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SUBSTRATE AVAILABILITY IN SOLID WASTE LANDFILLS

THESIS

Brian D. Benter, Captain, USAF

AFIT/GEE/ENV/99M-03

Approved for public release; distribution unlimited

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SUBSTRATE AVAILABILITY IN SOLID WASTE LANDFILLS

THESIS

Presented to the Faculty of the Graduate School of Engineering

Of the Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering and Environmental Management

Brian D. Benter, B.S.

Captain, USAF

March 1999

Approved for public release; distribution unlimited

SUBSTRATE AVAILABILITY IN SOLID WASTE LANDFILLS

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Brian D. Benter

Table of Contents

Page
Acknowledgementsii
List of Figuresv
List of Tablesvii
Abstractviii
I. Introduction
Background1Problem Statement4Purpose Statement5Research Questions5Scope/Limitations5
II. Literature Review
Abiotic Factors Influencing Biodegradation
Colborn Model 10 Reference Mode 10 Influence Diagram 11 Formulation 13 Testing 14
Kinetics 15 Monod Kinetics 15 First-Order Kinetics 16 Inhibition Kinetics 16 Shrinking Core Kinetics 17 Step Diffusion Kinetics 18 Other Formulations 18
Biofilm

III. Methodology	.22
Conceptualization	.22
Literature Review	.22
Reference Mode	.22
Influence Diagram	.23
Formulation	.23
Testing	.24
Structure and Parameter Verification Tests	.24
Extreme Conditions Test	.25
Boundary Adequacy Test	.25
IV. Results and Discussion	.26
Conceptualization	.26
Formulation	.30
Testing	.31
Structure and Parameter Verification Tests	.33
Extreme Conditions Test	.37
Boundary Adequacy Test	.48
V. Conclusions and Recommendations for Further Study	.50
Model Strengths	.51
Model Limitations	.51
Suggestions for Further Study	.52
Appendix A: Model Assumptions	.53
Appendix B: Model Structure	.54
Appendix C: Model Equations	.59
Bibliography	.65
Vita	.68

.

List of Figures

Figure 1. Theoretical Reference Mode
Figure 2. Basic Output of Colborn Model
Figure 3. Landfill Bioreactor Influence Diagram
Figure 4. Generic Flow Diagrams of the Colborn Model
Figure 5. Conceptual Model of Solid Substrate Surrounded by Biofilm27
Figure 6. Theoretical Reference Mode
Figure 7. Hydrolysis Influence Diagram
Figure 8. Hydrolysis Flow Diagram
Figure 9. Basic Output of Model
Figure 10. Basic Output of Colborn Model
Figure 11. Relationship between Organic Waste and Simpler Substances
Figure 12. Relationship between Bacteria Responsible for Degradation
Figure 13. Degradation Products
Figure 14. Gas Fraction, Inherent Depletion Rate Increased
Figure 15. Relationship between Organic Waste and Simpler Substances, Inherent Depletion Rate Increased
Figure 16. Degradation Products, Inherent Depletion Rate Increased
Figure 17. Gas Fraction, Inherent Depletion Rate Decreased
Figure 18. Relationship between Organic Waste and Simpler Substances, Inherent Depletion Rate Decreased
Figure 19. Bacterial Growth, Inherent Depletion Rate Decreased
Figure 20. Relationship between Organic Waste and Simpler Substances, Initial Radius Increased
Figure 21. Gas Fraction, Initial Radius Increased

Figure 22.	Bacterial Growth, Initial Radius Increased	45
Figure 23.	Gas Fraction, Initial Radius Decreased	46
Figure 24. Decreased	Relationship between Organic Waste and Simpler Substances, Initial Radius	46
Figure 25.	Degradation Products, Initial Radius Decreased	47

·

List of Tables

Table 1.	Typical	Temperature	Ranges for	Bacteria)
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Abstract

Numerous models exist to both predict and represent the many biological activities that occur in the modern landfill. These different models use varying methods of characterizing what is happening, what is thought to happen, or what should be happening based on both empirical data and theoretical reasoning.

The model presented here is an extension of the system dynamics model originally presented by Colborn in 1997. The revamped model presents a different perspective on what happens as solid organic waste is transformed to simpler substances. This new view involves a bacterial population performing hydrolysis whose growth is limited by the amount of surface area present throughout a number of spheres. Environmental factors no longer bear directly on the microbial population, but influence the rate at which hydrolysis occurs. In addition, the concept of an inherent depletion rate constant has been introduced. This parameter explains the rate at which a mass of organic waste is depleted in relation to both the surface area present throughout a number of spheres and time.

viii

SUBSTRATE AVAILABILITY IN SOLID WASTE LANDFILLS

I. Introduction

Background

Fifty-five percent of all waste generated in the United States in 1996 was ultimately disposed in sanitary landfills (EPA, 1998: 2). Although the number of landfills in the United States is decreasing, the total available capacity remains relatively the same, as recently constructed landfills are generally larger than their predecessors (EPA, 1998: 116). Because of the larger capacity of individual landfills and complex liner systems mandated by the Environmental Protection Agency (EPA), these solid waste landfills present a greater potential for significant negative environmental impact. This increased amount of barriers used in larger landfills allows for an amplified susceptibility to compromise, allowing leachate to seep through and ultimately causing groundwater contamination.

Two schools of thought exist on how landfill operations should be constructed. The EPA, under Subtitle D of the Resource Conservation and Recovery Act, currently mandates a containment, or isolation, philosophy when addressing all new sanitary landfills. This "dry tomb" approach uses existing natural hydrogeologic structures, manmade liners, and compacted covers in conjunction with both gas and leachate collection systems (Anex, 1996: 964). The goal is to contain the contents of the landfill, minimizing any potential for negative environmental impact caused by the landfill. Although contaminant leaks are minimized, the time required for the waste to completely degrade is often dramatically

increased, as conditions for biological activity (especially water) are suppressed. Thus, the risk of eventual uncontrolled release of environmental contaminants is increased through this "dry tomb" approach because the extended period the waste materials remain in a relatively undegraded state may outlast the life of the engineered containment systems.

The "wet cell" philosophy treats landfills as bioreactors, concentrating on the processes within the landfill. The internal conditions of the landfill are controlled in such a way as to encourage naturally occurring microbial degradation processes. The implementation of the "wet cell" approach reduces landfill stabilization time, defined as "a state in which negligible gas production is occurring, leachate does not constitute a pollution hazard, and maximum settlement has occurred" (Anex, 1996: 964). In addition, the requirement for long-term liner and cover maintenance is reduced, leachate is less potent, and the need for landfill monitoring is minimized (Anex, 1996: 964). The reduced times lead to a diminished possibility of negative environmental impacts of sanitary landfills (Wall and Zeiss, 1995: 214). On the other hand, a substantially larger flux of leachate is generated and must be dealt with.

In 1997, Capt Philip Colborn developed a system dynamics model describing the fundamental processes in the landfill bioreactor. He utilized as a reference a combination of two representations of gas generation in a solid waste landfill. The four-phase model includes aerobic degradation, anaerobic acid, accelerated methane, and decelerated methane production phases (Barlaz and Palmisano, 1996: 37-45). The other representation, a five-phase model, includes initial adjustment (I), transition (II), acid (III), methane fermentation (IV), and maturation (V) (Tchobanoglous and others, 1993: 384-387). The combination of these different methods is depicted in Figure 1.



Figure 1. Theoretical Reference Mode (after Tchobanoglous and others, 1993: 385; Barlaz and Palmisano, 1996: 37-45)



Figure 2. Basic Output of Colborn Model (Colborn, 1997: 66)

Colborn's model adequately simulated "the fundamental landfill gas generation behavior associated with biodegradation." Figure 2 shows how comparable Colborn's results were in comparison to the reference mode: "oxygen is depleted fairly quickly, hydrogen gas is produced, and methane and carbon dioxide eventually reach an equilibrium roughly splitting the composition of the landfill gas generated" (Colborn, 1997: 66).

Problem Statement

Although Colborn's model generated reasonable results, a major limitation was identified as "the mechanism associated with substrate availability." The term "substrate availability" describes the ability of microorganisms to gain access to the initial deposition of solid waste in the landfill and subsequently transform that solid waste into simpler substances. It was thought, "addressing this mechanism [will] improve the mechanistic nature of the structure of the model" (Colborn, 1997: 140). By tackling substrate availability concerns within the model, it is anticipated that the improved model will generate results more representative of the reference mode (Figure 1).

Other minor concerns with the current model include abrupt transitions in the model's output. In addition, an appreciable amount of initial organic waste required to generate those results—significantly more than what may be considered realistic in an actual landfill. By improving how some of the microbial processes within the model are depicted, these two minor concerns are expected to disappear.

Purpose Statement

The purpose of this research is to develop quantitative concepts that represent the dynamics of substrate availability in sanitary landfills. This is first achieved by identifying the applicable concepts and then developing the mechanisms that are necessary to (responsible for) the microbial degradation of solid organic waste. The resulting mechanisms are then applied to the existing system dynamics model developed by Colborn in an attempt to more accurately simulate the processes of microbial degradation in a sanitary landfill.

Research Questions

1. What mechanisms are responsible for limiting substrate access?

2. How is solid organic waste in a sanitary landfill depleted through microbial degradation? **Scope/Limitations**

As in the original model developed by Colborn, this system dynamics model uses proportional generation of landfill gases as a metric of landfill performance. Additionally, boundaries are set to isolate the interactions of the landfill structure to be modeled from external environmental conditions such as changing seasons and geographic and climactic influences.

As in many studies of landfills, "the major obstacle to much research is the heterogeneity of landfills, making it nearly impossible to conduct studies that provide a picture of the entire landfill" (Barlaz and Palmisano, 1996: 65). It is hoped that with both the definitions of the problem and purpose, along with a narrow focus, that the knowledge of one aspect of landfill dynamics can be advanced.

II. Literature Review

Abiotic Factors Influencing Biodegradation

Various abiotic and environmental factors affect the growth of a microbial population, which in turn affects degradation. Among these abiotic factors are temperature, radiation, pressure, salinity, water activity, movement, hydrogen ion concentration (pH), oxidation-reduction potential, magnetic force, and organic and inorganic compounds (Atlas and Bartha, 1993: 214-240). Of these factors, it is generally agreed that moisture content, the availability of nutrients, the presence of oxygen, pH, and temperature are the most significant (Barlaz and Palmisano, 1996: 93-100; El-Fadel and others, 1996: 313). These factors have an impact during different phases of a sanitary landfill's lifetime.

Moisture Content. Moisture content for solid waste depends on the waste's composition, the season of the year, and weather conditions—specifically humidity and rainfall. Moisture content for refuse in landfills located in the US typically varies from 15 to 45 percent (Tchobanoglous and others, 1993: 72; Barlaz and Palmisano, 1996, 61). Nutrients for microorganisms must be dissolved in water before they can be assimilated (Hamoda and others, 1998: 213). Thus, landfill moisture can provide an aqueous environment that facilitates the transport of nutrients and microbes (El-Fadel and others, 1997: 239).

Experiments aimed at showing the ideal moisture content of solid waste have been conducted in municipal solid waste (MSW) composting operations. These experiments determined that moisture content of 60 percent by weight yielded the best degradation

characteristics. At values above 60 percent, voids in the waste fill with water, resulting in the elimination of free air space. Values below 60 percent are not sufficient to allow for the solubilization of the solid organic matter. Both conditions reduce the efficiency of microbes in degrading organic matter (Hamoda, 1998: 213).

Oxygen. There are three basic categories of microorganisms with respect to oxygen. Strict or obligate aerobes are those that require oxygen to survive. Strict or obligate anaerobes are those microbes that are inhibited in the presence of oxygen. Occupying the middle ground between these two are facultative anaerobes, which can grow whether or not oxygen is present (Tchobanoglous and others, 1993: 673; Gaudy and Gaudy, 1988: 188; Atlas and Bartha, 1993: 238).

Oxygen is used by aerobic bacteria for two purposes. Oxygen is utilized as a terminal electron acceptor for the ultimate generation of energy. In addition, atmospheric oxygen is employed to facilitate certain enzymatic reactions (Gaudy and Gaudy, 1988: 188). Oxygen is initially present in a landfill at its atmospheric pressure, but is almost completely removed from the landfill environment by both aerobic hydrolysis and aerobic degradation within a matter of days (Tchobanoglous and others, 1993: 385).

Nutrients. For either aerobic or anaerobic degradation to occur, certain nutrients must be present within the landfill. In addition, these nutrients must be present in certain forms and within certain concentration limits in order to be utilized by the different microorganisms. Too much of any one nutrient may prove toxic to the microbial population (Atlas and Bartha, 1993: 237-240). Lack of a nutrient or nutrients may slow or even stop microbial activity, but landfill refuse provides an adequate amount of nutrients to prevent this condition (Barlaz and others, 1990: 575).

Aerobic bacteria use both oxygen (discussed below) and the available organic waste as nutrients. Anaerobic digestion requires nitrogen and phosphorous as major nutrients. Phosphorous is needed for energy and for the synthesis of nucleic acid and membrane phospholipids (Atlas and Bartha, 1993: 239). Other required nutrients required include sodium, potassium, calcium, magnesium, chlorine, and sulfur (Barlaz and Palmisano, 1996: 97)

pH. In general, microorganisms cannot tolerate extreme pH values (Atlas and Bartha, 1993: 232). Optimum values of pH for bacterial growth range from 6 to 8 (El-Fadel and others, 1996: 314; Tchobanoglous and others, 1993: 676). The pH of a microbial environment affects microorganisms and microbial enzymes directly or indirectly. Extreme values of pH (below 4.5 or above 9) allow the molecules of these acids or bases to enter the microbial cell and alter its internal pH, thereby damaging the cell (Tchobanoglous and others, 1993: 676). In addition, the dissociation and solubility of many molecules that indirectly influence microorganisms is affected by pH. This affect leads to varying levels of microbial nutrients and materials that may be toxic to microorganisms, influencing bacterial survival (Atlas and Bartha, 1993: 233, 241).

Later stages of biodegradation in a landfill are affected by varying values of pH. Fermentation, acetogenesis, and methanogenesis affect the pH in different ways. Fermentation increases the overall acidity in the landfill bioreactor. Accumulation of fermentation products results in lowered pH values and slowed microbial activity (El-Fadel and others, 1996: 314).

Acetogens and methanogens utilize the products of fermentation as a food source. Byproducts of acetogenesis and methanogenesis act as buffers and keep the pH of the landfill within the desired range.

<u>Temperature</u>. Bacteria in a landfill can be categorized as psychrophiles, mesophiles, and thermophiles according to the temperature range they live in, as seen in Table 1. Most landfills operate between in the temperature range of the mesophiles and thermophiles (Pacey, 1986: 363).

	<u>Temperature, degrees C</u>			
Туре	Range	Optimum		
Psychrophilic	-10 to 25	15		
Mesophilic	25 to 45	35		
Thermophilic	45 to 90	55		

Table 1. Typical Temperature Ranges for Bacteria (Atlas and Bartha, 1993: 215;

Tchobanoglous and others, 1993: 676)

The temperature ranges given above represent those ranges at which the microorganisms of that type may be able to survive. For each type, their ideal range is narrower, centered on the optimum temperature given. Temperatures above or below this value have a negative effect on growth rates (Tchobanoglous and others, 1993: 676). Growth rates of microorganisms double for every 10 °C increase in temperature until the optimum is reached. Above this critical temperature, the growth rate of the bacteria rapidly decreases (Barlaz and Palmisano, 1996: 96; Tchobanoglous and others, 1993; 676).

These temperature increases are significant factors in the microbial degradation of solid waste in landfills. Microbial processes generate heat. This rise in temperature, in turn, increases the rate of microbial degradation. The temperature and microbial activity will continue this trend until the critical temperature is reached, leading to a severe decline or halt in the growth and activity of the microbes (Colborn, 1997: 35). Controlling temperature in a landfill ensures continuous microbial activity leading to optimum waste degradation.

Composting experiments show that a starting temperature around 40 °C is the optimum for decomposition of organic matter. It has been postulated that this optimum temperature is due to the amount of lag time required for microorganisms to become accustomed to temperature. The optimum starting temperature is particularly true for thermophiles, which account for the largest percentage of organic waste degradation (Hamoda and others, 1998: 213).

Colborn Model

Reference Mode. Many previous research efforts have used landfill gas generation as a metric of landfill performance over time. Trends of landfill gas generation over time have been developed both theoretically and empirically (Barlaz and Palmisano, 1996: 40; Tchobanoglous and others, 1993: 385). Landfill gas generation is frequently used as a metric of landfill performance because it reflects the progression of biodegradation of organic waste within the landfill bioreactor (Colborn, 1997: 45). For a review of different gas simulation models, see "Gas Simulation Models for Solid Waste Landfills," by Mutasem El-Fadel and others (1997).

The reference mode is intended to narrow the thoughts of a modeler, and is established by both a review of applicable literature and consultation with experts in the field. Figure 1 is a depiction of the reference mode used in the Colborn model.

Influence Diagram. An influence diagram aids in both describing the components of a system and comprehending the interactions of the different components. The influence diagram is constructed from the reference mode and literature sources. The influence diagram developed by Colborn is seen in Figure 3.

Feedback loops primarily define the cause-and-effect behavior for the landfill bioreactor. They are primarily located between the bacteria and either the degradative step or the substrate identified with a particular strain of bacteria. The relationship between bacteria and degradation is defined as positive feedback; as the population of bacteria grows, the amount of degradation increases. Bacteria and substrate have a negative relationship; substrate disappears as the bacterial population grows (Colborn, 1997: 59)



Figure 3. Landfill Bioreactor Influence Diagram, Aerobic and Anaerobic (Colborn 1997: 57-58)

<u>Formulation</u>. The influence diagram is used as a reference to construct a flow diagram describing the entire landfill bioreactor system incorporating degradation of organic waste and bacterial growth and decline. The high-level conceptual flow diagram developed by Colborn is seen in Figure 4.



Figure 4. Generic Flow Diagrams of the Colborn Model (Colborn, 1997: 60)

The generic flow diagram serves as a template for constructing the more detailed model using system dynamics software. Within this construction, specific stoichiometric relationships for all the degradative steps are defined. Initial amounts of available substrate are depleted and the products of the depletion increase to be used as substrate for a subsequent degradative step performed by a different class of bacteria. The precise effects of environmental parameters on bacterial growth and decay are also constructed in the detailed model as they pertain to the different degradative steps (Colborn 1997: 59-65).

<u>Testing</u>. Using the system dynamics model based on Figure 4, simulations were conducted to compare the model's output to the reference mode, to validate the model, and to perform a sensitivity analysis. Model output with initial conditions and assumptions for the bioreactor system adequately mimics the reference mode (Colborn, 1997:65-66).

Numerous methods of verifying the model were then used to test the model. The model's structure was compared to that of biodegradation and microbial principles found in applicable literature (Colborn, 1997: 67-70). Parameters in the model were compared to those found in the literature as well. To ensure conceptually accurate and numerically plausible parameters when not found in the literature, advice was sought from experts (Colborn, 1997: 74-75).

Extreme condition testing was conducted by first identifying the most influential variables in the rate equations and then varying the variables between minimum and maximum values. Some of the more influential variables include initial levels of both substrate and bacteria, moisture content, nutrients, temperature, oxygen, and pH (Colborn, 1997: 82-99). Behavior reproduction and prediction testing conducted verified that the

model generated behavior similar to that of the real system. This test also demonstrated that the model reflected how different bacterial populations grow and decline in accordance with the different degradative steps in the model (Colborn, 1997: 99-108).

Kinetics

Microorganisms are capable of consuming substrate by various means. Different ways substrate can enter a cell include passive diffusion, facilitated diffusion, group translocation, proton-linked transport, and binding-protein-dependent transport. Many times, more than one of these mechanisms is involved in the uptake of the extracellular substrate by microbes (Zeng and Deckwer, 1995: 73). Rate expressions have been developed to describe many of these processes. More generally, the generation term in each can be defined in one of three ways, dependent on the component in the mass balance. This term can be either a rate of utilization, the difference between the accumulation of a component and that component's utilization, or a microbial growth rate (Barlaz and Palmisano, 1996: 89).

Monod Kinetics. Monod kinetics has been used extensively since first published in 1949. Both substrate and microbial populations must be defined before the Monod equation can be used (El-Fadel and others, 1997: 245). The Monod equation is expressed as:

$$\mu = \mu_{\rm m}(S/(K_{\rm s}+S)) \tag{1}$$

where $\mu = \text{specific growth rate (time}^{-1})$

 μ_m = maximum specific growth rate (time ⁻¹) S = concentration of substrate (mass/unit volume) K_s = half-saturation constant (mass/unit volume) The Monod equation remains the most widely used microbial growth model (Merchuk and Asenjo, 1995: 91).

<u>First-Order Kinetics</u>. Some data generated by experiments has suggested that organic matter degraded as a function of time follows first-order kinetics (Hamoda and others, 1998: 220):

$$dS/dt = -kS$$
(2)

where S = substrate concentration

 $\mathbf{k} =$ first order rate constant

First-order kinetics is a straightforward method of determining the loss of organic matter. The only parameter that needs to be estimated is the first order rate constant (Barlaz and Palmisano, 1996: 89). Additionally, first-order reactions can be linearized by fitting data on a semilogarithmic paper (Hamoda and others, 1998: 220).

<u>Inhibition Kinetics</u>. Some substances that are nutrients for one type of microbe may be inhibitory to another microbial population at higher concentrations (Atlas and Bartha, 1993: 237-240):

$$dS/dt = \mu_m X / \{Y[(K_s/S) + (S/K_1)]\}$$
(3)

where S = substrate concentration (mass/unit volume)

 $\mu_{\rm m}$ = maximum specific growth rate (time⁻¹)

X = concentration of bacteria (mass/unit volume)

Y = growth yield coefficient (mass of biomass/mass of substrate)

 $K_s = half-saturation constant (mass/unit volume)$

 K_1 = inhibition parameter

Inhibition kinetics modifies Monod kinetics to consider the toxic effects of some nutrients in its formulation (Barlaz and Palmisano, 1996: 90).

Shrinking Core Kinetics. This model assumes a spherical particle of organic waste present in a landfill that is hydrolyzed. The rate that substrate is depleted is proportional to the hydrolysis rate, the initial concentration of substrate, and the concentration of hydrolytic bacteria. The shrinking core model is described using the following expressions (Barlaz and Palmisano, 1996: 89-90):

$$d\phi/dt = -BX_h \tag{4}$$

$$dS/dt = -3BS_{o}\phi^{2}X_{h}$$
(5)

where $S_0 =$ initial substrate concentration (mass/unit volume)

 X_h = hydrolytic bacteria concentration (mass/unit volume)

 ϕ = dimensionless particle radius (= r/R_p)

 $\mathbf{r} =$ radius of particle at time t (length)

 R_p = initial radius of particle (length)

 $B = heterogeneous hydrolysis rate (volume*time^{-1}*mass^{-1})$

The shrinking core model, developed by Negri and others (1993:201-208), was used to model the production of volatile fatty acids from the organic fraction of municipal solid waste. Using a plug-flow reactor, it assumed that acidogenic microorganisms were responsible for the solubilization of solids, and that these acidogens then metabolized them to acids.

Experiments conducted by Mino and others (1995: 101) with starch as a substrate and pure cultures of aerobic, anaerobic, and anoxic bacteria performing hydrolysis confirm the proportional relationship between hydrolysis rates and biomass concentration.

<u>Step Diffusion Kinetics</u>. The step diffusional model takes into account the possible diffusion of degradation enzymes from the cells of microorganisms into the substrate. This semi-empirical equation has the degradation rate proportional to the square root of the substrate, as follows (Barlaz and Palmisano, 1996: 89-90):

$$- dS/dt = [v_{max}^{2} - k(S_{o} - S)]^{1/2}$$
(6)

where S = substrate concentration

- k = kinetic constant
- v_{max} = maximum substrate degradation rate

<u>Other Formulations</u>. In 1992, researchers in the Netherlands linked substrate availability to both its degradation and the growth of bacteria according to the following:

$$C_{t} = C_{o} + \int_{0}^{t} \frac{dS_{t}}{dt} - \frac{1}{V} * \int_{0}^{t} \frac{dQ_{t}}{dt}$$
(7)

where C_t = dissolved substrate at time t

 C_o = dissolved substrate concentration at time = 0 S_t = total amount of substrate per unit volume Q_t = amount of solid or adsorbed substrate

V = volume

Batch growth experiments conducted with naphthalene as a substrate showed good similarity to the theoretical curve of the above equation (Volkering and others, 1992: 548-550).

All of the kinetic models mentioned to this point have dealt with either the generation or decay of microorganisms, but not both. One way suggested by Peleg (1996: 225-230) to deal with both the growth and decay of microorganisms is by combining the

continuous logistic equation with Fermi's equation. The combination of the two gives the following:

$$N(t) = \frac{N_s \{1 + \exp[k_1(t - t_{cl})]\}}{1 + \exp[k_s(t_{cs} - t)]}$$
(8)

where N(t) = number of microorganisms at time t

 N_s = number of microorganisms the environment can support k_1 = decline or lethality rate constant t_{cl} = time to reach 50% survival k_g = growth rate constant

 t_{cg} = time to reach half the environmental capacity

This combined equation is an empirical model that can be used to describe and compare, rather than predict, different patterns of growth and decline. Other models, like variants of the Monod equation, are more suited for prediction.

Biofilm

Structure. Biofilms consist of many different microorganisms embedded in a matrix of extracellular substance. The structure of biofilms consists of voids, channels, cavities, pores, and filaments (de Beer and others, 1994: 1131). Voids form a network of channels through the biofilm, and can make up around 50 percent of the entire volume of an aerobic biofilm (de Beer and others, 1994: 1138). Cells in biofilms have been found to be distributed non-uniformly in many types of biofilms, including "methanogenic films from fixed-bed reactors, aerobic films from wastewater plants, nitrifying biofilms, and pure culture biofilms." The complex structure of biofilms may appear to be random, but is likely an optimal configuration designed for maximum uptake of nutrients by all microorganisms involved (de Beer and others, 1994: 1131).

Differences in the density of biofilms may be a result of either different populations and proportions of microorganisms or a reaction to hydrodynamic conditions surrounding the biofilm (Kwok and others, 1998: 403). Biofilm thickness is a function of substrate loading rate (the concentration of substrate present in the reactor) or biomass surface production rate. As loading rate increases, thickness is increased (Kwok and others, 1998: 407). For experiments, small biofilm thickness is favorable—thicker biofilms are sensitive to sloughing (Picioreanu and others, 1998: 101). For substrate removal efficiency, however, a thicker biofilm results in higher substrate removal efficiency (Wu and others, 1998: 376). As biomass surface production rate is increased, biofilms become "less dense and more fluffy, more protuberances, or rougher" (Kwok and others, 1998: 407).

<u>Mass Transfer</u>. Mass transfer rates differ between locations throughout a biofilm because of the complex structure and spatially varying reactivities of the biofilm. These variations take place both horizontally and vertically due to the heterogeneous nature of the biofilm. For instance, mass transfer coefficients increase just above the surface of the biofilm. Hydrodynamics also plays a role in the variation of mass transfer. Hydrodynamic influence decreases from the top to the bottom of the biofilm. Another factor that influences mass transfer is the interaction among the microbial community making up the biofilm (Yang and Lewandowski, 1995: 737-744).

Substrate Utilization

Numerous models have been developed to describe how substrate is utilized. Experiments have also been conducted to verify that these models accurately depict how substrate is utilized. In general, most models and experiments found in the literature assume a batch reactor and use some variation of Monod Kinetics. Although this may describe the

later stages of microbial degradation in landfills, the assumption may not be valid during a landfill's initial stages when the moisture content is relatively low. What follows is a description of a few of the models and experiments developed in the literature.

Lay and others (1998: 730-731) describe the relationship between the bacterial growth rate and the substrate utilization rate. The substrate utilization rate was subsequently related to the methane production rate in a landfill bioreactor. Although experimental data matched that predicted by their model, an initial value of 70 percent moisture content was used. This value is not typical of the 15 to 45 percent moisture content in an actual landfill (Tchobanoglous and others, 1993: 72; Barlaz and Palmisano, 1996, 61).

Some models and experiments have been developed to depict the relationships of biofilms and substrate. Wu and others (1998: 368-369) offer series of equations for both solid- and liquid-phase models, along with a "schematic illustration of a bioparticle." Their model and subsequent experiment, however, describes a biofilm attached to an inert surface and its use of substrate from a bulk liquid.

Other models that are applicable to the treatment of wastewater may be able to make the "jump" to the landfill bioreactor. One such experiment found that the rate-limiting step in converting "waste solids to fermentation products in the acid phase of anaerobic digestion is the hydrolysis of particulates to soluble substrates" (Eastman and Ferguson, 1981: 364). Although the experiment modeled domestic sludge in a completely mixed, semi-continuous flow anaerobic digester, their findings may be applicable to some extent to the landfill bioreactor.

III. Methodology

Conceptualization

Literature Review. The literature review and consultation with experts aid in the process of conceptualizing the model and its subsequent behavior. Under normal conditions, the model would have to be formulated from the ground up. Such is not the case in this instance. There is already a model in existence that mechanistically describes the process of biodegradation in a solid waste landfill. Because there is already a model, literature review and consultation focus on what aspects of the model need to be improved. By concentrating on the facets of the existing model that need to be improved, a new mental model emerges—perhaps a mental model that reflects a deeper understanding of how one part of landfill biodegradation progresses. Once strategies for improvement are established, focus switches to that of replication of the reference mode.

<u>Reference Mode</u>. The reference mode is intended to narrow the thoughts of a modeler (Randers, 1996: 122). A reference mode is established both through a review of applicable literature and consultation with experts in the field.

The description of the reference mode can be either graphical or verbal (Randers, 1996: 121). Both the graphical and written reference modes support the purpose of this research. The graphical depiction of the reference mode describes the anticipated overall output of the model. This graphical representation is already in existence because of Colborn's work (Colborn, 1997: 55). The verbal description of the reference mode answers two questions—what to change and how to change it.

Influence Diagram. The influence diagram describes the causal relationships between different entities that will appear in the subsequent model. An example of an influence diagram can be found in Figure 3 (see Chapter II). The different units in Figure 3 are joined together using arrows, indicating an affect or influence of one parameter on another. A positive influence is indicated with a plus (+) sign. One example of a positive affect is that of simpler substances on the process of fermentation (acidogenesis). As the amount of simpler substances is increased, more fermentation takes place. Fermentation (acidogenesis) has a negative relationship with simpler substances, as indicated by the negative (—) sign. As more fermentation takes place, the amount of simpler substances is decreased.

Formulation

The influence diagram describes the mechanisms of the system to be modeled. After developing the influence diagram, the next step is to build a flow diagram. The flow diagram that corresponds to the influence diagram in Figure 3 can be found in Figure 4 (see Chapter II). Instead of arrows defining causal relationships between the different units of the model, the units are defined more explicitly. A stock, indicated by a rectangle in the flow diagram, defines the amount of accumulation or depletion of an entity. A flow, shown as a circle-and-arrow combination on the representation, depicts how fast the entity is produced or depleted.

In the example of fermentation and simpler substances, simpler substances become a stock that can be either accumulated or depleted. Fermentation, the process of converting simpler substances to acids, acetate, alcohols, hydrogen, and carbon dioxide, is defined as a flow. The products of fermentation are also stocks, subject to ensuing flows.

After a plausible flow diagram has been established, the model is constructed in more detail using the data gathered from literature sources and consultation with advisors and experts. Differential equations describing the mass balance of substrate, byproducts, and bacterial populations are derived consistent with the flow diagram of the system. The system dynamics modeling software used for this research <u>STELLA Research 5.0</u>, by High Performance Systems. This software package is an upgraded version of that used by Colburn, but performs the same basic functions—translating stocks and flows of the flow diagram into different equations representing the mass balances for numerical integration over time.

Testing

Several tests are possible for building confidence in system dynamics models. Substantiating system dynamic models, however, differs from methods used to verify other types of models. In particular, "confidence in a system dynamics model accumulates gradually as the model passes more tests and as new points of correspondence between the model and empirical reality are identified" (Forrester and Senge, 1980: 209). Several different verification techniques may be used to build confidence in the new structure of the model. It should be noted that satisfying the following tests does not mean that the structure incorporated into the existing model is not contestable. This may not be the only mechanistically valid representation of the biodegradation processes in landfills (Randers, 1996: 129-130).

<u>Structure and Parameter Verification Tests</u>. This validation test as applied to system dynamics modeling involves constructing the model in such a way that it reflects what actually happens in the real system, in this case, the solid waste landfill. These tests are

conducted by subjecting the model to review by advisors. Model structure, assumptions, and parameters are verified so that the representation is consistent with both their knowledge and experience with the real system and relevant literature (Forrester and Senge, 1980: 212).

Extreme Conditions Test. The extreme conditions test is an important validation test. Not only may it reveal missing or flawed model structure, but may also enhance the usefulness of the model. By testing the model outside of normal conditions, confidence is built into the capability of the model to behave reasonably over a wide range of conditions (Forrester and Senge, 1980: 214).

The extreme conditions test is conducted by first identifying the most influential variables in the rate equations and then varying those parameters between their minimum and maximum values. Some of the more influential variables may include initial levels of substrate and bacteria, moisture content, nutrients, temperature, oxygen, and pH. For instance, if the initial value of bacteria in the system were zero, no degradation would occur and ultimately no landfill gases would be generated. The model should accurately reflect this behavior.

Boundary Adequacy Test. This verification procedure evaluates whether the structure of the model is adequate to address the goals set before constructing it. There are two aspects to this test. The first addresses whether the model includes all structure that is relevant to its intended purpose. The second determines if any part of the structure, which may be part of the real system, lies beyond the initial boundaries set (Forrester and Senge, 1980: 214-215). This verification test is accomplished by review of the completed model by advisors.
IV. Results and Discussion

Conceptualization

Hydrolysis of organic wastes into simpler substances is the first step in the degradation processes in a landfill, and occurs both aerobically and anaerobically. The aerobic processes in a landfill, however, play a minor role in decomposition and gas production in landfills (Barlaz and Palmisano, 1996: 9). This fact makes anaerobic hydrolysis the rate-limiting step in the overall degradation of solid waste and hence landfill gas production, the metric used here to measure landfill performance (Eastman and Ferguson, 1981: 364).

The initial model developed by Colborn utilized a fully mixed batch reactor and Monod Kinetics to describe the growth of both the aerobic and anaerobic bacteria performing hydrolysis. However, the initial value of moisture content in a sanitary landfill in the US has been found to comprise between 15 and 45 percent of the weight of material in a landfill (Tchobanoglous and others, 1993: 72; El-Fadel and others, 1996: 313). The use of a fully mixed batch reactor and Monod kinetics, therefore, may not be appropriate for modeling the initial stages of degradation in a landfill—namely, hydrolysis. Hydrolysis may have been wrongly depicted in the original model, which completes the first half of the verbal reference mode conveyed in Chapter III—what to change in the model. The second half of the verbal reference mode to be developed is how to change the formulation of hydrolysis. As a starting point the diagram in Figure 5 is given, formulated after Wu and others (1998: 368). As used in the literature, the biofilm was attached to beadshaped activated carbon and utilized substrate from a bulk solution surrounding it (Wu and

others, 1998: 368). The diagram in Figure 5, however, depicts a solid substrate surrounded by a biofilm, with the substrate changing to simpler substances to be utilized by the bacteria. Oxygen and moisture, however, infiltrate from the outside of the biofilm.



Figure 5. Conceptual Model of Solid Substrate Surrounded by Biofilm (after Wu and others, 1998: 368)

As shown in Figure 5, a biofilm has some thickness and that only some of the microorganisms making up the biofilm are exposed to the substrate to be utilized. Not only is the surface of the substrate all that is available for the bacteria to metabolize, but only the microorganisms closest to the surface are able to metabolize the substrate. This answers the second part of the verbal reference mode posed in Chapter III—how to change the model.

Both parts of the verbal description of the reference mode have been satisfied. The graphical reference mode utilized is the same as that in the original model as seen in Figure

1. The same figure is repeated here for convenience as Figure 6. The graphical reference mode is still valid because, although portions of the original model will be changed, the generation of gases by a landfill does not.





Monod kinetics is no longer valid in this stage. Prior to hydrolysis, the landfill is not fully mixed, and the moisture content is less than 100 percent. Upon first inspection, shrinking core kinetics seems appropriate to describe what is happening. The shrinking core model should not be used, however, because it is a variation of Monod kinetics and is based upon plug-flow. In addition, the shrinking core model does not represent environmental factors such as moisture content, temperature, and the presence (or absence) of oxygen.

There is also some carrying capacity related to the surface area of the substrate. In the previous model, the bacteria performing hydrolysis were allowed unbounded growth.

Using the above discussion involving verbal and graphical depictions of the reference mode, in addition to the conceptual model, an influence diagram is constructed to illustrate the causal relationships that impact hydrolysis in the landfill bioreactor. The resulting influence diagram can be seen in Figure 7.



Figure 7. Hydrolysis Influence Diagram

As illustrated by Figure 7, surface area now represents the population of bacteria performing hydrolysis. This approach allows for a more direct link between the rates of hydrolysis and the amount of organic waste available. In addition, environmental

parameters like temperature, moisture, and oxygen directly influence hydrolysis, as the amount of surface area present is independent of these factors.

Formulation

The influence diagram can now be used to construct a flow diagram of that part of the landfill system involving hydrolysis. The overall flow of the entire system can still be depicted as in Figure 4 (see Chapter II), with a few exceptions. For the initial step of hydrolysis, bacterial growth is replaced with surface area, which represents the population of microorganisms present around a sphere of organic waste. Because bacterial growth has been replaced, environmental factors no longer influence that entity, but rather the degradative step.

The stoichiometric ratio of hydrolysis is also replaced in the new formulation. This parameter represents the ratio between the mass of the organic waste present to the amount of simpler substances produced. The amount of products in this formulation is dependent on microbial activity. In the new representation, however, bacterial populations have been removed from the degradative step of hydrolysis and replaced with surface area. To deal with the new representation, an inherent rate of depletion has been formulated, with units of mass/(surface area * time). Because the Colborn model used stoichiometry, the new rate was formulated using information from literature and consultation concerning how hydrolysis progresses, along with the relative speeds at which aerobic and anaerobic hydrolysis occur.

The resulting flow diagram is shown in Figure 8. This flow diagram changes one degradative step in the overall flow to more accurately represent the process of hydrolysis.

The entire flow diagram, including how the new representation fits in, is included in Appendix B.



Figure 8. Hydrolysis Flow Diagram

Testing

After construction of the model, numerous simulations were conducted in order to compare the output of the model with the new formulations to that of the reference mode and for verification testing. The model containing the new formulation and parameters should reflect behavior similar to the reference mode found in Figure 6. The new model should also more accurately reflect the reference mode than the previous model without the new formulation. The previous model's output is found in Figure 2 (Chapter I). Figure 9 represents the output of the new model based on the initial conditions found in the landfill bioreactor.



Figure 9. Basic Output of Model

Figure 9 demonstrates that the model reasonably reflects landfill gas generation as depicted by the reference mode. Oxygen is immediately depleted preceding the production of hydrogen. Carbon dioxide is immediately built up, followed by its gradual decline as methane is produced. Eventually, methane and carbon dioxide reach equilibrium, indicating steady-state behavior in the landfill bioreactor. By comparing Figures 9 and 6, it can be seen that the formulation of the changed model largely, but not completely, recreates the general behavior of the reference mode.

Figure 2 is repeated here as Figure 10 for convenience. By comparing Figures 9 and 10, it can be seen that the two are similar. There are some differences in the two models' output, however. Oxygen is depleted immediately in the revised model, while in the previous model this process was completed around the 5-day point. The generation of hydrogen in the revised model is more characteristic of the reference mode. Carbon dioxide

and methane reach equilibrium sooner, with oscillations between the two fractions occurring slower once equilibrium is reached, indicating a steady state.



Figure 10. Basic Output of Colborn Model (Colborn, 1997: 66)

The revised model reflects the reference mode and is an improvement over the previous model. Confidence must now be built into the model through verification tests. After these tests can be performed, the new model can be regarded as fulfilling the requirement of more accurately reflecting the process of hydrolysis of organic waste in a solid waste landfill.

Structure and Parameter Verification Tests. The structure of the model must adequately describe the actual structure of the landfill bioreactor. This is done in a number of ways: comparison with the influence diagram, comparison with the reference mode, and discussion with advisors.

Model structure is built upon the influence diagram found in Figure 8. This influence diagram, in turn, was based upon previous studies found in the literature, the reference mode, and consultation with advisors. Because the influence diagram is grounded in what actually happens in a landfill, so is the model structure.

The reference mode shown in Figure 6 is derived from a combination of both experimental data and relevant literature. The model was constructed using entities from this same literature review in an effort to replicate the behavior of the reference mode. Because the basic output of the model mimics the reference mode, the model structure is assumed valid.

In another test of structure, the model, along with its basic output, is subjected to review by advisors. By comparing the sequential steps in the model to existing knowledge of the actual progression of biodegradation in a landfill, these experts confirm that the model structure is grounded in reality.

Parameter verification works in much the same way as structure verification. Parameters added to or changed in the model have been compared against available literature, verified through discussion, and compared to existing knowledge. One example lies in the inherent depletion rate of the surface area exposed to bacteria. Neither this specific rate, nor anything similar, was found through a literature review. It was found, however, that anaerobic hydrolysis is the rate-limiting step in biodegradation processes (Eastman and Ferguson, 1981: 364). In addition, the aerobic processes in a landfill play a minor role in decomposition and gas production in landfills (Barlaz and Palmisano, 1996: 9). Because of these two findings, it was postulated that anaerobic hydrolysis occurs at a rate that is orders of magnitude less than aerobic hydrolysis.

Other relationships can be used to verify both the structures and parameters involved in the model. Among these relationships is how fast organic wastes are depleted and simpler substances generated. Figure 11 depicts this relationship.



Figure 11. Relationship between Organic Waste and Simpler Substances

From Figure 11, it can be seen that the amount of organic waste is depleted very slowly. The significant amounts of mass, volume, and surface area left at the end of the simulation limit the amount of simpler substances produced. Although it cannot be seen from the scale of the graph, after the initial buildup of simpler substances the amount available falls to zero as subsequent processes immediately utilize them.

The limitation on the production of simpler substances is also reflected in subsequent degradation processes. The levels of bacterial populations responsible for these processes are shown in Figure 12. Simpler substances become different products utilized by the microorganisms responsible for successive processes. The ability of these populations to grow is based upon how much substrate is available. Because the amount of substrate is

now restricted, the microorganisms present essentially use the products as soon as they become available, resulting in relatively small population increases.



Figure 12. Relationship between Bacteria Responsible for Degradation

The limitation of the growth of the various microbial populations is reinforced by Figure 13. This figure depicts the amount of products generated during the subsequent degradative steps of the landfill process. Once again, the production of these substances is restrained by the amount of organic waste hydrolyzed to simpler substances. Once these substances are produced, however, they are quickly utilized by the corresponding population of microorganisms.

Figures 12 and 13 also illustrate the progression of degradation occurring in a landfill as a function of time. Trends shown in these figures show that bacteria responsible for the different stages of degradation appear in the order of their particular stage of degradation (Figure 12). In addition, substrates are depleted in the order they would be consumed or converted by the corresponding bacteria (Figure 13).



Figure 13. Degradation Products

Extreme Conditions Test. Testing the model outside of normal conditions may reveal flawed model structure and builds confidence in the model over a wide range of conditions. This test is performed by first identifying the system's most influential variables, followed by varying them over a wide range (Forrester and Senge, 1980: 214).

The most influential variables added or changed in the current model include the inherent rate of degradation and the initial value of the radius of a sphere of substrate. In order to build even more confidence in the model, tests performed by Colborn should be repeated. This task is left for later research efforts.

The inherent rate of degradation controls the speed at which hydrolysis takes place. As this rate is increased, depletion of organic waste to simpler substances is expected to take less time. Consequently, proportions of the different gases produced from the landfill will also be affected.

Figure 14 represents an increase in the inherent depletion rate by an order of magnitude. As can be seen, oxygen is again immediately depleted, and precedes a slightly more pronounced production of hydrogen. Carbon dioxide is again immediately built up, followed by a more gradual decline. Methane is also produced more gradually. Furthermore, methane and carbon dioxide do not reach equilibrium.



Figure 14. Gas Fraction, Inherent Depletion Rate Increased

When the inherent depletion rate is increased in this manner, it affects the amount of organic waste changed to simpler substances. Figure 15 indicates more of a decrease in the mass, volume, and surface area of the organic waste. Corresponding to the greater decrease in these entities is a greater amount of simpler substance production. Accordingly, it would be expected that there is a greater accumulation of degradation products. This can be seen in Figure 16.



Figure 15. Relationship between Organic Waste and Simpler Substances, Inherent





Figure 16. Degradation Products, Inherent Depletion Rate Increased

In the next case, inherent depletion rate was decreased by an order of magnitude to determine its effect. With this decrease of the inherent depletion rate, the opposite effect of that seen in the previous two figures should be expected. Figure 17 demonstrates this. Initially, it takes a longer for oxygen to bleed off. Hydrogen production is somewhat less. Carbon dioxide takes longer to build up, followed again by gradual decline as methane gradually increases. As was the case when the rate was increased by an order of magnitude, methane and carbon dioxide do not reach equilibrium. With a decrease in this value, however, the relative proportions of carbon dioxide and methane move away from 50 percent.



Figure 17. Gas Fraction, Inherent Depletion Rate Decreased

As with an increase in the inherent depletion rate, a decrease also has its effects on the processes that follow hydrolysis. When the rate is decreased, the amount of organic waste that is converted to simpler substances over the period of the simulation should also decrease. In addition, the bacteria associated with each step of the degradation process should not accumulate any more than in the basic model output. Figures 18 and 19 are a verification of this. The slope of the mass, volume, and surface area of the organic waste in Figure 18 are more horizontal, indicating the slower rate. Although not apparent at the scale on the graph, simpler substances exhibit the same behavior as that in the basic case and are immediately utilized by subsequent processes. The anaerobic bacterial populations shown in Figure 19, therefore, have less material to utilize as a substrate. Aerobic bacteria flourish largely in this scenario due to the longer time associated with the depletion of oxygen.



Figure 18. Relationship between Organic Waste and Simpler Substances, Inherent Depletion Rate Decreased



Figure 19. Bacterial Growth, Inherent Depletion Rate Decreased

The initial radius of a sphere of substrate controls the populations of both the aerobic and anaerobic bacteria performing hydrolysis. Initially, the radius of these spheres was set at 0.07 meters, corresponding to the typical particle size of waste in a landfill (Tchobanoglous and others, 1993: 75).

The radius of a sphere is inherent in both the volume and surface area of that sphere. When the radius of a sphere is increased, the volume of the sphere will increase by three times the amount of the surface area. This relationship is expressed in the following equation:

$$\frac{Volume}{SurfaceArea} = \frac{\left(\frac{4}{3}\right)\pi r^3}{4\pi r^2} = \frac{r}{3}$$
(9)

Because of this relationship, increases in the initial radius of the sphere increase the amount of surface area available for hydrolysis on one sphere of organic waste. This increase in radius, however, means that fewer spheres are available in the overall volume of organic waste. Because of the reduced number of spheres, the overall amount of surface area available for hydrolysis is also reduced. Correspondingly, decreases in the initial radius should increase the overall amount of surface area available for hydrolysis.

To perform the extreme conditions test as applied to the initial surface area, the initial radius of one sphere of substrate is first increased by a factor of ten from the original value of 0.07 meters. This will decrease the overall amount of surface area available, and should lead to less hydrolysis being performed.

An increase in the initial radius of a sphere of substrate has much the same effect on the output of the model as a decrease in the inherent depletion rate. The decrease in inherent depletion rate decreases the mass of organic waste changed to simpler substances in relation to surface area and time. Increasing the radius of the sphere, on the other hand, has the effect of decreasing the ratio between mass and the combination of surface area and time. This means that less material will be degraded, which can be seen in Figure 20. Note that the scale of the surface area graph is one order of magnitude lower than that in Figures 11, 15 and 18.

The gas fraction output of the model is seen in Figure 21. As expected, it is similar to that of a decrease in the inherent depletion rate of the substrate, but for the reasons mentioned previously. Figure 22 reinforces that an increase in surface area gives the same output as a decrease in inherent depletion rate, providing the same resulting bacterial growth. A lesser amount of simpler substances is produced. The anaerobic bacterial populations, therefore, have less material to utilize as a substrate. Aerobic bacteria flourish largely in this scenario due to the longer time associated with the depletion of oxygen.



Figure 20. Relationship between Organic Waste and Simpler Substances, Initial Radius

Increased



Figure 21. Gas Fraction, Initial Radius Increased



Figure 22. Bacterial Growth, Initial Radius Increased

Decreases in the initial radius of a sphere of organic waste increase the amount of surface area available for hydrolysis. A decrease in the initial radius of a sphere of organic waste should have an opposite effect as an increase. This decrease of radius should parallel an increase in the inherent depletion rate in the same way as an increase in radius parallels a decrease in the inherent depletion rate. These relationships are demonstrated in Figures 23 through 25.



Figure 23. Gas Fraction, Initial Radius Decreased



Figure 24. Relationship between Organic Waste and Simpler Substances, Initial Radius

Decreased



Figure 25. Degradation Products, Initial Radius Decreased

Figures 23 through 25 indicate that a decrease in radius of the initial sphere of organic waste has almost the same effect as increasing the inherent depletion rate. Figure 23 shows much the same results as Figure 14. There is an immediate depletion of oxygen preceding a pronounced production of hydrogen. Carbon dioxide is immediately built up, followed by a gradual decline. Methane is also produced gradually. Methane and carbon dioxide do not reach equilibrium, and their proportions may oscillate over a long period.

When the initial radius of a sphere of organic waste is decreased, it effects the amount of organic waste changed to simpler substances. Figure 24 relates more of a decrease in the mass, volume, and surface area of the organic waste than Figure 20. In addition, more simpler substances are produced. Accordingly, it would be expected that there is a greater accumulation of degradation products. This can be seen in Figure 25, which compares well to Figure 16.

Boundary Adequacy Test. This test verifies whether the model structure developed adequately addresses the objectives that were established before undertaking the structural changes. Initially, three problems were cited with the Colborn model: no mechanism associated with substrate availability, abrupt transition in model output, and an appreciable amount of organic waste required to generate those results.

By addressing the substrate availability problem, it was thought that the remaining problems would take care of themselves. This is only partially true. Substrate availability was addressed by redefining how hydrolysis occurs in the model. The new definition allows for a more reasonable amount of initial organic waste in the landfill model by many orders of magnitude.

The abruptness in the model, however, still exists. In most simulations, oxygen is depleted immediately and carbon dioxide is built up immediately. While there is a subsequent gradual decline in carbon dioxide during a gradual increase in methane, after the lines depicting these two entities cross they suddenly transition to more horizontal lines. This abruptness does not necessarily mean that there is a problem with the model, only that the model output doesn't mimic the smooth curves of the reference mode.

Limitations were also set before this task was undertaken. The most important of these are the boundaries that exclude external environmental conditions from influencing conditions within the model. These conditions, which include such things as changing seasons and geographic and climactic influences, may be part of the real system, but add complexity to the model that may not be warranted.

The boundary adequacy test is performed by a review of the completed model by advisors. With the above conditions and limitations identified, it was determined that the new model lies within the boundaries initially set forth.

V. Conclusions and Recommendations for Further Study

Models are used for two reasons. First, they are used to replicate known behavior of a particular system in an effort to further understand the process that produces that behavior. Second, models can be used to take existing conditions and a known process to predict the future behavior of a system.

Numerous models exist to both predict and represent the many activities that happen in the modern landfill. These different models use varying methods of characterizing what is happening, what is thought to happen, or what should be happening based on both empirical data and theoretical reasoning. The model presented here is no different in this respect.

What is different about the model presented in the previous pages is that it is one of only two system dynamics models developed to characterize the biodegradation processes in solid waste landfills. Whereas the previous system dynamics model was founded in experimental data coupled with an extensive literature review, this model departs midstream and utilizes theoretical considerations that have not yet been addressed in a laboratory.

The revamped model presents a different perspective on what happens as solid organic waste is transformed to simpler substances. This new view involves a bacterial population performing hydrolysis whose growth is limited by the amount of surface area present throughout a number of spheres. Environmental factors no longer bear directly on the microbial population, but influence the rate at which hydrolysis occurs. In addition, the concept of an inherent depletion rate constant has been introduced. This parameter explains the rate at which a mass of organic waste is depleted in relation to both the surface area present throughout a number of spheres and time.

Model Strengths

The purpose of this research was to develop quantitative concepts that represent the dynamics of substrate availability. The revised model clearly addresses this, as with the previous version there was no formulation that resulted in the hydrolysis of organic waste becoming the rate-limiting step in the landfill bioreactor. The revamped model presents a more accurate picture of not only the process of hydrolysis, but the entire landfill degradation process due to the reformulation.

Additional strengths of the model include its ability to adequately mimic the reference mode using a more reasonable amount of organic waste at the start. The amount of organic waste present at the beginning of model simulations better represents reality. The amount of landfill space limits the amount of waste that can be disposed.

Model Limitations

All models have limitations, and the model presented here is no exception. Some of the restrictions to the model are imposed before construction begins. Among these are the boundaries set to isolate the interactions of the landfill from external environmental conditions such as changing seasons and geographic and climactic influences.

Confidence is built in the model through testing. Although different verification tests were performed with the current model, they are not all-inclusive. The tests performed here concentrated on what was changed since the model's previous iteration. A more comprehensive battery of tests covering a broader scope of model parameters would add more validity to the overall performance of the model. Undertaking the tests performed by Colborn in the original model would further confirm the model's validity.

An additional constraint to performance of the model is the formulation of moisture. The processes of methanogenesis and aerobic degradation generate moisture, while hydrolysis and acetogenesis deplete moisture from the system. These processes are adequately addressed in the model. The location of moisture and its ability to be used by microorganisms is not addressed, however. In both this and the previous model formulation, any moisture present can be immediately utilized by microbial populations.

Suggestions for Further Study

Limitations in the model present opportunities for future research. By addressing these shortcomings, the model can be improved to become a more effective management tool. Some of the questions remaining to be addressed include:

- Does the new model formulation change the outcome of the verification tests originally performed by Colborn?
- What mechanisms are responsible for limiting or enhancing a microbial population's access to moisture?

How can the model more accurately account for the wide variety of waste that is
deposited in a landfill and how do these different things affect landfill performance?
 By addressing these limitations of the current model and filling gaps in current knowledge,
future iterations of this model can be utilized as a more effective tool to understand landfill
processes and subsequently predict landfill behavior.

Appendix A: Model Assumptions

- Anaerobic hydrolysis is the rate-limiting step in the overall degradation of solid waste.
- The use of Monod Kinetics is not appropriate for modeling hydrolysis in a landfill.
- The surface of the substrate is all that is available for microorganisms to metabolize.
- Only microorganisms closest to the surface of the substrate are able to metabolize that substrate.
- There is a carrying capacity related to the surface area of the substrate.
- Organic waste is present in spheres of radius 0.07 meters.
- Surface area represents the population of microorganisms present around a sphere of organic waste.
- Inherent depletion rate relates mass depleted per unit of surface area per unit of time.

Appendix B: Model Structure

Due to the size of the model structure, it is presented over the following four pages.







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Due to the number of model equations, they are presented over the following five pages.

Biomass Sector

```
Acetogens(t) = Acetogens(t - dt) + (Acetogen_Gr - Acetogen_Decay) * dt
```

```
INIT Acetogens = 100
Acetogen Gr =
IF(Oxygen=0)AND(Nutrients=1)THEN(Acetogens*(Aceto Gr Rate*Moisture Factor*
Temp Factor))ELSE(0)
Acetogen Decay = Acetogens*Aceto Decay Rate
Aerobic Bacteria(t) = Aerobic Bacteria(t - dt) + (Aerobic Growth -
Aerobic Bacterial Decay) * dt
INIT Aerobic Bacteria = 10000
Aerobic Growth =
IF(Nutrients=1)THEN(Aerobic Bacteria*(Aero Gr Rate*Moisture Factor*Temp Fa
ctor*Oxygen Factor))ELSE(0)
Aerobic_Bacterial Decay = Aerobic Bacteria*Aero Decay Rate
Fermentative Bacteria(t) = Fermentative Bacteria(t - dt) + (Ferm Growth -
Ferm Decay) * dt
INIT Fermentative Bacteria = 1000
Ferm Growth =
IF(Oxygen=0)AND(Nutrients=1)THEN(Fermentative Bacteria*(Ferm Gr Rate*Moist
ure_Factor*Temp Factor))ELSE(0)
Ferm Decay = Fermentative Bacteria*Ferm Decay Rate
Methanogens(t) = Methanogens(t - dt) + (Methano Growth - Methanogen Decay)
* dt
INIT Methanogens = 100
Methano Growth =
IF(Oxygen=0)AND(Nutrients=1)THEN(Methanogens*(Meth Gr Rate*Moisture Factor
*Temp_Factor*pH_Factor))ELSE(0)
Methanogen_Decay = Methanogens*Meth Decay Rate
Aceto Decay Rate = .1
Aceto Gr Rate =
MAX(Aceto_umax*((Acids)/(Aceto_K+Acids)),Aceto_umax*((Alcohols)/(Aceto_K+A
lcohols)))
Aceto K = 750
Aceto umax = .55
Aero Decay Rate = .1
Aero_Gr Rate = ((Aero_umax*Simpler_Substance)/(Aero_K+Simpler_Substance))
Aero K = 50
Aero umax = 1
Ferm Decay Rate = .1
Ferm Gr_Rate = ((Ferm_umax*Simpler_Substance)/(Ferm K+Simpler_Substance))
Ferm K = 500
Ferm_umax = .6
Meth Decay Rate = .01
Meth_Gr_Rate =
IF((H2_to_CO2<.18)AND(Hydrogen>0)AND(Acetate>0))THEN(MAX((Meth_umax*Carbon
Dioxide*Hydrogen)/((Meth K+Carbon Dioxide)*(Meth K+Hydrogen)),((Meth umax
*Acetate)/(Meth_K+Acetate))))ELSE((Meth_umax*Acetate)/(Meth_K+Acetate))
Meth K = 1000
Meth umax = .525
Nutrients = 1
Moisture_Factor = GRAPH(Percent Moisture)
```

(0.00, 0.00), (0.1, 0.45), (0.2, 0.66), (0.3, 0.8), (0.4, 0.865), (0.5, 0.89), (0.6, 0.905), (0.7, 0.925), (0.8, 0.95), (0.9, 0.975), (1, 0.995) Oxygen_Factor = GRAPH(Oxygen) (0.00, 0.005), (10.0, 0.085), (20.0, 0.205), (30.0, 0.295), (40.0, 0.41), (50.0, 0.495), (60.0, 0.615), (70.0, 0.705), (80.0, 0.795), (90.0, 0.905), (100, 0.995)

Gas Sector

Oxygen(t) = Oxygen(t - dt) + (- O2 Depletion) * dt

INIT Oxygen = 200000000

O2_Depletion =

(Aerobic_Hydrolysis*Aero_Hydro_Stoich)+(Aerobic_Growth*(1/Aerobic_Yield)*A
ero_Degr_Stoich)
Aero_Degr_Stoich = 1.2

Aero_Hydro Stoich = 9.2

Fraction CH4 = Methane/Total Gas

Fraction CO2 = Carbon Dioxide/Total Gas

Fraction H2 = Hydrogen/Total Gas

Fraction 02 = Oxygen/Total Gas

Total_CO2_Gen = (Aero_to_CO2+Ferm_to_CO2+Meth_to_CO2)-Meth_from_CO2

Total_Gas = Oxygen+Carbon_Dioxide+Hydrogen+Methane

Total_Methane_Gen = Meth_from_Acetate+Meth_from_CO2+Meth_from_H2

Moisture Sector

Moisture(t) = Moisture(t - dt) + (Aerobic_Moisture + Methano_Moisture -Moisture_Lost_to_Hydrolysis - Moisture Lost to Aceto) * dt

```
INIT Moisture = 400000000
Aerobic Moisture = Aerobic Growth* (1/Aerobic_Yield) *Stoich_Aero_Degr
Methano Moisture =
IF(H2 to CO2<.18)AND(Hydrogen>=8)AND(Carbon Dioxide>=44)THEN((Methano Grow
th*(1/Methano_Yield)*Stoich_Methano_H2)+(Methano_Growth*(1/Methano_Yield)*
Stoich Methano CO2))ELSE(0)
Moisture Lost to Hydrolysis =
Aerobic Hydrolysis*Stoich Aero Hydr+Anaerobic_Hydrolysis*Stoich_Ana_Hydr
Moisture Lost to Aceto =
(Stoich_Acid*Acetogen_Gr*(1/Aceto_Cell_Yield))+(Stoich_Acid*Acetogen_Gr*(1
/Aceto Cell_Yield))+(Stoich_Alc_to_Acetate*Acetogen_Gr*(1/Aceto_Cell_Yield
))+(Stoich Alc_to Acid*Acetogen Gr*(1/Aceto_Cell_Yield))
Percent Moisture = Moisture/(Organic Waste+Simpler Substance+Moisture)
Stoich Acid = .2
Stoich Aero Degr = .7
Stoich Aero Hydr = .1
Stoich Alc to Acetate = .4
```

 $Stoich_Alc_to_Acid = .3$

Stoich_Ana_Hydr = .04

Stoich_Methano_CO2 = .8

```
Stoich_Methano_H2 = 4.5
```

pH Sector

```
pH = GRAPH(Acids+Acetate)
(0.00, 7.80), (1e+011, 7.70), (2e+011, 7.60), (3e+011, 7.50), (4e+011,
7.40), (5e+011, 7.20), (6e+011, 7.00), (7e+011, 6.80), (8e+011, 6.60),
(9e+011, 6.50), (1e+012, 6.45)
pH_Factor = GRAPH(pH)
```
(4.00, 0.00), (4.40, 0.00), (4.80, 0.00), (5.20, 0.00), (5.60, 0.00), (6.00, 0.1), (6.40, 1.00), (6.80, 1.00), (7.20, 1.00), (7.60, 0.96), (8.00, 0.00)

Surface Area Sector

```
Initial_Radius = .07
Initial_Sphere_Vol = (4*PI*Initial_Radius^3)/3
Organic_Waste_Volume = Organic_Waste/Org_Waste_Rho
Org_Waste_Rho = 1352.631
Sphere_Number = INIT(Organic_Waste_Volume)/(Initial_Sphere_Vol)
Sphere_Radius = (3*Sphere_Volume/(4*PI))^(1/3)
Sphere_Volume = Organic_Waste_Volume/Sphere_Number
Surface Area = Sphere_Number*4*PI*Sphere_Radius*Sphere_Radius
```

Temperature Sector

Microbial_Activity =
GRAPH(Aero_Gr_Rate+Aceto_Gr_Rate+Ferm_Gr_Rate+Meth_Gr_Rate)
(0.00, 0.00), (0.35, 0.0438), (0.7, 0.0688), (1.05, 0.106), (1.40, 0.156),
(1.75, 0.206), (2.10, 0.3), (2.45, 0.4), (2.80, 0.575), (3.15, 0.775),
(3.50, 1.25)
Temperature = GRAPH(Microbial_Activity)
(0.00, 20.0), (0.125, 32.6), (0.25, 40.4), (0.375, 43.8), (0.5, 46.4),
(0.625, 49.0), (0.75, 51.4), (0.875, 53.2), (1.00, 55.6), (1.13, 57.6),
(1.25, 60.0)
Temp_Factor = GRAPH(Temperature)
(0.00, 0.00), (6.00, 0.025), (12.0, 0.08), (18.0, 0.24), (24.0, 0.61),
(30.0, 0.89), (36.0, 1.00), (42.0, 1.00), (48.0, 1.00), (54.0, 0.905),
(60.0, 0.005)

Waste Degradation Sector

Acetate(t) = Acetate(t - dt) + (Aceto_from_Acids + Aceto_from_Alc +
Ferm_to_Acetate - Meth from Acetate - Meth to CO2) * dt

```
INIT Acetate = 0
Aceto_from_Acids = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_from_Acid_Stoich
Aceto_from_Alc = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_from_Alc_Stoich
Ferm_to_Acetate = Ferm_Growth*(1/Ferm_Cell_Yield)*Ferm_to_Acetate_Stoich
Meth_from_Acetate =
Methano_Growth*(1/Methano_Yield)*Methano_from_Acetate_Stoich
Meth_to_CO2 = Methano_Growth*(1/Methano_Yield)*Methano_to_CO2_Stoich
Acids(t) = Acids(t - dt) + (Ferm_to_Acids + Aceto_to_Acid - Aceto_to_H2n -
Aceto_from_Acids) * dt
```

```
INIT Acids = 0
Ferm_to_Acids = Ferm_Growth*(1/Ferm_Cell_Yield)*Ferm_to_Acid_Stoich
Aceto_to_Acid = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_to_Acid_Stoich
Aceto_to_H2n = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_to_H2_Stoich
Aceto_from_Acids = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_from_Acid_Stoich
Alcohols(t) = Alcohols(t - dt) + (Ferm_to_Alc - Aceto_to_Acid -
Aceto_from_Alc - Aceto_to_H2_from_Alc) * dt
```

```
INIT Alcohols = 0
Ferm_to_Alc = Ferm_Growth*(1/Ferm_Cell_Yield)*Ferm_to_Alc_Stoich
Aceto_to_Acid = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_to_Acid_Stoich
Aceto_from_Alc = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_from_Alc_Stoich
Aceto to H2 from Alc =
```

```
Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_to_H2_from_Alc_Stoich
```

```
Carbon Dioxide(t) = Carbon Dioxide(t - dt) + (Ferm to CO2 + Aero to CO2 +
Meth to CO2 - Meth from CO2) * dt
INIT Carbon Dioxide = 0
Ferm to CO2 = Ferm Growth* (1/Ferm Cell_Yield) *Ferm to CO2_Stoich
Aero_to_CO2 = Aerobic Growth*(1/Aerobic Yield)*Degradation Stoich
Meth to CO2 = Methano Growth* (1/Methano Yield) * Methano to CO2 Stoich
Meth from CO2 =
IF((H2 to CO2<.18)AND(Carbon Dioxide>=44))THEN(Methanogenesis*Methano from
CO2 Stoich)ELSE(0)
Hydrogen(t) = Hydrogen(t - dt) + (Ferm_to_H2 + Aceto_to_H2n +
Aceto_to_H2 from Alc - Meth from H2) * dt
INIT Hydrogen = 0
Ferm to H2 = Ferm Growth* (1/Ferm Cell Yield) * Ferm to H2 Stoich
Aceto_to_H2n = Acetogen_Gr*(1/Aceto_Cell_Yield)*Aceto_to_H2_Stoich
Aceto to H2 from Alc = 
Acetogen Gr*(1/Aceto_Cell Yield)*Aceto_to_H2_from_Alc_Stoich
Meth from H2 =
IF((H2 to CO2<.18)AND(Hydrogen>=8))THEN(Methanogenesis*Methano_from_H2_Sto
ich)ELSE(0)
Methane(t) = Methane(t - dt) + (Meth from CO2 + Meth from H2 +
Meth from Acetate) * dt
INIT Methane = 0
Meth from CO2 =
IF((H2_to_CO2<.18)AND(Carbon_Dioxide>=44))THEN(Methanogenesis*Methano from
CO2 Stoich)ELSE(0)
Meth from H2 =
IF((H2 to CO2<.18)AND(Hydrogen>=8))THEN(Methanogenesis*Methano from H2 Sto
ich)ELSE(0)
Meth from Acetate =
Methano Growth* (1/Methano_Yield) *Methano_from_Acetate_Stoich
Organic Waste(t) = Organic Waste(t - dt) + (- Aerobic Hydrolysis -
Anaerobic Hydrolysis) * dt
INIT Organic Waste = 1000000000
Aerobic Hydrolysis =
Aero Depletion*(Surface Area)*Moisture Factor*Temp Factor*Oxygen Factor
Anaerobic Hydrolysis =
Anearo Depletion* (Surface Area) * Moisture Factor* Temp Factor
Simpler_Substance(t) = Simpler_Substance(t - dt) + (Aerobic_Hydrolysis +
Anaerobic Hydrolysis - Ferm to CO2 - Aero to CO2 - Ferm to H2 -
Ferm_to_Acids - Ferm_to_Alc - Ferm_to_Acetate) * dt
INIT Simpler Substance = 0
Aerobic Hydrolysis =
Aero_Depletion*(Surface_Area)*Moisture Factor*Temp Factor*Oxygen Factor
Anaerobic Hydrolysis =
Anearo_Depletion* (Surface Area) * Moisture Factor* Temp Factor
Ferm_to_CO2 = Ferm_Growth*(1/Ferm_Cell_Yield)*Ferm_to_CO2_Stoich
Aero_to_CO2 = Aerobic_Growth*(1/Aerobic_Yield)*Degradation Stoich
Ferm_to_H2 = Ferm_Growth*(1/Ferm_Cell_Yield)*Ferm_to_H2 Stoich
Ferm to Acids = Ferm Growth* (1/Ferm Cell_Yield) * Ferm_to_Acid_Stoich
Ferm to Alc = Ferm Growth* (1/Ferm Cell Yield) * Ferm to Alc Stoich
Ferm to Acetate = Ferm Growth*(1/Ferm Cell Yield)*Ferm to Acetate Stoich
Aceto Cell Yield = .4
```

```
Aceto_from_Acid_Stoich = 1.2
Aceto_from_Alc_Stoich = 1.3
Aceto_to_Acid_Stoich = 1.2
Aceto_to_H2_from Alc Stoich = .09
Aceto to H2 Stoich = .03
Aerobic_Yield = .6
Aero Depletion = 20
Anearo_Depletion = Aero_Depletion/10
Degradation Stoich = 1.5
Ferm_Cell_Yield = .5
Ferm to Acetate Stoich = .3
Ferm to Acid Stoich = .3
Ferm_to_Alc_Stoich = .2
Ferm_to_CO2_Stoich = .19
Ferm_to_H2_Stoich = .009
H2_to_CO2 = IF(Carbon_Dioxide>0)THEN (Hydrogen/Carbon_Dioxide) ELSE (0.18)
Methanogenesis = Methano_Growth* (1/Methano Yield)
Methano from Acetate Stoich = .3
Methano_from_CO2_Stoich = .4
Methano_from_H2_Stoich = 2
Methano_to_CO2\_Stoich = .7
Methano_Yield = .4
```

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