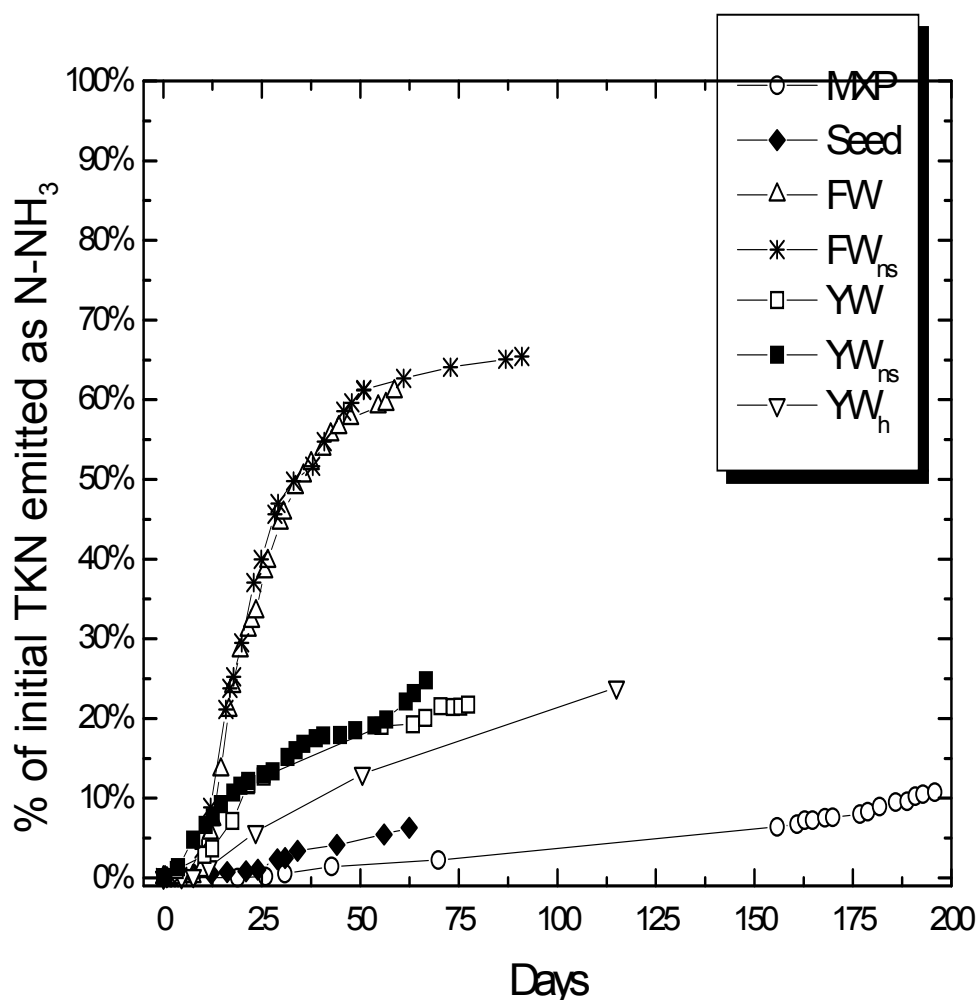


Figure 3-6. Cumulative percentage of total initial organic N emitted as N-NH₃ from different substrates during composting.

Based on the results of Table 3-2 and Figure 3-5, the effect of temperature on decomposition of different substrates is shown. The seeded yard waste CO₂ yields at thermophilic temperatures (YW) were approximately 67% higher than the corresponding yields at mesophilic temperatures. This indicates that thermophilic microbial cultures present in yard wastes achieved a higher extent of degradation of the substrate compared to the mesophilic species. Both the YW and YW_{ns} runs had approximately 60% of their carbon converted to CO₂, while the YW_{meso} run had approximately 33% of its initial total carbon converted to CO₂.

Mixed paper composted at mesophilic temperatures had a 53% dry mass reduction compared to a 35% dry mass reduction recorded for thermophilic temperatures. In contrast to yard wastes, microorganisms present in the seed used in both mixed paper runs was apparently

**Table 3-2. Experimental Results from Selected MSW Components During Composting
(Reduction Values Calculated from the End of a Run)**

Contents	CO ₂ (g C/dry kg ¹)	NH ₃ (g N/dry kg ²)	Dry mass rdc (%) ³	C rdc (%) ⁴	Fats / lipid rdc (%)	HWSM rdc (%)	Cellulose rdc (%)	Hemicel- lulose rdc (%)	Lignin rdc (%)	C closure (%) ⁵	N closure (%) ⁶
Seed	86.0	1.8	19.4	27.4	81.8	-5.3	36.2	23.9	-7.2	85.5	32.2
MXP _J ⁺	NM	NM	53.6	NM	-85.0	42.7	73.2	66.1	-9.9	NM	NM
MXP _O ⁺	NM	NM	53.4	NM	ND	33.9	73.7	76.6	-1.2	NM	NM
MXP	153.3	2.0	35.1	37.9	34.7	10.4	49.6	71.9	-28.8	93.2	33.9
YW	217.0	4.4	46.7	63.1	66.6	63.9	82.1	96.6	30.1	94.4	157.2
YW _{ns}	221.9	4.6	47.6	62.2	77.2	58.6	90.7	99.4	43.0	98.6	174.9
YW _n	265.2	5.2	53.9	66.4	74.0	60.4	89.8	100	38.5	101.7	51.8
YW _{meso} ⁺	121.0	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
FW	368.6	34.2	59.2	65.7	94	53.7	60.2	100	36.9	117.9	72.7
FW _{ns}	364.4	40.5	65.5	69.2	82.6	45.5	66.0	ND	61.6	108.5	77.5

HWSM = Hot water soluble matter.

ND = Not detected.

NM = Not measured.

ns = Nonseeded run.

rdc = Reduction mesophilic temperatures used.

¹ CO₂ yield in g C-CO₂ per dry kg of mixture (seed + component).

² Ammonia yield in g N-NH₃ per dry kg of mixture (seed + component).

³ Dry mass reduction (%) based on combined dry masses of seed and MSW component placed initially in digester.

⁴ Total carbon reduction or mineralizable carbon fraction (%) based on combined dry masses of seed and MSW component placed initially in digester.

⁵ Carbon closure defined as: emitted C-CO₂ / (total C in starting solid material including seed – total C in finished solid material).

⁶ N closure defined as: emitted N-NH₃ / (total N in starting solid material including seed + N added as nutrients – total N in finished solid material).

favorable by mesophilic temperatures. Mixed paper (MXP) had 35% of its initial carbon converted to CO_2 . The effect of temperature on the degradability of various organic substrates during composting has been summarized by Haug (1993).

Results show the effect of a different batch of grass in overall decomposition of yard waste. The YW_h run was prepared from grass clippings with a VS content of $89\% \pm 0.8\%$ (dry weight), while the grass used in all the other yard waste runs was $82\% \pm 0.5\%$ VS (dry weight). The CO_2 yield from the YW_h is approximately 20% higher than the yield from the other runs (see Table 3-2), when expressed on an initial dry weight basis. Sixty-eight percent of the initial organic carbon in the YW_h run was mineralized to CO_2 . Moisture was found to temporarily limit the CO_2 production rate for the YW_h run for a period of approximately 40 days, as is shown by the flat CO_2 cumulative profile for that substrate in Figure 3-5. Addition of moisture at the end of these 40 days did result in a slight increase in CO_2 yield shortly thereafter.

Food wastes had the largest carbon dioxide emissions of approximately 365 gr C- CO_2 / dry kg and the largest dry mass reduction of 65.5% among all substrates, as shown in Figure 3-5. Approximately 75% of the initial carbon found in food waste (in both FW_{ns} and FW runs) was converted to CO_2 . Although the FW and FW_{ns} runs were treated as replicates, it took approximately 90 days for the FW_{ns} run to reach its “full” extent of decomposition compared to 56 days for the FW run. The difference in decomposition rates is attributed to a seed effect, although seed did not appear to affect the CO_2 yields.

Seed had a CO_2 yield of 86 gr C/dry kg, the lowest among all components, probably because of its partial decomposition in the MSW composting plant from which the seed was collected. Only 23% of the initial carbon in the seed was converted to CO_2 .

As shown in Figure 3-6 and Table 3-2, unseeded food wastes had the largest ammonia emissions among all substrates of approximately 40 g N- NH_3 /dry kg. This is an apparent result of food waste having the largest initial nitrogen content of 6.2% (dw) among all substrates. The emission of 19% less ammonia from seeded food wastes is attributed to the fact that the seeded food wastes were terminated earlier than unseeded food wastes. Although carbon dioxide production rates were relatively low for seeded food wastes at that time, ammonia production rates were still relatively high indicating that ammonification still proceeded independent of organic carbon mineralization. Approximately 65% of the initial N content in food wastes was mineralized to ammonia. The rest was either not decomposed or was used for biomass production.

Yard wastes, with an initial N content of approximately 2.0% (dw) had the next largest ammonia emissions of approximately 4.5 gr N- NH_3 /dry kg. YW_h had slightly larger ammonia yields than the other runs, which can be partially explained by the fact that that run was terminated at 110 days compared to approximately 50 days for the YW and YW_{ns} runs. For the YW , YW_{ns} and YW_h runs, 21.7%, 24.8% and 23.9% of the initial nitrogen was mineralized to ammonia respectively.

The ammonia production from mixed paper alone (2.2 g N- NH_3 / dry kg) is partially attributed to the added nutrients. In particular, relatively high ammonia volatilization rates were observed for mixed paper after addition of nutrient salts on day 160, indicating that added

nutrients were in excess and thus volatilized. It is also likely that the relatively alkaline pHs observed at later stages of composting (de Bertoldi et al., 1983) induced volatilization of the added ammonium ions as ammonia. Generally, the low ammonia yields from mixed paper—regardless of nutrient addition—are expected due to the low initial N content of mixed paper, which was 0.35% dw (including the seed). The initial N content was raised to 1.85% (dw) after addition of the nutrient salts to mixed paper.

Seed had an initial N content similar to yard wastes (2.8% dry weight), but only 6.3% of that nitrogen was emitted as ammonia. The corresponding ammonia yield for the seed was 1.8 g N-NH₃/dry kg. Apparently, nitrogen-containing organic compounds were less prone to decomposition compared to the other substrates. This is attributed to the partial decomposition of the seed prior to the laboratory composting that led to the production of metabolic byproducts (e.g., microbial cells) that are resistant to further degradation.

Carbon mass balance closures ranged from 85.5% for the seed to 117.9% for food wastes. The average carbon mass balance closure from all runs was 99.9% with a coefficient of variation of 10.7%. Nitrogen mass balance closures ranged from 32.2% for the seed to 174.9% for yard wastes. The average nitrogen mass balance closure from all runs was 85.7% with a coefficient of variation of 67.3%. The relatively low nitrogen mass balance closure (compared to carbon) and greater variability is attributed to: (1) possible loss of nitrogen during spiking of the nutrient salt, (2) partial unavailability of the added nutrient to the microorganisms, (3) lack of nitrate/nitrite measurement, (4) accumulation at the bottom of the digesters from leachate movement, (5) volatilization of ammonia dissolved in the leachate during drying of the finished material, and (6) relatively (compared to C/CO₂) small amounts of N with the inherent resulting variability. Saturation of the ammonia trap in the case of food wastes was also occasionally observed.

Dry matter reductions ranged from 19.4% for the seed to 65.5% for unseeded food wastes and were correlated to the corresponding CO₂ yields. Total organic carbon reductions ranged from 27.4% for the seed to 70.5% for the mixture of food wastes and yard wastes.

Hemicellulose was the most degradable chemical group in all substrates, ranging from 23.9% (for the seed) to 100% decomposed at the end of the runs (Table 3-2). The lower molecular weight of hemicellulose compared to cellulose and its relative heterogeneity are the likely reasons for its higher decomposition extent compared to cellulose (Gray et al., 1971). Hemicellulose has also been found to be more degradable than cellulose and lignin by a variety of fungi in soil environments (Szegi, 1988). Hemicellulose degrades rapidly at the initial stages of mixed paper composting. The slight net increase of hemicellulose at the end of the MXP_j and MXP_o runs (as shown in Figure 3-4) is attributed to the synthesis of bacterial and fungal slimes and gums that are known to contain hemicelluloses (Tenney and Walksman, 1929).

Cellulose was the next most degradable compound with up to 90% of it decomposed in yard wastes. The lignin fraction was also degraded for all substrates but to a lesser extent than cellulose and hemicellulose. This is primarily a result of the lignin resistance to microbial attack, which has been well-documented (Crawford and Crawford, 1980; Vicuna, 1988). The high lignin reduction for unseeded food wastes might be a result of the different structure of the lignin fraction in that substrate, compared to the lignin fraction in mixed paper and in yard

wastes. Lignin in yard wastes was decomposed to the extent of 30.1% to 43%. The generation of humic substances or microbial proteins (both accounted for in the lignin/humus fraction) to a greater extent than lignin reduction appears to explain the net increase of the lignin/humus fraction for mixed paper by 28.8%. A slight lignin/humus net increase was also observed for the seed, MXP_j, and MXP_o runs, probably for the same reason.

Results of the VOC identification and quantification analyses are given in Chapter 6. As discussed there, mixed paper was the major source of various VOCs (primarily alkylated benzenes and naphthalene) compared to yard wastes and food wastes. Seed appeared to contribute to the emissions of seeded runs. GC/MS analysis performed for the MXP_j run identified the same types of VOCs (mostly alkanes, alkylated benzenes, terpenes) as a GC/MS analysis performed later for the MXP run. A high volatilization rate during the first 5 days, with a constantly decreasing trend thereafter, was observed for most VOCs during preliminary and actual runs. VOC measurements, however, were still under development during the preliminary runs and results must be considered preliminary.

A typical volatilization profile of eight VOCs identified and quantified in the seed is shown in Figure 3-7. Naphthalene, toluene, and *p*-isopropyltoluene were emitted in the largest amounts from that substrate. The yield of the eight VOCs during seed composting was 8.2 mg/dry kg.

3.3 Summary

This chapter presents a laboratory method to measure CO₂, NH₃, and VOC emissions and to follow solids decomposition during composting of MSW. Different runs with MSW components were performed and the reproducibility of the materials and methods presented was determined. Although the laboratory method was applied to the study of aerobic decomposition of MSW and its components, it can be used for the study of aerobic decomposition of virtually any solid organic substrate.

Results indicate that methods were reproducible for measuring CO₂ and NH₃ yields and for following solids decomposition during composting. The close to 100% carbon mass balance closures and the low biases of the CO₂ and NH₃ measurements verify the efficiency of the analytical techniques for these two gases. The aggregate recovery efficiencies (or biases) during measurement of CO₂, NH₃, and VOCs using the laboratory setup were 97.3%, 96.4%, and 94.6%, respectively.

Carbon mass balance closures ranged from 85% to 117% and nitrogen mass balance closures ranged from 32.2% to 174.9%. Precision and bias values for most of the analytical measurements used were less than 15%.

Thermophilic temperatures resulted in 65% higher CO₂ yields compared to mesophilic temperatures using yard wastes as the substrate. When mixed paper was the substrate, degradation at mesophilic temperatures resulted in approximately 50% more dry matter reduction compared to thermophilic temperatures.

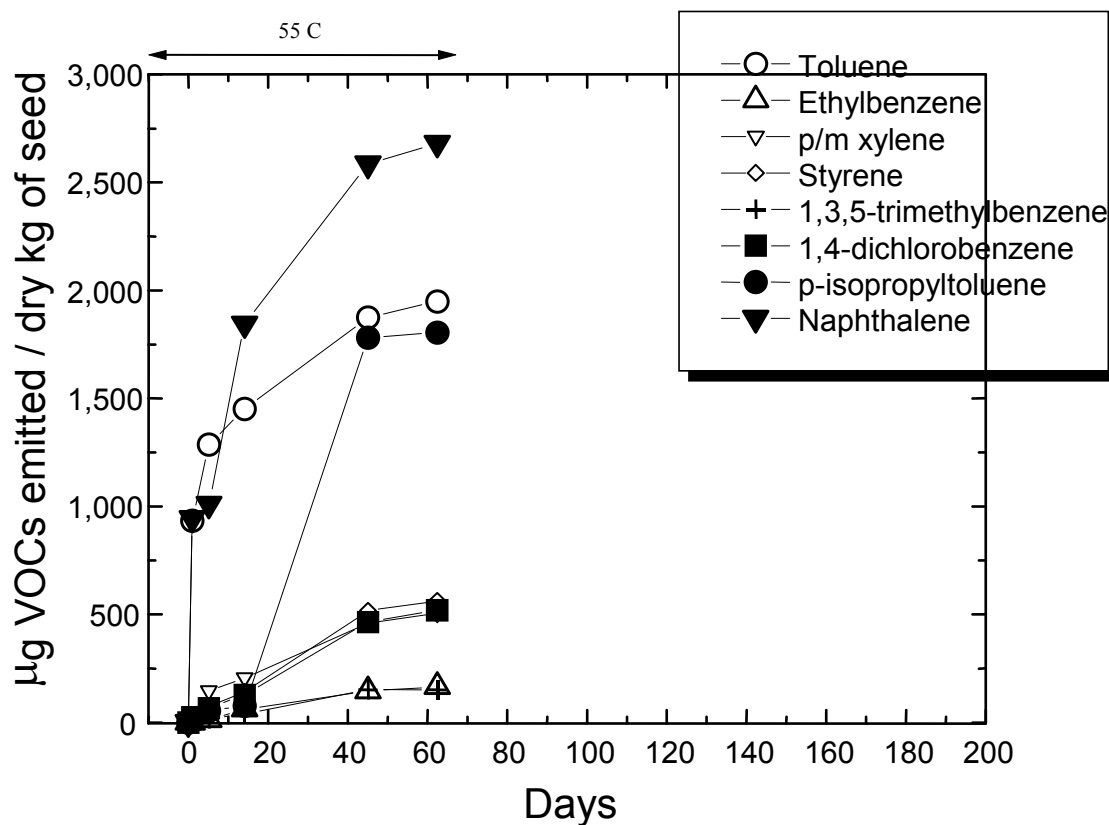


Figure 3-7. Cumulative production of eight VOCs during composting of seed at thermophilic temperatures (the period between data points corresponds to the time that one charcoal trap was continuously installed).

Food wastes produced the most CO_2 and NH_3 of the substrates tested, with approximately 365 g C-CO_2 /dry kg and 40 g N-NH_3 /dry kg. Yard wastes and mixed paper produced approximately 220 and 153 g C-CO_2 /dry kg, respectively, and 4.5 and 2.0 g N-NH_3 /dry kg, respectively. Seed emitted approximately 8.2 mg of eight VOCs per dry kg of starting material. VOC volatilization rates followed first order kinetics and no measurable VOCs were produced after approximately 50 days of composting at thermophilic temperatures.

4.0 Carbon Dioxide and Ammonia Yields During Composting

The objectives of the portion of the study presented in this chapter are to develop a tool for predicting CO₂ and NH₃ yields from MSW components or mixtures of components and to investigate whether mixing of different MSW components leads to additive gaseous yields based on yields from the individual components.

MSW was assumed here to consist of three biologically decomposable substrates: food wastes (FW), mixed paper (MXP), and yard wastes (YW), which are the major organic components of MSW (Tchobanoglous et al., 1993). Although separate composting facilities exist for residential municipal solid wastes and for yard wastes, the collective term of MSW composting will be used to describe them both.

To investigate interactions among components during composting, a laboratory method was developed that implemented a two-level, three-factor, full factorial experimental design. This design is an efficient way to study effects and interactions of parameters (Berthouex and Brown, 1994). In addition, a design based on the principles of a mixture experiment (Cornell, 1990) was used to develop a model that can estimate CO₂ and NH₃ yields on a per unit dry mass basis of MSW. Twelve laboratory runs were performed using the 25-L stainless steel digesters and methods described in the previous chapter under near optimal aerobic conditions. Carbon dioxide and ammonia yields as well as their production rates were measured for all experimental runs. It is noted that the same runs used in the full factorial design were also used during analysis of the data using the principles of a mixture experiment, with one additional run.

4.1 Statistical Experimental Designs

4.1.1 Full Factorial Analysis

The full factorial design was developed at two levels and included three factors (2³ factorial design). The two levels correspond to the presence or absence of a specific component in the mixture (high and low level). The three factors correspond to the three waste components: mixed paper waste (MXP), yard waste (YW), and food waste (FW). Eight runs were performed for the full factorial design.

Components were mixed according to the U.S. typical MSW composition after recycling reported by Tchobanoglous et al. (1993). Accordingly, the percentages of the components were set at 59.3% mixed paper, 27.4% yard wastes, and 13.3% food wastes, on a wet weight basis, which is approximately 80% mixed paper, 15.4% yard wastes, and 4.3% food wastes, on a dry weight basis. All MSW components and their mixtures were seeded using partially composted wastes, referred to as seed hereafter, from a MSW composting facility located near Portage, WI.

The seed was collected from the exit end of an enclosed digester, screened, and added at a ratio of approximately 1:10 of seed dry mass to component(s) dry mass for all runs.

The experimental responses for the full factorial design are the yields of either CO₂ or NH₃ (in g C-CO₂ or g N-NH₃) produced from the dry mass of the corresponding component(s) present in the digester.

To investigate the effect of seed on the overall emissions of each unseeded MSW component, three 2² (two factors at two levels) full factorial experiments were designed. The two factors were any of the three individual MSW components and the seed, respectively. The high and low levels corresponded to the presence or absence either of seed or any of the MSW components in the mixture. The three additional 2² factorial experiments are summarized in Table 4-1 and results of the analysis are shown in Table 4-2. They required four runs in addition to the eight runs required for the full factorial design as shown in Table 4-3. Table 4-3 also shows two additional runs, Y_{wns} and F_{wns} that are not part of the full factorial design.

The 2³ factorial design model has the generic form:

$$Y = n + (X_p/2) \times L_p + (X_Y/2) \times L_Y + (X_F/2) \times L_F + (X_{PY}/2) \times L_p \times L_Y + (X_{PF}/2) \times L_p \times L_F \\ + (X_{YF}/2) \times L_Y \times L_F + (X_{PYF}/2) \times L_p \times L_Y \times L_F + e \quad (4-1)$$

where

- | | | |
|--|---|---|
| Y | = | experimental response (in g C-CO ₂ or g N-NH ₃) |
| n | = | experimental mean (in g C-CO ₂ or g N-NH ₃) |
| $X_p, X_Y, X_F, X_{PY}, X_{PF}, X_{YF}, X_{PYF}$ | = | factor and interaction effects for mixed paper (X_p), yard wastes (X_Y), food wastes (X_F), mixed paper/yard waste mixture (X_{PY}), mixed paper/food waste mixture (X_{PF}), yard waste/food waste mixture (X_{YF}), and mixed paper/yard waste/food waste mixture (X_{PYF}) |
| L_p, L_Y, L_F | = | can take values of either -1 or +1 only, representing the absence (low level or -1) or presence (high level or +1) of each of the three components in an MSW mixture; the three components are the mixed paper wastes (L_p), yard wastes (L_Y), and food wastes (L_F) |
| e | = | errors (residuals) that are distributed normally with a zero mean and a constant variance. |

Table 4-1. 2² Full Factorial Experimental Runs to Investigate Interactions Between Individual MSW Components and Added Seed

Run title		CO ₂ response (as g C) ^a	NH ₃ response (as g N) ^a	
1 st 2 ² experiment				
	MXP _{ns} (0.803 dry kg)	Seed (0.0856 dry kg)		
Control (empty digester)	-	-	0	0
MXP _{ns}	+	-	4.45	0 ^b
Seed	-	+	7.36	0.15
MXP	+	+	136.3	1.76
2 nd 2 ² experiment				
	YW _{ns} (0.1545 dry kg)	Seed (0.0240 dry kg)		
Control (empty digester)	-	-	0	0
YW _{ns}	+	-	34.3	0.711
Seed	-	+	2.06	0.042
YW	+	+	38.7	0.793
3 rd 2 ² experiment				
	FW _{ns} (0.043 dry kg)	Seed (0.009 dry kg)		
Control (empty digester)	-	-	0	0
FW _{ns}	+	-	15.85	1.74
Seed	-	+	0.78	0.016
FW	+	+	18.97	1.78

+ = High level, indicating presence of either an individual component or seed in the mixture.

- = Low level, indicating absence of either an individual component or seed from the mixture.

MXP, YW, FW = 3 runs with seeded mixed paper, seeded yard waste and seeded food waste, respectively.

MXP_{ns}, YW_{ns}, FW_{ns} = 3 runs with unseeded mixed paper, unseeded yard wastes and unseeded food wastes, respectively.

Seed = Run containing seed only.

^a As g C (or g N) produced from the corresponding amounts (in dry kg) of individual components or mixtures of component and seed.

^b Nutrients were not added to the MXP_{ns} run.

Note: CO₂ emissions of 0.64 g subtracted from all CO₂ values (see Section 4.2). NH₃ not detected.

Table 4-2. Calculated Coefficients for the Three 2² Factorial Designs (based on responses shown in Table 4.1)

	CO ₂ (as g C)	NH ₃ (as g N)	CO ₂ (as g C)	NH ₃ (as g N)	CO ₂ (as g C)	NH ₃ (as g N)
Experimental mean (n)	36.9	0.48	18.8	0.39	8.90	0.88
Component (X _C /2)	33.2	0.40	17.7	0.37	8.51	0.88
Seed (X _S /2)	34.9	0.48	1.63	0.03	0.98	0.014
Component / seed (X _{CS} /2)	31.2	0.40	0.60	0.01	0.59	0.006

Table 4-3. 2³ Full Factorial Experimental Design to Investigate Main Effects and Interactions During Composting of Three Major MSW Organic Components

Run title	MXP (at 0.803 dry kg)	YW (at 0.155 dry kg)	FW (at 0.043 dry kg)	CO ₂ response (as g C) ^a	NH ₃ response (as g N) ^a	Days to emit 50% of CO ₂ yield
Control (empty digester)	-	-	-	0	0	0
MXP	0.803	-	-	123.2	1.59	27.0
YW	-	+	-	33.5	0.69	7.6
YW _{ns}	-	+	-	34.3	0.71	10.7
MXP/YW	0	+	-	237.0	0.56	25.0
FW	-	-	+	15.4	1.45	7.5
FW _{ns}	-	-	+	15.6	1.71	8.0
MXP/FW	+	-	+	198.7	0.92	24.4
YW/FW	-	+	+	59.5	2.86	9.5
MXP/YW/FW	+	+	+	265.3	0.46	19.0

+ = High level, indicating presence of material in the mixture.
 - = Low level, indicating absence of material from the mixture.

FW = Seeded food waste, present at a dry weight of 0.043 dry kg, as a mixture of lettuce, carrots, cooked pasta, cooked meat, milk, and raw potatoes in equal wet weight proportions.

FW/YW = A mixture of food wastes and yard wastes.

MXP = Seeded mixed paper waste, present at a dry weight of 0.803 kg, as a mixture of office paper (OFP), old corrugated cardboard (OCC) and old newsprint (ONP), at dry mass ratios of 1.0:2.1:1.7 respectively.

MXP/FW = A mixture of mixed paper and food wastes.

MXP/YW = A mixture of mixed paper and yard wastes.

MXP/YW/FW = A mixture of mixed paper, yard wastes and food wastes.

YW = Seeded yard waste, present at a dry weight of 0.1545 kg, as a mixture of grass clippings and leaves set at dry mass ratios of 1.5:1 respectively.

^a As g C (or g N) produced from the corresponding amounts (in dry kg) of component or mixture (including seed), as shown.

Note: CO₂ emissions of 0.64 g subtracted from all CO₂ values (see Section 4.2). NH₃ not detected. Note also that runs YW_{ns} and FW_{ns} are not part of the original full factorial design (see text).

The model for the 2² factorial design used to investigate seed interaction has the form:

$$Y = n + (X_C/2) \times L_C + (X_S/2) \times L_S + (X_{CS}/2) \times L_C \times L_S + e \quad (4-2)$$

where

- X_C, X_S, X_{CS} = factor and interaction effects for each of the three MSW components (X_C), the seed (X_S) and the interaction of component/seed (X_{CS})
- L_C, L_S = take values of either -1 or +1 and represent the absence (low level or -1) or presence (high level or +1) of the component or the seed in a mixture, where L_C corresponds to the MSW component - that is either mixed paper, yard wastes or food wastes - and L_S corresponds to the seed
- e = errors (residuals) that are distributed normally with a zero mean and a constant variance.

Other parameters are as defined previously.

4.1.2 Mixture Experiment

The full factorial design is based on mixtures of MSW components prepared based on a typical U.S. MSW composition. The resulting models and the main effects and interactions may not be applicable to MSW of a different composition. Therefore, to better describe CO₂ and NH₃ yields from any MSW mixture on a per dry unit mass basis, an additional design was set-up based on the principles of a mixture experiment. The analysis used the same runs included in the factorial analysis approach, with the addition of one run, referred to as the MSW_{1/3} run. In the MSW_{1/3} run, all three MSW organic components were mixed in approximately equal dry weight proportions and composted. The MSW_{1/3} run was considered necessary since four of the eight runs used in the full factorial analysis contained mixed paper at percentages higher than 80% on a dry weight basis. No seed was added to the MSW_{1/3} run, since yard wastes and food wastes had been shown to contain microbial populations adequate to maintain the decomposition process and to effectively inoculate mixed paper.

As part of the mixture experimental design analysis, the polynomial Equation (3) can be fitted to the data:

$$Y_{kg} = b_P \times F_P + b_Y \times F_Y + b_F \times F_F + b_{PY} \times F_P \times F_Y + b_{PF} \times F_P \times F_F + b_{YF} \times F_Y \times F_F + b_{PYF} \times F_P \times F_Y \times F_F + e \quad (4-3)$$

where

- Y_{kg} = either the CO₂ yield or NH₃ yield of an MSW mixture expressed in g C-CO₂/dry kg or g N-NH₃/dry kg of mixture, respectively

- F_P, F_Y and F_F = dry fractions of mixed paper, yard waste, and food waste, respectively, in the mixture, with each of the F_P, F_Y, F_F values ranging from 0 to 1 and with $F_P + F_Y + F_F$ always equal to 1
- $b_P, b_Y, b_F, b_{PY}, b_{YF}, b_{PF}, b_{PYF}$ = model coefficients
- e = errors (residuals) that are distributed normally with a zero mean and a constant variance.

All statistical analyses were performed with the MINITAB v12.2 statistical package (Minitab Inc., PA, USA).

4.2 Results and Discussion

Results of the experimental runs used in the three 2^2 designs are included in Table 4-1, and results of the experimental runs used in the 2^3 design are included in Table 4-3. Note that the gaseous yields shown in Tables 4-1 and 4-3 correspond to the dry masses of the materials shown in these two tables. For example, 0.803 dry kg of seeded mixed paper (MXP) produced 136.3 g C and 1.76 g N, respectively, as shown in Table 4-1.

The CO_2 emissions from the control run (empty digester) were 0.64 g (as C), measured over a period of 48 days, and were subtracted from the CO_2 yields of all experimental runs. No significant ammonia was detected during the control run. Based on the above, the CO_2 and NH_3 yields for the control run were always set to 0.

4.2.1 Seed Interaction

The model shown in Equation 4-2 was fitted to the CO_2 and NH_3 yield data of Table 4-1. The goal of each 2^2 factorial analysis was to investigate the magnitude of seed contribution to individual component yields and the effect of the seed/component interaction. The coefficients of Equation 4-2 are presented in Table 4-2. They are half of the values of the estimated main and interaction effects. Since there are no degrees of freedom during model fitting, no standard errors can be estimated for each model coefficient. The significance of each effect should be based, therefore, on the value of the corresponding coefficient as estimated during model fitting.

Based on Table 4-2, the seed main effects are 9.2% $[(1.63/17.7) \times 100]$ and 11.5% $[(0.98/8.51) \times 100]$ of the yard waste and food waste main effects, respectively, when predicting CO_2 yields. The seed/component interaction effects are 3.3% $[(0.60/17.7) \times 100]$ and 6.9% $[(0.59/8.51) \times 100]$ of the main component CO_2 yield effects for yard wastes and food wastes, respectively. This indicates that some minor additional amounts of CO_2 will be produced by seeding these two components, compared to the simple summation of the CO_2 yields from the individually composted component and individually composted seed. The fraction of the interaction-related CO_2 emissions due to additional decomposition of the component or additional decomposition of the seed cannot be determined.

In the case of mixed paper, seeding was necessary to initiate decomposition, since negligible CO_2 was produced from the MXP_{ns} run. This is also shown by the fact that the interaction effects are equal to the main component effects for both the CO_2 and NH_3 yields (see Table 4-2). The materials used to prepare mixed paper (office paper, cardboard, old newsprint) do not appear to have significant amounts of microbial populations present. In the case of mixed paper in particular, it is expected that the initial ratio of seed to substrate and the type of seed could have affected the decomposition rates and extent. Attempts to vary seed to substrate ratios were beyond the scope of this work. It is noted that the effect of seed to mixed paper is not a matter of additivity of individual CO_2 emissions. Seed was simply required to provide the minimal amount of microorganisms necessary to start the decomposition process for mixed paper.

The relatively small seed/component interaction effects for food and yard wastes (<7% compared to the main component effect) are explained by the fact that these components are likely to contain an indigenous microbial population capable of initiating and maintaining the aerobic decomposition process. According to Gray et al. (1971), composting of separated waste mixed refuse was not affected by the addition of several types of inocula due to the adequacy of the indigenous microbial population in degrading these materials. The slightly higher CO_2 seed/component interaction effect observed for food wastes than yard wastes can be explained by the former substrate containing cooked pasta, cooked meat, and pasteurized milk. These subcomponents account for 50% of the wet weight of food wastes and are all expected to have negligible amounts of microbial biomass prior to composting. In addition, seed was supplied in slightly higher ratios to food wastes (1:4.7 dry seed to dry component ratio) compared to yard wastes (1:6.5), which can also partially explain the higher seed/component interaction in the former substrate compared to the latter.

In the case of ammonia, the seed effect itself accounts for 8.1% and 1.6% of the yard waste and food waste main effects, respectively. The seed/component interaction effects are 2.7% and 0.7% of the yard waste and food waste main effects, respectively. Therefore, seed/component interaction effects for NH_3 are smaller than the corresponding interaction effects for CO_2 , for both yard wastes and food wastes. It is likely that a microbial population capable of ammonification processes is originally present in the unseeded food wastes and unseeded yard wastes. The almost negligible interaction effect of seed/food wastes (<0.7% of the main component effect) is also explained by the relatively large ammonia emissions from food wastes alone, compared to the ammonia emissions from other substrates.

Figure 4-1 shows the cumulative CO_2 yields. Based on Figure 4-1, seeding did appear to affect the CO_2 production rates, but not yields, for food wastes. Unseeded and seeded food wastes had similar CO_2 production rates until day 5. After day 5, unseeded food wastes had steadily lower CO_2 production rates compared to the corresponding rates of seeded food wastes. It took 56 days for seeded food wastes to reach more or less complete degradation, as opposed to a period of 90 days for the FW_{ns} run.

4.2.2 Calculating Gaseous Emissions from Seeded Runs

Results in the previous section indicate that the seed/component interactions for both food wastes and yard wastes are less than 10% of the corresponding main component effects

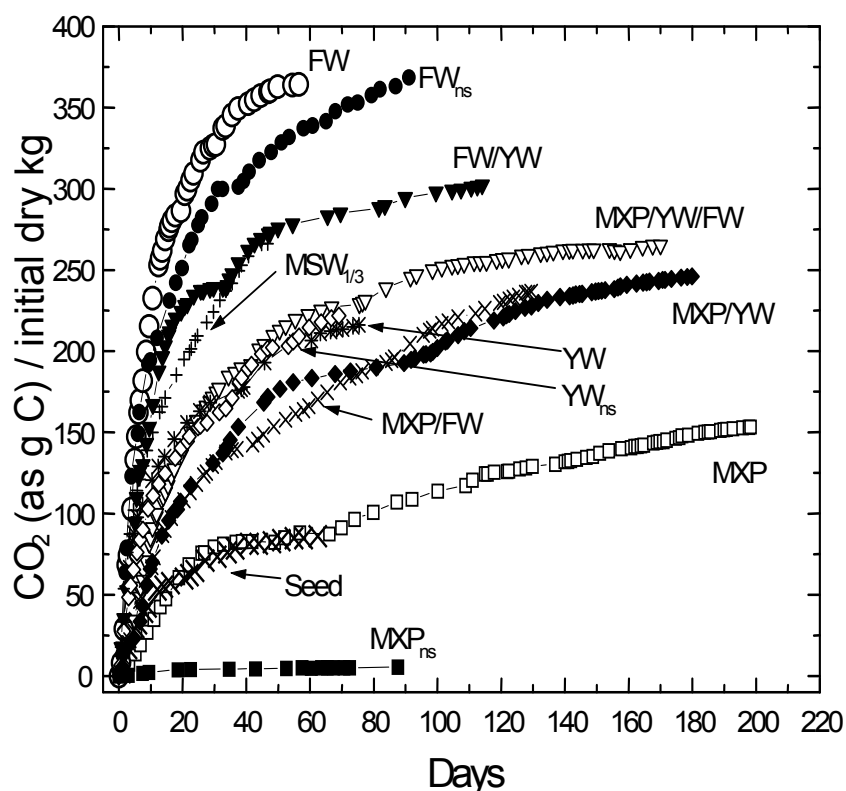


Figure 4-1. Cumulative CO₂ production (as g C) per dry kg of starting material (including seed).

when predicting CO₂ and NH₃ yields. The seed main effects are also relatively small (less than 10% of the main component effect). Due to the relatively small seed main effects and seed/component interaction effects, they will both be considered insignificant. Based on that, the gaseous yields from seeded components and seeded mixtures will be expressed as g of total C-CO₂ (or total N-NH₃) emitted per dry kg of total substrate (component + seed). The same approach is also followed for mixed paper. The cumulative CO₂ (as C/dry kg) and NH₃ (as N/dry kg) emissions from all components and mixtures are given in Tables 4-3 and 4-4 and are illustrated in Figures 4-1 and 4-2, respectively. Table 4-4 presents the fractions of each component in the mixture and the corresponding CO₂ and NH₃ yields, expressed on a per dry kg of substrate basis. This slightly differs from the expression of yields shown in Table 4-3; the difference simply reflects the format to which the numbers were fitted to Equation 4-1 (Table 4-3) and Equation 4-3 (Table 4-4).

Based on the assumptions stated above, the FW and FW_{ns} runs can be treated as replicates in terms of CO₂ and NH₃ yields. The average CO₂ and NH₃ yields from these two runs are 366.5 ± 2.97 g (as C)/dry kg and 37.35 ± 4.5 g (as N)/dry kg, respectively. Similarly, the YW and the YW_{ns} runs can be also treated as replicates with average CO₂ and NH₃ yields of 219.5 ± 3.46 g (as C) / dry kg and 4.5 ± 0.14 g (as N) / dry kg, respectively. Due to the large seed interaction for mixed paper, the MXP_{ns} run will not be considered as replicate to the MXP run.

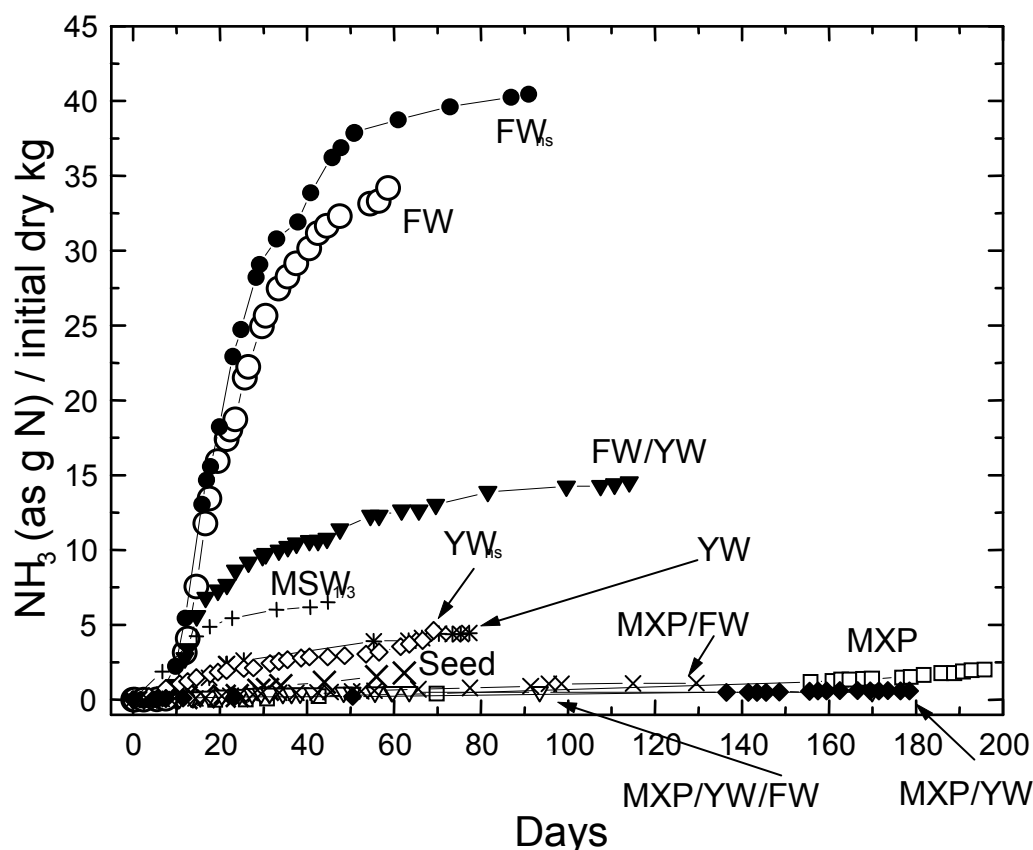


Figure 4-2. Cumulative NH_3 production (as g N) per dry kg of starting material (including seed).

Note: The result for MXP_{ns} was 0.0; values in parentheses indicate initial N content (in % dry matter) for specified substrate, including nitrogen added as nutrient to the MXP, MXP/FW, MXP/YW and MXP/YW/FW runs.

As Figure 4-1 shows, certain runs fully decomposed earlier than others, which explains the fact that some runs were terminated at 60 days (FW) and others lasted more than 150 days (MXP, MXP/YW). This appears to be a result of differences among hydrolysis rate constants for the different solid fractions of each component, assuming that solids hydrolysis is the rate-limiting step in the decomposition of all substrates, as is likely.

As illustrated in Figure 4-1, food waste is the largest producer of CO_2 among all components, producing 368 g CO_2 (as g C/dry kg), when unseeded. Seed produced only 86 g CO_2 (as g C/dry kg), which was the lowest yield among all substrates. Mixtures of two components result in CO_2 yields that—on a per dry kg basis—are always between the CO_2 yields of the individual components that constitute the mixtures. The flattening of the CO_2 cumulative curve observed for the YW/FW run between days 25 and 35 is due to substrate drying. Moisture

Table 4-4. Fractions of Components in Mixtures (dry mass basis) and Gaseous Yields for 12 Runs

Run	MXP	YW	FW	Dry seed / Dry component ratio	CO ₂ (g C / dry kg) ^a	NH ₃ (g N / dry kg) ^a	Initial N content (% dry weight) ^b	% of initial N mineralized to N-NH ₃ ^c
Seed	0	0	0	1	86.0	1.8	2.8%	6.3%
MXP	1	0	0	1:9.4	153.3	2.0	1.9% (0.35%)	10.7% (56.7%)
MXP _{ns}	1	0	0	0	5.5	0.0	0.09%	0.0%
YW	0	1	0	1:6.5	217.0	4.4	2.1%	21.7%
YW _{ns}	0	1	0	0	221.9	4.6	1.9%	24.8%
FW	0	0	1	1:4.8	364.4	34.2	5.6%	61.0%
FW _{ns}	0	0	1	0	368.6	40.5	6.2%	65.4%
MXP/YW	0.83	0.17	0	1:7.2	246.1	0.6	1.5% (0.72%)	3.9% (8.4%)
MXP/FW	0.96	0	0.04	1:9.9	236.6	1.1	1.9% (0.58%)	5.9% (19.1%)
FW/YW	0	0.78	0.22	1:7.4	301.9	14.5	2.9%	50.2%
MXP/YW/FW	0.80	0.155	0.045	1:7.4	265.3	0.5	1.7% (0.9%)	3.0% (5.6%)
MSW _{1/3}	0.34	0.37	0.30	0	266.3	6.5	2.6%	25.2%

NS = No seed.

^a Values represent total mass of emitted gas per dry kg of substrate (component + seed).

^b Values in parentheses indicate initial total organic nitrogen content prior to addition of nutrients in the specified runs.

^c Values in parentheses do not account for added nutrients in calculation of total initial N for the specified substrates.

was added on day 35 to this run, resulting in the continuation of its decomposition. This moisture limitation was also observed for the MXP run, between days 30 and 65, and for the YW_{ns} run, between days 25 and 35, with moisture added in both cases thereafter. As Figure 4-1 shows, low but steady CO₂ production rates were observed for the MXP, MXP/YW and MXP/FW runs for a relatively long period of time fully decomposed, indicating that more time might have been needed for these substrates to fully decompose. The runs were terminated, however, because of time constraints. In all runs including mixed paper, cardboard was the only subcomponent visually present in the digester at the termination of each run.

Figure 4-2 presents the time courses of the cumulative ammonia emissions from all runs, except MXP_{ns} that produced zero ammonia. Table 4-4 shows the initial N contents (in % dry matter) and the % of initial N that was mineralized to N-NH₃ for all 12 runs. As shown, ammonia yields correlate strongly with the initial N content of the substrate. Unseeded food wastes, with an initial N content of 6.2% (dw), produced 40.5 g NH₃ (as N/dry kg), which was the highest ammonia yield among all runs. Seeded food wastes had a NH₃ yield of 34.1 g N/dry kg. The 19% lower ammonia emission from seeded food wastes is partly attributed to the fact that the seed (which was in relatively large ratios in that run) produced minor amounts of ammonia and was included as part of the total substrate. In addition, ammonia production rates were still relatively high for the FW run at the time of its termination, despite the low CO₂ production rates, and therefore more ammonia could have been produced if the run was stopped at 90 days, as the FW_{ns} run, instead of 54 days.

Yard wastes were the next highest with ammonia yields of approximately 4.5 g NH₃ (as N)/dry kg. Although food wastes had an initial N content approximately three times higher than the yard wastes, they emitted approximately 10 times more ammonia than did yard wastes. This is likely a result of less nitrogen required for microbial biomass assimilation in the case of food wastes compared to yard wastes, therefore resulting in a higher release of excess nitrogen as ammonia in food wastes. Approximately 65% of the initial N of food wastes was mineralized to ammonia, while approximately 20% to 25% of the initial N for yard wastes was converted to ammonia.

Seed, despite its relatively high initial N content of 2.8% (dw) yielded less than half the ammonia than did yard wastes. This is probably because nitrogen is in a less bioavailable form in the seed compared to nitrogen forms in yard wastes and food wastes. This is likely because the seed was already partially decomposed. Generally, the forms of nitrogen in various organic substrates is expected to affect ammonia releases. Inoko et al. (1979) reported five forms of nitrogen in city refuse compost, with approximately 40% being in the form of amino acids, approximately 30% unidentifiable, and the rest in other forms.

Low ammonia emissions compared to other runs were recorded for all runs that had a mixed paper content of higher than 80% dry matter (MXP, MXP/FW, MXP/YW, MXP/YW/FW). It appears that N was limiting in these runs, even after the addition of nutrients that resulted in initial N contents approximately similar to the initial N contents for yard wastes. The relatively high ammonia yield from mixed paper alone is attributed to the addition of nutrients after day 160. These nutrients were probably not assimilated by the microbial biomass, due to mixed paper being at a relatively nonactive composting stage at the time of that addition.

Based on Figure 4-2, it appears that the FW and FW_{ns} might not have yielded all of their releasable ammonia, since ammonia production rates were higher than zero for both runs at the time of termination. It is likely that materials containing protein were still decomposing at the end of these runs.

4.2.3 MSW Component Interactions

Data in Table 4-3 were fitted to Equation 4-1. The unseeded YW and FW runs (YW_{ns} and FW_{ns}) were taken as replicates to the YW and FW runs as discussed. The MXP_{ns} run was not used during this analysis due to the negligible degradation observed for that run because of the lack of seed. The dry weights of materials shown in Table 4-3 are not the actual dry masses used in the digesters, but have been adjusted to equal the dry weights of each component used in the run MXP/YW/FW, for which the results are also presented per kg of dry mass.

4.2.3.1 CO₂ Yield—Main Effects and Interactions. The best reduced CO₂ yield factorial model was fitted using Minitab v12.2, so that errors were normally distributed with a mean of zero. The resulting model is shown in Equation 4-4:

$$Y_{\text{co}_2} = 116.2 (\pm 4.90) + 89.8 (\pm 4.90) L_p + 33.4 (\pm 4.97) L_Y + 17.0 (\pm 4.97) L_F + 11.7 (\pm 4.97) L_p L_Y \quad (4-4)$$

where

Y_{co_2}	=	mass of CO ₂ (as g C) emitted from a mixture of MSW
L_p	=	absence (-1) or presence (+1) of mixed paper in the mixture
L_Y	=	absence (-1) or presence (+1) of yard wastes in the mixture
L_F	=	absence (-1) or presence (+1) of food wastes in the mixture.

Levels (L) can take values of -1 or +1 only, defining the absence or presence of a component in the mixture. Values in parentheses represent the standard errors for the corresponding coefficients. The adjusted R² for Equation 4-4 is 97.7%, while residuals have a mean of zero and appear to follow a normal distribution. From Equation 4-4, all three main effects are considered statistically significant at a 95% confidence level. The mixed paper and yard wastes interaction effect appears to be statistically significant at the 90% confidence level.

According to Equation 4-4, the major contributor to the CO₂ yield is actually mixed paper, at the percentages that mixed paper is present in U.S. MSW composition. This would be expected since mixed paper accounts for 80% of the dry mass of MSW, based on the U.S. MSW composition used in the design of the experiment. Yard wastes and food wastes produce the next most significant amounts of CO₂, while the interaction of mixed paper and yard wastes (MXP/YW) appeared as marginally significant. The other two two-component interactions and the three-component interaction were insignificant.

The MXP/YW interaction significance can be explained by the fact that mixing of mixed paper with yard wastes—at the specified ratios—results in further seeding of the paper by the microbial population present in yard wastes. This additional seeding from yard waste provides a population able to further degrade slowly degradable components of the mixture—especially

mixed paper. The use of yard wastes may result also in an additional supply of nitrogen to the total mixture. Although nitrogen was added to the MXP run in the form of salts, it might still have been in limiting amounts. Such synergistic effects would be expected. For example, Szegi (1988) observed that lignin by itself decomposes more slowly than lignin incorporated in cell walls. The explanation given was that the presence of easily degradable matter in cell walls enables quicker multiplication of microorganisms, promoting the faster decomposition of lignin.

Cumulative production profiles for the seeded mixed paper (Figure 4-1) reveal that mixed paper decomposition could have continued, albeit at slow rates, after the experiment was terminated. Therefore, the amount and type of seed initially added to mixed paper alone might have simply resulted in the relatively slow decomposition rates, compared to runs with percentages of paper and other components (MXP/YW, MXP/FW). Inadequate seeding might, therefore, have resulted in the MXP run not reaching its “full” extent of decomposition within the time constraints under which the experiment was performed. If more time had been used for the MXP run—with the seed as used—the MXP yield would have been higher than that recorded in this study. To check that, higher CO₂ yields from the MXP run were input to the model. It was observed that the higher the CO₂ yields from the MXP run, the lower the interaction effect of mixed paper and yard wastes would become, until it would finally become statistically insignificant. It, therefore, appears that the slow decomposition rates of mixed paper that did not allow it to fully decompose finally resulted in the interaction of MXP/YW to appear as significant.

Exclusion of the MXP/YW interaction from Equation 4-4 results in an additive model. The adjusted R² for the predictive model, after excluding the interaction, becomes 96%, which is only slightly lower than the adjusted R² value of 97.7% of Equation 4-4. The above indicates that an additive model can also adequately describe CO₂ emissions from MSW. The additive CO₂ model is shown in Equation 4-5:

$$Y_{\text{CO}_2} = 116.2 (\pm 6.5) + 89.8 (\pm 6.5) L_P + 31.5 (\pm 6.5) L_Y + 18.9 (\pm 6.5) L_F \quad (4-5)$$

with parameters as defined previously. It is noted that residuals in Equation 4-5 are closer to being normally distributed compared to the distribution of the residuals from Equation 4-4.

4.2.3.2 NH₃ Yield—Main Effects and Interactions. In the case of NH₃ yield, the best reduced fit model is given as Equation 4-6:

$$Y_{\text{NH}_3} = 1.06(\pm 0.077) - 0.18(\pm 0.077) L_P + 0.06(\pm 0.079) L_Y + 0.37(\pm 0.079) L_F - 0.43(\pm 0.079) L_P L_Y - 0.56(\pm 0.079) L_P L_F \quad (4-6)$$

where

Y_{NH_3}	=	mass of NH ₃ (as g N) emitted from a mixture of MSW
L_P	=	absence (-1) or presence (+1) of mixed paper in the mixture
L_Y	=	absence (-1) or presence (+1) of yard wastes in the mixture
L_F	=	absence (-1) or presence (+1) of food wastes in the mixture.

The adjusted R^2 for Equation 4-6 is 91.6%. Values in parentheses represent the standard errors for the corresponding coefficients, while residuals for the model are normally distributed with a mean of zero and constant variance. As Equation 4-6 shows, the most important main effect is due to food wastes. The interactions of mixed paper and food waste (MXP/FW) and mixed paper and yard wastes (MXP/YW) are the only significant interactions and have negative coefficients. This means that inclusion of mixed paper in the MSW mixture reduces overall ammonia emissions. It is interesting to note that both the mixed paper and yard waste main effect are statistically insignificant (at the 95% confidence level). However to omit the main effect of either mixed paper or yard wastes from the model would be statistically wrong when interactions that involve these components appear statistically significant. The yard waste and food waste interaction and the three-component interaction were insignificant.

In the case of the NH_3 model (Equation 4-6), more interactions were significant compared to the CO_2 model (Equation 4-4). The high ammonia yields predicted for food wastes are a result of their high initial N content, as discussed. The addition of mixed paper in a MSW mixture reduces ammonia yields due to the relatively low initial N content of mixed paper despite the addition of nutrients. This addition of nutrients in mixed paper runs resulted in initial N contents approximately similar to the initial N contents of yard wastes, for which ammonia yields were much higher than that from the mixed paper runs. The lower ammonia yields from mixed paper can therefore be explained by an assimilation of all the nitrogen added to or present in mixed paper to form microbial biomass. It can also be explained by the fact that some of the externally added nitrogen (probably nitrates) might have become only partially available to the existing microbial population and therefore did not enter the N cycle. Leaching of the ammonium nitrate salt to the bottom of the digester is also suspected and could contribute to a probable low initial N content achieved for the mixed paper runs. Nitrogen losses could also have occurred during the addition of NH_4NO_3 to the substrate, prior to the initiation of a run. The nitrogen losses are also indicated by the less than 35% nitrogen mass balance closures for all runs involving mixed paper, namely, MXP, MXP/FW, MXP/YW, MXP/FW/YW.

4.2.3.4 Carbon Dioxide Production Rate Interactions. Mixtures of components appear to affect production rates. For example, the MXP/YW run had distinctively higher production rates than the MXP alone, as shown by the steeper CO_2 curve slope of the former compared to the latter during the first 10 days of the experiment (Figure 4-1). Because substrate utilization rates are usually a function of the substrate and biomass concentrations, the higher CO_2 production rates of MXP/YW compared to MXP appear to be a result of the presence of a more readily decomposable substrate (yard wastes), compared to mixed paper, and of a higher microbial population concentration compared to MXP alone.

Using the full factorial experimental design shown in Table 4-3, a statistical analysis was performed to investigate the main effects of components and interactions on the rates of CO_2 production. The response chosen was the number of days required for each run to emit 50% of its corresponding CO_2 yield, as shown in Table 4-3. The resulting equation is:

$$T_{\text{CO}_2_{50\%}} = 15.3(\pm 0.5) + 8.6(\pm 0.5) L_p + 0.4(\pm 0.5) L_Y - 0.06(\pm 0.5) L_F - 2.3(\pm 0.5) L_p L_Y - 2.1(\pm 0.5) L_p L_F - 1.4(\pm 0.5) L_Y L_F \quad (4-7)$$

where

$T_{\text{CO}_2_{50\%}}$	=	days required for the MSW mixture/component to emit 50% of its carbon dioxide yield
L_p	=	absence (-1) or presence (+1) of mixed paper in the mixture
L_Y	=	absence (-1) or presence (+1) of yard wastes in the mixture
L_F	=	absence (-1) or presence (+1) of food wastes in the mixture.

Values in parentheses represent the standard errors for the corresponding coefficients, while residuals for the model are normally distributed with a mean of zero. Equation 4-7 shows that presence of mixed paper in an MSW mixture ($L_p=+1$) significantly increases overall composting times compared to all other main and interaction effects. The main effects of both yard wastes and food wastes appeared statistically insignificant at the 95% confidence level. However, the two-component interactions were statistically significant. Therefore, as yard wastes or food wastes are introduced in a mixture containing mixed paper ($L_Y=+1$ or $L_F=+1$), composting times are reduced. In particular, the MXP/YW interaction effect results in the largest composting time decrease compared to the other two two-component interactions. The seeding of mixed paper with yard wastes appears to be the reason for the faster decomposition rates of the MXP/YW run, as discussed. In addition, mixing of yard wastes and food wastes also reduces composting times due to “seeding” of food wastes with the microbial population present in yard wastes as well as the additional supply of readily degradable substrate found in yard wastes. The negative value of the food waste coefficient, as opposed to the positive coefficients of mixed paper and yard wastes, indicates that food wastes degrade faster than either mixed paper or yard wastes. The three-component interaction was insignificant.

Solids hydrolysis appears to be the major rate-limiting step during composting for all substrates—except mixed paper—since nutrients, seeding, moisture, and oxygen supply were kept at near optimum values. Therefore, the initial steep slope in all cumulative CO_2 production curves (Figure 4-1) is a result of the breakdown of the readily hydrolyzable solid fraction contained in any of the substrates. This fraction is expected to contain starches and other water-soluble substrates (e.g., monosaccharides and fatty acids). After readily degradable material is decomposed, mineralization rates become a function of the concentration of the remaining slowly hydrolyzable solid fraction and the corresponding hydrolysis rates for that fraction. The slowly degradable fraction in all substrates is therefore responsible for the flattening of the cumulative CO_2 curves shown in Figure 4-1, as composting approaches the end. For mixed paper alone, inadequate seeding and nutrient limitation might be additional decomposition rate-limiting factors.

Production rate curves for CO_2 and NH_3 for the food waste and yard waste runs are shown as Figures 4-3 and 4-4 respectively. The highest CO_2 production rates occurred during the first 10 days for both substrates. Figures 4-3 and 4.4 show the characteristic lag between periods of highest CO_2 and NH_3 production, with NH_3 production lagging CO_2 production by 10 to 15 days. This NH_3 lag appears to be a result of the pH increase, commonly occurring at later stages of decomposition during MSW composting. This pH increase is a result of the consumption of organic acids that are normally produced during the active composting stage (Gray et al., 1971). pH values measured directly from the leachate contained at the bottom of the digester were 8.2 at the end of the FW/YW run, 8.7 at the end of the YW run, and 8.8 at the end of the YW_{ns} run. Ammonia is expected to be partially volatilized at such pH values and

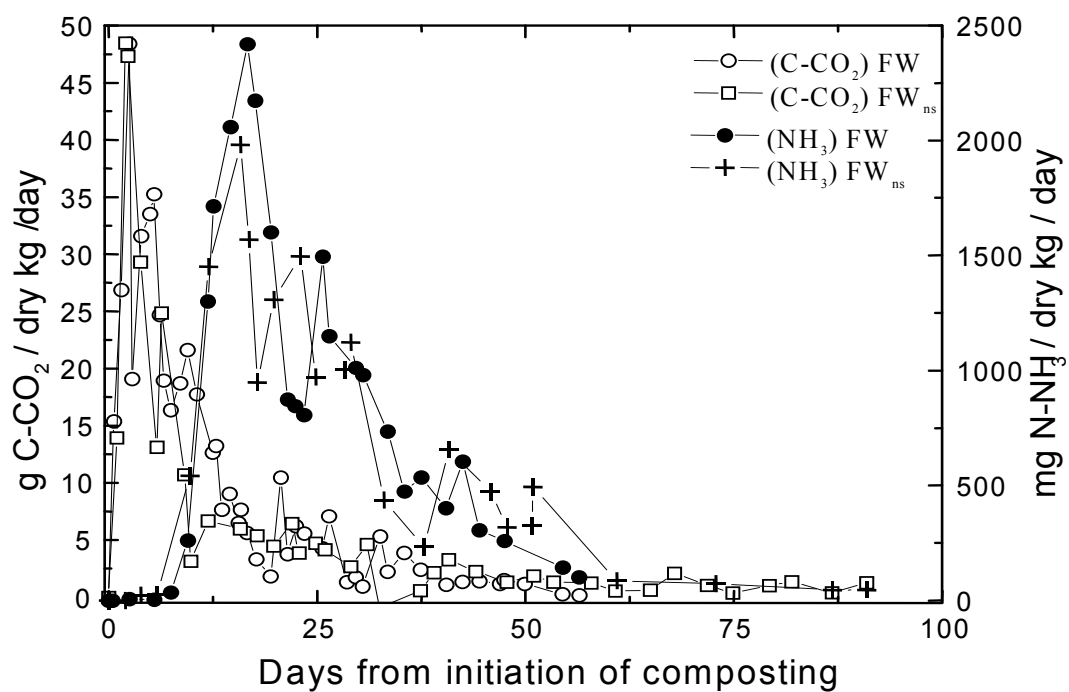


Figure 4-3. CO₂ and NH₃ daily production rates for the FW and FW_{ns} runs.

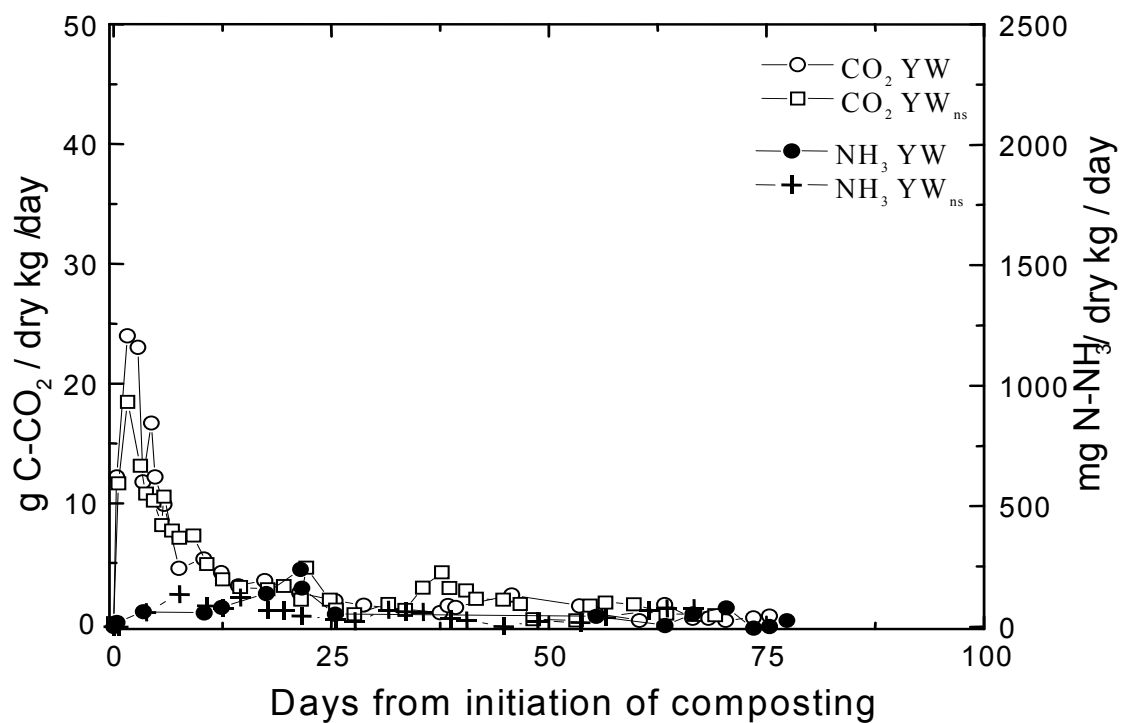


Figure 4-4. CO₂ and NH₃ daily production rates for the YW and YW_{ns} runs.

thermophilic temperatures. Lower production rates for CO₂ and much lower rates for NH₃ were obtained for yard wastes than for food wastes.

4.2.4 Mixture Experiment

Equations 4-4, 4-5, and 4-6 can describe yields of CO₂ (C) and NH₃ (N) (in gr) from a mixture of MSW depending on the relative percentages of mixed paper, yard wastes, and food wastes on which the experiment was based. These equations are useful to investigate main effects and interactions; however, they are based on the presence or absence of a given component and are not necessarily applicable when estimating yields from MSW of various compositions, which can be different from the typical U.S. MSW composition used in this experiment.

Based on the principles of mixture experimental design (Cornell, 1990; Draper and Smith, 1998), the results given in Table 4-3 were supplemented and then used to develop an equation to describe gaseous mass loadings per dry kg of MSW of various compositions. For this reason, run MSW_{1/3} (see Table 4-4) was also included in the data fitting. Similar to the factorial design approach, the FW_{ns} and YW_{ns} runs were considered replicates to the FW and YW runs, respectively. The MXP_{ns} run was not included during model fitting since negligible decomposition was observed for that run due to lack of seed.

Equation 4-3 was fitted to the data in Table 4-4 separately for the CO₂ and NH₃ yields. Table 4-5 presents the regression analysis results for the first-, second-, and third-order models. The second- and first-order models were fitted to the data by neglecting the third-order and second-order terms, respectively, from equation (4-3). Note that the term “order” is used in respect to the dependent variables (F_p, F_y, F_f). The order of the equations with respect to the model coefficients is 1. According to Draper and Smith (1998), the coefficient of determination R² is not defined for equations that have no intercept, as is the case for Equation 4-3. However, to allow comparison with Equations 4-4 and 4-6, the adjusted R² values were calculated based on the definition given in most statistics texts (Draper and Smith, 1998). These R² values are given in Table 4-5.

Using the third-order CO₂ predictive model, all model coefficients appear to be significant. However, values higher than 650 g C-CO₂ /dry kg are predicted from some mixtures of food wastes and mixed paper. Although the 3rd order model results in a higher adjusted R² than the other models, there are no experimental runs to support the predicted high yields. In addition, residuals for this model were not normally distributed and the standard errors for the second-order coefficients and the third-order coefficient were relatively large. The second-order model is inadequate, also due to the high standard errors for the second-order coefficients. The first-order model has a higher adjusted R² than the second-order model, while all residuals are normally distributed. Therefore the first-order model is considered the most adequate for describing CO₂ yields, based on the experimental runs mentioned in this paper.

In the case of NH₃, the second- and third-order models have large standard errors for their second- and third-order coefficients. In addition, the mixed paper coefficient (b_p) is statistically insignificant (at the 95% confidence level), but will be included in the final model

Table 4-5. Parametric Regression Analysis for Third-, Second-, and First-Order Models Based on Equation 4-3

Model	Coeff/SE	b_p	b_Y	b_F	b_{PY}	b_{PF}	b_{YF}	b_{PYF}	$R^2(\text{adj.})$
Third-order	CO ₂ coeff	154.6	219.8	366.3	674.0	1905	280.4	-6,858	99.7%
	SE (CO ₂)	15.6	11.0	11.0	135.3	540.7	105.5	1563	
	NH ₃ coeff	2.01	4.50	37.3	-12.4	-57.6	16.2	-38.9	98.1%
	SE (NH ₃)	2.6	1.8	1.8	22.3	89.2	17.4	257.8	
Second-order	CO ₂ coeff	202.3	222.2	365.8	303.0	-294.4	202.1		98.3%
	SE (CO ₂)	26.4	26.0	26.0	249.2	478.1	245.3		
	NH ₃ coeff	2.28	4.52	37.3	-14.5	-70.1	15.8		98.5%
	SE (NH ₃)	1.6	1.6	1.6	15.2	29.1	14.9		
First-order	CO ₂ coeff	217.4	237.3	370.5					98.5%
	SE (CO ₂)	19.3	21.2	24.1					
	NH ₃ coeff	-0.57	4.47	36.8					96.9%
	SE (NH ₃)	1.8	2.0	2.2					

SE is the standard error for the corresponding coefficient.

since the mixed paper / food waste interaction (b_{PF}) was found to be statistically significant in the second-order model (at the 95% confidence level). Therefore, a reduced second-order model was finally fit by ignoring the MXP/YW and FW/YW second-order terms and the third-order term. Based on the above, the best reduced models expected to adequately estimate CO_2 and NH_3 yields on a per dry kilogram of MSW mixture basis (in g C/dry kg and g N/dry kg, respectively) are Equations 4-8 and 4-9:

$$Y_{\text{kg_CO}_2} = 217.4 \times F_P + 237.3 \times F_Y + 370.5 \times F_F \quad (4-8)$$

$$Y_{\text{kg_NH}_3} = 1.29 (\pm 1.38) \times F_P + 5.15 (\pm 1.37) \times F_Y + 37.6 (\pm 1.56) \times F_F - 68.9 (\pm 23.4) \times F_P \times F_F \quad (4-9)$$

where

- $Y_{\text{kg_CO}_2}$ = mass of CO_2 (as g C) emitted per dry kg of MSW mixture
- $Y_{\text{kg_NH}_3}$ = mass of NH_3 (as g N) emitted per dry kg of MSW mixture
- F_P, F_Y and F_F = dry fractions of mixed paper, yard waste and food waste, respectively, in the mixture, with each of the F_P, F_Y, F_F values ranging from 0 to 1 and with $F_P + F_Y + F_F$ always equal to 1.

The adjusted R^2 is 98.5% for both Equations 4-8 and 4-9. The negative second-order coefficient in Equation 4-9 indicates that the mixing of paper and food wastes significantly reduces overall NH_3 emissions. This conclusion was also drawn and explained as part of the full factorial design analysis presented earlier.

The mixture experimental approach can also estimate interactions, also known as synergisms or antagonisms (Cornell, 1990), which are indicated by the positive or negative sign of the coefficient of the product of any of the F_i values in the equation (with i being either P, Y or F, as noted above).

4.3 Final Recommended Model(s)

The above statistical methodologies present models that can estimate CO_2 and NH_3 yields during MSW composting. The full factorial design based on Equations 4-1 and 4-2 are useful only in understanding whether the yields are additive and what interactions are important. Their applicability in estimating gaseous emissions for various MSW mixtures is limited, since they are based on the specific low and high levels used during the experiment. Therefore, Equations 4-4 and 4-6 estimate the mass of CO_2 or NH_3 (in g) emitted from the specified dry weights of the components (in kg) by setting the MXP/YW/FW substrate weight equal to 1 kg; Equations 4-8 and 4-9, however, are based on the grams of C- CO_2 (or N- NH_3) emitted per dry kg of each of the mixtures.

The mixture-experiment-based Equations 4-8 and 4-9 are based on the same runs used in the full factorial design, supplemented by one additional run. The additional run ($\text{MSW}_{1/3}$) was performed to investigate further the mixed paper/yard waste interaction that appeared as

marginally significant by the full factorial analysis. The results of this additional run could not have been included in the full factorial design.

Because errors were distributed normally for Equations 4-4, 4-6, 4-8, and 4-9, the adjusted R^2 values can be used to compare the above equations. Based on that, Equations 4-8 and 4-9 (with adjusted R^2 of 98.5% each) are more adequate for predicting CO_2 and NH_3 yields, respectively, than Equations 4-4 and 4-6 (with adjusted R^2 of 97.7% and 91.6%, respectively).

The highest residuals of Equation 4-8 are observed for the mixed paper and the mixture of yard wastes and food wastes (see also Figure 4-5). In the case of mixed paper, the predicted value from Equation 4-8 is 217.4 g C- CO_2 /dry kg, while the experimentally measured yield was 153.3 g C- CO_2 /dry kg. This deviation is probably attributable to the fact that mixed paper had not fully decomposed, probably due to inadequate seeding; therefore, the final expected yield for that run might have been equal to that predicted by the first order model. Based on that, the MXP run had yielded approximately 71% of its expected ultimate CO_2 yield during the experiment. According to the gas production rates of the mixed paper run at termination of that run, it would take approximately 200 additional days for mixed paper to reach its ultimate CO_2 yield, as is predicted by Equation 4-8.

According to Equation 4-8, no component interactions are statistically significant during degradation of MSW components to carbon dioxide, as long as these components reach their full extent of decomposition. An additive model was also suggested during the full factorial analysis, as shown by Equation 4-5. Figure 4-5 shows the actual and estimated CO_2 yields from the runs given in Table 4-4.

Based on the recommended Equation 4-9, yard wastes and food wastes are the only two statistically significant components, while only one two-component interaction is significant when predicting NH_3 yields. The full factorial analysis had shown that the mixed paper and yard wastes interaction was also significant in addition to the mixed paper and food waste interaction. The full factorial derived equation had shown that the yard waste main effect is insignificant, as opposed to the mixture equation predictions. These partially different conclusions are attributed to the different formats of Equations 4-6 and 4-9. Equation 4-6 estimates the yields of gases produced from the specific amounts of each component present in the mixture (e.g., 0.69 g N produced from 0.155 dry kg), while equation 4-9 estimates the yields per dry kg from each component or mixture. Equation 4-9 estimates NH_3 yields relatively well for all runs except for the runs that contain relatively large percentages of mixed paper (MXP, MXP/FW, MXP/YW, MXP/YW/FW). This lack of fit is probably due to the relatively high ammonia yield from the MXP run resulting from the late addition of nutrients. Figure 4-6 shows the actual and estimated NH_3 yields from the runs mentioned in Table 4-4.

Figures 4-5 and 4-6 are the response surfaces for the prediction of CO_2 and NH_3 yields according to Equations (4-8) and (4-9), respectively. Black dots indicate the “location” of experimental runs, showing the percentages at which components were combined in the mixture on a dry weight basis. The “flat” response surface of Figure 4-5 indicates that the predictive model is linear. The highest yield is observed when food waste is the sole component of MSW with a maximum yield of approximately 366 g C- CO_2 /dry kg of food wastes, which is the average value of the FW and FW_{ns} run CO_2 yields. The CO_2 yield predicted for mixed paper

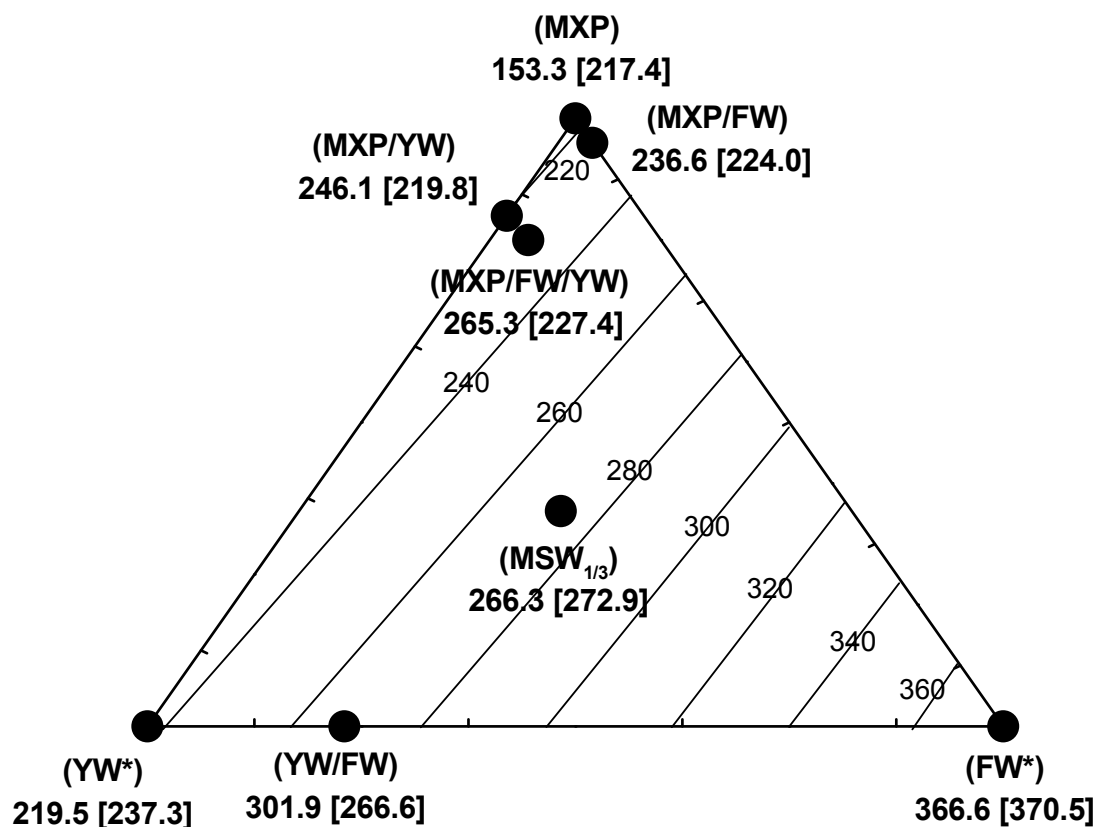


Figure 4-5. Response surface for estimation of CO₂ yields using Equation 4-8 (contour lines represent points of equal carbon dioxide yield expressed in g C-CO₂ per dry kg of substrate).

* Average experimental value from seeded and unseeded runs considered as replicates for corresponding component.

Note: Experimental data values shown left of the brackets; Equation 4-8 predictions shown in brackets.

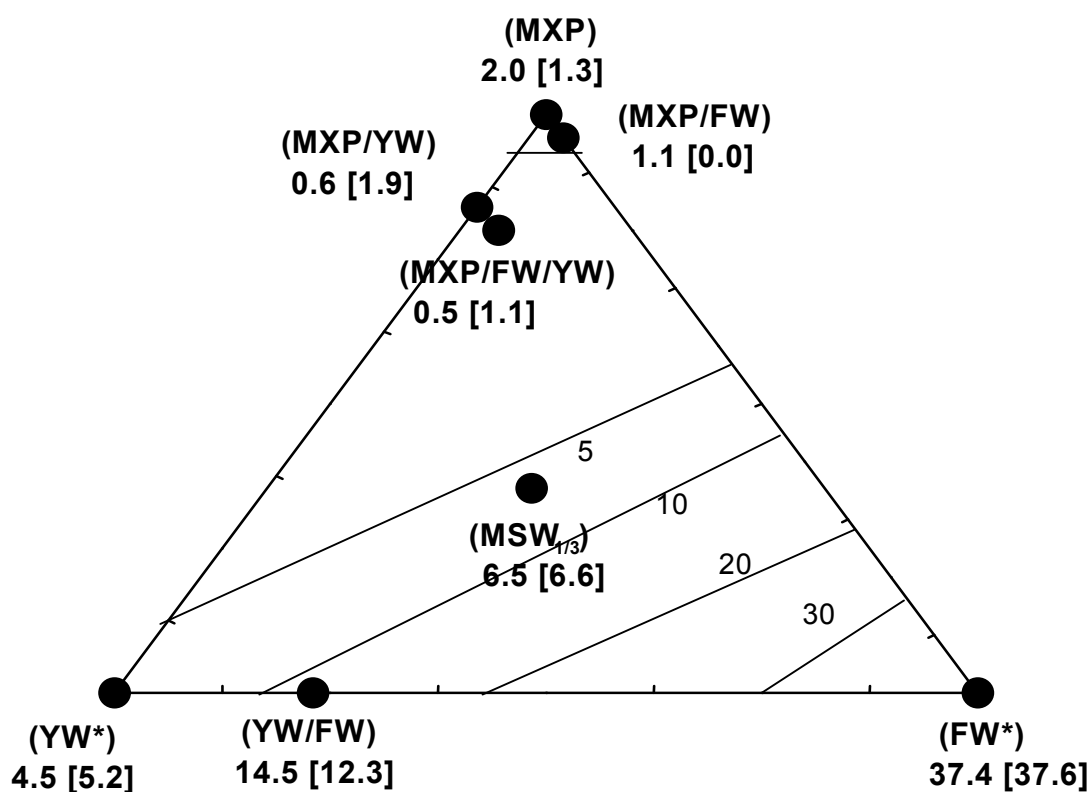


Figure 4-6. Response surface for estimation of NH₃ yields using Equation 4-9 (contour lines represent points of equal ammonia yield expressed in g-N-NH₃ per dry kg of substrate).

Note: Experimental data values shown left of the brackets; Equation 4-9 predictions shown in brackets. *: indicates average experimental value from seeded and unseeded runs considered as replicates for corresponding component.

(shown at the top of the triangle in Figure 4-5) is the expected ultimate CO_2 yield from that component, which would be observed had longer composting times or a better seed been used.

As Figure 4-6 shows, a plateau exists over approximately the top one third of the triangle representing negligible NH_3 yields from MSW mixtures with a dry weight mixed paper content higher than approximately 80%. A “slope” in the middle of the triangle toward food waste exists, reflecting the increase in NH_3 yields as the food waste percentage in MSW increases. The yield of 2.0 g N- NH_3 /dry kg of mixed paper represents a separate peak at the top of the triangle.

Figures 4-5 and 4-6 can be used for rapid estimation of CO_2 and NH_3 yields, respectively, from MSW of various compositions.

It is noted that all of the above analyses and conclusions are based on the use of mixed paper, yard wastes, and food wastes as the only organic components of MSW. Therefore, it is assumed that MSW has negligible amounts of other decomposable wastes, such as agricultural wastes, sewage sludge, etc. To express gaseous yields per unit mass of actual MSW that contains inorganic components, the yields predicted here—which are based only on the organic fraction—have to be reduced according to the percentage of inorganics in MSW.

In addition, Equations 4-8 and 4-9 were derived from fitting the data resulting from the experimental runs given in this paper. In this sense, Equations 4-8 and 4-9 are empirical models that describe (or estimate) these data but cannot be considered proven predictive tools.

5.0 Solids Decomposition During Composting

The objective of this chapter is to describe the decomposition of solids during MSW composting using the laboratory digestors. Seventeen experimental runs were performed using food wastes, yard wastes, and mixed paper, which are the primary degradable components in MSW. These components were composted individually and in mixtures, and selected subcomponent runs of grass, leaves, branches, and office paper were also performed. The loss of solid matter was followed by measurement of total carbon content, total nitrogen content, volatile solids content, and five organic chemical classes: hot water soluble matter (mostly sugars and starches), fats and lipids, cellulose, hemicellulose, and lignin/humus. This chapter also considers the concentrations of some of the solid parameters found in the composted substrates from the various runs in an attempt to derive compost maturity indicators.

The experimental runs performed were: seeded food wastes (FW), unseeded food wastes (FW_{ns}), seeded mixed paper (MXP), unseeded mixed paper (MXP_{ns}), seeded yard waste (YW), unseeded yard waste (YW_{ns}), mixed paper + yard wastes (MXP/YW), mixed paper + food wastes (MXP/FW), yard wastes + food wastes (YW/FW), mixed paper + yard waste + food waste (MXP/YW/FW), mixed paper + yard waste + food waste combined at approximately equal dry weight percentages (MSW_{1/3}), and the seed. The gas yields for these runs are reported and discussed in the previous chapter.

Additional individual subcomponents composted and considered in this chapter were grass, leaves, branches, and office paper (OFP); grass and leaves were used to prepare the yard waste mixtures (YW and YW_{ns}). Grass and leaves were composted without any prior shredding and without addition of seed. Because composting facilities for disposal of wood materials do exist in the United States, branches were composted individually without any shredding. Branches consisted of small twigs, 5 to 10 cm long, and were seeded with leaves at a ratio of 5.4:1, dry branches to dry leaves. Office paper, a subcomponent of mixed paper, was also composted individually. In contrast to cardboard and newsprint, which are mechanically treated wood pulps, a chemical process is associated with office paper manufacture that could affect its decomposition. Office paper was seeded with both seed and leaves in one run at a dry mass ratio of 10:1:1. Leaves were added to office paper to investigate the effect of (probably) different microbial populations on office paper decomposition.

In addition to the four individual subcomponents, a yard waste mixture (YW_h) was prepared from a batch of grass with a higher volatile solids content than the grass used in the YW and YW_{ns} runs. The high volatile solids grass had a volatile solids content of 89.8% dry weight (dw) as opposed to the latter batch with a volatile solids content of 81.6% (dw).

Moisture and nutrients were added to all the runs as needed. The materials and methods associated with setup of the laboratory experiment, substrate selection and preparation, analytical

techniques, and quality assurance and quality control results performed during operation of the laboratory runs are discussed in Chapter 3.

5.1 Results and Discussion

5.1.1 Initial Composition of Substrates

Table 5-1 provides initial chemical composition data for all runs. The five chemical classes presented are hot water soluble matter, fats and lipids, cellulose, hemicellulose, and lignin. Table 5-1 also includes initial volatile solids contents and initial organic carbon contents of the substrates used in the runs. The CO₂ yields are shown in Table 5-1.

Table 5-1 presents initial composition including the dry mass of seed present in the seeded runs. As Table 5-1 shows, cellulose is the dominant building block for almost all substrates. In particular, all runs that included paper had the highest average cellulose contents (>60% dry mass). Food waste runs were next highest with more than 42% cellulose content (dw). Mixed yard waste runs had cellulose contents of approximately 27% (dw), since grass, which had a 39.7% cellulose content, was the primary constituent. Leaves had the lowest cellulose content of 9.5% (dw) among all substrates. Leaves appear to have been partially decomposed naturally, as was indicated by the relatively low (compared to the other substrates) initial volatile solids content of 63.3% (dw). The highest cellulose content of 69.7% was measured for mixed paper (unseeded), which had a volatile solids content of 94.8% (dw).

The next most dominant component for almost all substrates was the lignin/humus fraction, which will be referred to as “lignin” hereafter. The measured lignin fraction includes lignin, humic acids, and acid-insoluble proteins (Tenney and Walksman, 1929; Inoko et al., 1979). Branches and leaves were the most lignified of all substrates with lignin contents of 42.9% and 33.9% on a dry weight basis, respectively. The three yard waste mixtures had lignin contents of 24.3% to 26.0% (dw). Food wastes had a lignin content of 12.03% and 14.3% (dw), with office paper (including the added leaves and the seed) having the lowest value of 6.5% (dw).

Hemicellulose, HWSM, and fats/lipids, in that order, were the next most dominant groups of compounds for almost all substrates. Hemicellulose was assumed to be a complex of two hexoses (D-galactose and D-mannose) and two pentoses (L-arabinose, D-xylose) only. Glucose was assumed to be derived only from cellulose. The highest hemicellulose content at 16.9% dry weight was found in grass and the yard waste mixtures. A 12.9% (dw) hemicellulose content was found in branches, while food wastes appeared to have negligible amounts of hemicellulose. All mixed paper mixtures had hemicellulose contents from 6.9% to 8.5% (dw).

The HWSM fraction is expected to be mostly sugars and starches but its composition might differ from component to component. Food wastes had the highest amount of HWSM, at 13.6% (dw), with grass and yard waste mixtures following at 10.6% and approximately 7.0% (dw), respectively. Mixed paper mixtures, leaves, and branches had HWSM contents of less

Table 5-1. CO₂ Yields and Initial Chemical Composition of Substrates from 17 Experimental Runs

Contents	CO ₂ (in g C/ dry kg) ^a	Fats/ lipids (% dw) ^b	HWSM (% dw)	Cellulose (% dw)	Hemicel- lulose (% dw)	Lignin/ humus (% dw)	VS (% dw) ^c	C (% dw) ^d	C/N ratio ^e	Cellulose/ lignin ratio	FHCHL/ VS ^f	Duration ^g
FW _{ns}	368.6	12.89	13.61	46.09	0.00	12.03	95.9	49.2	7.9	3.83	88.2	91
FW	364.4	11.57	12.26	42.51	0.73	14.33	91.7	47.1	8.4	2.97	88.7	57
YW _{ns}	221.9	2.49	6.93	27.20	11.25	24.34	73.8	36.2	18.7	1.12	97.8	69
YW	217.0	2.87	6.74	26.82	10.23	24.54	73.9	36.5	17.8	1.09	96.3	77
MXP _{ns}	5.5	.018	3.54	69.66	7.79	15.90	94.8	44.1	505.6	4.38	102.4	88
MXP	153.3	0.68	3.76	65.41	7.45	16.80	92.5	43.4	23.5 ^h	3.89	101.7	198
MXP/YW	246.1	1.15	4.32	57.97	8.49	18.57	89.7	42.5	27.5 ^h	3.12	100.9	179
MXP/FW	236.6	1.15	4.14	64.62	7.16	16.71	92.7	43.7	23.2 ^h	3.87	101.1	129
YW/FW	301.9	4.80	8.39	31.65	8.75	21.53	78.8	39.3	13.6	1.47	95.3	114
MXP/YW/FW	265.3	1.58	4.68	57.84	7.56	18.02	89.3	42.4	25.5 ^h	3.21	100.4	170
MSW _{1/3}	266.3	4.79	7.85	47.39	6.89	17.66	87.7	42.8	16.6	2.68	96.5	47
Seed	86.0	5.31	5.86	25.51	4.20	25.21	71.8	37.0	13.1	1.01	92.1	62
YW _h	265.2	2.48	7.23	27.73	16.05	26.00	79.8	39.2	18.0	1.07	99.6	110
Grass	202.0	2.41	10.62	39.67	16.89	17.63	81.7	40.6	17.5	2.25	106.8	27
Leaves	81.1	2.59	1.68	9.48	3.24	33.88	63.3	30.1	21.6	0.28	80.4	71
Branches ⁱ	82.7	1.04	3.20	14.71	12.87	42.89	81.7	40.4	13.1 ^h	0.34	91.5	54
Office paper ⁱ	112.5	0.74	3.72	68.13	6.71	6.50	86.9	39.2	27.6 ^h	10.48	98.8	61

FW = Seeded food wastes

FW_{ns} = Unseeded food wastes

MXP = Seeded mixed paper waste

MXP_{ns} = Unseeded mixed paper

MXP/YW = Mixed paper + yard wastes

MXP/FW = Mixed paper+food wastes

MXP/YW/FW = Mixed paper+yard wastes+food wastes

MSW_{1/3} = Mixed paper+yard wastes+food wastes mixed each at equal dry weight proportions

YW_{ns} = Unseeded yard wastes

YW = Seeded yard wastes

YW_h = Yard wastes with high volatile solids content

YW_{ns} = Unseeded yard wastes

YW/FW = Yard wastes+food wastes

^a CO₂ (as g C) per dry kg of total substrate.

^b % on a dry weight (dw) basis.

^c Volatile solids.

^d Total organic carbon.

^e Includes N added as N salt.

^f The ratio of the sum of fats, HWSM, cellulose, hemicellulose, and lignin/humus concentrations to the volatile solids concentration.

^g Experiment length (days).

^h Run to which NH₄NO₃ salt was added.

ⁱ Seeded with leaves and seed.

than 5% (dw). The fats and lipids fraction is expected to also contain waxes, resins (Tenney and Walksman, 1929), and probably alcohol-soluble proteins. Fats and lipids were at the smallest percentages of all five chemical groups for all substrates, except food wastes, which contained approximately 12% (dw) of fats.

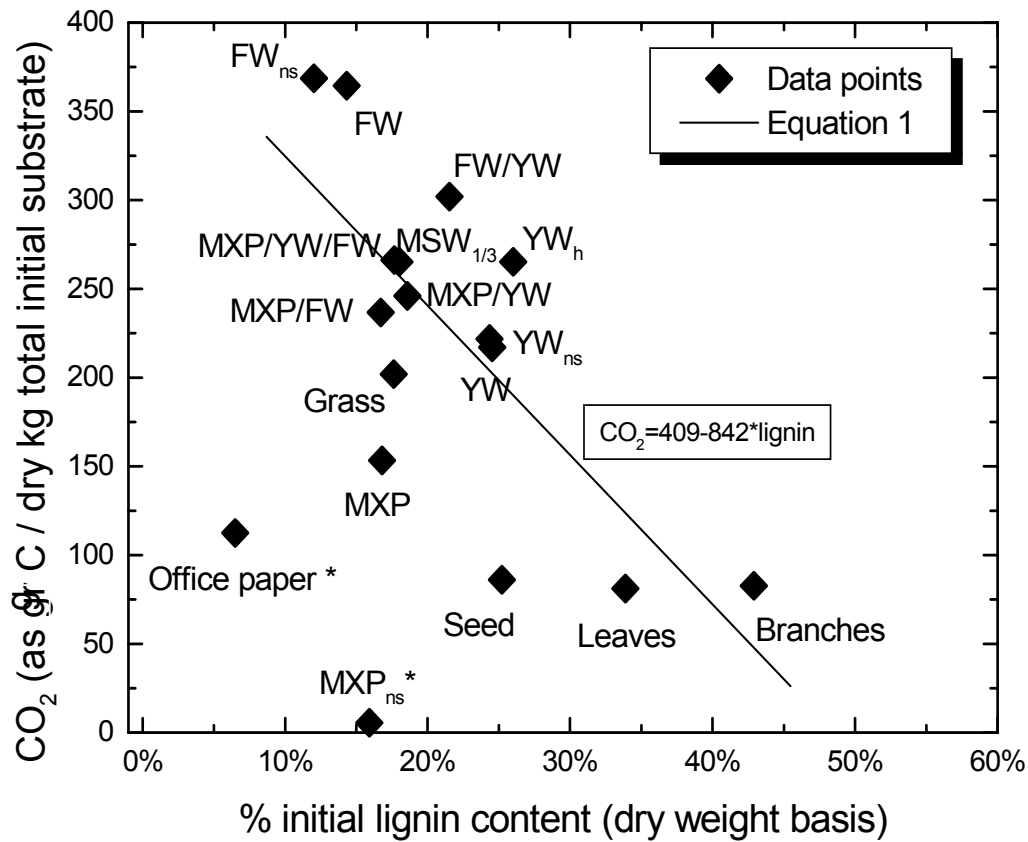
Table 5-1 shows that the volatile solids contents of all substrates used ranged from 63.3% (dw) for leaves to 95.9% for food wastes. The volatile solids content was approximately two times higher than the corresponding total organic carbon content for all substrates. The factor of 2 differs slightly from the factor of 1.8 suggested by New Zealand researchers (after Diaz et al., 1993) and used frequently since then. Differences are probably attributed to the use of different analytical techniques for the estimation of organic carbon or to the types of substrates used. The C/N ratio (also shown in Table 5-1) includes the weight of nitrogen added as NH_4NO_3 salt to some of the runs in order to achieve the suggested C/N optimum range of 25 to 30. The lowest C/N ratio of 7.9 was measured for food wastes, which had an initial N content of 6.1% (dw). The seed and the grass were the next most nitrogenous subcomponents, with N contents of 2.8% and 2.1% (dw), respectively.

It is noted that, because of time constraints, office paper had not fully decomposed, as was shown by the relatively low but steady CO_2 production rates prior to terminating that run. Mixed paper is suspected not to have reached its fully decomposed because of inadequate seeding, as discussed in Chapter 4.

5.1.2 Substrate Degradability as a Function of Lignin and HWSM Contents

Linear regressions (including an intercept) were made between the initial concentrations of the five chemical groups measured in the solids and the total carbon dioxide yields (Table 5-1) from 15 runs. Office paper was not included in these regressions because it had not reached its full extent of decomposition. The MXP_{ns} results were also not included since no decomposition occurred for this run due to lack of seed. Based on the regressions (multiple regressions were not tried), the correlation coefficients (adjusted R^2) for fats/lipids, HWSM, cellulose, hemicellulose, and lignin/humus were 0.33, 0.53, 0.14, -0.01 and 0.50, respectively. Therefore, the initial lignin content and initial HWSM content had the strongest correlation to mineralization extent. Components with high HWSM contents had high CO_2 yields, while components with high lignin content had low CO_2 yields. Figure 5-1 presents the carbon dioxide yields (in g C/dry kg) versus initial lignin contents.

The 15 data points were fitted by least squares to the linear equations shown as Equations 5-1, 5-2, and 5-3. Equation 5-1 relates the carbon dioxide yield to initial lignin content (dry weight basis), Equation 5-2 relates volatile solids reduction (expressed as a fraction) to initial lignin content (volatile solids basis), and Equation 5-3 relates carbon dioxide yield to initial HWSM content (dry weight basis). The equations, with standard errors and coefficients of correlation (adj. R^2), are:



* Not included in fitting to Equation 5-1.

Figure 5-1. Effect of initial lignin content on carbon dioxide yields.

Lignin fit:

$$\text{CO}_{2\text{yield}} = 409.9 (\pm 50.3) - 841.8 (\pm 215.6) \times \text{LGN}_{\text{dry}} \quad (\text{adj. } R^2=0.50) \quad (5-1)$$

$$\text{BVS} = 0.80 (\pm 0.09) - 0.91 (\pm 0.30) \times \text{LGN}_{\text{vs}} \quad (\text{adj. } R^2=0.37) \quad (5-2)$$

HWSM fit:

$$\text{CO}_{2\text{yield}} = 87.6 (\pm 37.2) + 2,019 (\pm 496) \times \text{HWSM}_{\text{dry}} \quad (\text{adj. } R^2=0.53) \quad (5-3)$$

where

- $\text{CO}_{2\text{yield}}$ = carbon dioxide yield (in g C / dry kg of component excluding seed)
- BVS = volatile solids reduction (as fraction)
- LGN_{dry} = the substrate's initial lignin content (dry weight expressed as a fraction of the total dry weight)
- LGN_{vs} = the substrate's initial lignin content (dry weight expressed as a fraction of the dry volatile solids)
- HWSM_{dry} = initial hot water soluble matter content (dry weight basis expressed as fraction).

Equations 5-1 and 5-3 can be used for estimating CO₂ yields from different lignocellulosic substrates by knowledge of their initial lignin and HWSM contents, respectively. As suggested by Figure 5-1 and Equations 5-1 and 5-2, lignin retards overall substrate decomposition. This retardation is thought to be due primarily to physical inhibition. Lignin is present between cellulose fibrils, decreasing the available surface area and preventing ready access to cellulose by invading microbes and enzymes (Szegi, 1988). Most of the information on the inhibition of lignin to decomposition in aerobic environments is found in studies of soil environments. Szegi (1988), in particular, showed that degradation of cellulose by certain fungi is actually retarded by lignin in soil environments as a result of physical inhibition rather than the simple presence of lignin. Lignin, however, is degradable aerobically, especially by white-rot fungi and brown-rot fungi (Kirk, 1984) and by bacteria to a much smaller extent (Vicuna, 1988).

The retardation of organic matter degradation due to lignin has been studied more extensively for anaerobic environments. Unaltered lignin is known to be nondegradable in anaerobic environments because its initial fragmentation requires molecular oxygen (Kirk, 1984). The retardation by lignin on the anaerobic degradability of several types of organic matter has been shown by Chandler et al. (1980). Retardation by lignin to the anaerobic degradability of paper wastes and various solid waste components has been shown by Stinson and Ham (1995) and Eleazer et al. (1997), respectively. Stinson and Ham (1995), in particular, showed that the retardation of cellulose decomposition in paper wastes was due to physical inhibition related to the sheathing of cellulose by lignin rather than to a chemical inhibition (e.g., adsorption of cellulolytic enzymes onto lignin).

Equation 5-2 allows comparison to a similar equation developed by Chandler et al. (1980) that applies to anaerobic environments. Chandler's predictive model is: $BVS = 0.830 - 2.8 LGN_{VS}$ ($R^2 = 0.94$), with terms defined as in Equation 5-2. The intercepts in Equation 5-2 and in Chandler's predictive model are very similar, suggesting that an organic substrate with no lignin content would achieve a maximum volatile solids reduction of 83% in anaerobic environments and 70% to 90% (0.80 ± 0.09) in aerobic environments. Based on the slope of the linear Equation 5-2—which is 0.91—and the corresponding slope of Chandler's equation—which is 2.8, it appears that the degree of retardation of substrate degradability due to lignin is approximately three times higher in anaerobic environments than in aerobic environments. This is probably a result of the negligible anaerobic decomposition of lignin compared to aerobic decomposition.

Care should be taken in comparing these two equations because different organic substrates were used as a basis to fit each equation. In addition, the Chandler equation was based on a range of lignin contents from 2.0% (VS basis) for corn meal up to 20.9% (VS basis) for newsprint, while the corresponding range for Equation 5-2 was 12.5% (VS basis) for food wastes to 53.5% (VS basis) for leaves. The lignin fraction, however, was determined using the 72% sulfuric acid extraction technique in both studies.

The variability observed in Equations 5-1 and 5-2 can be partly explained by the fact that the analytically measured lignin/humus fraction includes, apart from lignin, other chemical components that can have different degrees of availability or biodegradability and therefore have different degrees of inhibition to overall degradability. Lignin/humus in food wastes, for

example, was most degradable with an overall reduction of 74.1% during composting, while lignin/humus in branches was the least degradable with a reduction of 9.9%. This might partially explain the fact that food wastes had CO₂ yields higher than predicted by the model.

In addition, different types of lignin have different degrees of biodegradability. According to Shevchenko and Bailey (1996), grass lignin is different from softwood and hardwood lignins because of differences in the ratios of guaiacyl, syringyl, and *p*-hydroxy-phenylpropane units present in each type. Kirk (1984) mentions that a broader range of microbial populations is involved in the degradation of lignin in herbaceous plants—such as grass and leaves—compared to lignin in wood, making the former class of lignin more degradable than the latter. Allison (1973), by incubating woods and barks in soil aerobic environments, showed that there is a significant difference in degradability between hardwoods and softwoods and even between species within the softwood and hardwood families by factors up to 5.

In contrast to Equation 5-2, the Chandler formula does not have such a large variability, despite the range of organic substrate types used. This is probably because all types of lignin are similarly refractory to degradation in anaerobic environments but vary in degradability in aerobic environments.

The CO₂ yield from office paper is the major outlier to the lignin predictive models and was not used in curve fitting. Office paper's low lignin content should, according to the model, result in the highest CO₂ yield. Although office paper was provided additional seed at day 21 and phosphorus (P) and nitrogen (N) nutrients were added on day 54, the small increase in CO₂ production rate observed was typical after opening all digesters for inspection or moisture addition. It is likely seed, N, and P were not limiting decomposition. Explanations for the low decomposition rate of office paper are:

- Fillers and sizing agents of organic nature are added to office paper to prevent the feathering (spreading) of inks into the sheet. These agents are usually resin acids (e.g., abietic acid) that create a more hydrophobic surface, less prone to attack by microorganisms (Young, 1998).
- The moisture content ranged between 60% to 65%, with the office paper forming wet clods. This probably reduced oxygen access and therefore decomposition rates. A longer period of time would have resulted in more CO₂ generation, but the CO₂ rate at the conclusion of the run was very low, suggesting much additional time would be required to reach “full” decomposition.

The seed had also lower CO₂ yields compared to the model prediction from its lignin content. Since seed was partially composted MSW, it could contain materials such as plastics, textiles, leather or other organics, that can have a different degradation behavior than the other components (food waste, yard waste, paper) used in this experiment. If plastics were present, for example, they would be quantified as lignin/humus and could explain the relatively low CO₂ yield from seed, since plastics are generally considered nondegradable.

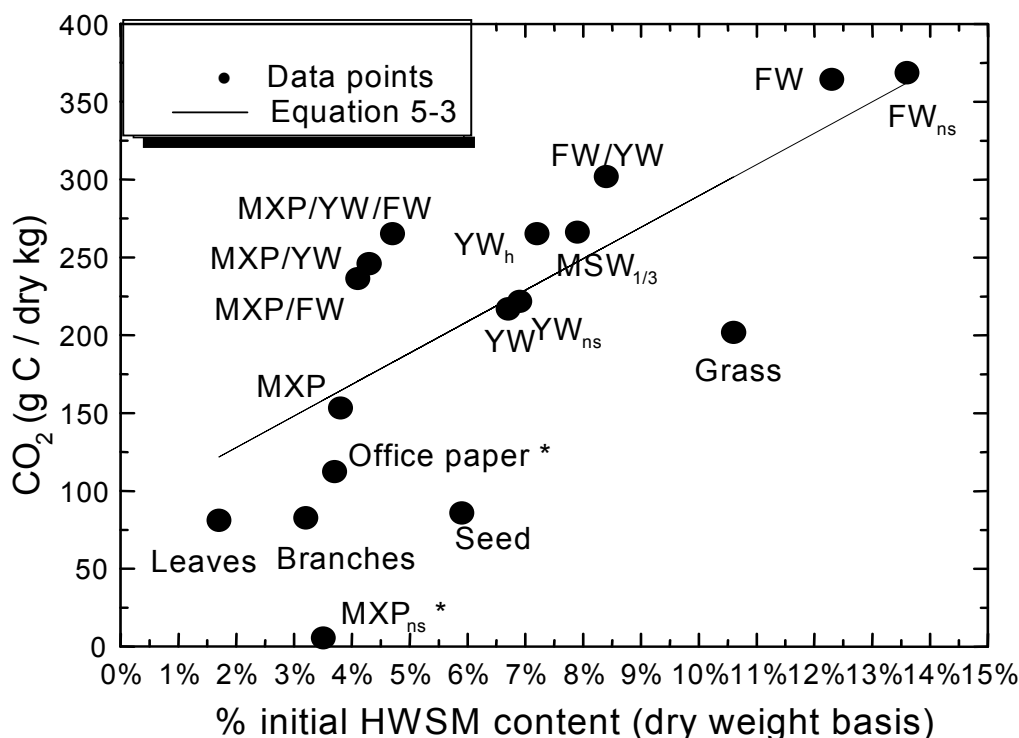
The correlation of CO₂ yield and initial HWSM content (adj.R²=0.53) is illustrated in Figure 5-2. This correlation is partially explained by the fact that the HWSM group contains relatively easily decomposable organic compounds, such as starches, monosaccharides, and amino acids (Inoko et al., 1979). Office paper was not included in the fitting since it may not have reached its full extent of decomposition, as discussed earlier. The seed appears to behave as an outlier in Equation 5-3. The presence of components in the seed other than food wastes, mixed paper, and yard wastes might partially explain the relatively large deviation of its value from Equation 5-3 estimations.

The correlation of total CO₂ yields to initial lignin content and initial HWSM content indicates that these values can be used as general predictors of ultimate CO₂ yields from various substrates when composted. The use of lignin and HWSM as CO₂ yield predictors does not mean, however, that these groups are the dominant biodegradable groups of the substrates used. This is because lignin has a low degradation extent, while HWSM has a relatively small initial concentration that ranges from 1.7% to 13.6% (dry weight) for all substrates. As will be shown in the next section, it is the degradability of other fractions, such as cellulose and hemicellulose, that controls the extent of substrate degradation. Based on the above, the variability of Equations 5-1 to 5-3 can be explained by the fact that substrates with similar initial lignin contents, or HWSM contents, can have different degradabilities not only because of degradability differences of the lignin, or HWSM, but also because of differences in the contents of the cellulose that the lignin sheaths.

5.1.3 Reduction of Chemical Components

The objective of this section is to discuss the extent of reduction of each of the five chemical groups during composting and the contribution of each component to total substrate degradability. Table 5-2 presents the extent of reduction for each of the five chemical groups for all runs. Table 5-2 also includes the dry matter reduction and the total organic carbon reduction. Figure 5-3 illustrates the total dry matter reduction for each run as shown by the length of each bar (positive values). Total dry matter reduction is further broken down to the dry loss of each chemical group. Table 5-3 shows the contribution of dry mass loss of each of the five chemical groups to total dry mass loss recorded for each run. The sum of the dry mass losses of the five chemical groups for each substrate is expected to be close to the total dry mass loss of that substrate. Deviations are primarily because certain chemical groups were not accounted for during solids measurements. Table 5-3 includes the dry mass reduction closure (in %). A positive closure value indicates an underestimation of the total dry mass loss, while a negative value indicates an overestimation of the total dry mass loss. Figure 5-3 also illustrates the dry mass reduction closure.

High solids loss is particularly apparent for food wastes; further, the unmeasured solids class was relatively large compared to other runs. The unmeasured dry fraction for food wastes is probably a water-insoluble chemical group (e.g., water-insoluble proteins) that is solubilized during acid hydrolysis but is not measured during HPLC analysis as any of the monosaccharides used for cellulose and hemicellulose determination. Negative values in Figure 5-3 indicate that an increase of the corresponding chemical group was observed during the process. For example, a lignin increase was observed for mixed paper, probably due to generation of humus and



*Not included in fitting to Equation 5-3.

Figure 5-2. Effect of initial hot water soluble matter (HWSM) content on carbon dioxide yields.

biomass (measured in the lignin/humus fraction) that was greater than overall lignin loss. An overestimation of the dry mass reduction was observed, especially for grass, MXP/FW, and YW_{ns}, probably due to overestimation of the cellulose and hemicellulose contents during HPLC analysis.

Figure 5-3 illustrates that cellulose was the major contributor to the total dry matter loss for most substrates. Cellulose dry loss contributed between 66.5% and 92.4% of the total dry losses recorded for the MSW_{1/3}, MXP/YW, grass, office paper, MXP/YW/FW, MXP/FW, and MXP runs, while it contributed approximately 50% of the dry loss of all yard waste runs (see Table 5-3). Based on Table 5-2, cellulose was degradable for all substrates at levels that ranged from 25% loss for office paper to 91% for yard wastes. The low cellulose decomposition of

Table 5-2. Correlation Matrix for Estimation of Compost Maturity Indicators Using the Reduction of Organic Chemical Groups During Composting

Substrate ^a	Average final CO ₂ production rate (g C/dry kg/day)	Fats/lipids reduction (%)	HWSM reduction (%)	Lignin reduction (%)	Cellulose reduction (%)	Hemicellulose reduction (%)	Dry mass reduction (%)	C reduction (%)	Cellulose/lignin reduction (%)	C/N ratio reduction (%)
MXP _{ns} ^b	0.02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MXP	0.25	34.7	10.4	-28.8	49.6	71.9	35.1	37.9	60.9	9.2
Leaves	0.26	69.6	-489.4	18.7	53.9	73.5	19.0	26.9	43.3	64.1
MXP/YW	0.26	67.1	58.9	26.7	82.1	91.5	62.4	66.3	75.6	31.3
Seed	0.26	81.8	-5.3	-7.2	36.2	23.9	19.4	27.4	40.5	9.8
MXP/YW/FW	0.28	77.1	56.6	24.2	87.8	87.4	62.5	68.1	83.9	38.1
FW/YW	0.31	88.7	47.0	33.4	89.5	95.0	55.1	70.5	84.3	29.4
YW	0.45	66.6	63.9	30.1	82.1	96.6	46.7	63.1	74.4	57.2
YW _n	0.50	74.0	60.4	38.5	89.8	100.0	53.9	66.4	83.3	38.0
FW/MXP	0.64	61.1	99.5	0.1	60.4	100.0	45.3	46.8	60.4	11.2
FW	0.75	94.0	53.7	36.9	60.2	100.0	59.2	65.7	36.9	-112.8
Branches	0.93	42.0	-80.6	9.9	-54.8	13.7	15.4	18.0	-71.8	-31.2
Yw _{ns}	1.02	77.2	58.6	43.0	90.7	99.4	47.6	62.2	83.7	56.3
FW _{ns}	1.03	82.6	45.5	61.6	66.0	0.0	65.5	69.2	11.6	-95.8
MSW _{1/3}	2.47	93.9	62.5	12.8	82.0	79.4	58.4	65.5	79.4	NM
Office paper	2.88	100.0	39.2	28.5	25.0	100.0	24.0	28.8	-5.0	NM
Grass	3.70	80.4	-27.6	12.1	88.0	93.8	44.7	54.7	86.3	NM
Correlation coefficient (R ²)		0.18	0.01	0.002	0.00	0.00	0.02	0.006	0.005	0.29

NM = Not measured.

^a Substrates are placed in ranking order from most mature (top of table) to least mature (bottom of table).

^b Negligible mineralization occurred for the MXP_{ns} run and therefore no solids measurements were performed for this run; all solids reduction values were set to 0 for this run.

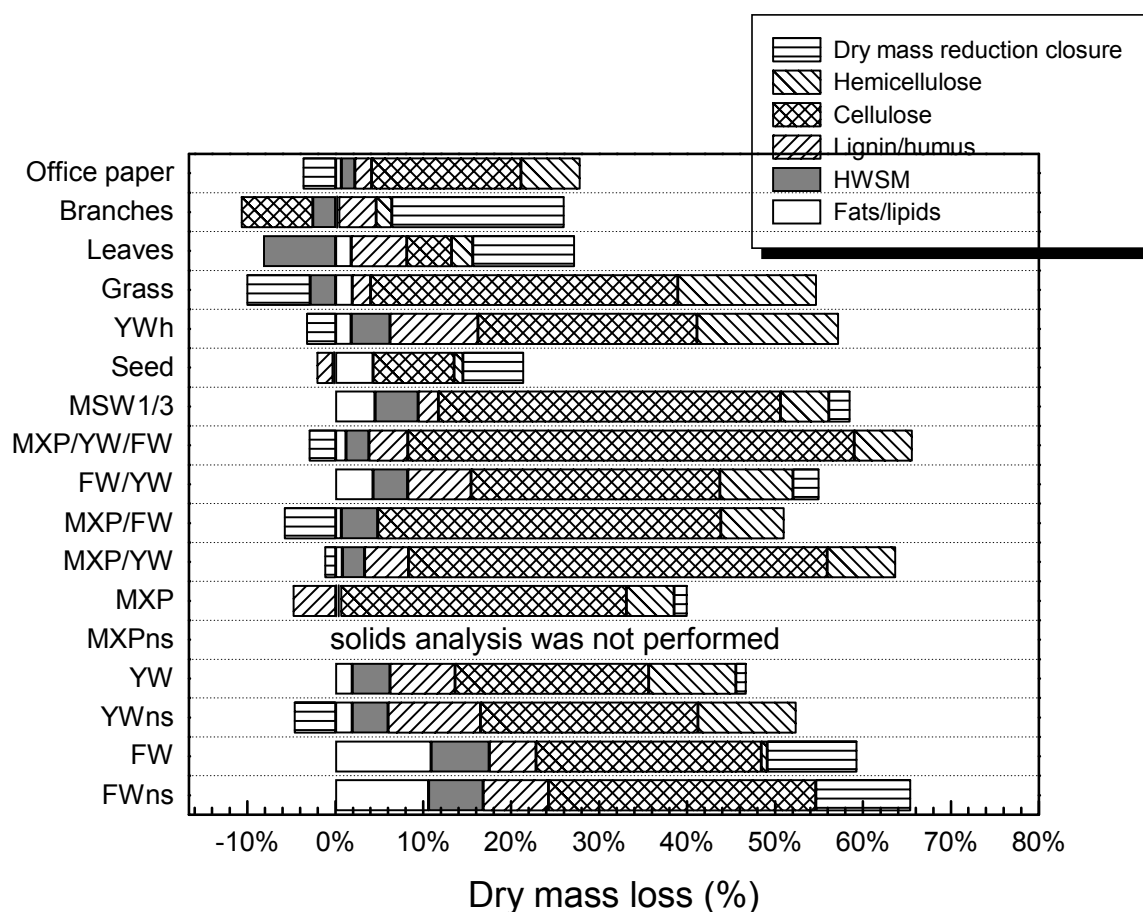


Figure 5-3. Dry mass loss for each chemical group during composting (in % of the total initial dry mass).

office paper is attributed to reasons discussed earlier for this substrate. Apart from the physical inhibition of lignin to cellulose decomposition, the binding of cellulose to humic matter during humification can also result in retardation of cellulose decomposition. Cellulose reduction in seed and leaves was 36.2% and 53.9%, respectively. The relatively low cellulose decomposition for these substrates, both of which were partially decomposed prior to composting in the laboratory, might be explained by the binding of cellulose to the generated humic matter. This is also indicated by the fact that seed and leaves have the highest initial lignin/humus contents of 25.2% (dw) and 33.9% (dw), respectively. Hänninen et al. (1995) suggested that carbohydrates in compost are covalently bound to the structures of humic acids and fulvic acids during composting. According to Hänninen et al. (1995), the binding of polysaccharides to humic matter during composting can be due to ester or ether bonds formed between the hydroxyl group of polysaccharides and phenolic acid groups of the humic matter. The polysaccharides to humic or fulvic acids are still subject to slow degradation, with polysaccharides associated with the humic acid fraction being more biologically stabilized compared to those associated with the fulvic acid fraction.

Table 5-3. Contribution of Dry Loss of Each Chemical Group to Total Dry Mass Loss of a Substrate (in %)

	Fats/ lipids ^a	HWSM ^a	Lignin/ humus ^a	Cellulose ^a	Hemicellulose ^a	Dry mass closure ^b
FW _{ns}	16.3 ^c	9.5	11.3	46.5	0.0	16.5
FW	18.4	11.1	8.9	43.2	1.2	17.2
YW _{ns}	4.0	8.5	22.0	51.8	23.5	-9.9
YW	4.1	9.2	15.8	47.1	21.1	2.6
MXP	0.7	1.1	-13.8	92.4	15.2	4.3
MXP/YW	1.2	4.1	7.9	76.2	12.4	-1.9
FW/MXP	1.6	9.1	0.1	86.2	15.8	-12.7
FW/YW	7.7	7.2	13.1	51.5	15.1	5.5
MXP/YW/FW	1.9	4.2	7.0	81.2	10.6	-4.9
MSW _{1/3}	7.7	8.4	3.9	66.5	9.4	4.1
Seed	22.4	-1.6	-9.3	47.7	5.2	35.7
YW _n	3.4	8.1	18.6	46.2	29.8	-6.1
Grass	4.3	-6.6	4.8	78.1	35.4	-16.1
Leaves	9.5	-43.2	33.3	26.9	12.6	61.0
Branches	2.8	-16.8	27.6	-52.3	11.4	127.2
Office paper	3.1	6.1	7.7	70.7	27.9	-15.5

^a A positive value indicates reduction and a negative value increase.

^b A positive value indicates a dry mass loss underestimation and a negative value indicates a dry mass loss overestimation. For example, the sum of dry mass losses of the five chemical groups in food wastes was 16.5% less than the measured total dry mass loss for that substrate, while the sum of dry mass losses of the five chemical groups in grass was 16.1% higher than the measured total dry mass loss for that substrate.

^c This means that 16.3% of the total dry loss recorded for food wastes was due to the reduction of fats/lipids.

Cellulose reduction in the MXP and MXP/FW runs was 49.6% and 60.4%, respectively. These values are lower than the corresponding cellulose reductions in MXP/YW (82.1%), MXP/YW/FW (87.8%), and MSW_{1/3} (82.0%). Cellulolytic microorganisms appear to be present in yard wastes, resulting in more vigorous degradation of cellulose present in mixed paper in the MXP/YW, MXP/YW/FW, and MSW_{1/3} runs. A lower amount of cellulolytic microorganism activity appears to be present in the seed as indicated by the low cellulose reduction values for the seed itself as well as for the seeded mixed paper (MXP). The relatively low (60.4%) cellulose reduction in the MXP/FW mixture is probably a result of the low concentrations of food in the MXP/FW mixture, which, therefore, did not adequately function as a cellulolytic seed. The presence of cellulolytic microorganisms in yard wastes is also indicated by the 91% cellulose reduction measured for unseeded yard wastes and the 88% cellulose reduction for the grass alone. The negative value of cellulose reduction for branches (as shown in Figure 5-3 and Table 5-2) is attributed to the low initial cellulose content and the resulting multiplier effect of analytical variability.

Based on Figure 5-3 and Table 5-3, hemicellulose appears to be the second largest contributor to total dry matter reduction for the yard waste runs, grass, leaves, and all mixtures with mixed paper. Hemicellulose contribution ranges from 12.6% to 35.4% of the dry losses for the above runs. Food wastes contained no hemicellulose while only 5% of the seed total dry loss was due to hemicellulose degradation. Based on Table 5-2, hemicellulose was more

degradable than cellulose in all components. Hemicellulose generally aids in the physical bonding of lignin to cellulose fibrils (Szegi, 1988) and has a lower molecular weight than cellulose (Gray et al., 1971). Szegi (1988), using several strains of soil fungi, showed that hemicellulose in soil was more degradable than cellulose and much more degradable than lignin. Hemicellulose was approximately fully degraded in the yard waste mixtures and the grass. Hemicellulose, in the MXP/YW, MXP/FW, and MXP/YW/FW runs, was decomposed at levels higher than 85% and was always more degradable than cellulose. The same microorganisms that degrade cellulose have been found to also degrade hemicellulose (Szegi, 1988). The higher degradation extent of hemicellulose compared to cellulose is explained by its lower molecular weight and its greater heterogeneity compared to cellulose. Branches had one of the lowest hemicellulose reduction extents, probably due to lignin inhibition.

Slightly lower cellulose reductions were observed by Michel et al. (1993) during composting of mixtures of grasses and leaves. Cellulose reduction values ranged from 61% to 78% and hemicellulose reduction ranged from 57% to 82%. The lower values could be attributed to the fact that all experiments were stopped after 43 days and, based on the CO₂ cumulative profiles, substrates had not reached their full extent of decomposition.

As shown in Figure 5-3 and Table 5-3, lignin/humus was degradable in almost all substrates. Lignin/humus loss contributed between 15.8% and 33.3% of the dry weight loss for yard waste runs, branches, and leaves. It contributed less to food wastes and the grass. Lignin is degradable under aerobic environments primarily by fungi and certain actinomycetes (Crawford and Crawford, 1980; Kirk, 1984). Based on Table 5-2, lignin reductions varied from 9.9% for branches to 61.6% for unseeded food wastes. Lignin reduction in seeded food wastes was 36.9%, probably because the lignin in the seed combined with the food wastes was less degradable than the lignin in food wastes. The variations in lignin degradability might be attributed to the different structures of lignin and different chemical groups included in the “lignin/humus” fraction, as discussed. Generally, lignin reduction values should be interpreted with caution, since the lignin/humus fraction that was quantified will contain humic matter and portions of microbial biomass, both of which are generated during composting (Tenney and Walksman, 1929). According to both the lignin theory and polyphenol theories of humus formation, lignin is the primary source of humus in soil (Stevenson, 1994). The contribution of polysaccharides to humus formation is still a subject for research (Shevchenko and Bailey, 1996).

As mentioned in the review by Szegi (1988), cellulolytic bacteria may be responsible for humus formation. This pathway might partially explain the negative value for lignin reduction observed for the MXP run and the seed if more humic matter and biomass were formed than lignin was decomposed. The same reason might explain the zero reduction of lignin/humus in the MXP/FW run. Since both the MXP and MXP/FW runs were seeded, it appears that no ligninolytic fungi were present in the seed used. This is further supported by the fact that a negative lignin reduction was recorded for the seed run alone. Seed was collected at the end of a 5-day retention time from a MSW composting facility. According to the succession and concentration of microorganisms during MSW composting (de Bertoldi et al., 1983), ligninolytic fungi and actinomycetes that are responsible for lignin degradation are present in high concentrations in the latter stages of composting. Though direct microbial population

measurements did not take place here, the microbial population in the seed used is expected to be dominated by heterotrophic bacteria rather than ligninolytic microorganisms.

According to Effland (1977), the degradation of lignin by fungi will result in some lignin being dissolved in the 72% sulfuric acid. Soluble lignin in hardwoods also can be up to 3% to 5%. Partial acid dissolution of the lignin fraction in food wastes might explain the high lignin reduction values for that substrate.

The addition of yard wastes to mixed paper in the MXP/YW or MXP/YW/FW runs appears to further “seed” mixed paper with a microbial population able to degrade lignin. This is shown by the fact that lignin reductions for the MXP/YW and MXP/YW/FW runs are on the order of 25%. The presence of ligninolytic fungi in yard wastes is further supported by the 43% lignin reduction measured for unseeded yard wastes, which was one of the highest lignin reduction values. Ligninolytic fungi are likely to be present in two subcomponents of yard wastes—grass and leaves—as was indicated by the 12% and 18.7% lignin reduction values for these two unseeded components, respectively. Michel et al. (1993) also recorded lignin/humus reduction values of up to 40% for mixtures of grass and leaves during composting.

Fats and lipids were in small amounts in almost all runs except food wastes. Decomposition of fats and lipids contributed approximately 16% of the total dry weight loss in food wastes (see Table 5-3). Fats and lipids in the seed were the greatest contributors to the degradation of that substrate (22.4%) because of the advanced decomposition stage of that substrate and the presence of relatively large concentrations of microbial biomass that is further depleted during endogenous decay. Fats/lipids contributed 9.5% of the dry loss of leaves, which was also at an advanced composting stage.

HWSM loss was responsible for the smallest contribution of the total dry loss of nearly all substrates, since it was in small concentrations initially. An exception was food wastes, since HWSM loss contributed approximately 15% to the total loss of that substrate. The increase of HWSM in leaves and grass is attributed to the generation of water-soluble humic compounds during composting (e.g., fulvic acids). The increase of HWSM in branches is partially attributable to the presence of leaves that were mixed with branches as seed.

Dry matter reduction values ranged from 15.4% for branches to 65.5% for unseeded food wastes. Volatile solids (VS) and total carbon (C) reduction values were similar. Carbon reduction ranged from 18.0% for branches to 70.5% for the mixture of yard wastes and food wastes. The relatively low reduction for branches undoubtedly contributed to the poor dry mass closure for branches (see Table 5-3) because of the multiplier effect of analytical variability. The correlation of CO₂ yield (as g C/dry kg) with dry mass reduction is as follows:

$$Y_{CO_2} = 489.3 (\pm 17.9) \times \text{DryRed} \quad (\text{adjusted } R^2=0.79) \quad (5-4)$$

where

$$\begin{aligned} Y_{CO_2} &= \text{CO}_2 \text{ yield (as g C / dry kg)} \\ \text{DryRed} &= \text{dry weight reduction (expressed as a fraction).} \end{aligned}$$

Equation 5-4 was developed with a zero intercept so no carbon dioxide will be produced at zero dry matter reduction. Equation 5-4 indicates that the maximum amount of carbon dioxide theoretically produced from a substrate, if all volatile solids were completely decomposed (100% reduction), would be approximately 490 g C/dry kg. However, the maximum dry matter reduction is less than 100% for all substrates tested in this report, indicating the formation of refractory organic residuals, such as humic matter and microbial biomass, that cannot be further decomposed and accumulated (Haug, 1993). This was also indicated by Equation 5-2, which predicts that the total decomposition of volatile solids during composting cannot exceed 80%. Equation 5-4 already accounts for the accumulation of biomass and humic matter and was developed based on a dry mass reduction range of 15.4% to 65.5% (see Table 5-2).

Dry mass reduction of a substrate during composting can be calculated on a constant ash basis by knowledge of the volatile solids contents of the starting and composted materials, as discussed in Komilis and Ham (1999). Using Equation 5-3, cumulative CO₂ production can be estimated this way at different locations within a composting facility.

5.1.4 Solids Degradation Rates

The objective of this section is to discuss solids decomposition rates during composting of grass and seeded mixed paper. Intermediate solid samples were collected and analyzed for two special runs performed under conditions similar to those used for results presented previously. The organic component concentrations, expressed as a fraction of the initial dry mass, are shown in Figures 5-4 and 5-5 for grass and mixed paper, respectively.

As Figure 5-4 illustrates, approximately 80% of the overall VS reduction of grass observed throughout the process occurred during the first 5 days, which coincides with the peak CO₂ production rates observed during that time. The initial high VS reduction is primarily due to the decomposition of cellulose. Overall cellulose reduction during the process was 88%, with 71% reduction occurring during the first 5 days. Glucose—the primary hydrolysis product from cellulose degradation—appears to be rapidly consumed, since no glucose was detected in HPLC analyses of the hot water extracts during any of the five decomposition sampling stages for grass.

The decomposition rate of each chemical group was calculated as the percentage of the loss of each component over time (i.e., mass of component decomposed over a time period / initial mass of component), as shown in Table 5-4. Table 5-4 indicates that initial cellulose degradation rates were 12.6% per day during the first 5.6 days and were the highest among all solid components. The cellulose decomposition rate between day 5.6 and day 14.7 was 0.91% per day, after which it stabilized at 0.7% per day until the end of the run. The relatively constant cellulose degradation rates after day 5 indicate that cellulose enzymatic hydrolysis was not a function of the cellulose concentration any more, but rather a function of other factors such as the crystalline structure of residual cellulose or availability of cellulose to hydrolysis if limited by lignin or other sheathing. Cellulose appears to have reached a constant final value of 8.6% (dw) at the end of the run. This could be due to a suggested binding of polysaccharides to humic or fulvic acids (Hänninen et al., 1995).

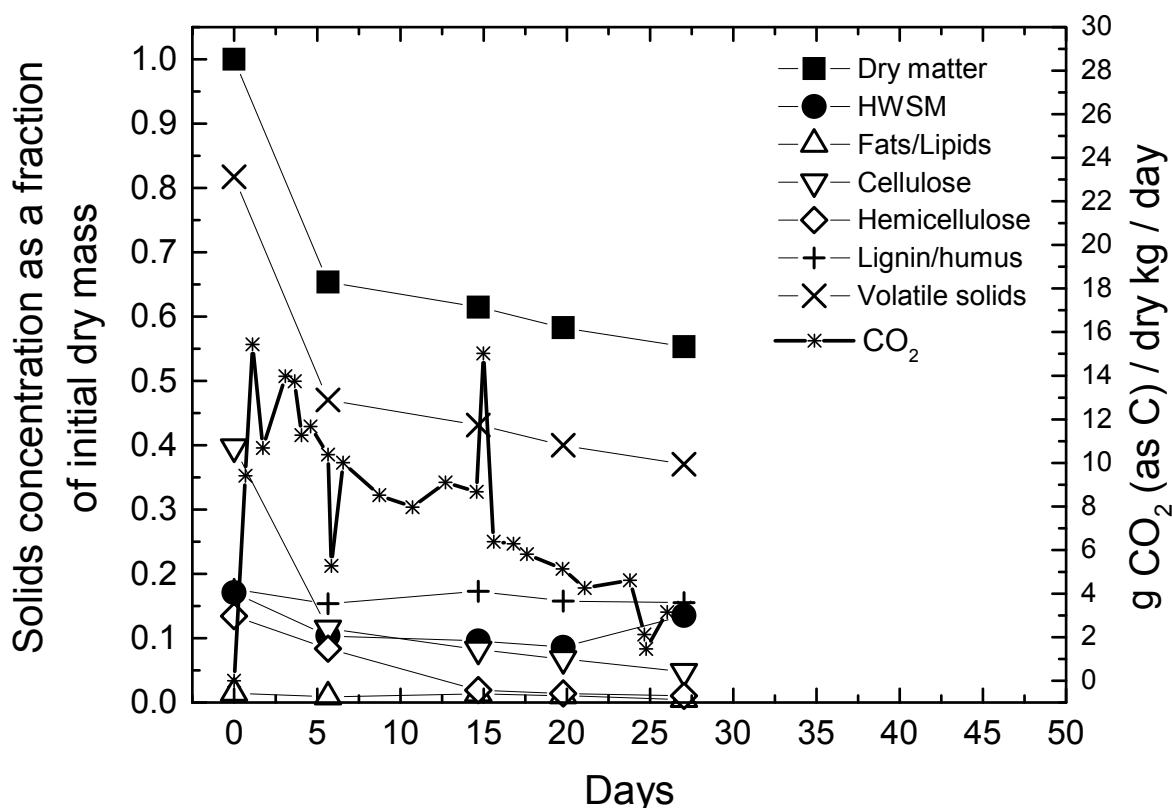


Figure 5-4. Concentrations of organic constituents and CO₂ production rate during composting of grass.

The easily degradable cellulose has apparently been degraded by day 5; hemicellulose degradation rates were 6.7% per day and 5.3% per day during the first 15 days and decreased to 0.74% per day and 0.37 per% per day until the end of the run, as shown in Table 5-4. Hemicellulose had therefore relatively constant decomposition rates during the first 15 days, after which it continued to degrade more slowly as it approached complete loss. Hemicellulose reduction was 93.8% by the end of the run.

HWSM, fats/lipids, and dry matter degraded at similar rates as hemicellulose during the first 5 days. Dry matter rates stabilized to relatively constant values after day 5.6, as was also observed for cellulose. An increase in the decomposition rate of the fats and lipids was observed after day 15, but the concentration of that chemical group was very low. The increase of HWSM at the end of the process is attributed to the generation of water-soluble humic matter, probably of fulvic acid origin. This is likely since fulvic acids are generated during the composting process (Riffaldi et al., 1986) and are soluble in all pH ranges (Stevenson, 1994).

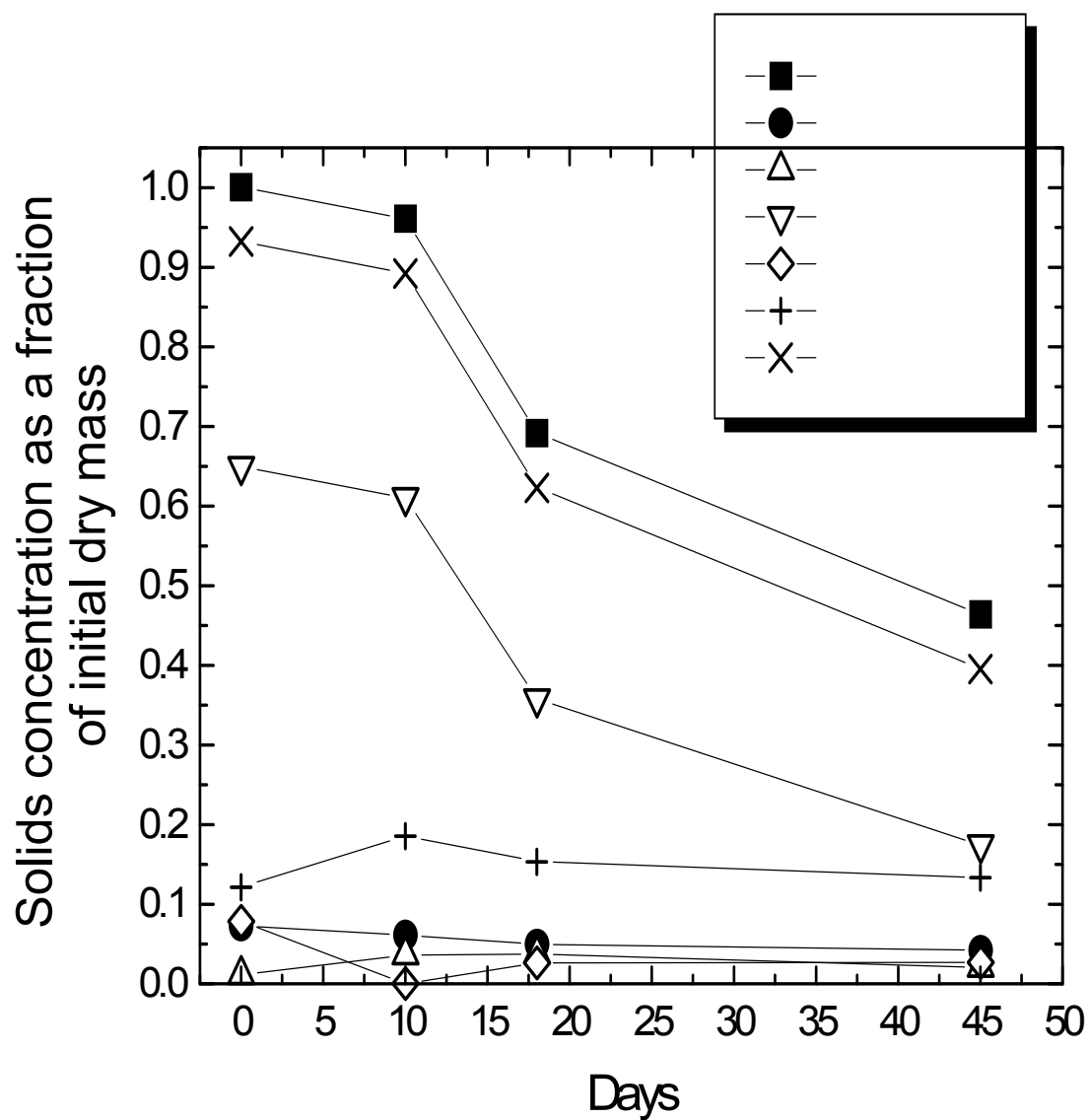


Figure 5-5. Concentrations of organic constituents during composting of seeded mixed paper.

**Table 5-4. Solids Decomposition Rates (As Percent of Dry Mass Decomposed/Initial Dry Mass/Day)
During Composting of Grass and Seeded Mixed Paper**

Grass						
Period (days)	Dry matter	Fats/lipids	HWSM	Cellulose	Hemicellulose	Lignin/humus
0-5.6	6.14	7.17	6.96	12.58	6.66	2.25
5.6-14.7	0.43	-3.60	0.51	0.91	5.32	-1.20
14.7-19.8	0.62	4.19	1.13	0.71	0.74	1.68
19.8-27.0	0.40	5.33	-3.98	0.70	0.37	0.22
Mixed paper						
Period (days)	Dry matter	Fats/lipids	HWSM	Cellulose	Hemicellulose	Lignin/humus
0-10	0.39	-22.74	1.58	0.61	10.00	-5.29
10-18	3.37	-0.81	1.99	4.87	-4.20	3.33
18-45	0.84	5.51	0.40	1.05	-0.01	0.61

Lignin/humus decomposition rates were highest during the first 5 days. A slight net increase of the lignin/humus fraction was observed from day 5 to 15, which can be explained by a net production of humus and biomass, accounted for in the lignin/humus fraction. Lignin, however, did not change much during the process, having an overall net reduction of 12.1% (see Table 5-2).

Decomposition rates for mixed paper are included in Table 5-4 and shown in Figure 5-5. For mixed paper, the initial cellulose decomposition rate was 0.61% per day, approximately 1 order of magnitude less than the initial decomposition rate for cellulose in grass. Cellulose decomposition rates increased between days 10 and 18 to 4.87% per day and decreased to 1.05% per day after day 18, which is a rate similar to the rate of cellulose decomposition in grass during the latter stages of composting. The initial cellulose persistence is probably because of the lag time required for the acclimation of cellulolytic microorganisms. Although mixed paper was seeded, the type and concentration of seed is expected to affect decomposition rates, as discussed earlier. A 30% residual cellulose content appears to remain at the end of the experiment, indicating potential residual cellulose binding to humus or lignin. The structure of cardboard might also retard mixed paper decomposition. Cardboard consists of sheets of paper attached together, which could make the invasion of the microorganisms between the sheets difficult.

Hemicellulose was highly degradable in the first 10 days with a decomposition rate of 10% per day. A slight increase in hemicellulose was detected after day 18 and is attributed to the synthesis of bacterial and fungal slimes and gums that are known to contain hemicelluloses (Tenney and Walksman, 1929).

HWSM decomposed slowly and at relatively constant rates during the first 18 days. Fats and lipids increased during the first 18 days, probably due to the generation of cells and cell lysis byproducts, which have a lipophilic nature. A slight decrease of fats and lipids was observed after day 18, indicating decomposition. An increase of lignin/humus was observed initially and reduction prevailed thereafter.

Dry mass reduction rates in mixed paper were similar to the rates of cellulose reduction since that is the dominant organic component. It is noted that this mixed paper run was performed at a mesophilic temperature, while an ascent from mesophilic to thermophilic temperature was used for the MXP run shown in Table 5-2 for the first 20 days after which thermophilic temperatures were maintained. The net overall reduction extents for the mixed paper run shown in Figure 5-5 were 53% for dry mass, 73.2% for cellulose, and 66.1% for hemicellulose; increases were 85% for fats/lipids and 9.9% for lignin/humus. Therefore, mixed paper was decomposed at higher extents in mesophilic compared to thermophilic temperatures and had a larger dry mass reduction extent compared to the grass.

This degradation profile of mixed paper is similar to observations made by Inoko et al. (1979), who followed solids decomposition in city refuse during composting in actual composting plants. Inoko et al. (1979) observed that hemicellulose was the component that decreased at the highest rates among all other solid constituents during the first 10 days of composting. Hemicellulose concentrations (in % dry mass basis) remained constant thereafter. They observed that cellulose percentages (expressed on a dry matter basis) increased during the

first 10 days, indicating that negligible cellulose decomposition actually occurred during that time. Cellulose reduction started to occur after approximately day 10, similar to that observed for the mixed paper run illustrated in Figure 5-5. The similarities are probably because city refuse is expected to contain high percentages of paper.

5.1.5 Compost Maturity Indicators

Whether finished composts derived from different initial substrates can have certain similar properties is a question of interest and a topic of research for decades (Mathur et al., 1993). Such similarities would aid in deriving commonly accepted compost maturity indicators. This would particularly apply to MSW for which differences in composition exist among countries or even municipalities.

The objective of this section is to discuss certain properties of the composted substrates used in these runs as to whether they could be used as potential compost maturity indicators. The average carbon dioxide production rate during the last 10 days of each of the runs, shown in Table 5-2, was selected as the basis for comparing the decomposition status of each substrate. It was therefore assumed that runs with low final average CO₂ production rates are closer to maturity than runs with higher final CO₂ production rates. This assumes that CO₂ production rates are not limited by factors such as nutrients, moisture, or seeding but only by the solids composition, that is the presence of refractory organics.

Based on the average values of CO₂ production rates, all runs were ranked from the most “mature” (top of Tables 5-2 and 5-5) to less “mature” (bottom of Tables 5-2 and 5-5). As Table 5-2 shows, mixed paper (MXP) had one of the lowest extents of VS reduction, but is defined as mature due to the minor CO₂ production rates recorded at the end of the run. As discussed earlier, inadequate seeding may be the reason for the low decomposition rate for that substrate. It was estimated in Chapter 4 that this component had reached 71% of its ultimate CO₂ yield at the time of termination of that run. The ultimate yield for that run would have been reached sooner had mixed paper been combined with other more degradable substrates.

Table 5-2 shows that the most mature component is MXP_{ns}, since it had negligible degradation due to lack of seed. The MXP_{ns} run was not included in the analysis to follow since decomposition was not induced for that run. Table 5-2 shows that office paper, grass, and the MSW_{1/3} had still relatively high CO₂ production rates at the time of the termination of the runs, indicating that they had not reached complete maturity by that time. The grass and MSW_{1/3} runs were terminated due to time constraints; it was estimated that they had yielded more than 90% of their CO₂ ultimate yield based on first order modeling in Chapter 4.

To derive indicators that could be useful for determining compost maturity, linear regressions were made between the average final CO₂ production rates for each run (Table 5-2) and various parameters for each substrate. The parameters were total reduction extents (in %) for the five chemical groups, the total organic carbon reduction, the C/N ratio (%), and the cellulose-to-lignin ratio (%) during composting. Linear regressions were also made with the concentrations of the five chemical groups in the composted (finished) substrates (expressed as

Table 5-5. Correlation Matrix for Estimation of Compost Maturity Indicators Using the Composted Substrate Chemical Composition

Substrate ^a	Fats/ Lipids (% VS)	HWSM (% VS)	Lignin content (% VS)	Cellulose (% VS)	Hemicel- lulose (% VS)	VS (% dw)	C (% dw)	C/N ratio ^b	Cellulose / lignin ratio
MXP ^c _{ns}									
MXP _{ns}	0.8	5.9	37.7	57.4	3.6	88.5	41.6	21.31	1.52
Leaves	1.8	22.3	62.2	9.9	1.9	54.7	20.2	7.77	0.16
MXP/YW	1.4	6.5	50.0	38.1	2.7	72.5	38.1	18.88	0.76
Seed	1.8	11.8	51.6	31.1	6.1	65.0	33.3	11.82	0.60
MXP/YW/FW	1.4	7.6	51.0	26.4	3.6	71.5	36.1	15.78	0.52
FW/YW	2.3	18.7	60.3	13.9	1.9	52.8	25.8	9.62	0.23
YW	3.5	8.9	63.2	17.7	1.3	51.0	25.2	7.60	0.28
YW _h	2.5	11.0	61.7	11.0	0.0	56.2	28.5	11.15	0.18
FW/MXP	0.9	0.0	35.2	53.9	0.0	86.7	42.5	20.63	1.53
FW	2.1	17.5	27.8	52.1	0.0	79.7	39.7	17.87	1.87
Branches	0.9	8.7	58.3	34.3	16.8	78.3	39.2	17.26	0.59
Yw _{ns}	2.2	10.9	52.9	9.7	0.3	50.0	26.1	8.17	0.18
FW _{ns}	7.4	24.4	15.2	51.5	0.0	88.1	43.8	15.55	3.39
MSW _{1/3}	1.0	10.1	52.7	29.1	4.9	70.4	35.5	N/m	0.55
Office paper	0.0	3.6	7.4	81.4	0.0	82.7	36.8	N/m	11.01
Grass	1.3	36.6	41.9	12.9	2.8	66.9	33.3	N/m	0.31
Correlation coefficient (R ²)	0.05	0.13	0.17	0.024	0.0	0.026	0.017	0.002	0.004 ^d
Cured MSW compost ^e	0.9%	7.2%	46.4%	24.1%	4.2%	63.1%	31.4%		0.52

^a Substrates are placed in ranking order from most mature (top of table) to least mature (bottom of table) as judged from the average CO₂ production rates during the last 10 days of each run.

^b No N measurements were performed for the grass, MSW_{1/3}, office paper, and the cured MSW compost.

^c Cured MSW compost chemical composition is given for comparison and was not included in the statistical analysis.

^d Office paper excluded from analysis (see text).

^e No solids measurements were performed for the MXP_{ns} run.

% of the volatile solids content), shown in Table 5-5. Regressions with final C/N ratio and final cellulose-to-lignin ratios were also made (Table 5-5). The linear regressions provided coefficients of determination (R^2) that were used to compare parameters in their ability to predict compost maturity. These correlation coefficients are included in Tables 5-2 and 5-5; they are useful only for comparison and are not meant to indicate the accuracy of predictive models

In addition to the above and as part of comparing the laboratory results with values observed in the field, cured compost was collected from an MSW composting facility near Portage, WI, and its solids composition measured. The chemical composition of the cured MSW compost is included in Table 5-5.

The correlation coefficients of Table 5-2 indicate that the C/N ratio reduction and the fats/lipids reduction correlate more strongly with the final CO_2 production rates than other reduction parameters, as illustrated in Figure 5-6.

A reduction in C/N ratio is generally observed as the substrate matures. This is evident from Figure 5-6 as well as from the initial and final C/N values for the various substrates shown in Tables 5-2 and 5-5. Generally, the C/N ratio decreases during composting due to greater reduction of carbon compared to the reduction of nitrogen (Epstein, 1997). Increases of C/N ratio during composting were observed only for food wastes (an increase from approximately 8.0 to approximately 16.0 at the end of the process). This is due to the high initial N content of food wastes. The reduction of C/N ratios during composting is generally well-documented (Mathur et al., 1993). Consideration of both the initial and final C/N ratios are required to calculate this reduction.

A C/N ratio of 10 has been suggested as a compost maturity indicator (Mathur et al., 1993). However, this was not shown in the above analysis. There is a generally wide range of C/N ratios for composted substrates, such as 7.8 for composted leaves and 21.3 for composted mixed paper (MXP) and no particularly good correlation was observed between the CO_2 production rates and the C/N ratio (as will be shown in Figure 5-8). Food-waste-derived compost C/N ratios are higher than 10 due to the relatively high residual carbon concentration present. Most of the mixed paper mixtures, however, had C/N ratios between 15 and 20, also due to a high residual carbon, mostly in the form of residual cellulose. Yard wastes and leaves had values lower than 10.

The reduction of fats and lipids during composting also had a stronger correlation than other parameters. However, as Figure 5-6 shows, this higher correlation is governed by the three data points with the highest residual CO_2 production rates, while the other data points are clustered together. The indicated increase of fats and lipids during composting might be due to the generation of biomass and cell lysis byproducts that are lipophilic. An increase of fats and lipids during composting was also shown earlier for mixed paper composting. Fats/lipids reduction extents should be used with caution as compost maturity indicators because of the relatively small concentrations of that organic group in both initial and final substrates.

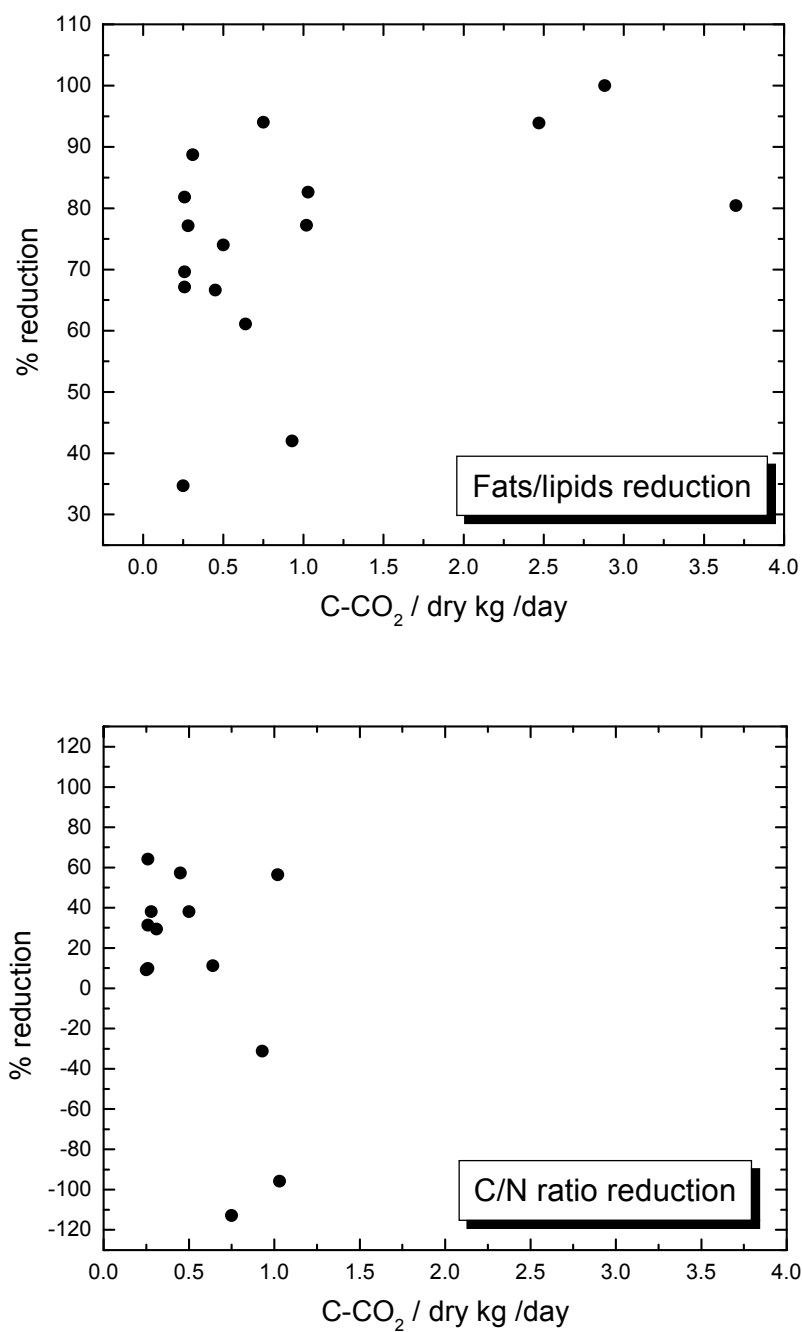


Figure 5-6. Correlation plots between final average CO₂ production rate and fats/lipids reduction and C/N ratio reduction.

Based on Table 5-5, final lignin/humus (as % VS) and final HWSM (as % VS) correlate more strongly with final CO₂ production rates than with other parameters describing the final waste composition. The correlation plots for lignin/humus and HWSM are included in Figure 5-7. Also shown are correlation plots for the other three chemical constituents (cellulose, fats/lipids, and hemicellulose). The final lignin/humus content appears to be a reasonable indicator of the concentration of the stabilized organic matter in compost, since it includes the slowly degradable lignin as well as the generated humic matter. Expressing lignin/humus content on a VS basis rather than a dry matter basis gives a better quantification of this organic group because the composted dry matter may have a high inorganic content, which is not degradable. The average lignin content for all composted materials shown in Table 5-5 is 48% ($\pm 3.4\%$) on a volatile solids basis. Most of the final lignin/humus concentrations, however, are above a threshold value of 50% (VS basis). Cured MSW, in particular, had a lignin/humus content of 46.4% (VS basis).

Figure 5-7 indicates that the lignin/humus concentration increases with composting. As materials mature, final lignin/humus concentrations appear to become greater than 50% (% VS) and approach a value of between 50% and 60% (VS). A threshold value of at least 50% (VS basis) for lignin/humus is suggested as a compost maturity indicator based on this study.

The FW and FW_{ns} runs had the lowest lignin contents in their composted substrates at 27.8% and 15.2% (VS basis), respectively. The low lignin values for food wastes are probably because lignin in food wastes is more degradable than lignin in the other MSW substrates or because the lignin/humus in composted food wastes was more soluble in the 72% sulfuric acid. In addition, humification might not have proceeded to a great extent in food wastes, making mineralization the primary pathway for conversion of the organic carbon found in the primary solid constituents. The composted substrates from the FW/MXP and MXP runs had lignin contents less than 40% because of the high residual cellulose content found in both composted substrates. Office paper had also not reached its full extent of degradation, as shown in Table 5-2. Therefore, the low decomposition rates probably resulted in limited formation of humic matter and biomass, so the residual lignin/humus content was only 7.4% (VS basis).

As shown by the correlation analysis, the extent of lignin/humus reduction did not provide a reasonable correlation and cannot be used as a compost maturity indicator.

The relatively high final HWSM content correlation with CO₂ production rates is governed primarily by the three least mature substrates (office paper, MSW_{1/3}, and grass). This is attributed to the formation of water-soluble humic matter, since these substrates still had not decomposed completely at the end of the runs. As Figure 5-7 shows, HWSM final contents range between 5% and 25% for the more mature substrates, while generally an increase of the HWSM content is observed during composting. Despite the correlation, HWSM final contents may not be suitable to indicate compost maturity due to their wide range in mature substrates.

Figure 5-7 also shows that a reduction in fats/lipids, cellulose, and hemicellulose occurs during composting. More apparent is the reduction of hemicellulose during composting, with final hemicellulose contents close to 0 for most of the substrates. Food wastes (unseeded) contained no hemicellulose in both the initial and final substrate.

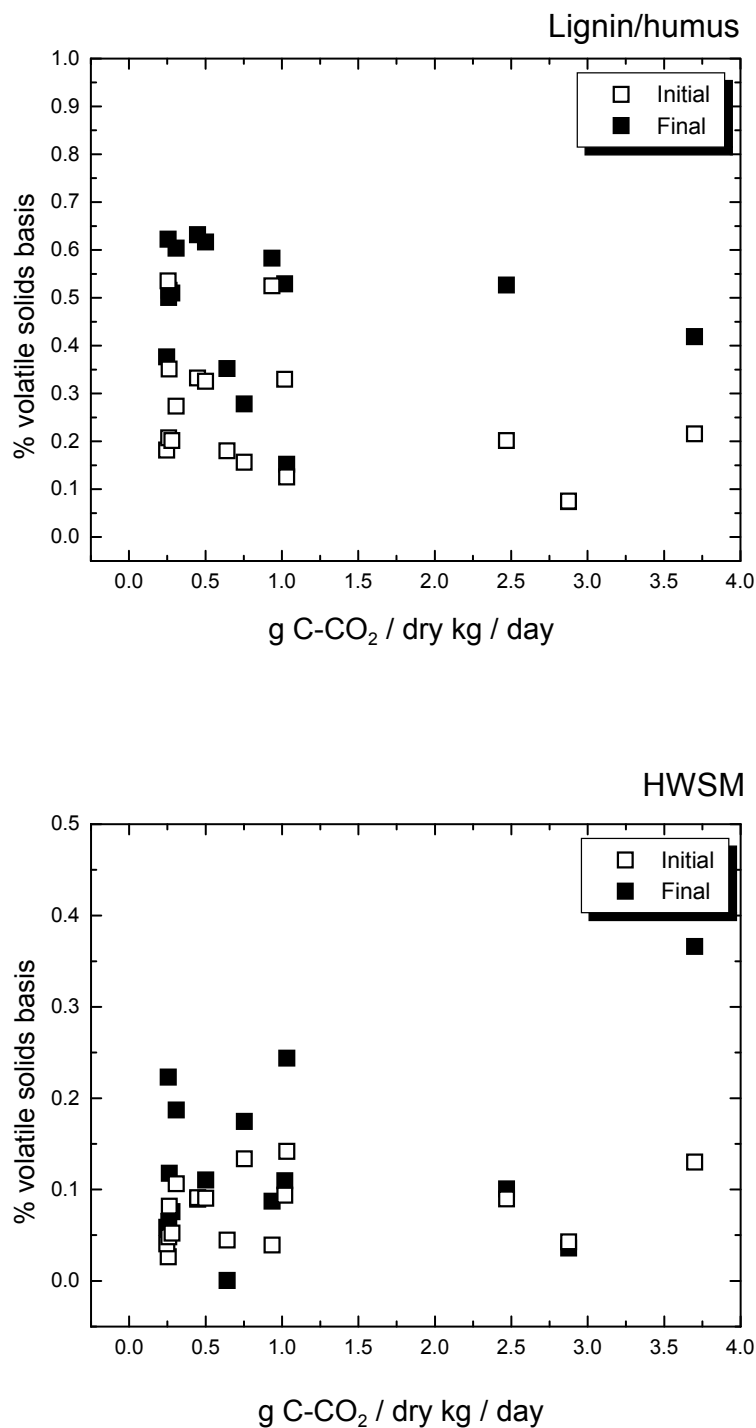


Figure 5-7. Correlation plots between final average CO₂ production rates and initial and final solids chemical composition (% VS basis).

(continued)

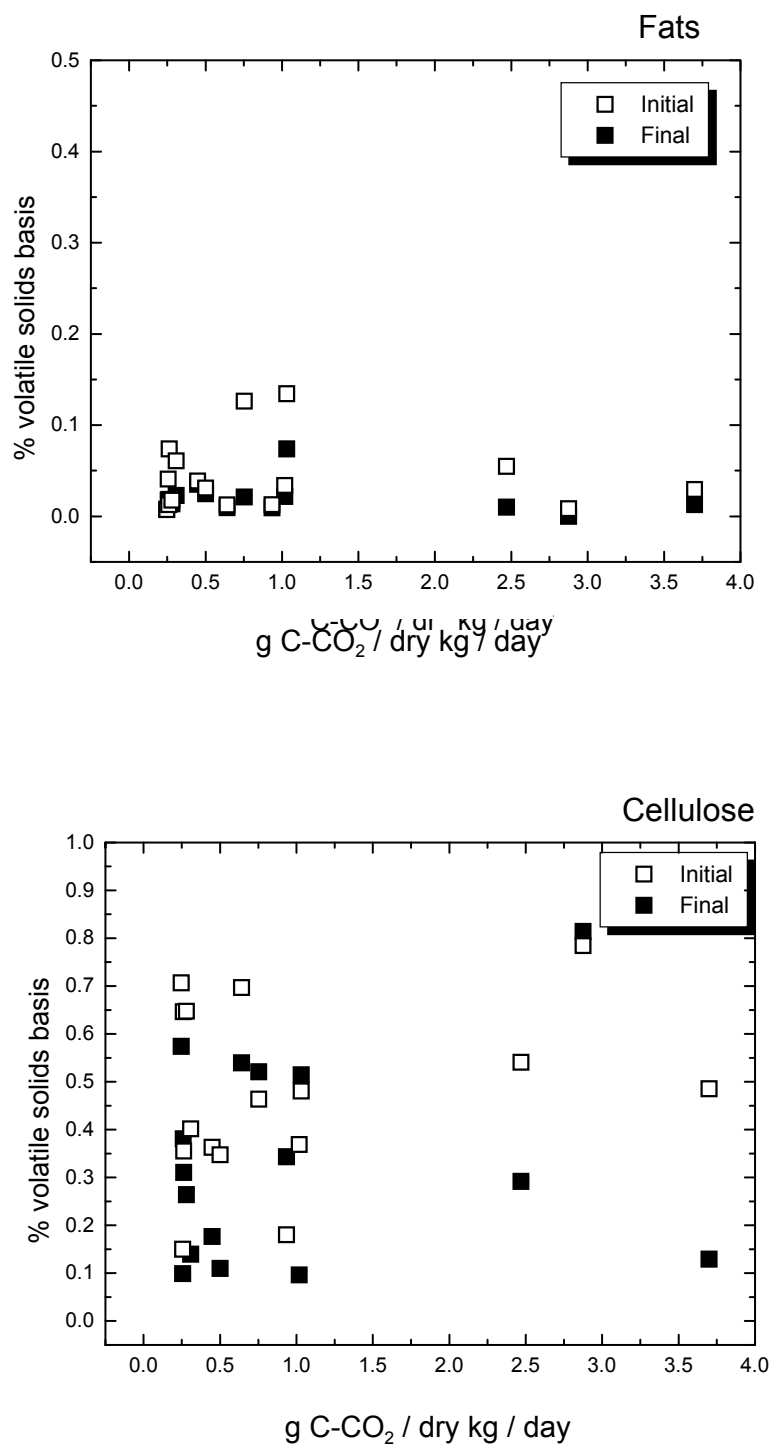


Figure 5-7. (continued)

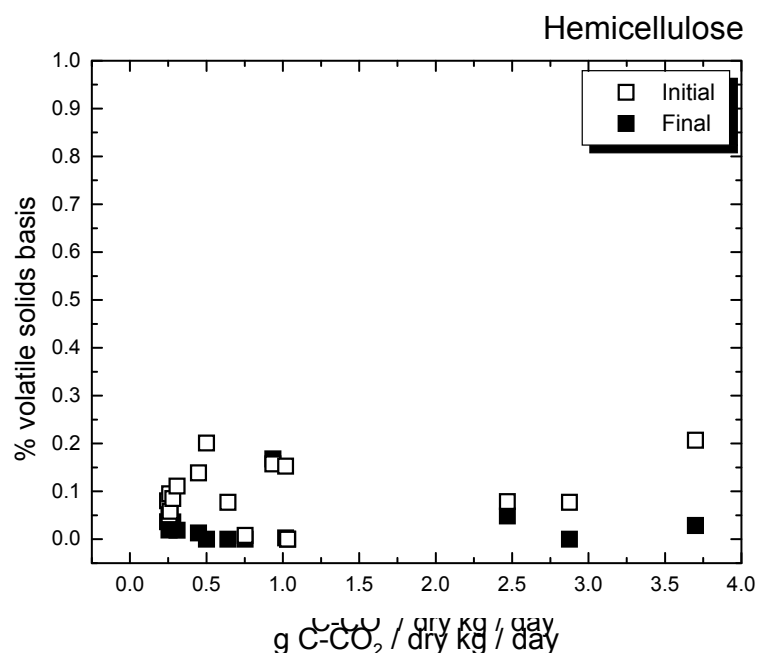


Figure 5-7. (concluded)

Although cellulose-to-lignin ratio (C/L ratio) in finished composts did not show any strong correlation, a decrease of this parameter was generally observed during composting (see Figures 5-8 and 5-9). Because this ratio has been used as an indicator for characterizing fresh and matured solid wastes in anaerobic environments (Bookter and Ham, 1982), it will be discussed here. Figure 5-8 shows the correlation plot between residual CO_2 production rates and initial and final C/L and C/N ratios. Figure 5-9 shows the initial and final C/L ratios for all substrates in a bar graph format. Based on Figure 5-8, it appears that most substrates approach a constant C/L ratio less than 0.5 during composting. The reduction of this ratio is explained by the fact that, although lignin does partially decompose during the process, the cellulose reduction is greater than that of lignin, resulting in a reduction of the C/L ratio from an average initial value of 2.3 (± 0.4) (Table 5-1). Higher than average initial C/L ratios were recorded for food waste and wastes containing mixed paper. Office paper is not shown in Figure 5-9 because of its significantly high C/L ratios compared to the other substrates. Yard wastes and its subcomponents had relatively low initial C/L ratios.

The composted food wastes had a relatively high C/L ratio compared to other composted materials. This is a result of the low lignin content of composted food wastes and the relatively high residual cellulose.

The increase of C/L ratio for branches might be explained by the uniquely low cellulose and high lignin contents of this material. In addition, branches had an increase in lignin during composting, probably due to a net increase in lignin/humus as a result of minimal degradation of lignin in branches and the generation of humus from both lignin and cellulose. This was also true for the mixed paper run.

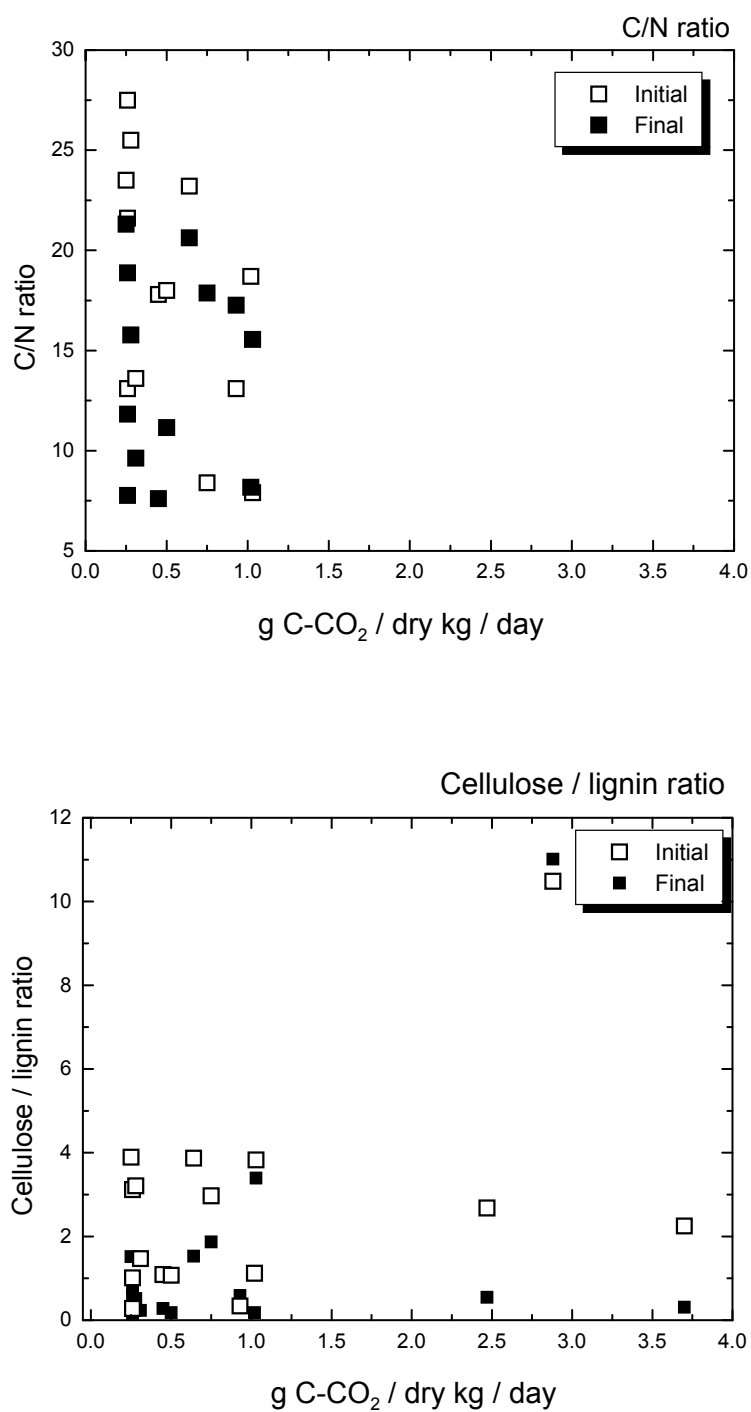


Figure 5-8. Correlation plot between final average CO₂ production rates and initial and final C/L and C/N ratios for various substrates.

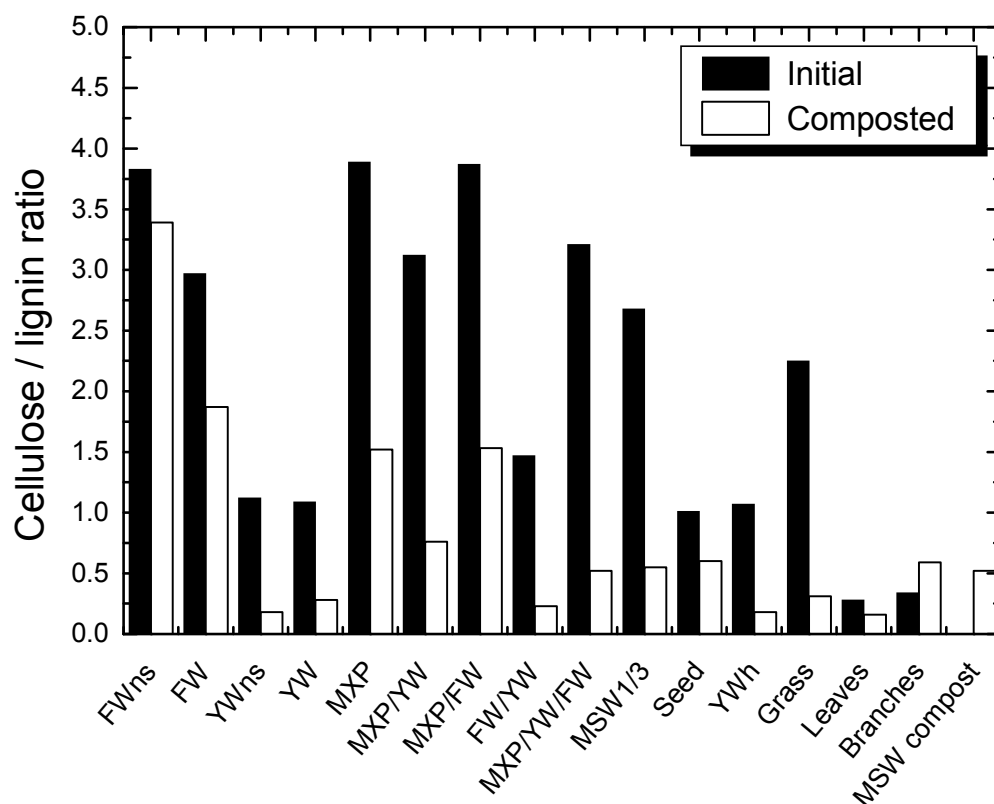
MSW-derived cured compost had a C/L ratio of 0.52, which is close to the value that most of the substrates appear to converge to during composting, as shown in Figure 5-8.

Based on the above it appears that a C/L ratio less than 0.5 could be used as a maturity indicator for various substrates. Ratios of approximately 0.8 have been recorded for 8-year-old refuse in landfills, and ratios of 0.16 to 0.24 have been recorded in older landfills (Bookter and Ham, 1982). In addition, Bookter and Ham reported fresh refuse with C/L ratios up to 4.04, a value close to the initial C/L ratio of several of the substrates used in this experiment. It should be noted that Bookter's analytical methods were different than those used in this paper, probably overestimating the amount of cellulose measured in his substrates.

The above analyses were based on regressions between the final average CO₂ production rates and final chemical composition of all substrates. The goal of the regressions was to compare potential compost maturity indicators and not to provide adequate predictive models. It is recommended that the above analysis be performed based on regressions of chemical composition and CO₂ production rates of materials not only at the end of a run—as was done here—but by using values throughout a run, based on intermediate sampling.

5.1.6 Errors in Analytical Measurements

The objective of this section is to evaluate sources of error in analytical measurements and to consider mass balances. Eleazer et al. (1997) have suggested that, in the case of anaerobic solid waste treatability studies, the ratio of the sum of cellulose, hemicellulose, and lignin to volatile solids concentration (all expressed on a dry weight basis) should equal 1.0. This was suggested by assuming that only cellulose, hemicellulose, and lignin are the dominant organic materials in the substrate. However, based on the methods used here, the dry mass of solid waste components was further fractionated to two additional chemical groups: fats and lipids and the hot water soluble matter. If only these five groups of organics are present in the substrate, the ratio of their sum to volatile matter concentration (all expressed on a dry mass basis) should equal 1.0. Table 5-1 shows that this ratio (defined as FHCHL/VS) ranges from 0.88 for food wastes to 1.07, with an average of $0.964 \pm 6.7\%$, for all starting materials. The relatively low value for food wastes (0.88) is attributed to dissolution of organic groups other than polysaccharides during acid hydrolysis as discussed previously. The low FHCHL/VS ratio for leaves (0.80), might be explained by partial dissolution of lignin, since leaves were already partially decomposed prior to initial analyses, making the lignin fraction more susceptible to acid solubilization (Effland, 1977). Table 5-6 includes the FHCHL/VS ratio for the composted materials. Most of the values are close to 1.0, indicating good accuracy in the determination of the five chemical groups. The low value for YW_{ns} (0.76) and the high value for branches (1.19) are attributed to analytical errors. The fact that the FHCHL/VS ratio for leaves increased from 0.80 in the starting material to 0.98 in the composted material might indicate the polymerization of compounds to humic compounds that are acid insoluble and quantified in the lignin/humus fraction. The average FHCHL/VS value from the composted substrates is $0.955 \pm 9.9\%$, a value very similar to the FHCHL/VS ratio reported for the starting materials.



* Office paper run not included due to high C/L values; no measurements were performed for the MXP_{ns} run

Figure 5-9. Cellulose to lignin (C/L) ratios for initial and composted materials from 15 experimental runs (plus compost from a MSW composting facility).

Table 5-6 also presents the carbon and nitrogen mass balance closures performed for all runs. The yields of carbon and nitrogen emitted during the process were quantified by CO₂ and NH₃. Carbon recovery values ranged from 85.5% to 117.9%, where recovery is defined as the amount of C captured as CO₂ divided by the carbon reduction in the solid phase. The average carbon recovery value was 100.5% ± 9.91% from all runs. Nitrogen recoveries had large variabilities ranging from 5.7% for MXP/YW/FW to 173.7% for yard wastes, where recovery is defined as the amount of N emitted as NH₃ divided by the nitrogen (TKN) reduction in the solid phase. Nitrogen added as nutrients was accounted for in the calculations. If nitrates were unavailable to the microbial population, and since they would not be measured during the final TKN analysis, nitrogen recoveries less than 100% were recorded, which may partially explain the low N recoveries for the mixed paper runs.

Table 5-6. Carbon, Nitrogen, and Solids Recoveries

Contents	C recovery (%)^a	N recovery (%)^b	FHCHL/VS^c
FW _{ns}	108.5	77.5	0.98
FW	117.9	72.7	0.99
YW _{ns}	98.6	173.6	0.76
YW	94.4	157.2	0.95
MXP _{ns}	NM	NM	NM
MXP	93.2	33.9	1.05
MXP/YW	90.2	7.4	0.99
FW/MXP	115.9	14.5	0.90
FW/YW	109.0	86.4	0.97
MXP/YW/FW	91.8	5.7	0.90
MSW _{1/3}	95.0	NM	0.98
Seed	85.5	32.2	1.02
YW _n	101.7	51.8	0.86
Grass	91.0	NM	0.95
Leaves	100.7	-23.3	0.98
Branches	114.3	37.9	1.19
Office paper	100.0	NM	0.92
Cured MSW compost			0.83

^a CO₂ yield (as C) / (total C in starting solid material – total C in composted solid material).

^b NH₃ yield (as N) / (total N in starting solid material + N added as nutrients – total N in composted solid material).

^c The ratio of the sum of fats, HWSM, cellulose, hemicellulose, and lignin/humus concentrations to the volatile solids concentration.

NM = Not measured.

6.0 Emissions of Volatile Organic Compounds During Composting

Certain runs presented in Chapters 4 and 5 were selected and used to provide VOC emissions data. VOC emissions were quantified for 11 runs. These runs were: seeded mixed paper (MXP), unseeded mixed paper (MXP_{ns}), seeded yard wastes (YW), unseeded yard wastes (YW_{ns}), seeded food wastes (FW), unseeded food wastes (FW_{ns}), a seeded mixture of mixed paper and yard wastes (MXP/YW), a seeded mixture of mixed paper and food wastes (MXP/FW), a seeded mixture of food wastes and yard wastes (FW/YW), and an unseeded mixture of food waste, mixed paper, and yard wastes (MSW_{1/3}). A run with only seed (obtained from an MSW composting facility) was also performed. Seed was added at approximately 10% of the component's weight (on a dry weight basis), and the relative amounts of each component in the mixture runs were set according to their relative amounts in the MSW.

VOCs emitted were captured on activated coconut charcoal traps and extracted with carbon disulfide (CS₂). Compounds were identified using GC/MS and quantified using a GC equipped with a flame ionization detector. Detailed methods are presented in Chapter 3.

The compounds identified may vary depending on the type of sorbent used during capture. The activated coconut charcoal used can effectively capture a wide range of organic molecules, but especially VOCs with two to five carbon atoms (Supelco, 1997). The porous surface of activated coconut charcoal makes it a more efficient sorbing material compared to graphitized carbon black. Wilkins (1994) and Tolvanen et al. (1998) used Tenax tubes, Eitzer (1995) used Tenax and graphitized carbon black traps, and Kim et al. (1995) and Brown et al. (1997) used charcoal traps.

The same experimental setup was also used to quantify emissions after spiking known amounts of VOCs. VOCs were spiked onto different MSW substrates in both liquid and vapor phases and under mesophilic and thermophilic temperatures. Two runs were performed by spiking ethylbenzene in liquid form to seeded newsprint and then to a mixture of yard wastes. Spikes were introduced through the exit port at the top of each digester. This was designed to simulate the introduction of VOCs originally introduced in MSWs through ruptured containers or broken bottles.

A mixture of toluene, ethylbenzene, *m*-xylene, and *o*-xylene (TEX) was spiked to simulate an MSW (mixture of food wastes, yard wastes, and mixed paper) in the vapor phase. A 125-mL glass bulb was connected to the tubing that directed air into the digester. Through a rubber septum located on the glass bulb, a known volume of a TEX liquid standard solution, prepared in methanol, was injected into the bulb via an airtight syringe. Both the digester and the glass bulb were kept in the thermophilic temperature range from 50 to 55 °C. The VOC mixture was rapidly vaporized at such temperatures and was carried by the air stream into the

MSW mixture. This setup might simulate the case where a VOC present in the center of a continuously aerated windrow will volatilize due to the development of thermophilic conditions and move through the compost mass by advection and/or diffusion.

The air flow rate was kept at approximately the same levels during the three spiked runs. During the spiked runs, VOCs were analyzed with GC/FID, using the internal standard technique.

6.1 Results and Discussion

6.1.1 Identification of VOCs from Biodegradable Fraction of MSW

Results of the identification of VOCs for 9 of the 12 runs are presented in Table 6-1. One Orbo charcoal trap from each run was used for VOC identification by GC/MS. Most charcoal tubes used for GC/MS analysis were collected during the first 5 days of the composting of a substrate, since most VOC volatilization was observed to occur during that time, as was shown by preliminary runs not presented here. In the case of the MXP run, the sample used for GC/MS was placed on the digester between day 29 and day 48 from the initiation of composting. This was done to collect VOCs for identification over the thermophilic temperature range used after day 29. Prior to day 29, a gradual ascent from mesophilic to thermophilic temperatures was used for that run only. For the MXP/YW run, the sample used for GC/MS VOC identification was collected between days 10 and 28 because of partial volatilization of the samples until day 10 for that run. The time period for VOC sampling by the charcoal tube used for VOC identification might be important because it reflects the decomposition stage for that run during that time period.

No GC/MS measurements are given in Table 6-1 for the seeded yard wastes (YW), the food waste and yard wastes (FW/YW), or the (MSW_{1/3}) runs. VOCs were not identified for these runs because the compounds emitted were not expected to differ from those emitted from the individual components that made up the mixtures or from the unseeded yard wastes.

Table 6-1 presents only the VOCs with a purity index (PI) higher than 70%, which is close to the common threshold value of 80% used by the State Laboratory of Hygiene (Madison, WI) for considering a compound as positively identified by MS only (personal communication. John Mathew, Director of GC/MS laboratory). Note that a purity index of 100% indicates the mass spectrum of a known standard organic compound (acquired from pertinent mass spectra databases) precisely matches the mass spectrum of an organic compound found in the mixture. VOCs with a purity index less than approximately 70%, although reported by the GC/MS, were not included in Table 6-1. Coelution of compounds usually confounds proper identification of compounds. Twenty-five VOCs were further targeted and tentatively identified using both GC/MS and retention times. Discussion of the selection of the 25 VOCs follows in a later section.

Table 6-1 presents the fraction (RAC) of the area counts of that compound, as measured during the GC/MS analysis, to the total area counts of all compounds identified in the charcoal

Table 6-1. VOCs Identified in Gaseous Emissions from Nine Runs^a

Unseeded mixed paper (MXP _{ns})		Seeded mixed paper (MXP) (cont.)	
Cyclopentasiloxane, decamethyl	5.0	Undecane	1.1
Dodecane	4.9	Limonene	1.0
2-ethyl-1 hexanol	4.1	2-pentyl furan	0.9
1,2,4-trimethylbenzene	4.0	Cyclopentasiloxane, decamethyl	0.9
Cyclotetrasiloxane, octamethyl	3.7	Bicyclo[2.2.1] heptan-2-ol, 1,7,7-trimethyl ester)	0.8
Undecane	3.3	Dodecane	0.8
Toluene	2.9	Camphor	0.8
Naphthalene	2.6	Naphthalene	0.8
Acetic acid, trifluoro-, octyl ester (or) 1 octanol	2.5	1-octanol	0.7
1 ethyl-4-methyl benzene	2.4	1,4-dichlorobenzene	0.7
3-cyclohexene-1-methanol, alpha	2.0	Heptanoic acid, 3,5-dimethyl-methyl (ester)	0.5
2,6 dimethyldecane	1.8	3-furancarboxylic acid, 2,5-dimethyl (ester)	0.4
Ethylbenzene	1.6	2-methyl 3 hexanone	0.3
Benzene, 1-methyl-2-(1-methylethyl)	1.6	2,3-dimethyl butanoic acid, methyl ester	0.3
3,8 dimethyl decane	1.6	3-heptanone	0.3
1-ethyl-2,3-dimethyl benzene	1.5	Benzene, 1-methoxy-4-methyl-	0.3
2 methyl decane	1.5	Benzaldehyde	0.3
Camphor	1.4	Benzene, 1-methyl-3-(1-methylethyl)-	0.2
2,6 dimethyl undecane	1.4	3-penten-2-one, 3-methyl	0.2
1,2-dimethoxy-benzene	1.3	Ethylbenzene	0.2
4-methyl undecane	1.3	p-xylene	0.1
Cyclotrisiloxane, hexamethyl	1.2	2-4 dimethyl pentanone	0.07
Docosane	1.2	Pyridine	0.03
1 dodecene	1.1	Unseeded yard wastes (YW_{ns}) RAC	
1,4-dichlorobenzene	1.1	A-pinene	13.5
Benzene, 1-methyl-2/4-(1-methylethyl)	1.1	Toluene	12.6
Cyclopentane, butyl	1.0	3-methyl-2-pentanone	5.5
3,4 dimethyl undecane	1.0	Camphene	5.3
Cyclohexene, 1-methyl-4-(1-methylethyl) (or) Limonene	0.9	Bicyclo [3.1.0]hexane, 4 methylene	4.8
Cyclohexanone 5-methyl-2-(1-methyl-)	0.9	Beta-pinene	4.7
Cyclohexanol, 5-methyl-2-(1-methyl)	0.9	Limonene	4.2
Decane	0.8	2 cyclohexen-1-one, 3,5,5 trimethyl-	3.5
2-butoxy-ethanol	0.7	2-cyclohexen-1-one	3.5
" -pinene	0.7	Camphor	2.5
1,3,5-trimethyl benzene	0.7	Dimethyl-disulfide	2.4
p-xylene	0.7	Cyclohexanone, 2-2-6 trimethyl	2.1
1-ethyl-2-methyl-benzene	0.6	2-Pentyl furan	2.1
1,2,3-trimethylbenzene	0.6	Tricyclo[2.2.1.02,6] heptane, 1,7,7 trimethyl	2.0
Camphene	0.5	Tricyclo-heptane	2.0
Propyl benzene	0.5	1,7-Nonadiene, 4,8-dimethyl	1.7
Beta ninene	0.4	4-methyl-3 hexanone	1.7
Seeded mixed paper (MXP) RAC		Benzene, 1-methyl-3/4-(1-methylethyl)	1.7
2-ethyl-1-hexanol	60.0	1.7-Nonadiene	1.7
2 cyclohexen-1-one, 3,4,4-trimethyl	3.7	Octane	1.2
Benzoic acid, methyl ester	2.5	Cyclohexanone, 3,3,5- trimethyl	0.9
1,2-dimethoxy-benzene	2.2	Bicyclo [3.1.0] hex-2-ene, 2 methyl	0.9
Cyclotrisiloxane, hexamethyl	1.9	Cyclopentane, 2-ethylidene- 1,-1 dimethyl	0.9
Toluene	1.5		

(continued)

Table 6-1. (continued)

Unseeded yard wastes (YW _{ns}) (cont.)		Seeded food wastes (FW)		RAC
Styrene	0.8	Dimethyl trisulfide		1.5
Pyrazine 2,5-dimethyl	0.7	Cyclopentasiloxane, decamethyl		1.4
2,5-Dimethyl pyrazine	0.7	A-pinene		1.2
1,4-Dichlorobenzene	0.6	Limonene		1.1
1,3-Cyclohexadiene, 1-methyl-4-(1-?)	0.6	Benzene, 1-methyl-4-(1-methylethenyl)		0.9
(+)-2-carene	0.6	1 hexanol, 2 ethyl		0.7
Cyclopentasiloxane, decamethyl	0.5	Ethylbenzene		0.4
Bicyclo [3.1.1]heptan-3-one, 2,6,6-trimethyl	0.5	p-xylene		0.4
Methyl isobutyl ketone	0.3	Beta-pinene		0.4
Nonane	0.3	Furan, 2-pentyl		0.4
3-cyclohexen-1-ol, 4-methyl- 1-(1-methyl?)	0.3	1-butanol, 3 methyl acetate		0.3
Dimethyl trisulfide	0.2	Bicyclo[3.10]hexane, 4-methylene		0.3
p/m xylene	0.2	Methoxy-benzene		0.2
Pyridine, 2-6 dimethyl	0.1	1,4-dichlorobenzene		0.2
3-cyclohexen-1-methanol, " - ,	0.1	1-undecene		0.2
Unseeded food wastes (FW_{ns})^c	RAC	Nonane		0.1
Dimethyl disulfide	10.8	Bicyclo[3.1.0] hex-2-ene, 2-methyl		0.1
Cyclopentasiloxane, decamethyl	3.5	Camphene		0.1
Dimethyl trisulfide	3.2	Undecane		0.1
Phenylethyl alcohol	3.1	Butanoic acid, 3-methyl ester		0.1
Butanoic acid, 3-methyl, 3-methyl	2.8	2-nonanone		0.09
Camphor	2.2	3-octanone		0.08
2-nonanone	1.7	Methyl ethyl disulfide		0.06
Benzene, 1-methyl-3-(1-methylethyl)	1.5	Mixed paper and food wastes (MXP/FW)	RAC	
Acetic acid, butyl ester	1.4	Toluene		9.6
1-hexanol, 2-ethyl	1.3	2-pentyl furan (or) 1,2,4-trimethylbenzene		3.7
Butanoic acid, butyl ester	1.2	Cyclopentasiloxane, decamethyl		3.4
Butyl 2-methylbutanoate	1.1	Dodecane		3.0
Limonene	1.1	2-heptanone		2.5
Pyrazine, trimethyl	1.0	p-xylene		2.5
1-undecene	0.9	Naphthalene		2.5
Phenol	0.9	1 hexanol, 2-ethyl		2.3
A-pinene	0.4	Undecane		2.1
Butanoic acid, 2-methyl	0.3	Limonene		2.0
Pyrazine, 2-5 dimethyl	0.3	Benzene, 4-ethyl-1, 2-dimethyl		1.9
4-heptanone 3 methyl	0.2	A-pinene		1.8
Ethylbenzene	0.2	2-nonanone		1.8
Butanoic acid, 3-methyl	0.2	3-octanone		1.7
Pyrazine, 2-6 dimethyl	0.2	1,4-dichlorobenzene		1.7
Toluene	0.2	Benzene, 1-ethyl-2-methyl		1.6
2-hexanone, 5-methyl	0.14	3-cyclohexene-1-methanol, alpha		1.6
Octane	0.09	Benzene, 2 ethenyl-1,4 dimethyl		1.3
Butanoic acid ethyl ester	0.08	Benzene, 1,2,4,5-tetramethyl		1.3
Butanoic acid, 3-methyl, ethyl ester	0.05	Benzene 1,2,3,4-tetramethyl		1.3
1 butanol	0.01	Undecane, 2-6 dimethyl		1.3
Toluene	37.6	Tetralin		1.1
Dimethyl disulfide	29.2	Benzene, 1-methyl-4-1(1-methylethyl) ²		1.1
Cyclotetrasiloxane, octamethyl	3.0	Camphor		1.1
Benzene, 1-methyl-4-(1-methylethyl) ^b	2.0	Ethylbenzene		1.0

(continued)

Table 6-1. (concluded)

Mixed paper and food wastes (MXP/FW) (cont.)		1 hexanol, 2-ethyl	2.5
Benzene, 2-ethyl-1,4-dimethyl	1.0	Cyclotetrasiloxane octamethyl	2.3
Decane	0.9	1,1-Tricosene	2.0
Decane, 3 methyl	0.9	Dodecane	1.9
Octane	0.8	Undecane	1.5
Naphthalene, decahydro-2-methyl-	0.8	Heptanoic acid, dimethyl, methyl ester	1.4
Benzene, 4-ethyl-1, 2-dimethyl	0.8	Hexanoic acid, methyl ester	1.3
Butyl benzene	0.8	Bicyclo[2.2.1]hepten-2-one, 1,3,3 trimethyl	1.3
Beta-pinene	0.7	Dimethyl disulfide	1.3
1,2,3-trimethyl benzene	0.7	Cyclohexanone, 5-methyl-2-(1-methyl)	1.3
Benzene, 1-methyl-2-(1-methylethyl)	0.7	1,4-dichlorobenzene	1.3
Camphene	0.6	Benzene, 1,2,4,5 tetramethyl	1.3
Propyl-benzene	0.5	2 pentanone	1.0
2-heptanone, 6-methyl	0.5	Benzene, 2-ethenyl-1,4-dimethyl	1.0
1,3,5-trimethylbenzene	0.5	2,4-dimethyl 3 pentanone	0.8
Benzene, 1-ethyl-3-methyl	0.5	4-heptanone	0.8
Cyclotrisiloxane, hexamethyl-	0.4	Benzene, 1-methyl-2-(1-methylethyl)	0.8
Benzene, 1 methylethyl ^d	0.4	Styrene	0.8
Methane, isothiocyanato	0.1	Methyl isobutyl ketone	0.7
Disulfide, dimethyl	0.1	A-pinene	0.7
Mixed paper and yard wastes (MXP/YW)		Decane	0.7
Hexanoic acid, 2-ethyl-methyl ester	20.1	1-ethyl-2-methyl benzene	0.6
Camphor	10.3	p-xylene	0.5
2-cyclohexen-1-one, 3,4,4 trimethyl	7.1	Beta-pinene	0.5
2-cyclohexen-1-one, 3,4,4- trimethyl	7.1	1-ethyl-4-methyl benzene	0.3
Limonene	5.2	1,3,5-trimethyl benzene	0.3
Bicyclo[2.2.1]heptan-2-one, 1,3,3-methyl	5.0	Cyclotrisiloxane, hexamethyl-	0.2
Nonanoic acid, methyl ester	3.3	Ethylbenzene	0.2
Cyclopentasiloxane decamethyl	2.9	2 hexanone	0.1
Cyclopentasiloxane, decamethyl	2.9	Control run RAC	
1,2-dimethoxy- benzene	2.7	2-ethyl 1 hexanol	38.3
2-pentyl furan	2.1	1-octanol	17.4
1-octanol, 2-butyl	1.7	Toluene	10.9
Benzene, 1-methyl-4-(1-methylethyl)	1.6	Cyclotrisiloxane, hexamethyl	6.2
Toluene	1.6	Cyclotetrasiloxane, octamethyl	5.3
2-ethyl-1-hexanol (P.I. 53%)	1.4	1-hexanol	3.7
1,4-dichlorobenzene	1.4	Benzene, isothiocyanato	2.7
Cyclotetrasiloxane, octamethyl	1.3	Cyclotetrasiloxane, decamethyl	1.6
Styrene	1.2	3-dodecene	0.8
A-pinene	0.7	Ethylbenzene	0.3
Ethylbenzene	0.7		
p-xylene	0.6		
Seed RAC		^a RAC is the ratio of area counts of corresponding compound to sum of area counts of all compounds measured in the specific run.	
Cyclopentasiloxane, decamethyl	5.1	^b p-Isopropyltoluene.	
2-cyclohexene-1-one, 3,4,4 trimethyl	4.6	^c Several acids and esters of acids with purity index less than 60%.	
Camphor	3.7	^d Isopropylbenzene.	
Limonene	3.5		
Toluene	3.1		
Naphthalene	2.8		

extract. For example, a ratio value of 1.5 indicates that the area counts for that compound account for 1.5% of the sum of the area counts of all compounds (excluding the solvent) measured during the specific run. This ratio value is useful only for relative comparisons of the concentrations of the compounds found in the specific sample. Compounds shown in Table 6-1 are ranked from highest to lowest relative concentrations in each sample, on an area count basis. Since only compounds at a purity index of 70% or higher are listed, the sums of the RACs for each substrate are less than 100.

Based on the results shown in Table 6-1, alkanes were frequently identified compounds, especially in three runs containing mixed paper (MXP, MXP_{ns}, MXP/FW). Undecane and dodecane, in particular, were found at high relative concentrations. Decane and methylated undecanes were found in unseeded mixed paper only. Decomposition or volatilization of these compounds might explain their absence from the MXP/YW run, since the charcoal trap used for VOC identification for that run was placed at an advanced composting stage (after day 9). Octane was detected in unseeded food wastes and the mixture of mixed paper and food wastes, indicating that food wastes might be a potential source of this hydrocarbon. All of the aforementioned alkanes were also detected in mixed waste headspaces but not in biological waste headspaces by Wilkins (1994).

Several alkylated benzenes were also detected, primarily from the same three mixed paper runs (MXP, MXP_{ns}, MXP/FW). A higher number of alkylated benzenes were present in the MXP_{ns} run compared to the MXP run. This might be attributed to partial decomposition of such compounds in the MXP run compared to MXP_{ns} run. This relates to the respective amounts of decomposition of the basic substrates in these two runs, since 153.3 g CO₂ (as C/dry kg) were produced during the MXP run compared to only 5.5 g CO₂ (as C/dry kg) from MXP_{ns}.

Of the alkylated benzenes, toluene and *p*-isopropyl toluene (cumene or 1-methyl-4-1-methylethyl benzene) were found at some of the highest relative concentrations for almost all runs shown in Table 6-1, while ethylbenzene was present in relatively high concentrations from the MXP_{ns} and MXP runs only. Toluene and ethylbenzene, in particular, have also been found in the highest ambient air concentrations at MSW composting facilities (Eitzer, 1995) compared to other alkylated benzenes. Styrene was found to be present in both yard waste runs and the MXP/YW run and the seed, but not in other runs. Styrene might be associated therefore with yard waste components. 1,4-Dichlorobenzene was the only chlorinated compound detected in the emissions of all runs, except unseeded food wastes. Naphthalene was detected at some of the highest relative concentrations in MXP, MXP_{ns}, and MXP/FW. The origin of naphthalene is suspected to be the carbon black contained in newsprint (Reinhart, 1993). Benzene could not be identified with the GC/MS techniques used, due to coelution with the extraction solvent.

All of the alkylated and chlorinated benzenes shown in Table 6-1 were also identified by Eitzer (1995) and by Wilkins (1994), primarily in the headspace of mixed wastes, as well as by Tolvanen et al. (1998). It is interesting to note that several compounds that Eitzer (1995) did not identify, or identified in negligible amounts, were also not identified in this work. These compounds were several chlorinated aliphatic and chlorinated aromatics, such as methylene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, trichloroethene, chlorobenzene, chlorotoluene isomers, the 1,2- and 1,3-dichlorobenzene isomers, and all trichlorobenzene isomers. However, trichlorofluoromethane, perchloroethane, and 1,1,1-trichloroethane were

quantified in relatively high concentrations by Eitzer (1995), but not in this study. This indicates that the source of these chlorinated compounds may be hazardous and industrial wastes and not the MSW components used here.

Methoxy-benzenes were detected from the MXP/YW, MXP, and MXP_{ns} runs. These compounds might be associated with the removal of lignin during paper manufacturing, since the structure of these VOCs is similar to moieties found in the lignin polymer.

Based on Table 6-1, the dominant VOCs from the yard waste and food waste runs were terpenes, alcohols, acids, esters of acids, and ketones. Most of these compounds are generally considered of biogenic origin (Wilkins, 1994). From the terpenes particularly, α -pinene and limonene were identified in all runs. These compounds have been found widely in several degradation environments, such as MSW composting facilities (Eitzer, 1995), sludge composting facilities (Van Durme et al., 1992), and landfills (Young and Parker, 1983). Wilkins (1994) also identified several terpenes, including α -pinene, β -pinene, and limonene. Terpenes have usually been associated with decomposition of wood chips found in composting (Wilber and Murray, 1990; Miller, 1993), but as results show here, woody material is apparently not the only source of such compounds.

Dimethyl disulfides and dimethyl trisulfides were found primarily in food waste emissions but also in yard wastes. According to Miller (1993), dimethyl disulfide can be a result of both biological (decomposition of proteins) and non-biological reactions. Butanoic acid and esters of butanoic acid were detected in food wastes and are probably partially responsible for the “strong” odor of decomposed food wastes (Miller, 1993). 2-Ethyl-hexanol was one of the compounds found in the largest amounts from the MXP_{ns}, MXP, and MXP/FW runs. Interestingly, the dominant compound in the MXP/YW run (as Table 6-1 shows) was the 2-ethyl hexanoic acid, indicating that partial oxidation of the 2-ethyl hexanol might have occurred. This could be a result of the more active decomposition in the MXP/YW run, compared to the other three runs. This is further suggested by the fact that the MXP/YW charcoal tube used during GC/MS was collected during an advanced composting stage compared to the other runs. The oxidation of alcohols to their corresponding carboxylic acids is a probable aerobic pathway.

Ketones were also dominant in almost all runs, with camphor found at some of the largest concentrations. Ketones have been associated with the decomposition of wood chips in composting facilities (Miller, 1993). Ketones are generally intermediate oxidation products of alcohols to acids and would therefore be expected to be present in aerobic environments. The presence of pyrazine in unseeded food wastes and yard wastes can be expected due to the abundance of nitrogen in both substrates, at least compared to the smaller nitrogen content of mixed paper, from which this compound was not detected. The lack of volatile acids in the MXP_{ns} run can be explained by the lack of significant decomposition for that run. The heptanoic acid found in the seeded mixed paper can be, for example, an oxidation product of the heptanal found in the MXP_{ns} run, since much more decomposition occurred in the first run compared to the latter.

Siloxane compounds (cyclopentasiloxane, cyclotetrasiloxane, and cyclotrisiloxane) were found at large relative concentrations in all runs except unseeded yard wastes and unseeded food wastes. The origin of these compounds is not known. Several of the alcohols, ketones, alkanes,

alkylated benzenes, and sulfuric compounds found in this study were also detected by Wilkins (1994) and Tolvanen et al. (1998).

Seed might be partially responsible for some of the emissions of seeded components. The seed would be expected to emit various VOCs because it was collected from an MSW composting facility and would therefore be expected to contain some hazardous and industrial wastes. Several xenobiotic compounds were identified in the seed, with toluene, limonene, and naphthalene being at the highest levels. The number of compounds identified in the seed were fewer than the number of compounds identified in the MXP_{ns} run. As will be discussed later, seed is not totally responsible for the amounts of selected VOCs produced from seeded MSW mixtures.

The emission of various VOCs from unseeded mixed paper (MXP_{ns}), for which negligible CO₂ production was recorded, indicates that these compounds were somehow embedded on the individual mixed paper components (cardboard, office paper, newsprint) and released upon simple wetting, heating, and probably air stripping. The ink in office paper and newsprint could be partially responsible for these emissions. Most of the compounds found in the MXP_{ns} run emissions appear to be in a less oxidized stage (e.g., several hydrocarbons and alkylated benzenes) compared to compounds found in mixed paper mixtures in which decomposition occurred (e.g., alcohols, ketones, acids). This indicates that VOCs were partially biologically oxidized in the latter runs as a result of decomposition of the basic substrate.

To further investigate the above hypotheses, leaching tests were performed separately for newsprint, office paper, and cardboard using the same dry mass of each component, with 60 °C water being the extracting agent. Water, however, may not completely dissolve all compounds, especially the nonpolar compounds such as alkanes and alkylated benzenes. Each component was placed in a jar filled with 250 mL of water to minimize headspace and let stand for approximately 1 hour at 60 °C. Using a sample size of 20 mL, a purge and trap instrument (Tracor LSC-2, sample concentrator), and a GC/FID, several chromatographic peaks were observed in water extracts from newsprint and no peaks were recorded from extracts of cardboard and office paper. Although no further identification of these compounds took place, it is suggested that newsprint was at least partially responsible for the production of VOCs from mixed paper. A similar extraction using carbon disulfide as a non-polar solvent on newsprint revealed no chromatographic peaks.

The presence of toluene and *p/m*-isopropyltoluene from unseeded food wastes is interesting. In distillation experiments designed to identify compounds responsible for the flavor of certain food products, some xenobiotic compounds, such as aromatic hydrocarbons and halogenated aromatics, were identified (Coleman et al., 1981; Heydanek and McGorin, 1981).

Some of the aforementioned VOCs were identified in a control run (Table 6-1). However, the total number of VOCs emitted from the control run, as well as the amounts, was smaller than the number of VOCs identified in all other runs. The VOCs in the control run appear to be a result of imperfect cleaning of the digester and the tubing prior to reuse.

6.1.2 Mass Loadings of Selected VOCs During the Composting Process

Twenty-five VOCs were selected for quantification, including 13 VOCs identified in Table 6-1 that are commonly found at the largest ambient air concentrations at MSW composting facilities (Eitzer, 1995). Because *p*- and *m*-xylene coeluted in the GC, they will be treated together; so, in effect, 12 VOCs were found at quantifiable concentrations. Some of these compounds are categorized as priority pollutants under the Clean Water Act, while others are hazardous air compounds under the 1991 Clean Air Amendments (see Table 6-2). The goal of the quantification was to provide mass loading information for these VOCs for each substrate separately (expressed on a per dry kg basis of substrate), and to study the rate of production of these VOCs during the composting process. The production rate was followed by using three or more charcoal traps in sequence for each run and by measuring the mass of each VOC in each trap. It is noted that except for the targeted VOCs, no quantification of the other VOCs listed in Table 6-1 was done, primarily due to time and budget limitations and the lack of readily available standards. Quantification was done using a standard mixture of 25 VOCs, supplied in methanol by Supelco. Appropriate dilutions in CS₂ were made to achieve the concentrations used during calibration. Multiple injections of the samples gave a coefficient of variation of between 1% and 3% for all VOCs.

Table 6-2 presents the VOC quantification results. Twelve of the 25 VOCs present in the standard were not identified by GC/MS (Table 6-1) and were not detected at reportable concentrations by GC/FID. They are not shown in Table 6-2. The 12 nonreported VOCs were: benzene, chlorobenzene, *o*-xylene, bromobenzene, 2-chlorotoluene, 4-chlorotoluene, 1,3-dichlorobenzene, 1,2-dichlorobenzene, *tert*-butylbenzene, *sec*-butylbenzene, 1,2,4-trichlorobenzene, and 1,2,3-trichlorobenzene. The following results and discussion are based only on the 12 identified VOCs.

Table 6-2 presents the yields of the 12 targeted VOCs emitted from 12 runs (including the seed and the control run) over the course of the composting process expressed in : g per dry kg of component or mixture initially placed in the digester. The units for the control run are in micrograms. Yields of the 12 VOCs reported in Table 6-2 have been reduced by the amounts of the corresponding VOC produced from the control run and from the seed present in each run by simple subtraction.

Table 6-2 indicates that seed produced the highest total yield of the 12 VOCs on a per dry kg basis. Toluene, *p*-xylene, styrene, 1,4-dichlorobenzene, 1,3,5-trimethylbenzene, and naphthalene were the major compounds produced from the seed. As noted earlier, seed would be expected to emit VOCs because it is partially composted MSW. It is worth noting that Kim et al. (1995), as part of another study, performed leaching tests with CS₂ directly on screened compost that had been collected from the same location as the seed used here, and they did detect both toluene and ethylbenzene in the extract.

Table 6-2. Yields of 12 VOCs from 12 Runs (in : g/dry kg Substrate)^{a, b}

Compounds	FW _{ns}	FW ^{c, d}	MXP _{ns}	MXP ^c	YW _{ns}	YW ^c	MXP/YW ^c	MXP/FW ^c	FW/YW ^c	MSW _{1/3}	Seed	Control ^e
Toluene ^{d, f, g}	(-) ^h	1,164	151.3	1,150.2	8.5	903.0	955.1	221.0	(-) ^h	75.5	1,906.4	7.3
Ethylbenzene ^{f, g}	(-) ^h		254.3	236.8		(-) ^h	219.8	72.4	34.0		70.5	16.3
<i>p</i> / <i>m</i> -xylene ^g		23	56.6	282.3	16.6	326.1	218.9	162.8	137.9	55.0	504.4	
Styrene ^g					62.7	517.8	195.9		196.6	140.2	563.2	
Isopropylbenzene								73.4				
Propylbenzene			23.0					50.9				
1,3,5-Trimethylbenzene			31.4			(-) ^h	29.6	55.5		70.8	151.3	
1,2,4-Trimethylbenzene ⁱ			608.0				(-) ^h	149.6				
1,4-Dichlorobenzene ^f		42	79.1	175.2	7.7	315.0	191.6	116.3	45.5	35.0	519.8	
<i>p</i> -Isopropyltoluene	327.8	1549	4,179.7	3,272.3	736.4	59.9		169.6	155.9	401.6	1,803.9	
<i>n</i> -Butylbenzene								90.1				
Naphthalene ^f			1,127.8	943.5				492.8		321.6	2,680.5	
Sum of 12 VOCs	327.8	2,778	6,511.2	6,060.3	831.9	2,121.8	1,810.9	1,654.4	569.9	1,099.7	8,199.9	23.6

^a VOC yields expressed per dry kg of component (only) after excluding the amount of VOCs emitted from the seed present in seeded mixtures and after correcting for the two VOCs emitted from the control run.

^b No entry indicates that this VOC was not identified by GC/MS.

^c Seeded runs.

^d Seed contribution was not subtracted for this run due to the relatively high component/interaction effect shown in Equation (6-3).

^e Values for the control run are expressed in : g and not in : g/kg.

^f Priority pollutant (designated under the Clean Water Act).

^g Hazardous air pollutant (designated under the 1991 Clean Air Act Amendments).

^h (-) indicates that value became negative after subtracting the corresponding VOC yield from the control run and correcting for the additive contribution from the seed.

ⁱ 2-Pentyl furan was identified at the same retention time of 1,2,4-trimethylbenzene except for the MXP_{ns} and MXP/FW runs.

Relatively high emissions of the 12 VOCs were produced from all seeded runs (except the MXP_{ns}), indicating that the seed is partially responsible for these emissions. To better investigate the potential seed and component interactions, a statistical analysis was performed as discussed in the next section.

6.1.3 Interaction of Seed and Component in Seeded Runs

A 2² factorial design approach, as described in Chapter 4, was implemented to investigate the interactions between seed and each MSW component using the VOC yield as a response. This was done because seed was indicated to be partially responsible for the VOC emissions of seeded individual components, as discussed earlier. On the basis of 1 dry kg of unseeded MSW component (mixed paper or yard waste or food waste), Equations 6-1, 6-2, and 6-3 present the results of the 2² factorial analyses.

$$Y_{\text{VOCP}} = 3,568 + 3127 L_p + 313 L_s - 128 L_p L_s \quad (6-1)$$

$$Y_{\text{VOCY}} = 1,168 + 581 L_y + 778 L_s + 191 L_y L_s \quad (6-2)$$

$$Y_{\text{VOCF}} = 1,353 + 492 L_f + 1,189 L_s + 328 L_f L_s \quad (6-3)$$

where

$Y_{\text{VOCP}}, Y_{\text{VOCY}},$ Y_{VOCF}	=	sum of the yield of 12 VOCs (in μg) emitted from a seeded mixture of mixed paper, yard waste, and food wastes, respectively
L_p	=	absence (-1) or presence (+1) of mixed paper in a mixture
L_y	=	absence (-1) or presence (+1) of yard wastes in the mixture
L_f	=	absence (-1) or presence (+1) of food wastes in the mixture
L_s	=	absence (-1) or presence (+1) of seed in the mixture.

Because no replication was used, no standard errors can be provided for the model estimates; whether an estimate is statistically significant or not is based only on the absolute value of that coefficient in the corresponding equation. Equation 6-1 indicates that L_p is more important than L_s , and the interaction of L_p and L_s is the smaller. Therefore seed contributes less than 10% of the sum of the yields of the 12 VOCs emitted from mixed paper alone in the seeded mixed paper run. The high VOC yield of unseeded mixed paper resulted in the interaction of mixed paper with the seed to appear to be relatively small (and negative), as shown from the $L_p L_s$ coefficient in Equation 6-1. Based on Equation 6-2, yard waste alone and seed contribute approximately similar amounts of VOCs in the seeded yard waste run. Based on Equation 6-3, L_s is more important than L_f indicating that the presence of VOCs in the seeded food waste runs is primarily due to seed. An exception is *p*-isopropyltoluene, which was identified in unseeded food waste emissions. The interaction factor in Equation 6-3 indicates that additional VOCs are emitted in seeded food wastes compared to the sum of the amounts emitted by the seed or food wastes individually. This is likely because the high extent of degradation of food wastes compared to the other components probably induces the degradation of the seed itself, resulting in additional release of VOCs attached to the seed. It is also likely that the high moisture content of food wastes aids in the solubilization and easy release of sorbed VOCs from the seed. The same explanation can be used for the yard waste and seed interaction, though this interaction is smaller compared to food wastes.

Equations 6-1 and 6-2 indicate that, because of the relatively small seed and component interactions for mixed paper and yard wastes, respectively, an additive contribution of seed to each of these components in the corresponding seeded run can be assumed. This cannot be done for seeded food wastes, however, because it might overestimate the amount of VOCs produced from that component alone. This is because it is not clear if the additional amount produced from the interaction is due to the seed or to the food waste alone, although the former is likely.

Table 6-2 includes the yields of the 12 VOCs from all runs excluding seed; that is, the amount of seed present in a seeded run and the VOC yield per dry kg of seed are calculated from the run with seed only. This was not done for food waste, as discussed. In addition, Table 6-3 presents the additive contribution of seed to total emissions. Table 6-3 shows that seed can contribute VOCs over a range of 10% to 20% for most of the compounds. Values higher than 100% indicate that seed might be solely responsible for the emissions of that VOC from the component/mixture. The fact that some compounds identified in the seed were not identified in some seeded mixtures (e.g., styrene in seeded food wastes) indicates that the compound might have been decomposed.

According to Table 6-2, the MXP_{ns} run had the highest amounts of the 12 VOCs among all other substrates except the seed, with *p*-isopropyl toluene and ethylbenzene accounting for 64% and 3.9% of the sum of the 12 VOCs, respectively. MXP_{ns} produced 1,2,4-trimethyl benzene, which was not emitted from other mixed paper mixtures, indicating that it might have been decomposed in the other mixed paper runs. It is noted that 2-pentyl furan would be reported at the same retention time as 1,2,4-trimethyl benzene so coelution is also a possible explanation. MXP_{ns} had the highest ethylbenzene and naphthalene yields followed by MXP, MXP/YW, MXP/FW, and MSW_{1/3} in that order. Because the amount of decomposition (loss of dry weight or CO₂ produced) followed the same ranking order for these four runs, it is likely that these two compounds are decomposed as a result of basic substrate decomposition. The probable presence of ligninolytic fungi in yard wastes, as discussed previously, could have induced the “complete” degradation of naphthalene in the MXP/YW run. BTEX compounds and polycyclic aromatic hydrocarbons (PAHs) are known to be efficiently degraded by a common ligninolytic fungus (Paszczynski and Crawford, 1995).

Although seed contribution was subtracted assuming an additive contribution, different seed/component interactions might exist separately for each of the 12 VOCs than the interactions predicted by Equations 6-1, 6-2, and 6-3 based on the sum of the 12 VOCs. As Table 6-2 shows, toluene was emitted at some of the largest amounts from runs that were seeded (footnoted in Table 6-2). Because toluene was at high amounts from the seed alone and in relatively low amounts from the unseeded runs (e.g. FW_{ns}, YW_{ns}, MXP_{ns}), it is expected that seed was partially responsible for these toluene emissions.

Butylbenzene and isopropylbenzene were found in the MXP/FW run, but not in the MXP/YW run. Assuming that these compounds are due to mixed paper only (as shown by the MXP_{ns} run), it is likely that the microbial culture present in the MXP/FW mixture did not

Table 6-3. Additive Contribution of Seed to the Emissions of Each of the 12 VOCs Emitted from a Seeded Mixture^{a,b}

	MXP	YW	MXP/YW	MXP/FW	FW/YW
Toluene	11.3	11.6	19.4	43.8	43.6
Ethylbenzene	2.3		3.8	8.4	8.3
<i>p</i> -Xylene	12.1	9.1	21.6	22.4	12.6
Styrene		6.8	25.4		10.6
Isopropylbenzene				0.0	
Propylbenzene				0.0	
1,3,5-Trimethylbenzene			37.0	20.3	
1,2,4-Trimethylbenzene					
1,4-Dichlorobenzene	18.1	9.6	24.4	29.2	23.2
<i>p</i> -Isopropyltoluene	4.2	38.8	466.1	48.7	23.3
<i>n</i> -Butylbenzene				0.0	
Naphthalene	17.5			33.3	

^a FW was excluded from this analysis due to the high seed/food waste interaction effect, as shown in Equation 6-3.

^b Assuming that X is the mass of a VOC emitted from a seeded mixture and Y is the amount of VOC expected to have been produced from the specific mass of the seed used during seeding (as can be calculated from the “seed” run), contribution is defined as $100 \times (X-Y)/X$.

degrade these compounds, while decomposition occurred in the MXP/YW run. Another potential explanation is that the presence of isopropylbenzene, found only in the MXP/FW run, was a result of decomposition of other alkylated benzenes.

p-Isopropyltoluene was present in all runs and at some of the highest amounts (as shown in Table 6-2). There was difficulty in the separation of that compound for the MXP and MXP_{ns} runs, due to the presence of 2-ethyl-1-hexanol, which was in very high concentrations and eluted close to *p*-isopropyltoluene during chromatographic analysis.

Styrene was found only in runs that included yard wastes, as discussed earlier, but was also detected in large amounts from the seed.

Isopropylbenzene, *n*-propylbenzene, and butylbenzene were generally present in relatively small amounts in the runs shown in Table 6-2, which coincides with the reported low concentrations for these VOCs by Eitzer (1995) in MSW composting facilities.

6.1.4 Empirical Models for Estimating VOC Yields from MSW Mixtures

To better investigate the production of these 12 quantified VOCs from an MSW mixture comprising three organic components only (food wastes, mixed paper wastes, and yard wastes), the results in Table 6-3 were modeled. The model is empirical, based on the principles of mixture experimental design, as discussed in Chapter 4. The resulting equation expresses the

sum of the yields of the 12 VOCs per dry kg of MSW, as a function of the fractions of each of the three organic components in any MSW mixture. The VOC yields from the unseeded individual components and for the seeded mixtures, as shown in Table 6-2, were used. The equation for estimating the production of the 12 VOCs from MSW is Equation 6-4 and was fitted using the MINITAB v12.2 statistical package (Minitab Inc., PA, USA).

$$Y_{\text{VOC}} = 4,162 (\pm 1,701) F_P + 831 (\pm 1,890) F_Y + 458 (2,340) F_F - 7,558 (\pm 17,662) F_P F_Y - 6,006 (\pm 28,770) F_P F_F \quad (6-4)$$

where

Y_{VOC} = sum of 12 VOCs volatilized from an MSW mixture, expressed in : g VOCs/dry kg of MSW

F_P , F_Y and F_F = dry fractions of mixed paper, yard waste, and food waste, respectively, in the mixture, with each of the F_P , F_Y , and F_F values ranging from 0 to 1 and with $F_P + F_Y + F_F$ always equal to 1.

The adjusted R^2 for Equation 6-4 is 0.33. The relatively low R^2 and the high standard errors of the coefficient indicate that Equation 6-4 may not be a good predictor for VOC emissions from MSW mixtures because various VOCs that may each behave differently were summed together. The seed correction may also contribute to the low coefficient of determination (R^2) of Equation 6-4. Equation 6-4 can still illustrate, however, that mixed paper is the greatest source of these 12 VOCs in an MSW mixture, as compared to the other two organic components. Combinations of yard wastes or food wastes with mixed paper result in a significant decrease of the sum of these 12 VOCs. As discussed earlier, this is likely a result of the decomposition of these VOCs due to degradation of the basic substrate. Mixed paper reached its full extent of degradation faster when combined with either food wastes or yard wastes, compared to when composted individually, as discussed previously. This probably affects the decomposition of VOCs as well.

Separate equations were also individually fitted by least squares to the results for each VOC. Parameters for which their confidence intervals contained zero were not included in the models; therefore, the following equations are the best reduced models. Errors were distributed normally and had a zero mean. Values in parentheses are the standard errors for the corresponding model coefficients.

Toluene fit (adj. $R^2=0.913$)

$$Y_{\text{TOLUENE}} = 306.2 (\pm 79.2) F_P + 4,663.5 (\pm 812.5) F_P F_Y - 5,322 (\pm 1,305) F_P F_F$$

Ethylbenzene fit (adj. $R^2=0.837$)

$$Y_{\text{ETHYLBENZENE}} = 214.7 (\pm 34.9) F_P - 1,090 (\pm 535.4) F_P F_F$$

p/m xylene fit (adj. $R^2=0.564$)

$$Y_{\text{XYLENE}} = 151.6 (\pm 47.8) F_P$$

Styrene fit (adj. $R^2=0.948$)

$$Y_{\text{STYRENE}} = 67.2 (\pm 27.1) F_Y + 1,218.5 (\pm 187.8) F_P F_Y - 1,012 (\pm 349.2) F_P F_F + 786.3 (\pm 197.5) F_Y F_F$$

n-propylbenzene fit (adj. $R^2=0.758$)

$$Y_{\text{NPROPYLBENZENE}} = 35.9 (\pm 7.3) F_P - 165.8 (\pm 65.7) F_P F_Y$$

1,3,5-trimethylbenzene fit (adj. $R^2=0.971$)

$$Y_{135} = 14.8 (\pm 8.5) F_P + 160.2 (\pm 86.7) F_P F_Y + 1,405.6 (\pm 139.3) F_P F_F$$

1,2,4-trimethylbenzene fit (adj. $R^2=0.608$)

$$Y_{124} = 375.6 (\pm 104.7) F_P - 1,734 (\pm 937.8) F_P F_Y$$

1,4-dichlorobenzene fit (adj. $R^2=0.819$)

$$Y_{14} = 109.2 (\pm 27.7) F_P + 408.2 (\pm 248.4) F_P F_Y$$

p-isopropyltoluene fit (adj. $R^2=0.302$)

$$Y_{\text{P-ISOPROPYLTOLUENE}} = 1,643 (\pm 819.2) F_P$$

n-butylbenzene fit (adj. $R^2=0.227$)

$$Y_{\text{NBUTYLBENZENE}} = 31.7 (\pm 18.1) F_P$$

Napthalene fit (adj. $R^2=0.653$)

$$Y_{\text{NAPHTHALENE}} = 765.7 (\pm 200.4) F_P - 2,401 (\pm 1,794) F_P F_Y$$

where

$$\begin{aligned} Y_{\text{VOC}} &= \text{mass of VOC volatilized per unit dry mass of substrate (in mg/dry kg)} \\ F_P, F_Y \text{ and } F_F &= \text{dry fractions of mixed paper, yard waste, and food waste, respectively, in the mixture, with each of the } F_P, F_Y, \text{ and } F_F \text{ values ranging from 0 to 1 and with } F_P + F_Y + F_F \text{ always equal to 1.} \end{aligned}$$

The above models show that mixed paper is the major VOC source except for styrene, for which yard wastes appears to be its primary source. Interactions between mixed paper and either yard wastes or food wastes are important and, in most cases, reduce VOC emissions due to decomposition of the basic substrate. This indicates that degradation of VOCs takes place after combining mixed paper with a more degradable component.

In the case of toluene, the interaction of mixed paper and yard wastes increases toluene yields. This could be due to additional toluene produced by the seed present in the MXP/YW run. A decrease of toluene is, however, observed when mixed paper is combined with food wastes. Degradation of ethylbenzene, n-propylbenzene, and 1,2,4-trimethylbenzene is observed when mixed paper is combined with either food wastes or yard wastes. In the case of styrene, only the interaction of mixed paper and food wastes results in a decrease of styrene emissions; increased emissions are observed when yard wastes are present in the mixture.

Additional release of 1,3,5-trimethylbenzene and 1,4-dichlorobenzene is observed upon combining mixed paper with food wastes or yard wastes, indicating that decomposition might be the reason for the production of that compound.

Reduction of naphthalene is observed upon combining mixed paper with yard wastes, probably because of ligninolytic microorganisms present in yard wastes.

6.1.5 VOC Volatilization Rates

The volatilization rates for the 12 VOCs were developed for some of the runs shown in Table 6-2. These profiles are helpful in further investigating the origin and behavior of the 12 targeted VOCs during composting. Volatilization rates for the MXP, MXP_{ns}, and the seed runs are shown in Figures 6-1, 6-2, and 6-3. The rates for these runs are more or less typical of all runs.

For the MXP run (Figure 6-1), the incubator temperature was gradually increased from 30 to 55 °C during the first 25 days of the run, after which thermophilic temperatures were maintained. This was done to simulate the typical temperature increase observed in the center of MSW compost windrows during active composting (Diaz et al., 1993). This gradual temperature increase was used for the MXP run only. Thermophilic temperatures were kept continuously for all other runs to accelerate decomposition. As seen in Figure 6-1, a relatively low volatilization rate was observed during the increasing temperature period for most VOCs. VOC emission rates started to rapidly increase at temperatures higher than approximately 45°C and stabilized to a maximum value. This profile indicates that these compounds are somehow attached to the solid matrix and released upon heating. The VOC yield might be affected by temperature; that is, higher VOC yields might have been measured if temperatures higher than 55°C had been used. In any case, this profile indicates that a fixed amount of VOCs is originally present in the solid matrix and released.

As shown in Figure 6-1, toluene had a relatively high volatilization rate from the beginning of the composting process due to its being the most volatile of the compounds with a boiling point (b.p.) of 110.6 °C. Ethylbenzene, the second most volatile after toluene, had the second highest volatilization rates during the initial 25-day period. Naphthalene, being less volatile than both compounds with a b.p. of 217.9 °C, had close to zero volatilization rates during that initial period. Between days 30 and 40, naphthalene rapidly increased to rates similar to those of toluene.

Most VOCs rapidly volatilized during the first 20 days for unseeded mixed paper (Figure 6-2) because this run was performed directly at thermophilic temperatures throughout. VOC emissions reached a constant value after approximately 20 days, except for *p*-isopropyltoluene, naphthalene, and 1,2,4-trimethylbenzene. These three compounds stabilized after approximately 60 days.

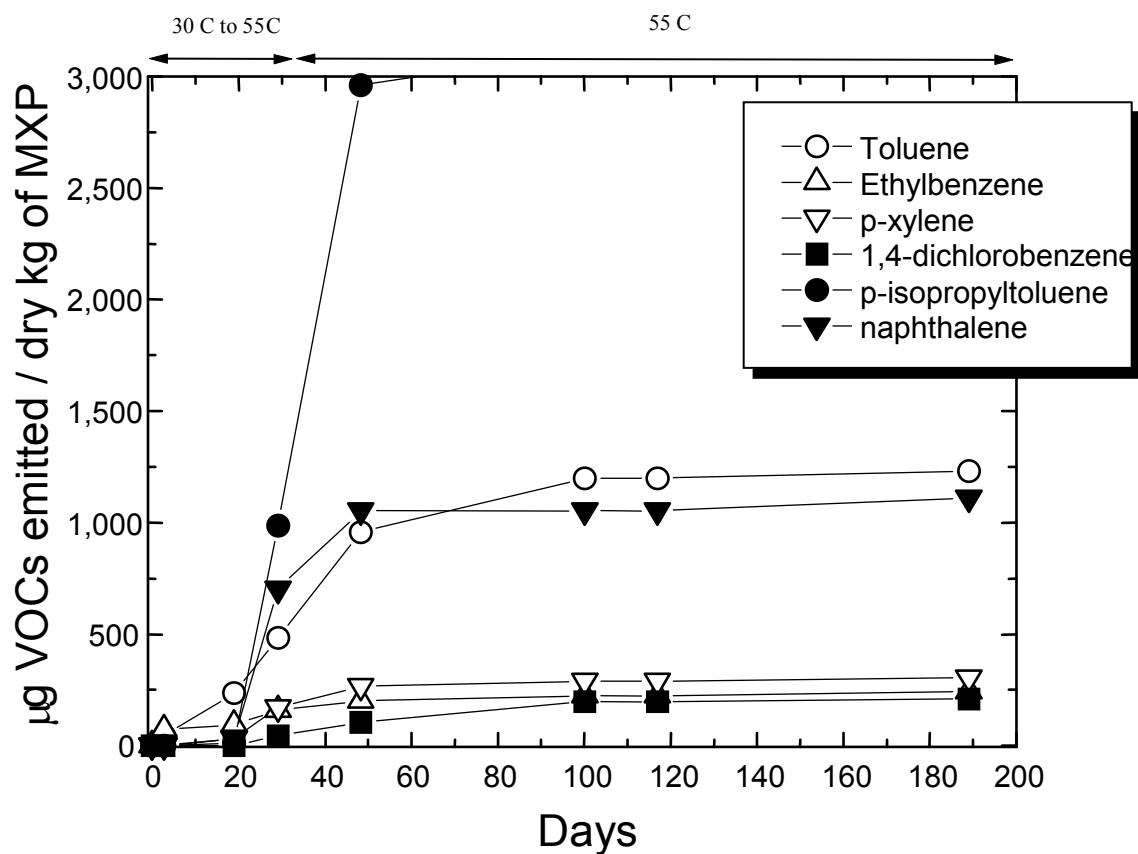


Figure 6-1. Cumulative production of six VOCs during composting of seeded mixed paper; yields have not been corrected for seed (the period between two data points corresponds to the time that one charcoal trap was in use continuously).

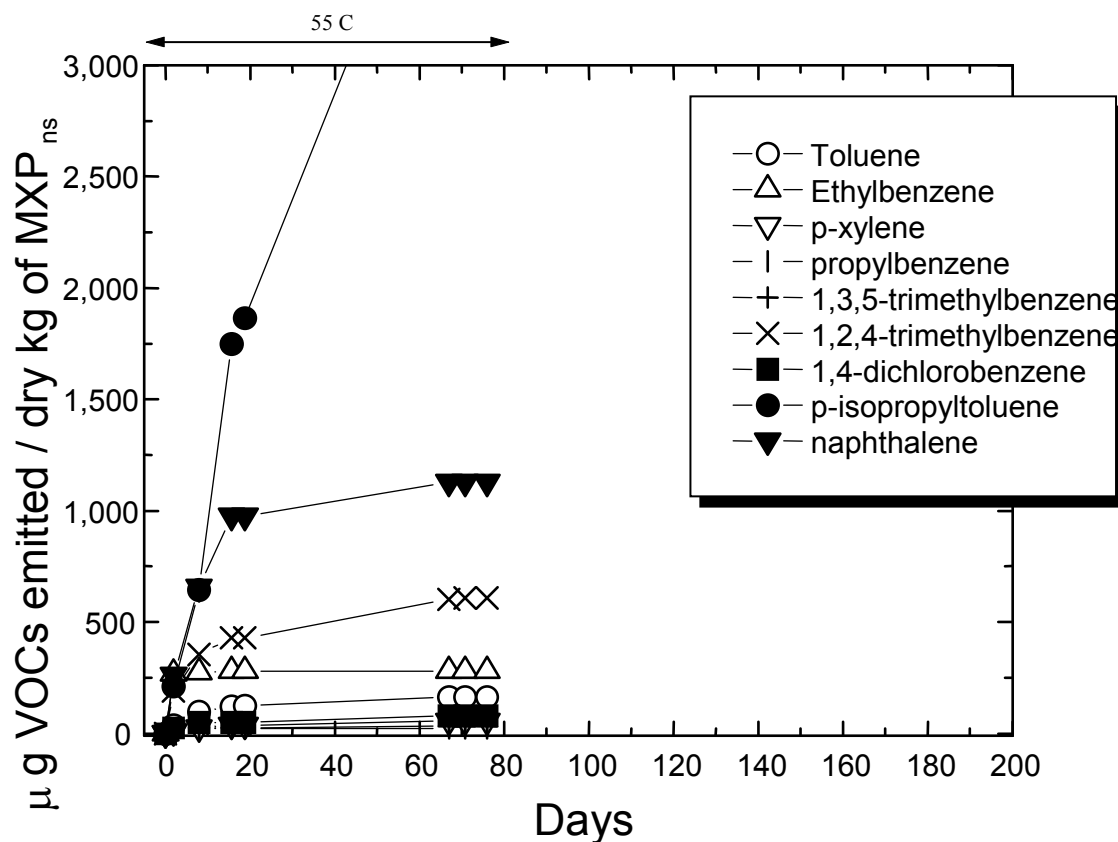


Figure 6-2. Cumulative production of nine VOCs during composting of unseeded mixed paper (the period between two data points corresponds to the time that one charcoal trap was in use continuously).

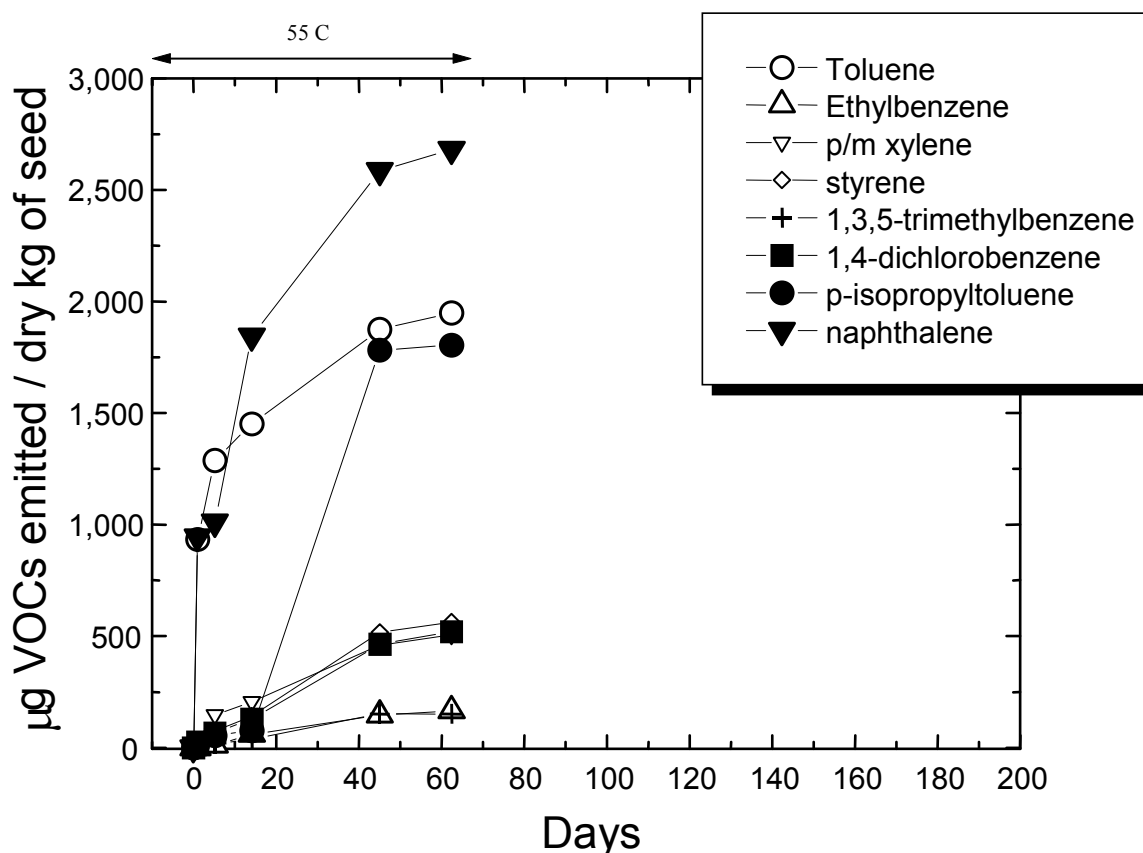


Figure 6-3. Cumulative production of eight VOCs during composting of seed (the period between two data points corresponds to the time that one charcoal trap was in use continuously).

In the case of seed (Figure 6-3), only *p*-isopropyltoluene appears to have a different volatilization profile compared to the other compounds. *p*-Isopropyltoluene appears to have a lower initial volatilization rate compared to the rate between days 15 and 40. Decomposition of this compound is rather unlikely during the initial time because it is water insoluble. It is likely that *p*-isopropyltoluene is more strongly attached to the solid phase than the other compounds, which explains its initial volatilization lag. The octanol-water partition coefficient $\log K_{ow}$ for *p*-isopropyltoluene is 3.66, while the $\log K_{ow}$ for naphthalene is 3.29, which indicates that *p*-isopropyltoluene will tend to sorb more onto the solid phase compared to naphthalene, despite the higher boiling point of the latter. As decomposition of the seed proceeds, however, the bound *p*-isopropyltoluene is released and volatilized.

6.2 Origin and Fate of VOCs

The results presented above do indicate that the 12 targeted VOCs are somehow bound to or embedded in the solids of all MSW components, but primarily mixed paper, and released upon heating and probably other mechanisms that affect their fate (i.e., sorption, water solubility). Decomposition of the basic substrate can reduce the yields of VOCs as indirectly indicated in Equation 6-4. However, definite conclusions cannot be made since the initial amount of VOCs present in each substrate is not known.

Some of the VOCs emitted from mixed paper—especially those frequently referred to as xenobiotic—might be produced due to the ink present in office paper and newsprint, as discussed earlier, or due to paper processing (e.g., wood bleaching) during which dissolution and degradation of lignin occurs that could give rise to some aromatic chemicals. However, this hypothesis needs more careful investigation, since lignin consists of oxidized aromatic rings, such as phenolic and methoxy groups (Kirk, 1984). The production of alkanes and aromatics, which are VOCs in a reduced oxidation stage, from lignin moieties would require anaerobic environments and high pressures that are not expected to occur during composting. Only the presence of methoxy benzene can be explained by the previous mechanism. Another potential explanation of the presence of VOCs in mixed paper could be atmospheric deposition.

The apparent decomposition of xenobiotic VOCs within the MSW environment is most likely a result of cometabolic processes; that is, carbon and energy sources are abundant for the composting cultures owing to the presence of the basic substrate. These cometabolic processes occur due to the generation of the required catabolic enzymes, which are used during basic substrate degradation as well as VOC decomposition. For example, oxygenases, which are commonly found in lignin degradation environments (Kirk, 1984), have also been shown to catalyze the biodegradation of several alkylated benzenes and PAHs (Gibson and Subramanian, 1984).

Decomposition of the basic substrate is expected to produce various VOCs, usually referred to as biogenic, such as terpenes, acids, acid esters, alcohols, and ketones. However, based on the results of this study, the identified biogenic VOCs also appear to be produced during the initial stages of composting as well as from substrates with negligible degradation (MXP_{ns}). Therefore, it is likely that production of some biogenic VOCs (e.g., limonene, which was found in some of the largest amounts in unseeded mixed paper) is also a result of simple volatilization. Biogenic VOC—though byproducts—could be also subject to further degradation depending on contact with the compost matrix.

Generally all types of VOCs measured in this study decreased as composting progressed and no VOCs appeared to be produced after a certain period, following the trend shown in Figures 6.1, 6.2, and 6.3. Volatilization rates appeared to follow first-order kinetics based on the 12 quantified VOCs. This decreasing trend in VOC emissions during composting was also observed by Eitzer (1995) for several VOCs, but not ketones, for which an opposite trend was observed. Eitzer (1995) did observe that all types of VOCs measured were emitted during shredding, where no extensive biodegradation usually takes place.

Equation 6-4 was developed based solely on the three organic MSW components (and the seed) used in this study. Other MSW components, such as inorganics or plastics, were not used and therefore their contribution to VOC emissions is not known. In addition, no hazardous or industrial wastes were used in the study, which would be expected to contribute to VOC emissions. Equation 6-4 predictions (given on a per unit dry kg basis of the sum of food wastes, yard wastes, and mixed paper) have to be multiplied by the percentage of the combined three components in typical MSW in order to express results on a per unit dry mass of “real” MSW.

The results given here are important because they indicate that hazardous and industrial wastes might not be the sole source of xenobiotic VOCs in MSW. Comparisons between studies of VOCs from solid wastes is important; however, attention should be given to the conditions under which VOCs are measured, the types of VOCs quantified, and the analytical techniques (such as VOC traps) used during measurement.

6.3 Spiking of VOCs to MSW Organic Substrates

To further investigate the effect of basic substrate decomposition on the fate of VOCs in MSW composting, separate runs were performed based on spiking known amounts of specific VOCs onto MSW components of different degradability.

6.3.1 Ethylbenzene Spike

The objective of this work was to investigate whether the decomposition of the basic substrate influences the decomposition and the fate of VOCs in a composting environment. This information would be important for predicting the fates of VOCs in MSW of various compositions, thus aiding in the development of standards concerning the disposal of household hazardous wastes in the MSW stream from different localities or countries.

Ethylbenzene was spiked separately to seeded newsprint and seeded yard waste at the same approximate initial concentration levels. Ethylbenzene was selected because it is the alkylated benzene found at the highest ambient air concentrations at MSW composting facilities (Eitzer, 1995) and can be used as a model for alkylated benzenes. These two runs were performed independent of the 12 runs described earlier in this chapter. Newsprint and yard wastes were selected due to their different degradation behaviors during composting, which might affect the fate and decomposition of the spiked VOC. Newsprint was chosen as one of the substrates instead of mixed paper to provide a relatively uniform substrate, allowing easier sampling of solids compared to mixed paper. Newsprint was seeded at the same proportions as the runs presented previously. Ethylbenzene was not spiked to food wastes because of solids sampling difficulties. Both runs were performed at mesophilic temperatures ranging from 30 to 35 °C. Mesophilic temperatures were selected to reduce extensive direct volatilization of the compound and, therefore, to allow better investigation of the potential degradation and metabolite production from this compound.

A total dry mass of 0.47 kg newsprint and 0.51 kg of yard wastes were used in the experiments. Ethylbenzene was spiked at concentrations of 9,100 ppm and 10,000 ppm (mg VOC/dry kg) onto the newsprint and yard wastes, respectively, by adding the VOC directly in liquid form through the exit port at the top of each digester. These values correspond to

approximately 3,600 ppm and 3,500 ppm (mg VOC/ wet kg), which are approximately 11 times the amounts of hazardous chemicals present in MSW, based on EPA estimations (Brown et al., 1997). The relatively high concentrations used in this run were selected to allow better identification of potential metabolites produced during the process.

Air was supplied intermittently during the first 5 days of the experiment to minimize volatilization of ethylbenzene and to induce acclimation of the biomass present in the solid wastes to the added VOC. Because of this inadequate aeration, however, relatively low CO₂ production was observed during the first 5 days from both substrates. Continuous air flow was applied beyond day 5 and a rapid increase in CO₂ production rates was observed as a result of these increased oxygen levels in the digesters. Air flow rates ranged from 200 to 400 mL/min, corresponding to approximately 400 to 800 mL/dry kg/min.

As shown in Figure 6-4, high ethylbenzene volatilization rates were observed immediately after spiking the VOC onto newsprint during the intermittent aeration period. Volatilization rates from yard wastes were lower than from newsprint, indicating that sorption or degradation of the ethylbenzene occurred rapidly after spiking. The potential rapid partitioning of ethylbenzene onto the solid matrix could be a result of the hydrophobic nature of ethylbenzene as well as the presence of hydrophobic groups (e.g., fats/lipids) in yard wastes. The fats and lipids in yard wastes, at a content of 2.5% dw, could therefore retain the hydrophobic VOC to a greater extent than newsprint, which has a fat/lipid content of 0.5% dw. Such hydrophobic binding has been suggested for humic substances, the hydrophobic surfaces of which can sorb nonpolar organic compounds (Sparks, 1995). It is also likely that ethylbenzene was more easily solubilized in the moisture present in yard wastes compared to newsprint if the initial moisture adjustment for newsprint provides less moisture compared to yard wastes. Note, however, that initial moisture contents were similar. Such initial dissolution would aid subsequent degradation of the compound.

The initiation of continuous aeration after the first 5 days of the experiment increased the mineralization rates for both substrates, as indicated by the rapid increase of the CO₂ production rate after 5 days (Figure 6-4). However, continuous aeration rates also induced temporary stripping of ethylbenzene from both substrates, as shown by the rapid increase of the volatilization rate of ethylbenzene after the fifth day. Volatilization rates did decrease thereafter, indicating that combined degradation and sorption mechanisms determined the fate of the remaining VOCs.

When ethylbenzene volatilization rates became approximately zero, VOC emissions sampling was stopped. Approximately 10 g of the wet mass of the solid material from each run was randomly collected and placed in 125 mL jars. One hundred milliliters of carbon disulfide was added to each jar and, after letting stand for 30 minutes, the extract was analyzed using direct injection to GC/FID. No ethylbenzene was measured during these tests. Such leaching tests, however, are not capable of measuring VOCs that may have been irreversibly sorbed onto the solid wastes as a result of potential biological humification processes or irreversible abiotic binding. Binding of chlorinated compounds onto humic acids during dehalogenation processes, based on biologically mediated radical formation, has been reported by Dec and Bollag (1994). Radical formation during degradation of alkylated benzenes by ligninolytic fungi (Barr and Aust, 1994) is possible since BTEX compounds have been shown to be degraded by a ligninolytic

fungus (Yadav and Reddy, 1993). Ligninolytic fungi are present in MSW composting (de Bertoldi et al., 1983), although primarily at later stages of composting. Biologically mediated radical formation of ethylbenzene could therefore result in covalent bonding with humic material. Further research is needed in this area as it applies to MSW composting environments.

From the initially spiked mass of ethylbenzene, 30.5% and 12% was volatilized from the newsprint and yard waste runs, respectively. Based on the MXP run discussed earlier, the ethylbenzene yield expected from newsprint without any spiking (baseline) should be approximately 200 to 300 : g/dry kg (Table 6-2), which is several orders of magnitude less than the approximately 3,000 mg/dry kg volatilized from the newsprint run after the spike. Since no ethylbenzene was detected in the final product, the nonvolatilized ethylbenzene must have been degraded to either intermediate byproducts or CO₂. Irreversible adsorption is also likely. Therefore, 88% and 69.5% of the initially spiked ethylbenzene was apparently decomposed in yard wastes and newsprint, respectively. Because the two substrates produced 121 g CO₂ (as C)/dry kg and 93 g CO₂ (as C)/dry kg, respectively, it appears that the degradation of ethylbenzene was influenced by decomposition of the basic substrate. However, a better comparison can be made by accounting for the yield of CO₂ exerted until the time the VOCs were completely volatilized, which was about 15 days from the initiation of the composting process. During these initial 15 days, 45.4 g CO₂ (as C)/dry kg and 35.8 g CO₂ (as C)/dry kg were produced from yard wastes and newsprint, respectively. This also suggests that more decomposition of the basic substrate (yard waste) is partially responsible for the corresponding increase in decomposition of ethylbenzene.

Therefore, yard wastes have either a higher concentration of microbial population, compared to newsprint, capable of degrading ethylbenzene or the microbial population in yard wastes is capable of degrading ethylbenzene to a greater extent than the population in newsprint. A cometabolic process is likely for such decomposition, as discussed earlier.

According to Gibson (1996), ethylbenzene can be oxidized to styrene by the presence of naphthalene dioxygenase; however, no styrene was detected in this study. This pathway may not be dominant during aerobic decomposition of ethylbenzene. Less volatile metabolites, such as 2,3-dihydroxyethylbenzene, are usually the preferred decomposition metabolites (Gibson, 1996).

The exact metabolic pathway cannot be concluded from this study. The use of radiolabeled compounds could have aided in the determination of the fraction mineralized and of the fraction attached to the solids; however, a radiolabeled compound could not be used, primarily because of concerns for safety and potential laboratory contamination from the highly volatile compounds studied.

6.3.2 Spike with a Mixture of Alkylated Benzenes

A separate run (TEX run) was performed to further assess the behavior of VOCs during MSW composting. The goal of this run was to assess the behavior of different alkylated benzenes when each is spiked at the same initial concentration levels during different stages of MSW composting. The selected VOCs were toluene, ethylbenzene, *m*-xylene, and *o*-xylene (referred to as TEX), which are commonly found in MSW composting facilities (Eitzer, 1995).

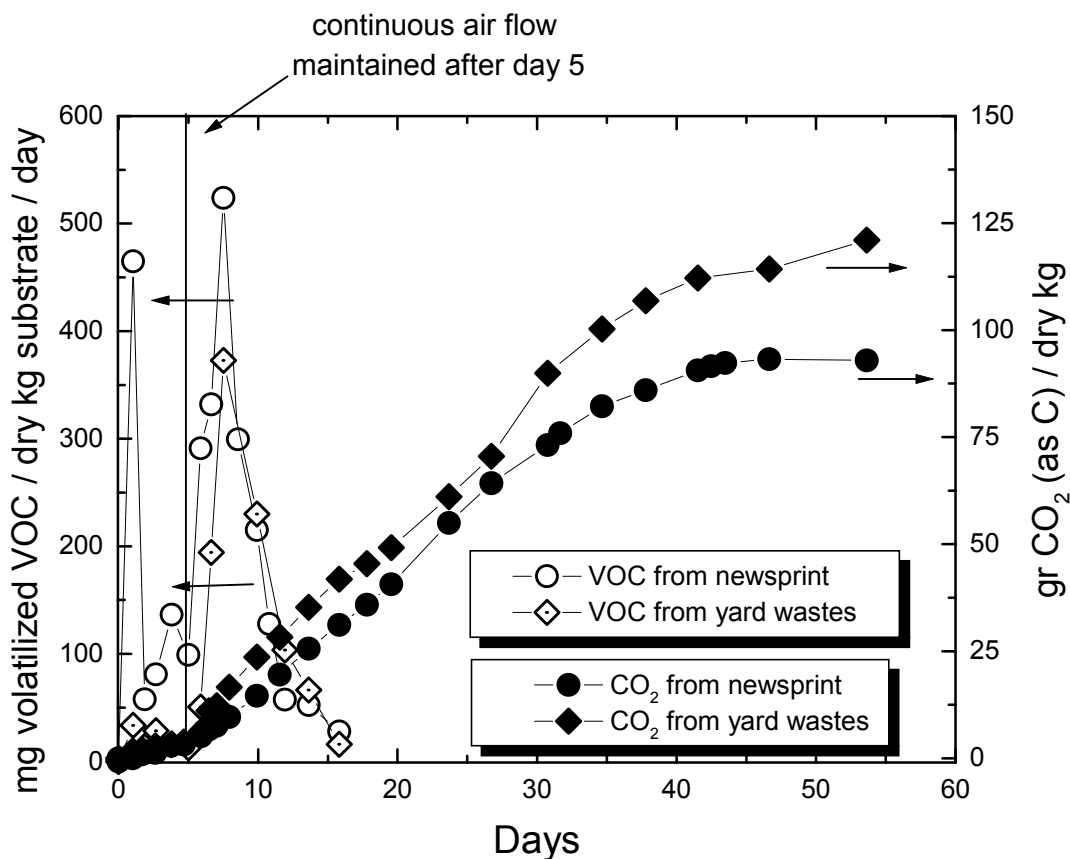


Figure 6-4. Volatilization rates of ethylbenzene and CO₂ cumulative production from newsprint and yard wastes during composting. (Ethylbenzene was spiked at initial concentrations of 9,100 and 10,000 mg per dry kg of newsprint and yard wastes, respectively.)

Certain key properties of these VOCs that are expected to affect their fate during composting are given in Table 6-4. These properties are boiling point, vapor pressure, solubility, octanol-water partition coefficient, and biodegradation half-lives based on aqueous (and soil) aerobic environments. VOCs were spiked to the mixture in the vapor phase, as discussed earlier.

As shown in Figure 6-4, decomposition of ethylbenzene in both substrates might have been limited during the first 5 days due to delayed aeration. The rapid increase in ethylbenzene volatilization after 5 days indicates that there is still a residual amount of VOC attached to the solid matrix of both substrates. Because this initial release was higher for newsprint than yard wastes, it is likely that the decomposition rate was higher in yard wastes compared to newsprint during the first 5 days.

Generally, decomposition of ethylbenzene in both substrates took place within the first 15 days after initiation of the experiments. No acclimation of the microbial population present in either substrate had taken place, which would probably have reduced decomposition times.

The temperature during the TEX run was kept at thermophilic levels to better simulate actual conditions, since such temperatures commonly occur during composting (Diaz et al., 1993). Since the goal was not to compare the effect of different substrates on the fate of VOCs, the basic substrate was set to be a mixture of mixed paper, yard wastes, and food wastes in proportions based on a typical U.S. MSW composition. Therefore, the organic fraction of MSW was simulated using 80% mixed paper, 15.4% yard waste, and 4.2% food wastes (all on a dry content basis), as used previously.

Since both microbial populations and organic matter change during composting (de Bertoldi et al., 1983), several spikes were performed to investigate potential effects of the different composting phases on VOC fate.

Table 6-4. Physicochemical Properties of VOCs Used in TEX Run
(La Crega et al., 1994; Howard et al., 1991)

Compound	Boiling point (°C)	Solubility (mg/L) ^a	Vapor pressure (mm Hg) ^a	Log K _{ow} (dim/less)	Biodegradation half-lives ^b
Toluene	110.8	515	22	2.73	96 / 528
Ethylbenzene	136.2	152	7	3.15	72 / 240
<i>m</i> -xylene	139.0	175	10	2.95	168 / 672
<i>o</i> -xylene	144.4	130	10	3.26	168 / 672

^a At 20 °C.

^b Low and high biodegradation half-lives (hours), respectively, in aerobic aqueous (and soil) environments (unacclimated), from Howard et al. (1991).

Five spikes of the mixture of these four VOCs were performed on days 0, 7, 23, 28, and 35 from the initiation of the run. Each VOC was spiked at a concentration of approximately 65 mg/dry kg of substrate, so that a total VOC concentration of approximately 265 mg/dry kg or approximately 150 mg/wet kg was achieved. This value is near the lower level of the VOC concentration range found in MSW (200 mg/kg to 1,500 mg/kg), as found in a study in King County, WA (Kissel et al., 1992). Because dry matter reduction occurred during composting, the masses of VOCs added during the fourth and fifth spike were approximately half of the masses used during the first three spikes. This was done in an attempt to maintain the spiking concentration at approximately 265 mg/dry kg of substrate at the time the spike was performed. The dry matter reduction during the process was calculated indirectly by measurement of the carbon dioxide yields. A continuous aeration regime was used during the first four spikes, and intermittent aeration was used during the fifth spike to minimize volatilization and to study the effect of such a change.

The cumulative volatilization profiles of all four VOCs during all four spikes are shown in Figure 6-5, and Table 6-5 summarizes the fractions (in %) of each of the initial masses of spiked VOCs volatilized. Table 6-5 also shows the time required for volatilization of 99% of the totally volatilizable mass of each VOC during each spike.

Toluene was detected in the breakthrough section of some of the traps during the second and third spike, indicating that some was lost. Therefore, the actual toluene volatilization fractions would have been higher than the values shown in Table 6-5. The significant breakthrough for toluene is probably attributable to the fact that it has the highest vapor pressure and lowest boiling point among the compounds tested.

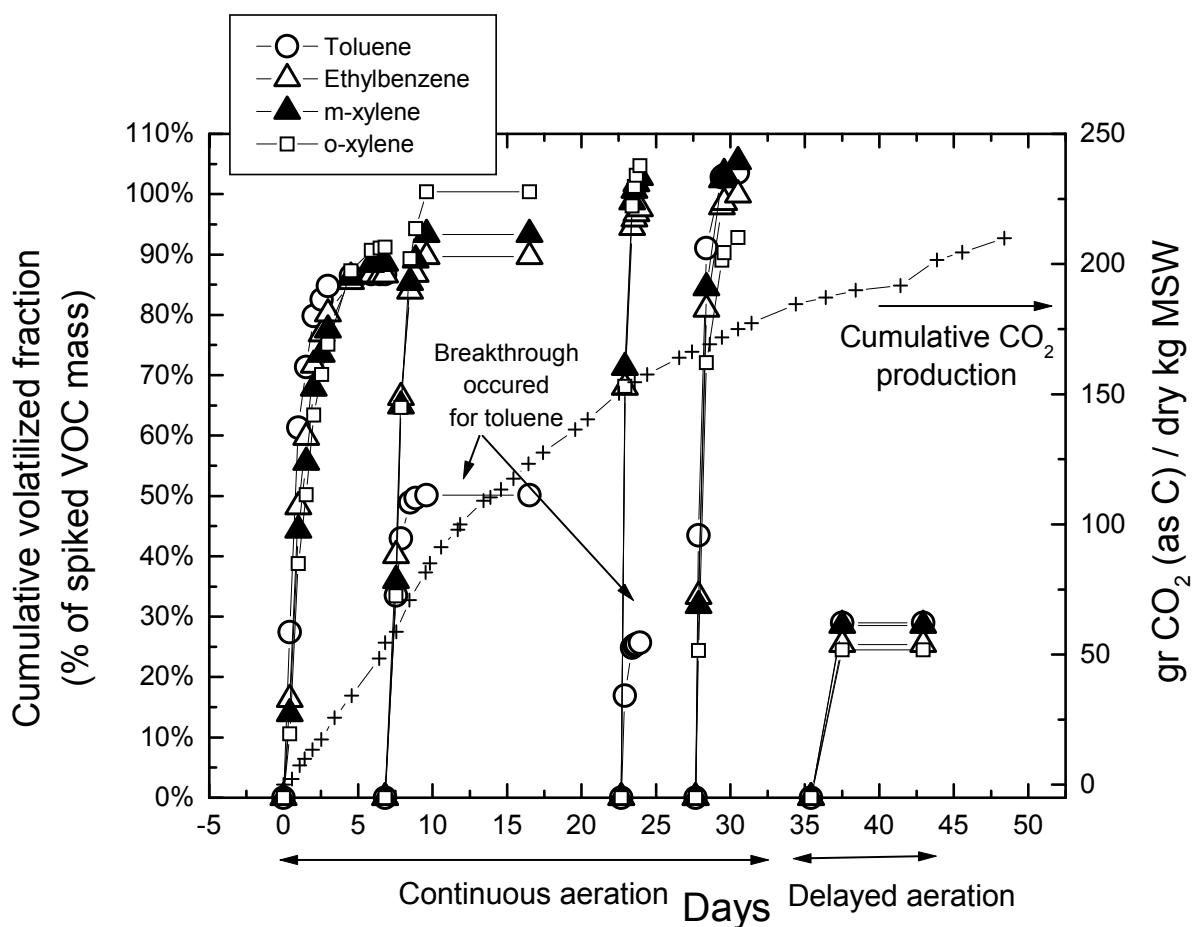


Figure 6-5. TEX cumulative volatilization profile and CO₂ cumulative production during composting of MSW.

Table 6-5. Volatilized Fraction (in %) of Initially Spiked VOC Mass During TEX Run and Length of Time (days) for Volatilization After Each Spike

	Toluene	Ethylbenzene	<i>m</i> -Xylene	<i>o</i> -Xylene
Spike 1	87% (3.5) ^a	87% (4.5)	89% (5.5)	91% (5.9)
Spike 2	50% ^b (-)	90% (2.6)	93% (2.7)	100% (2.75)
Spike 3	26% ^b (-)	98% (0.95)	103% (1.0)	105% (1.2)
Spike 4	104% (1.8)	100% (1.9)	105% (2.2)	93% (2.4)
Spike 5 ^c	29% (<2.1)	25% (<2.1)	29% (<2.1)	25% (<2.1)

^a Values in parentheses indicate days after each spike, that 99% of the VOC mass produced after that spike was volatilized.

^b Toluene breakthrough (loss) occurred and therefore a higher value would be expected.

^c Delayed aeration regime was used during this spike.

During the initial spike, lower volatilization percentages were observed for all VOCs compared to spikes 2, 3, and 4. The difference is attributed to degradation, because, during the first 5 days, the basic substrate was at its most active degradation stage (as shown by the relatively steep CO₂ cumulative curve during that time), which is primarily a result of decomposition of the readily degradable components (e.g., food wastes). Rapid sorption of the VOCs onto the substrate during the first spike, primarily onto food wastes and yard wastes that have a higher content of fats/lipids compared to paper, must have facilitated the retention of VOCs and their subsequent decomposition. All VOCs appear to be volatilized at similar levels of between 87% and 91% during the first spike. As Table 6-5 shows, the days required for volatilization of each VOC follow the same ranking order with the corresponding boiling points of these four VOCs, which is probably expected. It took from 3.5 to 5.9 days for these VOCs to volatilize during the first spike. Sorption might be partly responsible for the initial non-volatilized fraction, however, since all VOCs used are considered relatively decomposable, and decomposition is the likely dominant mechanism for their removal.

More than 90% of the VOCs, excluding toluene, volatilized during the second spike, and it took less time for the full volatilization of the four VOCs compared to the first spike. This is probably a result of dry matter reduction, which resulted in increased void space and a potential for increased channeling of the VOCs from the side of the digester, therefore reducing their contact with the solid matrix. It took approximately 2 to 3 days for all VOCs to volatilize during this spike and the same order of volatilization rates was observed as with spike 1. Assuming that the difference from 100% is decomposed VOCs, ethylbenzene appears to be the most degradable. Generally, ethylbenzene is one of the most degradable alkylated benzenes in various environments, as shown in Table 6-4 and as was reported by Yadav and Reddy (1993) for ligninolytic environments. *m*-Xylene and *o*-xylene had relatively similar apparent

decomposition extents during the second spike, which is in accordance with their similar degradation half-lives. It is noted, however, that *o*-xylene is generally considered the least degradable of BTEX compounds in several environments (Yadav and Reddy, 1993), which may explain its full volatilization during the second spike, despite it being the one with the highest boiling point and the highest log K_{ow} .

Higher volatilization percentages (approximately 100%) and even smaller volatilization times were observed during the third spike compared to the second and first spikes for all VOCs. The additional dry matter reduction was probably responsible for this, as discussed. Because the same mass of VOCs was spiked during the second and third spike compared to the first and additional dry matter reduction occurred, an increasingly higher mass of VOCs was spiked per unit dry mass of substrate in the digester as composting progressed.

In the fourth spike, the mass of VOCs added was reduced and corresponded to a total concentration of 149 mg (sum of VOCs) per dry kg of initial substrate. It is worth noting that the three most volatile VOCs (toluene, ethylbenzene, and *m*-xylene) totally volatilized, with only *o*-xylene having a lower volatilization fraction of 93%. Decomposition and sorption are both likely operable mechanisms reducing the release of this compound. *o*-Xylene is the least volatile and has the highest log k_{ow} among all VOCs, indicating a stronger retention in the solid phase. During the fourth spike, composting is already advanced and the corresponding generation of humic materials might be responsible for sorption of *o*-xylene. Decomposition is also likely, however, since acclimation of the biomass must have taken place as a result of the previous three spikes. The high volatility of the other three VOCs resulted in their total release.

During the fifth spike, intermittent aeration (5 minutes every 1 hour) was maintained to minimize the excessive volatilization that occurred during the previous spikes. This resulted in a decrease of more than 60% in the volatilization extents of all VOCs compared to the previous spikes. All VOCs volatilized within 2.1 days during the fifth spike. The potential for decomposition and sorption of the VOCs was increased during that spike due to delayed aeration. Ethylbenzene and *o*-xylene had the lowest volatilizable fractions at 25% among the four VOCs. A higher sorption is likely for both, compared to the other two compounds, due to their having relatively high log K_{ow} partition coefficients. However, a high sorption coefficient would retard degradation because the compound is probably retained in hydrophobic organic surfaces of the substrate. If partitioning between the solid and water phases takes place during composting, the initial sorption of compounds may result in relatively more subsequent degradation after all. Decomposition is more likely for ethylbenzene because it is generally the most degradable of these VOCs, and the previous experiment showed that no residual ethylbenzene remains on the solid. Generally the delayed aeration and the potential acclimation of the biomass by the fifth spike made decomposition the likely mechanism for the lower amounts volatilized. Ethylbenzene and *o*-xylene appear to be the most degradable of the four VOCs.

No absolute conclusions can be made regarding the decomposition of the four VOCs during this run since no solids analyses were performed. Heterogeneity of the material and the multiple spikes might have confounded such analyses. Based on the fifth spike, and assuming no VOCs were finally retained on the solids, it appears that 71% of toluene and *m*-xylene and 75% of ethylbenzene and *o*-xylene were decomposed when aeration was kept low so that no excessive

release of the compounds in the volatile phase occurred. Kim et al. (1995) reported that 6.2% and 0.2% of ethylbenzene and toluene, respectively, remain on solids during composting of MSW.

The close to 100% volatilization percentages recorded during the first four spikes of the TEX experiment (continuous aeration) are comparable to the findings by Brown et al. (1997). They determined that 100% of selected VOCs were volatilized in times similar to those reported here. Differences in the spiking techniques should be accounted for between the studies, since a vapor phase addition of the VOCs was used in the TEX run. Kim et al. (1995) concluded that 0% and 12.4% of ethylbenzene and toluene volatilizes during composting of MSW in a continuous aeration in-vessel plant, which partially contradicts the findings of this study. The different conclusions of Kim et al. (1995) might be attributed to the higher retention time of VOCs in the actual composting vessel compared to smaller retention times used in this study and by Brown et al. (1997).

7.0 Conclusions

This report presents a laboratory method to measure CO₂, NH₃, and VOC emissions and to characterize solids decomposition during composting of MSW. Different runs with different MSW components and mixtures of components were performed, and the reproducibility of the materials and methods was validated. The MSW components used (mixed paper, yard waste, and food waste) normally are the largest decomposable fractions of MSW. The close to 100% carbon mass balance closures and the low biases of the CO₂ and NH₃ measurements verify the usefulness of the methods and analytical techniques for these two gases.

The results of this study suggest the following conclusions.

Chapter 3

1. The laboratory method is reproducible in measuring yields of CO₂ and NH₃ and solids decomposition during composting.

Chapter 4

2. Seeding of yard wastes or food wastes did not significantly affect their decomposition. Seed is necessary for the decomposition of mixed paper.
3. The results using the mixture experimental design showed that CO₂ yields (in g C/dry kg) can be estimated by the additive model: $Y_{\text{kg_CO}_2} = 217.4 \times F_p + 237.3 \times F_Y + 370.5 \times F_F$, where F_p , F_Y and F_F are the dry fractions of mixed paper, yard waste, and food waste, respectively. The model indicates that all interactions were insignificant.
4. NH₃ yields (in g N/dry kg) from mixtures of MSW components can be estimated by the nonadditive model: $Y_{\text{kg_NH}_3} = 1.29 \times F_p + 5.15 \times F_Y + 37.6 \times F_F - 68.9 \times F_p \times F_F$, with parameters as defined in number 3, above. Inclusion of mixed paper in MSW mixtures resulted in a decrease of ammonia emissions because nitrogen is limited in mixed paper.
5. The interactions of mixed paper with either yard wastes or food wastes were significant in terms of rates of CO₂ production. Mixing mixed paper with either yard wastes or food wastes significantly reduced the composting time of the mixture compared to composting mixed paper alone.
6. The response surfaces shown in Figures 4-5 and 4-6 are based on the equations in conclusions 3 and 4 above, and can be used for rapid estimation of CO₂ and NH₃ yields from MSW of various compositions.

Chapter 5

7. Initial lignin and HWSM contents (dry weight basis) were important in determining CO₂ yields from different MSW substrates.
8. Lignin was less inhibitory to substrate decomposition in an aerobic environment than in an anaerobic environment. This is due to the physical association of lignin with cellulose (sheathing) and because lignin is relatively degradable in aerobic environments but refractory in anaerobic environments.
9. Cellulose and hemicellulose were responsible for more than 50% of the total dry mass loss for most of the substrates tested. Lignin/humus losses were responsible for up to 22% of the total dry mass loss of MSW substrates.
10. Hemicellulose was almost totally degraded in all substrates. Cellulose reduction ranged from 53.9% to 91.1% for all substrates that had approached “complete” degradation.
11. Lignin/humus reductions were 61.6% in food wastes, 43% in yard wastes, and approximately 26.7% in mixtures of yard and mixed paper wastes. A net increase of lignin/humus dry mass was observed in the mixed paper and the seed at the end of composting. A lignin/humus content of 50% or more of the volatile solids content was an indicator of maturity for most substrates.
12. Cellulose-to-lignin and C/N ratios decreased during composting. Cellulose-to-lignin ratios less than 0.50 indicated maturity for most of the MSW substrates.

Chapter 6

13. Various VOCs were identified in the gaseous emissions of mixed paper, yard waste, and food waste during composting. These waste components specifically excluded external sources of hazardous or industrial wastes.
14. Undecomposed mixed paper was a source of various VOCs, primarily alkanes and alkylated benzenes. From the latter group, *p*-isopropyltoluene, naphthalene, toluene, ethylbenzene, and 1,3,5-trimethyl benzene were found at the highest concentrations among the 12 quantified VOCs. Limonene and 2-ethyl-1 hexanol were also found at some of the highest relative concentrations in mixed paper. These VOCs are apparently in the solid matrix and are released upon wetting and heating.
15. Except for 1,4-dichlorobenzene, no chlorinated VOCs were found in the gaseous emissions from mixed paper, yard waste, or food waste.
16. The composting of seeded mixed paper and unseeded mixed paper produced approximately 6.1 and 6.5 mg of the targeted 12 VOCs, respectively, per dry kg of material.

17. Most of the identified VOCs in the emissions of food wastes and yard wastes during composting are biogenic, including organic sulfur compounds, terpenes, fatty acids, alkanes, ketones, and alcohols. Dimethyl disulfide and dimethyl trisulfide were dominant in food wastes emissions, while limonene was present in relatively large amounts from both substrates. Styrene was produced from unseeded yard wastes and the seed only.
18. The seed, as collected from an actual MSW composting facility, emitted 8.2 mg/dry kg of combined toluene, ethylbenzene, *p/m*-xylene, styrene, 1,3,5-trimethylbenzene, 1,4-dichlorobenzene, *p*-isopropyltoluene, and naphthalene.
19. All measured VOCs were emitted early in the composting process and followed a first-order-like decreasing trend as composting progressed.
20. Based on Equation 6-4, mixing of mixed paper with either yard wastes or food wastes resulted in reductions of VOC yields due to decomposition of the VOCs with the basic substrate. VOCs with more oxidized functional groups were found in the emissions of mixtures of mixed paper and other substrates, compared to the emissions of undecomposed mixed paper, indicating that VOCs were oxidized during the process.
21. Of the ethylbenzene, 88% and 69.5% was decomposed during composting when spiked to yard wastes and newsprint, respectively, at concentrations of approximately 10,000 mg/dry kg and at mesophilic temperatures. Ethylbenzene decomposition was apparently influenced by decomposition of the basic substrate, since yard wastes produced more CO₂ than mixed paper.
22. Approximately 90% of four alkylated benzenes spiked to MSW at total levels of 265 mg/dry kg were volatilized under continuous aeration regimes and at thermophilic temperatures at the beginning of the composting process, with the rest being decomposed or sorbed. The use of delayed aeration resulted in apparent decomposition of approximately 75% of the four VOCs, with ethylbenzene and *o*-xylene being the most degradable.
23. Significant decomposition and sorption of VOCs occurs during composting; most VOCs to be emitted are volatilized and stripped early in the composting process as a function of temperature and aeration rate.

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Appendix A

Audit Report

Audit Report
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Technical Services Branch

Quality Assurance	
Tracking Number	94017/III
Audit Type	Technical Systems and Performance Audit
Audit Dates	June 2-3, 1997
Project	Life Cycle Inventory of Municipal Solid Waste Composting
Project Officer	Susan Thorneloe
	Atmospheric Protection Branch (MD-63)
Auditors	Richard C. Shores, U.S. EPA
	Technical Services Branch (MD-49)
Audit Site	University of Wisconsin-Madison, WI
Site Contacts	Robert K. Ham, professor, University of Wisconsin-Madison.
	Dimitris P. Komilis, research assistant, University of Wisconsin-Madison

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Section 1

Introduction

1.1 Background

Treatment and disposal of solid waste are major concerns for most municipalities. Land filling has been the major method to dispose of solid waste; relatively few treatment systems are operational in the United States. Even with a treatment system, a landfill is still required for the disposal of residues, untreated materials, and so on. The lack of nearby landfill capacity has driven municipalities to find ways to divert several waste streams from landfills. One way is to divert the organic fraction of solid waste that can be treated by aerobic biological decomposition. This management option is called composting.

The composting process must be well-understood to be controlled and optimized. Unfortunately, the lack of such understanding has resulted in the construction of several inefficiently designed municipal solid waste composting facilities and the accumulation of the product due to a limited market. Because MSW is so heterogeneous, it is important to understand the physical and biochemical processes that govern the composting process with respect to individual organic components (e.g., food, paper, and yard waste).

The objective of this study is to characterize the composting process for certain MSW components under controlled aerobic conditions. This characterization will be achieved by conducting mass balances, primarily with respect to carbon. The components selected for characterization are:

- food waste
- paper waste (i.e., newsprint, office paper, corrugated cardboard), and
- yard waste (i.e., branches, leaves, grass clippings).

These waste components will be degraded either individually or in combinations, while air is forced into a vessel containing the wastes to maintain aerobic conditions. The air flow will be controlled so that the oxygen concentration in the exhaust gas is above 15% on a per volume basis. The air exiting the vessel is analyzed for CO₂, O₂, VOC, and NH₃.

Research Triangle Institute (RTI) has a cooperative agreement with the U.S. EPA-Air Pollution Prevention and Control Division (APPCD) and the University of Wisconsin at Madison is under contract with RTI to conduct these experiments. These experiments and the audit were conducted in Madison, Wisconsin.

1.2 Purpose

The results of these experiments will be used to manage and operate waste treatment facilities, and estimate the best alternative for waste management. The purpose of this audit was to evaluate the implementation of the Quality Assurance Project Plan (QAPP), prepared by The

University of Wisconsin at Madison, and to assure that the data from the field study satisfied the criteria specified in the QAPP. To accomplish this, a technical systems audit and a performance audit were conducted. The overall objectives of these audits, were as follows:

- Evaluate the implementation of the approved QAPP.
- Conduct a performance audit to evaluate the accuracy of gaseous measurement.

1.3 Audit Summary

The audit results indicated excellent agreement with the performance audit standards and that the method by which the experiment was being conducted was acceptable. This conclusion is based on performance audit results, where the experimental laboratory determined the concentration of audit gases.

Section 2.0 Audit findings

2.1 Technical Systems Audit Results

Technical Systems audits are intended to assess how well a QAPP was followed by field personnel and identify activities that will have an adverse effect on the data collected in the field. Observations made during the technical systems audit are listed below.

No specific problems were identified during the technical systems audit.

2.2 Performance Audit Results

Performance audits are intended to assess the accuracy of measurements made in the laboratory. The performance audit standards were two compressed gas cylinders, one containing carbon dioxide (CO₂) and oxygen (O₂) and the second containing ammonia (NH₄).

The results are presented in the following table. The columns identified as GC/TCD and Bubble Solution are the laboratory results.

Audit Gas	Audit Concentration ¹	GC/TCD ³	Bubble Solution ⁴
Carbon Dioxide, CO ₂	10.1% or 6.907 gms ²	10.19, 12.3, 10.13 or Average @ 10.87% 7.6% Diff. ⁶	6.78, 6.78, 6.88 or Average @ 6.81 gms or 1.4% Diff. ⁶

Oxygen, O ₂	15.16%	15.29, 14.8, 15.19% or Average @ 15.09% or 0.5 % Diff. ⁶	None ⁷
Ammonia, NH ₃	26.9 ppm or 3.256 mg5	None ⁷	3.026, 2.929, 3.263 or Average @ 3.073 mg or 2.4% Diff. ⁶

1. Cylinder gas concentration as reported by Scott Speciality Gases, NIST traceable to <+1- 5 percent.
2. Bubbling audit gas for 202.5 minutes at 189.5 accm and calculating the actual mass of carbon dioxide bubbled through the solution.
3. GC/TCD analysis of gas is used to ensure that the vessels are maintaining 15% O₂ and also as a check on the CO₂ concentration.
4. The mass balance calculations and waste product emissions are calculated using the bubbling solution concentrations.
5. Bubbling the audit gas for 946 minutes at 187.1 accm and calculating the actual mass of ammonia bubbled through the solution.
6. Difference calculated from $\{[(\text{Laboratory-Audit})/\text{Audit}] \times 100\}$ Laboratory values are GC/TCD and Bubbling Solution.
7. Oxygen concentrations are only measured using the GC/TCD and Ammonia is only measured using the bubbling technique.

Section 3.0 Audit Activities

3.1 Audit Preparation

Preparation for this audit included planning meetings with the Project Officer, review of the QAPP, prepared by the University of Wisconsin, discussions with both the RTI and the University of Wisconsin personnel.

Audit gases were obtained from Scott Speciality to evaluate the accuracy of concentrations measured in the University of Wisconsin Laboratory. These gases are described in the following table.

Cylinder Number	Component Gas	Certified Concentration	Certified Analytical Accuracy
BO02415	Carbon Dioxide Oxygen Nitrogen	10.10 percent/molar 15.16 percent/molar balance gas	+/- 5% +/- 5%
ALM058883	Ammonia Nitrogen	26.9 ppm-moles balance gas	+/- 5%

3.2 Supporting Documentation

Documentation referred to during this audit included the Quality Assurance Project Plan, prepared by the University of Wisconsin, dated October, 1996. This Quality Assurance Project Plan was reviewed and approved by the APPCD QA Staff. The specified date identifies the final revision, in response to the APPCD QA Staff review comments.

3.3 On-Site Activities

Monday, June 2, 1997

Traveled from RTP to Madison, Wisconsin. After arriving in Madison, drove to the Federal Express office and picked up the audit gas cylinders. Met a University of Wisconsin representative at the hotel and transported the cylinders to the laboratory building.

The audit began with an organizational meeting, to give everyone a chance to explain where roles. Auditors arrived at the University, the US EPA project officer, Susan Thorneloe gave a presentation of the Life Cycle project. This presentation included a discussion of what data was being collected and what organizations are interested in the results of the project. Richard Shores, the EPA auditor, gave an introduction on the activities associated with the audit and what was expected of the University Laboratory.

Went into the laboratory, reviewed the measurement systems and started the ammonia audit. It was important to start the ammonia gas bubbling to ensure that enough mass would be captured in the bubble solution. Ended the audit activities and traveled to the hotel.

Tuesday, June 3, 1997

Met at the Laboratory and began auditing activities immediately. The Ammonia bubbler was stopped and began the Carbon Dioxide bubbler. Reviewed the calibration and QC activities associated with the GC/TCD used for gas analysis. Observed ambient air and span gas analysis to ensure that the GC/TCD was functioning properly. Reviewed Ammonia and Carbon Dioxide analysis procedure. Completed the auditing activities with an exit meeting/discussion meeting with the University of Wisconsin personnel. Shipped the audit gases via Federal Express and flew back to RTP.

3.4 Auditing Activities

The concentration of the performance audit gases were evaluated using both the Varian 3300 GC/TCD gas analysis system and the bubbling system. Gas samples were analyzed using the GC/TCD by injecting a small volume of gas, with an air tight syringe into the GC/TCD. These gas samples included oxygen and carbon dioxide.

To evaluate the consistency of analysis and the consistency of gas concentration analysis, the audit cylinder gas was analyzed three times with the following results.

Date	Time	% O ₂ Concentration ^A	% CO ₂ Concentration ^B
June 2, 1997	15:36	15.29	10.19
June 2, 1997	16:05	14.8	12.3
June 2, 1997	16:30	15.19	10.13

^ATrue concentration of 15.16 %.

^BTrue concentration of 10.1 %.

These results would indicate that there is the potential for variability in the gas analysis concentrations determined using the GC/TCD and that any anomalous result should be reanalyzed. These results also emphasize the importance of calculating out the actual concentration from the GC/TCD results before proceeding with other work. Based on these results, the consistency of sample analysis when analyzing the vessel gases numerous times is acceptable and meets the project goals. Vessel # 5 was also analyzed numerous times to evaluate analysis variability when analyzing gases containing moisture. These results are as follows.

Date	Time	% O ₂ Concentration	% CO ₂ Concentration
June 2, 1997 ^a	14:48	8.2	10.96
June 3, 1997	10:37	13.25	8.06
June 3, 1997	12:16	14.38	7.84
June 3, 1997	13:06	14.9	7.14

^aLaboratory operator changed the vessel # 5 flow rate after this measurement because of the low oxygen concentration. Project goals were to maintain 15% oxygen concentration within the vessels.

The three samples collected on June 3 seem to indicate a trend where the oxygen concentration is approaching 15 %, in response to having the flow rate adjusted.