BEHAVIOR AND ASSIMILATION OF ORGANIC AND INORGANIC PRIORITY POLLUTANTS CODISPOSED WITH MUNICIPAL REFUSE

Volume I

by

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequency carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities.

This publication is one of the products of that research that provides the basis for an innovative approach to accelerate the stabilization of municipal solid waste landfills. The research clearly identifies how a bioreactor system can be maintained and restarted if necessary, as well as how to improve the predictability of the various physicochemical phases of the landfill. The data provided will guide the development of full scale operations with the ultimate goal of minimizing potential adverse health and environmental impacts.

E. Timothy Oppelt, Director
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PREFACE

The purpose of this research was to demonstrate and evaluate the capacity of landfill systems to assimilate and attenuate inorganic and organic priority pollutants loadings codisposed with municipal refuse, and to determine the fate and effect of the codisposed pollutants as landfill stabilization progressed under conditions of single pass leaching and leachate recycle.

In accordance with these objectives, ten simulated landfill columns, operated in pairs, with single pass leaching and leachate recycle were constructed and loaded with shredded municipal refuse (one pair), shredded municipal refuse and organic priority pollutants (one pair), and shredded municipal refuse, organic priority pollutants and increasing quantities of heavy metals (three pairs). The loaded columns were sealed, brought to field capacity by the addition of tap water and then operated for about 1500 days. Both leachate and gas samples were routinely analyzed for organic and inorganic priority pollutants as well as for an array of conventional parameters indicative of the sequential processes of landfill stabilization.

The results of this investigation demonstrated that the columns employing leachate recycle achieved waste stabilization more rapidly and completely than the columns operated with single pass leaching. This was evidenced by trends in gas volumes produced, gas production rates, gas composition and changes in leachate indicator parameters. Although the test columns receiving loadings of inorganic and/or organic priority pollutants exhibited reduced gas production, gas production rates and methane content of the gas, these effects were more severe for the single pass columns than for the similarly loaded recycle columns. Consequently, the stabilization in the recycle columns resulted in greater gas production, and concomitantly exhibited more complete assimilation of the priority pollutant than the single pass columns.

Conservative leachate constituents, such as chloride and sodium, reflected the effects of the leachate management techniques employed. Whereas these constituents were retained within the leachate of the recycle columns, as evidenced by the relatively constant concentrations, they were removed from the single pass columns primarily by washout. All other leachate constituents were affected by these operational strategies, with washout from the single pass columns serving to reduce concentration profiles. Operations with leachate recycle did not result in inhibition of landfill stabilization, although the applied priority pollutant loadings did cause some retardation. In contrast, the test columns containing priority pollutant loadings and operated with single pass leaching and resultant washout of leachate constituents exhibited inhibition of the stabilization and attenuation processes. Hence, the recycle columns possessed greater assimilative capacity for the organic and inorganic priority pollutants than that afforded by the single pass columns. This capacity was expressed in the case of the heavy metals by removal primarily through precipitation as hydroxides, carbonates or sulfides, and by reduction and matrix capture through encapsulation, sorption, ion-exchange and filtration. Similarly, the organic priority pollutants were attenuated primarily by abiotic and biotic transformation as well as by sorption within the waste matrix.

Based on the extensive database developed during the course of these investigations, it can be concluded that:

1. Controlled leachate containment, collection and recirculation offers opportunities for more rapid and complete stabilization of landfilled municipal solid waste, including attenuation of codisposed priority pollutants, than does single pass leaching operations more common to traditional landfill practices.

2. Loadings of codisposed priority pollutants in the form of heavy metals and/or selected classes of toxic organic substances, can cause retardation of the sequential phases of landfill stabilization. However, loading effects will be more severe with single pass leaching than with leachate recycle operations, as manifested by relative changes in leachate and gas characteristics.

3. Leachate and gas characteristics, described by various physical and chemical indicator parameters, can be used to reflect the progress of waste stabilization in terms of longevity and intensity of the acid formation and methane fermentation phases.

4. A threshold inhibition level, equivalent to highest inorganic priority pollutant loading, was established for recycle operations, whereas inhibition with single pass leaching was exhibited at the lowest loading. However, these effects would be site-specific and a function of loading and operational techniques employed.

5. Landfills possess a finite capacity to attenuate hazardous and nonhazardous organic and inorganic waste constituents through a wide array of biological and physicochemical mechanisms. These mechanisms principally include reduction, precipitation, and matrix capture for the heavy metals, and biotic or abiotic transformation with matrix interaction through sorption for the organic pollutants.

6. Controlled landfill systems, designed and operated as bioreactors through leachate containment, collection and recycle, enhance performance predictability and thereby minimize potential adverse health and environmental impacts, while encouraging innovation and associated regulatory and public acceptance.

ABSTRACT

Organic and inorganic priority pollutants codisposed with municipal solid waste (MSW) in ten pilot-scale simulated landfill columns, operated under single pass leaching or leachate recycle, were capable of being attenuated by microbially-mediated landfill stabilization processes. The results of the investigation have indicated that columns operated with leachate recycle stabilized more rapidly and completely than columns operated under single pass leaching. The behavior and attenuation of admixed priority pollutant loadings were reflected by changes in leachate characteristics and in the total gas production, the gas production rate, and the methane content of the gas produced by the simulated landfill columns. Leachate constituents were retained in the recycle columns, but were principally removed from the single pass columns due to washout. An explicit inhibition threshold for stabilization consequenced by the priority pollutant loadings was not observed for the recycle columns, although retardation was evident for the test column most heavily loaded with heavy metals. In contrast, stabilization in all single pass columns containing organic and inorganic priority pollutant loadings was inhibited. The organic priority pollutants appeared to have less impact on landfill stabilization than the heavy metals.

Both organic and inorganic priority pollutants loadings were assimilated within the landfill columns. This assimilation was greater in the recycle columns than in the single pass columns. Heavy metals (Cd, Cr, Hg, Ni, Pb and Zn) were subjected to a complex array of attenuation mechanisms within the MSW matrix, and were largely removed by precipitation as hydroxides, carbonates or sulfides, and by reduction and matrix capture through sorption, ion-exchange and encapsulation. The classes of codisposed organic priority pollutants (aromatic hydrocarbons, halogenated hydrocarbons, pesticides, phenols and phthalate esters) were primarily subjected to both abiotic and biotic transformation and physical-chemical sorption within the waste matrix. Reductive dehalogenation appeared to be a primary transformation mechanism for halogenated compounds, and reduction, ring cleavage and possible complete mineralization were indicated for the other codisposed organic compounds.

Collectively, the results of these investigations have established the efficacy of controlled landfill systems utilizing leachate containment and recycle for accelerated *in situ* stabilization of both nonhazardous and hazardous solid waste constituents.

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SECTION 1

INTRODUCTION

Effective management of increasing amounts of solid waste has become not only a local government and national challenge, but an international issue as well. Effective solid waste management includes an integrated multimedia approach that incorporates waste minimization, reuse/recycling, treatment/destruction, and ultimate disposal. Of all available solid waste management options, disposal in landfills is most frequently employed, primarily because of its economic advantage. Moreover, regardless of the emphasis on other solid waste management methods, the land will continue to serve as a final waste receptor, whether for incinerator ash, discards from recycling initiatives, or regulated hazardous waste.

Landfills are designed to comply with regulations allowing either "dry" or "wet" disposal, provided that adverse health and environmental impacts from potential leachate and/or gas generation are minimized. Therefore, two important features of modern landfills include leachate and gas management. Design requirements often specify that the landfills contain a double liner system, incorporating essentially impermeable natural and/or synthetic materials, and also a surface cap at closure. The two liners may be separated by a leak detection system which is intended to capture any leachate that may escape the first liner and to warn of loss in liner integrity and the potential release of leachate (or gas) into the surrounding environment. Directly above the innermost liner and below the disposed refuse, a leachate collection system may be installed to facilitate leachate management.

One of two fundamental leachate management strategies can be employed at full-scale landfills; one which strives for limited rainfall infiltration and single pass leaching, and the other employing leachate containment and *in situ* recirculation. During single pass leaching, leachate is collected and removed from the landfill and treated by separate biological and/or physical-chemical operations either on-site or off-site. In contrast, with leachate recirculation, leachate is collected and recycled back through the landfill, thereby converting the landfill into a large anaerobic biological reactor with attendant microbially-mediated, physical-chemical treatment capabilities. This latter approach is a more recent innovation that has been shown to provide cost-effective leachate treatment, while accelerating the waste conversion and stabilization processes occurring within the landfill environment.

The landfill cap typically consists of a composited impermeable natural or synthetic lower liner, an intermediate drainage layer, and an upper vegetative cover. The natural or synthetic liner is positioned on top of the refuse mass to limit moisture infiltration. The drainage layer, which is placed above the impermeable liner, serves to divert percolating infiltration away from the landfill. The vegetative cover, which is the uppermost layer, is provided to promote evapotranspiration and minimize surface erosion.

Landfill gas, produced as a result of the anaerobic biological waste stabilization occurring within the landfill, consists primarily of methane and carbon dioxide. Regulations require that the methane and other landfill gases be controlled in an environmentally sound manner, including flaring, controlled venting to the atmosphere, or recovery as a fuel source. Therefore, contemporary

landfill designs and operations include integrated leachate and gas management systems.

Because a landfill is essentially an anaerobic biological waste conversion and stabilization process during most of its active life, the same process fundamentals that apply to separate anaerobic treatment also apply to landfills, although effective retention times and opportunities for assimilation and attenuation of less available substrates associated with these separate anaerobic treatment processes are different than those provided by the landfills of today. Therefore, the purpose of this research was to emphasize this analogy between separate anaerobic treatment systems and landfills, and to demonstrate the behavior and assimilation of organic and inorganic priority pollutants codisposed with municipal refuse.

SECTION 2

GENERAL HISTORICAL PERSPECTIVE AND CURRENT STATUS OF LANDFILL PRACTICE

Landfill disposal of solid waste is common, because landfilling has been considered to be the simplest and most economically attractive of all available solid waste management options. However, increasing population growth and societal demands for more conveniences and a higher standard of living have increased solid waste management challenges, often resulting in a critical need for expanded landfill capacity. This increase in landfill capacity has aroused many environmental concerns, to some degree because landfills have historically been poorly managed and misunderstood, but also because inadequate attention has been given to protection of public health and the environment. For example, past landfill practices in the United States (USA) have resulted in 20% of the Environmental Protection Agency's (EPA) national priority list (NPL) of toxic waste clean-up sites being former municipal solid waste (MSW) landfills (Carra and Cossu[1]). These NPL landfills have contaminated groundwater with organic and inorganic constituents that have leached from the refuse and migrated into underlying aquifers.

The early history of land disposal, which dates back approximately 5000 years[2], is shown in Table 1. Within the USA, landfill disposal sites, often called "dumps" until the 1970's, consisted of the placement of solid waste in unlined excavations or mounds. Volume reduction was often achieved by setting the refuse on fire, thereby prolonging the useful life of the dump. However, as a result of the 1976 Resource Conservation and Recovery Act (RCRA), dumps were declared obsolete and are rapidly being replaced by more properly engineered landfills.[3]

Today, landfills may be classified into three basic categories based largely upon the type of waste being contained. "Sanitary" landfills are the most common and contain principally municipal solid waste (MSW) or refuse, "secure" landfills are developed to contain hazardous wastes, and the "controlled" landfills are designed to manage municipal refuse, but in a manner where both leachate and gas production safeguards are provided. Because it is recognized that refuse may contain some hazardous waste, this latter controlled landfill is specifically designed and operated to also provide assimilation of many of the hazardous waste constituents.[4] Such hazardous wastes may be codisposed with the MSW emanating from household or commercial activities, or from industrial activities; practices which have occurred in the past and may still occur today even though regulations generally prohibit large quantities of hazardous wastes from disposal in municipal landfills.

Contemporary landfills are designed and operated according to standards which vary from country to country. For example, Germany has established regulations that may require waste encapsulation and "dry" disposal, in which natural and/or synthetic liners are installed in combination with impermeable caps to minimize leachate generation. In contrast, the USA is also allowing "wet" disposal, where leachate is allowed to be produced and is collected and treated using a variety of techniques, including discharge to a Publicly Owned Treatment Works (POTW), on-site chemical and/or biological treatment, or recirculation back through the landfill. Practice in Sweden and Canada has indicated that leaching is an important part of the stabilization process and helps integrate the landfill into the surrounding environment, which is the ultimate goal. In the United Kingdom, codisposal of a restricted range of

TABLE 1. EARLY HISTORY OF MUNICIPAL SOLID WASTE TREATMENT AND DISPOSAL[2]

2000-3000 B.C.	New Stone Age Man	Kitchen middens-rubbish heaps
3500 B.C.	City of Ur Babylonia	Refuse piles
3500 B.C.	Mohenjo Daro, Harappa, Indus Valley	Covered conduits
1900 B.C.	Knossos, Crete	Circular walled refuse bioreactors (Kouloura)
900-400 B.C.	Mosaic Law	Tent/camp refuse accumulation prohibited
900-400 B.C.	Jerusalem	Perpetual refuse fires
494 B.C.	Rome, Italy	Street cleaning established
451 B.C.	Rome, Italy	Litter fines-corporal punishment introduced
350 B.C.	Pataliptra, India	Litter fines
1240	London, England	Refuse collection introduced
1294	Berwick, England	Litter fines (96 silver pennies)
1309	London, England	Surveyors appointed, fines introduced
1357	London, England	Royal order (imprisonment)
1494	City of Aberdeen	Street scavengers appointed
1530	England	Fermented refuse for gun powder manufacture
1656	England	Saltpeter digging banned
Late 19th-Early 20th Century	England	Hand sorting/refuse recycling
1900	Brazil	Refuse destructor commissioned (steam/ electricity generation)
1901	Budapest, India	Salvage works opened
1930	City of London	Ministry of health instructions and controlled tipping

industrial waste with MSW has been encouraged, because the landfill is believed to possess a capacity to attenuate key components of the industrial waste.[1]

The wastes disposed in a landfill can be pretreated by a variety of methods, largely to facilitate refuse volume reduction, and increase landfill capacity. Moreover, milling, shredding, and pulverizing the MSW can increase homogeneity and the surface area available for microbial attack, and also provide for incipient introduction of oxygen which serves to enhance an initial period of aerobic waste stabilization. Bailing and mechanical compaction increase refuse density, decrease permeability, and remove trapped air from void spaces. They may also impede moisture and nutrient distribution required for microbially-mediated stabilization. Sorting of MSW for the recovery of recyclable materials also reduces waste types and volumes to be landfilled, but probably does not affect stabilization of the remaining organic constituents unless such a practice causes adverse physical impacts on moisture and nutrient distribution.

Regardless of pretreatment, active landfills produce gas in composition reflecting a microbially-mediated succession of stabilization events. Methane is the primary gas produced, and can be recovered for use as a fuel depending upon economics and comparative energy prices. When collected and utilized, incremental cost of methane gas recovery can be decreased.

While landfilling is generally considered to be the least expensive method of MSW management, the true costs are probably significantly higher than have been generally recognized. The total cost of landfill disposal includes capital costs, operating expenses, and the cost of establishing and maintaining controls to prevent contamination from occurring or providing remediation if contamination does occur. As land costs increase and more stringent environmental controls are imposed, the total cost of landfilling will rise. Moreover, siting of new landfills has become increasingly difficult, resulting in increased collection and transportation costs with landfills being located more distant from generator areas.

The environmental impacts of improper landfill design and management practices have increased public awareness and concern. Instead of the traditional "out of sight, out of mind" approach, municipal solid waste management has received national (and international) focus, resulting in alarm over both short- and long-term environmental effects resulting from past mismanagement of MSW, and a resistance to development of new landfill facilities. In addition, population growth has eliminated many potential landfill sites, thereby compounding the siting problem.

2.1 MUNICIPAL SOLID WASTE

The residential, commercial, industrial, and agricultural sectors contribute to the total amount of solid wastes disposed in landfills. The combination of regulated residential and commercial refuse, usually defined as municipal solid waste (MSW), includes all solids, liquids, semi-solids, and contained gases discarded by a community. This quantity varies among countries, and as indicated by Table 2, a consistent categorization of MSW fractions does not exist.

In general, MSW is a diverse mixture of materials that vary in moisture content, size, chemical characteristics, density, and composition. The generator composition of MSW also varies as a function of location, socioeconomic status, time, and other site specific factors. Increased product packaging, household garbage grinders, and the trend toward expanded use of disposable products have significantly impacted MSW composition in recent decades. Selected data on the range of composition of MSW are presented in Table 3, and corresponding elemental constituency is provided in Table 4.

TABLE 2. EXAMPLE AMOUNTS OF MUNICIPAL SOLID WASTE GENERATED BY COUNTRY[1]

Country	Annual Total (10^6 tonnes/year)	Per Capita Amount (kg/person·day)
Austria	1.7	0.6
Canada[a]	25.0	2.7
Denmark[b]	1.3-3.4	0.7-1.8
Finland	2.0-3.0	0.5-1.6
France[c]	17.8-49.8	0.9-2.5
FRG	24.0	1.1
Italy	17.3	0.8
Japan	41.0	0.9-1.1
Netherlands[d]	8.5	1.6
Poland	-	0.6-1.3
South Africa	12.0	1.0
Sweden	2.5	0.8
Switzerland	6.3	2.6
UK	18.0	0.9
USA	72.0	1.6

Notes: [a]Figures only available for municipal and industrial-comercial combined.
[b]Household wastes include household, commercial, and bulky wastes.
[c]Household wastes include both household waste and industrial waste that is similar to household waste.
[d]Household, road sweep, etc., office/shop/service wastes are combined and reported as household waste.

TABLE 3. MUNICIPAL SOLID WASTE COMPOSITION[a]

Reference Source	(3)	(5)	(6)	(7)	(7)
Component/Character	Avg.	Avg.	Avg.	Range	Typical
Food Wastes	15.0	10.0	12.0	6-26	15.0
Garden Wastes	15.7	10.0		0-20	12.0
Paper	35.3	43.0	39.0	25-45	40.0
Cardboard			7.0	3-15	4.0
Plastics	5.0	3.0		2-8	3.0
Rubber and Leather	2.7	2.0	2.0	0-4	2.0
Textiles	1.7	3.0	3.0	0-4	2.0
Plastic Film			2.0		
Wood	3.8	3.0	7.0	1-4	2.0
Glass	10.6	9.0	10.0	4-16	8.0
Metallics			8.0		
Tin Cans				2-8	6.0
Non-ferrous Metals	1.0	1.0		0-1	1.0
Ferrous Metals	6.9	6.0		1-4	2.0
Dirt, Ashes, Brick		10.0	10.0	0-10	4.0
Miscellaneous	2.1				
Moisture Content				15-40	20.0

Note: [a]Percent by weight, wet weight basis.

TABLE 4. MUNICIPAL SOLID WASTE ELEMENTAL ANALYSIS[a]

Reference Source	(2)	(3)
Component	Average	Range
Carbon	25.5	15-30
Nitrogen	0.5	0.2-1.0
Hydrogen	3.4	2-5
Oxygen	20.3	12-24
Sulfur	0.2	0.02-0.1
Chloride	0.5	
Water	25.2	15-35
Inorganics	24.4	

Note: [a]Percent by weight.

As the difficulty in siting of new landfills increased, contemporary landfills have become larger and more sophisticated than those of the past, and many countries are seeking alternative methods of MSW management. The U.S. EPA has developed a hierarchy of solid waste management practices in which waste minimization at the source is emphasized as a first alternative, followed by recycling and reuse, treatment and destruction, and disposal.[8] However, industries and municipalities in the United States continue to favor the least cost method of solid waste management, which continues to be landfill disposal.

The relative percent of MSW managed by different methods is presented in Table 5, where MSW management methods employed by each country is shown to vary considerably. Only 20 to 30% of the MSW was reported landfilled in Switzerland and Japan, compared to 95% of the MSW generated in Finland, Poland, and Canada. In contrast, Japan, Sweden, and Switzerland are reported to incinerate 60 to 80% of the MSW compared to only 0 to 4% in Finland, Canada, and Poland. Hence, increased utilization of MSW incineration is becoming apparent for densely populated areas with decreased land available for new landfills. Continuing population growth in these areas also aggravates associated siting problems. Therefore, as the amount of MSW generated continues to escalate, integrated MSW management systems employing waste minimization, recycling and reuse, treatment and destruction, and ultimate disposal will become more common, and the relative costs of these options will eventually need to be reconciled with a desire to minimize potential adverse effects on both health and the environment.

2.2 LANDFILL STABILIZATION

2.2.1 Landfill Stabilization Processes

Stabilization processes occurring within a MSW landfill normally proceed through a series of physical, chemical and biological transformations. These changes include: biological decay of putrescible material, either aerobically or anaerobically, with the evolution of gases and liquids; chemical oxidation of waste constituents; dissolution and transport of organic and inorganic constituents by leaching liquids; diffusion and transport of gases; hydraulic liquid transport; movement of dissolved constituents as a result of concentration gradients and osmosis; and uneven settlement caused by waste degradation and consolidation of material into void spaces.[9]

The significance and longevity of the physical, chemical and biological stabilization processes are largely determined by climatological conditions, operational variables, management options, and control factors operative or being applied either external or internal to the landfill environment.[10] Through the measurement and analysis of certain leachate and gas parameters, these events can

TABLE 5. RELATIVE PERCENT OF MSW MANAGED BY DIFFERENT METHODS[1]

Country	Land-filled	Incin-erated	Recycled	Composted	No Service
Austria[a]	64	20		16	
Canada	95	4	1		
Denmark	31	50	18	1	
Finland	95	2	3		
France	47.9	41.9	0.6	8.7	
FRG	74	24		2	
Italy	83.2	13.9	0.6	2.3	
Japan[a]	29.6	67.6		2.8	
Nether-lands	51	34	15		
Poland	99.9[b]			0.1	
South Africa[c]	69.2	20.8	3.1	3.8	3.9
Sweden	35	60	5[d]		
Switzer-land	20	80			
UK	88	11	1.0[e]		
USA	83	6	11		

Notes: [a]Figures do not account for recycling.
[b]Includes waste disposed in controlled/uncontrolled dumps. Less than 1% of the dumps are true sanitary landfills.
[c]225 of 564 landfills are uncontrolled.
[d]Separation/composting facilities.
[e]Mostly waste-derived fuel.

be detected and followed. Initially, waste decomposition within the landfill proceeds aerobically, primarily utilizing the oxygen contained within the void spaces of the MSW during placement. After available free oxygen is depleted, stabilization continues anaerobically during the majority of the remaining active life of the landfill, somewhat analogous to a batch anaerobic digester, receiving finite inputs of waste and moisture and producing finite outputs of leachate and gas. However, the effective retention time in a landfill is on the order of years compared to days for most separate biological treatment systems.[10]

Most municipal solid waste landfills have also been shown to evolve through five relatively discrete and sequential phases of stabilization,[10] starting with an initial lag or adjustment phase which is prolonged until sufficient moisture develops to stimulate an active microbiological community and produce leachate. Thereafter, the phases of landfill stabilization or waste conversion can be characterized by leachate and gas composition and production rates, and the four phases after Initial Adjustment may be described to consist of Transition, Acid Formation, Methane Fermentation, and Final Maturation phases as defined in Table 6. The accompanying changes in gas production and leachate and gas composition during accelerated stabilization are illustrated in Figure 1.

Provided that sufficient moisture and nutrients exist during microbially-mediated stabilization, and toxic materials do not cause inhibition, the five phases of stabilization will occur at some time within each portion of a landfill. However, since the placement of MSW in a landfill occurs at different times as the component cells are developed, landfill stabilization phases tend to overlap. Moreover, the rate of stabilization also varies within each cell according to the physical, chemical and biological environment present. Thus, no landfill has a single "age", but rather a family of different ages associated with various compartments or cells within the landfill complex and their respective progress toward stabilization.[10]

2.2.2 Factors Affecting Landfill Stabilization

A principal aspect of the stabilization processes occurring in a landfill is the anaerobic microbial conversion of complex organic material to methane and carbon dioxide. Accordingly, anaerobic conversion of organic constituents may be described in four steps.[11] During the first step, complex and/or insoluble organic material is hydrolyzed to a size and form that can permeate into bacterial cells and be used as energy or nutrient sources.[12] During the second or acidogenic step, organic monomers are converted into simpler intermediates, such as the medium- and long-chain volatile organic acids and the short-chain acetic, propionic, butyric, and valeric acids, as well as hydrogen and carbon dioxide. During the third or acetogenesis step, the higher volatile organic acids are converted to acetic acid, carbon dioxide, and hydrogen. For all longer-chain volatile organic acids except propionic, the conversion to acetic acid occurs via β-oxidation, whereas the conversion of propionic acid to acetic acid occurs via α-carboxylation. Methanogenesis, the final step, consists of the conversion of acetic acid, carbon dioxide and hydrogen to methane. It is during the methane formation phase that the majority of waste stabilization takes place. The generalized pathways for this overall conversion are illustrated in Figure 2.

Microbially-mediated waste stabilization in landfills, as in separate anaerobic digestion processes, is influenced by a number of factors, including temperature, pH, the presence of toxic substances, and nutrient availability. Moreover, anaerobic processes generally occur best within either mesophilic (30 to 38°C) or thermophilic (50 to 60°C) temperature ranges. The optimum temperature range for mesophilic anaerobic digestion reported by McCarty[13] is 30-32°C. Henry and coworkers[11] performed experiments using two completely mixed reactors (CSTR's) operated at 35°C and at 55°C. The results indicated that at the higher temperature, carbohydrate, protein and organic matter conversion increased as did the volatile organic acid concentrations. However, the methane yield was lower

TABLE 6. MUNICIPAL LANDFILL STABILIZATION PHASES[10]

Phase I: Initial Adjustment

- Initial waste placement and moisture accumulation.
- Closure and initial subsidence of each landfill compartment or cell.
- Changes in environmental parameters are first detected to reflect the onset of stabilization.

Phase II: Transition

- Indicated field capacity is exceeded and leachate is generated.
- A transition from initial aerobic to anaerobic microbial stabilization occurs.
- The primary electron acceptor shifts from oxygen to nitrates and sulfates with the disappearance of oxygen and production of carbon dioxide in the gas.
- A trend toward reducing conditions is established.
- Measurable intermediates, such as volatile organic acids, appear and increase in concentration in the leachate.

Phase III: Acid Formation

- Intermediary volatile organic acids become dominant with the continuing hydrolysis and fermentation of waste and leachate constituents.
- A decrease in pH occurs with concomitant mobilization and possible complexation of metal species.
- Nutrients, such as nitrogen and phosphorus, are released and utilized in support of microbial biomass growth commensurate with prevailing substrate conversion rates.
- Hydrogen gas may be detected and affect the nature and type of intermediary metabolism and product formation.

-continued-

TABLE 6 (continued)

Phase IV: Methane Fermentation

- Nutrient consumption and conversion continues.
- Intermediary products, primarily volatile organic acids formed during the acid formation phase, are converted principally into methane and carbon dioxide.
- The leachate pH returns from a buffer level controlled by the volatile organic acids to one characteristic of the bicarbonate buffering system as the volatile organic acids are converted.
- Oxidation-reduction potentials (ORP) are at their lowest reducing levels with accumulation of reduced sulfur and nitrogen species.
- Complexation and precipitation of metal species proceed.
- Leachate organic strength is decreased dramatically in correspondence with increases in gas production.

Phase V: Final Maturation

- Relative dormancy following active microbial stabilization of the readily available organic constituents in the waste and leachate.
- Nutrients may become limiting.
- Measurable gas production diminishes.
- Environmental parameters reflect conditions of greater stability and diminished microbially-mediated activity.
- Oxygen and oxidized species may slowly reappear with a corresponding increase in oxidation-reduction potential.
- Microbially resistant organic materials may be slowly converted with the possible production of humic-like substances capable of complexing with and remobilizing heavy metals.

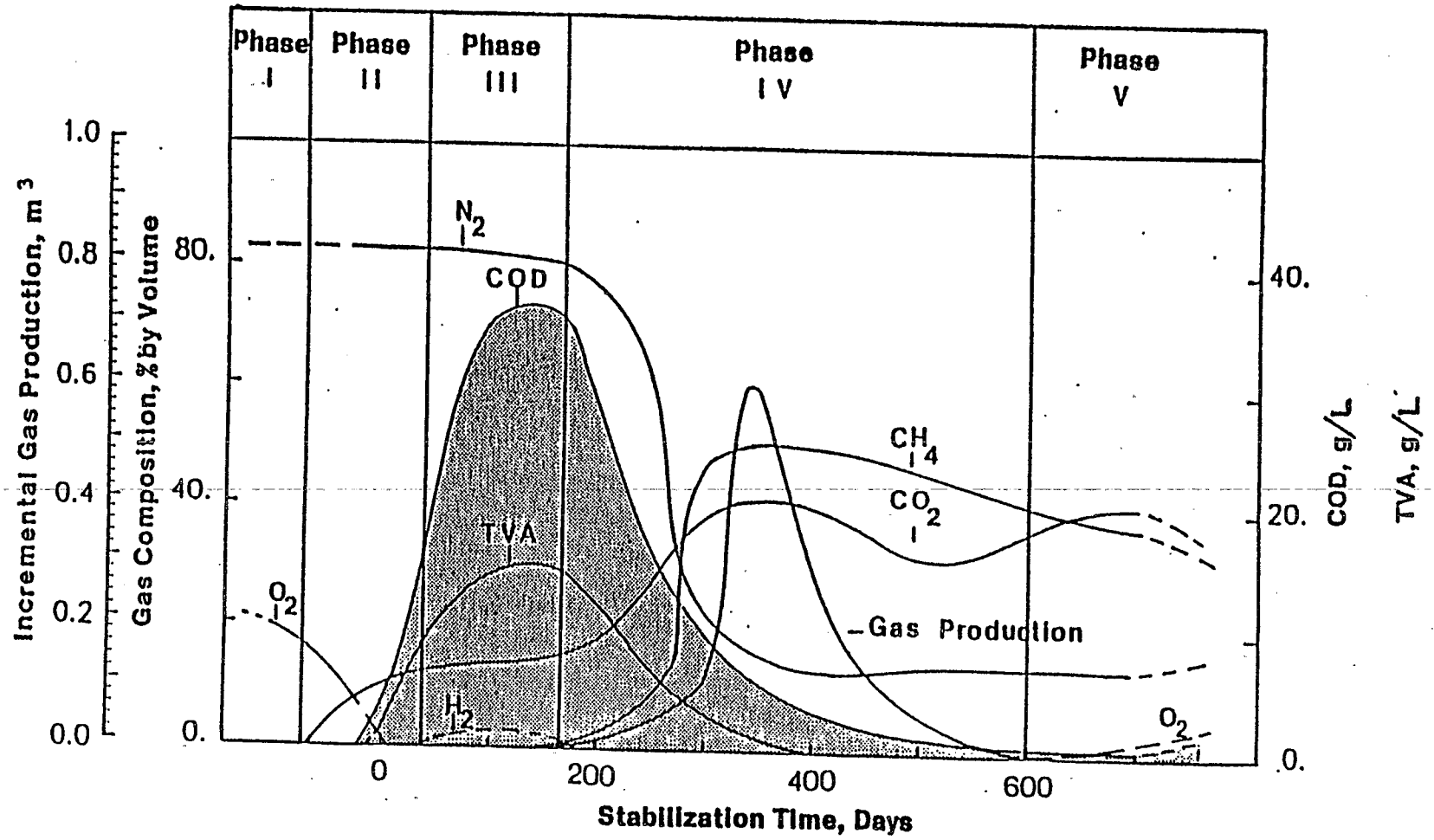


Figure 1. Changes in Selected Indicator Parameters During the Phases of Landfill Stabilization.[10]

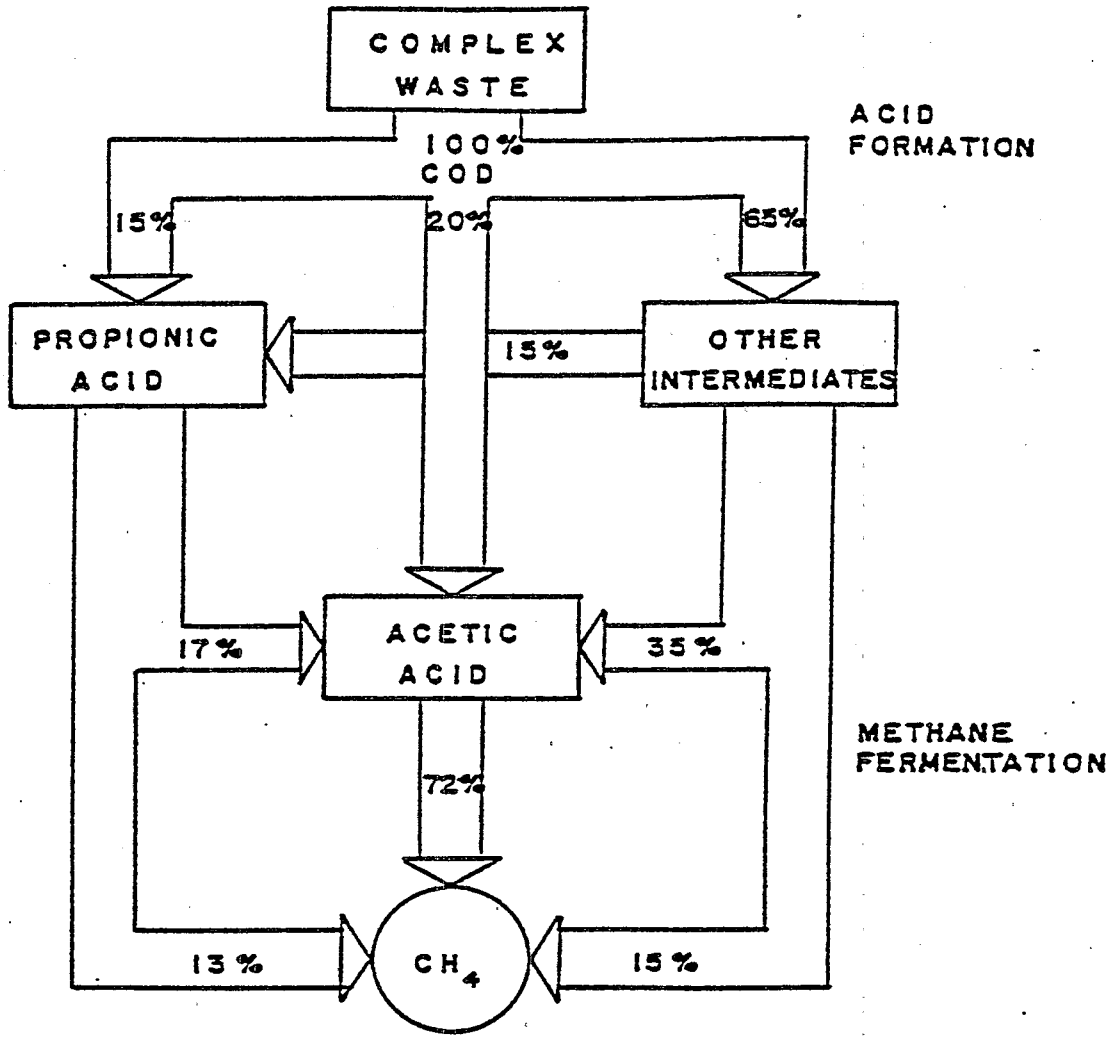


Figure 2. Generalized Pathways for Methane Fermentation of Complex Wastes.[13]

than that of the CSTR operated within the mesophilic temperature range. These results suggested that, while hydrolysis and liquefaction of feed substrate and acidification of soluble intermediates were improved under thermophilic conditions, methanogenesis was inhibited. The depressed gas production and increased acetate concentration in the thermophilic process indicated that the activity of the methanogens responsible for acetate conversion to methane was reduced at higher temperatures. Parkin and Owen[12] suggested that a temperature as close to 35°C as possible be maintained during anaerobic process start-up and recovery from upset. The rate of methane generation from solid waste disposed in existing landfills, studied between the temperature range of 21°C to 48°C, indicated that the optimum temperature was 41°C.[14]

Regardless of the operational temperature selected, the maintenance of uniform temperatures is considered to be fundamental to anaerobic stabilization process efficiency.[12] Since the processes of landfill stabilization occur under primarily anaerobic conditions, the same factors affecting separate anaerobic stabilization processes also influence landfill stabilization processes. However, temperatures within the landfill environment may display greater fluctuations than those of separate anaerobic processes, because landfill temperature is not externally controlled and generally reflects ambient temperature conditions, and the extent and effectiveness of insulation provided by the landfill configuration.

Maintenance of pH within an acceptable range is imperative for efficient anaerobic waste conversion. The generally accepted operational pH range is 6.5 to 7.6,[12,13] with the optimum pH being between 7.0-7.2.[13,15] Hydrolysis, liquefaction, and gas production efficiencies have been reported improved at near neutral pH levels.[11] This range of acceptable pH is primarily controlled by the bicarbonate buffering system, where buffer capacity may be measured in terms of alkalinity, and the maintenance of an adequate amount of alkalinity helps to buffer the anaerobic process from potential failure resulting from excess acid generation. Since the pH of an anaerobic system is a function of both the volatile organic acids and alkalinity concentrations, as well as the partial pressure of carbon dioxide gas evolved during stabilization, if the pH decreases due to an overproduction of acid, the magnitude of this pH change will be dependant upon the types of acids and bases present and their ability to displace the existing buffering system. During conditions when volatile acids accumulate (Acid Formation Phase), the pH may be lowered as the bicarbonate buffer system is displaced by the volatile acid buffer system.

The microbial stabilization processes occurring in an anaerobic digester or landfill may also be adversely affected by the presence of inhibitory substances, such as high concentrations of ammonia nitrogen, sulfides, heavy metals, toxic organic constituents, and excess volatile organic acids. The relative toxicity of any of these is a function of their physical-chemical nature, their concentration, and the possibility for microbial acclimation. In addition, hormesis,[16] or the stimulatory effects caused by low levels of potentially toxic materials, has been observed.[13] Accordingly, many potentially toxic substances may stimulate microbial reaction rates at low concentrations, however, increased concentrations may result in inhibitory or toxic effects.

Ammonia is produced during the decomposition of waste constituents containing nitrogen. Ammonia nitrogen mainly exists as either the ammonium ion at pH less than 7.2, or ammonia at higher pH values. Ammonia is generally considered inhibitory at a much lower concentration than the ammonium ion.[13] McCarty[13] reported that ammonia nitrogen concentrations between 50 and 200 mg/L can be beneficial to anaerobic processes, because ammonia nitrogen can serve as an essential nutrient; concentrations between 200 and 1000 mg/L were shown to have no adverse effects on anaerobic processes; concentrations ranging from 1500-3000 mg/L were shown to have inhibitory effects at higher pH levels; and concentrations above 3000 mg/L were toxic.

Alkali and alkali-earth metal salts such as sodium, potassium, calcium, and magnesium have also been reported as toxic[13] at concentrations of 0.005 M for divalent cations and 0.01 M for monovalent cations.[12] Similarly, soluble sulfides have been reported to cause significant decreases in methane production at concentrations in excess of 300 mg/L.[17] However, sulfide can be used in anaerobic systems to precipitate heavy metals as sparingly soluble sulfides which are not toxic because they are removed from solution and no longer in effective contact with the microbial populations inhabiting the landfill environment.

Some heavy metals, are required in trace amounts by microbial species for enzyme and coenzyme activation and/or functioning. Excess heavy metal toxicity is due primarily to disruption of enzyme structure and function by the binding of metals with functional groups on proteins or replacing naturally occurring metals in enzymes. Therefore, the toxicity of heavy metals is influenced by their speciation and partitioning within the anaerobic environment. Heavy metals may be precipitated under anaerobic conditions as sulfides, carbonates, hydroxides, or bound to waste ligands. Additionally, heavy metals may also be chelated and maintained in solution by conversion products, and may be subjected to sorption and ion exchange within the refuse matrix. Therefore, heavy metals that exist in solution as free cations are toxic to microbial life if present above some threshold concentration.[12]

Some organic substances, such as chlorinated hydrocarbons, are also considered toxic to anaerobic biological systems and are thereby capable of adversely affecting the landfill stabilization process. However, finite concentrations of halogenated organic compounds have been shown to be detoxified under anaerobic conditions, largely through reductive dehalogenation reactions beneficiated by reducing potentials.[10]

During anaerobic digestion, the predominant volatile organic acids (VOA) produced include acetic, propionic and butyric acids.[13,18,19] These acids have pK_a values between 4.75 and 4.87 and exist primarily in the dissociated form at the normal pH ranges of anaerobic digestion processes. Volatile organic acids are capable of inhibiting the digestion process in two ways. As the volatile organic acids dissociate, a hydrogen ion is released which causes the pH of the anaerobic system to decrease. This decrease in pH can have detrimental effects on the stabilization process, as previously discussed. Secondly, research by Zoetemeyer and coworkers[20] has indicated that volatile organic acids are also toxic to biological organisms in the undissociated form. During low pH conditions, the majority of the volatile organic acids exist in the undissociated form and are, therefore, able to penetrate the cell membrane. Once inside the cell, where pH is maintained at a higher level through the establishment of a pH gradient across the cell membrane by active transport of protons out of the cell, the volatile organic acids dissociate and reduce the internal cell pH. As the intercellular pH decreases, the cell consumes increasing amounts of energy to restore pH to its original condition. The loss of energy for maintenance of pH leaves less energy available to the cell for biomass growth and synthesis. Hence the growth rate declines and retards the waste conversion process.

McCarty[21] reported that VOA concentrations up to 6000 mg/L can be tolerated with no loss in methane production, provided that the pH is maintained in the optimal range. Propionic acid concentrations of 6000 mg/L also inhibited the acetogenic bacteria. McCarty and McKinney[22] suggested that VOA toxicity is not necessarily due to the acid anions themselves, but is related to salt toxicity from the cation of the base added to neutralize the acids. This premise was supported experimentally with sodium acetate, chloride, bicarbonate, and sulfate additions, all of which exhibited toxic effects at the same sodium levels.

The availability of nutrients in sufficient quantities is necessary to ensure that efficient anaerobic waste stabilization occurs. The major nutrients, nitrogen and phosphorous, are required in larger amounts, while only trace

quantities of iron, nickel, cobalt, sulfur, calcium, and some organics[12], as well as molybdenum, tungsten, and selenium[23], are required for biomass proliferation. Microorganisms in an anaerobic environment produce and excrete extracellular substances for the harvesting of trace metals by chelating and transporting them into the cell.[23]

2.2.3 Indicator Parameters Descriptive of Landfill Stabilization

Certain indicator parameters exist that are capable of being used to detect and describe the presence, intensity and longevity of each phase of landfill stabilization.[10] Because the majority of waste stabilization occurs during the Acid Formation and Methane Fermentation phases, monitoring of the stabilization process focuses on leachate and gas analyses during these phases. Hence, the leachate produced may be analyzed for a variety of physical, chemical and biological parameters capable of characterizing the progress of stabilization.

The concentration of volatile organic acids in leachate is an indication of the type and degree of waste conversion as well as the potential amount of methane and carbon dioxide that may be produced. Chemical oxygen demand (COD) and five-day biochemical oxygen demand (BOD_5) are chemical and biological parameters, respectively, and are assessed as an indication of the relative biodegradability of the waste substrate.[10] The variation in volatile organic acid concentrations is closely related to that of COD and BOD_5 because, during the Acid Formation Phase, the majority of the COD and BOD_5 is due primarily to the presence of high concentrations of volatile organic acids. Leachate nitrogen and phosphorous concentrations are measured and indicate the availability of these principal nutrients to the anaerobic system. Oxidation-reduction potential and pH are physical-chemical parameters and are reflective of the oxidation-reduction and acid-base conditions, respectively. Other parameters include leachate alkalinity (buffer capacity), heavy metal concentration (potential inhibitory effects), conductivity (ionic strength/activity), chloride concentration (constituent migration potential), nitrates and sulfates (oxidizing potential), and the presence of bacteria and/or viruses (health hazards).[10] Landfill leachate constituent concentration ranges and their significance in terms of the degree or phase of landfill stabilization, as observed during landfill stabilization, are presented in Table 7.

The intensity of these parameters will vary according to the prevailing phase of landfill stabilization and the manifestation of waste conversion. In addition to variations with the microbially-mediated stabilization processes, these parameters will be influenced by the amount of moisture entering the landfill, as dilution effects become more pronounced with increasing moisture flux. Although leachate concentrations may decline with increasing dilution, the overall mass capable of being transferred to the leachate is not affected by the leachate volume generated, provided that the leaching potential has been satisfied.

2.3 LEACHATE PRODUCTION AND MANAGEMENT

2.3.1 Leachate Generation

Leachate is produced when the liquid holding capacity of a landfill is surpassed as a result of rainfall infiltration, surface water drainage, and/or groundwater intrusion combining with the moisture content of the disposed waste. Rainfall infiltration is the primary cause of leachate formation, with the leachate serving as the principal transport medium for migration and leaching and also supplying the necessary moisture to support microbial activity. The amount of infiltration potentially contacting the waste is influenced by the type of containment (liner, cover), landfilling technique employed, and the surrounding hydrogeologic conditions. The quality and quantity of leachate produced will vary depending upon the nature of the waste disposed, climatic and hydrogeologic influences, state or extent of waste decomposition, and the chemical and physical

TABLE 7. LANDFILL LEACHATE CONSTITUENT CONCENTRATION RANGES AND THEIR AND THEIR RELATIVE SIGNIFICANCE IN TERMS OF THE DEGREE OF PHASE OF LANDFILL STABILIZATION[10]

Leachate Parameter	Phase of Landfill Stabilization			
	Phase II	Phase III	Phase IV	Phase V
Biochemical Oxygen Demand (BOD_5, mg/L)	100-10,900 Influence of dilution and aerobic solubilization of waste organics	1,000-57,700 Accumulation of biodegradable organic acids due to methanogenic lag	600-3,400 Conversion of biodegradable organics to gaseous end products (CH_4 and CO_2)	4-120 Influence of high molecular weight organic residuals (humics, fulvics)
Chemical Oxygen Demand (COD, mg/L)	480-18,000 Trending in a similar fashion to BOD_5	1,500-71,100 Trending in a similar fashion to BOD_5	580-9,760 Trending in a similar fashion to BOD_5	31-900 Higher influence of residual organics than in BOD_5 assay
Total Organic Carbon (TOC, mg/L)	100-3,000 Beginning to appear as a result of microbial solubilization	500-27,700 Increasing rapidly; accumulation due to methanogenic lag	300-2,230 Conversion of volatile acids to methane; decrease in aqueous carbon	70-260 Influence of higher molecular weight organics (humics, fulvics)
Total Volatile Acids (TVA, mg/L as CH_3COOH)	100-3,000 Beginning to appear as a result of microbial solubilization	3,000-18,800 Solubilization of organic polymers to monomers; β-oxidation to volatile acids	250-4,000 Conversion of volatile acids to methane; fermentation of acetic acid to methane	Essentially absent; methanogenic system undersaturated

-continued-

TABLE 7 (continued)

Leachate Parameter	Phase of Landfill Stabilization			
	Phase II	Phase III	Phase IV	Phase V
BOD_5/COD Ratio	0.23-0.87 Increasing biodegradability of organics due to solubilization	0.40-0.80 High bio-degradability	0.17-0.64 Decreasing bio-degradability due to methanogenesis	0.02-0.13 Low degree of biodegradability
COD/TOC Ratio	4.3-4.8 Low oxidation state of organics	2.1-3.4 Low to moderate oxidation state of organics	2.0-3.0 Moderate to high oxidation state of organics	0.4-2.0
Total Kjeldahl Nitrogen (TKN, mg/L)	180-860	14-1,970 May be low due to microbial assimilation of nitrogenous compounds	25-82 Low due to microbial assimilation of nitrogenous compounds	7-490 Residual in excess of that required for bioconversion
Nitrate Nitrogen (NO_3-N, mg/L)	0.1-5.1 Temporary increasing due to some oxidation of ammonia	0.05-19 Decreasing due to reduction to ammonia or N_2 gas	Absent Complete conversion to ammonia or N_2 gas	0.5-0.6
Ammonia Nitrogen (NH_3-N, mg/L)	120-125	2-1,030 Increasing due to nitrate reduction and protein conversion	6-430 Decreasing due to microbial assimilation	6-430 Residual in excess of requirement

-continued-

TABLE 7 (continued)

Leachate Parameter	Phase of Landfill Stabilization			
	Phase II	Phase III	Phase IV	Phase V
NH_3/TKN Ratio	0.1-0.9	0.0-0.98 Protein conversion; biological assimilation	0.1-0.84	0.5-0.97
Total Phosphate ($PO_4^{=}$-P, mg/L)	0.6-1.7	0.2-120 Microbial assimilation and metal complexation	0.7-14 Low due to microbial assimilation	0.2-14 Residual in excess of requirement
Total Alkalinity (mg/L as $CaCO_3$)	200-2,500	140-9,650 Increasing due to volatile acid formation and bicarbonate dissolution	760-5,050 Decreasing due to volatile acid removal	200-3,520
Total Solids (mg/L)	2,450-12,050	4,120-55,300 Increasing due to solubilization of organics/inorganics and mobilization of metals	2,090-6,410	1,460-4,640

-continued-

TABLE 7 (continued)

Leachate Parameter	Phase of Landfill Stabilization			
	Phase II	Phase III	Phase IV	Phase V
pH	6.7	4.7-7.7 Low due to volatile acid accumulation	6.3-8.8 Increasing due to volatile acid removal and bicarbonate dissolution	7.1-8.8
Oxidation-Reduction Potential (ORP, mV)	+40 to +80 Temporary aerobic effect	+80 to -240 Decreasing due to the depletion of oxygen	-70 to -240	+97 to +163
Total Coliform (CFU/100 ml)	10^0 to 10^5	10^0 to 10^5	Essentially absent	Absent
Fecal Coliform (CFU/100 ml)	10^0 to 10^5	10^0 to 10^5	Essentially absent	Absent
Fecal Streptococci (CFU/100 ml)	10^0 to 10^6	10^0 to 10^6	Essentially absent	Absent
Viruses (PFU/100 ml)	-	Essentially absent	Essentially absent	Essentially absent
Conductivity (μmhos/cm)	2,450-3,310	1,600-17,100 Increasing due to mobilization of metals	2,900-7,700 Decreasing due to metal complexation with sulfides	1,400-4,500 Expression of soluble residuals

-continued-

TABLE 7 (continued)

Leachate Parameter	Phase of Landfill Stabilization			
	Phase II	Phase III	Phase IV	Phase V
Chloride (Cl^-, mg/L)	30-5,000 Biologically stable; good indicator of washout	30-5,000 Stable; good hydraulic tracer	30-5,000 Stable; good hydraulic tracer	30-5,000 Stable; good hydraulic tracer
Sulfate 2($SO_4^=$, mg/L)	10-458 Increasing due to aerobic oxidation	10-3,240 Increasing initially due to aerobic solubilization, then decreasing as anaerobic conditions are established	Absent Complete conversion to sulfides	5-40 Reappearing due to possible aerobic oxidation
Sulfide ($S^=$, mg/L)	Essentially absent	0-818 Beginning to appear and increasing due to sulfate reduction under anaerobic conditions	0.9 Low due to heavy metal precipitation	Absent Reflection of demand for precipitation with metal loading

properties of the percolating water and adjacent soil or cover. For example, leachate volumes are greater and contain lower concentrations of the parameters indicative of the progress of landfill stabilization in moderate temperature and humid regions that receive high amounts of rainfall than in hot and arid regions that receive minimal rainfall.[10] In addition, a landfill containing both municipal and industrial wastes will produce leachate characteristic of both components. Hence, the leachate constituents originating from any industrial waste input will be superimposed upon the landfill leachate characteristics from the municipal solid waste. Representative variations in landfill leachate composition are presented in Table 8.

A landfill will accumulate moisture until field capacity is attained, develop an active microbiological community commensurate with substrate type and availability, and release leachate based upon the amount of moisture percolating into and through the landfill. The leachate produced will change in quantity and quality as stabilization proceeds. Initially, the leachate quality is reflective of the Acid Formation Phase of landfill stabilization, exhibiting a low pH, high organic content as indicated by COD, BOD_5, total organic carbon (TOC), and total volatile acids (TVA), an abundance of mobilized ions, and absence of dissolved oxygen concentrations. This leachate is characteristic of initial waste conversion and has a high pollutional potential if it were to escape the landfill boundaries. During the Methane Fermentation Phase, the leachate exhibits reduced TVA, increased pH, and the virtual elimination of readily degradable organic components. The COD of the leachate during the Methane Fermentation Phase is reflective of the remaining organics that are not easily biodegraded and/or the presence of humic-like compounds.

2.3.2 Leachate Management Strategies

Two fundamental leachate management strategies exist for conventional landfill operations, they are single pass leaching with leachate containment, collection and external treatment, and leachate containment, collection, and recirculation back into and through the landfill. The former is employed at nearly all full-scale landfill facilities where leachate is formed and managed. During single pass leaching, the moisture influx to the landfill is curtailed and the volume of leachate generated is collected and treated to remove the organic and inorganic contaminants present prior to ultimate disposal. Treatment may include a biological process to remove the organic fraction, followed by physical-chemical treatment to remove residual organics, inorganics, color and/or odor.[24] The treatment of landfill leachate by anaerobic biological processes has the advantage over aerobic biological processes with similar retention times, because methane is produced which can be used as an energy source, and the costly aeration necessary in aerobic systems is essentially eliminated.[10]

During leachate containment, collection, and recirculation, which has been the subject of extensive investigation and development by Pohland and coworkers,[10,24-27] the landfill is managed as both a biological and physical-chemical treatment system. Such leachate recycle has been shown to be an economical leachate pretreatment option by utilizing the landfill as a large anaerobic bioreactor.[1,27] As a result of this *in situ* leachate treatment, more effective use of the assimilative capacity of the landfill is attained through simultaneous attenuation of both hazardous and non-hazardous substances as biodegradation of organic compounds occurs. Once these substances are immobilized or converted within the landfill, and thereby removed from the leachate (or gas), the potential for adverse environmental impacts is greatly reduced should leachate migration from the landfill boundaries occur. In addition to the possibility of dramatically reducing leachate volumes through evaporation during leachate recycle by using surface infiltration,[1] a more rapid development of a viable population of anaerobic bacteria capable of waste conversion is promoted. The increased biological growth can be attributed to a more uniform availability of necessary nutrients contained within the recycled leachate, and continuing exposure of the microbial populations to leachate

TABLE 8. REPRESENTATIVE VARIATIONS IN LANDFILL LEACHATE COMPOSITION

Reference Source	(10)	(23)
Analysis	Range	Range
pH	4.7-8.8	4.9-8.4
Hardness (mg/L as $CaCO_3$)	-	30-13,100
Alkalinity (mg/L as $CaCO_3$)	140-9650	100-20,805
COD (mg/L)	31-71,700	246-750,000
BOD_5 (mg/L)	4-57,700	5.9-720,000
TOC (mg/L)	70-27,700	-
TVA (mg/L as CH_3COOH)	0-18,800	<100-10,000
Nitrate Nitrogen (mg/L as N)	0-51	5-196
Ammonia Nitrogen (mg/L as N)	2-1030	0.2-1106
Total Phosphate (mg/L)	0.2-120	-
Total Dissolved Solids (mg/L)	1460-55,300	1740-11,254
Sulfate (mg/L)	0-3240	24-1220
Potassium (mg/L)	35-2300	28-3770
Sodium (mg/L)	20-7600	85-1805
Cadmium (mg/L)	70-3900	-
Chromium (mg/L)	0.02-18	-
Copper (mg/L)	0.005-2.2	-
Iron (mg/L)	4-2200	2-1000
Lead (mg/L)	0.001-1.44	-
Magnesium (mg/L)	3-1140	-
Manganese (mg/L)	0.6-41	-
Nickel (mg/L)	0.02-79	-
Zinc (mg/L)	0.06-220	-

nutrients. As a result of the rapid development of a suitable microbial community, the time required for landfill stabilization is decreased from several decades to as few as 2 to 3 years.[10,27] Pohland[24] also found that by employing leachate recirculation along with pH control and sludge seeding, the time to achieve landfill stabilization could be further reduced to months rather than years. Moreover, evidence suggests that the cost of leachate recycle may be as low as 25% of the costs of corresponding separate treatment,[25] thus making leachate containment, collection and recirculation an attractive pretreatment option.

During research investigations by Pohland and coworkers,[27] two experimental simulated landfill columns (one single pass and one recycle) were loaded with shredded municipal solid waste, and tap water was added to bring the columns to indicated field capacity. After the attainment of field capacity, leachate was recirculated daily to the column employing that management strategy, and routine moisture additions to both columns were continued at intensities based upon local rainfall intensity. The experimental results indicated that the recycle column produced more gas than the single pass column, which was attributed directly to the opportunity provided by recycle to contain and more thoroughly stabilize the waste and leachate constituents. In contrast, the leachate from the single pass column, which contained much of the gas production potential in the form of volatile organic acids, was removed from the system. Hence, leachate was not discarded from the recycle column, and the gas production potential was not lost. In addition, if initial recirculation of high-strength leachate was too frequent, a delay in methane gas production could result. This effect was attributed to acid inhibition of the methanogens caused by high volatile organic acid concentrations in recycled leachate, which shifts the pH towards the pK_a of the volatile organic acid buffer system. For this same reason, gas production tended to occur earlier in the single pass column, because the potential inhibiting capacity of the volatile organic acids was removed by dilution and washout.

Pohland and coworkers[27] also observed that leaching in the recycle cell, although more uniform at higher liquid recycle flow rates and reduced short-circuiting, could adversely affect the localized microenvironments harboring methanogens within the refuse mass by penetrating the mass of refuse otherwise protecting them from high VOA concentrations and low pH. As indicated previously, because these microenvironments were present in the single pass column and were able to harbor and protect methanogens, gas production commenced earlier than in the recycle column. As a consequence of the delayed gas production in the recycle column, it was suggested that leachate be collected and stored, or the frequency and intensity of leachate recycle reduced, until the onset of rapid methane production could be promoted.

Pohland[24] found that less nitrogen and phosphorus, essential nutrients for the growth of biological populations, were present in recycled leachate due to the enhanced opportunity for distribution and utilization provided by this management strategy. In addition, residual contaminant concentrations in stabilized leachate were greatly reduced or completely removed due to the implementation of leachate recirculation, adjustment of the internal physical-chemical environment, and opportunities for precipitation, sorption, filtration and complexation within the landfill system.[26] Moreover, during the Final Maturation Phase of landfill stabilization, humic-like substances tend to persist and exert a remobilizing effect on heavy metals through complexation. Therefore, leachate recirculation should be discontinued when the Final Maturation Phase is reached, and the remaining leachate should be collected and removed for ultimate treatment and/or disposal.[27]

Few comprehensive reports of leachate recycle as an *in situ* treatment option in the United States have been published in the available literature. However, a demonstration project which may be considered to have been near full-scale has been conducted in Mountain View, CA.[10] Six field cells were

constructed, each having an average volume of 10,500 m^3 and refuse mass of 4825 metric tons, and operated under different combinations of water content, sludge seeding, nutrient levels and buffering. One of the six cells was operated using leachate recycle, and results illustrated the benefits of pH and moisture control and the increased gas volume produced by the implementation of leachate containment, collection and recirculation.

Information is also available concerning several field-scale landfills in Germany where leachate recycle is being used.[10] A two-stage approach was employed, where leachate was removed from a new landfill section and recirculated in an older section of the landfill. The results from this experiment indicate that the two-stage approach could be used to obtain consistent quantities of methane at minimum costs, since only a portion of the landfill would contain leachate recirculation and gas collection systems. Investigations conducted by the United States Environmental Protection Agency (USEPA) revealed that over 200 municipal solid waste landfills employ leachate recirculation as a leachate management method.[28] A full-scale leachate recycle study performed at the Lycoming County, PA MSW landfill indicated that leachate recycle systems promote a more rapid decomposition of organic waste, enhanced methane production, and increased stabilization rate.[28] The number of MSW landfill units employing various leachate management strategies is provided in Table 9. These findings suggest that leachate recycle is a viable option for design, operation and control of landfill disposal sites.

TABLE 9. NUMBER OF MUNICIPAL SOLID WASTE LANDFILL UNITS BY TYPE OF LEACHATE MANAGEMENT STRATEGY AND OPERATING STATUS[28]

Type of Leachate Management Practice[a]	Number of Landfills		
	Closed	Active	Planned
Recirculate by Spraying	40	158	185
Recirculate by Injection	10	36	16
Recirculate by Other Means	11	34	22
Land Spreading	15	84	60
Truck to POTW	48	76	245
Discharge to Sewer to POTW	53	118	135
Discharge to Surface Water	28	81	26
Other or Unknown Off-Site Treatment	5	21	23
On-Site Biological Treatment	41	102	108
On-Site Chemical/Physical Treatment	34	61	60

Note: [a]Some facilities have more than one type of leachate management practice.

2.4 CODISPOSAL OF MSW AND HAZARDOUS WASTE

The disposal of solid wastes in landfills is the most common method of management employed in the United States. Such landfill disposal has often included both municipal solid waste and hazardous waste. The hazardous waste codisposed with the MSW may have originated from industrial or commercial

sources, and from households. The RCRA small quantity generator exclusion has allowed limited amounts of hazardous waste to be codisposed with MSW. Codisposal is, however, restricted by regulations based upon a classification system often examining the behavior of the waste during laboratory testing. Accordingly, a solid waste is defined as hazardous by the US EPA if it meets one or more of the following criteria:[29] exhibits ignitability, corrosivity, reactivity, or TCLP toxicity as determined by standard tests; contains any of the toxic constituents named on published lists as having toxic, carcinogenic, mutagenic, or teratogenic effects on humans or other life forms; or, is listed on prescribed lists. However, a major problem exists in that laboratory test procedures are rarely indicative of waste behavior in an actual landfill environment. For example, the TCLP toxicity test employs a 24-hour leaching period, which may not be representative of an actual landfill circumstance.

The subject of codisposal of hazardous waste along with municipal solid waste has been studied extensively by Pohland and coworkers.[4,30-34] This research has indicated that landfills receiving municipal solid waste display a significant ability to also accommodate hazardous waste, including heavy metals and organic pollutants, up to a certain threshold. If this threshold is exceeded, the waste will tend to interfere with or prolong the normal stabilization processes occurring within the landfill environment. As long as the hazardous waste loadings remain below this level, attenuation mechanisms are often sufficient to compensate for the inherent toxic nature of the codisposed hazardous waste.[32]

Research reported by Pohland and Gould[32] included the development of four simulated landfill columns operated with leachate containment, collection and recirculation. Column 1 served as the control column and contained 400 kg of shredded municipal solid waste, while Columns 2, 3, and 4 received 33.6 kg, 65.8 kg, and 135.2 kg of metal plating sludge, respectively, along with 400 kg of shredded MSW. Leachate COD and TVA were used to illustrate changes in organic strength, and zinc (Zn), cadmium (Cd), nickel (Ni), and iron (Fe) were chosen to demonstrate the effects of the heavy metal loadings and interchange with the leachate and waste matrix during the experimental period. The control column, Column 1, produced leachate that was rapidly depleted of COD and TVA, which is characteristic of normal refuse stabilization. Column 2 displayed a similar but delayed pattern, suggesting that the corresponding metal sludge loading impeded, but did not totally inhibit, the stabilization process. In contrast, both Columns 3 and 4 exhibited behavior characteristic of inhibition. Because relatively uniform concentrations of COD and TVA were maintained in the leachate of the columns, failure in the normal process of waste stabilization was indicated. Additionally, results of this experiment indicated that the delay or inhibition of the natural stabilization process, as measured by COD and TVA, occurred in a cyclic fashion characterized by alternating periods of toxicity and acclimation. The concentrations of Zn, Cd, and Ni were barely detectable in the control column, while a behavior characteristic of washout followed by attenuation of mobilized metals was observed in Column 2 with regard to these heavy metals. Similar behavior was also observed in Columns 3 and 4, but to a lesser extent. The iron concentrations remained relatively high in all columns. Iron, which was present in the codisposed metal sludge, was also produced in all columns as a result of the corrosion of certain iron-containing refuse constituents.

Pohland and Gould[32] also observed some elevation of the concentrations of the codisposed heavy metals Zn, Cd, Ni, and Fe in the leachate during the last or Final Maturation Phase of landfill stabilization. . This increase in concentration was attributed to mobilization or remobilization of heavy metals by complexation with humic-like substances produced as a result of the degradation of more microbially-resistant organic materials that became predominant during the Final Maturation Phase. The effects of humic-like substances upon heavy metals include decreased toxicity and increased mobility.

A variety of mechanisms are considered responsible for the reactions that occur within the landfill environment and affect the ability of the landfill to attenuate codisposed heavy metals.[35] Metal solubilities in leachate increase as pH decreases, thus, the highest metal concentrations should be observed during the Acid Formation Phase when pH values are at a minimum. Secondly, heavy metals can be precipitated as sparingly soluble salts by many inorganic anions. Sulfide and hydroxide have wide precipitating capabilities, while others such as sulfate and chloride will combine only with a limited number of heavy metals. Heavy metals can also form complexes with many organic and inorganic ligands, thus affecting their solubility. In addition, oxidation-reduction processes influence metal speciation and behavior by both modifying the metal itself or transforming other species in the landfill environment. Solid/solute interactions such as adsorption, ion exchange, interactions with solid phase ligands, and heavy metal attenuation in interstitial waters provide opportunities for attenuation of codisposed heavy metals within the landfill. Finally, the mobility of dissolved heavy metals will be reduced within localized microenvironments of higher pH and alkalinity than occur in the landfill environment. In addition, sulfide or carbonate encapsulation of solids within these microenvironments will also reduce heavy metal mobility. As a result of these collective mechanisms, landfills receiving municipal solid waste have been found to exhibit a capacity to remove and minimize the mobility of heavy metals during the first four phases of landfill stabilization.

In view of the opportunity for significant attenuation and reduction of contaminant concentrations in leachate from landfills receiving both municipal and industrial wastes, it is possible that rigid and ultrarestrictive regulations concerning landfilling of such wastes may not be completely justified.[30] The use of leachate containment, collection and recirculation has not only been demonstrated to accelerate stabilization processes and establishment of microbially-mediated reducing conditions favorable for sulfide formation, but also provides an *in situ* physical-chemical process for immobilization of heavy metals and reduction of the potential for external environmental impairment.[31] Therefore, MSW landfills have the ability to attenuate and detoxify certain quantities of hazardous wastes without impeding the process of landfill stabilization or causing adverse environmental impacts on the immediate surroundings, and the remaining challenge is linking this ability to site-specific landfill circumstances.

2.5 FUNDAMENTALS OF ANAEROBIC TREATMENT APPLICABLE TO LANDFILL SYSTEMS

Waste degradation and stabilization within a landfill proceeds primarily under anaerobic conditions. Thus, the fundamentals of anaerobic waste treatment which describe other anaerobic processes such as anaerobic digestion, are applicable to landfill circumstance as well. Anaerobic treatment processes are conventionally employed for the stabilization of complex sludges, industrial wastes, and more recently, the treatment of dilute organic wastes. However, in spite of the capabilities of anaerobic treatment processes, they have not enjoyed a favorable reputation, largely due to lack of understanding of the associated fundamental concepts and mismanagement of existing facilities, whether these processes are utilized as suspended- or attached-growth systems.

Anaerobic biological treatment can have significant advantages over aerobic biological treatment, including: low organism growth rates, which translates into low biomass or sludge production requiring ultimate disposal; low nutrient requirements as a result of low organism growth rates; reduced energy cost, largely because aeration equipment necessary for aerobic treatment is not necessary; production of methane gas which can be purified and sold or used as fuel; tolerance to high organic loadings; precipitation and detoxification of heavy metals; potential for a high degree of waste stabilization; and, biodegradation of volatile compounds otherwise partially stripped during aerobic treatment.

The disadvantages of anaerobic treatment include: an incomplete understanding of microbiology and some lack of prudent process application; the sensitivity of the process to pH variations and the presence of high loadings of toxic compounds; the necessity of longer solid retention times for stable operation, thus requiring larger reactor volumes; and generally slower start-up and recovery from a shock or upset.

A fundamental knowledge of the anaerobic waste treatment process is necessary to the understanding of the progression of waste stabilization within a landfill, because a landfill exists in an anaerobic state for most of its active life.

2.5.1 Microbiological Processes During Anaerobic Stabilization

During anaerobic stabilization, complex organic materials are converted to methane and carbon dioxide by a variety of microorganisms. The four steps of anaerobic digestion, described in Section 2.2.2, include hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Each of these steps is performed by a separate and distinct microbial population, and successful waste conversion is dependant upon these microorganisms performing their respective functions separately or in concert.

The first step, hydrolysis, involves the transformation of complex insoluble organic material to less complex soluble material, a form which is then readily available for microbial utilization. Hydrolysis is primarily accomplished by extracellular, hydrolytic enzymes produced and excreted by the bacterial population for this specific purpose. However, not all organic material can be hydrolyzed to simpler soluble compounds capable of being assimilated by bacteria because of structure, inaccessibility, and complex non-hydrolytic linkages, among other factors.[12] This would suggest that the overall rate of stabilization can be limited by the ability to hydrolyze complex organic material such as present in solid wastes.

Acidogenesis is the formation of medium- and long-chain volatile organic acids, such as propionic, butyric and valeric acids, from the hydrolysis products. In addition, acetic acid, carbon dioxide and methane are also formed during this step. Toerien and coworkers[36] found that aerobic and facultative anaerobic acidogens comprised less than one percent of the total acid-forming bacterial population. Obligate anaerobic acidogens were found in numbers 100 to 200 times greater than aerobic and facultative anaerobic bacteria, confirming the importance of the establishment and maintenance of anaerobic conditions for successful waste conversion.

Chynoweth and Mah[37] have demonstrated that if soluble substrates, such as glucose, are introduced into an anaerobic digestion process, at concentrations in excess of those that can be readily metabolized, a shift in the biological population towards organisms that are capable of converting the excess substrate to acid end products will occur along with the accumulation of volatile organic acids. This shift in the acidogenic pattern was shown to result from the sudden selective growth of euryoxic bacteria normally present within anaerobic processes in low numbers.

Acetogenesis is primarily the conversion of longer-chain volatile organic acids to acetic acid, carbon dioxide and hydrogen. Two types of acetogenic bacteria may be recognized: the hydrogen-producing acetogens which obtain energy for growth by completely dissimilating alcohols of greater complexity than methanol, and volatile organic acids of longer chain length than acetic acid, into acetic acid, hydrogen and occasionally carbon dioxide; and, the hydrogen-consuming acetogens which catabolize carbohydrates, hydrogen and carbon dioxide or one-carbon compounds into acetic acid.[38] Hydrogen (or formate) has been shown to play a significant role in regulating volatile organic acid production and consumption as further described in Section 2.6. In order for these reactions

to become energetically favorable, the partial pressure of hydrogen must be maintained at low levels by hydrogen-utilizing bacteria, such as the carbon dioxide-reducing methanogens and hydrogen-utilizing acetogens.

The final step, methanogenesis, completes the anaerobic waste conversion with the ultimate production of carbon dioxide and methane. Three groups of methanogenic bacteria can be recognized: aceticlastic bacteria which produce methane and carbon dioxide through acetate cleavage; carbon dioxide-reducing methanogens which utilize hydrogen to reduce carbon dioxide to methane; and a final group of bacteria that utilize formic acid and methanol to produce methane. As indicated in Figure 2, approximately 72% of the methane formed in the anaerobic digestion of wastewater sludges originates from acetate cleavage, and the remaining 28% of the methane is produced by carbon dioxide reduction, with 13% of the 28% originating from propionic acid and 15% of the 28% coming from other intermediates.[13]

2.5.2 Volatile Organic Acid Production During Anaerobic Stabilization

Unbalanced stabilization can result from a rapid change in temperature, organic loading, or the addition of substances that are toxic to microorganisms responsible for waste conversion. Indications of unbalanced stabilization or digestion include increased volatile organic acid (VOA) concentrations, increased percentage of carbon dioxide in the gas phase, decreased pH, and a decrease in waste stabilization as evidenced by reduced methane production.[13] According to McCarty and coworkers,[21,22] the buildup of volatile organic acids is the result, not the cause, of unbalanced digestion. During unbalanced digestion, the main volatile organic acids that accumulate include acetic, propionic and butyric, indicating that the organisms responsible for their conversion are perhaps the most sensitive to environmental change.[22] If the increase in VOA concentration exceeds the system buffering capacity, pH will decrease as the excess volatile organic acids ionize and increase the concentration of hydrogen ions in solution. The increased levels of volatile organic acids could be the result of: the nutritional inadequacy of the acetogens responsible for their conversion to acetic acid, carbon dioxide and hydrogen, or a nutritional deficiency in the hydrogen-utilizing methanogens which must maintain low hydrogen levels to promote energetically favorable conditions for the conversion of higher volatile organic acids.[23] Pohland and Suidan,[39] in discussing pH stability in anaerobic systems, noted that increased amounts of carbon dioxide gas were produced during unbalanced digestion conditions at low pH due to inhibition of both hydrogen-utilizing and acetate-utilizing methanogens and a release of "stored" carbon dioxide as the pH was decreased.

Acetic acid, the most prevalent acid occurring during anaerobic digestion, is formed directly from fermentation of proteins, carbohydrates and fats, and also as an intermediate in the fermentation of longer-chained volatile organic acids. Propionic acid is formed primarily from carbohydrates, but is also produced from proteins containing odd-numbered-carbon amino acids and butyric acid is formed during the degradation of proteins and fats.[40] Jeris and McCarty[41] suggested that a sudden increase in the fat concentration entering an anaerobic digestion process could cause a backlog of volatile organic acids until the proper microorganisms were present in sufficient numbers to facilitate their removal.

Acetogenic bacteria are responsible for the conversion of longer-chained volatile organic acids to acetic acid, carbon dioxide and hydrogen. ß-oxidation, consisting of the separation of two-carbon groups from an even-numbered-carbon volatile organic acid until acetic acid remains, has been shown to be the major mechanism of degradation of medium- and long-chain even-numbered-carbon volatile organic acids.[41] If the medium- or long-chain VOA is comprised of an odd number of carbon atoms, β-oxidation will proceed until propionic acid remains, which then is converted to acetic acid by α-carboxylation.[42] Pohland and Bloodgood[43] presented evidence that the mechanism for degradation of even-chained volatile

organic acids was less affected by adverse environmental changes than the degradation of odd-chained volatile organic acids. The conversion of selected volatile organic acids to methane is shown in Table 10, along with the associated free energy changes descriptive of relative thermodynamic favorability.

TABLE 10. VOLATILE ORGANIC ACID (VOA) CONVERSION TO METHANE[a]

Reaction	ΔG_o (kJ/Mole)
Conversion of Higher VOA to Acetic Acid	
Propionic Acid $CH_3CH_2COO^- + 3H_2O \rightleftharpoons CH_3COO^- + HCO_3^- + 3H_2 + H^+$	+76.1
Butyric Acid $CH_3(CH_2)_2COO^- + 2H_2O \rightleftharpoons 2CH_3COO^- + 2H_2 + H^+$	+48.1
Valeric Acid $CH_3(CH_2)_3COO^- + 2H_2O \rightleftharpoons CH_3CH_2COO^- + CH_3COO^- + 2H_2 + H^+$	+48.1
Hexanoic Acid $CH_3(CH_2)_4COO^- + 2H_2O \rightleftharpoons 2CH_3CH_2COO^- + 2\frac{1}{2}H_2 + H^+$ $CH_3(CH_2)_4COO^- + 2H_2O \rightleftharpoons CH_3(CH_2)_2COO^- + CH_3COO^- + 2H_2 + H^+$ $CH_3(CH_2)_4COO^- + 4H_2O \rightleftharpoons 3CH_3COO^- + 4H_2 + 2H^+$	+48.1 +48.1 +96.2
Conversion to Methane	
Acetic Acid $CH_3COO^- + H_2O \rightleftharpoons HCO_3^- + CH_4$	-31.0
Bicarbonate $HCO_3^- + 4H_2 + H^+ \rightleftharpoons CH_4 + 3H_2O$	-135.6

Note: [a]Conditions of 25°C, 1 atm, pH 7.

Propionic acid has been shown to be an important intermediate produced during the anaerobic digestion of complex materials. According to Pohland and Bloodgood,[43] the mechanism for propionic acid degradation is the most sensitive to retarded conditions. In an experiment by McCarty and Brosseau,[21] four laboratory digesters were initially seeded with digested sludge from a municipal treatment plant, and were fed raw primary sludge diluted with an equal volume of tap water on a daily basis. Removal of digested sludge also occurred daily. The four digesters were spiked with 6000 mg/L (as acetic acid) of either acetic,

propionic or butyric acids that were neutralized to pH 7 using lime. One digester served as the control and received no acid addition. The results of this experiment indicated that the digesters receiving acetic and butyric acids exhibited increased gas production over the control digester, and the excess acids added were rapidly utilized. The highest gas production occurred in the digester receiving butyric acid. Alternatively, the added propionic acid had an initial inhibitory effect on gas production that was attributed to a lack of acclimation of the bacterial population. During this period of inhibition, no other volatile organic acids were produced, and the propionic acid concentration decreased proportionally with the theoretical washout curve, thereby suggesting that the organisms producing the volatile organic acids rather than those responsible for their decomposition were inhibited.

A second experiment was performed by McCarty and Brosseau[21] using four digesters, one control and three others spiked with a propionic acid concentration of 3000, 6000, or 8000 mg/L as acetic acid, respectively. The added propionic acid was neutralized to pH 7 using lime. These results indicated that addition of propionic acid resulted in decreased gas production when compared to the control digester. As the added propionic acid concentration increased, longer times were required for the recovery of gas production. This suggested that, because volatile organic acids did not accumulate and gas production declined when propionic acid was added, the introduction of propionic acid inhibited complex organic material degradation to both propionic and acetic acids. This is illustrated as Pathway A in Figure 3. Gas production was reduced because the major substrate source for methanogens, acetic acid, was not produced.

Research by Gorris and coworkers[44] has shown that an increase in organic loading affects propionate conversion more than butyrate conversion. The conversion of propionate was almost completely blocked at acetate concentrations greater than 500 mg/L, strongly inhibited at concentrations of 200 to 500 mg/L of acetate, and moderately inhibited at concentrations less than 200 mg/L of acetate. In addition, efficient propionate degradation only occurred after acetate levels less than 200 mg/L had been maintained for a sufficient time period. This information is consistent with the reports of Kaspar and Wuhrmann[45] in which high acetate concentrations and a high carbon dioxide partial pressure were found to inhibit propionate degradation by acetogenic bacteria.

Research by McCarty and coworkers[18,40] suggested that identification of individual volatile organic acids during upset digestion conditions yields clues as to the reason for the unbalance. An experiment was performed using four six-liter digesters, each fed one of the following acids, along with the necessary inorganic nutrients, as the sole substrate source at the rate of 1 g/l per day: formic acid, acetic acid, propionic acid or butyric acid. The digesters, seeded with strained and diluted (1:1) digested sludge from a municipal digester had a 30-day detention time and were mixed by gas recirculation. After the digesters were operated for a period of at least two months to purge them of a majority of the initial seed material, the substrate additions were suddenly increased to 1.5 g/l per day, which resulted in increased VOA concentrations within the digesters. Daily analysis of volatile organic acids was performed. In addition, 40 ml of active sludge from each digester was removed and mixed with 10 ml of solution containing the sodium salt of the different volatile organic acids in a 125-ml Warburg flask. The gas production from each acid salt was then measured manometrically. The results of this experiment are shown in Figure 4. These results indicated that the formic acid sludge, the sludge developed on formic acid, was not able to use any other acids. A sudden increase in formic acid concentration resulted in a rapid increase in its utilization and essentially no buildup of volatile organic acids. Formic acid was also found to be rapidly utilized by all four sludges developed in this experiment, however, no formic acid was ever detected in the volatile organic acids obtained from the digestion units. These results indicated that either formic acid was an important

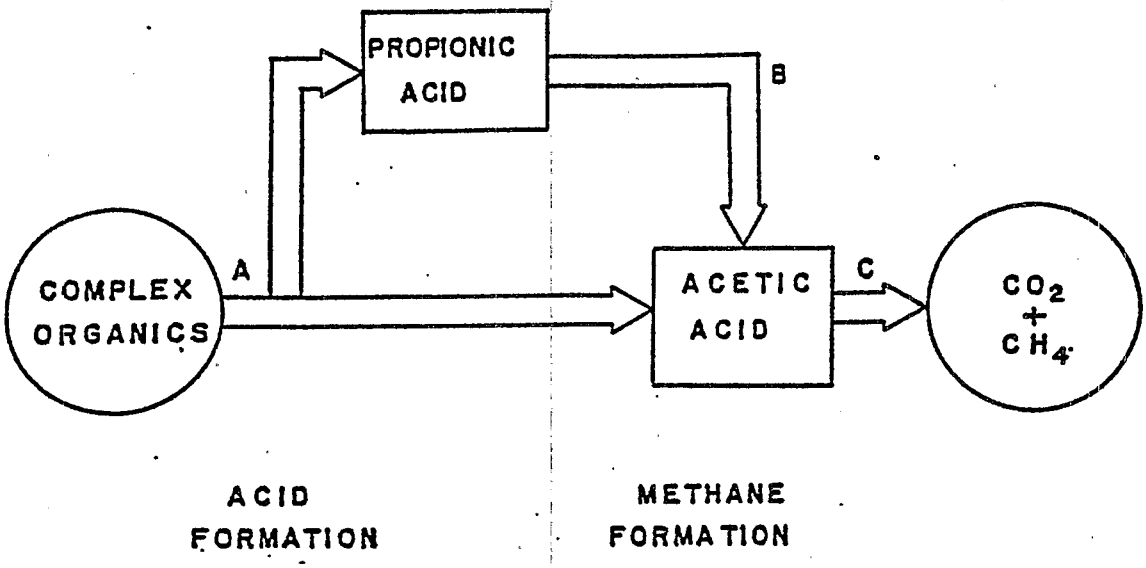


Figure 3. Generalized Pathways of Anaerobic Treatment of Complex Wastes.[21]

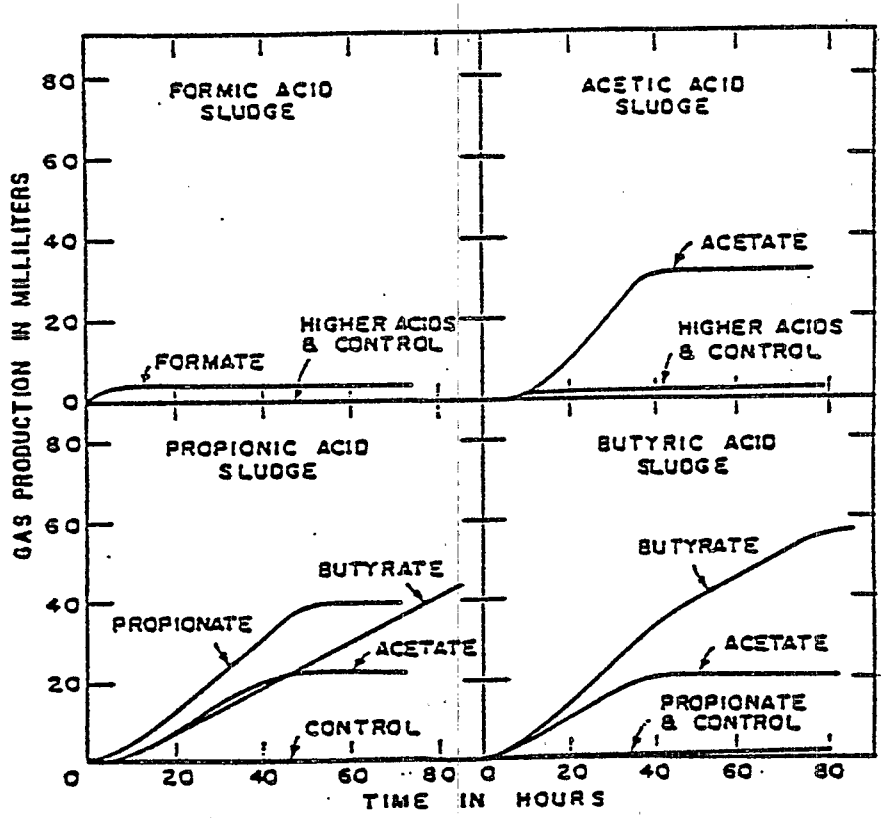


Figure 4. Volatile Acid Utilization by Volatile Acid Sludges.[40]

intermediate in the methane fermentation of all substrates and is readily fermented under most conditions, or sludge adapted to all other substrates was simultaneously adapted to formic acid.

The results also indicated that acetic acid sludge could only utilize formic acid and acetic acid. A sudden increase in the acetic acid concentration produced a gradual buildup of acetic acid. In addition, propionic acid sludge not only had the ability to ferment propionic acid, the intermediate acetic acid, and formic acid, but was also able to ferment butyric acid at a high rate. Moreover, all higher volatile organic acids through caproic acid could be utilized at a rate less than butyric acid. A sudden increase in the propionic acid concentration yielded not only a buildup of propionic and acetic acids, but several higher acids from butyric through caproic as well. These latter results are shown in Figure 5. When the propionic acid feed to the digester was reduced to the original rate of 1 g/l per day, the volatile organic acid concentration decreased and the higher acids disappeared.

Figure 5 also indicates that the butyric acid sludge was capable of utilizing all even-carbon volatile organic acids, but not propionic acid. Valeric acid, a five-carbon acid, was studied and found to split into acetic and propionic acids. The acetic acid was further fermented, while the propionic acid remained in solution. The six- and eight-carbon volatile organic acids were utilized at a lower rate than butyric acid. An increase in the butyric acid concentration in the digester yielded a buildup of butyric and acetic acids, as well as the next higher even-numbered-carbon acid, caproic (hexanoic) acid.

The combined results of these experiments indicated that, in the case of propionic and butyric acids, at high volatile organic acid concentrations, not only did the acids appear which are believed to be major intermediates, but also other "side acids" were formed.[18,40] These "side acids" were considered produced during the conversion of the major acids and occurred in lower concentrations than the primary acids. It was speculated that the reason butyric acid was utilized by propionic acid sludge was because butyric acid was also synthesized by propionic acid sludge. Moreover, during propionic acid fermentation, the synthesis of all higher acids through caproic acid was explained as synthesis of combinations of propionic acid and acetic acid, i.e., butyric acid can be formed by joining two acetic acid molecules, valeric acid is composed of one propionic acid and one acetic acid molecule, and caproic acid can be synthesized by joining either two propionic acid molecules or three acetic acid molecules.

A second experiment was performed by McCarty and coworkers[18,40] in which sludges were developed on octanoic and palmitic acids to represent intermediate- and long-chain volatile organic acids, respectively; glucose, starch and cellulose to represent carbohydrates of differing complexity; nutrient broth and leucine to represent proteinaceous material; and sewage sludge to represent a complex organic mixture. The organic loading to the digesters varied from 0.3 to 1.0 g/l per day, and the digesters were operated on a batch basis with a 15-day detention time and had approximately 0.75-1 capacity. An analysis procedure similar to that used in the previously described experiment by the same researchers was employed.

Fermentation of the 8-carbon octanoic acid and 16-carbon palmitic acid are shown in Figure 6. These acids were degraded by β-oxidation into other even-carbon volatile organic acids. All of the even-numbered-carbon volatile organic acids produced were fermented at a rate slower than butyric acid.

The results of the carbohydrate sludges are shown in Figure 7 along with the results of ethyl alcohol, which is a common intermediate in carbohydrate fermentation. The results for the three carbohydrates are very similar, and the relative rates of acetic and propionic acid utilization were much the same. The rapid utilization of butyric acid by the starch and cellulose sludges possibly signified that butyric acid is a significant intermediate in carbohydrate

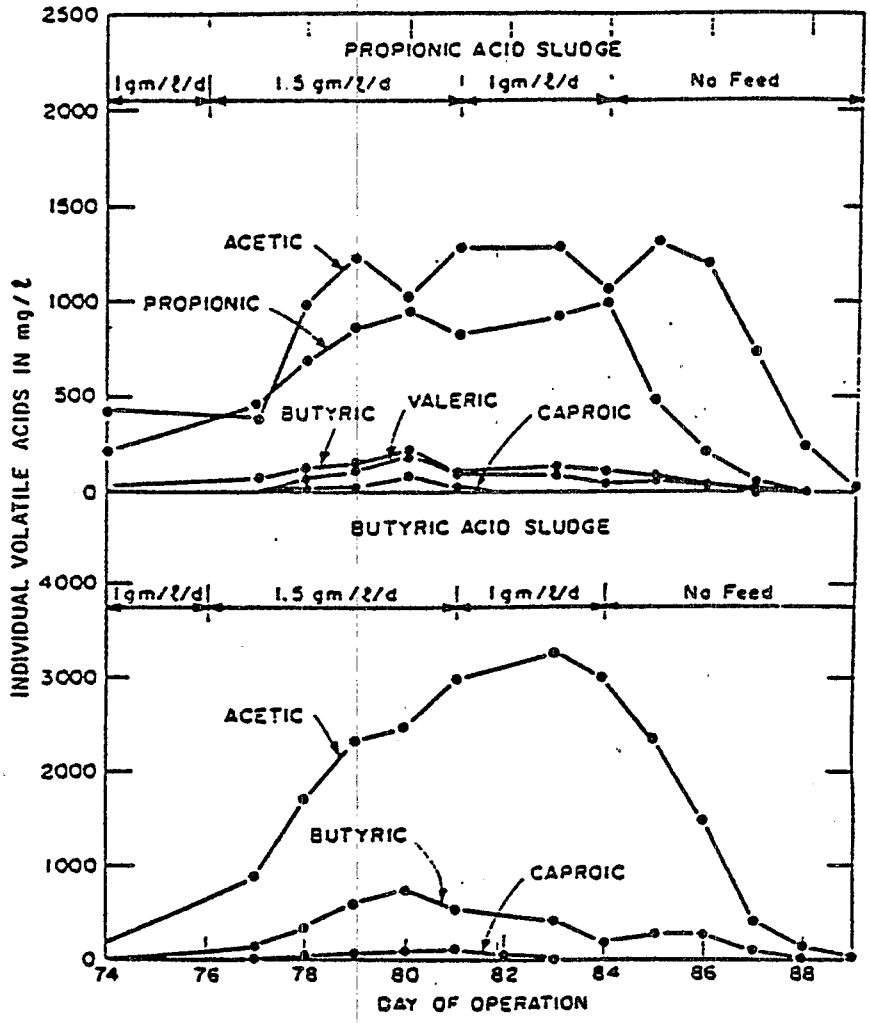


Figure 5. Volatile Acid Formation During Excessive Loading of Propionic and Butyric Acids.[40]

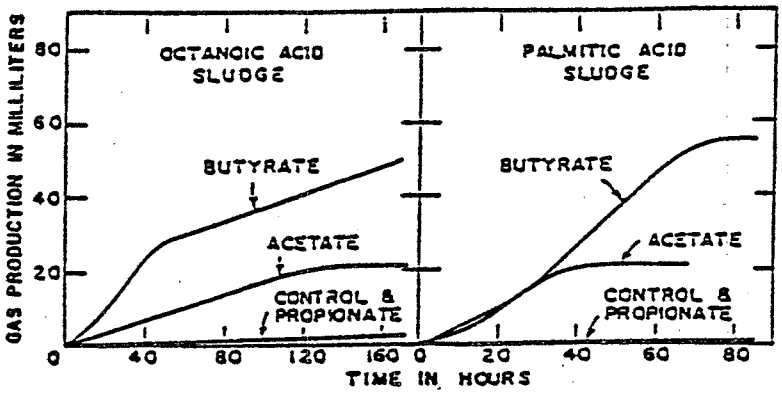


Figure 6. Volatile Acid Utilization by Fatty Acid Sludges.[40]

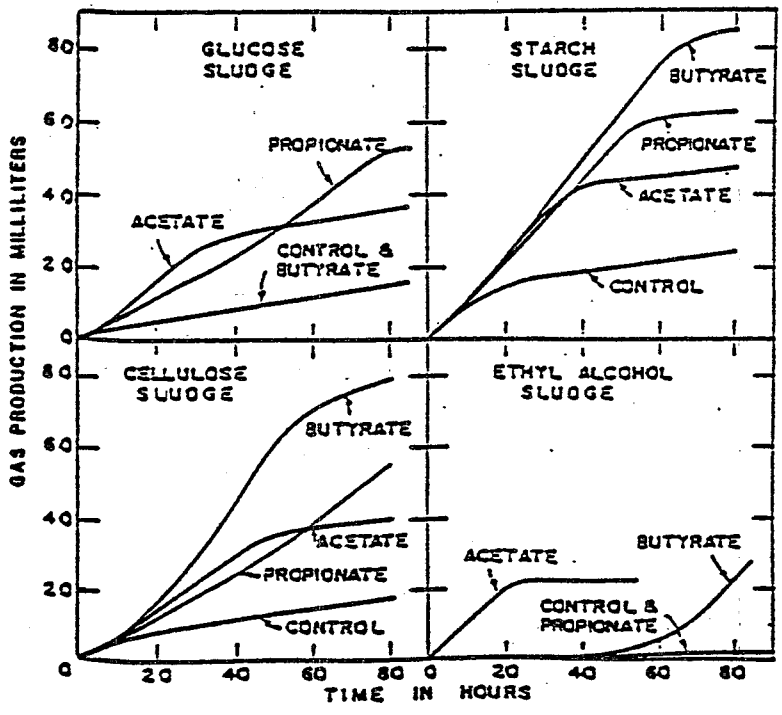


Figure 7. Volatile Acid Utilization by Carbohydrate Sludges.[40]

fermentation. However, no utilization of butyric acid was found to occur in the glucose sludge. These results were contradictory to the studies on propionic acid sludge, but the glucose sludge exception may have been the result of the presence of different propionic acid organisms in the glucose digester than in the starch, cellulose and propionic acid sludge digesters. Thus, the authors concluded that butyric acid and higher acids are not important in carbohydrate metabolism, and acetic and propionic acids are the major acids formed from carbohydrate fermentation.

Figure 8 shows the results for the protein sludges. Acetic acid was the primary acid formed in protein degradation. The butyric acid utilization rate was also quite rapid, perhaps suggesting the importance of ß-oxidation in converting amino acids to acetic acid. Propionic acid was also utilized at a lower rate than acetic acid or butyric acid, suggesting that propionic acid may be formed as an intermediate in the degradation of odd-numbered-carbon amino acids present in proteins.

The results for the digested sewage sludge are presented in Figure 9. The relative rates of utilization of acetic and propionic acids were similar to those determined for the protein sludges. However, the butyric acid utilization started slowly and increased significantly after about two days. Valeric and caproic acids were also utilized by this sludge.

Figure 10 shows the combined results of both experiments. The acids present in the various sludges are indicated by circles. Those acids that frequently occurred as major acids are indicated by large circles, and those which appeared, but always in lower concentrations as "side acids", are indicated with small circles. If an acid was utilized by the sludge as well, the circle was shaded. In most cases, acids found were also utilized, and acids which were not found were not utilized. The main volatile organic acid intermediates formed during methane fermentation of proteins, carbohydrates and fats are illustrated in Figure 11.

McCarty and coworkers concluded the following:[18,40] acetic and propionic acids are the most important volatile acids frequently occurring under unbalanced digestion conditions; acetic acid is the most prevalent volatile acid formed during the methane fermentation of carbohydrates, proteins and fats; propionic acid is an important intermediate acid formed during the methane fermentation of carbohydrates and proteins; other minor volatile acids frequently occur in low concentrations as a result of backup or side biochemical reactions, but are an unimportant result of upset conditions; formic acid is utilized rapidly by sludges developed on many different substrates, but usually is not present in high concentrations during upset conditions; and butyric acid is utilized rapidly by most sludges, but probably does not occur as a true volatile acid intermediate in methane fermentation. Experiments indicated that whenever β-oxidation is involved in substrate degradation, and in some cases where it is not (propionic acid fermentation), butyric acid was utilized. Therefore, the fact that butyric acid may be utilized by a sludge cannot be considered evidence indicating that butyric acid is a true intermediate.[18,40]

Research has also suggested that the oxidation-reduction potential of an anaerobic system affects the type of volatile organic acids present. Guenzi and Beard[46] studied the VOA concentration in a cattle manure slurry as a function of oxidation-reduction potential (E_h). The controlled redox system was sequentially lowered in 100 mV increments from +300 to -200 mV, and the desired E_h was maintained by titrating with oxygen. Pure oxygen was used to maintain the E_h at +300 and +200 mV, 20% oxygen was used to maintain the E_h at +100 mV, and 0.5% oxygen was used to maintain the E_h at 0, -100, and -200 mV. The experiment was conducted at a temperature of 35°C. Individual volatile acid concentrations of the suspensions were determined and are presented in Table 11. After a 7-day incubation period at +300 mV E_h, acetic acid was the only acid detected. As the oxidation-reduction potential was lowered to -100 mV, acetic acid concentrations increased and propionic acid was detected followed by iso-butyric acid. When the

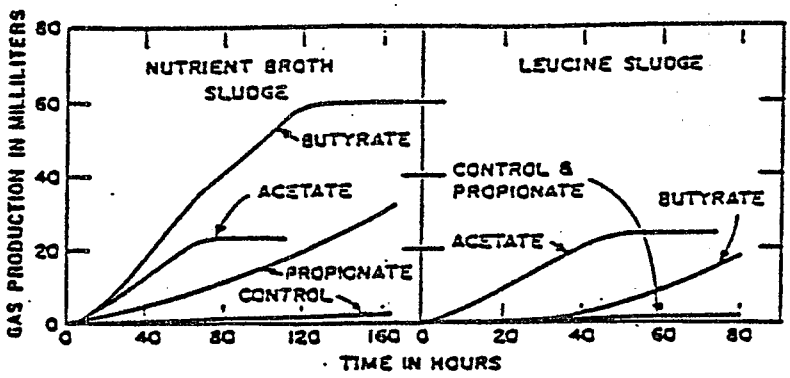


Figure 8. Volatile Acid Utilization by Protein Sludges.[40]

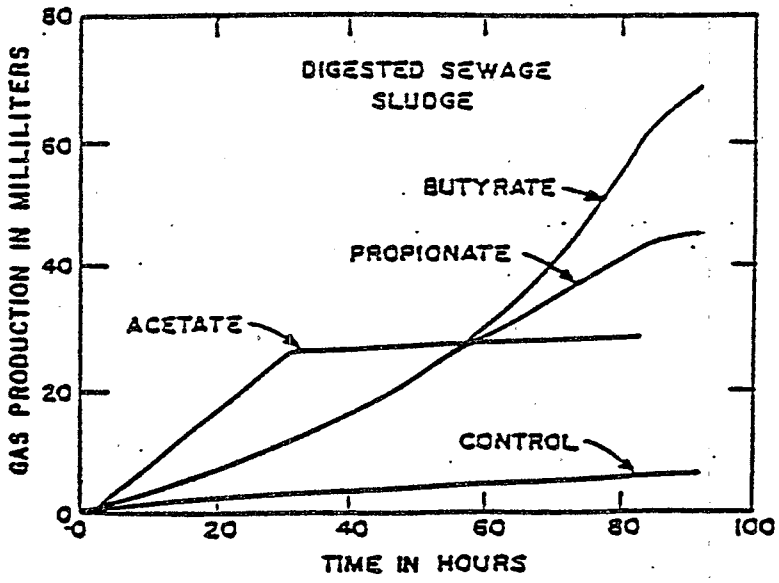


Figure 9. Volatile Acid Utilization by Sewage Sludge.[40]

TYPE OF SLUDGE	ACETIC	PROPIONIC	BUTYRIC	HIGHER
Fatty Acids				
Acetic	●			
Propionic	●	●	●	●
Butyric	●		●	●
Octanoic	●		●	●
Palmitic	●		●	●
Proteins				
Nutrient Broth	●	●	●	●
Leucine	●			○
Carbohydrates				
Glucose	●	●	○	○
Starch	●	●	●	●
Cellulose	●	●	●	●
Ethyl Alcohol	●			

Key: •Present as Major Acid •Present as Minor Acid
Shaded Circles - Acid Utilized by Sludge

Figure 10. Volatile Acids Formed during Digester Unbalance Compared with Those Utilized by Sludges.[40]

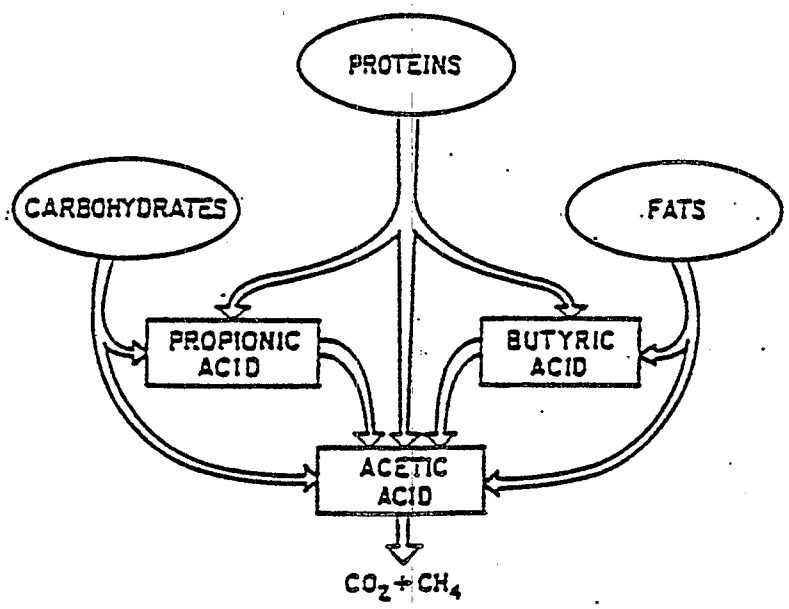


Figure 11. Volatile Acid Intermediate in Methane Fermentation of Proteins, Carbohydrates and Fate.[40]

TABLE 11. FREE VOLATILE ORGANIC ACID CONCENTRATIONS IN A MANURE SLURRY WITH CONTROLLED OXIDATION-REDUCTION POTENTIALS[46]

Time (Days)	ORP (E_h, mV)	Acetic Acid (mg/g)[a]	Propionic Acid (mg/g)[a]	Iso-Butyric Acid (mg/g)[a]	Butyric Acid (mg/g)[a]
1 hr	+300	3.82	0.40	0.05	0.63
7	+300	0.40	-[b]	-	-
8	+200	0.35	-	-	-
14	+200	0.18	-	-	-
15	+100	0.19	-	-	-
21	+100	0.16	-	-	-
22	0	0.17	-	-	-
28	0	0.16	-	-	-
29	-100	0.54	0.07	-	-
35	-100	2.46	0.30	0.07	-
36	-200	2.98	0.34	0.08	0.02
42	-200	9.12	1.16	0.12	0.09
45	-200	19.30	2.30	0.09	0.21

Note: [a](mg of acid)/(g of manure)
[b]None detected.

redox potential reached -200 mV, butyric acid was detected, and acetic, propionic, butyric and iso-butyric acids accumulated in that order, respectively. The rate of acid formation was considerably higher at -200 mV than -100 mV, except for iso-butyric acid which began forming at -100 mV E_h to -200 mV E_h, but remained consistently low. Decreasing the oxidation-reduction potential to around -300 mV would promote the conversion of volatile organic acids to methane and carbon dioxide.

2.5.3 Methanogenesis

Methane fermentation occurs by two primary mechanisms: cleavage of acetic acid to yield methane and carbon dioxide; and the reduction of carbon dioxide using hydrogen as the energy source. Research has shown that approximately 70 to 73% of the methane produced comes from acetate cleavage, and the remaining 27 to 30% originates from carbon dioxide reduction.[12,41,47-49] Table 10 and Figure 2 indicate the chemical transformations that occur and the generalized pathways for methane fermentation of complex wastes, respectively. As indicated in Table 10, one mole of methane gas is formed from one mole of acetic acid, and one mole of carbon dioxide produces one mole of methane gas. Research suggests that hydrogen-utilizing methanogens are more numerous than acetic acid-utilizing methanogens,[49] although a greater amount of methane is formed via acetic acid cleavage. In addition, the formation of methane by acetic acid is less energetically favorable than methane formation from carbon dioxide, as indicated by the comparison of ΔG values presented in Table 12.

According to Smith and Mah,[49] acetic acid is metabolized by an organism not involved in its production, as evidenced by the large extracellular pool and rapid turnover rate. Therefore, methane production is a function of the community of organisms involved in waste conversion, not just the actual methanogens. Within this consortia of organisms, some require symbiotic relationships for growth and proliferation.

TABLE 12. REDOX HALF-REACTIONS RESPONSIBLE FOR DEGRADATION OF SELECTED ORGANICS DURING ANAEROBIC TREATMENT[50]

Oxidations (electron donating reactions)[a]		ΔG_o (kJ)
Propionate ⇌ Acetate	$CH_3CH_2COO^- + 3H_2O \rightleftharpoons CH_3COO^- + H^+ + HCO_3^- + 3H_2$	+76.1
Butyrate ⇌ Acetate	$CH_3CH_2CH_2COO^- + 2H_2O \rightleftharpoons 2CH_3COO^- + H^+ + 2H_2$	+48.1
Ethanol ⇌ Acetate	$CH_3CH_2OH + H_2O \rightleftharpoons CH_3COO^- + H^+ + 2H_2$	+9.6
Lactate ⇌ Acetate	$CH_3CHOHCOO^- + 2H_2O \rightleftharpoons CH_3COO^- + HCO_3^- + H^+ + 2H_2$	-4.2
Acetate ⇌ Methane	$CH_3COO^- + H_2O \rightleftharpoons HCO_3^- + CH_4$	-31.0
Reductions (electron accepting reactions)[a]		
HCO_3^- ⇌ Acetate	$2HCO_3^- + 4H_2 + H^+ \rightleftharpoons CH_3COO^- + 4H_2O$	-104.6
HCO_3^- ⇌ Methane	$HCO_3^- + 4H_2 + H^+ \rightleftharpoons CH_4 + 3H_2O$	-135.6
Sulfate ⇌ Sulfide	$SO_4^= + 4H_2 + H^+ \rightleftharpoons HS^- + 4H_2O$	-151.9
	$CH_3COO^- + SO_4^= + H^+ \rightleftharpoons 2HCO_3^- + H_2S$	-59.9
Nitrate ⇌ Ammonia	$NO_3^- + 4H_2 + 2H^+ \rightleftharpoons NH_4^+ + 3H_2O$	-599.6
	$CH_3COO^- + NO_3^- + H^+ + H_2O \rightleftharpoons 2HCO_3^- + NH_4^+$	-511.4
Nitrate ⇌ Nitrogen gas	$2NO_3^- + 5H_2 + 2H^+ \rightleftharpoons N_2 + 6H_2O$	-1120.5

Note: [a]pH 7, 1 atm, 1 kg/mol activity

2.6 THE EFFECTS OF HYDROGEN ON ANAEROBIC STABILIZATION

Hydrogen is produced by acidogenic and acetogenic microorganisms present in anaerobic systems, and is used by methanogens during carbon dioxide reduction to methane. Although methane production from hydrogen is not the rate limiting step in complex waste conversion,[47] this process is crucial because the partial pressure of hydrogen must be maintained at values low enough to permit otherwise thermodynamically unfavorable reactions to occur. Some redox half-reactions are presented in Table 12 and suggest that the degradation of propionate and butyrate is energetically unfavorable at high hydrogen partial pressures.[50,51] Harper and Pohland[50] demonstrated that hydrogen at partial pressures greater than 10^{-4} atmospheres leads to accumulations of propionic and butyric acids, and inhibits their oxidation by obligate hydrogen-producing acetogens.

As reported by Smith and McCarty,[52] longer-chained volatile organic acids were produced when a continuously stirred tank reactor (CSTR) was perturbed with hydrogenic substrate. The hydrogen partial pressure increased due to the rapid utilization of the high-energy substrate, causing the formation of longer-chained volatile organic acids to become thermodynamically favorable. Smith and McCarty[52] also found that when the partial pressure of hydrogen declined, the direction of the equilibrium changed to again favor β-oxidation and the dissipation of longer-chained volatile organic acids. The longer-chained volatile organic acids produced may be a normal catabolic product of an organism present at low concentrations that multiplies rapidly when perturbation creates favorable growth conditions. The same researchers found that high molecular weight volatile organic acids were not formed in perturbed acetate enrichments, because hydrogen is not liberated during acetate cleavage.[52]

Kaspar and Wuhrmann[47] observed that an increase in the hydrogen partial pressure caused a linear accumulation of propionate and an accelerated decrease in acetate concentrations. Heyes and Hall[51] indicated that hydrogen affects the distribution of acids produced from glucose by inhibiting the formation of H_2 from NADH. This concept was also presented by Mosey,[53] as shown in Figure 12. When this reaction is inhibited, acidogens form more propionate and butyrate as electron sinks. Acidogens still produce hydrogen even when the NADH reaction is inhibited by the cleavage of ferredoxin and pyruvate.

Harper and Pohland[50] have reported that only two types of methanogens have been proven capable of acetate cleavage. These include the hydrogen-oxidizing aceticlastic methanogens (HOA) and the non-hydrogen-oxidizing aceticlastic methanogens (NHOA). HOA are apparently capable of three times the acetate utilization rate of NHOA at acetate concentrations above several hundred mg/L. Also, at hydrogen partial pressures greater than 10^{-4} atm, HOA use hydrogen and carbon dioxide in favor of acetate, whereas acetate cleavage by NHOA is unaffected by hydrogen partial pressure.

Research has shown that both sulfate- and nitrate-reducing bacteria, present in anaerobic systems, compete with methanogens for hydrogen and acetic acid.[50,54] Nitrate reduction is the most energetically favorable reaction, followed by sulfate reduction and, lastly, methane formation from both acetic acid cleavage and carbon dioxide reduction.[50,54]

Boone and coworkers[55] suggest that formate, not H_2, is used by some hydrogen-utilizing methanogens for the reduction of carbon dioxide to methane, and thus may be an important factor in mechanisms regulating the symbiotic relationships between anaerobic microorganisms. In most of the co-cultures studied, the methanogenic partner was able to utilize either formate or hydrogen as the electron acceptor, therefore, it is not clear which is the interspecies electron carrier. Free energy changes for syntropic propionate and butyrate oxidation coupled to methanogens via interspecies hydrogen or formate transfer are shown in Table 13. Boone and coworkers[55] calculated the potential hydrogen and formate diffusion between microbes and found that at hydrogen concentrations

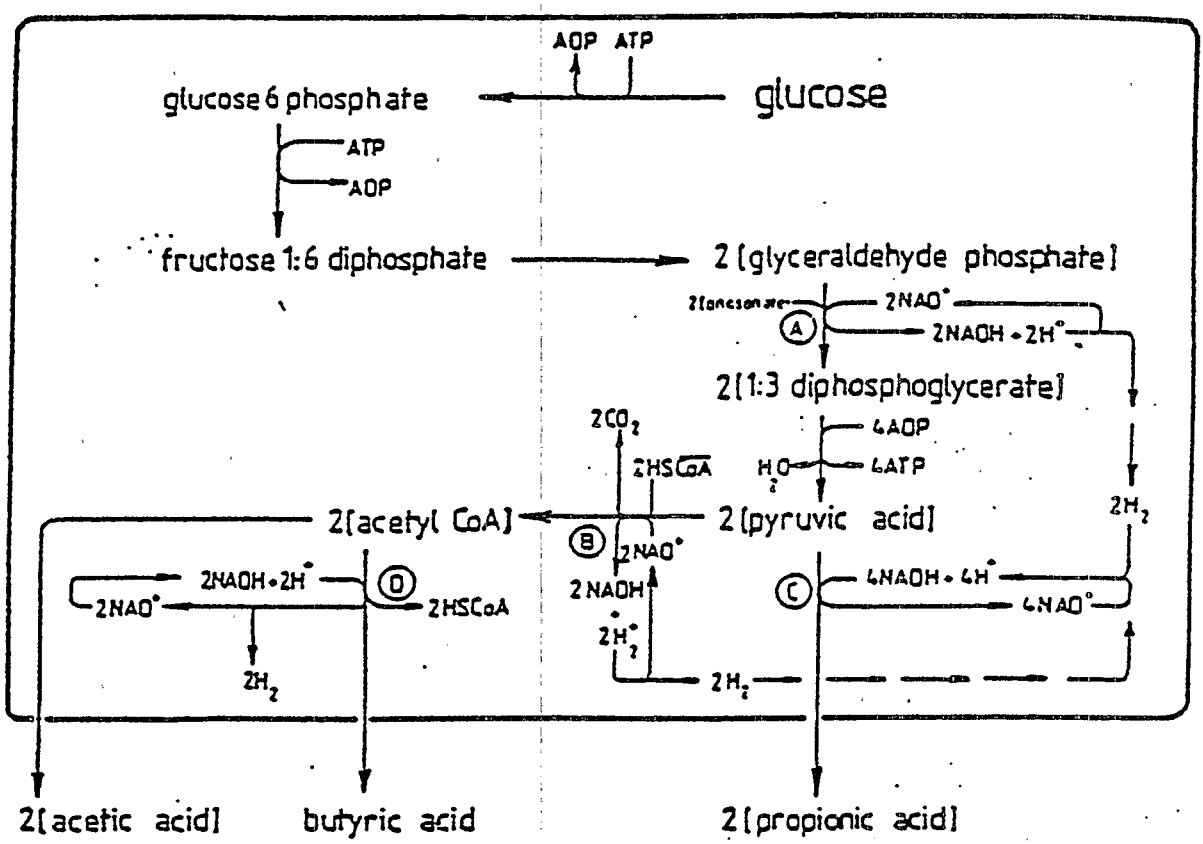


Figure 12. Glycolytic Pathway for Glucose Metabolism.[53]

TABLE 13. FREE-ENERGY CHANGES FOR SYNTROPHIC PROPIIONATE AND BUTYRATE OXIDATION COUPLED TO METHANOGENS VIA INTERSPECIES H_2 OR FORMATE TRANSFER[55]

Reactions	Equation	KJ/reaction
H_2 transfer		
(i) Methanogenesis	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	-130.747
(ii) Propionate oxidation	$CH_3CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CO_2 + 3H_2$	71.667
(iii) Butyrate oxidation	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	48.296
Formate transfer		
(iv) Methanogenesis	$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$	-144.543
(v) Propionate oxidation	$CH_3CH_2COO^- + 2H_2O + 2CO_2 \rightarrow CH_3COO^- + 3HCOO^- + 3H^+$	82.014
(vi) Butyrate oxidation	$CH_3CH_2CHH_2COO^- + 2HCO_3^- \rightarrow 2CH_3COO + H^+ + 2HCOO^-$	55.194
Net		
I + II or iv + v (Methanogenesis from propionate)	$CH_3CH_2COO^- + \frac{1}{2}H_2O \rightarrow CH_3COO^- + \frac{3}{4}CH_4 + \frac{1}{4}CO_2$	-26.393
I + III or iv + vi (Methanogenesis from butyrate)	$CH_3CH_2CH_2COO^- + H_2O + \frac{1}{2}CO_2 \rightarrow 2CH_3COO^- + H^+ + \frac{1}{2}CH_4$	-17.078

Calculated for a temperature of 37°C from free energies of formation from the elements.

commonly found in nature, hydrogen could not diffuse rapidly enough to dispersed methanogenic bacteria to account for the rate of methane synthesis, however, formate could.

2.7 THE EFFECTS OF HEAVY METALS ON METHANE PRODUCTION AND HYDROGEN LEVELS

Hickey and coworkers[56] found that the addition of heavy metals to an anaerobic system inhibited methane production. This decrease in methane production was not considered necessarily indicative of inhibition of the methanogens, because an accompanying buildup of volatile organic acids at levels greater than the control was not observed. These results suggested that the added heavy metals interrupted the substrate flow at other points in the complex waste degradation sequence other than the terminal or methanogenic reaction. Hickey and coworkers[56] also observed that samples inhibited by heavy metals showed a decreased rate of hydrogen accumulation in the headspace with increased inhibition of methane production. When complete inhibition of methane production occurred, no hydrogen accumulated in the headspace, thus, other organisms involved in the conversion of complex waste to methane were at least as severely inhibited as the methanogens. Because the decrease in methane production rate was not accompanied by a concomitant accumulation of volatile organic acids, it could be presumed that either all acetic acid produced was consumed, or no acetic acid was produced. This suggested that the acetate catabolizing population was inhibited by the added heavy metals. Thus, the authors postulated that the reduced hydrogen accumulation was a consequence of the added heavy metals serving as electron acceptors.

Hickey and coworkers[56] also indicated that the most significant consideration of heavy metal toxicity is the operating solids level. Higher total or volatile solids yielded better protection from heavy metal toxicity, because heavy metals could be bound by ligands contained on the cell membrane and extracellular polymer matrix. Complexation of heavy metals in the aqueous phase by soluble ligands and sulfides is a major factor determining the level of inhibition that occurs, as discussed previously in Section 2.2.2.

Collectively, these citations provide a basis for examining and understanding the microbially-mediated anaerobic processes of waste stabilization with intermediate formation and gas production in the landfill environment, a natural system analogous to controlled anaerobic digestion systems. Therefore, application of principles of understanding drawn from these processes should benefit the diagnosis and further development of controlled landfill systems.

SECTION 3

MATERIALS AND METHODS

The process of landfill stabilization, including concomitant changes in leachate and gas quantity and quality, was investigated under controlled operating conditions with simulated landfills columns constructed at the Georgia Institute of Technology. In order to assess the progression of the microbially-mediated stabilization events, 10 pilot-scale simulated landfill columns were prepared and operated as identical pairs. Five columns were operated in the single pass leaching mode, and the remaining five columns were operated with leachate containment, collection and recirculation.

All five pairs received equal quantities of shredded municipal refuse. One pair of columns (one single pass and one recycle) served as controls and received only shredded municipal solid waste. The remaining four pairs received equal amounts of selected organic priority pollutants. Three pairs of columns containing organic pollutants also received incremental loadings of heavy metals. The organic and inorganic priority pollutants were chosen to be representative of common toxic substances that may be codisposed with municipal solid waste in a sanitary landfill. Table 14 summarizes the loading and operation of the ten simulated landfill columns.

3.1 SIMULATED LANDFILL DESIGN

The design features characteristic of the single pass and recycle simulated landfill columns are presented in Figures 13 and 14, respectively.

3.1.1 Steel Jacket

The simulated landfill columns were fabricated using two sections of 3-mm (1/8-inch, 20-gauge) cold-rolled steel. The lower sections had been previously used in landfill experiments at the Waterways Experiment Station (Vicksburg, MS), and the upper sections were specially constructed to match and extend the lower sections. The lower sections consisted of a 1.83-m (6-ft) long cylinder with a diameter of 0.9-m (3-ft) and a curved bottom mounted on 0.6-m (2-ft) long legs. The legs were fabricated from 7.6-cm (3-in) angle iron with 6-mm (0.25-in) base plates, 100mm (4-in) square. A coal tar-base paint had been applied to the interior of the lower sections to prevent corrosion and/or leaching from the column surface. The upper column sections were 0.9-m (3-ft) diameter cylinders, 1.2-m (4-ft) long. The interiors of the upper sections were not painted.

The upper and lower column segments were joined together by bolting through the angle iron flanges contained on each piece. A coating of silicone rubber sealant was applied to the interior and exterior of the flanged joint, as well as between the iron flanges prior to bolting, to ensure that the junction would be water and gas tight.

A 5-cm (2-in) diameter hole at the center of the bottom of each column facilitated the installation of a leachate collection pipe. A 0.9-cm (3/8-in) bulkhead fitting was attached to the column bottom and served as a leak detection system for the high density polyethylene (HDPE) liner that was installed in each column as described in Section 3.1.6. (After column operation had begun, the HDPE liners were found to be leaking at the heat-welded seams joining the flat bottom to the cylindrical body of the liner. As a result, the 0.9-cm (3/8-in)

TABLE 14. SIMULATED LANDFILL COLUMN LOADING AND OPERATION

Column Number	Column Identity[a]	Operation	Organics	Inorganics
1	CR	Recycle	No	No
2	CS	Single Pass	No	No
3	OS	Single Pass	Yes	No
4	OLS	Single Pass	Yes	Low
5	OMS	Single Pass	Yes	Medium
6	OR	Recycle	Yes	No
7	OLR	Recycle	Yes	Low
8	OHS	Single Pass	Yes	High
9	OMR	Recycle	Yes	Medium
10	OHR	Recycle	Yes	High

Note: [a]Column Identity
- CR Control, Recycle
- CS Control, Single Pass
- OS Organics, Single Pass
- OLS Organics, Low Inorganics, Single Pass
- OMS Organics, Medium Inorganics, Single Pass
- OR Organics, Recycle
- OLR Organics, Low Inorganics, Recycle
- OHS Organics, High Inorganics, Single Pass
- OMR Organics, Medium Inorganics, Recycle
- OHR Organics, High Inorganics, Recycle

bulkhead fitting was connected directly to the leachate sampling system by means of a 0.9-cm (3/8-in) polypropylene tube to permit the collection of leachate from above the HDPE liner as well as between the liner bottom and steel column jacket.)

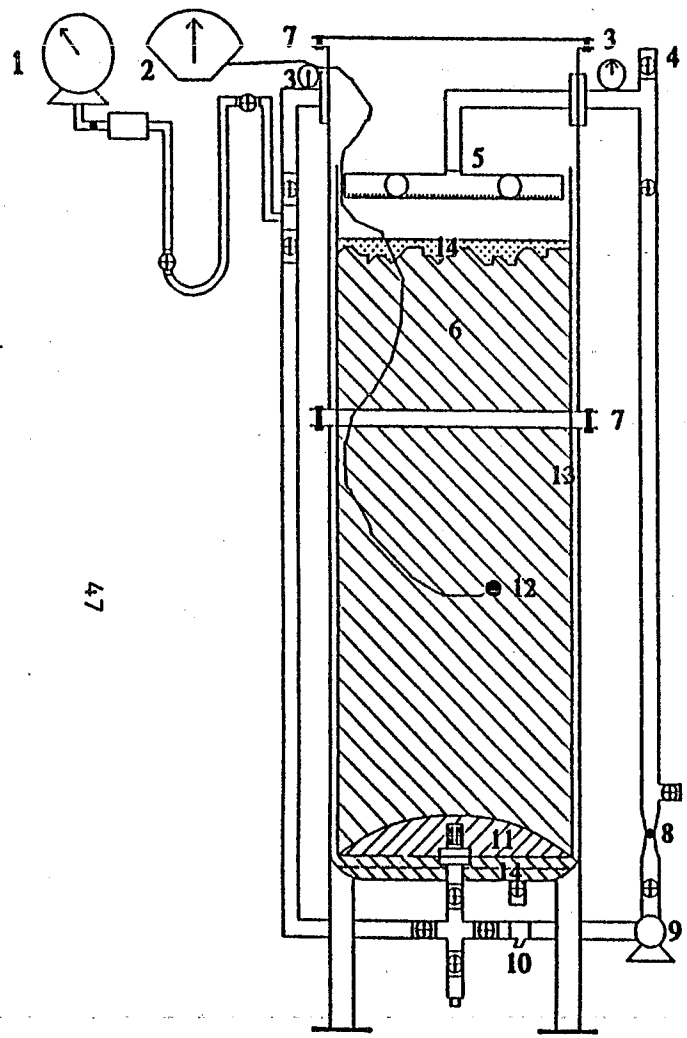
3.1.2 Liquid Addition/Distribution System

The single pass columns were designed to permit the addition of water directly to an internal distribution system through a 2.5-cm (1-in) PVC ball valve. The liquid distribution system was comprised of a six-armed pipe array and was constructed of 3.8-cm (1.5-in) perforated PVC pipe containing 0.9-cm (0.375-in) holes.

The recycle columns contained the same liquid distribution system as the single pass columns, with the exception that a leachate recirculation pump was joined to the liquid addition system by a 2.5-cm (1-in) PVC ball valve, a section of 2.5-cm (1-in) PVC pipe, and a one-way check valve to prevent the backwards flow of leachate. The leachate recirculation pump was also connected to the leachate sampling/collection system as described in Section 3.1.4.

3.1.3 Leachate Recirculation System

The leachate recirculation system included a liquid addition/distribution system, a leachate recirculation pump, a site glass system, and a leachate sampling/collection system. The site glass system consisted of a 2.5-cm (1-in)



1 Gas Meter
2 Temperature Readout
3 Pressure Guage
4 Ball Valve
5 Leachate/Water Distributor
6 Shredded Municipal Refuse
7 Silicone Sealed Bolted Joint
8 Check Valve
9 Recycle Pump
10 In-line Strainer
11 Gravel Underdrain
12 Thermistor
13 30 mil HDPE Lining
14 Gravel

Figure 13. Recycle Simulated Landfill Column.

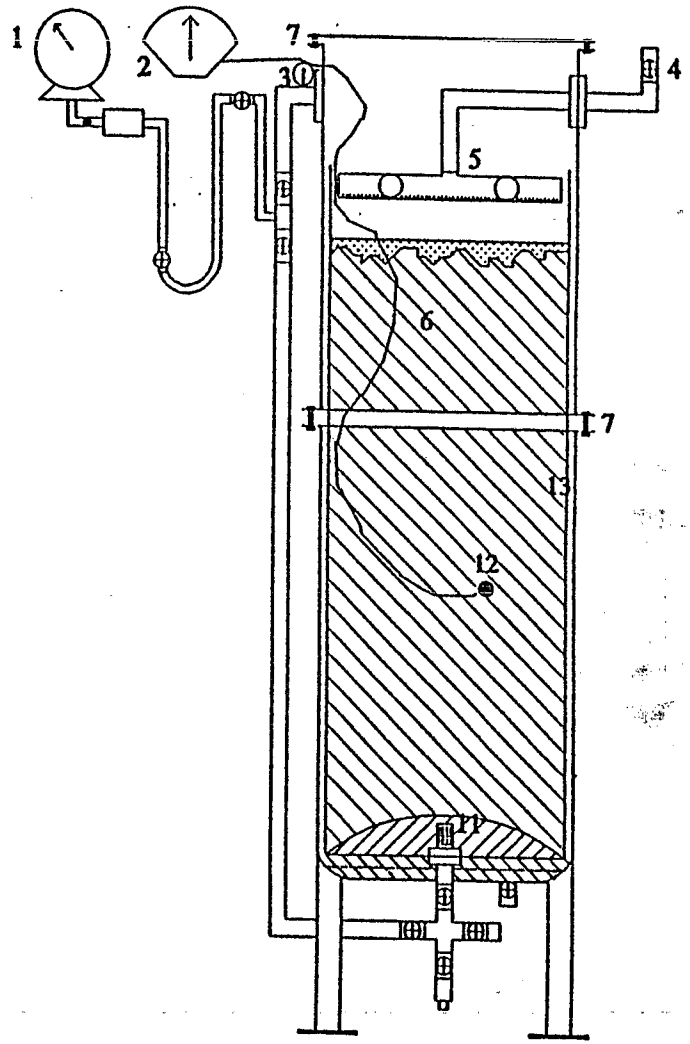


Figure 14. Single Pass Simulated Landfill Column.

transparent PVC pipe connecting the leachate sampling/collection system and gas measuring/sampling system. The site glass was used for determining leachate volume within the column, and was equipped with a liquid level controller that could be used to automatically recirculate leachate as it accumulated. The leachate recirculation pump was equipped with a 1.9-cm (0.75-in) PVC in-line strainer, mounted on the intake side to protect the pump from any abrasive particles that may be contained within the leachate.

3.1.4 Leachate Sampling/Collection System

The leachate sampling/collection system consisted of four 2.5-cm (1-in) ball valves connected to a 2.5-cm (1-in) PVC cross. The first ball valve was connected to the leachate collection system and served to isolate the external piping system from the internal leachate collection system if repairs and/or modifications were necessary; the second ball valve was used to facilitate the collection of leachate samples for analysis; and the third ball valve was connected to the site glass system previously described. A fourth ball valve was attached to the leachate recirculation pump on the recycle columns and was not functional on the single pass columns.

3.1.5 Gas Measuring/Sampling System

The gas measuring/sampling system was connected to a set of PVC flanges located at the top of the column by a 6-mm (0.25-in) tube fitting mounted between two, 25-cm (1-in) PVC ball valves. The tube fitting was attached to a tee fitting. One arm of this tee fitting was used as a sampling port, and the second arm was connected to a water-sealed U-tube to prevent air from entering the column head space. The water-sealed U-tube was connected to a volumetric gas meter.

3.1.6 HDPE Liner

High density polyethylene (HDPE) liners of 40-mil thickness (Poly-America, Inc.) were specially fabricated in a cylindrical shape with a heat-welded flat bottom to facilitate leachate containment and eventual refuse removal and analysis at the conclusion of these investigations. The liner also served to prevent direct contact between the refuse/leachate mass and the interior of the steel column jacket. The bottom center of the HDPE liner was fitted with a section of 3.8-cm (1.5-in) PVC pipe mounted on flanges both inside and outside of the HDPE liner. The 46-cm (18-in) outer pipe section penetrated the opening in the steel jacket and permitted the transfer of leachate to the leachate sampling/collection system. A 10-cm (4-in) long inner PVC pipe section was perforated with 0.6-cm (0.25-in) holes and equipped with a cap at the upper end to facilitate the collection of leachate from within the column.

3.1.7 HDPE Liner Placement

Each steel column was filled to a depth of 30 cm (12 in) from the bottom with washed 1.9-cm (0.75-in) gravel. A circular piece of geotextile, followed by a 1.3-cm (0.5-in) layer of sand and a second sheet of geotextile, was placed upon the gravel to prevent the HDPE liner from directly contacting the gravel. The cylindrical HDPE liner and leachate collection pipe were then placed inside the steel column jacket. A circular sheet of geotextile, followed by a 1.3-cm (0.5-in) layer of sand and a second piece of geotextile, was placed within the HDPE liner. In order to protect the base of the liner from direct refuse contact and to prevent clogging of the leachate collection pipe by the shredded municipal refuse, a layer of 0.6-cm (0.25-in) washed pea gravel was placed above the uppermost geotextile sheet in sufficient quantity to completely cover the perforated leachate collection pipe. The depth of gravel in the center of the liner was approximately 10 cm (4 in) and tapered to a depth of 5 cm (2 in) at the perimeter.

3.2 SIMULATED LANDFILL LOADING

Shredded municipal refuse, primarily of residential origin, was obtained from the DeKalb County, GA shredding facility. The refuse was divided into 9.1-kg (20-lb) portions and placed into plastic bags. During this weighing and bagging process, samples were obtained for the determination of refuse characteristics, including moisture content, calorific value, ash content, and percentage of carbon, hydrogen, and nitrogen. The results of these analyses are provided in Table 15.

The 10 simulated landfill columns were loaded with a total of 42 individual 9.1-kg (20-lb) bags of refuse (as received) within a period of about eight hours. The refuse was placed in the columns by loading five bags and manually compacting the loose refuse using a series of weighted hand tampers. Compaction was performed after the addition of each five bags [45 kg (100 lb)] of refuse to the column.

The organic and inorganic priority pollutants were simultaneously loaded with the refuse in the appropriate columns. The organic priority pollutants added to Columns 30S (Organics, Single Pass), 40LS (Organics, Low Inorganics, Single Pass), 50MS (Organics, Medium Inorganics, Single Pass), 60R (Organics, Recycle), 70LR (Organics, Low Inorganics, Recycle), 80HS (Organics, High Inorganics, Single Pass), 90MR (Organics, Medium Inorganics, Recycle), and 100HR (Organics, High Inorganics, Recycle) included aromatic and halogenated hydrocarbons, phenols, phthalate esters, and pesticides as indicated in Table 16. The organic priority pollutants were added to a closed glass container and completely mixed as a cocktail prior to their addition into the columns. After the placement of 30 cm (12 in) of compacted municipal refuse, the organic mixture was removed from the container and rapidly and uniformly distributed over the exposed refuse surface. The container that held the organic pollutants was rinsed twice with acetone, and the acetone rinsings were similarly distributed over the surface of the refuse as well, prior to immediate addition of the next refuse layer.

The inorganic priority pollutants added to Columns 40LS (Organics, Low Inorganics, Single Pass), 50MS (Organics, Medium Inorganics, Single Pass), 70LR (Organics, Low Inorganics, Recycle), 80HS (Organics, High Inorganics, Single Pass), 90MR (Organics, Medium Inorganics, Recycle), and 100HR (Organics, High Inorganics, Recycle) consisted of a mixture of two alkaline metal finishing waste treatment sludges with the characteristics shown in Table 17. The metal finishing sludges were supplemented with reagent-grade divalent metal oxides as indicated in Table 18. The metal sludges and metal oxides were admixed with sawdust to enhance leachate contact with the finely divided particulate matter, and to provide for even distribution of the mixture between the simulated landfill columns.

The metal sludge/metal oxide/sawdust mixture added to each column was thoroughly blended by manual mixing and divided into three equal portions for strategic placement within the column. The first addition of the metal mixture was made directly above the layer of refuse where the organic priority pollutants were placed. The second portion of the metal sludge/metal oxide/sawdust mixture was placed when the columns were approximately half full of manually compacted refuse, and the third addition of metals mixture was made approximately 30 cm (12 in) below the upper surface of the compacted refuse. Additionally, 100-g portions of the metal sludge/metal oxide/sawdust mixture were each admixed with 50 cc of 20-mesh Ottawa sand and placed within nylon mesh bags. Two bags were placed in each column receiving inorganic priority pollutants. One bag was placed in the lower layer of inorganic pollutants and the second bag was placed within the upper layer of inorganic pollutants in each column. In comparison to the overall mass loading of the metal sludge/metal oxide/sawdust mixture, the two bags constituted a negligible addition of less than one percent by mixture weight. The respective loading conditions are presented in Tables 19 and 20.

TABLE 15. CHARACTERISTICS OF SHREDDED MUNICIPAL SOLID WASTE ADDED TO SIMULATED LANDFILL COLUMNS

Sample Number	Moisture Content (%)	Calorific Value (cal/g)[a]	Ash Content (%)[a]	C (%)[a]	H (%)[a]	N (%)[a]
1a	27.3	4422	19.3	35.0	7.6	BDL[b]
1b	26.9	4272	14.2	40.0	5.2	5.1
2a	33.5	4835	13.5	36.0	5.3	0.7
2b	29.5	4654	13.4	36.0	5.0	0.7
3a	26.1	4279	10.8	40.0	5.3	1.5
3b	26.5	4458	15.9	39.0	5.3	0.9
4a	27.2	-	19.0	48.0	7.0	0.9
4b	27.8	-	14.1	47.0	6.8	0.9
5a	27.9	4318	14.4	38.0	5.3	2.7
5b	29.2	4494	16.4	40.0	5.9	0.9
6a	28.7	4376	13.6	37.0	4.8	BDL[b]
6b	26.2	4377	10.5	41.0	5.3	0.9
7a	35.0	4192	15.6	37.0	5.3	1.8
7b	32.0	4402	13.0	41.0	5.9	4.5
8a	39.2	4264	17.9	38.0	5.3	0.9
8b	38.1	4379	13.7	39.0	5.0	0.9
AVG	30.1	4409	14.7	39.5	5.6	1.5

Note: [a]Dry Weight Basis
[b]BDL = Below Detection Limit

3.3 SIMULATED LANDFILL CLOSURE

Upon completion of the simulated landfill column loading process, a 7.6-cm (3-in) layer of 1.2-cm (1/2-in) washed gravel was placed on the upper refuse surface to assist in the uniform distribution of leachate recycled and/or water added to the columns. The liquid distribution system was connected to the landfill covers to extend just above the gravel, and the covers were bolted to the columns and sealed water and gas tight using a silicone rubber sealant between the flanges. The silicone rubber sealant was also applied on the outside of the seal and on the bolt and nut heads as well. The total time required from the onset of loading until final column closure was approximately three days.

3.4 SIMULATED LANDFILL OPERATION

The 10 simulated landfill columns were loaded with shredded municipal solid waste and inorganic and/or organic priority pollutants on project Day 1. The columns were sealed water and gas tight on project Day 2, and pressure tests were conducted from project Day 3 through project Day 21 to ensure that the sealing operations were successful. Tap water additions were commenced on project Day 22 in order to attain immediate field capacity. Six liters of tap water were added to each column on project Day 22, and the water addition rate was increased to 12 liters per day between project Days 23 and 35 in order to expedite the attainment of field capacity on approximately project Day 35 with the cumulative addition of 162 liters of tap water to each column. Tap water additions

TABLE 16. ORGANIC PRIORITY POLLUTANTS LOADED TO SIMULATED LANDFILL COLUMNS

Compound	Formula	Physical Form	Mass Loading (g)
Dieldrin		Solid	30
1,4-Dichlorobenzene	$C_6H_4Cl_2$	Solid	120
2,4-Dichlorophenol	$C_6H_4OCl_2$	Solid	120
Hexachlorobenzene	C_6Cl_6	Solid	120
α-1,2,3,4,5,6-Hexachlorocyclohexane (Lindane)	$C_6H_6Cl_6$	Solid	120
Naphthalene	$C_{10}H_8$	Solid	120
2-Nitrophenol	$C_6H_5NO_3$	Solid	120
Dibromomethane	CH_2Br_2	Liquid	120
Bis-2-ethylhexylphthalate (Dioctyl Phthalate)	$C_{24}H_{38}O_4$	Liquid	120
Nitrobenzene	$C_6H_5NO_3$	Liquid	120
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	Liquid	120
Trichloroethylene	C_2HCl_3	Liquid	120

TABLE 17. CHARACTERISTICS OF METAL FINISHING WASTE TREATMENT SLUDGE LOADED TO SIMULATED LANDFILL COLUMNS

Constituent	DIF[a]	SAF[b]
Moisture Content (%)	78.7	79.7
Total Volatile Solids (%)	18.5	14.6
Metals (g/kg dry sludge)		
Cadmium (Cd)	7.2	167
Chromium (Cr)	21.6	0.4
Copper (Cu)	ND[c]	ND[c]
Iron (Fe)	204	2.3
Lead (Pb)	0.4	ND[c]
Mercury (Hg)	ND[c]	ND[c]
Nickel (Ni)	0.3	459
Zinc (Zn)	45.4	0.3

Note: [a]DIF - Dixie Industrial Finishing Company
[b]SAF - Saft America, Inc.
[c]ND - None Detected

TABLE 18. METAL SLUDGE/METAL OXIDE/SAWDUST MIXTURE LOADED TO SIMULATED LANDFILL COLUMNS

Constituent (as received)	Low Loading Level	Medium Loading Level	High Loading Level
DIF (kg)	5.0	10.0	20.0
SAF (kg)	0.8	1.6	3.2
Cr_2O_3 (g)	34.0	68.0	136.0
HgO (g)	22.0	44.0	88.0
PbO (g)	113.0	226.0	452.0
ZnO (g)	134.0	268.0	536.0
Sawdust (kg)	6.0	6.0	6.0

TABLE 19. PRIORITY POLLUTANT LOADING TO THE SIMULATED LANDFILL COLUMNS[a]

	Column Identity									
Pollutant	1CR	2CS	30S	40LS	50MS	60R	70L	80HS	90MR	100HR
Inorganics:										
Cadium	None	None	None	0.13	0.26	None	0.13	0.53	0.26	0.53
Chromium	None	None	None	0.17	0.35	None	0.17	0.7	0.35	0.7
Lead	None	None	None	0.4	0.8	None	0.4	1.6	0.8	1.6
Mercury	None	None	None	0.076	0.16	None	0.076	0.31	0.16	0.31
Nickel	None	None	None	0.28	0.56	None	0.28	1.1	0.56	1.1
Zinc	None	None	None	0.59	1.2	None	0.59	2.4	1.2	2.4
Organics:										
Dibromomethane	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
1,4-Dichloro-benezene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
2,4-Dichloro-phenol	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Dieldrin	None	None	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Dioctyl Phthalate	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Hexachloro-benzene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
1,2,3,4,5,6-Hexachloro-cyclohexane	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Naphthalene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Nitrobenzene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
2-Nitrophenol	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
1,2,4-Tri-chlorobenzene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Trichloroethylene	None	None	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45

Note: [a](g pollutant/kg dry shredded municipal refuse)

TABLE 20. SHREDDED MUNICIPAL REFUSE, ORGANIC AND INORGANIC PRIORITY POLLUTANTS, AND SAWDUST LOADINGS FOR EACH SIMULATED LANDFILL COLUMN

Constituent	Column Number and Type[a]									
	1CR	2CSP	30SP	40LSP	50MSP	60R	70LR	80HSP	90HR	100HR
	Mass, g									
Trichloroethene	-	-	120	120	120	120	120	120	120	120
Dibromomethane	-	-	120	120	120	120	120	120	120	120
2-Nitrophenol	-	-	120	120	120	120	120	120	120	120
1,4-Dichlorobenzene	-	-	120	120	120	120	120	120	120	120
Nitrobenzene	-	-	120	120	120	120	120	120	120	120
Naphthalene	-	-	120	120	120	120	120	120	120	120
1,2,4-Trichlorobenzene	-	-	120	120	120	120	120	120	120	120
2,4-Dichlorophenol	-	-	120	120	120	120	120	120	120	120
Hexachlorobenzene	-	-	120	120	120	120	120	120	120	120
Lindane	-	-	120	120	120	120	120	120	120	120
Bis-2-ethylhexylphthalate	-	-	120	120	120	120	120	120	120	120
Dieldrin	-	-	30	30	30	30	30	30	30	30
Cadmium	-	-	-	35	70	-	35	140	70	140
Chromium	-	-	-	45	90	-	45	180	90	180
Mercury	-	-	-	20	40	-	20	80	40	80
Nickel	-	-	-	75	150	-	75	300	150	300
Lead	-	-	-	105	210	-	105	420	210	420
Zinc	-	-	-	135	270	-	135	540	270	540
Sawdust	6,000	6,000	6,000	6,000	6,000	6,000	6,000	6,000	6,000	6,000
Shredded Municipal Refuse[b]	381	381	381	381	381	381	381	381	381	381

[a]C = Control, R = Recycle, O = Organic Pollutants, L = Low Metals, M = Medium Metals, H = High Metals, SP = Single Pass
[b]As placed refuse in kg

continued at a reduced rate of six liters per day between project Days 36 and 47 to ensure sufficient leachate production for recycle and/or sampling and analysis. Additionally, six liters of tap water were added on project Days 69, 76, 79, and 82. The two leachate management strategies, leachate recirculation and single pass leaching, were operative on project Day 104.

3.4.1 Single Pass Columns

To operate the landfill columns according to the changing leaching conditions of the landfill column, six liters of tap water were added to the five single pass columns approximately once every three days between project Days 104 and 471 on 123 separate occasions. During this time period, the total accumulated leachate was discarded every three days. The frequency of water additions was reduced to six liters every nine days from project Day 471 to 664. Between project Days 483 and 971, leachate was discarded at the rate of 1.8 liters every three days.

The columns were also seeded with anaerobic digester sludge to enhance the onset of methanogenesis after intentionally prolonged acid formation on 23 separate occasions between project Days 667 and 899. (The seeding procedure is described in Section 3.4.3.) During the seeding period, water additions of six liters per day were made to each column on project Days 675, 688, 694, and 713. In addition, 12 liters of tap water were added to Column 2CS on project Days 688 and 694, and four liters of tap water were added to Column 8OHS on project Day 729.

After the columns were seeded, tap water additions resumed at a rate of six liters every nine days from project Day 908 until project Day 954. During the time period between project Days 955 and 1016, water additions ceased in all columns except 8OHS. Water additions of six liters every nine days resumed between project Days 1017 and 1518. The total volume of leachate that had accumulated in each of the five columns was discarded on project Day 974. Afterwards, the total accumulated leachate was discarded once every three days between project Days 977 and 1540.

3.4.2 Recycle Columns

Water additions of six liters per month were made to each of the five recycle columns between project Days 104 and 645. The recycle columns, like the single pass columns, were seeded with anaerobic digester sludge on 23 occasions between project Days 667 and 899 to enhance the onset of methanogenesis. Tap water was added to all five recycle columns, with the exception of Column 6OR, on project Day 688 during the seeding period. The final tap water addition made to the recycle columns occurred on project Day 1192 when all columns, except Column 10OHR, received six liters of tap water.

Between project Days 288 and 661, one "dose" of leachate was recycled to the top of each column and was allowed to percolate through the refuse mass. The volume of recycled leachate was not measured at that time, however, it was later calculated as the amount of water present in the column in excess of field capacity during that time period. These volumes differed between the five simulated landfill columns due to the variance in the amount of water added to each column and the amount of leachate removed for sampling and analysis. During the seeding period, leachate was recycled seven to twelve times between project Days 723 and 778. Four of these recycles occurred prior to seedings four through eight to provide more substrate to the methanogens and permit their gradual development.

One to two liters of leachate were recycled 20 times during the time period between project Days 786 and 807. This leachate was also neutralized with a 150 g/L Na_2CO_3 solution to a pH between six and seven to avoid possible acid inhibition of the developing methanogens. The same volume of leachate was

recirculated and neutralized in each of the five recycle columns. Between project Days 808 and 833, leachate was recycled in all five columns, however, the frequency and amount varied between columns based upon the volume of accumulated leachate. Daily recycle of leachate was performed from project Day 834 to project Day 859, and the volume of recycled leachate varied between columns. Leachate recycle continued on a daily basis between project Days 860 and 915 with the recirculation of 12 liters per day in each column.

Beginning on project Day 916, the volume of leachate recycled was consistent between columns, but was limited to the volume produced by Column 60R. From project Day 916 until the end of the experimental time period, the volume of leachate produced by Column 60R gradually declined. This decrease in leachate was presumed to be the result of increased microbial activity and biomass growth, as well as a more complete saturation of the refuse mass and possible retention of leachate in the void spaces. Daily leachate recycle was performed between project Days 916 and 1063. The frequency of leachate recirculation was reduced to every other day between project Days 1064 and 1120, and the recirculation frequency was further reduced to every fourth day from project Day 1120 until the end of the experimental period on Day 1518.

3.4.3 Anaerobic Digester Sludge Seeding

After intentionally prolonged operation in the Acid Formation Phase of landfill stabilization, the 10 simulated landfill columns received sequential seeding of 23 separate additions of anaerobic digester sludge collected from the R. M. Clayton Wastewater Treatment Plant in Atlanta, GA. Prior to this seeding with anaerobic digester sludge, the columns were operated to intentionally maintain the Acid Formation Phase at a depressed pH and high chemical oxygen demand (COD) and total volatile acids (TVA) to observe the relative mobility of the codisposed organic and inorganic priority pollutants. Although methanogenic bacteria are normally present in the MSW and soil used for daily cover at full-scale landfills, the 10 simulated landfill columns were probably deficient in methanogens after prolonged operation in the Acid Formation Phase. It was, therefore, deemed appropriate to provide a seed of methanogens, using anaerobic digester sludge. The anaerobic digester sludge added had a pH of 7.9, alkalinity of 3.1 g/L as $CaCO_3$, and 2.5% total solids of which 60% were volatile solids.

The 23 anaerobic digester sludge additions were provided between project Days 667 and 899. A summary of the seeding procedure is presented in Table 21. The "seed" added consisted of the anaerobic digester sludge followed by an addition of one liter of tap water to rinse and prevent fouling of the liquid addition/distribution system. As indicated in Table 20, leachate was neutralized in some cases with a 150 g/L Na_2CO_3 solution and mixed with the anaerobic digester sludge to help decrease the effects of existing acid inhibition on the methanogens.

Seedings No. 1 through 8 consisted of the addition of five liters of anaerobic digester sludge, followed by one liter of tap water to rinse the liquid addition/distribution line of residual anaerobic digester sludge. Two to 4.5 liters of leachate were recirculated in Columns 1CR, 6OR, 7OLR, 9OMR and 1OOHR prior to seedings No. 4 through 8 to concomitantly provide substrate to the methanogens. Seedings Nos. 9 through 20 were conducted under a revised procedure, since the methanogic activity was only developing at a slow rate, presumably as a consequence of persistent acid inhibition. The new seeding procedure consisted of the addition of four liters of anaerobic digester sludge mixed with one liter of neutralized leachate to enhance substrate availability and utilization by the methanogenic bacteria. One liter of tap water was added following each seeding mixture.

Due to this revised seeding procedure, leachate was also recycled in the five single pass columns. However, the volume of leachate used and recycled in the single pass columns was not considered significant in the overall assessment

TABLE 21. SUMMARY OF ANAEROBIC DIGESTER SLUDGE ADDITIONS TO SIMULATED LANDFILL COLUMNS

Seeding Number	Date (Days Since Loading)	Anaerobic Digester Sludge (L)	Tap Water (L)	Leachate (L)	Total Volume Added (L)	Notes
1	July 16, 1987 (667)	5	1	0	6	
2	Aug. 3, 1987 (685)	5	1	0	6	
3	Aug. 21, 1987 (703)	5	1	0	6	
4	Sept. 11, 1987 (724)	5	1	0	6	
5	Sept. 28, 1987 (741)	5	1	0	6	
6	Oct. 7, 1987 (750)	5	1	0	6	
7	Oct. 19, 1987 (762)	5	1	0	6	
8	Oct. 28, 1987 (771)	5	1	0	6	
9	Nov. 2, 1987 (776)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
10	Nov. 19, 1987 (793)	2	3	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
11	Dec. 1, 1987 (805)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
12	Dec. 10, 1987 (814)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
13	Dec. 19, 1987 (823)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
14	Dec. 30, 1987 (834)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
15	Jan. 8, 1988 (843)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
16	Jan. 5, 1988 (850)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
17	Jan. 22, 1988 (857)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
18	Jan. 29, 1988 (864)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
19	Feb. 5, 1988 (871)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
20	Feb. 12, 1988 (878)	4	1	1	6	Leachate was neutralized to pH 6-7 using a 150 g/l Na_2CO_3 solution.
21	Feb. 19, 1988 (885)	5	1	0	6	
22	Feb. 26, 1988 (892)	5	1	0	6	
23	March 4, 1988 (899)	5	1	0	6	

of the leachate management strategy. As an additional measure to alleviate acid inhibition in the five recycle columns, one to two liters of leachate were neutralized prior to daily recirculation between project Days 786 and 807. Therefore, Seedings No. 21 through 23 were conducted according to the original seeding method of five liters of anaerobic digester sludge followed by one liter of tap water.

3.5 ANALYTICAL PROCEDURES AND METHODS

Leachate is produced in a landfill when field capacity is exceeded as a result of moisture accumulation from rainfall infiltration, groundwater intrusion, and waste degradation. The quantity and quality of leachate produced is influenced by the nature of the refuse, the state and extent of decomposition, and the chemical and physical characteristics of the percolating water and the adjacent soil and cover. In these studies, deliberate additions of tap water resulted in the attainment of indicated field capacity in the 10 columns on about project Day 35, after which leachate was produced for analysis and/or recirculation. (Rapid attainment of indicated field capacity was used as an experimental expediency which precluded operational delays otherwise incurred by liquid additions in accordance with natural rainfall events.)

The leachate was routinely analyzed for chemical, physical, and biological parameters indicative of the five phases of landfill stabilization. The codisposed organic and inorganic priority pollutants were also monitored to assess their potential for attenuation and mobility, and the possible generation of intermediary conversion products. Leachate samples from the 10 simulated landfill columns were analyzed for pH, conductivity, oxidation-reduction potential (ORP), total volatile acids (TVA), individual volatile acids (acetic, propionic, butyric, iso-butyric, valeric, iso-valeric and hexanoic), total organic carbon (TOC), five-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total alkalinity, conductivity, nitrogen, phosphorus, sulfates, sulfides, chlorides, bromide, iron, calcium, potassium, magnesium, manganese, sodium, ammonia, and the added organic and inorganic priority pollutants.

The total volume of gas produced was recorded, and gas samples were analyzed for carbon dioxide, oxygen, nitrogen, hydrogen, and methane. Some gas samples were analyzed for the volatile organic priority pollutants or conversion products in order to estimate possible losses due to volatilization. With the exception of the organic priority pollutant and gas analyses, Table 22 presents the analytical methodologies used in these studies.

Leachate collected from the 10 simulated landfill columns was analyzed for both semivolatile and volatile compounds. Semivolatile compounds were analyzed by solvent extraction and concentration followed by GC/MS analysis. A known volume of leachate sample was diluted to a volume of 500 ml with organic free water, and placed in a liquid-liquid vapor phase extractor (Kontes, Inc.). The diluted leachate was acidified to a pH less than 2.0 with concentrated hydrochloric acid, and a methylene chloride solution of the surrogate compounds was added. The leachate was heated and stirred during the eight-hour continuous extraction procedure. The methylene chloride extract was dried over anhydrous sodium sulfate, and a Kuderna-Danish concentrator was used to reduce the volume of methylene chloride to one ml. A solution of methylene chloride containing the internal standard was added to the concentrated methylene chloride, and the mixture was sealed and stored in a refrigerator until analysis with a capillary column GC/MS.

Volatile compounds were analyzed by purge and trap gas chromatography followed by mass spectrometric detection and identification. Known quantities of the internal standard and surrogate were added to a 5-ml leachate sample. The mixture was purged for nine minutes with nitrogen, and the purged compounds were collected and analyzed by capillary column GC/MS.

TABLE 22. SUMMARY OF ANALYTICAL METHODS USED DURING SIMULATED LANDFILL INVESTIGATIONS

Measurement	Procedure	Precision (σ)	Accuracy
Conductivity	EPA 600/4-79-020 Method 120.1	± 6%	95-105%
pH	EPA 600/4-79-020 Method 150.1	± 0.1	± 0.1
ORP	ASTM Method 1498-99	-	-
Alkalinity	EPA 600/4-79-020 Method 310.1	± 5%	95-105%
BOD_5	EPA 600/4-79-020 Method 405.1	± 20%	-
COD	EPA 600/4-79-020 Method 410.1	± 10%	90-110%
TOC	EPA 600/4-79-020 Method 415.1	± 10%	90-110%
Cl^-, SO_4^{-2}, PO_4^{-3}, S^{-2}	Standard Methods for the Examination of Water and Wastewater; Method 429	± 10%	90-110%
NH_3-N	EPA 600/4-79-020 Method 350.3	± 5%	90-110%
CH_4, CO_2, H_2	Gas Chromatography	± 5%	90-110%
Cadmium	EPA 600/4-79-020 Methods 231.1 & 213.2	± 10%	90-110%
Calcium	EPA 600/4-79-020 Method 215.1	± 5%	90-110%
Chromium	EPA 600/4-79-020 Methods 218.1 & 218.3	± 10%	90-110%
Iron	EPA 600/4-79-020 Method 236.1	± 10%	90-110%
Lead	EPA 600/4-79-020 Methods 239.1 & 239.2	± 10%	90-110%
Magnesium	EPA 600/4-79-020 Method 242.1	± 5%	90-110%
Manganese	EPA 600/4-79-020 Methods 243.1 & 243.2	± 10%	90-110%
Mercury	EPA 600/4-79-020 Method 245.1	± 20%	80-120%
Nickel	EPA 600/4-79-020 Methods 249.1 & 249.2	± 10%	90-110%

TABLE 22 (continued)

Measurement	Procedure	Precision (σ)	Accuracy
Potassium	EPA 600/4-79-020 Method 258.1	± 5%	90-110%
Sodium	EPA 600/4-79-020 Method 273.1	± 5%	90-110%
Zinc	EPA 600/4-79-020 Methods 289.1 & 289.2	± 10%	90-110%
Lithium	Standard Methods for the Examination of Water and Waste-water; Method 317B	± 5%	95-105%
Solid Waste Calorific Value	Parr Instruments Technical Manual #130	-	-
Solid Waste Moisture Content	Ohaus Instruments Technical Manual	± 5%	90-110%
Volatile Organic Acids	Direct Aqueous Injection Capillary Column Gas Chromatography	± 10%	90-110%

Note: EPA Methods[57]; Standard Methods[58]

The volume of gas produced, as indicated by liquid displacement measurements, was determined using plexiglass gasometers. Gas composition, measured as percent by volume, was determined for carbon dioxide, oxygen, nitrogen, hydrogen, and methane. Carbon dioxide, oxygen, nitrogen, and methane percentages were determined using a gas partitioner (Fischer, Model 25V) equipped with a thermal conductivity detector and operated at room temperature. Hydrogen was analyzed using a gas chromatograph (Perkin-Elmer, Model 900) which was also equipped with a thermal conductivity detector and operated at room temperature. The gas production data were converted to volumes at standard temperature and pressure (0°C and 1 Atm) using the ideal gas law to provide for their direct comparison.

Quality assurance/quality control (QA/QC) procedures were followed, which included the analysis of blanks, standards, duplicates, spiked samples, and control samples. Internal standards and surrogates were also analyzed to verify the validity of results obtained from extraction, gas chromatography, and gas chromatography/mass spectrometry (GC/MS) procedures.

3.6 SAMPLING PROCEDURES

The leachate samples collected for semivolatile and volatile organics analysis were managed in accordance with EPA 600/4-79-019, Section 8.2[57]. The containers consisted of thoroughly rinsed, oven-baked glass bottles with teflon-lined lids. Accordingly, the vials used for leachate collection for the analysis of volatile organics were completely filled, ensuring the absence of any head

space above the sample. Leachate samples for metal analyses were collected in acid-washed, screw-capped polyethylene bottles and preserved by digestion with nitric acid and hydrogen peroxide. The remaining leachate samples were collected in vials of the same type used for the metals analyses. Following collection of leachate samples, pH, conductivity, alkalinity, and ORP analyses were performed immediately, while other samples were collected and stored for a maximum of 24 hours at 4°C.

Gas samples were collected from the lysimeter head space for immediate analysis. Gas-tight syringes were used to collect gas samples from built-in sampling ports to prevent sample contamination.

All samples collected were logged into a data book by the analyst. The information recorded contained details regarding the sampler, type of analysis, and recipient personnel. The sample collected displayed a label with the following information: column number, date of sampling, master log book number, analysis to be performed, sample volume, preservative amount and type, sampler and general observations.

3.7 SIMULATED LANDFILL DISASSEMBLY

Upon completion of the study, the 10 simulated landfill columns remained standing for approximately six weeks prior to disassembly. During this time, leachate produced by each column was allowed to drained, collected, and discarded. The head-space gases were analyzed for the presence of hydrogen sulfide before opening the columns. During disassembly, samples of the waste matrix were retrieved for analysis, and appurtenances were inspected for changes in character or functionality.

SECTION 4

PRESENTATION AND GENERAL DISCUSSION OF RESULTS

During the simulated landfill studies, leachate and gas produced by the 10 simulated landfill columns were analyzed for the parameters reflective of the five phases of landfill stabilization as well as for the behavior and fate of the codisposed organic and inorganic priority pollutants. The total gas volume produced was measured, and gas composition was determined to reflect the progression of stabilization events within the landfill simulations. Leachate quantity and quality, which vary with time and extent of waste conversion, were evaluated as characteristic of the nature and extent of waste conversion. The chemical characterization of the leachate produced was also used to determine the potential adverse environmental impacts consequenced by mobilization of leachate constituents.

The 10 simulated landfill columns received tap water additions until indicated field capacity was attained and leachate production commenced. As a result, the first phase of landfill stabilization, Initial Adjustment, was significantly shortened. In addition, prior to project Day 667, the 10 simulated landfill columns were intentionally operated to maintain the Acid Formation Phase of landfill stabilization and to observe its effect on the relative mobility of the codisposed organic and inorganic priority pollutants. The columns were then seeded with anaerobic digester sludge on 23 occasions between project Days 667 and 899 to promote the Methane Fermentation Phase of landfill stabilization. Therefore, the following discussion concentrates on the Acid Formation and Methane Fermentation Phases of landfill stabilization within the 10 simulated landfill columns.

Leachate and gas data were obtained approximately once every two weeks. For purposes of consistent data presentation and interpretation, a sampling time period of every 14 days was developed, and "missing" sample values were determined using linear interpolation. In the event of more than one sample being obtained during a 14-day period, an average of the sample results was considered representative of that time period.

4.1 EXTERNAL TEMPERATURE

The temperature of the area in which the 10 simulated landfill columns were located was recorded and is presented in Figure 15 and Table A-1 (Appendix A). (Table A-1 also contains the vapor pressure of water at the measured temperature as determined using the Handbook of Chemistry and Physics.[59]) Internal column temperature, which was not determined because of a malfunctioning temperature probe, was assumed to be the same as the measured room temperature. The observed temperature fluctuated in accordance with ambient seasonal variations and ranged from 10.3°C to 31.1°C, with an average temperature of 22.9°C. During the majority of the experimental period, the temperature was below that characteristic of the optimum mesophilic range (30 to 38°C) for anaerobic stabilization. This suggests that some effects on biological conversion were due to temperature variations, but that these variations probably did not influence the final outcome other than to promote more rapid stabilization during higher temperatures and to reduce reaction rates during lower temperatures.

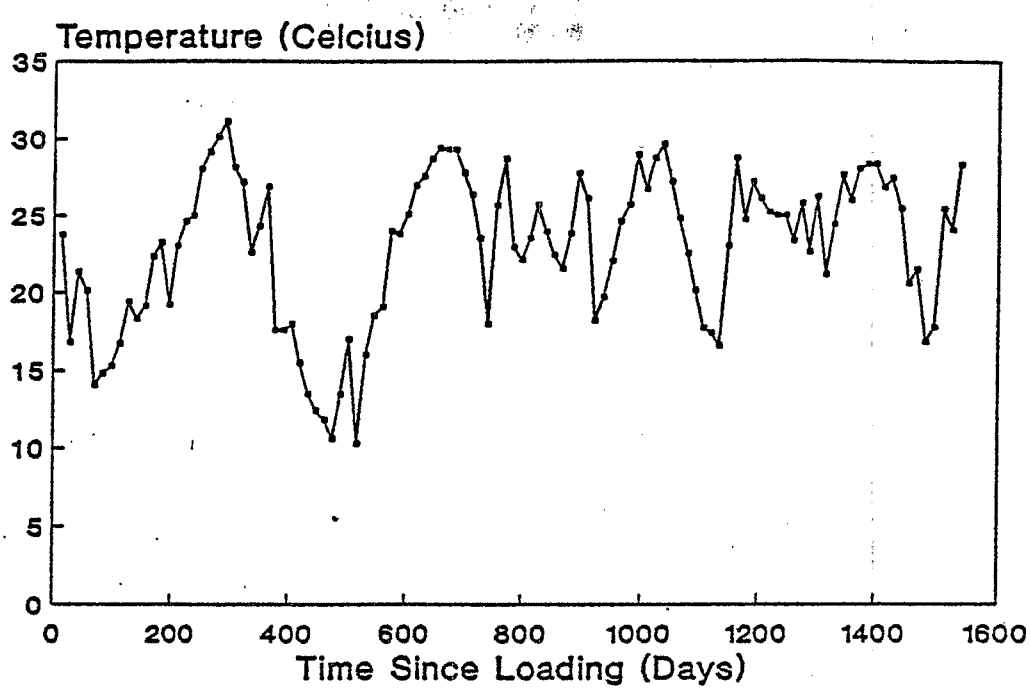


Figure 15. Ambient Temperature Variations during Simulated Landfill Investigations.

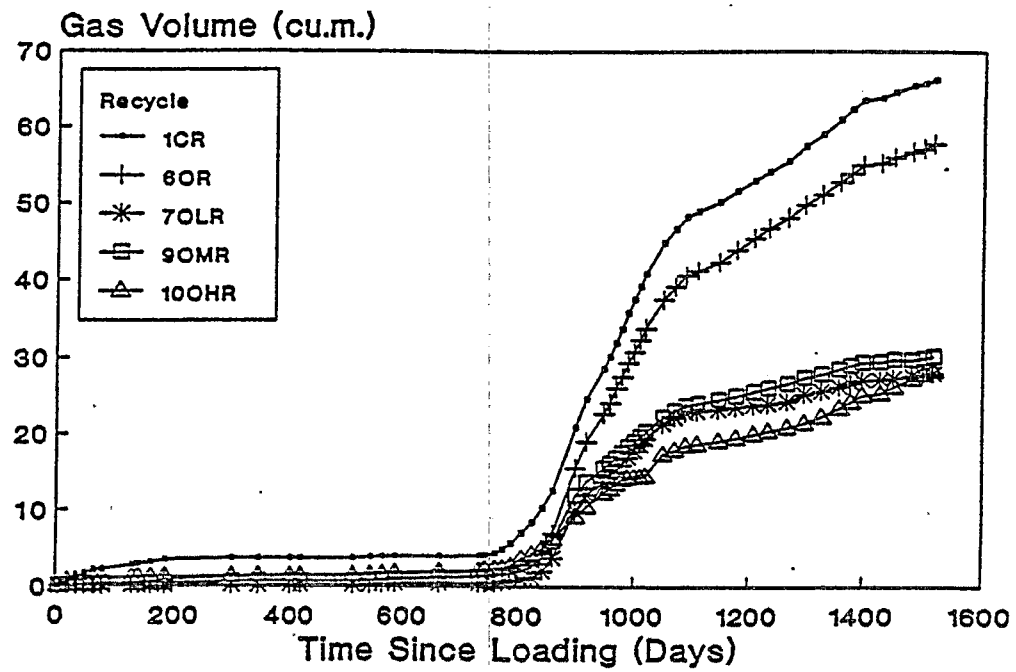
4.2 GAS ANALYSES

Gas volume and composition were determined as indications of the progression of landfill stabilization processes. Methane and carbon dioxide arethe primary end products of anaerobic biological waste stabilization and reflect the rate of biological activity and organic material conversion within the landfill environment. In addition, differences in gas volume and composition delineate the impacts of loading and type of leachate management strategy employed upon the anaerobic systems established within the 10 simulated landfill columns.

4.2.1 Gas Production

Cumulative gas volumes produced in the recycle and single pass columns are shown in Figure 16, and the corresponding data are presented in Table A-2 of Appendix A. Incremental gas volumes produced are presented in Figures 17 for recycle and single pass columns, respectively. The supporting data are included in Table A-3 of Appendix A.

The overall volume of gas produced was much larger in the recycle columns than in the single pass columns, and the maximum volume of gas produced during a two-week period was also greater for the recycle columns than for the single pass columns. This information, which is summarized in Table 23, indicates that stabilization proceeded more rapidly and thoroughly in the recycle columns than in the single pass columns. The higher degree of stabilization observed in the recycle columns can be directly attributed to the leachate recirculation strategy employed, since decomposable organic material such as the volatile organic acids, a principal substrate for methanogens, was removed due to leachate wasting in the single pass columns but was retained and recirculated as substrate in the recycle columns. Therefore, methanogens in the recycle columns experienced an increased



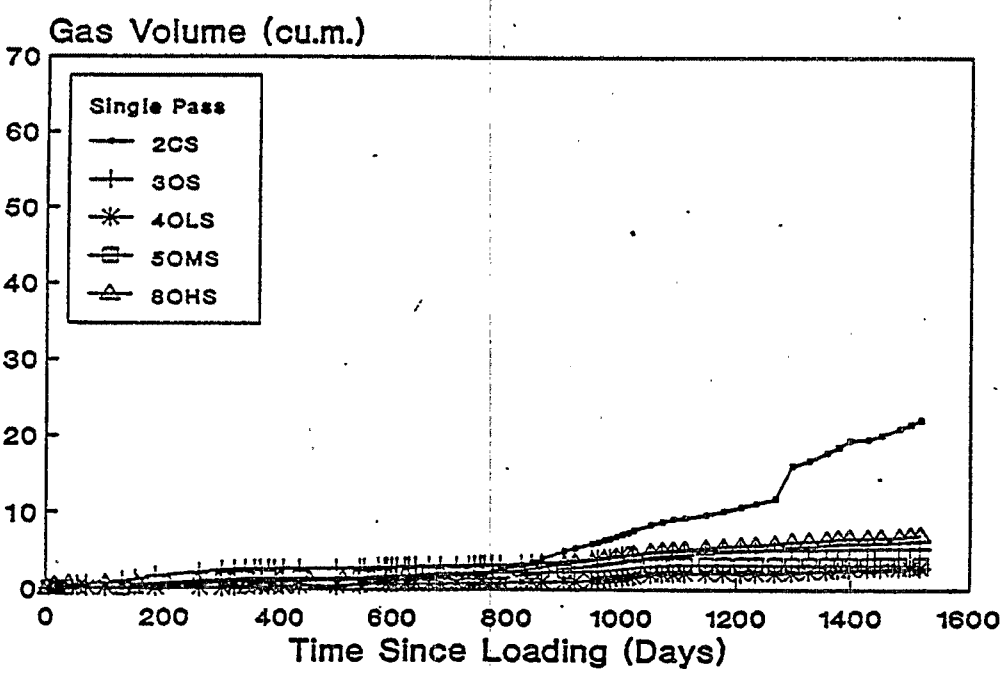
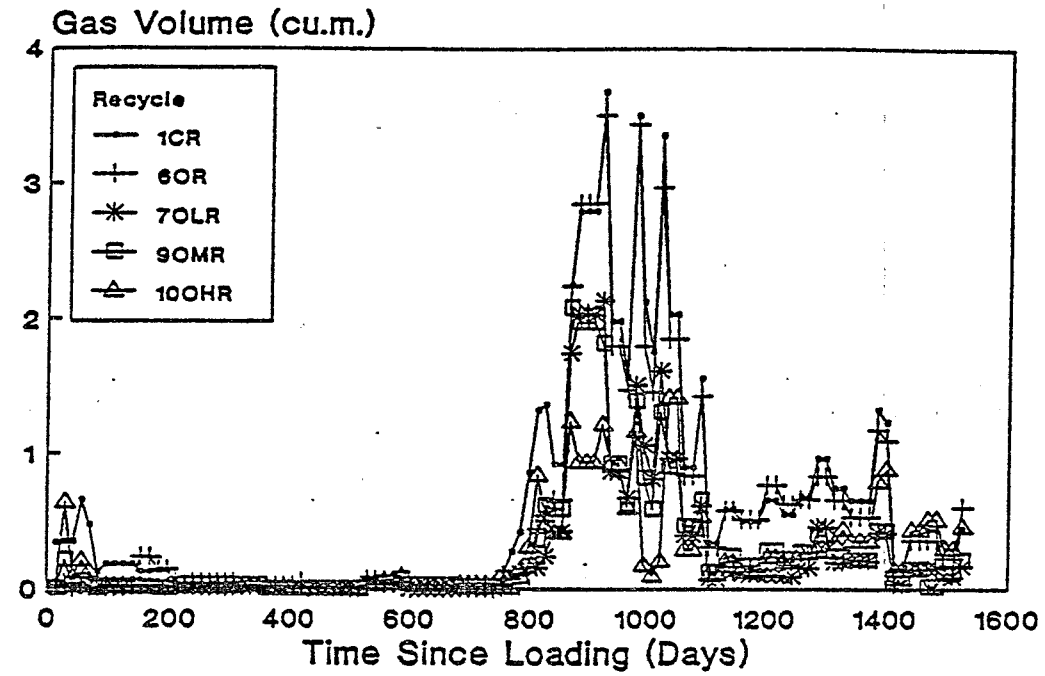


Figure 16. Cumulative Gas Production during Simulated Landfill Investigations.



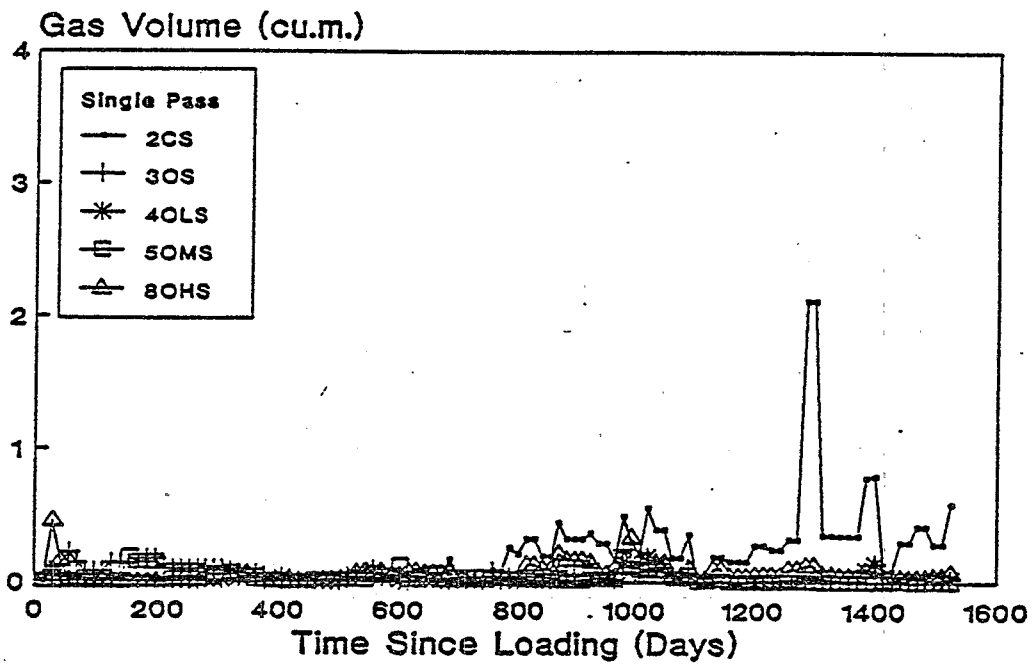


Figure 17. Incremental Gas Production during Simulated Landfill Investigations.

TABLE 23. COMPARISON OF GAS VOLUMES FROM SIMULATED LANDFILL COLUMNS

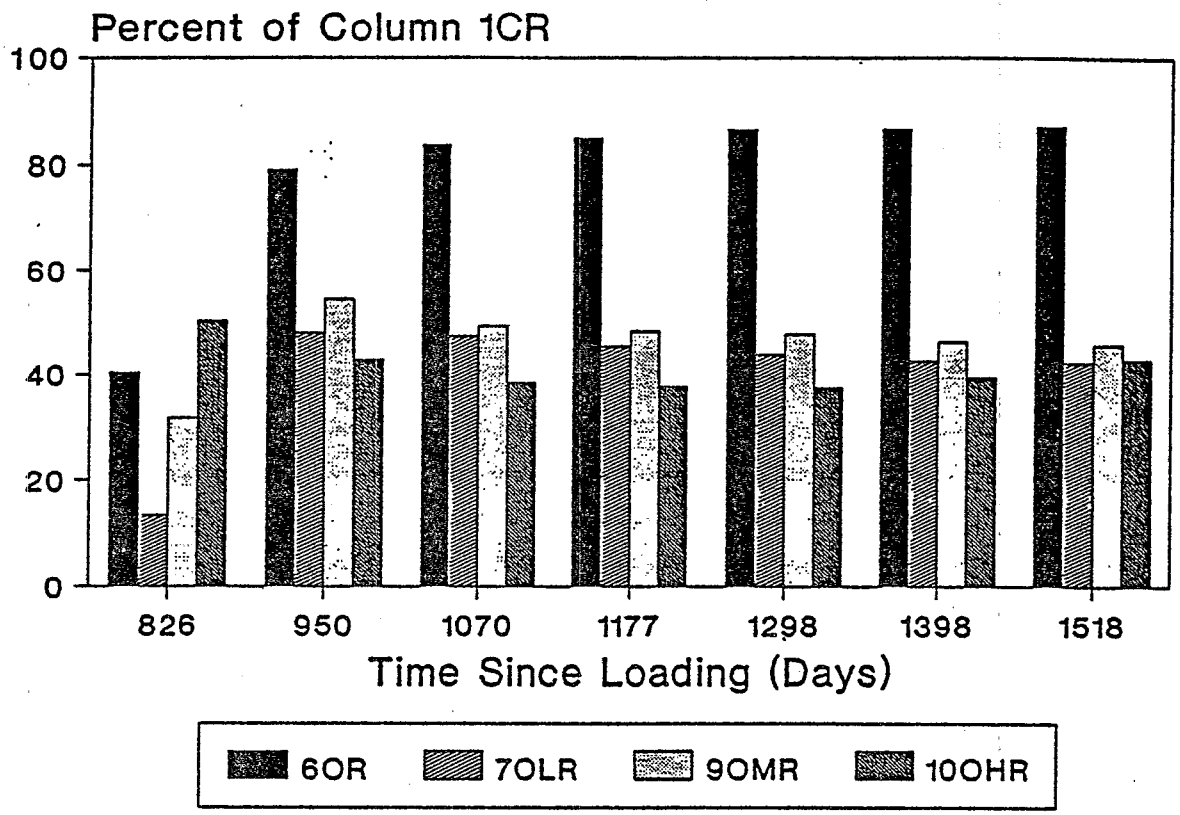
Column	Cumulative Gas Volume Produced (M^3)	Maximum Incremental Gas Volume Produced (M^3)
1CR	65.755	3.680
2CS	21.676	2.118
3OS	5.454	0.248
4OLS	2.893	0.193
5OMS	3.266	0.174
6OR	57.126	3.506
7OLR	27.872	2.128
8OHS	7.112	0.340
9OMR	30.007	2.081
10OHR	27.833	1.427

contact opportunity with the available substrate due to leachate recirculation.

Incremental gas production began to increase around project Day 793, which corresponds to the 10th seeding of anaerobic digester sludge added to promote methanogenesis. Beginning with the 9th seeding, a revised seeding procedure was adopted. In accordance with this procedure, leachate added along with anaerobic digester sludge and tap water was neutralized to pH 7, providing methanogens with a more acceptable substrate. After initiation of the revised seeding procedure, gas volume produced by all 10 simulated landfill columns increased dramatically.

Gas production from the control columns, Columns 1CR and 2CS, was greater than gas production in columns loaded with inorganic and/or organic priority pollutants, indicating the retarding effects of the applied admix priority pollutant loadings. For interpretive analysis, the experimental period was divided into the Acid Formation Phase of landfill stabilization, which lasted until approximately project Day 800, and the Methane Fermentation Phase which occurred from project Day 800 until the end of the experimental period. During both the Acid Formation and Methane Fermentation Phases, the control recycle column (Column 1CR) displayed the largest gas productivity, as expected, due to the absence of codisposed inorganic and organic priority pollutants. Column 6OR, the recycle column containing only organic priority pollutants, produced the next largest gas volume. The recycle columns receiving both organic and inorganic pollutants all displayed lower gas volumes when compared with Columns 1CR and 6OR, suggesting some retarding effect of the added inorganic priority pollutants. Although the inorganic priority pollutant loadings varied between Columns 7OLR, 9OMR, and 10OHR, the gas volume produced by each of these columns was similar, which implies that the landfill environment had the ability to accommodate and detoxify certain amounts of the pollutant loadings.

The relative gas production between the five recycle columns is shown in Figure 18. In Figure 18, gas volumes produced by columns loaded with inorganic and/or organic priority pollutants are compared to the volume of gas produced by the control recycle column, (Column 1CR) and the column with only organic



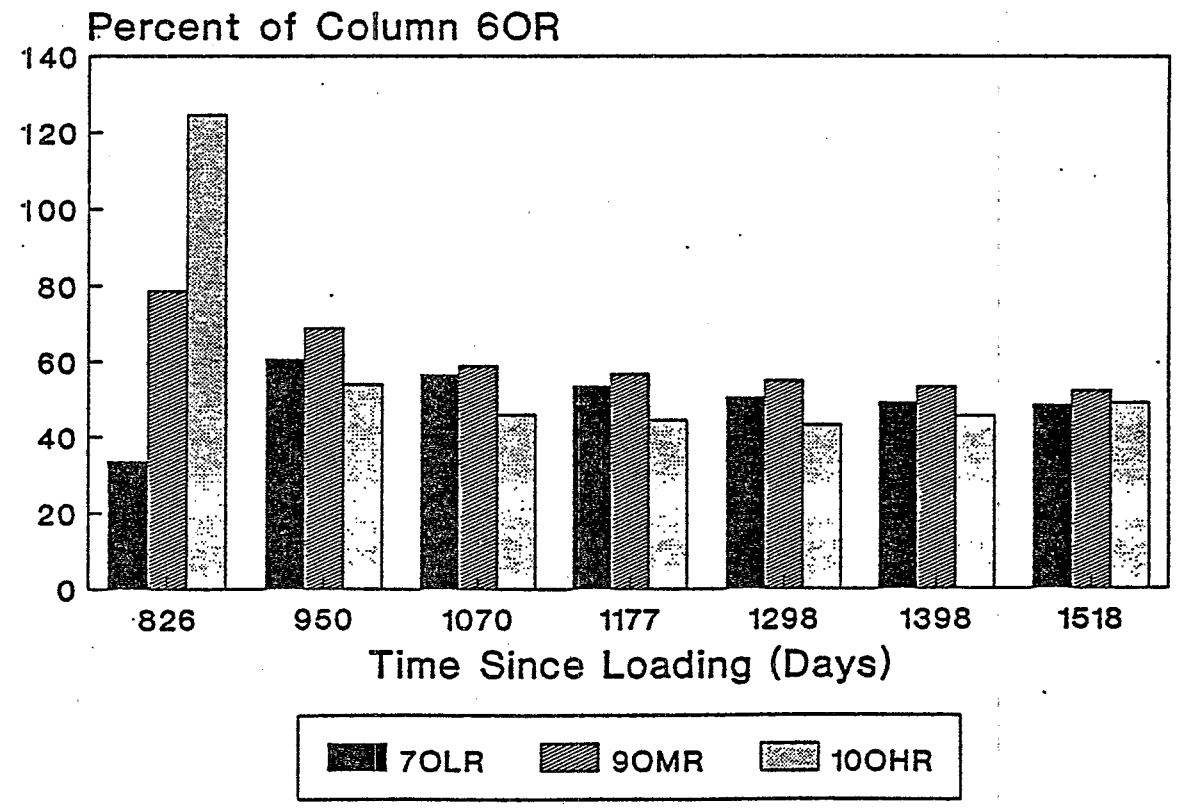


Figure 18. Relative Gas Production between Simulated Landfill Columns with Leachate Recycle.

priority pollutants added (Column 60R). Column 60R displayed increasingly greater gas volume produced in relation to Column 1CR, especially after rapid gas production commenced. The three recycle columns loaded with both organics and inorganics, Columns 70LR, 90MR and 100HR, displayed some retardation of gas production, but total inhibition was not observed. Towards the end of the experimental period, these columns were all producing about the same amount of gas, indicating that the effects of the codisposed inorganics and organics were being lessened as biodegradation and attenuation mechanisms became operative.

When the columns loaded with both organic and inorganic priority pollutants are compared to the column receiving only organic priority pollutants (Column 60R), the effects of the inorganic priority pollutant loading can be observed. During the early period of the Methane Fermentation Phase, specifically project Day 826, Columns 90MR and 100HR showed relatively high gas volumes produced compared to Column 60R. This may have resulted from some unavoidable waste heterogeneity or by other physical-chemical phenomena as the environment changed from the more acid conditions prevailing during the Acid Formation Phase (low pH) to the more favorable conditions established during the Methane Fermentation Phase (neutral pH). The column with the highest inorganic loading, Column 100HR, displayed the lowest gas production with respect to Column 60R, as expected, due to the high inorganic loading applied. However, as the experiment progressed, delineation between gas volumes produced from Columns 70LR, 90MR, and 100HR became increasingly less distinct as the inherent assimilative capacity of the landfill environment became operative.

The relationships between gas production in the single pass columns were not as predictable or logical as those in recycle columns. The control column, Column 2CS, produced the greatest gas volume, as expected, due to the absence of added organic and inorganic priority pollutants. However, during the Acid Formation Phase, Column 2CS did not produce the highest gas volume. It was only during the anaerobic digester sludge seeding period between project Days 667 to 899 that the gas production began to significantly increase. Column 2CS had the smallest leachate volume removed for sampling and wasting of the five single pass columns. Column 2CS also received the second highest volume of added tap water, giving this column the highest liquid volume retained in excess of indicated field capacity. (Water balance data are discussed in Section 4.3.) Therefore, substrates such as the volatile organic acids produced may have remained in Column 2CS, albeit to a lesser degree than in the recycle columns, but may have been diluted to less inhibitory levels. Subsequent to the anaerobic digester sludge seeding period, Column 80HS displayed the second highest gas volume and Column 40LS produced the smallest gas volume, which disagrees with expected results. Therefore, these findings suggest that the nature of the single pass operation distorted the effects of the inorganic and/or organic loadings due to washout of the codisposed pollutants.

Gas production rates were calculated during selected time intervals for both recycle and single pass columns. These time intervals differ between the recycle and single pass columns based upon variations in the slope of the respective cumulative gas volume produced figures. Recycle column gas production rates were determined during three time intervals and are presented in Table 24. In general, after the onset of the Methane Fermentation Phase, gas production rates increased initially to their highest values and decreased concomitantly as waste conversion progressed. During the time interval between project Days 920 and 1050, Column 1CR displayed the highest gas production rate, followed by Columns 60R, 70LR, 90MR and 100HR, respectively. During the third time period between project Days 1398 and 1518, Column 100HR showed the largest gas production rate, again suggesting the ability of the landfill to attenuate codisposed organic and inorganic priority pollutants.

Table 25 presents gas production rates for the five single pass columns during the latter part of the experimental period. Gas production rates for the single pass columns were much less than those observed for the recycle columns.

TABLE 24. RECYCLE SIMULATED LANDFILL COLUMN GAS PRODUCTION RATES

Column Identity	Project Days 920-1050 (M^3/Day) (L/Day)	Project Days 1050-1398 (M^3/Day) (L/Day)	Project Days 1398-1518 (M^3/Day) (L/Day)
1CR	0.157 156.6	0.053 53.2	0.023 22.9
6OR	0.142 142.2	0.050 50.1	0.023 23.1
7OLR	0.072 72.2	0.016 16.2	0.008 8.4
9OMR	0.065 64.9	0.021 20.7	0.007 7.3
10OHR	0.054 53.7	0.022 22.0	0.027 27.2

TABLE 25. SINGLE PASS SIMULATED LANDFILL COLUMN GAS PRODUCTION RATES

Column Identity	Project Days 826-1090 (M^3/Day) (L/Day)	Project Days 1268-1518 (M^3/Day) (L/Day)	Project Days 1050-1518 (M^3/Day) (L/Day)
2CS	0.023 22.8	0.041 41.4	
3OS			0.001 1.3
4OLS			0.002 2.2
5OMS			0.0004 0.4
8OHS			0.005 4.6

The control column, Column 2CS, showed an increase in gas production rate towards the end of the experimental period. Column 8OHS, which had the second highest gas volume produced, also had the second largest gas production rate, followed by Columns 4OLS, 3OS and 5OMS, respectively.

The higher gas production rates determined for the recycle columns further illustrate the benefits of leachate recirculation as a landfill management option in promoting a higher degree and more rapid rate of waste stabilization.

4.2.2 Gas Composition

Normalized gas composition for the 10 simulated landfill columns is presented in Figures 19 through 28 and Tables A-4 through A-13 of Appendix A. Oxygen, probably originating from within the refuse void spaces, was present in all columns until approximately project Day 550 in amounts ranging from 1 to 21% of the total gas volume. The initial presence and subsequent disappearance of oxygen is indicative of the transition from an initial aerobic to anaerobic environment within the columns. After the utilization of oxygen for initial aerobic waste stabilization and its displacement by carbon dioxide, the gas production rate decreased until methanogenesis was promoted by the seeding with digester sludge.

Hydrogen was present in all columns, but at less than 15% by volume until methane production commenced. Hydrogen completely disappeared in the gas from the recycle columns by project Day 980, and remained in the gas from the single pass columns for a longer period of time. Hydrogen eventually disappeared in columns except Column 8OHS. Column 8OHS, the heaviest loaded single pass column, contained hydrogen in the gas phase throughout the entire experimental period. This information is summarized in Table 26. The presence of hydrogen prior to active methane production corresponds to the possible impact of excessive hydrogen pressures on microbial activities during the Acid Formation Phase of landfill stabilization, and the disappearance of hydrogen corresponds to the more favorable conditions prevailing upon onset of methanogenesis, when hydrogen can serve as substrate for carbon dioxide-reducing methanogens. This observation is further corroborated by the changes in types and concentrations of volatile acids (Sections 4.4.2 and 4.5).

Nitrogen was present in the air entrained in the refuse void spaces during column loading operations. All 10 simulated landfill columns contained nitrogen until gas volumes produced were large enough to displace the nitrogen, as shown in Table 26. Nitrogen was displaced in the recycle columns by project Day 868 and was removed from Column 2CS by project Day 896. The remaining single pass columns, Columns 3OS, 4OLS, 5OMS, and 8OHS, apparently did not produce sufficient gas volumes to displace the nitrogen originally present. Of the single pass columns exhibiting lingering gas nitrogen content, Column 8OHS produced the largest gas volume, followed by Columns 3OS, 5OMS and 4OLS, respectively. Also, Column 8OHS had the lowest nitrogen percentage in the gas during the period from project Day 910 to 1428. Column 3OS had the next highest nitrogen gas percentage as expected, however, Columns 4OLS and 5OMS were reversed in the expected sequence as shown in Table 26. The unexpected results obtained from Columns 4OLS and 5OMS may have resulted from short-circuiting within Column 5OMS, thus allowing nitrogen gas to linger longer in the refuse void spaces.

The data in Table 26 also indicate that methane gas was produced in all columns at approximately the same time period, with the exception of Column 2CS, which produced some methane gas at a much earlier time. The early methane gas production in Column 2CS was attributed to the absence of possible inhibitory effects of organic and inorganic priority pollutants not contained within the control single pass column. Additionally, washout of the volatile organic acids produced, which have been shown to retard methanogenesis at high concentrations and low pH, provided a more favorable environment for the proliferation of methanogens, thus methane gas was produced earlier.

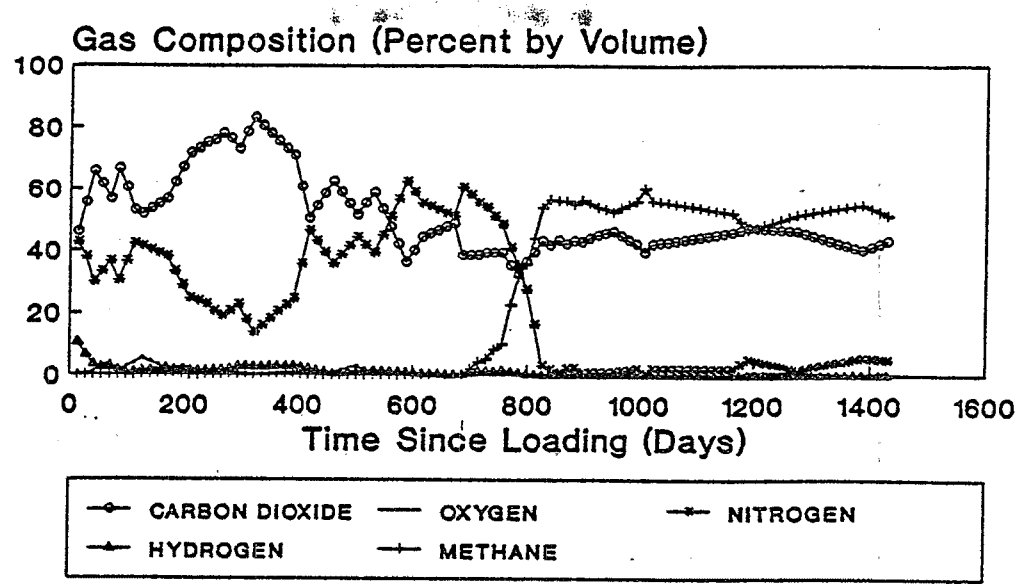


Figure 19. Normalized Gas Composition for Column 1CR.

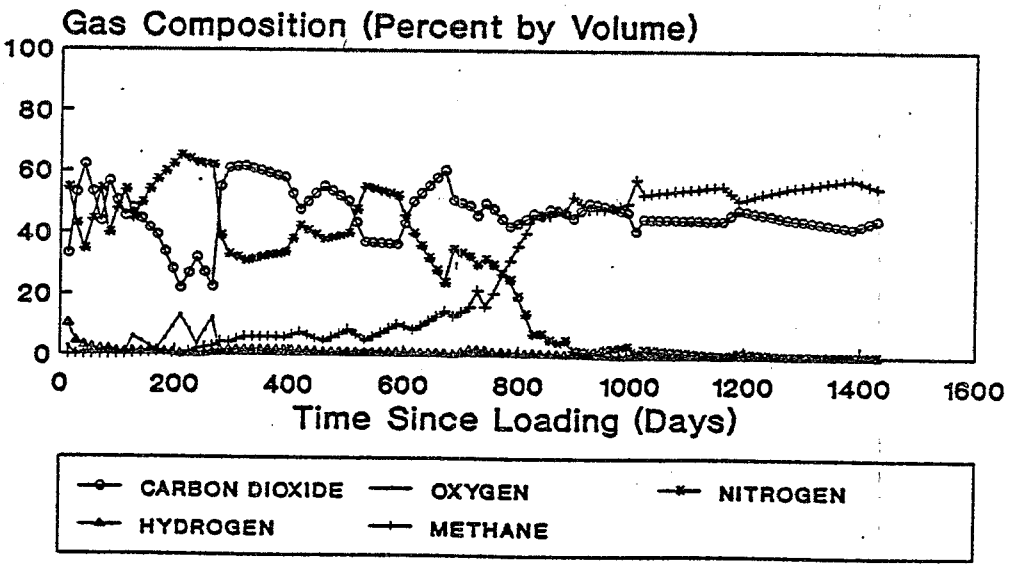


Figure 20. Normalized Gas Composition for Column 2CS.

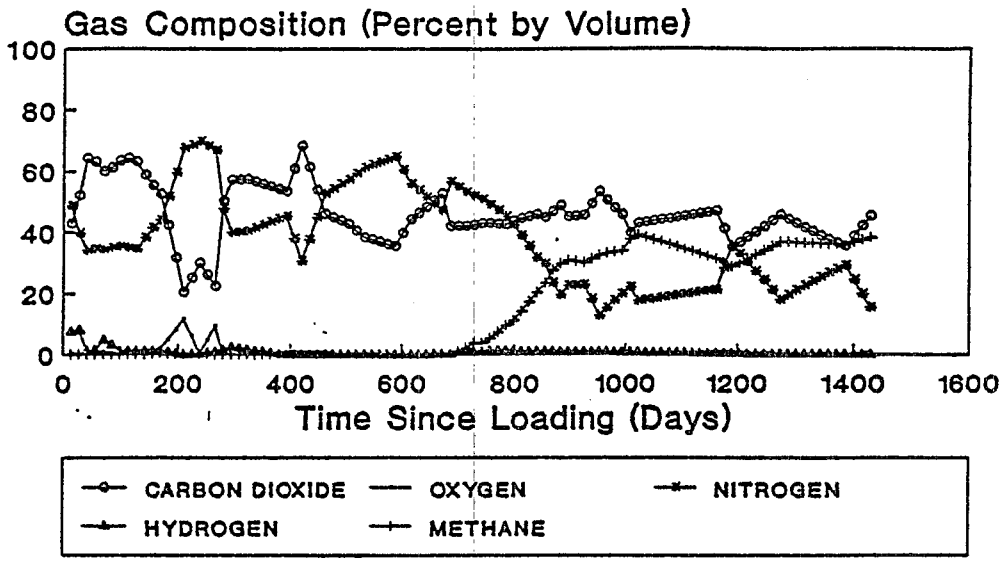


Figure 21. Normalized Gas Composition for Column 30S.

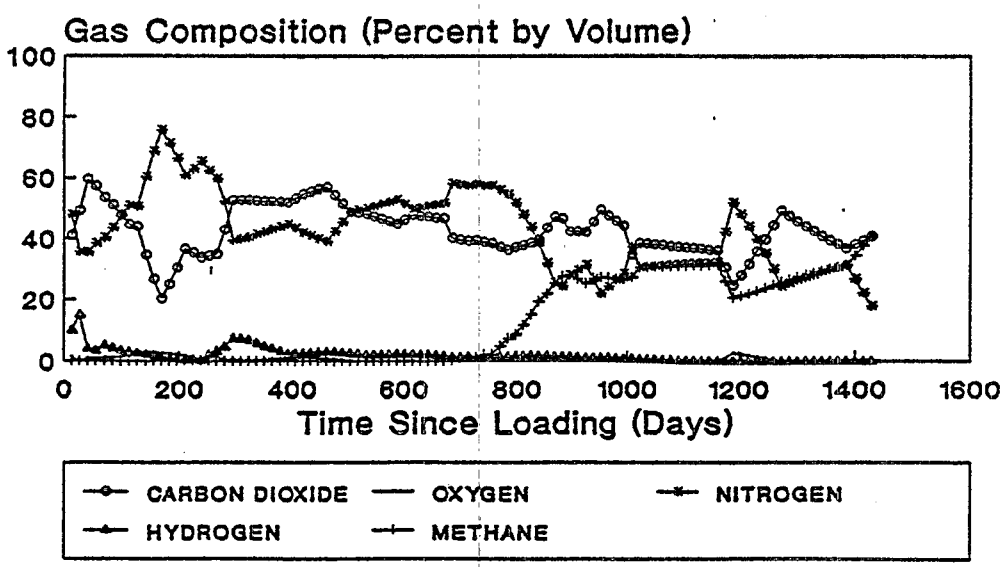


Figure 22. Normalized Gas Composition for Column 40LS.

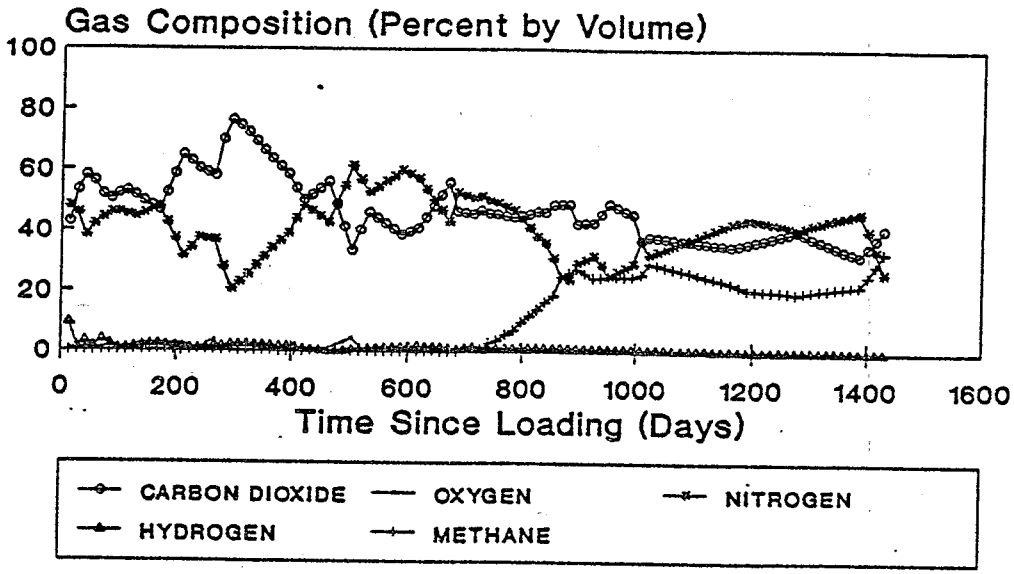


Figure 23. Normalized Gas Composition for Column 50MS.

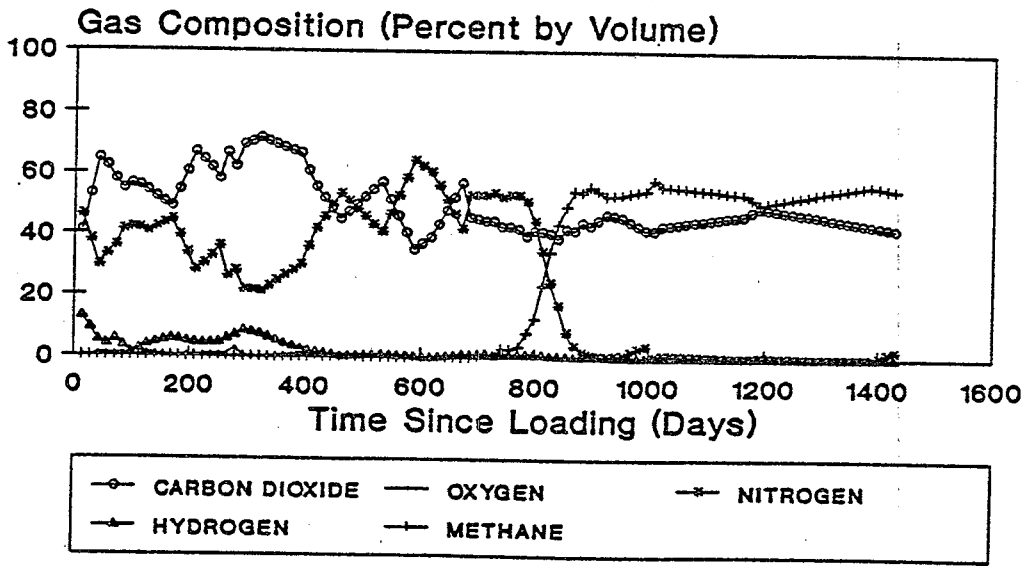


Figure 24. Normalized Gas Composition for Column 60R.

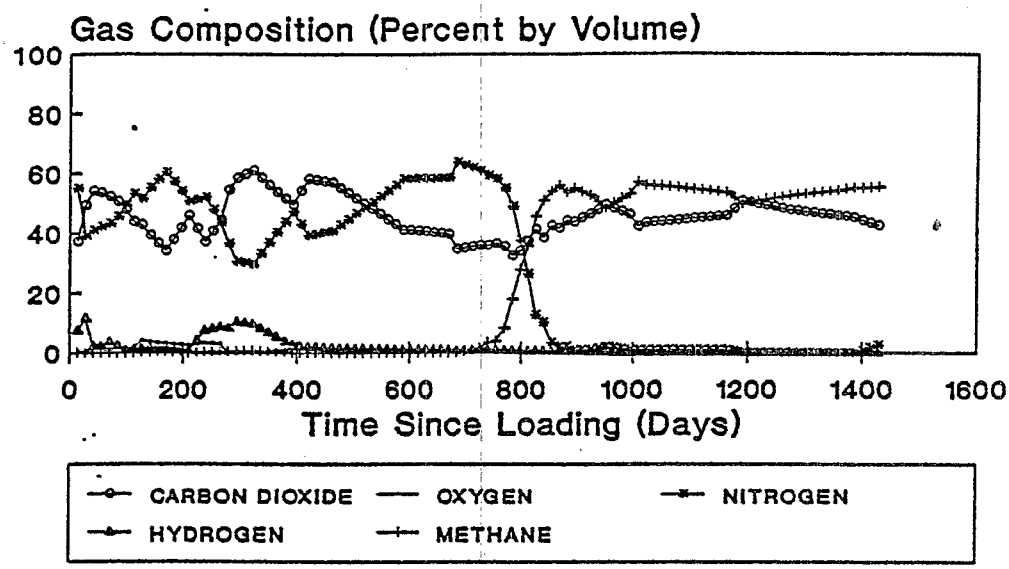


Figure 25. Normalized Gas Composition for Column 70LR.

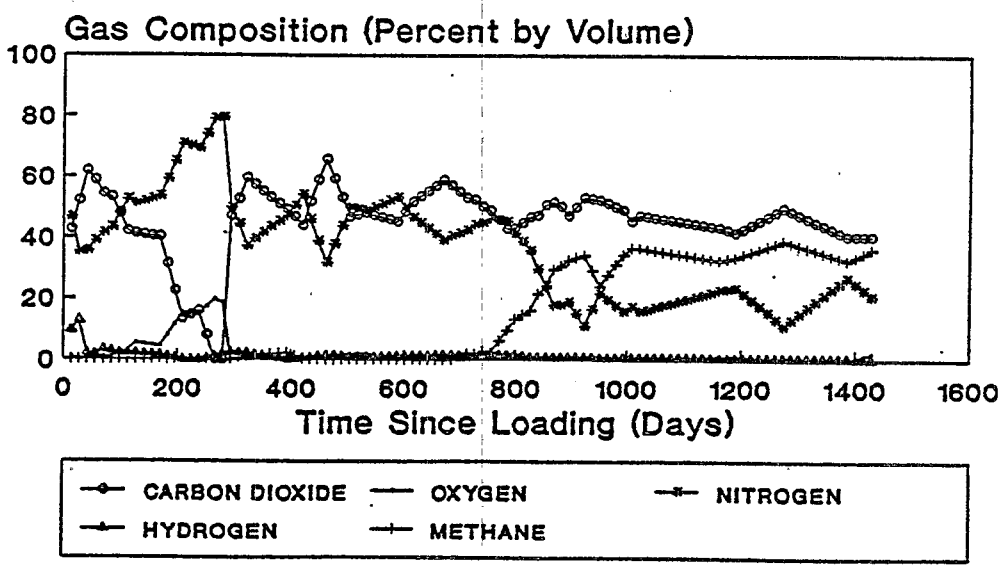


Figure 26. Normalized Gas Composition for Column 80HS.

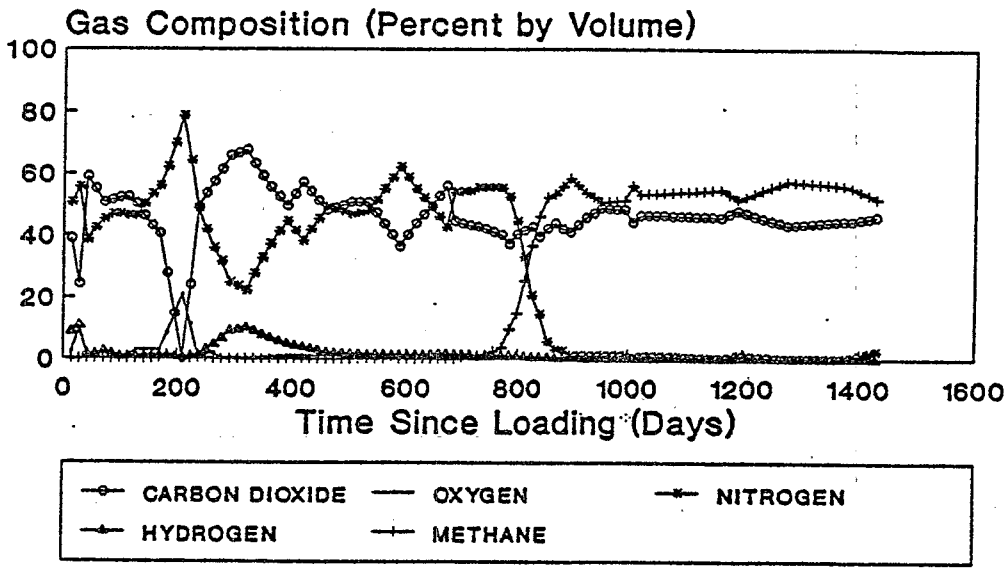


Figure 27. Normalized Gas Composition for Column 90MR.

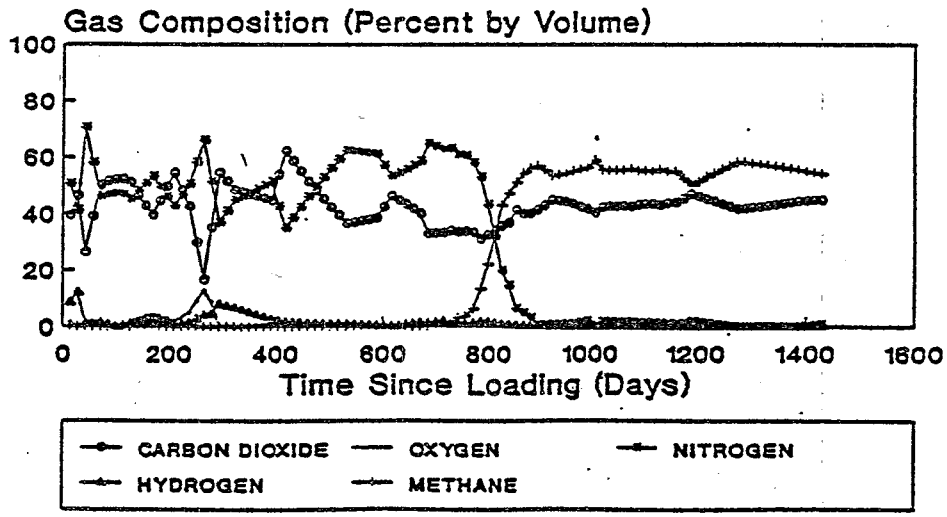


Figure 28. Normalized Gas Composition for Column 100HR.

TABLE 26. COMPARISON OF GAS COMPOSITION DURING SIMULATED LANDFILL INVESTIGATIONS

Column Identity	Project Day When N_2 Becomes Small (<5%)	Project Day When CH_4 Appears (>1%)	Average Gas Percentage During the Methane Fermentation Phase (Project Days 910-1428)		
			CO_2	N_2	CH_4
Recycle Columns					
1CR	826	700	44.02	2.77	52.81
6OR	868	742	45.17	0.67	54.14
7OLR	854	728	46.07	0.71	53.20
9OMR	868	728	45.42	0.61	53.96
1OOHR	868	714	43.54	0.95	55.44
Single Pass Columns					
2CS	896	238	45.37	0.79	53.74
3OS	-	700	42.96	21.95	34.36
4OLS	-	714	39.47	31.23	28.73
5OMS	-	714	38.21	37.74	23.77
8OHS	-	700	45.81	18.88	34.26

Examination of Figures 19 through 28 indicates for all recycle columns and Column 2CS an increase in methane production was accompanied by a concomitant decrease in nitrogen and carbon dioxide content. The decrease in nitrogen content was more pronounced because carbon dioxide as well as methane was produced during methanogenesis. Within recycle Columns 1CR, 6OR, 7OLR, 9OMR and 1OOHR, the average percentage of methane, carbon dioxide, and nitrogen present in the gas between project Days 910 and 1428 was very similar (Table 26). Methane comprised approximately 54%, carbon dioxide about 45%, and nitrogen less than 1% of the gas by volume.

In contrast, Columns 3OS, 4OLS, 5OMS and 8OHS all exhibited reduced gas carbon dioxide and methane percentages, and increased gas nitrogen percentages as a result of the retardation of stabilization processes arising from the combination of applied admix loading and the single pass leachate management strategy employed. In these four single pass columns, increased gas methane percentages were accompanied by decreased gas carbon dioxide and nitrogen percentages, with the decrease in nitrogen percentage being more pronounced.

4.3 WATER BALANCE

After the 10 simulated landfill columns were loaded and sealed water and gas tight, tap water was added until indicated field capacity was attained on or about project Day 35. Subsequently, water additions continued to the single pass columns in accordance with that management strategy, and water was added to the

recycle columns to compensate for leachate removal. Leachate was removed from recycle columns for sampling purposes only, and leachate removals from the single pass columns facilitated sampling and wasting, which was an integral part of the single pass leaching strategy.

Leachate was also removed from each column as a result of moisture losses during gas production. Therefore, the amount of moisture lost due to gas production was calculated for each column based upon the following assumptions. Total system pressure (P_T) was assumed to be one atmosphere, since the simulated landfill columns were not operated to allow a pressure buildup; the volume of gas collected was assumed to be saturated with moisture; the density of water was assumed to be 1000 g/L; and temperature fluctuations were neglected. Within the temperature range encountered in the simulated landfill columns (10 to 30°C), the variation in water density with temperature was minimal (999.73 g/L at 10°C, 995.67 g/L at 30°C).[60] Therefore, 55.6 moles/l of H_2O was taken as constant with temperature. Finally, all gases were assumed to behave as ideal gases, therefore, the volume fraction of gas produced was taken as mole fractions.[61]

Based upon these assumptions, the volume of moisture lost due to gas production was calculated using gas density, which is a function of gas composition, and specific humidity, which is dependant upon total pressure and water vapor pressure at a given temperature. The volume of liquid lost due to gas production was calculated as follows:

$$V_{LOST} = \frac{q * \rho_{GAS}}{(MW_{H2O}) * (55.6\ Moles/L)} \qquad (1)$$

where;

V_{LOST} = Volume of liquid lost due to gas production [L H_2O/L gas]
q = Specific humidity [g H_2O/g gas]
ρ_{GAS} = Gas density [g/L]
MW_{H2O} = Molecular weight of water [18.015 g/mole]

The specific humidity, which is the mass of water vapor contained within a unit mass of moist space, can be calculated using the following expression:[62]

$$q = \frac{0.622 * (VP)}{P_T - [0.378 * (VP)]} \qquad (2)$$

where;

q = Specific humidity [g H_2O/g gas]
VP = Water vapor pressure at specified temperature [millibars]
P_T = Total system pressure [millibars]

The gas density can be calculated using the ideal gas law, provided that the molecular weight of the gas is known. The molecular weight of the gas produced varies with gas composition, and based upon the assumption stated above, was determined using the following relationship:

$$MW_{GAS}=MW_{CO2}*X_{CO2}+MW_{O2}*X_{O2}+MW_{N2}*X_{N2}+MW_{H2}*X_{H2}+MW_{CH4}*X_{CH4} \quad (3)$$

where;

MW_{GAS} - Molecular weight of gas mixture [g/mole]
MW_i - Molecular weight of each component gas [g/mole]
MW_{CO2} - 44.010 g/mole
MW_{O2} - 31.999 g/mole
MW_{N2} - 28.013 g/mole
MW_{H2} - .2.016 g/mole
MW_{CH4} - 16.043 g/mole
X_i - Mole fraction of gas$_i$ [moles gas$_i$/total moles gas]

Therefore, the gas density was determined using the ideal gas law and the result of Equation (3), or:

$$\rho_{GAS} = \frac{MW_{GAS} * P_T}{R * T} \quad (4)$$

where;

ρ_{GAS} - Gas density [g/L]
MW_{GAS} - Molecular weight of gas mixture [g/mole]
R - Universal Gas Constant [0.0821 L*atm/°K*mole]
T - Temperature [K]

Thus, by combining Equations (3) and (4) and substituting along with Equation (2) into Equation (1), the volume of liquid removed by the gas produced was determined. Results of these calculations are presented in Tables B-1 through B-10 of Appendix B and are summarized in Table 27. As indicated in Table 27, the columns producing the most gas lost the highest volume of liquid, as expected. However, the cumulative volume of liquid removed by gas production was determined to be insignificant in comparison with the volume of liquid removed for sampling and wasting.

After calculating the volume of moisture lost due to gas production, it was necessary to determine the volume of moisture retained in each column in excess of indicated field capacity. The water balance information, presented in Tables B-11 through B-15 for the recycle columns and Tables B-16 through B-20 for the single pass columns, is included in Appendix B. Leachate recycle volumes are also included in Tables B-11 through B-15 for those columns employing leachate recirculation. The amount of moisture retained in each column was calculated as follows:

$$V_{EX} = V_A - V_R - V_{LOST} \quad (5)$$

where;

V_{EX} - Volume of liquid retained in excess of indicated field capacity [L]
V_A - Volume of fresh water added [L]
V_R - Volume of leachate removed for sampling or wasting [L]
V_{LOST} - Volume of liquid removed by gas production [L]

TABLE 27. CUMULATIVE LIQUID REMOVED DUE TO GAS PRODUCTION

Column	Cumulative Gas Production (M^3)	Cumulative Fresh Water Added (L)	Volume of Liquid Removed by Gas (L)	Cumulative Leachate Removed (L)
1CR	65.755	355.0	1.449	184.640
2CS	21.676	1445.0	0.469	1090.347
3OS	5.454	1415.0	0.135	1173.921
4OLS	2.893	1415.0	0.070	1191.639
5OMS	3.266	1415.0	0.089	1217.835
6OR	57.126	345.0	1.271	129.522
7OLR	27.872	363.0	0.623	103.461
8OHS	7.112	1460.0	0.174	1171.679
9OMR	30.007	351.0	0.222	107.770
10OHR	27.833	357.0	0.568	141.368

Thus, the amount of moisture retained in each of the 10 simulated landfill columns in excess of indicated field capacity was determined during each time interval and is presented in Tables B-11 through B-20 of Appendix B. These calculations are used later to determine mass fluxes of leachate constituents.

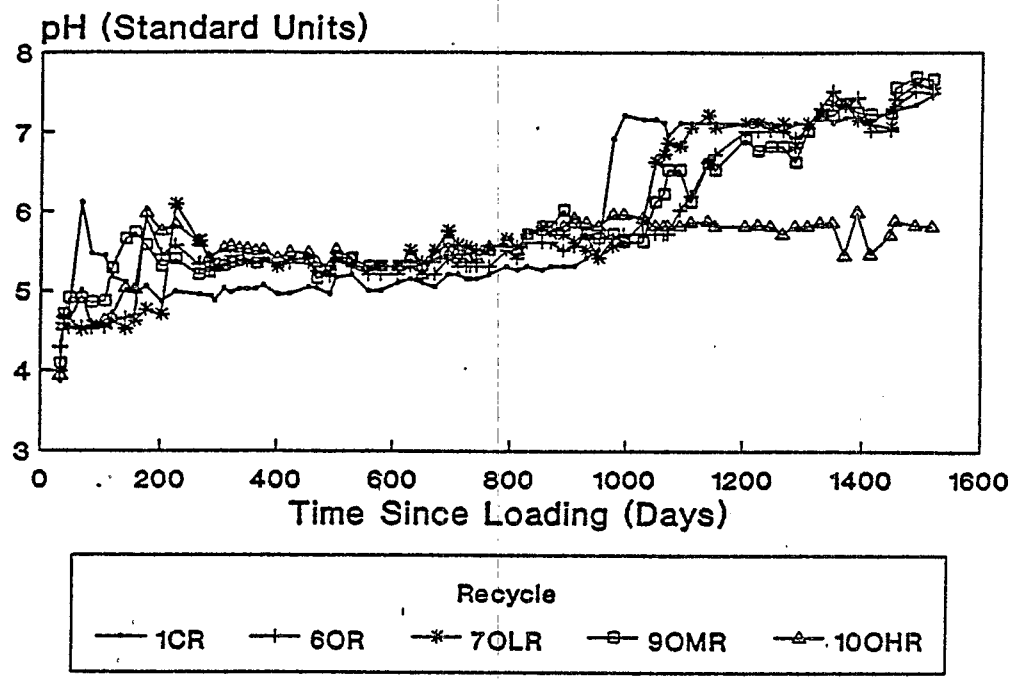
4.4 LEACHATE ANALYSES

Leachate, which provides moisture, nutrients and a principal substrate for biological activity and serves as a transport medium, reflects the progression of landfill stabilization events. Therefore, through the analysis and interpretation of certain leachate parameters, an insight could be gained regarding the extent of biological waste conversion and the behavior of the codisposed organic and inorganic priority pollutants as well.

4.4.1 pH

The pH of an anaerobic system such as a landfill is an indication of the intensity of the prevailing buffer system, and also affects species ionization. The prevailing pH is dependent upon interactions between volatile organic acids, alkalinity, and partial pressure of evolving carbon dioxide gas. During the Acid Formation Phase of landfill stabilization, pH values are generally low due to the presence of volatile organic acids (VOA) and their effect on system pH. During periods of low pH, an abundance of mobilized ions may appear in the leachate along with volatile organic acids. When available VOA are converted to methane and carbon dioxide during the Methane Fermentation Phase, pH usually rises to values characteristic of the bicarbonate buffering system, and may continue to rise with excess ammonia generation.

Leachate pH values for the recycle and single pass simulated landfill columns are presented in Figure 29. Measured leachate pH values are presented in table A-14 of Appendix A. Recycle column pH, shown in Figure 29, remained between 5.0 and 5.5 during the Acid Formation Phase, which corresponds to the period of dominance by the volatile organic acids. As volatile organic acids began to decrease between project Days 800 to 1000, pH increased to the 5.5 to 6.0 range. After project Day 1000, when VOA began to be reduced to very low



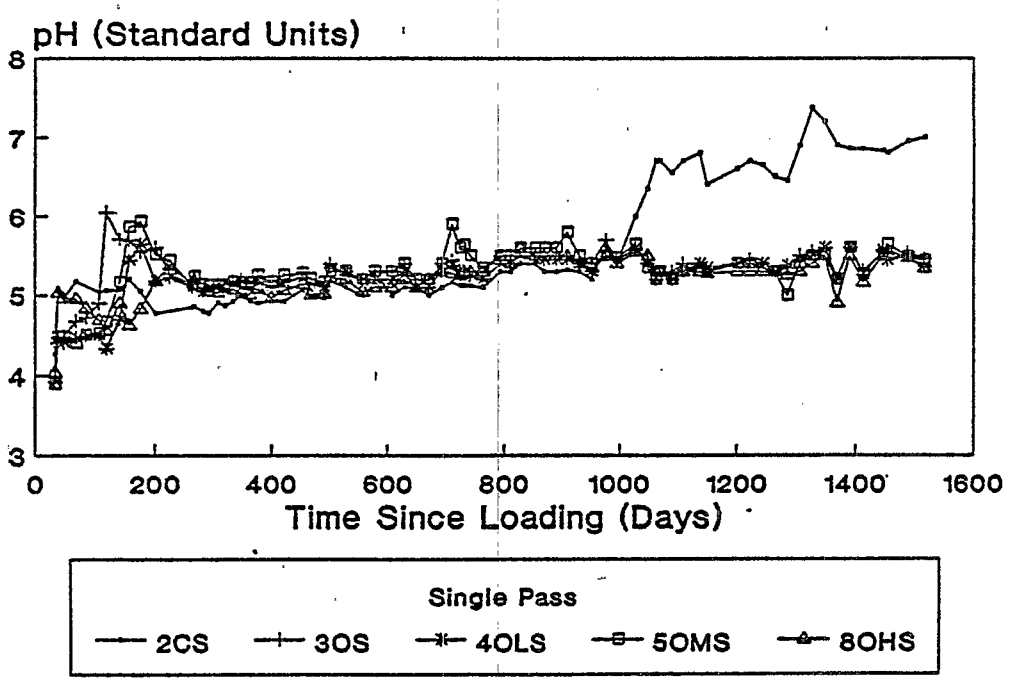


Figure 29. Leachate pH during Simulated Landfill Investigations.

concentrations due to their utilization by the methanogens, pH increased to a range of 6.4 to 7.5, which is characteristic of a bicarbonate buffering system. This behavior was observed in all recycle columns except Column 100HR, the heaviest heavy metal-loaded recycle column. Leachate pH for Column 100HR remained between 5.0 and 6.0 throughout the experimental period, and total volatile acid (TVA) concentrations never decreased significantly after project Day 800. These results suggest that a similarly viable population of methanogens never developed in Column 100HR, as evidenced by the absence of a decline in TVA concentrations and by gas production trends (Table 24).

Single pass column pH, except for Column 2CS, remained between 5.0 and 5.5 during the experimental period. These values are well below the acceptable pH range of 6.5 to 7.6 for active methanogenesis (Section 2.2.2), suggesting that for Columns 30S, 40LS, 50MS and 80HS, a transition from the Acid Formation Phase to the Methane Fermentation Phase of landfill stabilization, as evidenced by increased leachate pH due to VOA consumption by methanogens, was not evident. This conclusion is supported by the relatively constant TVA concentrations remaining after the apparent washout of volatile organic acids, and the apparent washout of buffer capacity from the single pass columns. These concepts are discussed further in Sections 4.4.2 and 4.4.3, respectively.

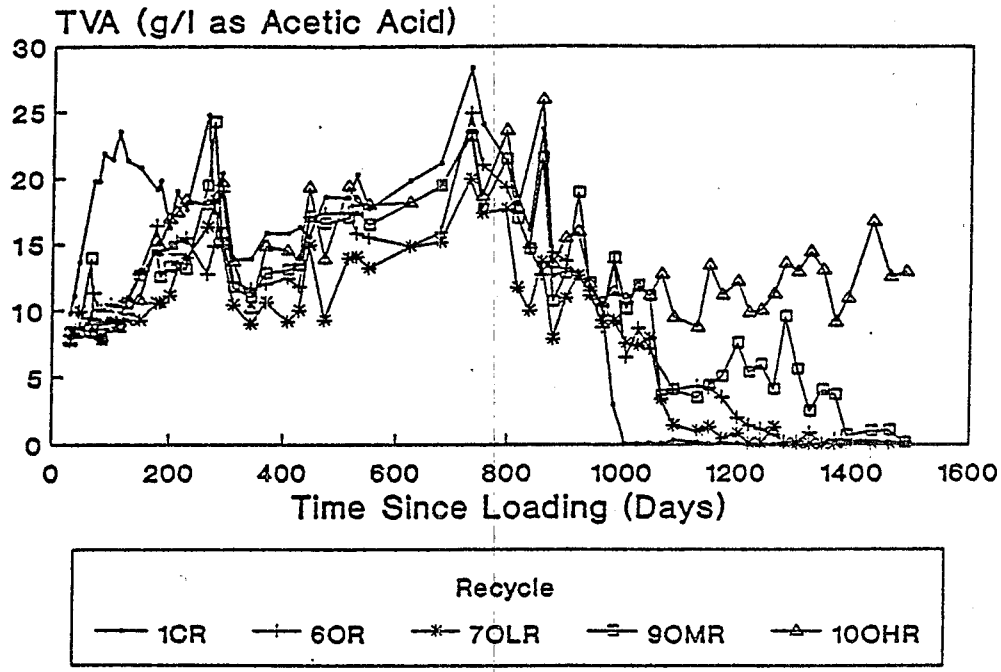
The control single pass column, Column 2CS, displayed a behavior similar to that observed for the recycle columns. A decrease in TVA concentration around project Day 1000 was accompanied by a concomitant increase in pH as shown in Figure 29, implying that increased system pH during methanogenesis resulted primarily from VOA conversion to methane and carbon dioxide and the establishment of a pH characteristic of the bicarbonate buffering system.

4.4.2 Total Volatile Acids

Volatile organic acids are produced during degradation of organic material and provide substrate for the methanogens. Total volatile acids (TVA) represent the combination of individual volatile acids, usually expressed as an equivalent amount of acetic acid. Leachate TVA concentrations for the recycle and single pass columns are presented in Figure 30. Measured leachate TVA concentrations are presented in Table A-15 of Appendix A.

The five recycle columns exhibited similar behavior regarding leachate TVA concentrations during the first 1000 days of column operation. Leachate TVA concentrations increased gradually until project Day 800, which corresponds to the Acid Formation Phase of landfill stabilization. Between project Days 800 and 1000, leachate TVA concentrations began to decline concomitantly with the development of a viable population of methanogens, as indicated previously by increased gas production and percent methane. After project Day 1000, leachate TVA concentrations declined rapidly for Columns 1CR, 60R, 70LR and 90MR in accordance with the influence of active methanogenesis. However, Column 90MR showed signs of slight retardation during the Methane Fermentation Phase, as evidenced by lingering TVA concentrations until approximately project Day 1400. This slight retardation suggests that the loadings to Column 90MR stressed the anaerobic bacterial population, but could be accommodated with a small lag in stabilization. Column 100HR, the heaviest heavy metal-loaded recycle column, showed signs of more severe retardation. Leachate TVA concentrations did not decline during methanogenesis, suggesting that the applied loading more significantly retarded the growth of organisms responsible for conversion of volatile organic acids to methane.

Because leachate was contained and recirculated in the five recycle columns, VOA produced remained in the systems and were removed primarily due to conversion to methane and carbon dioxide. Additional support for this conclusion is evidenced by noting that the period of increased gas production and increased methane percentage in the gas corresponded to the time period when leachate TVA concentrations declined and system pH increased from values characteristic of the



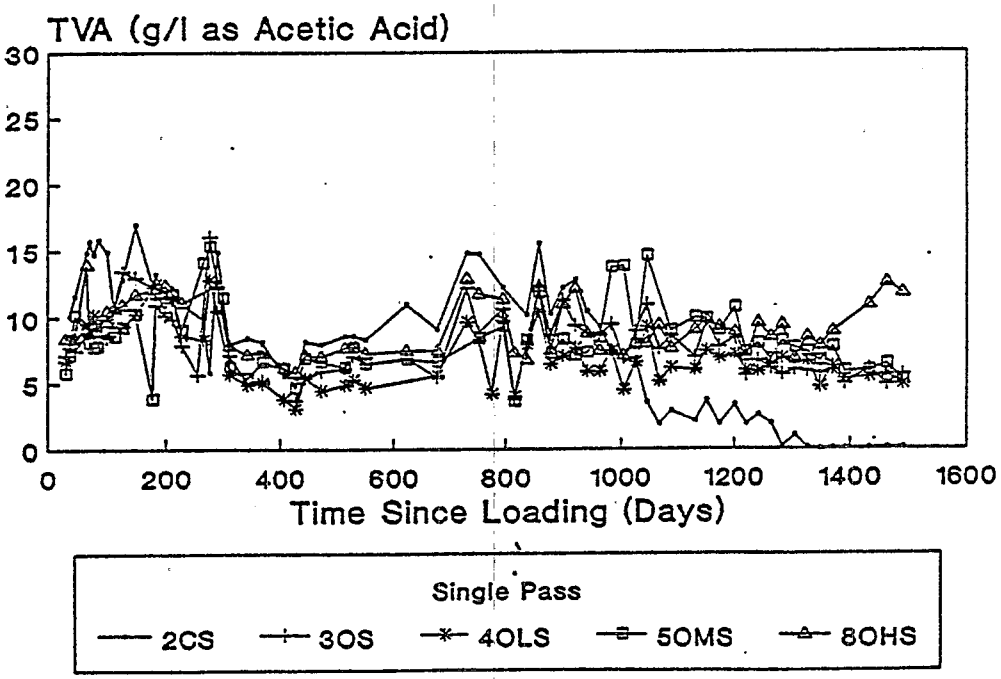


Figure 30. Leachate Total Volatile Acids during Simulated Landfill Investigations.

VOA buffering system to those of the bicarbonate buffering system. Thus, leachate recirculation provided more intimate contact between the substrate contained within the leachate and the existing anaerobic bacterial populations, thereby promoting the development of viable populations of acidogens, acetogens, and methanogens responsible for anaerobic waste stabilization. This conclusion is further evidenced by the ability of the recycle columns to accommodate applied loadings of inorganic and/or organic priority pollutants, as reflected by trends in gas production, gas composition, pH, and leachate TVA concentrations. However, increased priority pollutant loadings can cause some retardation of stabilization, as also evidenced by the behavior of the aforementioned parameters observed for Columns 90MR and 100HR.

Leachate TVA concentrations observed in the single pass columns were lower than those measured in the recycle columns, which was primarily attributed to dilution and washout effects. The changes in the TVA concentrations for the control single pass column, Column 2CS, were similar to the behavior observed in the recycle columns. However, a delay was observed compared to the control recycle column, Column 1CR. This delay implies that the leachate recirculation management strategy affords an opportunity for more complete and rapid stabilization when compared to the single pass leaching option.

The behavior of Columns 30S, 40LS, 50MS and 80HS was characteristic of inhibition. Leachate TVA concentrations remained relatively constant throughout the Methane Fermentation Phase, indicating that applied loadings under conditions of washout adversely affected TVA conversion to methane and carbon dioxide. (These four single pass columns also had the lowest volume of gas produced and the smallest percentage of methane in the gas of all 10 simulated landfill columns.) Leachate TVA concentrations were high during the Acid Formation Phase between project Days 0 and 300, and decreased slightly between project Days 300 and 800 as dilution and washout became operative. Thus, the volatile organic acids produced were removed primarily by washout as evidenced by relatively constant leachate TVA concentrations during the Methane Fermentation Phase, low gas volumes produced, and low percent methane in the gas.

Overall, the results of total volatile acids analyses suggest that the recycle columns were able to accommodate higher inorganic and organic loadings than the single pass columns. Moreover, because the recycle columns were able to achieve volatile acid conversion and waste stabilization earlier than similarly loaded single pass columns, leachate produced and not converted by the single pass columns exhibited a greater requirement for external treatment and potential of imposing adverse environmental impacts.

4.4.2.1 Mass of Volatile Acid Lost due to Leachate Removal--

During operations of the recycle and single pass simulated landfill columns, leachate was removed for sampling and analysis, and leachate was also wasted from the single pass columns in accordance with that management strategy. The leachate removed contained, among other things, volatile organic acids that could serve as substrate for methanogens.

As discussed in Section 4.2.1 and illustrated in Figure 16, the five recycle columns produced considerably more gas than the five single pass columns. This difference in cumulative gas production may have resulted because more substrate (VOA) was removed by washout from the single pass columns than from recycle columns, thus depriving methanogens in the single pass columns of their food source, with resultant lower gas production.

In order to determine if the single pass columns had the same gas production potential as the recycle columns, the potential gas volume lost due to acid removal was calculated based upon leachate TVA concentrations (Tables C-1 through C-10 of Appendix C). The mass of volatile acids in the leachate removed was determined as the product of leachate volume removed and measured TVA concentration expressed as acetic acid for each of the 10 simulated landfill

columns. This calculation assumed that all volatile acids removed, expressed as TVA as acetic acid, would have been converted into methane and carbon dioxide. Also, the hydrogen produced during the conversion of individual volatile acids to acetic acid was ignored, as was the carbon dioxide produced during the α-carboxylation of propionic acid to yield acetic acid.

The hydrogen produced during the conversion of individual volatile acid (IVA) to acetic acid exists both as the hydrogen ion and as hydrogen gas. Released hydrogen is utilized both in the production of methane from carbon dioxide and in the condensation of lower molecular weight IVA to form higher molecular weight IVA. (As indicated previously, the percentage of hydrogen gas measured by volume decreased to zero as landfill stabilization progressed.) Carbon dioxide released during propionic acid degradation can be utilized to produce methane and can exist, as can hydrogen, in either an aqueous or gaseous state. Because the purpose of this calculation was to determine the gas production potential lost due to acids removal and to compare these results between the 10 simulated landfill columns, the additional effort required and the benefits derived by including these calculations was not considered justified and beyond the scope of these investigations.

Calculations of the potential gas volume lost due to leachate removal were based upon the relationship that one mole of methane and one mole of carbon dioxide are produced from one mole of acetic acid. Therefore, the number of moles of gas removed could be determined by:

$$n_{RMVD} = \frac{(M_{RMVD}) * (2 \frac{moles\ gas}{mole\ CH3COOH})}{(MW_{CH3COOH})} \qquad (6)$$

where;

n_{RMVD} = Moles of gas removed [moles]
M_{RMVD} = Mass of TVA as acetic acid removed [g]
$MW_{CH3COOH}$ = Molecular weight of acetic acid [60.053 g/mole]

The potential gas volume lost could then be found using the ideal gas law:

$$V_{LOST} = \frac{n_{RMVD} * R * T}{P_T} \qquad (7)$$

where;

V_{LOST} = Potential gas volume lost due to leachate removal [L]
n_{RMVD} = Moles of gas removed [moles]
R = Universal Gas Constant [0.0821 L*atm/K*Mole]
T = Temperature [K]
P_T = Total pressure [atm]

The results of these calculations for the 10 simulated landfill columns are presented in Tables C-1 through C-10 of Appendix C and are summarized in Table 28. As presented in Table 28, the single pass columns lost a greater mass of acid and greater gas production potential due to leachate removal than the recycle columns where leachate was retained. In fact, the percentage of potential gas volume lost due to leachate removal was 24.9 to 72.9% for the single pass columns compared to 2.2 to 5.4% for the recycle columns.

TABLE 28. GAS PRODUCTION POTENTIAL LOST DUE TO LEACHATE REMOVAL DURING SIMULATED LANDFILL INVESTIGATIONS

Column Identity	Total Mass of Acid Removed in Leachate (g TVA as Acetic)	Total Potential Gas Volume Lost Due to Leachate Removal (M^3)	Measured Total Gas Volume (M^3)	Potential Total Gas Volume (M^3)	Percent of Total Gas Volume Lost (%)
1CR	2584	2.153	65.755	67.908	3.2
2CS	8680	7.199	21.676	28.875	24.9
3OS	9284	7.746	5.454	13.200	58.7
4OLS	8340	6.970	2.893	9.863	70.7
5OMS	10506	8.787	3.266	12.053	72.9
6OR	1536	1.281	57.126	58.407	2.2
7OLR	964	0.804	27.872	28.676	2.8
8OHS	10959	9.139	7.112	16.251	56.2
9OMR	1297	1.077	30.007	31.084	3.5
10OHR	1910	1.579	27.833	29.412	5.4

In comparing the potential cumulative gas production for the recycle and single pass columns, calculated values show that the single pass columns consistently produced less gas than the recycle columns. Therefore, the single pass columns, by virtue of the leachate management strategy employed, did not exhibit the same gas production potential as the recycle columns. Moreover, the decreased gas production observed in the columns receiving inorganic and/or organic priority pollutants, compared to the respective recycle and single pass control columns, was not due to differences in column operation, but was attributed to loading effects upon the anaerobic stabilization process.

4.4.3 Individual Volatile Organic Acid Concentrations

During the simulated landfill investigations, leachate concentrations of seven VOA were measured by the methods described in Section 3.5. These volatile acids included acetic, propionic, butyric, iso-butyric, valeric, iso-valeric, and hexanoic acids. The measured leachate concentrations of these seven acids are included in Tables C-11 through C-17 of Appendix C and are plotted for each column in Figures 31 through 40. As these figures indicate, the predominant acids found in each column included acetic, propionic, and butyric acids. The average concentrations of the seven acids between project Days 30 and 623, prior to anaerobic digester sludge seeding, were calculated and are presented in Table 29. The five recycle columns exhibited similar trends regarding acid concentrations in that butyric acid was found in the highest concentration followed by acetic, propionic, hexanoic, iso-butyric, valeric, and iso-valeric acids, respectively. This behavior was also observed for the control single pass column, Column 2CS.

Acetic acid was most prevalent in the leachate of single pass Columns 4OLS and 8OHS, and butyric acid was found in the highest concentrations in that of

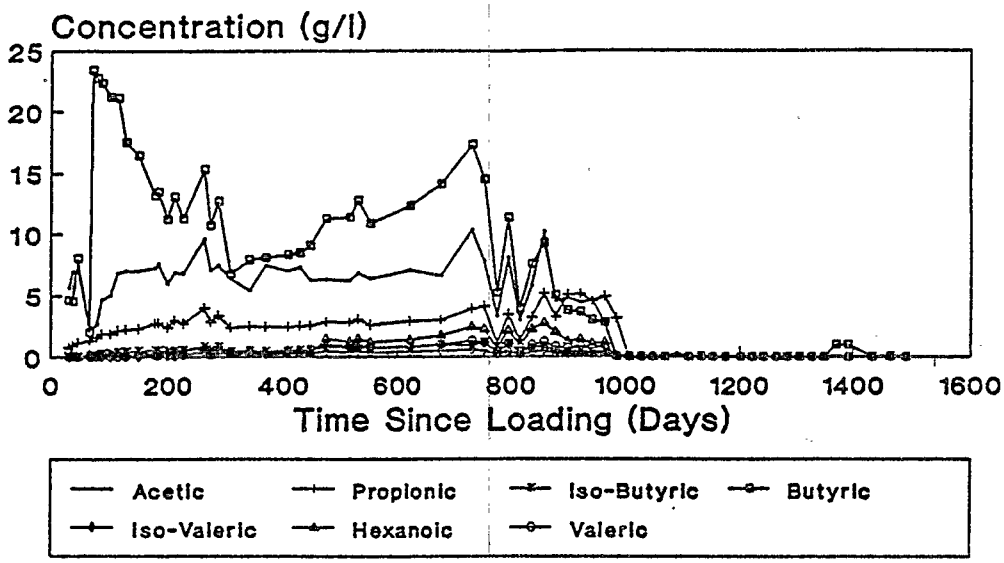


Figure 31. Leachate Individual Volatile Acids for Column 1CR.

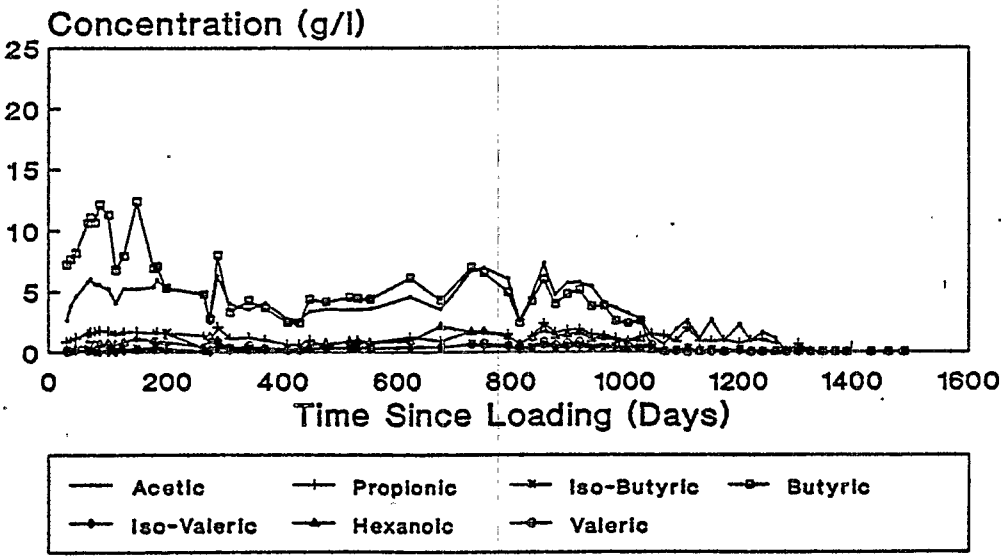


Figure 32. Leachate Individual Volatile Acids for Column 2CS.

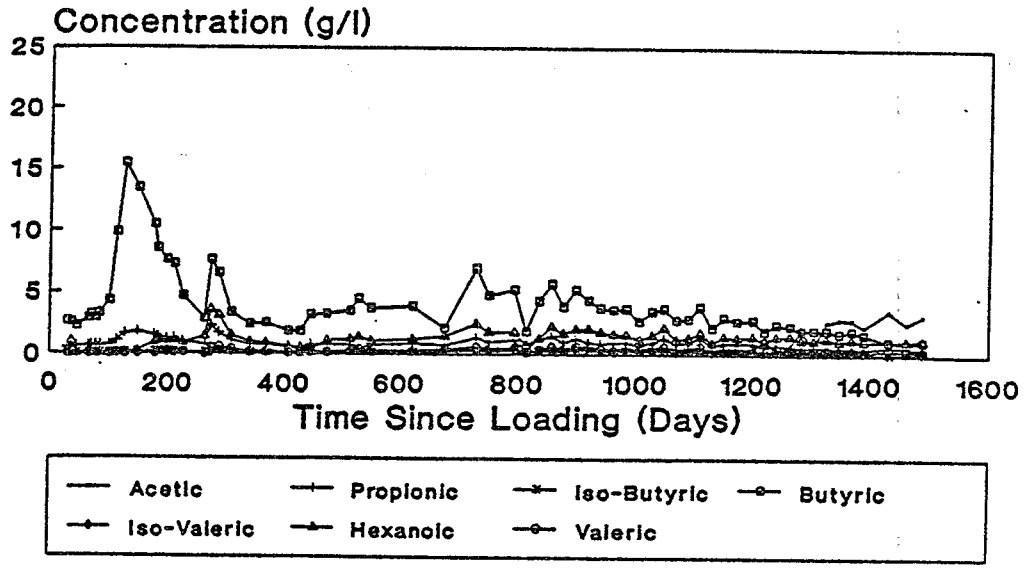


Figure 33. Leachate Individual Volatile Acids for Column 30S.

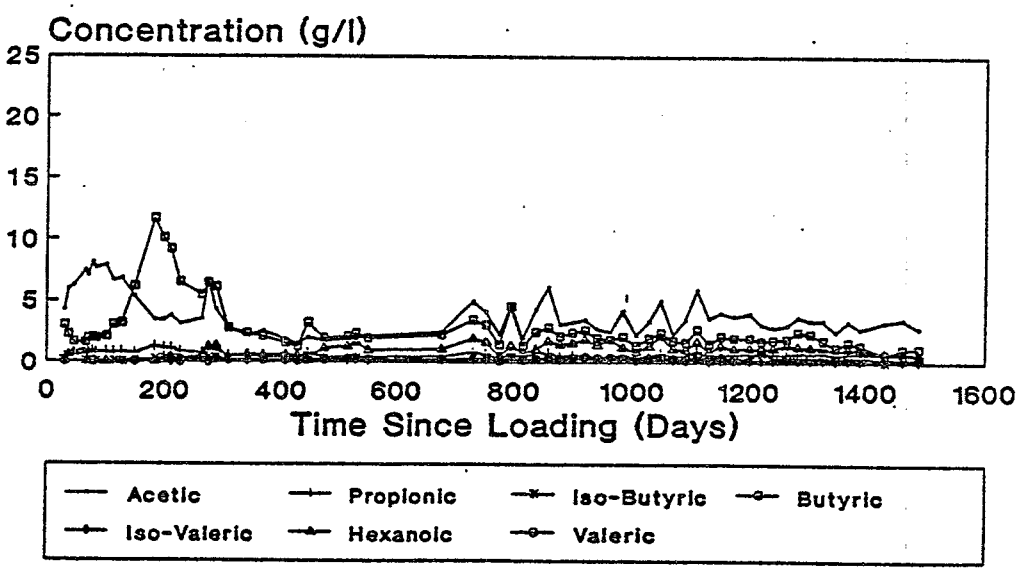


Figure 34. Leachate Individual Volatile Acids for Column 40LS.

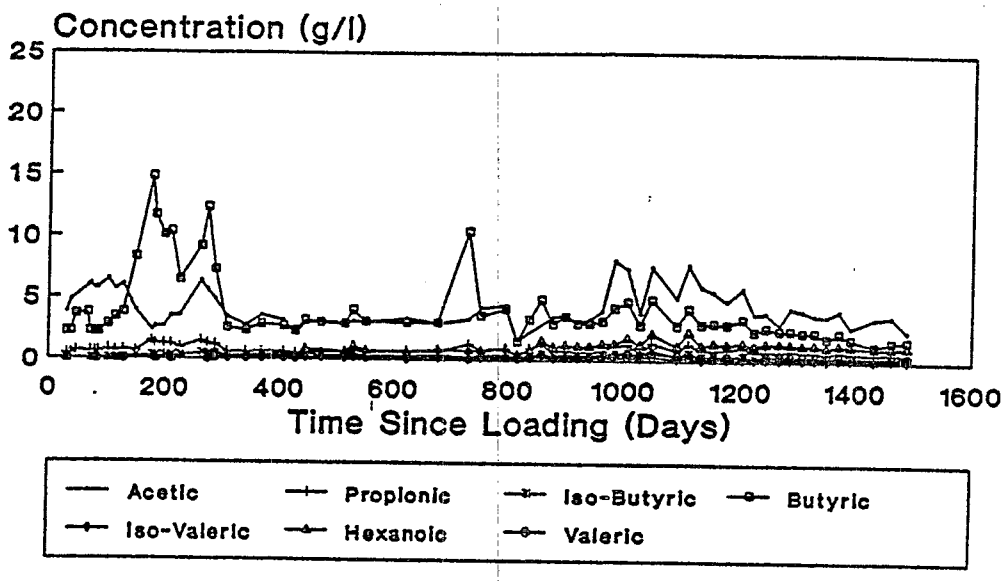


Figure 35. Leachate Individual Volatile Acids for Column 50MS.

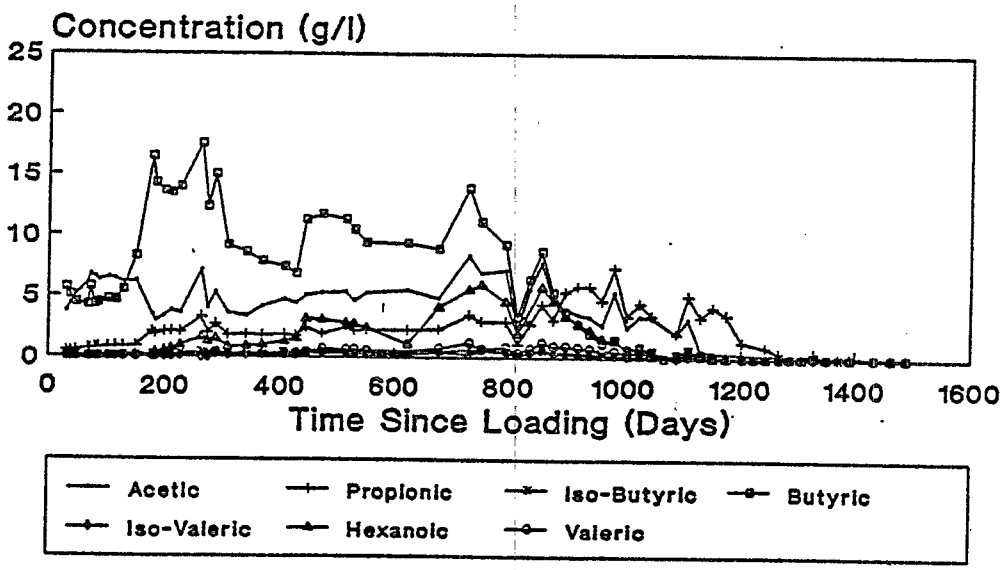


Figure 36. Leachate Individual Volatile Acids for Column 60R.

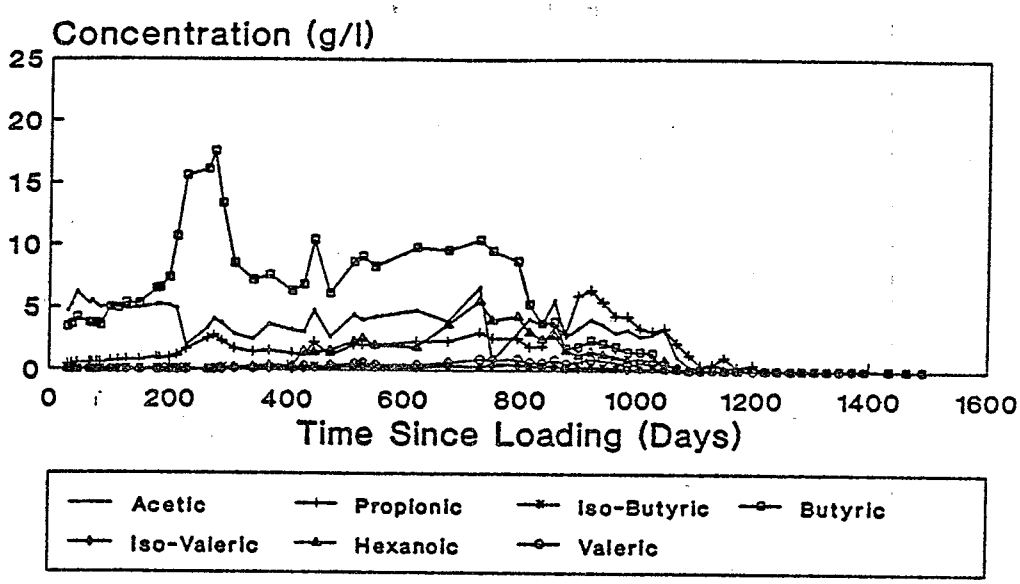


Figure 37. Leachate Individual Volatile Acids for Column 70LR.

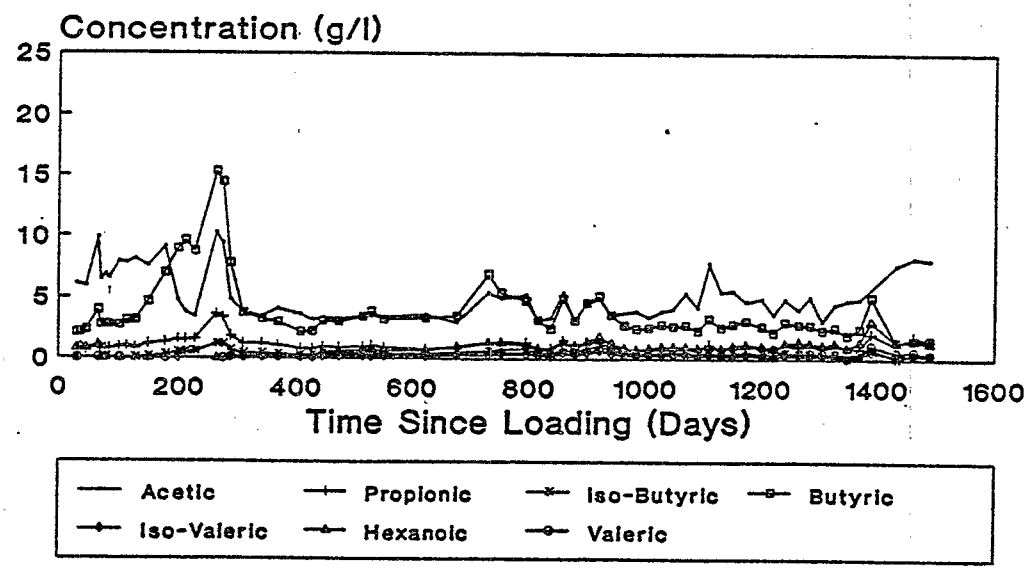


Figure 38. Leachate Individual Volatile Acids for Column 80HS.

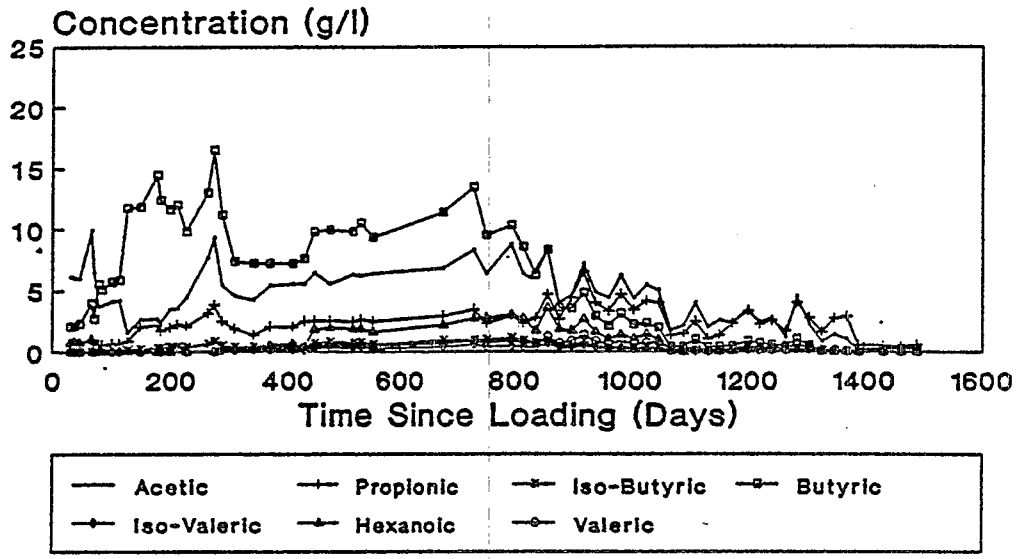


Figure 39. Leachate Individual Volatile Acids for Column 90MR.

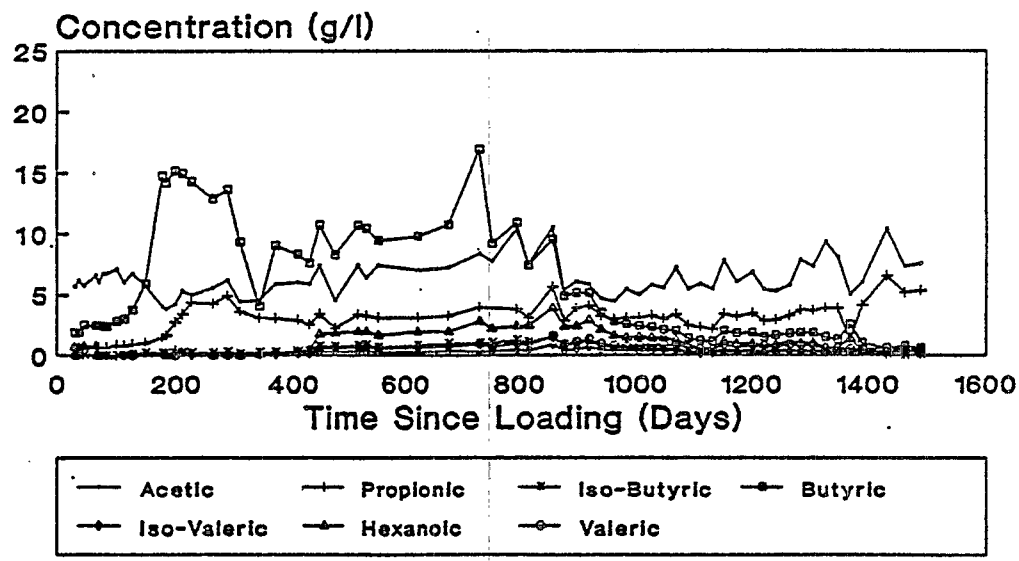


Figure 40. Leachate Individual Volatile Acids for Column 100HR.

TABLE 29. AVERAGE LEACHATE INDIVIDUAL VOLATILE ACIDS DURING THE ACID FORMATION PHASE OF THE SIMULATED LANDFILL INVESTIGATIONS

Individual Volatile Acid	Concentration (g/L)									
	1CR	2CS	3OS	4OLS	5OMS	6OR	7OLR	8OHS	9OMR	10OHR
Acetic	6.328	4.408	0.964	4.366	4.107	4.970	4.364	5.637	5.164	5.885
Propionic	2.389	1.275	0.953	0.697	0.815	1.639	1.319	1.189	1.800	2.271
Butyric	12.419	6.601	5.088	3.795	5.037	9.225	7.639	4.769	8.470	7.874
Iso-Butyric	0.512	0.366	0.127	0.181	0.259	0.202	0.154	0.429	0.392	0.287
Valeric	0.308	0.276	0.204	0.141	0.134	0.197	0.127	0.158	0.219	0.269
Iso-Valeric	0.178	0.156	0.118	0.100	0.087	0.102	0.063	0.091	0.127	0.123
Hexanoic	0.564	0.686	0.904	0.616	0.405	1.006	0.657	0.421	0.623	0.751

single pass Columns 3OS and 5OMS. In Columns 3OS, 4OLS and 5OMS, hexanoic acid was found in higher concentrations than valeric, iso-valeric, and iso-butyric acids, and hexanoic acid was found in higher concentrations than valeric and iso-valeric acids in Column 8OHS.

Moreover, the behavior of the IVA was reflected in measured TVA concentrations previously presented in Figure 30. The decline in TVA concentration for Columns 1CR, 6OR, 7OLR, 9OMR and 2CS was accompanied by a concomitant decrease in individual volatile acids concentrations, as expected. Elevated TVA concentrations present in Column 10OHR during the Methane Fermentation Phase was due to lingering propionic and acetic acid concentrations, as illustrated in Figure 40. Single pass Columns 3OS, 4OLS and 5OMS all displayed higher TVA concentrations during the Methane Fermentation Phase, which can be attributed to lingering acetic acid concentrations. The increase in TVA concentration for Column 8OHS towards the end of the experimental period can be explained by increased acetic acid concentrations.

In general, the recycle columns exhibited higher individual volatile acids concentrations during the Acid Formation Phase of landfill stabilization than the corresponding single pass columns. This trend can be attributed to washout and dilution of acids in the single pass columns, which did not significantly occur in the recycle columns because leachate was not wasted but contained within the system. Therefore, in order to avoid dilution and washout effects influencing comparison of results between the 10 simulated landfill columns, the acids produced were compared on a mass basis instead of employing a concentration-based comparison. A comparison of the mass of acid produced is discussed in Section 4.5.3.

4.4.3.1 Mass Production of Individual Volatile Acids--

The process of anaerobic conversion of organic material to produce methane and carbon dioxide occurring in a landfill environment is the same as that occurring in separate anaerobic treatment systems, with the exception that the effective retention time in a landfill is on the order of years compared to days for separate anaerobic processes. As in separate anaerobic systems, VOA are produced in landfills as a result of waste degradation, and the identification

of the type and quantity of IVA produced can provide evidence regarding the progression or inhibition of landfill stabilization processes.

The production of IVA cannot be measured simply as leachate IVA concentrations because the effects of dilution, washout, and operational differences between columns tend to obscure the results. More correctly, IVA production should encompass both the mass of IVA transferred to the leachate and the mass of IVA transformed into methane gas.[11] The mass of acid transferred to the leachate should include both the leachate removed from the column for sampling and/or wasting and the leachate retained in the column in excess of indicated field capacity. The mass of acid produced can be determined by performing a mass balance around the column control volume as shown in Figure 41. The mass of volatile acids recirculated in the five recycle simulated landfill columns is considered internal to the column control volume. The mass balance is performed as follows:

$$\frac{dM}{dt} = INFLOW - OUTFLOW + PRODUCTION - UTILIZATION \qquad (8)$$

The change in volatile acids mass per unit time (dM/dt) is a function of the mass of acids added, removed, produced and consumed. Because anaerobic processes progress slowly relative to the sampling time scale, the mass of acids accumulated from one sampling period to the next will be negligible in comparison with the mass of acids utilized, lost in the effluent, or recycled. Thus, dM/dt can be assumed to be zero. Therefore, for each IVA:

$$0 = [V_I(i) * C_I(i)] - [[V_W(i) * C_E(i)] + \\ + [\frac{C_E(i-1) + C_E(i)}{2} * V_{EX}(i)]] + M_{PRO}(i) - M_{UTIL}(i) \qquad (9)$$

where;

i	=	Sampling time period
M_{PRO}	=	Mass of IVA produced [g]
M_{UTIL}	=	Mass of IVA transformed into methane [g]
C_I	=	Concentration of IVA in feed [g/L]
C_E	=	Concentration of IVA in leachate sample [g/L]
V_I	=	Volume of liquid input to column [L]
V_W	=	Volume of leachate wasted [L]
V_{EX}	=	Volume of liquid in excess of indicated field capacity [L]

The third term in Equation (9) represents an average concentration of IVA in the liquid retained in the column in excess of indicated field capacity, because the assumption of a uniform concentration throughout the column is not necessarily valid. Equation (9) can be further simplified because only tap water was added to each column. Thus the input concentration, C_I, was zero. Rearranging Equation (9) yields:

$$M_{PRO}(i) = [V_W(i) * C_E(i)] + [\frac{C_E(i-1) + C_E(i)}{2} * V_{EX}(i)] + M_{UTIL} \qquad (10)$$

The first two terms in Equation (10) represent the mass of acids released into the leachate, and the last term, M_{UTIL}, is the mass of IVA transformed into methane.

In order to determine M_{UTIL}, the volume of methane produced by each column

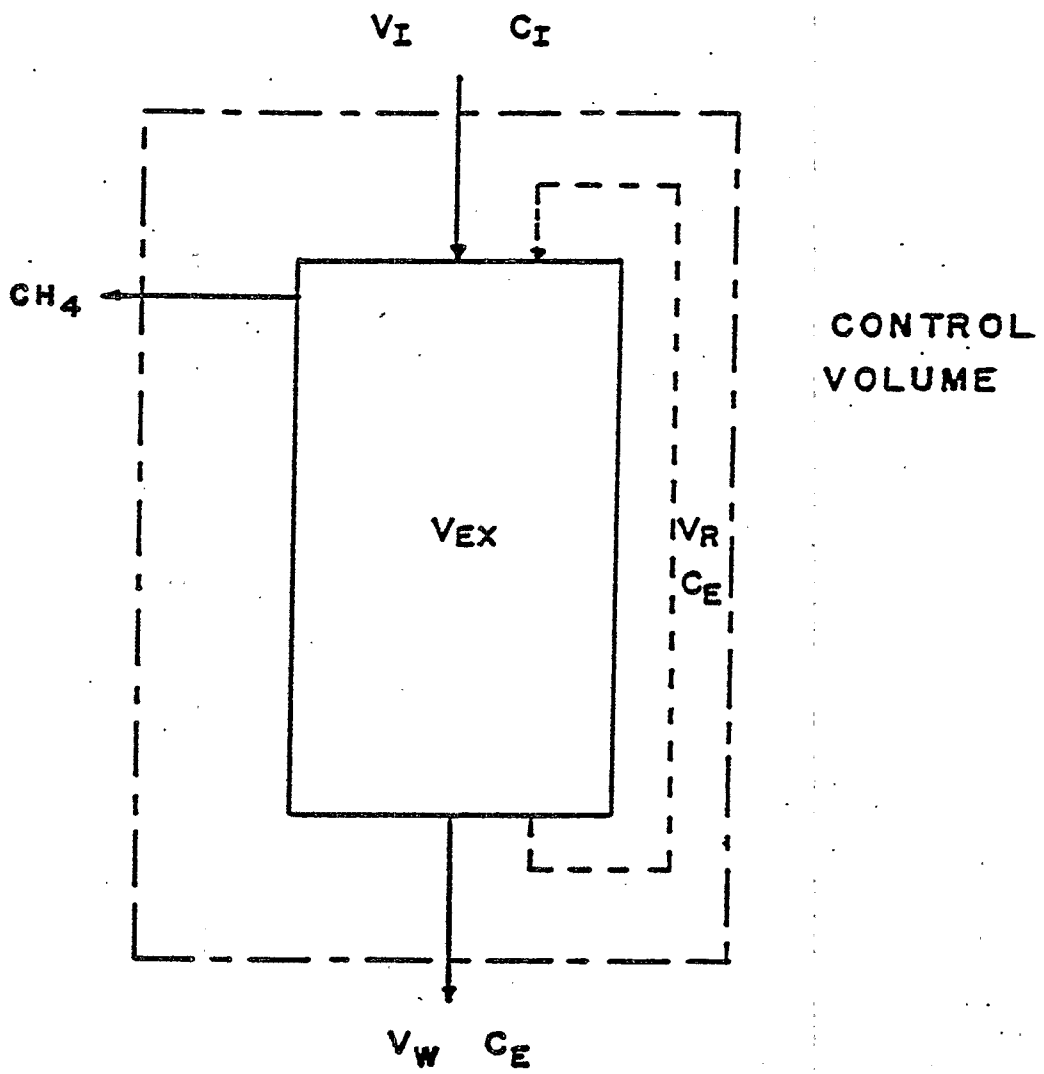


Figure 41. Mass Balance on Simulated Landfill Column Control Volumne.

was calculated. Because methane exists in both the gaseous and dissolved forms, the volume of methane gas was calculated as follows:

$$V_{MG}(i) = V_{GAS}(i) * F_{CH4}(i) * \left(\frac{273.15}{273.15+T(i)}\right) * \left(1-\frac{VP(i)}{760}\right) \quad (11)$$

where;

V_{MG} = Volume of methane gas produced [L]
V_{GAS} = Total volume of gas produced [L]
F_{CH4} = Fraction of methane in gas
T = Temperature [°C]
VP = Water vapor pressure at indicated temperature [mm Hg]

The last two terms in Equation (11) are a correction of the gas volume produced to standard temperature (0°C) and pressure (1 atm). The volume of dissolved methane was calculated by assuming that methane behaves as an ideal gas and that the density of water does not change significantly with temperature, as discussed previously. Thus:

$$V_{DM}(i) = \frac{F_{CH4}(i) * \left(1-\frac{VP(i)}{760}\right)}{H(i)} * 55.5 \frac{MOLES\ H20}{L} * \frac{}{R * (273.15+T(i)) * V_{EX}(i)} \quad (12)$$

where; H(i) is Henry's constant for methane [atm], which varies with temperature according to:

$$H(i) = ALOG\left(\frac{-\Delta H}{R * T} + K\right) \quad (13)$$

and;

ΔH = 1540 kcal/kmol
R = Universal Gas Constant [1.987 kcal/kmol*K]
T = Temperature [K]
K = 7.22 [dimensionless constant]

The total volume of methane produced (V_{CH4}) was determined as:

$$V_{CH4}(i) = V_{MG}(i) + V_{DM}(i) \quad (14)$$

The volume of methane produced, computed from Equation (14), can be converted to COD using the following expression:

$$COD_{CH4}(i) = V_{CH4}(i) * \left(2.857 \frac{g\ COD}{L\ CH4}\right) \quad (15)$$

where;

COD_{CH4} = Methane COD [g]

The calculation of the COD of methane produced is presented for the 10 simulated landfill columns in Tables C-18 through C-27 of Appendix C.

It was then necessary to determine the fraction of methane produced that could be attributed to each of the seven individual volatile acids monitored during these studies. This calculation was performed using a ratio of the COD of the individual volatile acid under consideration in the leachate to the total leachate individual volatile acid COD. This ratio was determined for each of the seven individual volatile acids during each sampling period and was determined as follows:

$$MC(n,i) = \frac{IVA(n,i) * COD(n)}{\sum [IVA(n,i) * COD(n)]} \qquad (16)$$

where;

- n = Acetic, propionic, butyric, iso-butyric, valeric, iso-valeric, or hexanoic acid
- i = Sampling time period
- MC = Fraction of methane attributable to IVA_n during time period i
- IVA = Leachate concentration of IVA_n [g/L]
- COD = COD equivalent of IVA_n

Calculations of the fraction of methane attributable to each IVA in each of the 10 simulated landfill columns are presented in Tables C-28 through C-37 of Appendix C.

Lastly, the mass of acid transformed into methane (M_{UTIL}) can be determined using Equation (17) and substituting the result into Equation (10) to yield the mass of acid produced.

$$M_{UTIL} = \frac{COD_{CH4} * MC(n,i)}{COD_n} \qquad (17)$$

The mass of the seven IVA produced in each of the 10 simulated landfill columns was calculated, and sample calculations for the seven IVA are presented in Tables C-38 through C-44 of Appendix C. Tables C-45 through C-54 of Appendix C summarize, for each simulated landfill column, the mass of IVA released into the leachate; and Tables C-55 through C-64 of Appendix C summarize, for each simulated landfill column, the mass of IVA transformed into methane. Results are presented graphically in Figures 42 through 51 for each simulated landfill column. These figures display the mass of each of the seven IVA released into the leachate as well as the total mass of acid transformed into methane gas. To assist in graphic display, the results are presented in stacked bar format at selected time intervals, approximately every 70 days.

Upon examination of Figures 42 through 51, some general trends regarding the release and transformation of IVA were observed. An increase in the mass of IVA released occurred with the progression of the Acid Formation Phase of landfill stabilization in Columns 1CR, 6OR, 7OLR, 9OMR and 2CS. The mass of volatile acids released declined concomitantly with the production of methane and the resulting utilization of these available acids.

The IVA in the leachate were effectively removed by conversion to methane and carbon dioxide in Column 1CR by project Day 1022. After this time, methane continued to be produced, suggesting that VOA were still being generated. However, they were utilized as quickly as they were released, thus VOA were

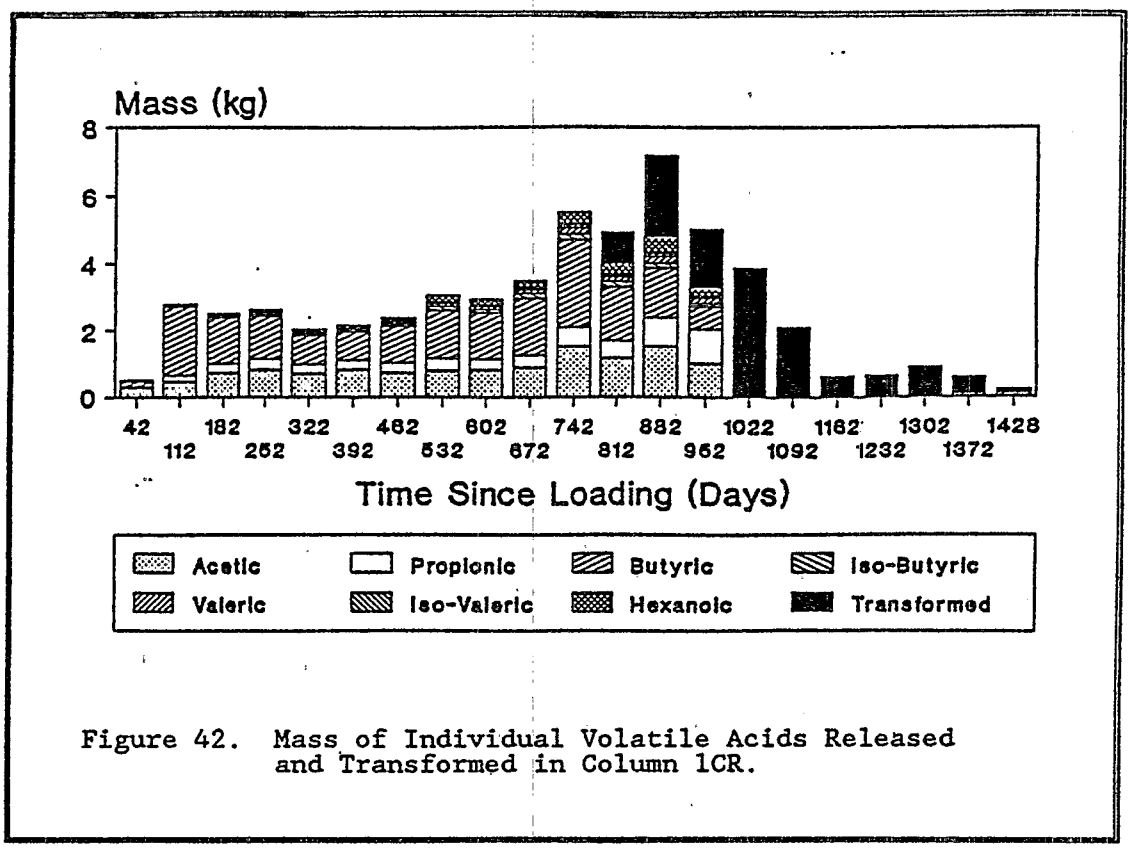


Figure 42. Mass of Individual Volatile Acids Released and Transformed in Column 1CR.

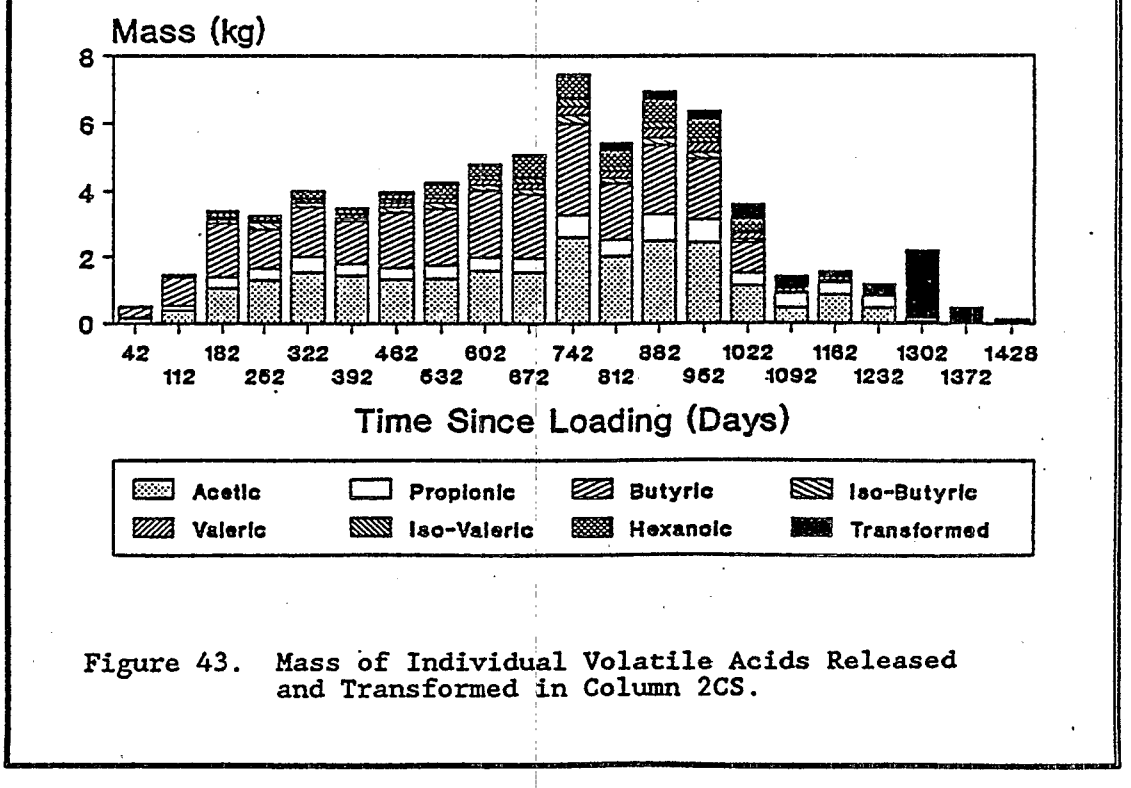


Figure 43. Mass of Individual Volatile Acids Released and Transformed in Column 2CS.

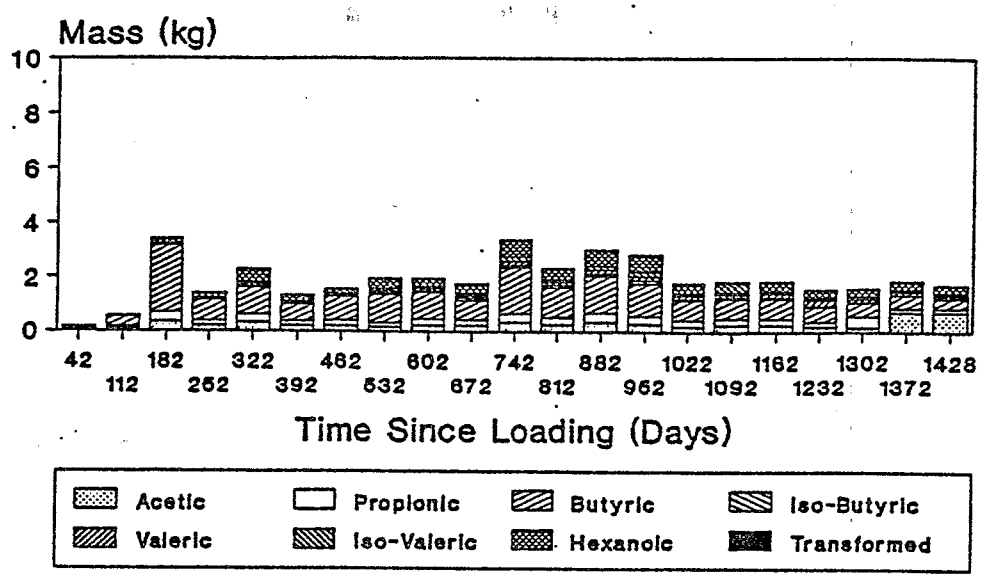


Figure 44. Mass of Individual Volatile Acids Released and Transformed in Column 30S.

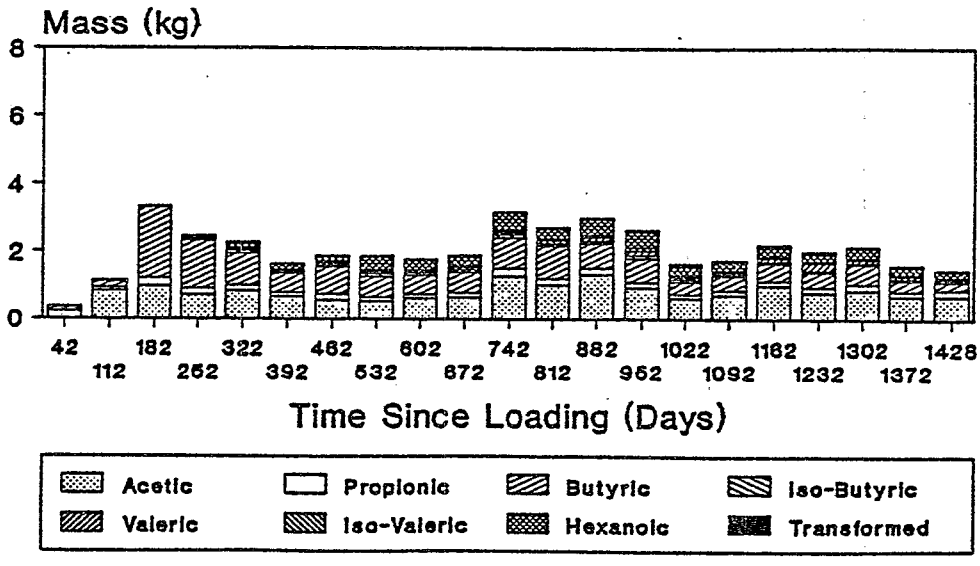


Figure 45. Mass of Individual Volatile Acids Released and Transformed in Column 40LS.

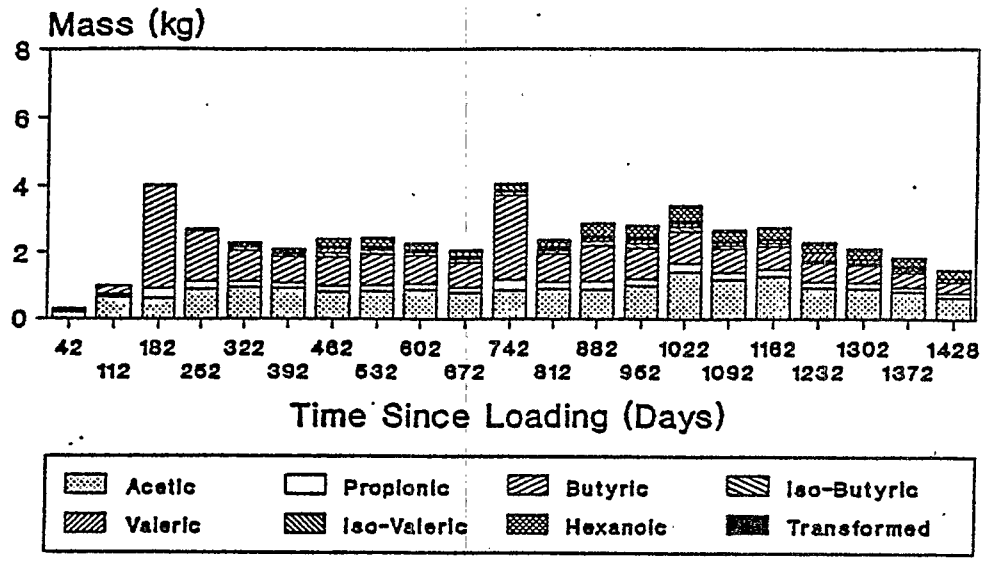


Figure 46. Mass of Individual Volatile Acids Released and Transformed in Column 5OMS.

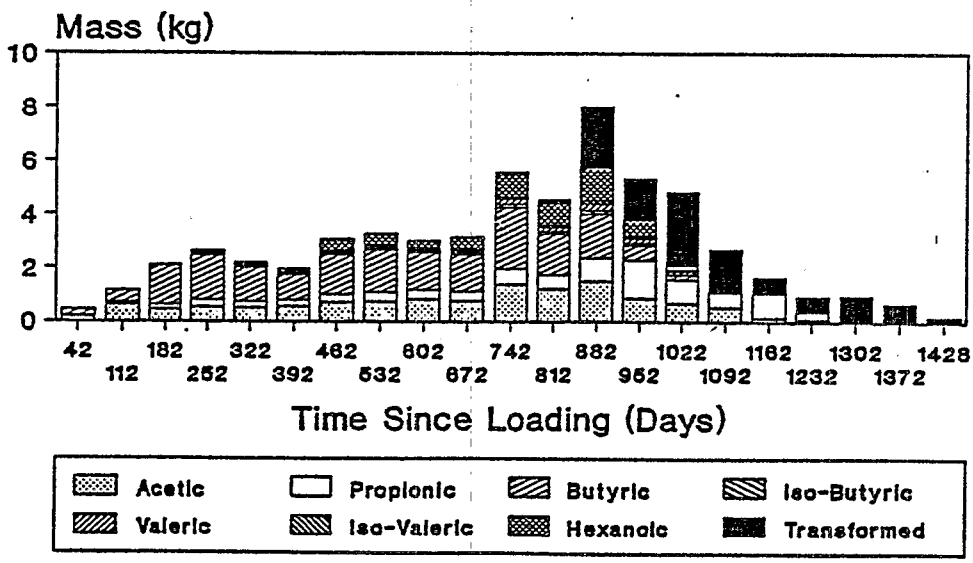


Figure 47. Mass of Individual Volatile Acids Released and Transformed in Column 6OR.

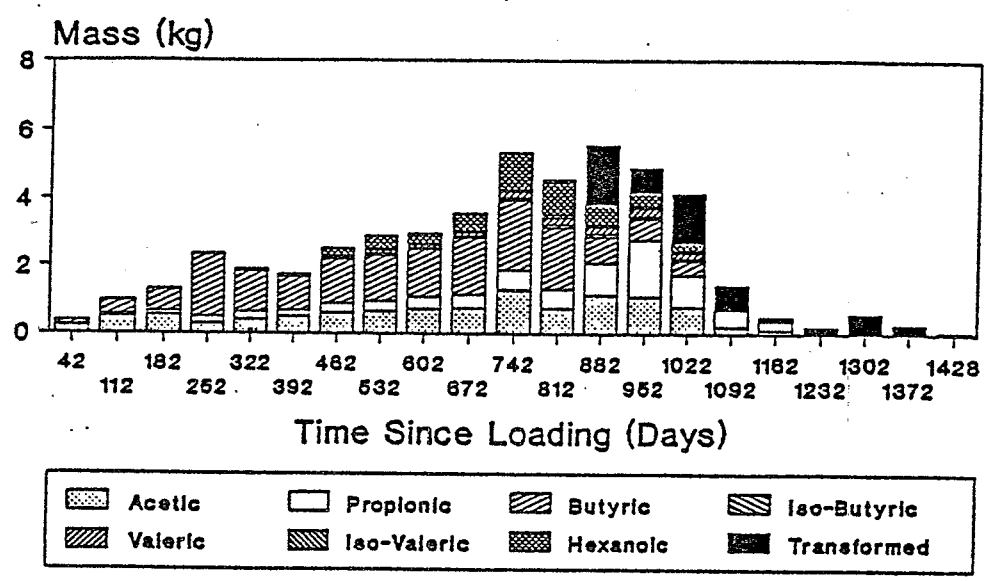


Figure 48. Mass of Individual Volatile Acids Released and Transformed in Column 70LR.

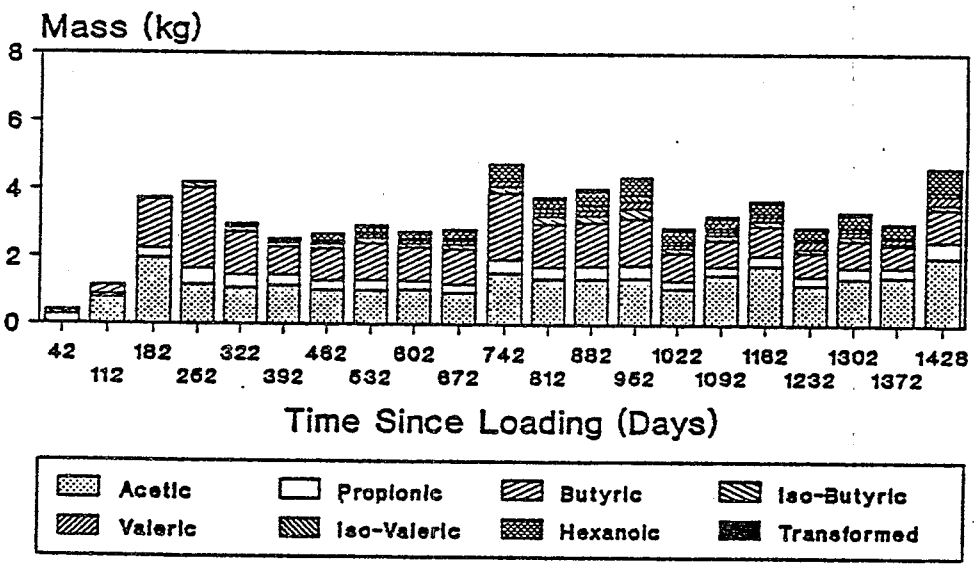


Figure 49. Mass of Individual Volatile Acids Released and Transformed in Column 80HS.

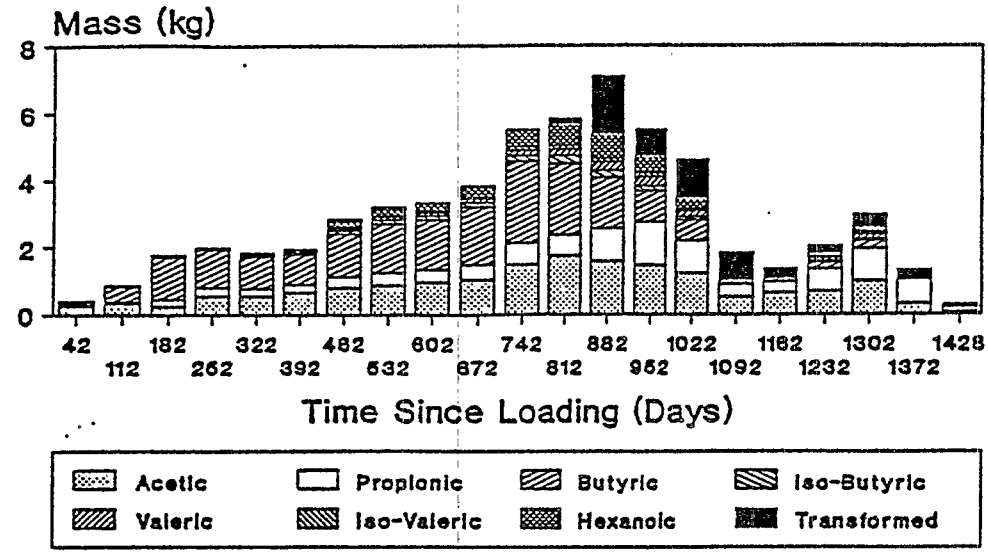


Figure 50. Mass of Individual Volatile Acids Released and Transformed in Column 90MR.

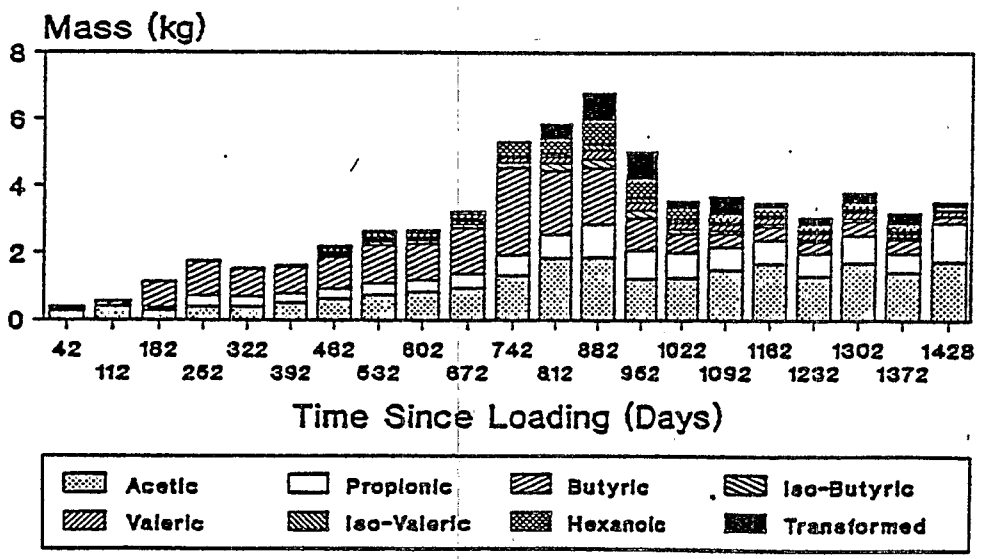


Figure 51. Mass of Individual Volatile Acids Released and Transformed in Column 100HR.

difficult to detect in the leachate. Towards the end of the experimental period at project Days 1372 and 1428, butyric acid began to appear along with low masses of acetic and propionic acids. The appearance of these acids probably resulted from the onset of degradation of more microbially resistant materials. Additionally, Column 1CR had the highest mass of acids transformed into methane, signifying the most viable and greatest degree of waste conversion.

Column 6OR displayed similar behavior to Column 1CR, however, a delay in the removal of acids from the leachate occurred. Volatile organic acids were not significantly removed until project Day 1302, a probable result of the added organic priority pollutant loadings applied to this column.

Similar to Column 6OR, Column 7OLR also displayed a delay in the removal of volatile organic acids from the leachate compared to Column 1CR, but acids mass was significantly reduced by project Day 1232. Also, Column 7OLR showed smaller masses of acids being initially transformed into methane, providing evidence of the retarding effects of the added inorganic and organic priority pollutants.

Column 9OMR exhibited a slow decline in the mass of volatile organic acids released. However, the VOA were never reduced to the low levels achieved by Columns 1CR, 6OR, and 7OLR. This behavior was attributed to the higher inorganic priority pollutant loading present in Column 9OMR.

The control single pass column, Column 2CS, also behaved similarly to the control recycle column, Column 1CR. The mass of volatile organic acids released to the leachate was removed by project Day 1372 by both washout and conversion to methane and carbon dioxide. Although Column 2CS produced methane, the mass of acid utilized to form this methane was much lower in Column 2CS than in Column 1CR, suggesting that leachate recirculation promoted more thorough waste conversion by providing a more complete contact between the microorganisms and usable substrate.

The most heavily loaded recycle column, Column 10OHR, exhibited behavior characteristic of severe retardation due to applied organic and inorganic waste loadings. The mass of volatile organic acids released increased until approximately project Day 882, followed by a slight decline commensurate with the onset of methane production. However, the mass of volatile organic acids released remained relatively constant from project Day 1022 until the end of the experimental period. Because Column 10OHR released about the same mass of acids into the leachate, and had a significantly lower mass of acids transformed into methane, it is likely that the applied loadings adversely affected the acetate utilizing methanogenic population.

The remaining four single pass columns, Columns 3OS, 4OLS, 5OMS and 8OHS, displayed lower masses of volatile organic acids released than from Column 2CS. Additionally, all of these four columns displayed a negligible mass of acids transformed into methane, and relatively constant mass of acids released throughout the experimental period after an initial lag of 182 days. These results suggest that the combination of loading applied and leachate management strategy employed adversely affected both the acid forming and methane forming populations.

In general, the five recycle columns displayed a greater mass of individual volatile acids transformed into methane than did the single pass columns. Also, recycle Columns 6OR, 7OLR, 9OMR and 10OHR showed more volatile organic acids released than the corresponding single pass columns, while the control single pass column, Column 2CS, had a higher mass of acids released than did the control recycle column, Column 1CR. These results imply that the environment in the recycle columns, in general, was more favorable to acid formers and methanogens, which can be attributed to increased contact opportunities between biomass, nutrients and substrate offered by this leachate management strategy. Because

the single pass columns were more severely affected by the codisposed inorganics and/or organics, as evidenced by the relatively constant mass of volatile organic acids released throughout the experimental period, leachate produced in the single pass systems would require external treatment and had a greater possibility of adversely affecting the environment if it were to escape the landfill boundaries.

The primary acids released by the 10 simulated landfill columns included acetic, propionic, and butyric acids. Of these acids, butyric acid was the most predominant during the Acid Formation Phase, followed by acetic and propionic acids, respectively.

All seven individual volatile acids were released into the leachate of the 10 simulated landfill columns, however, the mass of IVA released differed between columns. In general, columns that exhibited the progression of anaerobic waste stabilization processes similar to those displayed in Figure 1 (Columns 1CR, 2CS, 6OR, 7OLR, 9OMR and 10OHR) released more IVA into the leachate than those columns exhibiting signs of retardation of the stabilization process (Columns 3OS, 4OLS, 5OMS, and 8OHS). The columns that released the lowest mass of IVA into the leachate and displayed signs of retardation were all single pass columns that received inorganic and/or organic priority pollutant loadings. These findings suggest that a combination of the single pass leaching management strategy and priority pollutant loadings inhibited the decomposition of soluble organic material into volatile organic acids. (Factors affecting the waste stabilization process were discussed in Section 2.2.2.) Therefore, higher masses of IVA released and transformed into methane were observed in Columns 1CR, 2CS, 6OR, 7OLR, 9OMR and 10OHR, while lower masses of IVA released and transformed were observed in Columns 3OS, 4OLS, 5OMS and 8OHS.

Upon examining Figures 42 through 51, and studying supporting data, some interesting relationships among the IVA was observed. Probably the most significant of these relationships occurred between the mass of hexanoic and butyric acids released into the leachate. Hexanoic acid was detected in the leachate of all 10 simulated landfill columns, however, hexanoic acid was released into the leachate earlier in single pass columns than in recycle columns. Additionally, an increase in the mass of butyric acid released into the leachate was accompanied by an increase in hexanoic acid mass released.

Similar results regarding the formation of longer chain IVA due to increases in lower molecular weight VOA were reported by McCarty and coworkers[18,40] using laboratory-scale anaerobic digesters. An explanation of hexanoic acid production during periods of high butyric acid mass is the thermodynamic favorability of the condensation of butyric and acetic acids to form hexanoic acid. Once hexanoic acid was produced, it was present in the leachate until methane fermentation commenced, which promoted a reduction in the mass of butyric acid in the leachate. Additionally, the decline in hexanoic acid mass released was accompanied by decreases in butyric and acetic acid mass as well. This relationship may result from the breakdown of hexanoic acid into butyric and acetic acid, and the breakdown of butyric acid to form acetic acid.

A second interesting behavior was observed between propionic, valeric, and hexanoic acids. Within all 10 simulated landfill columns during the Acid Formation Phase of landfill stabilization, it was observed that increases in the mass of propionic acid released were accompanied by concomitant increases in the mass of hexanoic and valeric acids released. This relationship may be explained by the condensation of two moles of propionic acid to form hexanoic (caproic) acid, and the combination of propionic and acetic acids to produce valeric acid. These reverse reactions become favorable when the mass of released propionic acid is high. Propionic acid, which is produced during the anaerobic conversion of carbohydrates and proteins, may be released in large masses as a result of the conversion of these constituents during stabilization processes.

As mentioned previously, the primary acids released in all 10 simulated landfill columns included butyric, acetic, and propionic acids. Hexanoic acid masses became significant toward the end of the Acid Formation Phase and beginning of Methane Fermentation Phase for those columns exhibiting significant progress toward complete anaerobic waste stabilization. These columns included Columns 1CR, 6OR, 7OLR, 9OMR, 1OOHR and 2CS. Within these columns, hexanoic acid masses were reduced upon commencement of methane production. However, in single pass Columns 3OS, 4OLS, 5OMS and 8OHS, hexanoic acid masses were significant throughout the experimental period. These results suggest that the more sensitive members of the anaerobic microbial consortia were adversely affected by the leachate management strategy, simulated landfill column pH, and/or presence of toxic materials. Thus, it appears that the organisms responsible for both the production (acidogens) and subsequent degradation (acetogens) were inhibited, as evidenced by lower masses of volatile organic acids produced and the composition of individual volatile acids produced.

4.4.4 Total Alkalinity

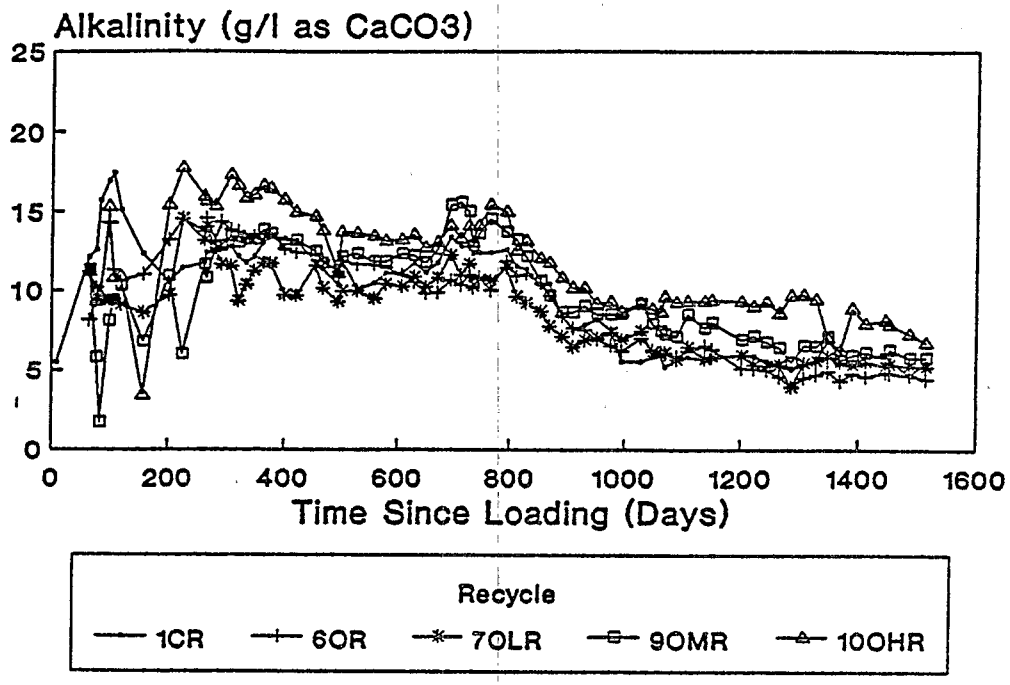
Total alkalinity is a measure of system buffer capacity. The measured leachate alkalinity concentrations for the recycle and single pass columns are provided in Figure 52. Measured leachate alkalinity concentrations are presented in Table A-16 of Appendix A. Alkalinity concentrations for the five recycle columns closely paralleled the measured TVA concentrations. During the Acid Formation Phase, leachate alkalinity remained relatively constant which, along with high TVA concentrations and low pH (5.0 to 5.5), suggested that a volatile organic acid buffering system predominated. As methanogens utilized the available VOA as substrate, pH increased and the total alkalinity concentrations tended to decrease. As previously discussed, Column 1OOHR was adversely affected by applied pollutant loadings as evidenced by lingering leachate TVA concentrations and depressed pH during the Methane Fermentation Phase. Further evidence of retardation was demonstrated by higher total alkalinity concentrations for Column 1OOHR than for the other recycle columns.

Single pass column leachate alkalinity concentrations were high initially until project Day 150, and decreased thereafter primarily due to washout. Alkalinity concentrations remained consistently low during the Methane Fermentation Phase, even though TVA concentrations were relatively stable, which provides further evidence of washout. Column 2CS exhibited a slightly different behavior than the other four single pass columns during the Methane Fermentation Phase, in that alkalinity concentrations declined to lower values around project Day 1100, which was accompanied by a concomitant decline in TVA concentration.

4.4.5 Organic Strength Indicators

Leachate chemical oxygen demand (COD) and total organic carbon (TOC) were measured as indicators of organic strength and the potential pollutional impact that may result if leachate is released. Leachate COD concentrations for the recycle and single pass columns are presented in Figure 53 and TOC concentrations for the recycle and single pass columns are provided in Figure 54. Measured leachate COD and TOC concentrations are presented in Tables A-17 and A-18 of Appendix A.

Recycle column leachate COD and TOC concentrations closely paralleled those of the TVA, since TVA represent a large portion of COD and TOC especially during the Acid Formation Phase. Leachate COD and TOC both remained relatively constant at their highest concentrations during the Acid Formation Phase. After seeding with anaerobic digester sludge and neutralization promoted the onset of methanogenesis, leachate COD and TOC concentrations declined in accordance with the progression of microbially-mediated stabilization processes. Decreases in COD and TOC concentrations, as well as TVA concentrations, occurred along with corresponding increases in gas production. This relationship indicates that much of the leachate organic content was removed by *in situ* treatment and conversion



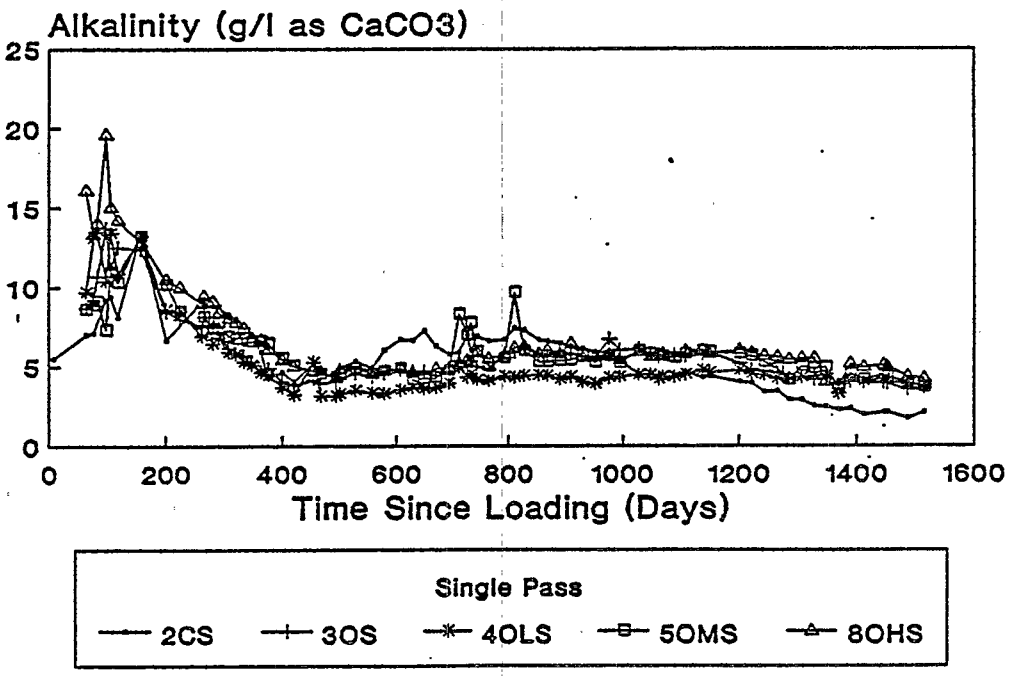
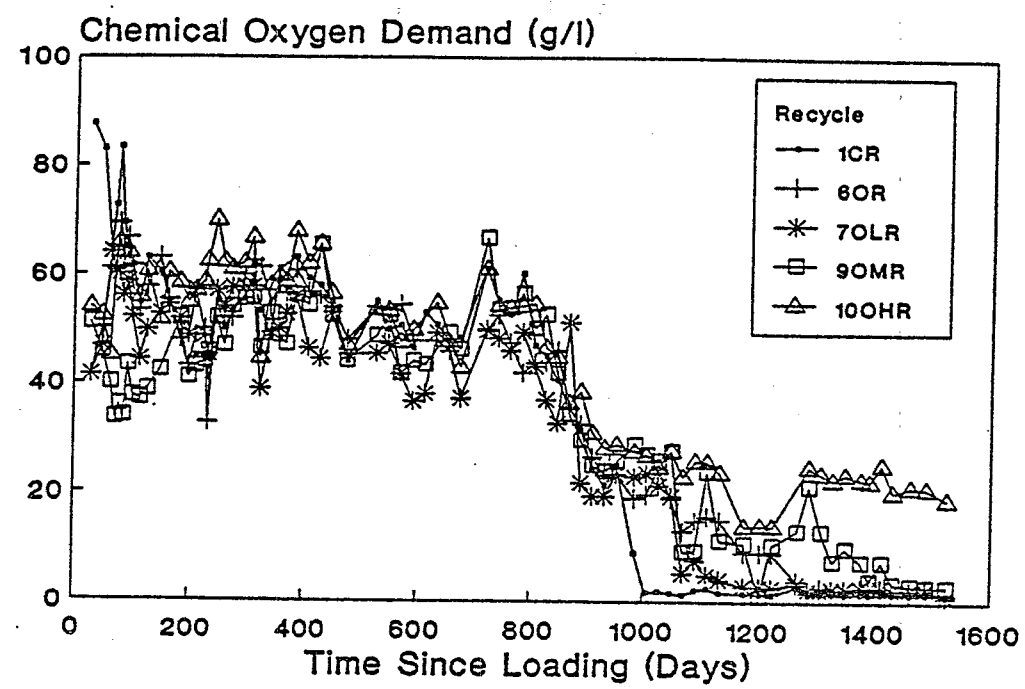


Figure 52. Leachate Alkalinity during Simulated Landfill Investigations.



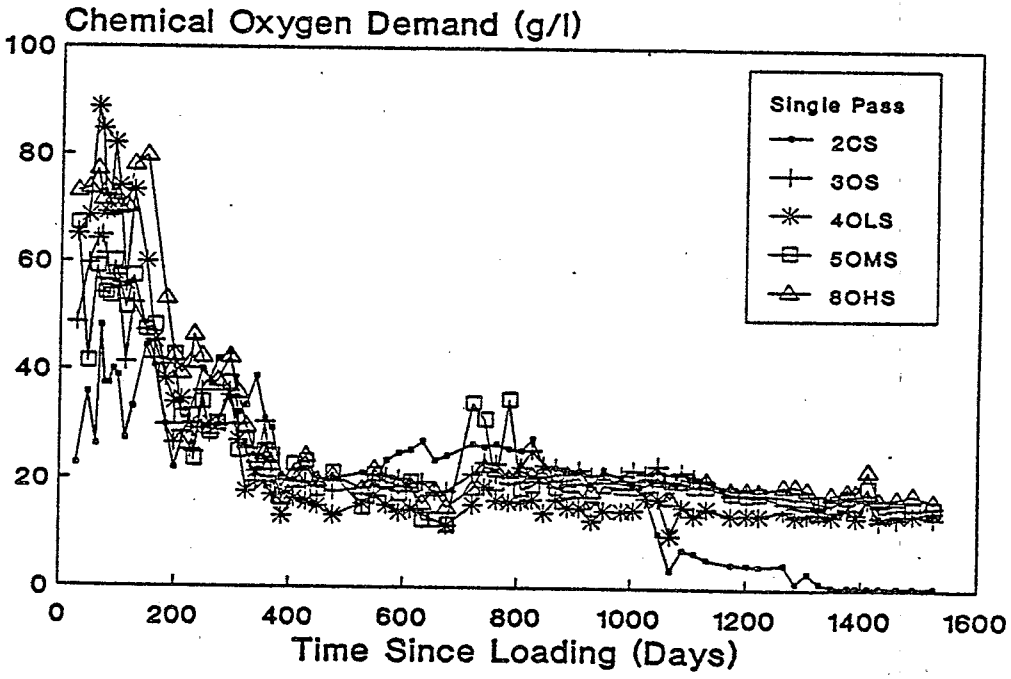
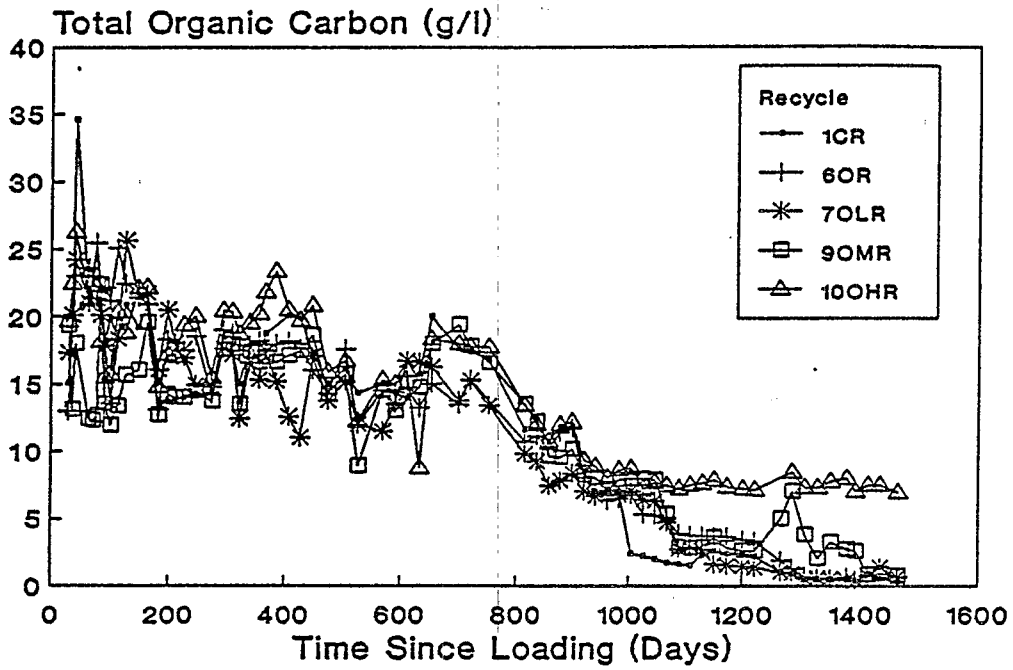


Figure 53. Leachate Chemical Oxygen Demand during Simulated Landfill Investigations.



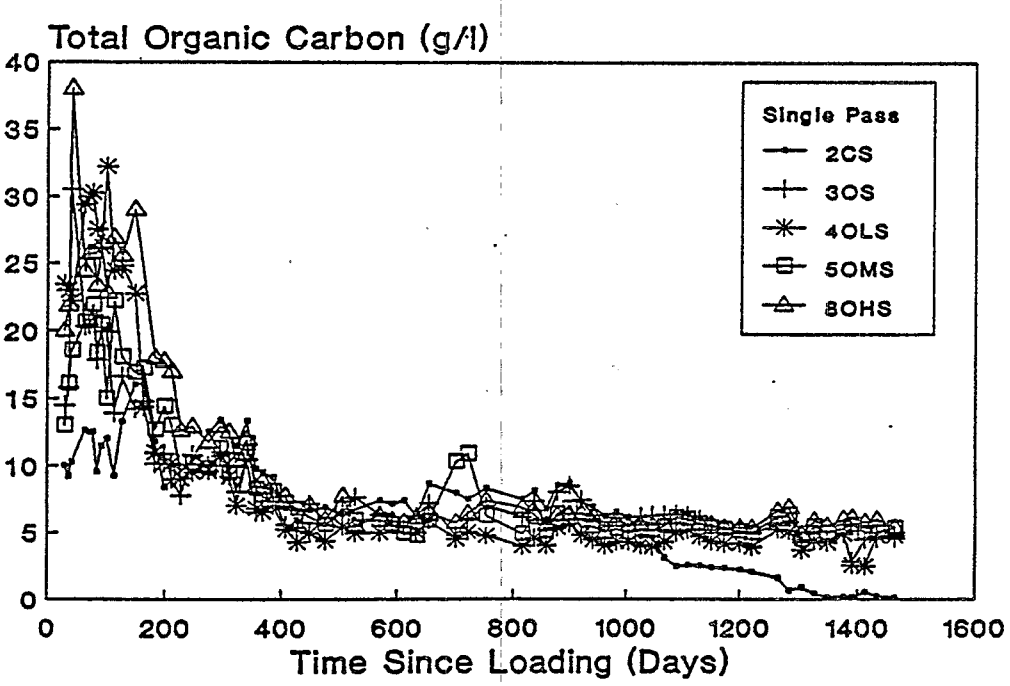


Figure 54. Leachate Total Organic Carbon during Simulated Landfill Investigations.

to methane and carbon dioxide, since leachate was essentially not wasted from the recycle columns. Column 100HR continued to show signs of retardation, as indicated by higher relative COD and TOC concentrations during the Methane Fermentation Phase. The high removal rate of organic material from the leachate of the recycle columns can be attributed to the nature of leachate recirculation management strategy and continuing exposure of anaerobic microorganisms to available substrate.

Single pass column COD and TOC concentrations exhibited effects characteristic of washout as indicated by the rapid decline in concentration until project Day 400 and the absence of significant methane gas production during this time period. Although some organic material stabilization occurred during the Methane Fermentation Phase, as evidenced by some methane gas production, the majority of the leachate organic content was removed by washout. However, Column 2CS, displayed signs of increased biological conversion of organic material when compared to other single pass columns, in that both COD and TOC concentrations were reduced around project Day 1050 to levels lower than those existing in the leachates of the other four single pass columns.

These results again suggested that the leachate recirculation management option provided for more complete organic material conversion than did the single pass leaching management strategy. Stabilization of organic material released to the leachate of the recycle columns surpassed that of the single pass columns, as illustrated by increased gas production, and larger percent methane in the gas phase, and decreased leachate COD, TOC and TVA concentrations. In addition, inorganic and/or organic loadings applied to recycle columns were apparently accommodated by the landfill environment present, whereas similar loadings applied to the single pass columns were inhibitory to waste stabilization processes.

4.4.6 Oxidation-Reduction Potential

Oxidation-reduction potential (ORP) measured during these studies indicated the oxidizing or reducing conditions present in the 10 simulated landfill columns. Measured leachate ORP values for recycle and single pass columns are presented in Figure 55 and the supporting data are included in Table A-19 of Appendix A.

As indicated by Figure 55, leachate ORP values for the recycle columns remained characteristic of a reducing environment, however, dramatic fluctuations during the Acid Formation Phase were observed. After the onset of active methane production around project Day 800, variations in leachate ORP were dampened, and ORP values declined to a low of approximately -350 mV on project Day 1348 for all recycle columns except Column 100HR. After this minimum ORP value was achieved, leachate ORP values began to become less negative. Leachate ORP values measured in Column 100HR followed a pattern similar to the other four recycle columns, however, the minimum value reached was -181 mV. Despite the analytical sensitivity of ORP measurements, these results further support the conclusion that methanogens in Column 100HR were adversely affected by the applied loading, because an ORP of at least -300 mV is generally required for proliferation of methanogens.

Leachate ORP values measured for the single pass columns were generally less negative (or in some cases positive) than those measured for the recycle columns. Column 2CS, the control single pass column, displayed a behavior similar to the recycle columns during the Methane Fermentation Phase, in that ORP values declined concomitantly with more active methane production and reached their lowest value of -279 mV on project Day 1327. After achieving this value, leachate ORP values increased similarly to the behavior of recycle columns. During the Acid Formation Phase, ORP values measured in the single pass columns were sometimes positive or only slightly negative, which can partially be attributed to displacement of air originally present in refuse void spaces. The

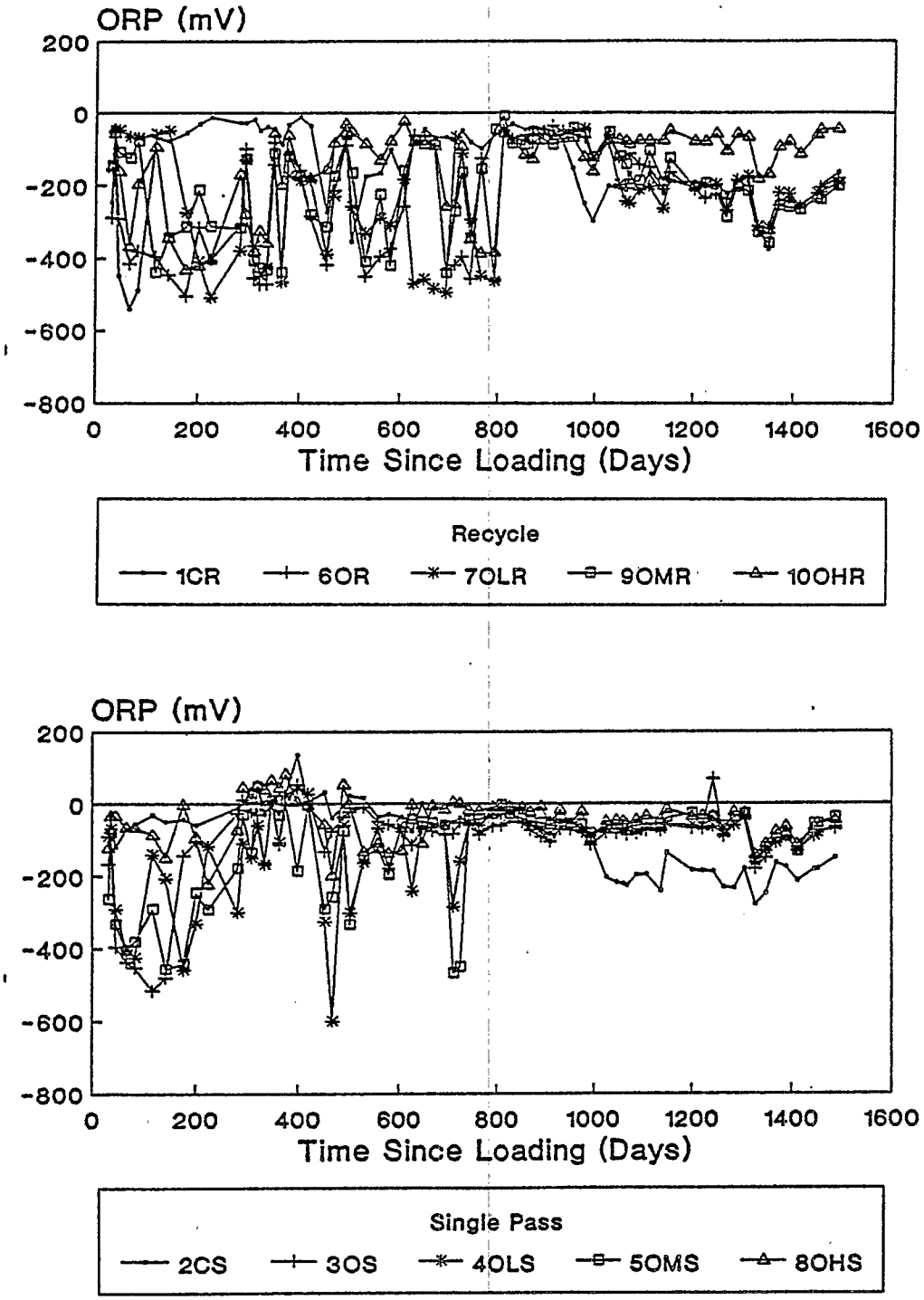


Figure 55. Leachate ORP during Simulated Landfill Investigations.

remaining four single pass columns, Columns 30S, 40LS, 50MS and 80HS, reached their minimum ORP values of approximately -160 mV on project Day 1327. The ORP values maintained by these columns during the Methane Fermentation Phase were less conducive to the establishment of a viable population of methanogens, as evidenced by low gas production volumes, low percent methane in the gas, and lingering leachate TVA, COD, and TOC concentrations.

4.4.7 Chloride

In order to observe the effects of leachate management strategies upon priority pollutant behavior and fate, leachate chloride was measured as a conservative tracer, not affected by biological conversion. Chloride concentrations for the recycle and single pass columns are presented in Figure 56, and measured leachate chloride concentrations are presented in Table A-20 of Appendix A. Leachate chloride concentrations in the recycle columns decreased slowly due to dilution effects after an initial period of leaching and mobilization. In contrast, leachate chloride concentrations for the single pass columns exhibited a behavior characteristic of washout of a conservative tracer, as evidenced by the rapid decline in concentrations.

4.4.8 Ammonia

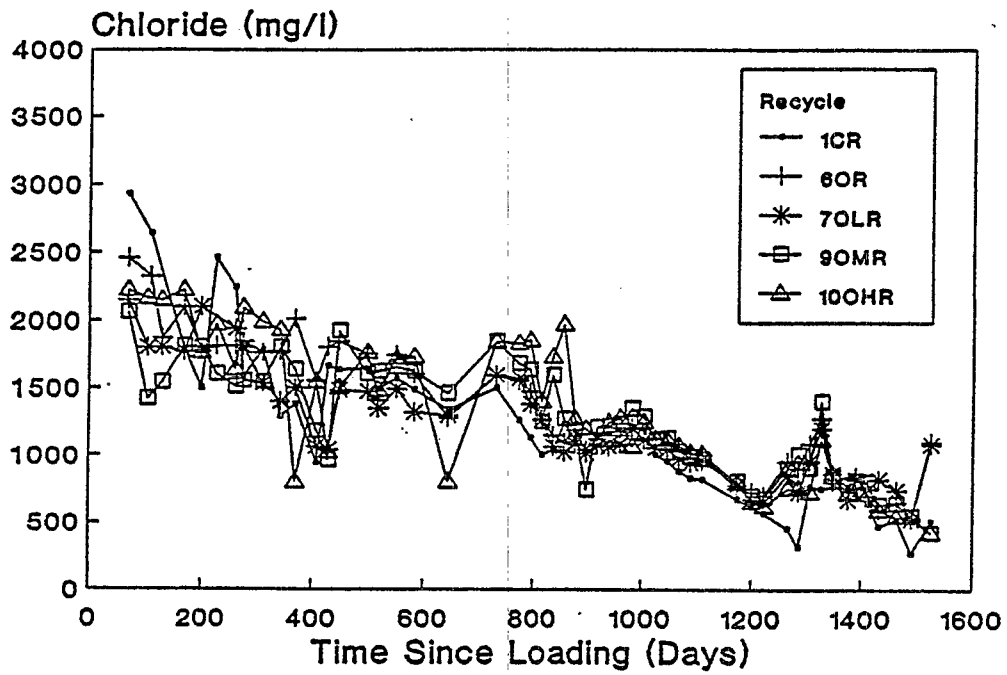
Ammonia is an essential nutrient derived directly from the waste input or produced during decomposition of organic material containing nitrogen. Leachate ammonia concentrations were measured as an indication of nutrient availability and buffer within each of the 10 simulated landfill columns. Within the pH range existing in the columns, ammonia was primarily present as the ammonium ion, which is less toxic than ammonia gas produced at a higher pH. Measured leachate ammonia concentrations for the recycle and single pass columns are shown in Figure 57 and corresponding data are presented in Table A-21 of Appendix A. Ammonia concentrations for the recycle columns remained relatively constant throughout the experimental period, with the exception of a decline in all columns around project Day 600. Ammonia concentration behavior was attributed directly to the nature of the leachate recirculation management strategy, whereby available nutrients are contained and recirculated within the column, providing an increased opportunity for their accumulation and/or removal through biological assimilation. The range of ammonia concentrations observed for the recycle columns was between 600 and 1200 mg/L, which has been shown to exert no adverse effect upon anaerobic processes.[13]

Ammonia concentrations in the leachate from the single pass columns displayed evidence of washout, although concentrations were maintained above 200 mg/L at all times during the experimental period, thereby indicating availability for establishing a viable microbial population.

4.4.9 Sulfate and Sulfide

Sulfate was present in the refuse and the metal sludge mixture added to six of the 10 simulated landfill columns. Leachate sulfate concentrations measured for the recycle and single pass columns are shown in Figure 58, and measured leachate sulfate concentrations are presented in Table A-22 of Appendix A. Sulfate was present in the recycle columns until methane production began on or about project Day 800. The decline in leachate sulfate concentration resulted from the establishment of highly reducing conditions and the ensuing reduction of sulfate to sulfide. Sulfate was removed from the leachate of single pass columns mainly by washout, as evidenced in Figure 58.

The removal of sulfate from the leachate of the recycle and single pass columns was accompanied by the appearance of sulfide around project Day 800, which becomes possible at low ORP values (below -200 mV). Moreover, sulfide is a potent precipitant of heavy metals, thereby removing the potential toxic effects of heavy metals on the biological populations. As discussed in Section



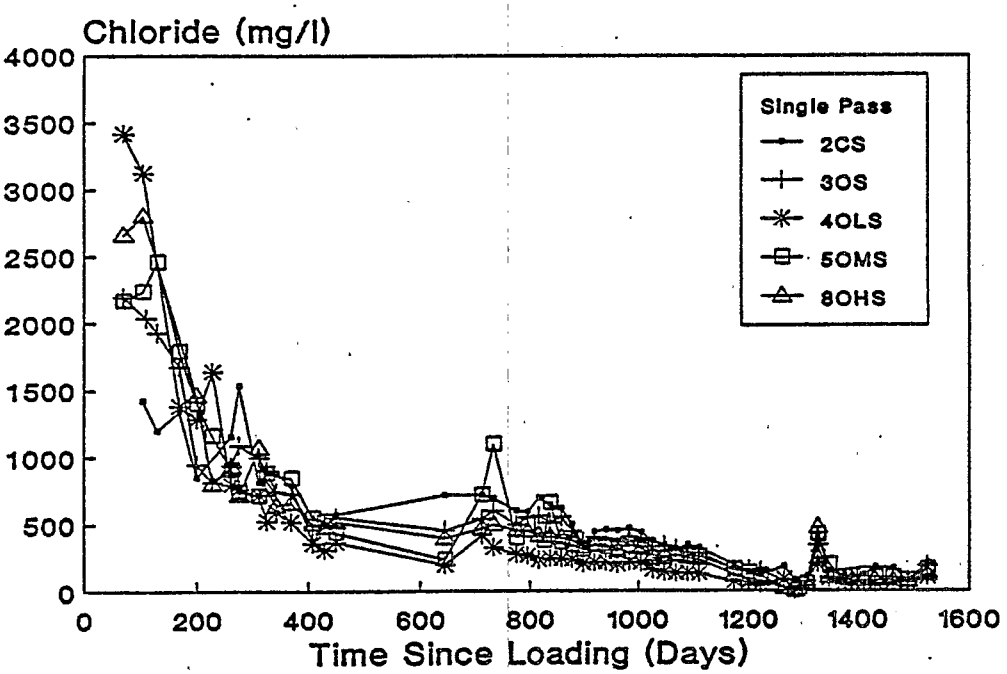
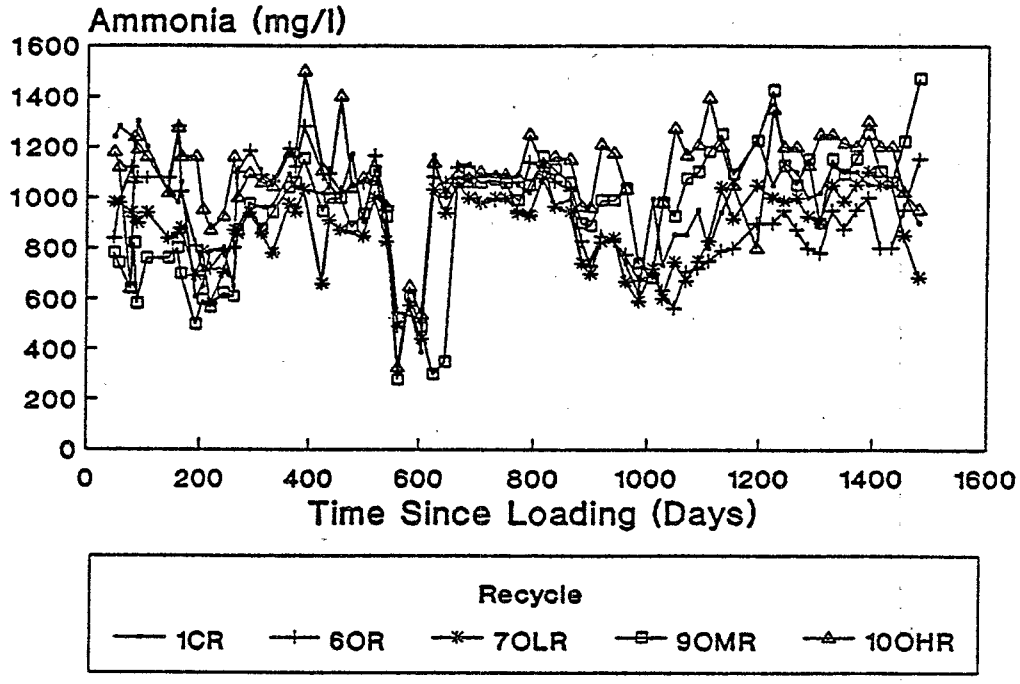


Figure 56. Leachate Chloride during Simulated Landfill Investigations.



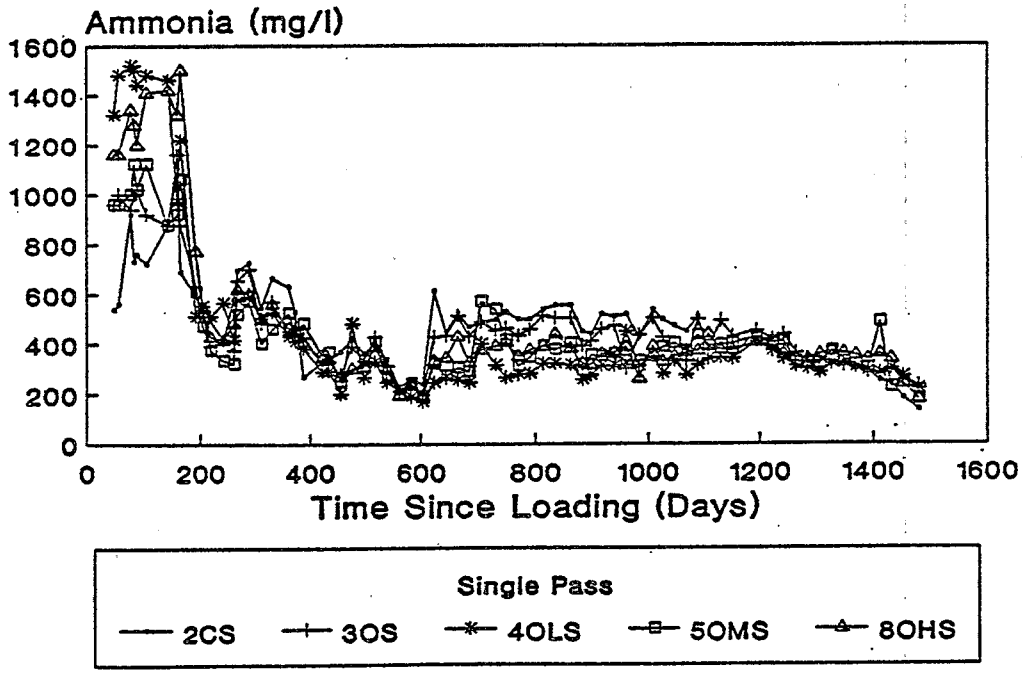
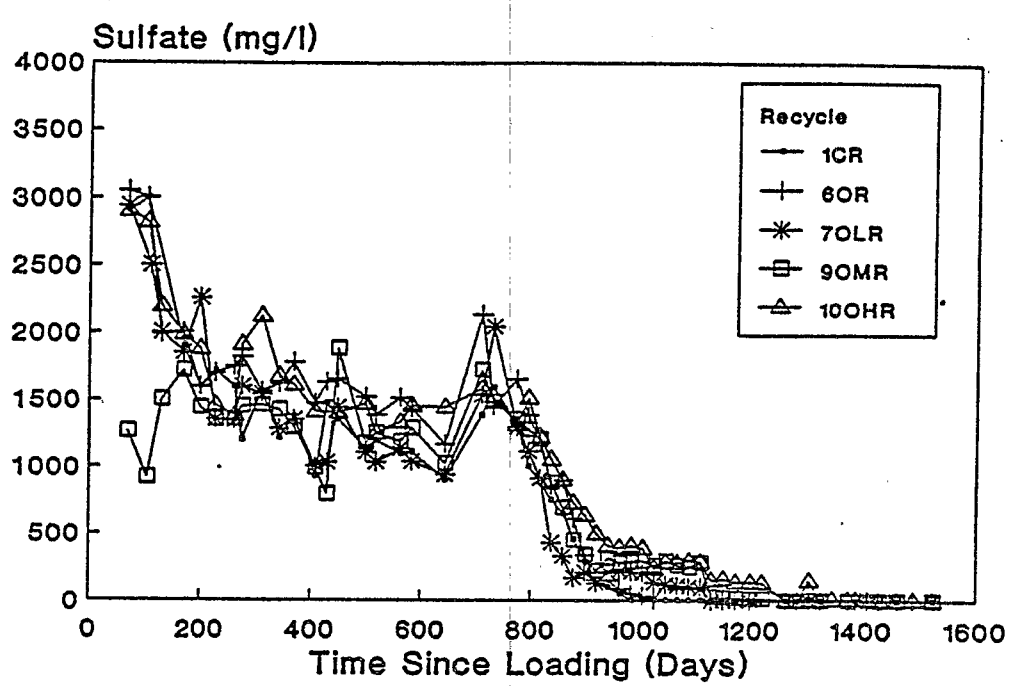


Figure 57. Leachate Ammonia during Simulated Landfill Investigations.



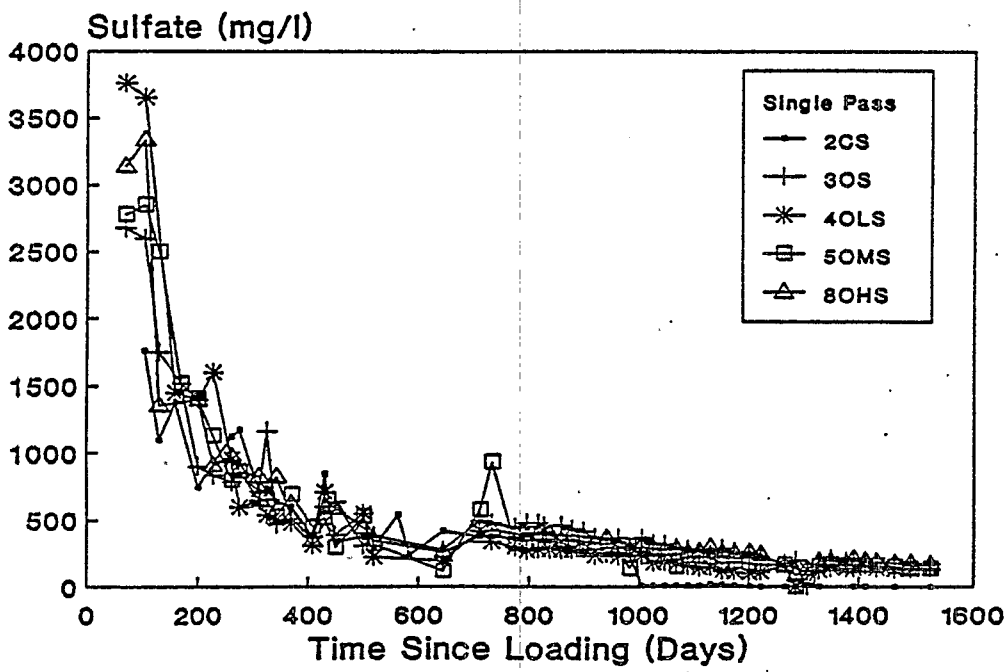


Figure 58. Leachate Sulfate during Simulated Landfill Investigations.

4.4.11, heavy metal concentrations were observed to decline concomitantly with the appearance of sulfide. Sulfide concentrations for the recycle and single pass columns are presented in Figure 59, and measured leachate sulfide concentrations are included in Table A-23 of Appendix A.

4.4.10 Organic Priority Pollutants

Twelve organic priority pollutants were added to Columns 3OS, 4OLS, 5OMS, 6OR, 7OLR, 8OHS, 9OMR and 1OOHR. A summary of the type and amount of organic priority pollutant added to these eight test columns was presented previously in Tables 19 and 20. Measured leachate concentrations of eight of the twelve organic priority pollutants are included in Figures 60 through 67, and measured leachate concentrations of the organic priority pollutants are included in Table A-24 through A-31 of Appendix A.

Five non-polar organic priority pollutants were added to the eight columns and included naphthalene, lindane, dieldrin, dioctyl phthalate and hexachlorobenzene. As indicated by Figure 60, naphthalene showed significant mobility, but was also detected in the leachate from the control columns, Columns 1CR and 2CS. Lindane was generally retained within the columns, being detected in concentrations less than 20 μg/L only near the end of the experimental period. Hexachlorobenzene, dieldrin, and bis-2-ethylhexyl phthalate were never detected in the leachate from any column.

Two organics measured by the purge and trap method of analysis, dibromomethane and trichloroethylene, were also added to the eight simulated landfill columns and their leachate concentrations are shown in Figures 61 and 62. These compounds were detected early in the leachate and were highly mobile, particularly during the Acid Formation Phase.

Two extractable organic compounds were also added to the columns, which included dichlorobenzene and trichlorobenzene. These compounds, shown in Figures 63 and 64, exhibited low mobility as evidenced by their slow evolution and low leachate concentrations.

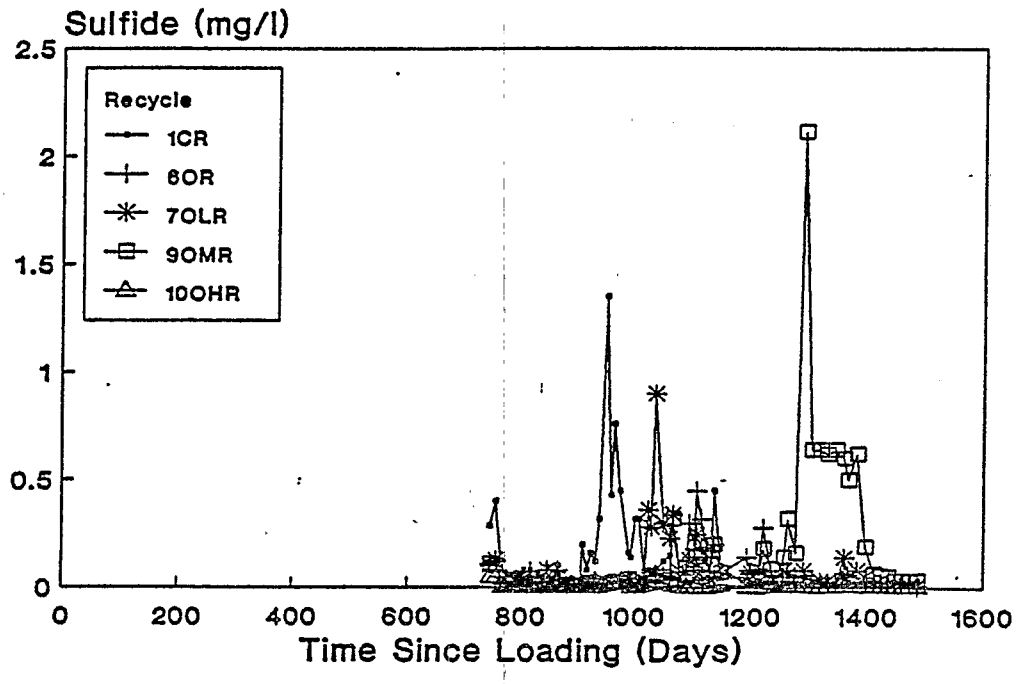
Nitrobenzene, nitrophenol and dichlorophenol, three polar semi-volatile organic priority pollutants, were also added to the eight test simulated landfill columns. Nitrobenzene and nitrophenol, shown in Figures 65 and 66, exhibited slow yet distinct but diminishing mobility, especially during the Methane Fermentation Phase. Dichlorophenol, shown in Figure 67, seemed to be mobilized during methane fermentation, possibly as a consequence of the more neutral pH.[34]

The possible attenuation mechanisms affecting the codisposed organic compounds included dispersion, fractionation, volatilization, sorption, and biodegradation. Reductive dehalogenation was suggested by the appearance of elevated leachate bromide concentrations, shown in Figure 68, as dibromomethane concentrations decreased, and by the detection of vinyl chloride shown in Figure 69, a probable transformation product of trichloroethylene, in the headspace gas as this compound diminished in leachate concentration. Leachate bromide and headspace vinyl chloride concentrations are presented in Tables A-25 and A-26 of Appendix A. A more in-depth analysis of the attenuation mechanisms is provided by Pohland and coworkers[34] and in Section 5.1.

When examined relative to effects upon the progress of landfill stabilization, the applied organic priority pollutant loadings present, in the absence of admixed heavy metals, were apparently readily accommodated as evidenced by gas production, gas composition and reductions in TVA concentrations.

4.4.11 Metals

Metal toxicity is a function of speciation and metal partitioning in the



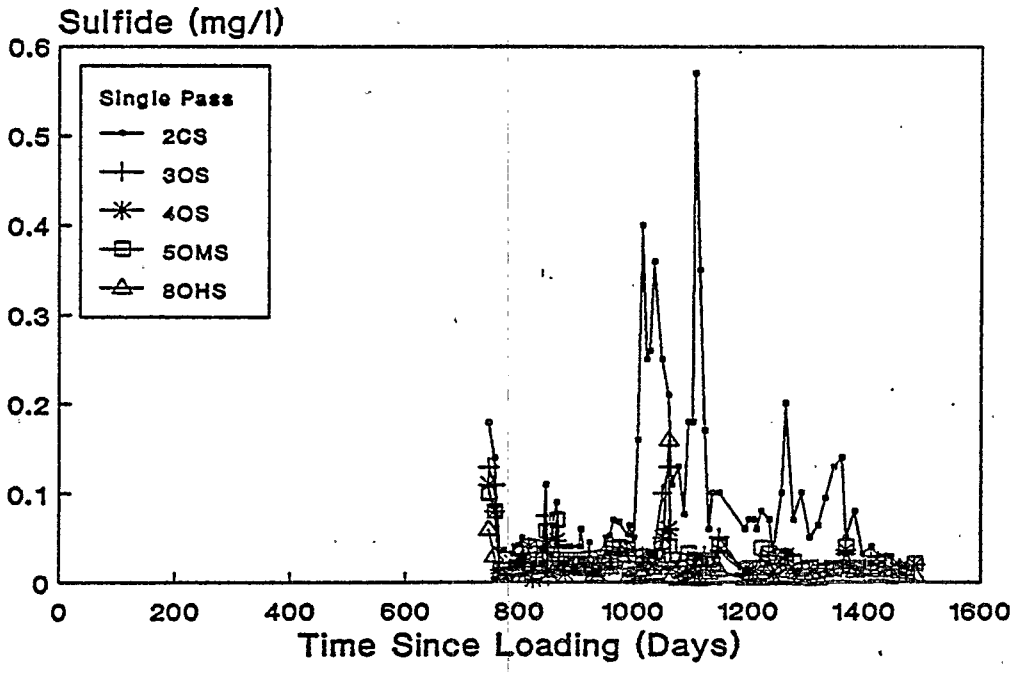
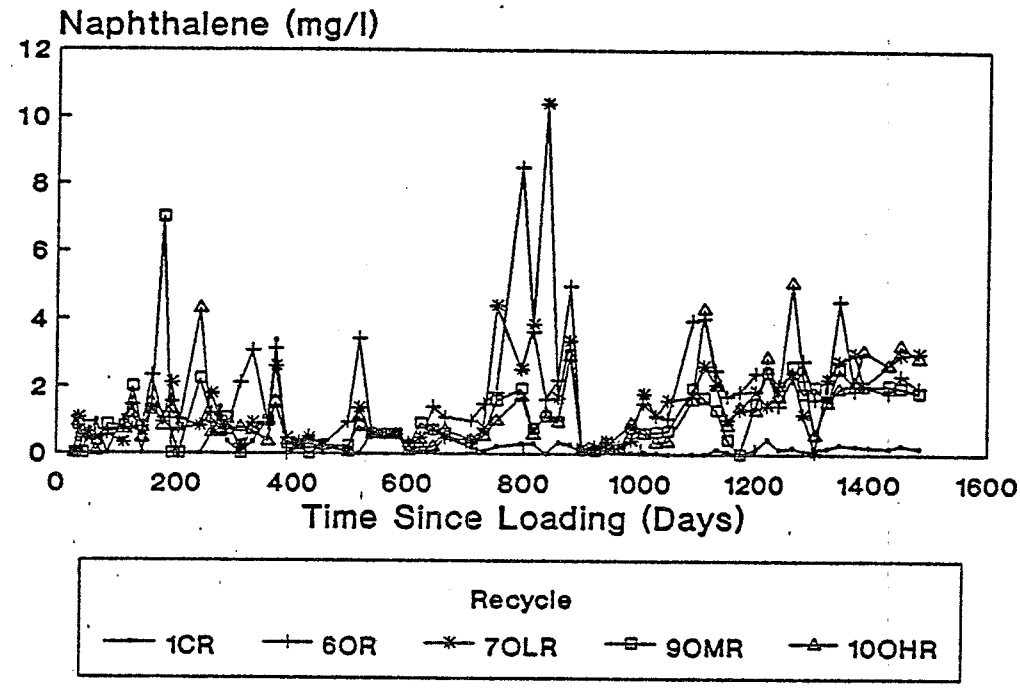


Figure 59. Leachate Sulfide during Simulated Landfill Investigations.



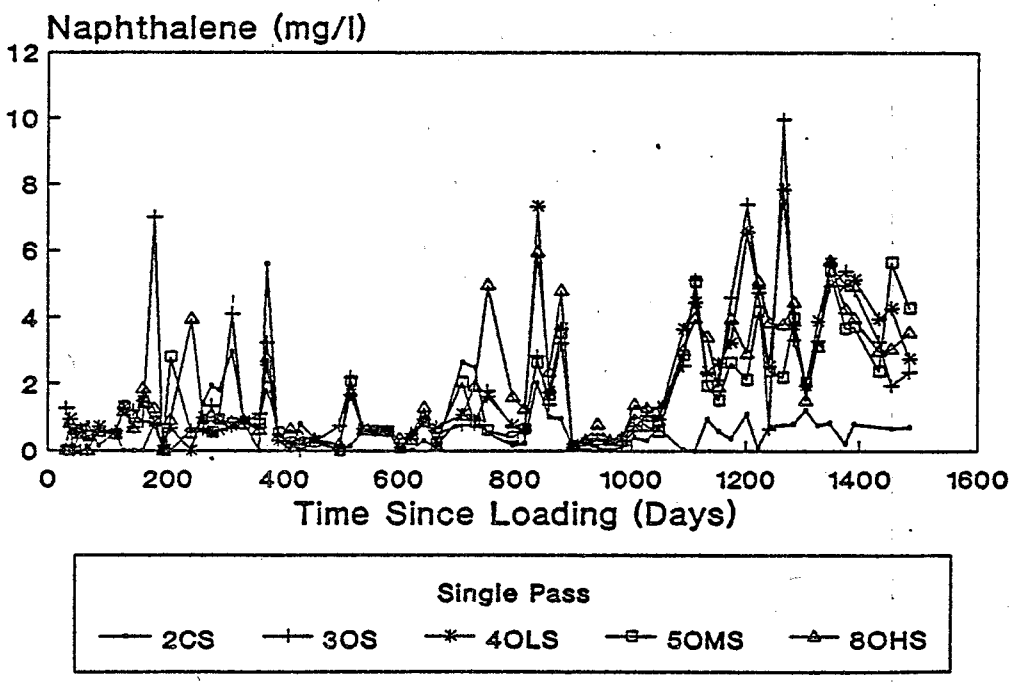
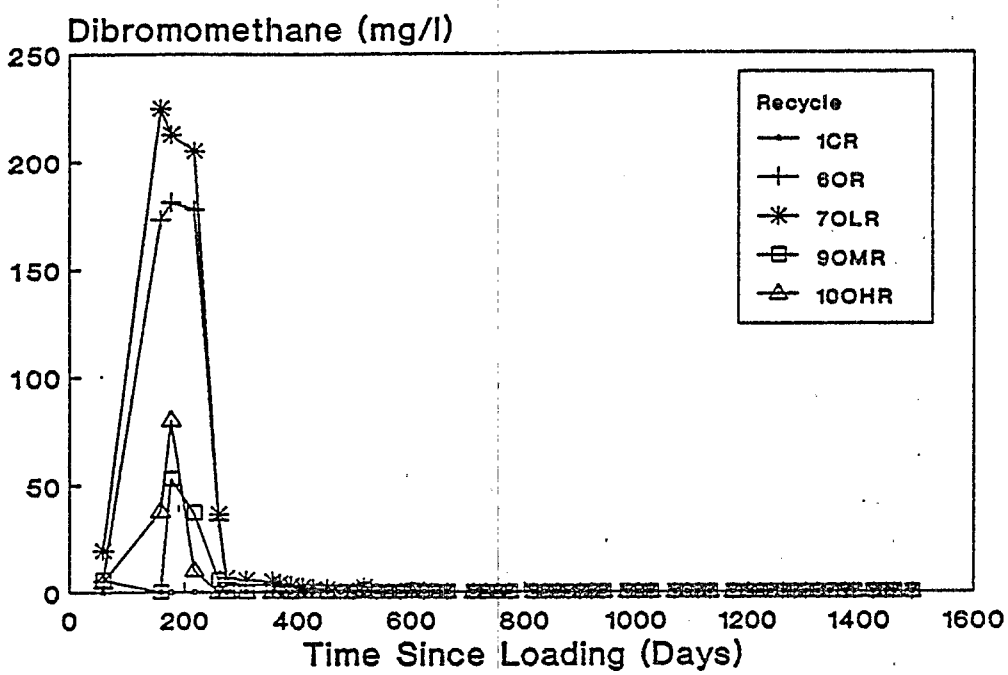


Figure 60. Leachate Naphthalene during Simulated Landfill Investigations.



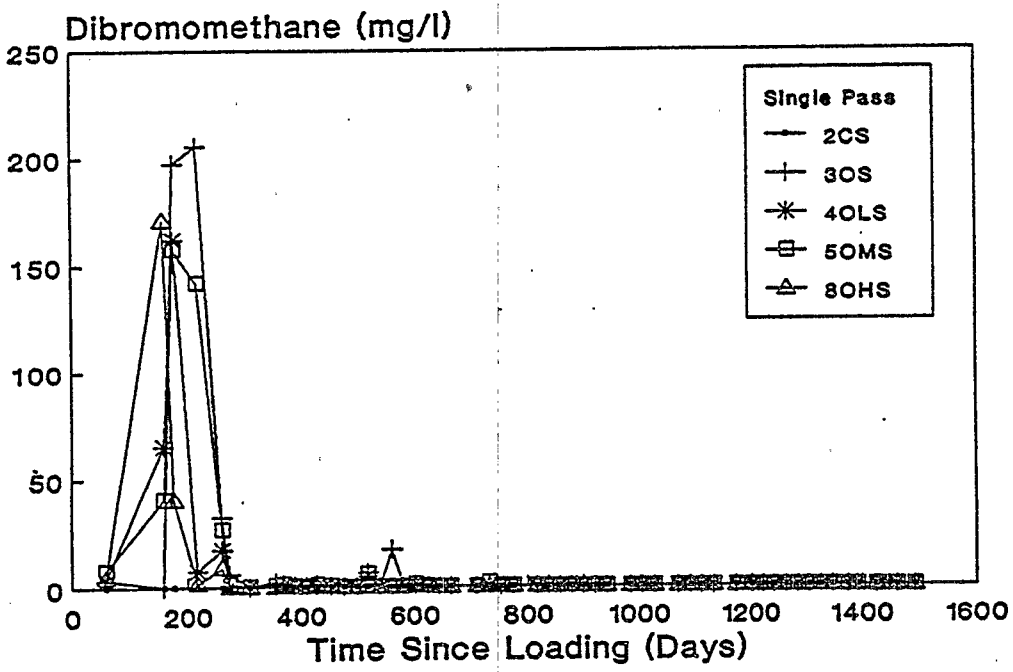
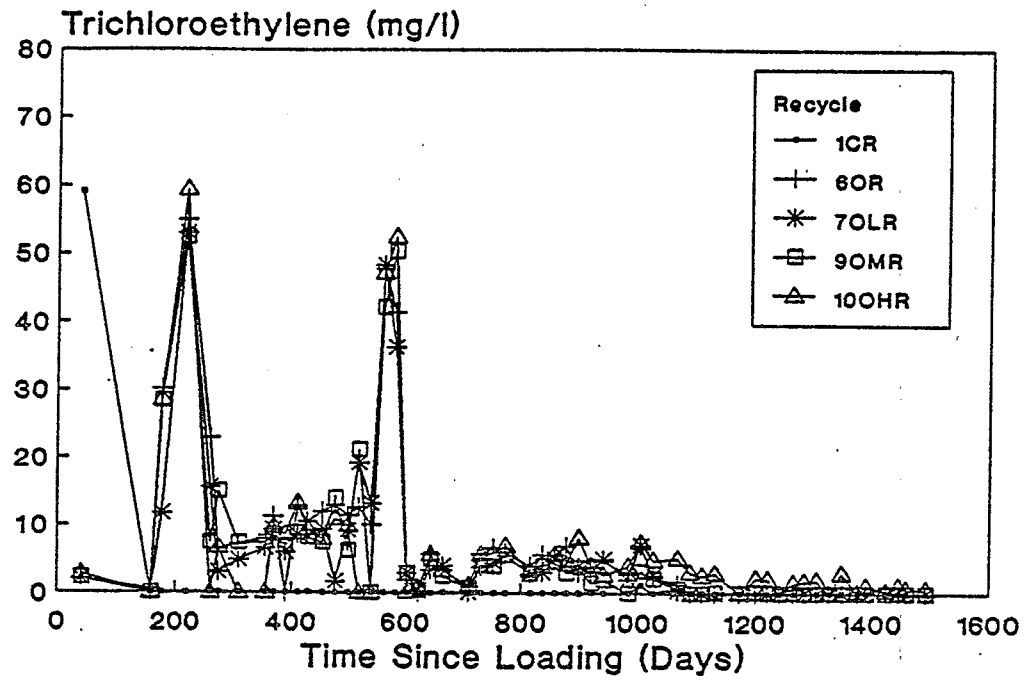


Figure 61. Leachate Dibromomethane during Simulated Landfill Investigations.



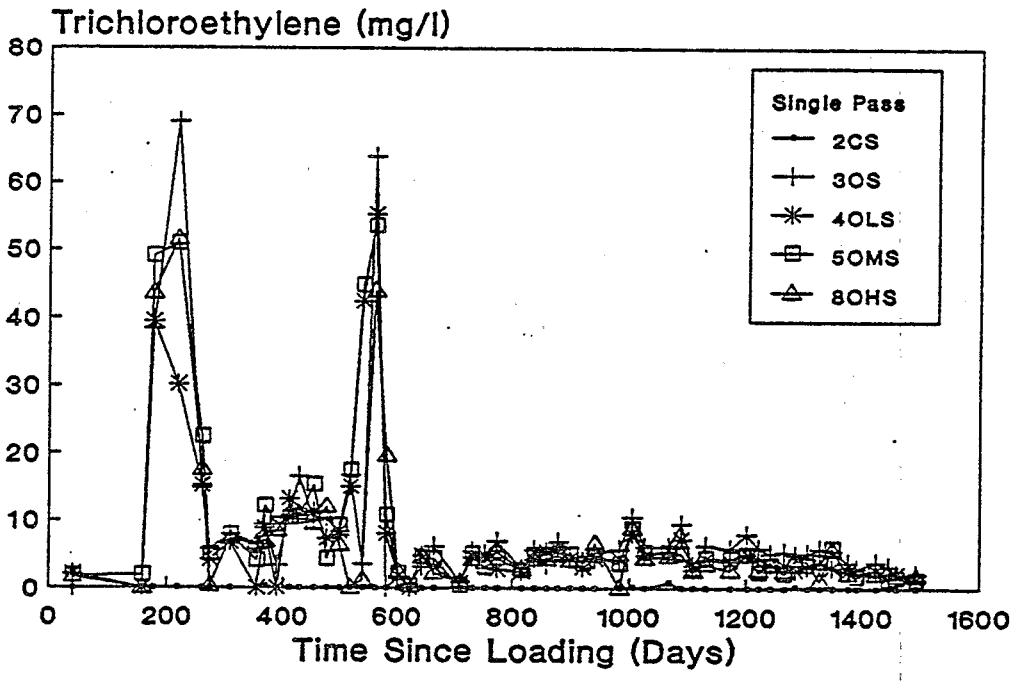
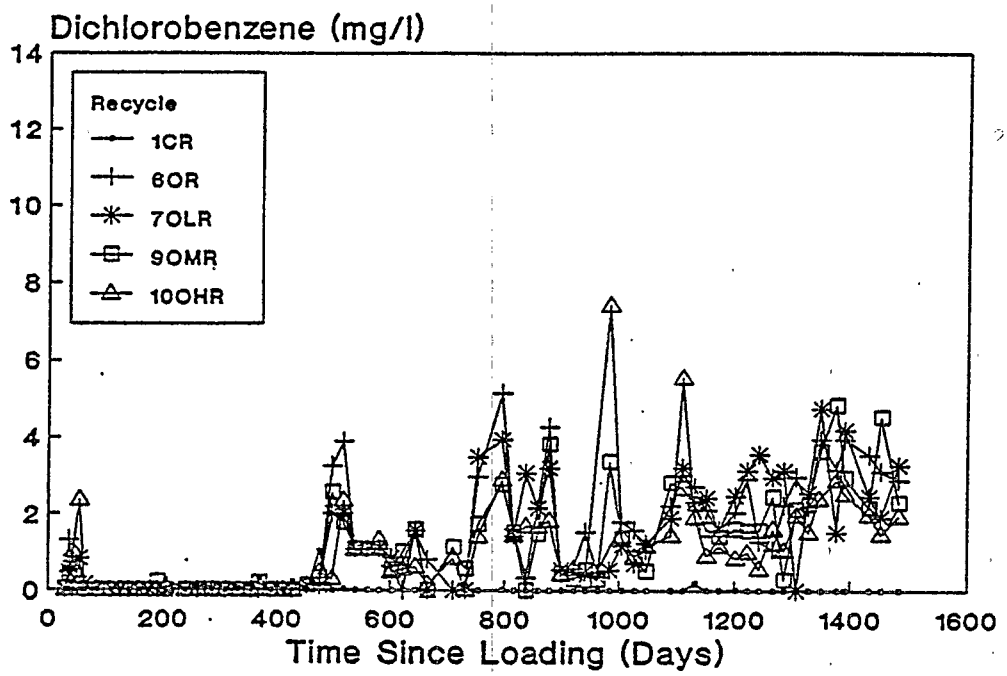


Figure 62. Leachate Trichloroethylene during Simulated Landfill Investigations.



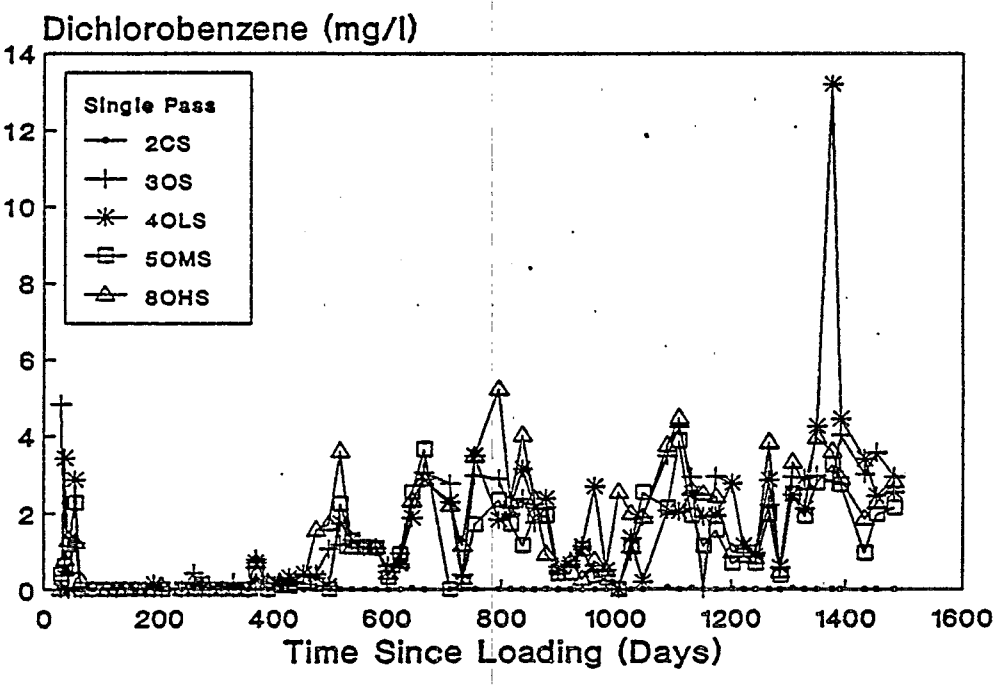
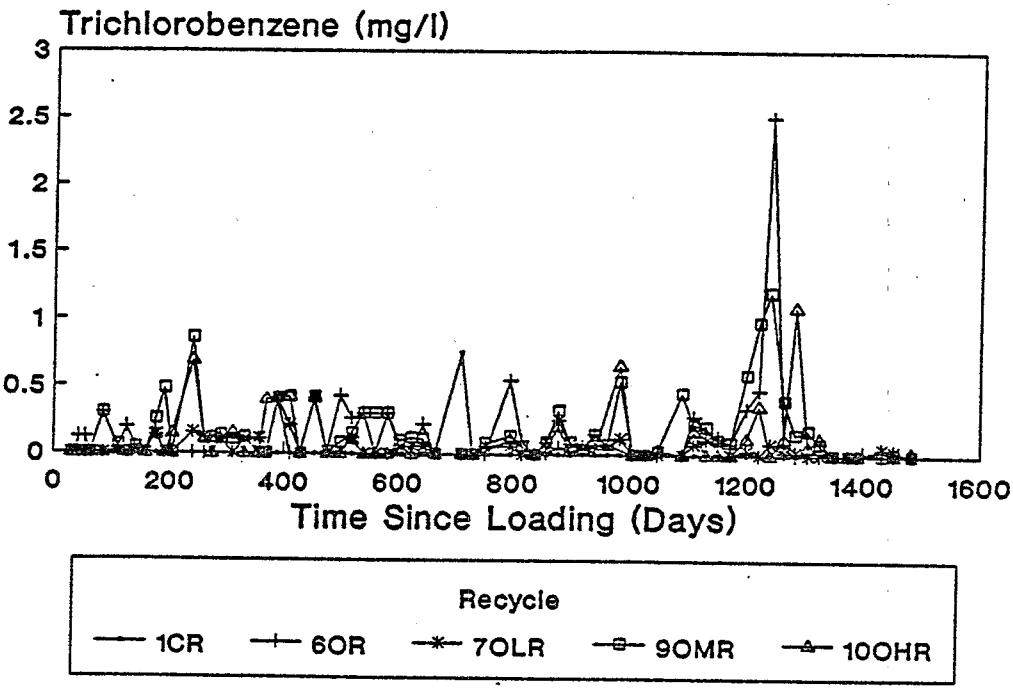


Figure 63. Leachate Dichlorobenzene during Simulated Landfill Investigations.



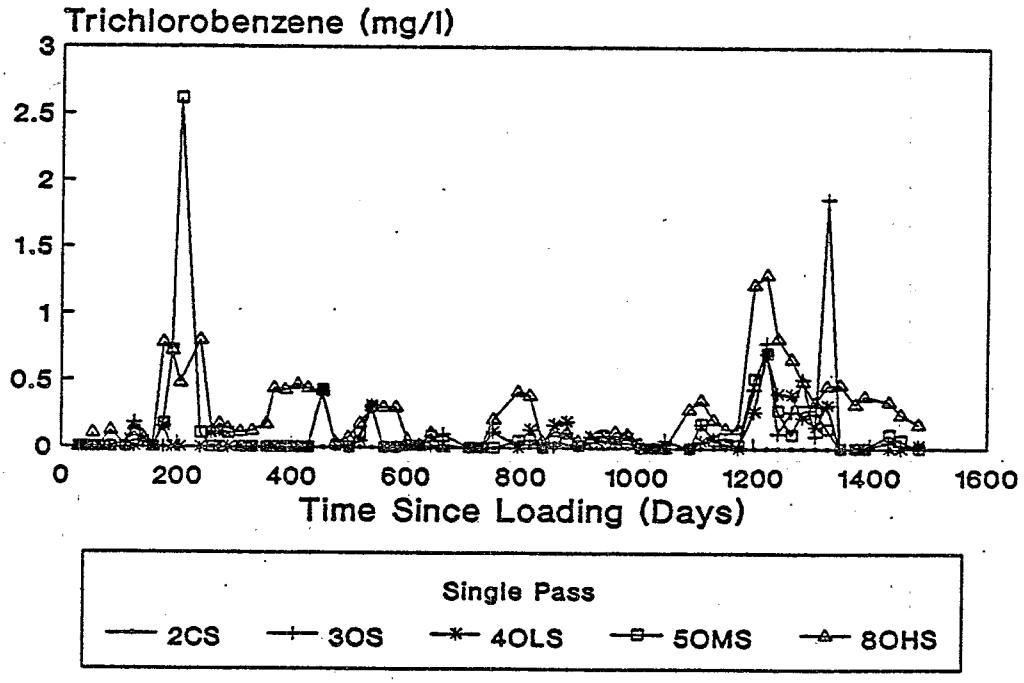
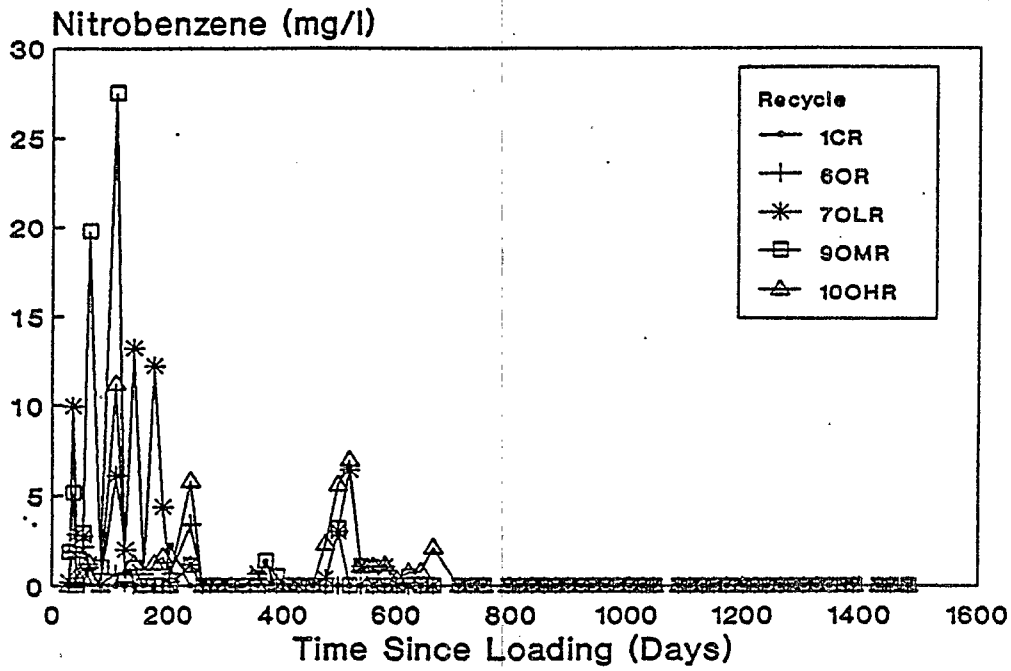


Figure 64. Leachate Trichlorobenzene during Simulated Landfill Investigations.



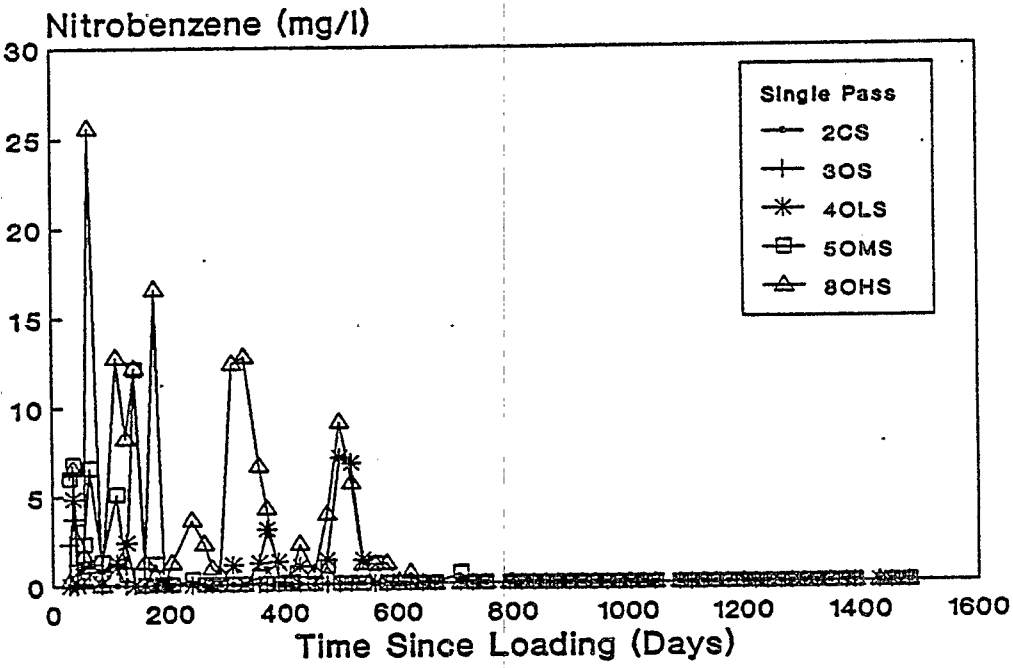
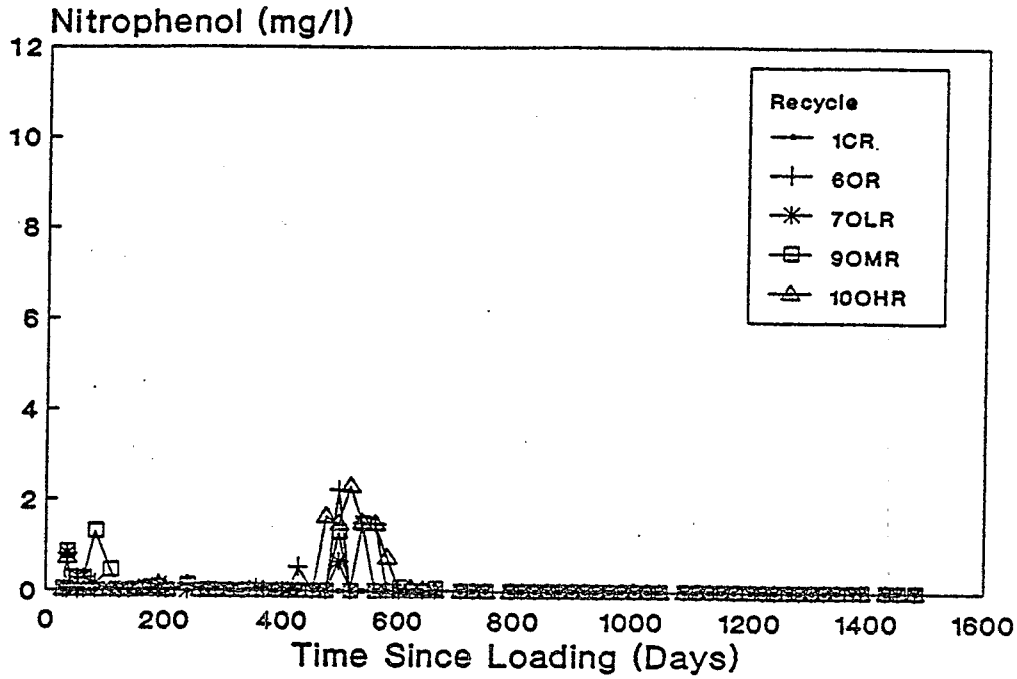


Figure 65. Leachate Nitrobenzene during Simulated Landfill Investigations.



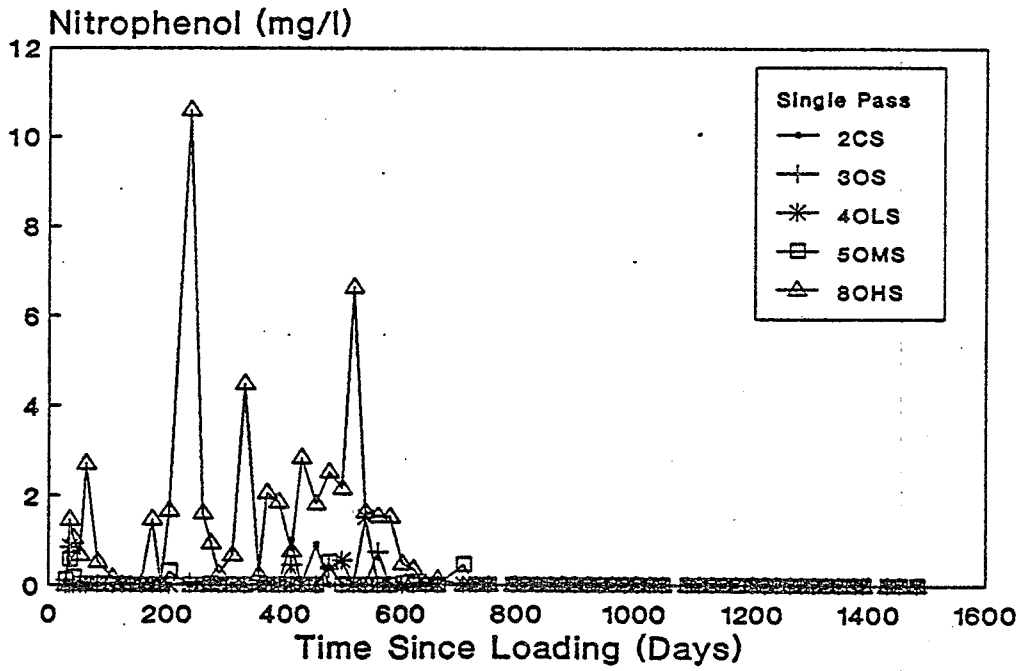
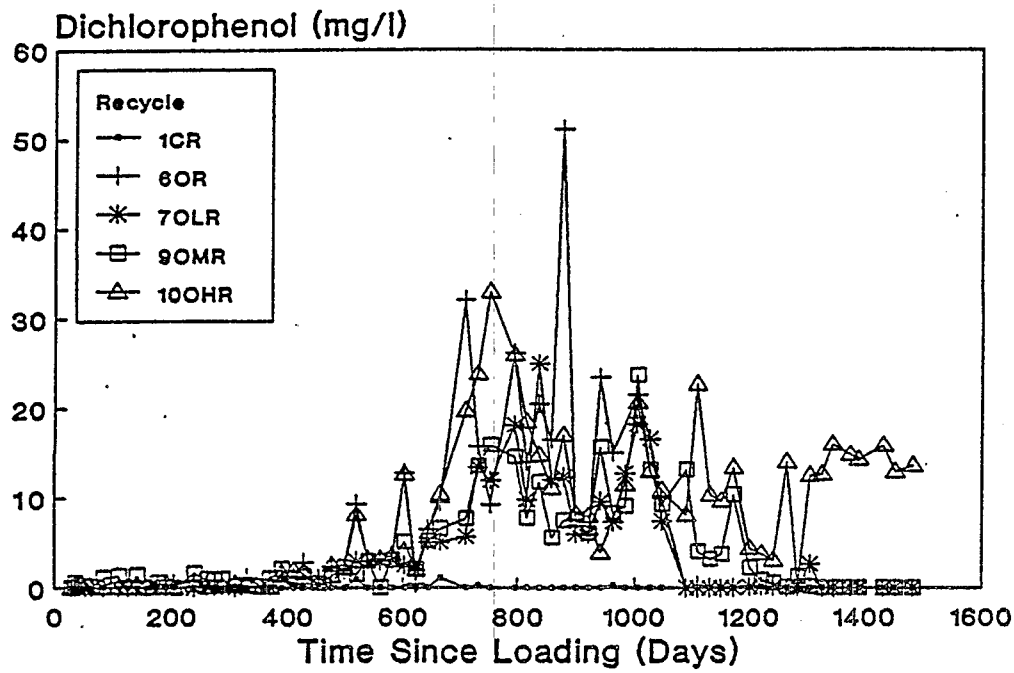


Figure 66. Leachate Nitrophenol during Simulated Landfill Investigations.



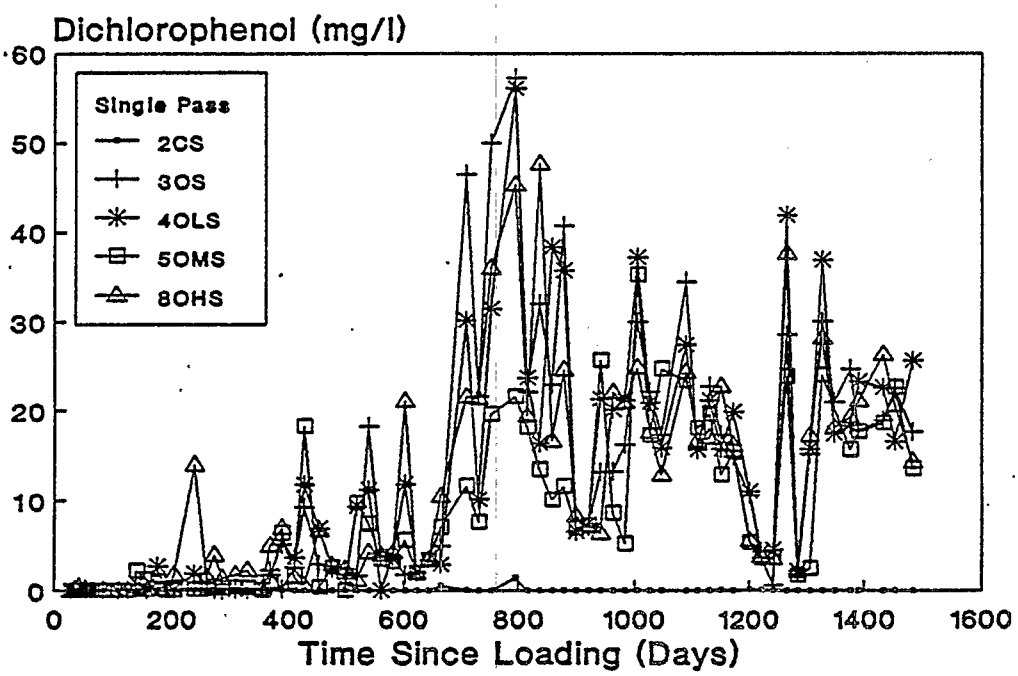
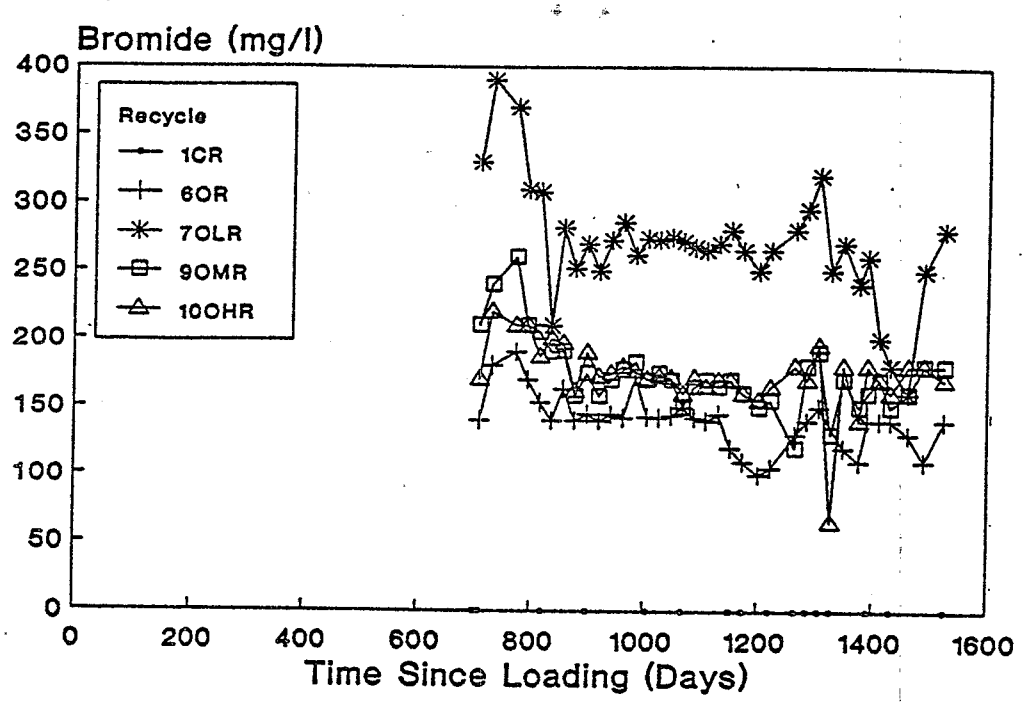


Figure 67. Leachate Dichlorophenol during Simulated Landfill Investigations.



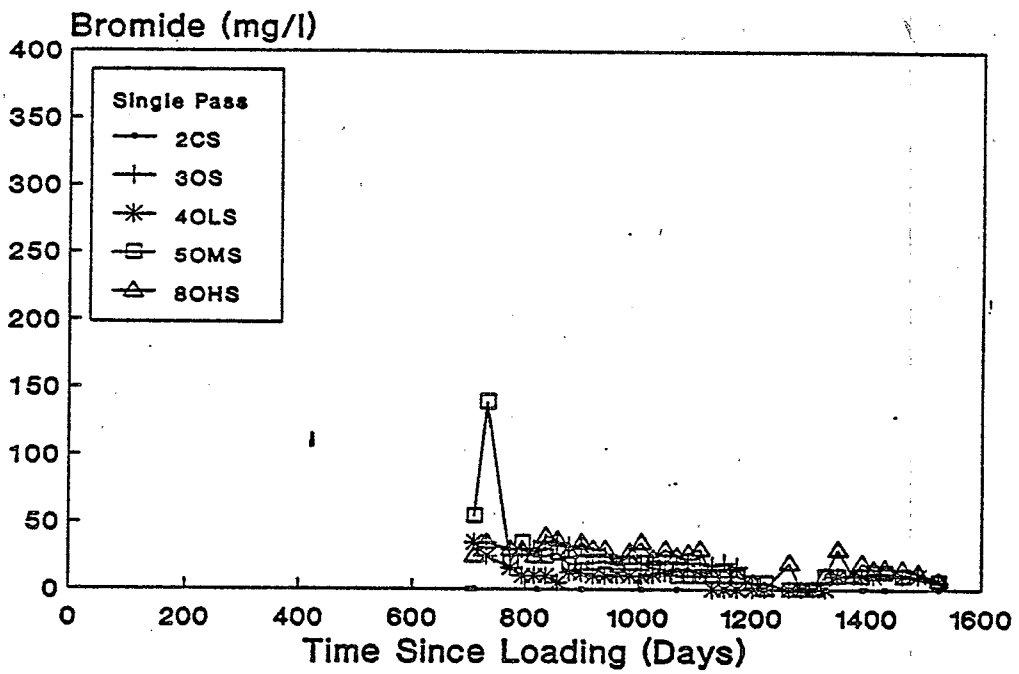


Figure 68. Leachate Bromide during Simulated Landfill Investigations.

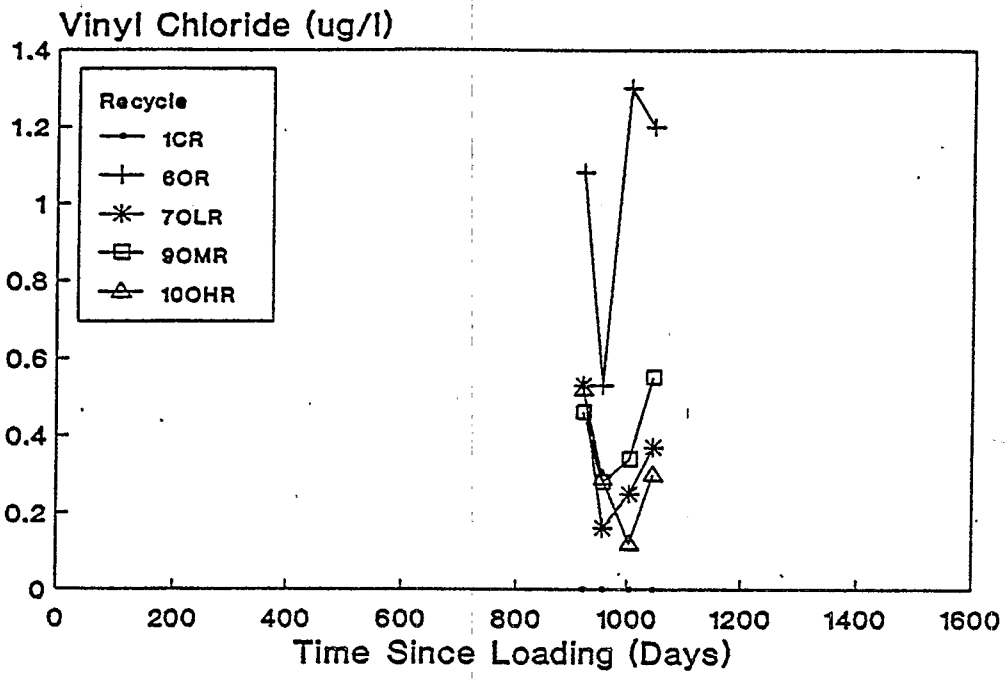


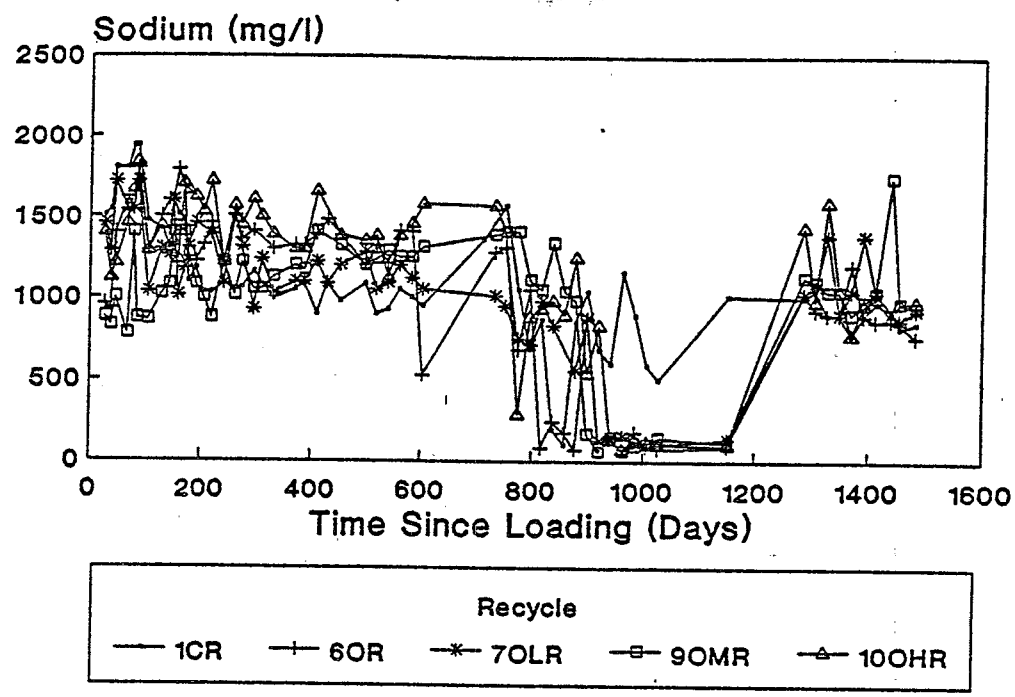
Figure 69. Headspace Vinyl Chloride during Simulated Landfill Investigations.

anaerobic environment. Metal solubility is a function of numerous factors, including pH, ORP, dilution, presence of complexing ligands, and the presence of precipitators such as sulfide and hydroxide, as discussed in Section 2.4. Analyses for 12 leachate metals included sodium, potassium, magnesium, calcium, iron, manganese, chromium, cadmium, nickel, zinc, lead and mercury. Six columns received incremental loadings of heavy metals, and the type and quantity of each heavy metal added was previously summarized in Tables 19 and 20. Measured leachate metal concentrations are presented in Tables A-27 through A-28 of Appendix A. The 12 metals studied were divided and discussed according to their periodic table groupings.

The alkali metals, Group IA, include sodium and potassium. Leachate sodium concentrations are presented in Figure 70, and leachate potassium concentrations are illustrated in Figure 71. Both sodium and potassium showed evidence of washout from the single pass columns. However, leachate sodium and potassium concentrations in the recycle columns exhibited a behavior that suggested possible increased ion exchange reactions and dilution effects were predominant.

The alkali-earth metals, Group IIA, include calcium and magnesium. Leachate calcium and magnesium concentrations are presented in Figures 72 and 73. Both calcium and magnesium are relatively conservative metals, which was reflected in their behavior within the simulated landfill columns. Both alkali-earth metals displayed behavior characteristic of dilution in recycle columns and washout in single pass columns. Also, the possibility for the precipitation of calcium existed after project Day 1150 as a result of the rise in pH which would increase the possibility of a reaction between calcium and available carbon dioxide.

Selected heavy metals were codisposed with the refuse and organic priority pollutants in Columns 40LS, 50MS, 70LR, 80HS, 90MR and 100HR. These heavy metals



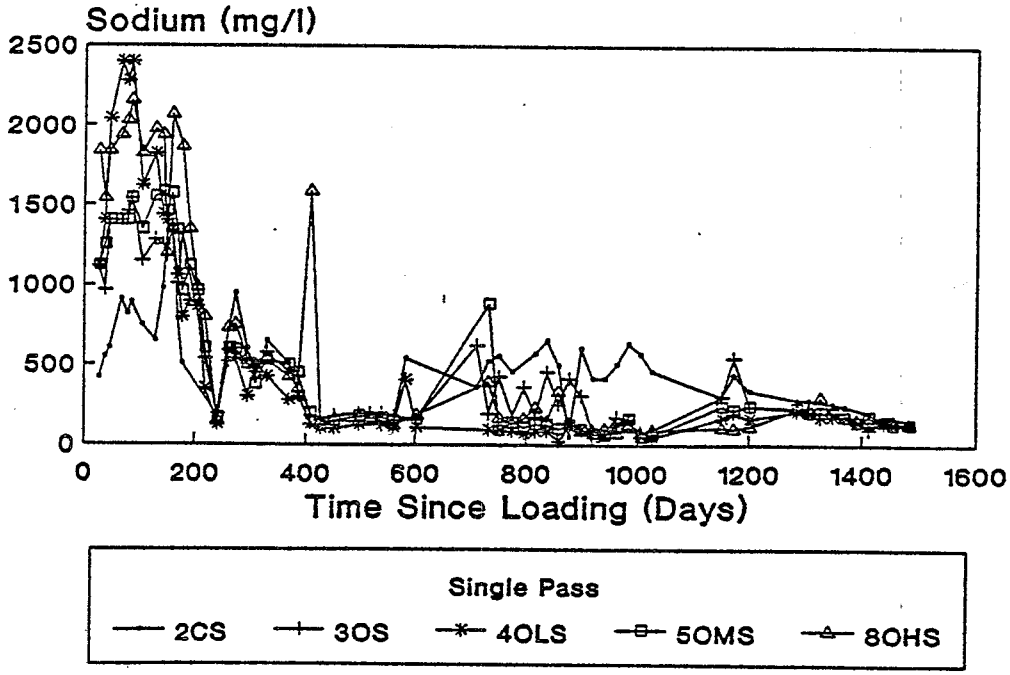
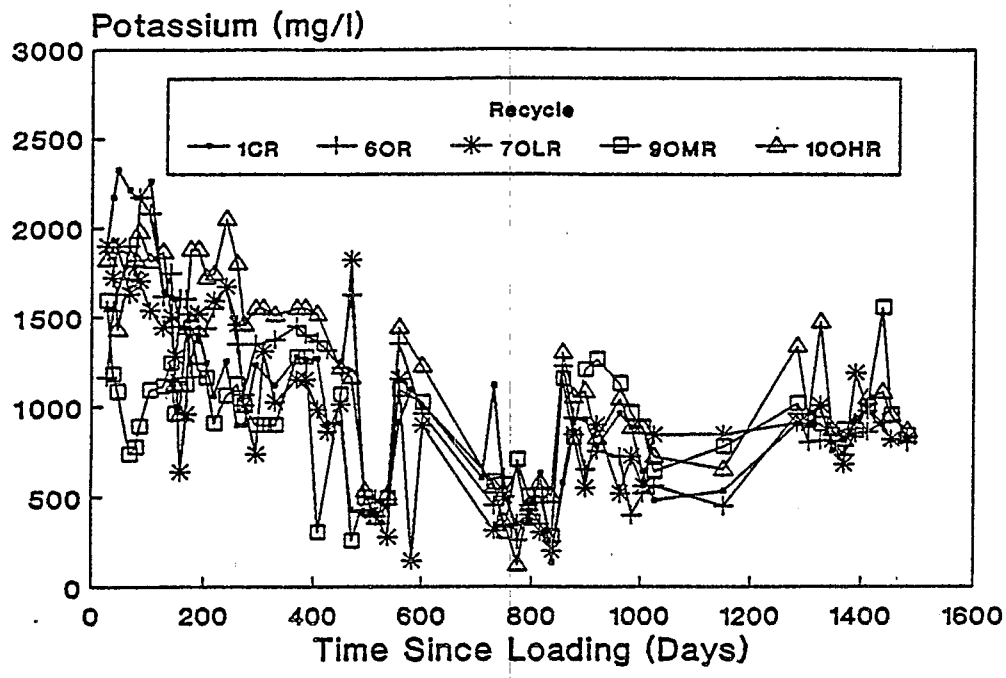


Figure 70. Leachate Sodium during Simulated Landfill Investigations.



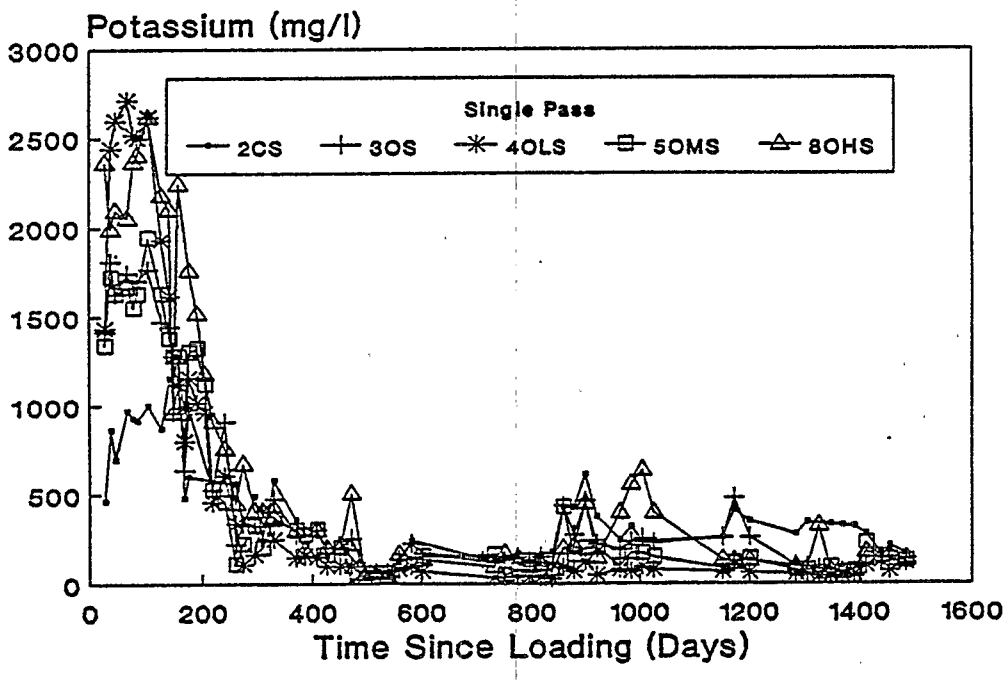
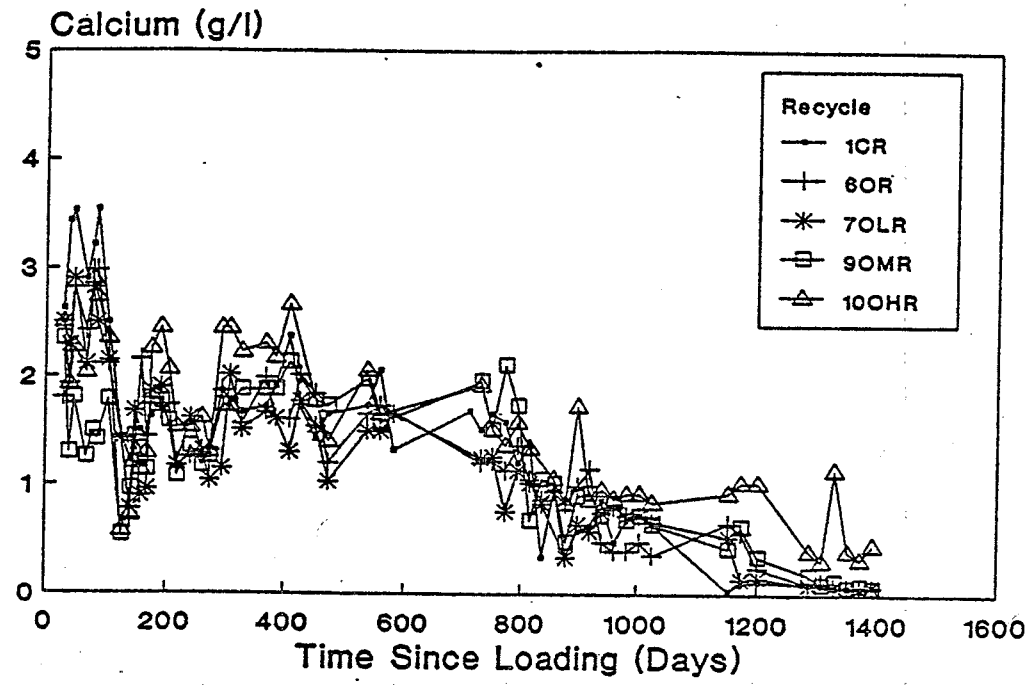


Figure 71. Leachate Potassium during Simulated Landfill Investigations.



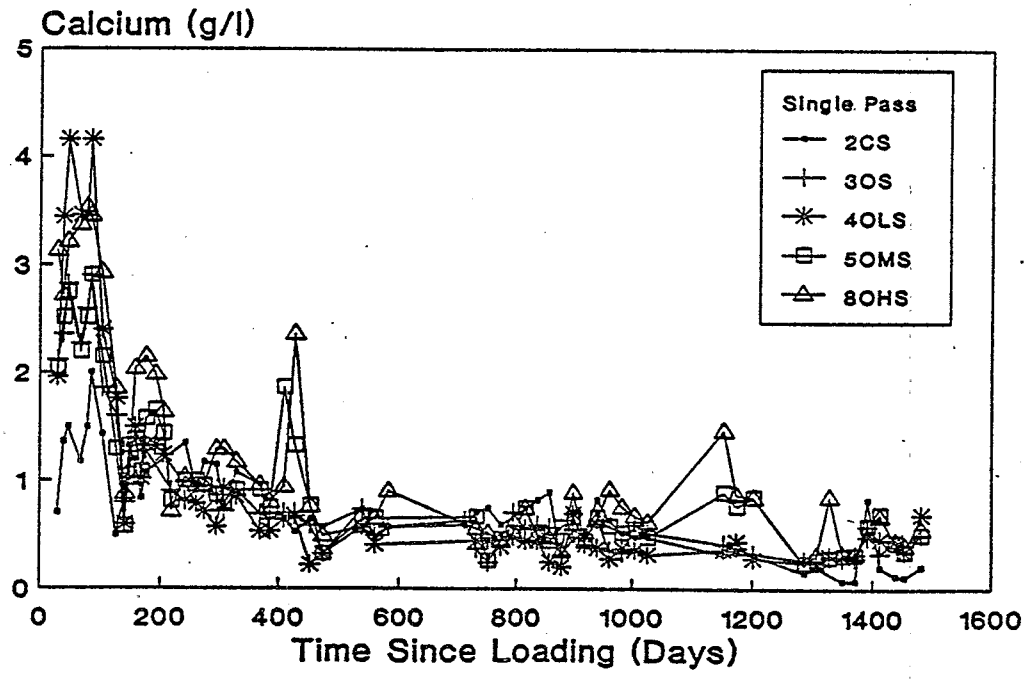
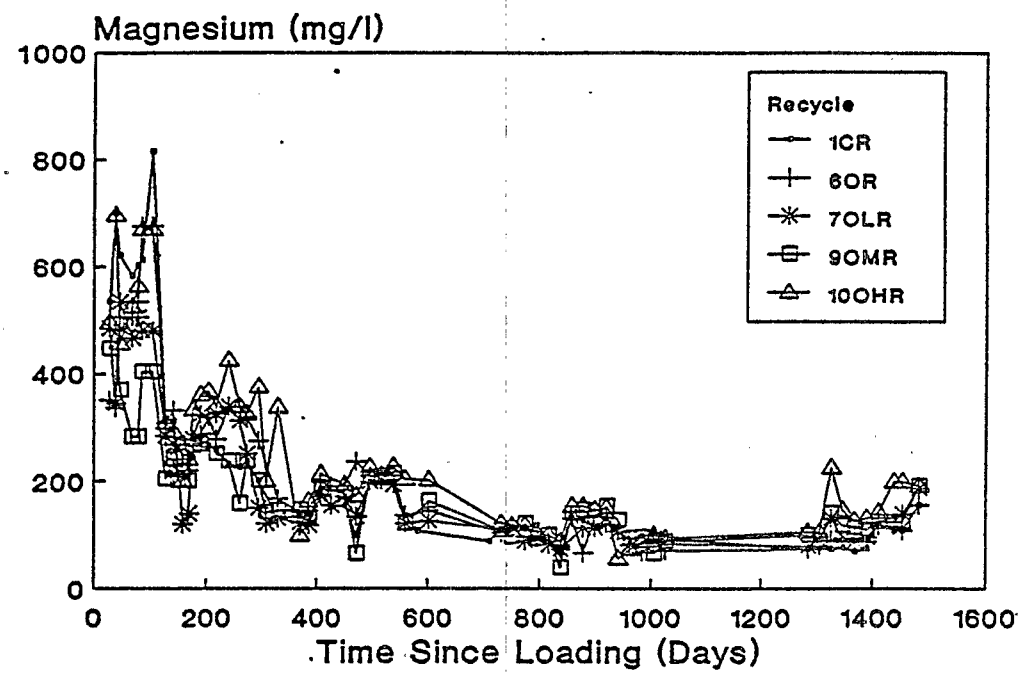


Figure 72. Leachate Calcium during Simulated Landfill Investigations.



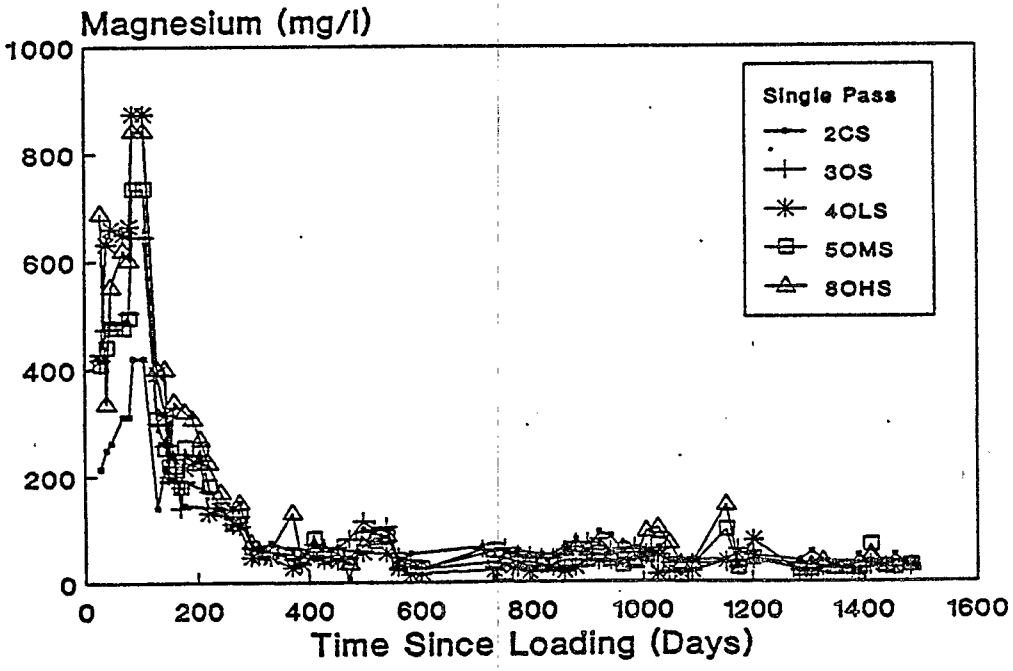


Figure 73. Leachate Magnesium during Simulated Landfill Investigations.

consisted of iron, cadmium, chromium, lead, manganese, nickel, zinc and mercury. Iron was present in the codisposed metal sludges and is also present in municipal solid waste. Therefore, iron was detected in leachate originating from all 10 simulated landfill columns. Leachate iron concentrations for the recycle and single pass columns are presented in Figure 74. Iron was initially present in the Acid Formation Phase as Fe^{3+}, but was then most likely reduced to the more soluble Fe^{2+} during the Methane Fermentation Phase due to the highly reducing conditions established. This change in speciation offers an explanation of the increasing iron concentration in single pass columns towards the end of the Methane Fermentation Phase. Recycle iron concentrations decreased during the Methane Fermentation Phase, which was attributable to precipitation as sulfide.

Cadmium, chromium, lead, manganese, nickel and zinc leachate concentrations are presented in Figures 75 through 80. Reductions in leachate heavy metal concentrations in the recycle columns were attributable to precipitation as the sulfide under reducing conditions, or chromium precipitation as the hydroxide.[34] Heavy metal removal occurred in the single pass columns as well, but the primary mechanisms of removal was washout and, to a lesser degree, precipitation. These chemical attenuation mechanisms are discussed in more detail in Section 5.2.

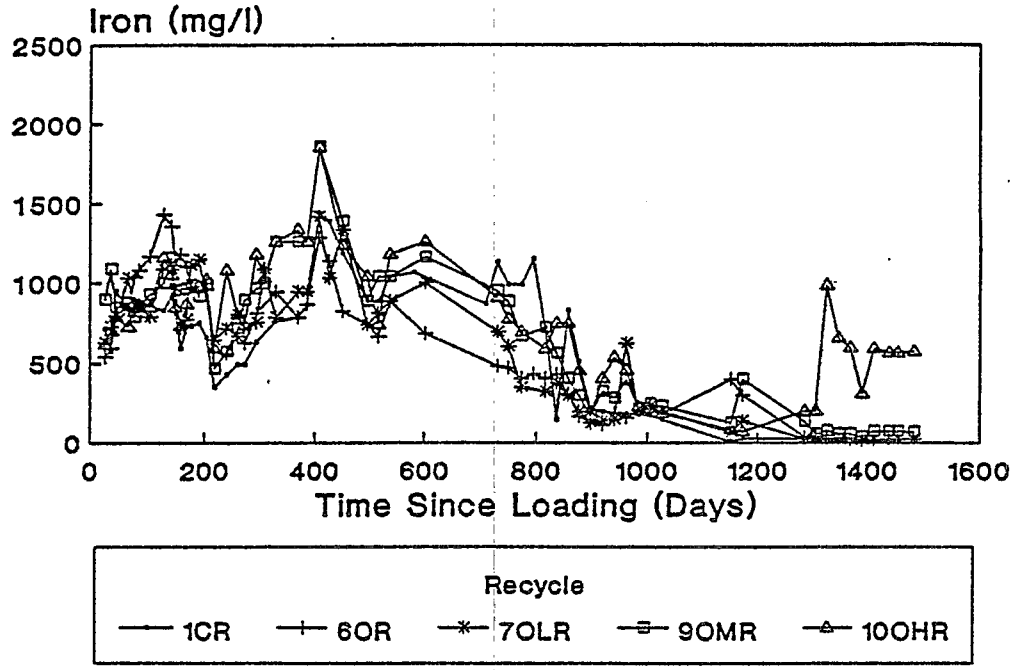
Leachate mercury concentrations were also measured and are shown in Figure 81. Mercury removal in the recycle columns probably resulted initially from precipitation as the sulfide, but later removal may have been accomplished by conversion to metallic mercury when the landfill environment became highly reducing, as is also discussed in more detail in Section 4.7. Additionally, mercury was removed in the single pass columns, principally by washout, as well as by precipitation.

Superimposed upon the primary heavy metal attenuation mechanisms were opportunities for encapsulation, sorption, ion exchange, complexation and void space containment consequenced by the method of loading, the associated reaction opportunities, and the physical characteristics of the waste matrix.[34] Precipitation or other mechanisms, including filtration of heavy metals within the waste matrix in the five recycle columns, apparently lowered leachate total metal concentrations below an apparent threshold, below which methane fermentation could occur. However, since methane was produced in all columns containing heavy metals, the applied loadings could be accommodated, but at delayed cumulative gas production which was less as heavy metal loadings increased. Moreover, gas production was occurring at similar or increasing rates for all metal-loaded recycle columns at the end of the experimental period, thereby indicating that gas production similar to that of the control recycle column could be projected to be eventually attained.

4.5 INHIBITION LEVELS

Based upon the behavior of the 10 simulated landfill columns and their respective progression toward anaerobic waste stabilization, a priority pollutant loading can be determined above which the stabilization process is inhibited. This inhibition level differs according to the leachate management strategy employed.

None of the five recycle simulated landfill columns experienced complete inhibition of the waste stabilization process as reflected by gas volume produced, gas composition, leachate analyses, and mass of IVA released and transformed. However, increased retardation of waste stabilization processes was experienced with increased priority pollutant loadings, as anticipated. Column 90MR displayed behavior characteristic of slight retardation, and Column 100HR showed signs of more severe retardation. The codisposed priority pollutant loadings were accommodated in all five recycle simulated landfill columns, therefore, no inhibition level was determined for these columns within the range of codisposed priority pollutants examined in these investigations. (Table 19 provides the priority pollutant loading for each simulated landfill column on a



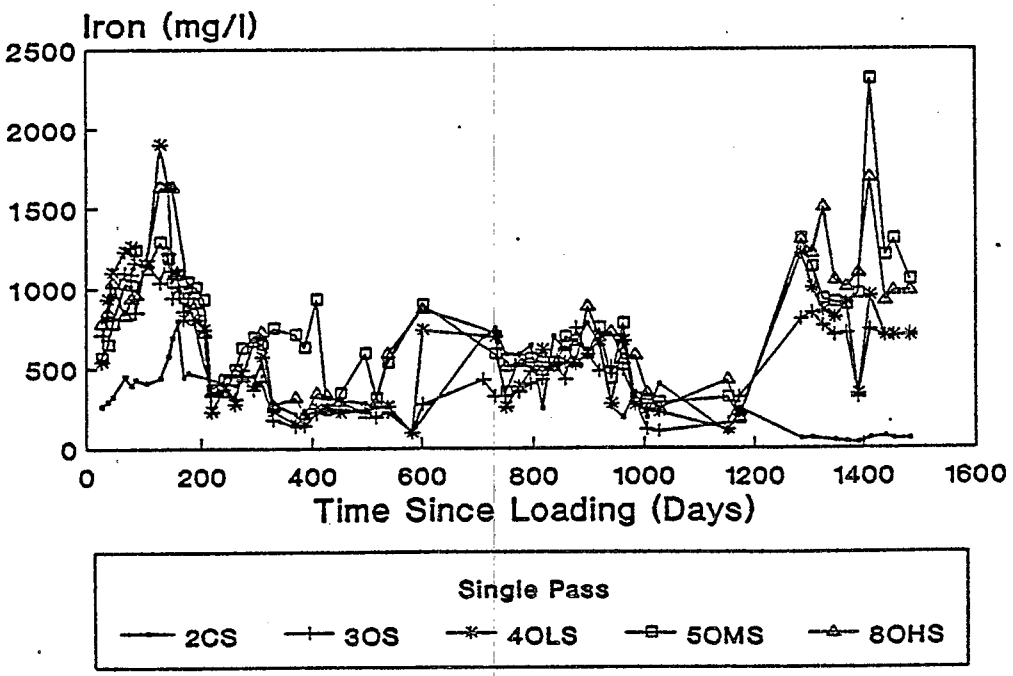
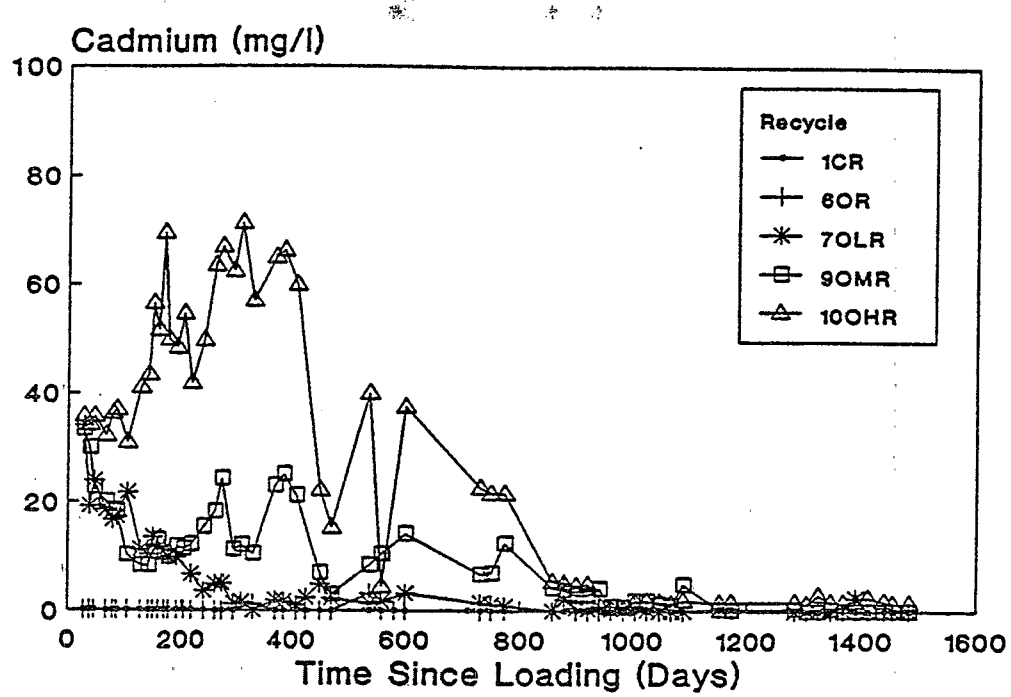


Figure 74. Leachate Iron during Simulated Landfill Investigations.



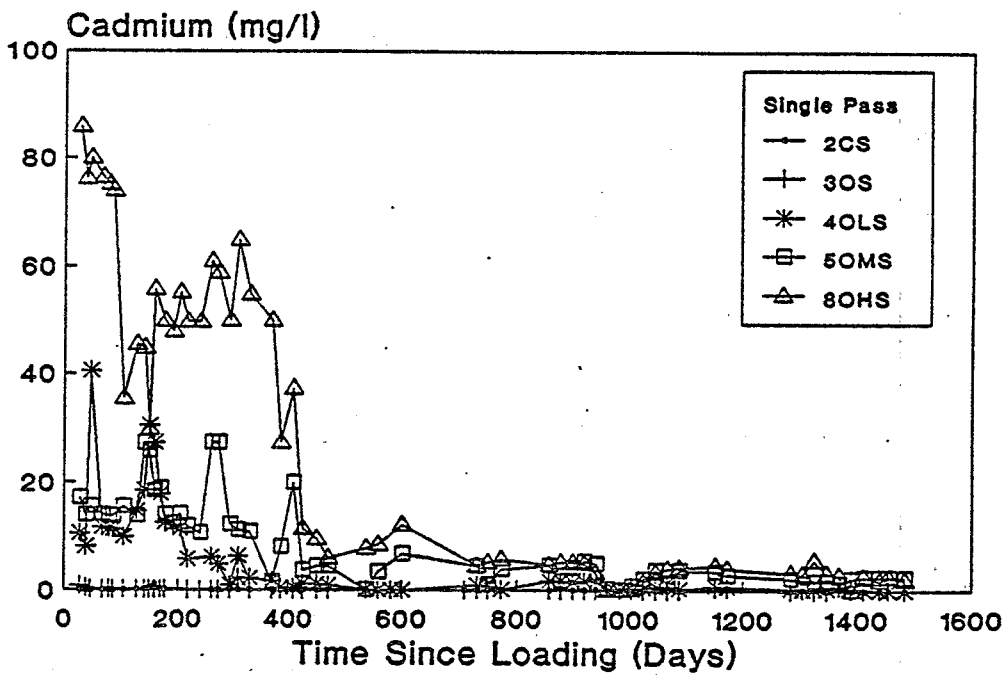
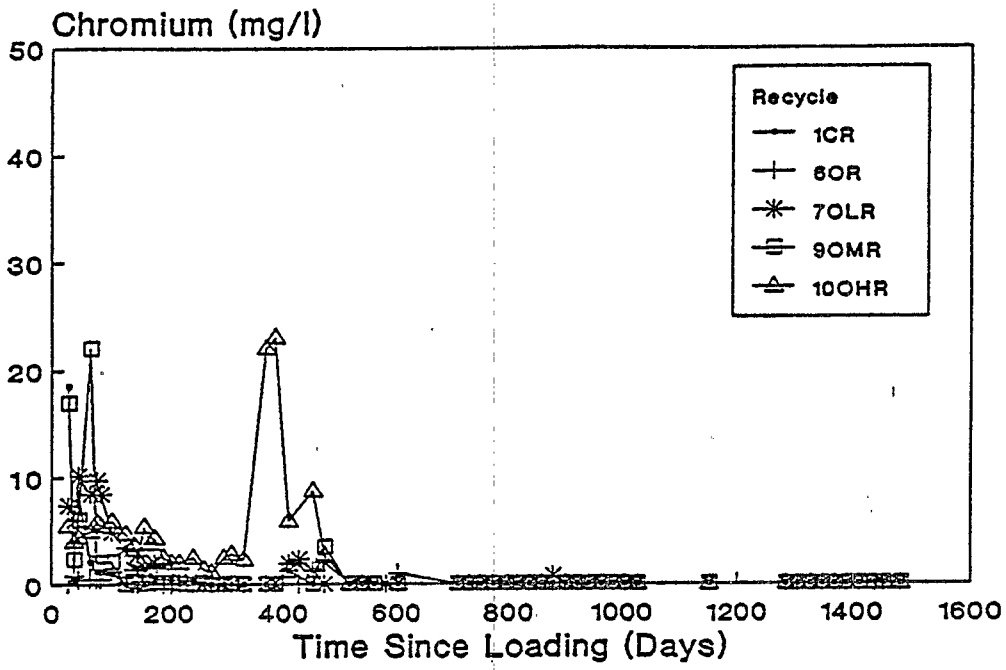


Figure 75. Leachate Cadmium during Simulated Landfill Investigations.



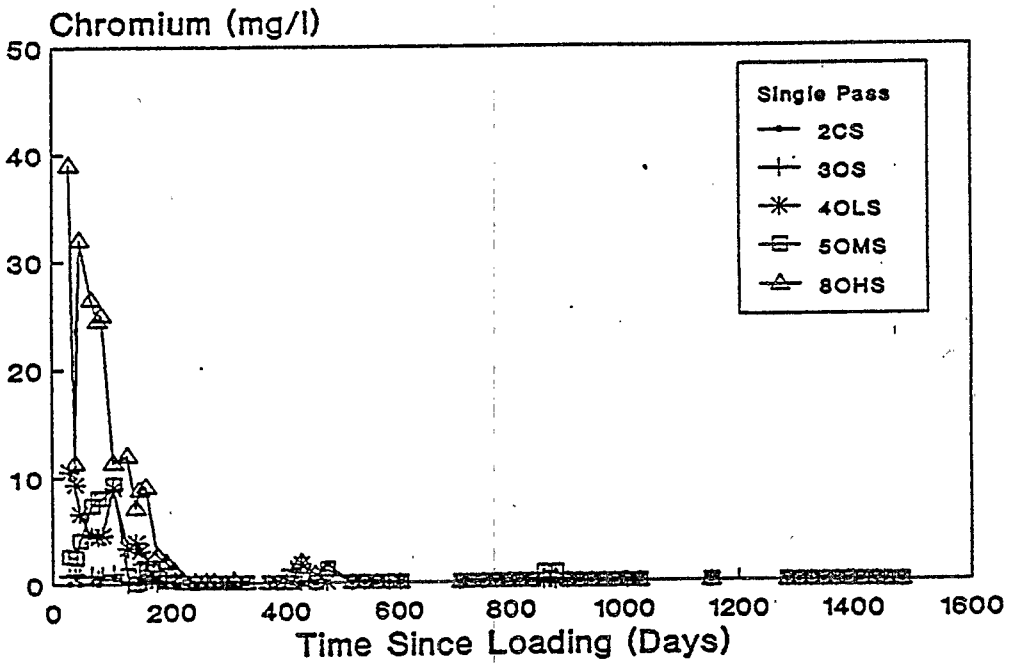
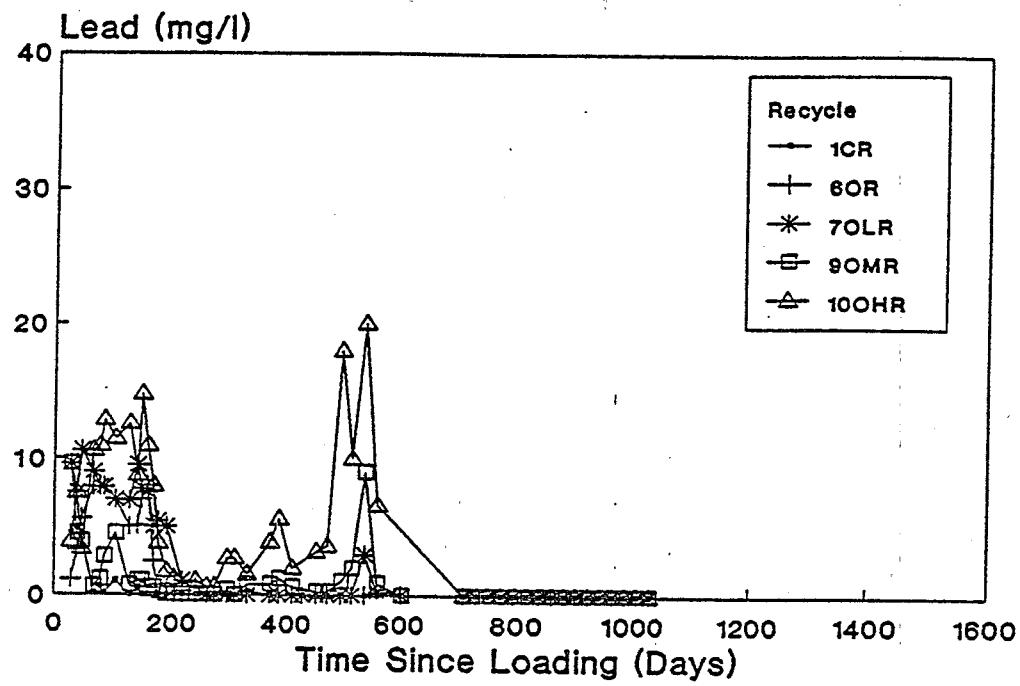


Figure 76. Leachate Chromium during Simulated Landfill Investigations.



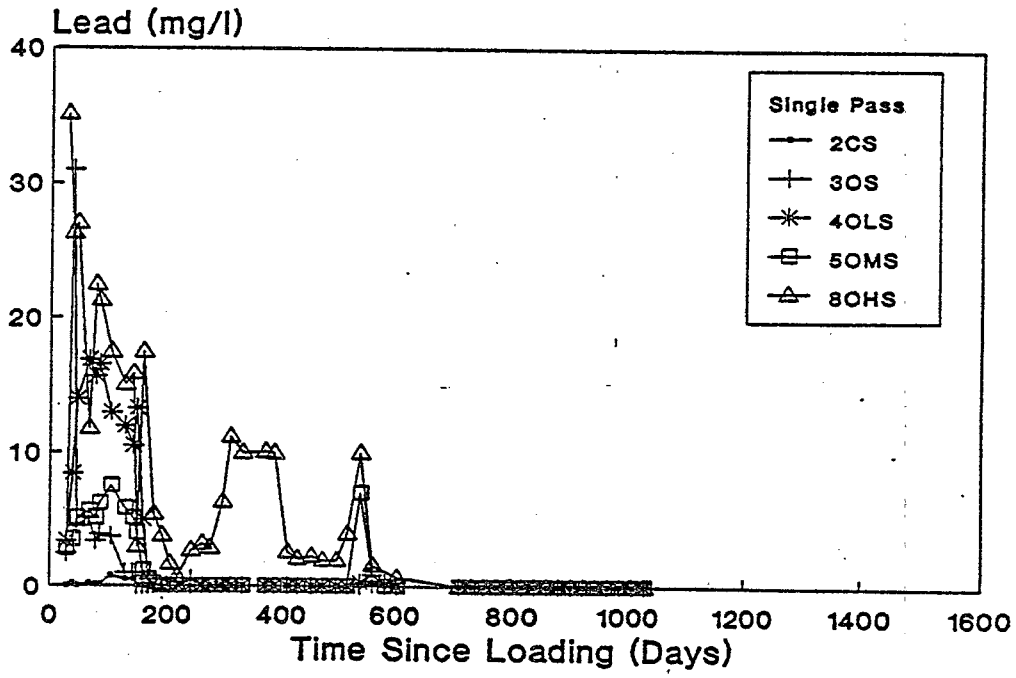
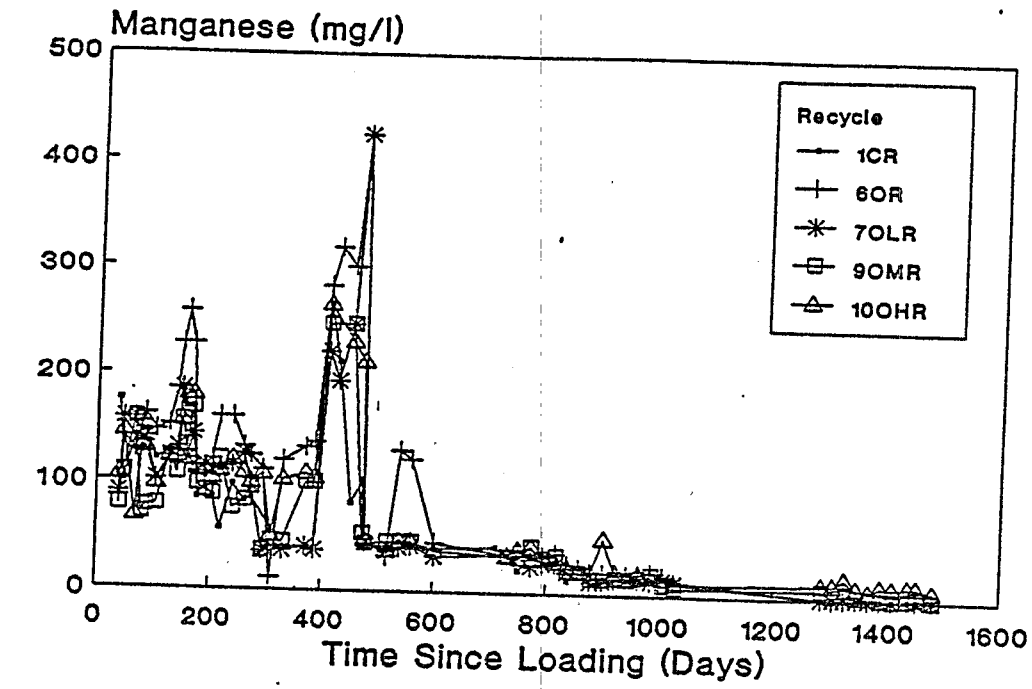


Figure 77. Leachate Lead during Simulated Landfill Investigations.



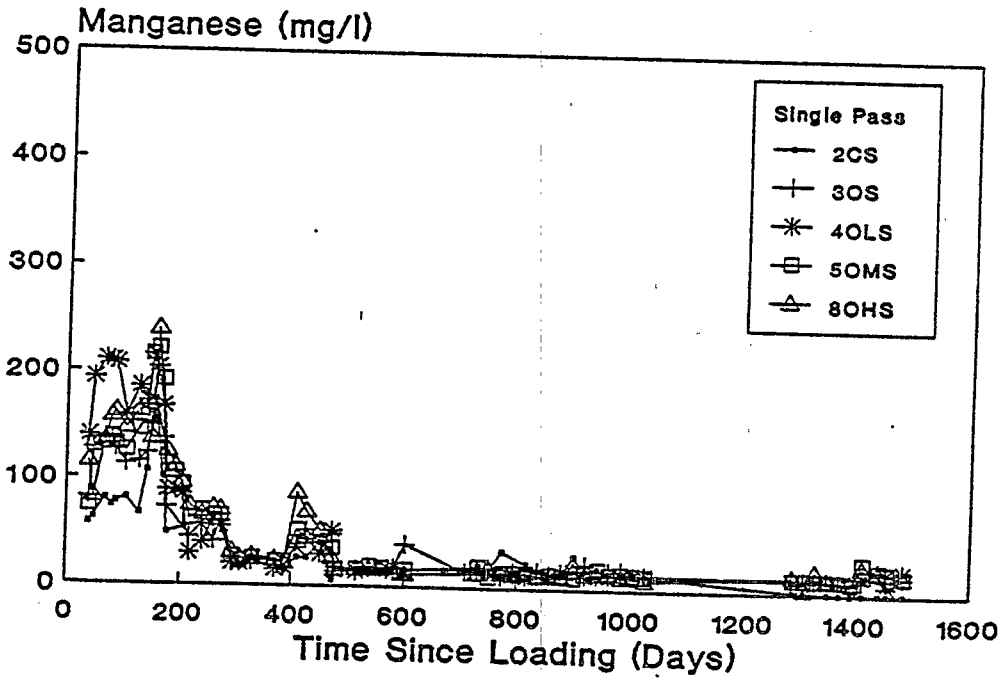
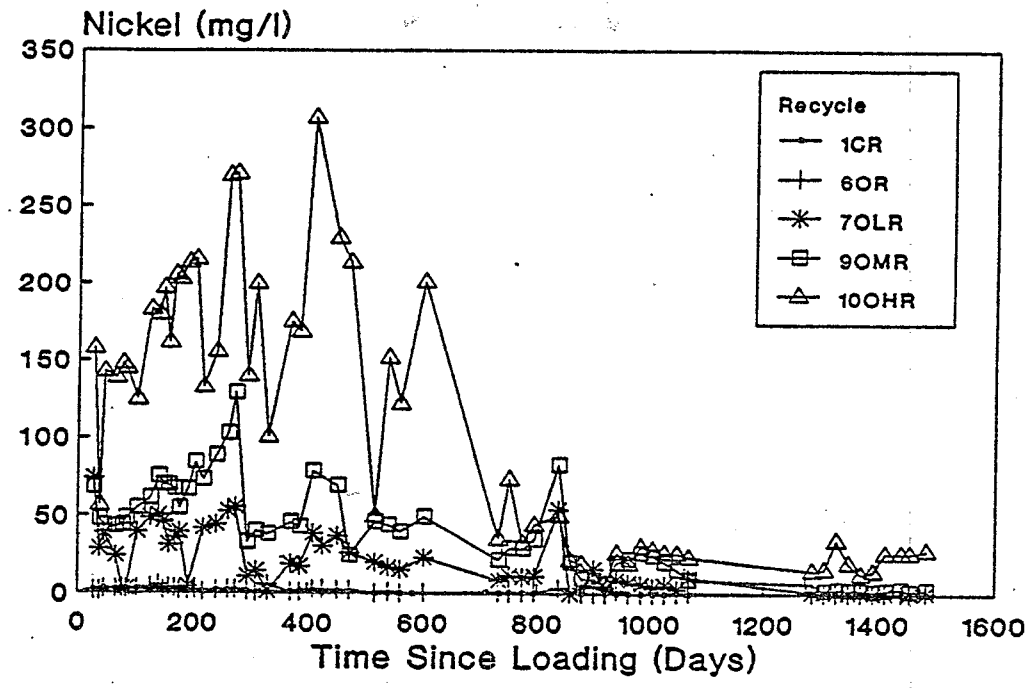


Figure 78. Leachate Manganese during Simulated Landfill Investigations.



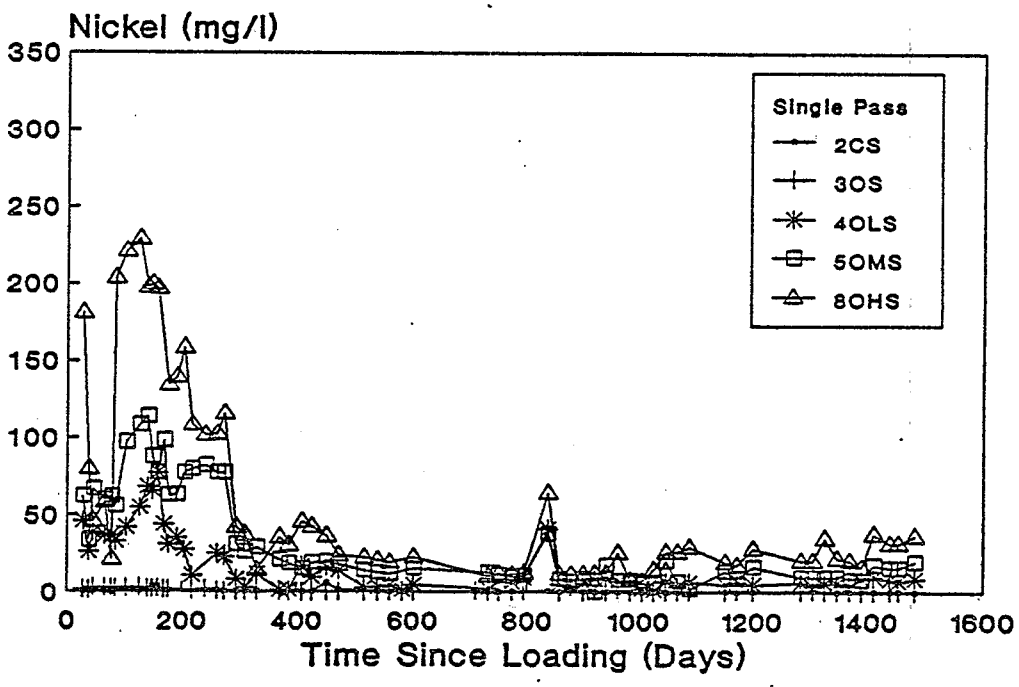
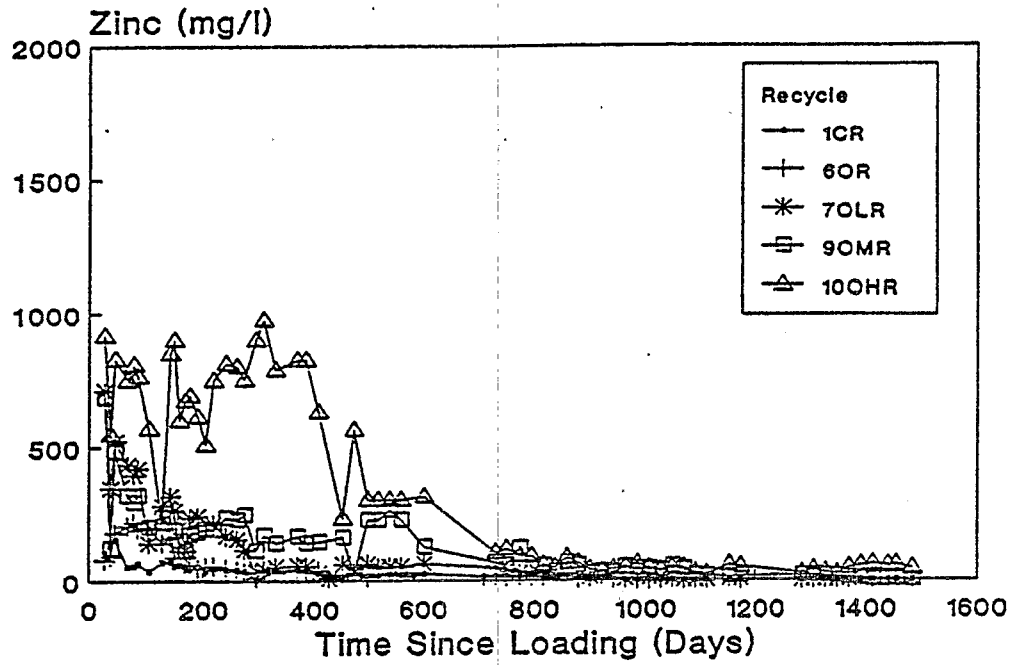


Figure 79. Leachate Nickel during Simulated Landfill Investigations.



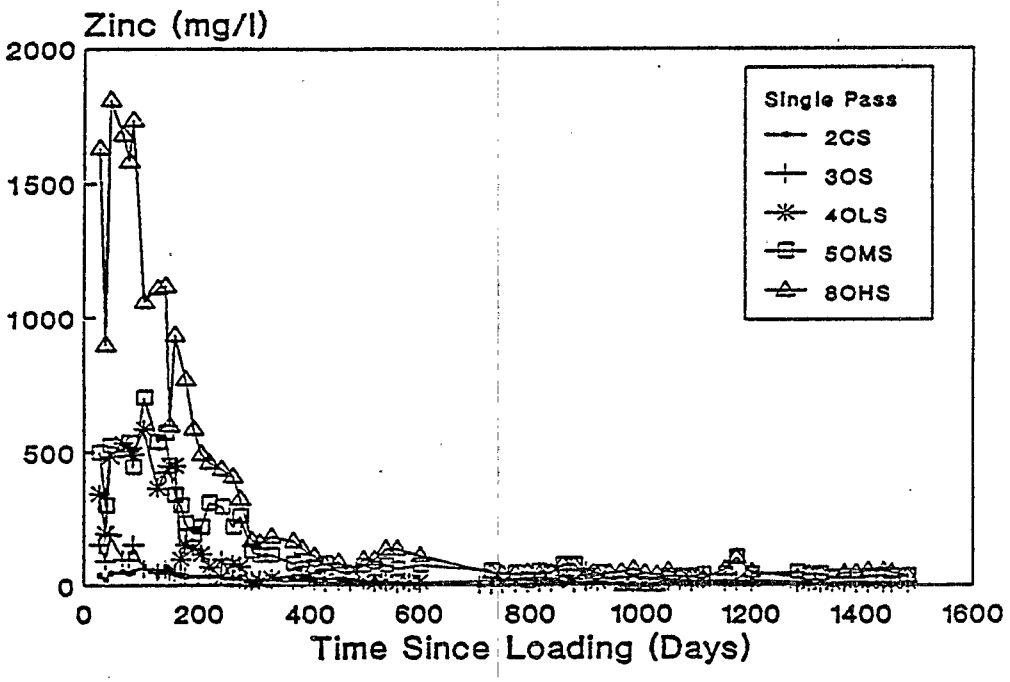
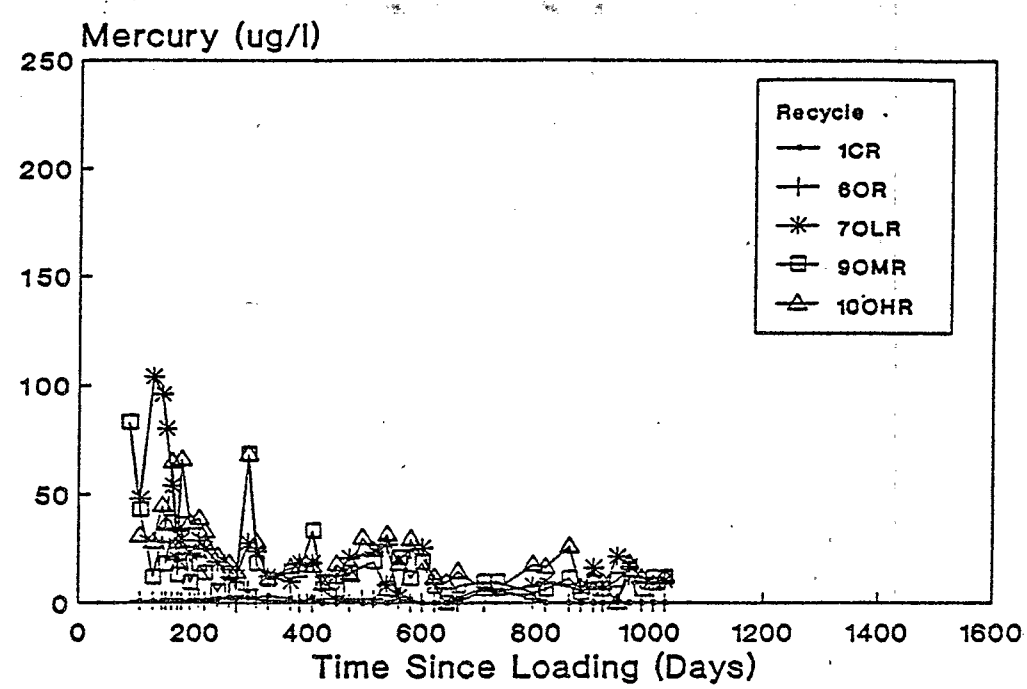


Figure 80. Leachate Zinc during Simulated Landfill Investigations.



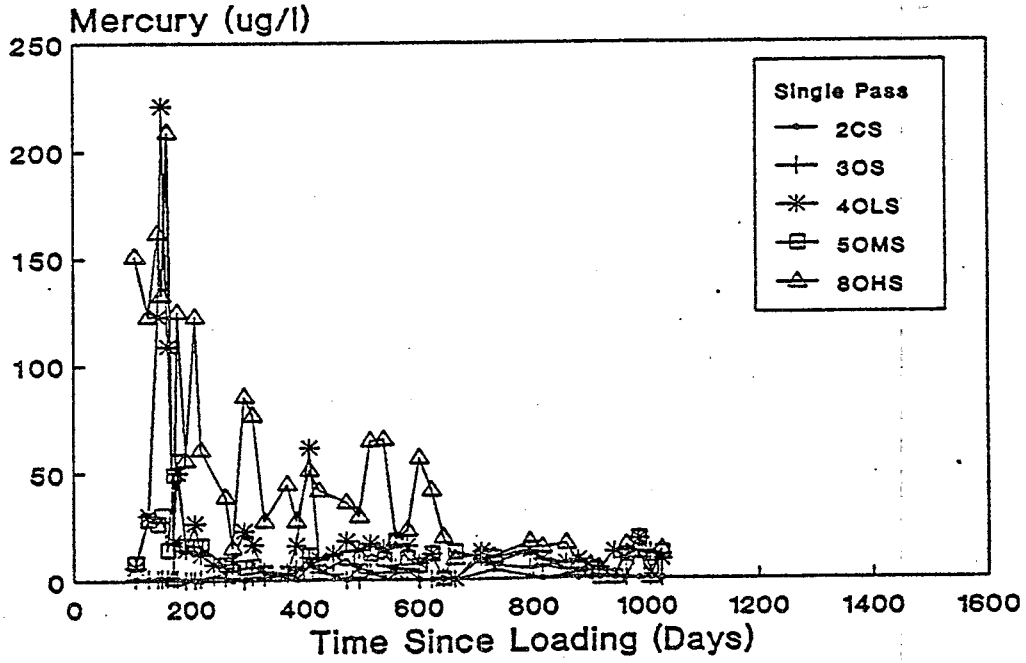


Figure 81. Leachate Mercury during Simulated Landfill Investigations.

mass of pollutant per mass of municipal solid waste basis.)

A different behavior was observed in the five single pass simulated landfill columns. The control single pass column, Column 2CS, behaved similar to the recycle columns in that waste stabilization processes progressed in a predictable fashion. Single pass columns that received priority pollutant loadings, Columns 3OS, 4OLS, 5OMS and 8OHS, displayed behavior characteristic of inhibition as reflected by gas volume produced, gas composition, leachate constituent analyses, and mass of IVA released and transformed. Therefore, no priority pollutant loadings applied to single pass simulated landfill columns during these investigations could be tolerated.

4.6 LITHIUM TRACER STUDIES

At various times during the course of these studies, lithium chloride was added to the columns for the purpose of ascertaining the nature of the flow through the columns and estimating the approximate retention times within the columns. Data obtained from these studies were analyzed by the following equation, with elaborations based on the nature of the lithium spiking procedure and the column operation methodologies as discussed subsequently.

$$t_r = \sum (C_{Li} * t) / \sum C_{Li} \qquad (18)$$

where;

t_r = retention time
C_{Li} = concentration of lithium
t = time at which that concentration has been measured in days since addition of the lithium

4.6.1 Single Pass Column/Retention Times

The lithium breakthrough curves for the single pass columns (Columns No. 2, 3, 4, 5 and 8) are shown in Figures 82 through 86. In all cases, simple unimodal breakthrough curves were obtained. In the cases of Columns 3 and 5, a second lithium spike was added after the first spike had substantially exited the columns in an effort to evaluate the possible impact of time-dependent compaction on the retention times. In those cases, the retention time was based on the date of addition of the second lithium spike taken as day zero of the measurement. The retention time results of these tracer studies are included in Table 30.

As indicated, the initial retention times ranged from 200 to 278 days for all single pass columns with the exception of Column 8 which had an initial retention time of 373 days. The cause of this difference is not clear, although it may have been a consequence of some anomaly in the loading of waste added to the columns. Hence, these data suggest that, even with attention to the loading of the columns, their development may proceed in a more heterogeneous manner and total consistency in retention time behavior may be very difficult to obtain.

The second lithium spikes to Columns 3 and 5 resulted in breakthrough curves indicative of increases in retention times of greater than 100% in both cases (102 and 132%, respectively). These increases were consistent with the trend in additional compaction of the waste matrix and more active microbial development with time. With this increase in retention times as column operations progressed through the phases of waste stabilization, the ability to act as a more efficient microbially-mediated treatment medium was likely enhanced.

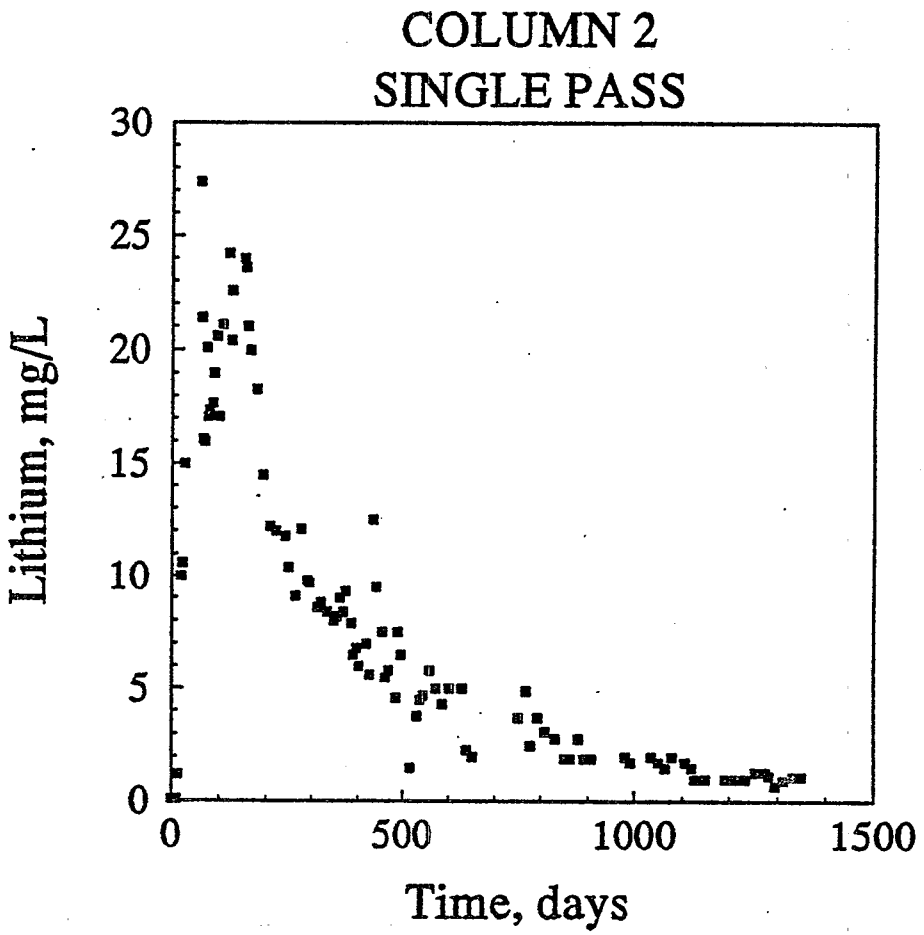


Figure 82. Lithium Breakthrough Curve for Single Pass Column 2 (Single Spike).

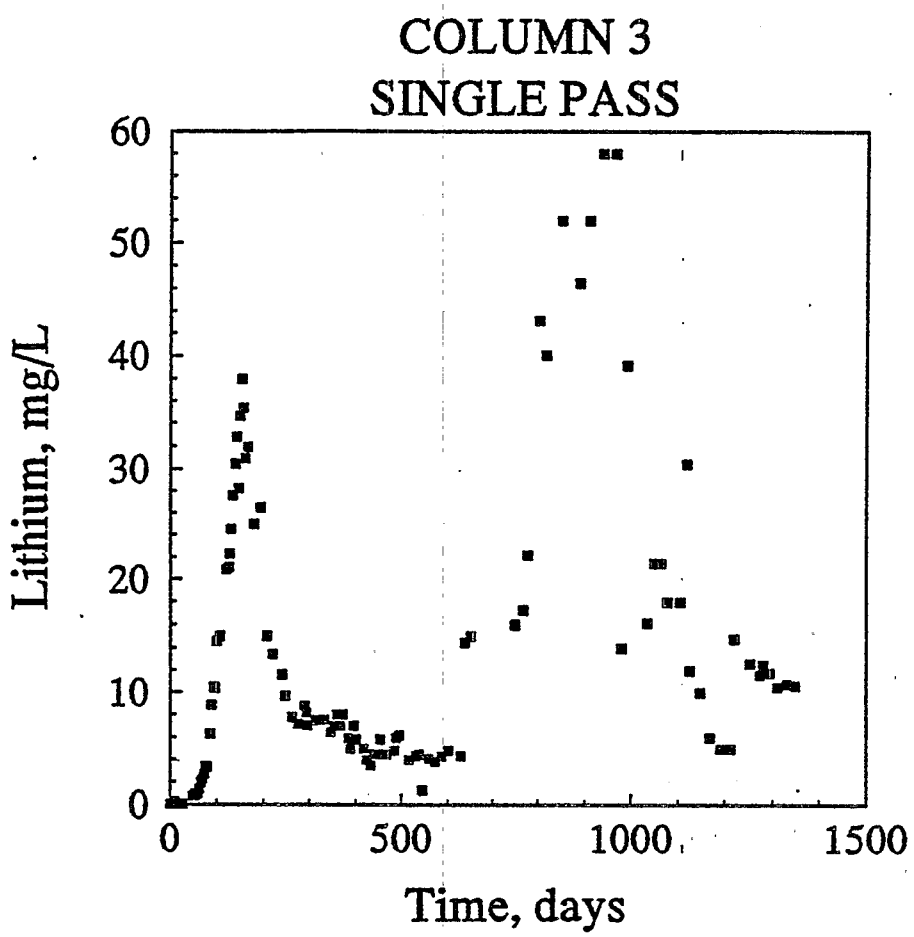


Figure 83. Lithium Breakthrough Curves for Single Pass Column 3 (Double Spike).

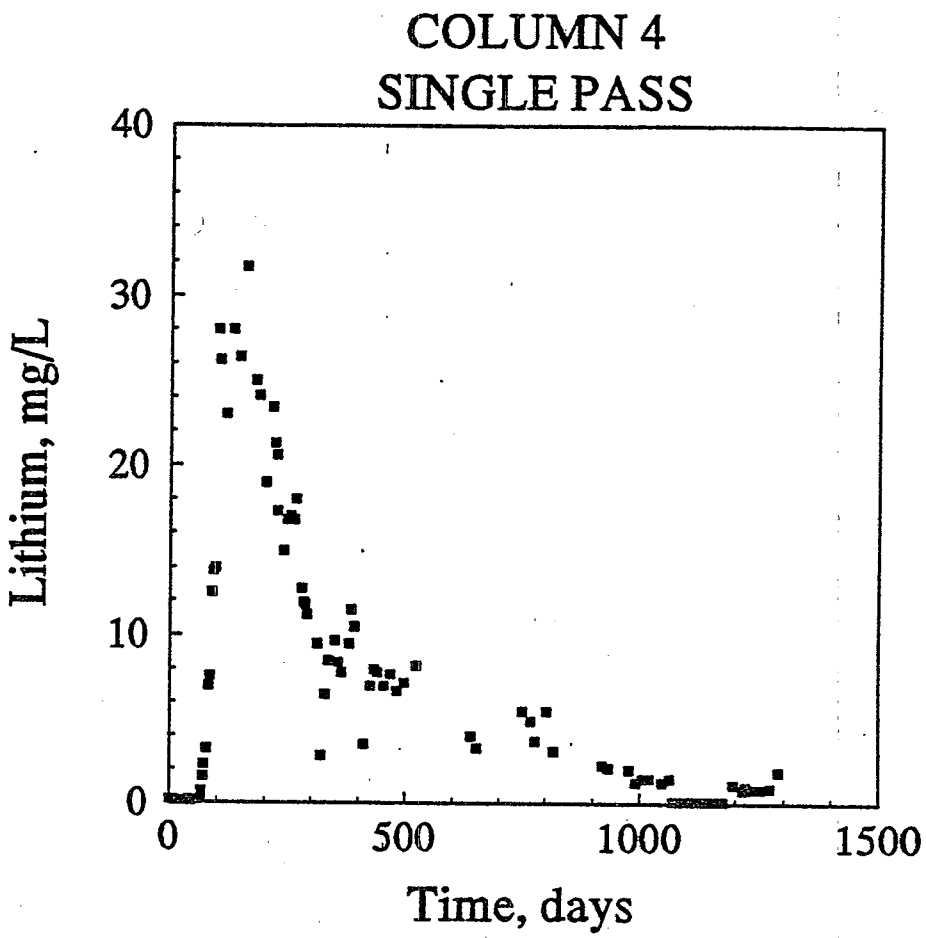


Figure 84. Lithium Breakthrough Curve for Single Pass Column 4 (Single Spike).

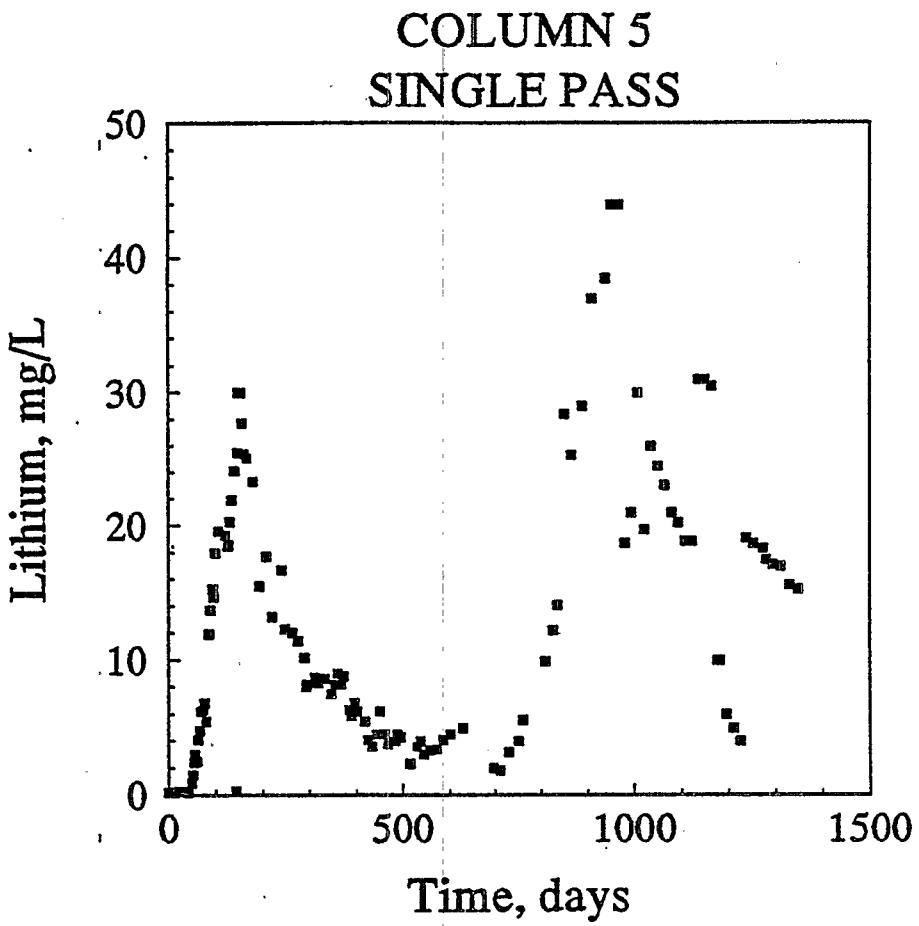


Figure 85. Lithium Breakthrough Curves for Single Pass Column 5 (Double Spike).

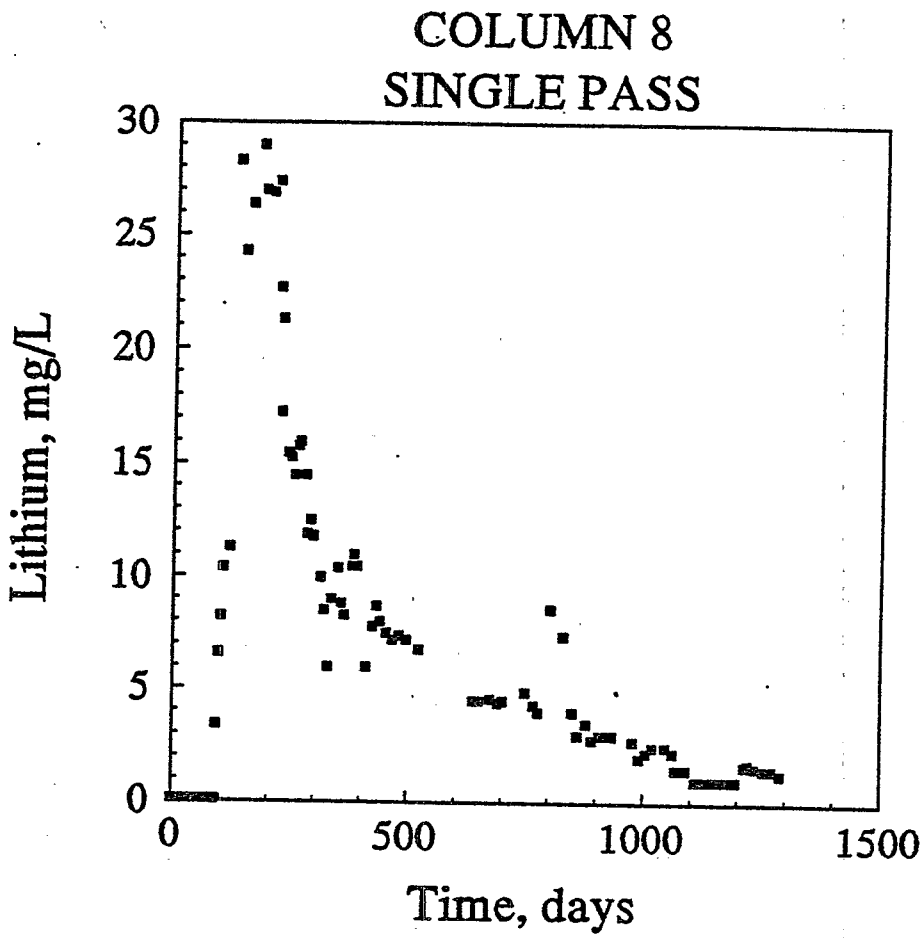


Figure 86. Lithium Breakthrough Curve for Single Pass Column 8 (Single Spike).

TABLE 30. INDICATED RETENTION TIMES OF SINGLE PASS SIMULATED LANDFILL COLUMNS

Column Identity	Retention Time, Days	
	First Spike	Second Spike
2CS	264	--
3OS	206	417
4OLS	278	--
5OMS	200	465
8OHS	373	--
Average	264.2	--

4.6.2 Recycle Columns/Retention Times

Analysis of retention times for the recycle columns (Columns No. 1, 6, 7, 9 and 10) posed a problem related to the manner in which the lithium was added. As a result of being added to the top of the opened recycle lines, the lithium was not introduced immediately onto the top of the waste matrix, but into the sump from which samples were drawn for analysis and from which leachate was recycled to the columns. The results of this mode of addition are clearly evident in the breakthrough curves from these columns (Figures 87 through 91) where very high initial lithium concentrations first diminished rapidly with leachate recycle to levels essentially characteristic of the background concentrations in all columns. Following this, all columns showed typical unimodal breakthrough curves, except that these curves tended to reach minima at levels in excess of the leachate background concentrations. Since lithium was being recycled, this was not unexpected. The appearance of a second breakthrough as the first lithium pulse was recycled to the top of the waste in the columns and re-emerged from the bottom of the column indicated a similarity in magnitude to the first breakthrough curve. This suggested that dispersion of lithium was limited during passage through the columns, and that for the conservative lithium tracer or other conservative materials, one pass through the columns would closely resemble the next. Therefore, in the analysis of these data, the day of the first, post-spiking minimum was taken as Day 0 for the first breakthrough and, where the second breakthrough was sufficiently developed to permit analysis, the minimum point between the completion of the first breakthrough and initiation of the second was taken as Day 0 for the second breakthrough. The results of these analyses are presented in Table 31.

As indicated in Table 31, The estimated retention times in the recycle columns for the first lithium pulse were characterized by substantial variability (256 to 432 days) and averaged about 30% longer than in the single pass columns (265 to 345 days). The second breakthrough was measured in Columns No. 1 and 6 and found to have increased, but to a significantly smaller extent (23 and 50%, respectively) than observed in the single pass columns. These variations could again be accountable to the difference in single pass and recycle operations and the more rapid progression toward stabilization established in the recycle columns as a consequence of leachate recycle. However in either case, the extended time of passage of the liquid transport phase provided a bioreactor circumstance beneficial to *in situ* adaptation and assimilation of both solid waste constituents and admixed loadings of organic and inorganic priority pollutants.

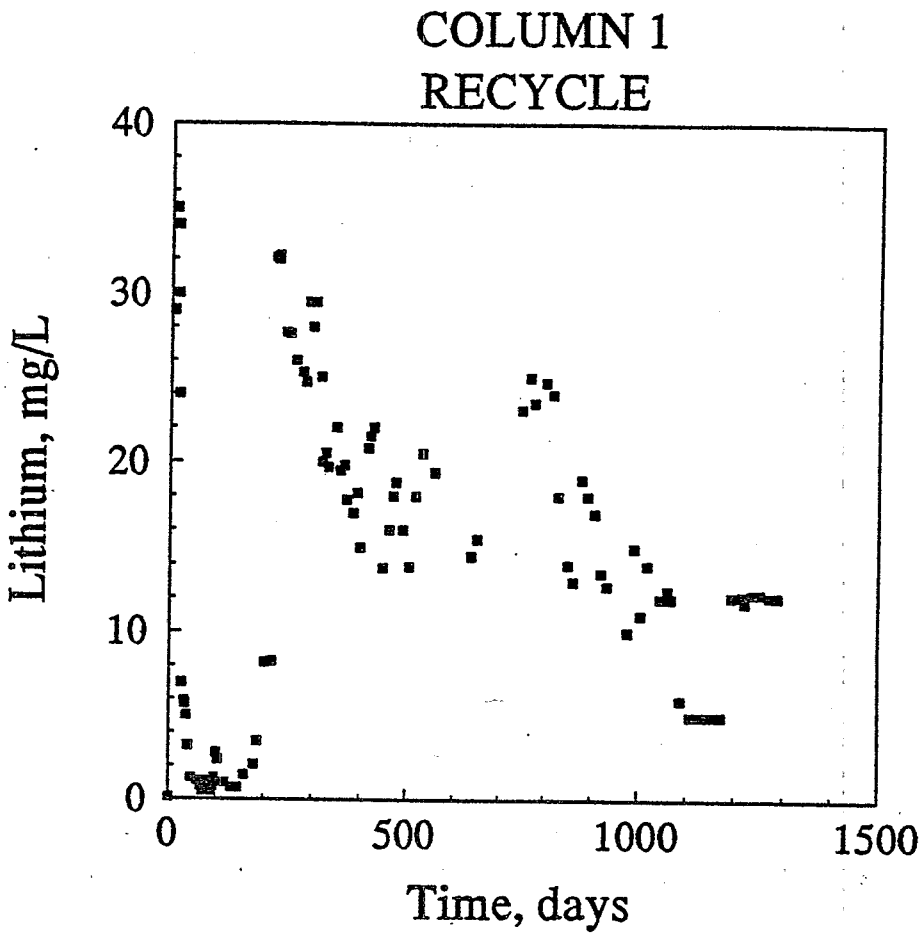


Figure 87. Lithium Breakthrough Curves for Recycle Column 1 (Single Spike).

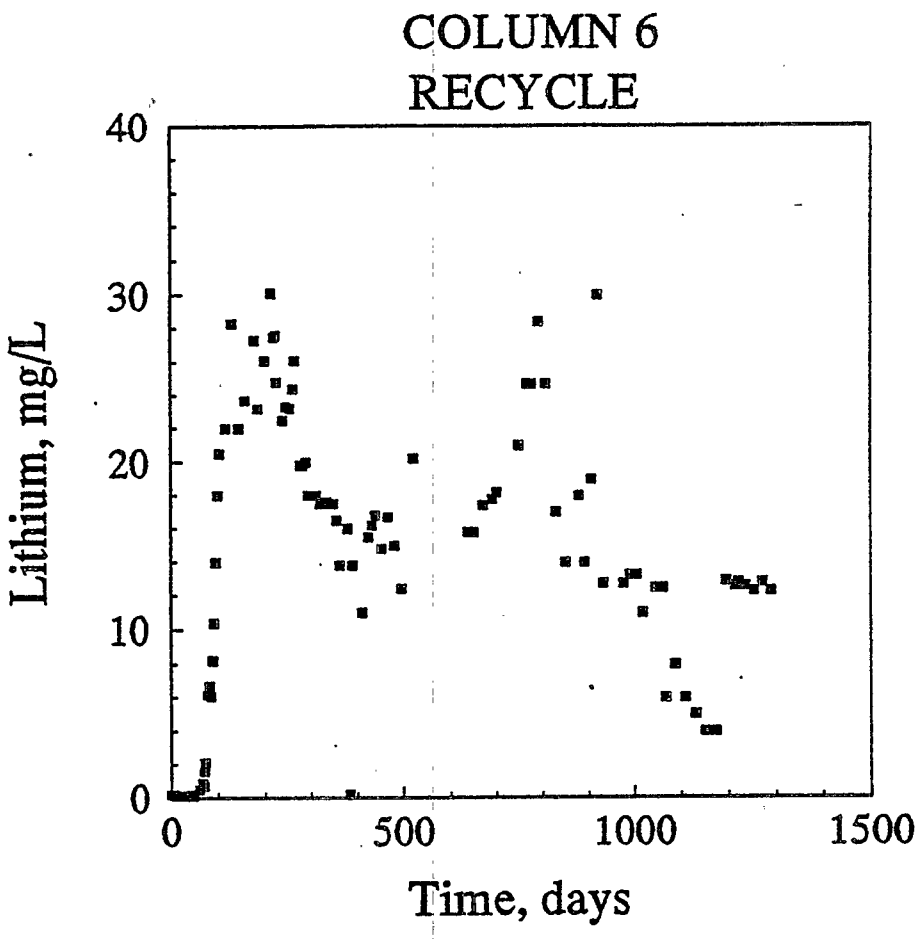


Figure 88. Lithium Breakthrough Curve for Recycle Column 6 (Single Spike).

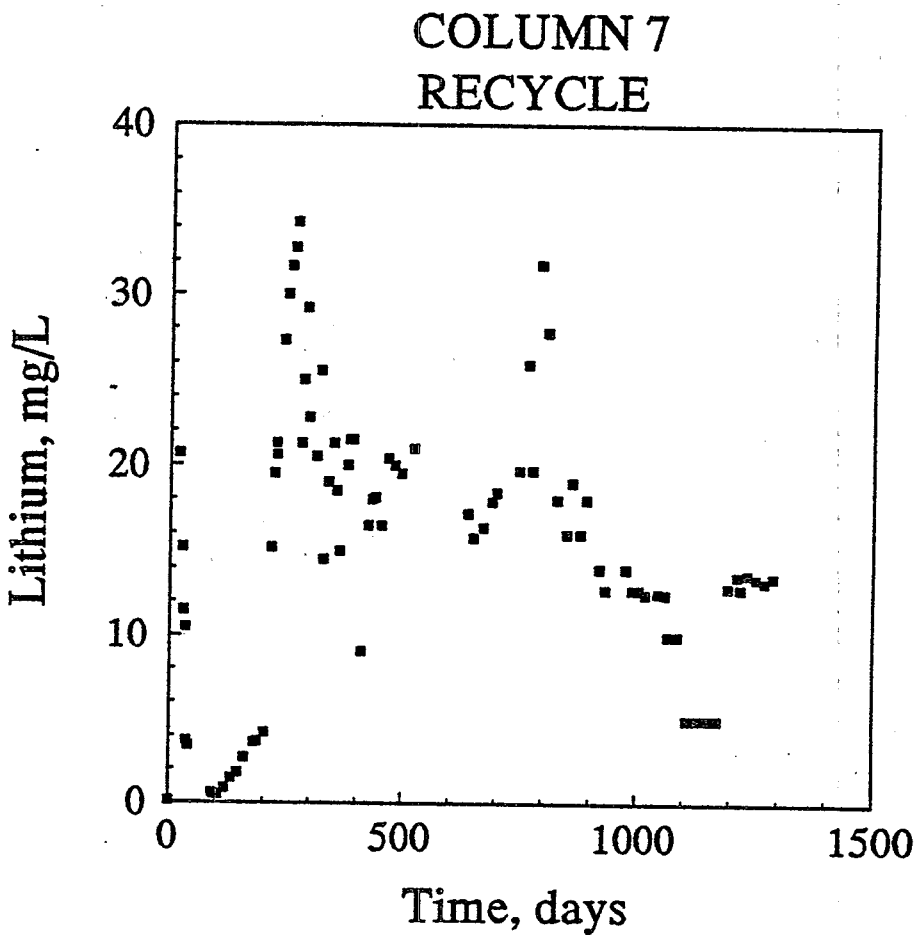


Figure 89. Lithium Breakthrough Curves for Recycle Column 7 (Single Spike).

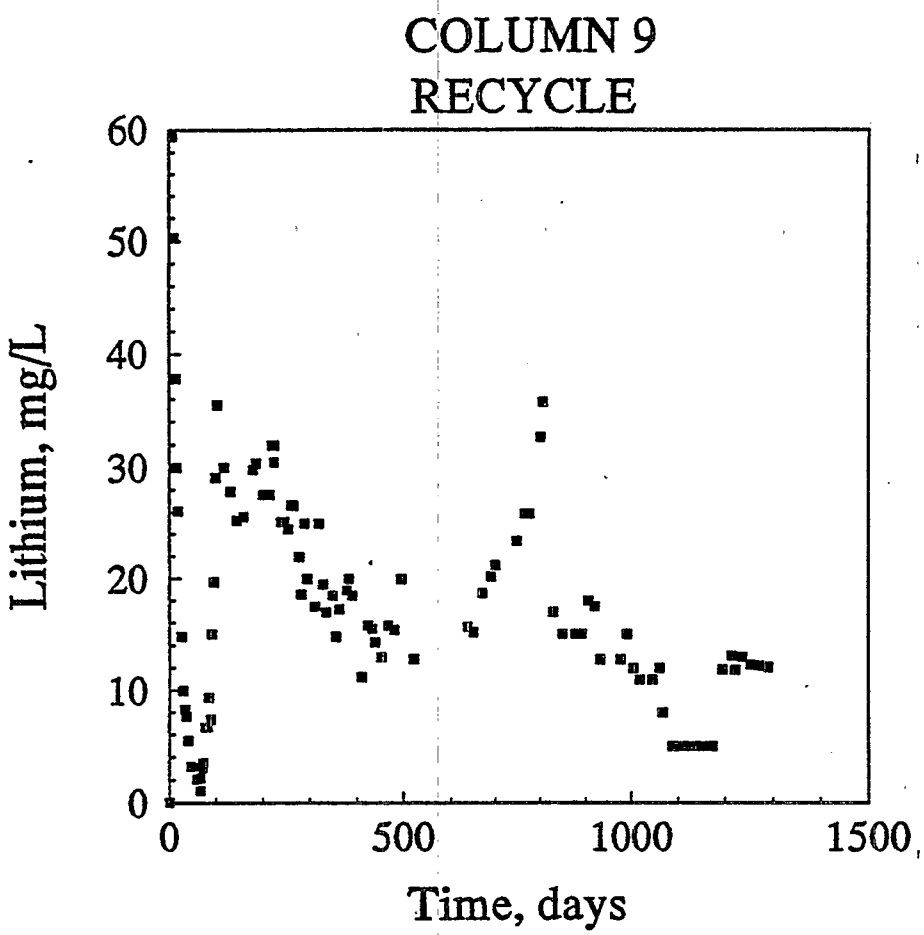


Figure 90. Lithium Breakthrough Curves for Recycle Column 9 (Single Spike).

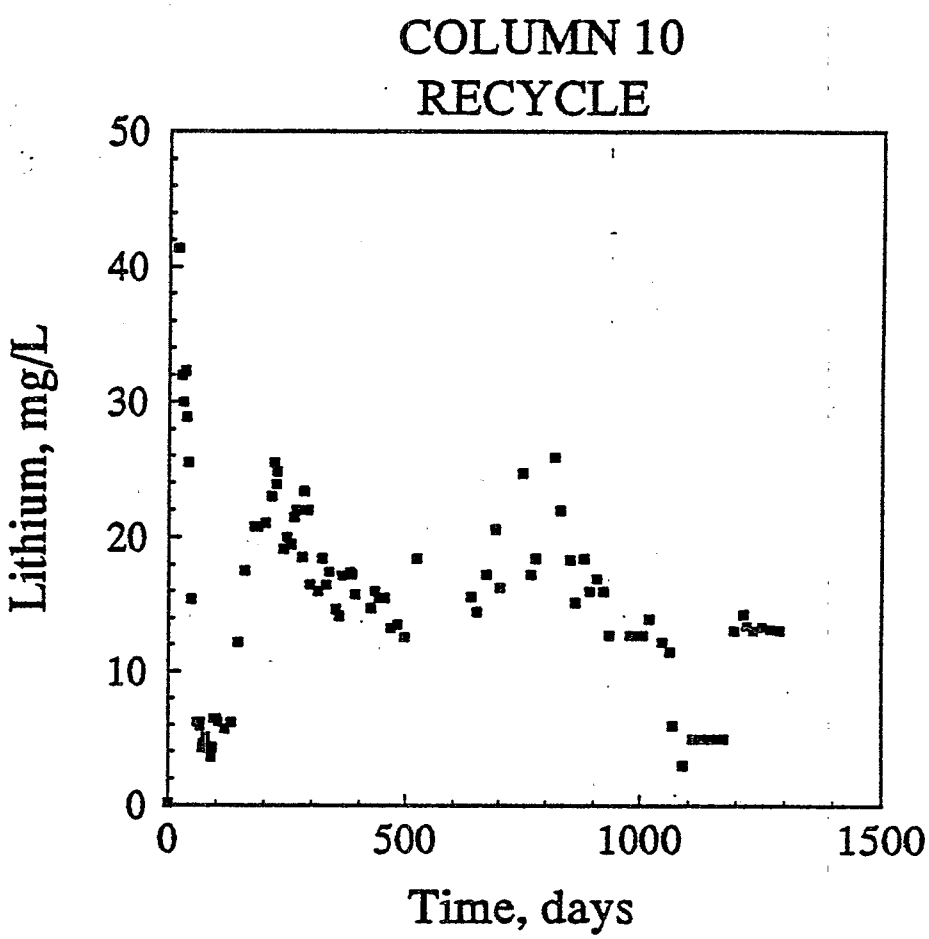


Figure 91. Lithium Breakthrough Curves for Recycle Column 10 (Single Spike).

TABLE 31. INDICATED RETENTION TIMES OF RECYCLE SIMULATED LANDFILL COLUMNS

Column Identity	Retention Time, Days	
	First Pass	Second Pass
1	256	315
6	262	399
7	432	--
9	372	--
10	407	--
	345.8	--

4.7 Simulated Landfill Column Disassembly

At the completion of the simulated landfill column operations (~ Day 1518), the 10 simulated landfill columns were allowed to remain dormant for approximately six weeks (40 days) before column disassembly was commenced. During this time, the accumulated leachate was drained periodically from the columns and discarded. However, prior to opening the columns for sampling and disassembly, head space gases were analyzed for the presence of hydrogen sulfide. The results of these analyses are included in Table 32 and indicate that H_2S was detected for all simulated landfill columns except for the column with the highest metal sludge loading (Column No. 10OHR). In addition, the highest H_2S level was in the headspace of the control recycle column (Column No. 1 CR), with the recycle columns generally exhibiting more H_2S, but moderated by the presence and/or effects of heavy metals. Therefore, H_2S utilization in precipitation reactions and precipitate production by sulfate reduction were influenced by the presence and intensity of the heavy metal loadings.

After the tele-thermometers and gas meters were disconnected and the column tops removed, several additional observations concerning the ten simulated landfill columns were made subsequent to their disassembly. First, all columns had settled uniformly across the surface during the experimental period. The depth of the stabilized refuse was determined by measuring from the top of the column to the surface of the gravel layer and adding to this the depth of the gravel. This result was then compared to the measurement originally taken prior to closure as indicated in Table 33. Based on these measurements, the refuse/waste mass had settled or compacted an average of 28% (19 to 36%), with the greatest and least settlement exhibited in the recycle control and highest metal loaded columns, respectively. Secondly, a uniform layer of black sludge, having an approximate depth of 1.0 to 2.0 cm (7/16 to 8/16 in), covered the entire gravel surface of the recycle columns. This sludge layer was shallower in the single pass columns and was confined only to a small portion at the center of the column. This again indicated a possible distribution of heavy metal precipitates in the presence of sulfides not only throughout the waste matrix, but in drainage gravel layers as well. Part of this layer, however, was attributable to the sludge seeding procedures introduced during landfill operations to initiate methane fermentation as described previously (Section 3.4.3).

TABLE 32. HEADSPACE H_2S CONTENT AT COLUMN DISASSEMBLY

Column Identity	Gas-Phase H_2S Concentration, mg/m^3
1 CR	50
2 CS	2
3 OS	2
4 OLS	2
5 OMS	1
6 OR	10
7 OLR	1
8 OHS	1
9 OMR	20
10 OHR	BDL[a]

Note: [a]Below Detection Limit (<1 mg/m^3)

TABLE 33. NET SETTLING OR COMPACTION IN SIMULATED LANDFILL AT COLUMN DISASSEMBLY

Column Identity	Original Refuse Depth, cm	Final Refuse Depth, cm	Change in Refuse Depth, cm	Settling, %[a]
1 CR	185	119	66	36
2 CS	193	127	66	34
3 OS	188	135	53	28
4 OLS	178	130	48	27
5 OMS	190	137	53	28
6 OR	183	124	59	32
7 OLR	188	130	58	31
8 OHS	190	147	43	23
9 OMR	185	137	48	26
10 OHR	198	160	38	19

Note: [a]% settling $\left(\frac{\text{original refuse depth - final refuse depth}}{\text{original refuse depth}}\right)_{*100}$

Core samples of the stabilized waste were obtained from the 10 columns in order to determine the distribution of the residual organic priority pollutants codisposed in the columns. These samples were obtained using a core sampler at depth increments of about 30 cm, and were extracted with methylene chloride using a Soxhlet extractor. The concentrated methylene chloride extract was analyzed using the same GC/MS methods described for the leachate samples. The results of these analyses are presented and discussed in more detail in Section 5.1, and the corresponding analyses of supplemental heavy metal sludge samples retrieved from the columns during disassembly are presented and discussed in Section 5.2.

When the stabilized refuse was removed from the columns, visual observations were also made with regard to the physical appearance of the refuse, the sand/gravel/geotextile underdrain system within the HDPE liner, and the sand/geotextile/gravel system between the HPDE liner and the steel containment shell of the columns. Much of the inert materials such as metal, glass and plastic were readily recognizable, as was a considerable amount of cardboard and

newsprint, some indicating little apparent physical or chemical change. Sections of newspapers were still readable, although these waste materials appeared stained from exposure to and reaction with the leachate over the experimental period. Because the original refuse was shredded, it was difficult to discern other differences in component characteristics, with exception of the greater compaction discussed previously.

The layers of sand, geotextile and gravel composing the underdrain system appeared to be unchanged from when it was initially placed in the columns. In a few instances, the materials were slightly discolored by what visually appeared to be rust stains. These stains were neither uniform nor widespread through the underdrain systems and there was little indication of either biological growth or precipitation/cementation within the underdrain materials. Similarly, the layers of materials contained between the HDPE liner and the steel column shell were alike in appearance to those same materials within the HDPE liner, with the exception of the rust stains and apparent moisture content. These materials did not show the discoloration attributed to iron oxide precipitation noted previously, but in some instances appeared to be somewhat less moist than the inner liner contents. Again, there was little evidence of microbial or chemical interaction within the sand/gravel/geotextile base materials, and all drainage systems and appurtenances appeared to have retained their functionality.

SECTION 5

EVALUATION OF ORGANIC AND INORGANIC PRIORITY POLLUTANTS

5.1 BEHAVIOR OF ORGANIC PRIORITY POLLUTANTS

In addition to the previous presentation and discussion of the routine analytical parameters, particular attention was focused on the behavior of the organic priority pollutants codisposed with the municipal refuse in the simulated landfill columns (Table 16).

5.1.1 Chemical and Physical Properties

The chemical and physical properties affecting the potential mobility of the organic priority pollutants are included in Table 34. Accordingly, the expected mobility of the test compounds in the liquid and gas phases associated with the refuse matrix can be summarized as follows:

Halogenated Aliphatic Compounds--(trichloroethene, TCE, and dibromomethane, DBM); high volatility and mobility in liquid and gas phases as indicated by high solubility and vapor pressure and low octanol/water partition coefficient (K_{ow}).

Chlorinated Benzene Compounds--(1,4-dichlorobenzene, DCB, and 1,2,4-trichlorobenzene, TCB); relatively volatile with low mobility in the liquid phase as indicated by low solubility and high K_{ow}.

Phenolic and Nitro-Aromatic Compounds--(2,4-dichlorophenol, DCP, 2-nitrophenol, NP, and, nitrobenzene, NB); relatively mobile in liquid phase, low volatility and mobility in the gas phase as indicated by high solubility, low vapor pressure and K_{ow}.

Hexachlorobenzene (HCB), Polynuclear Aromatic Hydrocarbons--(naphthalene, NAP), Pesticides (lindane, LIN, and dieldrin, DIEL), and Phthalic Acid Esters (Bis(2-ethylhexyl)phthalate, BEHP); low volatility and mobility as indicated by low solubility and vapor pressure and high K_{ow}.

To assist in the interpretation of data descriptive of the behavior of the organic priority pollutants, sorption isotherms were developed in separate laboratory tests for each of the test compounds with the exception of DIEL, HCB, and BEHP by Reinhart[65]. All resulting isotherms confirmed a strong linearity between sorbed and solute concentrations, and from a least squares regression analysis, the coefficients of linearity or sorption partition coefficients, K_p, for each compound were calculated and are presented in Table 35. K_p could then be used to calculate a retardation factor, RET, or:

$$RET = 1 + \rho K_p/\theta_w \qquad (19)$$

where;

ρ = refuse bulk density
θ_w = moisture content

Since RET is a measure of the rate of movement of the test compound

TABLE 34. PHYSICAL AND CHEMICAL PROPERTIES OF ORGANIC PRIORITY POLLUTANTS LOADED TO THE SIMULATED LANDFILL COLUMNS[a]

Organic Compound	Molecular Weight	Aqueous Solubility	Vapor Pressure at 100°C (KP_a)	Log Octanol/ Water Partition Coefficient	Henry's Law Constant
Trichloroethene (TCE)	131.4	1,100 (20°C)	150	2.29	0.37
Dibromomethane (DBM)	173.9	11,700 (15°C)	101	1.45	0.038
1,4-Dichlorobenzene (DCB)	147.0	49 (22°C)	8.1	3.38	0.117
Nitrobenzene (NB)	123.1	1,900 (20°C)	3.3	1.85	0.00046
2-Nitrophenol (NP)[b]	139.1	2,100 (20°C)	2.5	1.76	0.0032
Naphthalene (NAP)	128.2	26.2 (20°C)	2.5	3.37	0.015
2,4-Dichlorophenol (DCP)[c]	163.0	4,500 (20°C)	1.9	2.75	0.0017
1,2,4-Trichlorobenzene (TCB)	181.5	19 (22°C)	3.3	4.04	0.216
Lindane (LIN)	290.9	17 (24°C)	0.17	3.72	1.3×10^{-5}
Dieldrin (DIEL)	381.0	0.1 (25°C)	2.39×10^{-5}	---	---
Bis(2-ethylhexyl)phthalate (BEHP)	391.0	0.285 (24°C)	0.0002	5.20	---
Hexachlorobenzene (HCB)	284.8	0.11 (24°C)	133 (114.4°C)	5.61	---

[a]From Callahan, et al.[63] and Verschueren[64]
[b]Log dissociation constant = 7.21
[c]Log dissociation constant = 7.85

TABLE 35. CALCULATION OF RETENTION TIME FOR SELECTED ORGANIC PRIORITY POLLUTANTS LOADED TO THE SIMULATED LANDFILL COLUMNS[a]

Organic Compound	Coefficient Partition, K_p ml/q	Retardation Factor, RET[b]		Retention Time[c], yr	
		min	max	min	max
Dibromomethane (DBM)	7.3	4.86	6.18	0.93	1.36
Trichloroethene (TCE)	36.6	20.4	26.9	3.91	5.94
Nitrobenzene (NB)	17.4	10.2	13.4	1.96	2.96
2-Nitrophenol (NP)	29.5	16.6	21.9	3.18	4.84
2,4-Dichlorophenol (DCP)	285	152.0	203.4	29.15	44.92
1,4-Dichlorobenzene (DCB)	126	67.8	90.5	13.00	19.98
1,2,4-Trichlorobenzene (TCB)	1350	716.5	959.5	137.41	211.99
Lindane (LIN)	853	453.0	606.6	86.88	133.95
Naphthalene (NAP)	216	115.5	154.4	22.15	25.50
Bis(2-ethylhexyl)phthalate (BEHP)	10^6	$5x10^5$	$7x10^5$	$9.6x10^4$	$1.5x10^5$
Dieldrin (DIEL)	10^6	$5x10^5$	$7x10^5$	$9.6x10^4$	$1.5x10^5$
Hexachlorobenzene (HCB)	10^6	$5x10^5$	$7x10^5$	$9.6x10^4$	$1.5x10^5$

[a]After Reinhart[65]
[b]RET = $1 + \rho K_p/\theta_w$; ρ = density, g/ml; θ_w = moisture content, fraction
[c]Retention time = RET X V/Q; V = volume of water in column, L; Q = average leachate flowrate, L/yr

relative to the bulk water movement, from average leachate flowrates through the columns and the calculated RET, the expected relative retention time, presented in Table 35 for each organic compound, could be calculated. However, because of the opportunity for some dispersion and the possibility of shortcircuiting, the compound may tend to appear in the leachate before and after the calculated retention time. From predicted retention time ranges (Section 4.6) and in the absence of bioconversion, only TCE, DBM, NP and NB were thereby expected to elute during the time period of the investigation. Although DCP had an indicated retention time of 13 to 20 years, the extremely high aqueous solubility indicated a probability of appearance in the leachate toward the end of the investigations. In addition, as already indicated, this physical-chemical behavior was expected to be modified by microbially-mediated processes of attenuation.

5.1.2 General Observations

The fate of the organic priority pollutants in the recycle and single pass columns, based on leachate and waste matrix analysis after the simulated landfill columns were disassembled, is summarized in Tables 36 and 37, respectively. Details of the analyses of extracted core samples and mass balances for each column at the end of the project period are provided in Tables D-1 through D-4 of Appendix D. Mass not accounted for in the leachate or on the waste is assumed to have been "transformed." Such transformation is not explicitly defined and is not meant to imply complete mineralization, since, in most cases, all potential byproducts were not identified nor quantified. In addition, although limited gas analysis indicated that volatilization was a minor pathway for several of the more volatile compounds, because sufficient data were not available to completely quantify volatilization, mass possibly lost to the gas phase is also included in the total mass transformed.

Notwithstanding these limitations, several general conclusions can be drawn from the indicated mass balances regarding the fate of the organic priority pollutants. The more hydrophilic compounds (log K_{ow} less than 2.29), including DBM, TCE, NP and NB (Figures 61, 62, 65 and 66), appeared in the leachate very early in the investigations at relatively high concentrations (up to 225 mg/L). In addition, the order in which the compounds appeared in the leachate was approximately proportional to their respective K_{ow} values. Thus the more hydrophobic the compound, the longer it was retained, presumably as a result of some interaction with the waste matrix. However, appearance of these compounds was relatively brief and most had either disappeared or dramatically declined in concentration (to the μg/L range) within the first year. Overall transformation of these compounds, as indicated in Tables 36 and 37, was very efficient, approaching 100% of the mass placed in most cases.

Compounds with intermediate hydrophobicity (log K_{ow} between 2.75 and 4.04), such as DCP, NAP, DCB, LIN and TCB (Figures 57, 60, 63 and 64), were detected in the leachate and, with the exception of DCP, were measured at relatively low concentrations. Most of these compounds exhibited moderate (30 to 60%) overall transformation, however, the extent varied significantly from one column to another. DCP was much more mobile in the liquid phase than the remaining compounds in this category, particularly at more neutral pH values.

The extremely hydrophobic compounds (K_{ow} greater than 5), DIEL, HCB and BEHP, were never detected in the leachate, i.e., DIEL and BEHP were completely retained or transformed in all columns. In contrast, HCB retention or transformation varied from zero to 100%.

As indicated previously, volatilization was not well quantified during the investigations. Only TCE, DCB, and TCB were detected in the gas phase. This could be expected, since these compounds have Henry's Law constants in excess of 0.117 (Table 34).

TABLE 36. MASS BALANCE SUMMARY ON ORGANIC PRIORITY POLLUTANTS FOR THE SINGLE PASS SIMULATED LANDFILL COLUMNS[a]

Compound	% Leached	% Retained	% Transformed[b]
Dibromomethane (DBM)	14.1 (6.1-27.4)	0	85.9 (72.6-93.9)
Trichloroethene (TCE)	10.7 (7.77-14.58)	0	89.3 (85.42-92.23)
Nitrobenzene (NB)	0.75 (0.02-2.31)	0	99.25 (97.69-99.98)
2-Nitrophenol (NP)	0.31 (0.03-1.16)	0	99.69 (98.84-99.97)
2,4-Dichlorophenol (DCP)	10.9 (8.66-11.81)	15.4 (0.74-25.2)	73.6 (57.71-87.75)
1,4-Dichlorobenzene (DCB)	3.8 (2.53-5.98)	48.4 (30.96-68.63)	47.8 (28.55-81.27)
Naphthalene (NAP)	1.2 (1.04-1.34)	46.8 (17.48-59.53)	52.0 (39.13-81.27)
Lindane (LIN)	0	52.2 (0-100)	47.8 (0-100)
1,2,4-Trichlorobenzene(TCB)	0.17 (0.08-0.32)	39.7 (6.67-60.0)	60.1 (42.00-93.01)
Dieldrin (DIEL)	0	0	100
Hexachlorobenzene (HCB)	0	57.1 (0-96.67)	42.9 (3.33-100)
Bis(2-ethylhexyl)phthalate (BEHP)	0	0	100

[a]Ranges in parentheses
[b]Mass not accounted for in the leachate or recovered from the waste

TABLE 37. MASS BALANCE SUMMARY ON ORGANIC PRIORITY POLLUTANTS FOR THE RECYCLE SIMULATED LANDFILL COLUMNS[a]

Compound	% Leached	% Retained	% Transformed[b]
Dibromomethane (DBM)	1.71 (0.12-2.66)	0	98.29 (97.34-99.88)
Trichloroethene (TCE)	0.57 (0.40-0.83)	0	99.43 (99.04-99.60)
Nitrobenzene (NB)	0.07 (0.02-0.10)	0	99.93 (99.90-99.98)
2-Nitrophenol (NP)	0.03 (0.01-0.04)	0	99.97 (99.96-99.99)
2,4-Dichlorophenol (DCP)	2.55 (0.41-8.73)	25.17 (6.50-41.99)	72.29 (41.99-94.39)
1,4-Dichlorobenzene (DCB)	1.20 (0.21-3.90)	35.37 (18.99-48.89)	63.44 (50.79-80.80)
Naphthalene (NAP)	0.41 (0.09-1.32)	48.28 (21.75-63.31)	53.00 (21.2-78.16)
Lindane (LIN)	0	66.29 (33.75-93.17)	33.71 (6.83-66.25)
1,2,4-Trichlorobenzene(TCB)	0.05 (0.0-0.17)	38.15 (32.58-43.75)	61.81 (37.42-67.40
Dieldrin (DIEL)	0	0	100
Hexachlorobenzene (HCB)	0	86.31 (46.42-100)	13.69 (0-53.58)
Bis(2-ethylhexyl)phthalate (BEHP)	0	0	100

[a]Ranges in parentheses
[b]Mass not accounted for in the leachate or recovered from the waste

5.1.3 Behavior of Specific Organic Priority Pollutants

5.1.3.1 Dibromomethane--

Dibromomethane (DBM) appeared in all column leachates early in the investigations, rapidly reaching a maximum leachate concentration, and then disappearing within the first year (Figure 61). As would be expected from its relatively high solubility, concentrations observed for DBM were the highest measured for all test compounds. Transformation of DBM is expected to produce bromide, and possibly methane or ethylene, as observed by Wade and Castro[66]. Ion chromatographic analysis, initiated on Day 700, confirmed the presence of bromide in all test column leachates (Figure 68) and accounted for 30 to 100% of DBM transformed. A close mass balance on DBM was not possible, since bromide data were unavailable before Day 700. Moreover, as could be expected, the bromide concentrations remained relatively constant in the recycled leachate. However, in the leachate of the single pass column, it decreased significantly after Day 1200, at which point most of the DBM should have eluted, as suggested by the calculated retention time (Table 35).

Microbially-mediated bromine removal from the DBM molecule appeared to be independent of column ORP, unlike dechlorination as is discussed subsequently. However, because of the lesser relative strength of the carbon-bromine bond as compared to carbon-chlorine bond, debromination rates are greater and acclimation periods shorter than those of dechlorination as reported by Suflita, et al.[67].

5.1.3.2 Trichloroethene--

Trichloroethene (TCE) also appeared in leachates early in the investigations (Figure 62), and reached maximum leachate concentration soon after DBM. Thereafter, concentrations of TCE declined and were below detectable levels by Day 1026 in columns with ORP values consistently below -200 mV (recycle columns, excluding Column 10 OHR). For columns with leachate ORP above -200 mV, TCE was detected throughout the study. Moreover, the calculated retention time for TCE (Table 35) exceeds the time period of the investigations. Thus the continued presence of TCE would be expected, particularly if transformation mechanisms were inhibited in some manner.

Like many halogenated aliphatic compounds, reductive dehalogenation appears to be a major pathway for the transformation of TCE under anaerobic conditions. Observed byproducts include cis- and trans-dichloroethene, vinyl chloride and carbon dioxide (Bouwer and McCarty,[68]; Wilson,[69]. Reductive dehalogenation, however, becomes less predominant as the ORP increases[70], and ceases for many aliphatic compounds under aerobic conditions[67]. Vinyl chloride was measured in the gas phases for all test columns containing TCE (Figure 69).

While TCE transformation was indicated as nearly complete, the continued presence and possible intermediary product formation of TCE in some column leachates at the end of the investigation suggest that some TCE remained in the columns (particularly those with relatively high ORP) and was not measured during waste extraction. However, the waste extraction procedure used, which involved relatively high extraction temperatures and an evaporative concentration step, may not have efficiently captured some of the highly volatile compounds such as TCE.

5.1.3.3 Nitroaromatics--

Nitrophenol (NP) and Nitrobenzene (NB) behavior was sufficiently similar to be considered together. Both compounds appeared at low concentrations in the leachates soon after the investigations began, with NB detected just prior to NP (Figures 66 and 65). By Day 200, NP and NB concentrations had decreased below detectable levels, however, the compounds were again detected during subsequent periods whenever the ORP rose above -200 mV. After Day 800, neither compound was observed in the leachate, even during periods when the ORP exceeded -200 mV. It was assumed that by Day 800, either all the NP and NB had been transformed, or conditions within the columns supported transformation despite the elevated ORP.

This period of the investigation also coincided with the onset of methanogenesis in most columns, and a time when pH increased significantly due to the consumption of the volatile acids (Figures 29 and 30). It has been observed by Macalady, et al.[71], that the standard potential for reduction of nitro-moieties is highly pH dependent, i.e., as the pH increases, the minimum ORP for reduction appears to decrease. Moreover, increases in pH may have reversed the sorptive capacity of the waste matrix for phenolic compounds.

While daughter products of NP and NB transformation were not identified, it is assumed that nitro-groups were reduced to aryl amine groups as has been widely observed for a variety of compounds by Kobayashi and Rittman[72], Macalady, et al.[71], Weber and Wolfe[73]. The resulting aryl amine has been reported to rapidly react with carbonyl and quinone moieties commonly found in humic substances by Parris[74]. Ring cleavage for the mineralization of nitroaromatic and aryl amine compounds has been reported to be strongly inhibited under reducing conditions Macalady, et al.[71]. Moreover, because of the nitro- and amine groups, the aromatic ring has a low electron density and is resistant to electrophilic attack. In contrast, the presence of the phenolic hydroxyl group improves the probability of transformation of nitrophenols over nitrobenzenes. Indeed, NP was detected in column leachates at lower concentrations than NB, and its presence in the leachate appeared to be less sensitive to excursions in leachate ORP (Figure 55).

5.1.3.4 2,4-Dichlorophenol--

Leachate DCP (Figure 67) reached relatively high concentrations by Day 400 and remained at concentrations greater than 10 mg/L throughout the remainder of the investigations in the single pass columns and Column 10 OHR, where the ORP was higher than -200 mV. In the remaining recycle columns, leachate DCP concentrations decreased between Day 400 and Days 1000 to 1300 when they were no longer detected. By the end of the investigations, only a small fraction of DCP had eluted from the columns (3 to 10%), 15 to 25% still remained on the refuse, and the remainder had been transformed in some manner. The delayed appearance in the leachates and significant retention by the refuse is consistent with the pH effect and relatively long calculated retention time (Table 33).

Chlorophenols are degraded through the reductive removal of aryl halogens followed by the mineralization of the aromatic moiety (Krumme and Boyd[75]; Mikesell and Boyd[76], Knoll and Winter[77]. In addition, chlorinated phenolic compounds were observed by Artiola-Fortuny and Fuller[78] to react with humic substances present in leachate. Sawney and Kozloski[79], however, reported that phenolic compounds leached from soils more readily under anaerobic conditions and suggested that phenolic polymerization observed under aerobic conditions was inhibited. Here again, the change in leachate pH from acidic to more basic levels as landfill stabilization proceeded from the Acid Formation Phase through the Methane Fermentation Phase probably affected the relative sorption and consequent mobility of DCP.

5.1.3.5 Chlorinated Benzene Compounds--

Both TCB and DCB exhibited some displacement up the landfill columns, as indicated in Tables D-1 and D-2 of Appendix D, presumably moving in the gas phase as a result of their volatility. Both DCB and TCB were detected at low concentrations in the leachate (Figures 63 and 64), due in part to background DCB levels in the refuse as well as volatility-enhanced movement. As indicated in Tables 36 and 37, DCB was moderately transformed (30 to 50%), while TCB transformation was as high as 93%. In contrast, HCB, an extremely hydrophobic compound, was not detected in the column leachates. This limited distribution also curtailed transformation opportunities, although indicated containment or transformation ranged up to 100 percent, possibly by conversion into TCB or DCB daughter products.

The type and position of a substituent group on an aromatic compound affects its potential biodegradability. The carboxy-, methoxy-, hydroxy- and

bromo-groups apparently facilitate degradation, whereas fluoro-, amino- and nitro-groups retard degradation Bouwer and McCarty[80]; Horowitz[81]. Oxygen in the substituent group appears to be required for effective anaerobic degradation Zeyer, et al.[82], and unsubstituted aromatic compounds are devoid of activating sites that facilitate cleavage. Therefore, benzene and alkylbenzenes have been reported to be recalcitrant Zeyer, et al.[82]. However, the complete mineralization of toluene, benzene, ethylbenzene, and o-xylene has been observed in anaerobic microcosms composed of aquifer materials previously exposed to benzene by Wilson[69], a period of 120 weeks was required for mineralization of all compounds except toluene, which required only 40 weeks.

Fathepure[83] identified two degradation pathways for the anaerobic transformation of HCB. One pathway sequentially removed chlorine atoms to eventually produce a stable trichlorobenzene, while the other involved 1,2,4-trichlorobenzene and produced three stable dichlorobenzene isomers, including 1,4-dichlorobenzene. Thus, the successful transformation of TCB and DCB during the simulated landfill investigations is not surprising, particularly since the extended adaptation and reaction period afforded by the hydrophobicity of TCB and DCB as well as the relatively long leachate retention times (Section 4.6) provided enhanced opportunities for dehalogenation and, possibly, mineralization to occur.

The extent of containment or transformation of DCB, TCB and HCB (as well as LIN and NAP as discussed subsequently) varied from one column to another. The extent in the single pass columns sometimes exceeded that of recycle columns. Transformation in columns containing medium and high loading levels of heavy metals was much higher than for columns containing no admixed heavy metals or low metals loading levels, and was independent of leachate ORP. It is possible that the metals (or alkaline conditions) took part in a metal and/or hydroxide-catalyzed reductive and/or abiotic reactions. In addition, in the presence of localized high concentrations of heavy metals and organic compounds, biological activity may have been sufficiently inhibited to preclude extensive microbially-mediated transformations.

5.1.3.6 Naphthalene--

Naphthalene (NAP) was detected in all column leachates, including the control columns (Figure 60). Therefore, the presence of NAP in the leachates is assumed to be related to background contamination of the refuse and not to significant mobility of this fairly hydrophobic compound. NAP transformation varied significantly among the test columns, with increasing transformation efficiency indicated with increasing metal loading.

Polynuclear aromatic hydrocarbon degradation has been observed to be strongly affected by the redox environment and the nature of substituent groups, and several laboratory investigations have determined naphthalene to be recalcitrant at low ORP[84, 85]. However, in the present investigations, some transformation apparently occurred again likely as a consequence of long retention times or the localized conditions described previously.

5.1.3.7 Lindane--

Lindane (LIN) was not observed in the test column leachates. Transformation followed the variable patterns described previously for DCB, TCB and NAP, ranging from low to negligible in columns with no or low levels of heavy metals to high (100% in one column) for those columns with medium and high metal waste loadings. The significance of the metal loadings on LIN transformation was not explicitly established, but may have shunted normal degradative pathways in favor of partial dehalogenation.

Several investigators have reported anaerobic degradation pathways for gamma-hexachlorocyclohexane (lindane) Bachman, et al.[86]; Hill and McCarty[87]; Buisson[88]; Fries[89], with the production of penta- and tetra-chlorocyclohexane as well as tri- and tetra-chlorobenzenes. Conversion of lindane has even been

observed to proceed after biological activity was arrested, suggesting an abiotic pathway.

5.1.3.8 Dieldrin--

Dieldrin (DIEL) was not observed in any test column leachates and experienced consistent and complete transformation in all columns. Buisson[88] concluded that dieldrin (1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7,8,8a,-octahydro-1,2,-endo,exo-5,8-dimethanonaphthalene) was resistant to biodegradation during anaerobic digestion of primary and mixed municipal wastewater sludges. However, other research has indicated biotransformation of dieldrin to photodieldrin or to several water-soluble metabolites under reducing conditions[89,90].

5.1.3.9 Bis(2-ethylhexyl)phthalate--

Bis(2-ethylhexyl)phthalate (BEHP) was not detected in test column leachates. Like DIEL, BEHP was apparently consistently and completely transformed in all columns. Phthalic acid esters have been shown to be susceptible to anaerobic degradation by Johnson, et al.[91], and the length of the alkyl side chains profoundly affects the ease and rate of biodegradation, with short chain groups more readily removed than long chain groups. Following this side chain removal, the acid can be decarboxylated and then mineralized, but is reported to be slowly degraded anaerobically[89].

5.1.4 Major Findings during Landfill Column Operative and Disassembly

Major findings related to the behavior of organic priority pollutants loaded to the simulated landfill columns include:

- The mobile, more hydrophilic compounds, including dibromomethane, trichloroethene, 2-nitrophenol, nitrobenzene and 2,4-dichlorophenol eluted from the columns in the approximate order of increasing affinity for the waste matrix.

- The mobile, hydrophilic compounds were assimilated within the landfill systems, apparently enhanced by microbially-mediated transformation. In the case of dibromomethane and trichloroethene, the detection of transformation byproducts confirmed this as a contributing mechanism.

- The transformation of certain chlorinated and nitroaromatic compounds (trichloroethene, 2,4-dichlorophenol, 2-nitrophenol, and nitrobenzene) appeared to be inhibited by ORP levels more positive than -200 mV. However, partial transformation of each class of compound was observed.

- The more hydrophobic compounds, including 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, lindane, dieldrin, bis(2-ethylhexyl)phthalate, and hexachlorobenzene, were not readily released to the leachate, and were apparently retained within the landfill systems as a result of an association with the solid matrix. Such retention and consequential delayed migration enhanced opportunities for the *in situ* attenuation and assimilation within the simulated landfill columns, thereby affording a greater possibility for more complete transformation.

- The degree of apparent transformation for 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, lindane, and hexachlorobenzene was significantly higher in columns containing medium and high metal waste loadings as compared to that of columns without or with low metal waste loadings.

- Complete retention and transformation of dieldrin and bis(2-ethylhexyl)phthalate were observed for all columns.

5.2 BEHAVIOR OF INORGANIC PRIORITY POLLUTANTS

5.2.1 Preliminary Considerations

As with the organic priority pollutants, a primary component of this investigation was to examine the behavior of toxic heavy metals codisposed as sludges with the municipal refuse. To meet this objective, cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) were added as either actual industrial sludges or as analytical grade metal oxides at the three column loadings of low, moderate and high to the three pairs of recycle and single pass simulated landfill columns (Tables 17 and 18). The remaining two pairs of simulated landfill columns served as controls with no priority pollutants added or with only organic priority pollutants added. With the exception of the Cr, which was added as chromic oxide (Cr_2O_3) with an oxidation state of +3, all metals were added in the +2 oxidation state. In addition to these metals, analyses for concentrations of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe) and manganese (Mn), and lithium (Li) tracer studies (Section 4.6), were also performed after column operations had begun.

The complex chemical and physical environment of the landfill columns, as exemplified by the observed leachate properties and other characteristics, mediated the behavior of both codisposed and indigenous heavy metals. For example, the leachates were rich in an array of inorganic anions and, in particular, chloride and sulfate which were present in all columns at levels well in excess of 1,000 mg/L at the start of leachate management operations (Figures 56 and 58). Both anions could act as reasonably conservative tracers in the single pass columns and showed clear evidence of washout. As indicated previously, sulfate was also subject to microbially-mediated transformations which resulted in its eventual conversion to sulfide with substantial implications in terms of metal behavior. Indeed, its role as a powerful precipitant for metals was one of the most important factors determining the fate of many of the heavy metals. Sulfate reduction with consequent formation and release of sulfide began to a significant degree coincidentally with the onset of methanogenesis (Figure 59). In addition, carbon dioxide production provided a potential source of bicarbonate and carbonate anions once the Acid Formation Phase was completed and leachate pH levels increased (Figure 29). In those columns to which dibromomethane (CH_2Br_2) had been added as an organic priority pollutant, substantial concentrations of bromide were released into the leachates as a result of debromination of the compound (Figure 68). However, with respect to its impact on the behavior of the metals, bromide can be considered to act essentially identically to the much more abundant chloride and, therefore, will not be examined further. Nitrate, nitrite and o-phosphate were not detected at levels which could impact on metal behavior during this project.

The other significant inorganic cation in addition to the metals and hydrogen ion present during these studies was the ammonium ion (NH_4^+) (Figure 57). In terms of potential reactivity with the heavy metals, this cation is largely nonreactive. If the pH had risen high enough to permit significant dissociation of ammonium to form ammonia ($pK_a = 9.3$), some complexation might have occurred, especially with Cd, Hg, Ni, Zn and Fe. Since the column pH (Figure 29) never reached levels which would have resulted in significant formation of free ammonia, its impact on the behavior of metals in these systems was neglected. Leachate pH levels were typical acid during the Acid Formation Phase initially, and then increased to levels somewhat in excess of neutrality following the onset of methanogenesis.

Due to problems associated with the maintenance of ORP probes implanted in the columns, it was necessary to measure ORP on leachate samples withdrawn from the columns. Hence, in spite of care in making the ORP measurements, the potentials observed were likely less reducing than those actually present within the columns. Furthermore, it is probable that some degree of waste matrix heterogeneity and possible shortcircuiting promoted development of

microenvironments which may have been very much more reducing than indicated by ORP levels externally measured in the leachate. The ORP values throughout the investigations were sufficiently reducing (Figure 55) to permit the reduction of sulfate to sulfide with eventual complete depletion of leachate sulfate in the recycle columns.

The column leachates were also characterized by high concentrations of organic carbon. The nature of this organic matter was necessarily complex, arising as it did from both washout of soluble materials from the refuse mass and from products of chemical and biological conversion. In addition, there was a time dependency which, during the initial acetogenic phase of landfill evolution, resulted in a major portion of the leachate organic content being contributed by the volatile organic acids (Figures 30, 53 and 54). The volatile organic acid homologues (Figures 31 through 40) have fairly uniform strengths with pK_a values in the range of 4.8 to 5.0. As a result, the acids were significantly dissociated during the acetogenic phase of column evolution with correspondingly significant concentrations of the corresponding anions being present. However, with the onset of methanogenesis and increased pH levels, any of the remaining unionized acids present would have been virtually entirely ionized. The increase of pH and corresponding rapid and essentially complete consumption of the volatile acids, diminished the effect of pH on the behavior of the organic acids during this phase. In contrast, during the acetogenic phase, these acid anions might have had a significant impact on the behavior of the heavy metals due to their relative abundance and a possibility of acting as competing ligands. On the other hand, the formation constants for complexes between these anions and the metals of interest are quite low, and the degree of formation of metal-carboxylate complexes was therefore considered insignificant compared to other potential interactions of the heavy metals within the waste matrix.

A second group of organic substances of concern was that resulting from both the leaching and decomposition of components of the waste mass. These substances are similar to the moderate and high molecular weight compounds found in all natural waters and characterized as humic-like substances. They are of poorly defined structures and are considered composed of mixtures of compounds of varying character and molecular weight. They have, however, been associated with significant heavy metal complexation capabilities Singer[92], and it is probable that they may have had some impact on the behavior of metals in these investigations. Indeed, earlier studies[93] on similar simulated landfill systems had provided some indication that humic-like substances, as quantified by the Folin-Dennis analysis[94] for aromatic hydroxyl groups, were imparting a possible mobility to the metals as a consequence of formation of soluble complexes. However, this suspected remobilization could not be explicitly confirmed and, on further examination of the Folin-Dennis Method, it was determined that the method was subject to strong and unavoidable positive interferences resulting from the presence of high concentrations of reduced iron and manganese in the leachate. Calculations of the quantitative impact of these metals on the aromatic hydroxyl measurements led to the conclusion that the analytical response could have been due to iron and manganese, and that reliable estimates of the presence and activity of the aromatic hydroxyl groups in the leachate matrix was not possible. As a consequence, measurements of aromatic hydroxyl groups were suspended, and no attempt was made to relate such measurements to metal behavior in the final analysis.

These same studies[93] examined information on ionic strength and its potential impact on activity in the leachates by application of the empirical relationship developed by Lind[95] in studies on groundwaters. This equation relates the ionic strength, μ, to the conductivity as follows:

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity in } \mu\text{mhos} \qquad (20)$$

Using this expression, and the leachate conductivity measurements indicated in Figure 92 and Table D-5 of Appendix D, a series of estimates of ionic strength were obtained and these were in turn used to develop estimates of the activity coefficients in the leachates by application of the extended DeBye-Huckel Equation[96], or

$$-Log\ \gamma_i = \frac{0.5\ Z^2\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (21)$$

In general, it was determined that the activity corrections displayed virtually no relationship to time of column operation with standard deviations for this parameter being on the order of 0.02 units for all values of Z (the charge on the ion under consideration). For monovalent ions such as Na^+, K^+, Cl^-, etc. the value of γ averaged 0.78 units. Divalent ions such as Ca^{2+}, Ni^{2+} and SO_4^{2-} had γ values which averaged 0.41 units. Trivalent ions which were unlikely to be present at any significant levels in these leachates had a γ value of 0.12 units. Although these values are of some interest in developing ionic equilibria, considering both the magnitudes of the activity corrections and the uncertainty associated with their estimation based on conductivity and an empirical equation derived from groundwater systems, evaluation of suggested equilibrium behavior of leachate components in terms of these coefficients did not appear to offer results of sufficient reliability to justify the effort and adjustments entailed. Moreover, some difficulty was encountered with leachate conductivity measurements during the respective acid formation and methane fermentation phases due to difficulties in instrumental analyses. The analyses that follow are sufficiently instructive to obviate such a refinement in a matrix as complex as the column leachates.

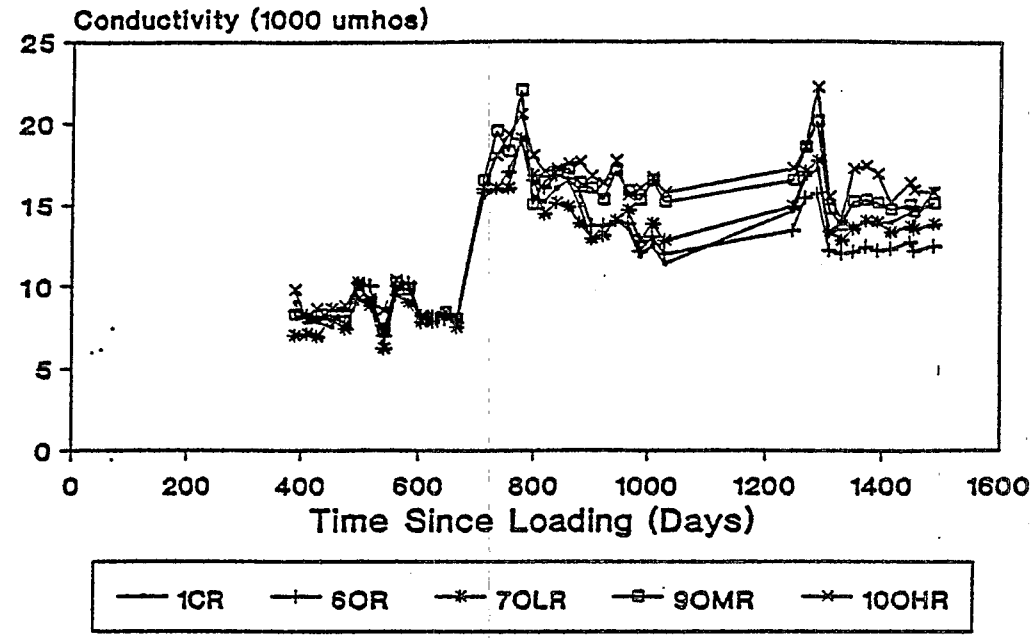
In addition to chemical impacts, the physical environment of the landfill columns could also have influenced the behavior of the metals. Accordingly, the landfill columns might be regarded as large chromatographic partitioners, complicated by irregular packing of the potentially adsorbent refuse solids, and by intermittent and potentially nonuniform flow of the eluant water/leachate. In a system of this type, adsorption of the metals would be expected to be important to leachate mobility, especially in the case of the more polar metals of higher atomic weights such as mercury and lead. However, even the lower atomic weight metals will be subject to physical interactions with the refuse solids, a mechanism not directly assessed during the course of the investigations.

Finally, the simulated landfill systems were devised to be biologically active with a short-term aerobic condition followed by a much longer-tenured anaerobic condition as oxygen introduced with waste placement was rapidly depleted and reducing conditions were established. Hence, while the nature of the biological processes underwent significant change, anaerobic microbial activity predominated and was of greatest significance in terms of the behavior of the heavy metals.

5.2.2 Properties of the Metals

5.2.2.1 Sodium and Potassium--

Sodium and potassium presented the simplest chemistry of all the metals of concern. There exists no significant precipitant for these elements, they do not participate in any considerable way in complexation reactions, and they exist in only one oxidation state (+1) in the landfill systems. Thus, their behavior was expected to be that of a conservative tracer throughout these studies. Indeed, as indicated in Figures 70 and 71, these elements were washed out of the single pass columns, and concentrated to an essentially constant level in the recycle columns.



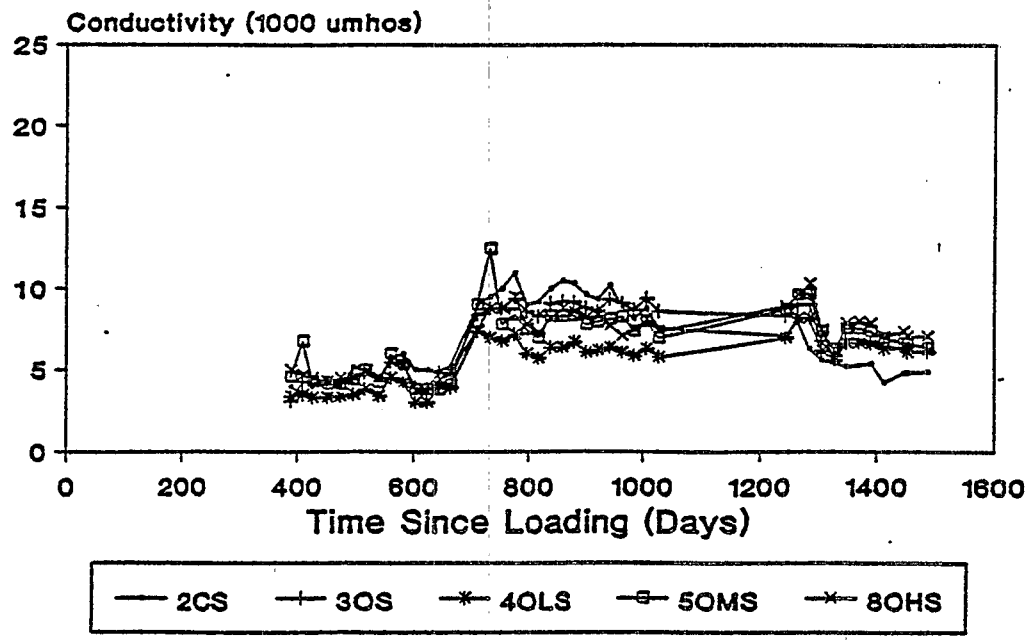


Figure 92. Leachate Conductivity during Simulated Landfill Investigations.

5.2.2.2 Calcium and Magnesium--

Calcium and magnesium are only slightly more chemically complicated than sodium and potassium, with the primary difference being that both have available and potential precipitants. In the case of calcium, the potential precipitant is carbonate ($CaCO_3$, pK_{so}=8.4), while magnesium is subject to precipitation as the hydroxide ($Mg(OH)_2$, pK_{so}=11.1). (Neither of these precipitants attained high concentrations in the landfill columns, although some precipitation to the corresponding salt was possible.) Otherwise, calcium and magnesium participate in complexation reactions only to a slightly greater degree than do sodium and potassium, and each has only the +2 oxidation state. Hence, like sodium and potassium, calcium and magnesium were expected to act somewhat as conservative tracers although, due to their higher charges and atomic weights, subject also to a greater degree of adsorption in the waste matrix.

5.2.2.3 Iron and Manganese--

Iron and manganese present a more complicated circumstance than those discussed previously. In particular, each has more than one easily accessible oxidation state. In the case of iron, the states are the +2 or ferrous state and the +3 or ferric state. Manganese could be expected to exist in either the +2 or +4 oxidation states. Under strongly reducing conditions, as was the case during the majority of the simulated landfill investigations, the +2 oxidation state is the preferred state for both metals. In the +2 oxidation state, both metals are characterized by their fairly high solubilities at pH levels below ≈9 (Figures 93 and 94) and the potential for forming sparingly soluble sulfides (FeS, pK_{so}=18.6; MnS, pK_{so}=14.0).

5.2.2.4 Cadmium, Nickel and Zinc--

Cadmium, nickel and zinc can be treated together due to their considerable degree of similarity. All three of these metals exist in only the +2 oxidation state, and are subject to precipitation as sparingly soluble sulfides (CdS, pK_{so}=26.1; NiS, pK_{so}=24.0; ZnS, pK_{so}=23.8). None of these metals is subject to significant complexation with any of the important inorganic ligands in the leachates. (The hydroxides of these metals, while sparingly soluble at alkaline pH level ($pK_{so}\leq 17$), are unlikely to have controlled solubility at any pH level observed in the leachates from the simulated landfill columns over the course of the investigations.) With the generation of significant concentrations of sulfide through sulfate reduction, little else was present in the columns which would have otherwise acted to precipitate cadmium, nickel and zinc. Once active sulfate reduction/sulfide generation commenced, these elements could be expected to be removed by precipitation as the respective sulfides and physical entrapment in the waste matrix.

5.2.2.5 Chromium--

Chromium presents a somewhat different situation from that of the aforementioned metals. Chromium is much like iron in that it can exist in the +2 (chromous) and the +3 (chromic) oxidation states. Unlike iron, however, the redox potentials needed to reduce chromium from the chromic state to the chromous state are more strongly reducing then could be expected to be attained in the simulated landfill columns (E^o=-0.41V). Thus, while the chemistry of iron in these systems is that of the ferrous ion, Fe^{2+}, chromium chemistry is entirely in the domain of the chromic ion, Cr^{3+}. One consequence of this is that, uniquely among the heavy metals added to the columns, chromium does not form insoluble sulfides and will not be removed as a result of the generation of sulfide. On the other hand, the chromic ion forms one of the more sparingly soluble of all hydroxides, $Cr(OH)_3$, with a pK_{so} of 30.8. This is sufficient to result in significant removal of chromium as the hydroxide, even at acidic pH values (Figure 95).

5.2.2.6 Lead--

The chemistry of lead is complicated by the array of available chemical interactions. While lead can exist in a +4 oxidation state, the redox potentials observed in the simulated landfill systems limit lead to the +2 oxidation state.

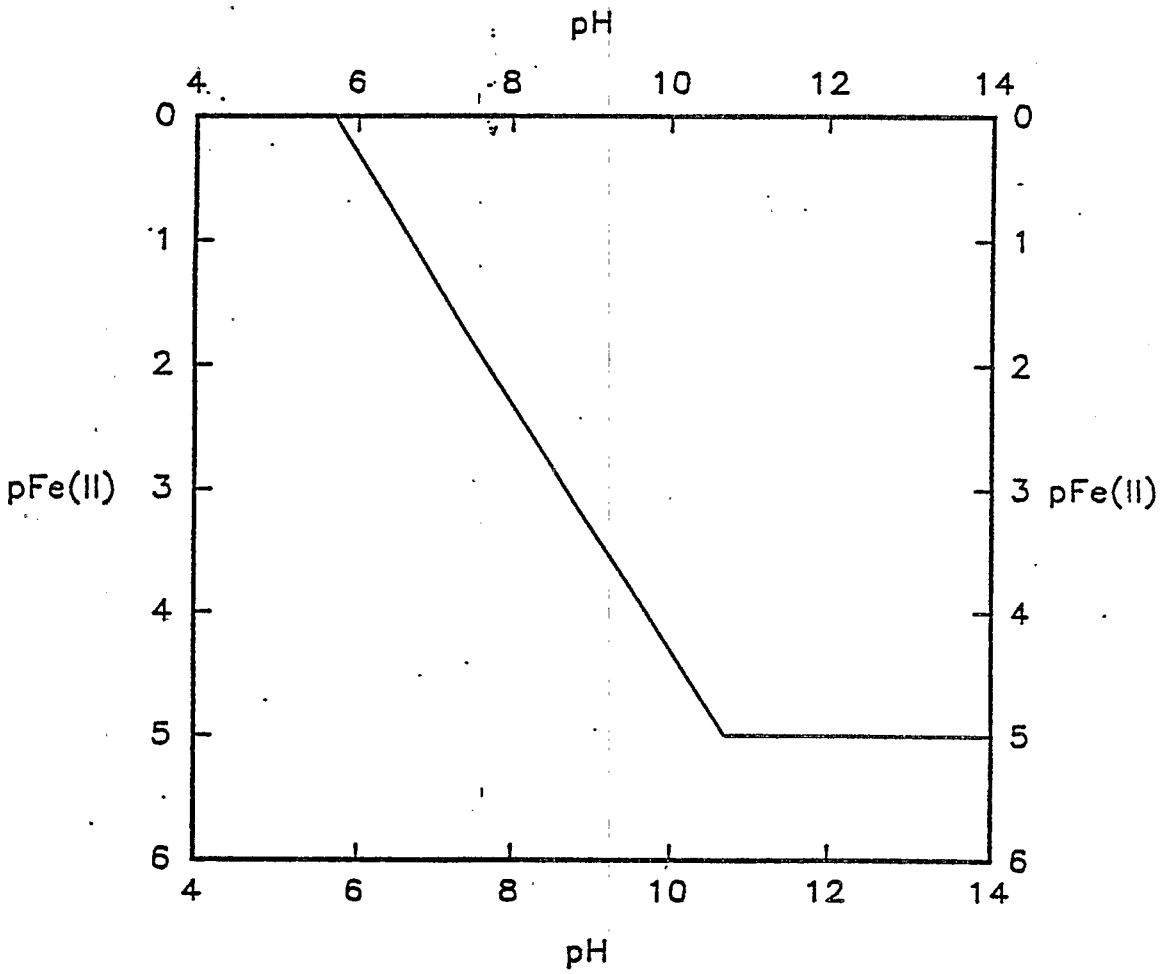


Figure 93. pH-pFe(II) Distribution Diagram.

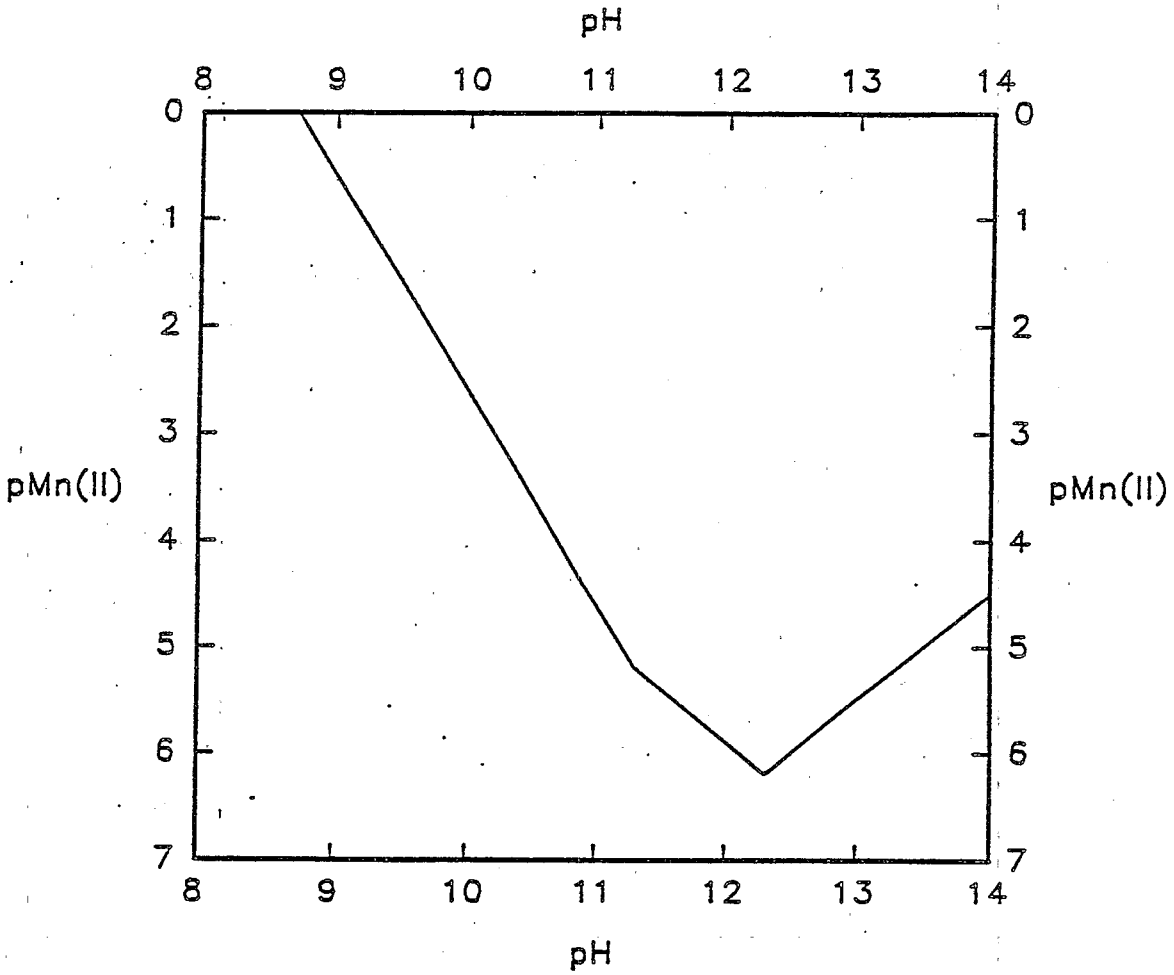


Figure 94. pH-pMn(II) Distribution Diagram.

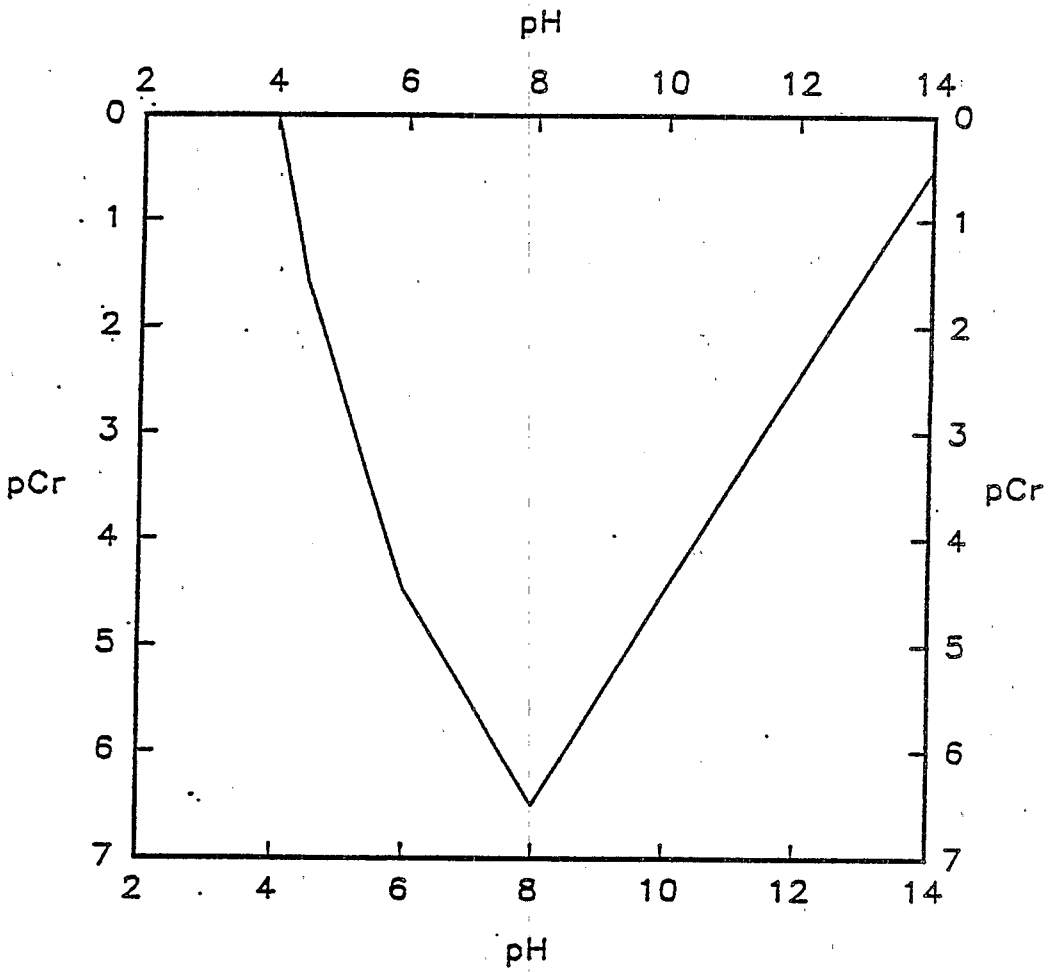


Figure 95. pH-pCr Distribution Diagram.

Lead in that state can form strong complexes with hydroxide, chloride and sulfate, and five different sparingly soluble salts with these anions and with sulfide (Table 38). Thus, while the four heavy metals described earlier display relatively simple chemical behavior, lead is affected by a much more complex range of controls. With respect to solubility control, an examination of Figure 96 indicates that, prior to the onset of sulfate reduction, the controlling solid species was most probably the sulfate. Based on this assumption and the equilibria presented in Table 39, and taking into account the approximate concentrations of leachate sulfate and chloride, the mole percent distribution of lead among the expected important complexes is also presented in Table 39. Based on these results, it was anticipated that the total lead concentration in the leachates during the acetogenic phase of landfill evolution would be on the order of 16 times the concentration of free, uncomplexed lead as calculated on the basis of the indicated concentration of sulfate and the solubility product of lead sulfate.

With the onset of sulfate reduction/sulfide production, it was expected that the very sparingly soluble lead sulfide (PbS with its $pK_{so} = 28.0$) would become the controlling solid, and that the lead concentrations would rapidly decrease to very low leachate levels (Figure 97).

5.2.2.7 Mercury--

Mercury was the most complicated of the heavy metals included in the investigations. Under the reducing conditions extant in the columns, mercury has ready access to three oxidation states, the +2 or mercuric state, the +1 or mercurous state, and the neutral or free metal state. In the latter case, this implies reduction of the ionic form to metallic mercury. The mercuric ion is subject to unusually strong interactions with many inorganic ligands and, in particular, with halide ions such a chloride (Table 38). Examination of the equilibria indicates that, under the conditions present prior to significant sulfide formation, all but a trace of soluble mercury would be present as chloride complexes (Table 40). The redox behavior of mercury is also significant as indicated earlier. A pH-pε diagram was generated using the indicated conditions expected in the columns during the acetogenic phase (Figure 98). On examination of this diagram, it was clear that, even when complexed with chloride, the mercury could be easily reduced to the neutral metal. (It might be noted incidentally that one conclusion drawn from the computations involved in the generation of this diagram was that the mercurous ion, Hg_2^{2+}, was not thermodynamically stable in these systems). A similar diagram was generated assuming the presence of sulfide in the solutions and the consequent existence of solid mercuric sulfide, HgS (Figure 99). In this case, while reduction of the mercury to the neutral metal remains possible under the column conditions, the situation is not as clear, and it is possible that formation of the sulfide might hinder reduction of the mercury to the metal. Reduction of mercury to the metal opens one unusual pathway for the loss of mercury by transport in the vapor phase; metallic mercury is volatile even at ambient temperatures. Finally, mercury is capable of forming organomercury compounds under conditions such as those anticipated to be present. The formation of such substances as methylmecuric chloride (CH_3HgCl) by microorganisms in aquatic systems has been well documented Hughes[99]; Jernelöv[100], and the possibility of this occurring in the simulated landfill investigations could not be dismissed.

5.2.3 Observed Leachate Metal Behavior

5.2.3.1 Sodium, Potassium, Calcium and Magnesium--

As indicated earlier, it was anticipated that no significant precipitants would be present for sodium, potassium, calcium and magnesium during the operation of the simulated landfill columns, with primary behavior as conservative tracers. Examination of Figures 70 through 73 indicates that these metals did indeed behave in a fashion consistent with that expectation. This is most obvious in the case of sodium and potassium, which demonstrated clear washout patterns in the single pass columns with net removals of the metals

TABLE 38. SIGNIFICANT EQUILIBRIUM CONSTANTS FOR METAL COMPLEXES[97, 98]

Solubility Products, log K_{so}		Cumulative Formation Constants	
PbS	-26.6	$PbSO_4$	2.8
$PbSO_4$	-7.8	$Pb(SO_4)_2^{-2}$	3.6
$Pb(OH)_2$	-15.5	$PbCl^+$	1.3
$PbCl_2$	-4.7	$PbCl_2$	1.7
PbOHCl	-13.7	$PbCl_3^-$	1.9
$Pb_2Cl(OH)_3$	-36.1	$PbCl_4^{-2}$	1.5
HgS	-52.0	$HgCl_2$	13.9
$Hg(OH)_2$	-25.7	$HgCl_3^-$	14.8
CdS	-27.2	$HgCl_4^{-2}$	15.8
NiS	-23.8		
ZnS	-24.8		

Acidic Dissociation Constants

H_2S Log K_{a1} = -7.0
Log K_{a2} = -13.6

TABLE 39. DISTRIBUTION OF LEAD SPECIES IN TYPICAL LEACHATE*

Species	Distribution
Pb^{+2}	6%
$PbCl^+$	5%
$PbCl_2$	1%
$PbSO_4$	77%
$Pb(SO_4)_2^{-2}$	11%

$[Pb]_T = [Pb^{+2}] + [PbCl^+] + [PbCl_2] + [PbSO_4] + [Pb(SO_4)_2^{-2}] = 16\ [Pb^{+2}]$

*Chloride and sulfate at 1,500 mg/L, pH = 5.3

TABLE 40. DISTRIBUTION OF MERCURY SPECIES IN TYPICAL LEACHATE*

Species	Distribution
$HgCl_2$	66%
$HgCl_3^-$	23%
$HgCl_4^{-2}$	11%

$[Hg]_T = [HgCl_2] + [HgCl_3^-] + [HgCl_4^{-2}] = 2 \times 10^{11}\ [Hg^{+2}]$

*Chloride and sulfate at 1,500 mg/L, pH = 5.3

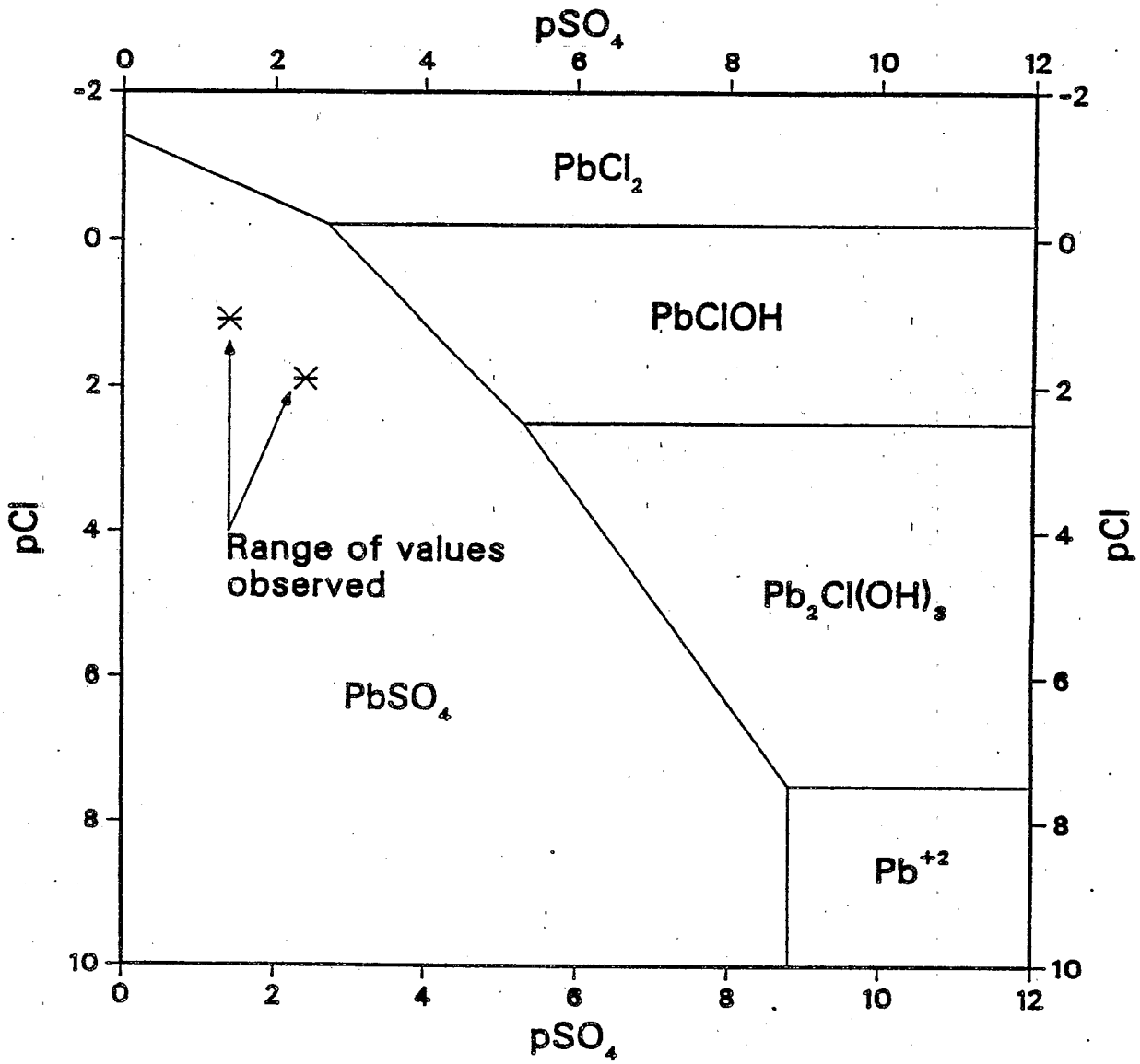


Figure 96. Predominance Area of Diagram for the System $Pb^{+2}/SO_4^{-2}/Cl^-/OH^-$.

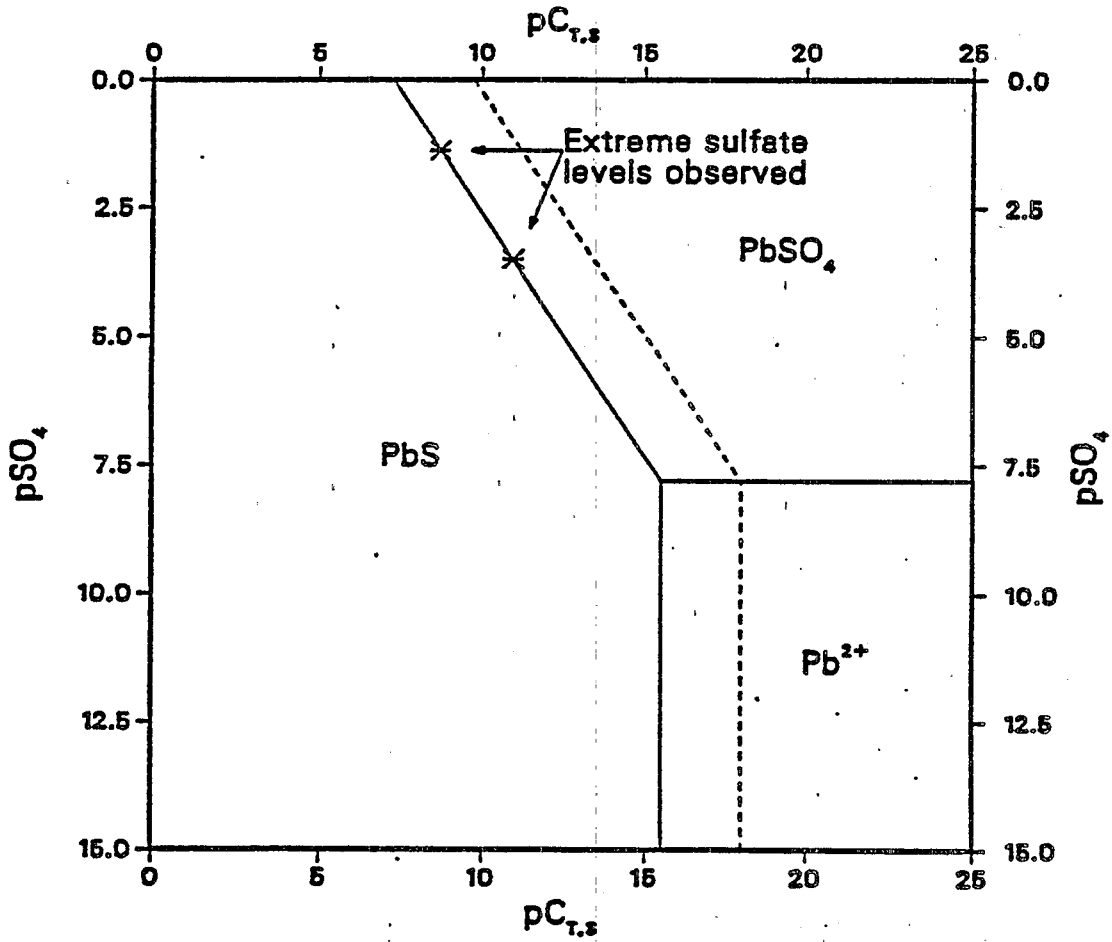


Figure 97. Predominance Area Diagram for the System Pb2+/SO42-/Sulfide (— pH = 5.5, --- pH - 7.5).

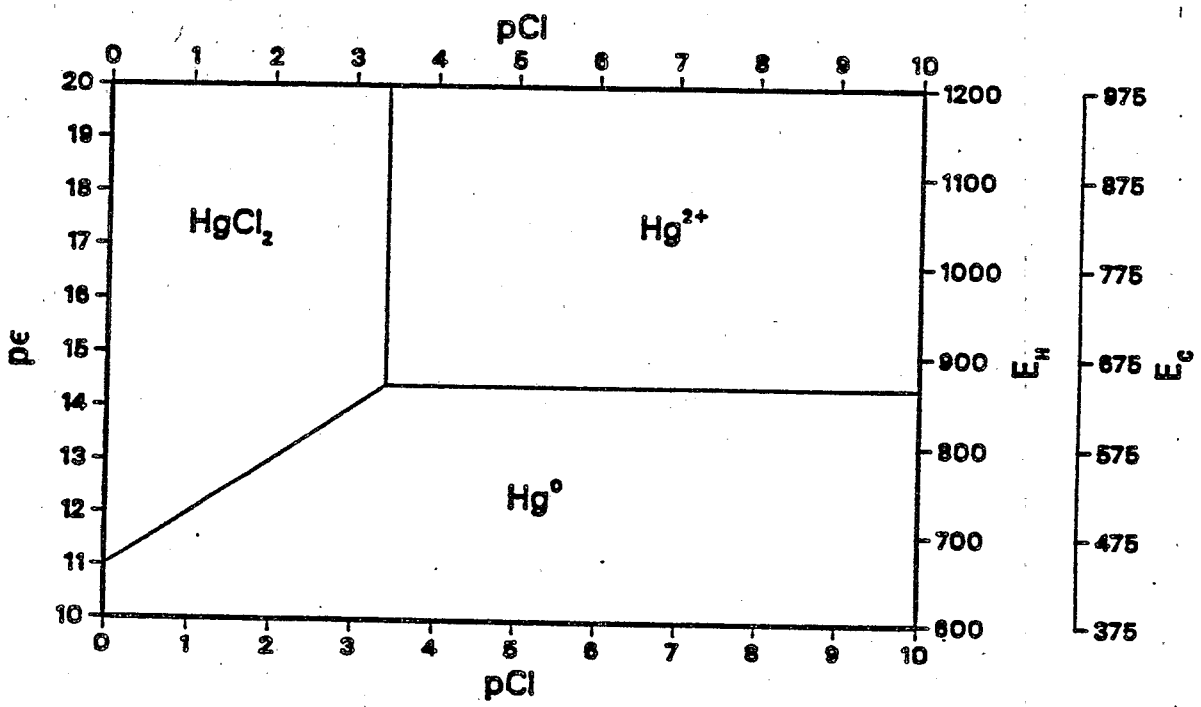


Figure 98. pCl-pε Diagram for Mercury in Absence of Sulfide.

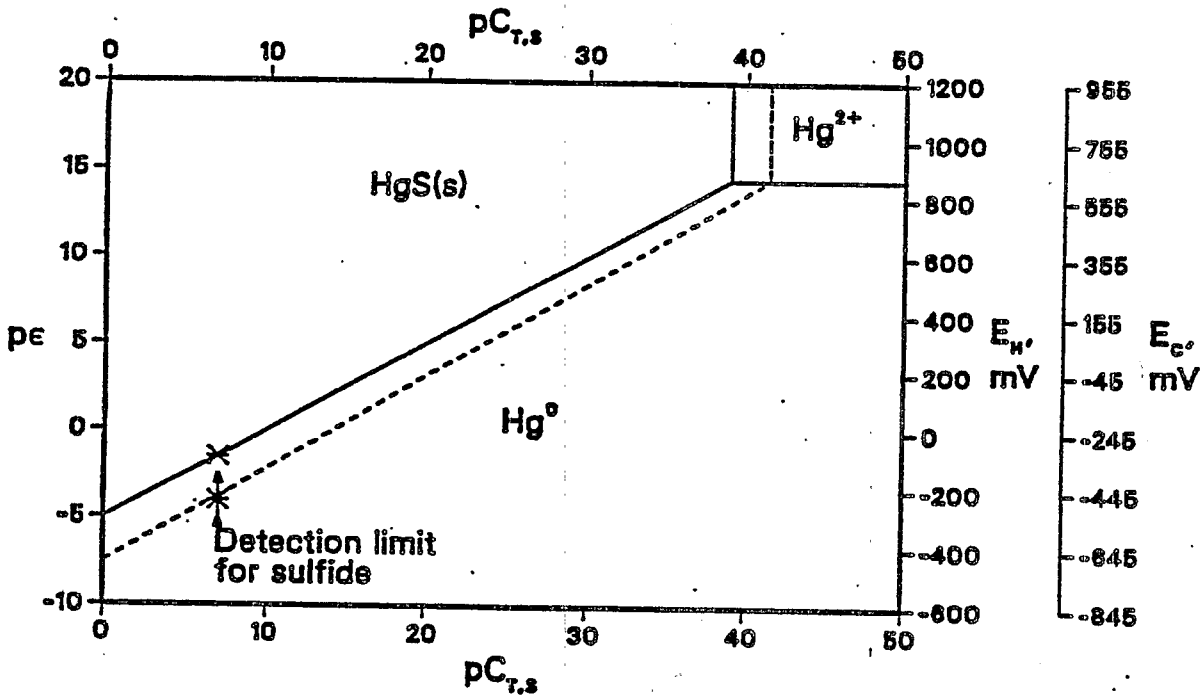


Figure 99. $pC_{T,S}$ - pe Diagram for Mercury in Presence of Sulfide (——pH = 5.5; ---pH = 7.5).

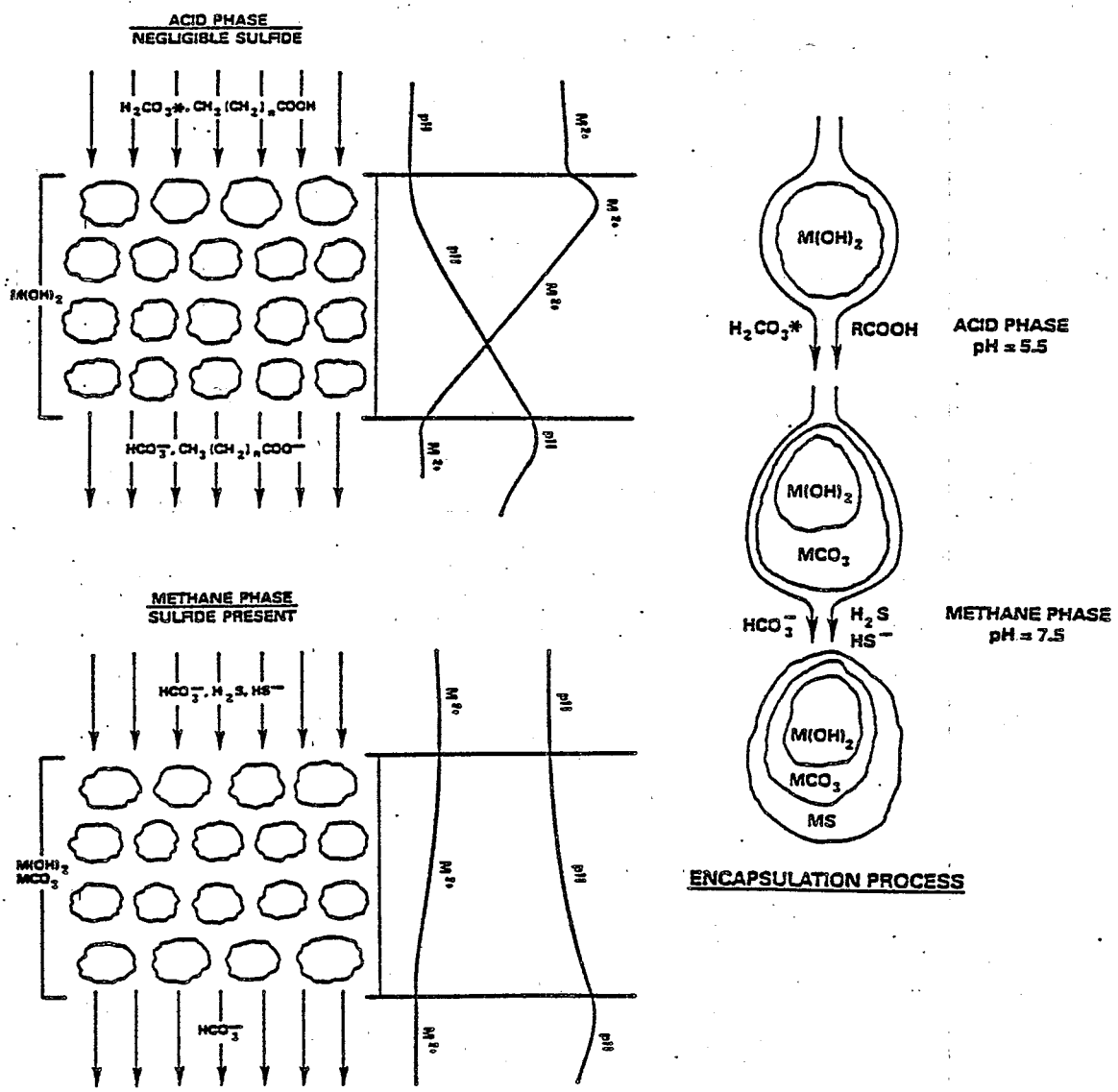


Figure 100. Encapsulation of Heavy Metal Sludge Solids in Simulated Landfills.

observed. Since the onset of methane formation was associated with an increase in leachate pH, the solubility of chromium would be expected to be further limited, an expectation borne out by recorded observations.

5.2.3.5 Mercury--

Upon consideration of the significant equilibrium constants for mercury (Table 38), two facts are evident. Sulfide can function as a powerful precipitant for mercuric ions, even at extremely low equilibrium concentrations, and any soluble mercury present should be associated in a complex interaction with the ligand, chloride. The actual concentrations of mercury measured in the leachates during this study are presented in Figure 81, and chloride concentrations are shown in Figure 56. The data of Figure 81 give evidence that, following early increases in the mercury concentrations, leachate levels for all simulated landfills to which mercury had been added decreased rapidly to ≈20 μg/L (≈0.1 μM) at Day 300, and showed only minor variations around that level thereafter. If it were assumed that the mercury was present in the leachates in the same oxidation state as that which was placed in the columns initially (+2), on the basis of equilibria presented in Table 38, mercury speciation would be dominated by chloro-complexes (Table 40), and the total concentration of soluble mercury would, at the approximately 1,500 mg/L of chloride in the leachates, equal approximately 1.8×10^{11} times the concentration of "uncomplexed" Hg^{2+}. Since the leachates contained approximately 0.1 μM total soluble mercury, this implies a "free" mercuric concentration of 5×10^{-19} M. Based on mercuric sulfide solubility, H_2S acid dissociation constants, and the leachate pH levels during the acetogenic phase, this mercury concentration would be in equilibrium with extremely low levels of total sulfide ($\leq 10^{-20}$ M). However, since it is not possible to analyze sulfide at such low concentrations, direct substantiation of the participation of sulfide to control mercury behavior was not possible.

An alternative rational for the observed behavior of mercury, which is compelling both on the basis of its relative simplicity and its reasonable consistency with the observed behavior in these columns, can be developed. Shown in Figure 98 is a pCl-pε diagram for the mercury-chloride system. This diagram was developed assuming no participation of sulfide in the control of the mercury. It should also be noted that in developing this diagram, it was found that the mercurous ion was thermodynamically unstable with respect to the other species in the system. Based on the oxidation-reduction potentials (ORP) measured in the leachates as shown in Figure 55, it is clear that the columns had been operating from the start of the investigations at redox potentials in excess of 500 millivolts more negative than needed to reduce the mercuric chloride complex to metallic mercury. Therefore, it is proposed that the rapid early decrease in leachate mercury concentrations was a result of the reduction of divalent mercury to neutral metallic mercury, and since the rate at which the mercury concentration decreased is consistent with this premise, it is highly unlikely that significant sulfate reduction/sulfide formation could have taken place soon enough to effect the observed decrease in leachate mercury concentrations. In addition, it has been reported[101] that metallic mercury has a solubility in water of 20 to 40 μg/L, a concentration range consistent with that observed in these investigations. This transformation of mercury would permit volatile mercury metal to undergo mobilization in the gases emitted from such landfill systems, particularly during the methane generation phase when large volumes of gas are characteristically produced.

In further support of the reduction of mercury to the metallic form, it was noted that, even after the onset of active sulfide formation, the mercury concentrations in the leachates remained at the 20 to 40 μg/L observed previously. These levels of mercury should not be possible in the presence of 0.1 to 1.0 mg/L of sulfide, unless the mercury was not able to be precipitated by the sulfide, a condition met uniquely by neutral, metallic mercury. Even at sulfide concentrations as high as 1 mg/L, the potentials in the columns were sufficiently reducing to permit mercury reduction (Figure 99).

approaching 95% of the metals originally present. In the recycle columns, the concentrations of sodium and potassium in the leachates decreased approximately 25 to 30% over the duration of the study, a phenomenon which could be ascribed to removal of leachate during sampling and replacement of these withdrawals with tap water. Calcium and magnesium behaved in a somewhat more complicated fashion. In the case of magnesium, washout was apparently the dominant process in the single pass columns while, in the recycle columns, following a substantial increase during the first 100 days of operation, concentrations decreased to and were maintained at essentially uniform levels of approximately 100 mg/L for the duration of the study. It is likely that this early surge of magnesium was a result of concentration of the metal in the initial leachate front, after which it rapidly became dispersed more uniformly throughout the leachate pool as a consequence of leachate recirculation. No evidence of any significant chemical controls on the behavior of magnesium was observed.

In the single pass columns, washout of calcium was again the predominant process, whereas in the case of the recycle columns the behavior of calcium was not as obvious. An initial increase in calcium concentrations during the first 100 days similar to that for magnesium was observed, after which calcium concentrations decreased to approximately 1,500 mg/L and were maintained at that level until approximately Day 750. Following Day 750, the calcium concentrations in the leachates from the recycle columns decreased steadily in an apparently linear fashion for the remainder of the study. The most likely cause for this behavior is a combination of a modification of operational methodology and the progression of the columns to a new phase in their evolution. At a time approximately coincident with the initiation of the decline in calcium concentrations, it was decided to augment the onset of methanogenesis by additions of sodium bicarbonate for pH adjustment. Several such additions were carried out and, with each addition of sodium bicarbonate, an increment of carbonate ion equal to approximately one percent of the bicarbonate added was introduced to the columns in accordance with the acid-base equilibria of the carbonic acid system. This carbonate could have acted effectively as a precipitant for the calcium and contributed to its removal from the leachates. In addition, with the onset of methane formation between Days 900 and 1,000, the pH of the leachates increased rapidly, thereby favoring further production of carbonate through dissociation of bicarbonate and dissolution and dissociation of carbon dioxide released during anaerobic stabilization. Thus, it appears that carbonate precipitation of calcium played a role in reducing the concentration and mobility of this metal.

5.2.3.2 Manganese and Iron--

The behavior of manganese and iron (Figures 74 and 78) could be explained on the basis of a combination of washout and sulfide precipitation. In the case of the manganese, washout appeared to dominate in the single pass columns, with only a slight indication of sulfide precipitation in the control column after Day 1250. In the recycle columns, manganese behaved much as did calcium and magnesium, with an initial increase in the first 100 days followed by a decrease to a constant concentration by Day 450, and a further decrease in concentration approximately coincident with the onset of sulfide production (Figures 58 and 59) at about Day 750.

In contrast to manganese, the behavior of iron was more difficult to interpret. For the single pass columns, little evidence of washout was apparent. In addition, the only period during which sulfide precipitation might have been important was a brief interval between Days 1,000 and 1,150, and it is not evident that sulfide was a controlling factor over this interval, except possibly in the control column. The most reasonable explanation for this behavior relates to the forms in which iron is available. While present in metal sludges added to the columns, iron is also present in abundant but slowly releasing forms as iron minerals in soils and metallic iron present in the waste mass. Thus, the reservoir of iron likely far exceeded both the ability of simple washout to deplete it in the time interval of this investigation, and the capacity of the sulfide generated to precipitate it.

In the single pass columns, the continued addition of tap water to the simulated landfill columns resulted in a steady release of iron from the reservoir sources in quantities unlikely to be much influenced by such removal mechanisms as sulfide precipitation, except in the case of the control column where no other significant metal concentrations were present as competition and where sulfide concentrations were highest of the single pass columns (Figures 58 and 59). On the other hand, the leachate from the recycle columns was nearer equilibrium with the iron reservoir, and the impact of sulfide was more apparent. In these columns, the leachate iron concentrations were essentially constant from the initiation of the investigations until approximately Day 750, at which point a steady decrease in iron concentrations commenced. The relationship of this decrease to the onset of sulfate reduction/sulfide formation is clear and, therefore, provides the most obvious explanation for the observed behavior.

5.2.3.3 Cadmium, Nickel and Zinc--

Cadmium, nickel and zinc (Figures 75, 79 and 80) in the single pass columns were present at high concentrations, although in no case at concentrations which approached those expected on the basis of considerations of the solubility equilibria of the corresponding hydroxides. After a period of time, which ranged from approximately 200 days for zinc to approximately 400 days for cadmium, the concentrations of the metals decreased rapidly to much lower concentrations and were maintained low thereafter until the investigations were terminated. In no case was either washout or sulfide precipitation observed, which would have been expected to occur as sulfate was reduced. Therefore, it is postulated that the initial surge of metals was a consequence of the leaching of metals from the codisposed sludge layers, limited by such factors as incomplete contacting of the sludge by the leachate, the kinetics of the dissolution of the sludge solids, the reprecipitation of metal salts in the alkaline microenvironment of the hydroxide sludge layers and encapsulation of sludge particulates with other anions such as carbonate and, possibly, some small quantities of sulfide being produced even during these early phases of the studies. It is also probable that sorption processes involving the solids of the waste matrix were acting to retard mobility of the metals, a process which might have been enhanced by complexation of the metals with high molecular weight and polar humic-like materials in the leachate.

The rapid decrease in leachate concentrations of the metals in the single pass columns may reflect the completion of encapsulation processes, again with sulfide being the most likely candidate for this encapsulation. In the case of the recycle columns, the initially high concentrations of these metals were maintained until the onset of sulfide generation, an event which very clearly led to precipitation of the metals. In this case, the initial dissolution of the sludges yielded metal concentrations quite similar to those observed for the single pass columns, while encapsulation of the sludge solids and sludge mass precipitation of the metals acted to limit further dissolution of the metals in the leachates upon subsequent recycling events. With the onset of sulfide formation, the metals were precipitated more rapidly than they could be redissolved from the modified sludge solids, and the metal concentrations commenced to decline and reach a new equilibrium level at approximately 900 Days, a level which was maintained thereafter. These hypothesized mechanisms are illustrated in Figure 100 for the Acid Formation and Methane Fermentation Phase of landfill stabilization, as discussed in more detail in Section 5.2.5.

5.2.3.4 Chromium--

The behavior of chromium (Figure 76) gave every indication of being directed largely by hydroxide solubility equilibria, with leachate levels decreasing rapidly (except for a brief and unexplained concentration increase around Day 350) in the leachate of the recycle columns from initially high concentrations to levels below one mg/L in all columns. Neither the operational mode nor sulfide generation had an impact on the behavior of this metal. It should be noted here that, at the observed pH of ≈5.5 in the acetogenic phase of landfill evolution, the predicted concentration of chromium in equilibrium with $Cr(OH)_3$ would be about one μM (0.06 $\mu g/L$) which is consistent with the results

While it is possible that some conversion of mercury to alkylmecuric compounds took place in the environment of the columns, efforts at detecting such species by cold vapor analysis of undigested leachates were unsuccessful and their possible existence was, therefore, not confirmed.

5.2.3.6 Lead--

During the acetogenic phase of column operation, leachate lead concentrations varied, but tended to remain in the range of 1 to 10 mg/L (Figure 77). As discussed earlier, operating conditions were such that the solubility of lead during that phase, assuming the absence of any sulfide, would have been dominated by sulfate species and only a small amount of chloride complexation (Figure 96). Under these conditions, the total soluble lead concentration would have been equal to approximately 16 times the concentration of free Pb^{2+} as indicated previously (Table 39). On the basis of the solubility product of lead sulfate ($PbSO_4$) and an average leachate concentration of sulfate of 1,500 mg/L during the Acid Forming Phase, the equilibrium concentration of "uncomplexed" lead would be expected to have been approximately one micromolar, and the total soluble (complexed + uncomplexed) lead concentration would have been 16 μM or approximately 3 to 4 mg/L. Given the analytical complexities associated with the leachate matrix and the inherent variability of the parameters measured in this study, this is in excellent accord with the concentrations of lead actually measured in the leachates.

With the onset of active sulfate reduction/sulfide production, lead concentrations decreased in the leachates to levels well below 1 mg/L. This again is consistent with the very limited solubility of lead sulfide (pK_{so}=26.6), which would yield estimated equilibrium lead concentrations many orders of magnitude below detectability by conventional analytical methods. Therefore, it could be surmised that lead was highly responsive to removal as the sulfide once this precipitant began to be formed in the landfill columns coincident with the onset of methanogenesis.

5.2.4 Major Findings During Landfill Column Operations

Based on the results obtained during the simulated landfill operations, several conclusions concerning the behavior of the codisposed inorganic priority pollutants could be drawn.

- The landfill columns had substantial assimilative capacities for the codisposed heavy metals.
- The assimilative mechanisms were diverse and dependent on the chemical characteristics of the heavy metals as well as the environmental conditions to which they were exposed.
- Chromium removal was controlled by precipitation of $Cr(OH)_3$ and was essentially complete very early after column operation commenced. As expected, sulfide generation did not influence the behavior of chromium.
- The behavior of cadmium, nickel, lead and zinc was controlled during the early phases of column operation by sorptive interactions between components of the waste matrix and the metal ions. With the onset of sulfate reduction, removal of these metals was then controlled by of sulfide generation and precipitation of sparingly soluble sulfides.
- Mercury was very rapidly reduced to metallic mercury, and the subsequent behavior of the metal was controlled by the properties of the neutral element. Leachate concentrations of mercury were in excellent agreement with solubility expected for metallic mercury, and sulfide formation had little significant impact on residual leachate mercury concentrations. In this context, vapor phase removal of volatile metallic mercury may be an important transport mechanism for mercury, particularly during high generation periods.

- Once sulfate reduction/sulfide generation had commenced, even the higher loadings of added metals were assimilated within the simulated landfill columns. However, the ability of the metals to retard or prevent entirely the onset of microbially-mediated sulfate reduction or methane fermentation by exertion of toxic or inhibitory effects must be considered in any decision regarding acceptable metal loadings to landfills subjected to the codisposal of heavy metals.

- Based on the observed performance of the simulated landfill columns, it can be concluded that they could readily assimilated the lowest metal sludge loading, while the moderate loading was a near limit for the codisposal method employed without dramatically interfering with the progress of waste stabilization.

- Leachate containment and recycle enhanced the landfill stabilization processes associated with assimilation of the heavy metals, and reduced the potential for uncontrolled discharge to the environment and the need for separate treatment by fixing the dissolved metals *in situ* within the waste matrix. It also acted to increase the opportunities for beneficial metal-refuse mass and sludge solids interactions, and tempered the need for codisposal and ultimate discharge control.

5.2.5 Characteristics of Supplemental Metal Sludge Samples

The codisposed metals contained in the test columns were added in the form of typical alkaline sludges beneficiated as necessary by metal oxides (Tables 17 and 18). While the primary objective of these additions was to acquire information regarding the potential for release of metals from these sludges into the column leachates as landfill stabilization progressed and the relative impacts on microbial mediation, it was also desired to obtain corresponding data on the effect of the landfill environment during acid formation and methane fermentation on the sludges and the implications of resulting changes in their characteristics and associated behavior. In order to facilitate the acquisition of this information, to each test column to which metals were added, supplemental packets of sludge, contained in mesh bags (nylon stockings) and tied with bright yellow plastic cord to facilitate recovery during column disassembly, were also added. These packets were placed in the columns at the same locations as the sludge loadings and each packet contained the same metal sludge/oxide mixture added in bulk to the columns with the exception that these sludges contained clean Ottawa sand rather than sawdust admixed to facilitate permeability to the leachate. While the results presented in Figure 101 apply to the sludge/metal oxide/sand mixtures, the values in Tables 41, 42 and 43 have been corrected for the sand content of the mixture and, hence, apply only to the metal sludge/metal oxide mix.

5.2.5.1 Initial Considerations--

It has been hypothesized from the beginning of the experimental investigations that the alkaline metal sludges codisposed in the simulated landfill columns would react in a fashion affected by the composition and consequent chemistry of the sludges and their potential to serve as a reaction site within the waste matrix. In particular, the metal sludges, placed as they were in three discrete layers rather than distributed uniformly throughout each test column, were expected to provide regions of high alkalinity which could locally moderate the acidic nature of the columns during the early phases of landfill stabilization and, in the process, undergo chemical modification themselves. Furthermore, by providing such an alkaline microenvironment, eventual encapsulation of the sludges by sulfides during the methane formation/sulfate reduction phase of landfill stabilization would strongly influence the degree of long-term mobility of metals originating from the sludges.

The encapsulation process, previously introduced schematically in Figure 100, is a recognized process whereby a particle of metal hydroxide sludge is impacted during the acid formation phase of landfill stabilization by both carbonic acid and volatile organic acids with, as the primary effect, the release

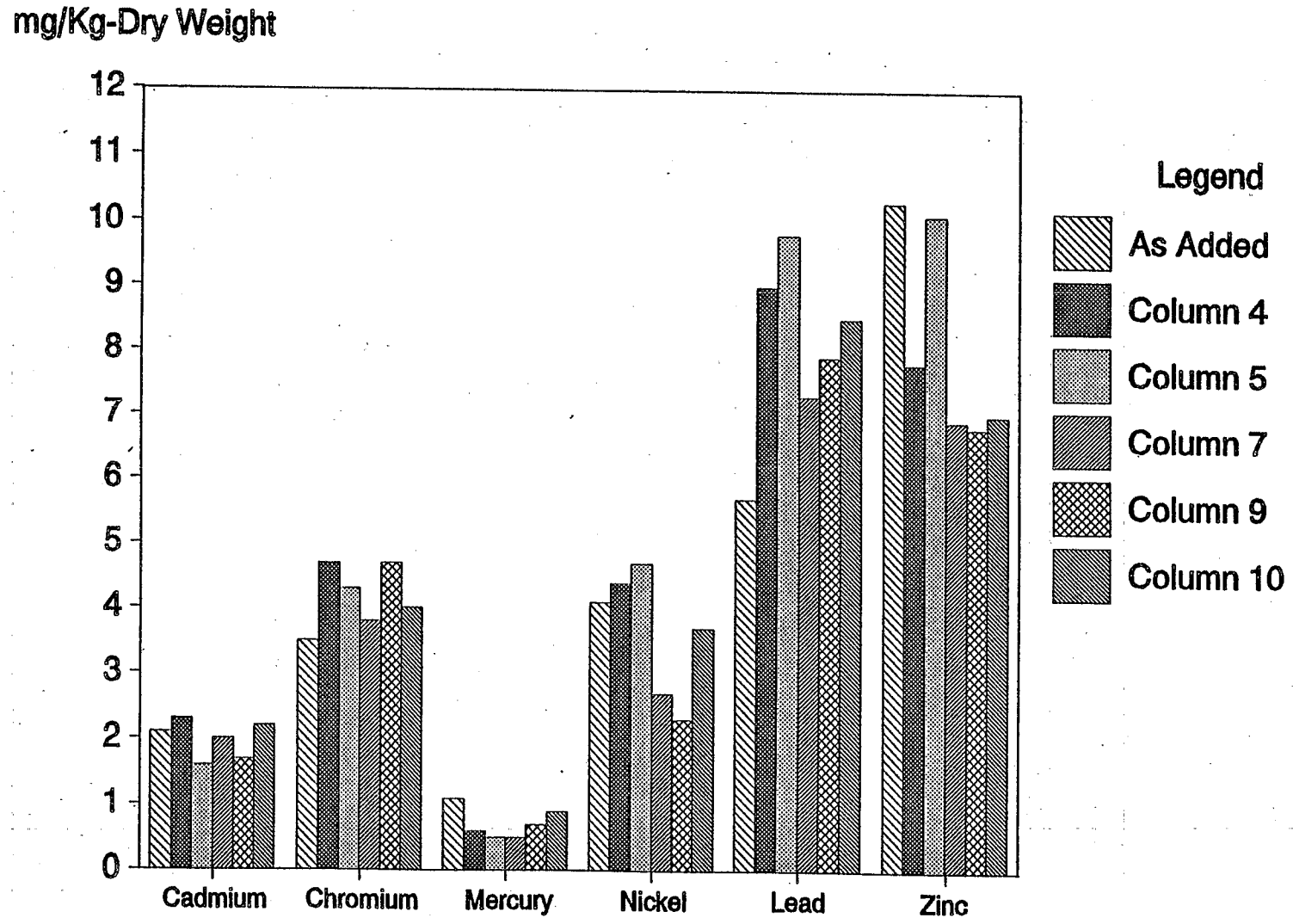


Figure 101. Comparison of Heavy Metal Content of Supplemental Sludge Samples.

TABLE 41. SELECTED ANALYSIS OF SUPPLEMENTAL METAL SLUDGE CODISPOSED IN SIMULATED LANDFILL COLUMNS

Column Identity	Sludge Solids, %[a]	Sulfide, mg/kg (dry)[b]	Inorganic Carbon, % (dry)[c]
4 OLS	63.3	56,000	8.2
5 OMS	61.4	8,600	8.0
7 OLR	66.5	3,300	8.0
9 OMR	64.8	1,300	8.8
10 OHR	60.1	110	7.8

Note: [a]Includes Ottawa sand added with sludge in mesh bags.
[b]Original sulfide content < 5 mg/kg (dry)
[c]Original inorganic carbon content 1.9% (dry)

TABLE 42. TOXIC METAL CONTENT OF SUPPLEMENTAL SLUDGE CODISPOSED IN SIMULATED LANDFILL COLUMNS

Column Identity	Constituent Toxic Metal[a]											
	Cd		Cr		Hg		Ni		Pb		Zn	
	mg/g	%	mg/L	%	mg/g	%	mg/g	*	mg/g	*	mg/g	%
4 OLS	18.0	110	37.5	142	5.4	63	35.2	110	70.4	167	61.0	75
5 OMS	12.5	76	33.6	127	4.6	54	37.5	117	76.6	181	79.7	98
7 OLR	15.6	95	29.0	109	4.5	53	23.5	73	58.6	139	54.7	67
9 OMR	13.3	81	38.3	143	5.5	64	19.6	61	61.8	146	53.9	67
10 OHR	17.2	105	31.3	118	7.0	82	28.9	90	66.5	157	54.7	68
Average		93		128		63		90		158		75

Note: [a]Original Cd, Cr, Hg, Ni, Pb and Zn added; 16.4, 26.6, 8.6, 32.1, 42.2 and 81.3 mg/g (dry), respectively
% = % of original metal level added.

TABLE 43. NON-TOXIC METAL CONTENT OF SUPPLEMENTAL SLUDGE CODISPOSED IN SIMULATED LANDFILL COLUMNS

Column Identity	Constituent Non-Toxic Metal, mg/g (dry)					
	Na	K	Ca	Mg	Fe	Mn
4 OLS	5.8	0.3	<0.1	47.7	18.8	39.1
5 OMS	1.9	0.5	<0.1	57.9	20.3	32.1
7 OLR	5.4	1.0	0.4	36.7	27.4	50.0
9 OMR	10.9	1.1	0.3	80.5	27.4	40.7
10 OHR	9.8	1.1	0.4	72.7	28.9	43.0

of some metals to the leachate. Countering this process is a concomitant buildup of a layer of metal carbonates analogous to ion exchange at the particle surface. This initial encapsulation process would thereby hinder the further mobilization of the metals during the acid formation phase of landfill stabilization.

With the initiation of sulfate reduction coincident with the onset of methane fermentation, a second ion exchange-type process could result in the replacement of carbonate at the particle surface by sulfide. Given the extremely low solubilities of most heavy metal sulfides, this second encapsulation would have the effect of essentially terminating the mobilization of most metals at the neutral and higher pH levels characteristic of the landfill environments during the methane phase and thereafter. The corresponding impact of the sludge on the characteristics of the contacting leachates is illustrated in (See Figure 100). During the acid formation phase, the conversion of carbonic acid to carbonate ion and the neutralization of the organic acids would be expected to result in a sharp local increases in the pH of the leachate, with a corresponding decreases in heavy metal solubilities. Consequently, the alkaline environment of the sludges could be expected to actually hinder the mobilization of the heavy metals into the leachates during the acid formation phase of operations (Figure 101), while, during the methane fermentation phase, the heavy metal concentrations, already diminished as a consequence of the elevated pH levels characteristic of the later portions of this phase and ensuing conditions, would be further decreased by precipitation as sulfides in the alkaline microenvironment of these sludge layers.

5.2.5.2 Sludge Compositions--

Following termination of the experimental studies, samples of metal sludge were recovered from test Columns No. 40LS, 50MS, 70LR, 90MR and 100HR. (The packets contained in Column 80HS could not be found.) The retrieved samples were analyzed for solids content, sulfide, inorganic carbon, heavy metals and for the six other metals routinely analyzed in the leachates. The solids in these sludge samples were estimated after drying at 107° C. The results are presented in Table 41, and varied only slightly between columns, averaging about 63%. These determinations were then used to express other measurements on a dry weight basis.

Sulfide levels in the sludge samples were estimated in accordance with Standard Methods and EPA methods (Table 22) by purging acidified suspensions of sludge into an alkaline ascorbic acid using nitrogen gas. The sulfide trapped was then measured by means of a sulfide electrode calibrated against a standardized (Lead Titration) sulfide solution. The resulting values were normalized on a dry weight basis and are also presented in Table 41.

The most striking finding with respect to sludge sulfide levels was the wide range of values measured, varying in excess of three orders of magnitude. While the data are too few to draw an unequivocal conclusion regarding trends, it does appear that the higher the metal sludge loading in a column, the lower the sludge sulfide level. Moreover, the effect is far too obvious than to be rationalized simply on the basis of increased capacity for sulfide formation resulting from heavier sludge loadings, since the range is out of proportion to the variation in sludge loadings. However, it is possible that the increased metal loadings hindered the microbially-mediated reduction of sulfate to sulfide and thereby reduced the amount of sulfide available for encapsulation. Therefore, encapsulation and its effect on long-term metal mobilities is considered significant and worthy of further investigations under a variety of landfill loading and operational conditions.

Inorganic carbon levels were measured in a similar manner to sulfide levels, except that reagent grade sodium hydroxide was used to trap the CO_2 and the inorganic carbon was analyzed using a Beckman Total Carbon Analyzer. No significant trend in the inorganic carbon levels in the retrieved sludge samples was observed (Table 41), and all values ranged from 7.8 to 8.8% on a dry weight

basis as compared to approximately 1.9% for the sludge as added. Therefore, some encapsulation by inorganic carbon was indicated in accordance with the process previously described.

The heavy metals (Cd, Cr, Hg, Ni, Pb, Zn) added to the columns were analyzed by digestion of the sludges in strong acid followed by flame atomic absorption spectrometry. The results of these analyses are presented in Table 42 and Figure 101. The results indicate an interesting pattern in terms of metal accumulations and releases. In the case of cadmium and nickel, these two metals appear to have been largely conservative, with small average reductions in metal content in the sludges and somewhat erratic behavior. Nevertheless, the combined effects of encapsulation and the alkaline sludge environment likely served to minimize mobilization of cadmium and nickel. In comparison and for reasons which are not clear, zinc levels in the sludges decreased substantially (≈25%), which is somewhat surprising when compared with the behavior of its close chemical relative, cadmium, which exhibited a minimal decrease in sludge levels. Apparently, some unknown factor in these systems was acting to enhance zinc mobility, but the exact nature of the factor cannot be ascertained with the available data. Likewise, mercury was the most diminished of the metals (≈37%), a finding which was most likely attributable to the loss of mercury as a consequence of reduction of the mercuric ion and volatization of metallic mercury as discussed previously (Section 5.2.3.5).

In contrast, lead and chromium accumulated significantly (158 and 128%, respectively) in the sludges, thereby suggesting chemical precipitation within or on the sludge solids. Precipitation of chromium as hydroxide ($Cr(OH)_3$) and lead as sulfide and/or sulfate, both sparingly soluble species, in or on the alkaline sludge mass would be an expected reaction as also discussed previously (Sections 5.2.3.4 and 5.2.3.6. It should be observed here that this accumulation results from either single pass or recycle liquid phase transport of metals from higher levels of concentration in the columns

The sludge samples were also analyzed for the group of nontoxic metals monitored routinely in the leachates (Na, K, Ca, Mg, Fe and Mn) as presented in Table 43. Most of these metals were present at extremely low levels in the sludges, thereby reflecting their relative mobilities in the leachate of the simulated landfills. Indeed, only iron and manganese, both subject to precipitation as very sparingly soluble sulfides in the +2 oxidation states expected for both metals, and magnesium, which forms a very sparingly soluble hydroxide, were present at significant levels. The others of these metals, deprived of reaction opportunity with sulfide or hydroxide, were found to be present only at very low levels in the sludge.

5.2.5.3 Implications of Results from Retrieved Sludge Sample Analyses--

Based on the results of these analyses, there is every indication that metal sludge codisposed with refuse in a landfill will react in a complex fashion, resulting in modifications of both the localized landfill environment and the sludge itself. Encapsulation of sludge particles with both carbonate and sulfide can occur, but elevated metal levels may hinder microbially-mediated sulfide formation with resultant reduction of both metal complexing capabilities and encapsulation behavior. Therefore, it may also be concluded that the metal sludges in the simulated landfill columns actually acted as sinks for metals transported from other regions of the landfill (Pb and Cr) and that, although no parallel studies on the chemical constituency and behavior of more homogeneously distributed sludges were available, layering of the sludge in high concentrations zones enhanced this beneficial immobilizing behavior. In addition, leachate recycle facilitated opportunities for both metal deposition in or on the sludge layers and resultant encapsulation of sludges with mobility retardants such as carbonate and sulfide. Consequently, it could be concluded that the manner in which toxic metal sludges are added to a landfill and the method of landfill operation can significantly impact mobilities and ultimate behavior of metals contained in such sludges.

SECTION 6

SUMMARY AND CONCLUSIONS

The purpose of this research was to demonstrate and evaluate landfill assimilative capacity in terms of the ability to accommodate inorganic and/or organic priority pollutants codisposed with municipal refuse without inhibiting the microbially-mediated processes of waste stabilization. In accordance with this objective, the experimental results can be summarized as follows:

1. In general, simulated landfill columns employing the leachate recirculation management strategy achieved waste stabilization more quickly and completely than simulated landfill columns operated with single pass leaching as reflected by trends in gas volumes produced, gas production rate, gas composition, and leachate indicator parameters. In addition, a greater mass of volatile organic acids were released into the leachate during the Acid Formation Phase and transformed into methane during the Methane Fermentation Phase in the recycle columns than in the single pass columns. This more complete and rapid waste stabilization in the recycle columns was attributed to the more favorable environment that was developed in the recycle columns in comparison with the single pass columns. Within the recycle columns, leachate was contained and recirculated, thus the biomass generated within the columns had an enhanced and controlled contact opportunity with substrate, nutrients and moisture needed for growth and proliferation. In contrast, biomass within the single pass columns did not have the same contact opportunity, because leachate was routinely removed from the system. Therefore, the environment within the recycle columns was more uniform than that within the single pass columns, because the nutrient-rich leachate was removed and lost with the single pass leaching management strategy. Moreover, leachate produced by facilities employing single pass leaching would incur greater treatment challenges and pollutional potential in terms of adverse environmental and health impacts if it were to migrate from landfill boundaries.

2. The consequences of the applied admix loadings of inorganic and/or organic priority pollutants were reflected by reduced gas production, gas production rates, and percentage of methane in the gas. In addition, simulated landfill columns that received priority pollutant loadings generally exhibited different trends in leachate indicator parameters than the control columns, as discussed subsequently. However, the effects of the organic and inorganic priority pollutant loadings upon the single pass columns were more severe than for similarly loaded recycle columns as reflected by differences in gas production, gas composition, and leachate indicator parameters.

3. The recycle columns displayed greater gas production than single pass columns and, although increases in priority pollutant loadings in the recycle columns were accompanied by temporary decreases in gas production, eventual assimilation of the priority pollutants was achieved. In contrast, this behavior was not clearly reflected in the single pass columns because both substrate and priority pollutants were removed by washout, thereby affecting the assimilative capacity as well as the quality of the leachates and gas discharges.

4. Carbon dioxide, methane, oxygen, hydrogen and nitrogen gas were detected from all ten simulated landfill columns. Oxygen and nitrogen, introduced during waste loading and contained within refuse void spaces, was removed in all ten columns when anaerobic conditions predominated, and nitrogen was displaced by gas production. All five recycle columns and the control single pass column produced adequate gas volumes to displace the nitrogen, however, nitrogen was present throughout the entire experimental period in the remaining single pass columns because of insufficient gas production. The lack of sufficient gas production in the single pass columns containing priority pollutants was attributed both to the admix priority pollutant loadings and washout promoted by the leachate management strategy employed.

5. Similar behavior was observed between the ten simulated landfill columns with respect to the leachate indicator parameters of pH, alkalinity, TVA, COD, TOC and ORP. Recycle Columns 1CR, 6OR, and 7OLR demonstrated the greatest degree of waste stabilization as determined by trends in these indicator parameters, and Column 9OMR displayed signs of slight retardation. Column 1OOHR, however, showed signs of more severe retardation due to the applied priority pollutant loading as evidenced by lower pH, lingering TVA concentrations, higher COD and TOC concentrations, higher alkalinity concentrations, and less negative ORP. The control single pass column, Column 2CS, exhibited the greatest degree of waste conversion of the five single pass columns as reflected by these same parameters. The remaining single pass columns, Columns 3OS, 4OLS, 5OMS and 8OHS, showed signs of inhibition consequenced by applied loadings and washout due to the type of leachate management strategy employed.

6. Leachate chloride and sodium concentrations, as well as lithium tracer studies, were useful in determining the effects of leachate management upon leachate constituent behavior. These analyses indicated that leachate constituents within the recycle columns were retained within the column, but decreased in concentration somewhat due to dilution. However, leachate constituents within the single pass columns were removed primarily by washout, as evidenced by the rapid decline in chloride concentration. Liquid retention times within the landfill columns increased as landfill stabilization progressed and was on the order of several hundred days.

7. The mass of volatile organic acids removed due to leachate withdrawal was much greater in the single pass columns than in the recycle columns. Most of the generated leachate was contained within the recycle columns with only a minor amount removed for sampling. Calculation of the potential gas volume lost due to the removal of VOA, which serve as the primary substrate for methanogens, revealed that the single pass columns did not exhibit the same gas production potential as the recycle columns. This decreased gas production potential observed for the single pass columns was attributed to the less favorable biological environment present in these columns, as well as the effects of washout.

8. Based upon calculations of the mass of individual volatile acids (IVA) released into the leachate of the simulated landfill columns, the primary IVA released in all columns included acetic, propionic and butyric acids. These results agree with those reported in the literature concerning separate anaerobic treatment processes. The mass of IVA released into the leachate increased until the onset of methanogenesis. Thereafter, IVA masses released declined commensurate with IVA transformation into methane in Columns 1CR, 2CS, 6OR, 7OLR and 9OMR. Columns 1OOHR, 3OS, 4OLS, 5OMS and 8OHS were adversely affected by applied priority pollutant loadings, as evidenced by the relatively constant mass of acid released into the leachate. Additionally, IVA were released into the leachate of the control recycle and single pass columns towards the end of the

experimental period, which was attributed to the decomposition of more microbially resistant organic material. The mass of IVA released into the leachate declined as priority pollutant loadings increased in the four single pass test columns, while the mass of IVA released into the leachate of the recycle test columns remained relatively constant as priority pollutant loadings increased.

9. The mass of IVA transformed into methane increased commensurate with the decrease of the mass of IVA released into the leachate of Columns 1CR, 2CS, 6OR, 7OLR and 9OMR. However, Columns 1OOHR, 3OS, 4OLS, 5OMS and 8OHS displayed a negligible mass of IVA transformed into methane. As priority pollutant loadings increased within the ten simulated landfill columns, the transformation of IVA into methane was both delayed and diminished, however, the effects of priority pollutant loadings were more severe in the single pass columns than in the recycle columns.

10. A relationship between the mass of hexanoic and butyric acid released into the leachate was observed in the simulated landfill columns, as well as a relationship between released propionic, hexanoic and valeric acid mass. An increase in the mass of butyric acid released was accompanied by increased hexanoic acid mass, and increases in the mass of propionic acid released occurred concomitantly with increased releases of hexanoic and valeric acid mass. Additionally, hexanoic acid was released earlier in the single pass columns than in the recycle columns.

These results can be explained by the thermodynamic favorability of the condensation of butyric and acetic acids to form hexanoic acid during periods of high leachate butyric acid mass, and, similarly, the condensation of two moles of propionic acid to form hexanoic acid and the condensation of propionic and acetic acids to form valeric acid during periods of high leachate propionic acid mass. The mass of hexanoic acid released into the leachate remained high until methane production commenced, after which butyric and hexanoic acid mass were observed to decrease. However, in the single pass test columns, the mass of released hexanoic acid was significant throughout the experimental period. Similar results regarding the production of higher molecular weight IVA have been reported and it appears that the microbial populations responsible for both the production (acidogens) and subsequent degradation (acetogens) of IVA were inhibited as evidenced by a lower mass and varying composition of IVA produced.

11. The inhibition threshold, or priority pollutant loading below which inhibition of landfill stabilization was not observed, was determined for recycle and single pass simulated landfill columns. The recycle columns did not exhibit inhibition of stabilization processes, although the applied priority pollutant loadings did cause retardation (or a delay) of stabilization processes. All four single pass columns containing priority pollutants were inhibited by the applied loadings.

12. Both organic and inorganic priority pollutant loadings were assimilated within the landfill columns. This assimilation was greater in the recycle columns than in the single pass columns. Heavy metals were largely removed by precipitation as hydroxides, carbonates or sulfides, although reduction and matrix capture by sorption, ion exchange and encapsulation were also operative. The organic priority pollutants were also attenuated, largely by abiotic and biotic transformations, as well as by partitioning within the waste mass. Reductive dehalogenation appeared to be a principal mechanism for halogenated compounds, whereas some evidence of reduction, ring cleavage and possible complete mineralization was present. Overall conversion of the organic priority pollutants was more evident in the recycle than the single pass columns, and the degree of conversion was also related to the inhibition or retardation exhibited at

higher heavy metal loadings.

The following conclusions are drawn based upon the experimental results obtained during the course of these investigations.

1. The leachate recirculation management strategy offers opportunities for more complete and rapid waste stabilization, including attenuation of codisposed priority organic and inorganic pollutants, than the single pass leaching management strategy, thereby providing a controlled and more favorable environment for accelerated microbiological growth and concomitant waste stabilization.

2. Admix inorganic and/or organic priority pollutant loadings exhibited retardation of the landfill stabilization process in both recycle and single pass columns. However, single pass columns were more severely affected than the similarly loaded recycle columns, and greater attenuation and detoxification was achieved with leachate recycle.

3. Trends in leachate indicator parameters such as pH, alkalinity, TVA, COD, TOC and ORP, provide insight into the status of the progress of waste stabilization, and can reflect the magnitude of stress imposed upon the system such as introduced by the applied priority pollutant loadings and/or the type of leachate management strategy employed.

4. Both acid-forming and methane-forming populations within the recycle columns were essentially unaffected by the applied priority pollutant loadings. However, these same populations were adversely affected within the single pass columns, as evidenced by the type and quantity of IVA released into the leachate and the relative efficiency of their conversion to gas.

5. The threshold inhibition level for the recycle columns was equivalent to the inorganic priority pollutant loading applied to the highest loaded column, whereas the threshold inhibition level for the single pass columns was determined to be the lowest codisposed priority pollutant loading.

6. Landfills possess a finite capacity to attenuate hazardous and nonhazardous organic and inorganic constituents through microbially-mediated physicochemical processes of reduction, precipitation, sorption and matrix capture of heavy metals, and fixation and sorptive matrix capture and both biotic and abiotic conversion of complex organic substances.

7. Controlled landfill systems, designed and operated as bioreactors with both leachate and gas management, enhance predictability, minimize potentials for adverse health and environmental impacts, and encourage further innovations responsive to regulatory and public concerns.

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