Denitrification in a Landfill Bioreactor with the Use of Methane as a Source of Carbon and/or Electron Donor for Denitrification

By

Rawa Aljarallah

B.Sc., Kuwait University, Kuwait; M.Sc., Oregon State University, Oregon USA
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Department of Civil Engineering

The University of British Columbia

Vancouver, Canada

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Abstract

Recycled landfill leachate is often characterized by its high ammonia content, which can be nitrified in an aerobic bioreactor. This research investigates the capability of landfill bioreactors to remove nitrate by denitrification with a focus on utilizing the methane flow as a carbon source. Eight lysimeters that contained synthetic municipal solid waste were operated for 510 days to demonstrate the feasibility of converting nitrate, at concentrations between 20 and 2000 mg/L, to nitrogen gas.

The results show that the landfill as a bioreactor is capable of denitrifying this wide range of nitrate concentrations with an efficiency up to100%. At low nitrate concentrations (20-100 mg-N/L), denitrification was feasible with high efficiency in young and mature landfills, without affecting landfill activities (i.e. extent of waste degradation). However, denitrification with high nitrate concentrations (800-2000 mg-N/L) was associated with less gas production and hence less waste degradation. As the nitrate concentration increases, this effect also increases. In addition, at high nitrate concentrations, the denitrification efficiency decreases as the landfill ages due to carbon deficiency. The results also suggest that the carbon deficiency causes incomplete denitrification.

The use of methane as a carbon source for denitrification was not detected during the early stages of the landfill life. In mature landfills, methane gas enhanced denitrification efficiency, even at high nitrate concentrations (1500 mg-N/L).

Finally, testing was conducted to evaluate the kinetics of denitrification supported by methane or leachate. Results show that denitrifiers can grow on leachate, and consume nitrate at a rate faster than when growing on methanol. Denitrifiers were able to grow on methane, but at a much slower rate.

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List of Nomenclature

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
ED	Electron Donor
EPA	Environmental Protection Agency
GHG	Green House Gas
GVRD	Greater Vancouver Regional District
HRT	Hydraulic Retention Time
LR	Leachate Recirculation
MLVSS	Mixed Liquor Volatile Suspended Solids
MSW	Municipal Solid Waste
OD	Oxygen Demand
ORP	Oxidation Reduction Potential
QA	Quality Assurance
QC	Quality Control
SD	Standard Deviation
SP	Single Pass
TKN	Total Kjeldahl Nitrogen
THOD	Theoretical Oxygen Demand
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UBC	University Of British Columbia
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solids
WWTP	Waste Water Treatment Plant

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Dedication

I would like to dedicate this work to my beloved husband, Khaled.

1 Introduction

The normal operating practice at a modern landfill is to rapidly add refuse on top of an impermeable bottom liner and then close the site with an impermeable cap immediately after filling. Under such a moisture control system, the modern landfill will serve as a temporary storage device with limited degradation, a consequence of the absence of adequate moisture conditions essential to the degradation of the organic waste fraction. Once the environmental barriers (caps and liners) fail, and the introduction of moisture is permitted, the subsequent biological activity may result in elevated gas and leachate production, and thus may have potentially adverse environmental impacts.

The future of landfill management is to treat the landfill as a bioreactor. The landfill bioreactor is a relatively new management system that uses the landfill bed to serve as an anaerobic bioreactor to degrade solid waste. This approach is made possible by recirculating the leachate. The popularity of this management system is increasing because by simple and inexpensive methods it accelerates landfill stabilization, reduces landfill active life, reduces the carbonaceous strength of the leachate and increases the landfill gas production. However, this practice does negatively impact the environment. Landfill bioreactors usually produce leachate that is rich in ammonia, and this has caused serious challenges to treatment systems.

Landfill gas is another product of solid waste stabilization. Landfills that practice leachate recirculation (LR) have higher rates of gas generation. Large numbers of landfills fail to manage their gas emissions properly and, hence, make additional contributions to the Green House Gas (GHG) budget.

Thus, ammonia nitrogen and methane gas, two by-products of landfill bioreactors considered harmful to the environment, require treatment for this current approach to solid waste management to prove truly beneficial. In this research, these two compounds were targeted, by introducing a new method to manage the nitrogen. The objective of this research was to investigate the denitrification portion of the nitrogen treatment process, using landfill bioreactor techniques. Moreover, the effect of the denitrification on waste

degradation processes and the use of methane as a carbon source and/or electron donor (ED) to support denitrification were also elucidated. Finally, the use of landfill leachate as a carbon source for denitrification was studied.

In the following chapter, a summary of the available literature on landfill bioreactors, denitrification and landfill stabilization are presented. The objectives, hypothesis and problem statement for this study are given in Chapter 3. The experimental design, set-up and procedure are described in Chapter 4. The sampling and analytical methods are described in Chapter 5. The results of this study, along with their potential application, are presented and discussed in Chapter 6. Finally, Chapter 7 presents the conclusions and recommendations for future work.

2 Literature Review

The literature review for this thesis is divided into three sections. The first section focuses on the process of leachate recirculation, discussing the practical aspects of its implementation, its advantages and disadvantages, its impact on the environment, and related issues requiring further investigation. The second section outlines the management of nitrogen with special emphasis on nitrate removal through the process of biological denitrification, the feasibility of using the landfill bed as an anoxic reactor, and the potential for the leachate and/or methane to support the process of denitrification. In the final section of the literature review, landfill stabilization processes and products are discussed.

2.1 Introduction

The primary mechanisms responsible for degradation of landfill solid waste are the microbial biochemical processes. The rate of biological degradation can be enhanced, stimulated and controlled within certain limits and under proper conditions. Minimizing the degradation time is a goal because it eases the requirement for leachate treatment, reduces the liability period and makes successful reclaiming of the landfill site possible. The principal environmental conditions essential for waste degradation enhancement include the following: 1) appropriate pH and temperature; 2) absence of toxins; 3) availability of nutrients; 4) optimal particle size (of the waste), 5) specific oxidation – reduction potential (ORP); 6) availability of inoculum; and 7) optimal moisture content.

Of these, moisture content has been identified as the most critical parameter affecting municipal solid waste (MSW) biodegradation (Chugh *et al.* 1998). Laboratory and pilot-scale studies have shown that ideal moisture content permits rapid stabilization of waste and enhances gas production, thereby improving leachate quality, reducing the long-term environmental consequences and the liability of waste storage and boosting the economic viability of landfilling (Doeden and Cord-Landwehr 1989, Anex 1996, Reinhart and Al-Yousfi 1996, Al-Yousfi and Pohland 1998, Warith and Sharma 1998).

2.2 Leachate Recirculation (LR)

Leachate recirculation refers to the collection of leachate discharged from a landfill and its redistribution through the refuse. This technology uses the landfill bed to anaerobically stabilize and promote sequential conversion of complex materials through intermediate to final end-products. The process combines anaerobic treatment within the landfill with evaporation that occurs during the distribution of leachate at each cycle.

With LR, the landfill is known as a bioreactor. When aeration is involved, it is then called an aerobic bioreactor. The issues surrounding aerobic bioreactors are relatively new and many studies are currently in progress in order to develop a greater understanding pertaining to them (Reinhart and Townsend 2001, Stessel and Bernreuter 2001, Weathers *et al.* 2001, Yazdani and Augenstin 2001).

In LR, leachate is collected, usually stored and then pumped through a number of pipes laid over the landfill cover. The pipes are perforated on their upper side at regular intervals to allow leachate to run onto the cover for infiltration into the refuse. Other options include placing a number of sprinkler jet nozzles to spray the leachate uniformly over the entire surface of the landfill or using injection wells so that the leachate is recycled directly into the refuse. Choosing either of these methods would depend on the ease with which the pump and sprinkler could be installed. The success of the process depends on the ease with which the leachate infiltrates through the soil cover of the landfill.

When viewed as a biological reactor, the landfill can be considered a stationary fixed film reactor in which poor mixing is the most significant constraint on bacterial activity and, hence, waste degradation. Physical mixing of the waste within the site is impractical, thus, leachate recirculation provides the only way of addressing this issue. Leachate movement could be anticipated to increase waste degradation rates as a result of better moisture distribution throughout the waste (creating more areas within the waste where bacteria may grow), enhanced access of bacteria to soluble nutrients and removal of inhibitory compounds.

LR has been a subject of considerable research around the world (Pohland 1980, Otieno 1989, Doeden and Cord-Landwehr 1989, Reinhart 1996, Warith and Sharma 1998). In the mid 70's Pohland (1980) found that once generated leachate is recycled, rapid conversion of readily available organic constituents occurs. Many studies confirmed that the leachate quality in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and volatile fatty acid (VFA) is improved by applying LR (Mata-Alvarez and Martinez-Viturtia 1986, Barlaz *et al.* 1989, Doeden and Cord-Landwehr 1989, Otieno 1989, Barber and Maris 1992, Reinhart 1996). The effects of LR on leachate characteristics are discussed in the following section.

2.2.1 Impact of LR on Leachate Characteristics

The relative efficiency of LR in enhancing leachate treatment at full-scale is difficult to quantify because it requires parallel operation of conventional single pass (SP) and LR landfills. To achieve such a situation, Barber and Maris (1992) tried to put the parallel operation into practice and noted that the differences in waste age and the heterogeneity of conditions found in each landfill may cause problems in measuring the relative efficiency. Nevertheless, many studies continue to investigate the process of LR and its impact on the environment (Mata-Alvarez and Martinez-Viturtia 1986, Barlaz *et al.* 1989, Doeden and Cord-Landwehr 1989, Otieno 1989, Reinhart 1996, Reinhart and Al-Yousfi 1996).

Reinhart and Al-Yousfi (1996) analyzed data from full-scale landfills with LR and compared them to SP operated landfills. The results of their work are summarized in Table 1, which shows that landfills practicing LR produce higher quality leachate. In the same study, the authors studied the leachate characteristics from LR and SP landfills as the landfills aged: leachate from LR versus SP landfills were compared as a function of landfill stabilization phase[1] (Table 2). Although it is difficult to define explicit transitions between stabilization phases, boundaries were delineated based on the approximate

[1] The phases of landfill stabilization are illustrated and discussed later in section 2.4.

magnitude of leachate and gas strength obtained from site records. Table 2 shows that the practice of LR reduces the concentration of the BOD and the COD of the leachate; however, it does not provide the same effect on the concentration of ammonia and the leachate conductivity.

Table 1 Leachate constituents of single pass and leachate recirculation landfills.

Parameter (mg/L)	Single Pass	Leachate Recirculation
BOD	20-40000	12-28000
COD	500-60000	20-34560
Ammonia	30-3000	6-1850
Iron	20-2100	4-1095
Chloride	100-5000	9-1884
Zinc	6-370	0.1-66

(Adapted from Reinhart and Al-Yousfi, 1996)

Table 2 Landfill constituent concentration ranges as a function of the degree of landfill stabilization.

Phase	Phase 2 Transition		Phase 3 Acid Formation		Phase 4 Methane Formation		Phase 5 Final Maturation	
Parameter	SP	LR	SP	LR	SP	LR	SP	LR
BOD (mg/L)	100-1000	0-6893	1000-57700	0-28000	600-3400	100-10000	4-120	100
COD (mg/L)	480-18000	20-20000	1500-71000	11600-34550	580-9760	1800-17000	31-900	770-1000
VFA (mg-Ac/L)	100-3000	200-2700	3000-18800	0-30730	250-4000	0-3900	0	0
BOD/COD	0.23-0.87	0.1-0.98	0.4-0.8	0.45-0.95	0.17-0.64	0.05-0.8	0.02-0.13	0.05-0.08
Ammonia (mg/L)	120-125	120-125	**2-1030**	**0-1800**	**6-430**	**32-1850**	6-430	420-580
pH	6.7	5.4-8.1	4.7-7.7	5.7-7.4	6.3-8.8	5.9-8.6	7.1-8.8	7.4-8.3
Conductivity (μmhos/cm)	2450-3310	2200-8000	1600-17100	10000-18000	2900-7700	4200-16000	1400-4500	NA

(Adapted from Reinhart and Al-Yousfi, 1996)

2.2.1.1 Organic Strength

The effect of the treatment method on the organic strength is important. Therefore, the comparison between SP and LR based on the organic strength of the leachate is essential. Data from Table 2 show that leachate of landfills with LR follows a pattern similar to that of landfills with SP. In the early stages of waste degradation, higher values of BOD and VFAs may be associated with LR. Such phenomena can be explained by the fact that uniform high moisture contact opportunities exist in the LR landfills. This environment

increases the hydrolysis and solubilization of organic material. On the other hand, areas of SP landfills, which experience fewer chances of moisture contact, hence, have less opportunity for waste degradation.

Although LR may promote leachates with higher organic strength, the duration of the release of the organics is about one order of magnitude lower than that of SP landfills (Reinhart, 1995). Table 2 also shows that once methanogenesis is established, the leachate organic strength declines (Barlaz *et al.* 1989).

In addition, the organic strength of the leachate is primarily treated inside landfills, where LR is in practice. In this case, the landfill is used as an effective bioreactor, utilizing its storage and degradation capacity. The leachate produced is repeatedly recirculated back into the landfill until its strength diminishes and stabilizes. Therefore, no extra liability and/or handling requirements are needed. In this respect, the frequency of recirculation (which is discussed in section 2.2.3.2) can be employed as a new control measure to optimize landfill operation and alter leachate characteristics as desired (Otieno 1989, and Reinhart 1996).

Otieno (1989) found that recirculation of leachate in landfills over a given period of time resulted in good quality leachate; this conclusion was based on leachate BOD, COD and pH. In some cases, the leachate quality had improved to such an extent that it could be discharged into the existing sewers without incurring sewer surcharges. Barber and Maris (1992) found that the organic strength of a leachate that has been recirculated decreased markedly relative to that from SP.

2.2.1.2 Ammonia-N

Ammonia is produced during the decomposition of the proteinaceous fraction of solid waste due to hydrolysis and fermentation. The LR as a landfill management option negatively affects the leachate ammonia concentration. The recirculation of leachate enhances waste degradation, which increases the strength of the VFA and ammonia in the leachate. LR can result in further degradation of the VFAs, but it does not reduce the

concentration of the ammonia (Table 2). Therefore, at landfills where LR is practiced, ammonia tends to accumulate and to reach high concentrations.

Onay (1995) reported that the average ammonia concentration from 26 different U.S. landfills was 84 mg-N /L, with a maximum of 1024 mg-N /L. A higher range -between 600 and 2300 mg-N/L- was reported in landfills within the United Kingdom (Shibani 1987). Ammonia concentration behavior was attributed directly to the leachate management option. At landfills where LR was practiced, ammonia concentrations accumulated to higher levels during the acidic and methane formation phases than the ammonia concentrations in SP landfills (Table 2).

Although microorganisms use part of the ammonia nitrogen for assimilation purposes during the active decomposition phase, the excess finds its way into the leachate. Under LR conditions, ammonia accumulates because the anaerobic landfill bioreactor does not provide an effective way to treat the ammonia nitrogen. During the final maturation phase, the utilization of ammonia is limited because the readily biodegradable organics are essentially exhausted. These limitations increase the accumulation of ammonia and cause it to reach a higher concentration which then creates an ultimate discharge challenge.

LR preserves the existing ammonia pool in addition to enhancing its additional formation. Interestingly, the range of ammonia nitrogen concentrations observed at LR landfills has been shown to have no adverse effects on the anaerobic processes of the landfill bioreactor. However, nitrogen management is a key factor in the discharge of this leachate.

2.2.1.3 Metals

In SP landfills, the primary removal mechanism for metals appears to be wash out; thus, a limit exists on the amount of metals that can be chemically precipitated. In contrast, LR has important consequences regarding metal contamination. Gould *et al.* (1989) found that LR stimulated reducing conditions which enhanced the reduction of sulfate to

sulfide. Sulfide and hydroxide precipitation appeared to be the primary metal removal mechanisms at LR landfills (Reinhart and Al-Yousfi 1996).

Chian and Dewalle (1976) reported that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In addition, leachate with neutral or above neutral pH (promoted by LR) enhanced the precipitation of metal hydroxides. As a result of precipitation, leachate metals are moderated to very low concentrations (Table 1).

2.2.2 Impact of LR on Gas Production

Landfill gas is one of the major products generated by waste decomposition. In young landfills, the gas is mainly composed of CO_2 and H_2, while in mature landfills, CH_4 and CO_2 are the major constituents in landfill gas (Figure 1). In addition to the economic value of methane as an energy source, it is also used as an indicator of waste stabilization. To achieve high rates of methane production, many enhancement techniques have been used including LR and the addition of nutrients, buffers and municipal sewage sludge.

Increasing the leachate recirculation rate enhances gas production. Al-Yousfi and Pohland (1998) reported that the overall rate of methane production at a landfill bioreactor was about 20 times greater than that at an SP landfill. They also observed that there was no distinct methane peak developed in the SP landfill, indicating an incomplete stabilization potential. The study found that the time needed for the methanogenic phase to prevail under LR operation is longer. This delay in methane production may be due to the intensive acidogenic conditions present in the LR landfills.

Delaware Solid Waste Authority (1993) operated parallel one-acre cells and compared SP operation to LR operation. The results of their work showed a twelve-fold increase of gas production in the LR cell over that of the SP cell. Gas emission measurements made by researchers at LR landfills in Alachua County, Florida, revealed a doubling in gas production rates from waste located in wet areas of the partially LR landfill relative to comparably aged waste in dry areas (Miller *et al.* 1994).

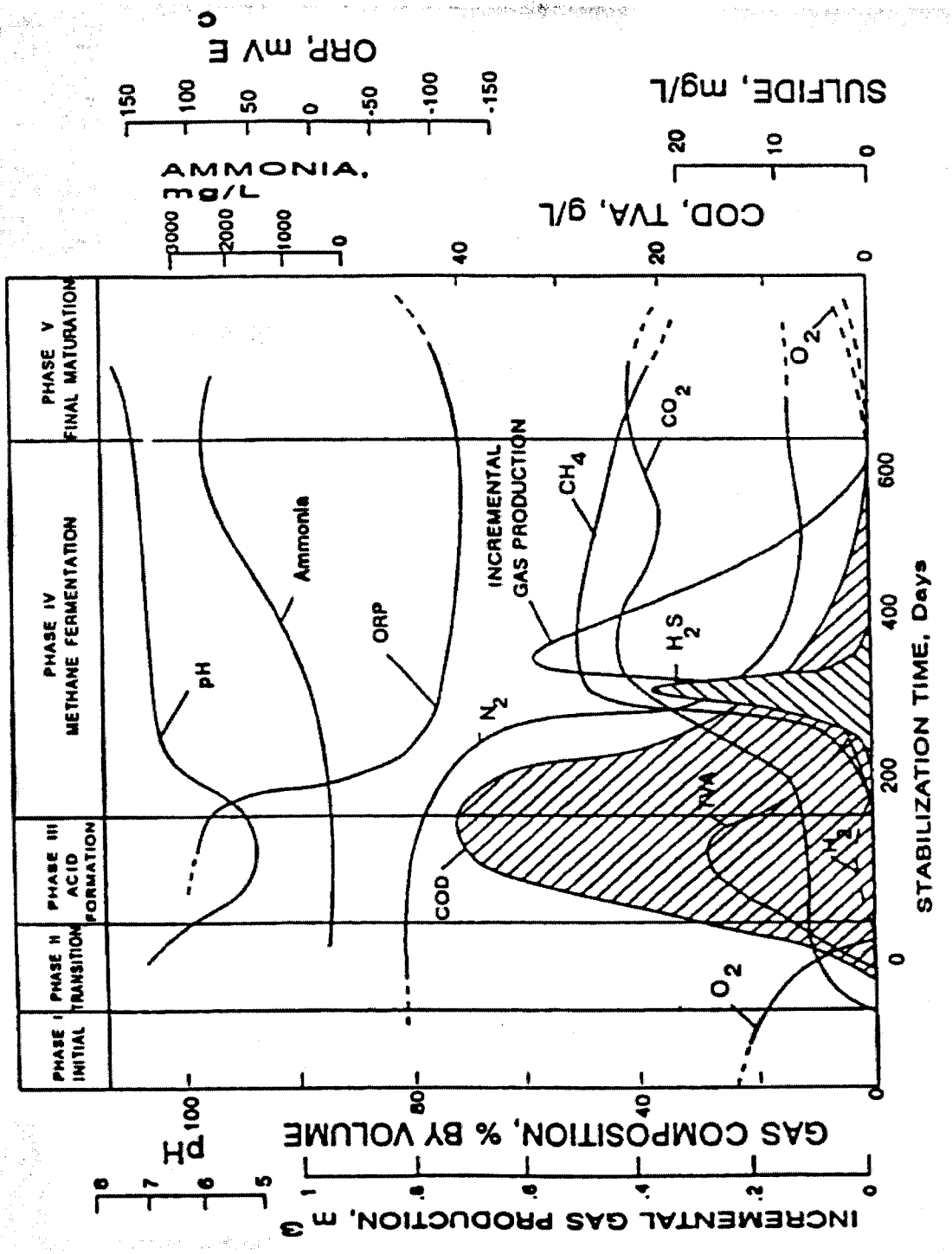

Figure 1 Changes in selected indicator parameters during the phases of landfill stabilization

(Adapted from Onay 1995)

Lay *et al.* (1998) conducted a study to model methane production from landfill bioreactors treating the organic fraction of MSW. They determined that LR significantly enhanced the carbohydrate consumption in shortening the lag phase of methane production under neutral pH; however, results showed that the effect of LR on protein and lipid consumption was negligible. LR significantly shortened the overall lag phase. They concluded that once methane production was started, whether or not LR was employed, the methane production rate (2.6 mL/gVSS· d) showed no significant difference.

Doedens and Cord-Landwehr (1989) investigated the effect of leachate recirculation under different scenarios. They found that an LR cell was equally likely to be associated with high methane production rates as was an SP cell provided with the same amount of moisture. The results of their work suggest that the availability of moisture is the vital parameter that enhances waste degradation.

From all of the above, it can be concluded that faster and/or higher gas production tends to be associated with LR. In addition, Pohland and Al-Yousfi (1994) suggested that gas production at larger sites is significantly enhanced as a result of both accelerated waste stabilization as well as the return of organic material in the leachate to the landfill for conversion to gas (as opposed to washout in a SP landfill).

The results show that LR enhances and accelerates gas production, yet the majority of the landfills fail to manage the gas produced, which is ultimately released to the atmosphere (David 1997). Since the release of landfill gas has an adverse effect on the environment (see section 2.4.2.1), this issue needs to be considered and preferably resolved before adopting LR.

2.2.3 Impact of LR on Landfills

Adopting LR as a landfill management option introduces the landfill operators to new terms such as the quantity of leachate recycled and/or disposed, the frequency of recycling and the need for leachate storage. In the following sections, the new terms in LR are introduced.

2.2.3.1 Leachate Quantity and Disposal

The amount of leachate produced from landfills with LR is larger than that produced from SP landfills, and it increases as recirculation rates increase. With current landfill capping practices, the volumes of the recirculated leachate will become especially dominant after landfill closure. Reinhart (1996) studied and analyzed a number of landfills with LR and found that leachate generation rates ranged from 1.1 to 13.5 $m^3/ha \cdot d$ with LR representing 40 to 70% of the leachate generated. As with SP landfills, leachate generation depends on the climate and the site characteristics.

According to the same study, 0 to 59% of the leachate generated required off-site disposal. At sites where large storage volumes were provided, (greater than 700 m^3 of storage /ha of landfill), off-site management of leachate was minimized. Reinhart (1996) also observed that sites with relatively little storage were compelled to recirculate leachate at much higher rates than those with large storage volumes. Otieno (1989) found that recirculation of leachate may provide a high quality effluent that could be discharged directly to the receiving water without further treatment.

Doeden and Cord-Landwehr (1989) found that under German climatic conditions, complete evaporation of leachate by LR would not be possible even with sufficient storage capacity. The amount of excess leachate was estimated to be 2 $m^3/ha \cdot d$ with LR, and 4 to 5 $m^3/ha \cdot d$ with SP. Barber and Maris (1992) conducted LR studies in the United Kingdom under climatic conditions with high precipitation, where rainfall exceeds the potential evaporation. While the authors concluded that LR offered benefits in the form of reducing leachate volume and strength, they concluded that under such circumstances, LR did not offer a complete solution to leachate discharge. It was determined that additional treatments of leachate at some stage may be required.

2.2.3.2 Rates of Recirculation

The process of recirculation starts with low rates and frequencies during the early acidogenic phase to avoid any potential inhibitory effects on the overall process. The

rates are then gradually increased as methanogenesis becomes established (Pohland 1980, Cossu *et al.* 1993, Pohland and Al-Yousfi 1994).

The total quantity of accumulated leachate should be restricted to the amount needed to effectively operate the landfill system as a bioreactor. In addition, the eventual quantity that requires ultimate disposal, with or without post-treatment after landfill stabilization, should be minimized.

Many researchers have examined the effect of variable rates of LR on solid waste stabilization and the leachate generation rate (Klink and Ham 1982, Al-Yousfi and Pohland 1998, Chugh *et al.* 1998). Al-Yousfi and Pohland (1998) recycled 25% to 100% of the total leachate generated and found that the higher the leachate-recycling rate, the greater the quantity of methane gas produced. This observation was related to the higher quantities of organic substrate made available during high rates of LR. However, higher LR rates resulted in longer lag times before methane generation began. Under such conditions, it is likely that the microbial populations are better adapted and therefore, ensure higher conversion and more complete stabilization.

Another study by Chugh *et al.* (1998) examined the effect of the volume of recirculated leachate on waste degradation with volumes ranging from 2% to 30% of waste volume. They found that the highest percentage of recirculation resulted in the largest amount of gas production accompanied by the maximum methane content. They also noted that the earliest methane peak corresponded to the highest recirculation rate. In terms of duration, these results disagree with the earlier results by Al-Yousifi and Pohland (1998); however, there is agreement on the fact that increasing the percentage of recirculated leachate will increase gas production. These results also agree with those obtained from the studies carried out by Klink and Ham (1982), who concluded that moisture flow through a refuse bed increased the rate of methane production by 25% to 50%, relative to refuse at the same moisture content with no moisture flow.

2.2.3.3 Other Parameters

Settlement: One of the consequences of LR is that it keeps the cell wet, and this in turn enhances waste compaction. Studies of the impact of LR on settling have shown that the wet technology enhances the rate and extent of subsidence (Pohland and Al-Yousfi 1994, Reinhart and Al-Yousfi 1996). Wetting of waste as it is placed has been practiced for many years as a method of increasing compaction efficiency. Rapid and predictable settlement can provide an opportunity to utilize valuable air space prior to closure of the cell. Enhancing the degradation rate through LR can provide a way to meet mandated waste volume reduction in some parts of the world. Landfill reclamation and final site use are also facilitated by timely volume reduction provided by moisture control.

Economy: Long-term liability can be minimized if the waste is quickly treated to a point where further degradation will not occur or will occur so slowly that leachate contaminants and gas production are sufficiently minimized to no longer pose a threat to the environment. Using the COD declining slope, the COD half-life was measured to be about 10 years for SP landfills and between 230 to 280 days for landfills with LR (Reinhart 1995). A design life of 20 years for geosynthetic membrane may not provide adequate protection for the conventional landfill with stabilization periods of many decades.

With LR, gas production confined to a few years rather than decades, provides opportunity for more efficient control and destruction of airborne toxins and GHGs. A cost saving of about $U.S. 2500/acre is expected at LR landfills because of the reduction in long-term care and liability and the potential for landfill and space recovery (Reinhart and Al-Yousfi 1994).

Treatment: Due to the specific characteristic of the recirculated leachate coupled with the increase in LR implementation, the treatment of such leachate requires more study. Diamadopoulos (1994) experimented with many types of treatments for leachate, concluding that the physio-chemical treatments were most effective due to the low BOD/COD ratio in the resulting recirculated leachate. Alternatively, the same study investigated one biological method: a stabilization pond. The settling pond proved

effective in removing BOD and ammonia as well as serving as an equalization pond. The only limitation of the latter approach was the large area required for a pond.

Diamadopoulos (1994) investigated ammonia treatment through a stabilization pond and air stripping. The former exhibited good results but required a large area, while the latter was found to be very expensive.

Onay and Pohland (1998) conducted a study that focused on the potential for *in situ* nitrogen removal in dedicated nitrification/denitrification zones at the landfill. Their research was conducted because of the popularity of LR and the high ammonia associated with the effluent leachate. They divided the landfill into three zones: aerobic, anaerobic, and anoxic. In the aerobic zone, the reactor was aerated to supply the oxygen required for nitrification. The nitrified leachate was then passed to the anoxic zone for denitrification. They succeeded in removing the nitrogen with separated reactors; however, once the processes were combined, the efficiency of nitrogen removal was significantly lowered. To date, Onay and Pohland are the only researchers who have investigated this particular method. However, they used a compost material instead of MSW. Compost contains less carbon and more nitrogen than MSW and this fact may have an effect on the resulting biological treatment. The denitrification zone may face carbon deficiency, which could potentially lower the efficiency of the process. On the other hand, the high nitrogen content may add some difficulties to the process of nitrification. Moreover, this study focused on the nitrogen treatment without exploring the effects of such a method on the landfill stabilization activities.

2.2.4 Additive and Environmental Conditions

In various laboratory studies, leachate recycling was found to both enhance the waste decomposition and improve leachate quality when a variety of materials, such as buffers, nutrients and microbial inoculum were added to the leachate and recirculated through the solid waste (Mata-Alvarez and Martinez-Viturtia 1986, Barlaz *et al.* 1989, Bonger 1990).

pH: The findings of the above studies all agreed that buffering the leachate being recycled enhanced decomposition by allowing the proper pH to be established faster.

Mata-Alvarez and Martinez-Viturtia (1986) found that buffer addition was necessary only for the start up of digestion: once a neutral pH (ranging from 6.8 to 7.4) was reached, rapid methane production commenced.

Nutrients: Stegmann (1983) observed that the addition of nutrients such as nitrogen and phosphorus to the recycled leachate significantly shortened the initial phase of degradation, and methane generation commenced earlier. However, the continued addition of nutrients after methane production had started did not improve the methane production rate above what was experienced through buffer addition alone. In contrast, Mata-Alvarez and Martinez-Viturtia (1986), found that the addition of nutrients was not required because of the composition of the waste.

Temperature: Mata-Alvarez and Martinez- Viturtia (1986) investigated the kinetics of waste fermentation using five test cells operated at different temperatures. The aim was to enhance and optimize the rate of methane production and increase the ultimate methane yield. This was accomplished through the use of LR with supplemental water spiked with buffer, nutrients and inoculum. The temperatures studied ranged from 30 to 46°C. The optimal range for landfill operation was found to be between 36 and 38°C. Mata-Alvarez and Martinez- Viturtia (1986) concluded that a landfill operated under the optimum conditions would have a life of 1.5 to 2 years and that 95% of the biodegradable matter would be reduced during the first year.

The need to conduct more studies on the treatment of recirculated leachate is rising both because of the current limited data and the growing popularity of the LR practice. In the following section the advantages and disadvantages of LR are given.

2.2.5 LR: Advantages, Disadvantages, and Concerns

According to the research results available to date, the process of LR has been found to offer many advantages. First, it is a simple method that has a low cost for equipment and maintenance and does not require additional land space. Also in many cases, adopting LR provides a solution for the treatment of the discharged leachate (see section 2.2.3.1). Even at landfills where the ultimate need for leachate treatment exists, LR significantly

reduces BOD_5 from young landfills (see section 2.2.1.1), and promotes neutral pH, both of which reduce the challenge and cost of subsequent treatment.

In addition, the leachate volume can be reduced at various levels by evapo-transpiration and retention by unsaturated refuse in the landfill; hence, LR provides a potential to eliminate or reduce the need for the transportation of leachate off-site. Also, LR was found to accelerate biological stabilization of landfills with high biodegradable organic materials (see section 2.2.2). Another advantage of this practice is that it helps to ease the threat of contamination of surface and ground waters and provides stabilization of some inorganics by oxidation and precipitation.

On the other hand, the process of LR has drawbacks such as the additional capital cost involved, the operating cost and the potential for surface ponding, channeling and/or short-circuiting in the movement of leachate. By practicing LR as a management option for landfills, there is a possibility for problems to arise such as clogging of leachate distribution and collection systems, surface run-off, odor problems and the introduction of oxygen into the anaerobic zone causing inhibitory effects on organic decomposition.

Furthermore, LR does not decrease the concentration of ammonia, or some metals and inorganic constituents in the leachate and does not remove refractory COD from old landfills. In addition, the buildup of chloride, sulfates and dissolved solids with continued recirculation might affect the evaporation rates. Also, the increase of the hydraulic loading on the landfill liners may cause groundwater contamination. Finally, the increase in the release of methane into the atmosphere from the landfill with LR contributes to the effect of GHGs in global warming (see section 2.4.2.1 for more details).

The process of LR is relatively new, yet it is popular. Due to the increasing popularity of this process, it has attracted numerous researchers. However, there is still a need for further research to investigate certain issues. A few examples of essential issues that require further investigation are discussed below.

First, the treatment of leachate used in landfill bioreactors is poorly documented in the literature. The characteristics of the leachate stabilized through a landfill bioreactor are

well documented (see section 2.2.1), yet the optimal treatment of this leachate requires further research. In addition, the high ammonia content of leachate is considered to be an important issue that requires more study.

Furthermore, most researchers welcome the increase in landfill gas production that comes along with LR; however, the environmental effect of such high gas production on global warming has not been taken into account as a part of the LR practice.

Moreover, the literature covers the general practice of the process without detailing the scientific theory behind it (how does LR affect waste degradation and methane generation). It is assumed that the availability of the moisture enhances the degradation, together with its movement through the landfill bed. However, researchers are still debating the optimum moisture content.

Another point worth exploring is an economic investigation that studies the big picture of applying LR, incorporating features such as leachate production, leachate treatment, transportation, landfill liability, gas production and gas recovery.

Finally, the production of ammonia-rich leachate and the high rate of methane released to the atmosphere are often associated with LR. In the following section (2.3), the removal of ammonia from leachate is discussed, with a special focus on utilizing landfill products (i.e. leachate and gas) to support denitrification.

2.3 Nitrogen: Impact, and Removal

Nitrogen is an essential element to the function of any natural ecosystem and may exist in many forms. However, some forms at certain concentrations are hazardous to humans as well as to the ecosystem. The most significant problems associated with discharging effluents that are high in nitrogenous compounds are eutrophication of surface water, depletion of surface water dissolved oxygen (DO), toxicity to aquatic life and public health (U.S. EPA 1993).

The excessive growth of plant and algae in surface water (i.e., eutrophication) requires the presence of nitrogen, phosphorus, carbon dioxide and light. Often, nitrogen is the

growth-limiting parameter especially in marine environments; therefore, discharging nitrogen to surface waters may promote algal production. The impact of biostimulation includes poor appearance of the surface water, odor problems and oxygen depletion due to plant decomposition. In addition to plant decomposition, biological nitrification of ammonia can further decrease the DO level. Respiration of aquatic environment organisms can be affected by the low DO concentrations.

Furthermore, ammonia toxicity to aquatic life is an important factor to consider. In aqueous solution ammonia react as:

Equation 1 Ammonia equilibrium equation in the aquatic environment

$$NH_4^+ \leftrightarrow NH_3 + H^+ \quad \text{at 25°C (Sawyer } et\ al. \text{ 1994)}$$

Ammonium ion un-ionized ammonia Hydrogen ion

The equilibrium equation presented is pH-, temperature- and salinity- (i.e., ionic strength) dependent. The term ammonia refers to the total ionized and un-ionized ammonia. Of the two ammonia forms, un-ionized ammonia is more toxic to aquatic life as it is lipid soluble; therefore, it is able to pass through fish membranes into the blood stream (Nova Tec 1996). Toxicity usually manifests itself through neurological disorders and /or the thickening of gill membrane, effectively reducing oxygen diffusion capacity, both effects eventually resulting in death of the organism (Haywod 1983). The toxicity limit for NH_3-N is 0.02 mg/L (Sawyer *et al.* 1994). Ionized ammonia is also toxic to fish but only in much higher concentrations (Lewis 1988); therefore designs are most often based on the NH_3-N concentration.

Nitrate is the most oxidized form of the nitrogen and it is a product of the biological nitrification of ammonia. Drinking water with high nitrate concentrations is associated with a fetal blood disorder infant methemoglobinemia (Azevedo 1993). Nitrate inactivates hemoglobin and the infant suffocates, producing the diagnosis of blue babies syndrome. Another potential health impact is the possibility that nitrates are cancer-causing agents; because nitrates can react with amines and amides to form N-nitroso compounds. These compounds have been found to be carcinogenic (U.S. EPA 1993).

As discussed in section 2.2.5, one of the important disadvantages of adopting the practice of LR is the production of ammonia-rich leachate. Due to the impact that nitrogen has on the environment and public health, it must be treated. In the following section several alternatives for removing ammonia are discussed.

2.3.1 Leachate Nitrogen Removal

Leachate with a high ammonia-N concentration is a concern when dealing with leachate disposal and/or treatment. The biological treatment of ammonia-N requires nitrification under aerobic conditions, then denitrification under anoxic conditions. Another way of removing leachate ammonia is by using physical-chemical methods. In this section, both biological and physical-chemical treatments are discussed.

Physical-chemical Treatment: Physical-chemical methods for ammonia removal from stabilized leachate include air-stripping, ion exchange and reverse osmosis. Chemical coagulation and filtration are considered only when organic nitrogen is present in high concentrations. The advantages of these techniques are the short start-up time, the uniform removal efficiency, the relative insensitivity to toxins and temperature and the minimal production of sludge. The high cost associated with physical-chemical treatments may be considered the main disadvantage (Ehrig 1985, Diamadopoulos 1994). After Ehrig (1985) investigated several physical-chemical methods for treating leachate, he reported that biological treatment was the most effective system.

Biological removal: Nitrification is the conversion of ammonia to nitrate by microbial action. This process is carried out by two categories of microorganisms. The oxidation of ammonia to nitrite and then to nitrate is an energy yielding process. Microorganisms use the generated energy to assimilate carbon dioxide. Carbon requirements for nitrifiers are satisfied by carbon dioxide, bicarbonate or carbonate. Nitrification is favored by the presence of oxygen and sufficient alkalinity to neutralize the hydrogen ions produced during the oxidation process.

Most studies on leachate treatment have concentrated on the removal of the COD and BOD components. Mavinic and his co-workers have completed studies on biological

ammonia removal from leachate (Dedhar and Mavinic 1986, Carley and Mavinic 1991, Azevedo 1993, Ilies 1999). Few studies have been done on such treatment for stabilized leachate through LR (Diamadopoulos 1994, Onay and Pohland 1998). Since LR through landfills promotes the methanogenic phase of refuse decomposition and enhances gas production, there is a current interest in its application. Therefore, more stabilized leachate with low concentrations of degradable carbon compounds but high concentrations of ammonia nitrogen will be produced.

Onay and Pohland (1998) conducted an experiment using laboratory-scale simulated landfill units to demonstrate the feasibility of extending the stabilization to *in situ* nitrification and denitrification at controlled landfills operated with LR. They developed a three-component simulated landfill system to include anoxic, anaerobic and aerobic zones. The experiment was conducted in three stages: SP separate reactors, internal and external LR combined reactors and external LR combined reactors. Results from these three simulated operational stages of methanogenesis, nitrification and denitrification indicated that the efficiency of nitrogen conversion was dependent on the operational stages and both separate and combined reactor operations with internal leachate recycling around each reactor provided 95% nitrogen conversion. In contrast, combined reactor operation, without internal recycling provided a conversion efficiency per cycle ranging between 30 to 52% for nitrification and 16 to 25% for denitrification, with a suggestion of increasing efficiency as they acclimatized.

Since the feasibility of *in situ* nitrification and denitrification in a bioreactor landfill was demonstrated, design modifications, involving an anaerobic zone associated with the leachate underdrain system and an anoxic zone associated with a surficial leachate distribution system below the final cap or vice versa, have been recommended (Onay and Pohland 1998).

Diamadopoulos (1994) used an artificial pond to treat recycled leachate. The facultative pond removed 88% of the ammonia-N. The high degree of nitrogen removal at the pond shows that it acts as an important pretreatment step, significantly reducing the cost of any subsequent treatment required for nitrogen removal.

The process of nitrification produces nitrate, which requires further treatment. In the following section, the removal of nitrate is discussed, with the emphasis on the feasibility of utilizing landfill products to support denitrification.

2.3.2 Denitrification

Microorganisms use ammonia as a source of nitrogen, for cell synthesis. In the absence of ammonia, nitrate is reduced to ammonia, which is then used to synthesize protein in a process called *Assimilative Nitrate Reduction* (Azevedo 1993). The assimilative reduction of nitrate is minor if ammonia is available. On the other hand, the dissimilative reduction of nitrate to nitrogen gas is the major method for removal of nitrate. This practice is also known as denitrification or nitrate respiration. In this respiratory process, nitrate serves as the electron acceptor in the absence of oxygen. The process results in the generation of energy that can be applied for the maintenance of the existing cell mass and the synthesis of a new cell mass. Denitrification produces nitrous oxide and nitrogen gas, with nitrogen gas liberation being the predominant output of denitrification. The overall reaction, using methanol as a source of carbon, to remove nitrate is shown in the following equation:

Equation 2 The overall nitrate removal reaction

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow 0.065C_5H_7O_2N + 0.47N_2 + 2.44H_2O + 0.76\ CO_2$$

2.3.2.1 Microbiology

Denitrifying bacteria are facultative aerobes; they are able to use oxygen and nitrate as electron acceptors. Since reducing oxygen yields more energy, denitrifiers prefer oxygen to nitrate as an electron acceptor. Denitrifying bacteria are active at anoxic conditions; yet, the occurrence of denitrification under aerobic conditions in wastewater environments has also been reported (Mateju *et al.* 1992). The extent to which the process proceeds, and the circumstances affecting the onset of denitrification, are complex and variable. One of the general rules of denitrification is that it is considered to be an anoxic process, occurring in the presence of nitrate and the absence of molecular oxygen. Bacterial genera that are known to contain denitrifying species include *Achromobacter, Alcaligenes, Bacillus, Chrombacter, Corynebacterium, Halobacterium,*

Methanomonas, Moraxella, Paracoccus, Propionibacterium, Pseudomonas, Spirillum, Thiobacillus and Xanthomonas (Gayle *et al.* 1989).

Reduction of nitrate to nitrogen gas proceeds in four consecutive steps according to the following scheme (Gayle *et al.* 1989):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Each step in the denitrification process is catalyzed by a separate enzyme: a nitrogen oxide reductase that transfers the electron from the chain to the particular intermediate of the denitrification pathway. The first step involves energy conservation and is catalyzed by a Mo-dependent reductase (Kroneck and Zumft 1991). The second step is carried out by two distinct nitrite reductases (one has a copper center and the other has two hemes), with the same physiological reaction (Mateju *et al.* 1992). The third step is the least well-characterized of the enzymatic steps associated with denitrification. The last step is catalysed by a copper-containing reductase, and is coupled to ATP formation (Kroneck and Zumft 1991, Mateju *et al.* 1992). Denitrifying bacteria as a group are metabolically versatile and genetically diverse, and hence, factors affecting induction and repression of the enzyme systems are not universal.

In addition, denitrifiers are less sensitive to toxic chemicals than are nitrifiers. However, ammonia concentrations ranging from 1500 to 3000 mg/L were shown to be toxic to the anoxic process (McCarty 1964). Mineral nutrients such as PO_4^{4-}, SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+} and Ca^{+2} are required for reduction of nitrate in the presence of a carbon source. Various trace elements such as Mo, Fe, Cu and Mn are reported to be necessary for the successive enzymatic steps (Onay 1995).

The optimum pH range for denitrification is between 7.0 and 8.5. The process of nitrification produces H^+, which tends to lower the pH, while denitrification, as shown in Equation 2, consumes the hydrogen ion. It has been found that denitrification can overcome half of the acidity produced in nitrification (U.S. EPA 1993). Therefore, operating a denitrification stage before and/or after nitrification helps in neutralizing the leachate and maintaining the pH in the optimum range (Ilies 1999).

2.3.2.2 Kinetics

It is important to study the kinetics of the process of denitrification, as it provides the parameters needed to evaluate the efficiency of the progression. These parameters include the growth rate, the maximum specific growth rate and the nitrate consumption rate. In denitrification, the important factors that affect the process design and kinetics are the concentration of the nitrate and the carbon source, which also serves as an ED for the reaction. The type of ED used in engineered denitrification processes is chosen based on efficiency and economics.

Suspended growth: If simple Monod kinetics are assumed to apply to suspended growth, then the rate of growth (dX/dt) is expressed in terms of microorganism concentration (X) as in Equation 3:

Equation 3 Growth rate

$$dX/dt = (K_o \cdot X \cdot S) / (K_s + S),$$

where K_o is the maximum specific growth rate, S is the concentration of growth-limiting substrate and K_S is the half velocity constant or the substrate concentration at one-half the maximum growth rate.

For denitrification with nitrate concentrations > 10 mg-N/L, it is safe to assume that the nitrate concentration is considerably greater than the half velocity constant, which has been reported to be 0.08 mg/L (Barnes and Bliss 1983); therefore, the equation can be simplified to:

Equation 4 Growth rate (substrate is not limited)

$$dX/dt = K_o \cdot X$$

where, $S >> K_S$

Hence the rate of denitrification is first order, dependent on the biomass concentration and independent of nitrate concentration.

The denitrification rate can also be expressed in terms of the nitrate loss. For high nitrate concentrations, the rate is zero order (Moore and Schroeder 1971, as cited by Barnes and Bliss 1983, U.S. EPA 1993) with respect to nitrate concentration:

Equation 5 Nitrate utilization rate

$$- d(NO_3\text{-}N)/dt = K_o$$

The rate of denitrification is also dependent on the quantity and the quality of the ED. Theoretically, the dependence is significant only if there is a deficiency in the amount of the electron donor (McCarty *et al.* 1969, Picard and Faup 1980, as cited by Barnes and Bliss 1983). For a mixture of ED's, for example as in leachate, it is difficult to predict the concentration of the ED and how it changes with time.

Fixed film: A landfill bioreactor may be described as a fixed film reactor with poor mixing. The process of denitrification through a landfill bioreactor is closer to that of a fixed film reactor than to a suspended growth process. In fixed film reactors, the rate is dependent upon the availability of nitrate and ED's in a particular layer of the biomass.

In layers of biomass where nitrate is present and the required amount of ED is available, the process proceeds as in suspended growth. Such conditions can be anticipated for thin films of biomass and/or high concentrations of nitrate (Harremoes 1977, as cited by Barnes and Bliss 1983) and ED. In thick films, the concentration of the nitrate and the ED is depleted near the media (solid waste) supporting the biomass. The availability of substrate depends on the diffusion of that substrate through the outer layer of the biomass. If the partial penetration of the ED limits its availability, the zero-order denitrification rate is considered as half-order or first-order (Harremoes 1977, as cited by Barnes and Bliss 1983 and 1982).

In landfills, it is expected that the biomass film will build up over time to form a thick layer. However, recirculation of leachate may help reduce that thickness. For thick films of biomass, the reaction rate is dependent on the concentration of the nitrate, the concentration of ED, the availability of the substrate at the denitrification sites, the rate of diffusion of the substrate through the biomass, the thickness of the biomass and the

distribution of the film thickness (Harremoes 1977, as cited by Barnes and Bliss 1983 and 1982). The accumulation of the reaction products may inhibit the reaction if alkalinity accumulates in local areas and pH rises to high levels.

For design purposes with both suspended growth and fixed film, a slight surplus of ED must be supplied to confidently assume no dependence on concentration. It is important to stress the fact that, although the rate of denitrification is independent of the concentration of the ED (at high concentrations), the rate of denitrification is still affected by the type of the ED (McCarty *et al.* 1969). Higher rates of denitrification are expected with EDs such as acetic acid and ethanol compared to denitrification with methanol (McCarty *et al.* 1969, and Tam *et al.* 1992, Æsoy *et al.* 1998).

Due to the importance of the sources of EDs, several EDs and their efficiency are discussed in the following section, with the focus on sources that are related to landfills (leachate and methane).

2.3.2.3 Sources of Carbon and Electron Donor for Denitrification

Denitrification is classically considered to be a heterotrophic process conducted by microorganisms that require organic carbon for energy and cell synthesis. Therefore, in order for denitrification to occur, the availability of readily biodegradable carbon is essential. The most popular carbon source supplied is methanol, which was recommended by the Environmental Protection Agency (EPA) based on the work done by McCarty *et al.* (1969).

In that study (done by McCarty *et al.*), methanol, acetic acid, ethanol, sugar and acetone were investigated as carbon sources. Although denitrification with methanol was slower than acetic acid and ethanol, the final preferred carbon source was methanol, and this was based on the equivalent cost.

The amount of methanol required for complete denitrification and the quantity of biomass produced were calculated from Equation 6 and Equation 7, based on Equation 2:

Equation 6 Methanol required for complete denitrification

$$C_m = 2.47\ N_o + 1.53\ N_1 + 0.87DO$$

Equation 7 Quantity of biomass produced

$$C_b = 0.53\ N_o + 0.32\ N_1 + 0.19\ DO$$

Where

C_m = concentration of methanol required, mg/L

C_b = biomass produced, mg/L

N_o = initial nitrate concentration mg-N/L

N_1 = initial nitrite concentration mg-N/L

DO = initial DO concentration mg/L

The cost of methanol was $3.80 U.S. per 100 pound in 1969. Presently (2001), the same amount of methanol costs approximately $40.50 U.S. The following table compares the cost of methanol and acetic acid with the results from McCarty *et al.* (1969).

Table 3 Cost of methanol and acetic acid in 1969 and current cost

Carbon Source	Cost (US cents) /100 equivalent (1969)	Cost (US cent) /100 equivalent (2001)
Methanol	4.5	47
Acetic acid	23	200
Ethanol	7.6	NA
Sugar	14.5	NA

Acetic acid and ethanol were found to be better than methanol for denitrification; however, both are more expensive. The high cost of acetic acid prompted the researchers to look for an inexpensive alternative source of acetic acid, while the continuous increase in methanol prices has forced a search for new, cheap sources of carbon.

In the late 1980's, the interest in using sludge as a carbon source increased, because using sludge was beneficial from both an economic and ecological point of view. Several studies have been conducted with the goal to make sludge more attractive for denitrifiers

(Æsoy and Odegaard 1994, Abufayed and Schroeder 1996). The organic matter content of the sludge is slowly biodegradable; hence, biological, thermal or chemical hydrolysis of the sludge solubilizes the particulate organic matter, making it easier to utilize and more efficient to use (Barlindhaug and Odegaard 1996).

Primary sludge has been found to be an excellent source of organic carbon (Abufayed and Schroeder 1996). Most of the carbonaceous and nitrogenous matter provided by primary sludge is present in particulate form. Therefore, the feasibility of utilizing primary sludge for denitrification is governed by the relative amounts of carbonaceous and nitrogenous compounds hydrolyzed and the uptake rate of these compounds by the denitrifying organisms. The main advantages with biological hydrolysis are the high fraction of the readily biodegradable COD that may be produced and the simple process design (Æsoy and Odegaard 1994).

Other than sludge, VFAs from anaerobic digesters and wastewater from food and beverage industries have been found to support denitrification with rates equal to or higher than that supported by methanol (Fass *et al.* 1994).

Leachate: Leachate may be considered as an industrial waste that has a potential to support denitrification. Although many industrial wastes (such as wastes from wineries and food producers) have been used to provide carbon for denitrification, landfill leachate was not included. The leachate constituents may pose a threat to microbial activity at the wastewater plant. In addition, landfills may not be able to provide consistent quality and/or quantity of ED and carbon for denitrification. The quantity of the leachate varies as the seasons change, while its quality changes as the landfill ages. Therefore, a full-scale denitrification process that depends on leachate may require frequent analysis and modification. Despite the drawbacks of using leachate, young leachate may be an attractive source of ED and carbon. Young leachate is rich in VFA, which have been found to provide a high rate of denitrification (Fass *et al.* 1994, Ganaye *et al.* 1996).

Using leachate for denitrification reduces the cost of the denitrification process. In addition, treating leachate provides a form of income to the treatment plant. The treatment plant may even be able to trade the solid waste that it generates for the leachate

with a nearby landfill. Nevertheless, this requires further studies, since the literature lacks the information needed to use leachate as a carbon and ED source for denitrification.

Methane: One of the low-cost carbon sources that is usually available at treatment plants is methane. Biogas, containing approximately 60% methane, can also serve as a sole carbon source in denitrification (Barrenstein *et al.* 1986). The following equation provides the stoichiometric relationship for methane as the sole source of carbon (Barrenstein *et al.* 1986):

Equation 8 Denitrification with methane

$$5CH_4 + 8NO_3^- + 8H^+ \rightarrow 4N_2 + 5CO_2 + 14H_2O,$$

Davies (1973) was the first to claim that methane could be an ideal carbon source in commercial units. His work concluded that nitrate can be denitrified with methane as the only source of carbon and that denitrifying bacteria can adapt to methane after they had been adapted to methanol.

Investigating Davies's work, techniques and materials showed significant problems in the study. Davies (1973) used a denitrification medium that was named "organic carbon-free denitrification medium". This medium had 1 mL of vitamin B solution and 1 mL of vitamin E solution per L of the carbon-free medium. The composition of these two solutions was illustrated in a study by Toerien and Siebert (1967). Table 4 shows the composition of these two vitamin solutions and the total amount of the carbon contained. The last column shows the concentration of these components in the final medium used as a carbon-free medium for denitrification. Obviously, what was supposed to be a carbon-free medium was rich in carbon, especially with ethanol. This is deemed to be a misleading fact, and therefore, Davies'conclusion was based on an inappropriate assumption.

Table 4 Carbon concentrations in vitamin solutions

Vitamin B	Concentration in the vitamin solution (mg/L)	Concentration in Final solution (mg-C/L)
Aneurine HCl	NA	NA
L- Ascorbic acid	500	0.2
Riboflavin	500	0.2
Biotin	2000	1.0
Pyridoxinum Hcl	1000	0.3
Folic acid	200	0.1
p. Aminobenzoic acid	1000	0.6
Nicotinic acid	500	0.3
Choline	500	0.3
Vitamin E		
α tocopherol	625	0.5
Ethanol	999,500	**521**

Furthermore, Davies' study claimed to provide "good results", which were supposed to direct the focus to the use of methane for denitrification. Yet, little work has been done to confirm his results or to investigate the mechanism and characteristics of the process.

Sollo *et al.* (1976) conducted a study that investigated the feasibility of using methane as the only carbon source for wastewater denitrification. The results of his work were negative and contradicted the results of Davies' study. Sollo *et al.* (1976) did not use the vitamin solutions and hence concluded that denitrification with methane was not an economical process. The research done by Sollo and his co-workers provided little documentation and did not present much of the information required to understand the process, such as the nitrate concentration, flow rate and HRT. Aside from the missing information, the research was very focused on how to make the process successful without trying to understand the microbiology.

No further attention was given to the process except for a few studies that included methane oxidation prior to denitrification (Mechsner and Hamer 1985, Werner and Kayser 1991, Thalasso *et al.* 1997, Costa *et al.* 2000, Eisentraeger *et al.* 2001). In these studies, methane was used as a carbon source in denitrification in the presence of oxygen. Methanotrophic bacteria oxidized methane to methanol or acetate, which was then used as a carbon source in denitrification (Mechsner and Hamer 1985, and Werner and Kayser 1991). There are two main hypotheses presented in the literature to explain the results. The first is that the denitrifying bacteria are able to use methane as an electron donor in

the presence of oxygen. The second hypothesis is that consortia of methanotrophic bacteria produces an organic intermediate, which serves as a carbon source for the anaerobic denitrifying bacteria (Thalasso *et al.* 1997).

Several studies have demonstrated the second hypothesis and two possible intermediate carbon compounds have been determined, both of them are produced by the methanotrophic bacteria; acetate (Costa *et al.* 2000) and methanol (Werner and Kayser 1991, Thalasso *et al.* 1997, Rajapakse and Scutt 1999).

Denitrification can also be accomplished by autotrophic bacteria, which can use hydrogen or various reduced-sulfur compounds as energy sources. Under autotrophic growth conditions, no organic carbon is required, rather carbon dioxide or bicarbonate is used for cell synthesis.

2.3.3 Landfill Bioreactor Denitrification

The information available shows that the use of a landfill as an anaerobic bioreactor is becoming more popular due to the high efficiency in treating the leachate BOD. The introduction of nitrate-rich leachate changes the environmental conditions from anaerobic to anoxic, which promotes nitrate reduction to nitrogen gas. However, this requires an available carbon substrate.

On the other hand, VFAs have been found to be an attractive source of carbon for denitrification. As long as the landfill leachate is rich in VFAs, there is a potential for denitrification in a landfill bioreactor. In addition, denitrification generates alkalinity and this may help in establishing faster waste degradation. Therefore, it is expected that denitrification at a landfill bioreactor, may proceed with few complications under the presence of VFAs. However, in the absence of VFAs, leachate BOD may not be sufficient to support denitrification. As a result, another source of carbon and ED would be required.

In addition to VFAs, methane is a source of carbon that is available at landfill sites. However, although the feasibility of utilizing methane as a carbon and ED for denitrification is surrounded with uncertainties, there is a potential for it to work. The

microbial utilization of VFAs yields more energy than with methane; therefore, the utilization of methane is expected to be feasible only when VFAs are not sufficient to provide the carbon needed for denitrification. This potential is worth investigation. The utilization of methane by denitrification may also provide a solution for the problem of GHG emissions. Nevertheless, due to the low solubility of methane, the effect of methane utilization by denitrifiers on the methane contribution to GHGs is expected to be minor.

Under the assumption that denitrification at a landfill bioreactor is possible, there are several questions that require answers. These questions are as follows: 1) does the process of denitrification affect the existing landfill activities; 2) are VFAs always available in leachate; and 3) is methane always available at an amount sufficient to support denitrification?

In order to be able to denitrify using an anoxic landfill bioreactor, the landfill activities and products have to be studied. In the following section, the landfill stabilization phases and the stabilization products are discussed to provide a complete understanding of the process. In addition, the effects of denitrification on landfill activities are studied to explore the feasibility of the anoxic bioreactor system.

2.4 Landfill Stabilization

With a view to evaluating the feasibility of the anoxic bioreactor system, this section discusses the phases that the landfill undergoes to reach complete stabilization, the products of these phases, and the parameters that influence waste stabilization. Finally, the consequences of the application of LR technology and the effects of denitrification on the process of landfill stabilization are discussed.

Landfill solid waste undergoes many simultaneous biological, chemical and physical changes. These changes have been reported (Onay 1995) as:

- biological decomposition of organic material, with gas production;
- biochemical oxidation-reduction of organic and inorganic fractions in the solid waste;

- diffusion and transport of gases;
- dissolution and transport of constituents by leaching;
- sorption on the waste matrix;
- hydraulic liquid transport;
- movement of dissolved materials as a result of concentration gradients; and
- differential settlement caused by waste degradation and consolidation of material into void spaces.

The composition of generated leachate is governed mainly by the activities of landfill microorganisms. However, microorganism populations vary with changes in refuse composition. Both aerobic and anaerobic activities have been documented in landfills and are considered responsible for the biodegradation of solid waste under mesophilic as well as thermophilic conditions (Zinder 1993).

Aerobic microorganisms are of less significance in comparison to anaerobic ones, in terms of the scale of waste decomposition they affect. This is due to the fact that the aerobic phase lasts for only a short period of time during the initial period of landfill stabilization: at the outset, oxygen is supplied from air trapped with fresh refuse during placement, through infiltrating rain, and by the induced air flow associated with over-extraction of landfill gas. Aerobic activity decreases, however, as oxygen is depleted, favoring the enrichment of facultative anaerobic bacteria. Thus, the initial aerobic conditions are quickly followed by an anaerobic environment, which ultimately controls leachate and gas quality during most of the landfill life.

The anaerobic decomposition of the solid waste is a multistage biochemical process involving many different types of organic materials. The landfill stabilization process is divided into three degradation phases (Stronach *et al.* 1986). In the first stage, hydrolytic bacteria use cellular enzymes to convert complex organic solids, cellulose, proteins and lipids into soluble fatty acids, alcohols, carbon dioxide and ammonia. In the second stage,

acetogenic bacteria convert the products of the first stage into acetic acid, propionic acid, hydrogen, carbon dioxide and other low molecular weight organic acids. In the third and final stage, methanogenic bacteria provide the completion of waste conversion, via the production of carbon dioxide and methane.

The three steps often occur simultaneously, so that there is little accumulation of intermediates over time. However, because landfills are heterogeneous, batch-wise systems, the activities of acid-forming and methane-forming bacteria are not equal at any location at one time. As a result, landfills are often characterized as temporal stages created by a dominance of different microorganisms at different times.

Other researchers suggested that refuse decomposition occurs in five basic stages rather than three phases (Pohland 1991, Reinhart and Al-Yousfi 1996, Warith and Sharma 1998). Pohland and his co-workers have added two phases to the former model as shown in Figure 1 (shown in page 10). Their system consists of initial adjustment, transition, acid formation, methane formation and final maturation. In the initial adjustment phase, the waste is placed and the preliminary moisture is accumulated. Changes in environmental parameters are first detected, reflecting the onset of the stabilization process.

In the transition phase, the field capacity[2] is approached, and the system shifts from aerobic to anaerobic. In this phase, the primary electron acceptor shifts from oxygen to nitrates and sulfates with the displacement of oxygen by carbon dioxide in the gas phase. By the end of this phase, the accumulation of volatile organic acids has started. In the acid formation phase, intermediary volatile acids become dominate with the hydrolysis and fermentation of the waste. Due to the accumulation of these acids, the pH decreases. Nutrients (nitrogen and phosphorus) are released by the degradation of the organic materials and are utilized to support the growing biomass.

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[2] The field capacity of a landfill cell is the total amount of moisture that can be retained in that cell.

In the methane formation phase, methanogenic bacteria are the active microorganisms. They produce methane and carbon dioxide from volatile organic acids. As a result, the pH of the system increases. At low sulfate concentrations, methanogenic bacteria produce methane from carbon dioxide and hydrogen. The mass of the organics released is shifted from the leachate to the gas stream. This phase is characterized by low oxidation-reduction potentials, due to the low concentrations of sulfates and nitrates, which have been reduced to sulfides and ammonia (Paul and Clark 1989) in the previous phases.

In the final maturation phase, biological stabilization of readily available organic material has been completed. The gas production dramatically decreases and nutrients may become limiting. Oxygen and oxidized species may slowly reappear with an increase in oxidation-reduction potential.

The second model with five stages is more popular, probably because it provides a better understanding of the landfill system. The biodegradation of solid waste usually starts with an aerobic phase. This phase was not included in the first model. The aerobic phase is followed by a short anoxic phase, which occurs before the system is completely anaerobic. The anoxic phase is also neglected in the first degradation model. In addition, the first model assumes that the last stage in the landfill cycle is the methane formation phase. However, this is not the case in practice, since the level of the methanogenic activity is found to be low after most of the available organics have been degraded. Therefore, the second model, which includes a final maturation phase, provides a better representation of the landfill activities.

Variations between real and typical stabilization progressions should be expected due to various physical, chemical and biological factors within the landfill environment. However, in the absence of inhibition, stabilization in landfills always proceeds, even though the time needed for completion can vary and often can be controlled by operational and management measures such as LR.

2.4.1 Landfill Leachate

Leachate is defined as the liquid that has percolated through solid waste and has extracted dissolved and/or suspended materials. Sources of moisture can include surface drainage, precipitation, groundwater, liquid squeezed out due to the waste pressure and moisture produced from waste decomposition. Precipitation and moisture at placement are the foremost contributors to leachate generation.

Both quality and quantity of leachate are important issues for landfill design; however, leachate characteristics vary widely (Table 5), and no general method has been developed to predict the exact composition of leachate in a particular landfill at a specific time. The factors that affect the quality and quantity of leachate the most include the following: 1) the nature of the waste disposed; 2) the climatic and hydrologeologic influences; 3) the state or extent of waste decomposition; 4) the chemical and physical properties of the percolating water; and 5) the adjacent soil cover (Ontario Ministry of Environment and Energy 1995).

Moisture accumulates in the refuse until the field capacity is reached. Then, active microbiological environments develop, and waste degradation takes place. The extent of the biological individual reactions in a landfill is a function of the moisture content after the field capacity is reached. The leachate is released based upon the amount of moisture percolating into the landfill. Leachate is characterized as an industrial wastewater due to its strength and toxicity. Typical leachate characteristics are shown in Table 5.

Treatment of leachate is required to reduce and/or eliminate its impact on the environment. Leachate treatment is site-specific and must be dealt with on a case-by-case basis. The selection of leachate treatment method depends on leachate volume and characteristics, as well as the effluent criteria desired for each landfill. The Ontario Ministry of Environment and Energy (1995) conducted a comprehensive study on leachate treatment and suggested the use of biological treatment to remove ammonia, both for new leachate with high BOD:COD ratios, as well as for old leachate. The leachate BOD and ammonia are biodegradable, and there is extensive literature available that discusses different biological methods to treat them. For leachate with high BOD

(more than 1 g/L), anaerobic treatment may be considered as a pre-treatment, while for low strength leachate, lagoons can be considered effective. For old leachate, physical-chemical treatment is more suitable for removing leachate COD.

Table 5 Typical landfill leachate characteristics

Constituent	Value in mg/L (except pH)		
	New landfill (less than 2 years)		Mature landfill (greater than 10 years)
	Range	Typical	
BOD	2000-30000	10000	100-200
TOC	1500-20000	6000	80-160
COD	3000-60000	18000	100-500
Total Suspended Solids	200-2000	500	100-400
Organic nitrogen	10-800	200	80-120
Ammonia	10-800	200	20-40[3]
Nitrate	5-40	25	5-10
Total phosphorus	5-100	30	5-10
Ortho-phosphorus	4-80	20	4-8
Alkalinity as $CaCO_3$	1000-10000	3000	200-1000
pH	4.5-7.5	6	6.6-7.5

Adapted from Tchobanoglous *et al.* (1993)

In order to achieve complete treatment for leachate, neither biological treatment nor physical-chemical treatment alone can produce an effluent of high standard. The high cost associated with leachate treatment and the long associated stabilization time support the use of a landfill bioreactor (section 2.2). However, this management option produces high ammonia leachate requiring further treatment.

2.4.2 Landfill Gas Formation, Impact, and Control

Landfill gas is produced as a result of the waste degradation that takes place in the landfill bed, a process that starts soon after waste placement. The process of waste degradation has been divided into several phases as discussed earlier (see section 2.4).

The composition of landfill gas is highly dependent on the decomposition stage within the landfill. Investigators have identified several major steps characterizing the anaerobic decomposition phase during which organic materials are converted to methane and

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[3] This range is considered to be low and does not agree with other studies such as those summarized in Table 1 and Table 2.

carbon dioxide (Reinhart and Al-Yousfi 1996, Warith and Sharma 1998). These steps are highly interdependent and include hydrolysis, acidogenesis, acetogenesis and methanogenesis. Under stabilized methanogenic conditions, methane and carbon dioxide are, by far, the two principal components of landfill gas and form more than 90% of the total gas generated. Methane and carbon dioxide generation occurs primarily through acetate cleavage. Methane is also produced through carbon dioxide reduction with hydrogen. In a landfill environment, methane generation from the latter route is often limited by the lack of hydrogen, which is consumed by sulfate reducers.

Nitrogen and oxygen are normally present in small amounts primarily as a result of air entrapment during waste deposition, atmospheric air diffusion through the landfill cover, especially in the near surface layers, or air intrusion from negative landfill pressure when landfill gas is extracted. The composition of the landfill gas is time dependent. Figure 1 (page 10) shows that as time passes, the composition of the gas changes. Table 6 summarizes the composition of a typical landfill gas.

Table 6 Landfill gas composition

Component	Concentration Range (% dry volume)
Methane	40-70
Carbon Dioxide	30-60
Carbon Monoxide	0-3
Nitrogen	3-5
Oxygen	0-3
Hydrogen	0-5
Hydrogen Sulfide	0-2
Trace Compounds	0-1

Adapted from El-fadel *et al.* 1997

Quantitatively, the gas yield is of special interest because of the potential value of landfill gas as an energy source and its impact on the environment. Generation rates of landfill gases are the controlling factors in assessing the feasibility of exploiting a landfill site. Estimation of gas generation rates is a very important process, which usually depends on experimental studies. Lab-scale experiments are not reliable sources of information for predicting gas generation rates. Therefore, test-cells are recommended. While experimental studies result in gas generation rates on the order of 0 to 488 L/kg· yr, estimates from measurements at full-scale landfills fall within a narrower range of 1 to 14

L/kg· yr (Abufayed and Schroeder 1996). The variables that are expected to influence the volume and rate of emission are waste characteristics, moisture content, temperature, pH, the availability of nutrients and microbes, the presence of inhibitors, and the adoption of enhancement techniques, if any (U.S. EPA 1993).

Landfills that fail to control the release of gas tend to harm the environment. In the following section, the effects of methane on the environment are discussed.

2.4.2.1 Potential Environmental Impacts of Methane

The United States EPA estimated methane emission from landfills (in North America) to be in the range of 25 to 40 Tg/yr[4] (U.S. EPA 1990). Gas control systems can successfully reduce the following impacts and, therefore, lower the liabilities associated with landfill operations.

Landfill methane accounts for 3 to 19% of the global anthropogenic sources of methane (David 1997). Methane has a global warming potential 20 to 25 times greater than that of carbon dioxide (El-Fadel *et al.* 1997). On a global basis, atmospheric methane is increasing at about 1% per year while CO_2 is increasing at about 0.4% per year (David 1997). Methane is thought to be responsible for approximately 20% of the current increase in global warming (U.S. EPA 1990). In Canada, methane is the second most important GHG after carbon dioxide, and landfill gas is one of the largest sources of methane emissions to the atmosphere. Combustion of landfill gas reduces the global warming impact by 95% through the conversion of methane to carbon dioxide; moreover, it destroys many other contaminants such as volatile organic compounds.

Other impacts of methane may depend on the pathway by which the gas migrates to areas of human activity and the environment. Migrating gas produces a number of problems. The most obvious is odor; however, other hazards are more serious. Methane gas can collect in basements and other subterranean areas and can be explosive in concentrations

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[4] Teragram (Tg) is 1 million metric tonnes or 10^{12} grams

as low as five percent. It can also be harmful to vegetation (Hill 1991). For these reasons, the demand for control of landfill gas is rising.

2.4.2.2 Methane Control

To reduce methane emissions from landfills, two strategies are currently being used. The first strategy stimulates methane production at an isolated landfill. Under this situation, an impermeable layer caps the landfill to prevent gas emission. The generated waste gas has to be removed to protect the cap from rupture. The gas is collected in recovery wells inside the landfill and withdrawn by pumping. Recovery efficiencies of 50 to 85% are possible, with methane concentrations varying from 40 to 70% (U.S. EPA 1990, Hill 1991, David 1997). The gas can either be used for energy production or burned in a flare.

The second strategy is to inhibit methane production by maintaining an aerobic landfill and/or reducing the amount of organic waste in landfill. In an aerobic landfill, the ratio of CH_4 to CO_2 production shifts towards CO_2 production as a consequence of the improved oxidation in the landfill. Instead of being fermented, the waste is composted. Another way to reduce methane emission is to reduce landfilling of organic waste. Biological, chemical and/or thermal processes may treat the organic fraction of the MSW.

2.4.3 Factors Controlling Landfill Stabilization

Waste decomposition and in particular, methane production, are affected by several factors in the landfill environment such as oxygen, pH, moisture content and inhibitors. These parameters may be influenced by the landfill management procedures. The processes of waste degradation have been studied with the focus on the methanogens. This may be due to the importance and/or sensitivity of methanogens. The degradation processes –excluding methanogenesis- are poorly documented and rarely investigated. The effects of individual factors on waste degradation are discussed in the following paragraphs.

Moisture content: The availability of moisture at a level of 25 to 60% has been shown to exponentially increase methane gas production (Mata-Alvarez and Martinez-Viturtia

1986, Westlake 1995, Warith and Sharma 1998). The benefits of the increased water content in a landfill include the limiting of oxygen transport from the atmosphere, the facilitating of exchange of substrate, nutrients and buffer, the dilution of inhibitors and the spreading of microorganisms within the landfill.

The optimum water content varies between 40 to 80% depending on the waste composition and landfill environmental conditions (Munasinghe 1997). A decrease in gas production has been reported with relatively high moisture content, especially in shallow and poorly insulated sites (Barlaz *et al.* 1989, Westlake 1995, Munasinghe 1997).

Oxygen: Methanogens have the reputation of being the strictest anaerobes. It is considered that methanogens need an oxidation/reduction potential of –0.3 V (Zinder 1993). Extensive gas recovery pumping may create a substantial vacuum in the landfill. This would extend the aerobic zone in the landfill waste and eventually prevent formation of methane in these layers. However, under normal conditions, aerobic bacteria at the top of the landfill consume the oxygen and limit the aerobic zone to less than 1 m of compacted waste (Christensen and Kjeldsen 1987).

New findings show that methanogens can withstand oxygen, especially in granular sludge (Bitton 1999), or in a microenvironment where they are protected from the detrimental effects of oxygen. Landfills are rich in microenvironments where methanogens are able to grow in the presence of limited amounts of oxygen.

pH: Most methanogens function within a pH range of 6.7 to 7.4, but the optimum pH is between 7 and 7.2; however, the process of methanogenesis may fail if the pH falls to 6. Acidogenic bacteria produce organic acids, which tend to lower the pH of the leachate. Under normal conditions, this pH reduction is buffered by bicarbonate produced by methanogens (Bitton 1999).

On the other hand, if the methanogenic activity is low, the conversion of hydrogen and acetic acid decreases. This causes hydrogen pressure to build up, and at elevated partial pressures, acetogenic bacteria cannot convert volatile fatty acids, particularly butyric and propionic acid (Christensen and Kjeldsen 1987). The accumulation of these acids

consequently lowers the pH within the landfill and eventually stops methane production. The methanogenic system in the landfill is rather delicate. Balanced relations between various bacterial groups are crucial for optimal methane production.

Monitoring the ratio of total volatile acids (as acetic acid) to total alkalinity (as calcium carbonate) has been recommended to ensure that it remains below 0.1 (Bitton 1999). A buffer material, such as demolition waste or soil could be added to the landfill so that an appropriate pH level is maintained (Warith and Sharma 1998).

Temperature: Methanogens are found in a wide variety of thermal regimes ranging from 2°C to 100°C (Zinder 1993). There is a great diversity of psychrophilic, mesophilic, and thermophilic methanogens. The optimum temperature for methanogenic activity was found to lie near 35°C (McCarty 1964, Mata-Alvarez and Martinez-Viturtia 1986). To adapt methanogens to high temperatures, an organism must ensure that its macromolecules (proteins, nucleic acids, and lipids) can maintain their structure and function at elevated temperatures.

It was indicated that in a deep landfill with a moderate flux, a temperature of 30° to 45°C is expected, even in temperate climates (Christensen and Kjeldsen 1987). This was attributed to a low heat flux from the landfill to the surroundings due to the insulating effect of the waste. The anaerobic decomposition process generates the heat.

Sulfate: Methanogens and sulfate-reducing bacteria may compete for the same electron donors, acetate and hydrogen. Sulfate-reducing bacteria have a higher affinity for acetate (K_s = 9.5 mg/L) than methanogens (K_s = 32.8 mg/L) (Bitton 1999). This means that sulfate-reducing bacteria can out-compete methanogens under low acetate concentrations. This competitive inhibition results in the shunting of electrons from methane generation to sulfate reduction.

Sulfate reducers and methanogens are very competitive at COD/SO_4^{2-} ratios of 1.7 to 2.7 (Bitton 1999). An increase in this ratio is favorable to methanogens, whereas a decrease in the ratio is favorable to sulfate reducers.

Inhibitors: In addition to the inhibitory effects of oxygen, hydrogen and sulfate, it has been suspected that carbon dioxide, salt ions, sulfide, heavy metals and ammonia are potential inhibitors of methane production. It was reported that at carbon dioxide partial pressures between 0.2 to 1 atm, the conversion of acetic acid decreases (Christensen and Kjeldsen 1987). Cations such as sodium, potassium, calcium, magnesium and ammonium have been observed to stimulate anaerobic decomposition at low concentrations while they inhibit it at high concentrations (Christensen and Kjeldsen 1987).

Nutrients: Microorganisms that participate in the anaerobic degradation of waste require nitrogen and phosphorus as well as sulfur, calcium, magnesium, potassium, iron, zinc, copper, cobalt and selenium. These nutrients are found in most landfills. However, insufficient homogenization of the waste may result in a nutrient-limited environment. It was reported that optimal ratios between organic matter (expressed as COD mg/L), nitrogen and phosphorus are as 100:0.44:0.08 (Christensen and Kjeldsen 1987). In cases where there is a limiting nutrient for anaerobic degradation, phosphorus would be the most likely limiting element (Warith and Sharma 1998).

Salinity: Methanogens can be found over the complete range of salinities, from fresh water to hyper-saline water. Fresh water methanogens require a minimum concentration of 23 ppm Na^+ (Zinder 1993). Fresh water methanogens may be found in the marine environment after an adequate adaptation period. Adaptation to the marine environment causes a drop in the maximum growth temperature from 55°C to 45°C. Salt-adapted cells can be slowly adapted back to fresh water (Bitton 1999).

Management Procedures: Waste degradation is enhanced by several measures that may be used as part of a landfill management system. These procedures include LR, the addition of sludge as a source of microorganisms and nutrients, the reduction of particle size, the addition of enzymes and the reduction of the height and density of the waste layer (Warith and Sharma 1998). Adapting one or more of these options may result in faster degradation.

2.4.3.1 Effect of Denitrification on Waste Degradation

The idea of using a landfill bioreactor was introduced to enhance and accelerate waste stabilization. The feasibility of using this bioreactor to treat nitrate depends on its impact on waste degradation. Although waste degradation passes through many phases, the literature does not address the effects of the denitrification on all the phases. A few studies have been conducted to examine the effect of the denitrification process on methanogens during wastewater treatment (Westermann and Ahring 1987, Chen and Lin 1993, Hendriksen and Ahring 1996, Akunna *et al.* 1998, Fang and Zhou 1999).

Methanogens and denitrifying bacteria both share the same source of carbon and electron donors (Westermann and Ahring 1987). At low substrate concentrations, bacteria with higher kinetic constants are able to survive. Fang and Zhou (1999) have investigated the interactions between methanogens and denitrifiers in an anaerobic sludge digester. They found that denitrifiers out-competed methanogens for substrates. They determined that methanogenesis occurred only at COD/NO_3-N ratios greater than 3.34. Below this ratio, methanogenesis stopped, and denitrification became incomplete due to an insufficient supply of substrate.

In surplus carbon conditions, both populations can coexist if either are separated in time or space (Chen and Lin 1993, Hendriksen and Ahring 1996, Akunna *et al.* 1998). If the two groups of bacteria are not separated, denitrification completely inhibits methanogenesis even under surplus carbon conditions. Yet, this inhibition is reversible and temporary. According to Hendriksen and Ahring (1996), methanogenic activity resumes soon after nitrate depletion. They claim that denitrification influences the kinetics and population of the methanogenic bacteria, since certain substrates are preferred and thus exhausted by denitrifiers.

As mentioned previously, methanogenic bacteria require environments with very low redox potential (E_h). Therefore, it is expected that the relatively high redox potential associated with the presence of nitrate might be one cause of the inhibition. Akunna and others (1998) have investigated the effect of nitrate and hence the high redox potential on the methanogens' activities. Their results confirm that the methanogens' activities were

reduced in the presence of nitrate and carbon at low redox potential[5] (-300 mV). However, these activities were re-established after all nitrogen oxides had been reduced. Studies have shown that the inhibition of methanogenesis could not be attributed entirely to the higher redox potential associated with the presence of denitrification (Chen and Lin 1993, Akunna *et al.* 1998). Akunna and his co-authors (1998) stress the feasibility of simultaneous denitrification and methanogenesis processes in zones of different concentrations.

A few researchers have suggested that the inhibition of methanogens by denitrification may be due to poisoning (Westermann and Ahring 1987, Chen and Lin 1993). However, they found that methanogen activity resumes immediately after the disappearance of the nitrogen oxides from the system.

The studies in the literature agree on the inhibition effects of denitrification on methanogens. Therefore, the design of a denitrification landfill bioreactor may be a challenge, with more difficulties expected to rise in practice.

2.5 Overview

The method of LR was introduced as a landfill management option in the 1970s. Since then, the practice has flourished and more landfills are adopting this system as a management strategy. The popularity of LR is due to its ability to accelerate landfill stabilization, improve the quality of leachate and its ease of operation. However, a few issues arise as a consequence of adopting this management strategy.

Landfills with LR produce leachate with high ammonia that is toxic to many aquatic organisms and requires challenging and expensive treatment. In addition, these landfills generate more gas. As most of the landfill operations fail to manage their gas properly, landfill bioreactors release it into the atmosphere, contributing to the total GHG load.

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[5] This low ORP was obtained by using cultures containing cysteine solution.

The use of landfill bioreactors to treat the leachate nitrogen with landfill by-products may be a promising option; however, it is also surrounded with challenges and uncertainties. Nevertheless, this technology has too great a potential for this idea not to be pursued.

The suggested system is shown in Figure 2. The system is proposed to treat leachate nitrogen in two steps. In the first step, the leachate is nitrified in an old cell (no carbon) using an aerated landfill bioreactor. In the second step, the nitrate-rich leachate is denitrified in either an old or a new cell. Leachate and methane provide the sources of carbon and ED needed for denitrification. Recycling and bypassing may be used at any point, depending on the need to optimize the process.

The literature reviewed in this chapter suggests that this process is feasible. In this research, only the second step of the process (denitrification) is investigated.

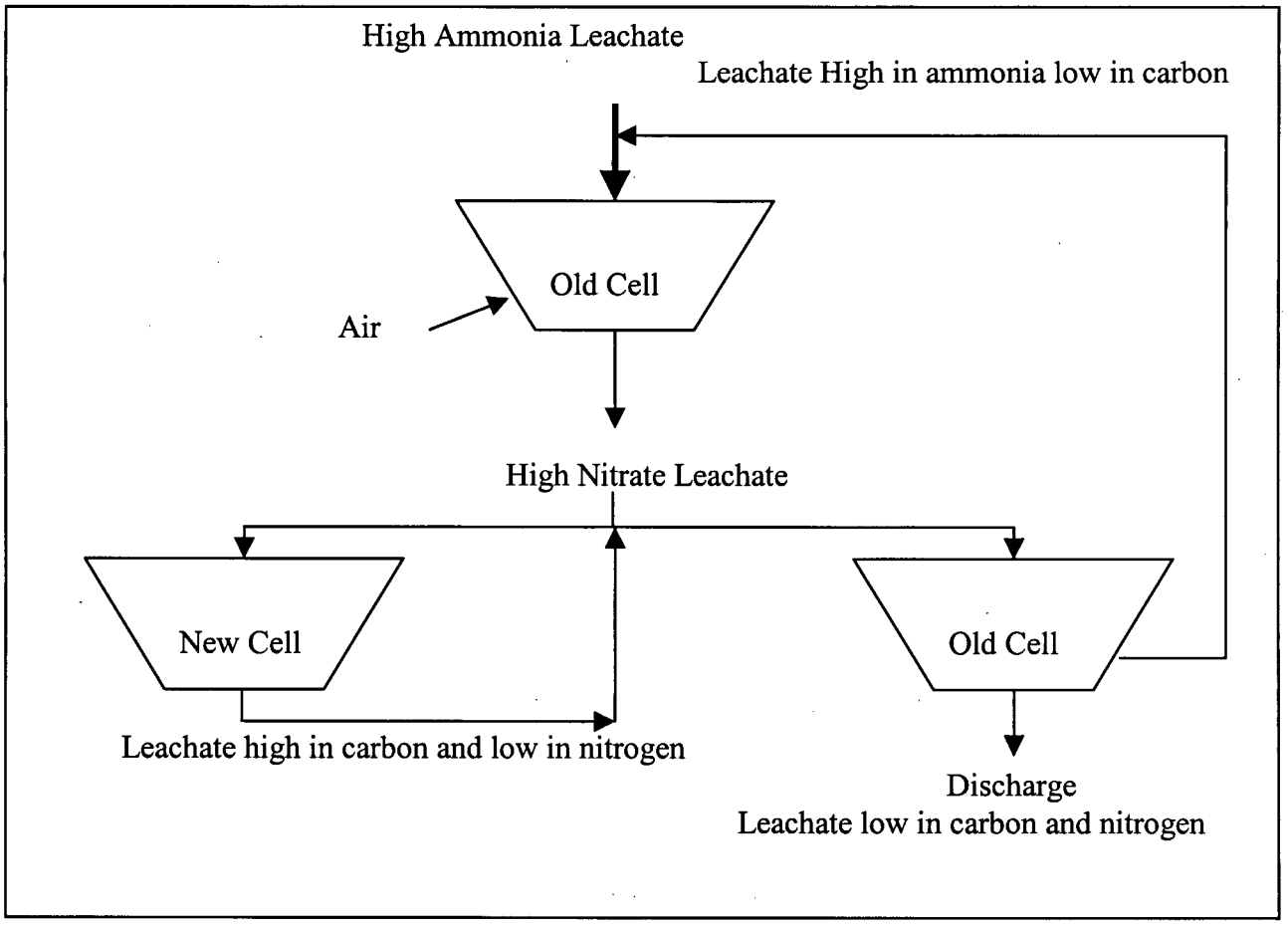

Figure 2 Suggested system to remove leachate nitrogen.

3 Research Objectives

LR produces high ammonia leachate. Assuming that ammonia is nitrified either using the aerobic landfill bioreactor or an external treatment method, the nitrified leachate will be rich in nitrate. This nitrate is harmful to the receiving water and requires further treatment. Another problem that is associated with LR is that these landfills generate more gases that harm the environment if not managed properly.

The use of LR to treat nitrified leachate seems to be feasible but challenging. Landfill gas and leachate have potential to serve as sources of ED and carbon to support denitrification. Alternatively, denitrification has been found to inhibit methanogens. Therefore, having an anoxic zone in a landfill bioreactor without introducing adverse effects to the rest of the system may be tricky, but still may be possible. This research was conducted to investigate the possibility of the second part of the process discussed earlier in section 2.5 and shown in Figure 2.

The objectives of this research were to investigate the following.

1. the use of the landfill bed to biologically denitrify the nitrified leachate;
2. the utilization of the leachate BOD as a carbon source for denitrification;
3. the utilization of landfill gas as a source of carbon for denitrification;
4. the reduction of the emission of methane gas to the atmosphere.

The research was conducted to answer the following questions.

1. Is the landfill capable of providing nitrate removal?
2. Can the process of denitrification in a landfill bioreactor be self-sufficient (i.e., no need for external source of ED and carbon)?
3. Can an anoxic landfill bioreactor proceed without disturbing accelerated waste degradation?

4. Is the system capable of utilizing methane as a carbon source for denitrification?

5. Will the system be able to provide a solution for the released methane as a GHG?

6. How does the system perform with different leachate strengths?

7. Can the system tolerate changes in leachate characteristics?

8. What is the maximum nitrate concentration that the system will be able to treat?

9. What is the maximum nitrate removal rate that the system can achieve?

To answer each of these research questions, two sets of experiments were designed. The full description of these experiments is shown in the following chapter.

4 Experimental Methodology

Two experiments were designed and run based on the methodology defined and illustrated in this chapter. The two experiments were as follows: 1) the "Landfill Bioreactor Denitrification Experiment"; and 2) the "Denitrification Batch Test Experiment". This chapter outlines and describes the materials used in constructing and running the experiments and the methods used to operate the experiments. The chapter is divided into three sections; the first section outlines the research scheme, the second section describes the materials and methods of the first experiment and the last section describes the materials and methods of the second experiment.

4.1 Research Scheme

Table 7 provides a summary of the two experiments.

Table 7 The outline for the experiments scheme

	Experiment 1	**Experiment 2**
Name	Landfill Bioreactor Denitrification	Denitrification Batch Test
Objective	To investigate the feasibility and the efficiency of denitrification in a landfill bioreactor using methane and/or leachate as the carbon source.	To investigate the kinetics of denitrification using landfill end-products as the carbon and ED source.
Reactors	Lysimeters (30 L)	Batch test (0.5 L)
Preliminary phase	Yes	Yes
Number of Phases	5	2
Duration (day)	510	90

4.1.1 Experiment (1): Landfill Bioreactor Denitrification

In the first experiment, "Landfill Bioreactor Denitrification", eight lysimeters were used to investigate the feasibility of denitrification in landfill beds and to examine the ability of leachate and/or methane to support denitrification. The lysimeters were designed to represent a zone in the landfill column where denitrification takes place. The detailed information about the lysimeters design, material and fill are in section 4.2.

This experiment started with a few preliminary studies, which were followed by five experimental phases as described in Table 8. The preliminary studies were conducted to

determine the characteristics of the lysimeters (such as moisture content and HRT). The overall experiment lasted for 510 days.

Table 8 Description of the phases of the first experiment

Phase	Objective	Duration (weeks)	Number of lysimeters used
Preliminary	Specify the initial characteristics of the lysimeters.	15	8
1.1	Activate denitrifiers and investigate their efficiency.	15	8
1.2	Investigate the effect of changing nitrate concentration on denitrification efficiency.	7	8
1.3	Evaluate the long-term performance of the anoxic bioreactor at low nitrate concentration (100 mg-N/L).	17	5
1.4	Evaluate the long-term performance of the anoxic bioreactor at high nitrate concentration (1500 mg-N/L).	17	5
1.5	Investigate the ability of methane to serve as the potential carbon and ED source for denitrification.	15	2

The first phase (1.1), investigated the possibility of denitrification in a landfill bioreactor over a period of 15 weeks. To achieve this objective, the lysimeters were fed with a nitrate solution, and the nitrogen contents of the leachate and gas were determined. In this phase (1.1), the effect of denitrification on waste degradation was also investigated. To increase the possibility of denitrification, the nitrate concentration in two of the lysimeters was set as low as 20 mg-N/L. To determine the range of nitrate concentrations that the reactor could tolerate, nitrate concentrations were varied from 20 to 800 mg-N /L. The capability of leachate and gas to support denitrification was also explored in this phase (1.1), as well as in all of the following phases of this experiment. For Quality Assurance and Quality Control (QA/QC) purposes, two lysimeters were set as controls and received tap water. The detailed concentrations are given in section 4.2.6 and the results of this experiment are shown and discussed in section 6.1.2.

The second phase (1.2) investigated the effect of changing the nitrate concentration on the landfill behavior and continued investigating the effect of denitrification on waste degradation. The detailed description of the method used is given in section 4.2.7 and the results are shown and discussed in section 6.1.3. This phase lasted for seven weeks.

The third (1.3) and fourth (1.4) phases were conducted in parallel to determine the effect of the lysimeter carbon content (i.e. landfill age) on denitrification at low and high nitrate concentrations. The detailed methods for the third and fourth phases are given in section

4.2.8 and section 4.2.9 respectively, while the results of the two phases are shown and discussed in section 6.1.4 and section 6.1.5 respectively. Both phases lasted for 17 weeks.

The last phase (1.5) of this experiment was conducted to specifically investigate the feasibility of using methane as a carbon source to support denitrification. Because the lysimeters were designed to represent an anoxic zone, the methanogens were not expected to provide sufficient amounts of methane, and therefore, methane gas was supplied to the lysimeters. Only two lysimeters were used for this purpose. The fifth phase (1.5) lasted for 15 weeks and its method is described in section 4.2.10. The results of this phase are shown and discussed in section 6.1.6.

The first experiment (Landfill Bioreactor Denitrification) examined the behavior of the denitrifying bacteria in a complex environment. Under such conditions, bacteria exist in a mixed culture and many factors may affect the results. Thus, it seemed necessary to investigate the behavior of the denitrifying bacteria with a higher level of control over the environment. The second experiment was conducted to achieve this goal.

4.1.2 Experiment (2): Denitrification Batch Test

The second experiment, "Denitrification Batch Test", was divided into two phases. The first phase (2.1) investigated the potential of denitrifiers to grow on methane. In addition, a kinetic study was performed to compare denitrification with methane to that with methanol, VFAs, and leachate. The method for phase 2.1 is given in section 4.3.1.3, and the results are shown and discussed in section 6.2.1.

In the second phase (2.2) of the second experiment, a few batch tests were conducted to evaluate the use of leachate as a source of carbon and/or ED for denitrification, and to explore the effect of the leachate strength on denitrification. The experimental method for phase 2.2 is described in detail in section 4.3.2.3, while the results are given in section 6.2.3.

Table 9 Description of the phases and tests of the second experiment

Phase	Test	Objective	Number of runs	Number of reactors used
2.1	Preliminary	To test the procedure designed for the following phases, and determine the design parameters.	1	8
	Methanol	To test the kinetics of denitrification using methanol as the only carbon source.	5	3
	Methane	To test the kinetics of denitrification using methane as the only carbon source.	5	3
	Leachate	To test the kinetics of denitrification using leachate and its acids as the carbon sources.	1	8
2.2	Leachate	To evaluate the effect of the leachate strength on the denitrification kinetics	1	33

4.2 Experiment (1): Landfill Bioreactor Denitrification

This experiment was designed to examine denitrification in an anoxic zone of a landfill bioreactor treating nitrified leachate (i.e. rich in nitrate). As described in section 4.2.2 and shown in Figure 3, eight lysimeters were constructed, filled with refuse (see section 4.2.1 for refuse composition and characteristics), and fed with nitrate solution. The lysimeters were supported by a steel frame. Each lysimeter was connected to a gas meter to record gas production. Diligence was exercised in having identical lysimeter configurations; however slight variations were still expected due to unavoidable differences in the orientation, level of placement and organic waste characteristics.

This experiment began with preliminary tests. After these initial tests, five experimental phases (phases 1.1 to 1.5) were run. Full descriptions of the operating methods for each phase are given in sections 4.2.5 through 4.2.10. This experiment was completed in five phases, over a 510-day period as described in Table 8 and Table 10. Testing was conducted in a controlled temperature room to avoid temperature changes and to simulate an ideal landfill temperature. The control temperature was set at 31°C.

Table 10 Phases of the Landfill Bioreactor Denitrification Experiment

Phase	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M
Preliminary	**15 weeks**																
Phase 1.1				**15 weeks**													
Phase 1.2								**7 weeks**									
Phase 1.3										**17 weeks**							
Phase 1.4										**17 weeks**							
Phase 1.5														**15 weeks**			

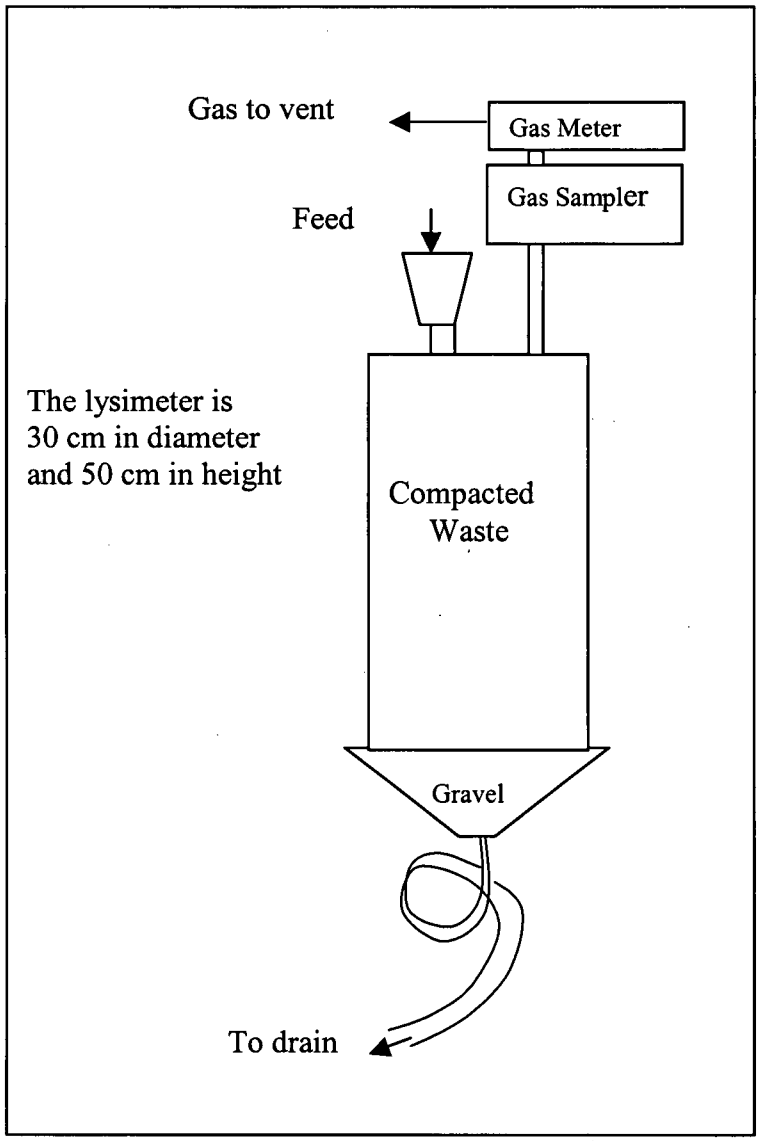

Figure 3 The lysimeter set-up

4.2.1 Refuse

A previous study by Munasinghe (1997) was conducted in the Department of Civil Engineering at the University of British Columbia (UBC) to investigate the effect of HRT on landfill end-products. In order to remain consistent with that study (Munasinghe 1997), the same refuse proportion was used. The composition of refuse is illustrated in Table 11. This composition is based on refuse generated within the Greater Vancouver Regional District (GVRD) where a plastic, glass, metal and paper recycling program is in effect.

Table 11 Waste composition

Waste	Weight %
Organic (food and yard)	52.8
Paper	31.7
Glass	4.1
Metal	5.7
Plastic	5.7

Adapted from Munasinghe, 1997.

Food waste was collected from The University of British Columbia's family housing complex. Other categories were collected from the Vancouver KENT Transfer Station.

Refuse physical parameters such as particle size and waste density were controlled to reduce the effect of the heterogeneous media on the experimental results. Food, yard, paper, metal and plastic were shredded to a 2 to 5 cm particle size. Glass was broken into 2 to 5 cm pieces. All categories were mixed together using a concrete mixer according to the proportions shown in Table 11.

4.2.2 Lysimeters

Eight lysimeters were constructed as anoxic bioreactors for denitrification. The lysimeters were constructed using 30 cm diameter PVC pipes having a height of 50 cm. The lysimeters had a flange at the top and a cone at the bottom, both of which were of fiberglass fabrication.

The top was sealed with a lid to secure the system and prevent gas from escaping. Gas was collected from the top, sampled, measured by a wet gas meter and then vented to the

atmosphere. A chemical feed was needed to aid in the denitrification process. The feed was introduced to the refuse from the top of the lysimeter using a ring of plastic tubing to ensure even distribution.

The bottom was filled with 19 mm gravel with a layer of pea gravel on top. Leachate was collected at the bottom using a U-shaped 12 mm tube equipped with a valve to prevent air entry from the bottom. The leachate was discharged into a drain unless samples were needed. Another tube passed through the fiberglass cone and the gravel to deliver methane gas to the refuse (for lysimeter number 8 only). The tube was connected to a valve to control the gas flow. A frame was constructed to provide adequate support for the lysimeters. The lysimeter set-up is shown in Figure 3.

Each lysimeter was filled with five batches of the waste mixture. The batch container used was designed specifically for this purpose. The batch container had the same diameter (30 cm) as the lysimeter and a removable bottom. Each batch was filled with 3.22 kg of mixed waste; the waste was compacted by tapping it down to a height of 8 cm. Then the bottom was removed, and the batch was placed on the top of the lysimeter. The waste was then transferred to the lysimeter by applying pressure to the top of the batch. After the fifth batch, the waste reached a height of 40 cm and had a density of 570 g/L.

4.2.3 Gas-meters

Eight wet gas meters (manufactured by the UBC civil and mechanical machine shop) were used to measure gas production. The gas meters were calibrated and then attached to each of the lysimeters using plastic tubing. Once the gas meter was connected, the system was completely sealed against air entry.

4.2.4 Feed

A nitrate solution was used as a feed and a simulated precipitation for the lysimeters. Potassium nitrate (KNO_3) was used to provide the nitrate concentration required for denitrification. The feed was purged with nitrogen gas in the fifth phase. Pure methane gas was used for lysimeter 8 in the fifth phase.

Two liters of sludge from the UBC pilot plant operated by the Environmental Engineering Group at UBC were added to the top of the lysimeter to shorten the lag phase. The leachate had sufficient nutrients and the process of denitrification did not require the addition of any kind of buffer.

4.2.5 Methodology –Preliminary studies

The first objective of this phase was to insure that the lysimeters built (as described in section 4.2.2) and filled with the waste (as specified in section 4.2.1), were identical. The second objective was to specify the initial characteristics of the lysimeters.

The moisture content of the mixture was measured prior to filling the lysimeters. It was assumed that the paper moisture content was 6% (Tchobanoglous *et al.* 1993), and that glass, metal and plastic had a moisture content of zero. Therefore, the main source of the waste moisture content was the organic waste (food and yard waste). Representative samples were chosen from the food and yard wastes. The weight of each sample was measured initially. Samples were then put into an oven to dry at 105 °C. The weight of each sample was measured on a daily basis until it stabilized within a 5% difference. The difference between the initial and final weight was calculated, and the moisture content was determined.

After all lysimeters were filled and compacted, the lysimeters were then flooded with water and allowed to stand for four days so that the refuse was well wetted. The saturated water was then drained and measured to find the refuse sorption capacity. Then each lysimeter was seeded with the 2 L of sludge.

After the lysimeters were seeded, they were covered at the top and sealed to avoid air entry. The lysimeters were then ready to start the first phase of operation.

4.2.6 Methodology –Phase 1.1

The aim of this phase was to ensure that the denitrifier culture was active so that the efficiency of denitrification in the lysimeters could be evaluated. Therefore, nitrate as potassium nitrate (KNO_3) was added to six lysimeters with concentrations as shown in

Table 12, and at a constant rate of 400 mL/day to all the lysimeters. The nitrate concentration range was chosen based on the typical leachate ammonia concentration reported in the literature (Pacey 1989, Reinhart and Al-Yousfi 1996), with an assumption that local precipitation would have some dilution effect (at least 20%). This would possibly reduce the nitrate concentration. The range was set to cover all of the phases that the landfill passes through.The lysimeters were run in pairs, so that each concentration was applied to two lysimeters. The flow rate was constant for all phases of the experiment. The influent nitrate concentration remained constant throughout phase (1.1). The leachate was analyzed for COD, BOD_5, VFA, pH, ORP, NO_x^-, NH_4^+, and PO_4^{2-}. The gases produced were measured and analyzed. This phase occurred over a period of 15-weeks.

Table 12 Operating conditions for the anoxic lysimeters

Lysimeter Number	Nitrate Concentration (mg-N/L)
1-2	0 (control)
3-4	400
5-6	20
7-8	800

4.2.7 Methodology –Phase 1.2

In this phase, the nitrate concentrations were changed to evaluate the effect of the changes on gas production and composition. Starting from the first day of the phase, the concentrations were changed gradually (the new load was either increased or decreased by 10%/day) to avoid shock loading. Table 13 shows the changes in nitrate concentrations. Table 13 also shows that duplicate lysimeters were run during this phase. The feed flow rate remained at 400 mL/day for all the lysimeters. This phase lasted for 7 weeks.

Table 13 Nitrate concentrations during the second phase

Lysimeter Number	Nitrate Concentration mg-N/L	
	Phase –1.1	Phase –1.2
1-2	0 (control)	0 (control)
3-4	400	600
5-6	20	100
7-8	800	600

4.2.8 Methodology –Phase 1.3

In this phase, the behavior of the lysimeters was monitored to evaluate the long-term performance of a bioreactor with relatively low nitrate loadings. Two lysimeters were used as control, with a zero nitrate feed, and three lysimeters were used as anoxic bioreactors. The three lysimeters chosen for this phase were 5, 6, and 7. The nitrate concentration was 100 mg-N /L and the flow rate was 400 mL/d. This phase (1.3) lasted for 17 weeks and was completed in parallel with the following phase (1.4).

Table 14 Nitrate concentration during phase 1.3

Lysimeter Number	Nitrate Concentration (mg/L)
1-2	0
5	100
6	100
7	100

4.2.9 Methodology –Phase 1.4

The objective of this phase was to evaluate the effect of the carbon content of the lysimeter on denitrification. Three lysimeters (3, 4 and 8) were chosen based on their carbon content to represent situations of low, medium and high carbon content. This was achieved by calculating the carbon released during the previous phases (assuming that all the lysimeters start with the same carbon content). Lysimeter 4 was found to be low in carbon, lysimeter 3 was found to have low to moderate amount of carbon while lysimeter 8 was found to be high in carbon. All of the three lysimeters were fed with nitrate solution of 2000 mg-N/L at a flow rate of 400 mL/d. Lysimeters 1 and 2 were used as controls and received tap water at the same flow rate. After three weeks, the nitrate concentration was lowered to 1500 mg-N/L. This phase (1.4) lasted for 17 weeks.

Table 15 Nitrate concentration during the phase 1.4

Lysimeter Number	Nitrate Concentration (mg/L)	
	3 weeks (initially)	14 weeks
1-2	0	0
3	2000	1500
4	2000	1500
8	2000	1500

4.2.10 Methodology –Phase 1.5

The objective of this phase was to verify that methane can be used as a carbon and/or energy source for the process of denitrification in landfill bioreactors. To reach this goal, two lysimeters were chosen (3 and 8) and fed with 400 mL/d of nitrate solution at 1500 mg-N/L. The feeding continued until the BOD_5, TOC and VFAs were found to be inadequate to support denitrification (two weeks). Then methane gas was introduced into lysimeter 8 from the bottom, while lysimeter 3 was used as a control. Methane was introduced at a rate of 40 to 60 mL/min for 8 hr/d. Methane addition proceeded for 5 weeks. The nitrate feeding continued at the same rate and concentration for the entire phase (15 weeks).

4.3 Experiment (2): Denitrification Batch Test

The goal of this experiment was to investigate more closely the ability of denitrifiers to use landfill products such as methane and leachate for growth and energy with higher levels of control over carbon sources . In order to have a clear understanding of the denitrification efficiency, another carbon source (methanol) was also tested. All of the tests were conducted at 31°C, and were provided with nutrients and a buffer as described in section 4.3.1.2 and 4.3.2.2.

This experiment consisted of two phases. Each phase used a different batch system as described in section 4.3.1 and 4.3.2. In the first phase (2.1), 'Denitrification with Methane'; the use of methane as a source of carbon and/or ED was explored. This phase also tested and compared other carbon sources such as leachate and methanol. The second phase, 'Denitrification with Leachate', focused on the leachate as the carbon and/or ED source for denitrification.

The following section describes the materials used to conduct the first phase of this experiment (2.1) and the procedure followed to run it. The materials and methods used for the second phase (2.2) are given in section 4.3.2.

4.3.1 Denitrification With Methane

4.3.1.1 The Batch Reactor

Each batch test utilized a 500 mL flask with a side arm that was connected to a water basin to avoid air entry (as shown in Figure 4). For the methane test, the side arm was connected to a gas meter to monitor the gas flow rate. The top of the flask was sealed using a rubber bung. A hole was made in the bung so that a septum could be inserted. The septum was connected to capillary tubing that extended to approximately two thirds of the solution depth. A plastic syringe was used to collect samples when needed. For the methane test, another hole was made in the bung to supply the gas.

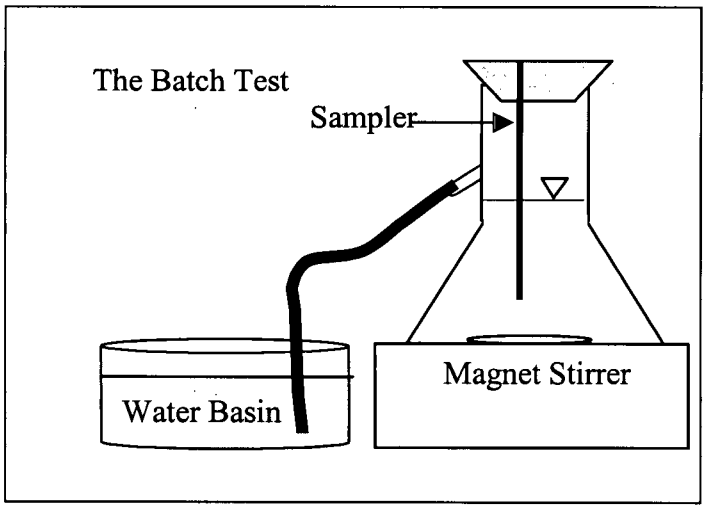

Figure 4 The batch set-up

4.3.1.2 Chemicals

Each batch was provided with nitrate, seed, nutrients, carbon and vitamins. Potassium nitrate was used to provide the required nitrate concentration. Leachate from lysimeter number 8 was used as the source of seed. Nutrient solutions were made to provide all essential elements such as P, Mg, Ca, Fe, Na, K, Co, Cu, Mn, Ni, and Zn. All nutrients were provided in excess to avoid any deficiencies. In addition, phosphate buffer (Eaton *et al.* 1995) was added initially in each test to provide a suitable environment. Vitamins B and E were also added to support growth. The nutrients solution, buffer solution and

vitamins solution were prepared as specified in Davies (1973), Eaton *et al.* (1995) and Toerien and Siebert (1967) respectively.

Methanol, acetic acid, propionic acid, leachate and methane were used as sources of carbon. The carbon was provided in excess so that there would be no shortage of carbon. The sources of leachate for the leachate test (2.1- leachate from Table 9) were lysimeters 3 and 8. Leachate from both lysimeters was mixed and then analyzed for nitrate and TOC (Table 16). Because the leachate was found to be low in carbon, it was spiked with propionic acid and acetic acid to overcome the lack of carbon. In the methane test (2.1-Methane from Table 9), natural gas was used as a source of methane. The composition of natural gas is shown in Table 17.

Table 16 Leachate characteristics

Parameter	Leachate mixture
TOC mg/L	60
NOx (mg-N/L)	1.5

Table 17 Natural gas composition and characteristics

Component	Percentage[6]	Aq. Sol.[7] (mol/dm^3)	Log H_a[8] ($kPa.dm^3/mol$)
Methane	95.5	0.41	4.85
Ethane	2.9	0.081	4.9
Propane	0.5	0.013	4.86
Nitrogen	0.7	0.00062	5.19
Carbon Dioxide	0.2	0.033	3.47
n-Butane	0.1	0.0026	4.98
Iso-Butane	0.05		
Pentane	0.05		

4.3.1.3 Methodology –Phase 2.1

In this phase the kinetics of denitrification were determined using different carbon sources. The sources of carbon were chosen based on their availability in the landfill

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[6] Emergency Dispatch Center, BC Gas, 2001.

[7] Valsaraj, 1995.

[8] Valsaraj, 1995.

system or on their popularity at treatment plants. Batches of 400 mL were set for denitrification as described in section 4.3.1, while nutrients, seed and chemicals were added as described in section 4.3.1.2.

This phase consisted of four tests (see Table 9 for details). To eliminate the effect of parameters other than the source of carbon, a preliminary test was conducted in advance. Then, three tests were performed with methanol, methane and leachate.

The number of reactors was varied in each test as shown in Table 18, depending on the parameters that needed to be tested. The reactors were run in a controlled temperature room at 31°C and were mixed by a magnetic stirrer. Frequent samples were taken, depending on the rate of denitrification as specified in the following sections. Samples were analyzed for nitrate and TOC.

Table 18 Reactors used for this phase (2.1)

Batch Test	Number of reactors used
Preliminary	8
Methanol	3
Methane	3
Leachate	8

4.3.1.3.1 Preliminary Test

The purpose of this test was to determine the procedure for subsequent testing. Several parameters were determined by this test: 1) the volume of the seed; 2) the adequate nitrate concentration; 3) the required HRT and reactor volume; 4) the need for a buffer and 5) the effect of the vitamin solutions. Eight reactors were operated (as shown in Table 19) in parallel to perform the preliminary tests. Four reactors (number 1, 2, 3, and 4) did not have any carbon addition; two of them (number 1, and 2) were not seeded. In this test, all reactors were fed with nitrate solution to provide an initial concentration of 50 mg-N /L. The carbon was set to 200 mg-C /L of methanol for two reactors (5 and 6), 400 mg –C/L for one reactor (8) and 100 mg-C /L for the last one (7). Vitamin E was excluded from the subsequent tests.

Table 19 Preliminary test conditions

Reactor number	1	2	3	4	5	6	7	8
Seed (mL)	0	0	4	4	2	2	4	4
Methanol (mL)	0	0	0	0	0.5	0.5	0.25	1

4.3.1.3.2 Methanol

Methanol is the most popular source of carbon for denitrification and is commonly used in wastewater treatment plants. The methanol test was used to evaluate the performance of denitrification with leachate and methane as compared to denitrification with methanol. Methanol testing was carried out five times in three identical batch reactors. The purpose of the first run was to activate the system and avoid a lag period in the following runs, while the purpose of the last run was to consume all the residual carbon to prepare the reactors for the following test. The three runs in between were the key runs for methanol and their results are shown and discussed in Chapter 6, while the data for all the runs are presented in Appendix 2.

The nitrate concentrations for each batch at all runs are shown in Table 20. In each case, a ratio of 1:4 of N: C was used. Samples were analyzed for nitrate and TOC. The frequency of sampling varied depending on the rate of denitrification.

Table 20 Nitrate concentration (in mg-N/L) for methanol test

Test number	1	2	3	4	5
Batch 1	38	56	7.2	10	10
Batch 2	62	55	6.6	10	9
Batch 3	61	55	12	10	9

4.3.1.3.3 Methane

Two identical batches were used to perform denitrification kinetic tests with methane as the carbon source. Another batch was set with no methane as a control. Natural gas was used as the source of methane. The flow rate was set at 30 mL/min. Samples for nitrate were taken on a daily basis while TOC samples were taken less frequently (about twice a week).

The test was carried out five times. In the first run, the denitrification kinetics were measured. Then the methane flow was discontinued in the first reactor to ensure that it

was the only substrate that the denitrifiers could use. The control batch was stopped after the first run. Samples were analyzed for methane, VFA, methanol, acetic acid and acetate.

In the second run, the flow rate of the natural gas was increased to 300 mL/min to determine whether higher rates of denitrification could be achieved with higher flow rates. In the third run, pure methane was used instead of natural gas for QA/QC purposes.

In the last two runs, fixed film media were added to the reactors as an attempt to improve the process. Two kinds of media were used: plastic synthetic sponge and flexible plastic tubes. Both were cut into small pieces to provide maximum surface area. The total volume of the media was less than 20% of the total volume of the reactor. The sponge medium was washed, submerged in methane-saturated water and then added to the solution. The test was conducted twice.

4.3.1.3.4 Leachate, Acetic Acid and Propionic Acid

The objective of this test was to investigate the effectiveness of using leachate for denitrification and the effect of the leachate matrix on the rate of denitrification. To achieve this goal, denitrification with leachate, acetic acid, propionic acid and a mixture of both acids were investigated.

Acetic acid and propionic acid were found to be the major VFAs present in the leachate. Therefore, these acids were chosen for the denitrification kinetic test. Eight batches were run, two with acetic acid, two with propionic acid, two with a mixture of both and two with leachate. The leachate batches were run with 100 mL of leachate to provide a 25% leachate strength. The Leachate source and characteristics are mentioned in section 4.3.1.2. Leachate was found to be low in carbon; therefore leachate batches were spiked with acetic acid and propionic acid. In all cases, the acids were the only source of carbon available for denitrification. Acids were added to provide a 1:4 ratio of N: C. The nitrate concentration was set to 10 mg-N/L. Samples were taken 4 times per hour and analyzed for nitrate and TOC.

4.3.2 Denitrification With Leachate

4.3.2.1 The Batch Reactor

In the first run, three reactors were used as batch reactors. The liquid volume in each reactor was 2 L. The reactors were set in a controlled temperature room (31°C) and were completely mixed. For the second run, three sets of ten 200 mL dark bottles were used as the reactors. An incubator was used to provide them with the mixing and the required temperature (31°C).

4.3.2.2 Chemicals

The nitrate, leachate and nutrients (not carbon) were provided to this test as in section 4.3.1.2. The first test had 25% leachate and 75% distilled water, the second test had 50% leachate and 50% distilled water and the third test had 100% leachate.

The nitrate concentration for all tests was 20 mg-N /L. The leachate used was low in carbon; therefore batches were spiked with acetic acid, propionic acid, valeric acid and butyric acid to provide a ratio of 1:4 as N: C. A carbon solution was made of the four acids (15 mL acetic acid, 10 mL propionic acid, 0.5 mL butyric acid and 0.25 mL valeric acid in 50 mL distilled water) and 2 mL of the carbon solution was fed to the reactors, each of which contained a different strength of leachate.

4.3.2.3 Methodology –Phase 2.2

The purpose of this phase was to investigate more closely the use of leachate as a carbon source for denitrification and to study the effect of the leachate strength on the performance of the process. Two runs were completed at three different leachate strengths 25%, 50% and 100%.

The purpose of the first run was to activate the denitrification process and to avoid a lag phase in the second run. The 2 L reactors were provided with all the nutrients and spiked with 2 mL of carbon solution and 20 mg-N /L of nitrate. Samples were taken before and after the run. Samples were analyzed for NO_x, VFAs and TOC.

In the second run, the solution in the 2 L reactor was transferred to ten small dark bottles. This step was carried out for all three of the 2 L reactors with the three different leachate strengths. The bottles were set in an incubator that provided a temperature of 31°C and a mixing speed of 75 rpm. At each time interval (about 15 minutes), a bottle was taken and sampled for NO_x, NO_2, VFAs, TOC and solids analysis.

5 Sampling and Analytical Procedures

This chapter explains the analytical procedures for the 'Landfill Bioreactor Denitrification Experiment' and the 'Denitrification Batch Test Experiment'. It describes the sampling protocol, the parameters used for data analysis and the methods applied. It also discusses the QA/QC methods for each category in this chapter.

5.1 Sampling Protocol

Three types of samples were taken: leachate, gas and batch test samples. In the " Landfill Bioreactor Denitrification" experiment, leachate and gas samples were taken once a week unless otherwise specified, while in the "Denitrification Batch Test" experiment, the frequency of sampling varied in each phase. The frequency of sampling for both experiments was based on the rate of change in the concentration of the analyte of interest.

5.1.1 Leachate Samples

Initially, leachate samples were collected every the other day and analyzed for NO_x, PO_4, COD, BOD, pH and ORP. The results of these tests showed minimal variation. Starting from the second week, leachate samples were taken on a weekly basis for the first four phases of the first experiment. Samples were analyzed for VFAs once a week during the first phase (1.1), and once a month after that. During the fifth phase (1.5), samples were analyzed for NO_x three times a week and TOC once or twice a week. The leachate outlets were closed for twenty-four hours before sampling to allow the leachate to accumulate in a sufficient volume. Samples were preserved according to Standard Methods (Eaton *et al.* 1995) and then analyzed. Sample storage time before analysis was kept to a minimum. COD, BOD, pH and ORP analyses were made on the day of sampling.

To ensure results of high quality, a number of measures were undertaken. A small volume of leachate was discharged before sampling. Initially, duplicate samples were used for all tests. Random duplicate samples were used for tests that showed high

precision and accuracy with parameters such as COD. Triplicate and even quadruplicate samples were used for tests with low precision and accuracy such as BOD. All glassware used was washed five times with tap water, twice with distilled water, and then washed with the sample. Glassware previously washed with nitric acid was avoided. Blank samples were analyzed for all tests on a weekly basis to account for any interference of preservation and/or acidification techniques. Spiked samples were also included to ensure accuracy of the methodology.

5.1.2 Gas Samples

Gas samples were taken on weekly basis so that they would correspond with leachate samples. Samples were taken before the feed to avoid air contamination. Gas analysis was made on the same day of sampling. The sampling apparatus was washed with the gas before the sample was taken. Duplicate samples were taken randomly.

5.1.3 Denitrification Batch Test Samples

Batch tests samples were collected based on the denitrification rate. Sampling frequency was every five minutes for fast rates and once a day for slow rates. All the samples were analyzed for NO_x. Samples were also analyzed for TOC, NO_2^-, VFAs, CH_4, CH_3OH and/or solids, as needed. A 5 mL syringe was used for sampling.

To ensure results with high quality, a number of measures were undertaken. First, the reactor had to be well mixed before taking the sample. The sample was taken one-third of the liquid depth from the bottom of the reactor. In addition, a small volume was flushed first to rinse the syringe before sampling. Moreover, all dishware used was washed five times with tap water and twice with distilled water and then washed with the sample. Dishware previously washed with nitric acid was avoided. For each test, a blank sample, test solution and at least one standard were included in each run. The number of duplicate samples taken was minimal because of the size of the reactor.

5.2 pH

To determine the pH of the leachate, a Beckman 44 pH meter was used. This pH meter was equipped with automatic temperature compensation and connected to an Oakion WD-35801-00 probe. The time between sampling and analyzing was kept to a minimal. Samples were covered before analysis to minimize air exposure.

The meter was calibrated prior to measurements using two standard buffer solutions of pH 4.0 and 7.0 during the initial phases of the lysimeters, and it was calibrated to 7.0 and 10.0 for the methane formation and maturation phase of the lysimeter. To evaluate the precision and the accuracy of the readings, another pH meter was used with the same probe and a different probe. The results of the two meters and probes matched with less than 5% deviation.

5.3 Oxidation-Reduction Potential (ORP)

ORP of weekly collected leachate samples were measured using a Cole-Parmer Chemicadet pH/mV meter (model 5986-60) connected to a Broadley James Corporation ORP electrode. The ORP measurements were recorded weekly in mv. Data proved to be unreliable. Results of duplicate and replicate samples always had more than a 50% difference; therefore, testing was discontinued after 10 weeks. Results of the first 10 weeks are shown in Appendix 1.

5.4 Carbon Analysis

Carbon appears in leachate and gas in both organic and inorganic forms. The leachate carbon can be estimated from the COD and/or VFA or can be more accurately measured by the carbon analyzer. For the batch test, the carbon analyzer was not sufficient because it lacked the ability to measure methane in solution. Therefore, in addition to the TOC analyzer, a gas chromatograph was used to measure the concentration of soluble methane. For QA/QC purposes, standards, blank, and duplicate samples were used.

5.4.1 Total Organic Carbon

TOC was determined by using a Shimadzu Total Organic Carbon Analyzer (Model TOC-500) with an automatic sample injector. Samples were acidified with (5% to 50%) phosphoric acid based on sample alkalinity to reduce the pH to below 2, then purged to remove inorganic carbon. Duplicate samples were sent infrequently to another carbon analyzer (Tekmar/Dohmann Apollo 9000 high temperature). The replication shows a 5% to 10% error for both instruments with an analytical error equal to or less than 5%.

For the second phase of the batch experiment, samples were filtered before analyzing. Single use 0.2 μm filters were washed with distilled water several times to avoid carbon contamination.

5.4.2 Volatile Fatty Acids

The VFA analysis was done using a Hewlett-Packard 5880A gas chromatograph, equipped with a Flame Ionization Detector and Autosampler. Helium was used as the carrier gas with a flow rate of 20 mL/min. A 1 m glass column (25 mm ID) was used, and packed with 0.3 CARBOWAX 20M/0.1% H_3PO_4. The temperature at the injection point was 175°C and 200°C at the detector. The oven temperature increased from 105°C to 150°C gradually (10°C per minute). The concentrations represented by the response peaks were estimated by comparison with external standard.

Samples were collected and preserved with (5 to 50%) phosphoric acid to bring the pH below 2 and then stored at 4°C. Due to the volatile nature of the samples, the time between sampling and preservation was kept to a minimum. Analysis for volatile fatty acids included acetic, propionic, butyric, iso-butyric, and valeric acid. Duplicate samples were run randomly as well as blanks, standards, and spiked samples.

5.4.3 Methanol

The concentration of methanol in samples was measured by a Hewlett-Packard 5890 gas chromatograph, with a 30 m long wide bore capillary column (DBWAX 0.53 MMID, J & W Scientific, Folsom, CA, USA) and a flame ionization detector.

5.4.4 Methane in Solution

The methane measurements were made using a Hewlett-Packard 5880A gas chromatograph. Helium was used as a carrier gas with a flow rate of 30 mL/min. A 2 m long, 0.25cm OD, stainless steel column was used, and packed with Porapak Q. The temperature at the injection point was 150°C and 200°C at the detector. The oven temperature was 60°C. The concentrations represented by the response peaks were estimated by comparison with external standard.

Samples were collected as described in 5.1.3, and preserved with (50%) phosphoric acid to bring the pH below 2 and measured immediately. Due to the volatile nature of the samples, extra care was paid in handling, sampling, preservation, and analyzing.

Standards for measuring methane concentration in solution were made by injecting a known volume of methane in a capped solution. Then, a sample from the well-mixed methane standard was taken, and injected to the gas chromatograph. The peak area was then used to calculate the methane concentration.

5.5 Nitrogen Analysis

5.5.1 Nitrate and Nitrite (NO_x^-)

The NO_x^- concentration was measured using a Lachat Quikchem Automated Ion Analyzer in accordance with the methods manual for the instrument (NOx-N, 20-107-04-1-Z). Samples from the "Landfill Bioreactor Denitrification" experiment and the "Denitrification Batch Test", were passed through the same preservation, storage, and analyzing procedure. Samples with high suspended solids were filtered, preserved with mercury acetate, and refrigerated at 4°C prior to being analyzed.

NO_x^- analysis reduces nitrate to nitrite by a copper-cadmium reduction column, and then measures the total nitrite to represent the nitrate and nitrite in the sample. The accuracy of the NO_x^- analysis depends on the conversion efficiency of the column, which lies between 80 and 95% based on the life of the column used. The accuracy of the column was determined using nitrate and nitrite standards, and then results were corrected.

A screening method (the UV spectrophotometric method) for NO_x^- was attempted as described in Standard Methods (Eaton *et al.* 1995). However, the screening method did not succeed in measuring the leachate nitrate. The results failed even with filtered samples of leachate. Thus, the screening method was considered inaccurate for this particular application. The inaccuracy of this method was attributed to the interference from the high level of refractory organics in the leachate. The screening method was attempted using UV-Visible Spectrometer Spectronic Tnicam.

This method was revisited when performing the denitrification batch test, which has relatively low solids concentration, however the replicate test also failed.

5.5.2 Nitrite (NO_2^-)

The analytical method and the chemicals used were identical to those used in measuring NO_x^-, except that the copper-cadmium column was not used.

5.5.3 Nitrate (NO_3^-)

The Nitrate concentration was calculated by subtracting the nitrite (NO_2^-) from the total NO_x.

5.5.4 Ammonia

The term ammonia, ammonia-N, NH_4^+, and NH_3 in this work, refers to the sum of the free ammonia-N and the ammonium ion-N. Leachate samples were collected once a week from each column to be analyzed for ammonia-N. Samples with high suspended solids were filtered and then immediately preserved to a pH level below 2 by the addition of several drops of concentrated sulphuric acid, and refrigerated at 4°C prior to analysis. A Lachat Quikchem Automated Ion Analyzer was used to measure ammonia concentrations. As per the method manual (QuikChem 10-107-06-1-Z), samples with high ammonia were diluted with distilled water when necessary. Standards, blanks, and spiked sample were used at each run.

5.5.5 Total Kjeldahl Nitrogen (TKN)

TKN measures the inorganic ammonia and organic nitrogen in a system by converting all organically bound nitrogen to ammonia. The level of ammonia in the sample is then measured as an indication of the total tristate nitrogen in the sample. In this experiment, the TKN values were assumed to represent the leachate ammonia and the organically bound nitrogen.

Total Kjeldahl Nitrogen was measured by digesting the samples in BD-40 Technicon Block Digester with concentrated H_2SO_4 and K_2SO_4 to liberate all organically bound nitrogen. Analysis was performed colorimetrically, following the instruction in the Lachat Quick Chem Automated Ion Analyzer according to QuickChem Method No. 10-107-06-2-E. The TKN results were usually as high as the ammonia-N results. Therefore, the test was revisited once at each phase to confirm that ammonia is the main source of TKN. As a result of this, the TKN data were not used as part of the discussion.

5.6 Ortho-phosphate

Ortho-phosphate levels were analyzed from filtered samples using a Lachat Quikchem Automated Ion Analyzer in accordance with the equipment instructions (10-115-01-1-7). This analysis took place in parallel with the NO_x^- analysis. Methods employed in NO_x^- analysis were also used to determine ortho-phosphate levels.

5.7 Chemical Oxygen Demand

The leachate COD was measured on a weekly basis. Samples were prepared using the COD acid reagent and the COD digestion reagent. Samples were analyzed using the HACH heating COD reactor and the HACH DR/2000 direct reading spectrophotometer apparatus. The presence of chloride in the leachate sample required the addition of mercuric sulphate during digestion.

Samples were diluted with distilled water to be within the range of 100 to 900 mg-COD/L. A full range of standards (50, 100, 200, 400, and 800 mg-COD/L) was run with every new prepared batch of COD test tubes (approximately 150 tubes per batch). One

standard and a blank were run with every test on a weekly basis. Sample duplicates were run on a monthly basis.

5.8 Biochemical Oxygen Demand

The BOD test was performed only on leachate samples. The dilution ratio varied according to the BOD_5. Initially, 20 μL of aerobic sludge was used as a seed. The results of the first ten weeks were not consistent. For the following weeks, synthetic seed, (Polyseed) specifically made as a BOD seed inoculum, was used. This seed provided better and more consistent results. The initial and final dissolved oxygen (DO) concentrations were measured by the YSI-52 Dissolved Oxygen Meter with a YSI 5905 BOD Probe. For QA/QC purposes, blanks, and seeded blank samples were run in duplicate with each run. Samples with quadruplicates were analyzed to provide results of higher quality.

5.9 Suspended Solids

The total suspended solids (TSS) and the volatile suspended solids (VSS) were measured only in the denitrification batch test experiment to monitor the increase in biomass over time and hence, to develop a utilization rate for nitrate. The frequency of this test depended on the total depletion rate of NO_x. The test was carried according to Standard Methods (Eaton *et al.* 1995)

5.10 Gas Analyzer

This analysis was conducted for the first experiment. Gas sampling was conducted on a weekly basis and samples were taken before the batch feed to avoid air contamination. Sampling was done from each lysimeter through the gas sampling ports using a 1 mL Hamilton syringe. The syringe was flushed several times with the gas sample. The sample was then injected into a Fisher-Hamilton Gas Partitioner (Model 29), which uses helium as the carrier gas. Comparing the peak areas with known standards identified the gases. Standards were used to determine the response factors. The gas partitioner was

used to quantify nitrogen, oxygen, carbon dioxide, and methane. One replicate was run on a weekly basis.

6 Results and Discussion

In this chapter, the results of the first and the second experiment are presented and discussed. The raw data for both experiments are summarized in Appendix 1 and 2 (section 9.1 and 9.2). The experiments were performed using the methodology described in Chapter 4.

6.1 The Landfill Bioreactor Denitrification Experiment

This experiment included eight lysimeters, each serving as a zone within a landfill bioreactor. It started with a preliminary test, which was followed by five experimental phases. In the first two phases, all of the lysimeters were used, whereas in the third and fourth phases, only half of the lysimeters were used. The fifth phase used only two lysimeters. The results presented in this section focus on the leachate and gas produced from the lysimeters as indicators of denitrification in the bioreactors. Terse

6.1.1 Experiment (1) –Preliminary Studies

Before starting the full experiment, studies were performed to measure the waste moisture content (mc), the volume of the anoxic reactor, HRT, and initial leachate characteristics. The mc was calculated according to Equation 9 before waste placement (Table 21).

Equation 9 Moisture Content

mc = (weight of water / weight of water and weight of dry mass) · 100%

Table 21 Moisture content of organic waste

	Food waste	Yard waste	Paper waste
Moisture content	80 %	65 %	6%[9]
Percentage (to the total waste)	32.8 %	20.0 %	31.7 %

The total waste moisture content was measured based on the following equation:

[9] The paper mc is based on typical values in the literature (Tchobanoglous, 1993)

Equation 10 Total moisture content

$$mc = [\Sigma ((w_i\ \%) \cdot\ mc_i)] / 100$$

where :

mc is the moisture content of the total waste,

w_i % is the percentage weight of this specific waste to the total waste,

mc_i is the specific moisture content of the specific waste type,

i represents the waste type, i.e. food, yard, paper ...etc.

The terms of this equation are shown in Table 22, where the total moisture content is shown to be 41% based on wet weight. The moisture content of 41% was assumed to be valid for all of the lysimeters. This percentage represents 6.61 L of water in each lysimeter.

Table 22 The total moisture content (mc) of the waste matrix and individual moisture content (mc_i) of the components of the waste matrix

Component of waste	Mass fraction of mixed waste %	Component moisture content (mc_i)	Contribution to moisture content (mc) of mixed waste (%)
Food	32.8	80.0	26.2
Yard	20.0	64.5	12.9
Paper	31.7	6.0	1.9
Glass	4.1	0	0
Metal	5.7	0	0
Plastic	5.7	0	0
Total	100.0	41.0	41.0

The volumetric holding capacity (also called storage capacity) of each lysimeter was calculated based on the amount of water that it retained and its mc. A test was made to determine the capacity of each lysimeter to retain water. The results of this test are shown in the second column of Table 23. The third column of this table shows the storage capacity in L for each lysimeter as calculated with the following equation:

Equation 11 Landfill volumetric storage capacity

Volumetric storage capacity (L/L) =[($mc_{of\ waste}$ · waste weight[10]) + volume of water retained] / Volume of waste

The fifth column in Table 23 shows the HRT of each lysimeter. The HRT was calculated using the flow rate and the storage capacity based on the following equation (Munasinghe, 1997):

Equation 12 Landfill HRT

HRT = S/Q

Where;

S is the storage capacity (L), which is obtained by: (volumetric storage capacity (Equation 11) (L/L) · volume of solid waste in the landfill (L)).

Q is the flow rate through the landfill (L d^{-1})

Table 23 Lysimeters capacity to retain water and HRT

Lysimeter	Water retained (L)	Moisture Content (L)	Storage capacity %	HRT (d)
1	1.50	6.6	28.5	20.0
2	4.00	6.6	37.3	26.5
3	3.75	6.6	36.4	26.0
4	3.25	6.6	34.7	24.5
5	1.50	6.6	28.5	20.0
6	3.00	6.6	33.8	24.0
7	2.00	6.6	30.2	21.5
8	2.00	6.6	30.2	21.5
Average	2.60	6.6	33.0	23.0
SD	1.00	-	3.5	2.5

Since the waste moisture content was assumed constant for all lysimeters, the storage capacity differed from one lysimeter to another, due to changes in the water the lysimeter was able to retain. Despite all efforts to make these lysimeters identical, differences were observed in the water retained, and hence the HRT. The HRT values ranged between 20.0

[10] Assuming that the volume of 1 kg of water is 1 L.

and 26.5 days, with an average HRT of 23 days. Although the standard deviation (SD) of the water retained was 1 L (about 38% of the average), the SD of the storage capacity and the HRT were 3.5% and 2.5 d (approximately 10% of the average). The results of the preliminary test are summarized in Table 24.

Table 24 Lysimeters characteristics

Parameter	Average	Range
Waste volume (L)	28.3	28.0-28.9
Waste weight (kg)	16.1	16.0-16.2
Waste density (g/L)	570	
Waste moisture content (wet weight %)	41	
Waste storage capacity (L water / L waste)	0.33	0.29-0.37
Lysimeter HRT (d)	23.0	20.0-26.5

6.1.2 Experiment (1) –Phase 1.1

In this phase, the feasibility of denitrification through landfill bioreactors was investigated using different influent nitrate concentrations. The nitrate concentration range was chosen based on the typical leachate ammonia concentrations and it was set to cover all of the phases that the landfill passes through.

In this experimental phase, all eight lysimeters were used. Although great effort was exerted in building identical lysimeters, replicates still showed a few differences. Lysimeter 4 behaved differently. This lysimeter passed the first phase very quickly in comparison with the rest of the lysimeters, and as a result, had a higher gas production, a higher pH, and a lower leachate COD and BOD. Unless otherwise specified, the results for this phase represent the average of replicate readings from the lysimeter pairs.

6.1.2.1 Denitrification Efficiency

In the process of denitrification, nitrate is reduced to nitrogen gas. The efficiency of the process is an important parameter that is considered for evaluation and is determined by the removal of nitrate. In this experiment, lysimeters were fed with different nitrate concentrations, and the effluent leachate was analyzed to measure the total amount of nitrate and nitrite. The efficiency of the process of denitrification was calculated by the following equation:

Equation 13 Denitrification efficiency

$$E = [(Nitrate_{in} - (Nitrate_{out} - Nitrate\ Control_{out})) / Nitrate_{in}] \cdot 100\%$$

Where E is the efficiency of denitrification. The influent concentrations (Table 25) were held constant throughout the phase. The effluent concentrations were found to be low, resulting in high removal efficiencies even with the high nitrate feed (Table 25 and Figure 5). The removal efficiency was calculated based on the average effluent concentration after five weeks. The first five weeks were not included in the calculation to provide sufficient time to activate the microbial activity and to flush all the water used for the preliminary studies. The high removal of nitrate was expected, because of the initial condition of a high oxygen demand and the availability of nitrate to serve as an electron acceptor.

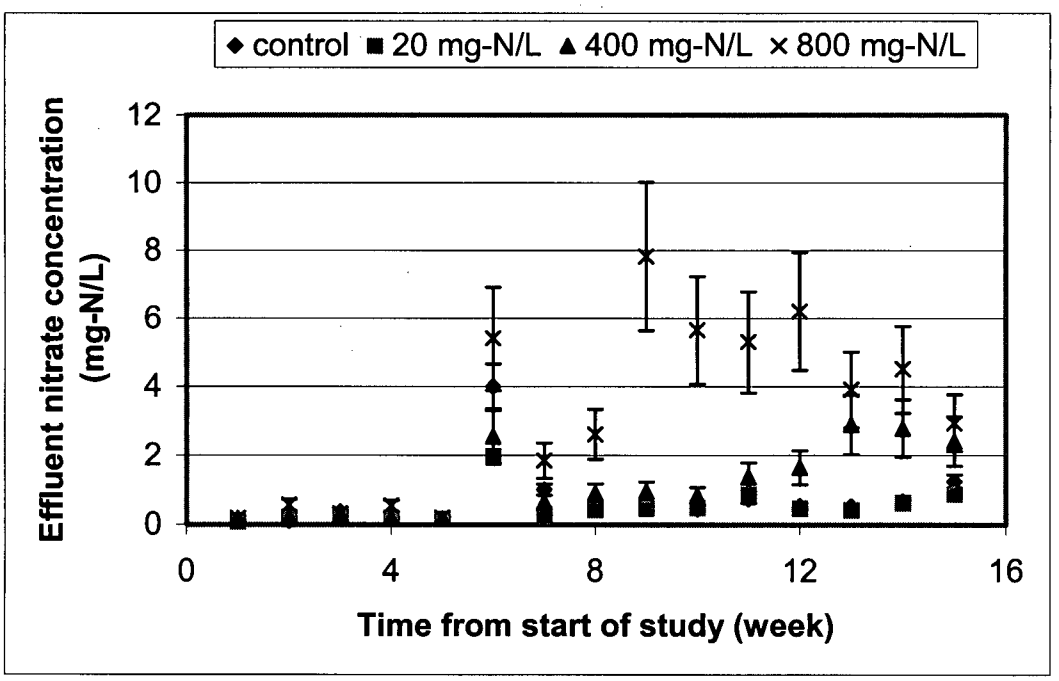

Figure 5 Comparison of average effluent leachate NO_x concentration for different nitrate feed concentrations during phase 1.1[11]

[11] The error bars in this figure (as well as in other figures in this document) represent the deviations between replicates reading and the average.

The denitrification efficiencies shown and discussed above were calculated based on the total nitrate and nitrite released. To confirm this high efficiency, a mass balance on nitrogen was conducted. Results of the averaged mass balance are shown in Table 26. The mass balances were done with the nitrate feed representing the input for the nitrogen, the effluent nitrate and nitrite and nitrogen gas representing the output for the nitrogen. Ammonia in the leachate was not considered as a part of the equation. Dissolved nitrogen gas in leachate was also not included due to its limited solubility (Table 27). The same assumptions –for ammonia and nitrogen- were considered valid at all of the following phases. A sample calculation of nitrogen concentration in gas is shown in Appendix 3, section 9.3.1

Table 25 The average efficiency of denitrification during phase 1.1.

Lysimeter Feed	**Nitrate (in) mg-N/L**	**Nitrate (out) mg-N/L**	**Number of samples**	**Average Efficiency %**
Control	0	0.6	20	-
Low nitrate concentration	20	0.5	20	100
Medium nitrate concentration	400	1.6	20	99.8
High nitrate concentration	800	5.6	20	99.6

Table 26 Nitrogen mass balance during phase 1.1

Nitrate load	Nitrogen in g-N during phase 1.1	Nitrogen out g-N during phase 1.1			Mass out/ Mass in (%)	Number of samples included (leachate + gas)
		Leachate	Gas	Total		
Control[12]	-	0.56	7.00	7.56	N/A	60
Low	0.84	0.33	5.17	5.50	654	60
Medium	16.80	0.75	14.67	15.42	91.8	60
High	33.60	2.02	31.26	33.28	99.0	60

Table 27 Aqueous solubility and Henry's coefficient (H_a) for nitrogen and the major components of landfill gas (Valsaraj 1995)

Compound	Aqueous solubility (mol/dm^3)	Log H_a ($kPa \cdot dm^3/mol$)
Nitrogen	6.2E-4	5.19
Carbon dioxide	3.3E-2	3.47
Methane	4.1E-1	4.85

[12] The control is based on lysimeter 1. The results of lysimeter 2 are not included in this Table, because the SD was high (9 g-N).

Table 26 shows that during phase 1.1, all the lysimeters were releasing nitrogen. The lysimeters with low nitrate feed released 6.5 times more nitrogen than the mass that they received. The mass of nitrogen detected in the gas stream may have been due to the release of the air trapped within the waste. A previous study by Munasinghe (1997) showed that lysimeters produce nitrogen during the early stages of landfilling.

As previously mentioned, the nitrogen gas dissolved in tap water (6.6 mg-N/L at 30°C) was ignored. In the case of the low nitrate feed this is a significant contribution, 0.3 g-N during phase 1.1 as compare to the input 0.84 g-N. However, it does not significantly change the mass balance error (500%).

The results of Table 26 also show that the ratio of nitrogen mass introduced to the system to the nitrogen mass produced from the system was close to 1 for the lysimeters with the medium and high nitrate feed. The previous assumption, which states that the nitrogen was emitted during the early stages of landfilling due to the release of the air trapped with the waste, is still valid at this case. This release may have helped in closing the nitrogen mass balance with low percentage of error (less than 10%).

The objective of investigating the ability of the lysimeters to remove the nitrate was achieved. However, the results of this phase (1.1), are only applicable to young landfills where the carbon source for heterotrophic bacteria is abundant. The situation at old landfills was investigated in the following phases: 1.2 to 1.5. The effects of this practice on waste degradation and landfill stabilization require more study. The following section explores denitrification effects on gas production as a key to waste degradation.

6.1.2.2 Gas Production

Landfill gas is a major by-product of waste degradation. The anaerobic breakdown of organic matter proceeds sequentially from the complex to the simple and produces carbon dioxide and methane as end-products. In the last step of degradation, methanogens use mainly acetic acid to produce carbon dioxide and methane. The environment surrounding methanogens has a strong impact on their biological activity.

The data produced from this research strongly suggest that the presence of nitrate and hence the process of denitrification, is associated with lower gas production (Figure 6). The results show that the lysimeters that received high levels of nitrate (800 mg-N/L), released 50% less gas compared to the control lysimeter. Although the denitrification in the high nitrate lysimeters produced nitrogen gas that contributed to the total gas produced (1 to 2 L/week), these lysimeters produced less gas in total.

The results from the lysimeters that received the low and medium nitrate feed did not show a clear relationship between the nitrate feed concentration and the cumulative gas production (Figure 7) [13]. However, the deviation in gas production rate, between the replicates of lysimeters receiving low nitrate concentration feed, was decreasing as time passed. This may be attributed to many factors. First, we have to acknowledge that lysimeters are extremely heterogeneous systems due to the nature of the waste, and that the effect a parameter (such as nitrate concentration) is strongly dependent on the path of the feed and the existence of microenvironments. Second, more differences are expected in leachate characteristics during the initial phases of landfill stabilization, due to the rapid degradation that occurs in these phases. It also must be recognized that the choice of the nitrate concentrations for the low and medium nitrate lysimeters may not be adequate to represent significant variations.

Lysimeters 3 and 4 both received a feed of medium nitrate concentration (400 mg-N/L). Lysimeter 4, passed the lag phase very quickly and started forming gas at high rates, showing insignificant effects of the nitrate concentration on its cumulative gas production (Figure 7). In contrast, lysimeter 3 behaved differently. The results of lysimeter 3 were similar to the results of the lysimeters with high nitrate feed. The average cumulative gas, produced from the two lysimeters (3 and 4), lies between the cumulative gas produced from the lysimeters wit the low and high nitrate feed. However, due to the limited

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[13] The slope of the cumulative gas production line was 45 L/week and 38 L/week for lysimeters 5 and 6 respectively with 15% difference. While the slope of the cumulative gas production line was 29 L/week and 52 L/week for lysimeters 3 and 4 respectively with 45% difference.

number of replicates and the high SD, results of the lysimeters receiving medium nitrate feed will not be discussed in this phase (1.1).

Figure 8 shows that nitrate at low and high concentrations reduce the methane production rate, with stronger effects associated with the high nitrate feed. The effect of nitrate on gas production can be explained in two ways: either the denitrifiers consume methane or the process of gas formation is inhibited by the presence of nitrate or denitrification.

If the first assumption is valid, then denitrification proceeds according to Equation 8. Under such conditions, methane is utilized, while carbon dioxide is produced. For each mole of methane consumed, 0.64 mole of carbon dioxide must be produced. For this assumption to be valid, the methane production rate must be reduced and the carbon dioxide production rate must be increased. According to this explanation, the composition of the gas is changed while the total gas production rate is not affected to the degree shown in Figure 6. In addition, Figure 9 shows that a low carbon dioxide production rate was associated with a low nitrate concentration feed, and that the carbon dioxide production rate showed a further decrease in the lysimeters with the high nitrate feed. Therefore, this assumption may not be valid.

The goal of detecting denitrification activities, supported by methane, was not achieved during this phase (1.1). This does not mean that the process is unfeasible, or that it did not occur. The preference for VFAs, over methane, may possibly limit the presence of methane utilization. During this phase, in which leachate is rich in attractive sources of carbon, the denitrifiers may not use methane. However, this may not be the case at old landfills where leachate has low BOD and almost no VFAs. Nevertheless, the issue of utilizing methane for denitrification should not be neglected. Evaluating the ability of denitrifiers to grow on methane was one of the objectives of this research. In fact, it was addressed later, when lysimeters were old enough to provide the environment needed for this process (refer to section 6.1.6 for more details).

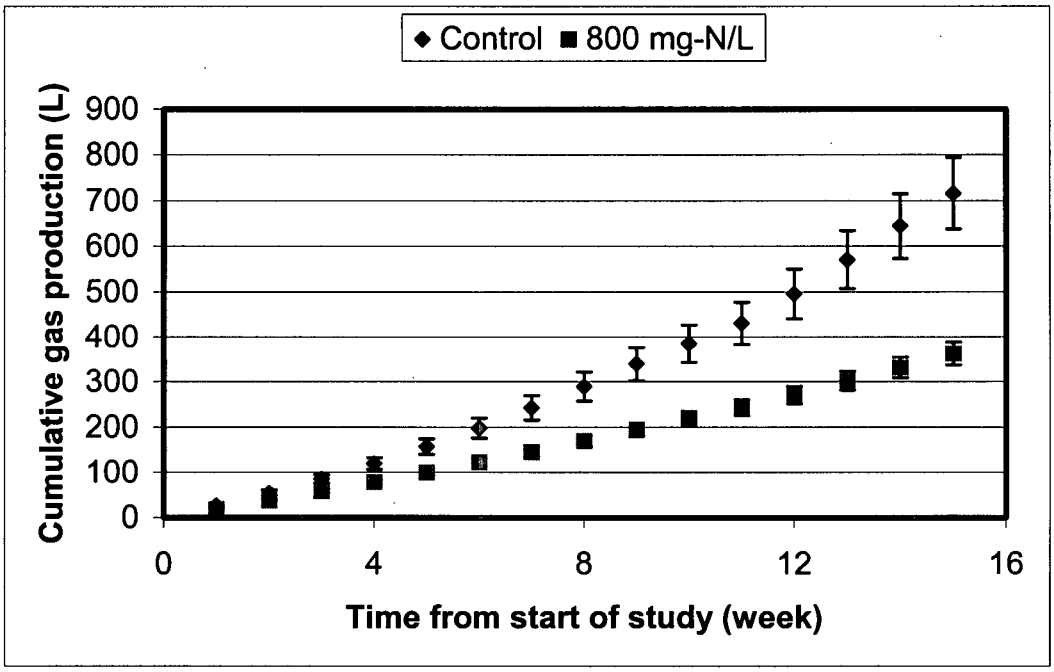

Figure 6 Average cumulative gas production for high nitrate concentration (800 mg-N/L) during phase 1.1

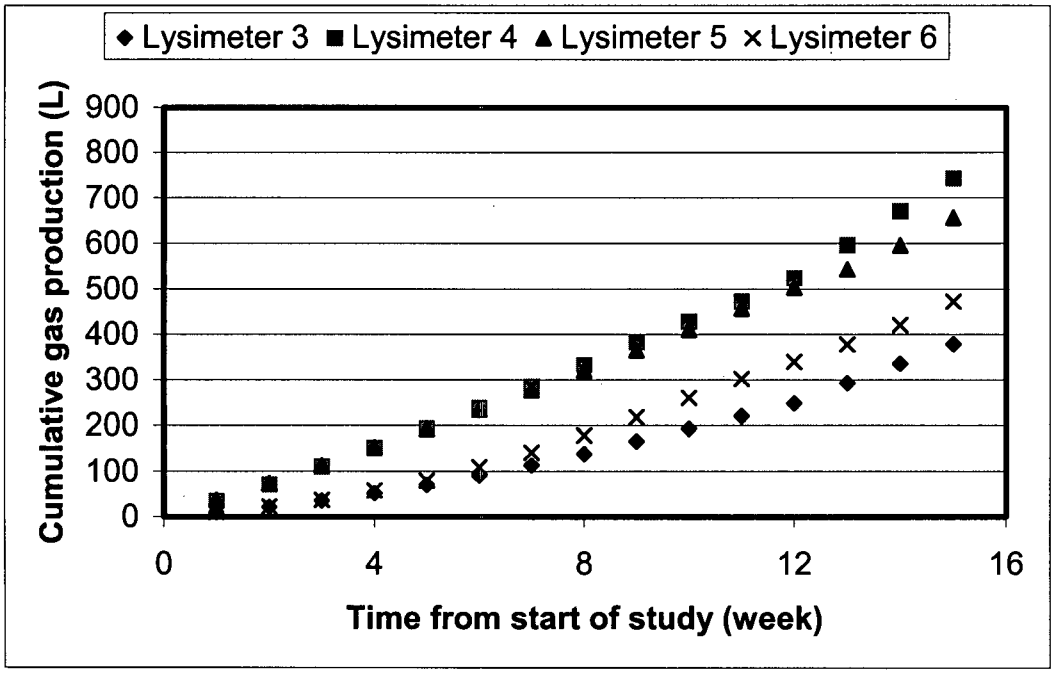

Figure 7 Comparison of cumulative gas production for lysimeter replicates at low nitrate feed concentration (lysimeters 5 and 6 at 20 mg-N/L) and medium nitrate concentration (lysimeters 3 and 4 at 400 mg-N/L) during phase 1.1

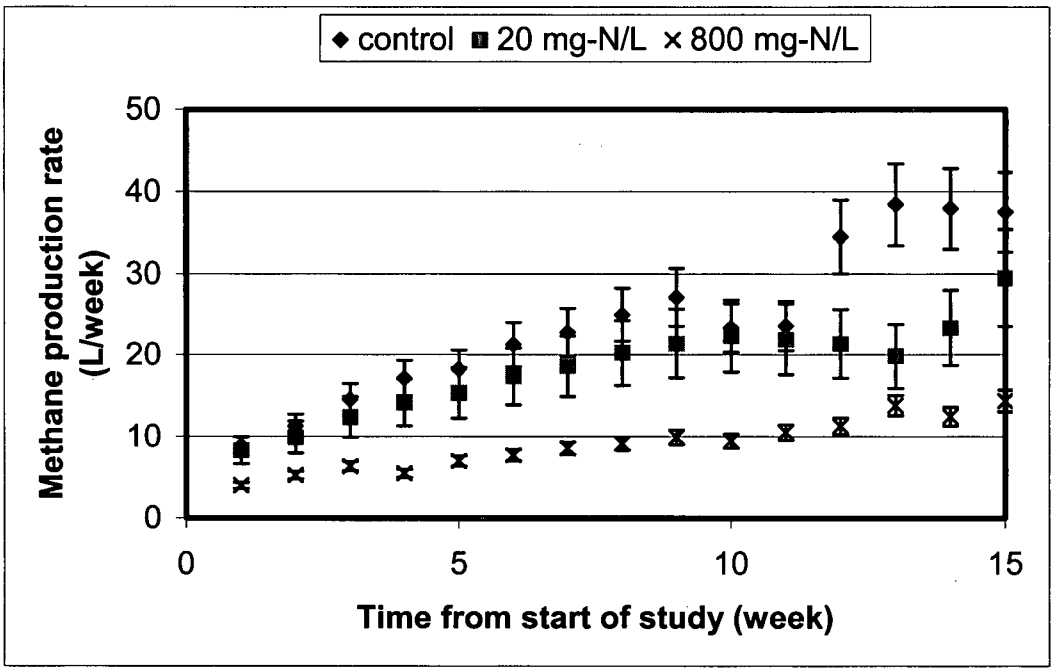

Figure 8 Comparison of average methane production rate at different nitrate feed concentration during phase 1.1

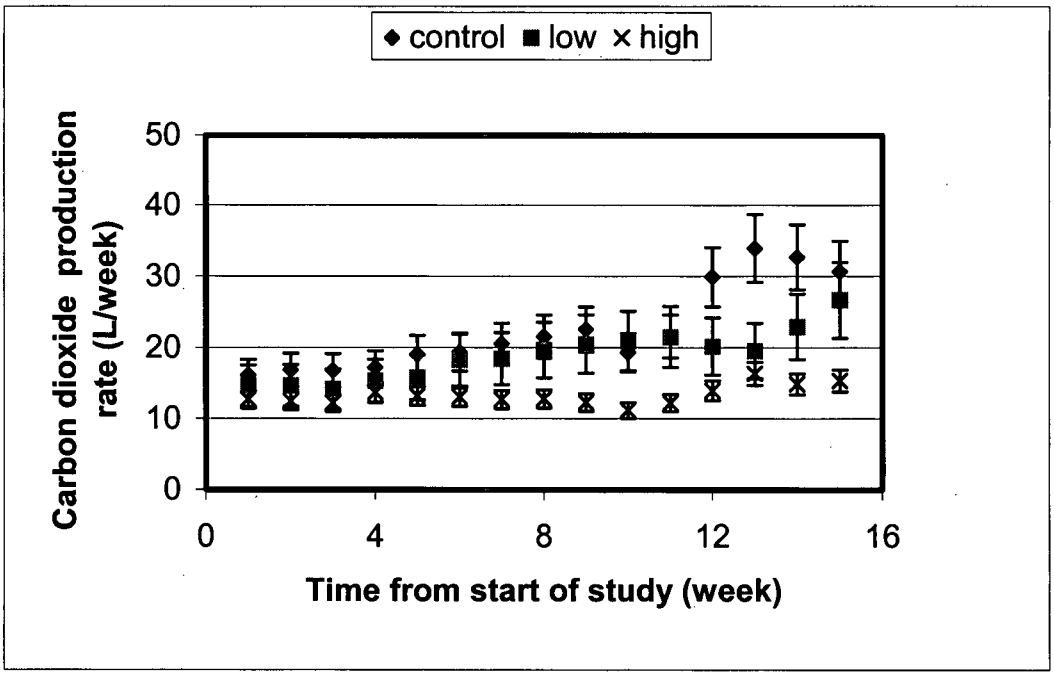

Figure 9 Carbon dioxide production rate at low and high nitrate concentrations during phase 1.1

On the other hand, denitrification supported by VFAs should result in a higher production rate of carbon dioxide. Comparing the results presented in Figure 10, Figure 11, and Figure 12 shows that as the nitrate concentration in the feed increased, the carbon dioxide production rates had higher values than those of methane production; this can be attributed to the process of denitrification. However, comparing carbon dioxide production rates at low and high nitrate levels (Figure 9) with the carbon dioxide produced from the control lysimeters (Figure 10), shows that lower carbon dioxide production rates were associated with denitrification. This data supports the second hypothesis (inhibition of gas production), which may be the answer to the gas reduction.

Nitrate or denitrification at high nitrate levels may hinder the process of gas formation. From Figure 8, it can be seen that methane produced from the high nitrate lysimeters was about one third of that produced from the control lysimeters and one half of that produced from the low nitrate lysimeters. There is an inverse relationship between influent nitrate concentration and methane production.

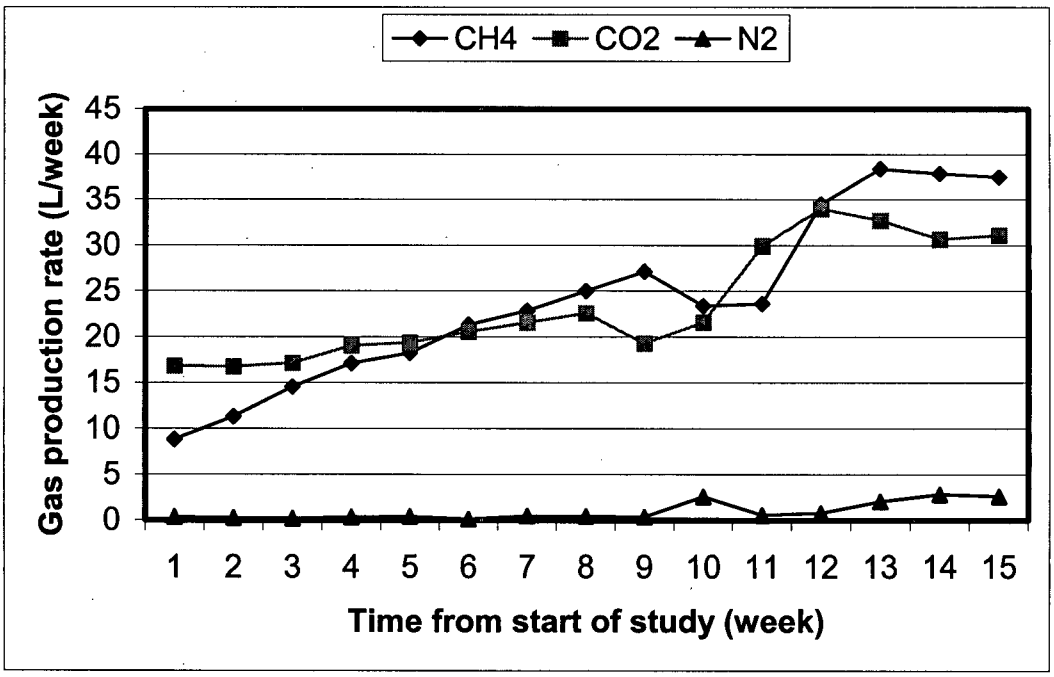

Figure 10 Production rate for methane, carbon dioxide, and nitrogen, for the control lysimeters during phase 1.1

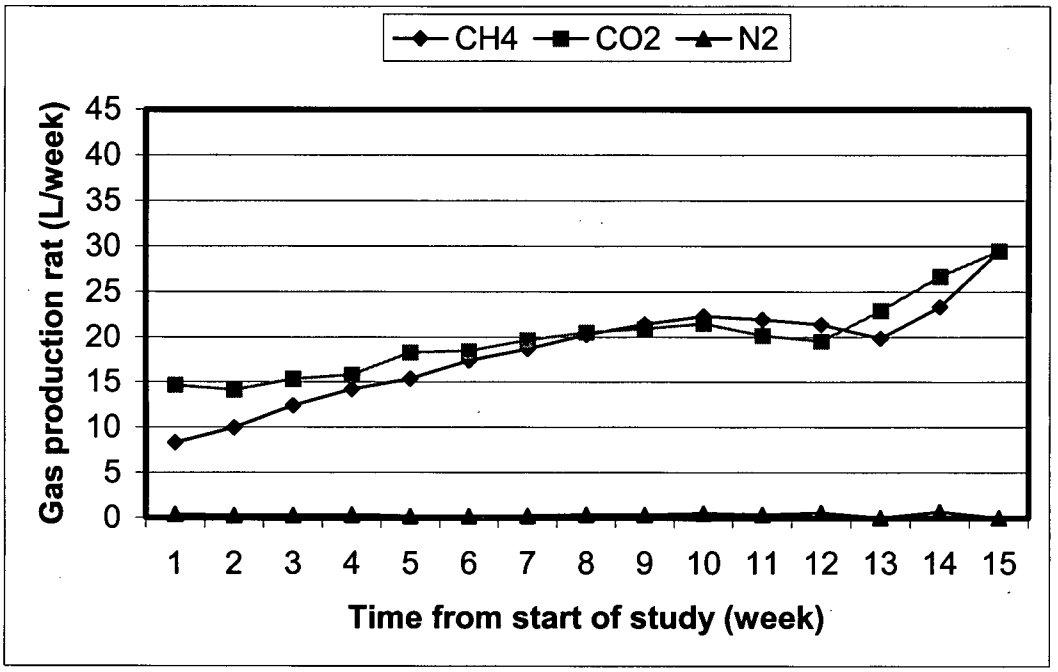

Figure 11 Production rate for methane, carbon dioxide, and nitrogen, for the lysimeters receiving the low nitrate feed, during phase 1.1

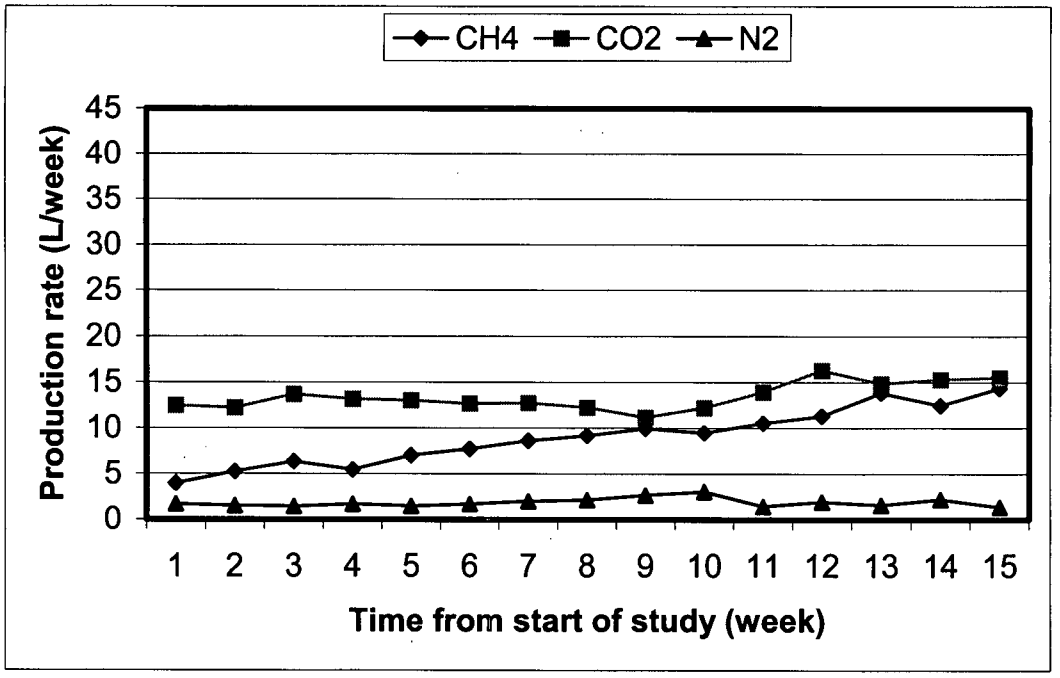

Figure 12 Production rate for methane, carbon dioxide, and nitrogen, for the lysimeters receiving the high nitrate feed during phase 1.1

Researchers, over the past decades, have not developed a complete explanation for this relationship; however, several attempts have been made to explore this phenomenon, including studies by Balderston and Payne 1976, Fischer and Thauer, 1990, Culotta and Koshland 1992, Fetzer and Conrad 1993, Zumft 1993, Akunna *et al.* 1994, Achtnich *et al.* 1995, Roy *et al.* 1997, and Kluber and Conrad 1998a and b. Researchers who noticed the effect of nitrate on methane production suggested three hypotheses: inhibition of methanogens due to high redox potential; electron donor competition; and buildup of denitrification intermediates.

In the current study, positive redox potentials (up to +100 mV) were observed in all but one lysimeters. All of the lysimeters were able to produce gas although it should be noted that it was the lysimeter (4) with the fastest degradation that was consistently negative.

In addition, recent findings show that high positive redox potential (up to +420 mV) neither prevented the initiation nor the growth of methanogens in soil, sediments, and anaerobic reactors (Balderston and Payne 1976, Fetzer and Conrad 1993, Akunna *et al.* 1994, Roy *et al.* 1997, Kluber and Conrad 1998b). Therefore, the high redox potential is no longer considered a valid explanation.

The second hypothesis may be valid at a low C:N ratio (Roy and Conrad 1999). However, methane production was suppressed by nitrate, even when carbon was present in excess (as VFAs in leachate). This leads to the conclusion that competition for substrate between denitrifiers and methanogens was not the main mechanism that inhibited methanogens.

The last possible explanation is that the NO_2, NO, and N_2O are toxic to methanogenesis. Researchers (Achtnich *et al.* 1995, Kluber and Conrad 1998a and b) recently found that denitrification intermediates are toxic to methanogenesis in salt marsh sediments and rice soils. Nitric oxide is especially toxic to bacteria when it attacks the Fe containing enzymes (Culotta and Koshland 1992). Other enzymes that are crucial for methanogens may also be inhibited by N_2O (Fischer and Thauer 1990), which is known to inactivate cobalamin-dependent enzymes. Also, other enzymes may be susceptible to inhibition by NO or NO_2, both of which may form metal-nitrosyl complexes (Zumft 1993). Based on

these considerations, the inhibition by toxic denitrification intermediates better explains the phenomenon, but a greater understanding is needed. Although in this phase, evidences of incomplete denitrification or conditions of carbon shortage were not present.

At this point, denitrification through landfill bioreactors has been demonstrated; however, it does reduce gas production. A question remains: does denitrification affect waste degradation? This is discussed in the following section.

6.1.2.3 Effect of Denitrification on the Carbon Emitted to the Environment During Phase 1.1

One of the goals of adopting landfill bioreactors as a management option is to provide faster degradation and stabilization of the landfill. Since leachate recirculation proved to enhance waste stabilization by converting the landfill bed into an anaerobic biological reactor, it can be concluded that the presence of nitrate converts it to an anoxic reactor. The effect of the latter conversion on degradation is investigated in this section. The total carbon released to the environment is the key to estimating the level of waste degradation.

Solid waste is degraded biologically from complex to simple matter in consecutive processes (see section 2.4 for details). Hydrolysis is the first and the most critical process; after that, acidogenesis and then acetogenesis occur. The last step is methanogenesis. The products of each step may be passed to the following process or removed from the system either through the leachate or the gas. In the initial stage of landfill stabilization, methanogens are not well developed and leachate is the main outlet.

The cumulative masses of carbon released in the leachates are shown in Figure 13[14]. The data suggest that the effect of low nitrate concentration (20 mg-N/L) on carbon released to the environment through leachate was small, and in fact, it could be neglected, when compared to the cumulative mass of carbon released from the control lysimeters.

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[14] The SD for the control, low, and high nitrate feed was 10.4%, 6.6%, and 6.6% respectively.

Landfill gas is another stream that contributes to the total carbon released to the environment. The carbon calculations are shown in Appendix 3, section 9.3.3. The total carbon released in the gas was calculated at each week and added to the following week to present the cumulative amount of carbon. The data in Figure 14 show that the high nitrate feed was associated with a lower release of carbon than for the control and for low nitrate feed. The difference in the mass of carbon released between the high nitrate feed lysimeters and the control lysimeters was significant (52%). This difference may be attributed to the effect of nitrate on methanogenic activities. On the other hand, the difference in the results of the cumulative amount of carbon released, between the control lysimeters and the lysimeters with the low nitrate feed, was not clear (high variations between replicates of the low nitrate feed lysimeters (24%)). This may suggest that the effect of the low nitrate feed concentration on waste degradation was minimal.

Examining the total carbon released and its components may lead to a better understanding of the effect of nitrate on the process of waste degradation. The carbon in leachate and gas was summed and the results are shown in Figure 15. The figure shows that the highest degradation (437 g-C with SD of 4%) was achieved with the control lysimeter, and that the lysimeters with low nitrate feed were almost as high (383 g-C with SD of 17%). The lysimeter with the high nitrate feed exhibited the lowest level of degradation: 263 g-C with SD of 2%. This is 40% less than that achieved by the control lysimeters and 31% less than that achieved by the low nitrate feed lysimeters. The data in Figure 15 suggest that denitrification reduces the carbon released to the environment and that larger effects are associated with higher nitrate concentrations.

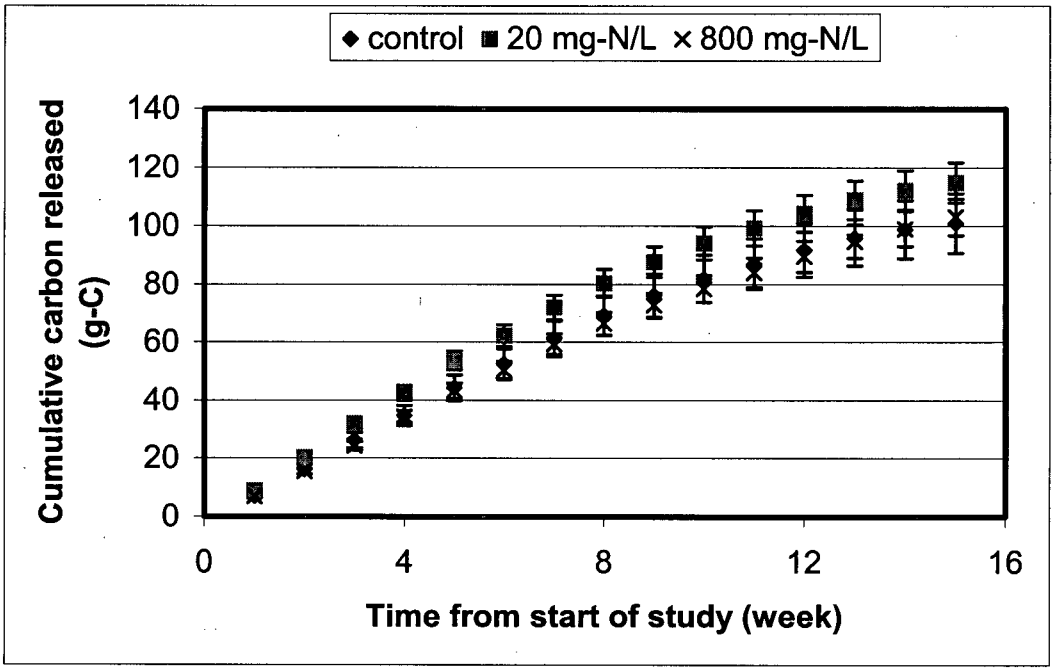

Figure 13 Comparison of average cumulative amount of carbon released by leachate from lysimeters receiving different nitrate feed concentrations during phase 1.1

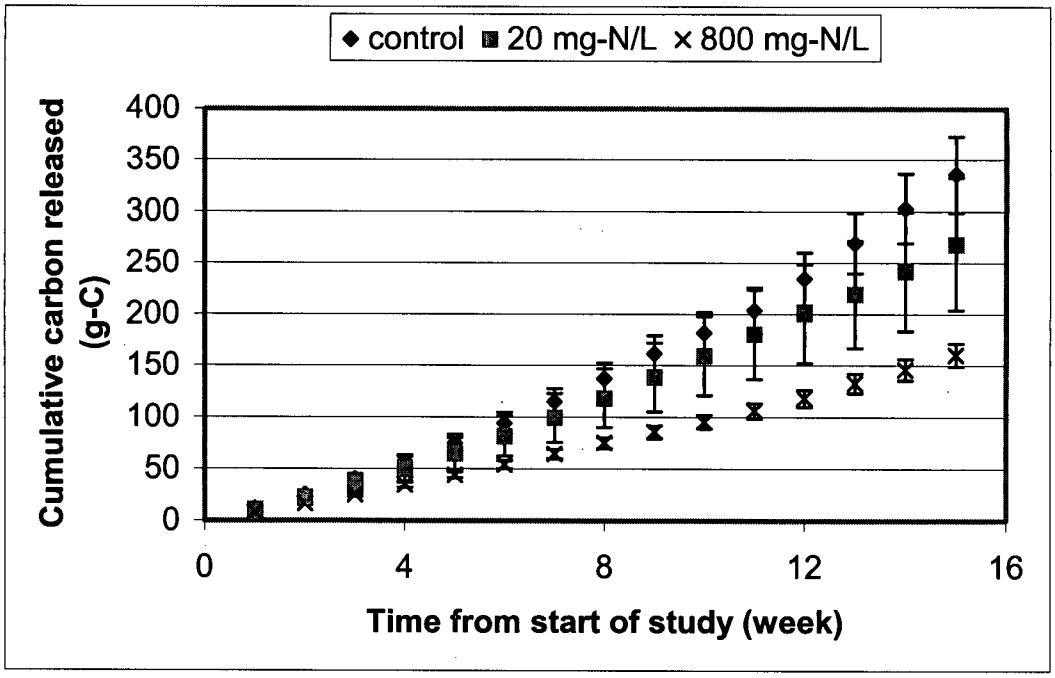

Figure 14 Comparison of average cumulative amount of carbon released by gas from lysimeters receiving different nitrate feed concentrations during phase 1.1

The results of the previous section (6.1.2.2) suggest that denitrification reduces gas formation, while the results of this section suggest that denitrification reduces carbon release through the gas, without affecting its release through the leachate. As the nitrate concentration increased, less carbon was released to the environment (Figure 15); hence, the amount of waste degradation was less. This can be explained by the hypothesis that the consequences of denitrification start with methanogenesis and the effects pass through all the processes of waste degradation to reach hydrolysis. The mechanism of this behavior is presented in the following section.

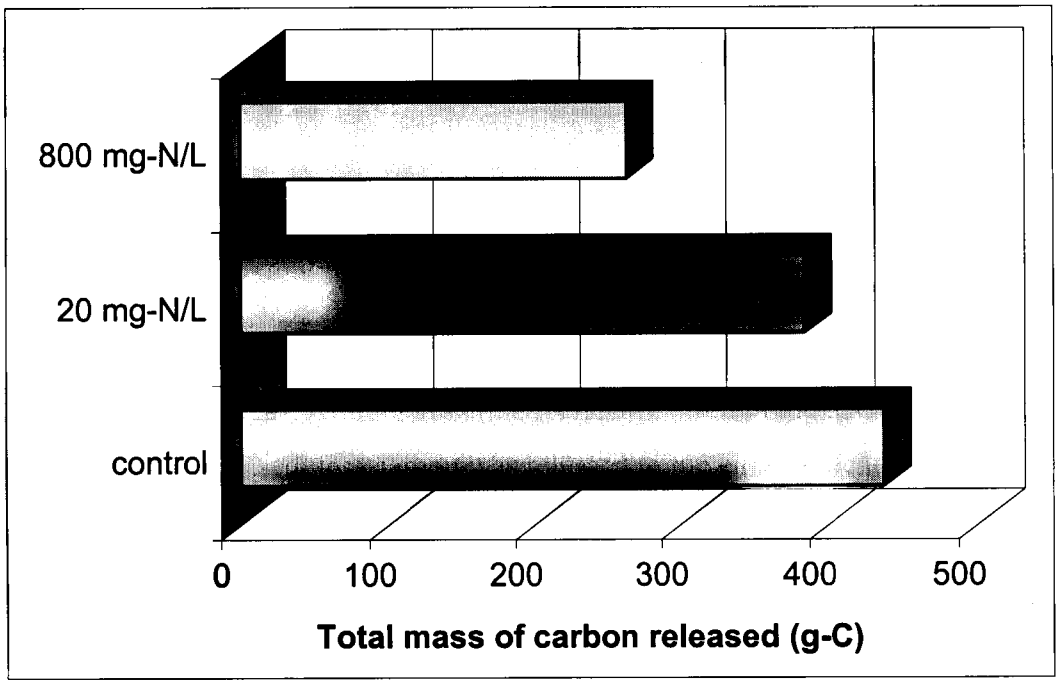

Figure 15 Total carbon released from low and high nitrate feed during phase 1.1

6.1.2.3.1 Effect of Inhibition of Methanogenic Activities on Waste Degradation

The data from this phase (1.1) have shown that denitrification was associated with reduced gas formation. Several studies have found that denitrification inhibits methanogenesis (Westermann and Ahring 1987, Chen and Lin 1993, Hendriksen and Ahring 1996, Akunna *et al.* 1998, Fang and Zhou 1999). The inhibition of methanogenesis affects the overall process of waste degradation, as shown in the previous section.

At low levels of methanogenic activity, the rate of hydrogen, carbon dioxide and acetate consumption may be less than the production rate of hydrogen and acetate. Under such conditions, acetate and hydrogen accumulate, and other fermentation products –such as propionate and butyrate- may be formed (McInerney and Bryant 1983, as cited by Munasinghe 1997). In addition, the accumulation of carbon dioxide may further reduce methanogenic activities (Munasinghe 1997).

The accumulation of acetate reduces the pH, which increases the inhibition effect on methanogens. Furthermore, high levels of acetate may inhibit acetogenic reactions by thermodynamic mechanisms (Zinder, 1993). At low levels of acetogenic activities – promoted by low methanogenic activities-, longer chain organic acids (such as propionate and butyrate) accumulate (Chynoweth and Pullammanappallil 1996). The accumulation of these end-products reduces the driving force for further degradation and may introduce inhibitory effects (Zinder 1993).

The overall process of waste degradation, therefore, is highly dependent on the interaction between different microbial species to provide a balance between substrates and end-products. Overproduction or accumulation of acetate, hydrogen, and carbon dioxide resulting from the under-utilization of these substrates by methanogenic bacteria, produces fermentation products at inhibitory levels. This results in the cessation of waste decomposition.

This may explain the results presented in Figure 15, which shows that denitrification at a high level reduces the release of carbon by 50%. Lysimeters that receive high nitrate feed, have a high inhibition effect on methanogenic bacteria, and this upsets the balance between bacterial activities. Under such conditions, acetogenic, acidogenic, and hydrolysis activities may be affected, due to the accumulation of end-products which affect the system thermodynamics. On the other hand, denitrification at the low level of nitrate did not show a significant effect; this suggests that the nitrate concentration was not sufficient to produce a substantial inhibitory environment for methanogeneic bacteria.

6.1.2.4 Basic Leachate Characteristics

6.1.2.4.1 Effect of Nitrate Concentration on Leachate pH

The presence of nitrate by itself does not have a strong influence on the pH of a solution, but the biological processes and their by-products do. The availability of nitrate, in an anoxic environment that is rich in microorganisms and which has sufficient nutrients, favors the biological process of denitrification. In this process, nitrate is ultimately reduced to nitrogen gas in a biochemical reaction that produces alkalinity, a condition that has a significant effect on the pH of the reactor. In this experiment, the process of denitrification takes place in the lysimeters and the effect of denitrification on the pH, if any, is observed through the change in leachate pH.

The pH of the leachate was measured on a weekly basis for all lysimeters. The results of these measurements for the control lysimeters, low nitrate feed lysimeters, and the high nitrate feed lysimeters are shown in Figure 16. The data from replicates showed high level of similarity with the standard deviation having values between 0.4 and 2%. The fifteenth week was found to be a critical time for the pH results; therefore, the time frame in the figure was extended to include data from the following four weeks (16 to 19) to provide a better understanding of the results.

The pH's of the three lysimeters pairs exhibited similar trends (Figure 16). The pH was around 5.2 for the first few weeks, and then it started to increase. The pH of the leachate increased due to two processes; methane formation and denitrification.

In methane formation, methanogens use acetate or hydrogen as substrates for the production of methane. This process increases the pH, prevents the accumulation of acetate, and reduces the hydrogen partial pressure. In this way, it provides an adequate environment for methanogenic, acetogenic, and acidogenic bacteria, which as a consortium, continue the cycle by degrading more organic materials. This situation may take place in the control lysimeters. If, for any reason, methane formation fails, the acetate and hydrogen accumulate, generating a higher hydrogen partial pressure. Fermentative bacteria generate butyric acid and propionic acid at high hydrogen pressure

(McInerney and Bryant, 1983, as cited by Munasinghe 1997). Acetogenic bacteria can further utilize these acids at low hydrogen partial pressures; however, at partial pressures higher than $9 * 10^{-5}$ atm, the acids accumulate with no further degradation (Christensen and Kgeldesen 1989).

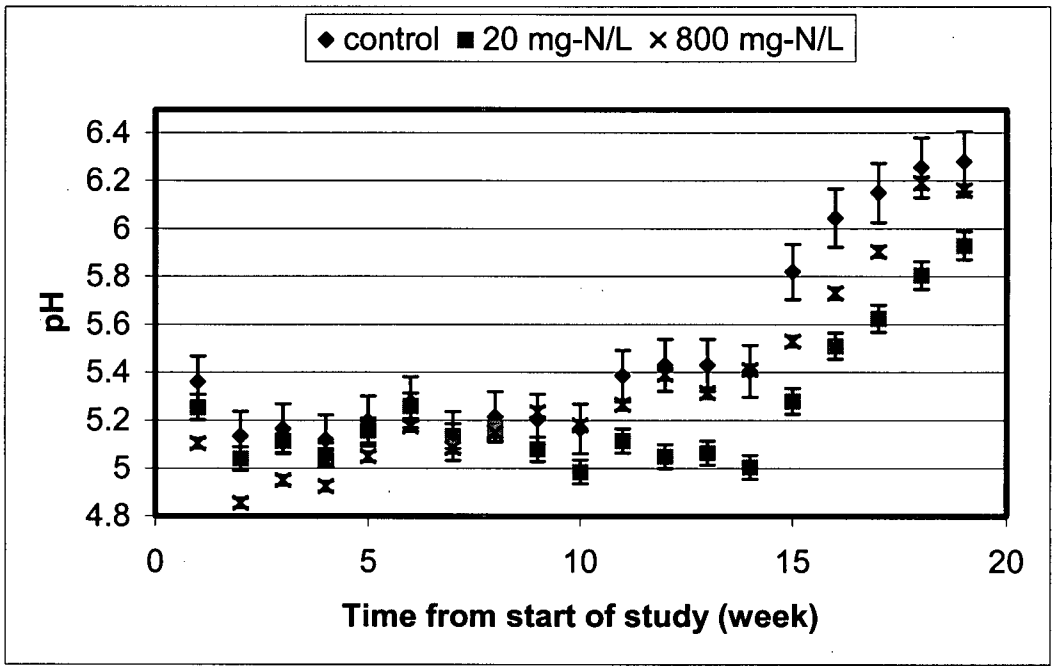

Figure 16 Comparison of the average effluent leachate pH from different nitrate feed concentrations during phase 1.1

In the presence of denitrification, methanogenic activities are reduced (Westermann and Ahring 1987, Chen and Lin 1993, section 6.1.2.26.1.2.3), and as a consequence, organic products of waste degradation (such as acetate, propionate, and butyrate) accumulate (Chynoweth and Pullammanappallil 1996), and reduce the pH of the leachate. This situation may have occurred in the lysimeters that received nitrate feed, with stronger inhibition effects in the high nitrate feed lysimeters due to the high concentration of nitrate. However, Figure 16 shows that lower pH values were associated with the low nitrate feed lysimeters rather than the high nitrate feed lysimeters. This can be reasonably explained by the effect of denitrification on pH.

The process of denitrification generates alkalinity (Equation 14). Theoretically, 3.57 mg of alkalinity as $CaCO_3$ is produced per 1 mg of nitrite-N reduced to nitrogen; however,

for practical purposes a value of 3 is recommended for use in process calculations (U.S. EPA 1993). Assuming that 3.0 mg of alkalinity is produced per 1.0 mg of nitrate-N reduced, then 60, and 2400 mg of alkalinity would have been produced from the lysimeters with low and high nitrate concentration respectively. The alkalinity produced increases the pH. The effect of this alkalinity may explain the increase in the pH of the lysimeters with the high nitrate feed over the lysimeters with the low nitrate feed.

Equation 14 Alkalinity generated by denitrification

$$NO_3^- + 0.83\ CH_3OH \rightarrow 0.5\ N_2 + 1.16\ H_2O + 0.83\ CO_2 + OH^-$$

Denitrification through landfill bioreactors was found to affect the leachate pH during the initial phase of degradation. Since denitrification has an influence over the leachate pH, other factors such as leachate BOD may be influenced. In the following sections, the effect of denitrification on leachate COD and BOD are examined.

6.1.2.4.2 Effect of Nitrate on COD and BOD

Initially, the BOD tests were not successful for about two months. Different dilutions were used; however, the results were not satisfactory (high SD between relicates of the same sample). The leachate strength and the seed sensitivity may have caused this failure. By the eighth week a new source of seed –made specifically for BOD testing– was used and the results were acceptable (results of replicates had low SD). Due to the biological nature of this test, higher deviations between sample replicates were expected. Because of all these difficulties and uncertainties, COD was used instead of BOD to interpret the results, with the assumption that the BOD was the major contributor to the COD values (about 80%) during the first phase. To validate this assumption, an analysis was performed, and the results are shown in Table 28.

An alternative way to look at the BOD is to measure the VFAs oxygen demand. In the early stages of degradation, VFAs are the main component of BOD. To confirm this assumption, the VFAs were analyzed and their theoretical oxygen demand (THOD) was calculated and then compared to the COD. The THOD of each acid was calculated based on the equations shown in Appendix 3, section 9.3.4. Equation 15 was used to calculate

the THOD of the VFAs at any point during the first phase. The results of these calculations (Table 28) show that it is safe to assume that during the first phase, the BOD was the major contributor to the COD (about 80%). Therefore, the COD results may be used as an indicator of the BOD concentration during this phase.

Table 28 The ratio of THOD to COD for the control, low nitrate feed and high nitrate feed lysimeters during phase 1.1

Parameter	Control lysimeters	Low nitrate feed lysimeters	High nitrate feed lysimeters
Range of THOD/COD	0.70-0.94	0.69-0.90	0.6-0.87
Average THOD/COD	0.80	0.80	0.78
Number of samples	22	22	22
SD for replicates lysimeters (%)	2.6	4.0	2.7

Equation 15 Total oxygen demand for VFAs

THOD-VFAs (mg/L) = 1.0 acetic acid (mg/L) + 1.5 propionic acid (mg/L) + 1.8 butyric acid (mg/L) + 2.0 valeric acid (mg/L)

All lysimeters started with a high COD of 20 to 30 g/L and sustained this level for five weeks (Figure 17), after which, the COD started to decrease. At the end of this phase, the COD was between 5 and 15 g/L (Figure 17). The rate of decreasing of COD concentration (Table 29) was calculated based on the COD values obtained from week 6 to week 15. The results of Table 29 show that the lysimeters with the high nitrate feed had lower COD decreasing rates (less than 45%) than the control and the low nitrate feed lysimeters. In addition, Figure 17 shows that by the end of the phase, the COD values of the high nitrate feed lysimeters were about 50% higher than the control and the low nitrate feed lysimeters. The results (Table 29 and Figure 17) also show that there were no significant differences (3.5% difference in the in the dCOD/dt rate, and SD of 10% in COD values) between the low nitrate feed and the control lysimeters

Table 29 The COD decreasing rate for the control, low nitrate feed and high nitrate feed lysimeters during phase 1.1 (week 6-15)

Parameter	Control lysimeters	Low nitrate feed lysimeters	High nitrate feed lysimeters
dCOD/dt (g-COD/week)	2.7	2.8	1.2
R^2	0.9854	0.9748	0.9326

In the early phases of waste decomposition, organic compounds represent a high portion of the COD, with the BOD:COD ratio between 0.4 and 0.8 (Table 1 and Table 2). The high nitrate concentration in the feed may introduce an environment that inhibits methanogenic bacteria. Thus, carbon in the leachate increases, and this increase is represented as effluent leachate COD. The presence of the denitrification process limits the transformation of carbon from the leachate to the gas. Therefore, denitrification with high levels of nitrate is associated with higher COD leachate.

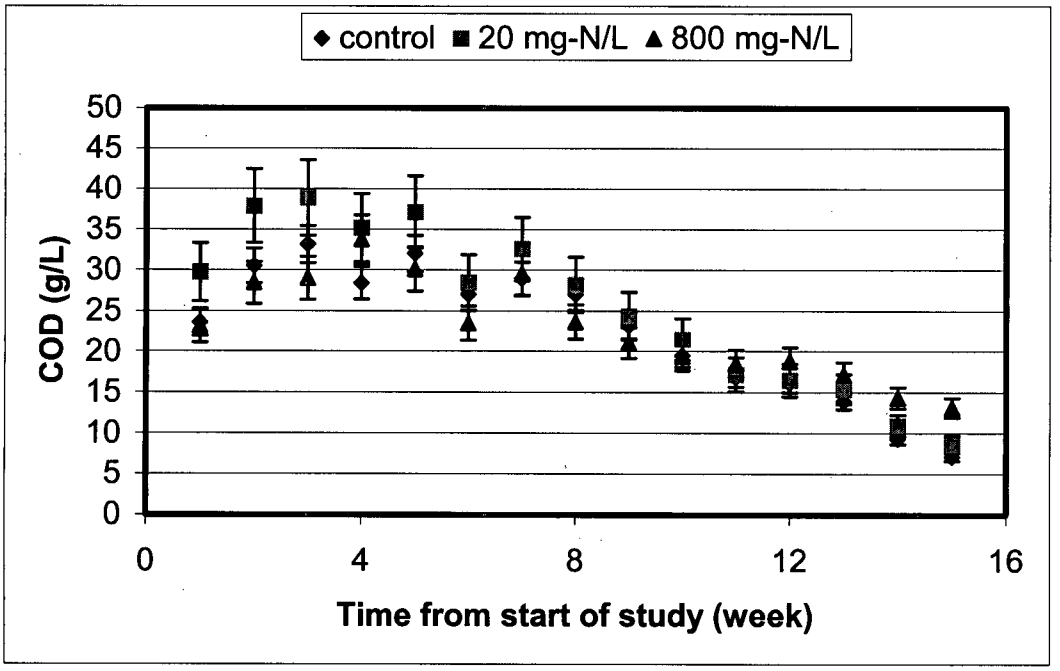

Figure 17 Comparison of the average effluent leachate COD from different nitrate feed concentrations during phase 1.1

The COD results also support the previous hypothesis, which stated that denitrification reduced methane formation and hence the process of waste degradation. The high nitrate feed was associated with a lower rate of decreasing of COD concntration, which resulted in higher leachate COD values. On the other hand, the control lysimeters and the low nitrate feed lysimeter exhibited similar COD values and removal rates.

6.1.2.5 Overview –Phase 1.1

This phase demonstrated that denitrification is feasible using landfill bioreactors, however, denitrification –at high nitrate concentrations- reduces the total gas production rate. Moreover, the use of this gas to support denitrification was not apparent. During this phase, there were signs that denitrification, at high nitrate concentrations, hindered waste degradation, possibly by inhibiting methanogens, which tends to disturb the balance between bacterial species. Finally, yet importantly, the effect of denitrification on waste degradation, at a low nitrate concentration, was insignificant (less than 13% compared to the control).

6.1.3 Experiment (1) –Phase 1.2

The objective of this phase was to explore the ability of aging leachate to serve as an electron donor and a carbon source for denitrification. As a landfill approaches the maturation phase, the leachate BOD and hence carbon availability decreases. Denitrification supported by leachate carbon may suffer from carbon deficiency. In addition, this phase (1.2) was performed to evaluate the effect of an increase and decrease in nitrate concentrations on landfill end-products. The change in nitrate concentration was shown in Table 13. The concentration of the low nitrate feed was increased by a factor of five, from 20 mg-N/L to 100 mg-N/L, while the concentration of the medium nitrate feed was increased by 50%, from 400 mg-N/L to 600 mg-N/L. The concentration of the high nitrate feed was decreased by 25%, from 800 mg-N/L to 600 mg-N/L. It was expected that the changes made to the feed concentrations were sufficient to produce significant effects on the gas and leachate characteristics.

The results of this phase are divided into three sections. The first section discusses the effect of aging leachate on denitrification efficiency, while the second section discusses the effect of denitrification on waste degradation during the second phase (1.2). The last section evaluates a case in which the nitrate was either increased or decreased and compares this change with that observed in the control lysimeters.

6.1.3.1 Denitrification Efficiency

The efficiency of denitrification was closely observed throughout all the phases. During this phase (1.2), denitrification was also assessed based on Equation 13 and the method discussed in section 6.1.2.1. It was expected that the available carbon would decrease with time and hence, the efficiency of denitrification would decrease as well. Figure 18 shows the total organic carbon (TOC) concentration in the effluent leachate. The data show that the effluent TOC values for the control lysimeters and lysimeters 5, 6, 7 and 8 were decreasing, while the TOC values of lysimeters 3 and 4 were constant. As a landfill ages, it is expected that the carbon content of the leachate decreases. The constant release of carbon by lysimeters 3 and 4 may be due to the increase in the feed nitrate concentration, which will be discussed later.

Although the TOC was decreasing with time (Figure 18), the efficiency of denitrification remained high (Table 30, and Figure 19). The lowest efficiency was observed in the 23rd week with lysimeter 3 and was calculated to be 98.3%.

Table 30 The average efficiency of denitrification during phase 1.2

Lysimeter number	Nitrate (feed) mg-N/L		NO_x (leachate) mg-N/L	Number of samples	Average Efficiency %
	Phase 1.1	Phase 1.2			
5 – 6	20	100	1.0	14	99.8
3 – 4	400	600	1.9	14	99.8
7 – 8	800	600	2.8	14	99.7

During this phase, denitrification in the landfill bioreactor was able to remove almost all the nitrate and the nitrite. The carbon source for denitrification was still thought to be the VFAs in the leachate. The hypothesis of using methane as a carbon source for denitrification did not appear to be valid; because under such conditions, it was expected that higher carbon dioxide production rates and lower methane production rates would be observed as discussed previously in section 6.1.2.2. However this is not the case, since production rates for both gases were similar (Figure 20 through Figure 23).

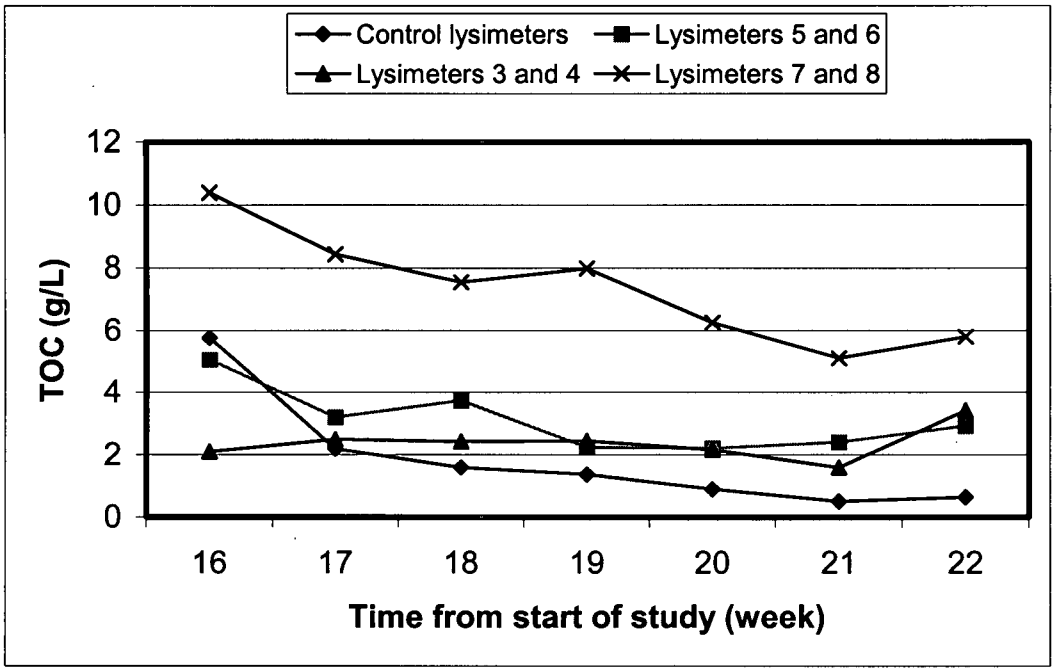

Figure 18 Comparison of the effluent TOC for the lysimeters during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

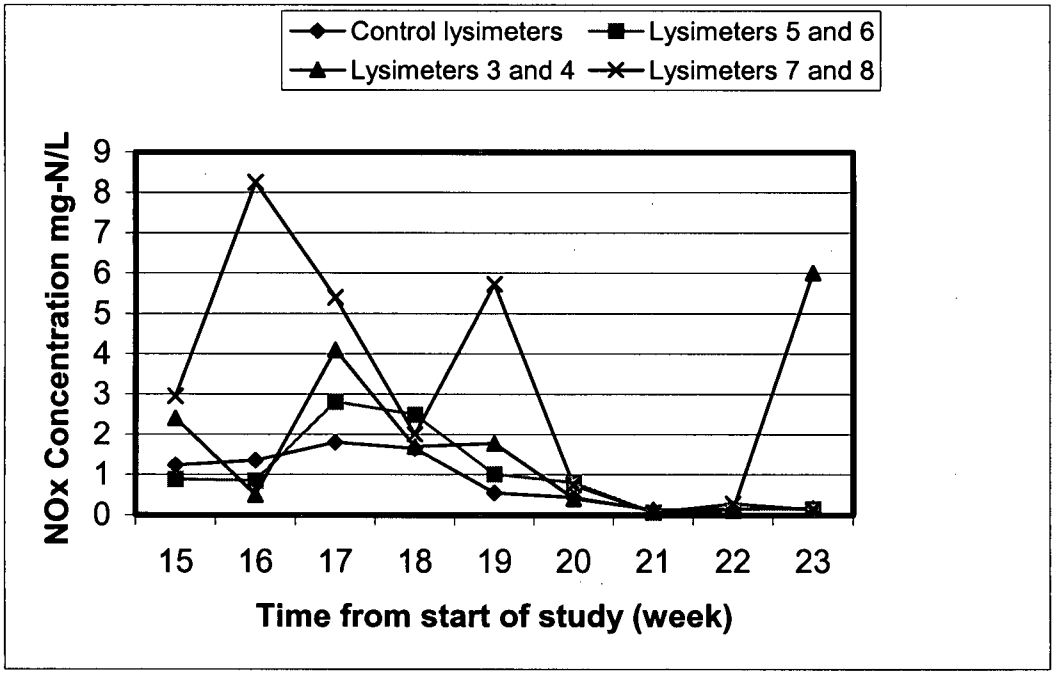

Figure 19 Comparison of the average effluent nitrate concentration from different nitrate feed concentrations during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

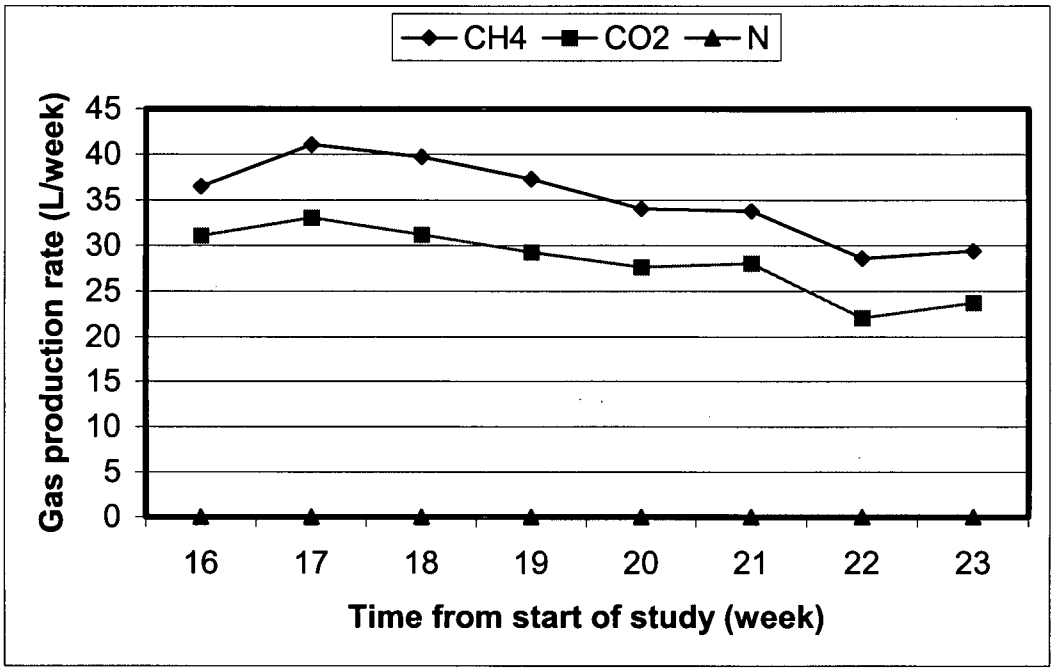

Figure 20 The average production rate for carbon dioxide, methane and nitrogen during phase 1.2 from the control lysimeters

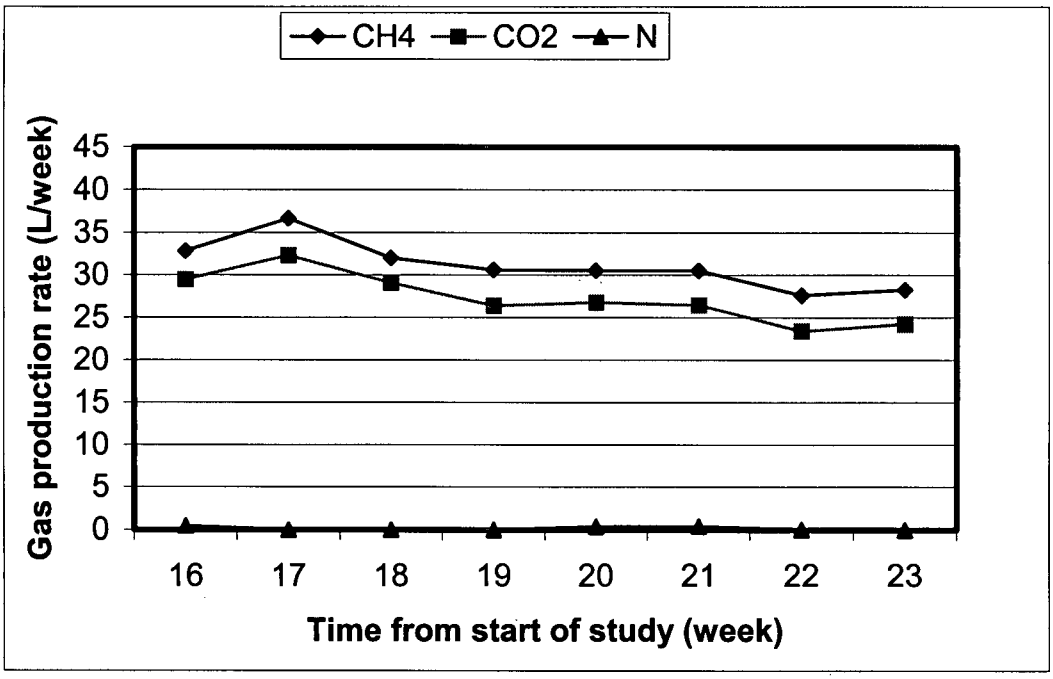

Figure 21 The average production rate for carbon dioxide, methane and nitrogen during phase 1.2 from lysimeters 3 and 4 (with nitrate feed concentration of 600 mg-N/L)

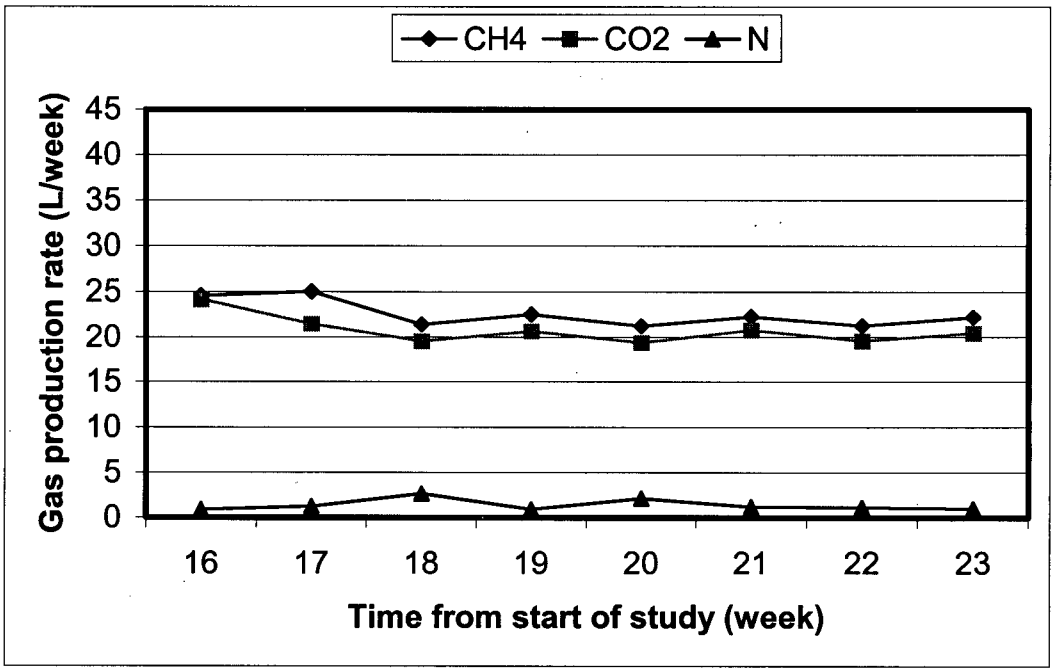

Figure 22 The average production rate for carbon dioxide, methane and nitrogen during phase 1.2 from lysimeters 5 and 6 (with nitrate feed concentration of 100 mg-N/L)

Carbon availability during this phase helped in maintaining the high denitrification efficiency (Figure 18). Other studies have shown that a range of 2 to 4 g-C is needed per 1 g of nitrate-N, depending on the carbon source (McCarty 1969, Carley 1988). The data in Figure 18 show the TOC remained –as a surplus- in leachate after denitrification.

To confirm the efficiency results, a mass balance calculation on nitrogen was done and the results are shown in Table 31. The results are based on the average amount of nitrogen released to the leachate and gas from week 19 until week 22. The results of this phase were lower than the results of the previous phase (1.1) (Table 26). This supports the hypothesis that the high percentage of recovery in nitrogen mass balance, observed during phase 1.1, is related to air trapped within the waste at placement.

The results of phase 1.2 show that the ratios between the masses of nitrogen produced from the lysimeters to the mass of nitrogen introduced to the lysimeters fall in a wide range (between 48 and 117%). A high percentage of error (52%) was associated with lysimeter 6, which was receiving 100 mg-N /L. This error can be attributed to the limited

ability of the gas partitioner to detect/measure gases at low concentrations[15]. The gas partitioner was not successful in providing reliable results at low nitrogen concentrations.

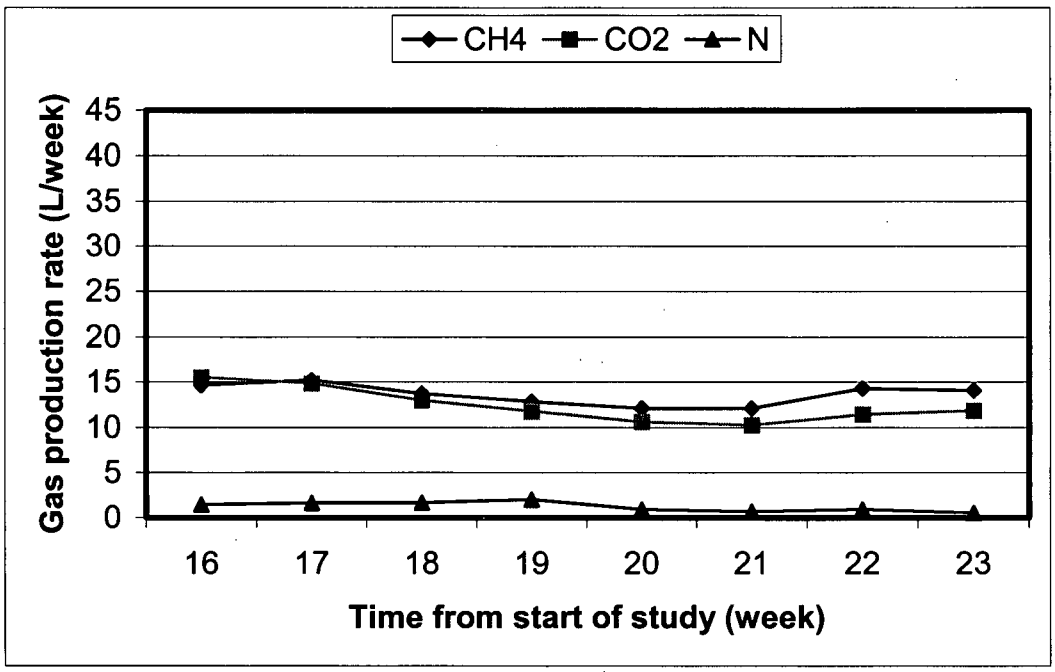

Figure 23 The average production rate for carbon dioxide, methane and nitrogen during phase 1.2 from lysimeters 7 and 8 (with nitrate feed concentration of 600 mg-N/L)

Table 31 Nitrogen mass balance for all the lysimeters during phase 1.2

Nitrate load mg-N/L	Lysimeter number	Nitrogen in g-N during week 19-22	Nitrogen out g-N during week 19-22			Mass out/ Mass in (%)	Number of samples included (leachate + gas)
			Leachate	Gas	Total		
0	1	-	0	0	0	N/A	8
0	2	-	0	0	0	N/A	8
100	5	1.12	0	1.31	1.31	117	8
100	6	1.12	0.01	0.52	0.53	48	8
600	3	6.72	0.01	6.30	6.31	94	8
600	4	6.72	0	5.01	5.01	75	8
600	7	6.72	0.02	4.90	4.92	73	8
600	8	6.72	0.02	5.10	5.12	77	8

Alternatively, the results for the lysimeters that received nitrate feed of 600 mg-N /L (4,7 and 8), fall in a narrow range of 73 to 77%, with lysimeter 3 having a higher value of

[15] The detection limit of the gas partitioner was found to be 3%.

94%. The 25% error in the nitrogen mass balance for lysimeters 4, 7 and 8 may be attributed to incomplete denitrification. Since the process of denitrification involves four consecutive steps, by which nitrate is reduced to nitrogen gas, incomplete denitrification may occur if the denitrification process stops before reaching the end of the fourth step. Incomplete denitrification produces one or more of the nitrogen intermediates (nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O)) as end-products in addition to nitrogen gas. These three intermediates have undesirable attributes for the environment and microbial growth.

Several studies have reported that carbon availability strongly influences the extent of nitrate reduction (Hanaki *et al.* 1992, Weier *et al.* 1993, Parton *et al.* 1996, Percheron *et al.* 1999). During this phase, the ratio of carbon: nitrate was below the recommended level of 3 (Carley 1988) as shown in Figure 24. Hanki *et al.* (1992) support the hypothesis of incomplete denitrification at low carbon: nitrate ratio. They found that a low carbon: nitrate ratio favored the production of nitrous oxide. At a low carbon: nitrate ratio, the reduction of the intermediate products may not be complete and nitrogen oxides gases may be produced instead of nitrogen gas.

Other factors, such as high nitrate and/or nitrite concentrations and low moisture content, have been reported to increase the N_2O: N_2 ratio (Hanaki *et al.* 1992, Weier *et al.* 1993, Parton *et al.* 1996, Percheron *et al.* 1999). The concentration of the influent nitrate feed for lysimeters 3, 4, 7 and 8 (600 mg-N/L) is considered to be high relative to the nitrate concentration used in these studies (less than 600 mg-N /L). Percheron *et al.* (1999) found that N_2O was a major component of the nitrogen mass balance, with the ratio of N_2O:N_2 falling in the range of 0.3 – 1.6. Also the higher the initial nitrate concentration, the higher the N_2O:N_2 ratio. Weier *et al.* (1993) suggested that the high nitrate and/or nitrite concentrations inhibit the reduction of nitrous and nitric oxides.

Although no accumulation of nitrate or nitrite was observed during this phase (1.2), a high concentration may be present at any point during the process of denitrification.

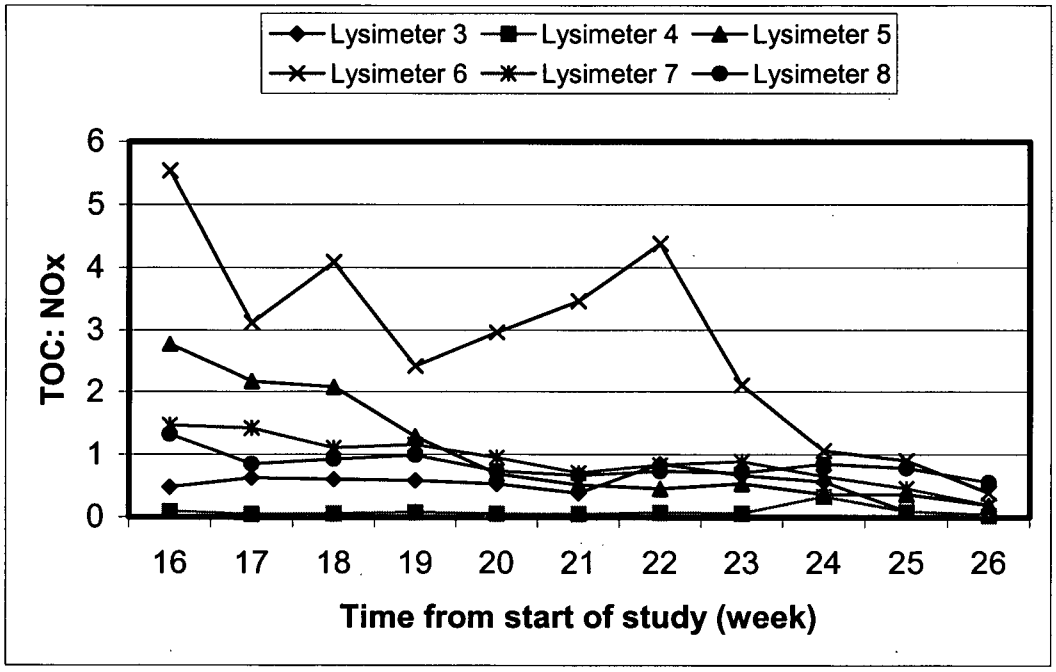

Figure 24 The carbon: nitrate ratio for all the lysimeters during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

6.1.3.2 Effect of Denitrification on the Carbon Emitted to the Environment During Phase 1.2

As mentioned previously in section 6.1.2.3, carbon is released from the waste into the environment through the landfill gas and leachate. The leachate carbon in this phase was calculated based on the results of TOC as in Equation 16. This value was then added to the value for the previous week to obtain the cumulative carbon release from leachate.

Equation 16 TOC (g-C/week)

$$\text{TOC g-C/ week} = \text{TOC g/L} \cdot \text{Q (0.4 L/d)} \cdot \text{7 d/ week}$$

The other source of carbon is landfill gas, where carbon is present as carbon dioxide and methane. The amount of carbon was calculated based on Equation 20 and Equation 27 shown on page 220 and 224 respectively. The concentration of each gas at these conditions = $4 \cdot 10^{-2}$ mole/ L (see section 9.3.3 in Appendix 3 for more details). Knowing that each mole of gas (CO_2 or CH_4) has 1 mole of carbon per 1 mole of compound, and

that the carbon molecular weight is 12, the concentration of carbon in the gas stream is 0.48 (g-C /L).

The amount of carbon produced weekly was calculated using Equation 28 through Equation 30 shown on page 224. This value was added to the value for the previous week to get the cumulative amount of carbon emitted in the gas stream during this phase. The results of the cumulative carbon released during this phase (1.2) are shown in Figure 25, Figure 26 and Figure 27. The values shown in these figures are for this phase only; this means that carbon produced during the first phase was not included.

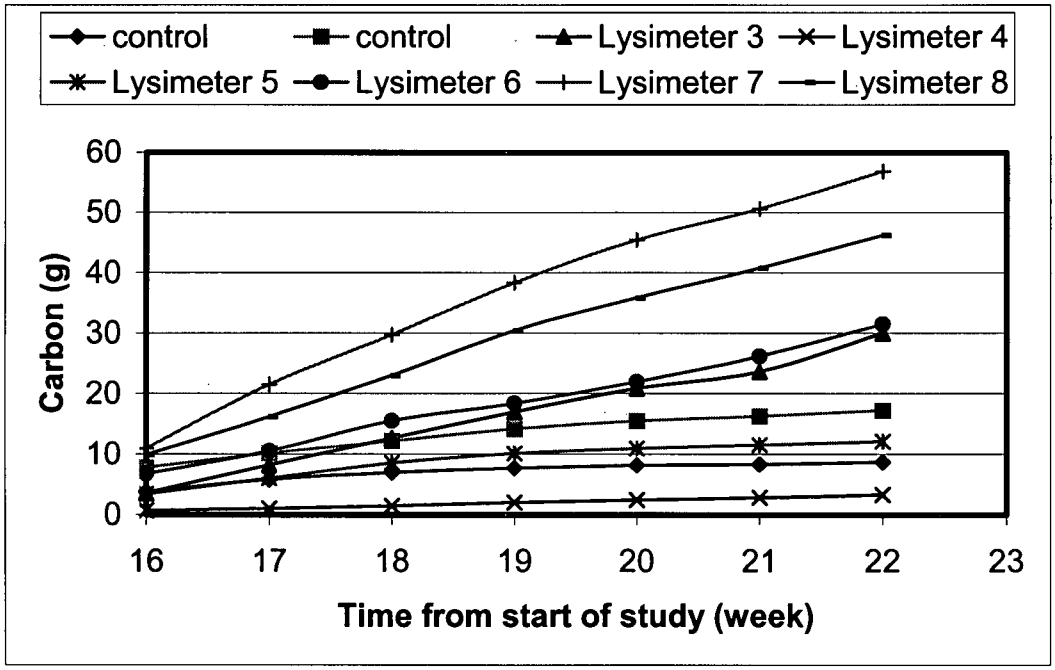

Figure 25 Comparison of the cumulative carbon released by leachate from each lysimeter during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

The data in Figure 25 and Figure 26 show that the lysimeters with nitrate feed of 100 (5 and 6) and 600 mg-N /L (3 and 4) have similar trends and values when compared to the control lysimeters (1 and 2). They also show that the effect of nitrate on the carbon release is minor during this phase, in which nitrate concentrations are between 100 and 600 mg-N /L (for lysimeters 3 to 6). Lysimeters 7 and 8, which were receiving nitrate

feed of 800 mg-N /L during the previous phase (1.1), and 600 mg-N /L during this phase (1.2), emitted the highest amount of carbon from leachate and the lowest amount of carbon from gas (Figure 27).

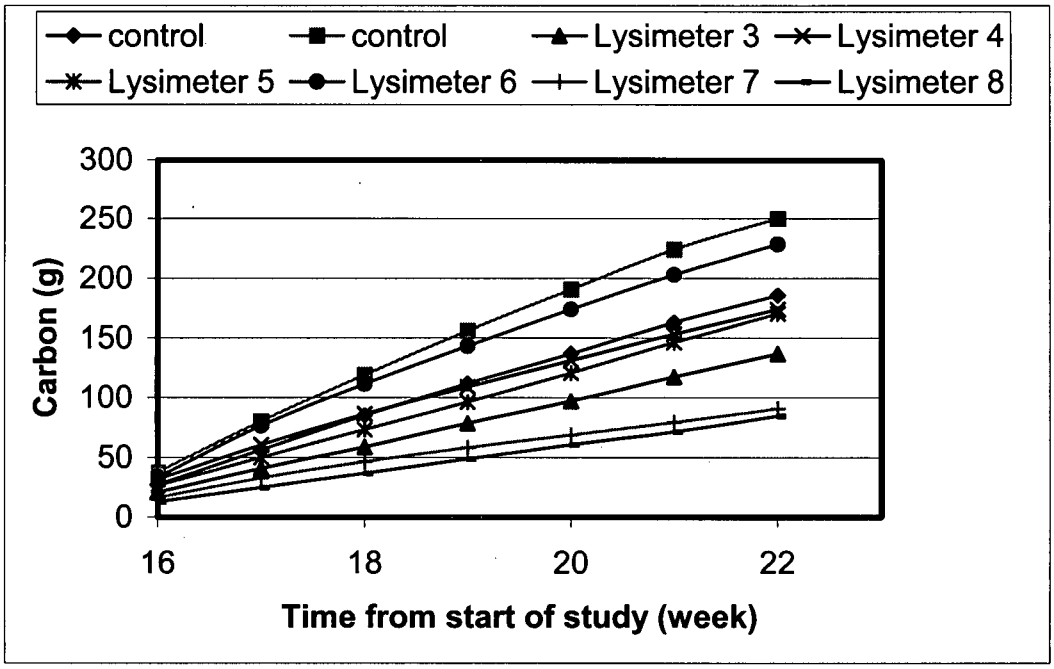

Figure 26 Comparison of the cumulative carbon emitted by gas from each lysimeter during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

Figure 27 shows the total carbon released during this phase (week 16 to week 22). The data show that the gas was the major contributor to the total carbon emitted (61% to 96%). The control lysimeters (1 and 2) have the highest mass of carbon emitted. This is due to the high efficiency of methanogenic bacteria, which are able to degrade the organic materials and convert the soluble carbon in leachate to gas, before it leaves the lysimeter. The high level of methanogenic activity also helps in enhancing the overall process of waste degradation.

The average of the total carbon emitted from lysimeters 3, 4, 5 and 6 during phase 1.2 (196.5 g-C) was 14% less than the average total emitted by the control lysimeters. Therefore, the effect of denitrification on waste degradation was found to be minimal

(14%) during this phase (1.2). Alternatively, lysimeters 7 and 8 released less carbon[16] in total than the other lysimeters, which received the same nitrate concentration (lysimeters 3 and 4[17]). The difference in the amount of carbon released may be attributed to the effect of the high nitrate feed (800 mg-N /L) of lysimeters 7 and 8 during the first phase (1.1). Even during this phase (1.2), methanogenic activities, in lysimeters 7 and 8, were still suffering from the inhibition effect of the high nitrate concentration during the previous phase (1.1).

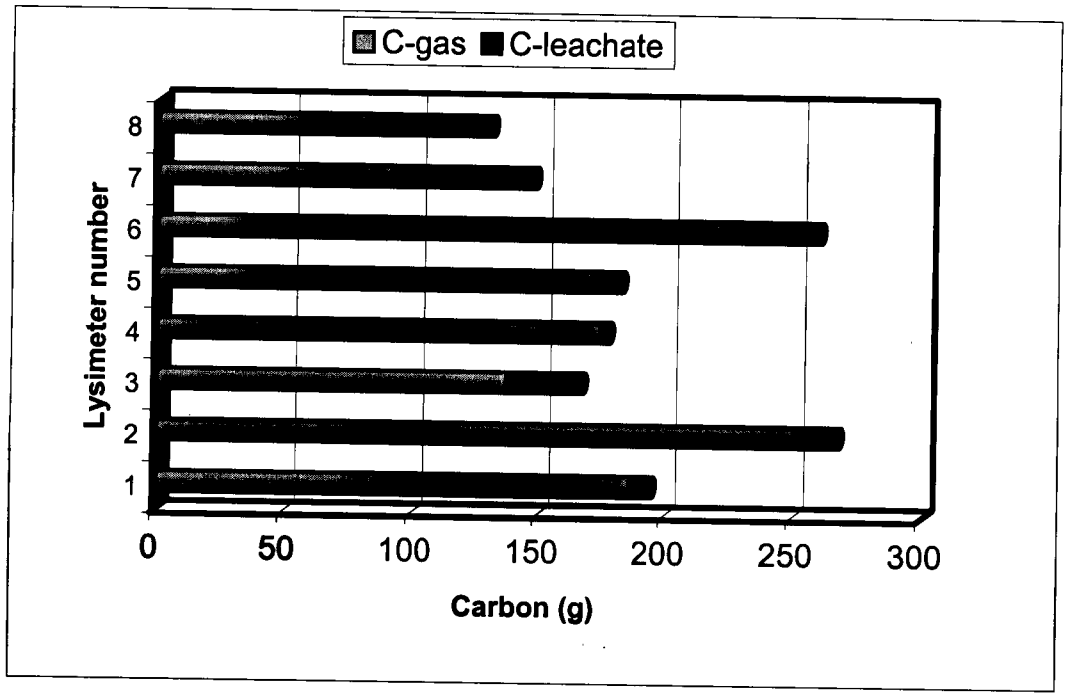

Figure 27 Comparison of the total carbon released to the environment from each lysimeter during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

A study by Percheron *et al.* (1999), found that the higher the nitrate concentration, the lower the amount of methane produced. Although increasing the nitrate concentration

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[16] The average total carbon released from lysimeter 7 and 8 was 40% less than the control and 30% less than the average total carbon released from the other lysimeters.

[17] Lysimeters 3 and 4 received nitrate feed of 400 mg-N/L during phase 1.1 and 600 mg-N/L during phase 1.2.

from 161 to 281 mg-N /L reduced the gas production by 30%, further increasing the nitrate concentration to 560 mg-N /L reduced the gas production by 33% (the difference was only 3%). This result suggests that there might be an optimum nitrate concentration above which higher nitrate concentrations do not effect the gas production, as long as the process of methane formation has been established.

The results of the carbon release during this phase (1.2) and the previous phase (1.1), show that the inhibition effect of denitrification on the methanogenic activities is minor once these activities are well established. It also shows that as long as methanogenic activities have reached their optimum level, the effect of the nitrate concentration is minimal. On the other hand, the effect of denitrification at high nitrate concentration during the initiation of these activities (phase 1.1) was significant (30% less compared to the lysimeters receiving medium nitrate concentration during phase 1.1, and the same nitrate concentration during this phase (1.12)). Decreasing the high nitrate concentration by 25% did not help in increasing the gas production rate.

6.1.3.3 Effect of Changing Nitrate Concentration on the Characteristics of Landfill Gas and Leachate

The feed nitrate concentrations were changed to evaluate the effect of this change on the landfill gas production rate and the leachate strength. Understanding the behavior of the control lysimeters helps in better interpretation of the effect of nitrate during this phase. As time passes, it is expected that the leachate strength would decrease, due to the limilted availability of degradable organic materials. This results in decreasing the BOD:COD ratio. The results for the control lysimeters were as expected. The effluent leachate strength in terms of BOD, and COD decreased sharply (Figure 28), and the average BOD:COD ratio decreased as well (Figure 28). In addition, the results of the gas production rate show that the production rate did not increase (the production rate was constant for lysimeter 1 and decreasing for lysimeter 2 (Figure 29)). These results, shown in Figure 28 and Figure 29, confirm the expectation that the lysimeters were approaching the maturation phase, where the amount of soluble organic materials is limited.

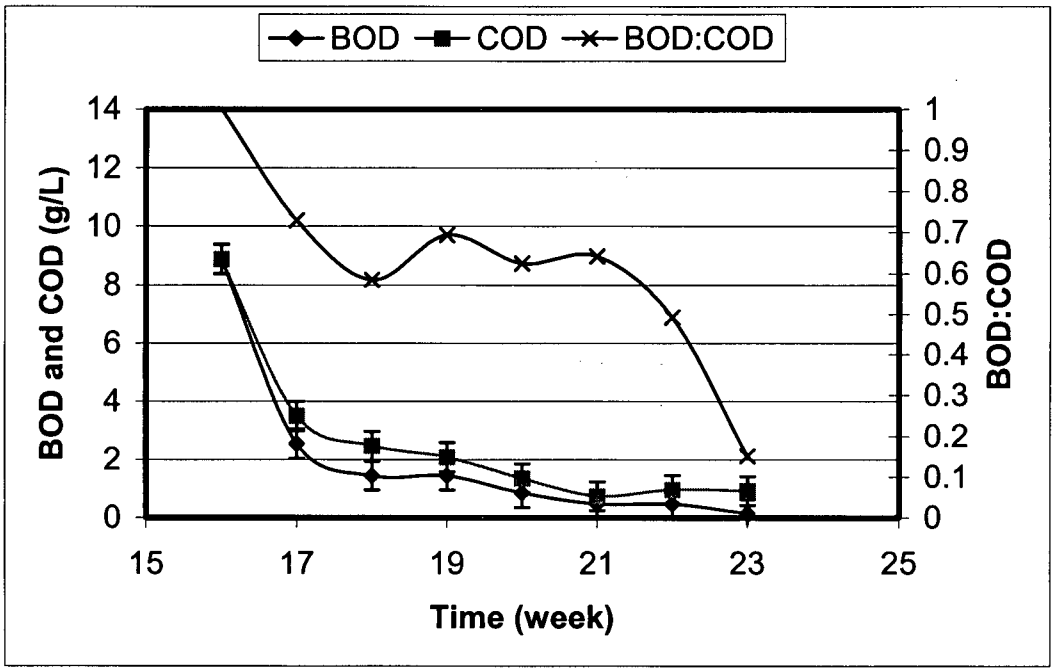

Figure 28 The average leachate characteristics in terms of BOD, COD and BOD:COD ratio for the control lysimeters during phase 1.2

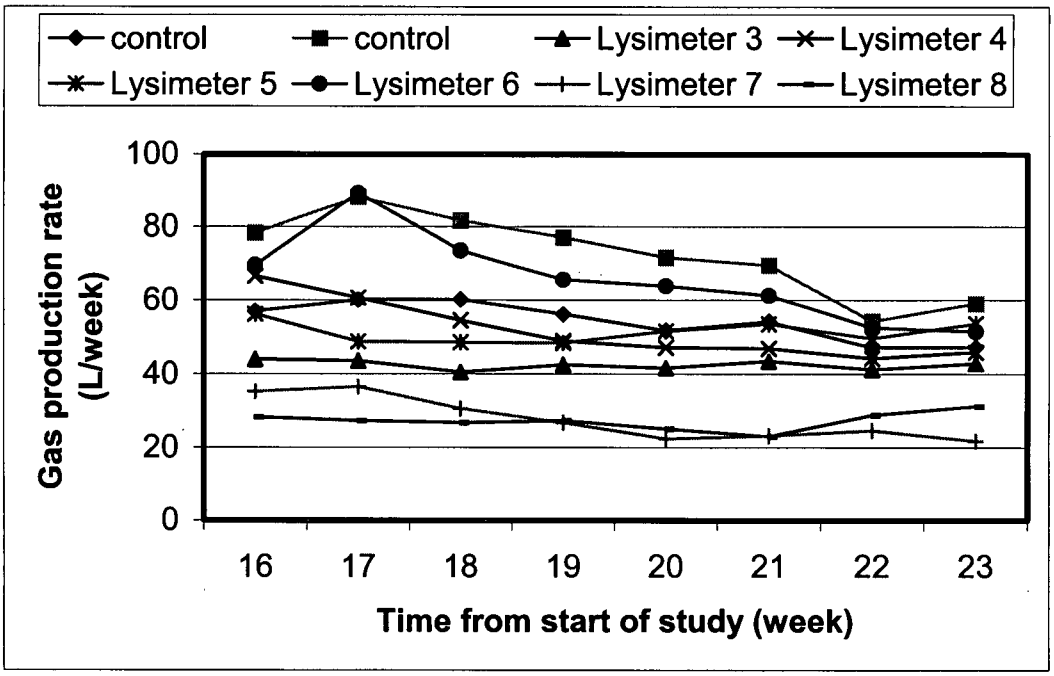

Figure 29 The gas production rate for all the lysimeters during phase 1.2 (the nitrate feed was 100 mg-N/L for lysimeters 5 and 6, and 600 mg-N/L for lysimeters 3, 4, 7 and 8)

6.1.3.3.1 Decreasing the Feed Nitrate Concentration

During the first phase (1.1), lysimeters 7 and 8 were receiving 400 mL/d of solution with the nitrate concentration at 800 mg-N /L. In this phase, the nitrate concentration was decreased by 25%, i.e. these two lysimeters received a nitrate level of 600 mg-N /L. It was expected that this decrease would be sufficient to produce changes, such as an increase in the gas production rate and a decrease in the leachate strength. Nevertheless, the changes were minor. Figure 30 through Figure 32 show the data for COD and BOD_5, while Figure 29 and Figure 33 show the gas production rate for lysimeters 7 and 8.

Hypothetically, the reduction in nitrate concentration should aid the process of methane formation, by providing a better environment with fewer toxins and less competition for substrate. With more gas production, carbon in the leachate diminishes and leachate with low BOD_5 is expected. On the other hand, the limited availability of carbon in the leachate may affect the process of denitrification, which depends on leachate for its growth and energy.

Results were not exactly as expected. The gas produced from these lysimeters did not show any increase in its production rate (Figure 29). Comparing the production rate of this phase (1.2) to the production rate of the previous phase (1.1), it can be confirmed that the reduction in influent nitrate concentration did not enhance gas production (Figure 33). This steady production rate may be due to the inhibition effects of the high influent nitrate feed on the initiation of methanogens during the first phase, which persisted even after the feed nitrate concentration was reduced.

The COD data (Figure 31) show that the average COD of the effluent leachate decreased at the same rate during both phases (1.1 and 1.2), which neglect the effect of decreasing the feed nitrate concentration on the leachate COD. Comparing the slope of the COD line from lysimeters 7 and 8 to that from the control lysimeters, it can be shown that the COD of the control lysimeters was decreasing in a faster rate in .

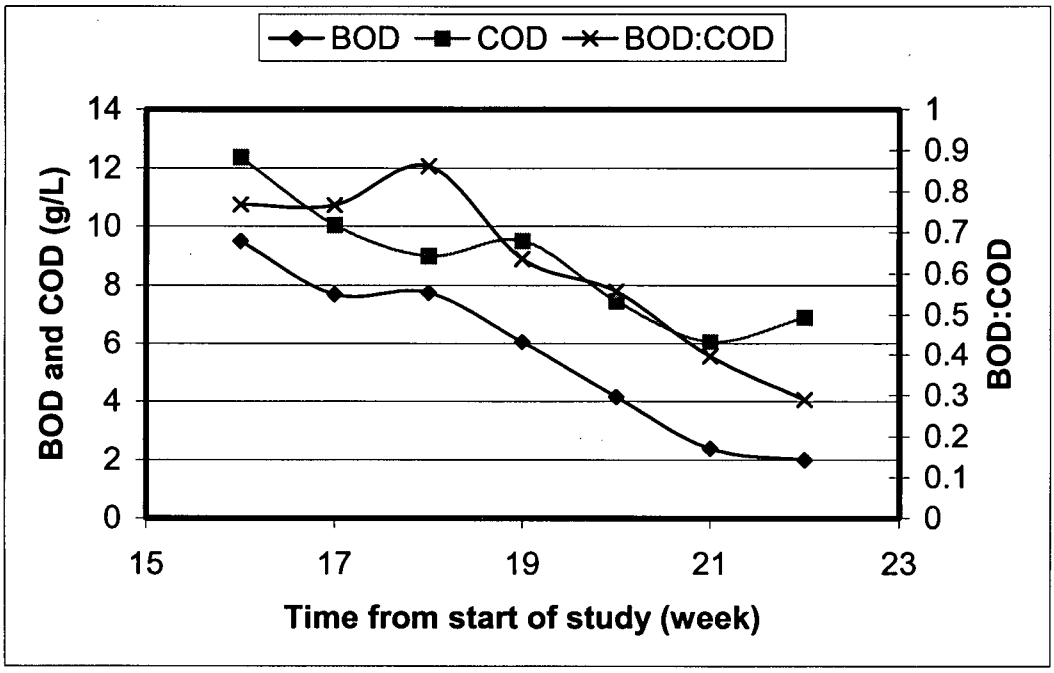

Figure 30 The average leachate characteristics in terms of BOD, COD and BOD:COD ratio for lysimeters 7 and 8 during phase 1.2

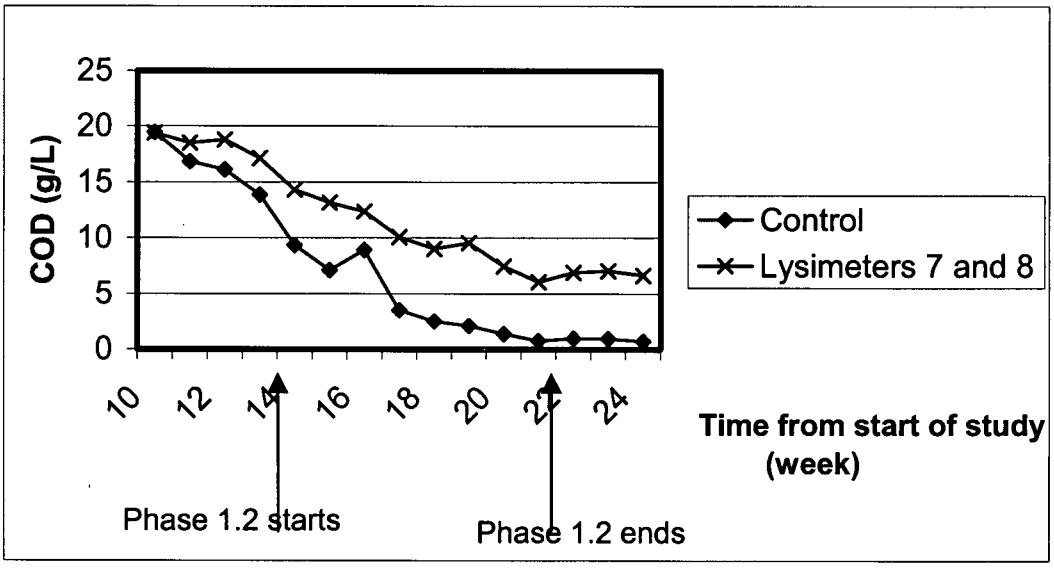

Figure 31 The average COD values for lysimeters 7 and 8 during phases 1.1 and 1.2

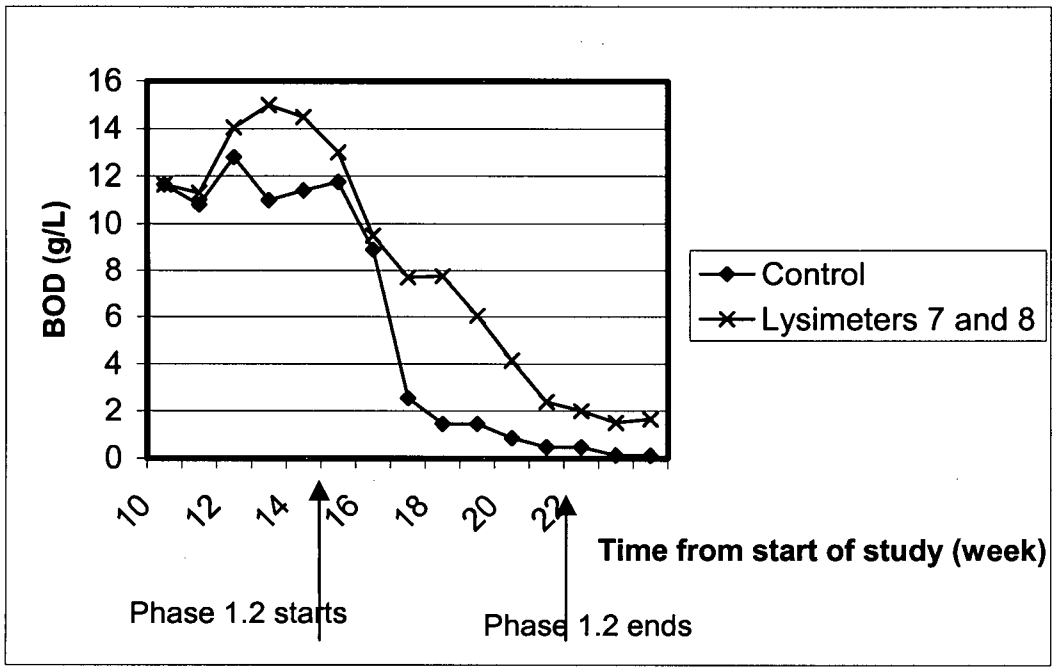

Figure 32 The average BOD values for lysimeters 7 and 8 during phases 1.1 and 1.2

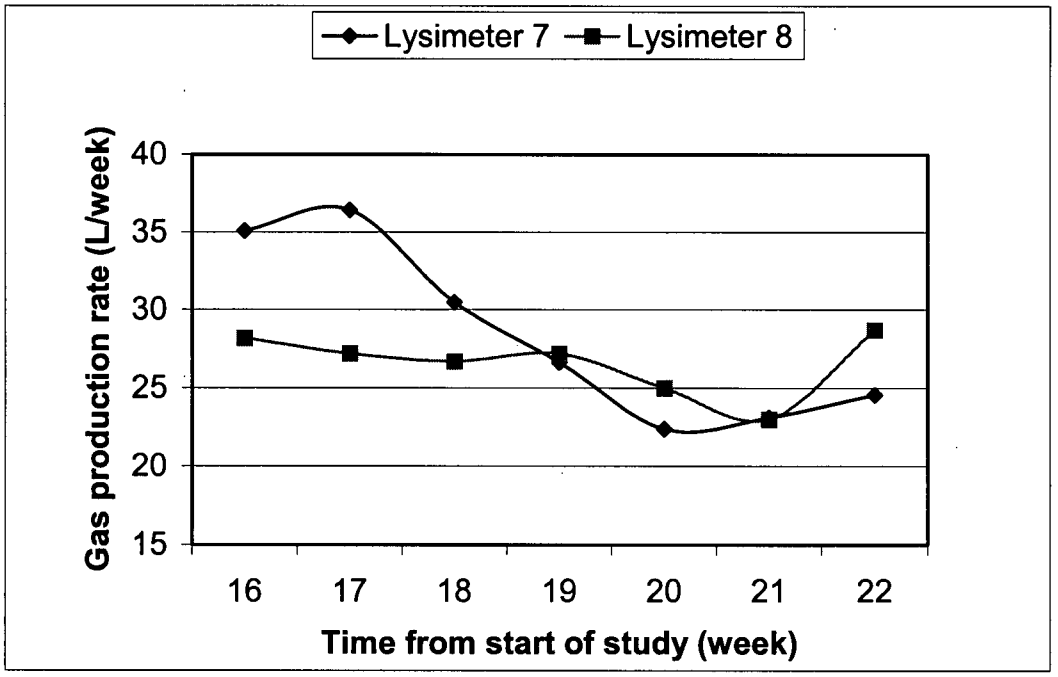

Figure 33 The gas production rate for lysimeters 7 and 8 during phase 1.1 and 1.2

The BOD results (Figure 32) were different than the results of the COD (Figure 31). The average BOD of the effluent leachate from lysimeters 7 and 8 did show a change in its trend at the beginning of this phase (1.2) (Figure 32). The BOD had started to decrease at a sharp rate by week 15. Comparison between the slope ofs the BOD line from the control lysimeters with the slope line from lysimeters 7 and 8 show minimal differences. This decrease may be due to the decrease in the feed nitrate concentration or it may be due to the fact that the lysimeters were aging. By week 17, the BOD removal rate from lysimeters 7 and 8 was slower than that from the control lysimeters.

The effect of nitrate reduction on leachate and gas characteristics was small. Several factors may have caused this behavior. First of all, it is important to stress the fact that evaluation of such an effect in a landfill environment is a very difficult task, because the landfill is a heterogeneous and diverse system, and the system characteristics change with time. Therefore, this comparison requires the use of identical wastes that have the same history. Since it is almost impossible to expect the same storage content of waste and bacteria at any time of the experiment, variations in results are anticipated.

A possible explanation for this behavior may be that the feed nitrate concentration during the first phase was very high (800 mg-N /L), so that it affects the results of the following phases. Roy and Conrad (1999) have studied the effected of different nitrate concentrations (1 to 10 mM) on methane production. They found that a high nitrate concentration led to a long period of inhibition to methanogenic bacteria after the complete reduction of nitrate. They also found that the higher the nitrate concentration, the longer the inhibition period was (2.8 days per mM of nitrate). Thus, the lysimeter system would require 160 days to overcome the effect of the initial nitrate concentration (800 mg-N /L); this suggests that the duration of the second phase was too short (49 days) for a change in system behavior to arise.

Another possible reason for these results is that the change in the concentration (25%) was not significant. The new concentration of 600 mg-N /L was not low enough to show significant evidence of an effect.

Kluber and Conrad (1998b) have shown that methanogenic bacteria start to produce methane after the complete reduction of nitrate. According to their results, methane production increased linearly, but its maximum was 30% less than its initial production rate (before nitrate addition). The results of the research done by Kluber and Conrad (1998b) and Roy and Conrad (1999) agreed with the low gas production rate observed in lysimeters 7 and 8.

6.1.3.3.2 Increasing the Nitrate Feed Concentration

In contrast with the previous test, this test examined the effect of increasing the feed nitrate concentration on landfill end-products. In the first case (low nitrate), the concentration was increased by 500% from 20 to 100 mg-N /L, while in the second case (the medium nitrate), it increased by 50% from 400 to 600 mg-N/L. The changes in the concentrations started by the first day of week 16.

As the feed nitrate concentration increased, it was expected to result in less gas production and stronger leachate. The comparison between the general trends of the BOD and COD measurements (Figure 34 and Figure 35), to the BOD and COD measurements of the control lysimeters (Figure 28), show few differences. The lysimeters that subjected to an increase in their nitrate feed, exhibited less COD decreasing rate. In addition, a gap was initiated between the COD and BOD lines from lysimeters 3, 4, 5 and 6, while there was no gap initiated between the two lines from the control lysimeters.

A possible explanation is that the increase in the nitrate concentration disturbs the process of waste degradation. Denitrification inhibits methanogenic activity, which fails to utilize acetate and hydrogen. The accumulation of acetate and hydrogen inhibits acetogenic bacteria. Other bacteria responsible for hydrolysis and acidogenesis may be inhibited due to the accumulation of end-products. Thus, degradation activities, of materials that were in between processes, were reduced, and these materials were flushed as leachate COD. Due to the difficulties associated with degrading long-chain organic materials, these materials did not contribute to the BOD_5 measurements.

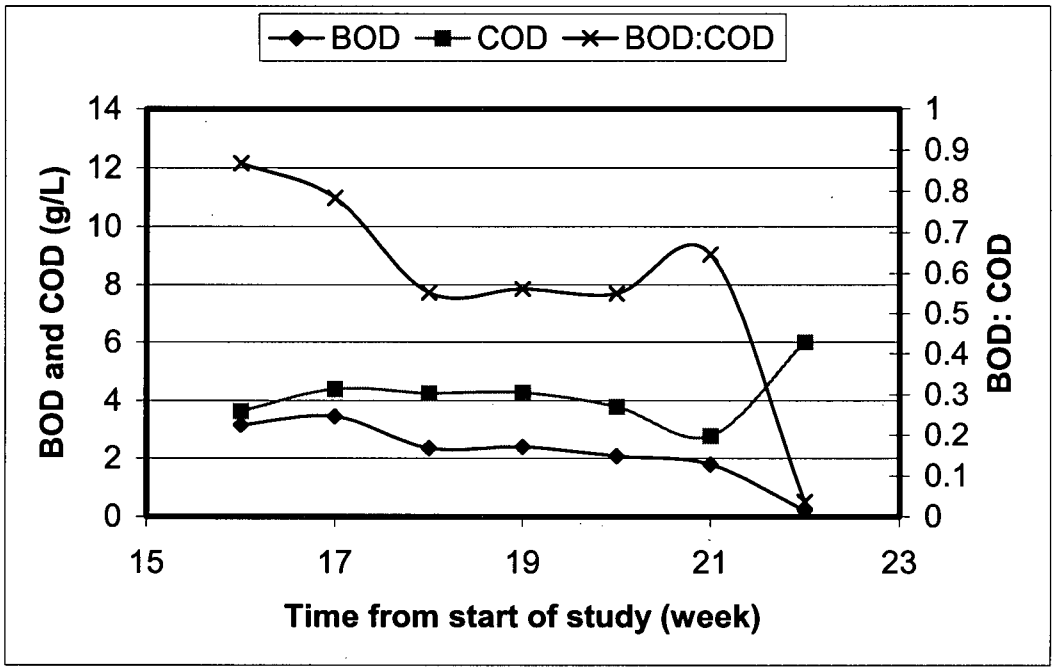

Figure 34 The average leachate strength in terms of BOD and COD for lysimeters 3 and 4 during phase 1.2

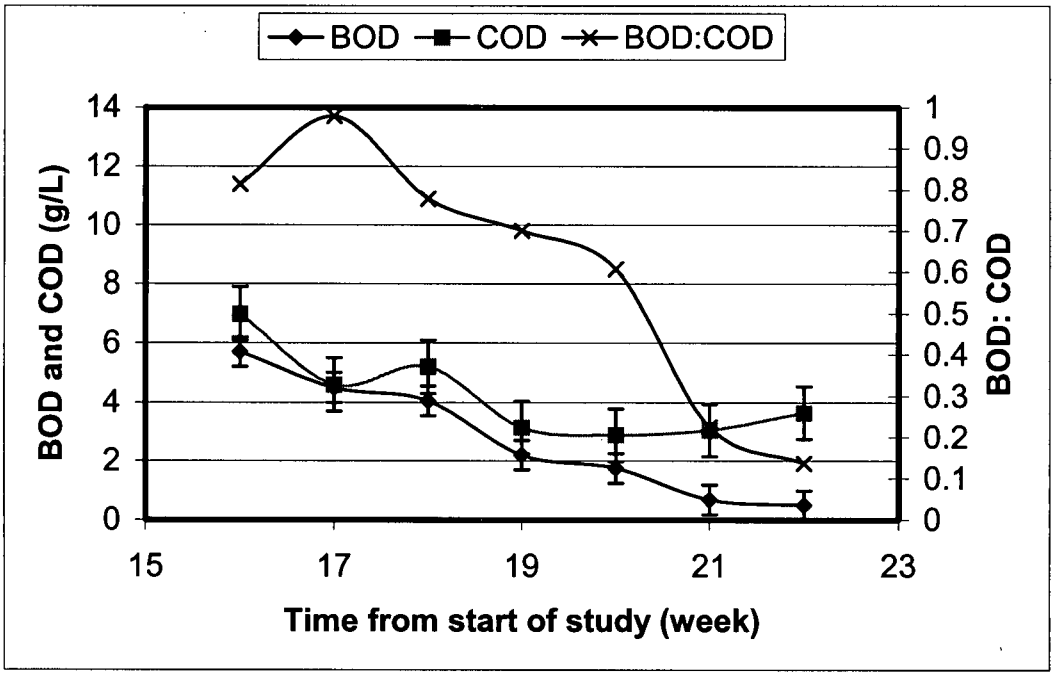

Figure 35 The average leachate strength in terms of BOD and COD for lysimeters 5 and 6 during phase 1.2

On the other hand, denitrification was found to inhibit methanogenic bacteria, therefore, it was expected that the gas production rate for lysimeters 3, 4, 5 and 6 would be reduced. Figure 36 and Figure 37 show that the gas production rates started decreasing between week 15 and 18. This decrease may be due to the effect of increasing the nitrate feed concentration and/or due to the fact that the lysimeters were approaching the maturation phase. During the maturation phase, the substrate available for methane formation reached its minimum value's, indicating that less carbon was available in the waste. Comparison of the total amount of carbon released to the environment from lysimeters 3, 4, 5 and 6, with the total amount of carbon released by the control lysimeter (Figure 38), supports the contention that these lysimeters were aging, while the effect of nitrate on gas production rate was still not confirmed.

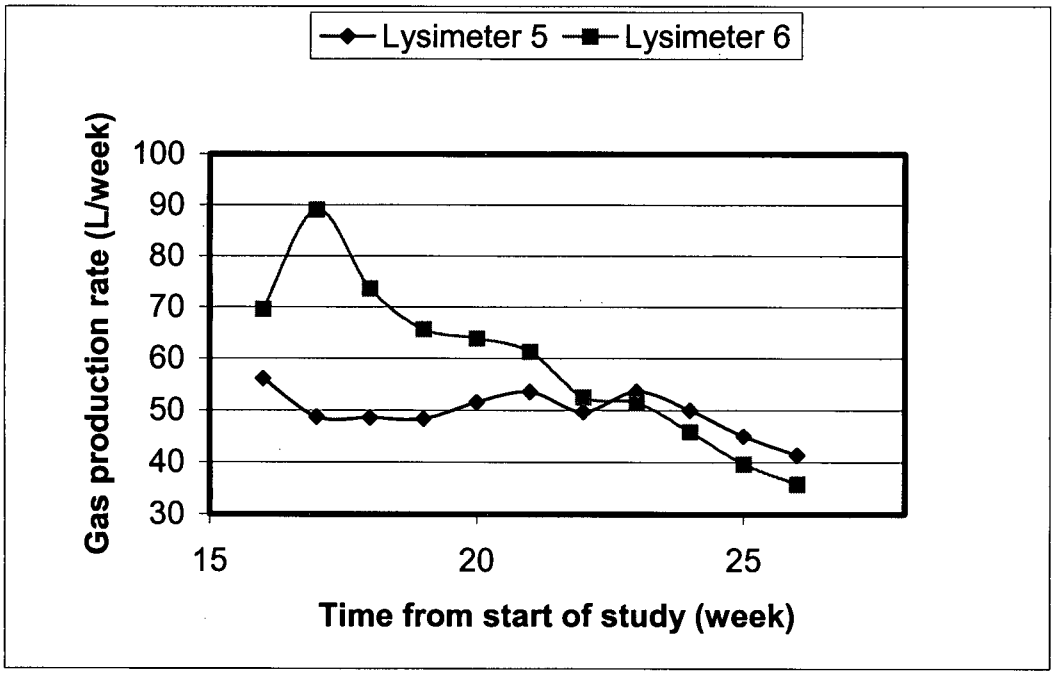

Figure 36 Gas production rate for lysimeters 5 and 6 during phase 1.2

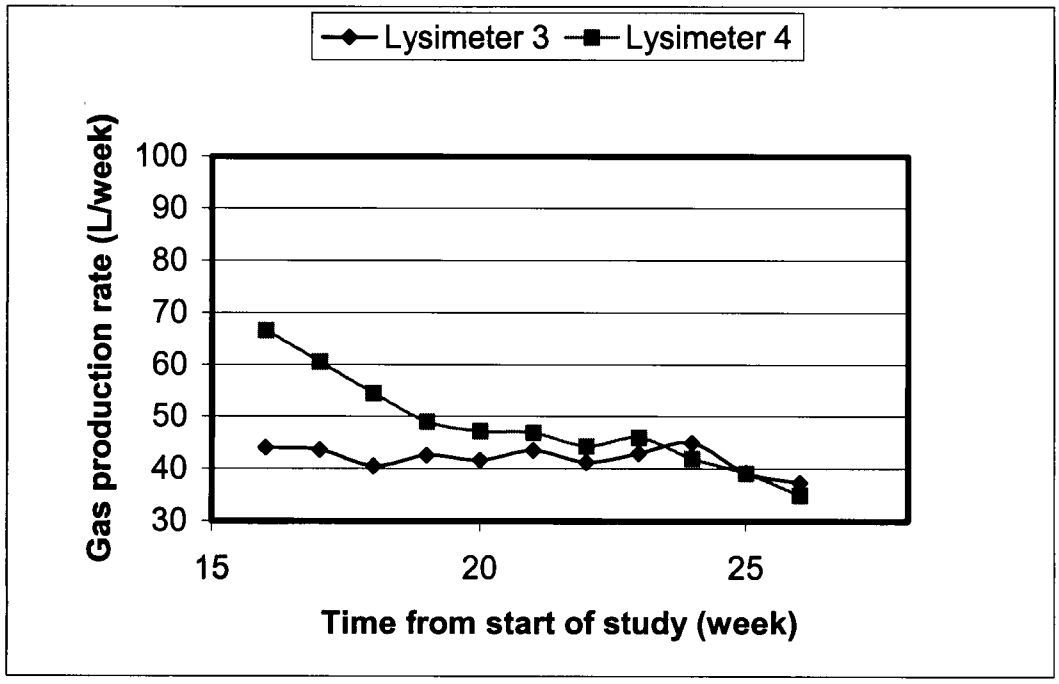

Figure 37 Gas production rate for lysimeters 3 and 4 during phase 1.2

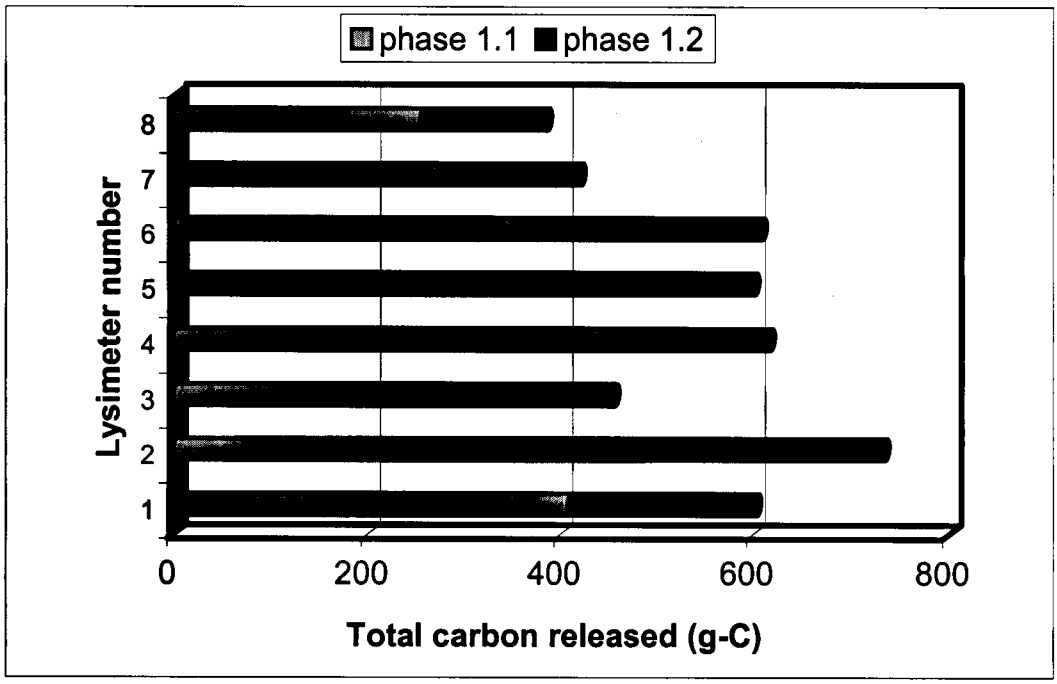

Figure 38 The total carbon release during phase 1.1 and phase 1.2 by each lysimeter

6.1.3.4 Overview –Phase 1.2

The results of this phase confirm the feasibility of denitrification in a landfill bioreactor; however, it may be associated with incomplete denitrification. The effect of

denitrification on the carbon released to the environment, and hence waste degradation was found to be minor, as long as methanogenic activities are well established.

The effects of decreasing the nitrate feed on characteristics of landfill gas and leachate were minor. This may be due to the effect of the high nitrate concentration during the initiation of the methanogenic activities. The inhibition effect of denitrification on methanogenic bacteria was found to persist, even after reducing the high nitrate concentration by 25%.

Increasing the low and medium nitrate concentration reduces the COD decreasing rate, while the effects on gas production were not confirmed. The results also support the hypothesis of the previous phase (1.1), that denitrification affects the overall process of waste degradation.

6.1.4 Experiment (1) –Phase 1.3

The objective of this phase was to evaluate the long-term performance of the denitrification bioreactors. This evaluation was based on two criteria; the efficiency of the bioreactor to denitrify the feed during the maturation phase in which carbon is limited, and the ability of the bioreactor to degrade the organic materials. Another goal of this phase was to investigate the feasibility of using methane to support denitrification in a mature landfill. An influent nitrate concentration of 100 mg-N /L was chosen for this phase. The flow rate of the nitrate feed remained at 400 mL/day. Three lysimeters (5, 6, and 7) were used in this phase in addition to the control lysimeters (1 and 2). Lysimeters 5, 6 and 7 received different nitrate concentrations during the previous phases as shown in Table 32.

Table 32 History of the lysimeters used in phase 1.3

	Nitrate Concentration (mg-N/L)		
Lysimeter number	Phase 1.1 (15 weeks)	Phase 1.2 (7 weeks)	Phase 1.3 (17 weeks)
5	20	100	100
6	20	100	100
7	800	600	100

As a landfill ages, the leachate strength (COD and BOD) decreases, and hence the carbon available for denitrifying bacteria decreases; this decrease may affect the denitrification efficiency. The leachate characteristics (Figure 40 and Figure 41) show that the lysimeters were in the mature phase, where the COD was lower than 500 mg/L, and the BOD was lower than 100 mg/L. Due to the limited carbon availability associated with matured leachate, low denitrification efficiency was expected. Nevertheless, the efficiency of denitrification during this phase (1.3) remained high (between 99.6% and 100%), with very low NO_x in the effluent leachate (Figure 39). The low effluent NO_x concentrations show that the mature lysimeters were able to reduce nitrate and nitrite, and decrease their concentrations in the leachate substantially. Therefore, denitrification in mature lysimeters did not appear to suffer from carbon deficiency during this phase (1.3).

The source of carbon used for denitrification was unlikely to be the leachate itself (i.e. VFAs). The TOC and BOD of the effluent leachate were not sufficient to support denitrification. Carley (1988) found that the minimum amount of carbon required for complete denitrification ranged between 3 and 4 g-C / g-N depending on the type of carbon. Values obtained from the effluent leachate TOC show that the ratio of carbon: nitrate-N for all lysimeters was below the recommended ratio (Figure 42). However, the effluent TOC concentration may be less than the leachate TOC concentration in the denitrification zone.

The gas production provides a better interpretation of the leachate TOC concentration at different points of the lysimeter. The gas production rate for the three lysimeters decreased during this phase (Figure 43). The gas meter of lysimeter 7 was not working properly after week 30; hence the data from week 31 are not reliable.

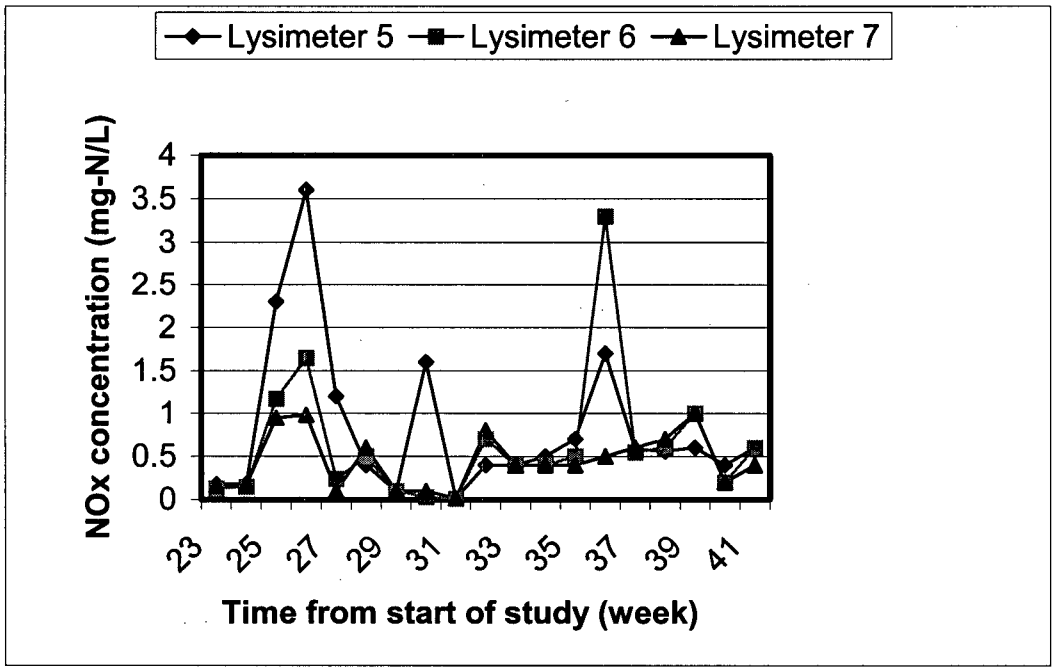

Figure 39 Comparison of effluent NO_x concentration from lysimeters 5, 6 and 7 during phase 1.3

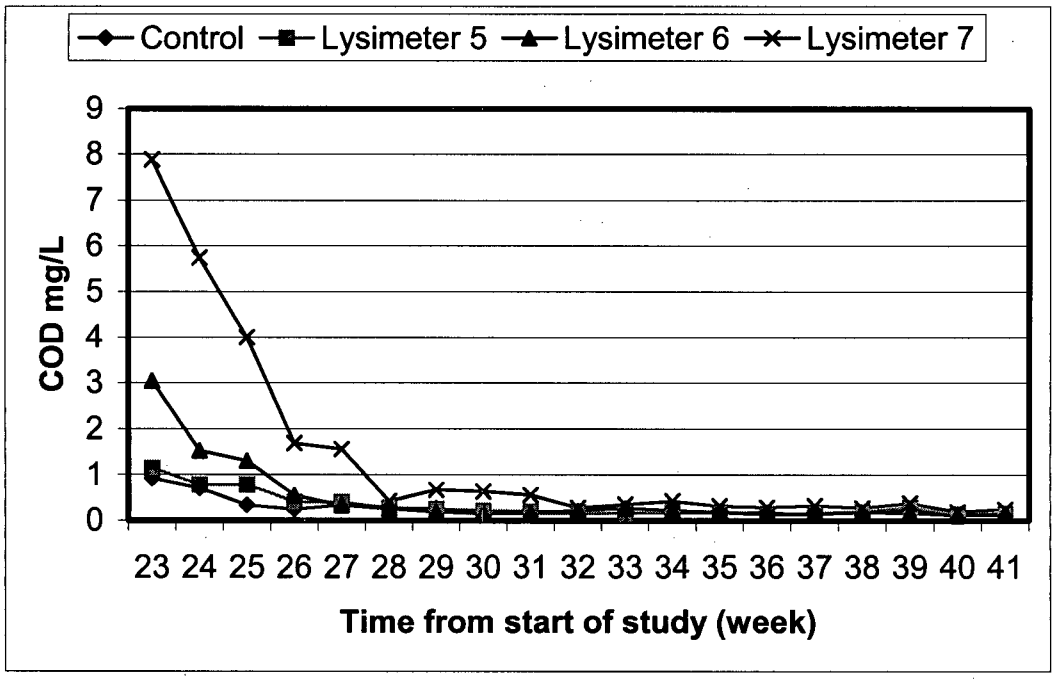

Figure 40 Comparison of effluent COD concentration from lysimeters 5, 6 and 7 during phase 1.3

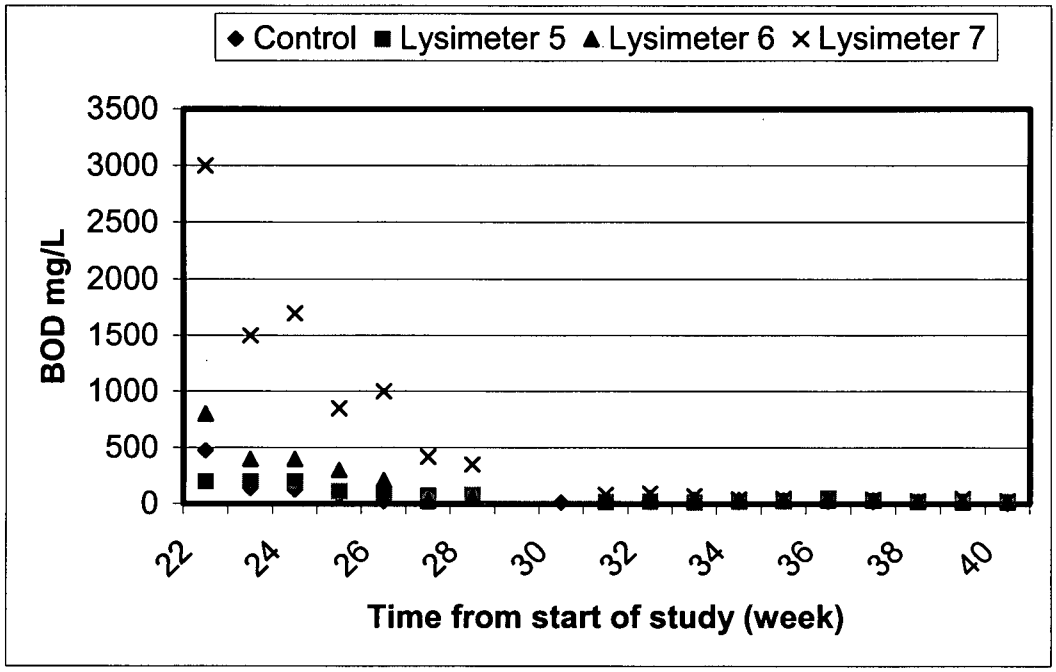

Figure 41 Comparison of effluent BOD concentration from lysimeters 5, 6 and 7 during phase 1.3

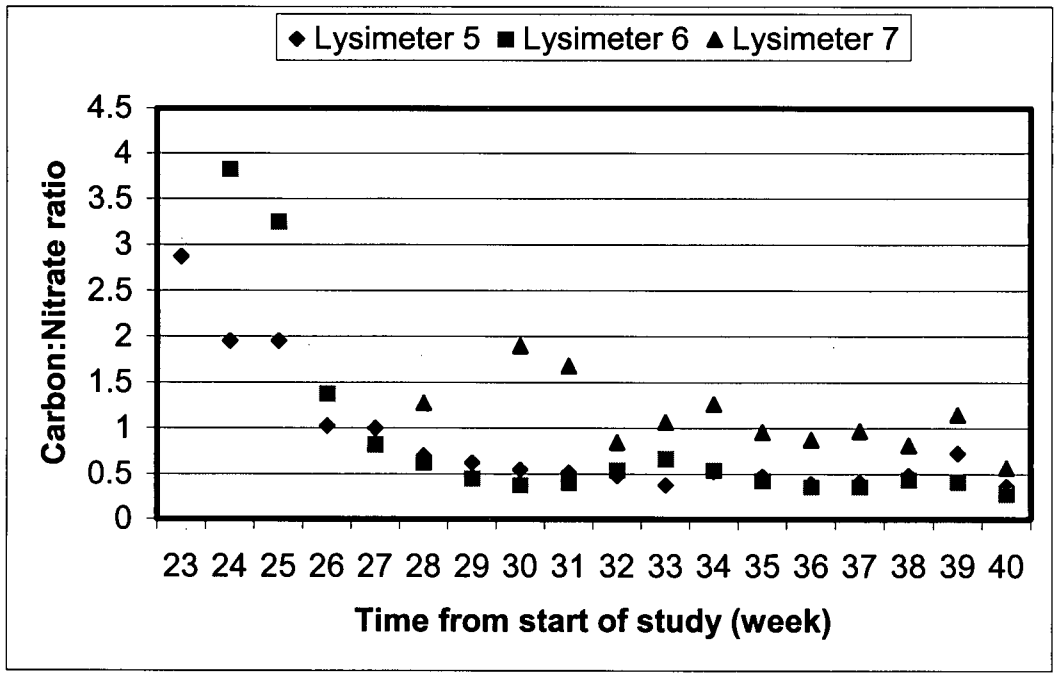

Figure 42 Comparison of carbon:nitrate-N ratio from lysimeters 5, 6, and 7 during phase 1.3

The decreasing trend of the gas production rate shows that the lysimeters were aging and that the TOC concentration in the leachate was decreasing in the lysimeter. In such conditions, there is a better opportunity for methane to be utilized as a carbon source for denitrification. According to Equation 8, an influent nitrate concentration of 100 mg-N /L would consume 0.3 L-CH_4 /week to produce 0.3 L-CO_2/week, assuming that 100% of the denitrifying bacteria are growing on methane. The production rate for carbon dioxide and methane are shown in Figure 44, Figure 45 and Figure 46 for lysimeters 5, 6 and 7 respectively. The quantity of methane consumed by denitrifiers bacteria is insignificant (0.5% to 3%), compared to the quantity produced by methanogenic bacteria; therefore, the methane production rate is not sufficient evidence to prove that methane was utilized to support denitrification.

Moreover, Figure 44, Figure 45 and Figure 46 show no signs of nitrogen gas production. The absence of nitrogen gas was attributed to the low concentration of nitrogen gas relative to the other gases present and to the low sensitivity of the gas partitioner. Therefore, the results of the mass balance on nitrogen are also not reliable for this phase. Incomplete denitrification is not expected to be responsible for the absence of nitrogen gas due to the relatively low nitrate feed concentration (100 mg-N/L).

The effect of denitrification on waste degradation was also investigated during this phase (1.3). The waste degradation was measured by the amount of carbon released into the environment through the leachate and gas. The results for lysimeters 5 and 6 show that denitrification, with an influent nitrate concentration of 100 mg-N /L, did not hinder the process of waste degradation (Figure 47). The difference in the total amount of carbon emitted by each lysimeter (5 and 6) compared to the total amount of carbon emitted by the control lysimeters was insignificant (less tan 6%). Alternatively, the results of lysimeter 7 show that the amount of carbon released was reduced by denitrification. This was attributed to two factors: the fact that this lysimeter received a high nitrate concentration influent during the first phase, and the gas meter was not working properly during this phase (1.3).

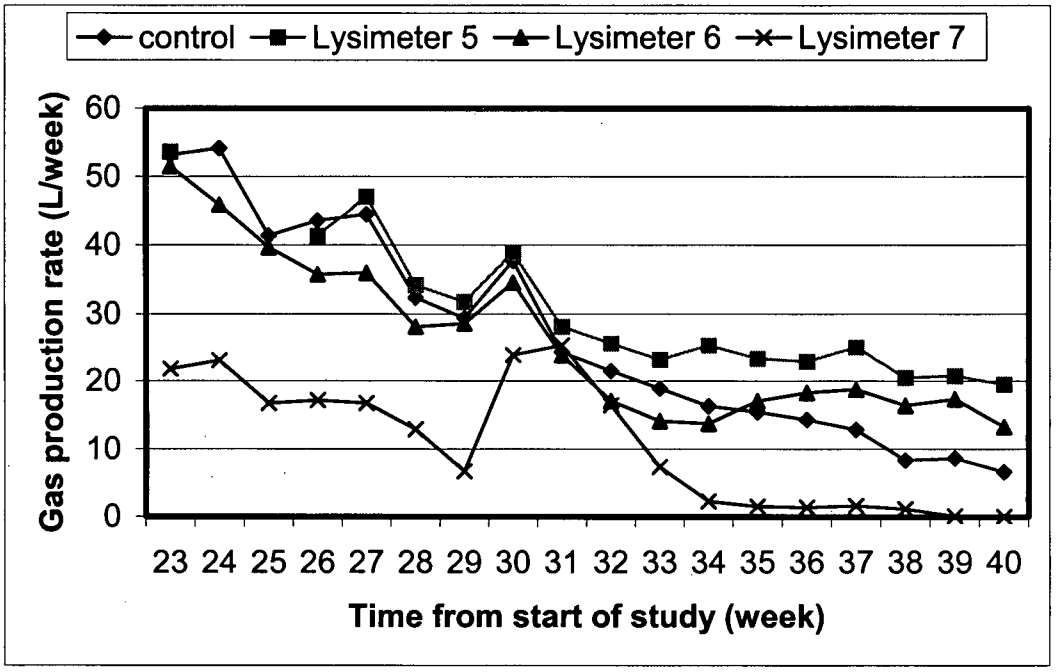

Figure 43 Total gas production rate for lysimeters 5, 6, and 7 during phase 1.3

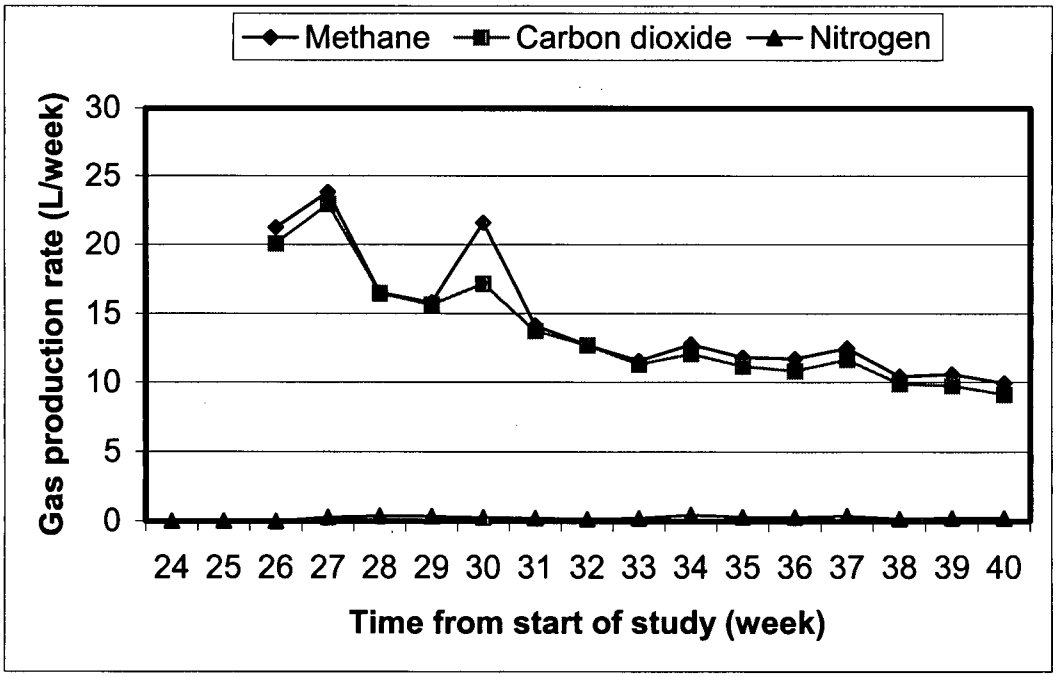

Figure 44 Gas production rate for lysimeter 5 during phase 1.3

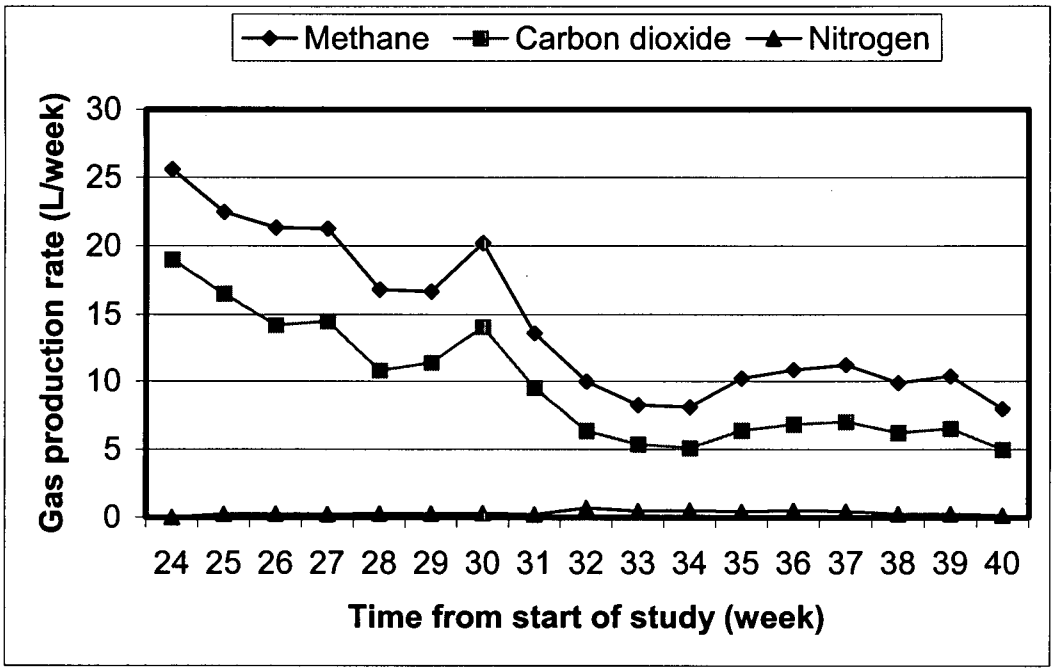

Figure 45 Gas production rate for lysimeter 6 during phase 1.3

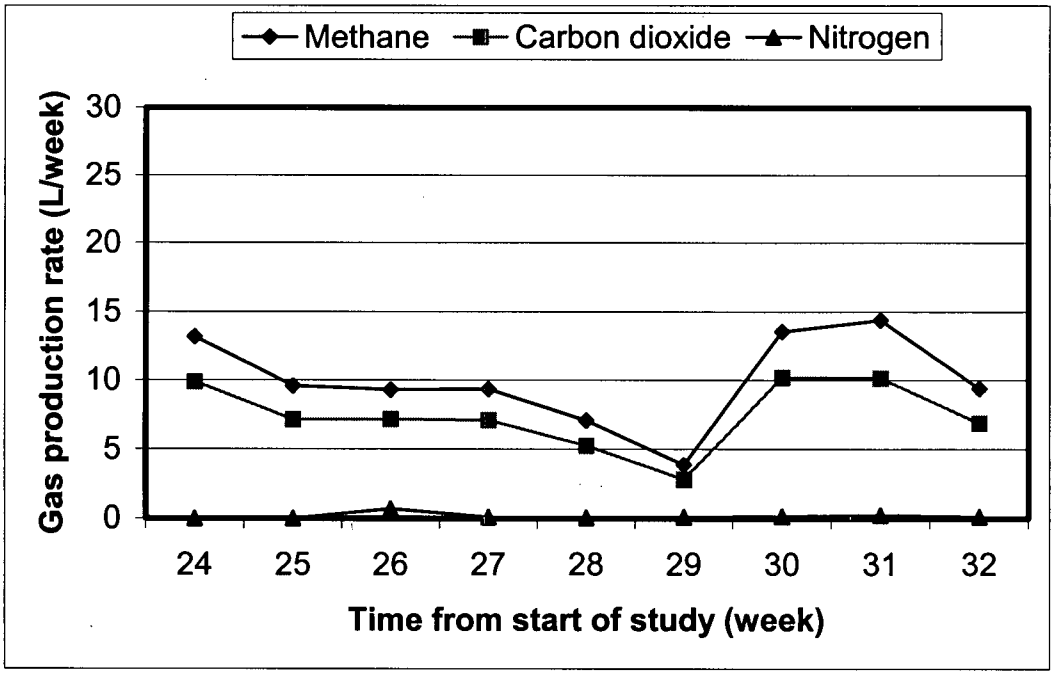

Figure 46 Gas production rate for lysimeter 7 during phase 1.3

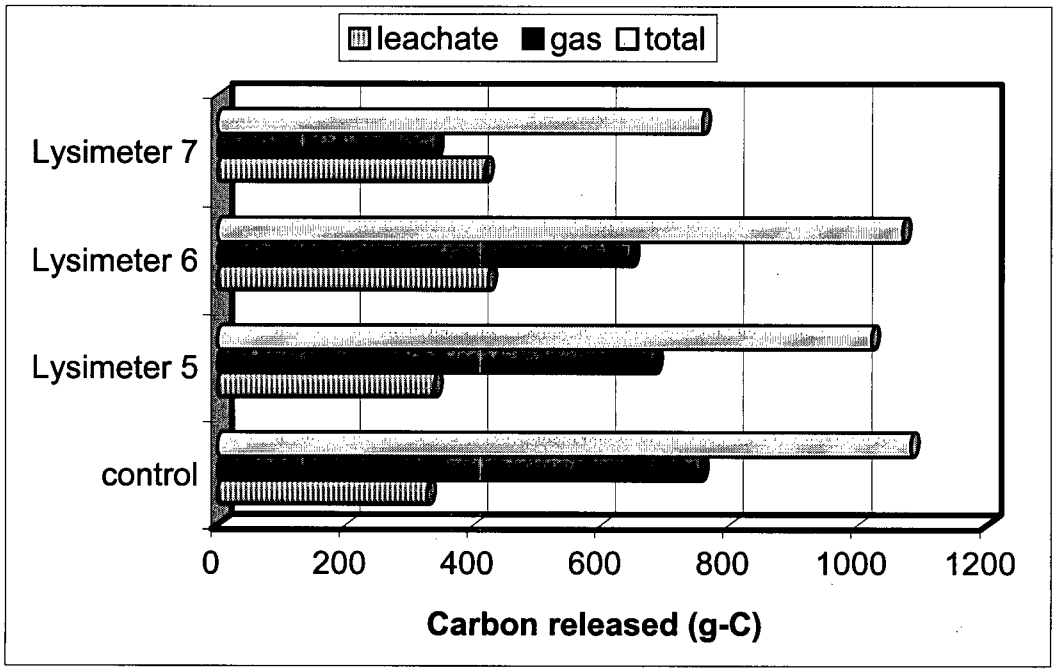

Figure 47 The cumulative carbon released by leachate, by gas and the total carbon released during phases 1.1, 1.2 and 1.3 for lysimeters 5, 6 and 7 compared to that released from the control lysimeters

6.1.4.1 Overview –Phase 1.3

The leachate and gas data show that the lysimeters were in the maturation phase, and that under such condtions, denitrification with high efficiency was feasible. In addition, denitrification (at a nitrate concentration of 100 mg-N /L) did not hinder the process of waste degradation during the period of 510 days. The use of methane, as a carbon source for denitrification, was not detected in this phase (1.3). As such, increasing the nitrate concentration was thought to provide stronger evidence towards the feasibility of the process of denitrification supported by methane. Therefore, in phases 1.4 and 1.5, the concentration of the nitrate feed was increased to evaluate and prove the process of denitrification with methane as a source of carbon.

6.1.5 Experiment (1) –Phase 1.4

The objective of this phase (1.4) was to evaluate the effect of landfill carbon content[18] on the process of denitrification, using a higher nitrate feed concentration. As a landfill ages, the strength of the leachate (as BOD and TOC) decreases, and this decrease reflects the decrease in the amount of carbon stored in the MSW. The limited carbon availability is expected to affect the process of denitrification, which requires the carbon to be at certain levels[19]. Therefore, the effect of the lysimeter carbon content on the efficiency of denitrification was investigated in this phase.

Three lysimeters with three different carbon contents were used in this phase (1.4). Assuming that all of the lysimeters started with the same carbon content, calculations of the total carbon released (Figure 48) showed that lysimeter 4 released the most carbon; hence, it retained the lowest carbon content by the 23rd week. The results also showed that lysimeter 8 had released the least carbon at the same time. Lysimeter 3 was included to reflect the effect of the medium carbon content on the efficiency of denitrification. The phase lasted for 17 weeks starting at the 23rd week, and ended by the 40th week. The influent nitrate concentration for all lysimeters started with 2000 mg-N/L. This concentration was maintained only for three weeks. By the fourth week, the nitrate feed was reduced to 1500 mg-N /L, instead of 2000 mg-N /L, to maintain the low NO_x concentration of the leachate. The current and previous influent nitrate concentrations for the three lysimeters are shown in Table 33.

The other objective of this phase was to prepare the lysimeters for the following phase (Experiment (1) –Phase 1.5), which investigated the ability of methane to serve as a carbon source for denitrification. The preparation included the consumption of the carbon

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[18] The landfill carbon content represents the amount of organic carbon that is stored in the lysimeter and has a potential to be released.

[19] Complete denitrification requires carbon to be not less than 3 to 4 g-C /g-N depending on the source of carbon (Carley 1988).

content so that the BOD, TOC and VFA were low and that the lysimeters were adapted to a high nitrate concentration as feed stock.

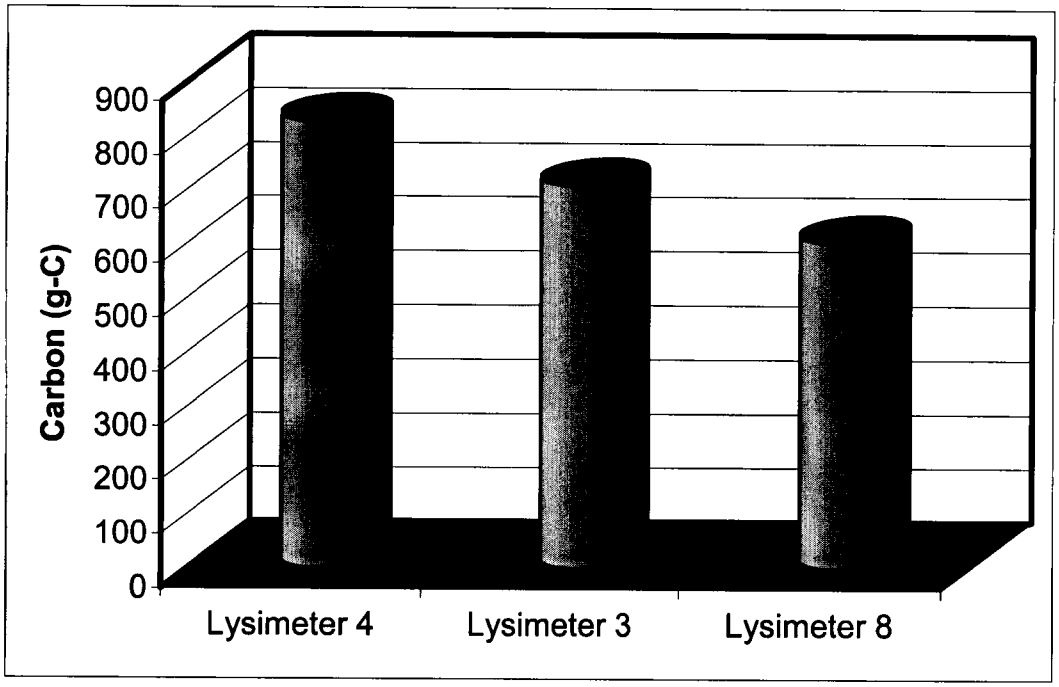

Figure 48 Comparison of the total carbon released from lysimeters 3, 4 and 8 during phases 1.1 and 1.2

Table 33 The influent nitrate concentration for lysimeter 3, 4 and 8 during phases 1.1, 1.2, and 1.4

	Nitrate Concentration (mg-N/L)		
Lysimeter number	Phase 1.1 (15 weeks)	Phase 1.2 (7 weeks)	Phase 1.4 (17 weeks)
3	400	600	2000-1500
4	400	600	2000-1500
8	800	600	2000-1500

6.1.5.1 Denitrification Efficiency

The influent nitrate concentration was increased gradually during the first week of this phase from 600 mg-N /L to 2000 mg-N /L. The leachate nitrate concentration started to increase (for the low and medium carbon content lysimeters) as a result of the increase in the feed concentration (Figure 49). The data (Figure 50) demonstrate the efficiency of denitrification at three levels of carbon contents during this phase (1.4). The data show that higher efficiency was associated with a higher carbon content.

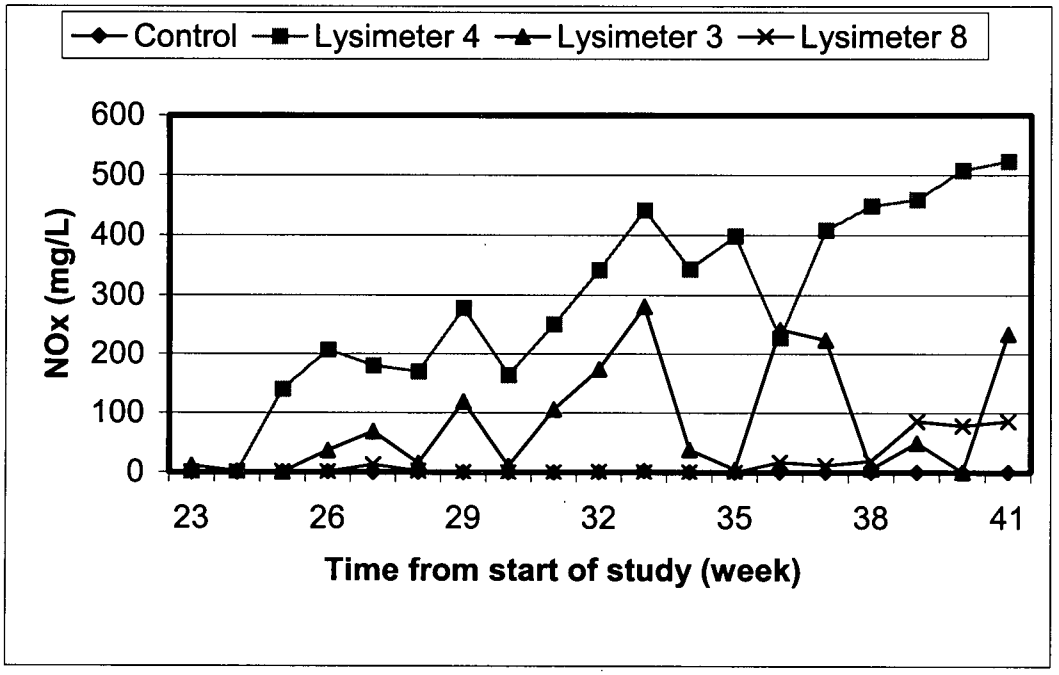

Figure 49 Comparison of effluent NO_x concentration for lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

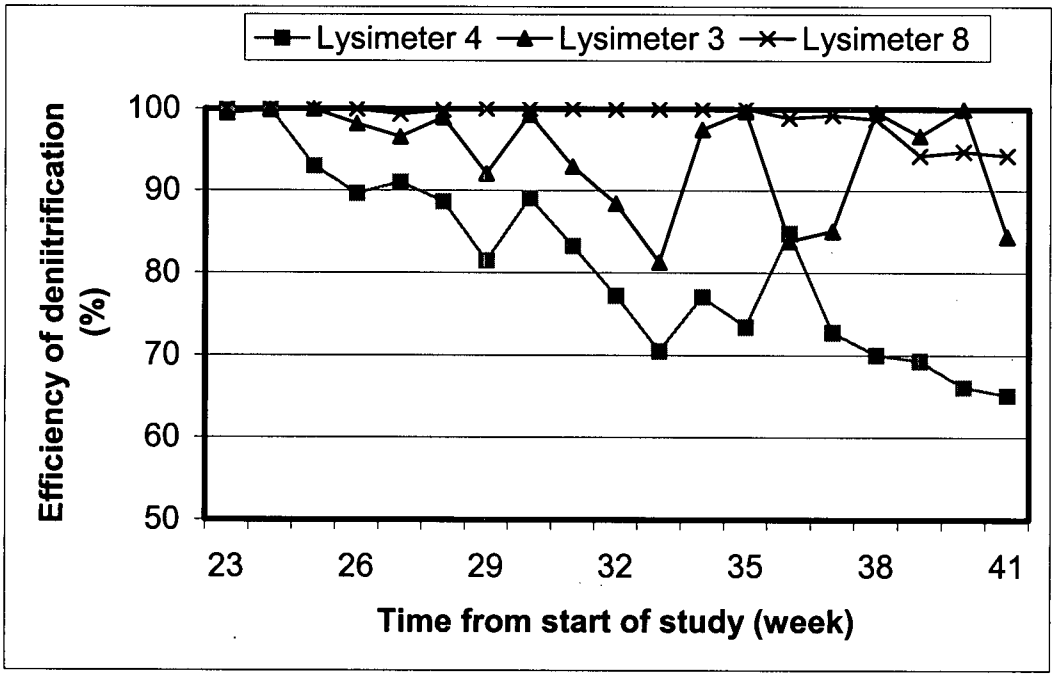

Figure 50 Comparison of efficiency of denitrification for lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

By the 29th week, the leachate nitrate concentration increased, reaching 300 mg-N /L for the low carbon content lysimeter and 100 mg-N /L for the medium carbon content lysimeter. This increase in the leachate nitrate concentration reduced the denitrification efficiency to 81% and 92% for the low and medium carbon content lysimeters respectively. By the 30th week, the nitrate concentration in the leachate decreased, as the effect of reducing the feed nitrate concentration started to be evident. However, soon after, it started to climb again, reaching a maximum by the 33rd week. Both the low and the medium carbon content lysimeters exhibited the same trend but with different values until the 33rd week. The leachate nitrate concentration of the low carbon content lysimeter was higher than the medium carbon content lysimeter by approximately 150 mg-N /L. After the 33rd week, the leachate nitrate concentration of the lysimeter with the low carbon content continued to increase, reaching 500 mg-N /L at the end of the phase, with a denitrification efficiency of 65%.

The lysimeter with the high carbon content continued to denitrify with high efficiency throughout this phase (1.4). However, by the 39th week, the leachate nitrate concentration started to increase, reducing the denitrification efficiency to 94%. This supports the well-known fact that denitrifying bacteria require a readily decomposable substrate (carbon) before reduction of nitrate can occur (Barnes and Bliss 1983, Carley 1988, McCarty 1969). At low carbon concentrations (lower than 3 g-C/ g-NO_3-N), nitrate may start to show up in the effluent (Carley 1988).

The efficiency of denitrification was also checked based on a nitrogen mass balance. The mass balance on nitrogen was calculated based on the average nitrogen released to the environment during this phase (after the reduction of the nitrate feed). The results (Table 34) show that the percentage of error was high (about 55%). Since the nitrate feed was high (1500 mg-N /L), the detection limit of the instrument, used to detect the quantity of the gas, cannot be claimed for this error. Therefore, incomplete denitrification may be a possible explanation. Previous studies have found that incomplete denitrification was associated with limited carbon availability, high nitrate concentrations, and low carbon: nitrate ratio (Hanaki *et al.* 1992, Weier *et al.* 1993, Parton *et al.* 1996, Percheron *et al.* 1999) as discussed previously in section 6.1.3.1.

Comparing the results of this phase with the results of the previous phases (Table 26, and Table 31) shows that, as the landfill ages, the error in nitrogen mass balance increases. This behavior may be due to the reduction in carbon availability, which tends to be associated with incomplete denitrification. During this phase (1.4), the carbon: nitrate ratio was below the recommended level of 3 to 4 g-carbon /g-nitrate-N, as shown in Figure 51.

Moreover, the influent nitrate concentration (1500 mg-N /L) during this phase (1.4) was considered to be high compared to the previous phases (400 and 800 during phase 1.1 and 600 during phase 1.2) and to the concentrations reported in the literature for similar studies (Weier *et al.* 1993, Percheron *et al.* 1999). The incomplete denitrification produces nitrous oxide and nitric oxide; both of these nitrogen oxide gases are considered to be GHGs, with nitrous oxide being a particular concern from the perspective of global warming.

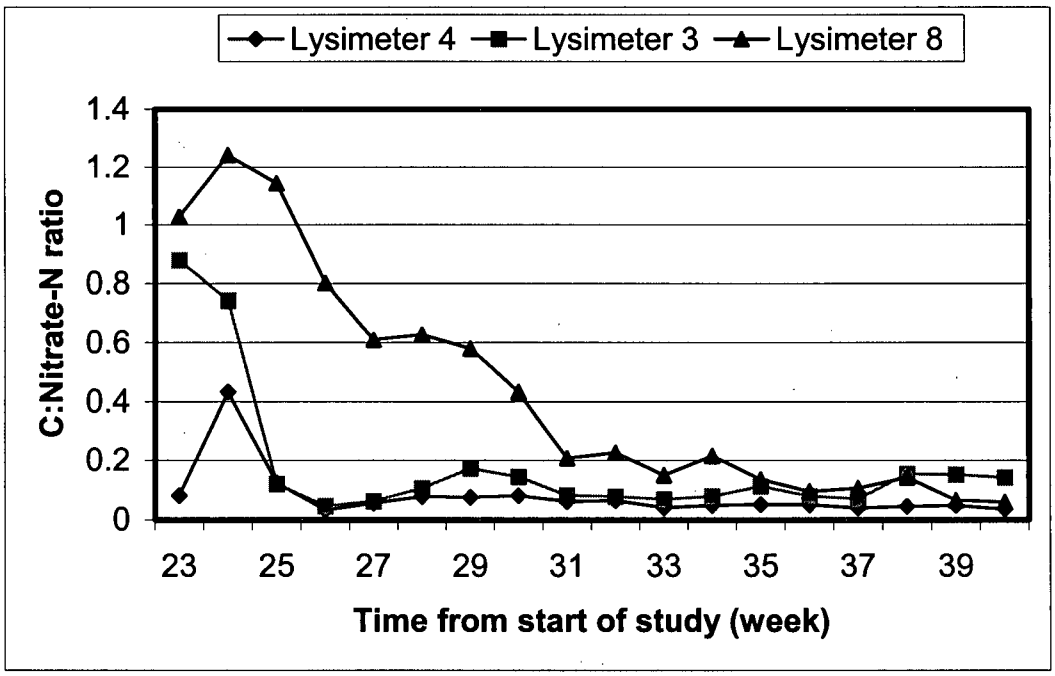

Figure 51 Comparison of carbon:nitrate-N ratio for lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

Kluber and Conrad (1998a) have shown that the accumulation of the intermediate products of denitrification (nitrite, nitrous oxide, and nitric oxide), inhibits methanogenic bacteria, with the strongest inhibition caused by nitric oxide. They concluded that different species of methanogenic bacteria react differently upon treatment with the different nitrogen compounds.

The high influent nitrate concentration, together with the low carbon availability during this phase (1.4), favor incomplete denitrification. The results of the nitrogen mass balance support a hypothesis of incomplete denitrification. Assuming that incomplete denitrification was occurring during this phase, then, the high efficiency of denitrification, which was calculated based solely on nitrate and nitrite removal in leachate, may be misleading.

Table 34 Mass balance for nitrogen during phase 1.4

Lysimeter carbon content	Lysimeter number	Nitrogen (in) (mg/week)	Nitrogen (out) (mg/week)	Number of samples	Mass (out)/ Mass (in) %
Low	4	4200	1778	17	42
Medium	3	4200	1880	17	45
High	8	4200	1816	17	43

6.1.5.2 Basic Leachate Characteristics

The leachate was characterized for pH, COD, BOD, TOC and ammonia. The effects of denitrification, carbon content and time on these parameters are discussed in this section. Figure 52 shows the pH of the lysimeters during this phase. Initially all lysimeters started with a neutral pH level (6.4 to 6.9). The pH of the control lysimeter was approximately 6 during this phase. It slowly decreased with time, reaching its minimum (5.8) by the end of the phase. On the other hand, all of the denitrification lysimeters exhibited an increasing trend. The pH level increased for three months. After that, the pH for the low, medium and high carbon content lysimeters remained between pH 7 and 8. There was no clear correlation between the carbon content of the reactor and the pH.

The pH results of the control lysimeters were not as expected. As a landfill ages, the methanogenic activities are well established, which help in consuming the VFAs. During the maturation phase, the leachate VFAs concentration is very low. Therefore, it is

expected to show higher pH values (above neutral pH) during this phase (1.4) (Figure 1). The reason for this particular behavior in pH is unknown. On the other hand, the denitrification lysimeters have pH values that are in the expected range for this phase of landfill stabilization (Figure 1). However, this may be due to the fact that denitrification produces alkalinity (as discussed earlier in section 6.1.2.4.1), which helps in maintaining the pH above neutral (U.S. EPA 1993).

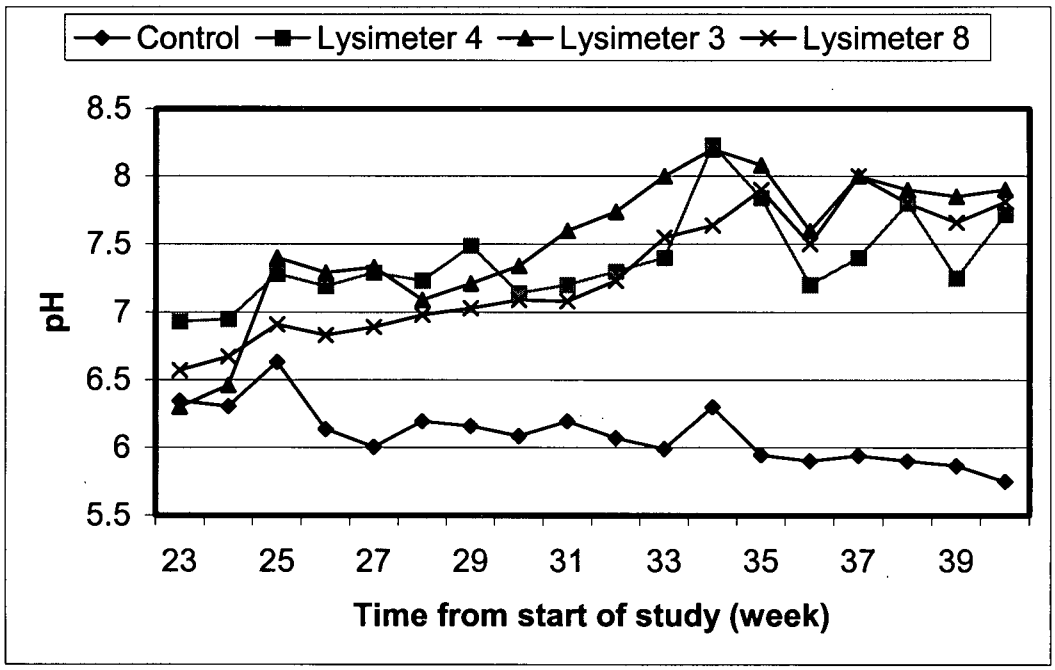

Figure 52 Comparison of the effluent pH from lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

The COD and BOD for all of the lysimeters continued to decrease during this phase, as illustrated in Figure 53 and Figure 54. As seen in these figures, eventually, all lysimeters achieved low values for COD (below 1 g/L) and BOD (below 100 mg/L). However, the lower the carbon content, the faster the rate of decline. By the 38th week, the COD of the medium carbon content lysimeter increased from 0.5 g/L to 1 g/L (not as expected).

The low values of COD and BOD show that the lysimeters were in the maturation phase (Figure 1). Several other studies have shown that during this phase of landfill stabilization, the amount of soluble and/or degradable materials are substantially reduced,

hence, leachate with low COD and BOD is produced (Pohland 1991, Reinhart and Al-Yousfi 1996, Warith and Sharma 1998).

The results of the release of ammonia (Figure 55) show that there was no consistency in the correlation between the carbon content of the lysimeter and the concentration of ammonia in the leachate. It is also shown that the effluent concentration was stable throughout the phase.

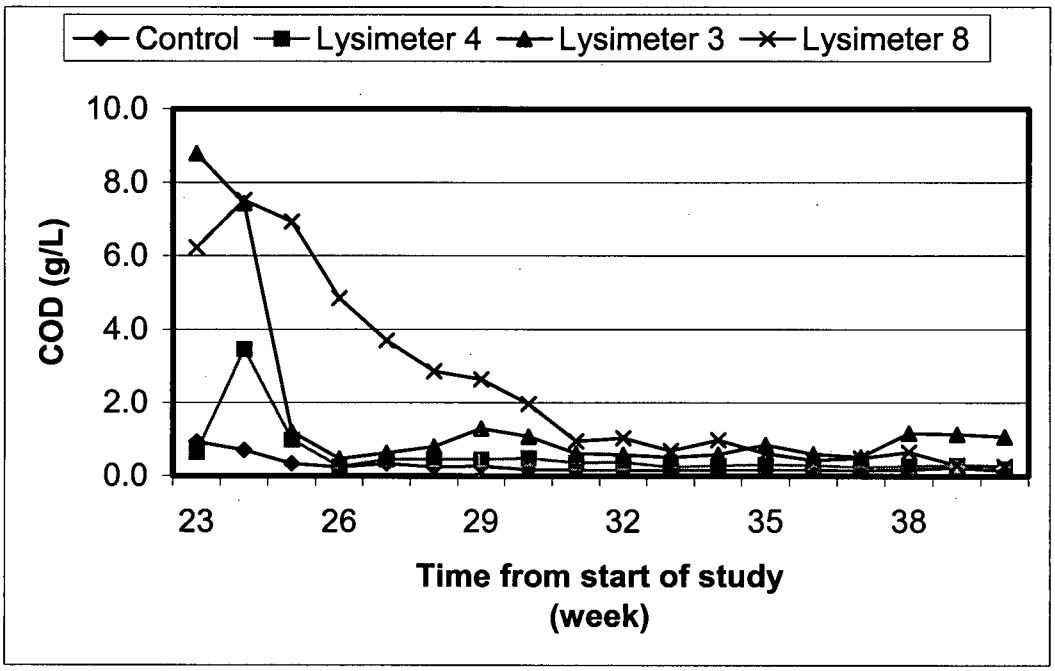

Figure 53 Comparison of the effluent COD from lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

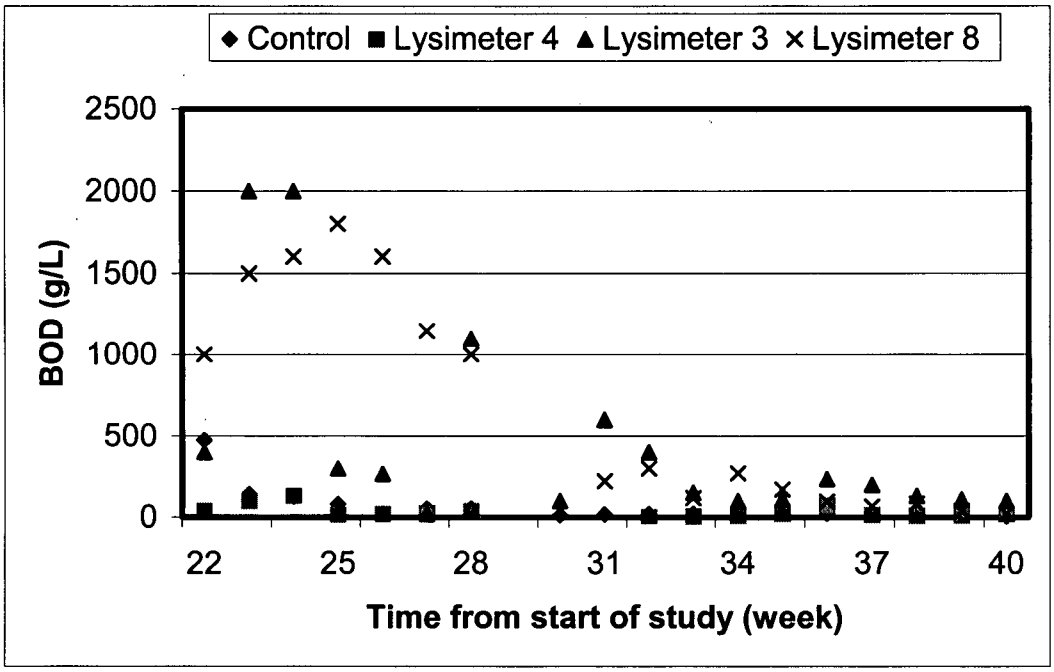

Figure 54 Comparison of the effluent BOD from lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

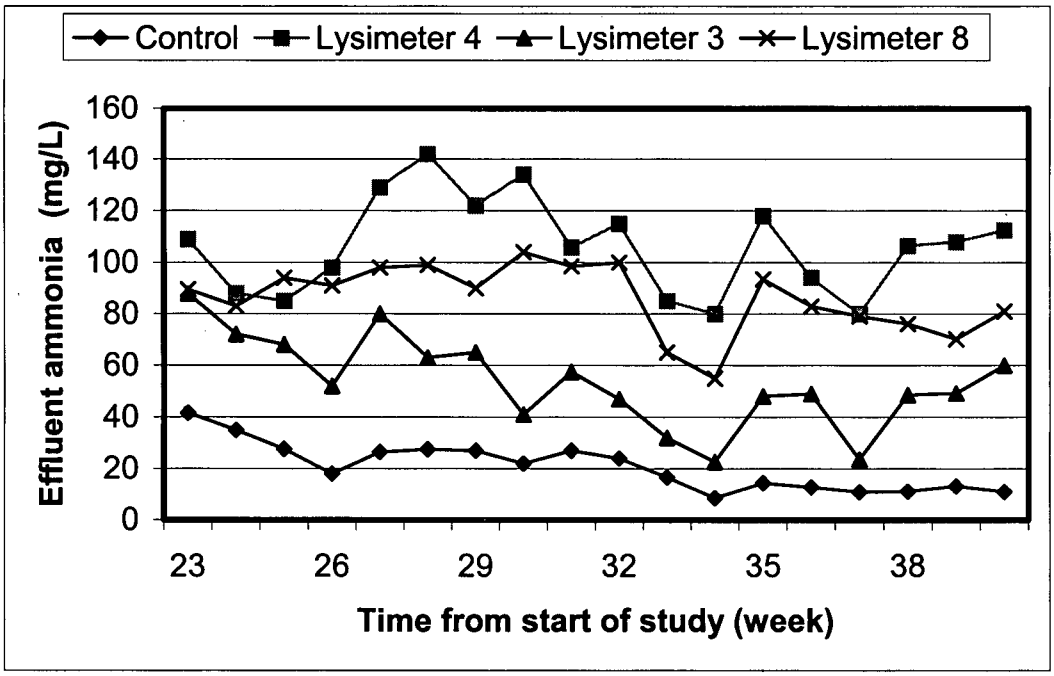

Figure 55 Comparison of the effluent ammonia concentration from lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

6.1.5.3 Gas Production

The gas production rate reflects the activity of the methanogens. In this phase, all of the lysimeters exhibited a reduction in their gas production rates (Figure 56). This decline, in the gas production rates, may be explained by the decline in the substrate available for methanogens in microenvironments (Figure 51 and Figure 54).

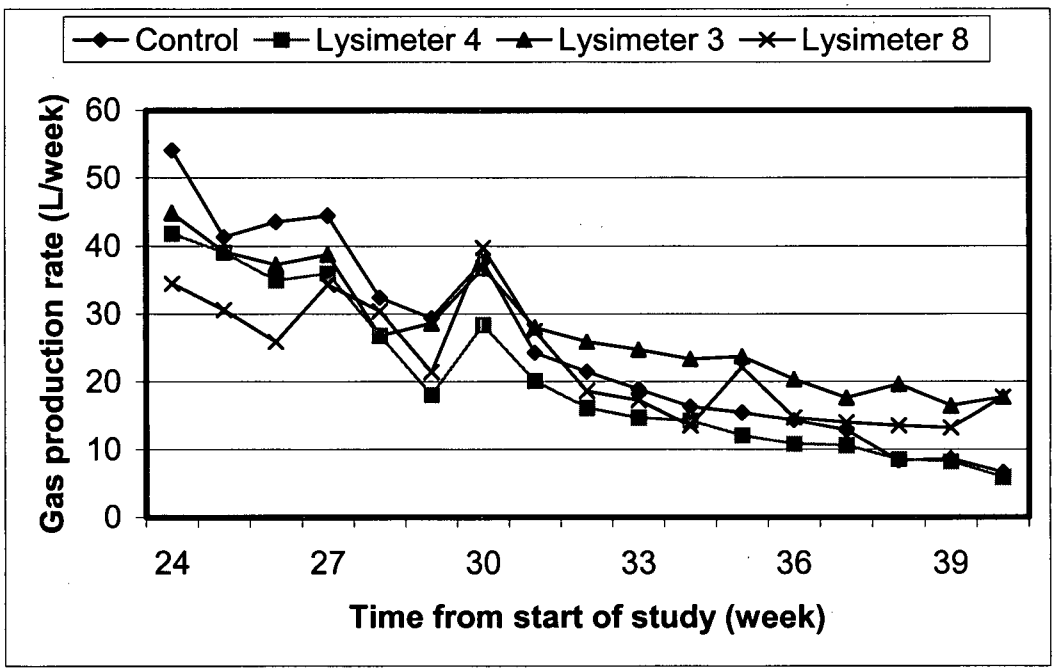

Figure 56 Comparison of the weekly gas production rate from lysimeters 4, 3 and 8 (with low, medium and high carbon content respectively) during phase 1.4

The production rate for methane, carbon dioxide, and nitrogen were monitored throughout this phase and the results are shown in Figure 57 through Figure 59. From these figures, it can be seen that methane content was always higher than carbon dioxide, but the difference was minor. Due to the high pH of the leachate (around 7.5 as shown in Figure 52), there is potential for the carbon dioxide to move from the gas to the leachate, reducing its contribution in the total gas. The use of methane as a carbon source for denitrification may be suggested at this point (due to the high demand for carbon), yet not confirmed. Further studies were conducted (Experiment (1) –Phase 1.5) to provide a higher level of certainty for this assumption.

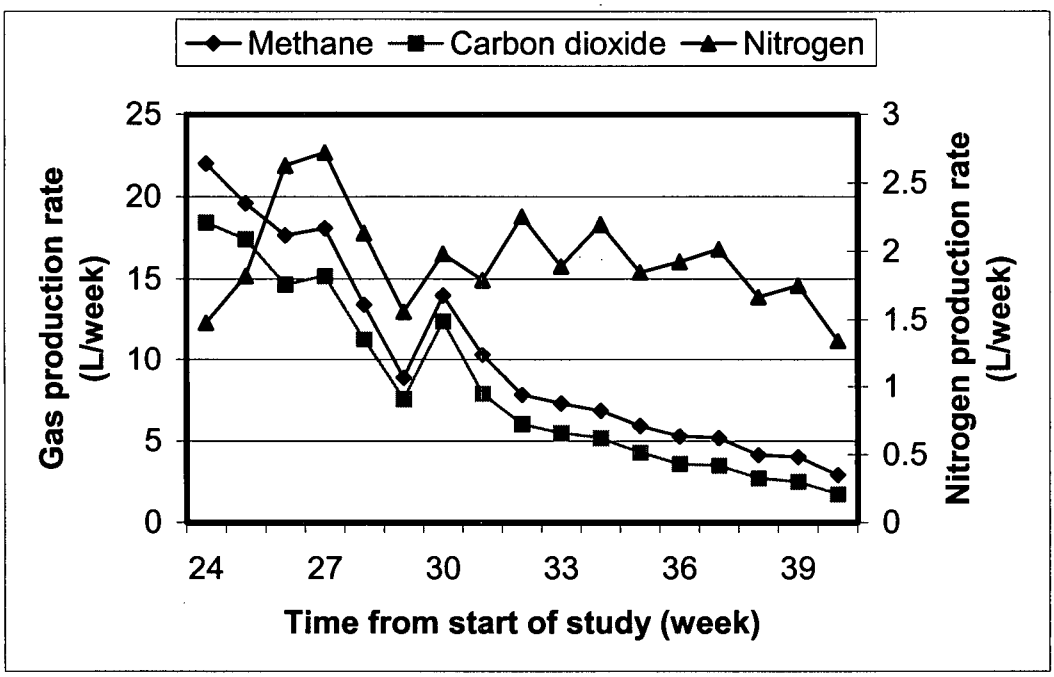

Figure 57 The weekly gas production rate from lysimeter 4 (low carbon content) during phase 1.4

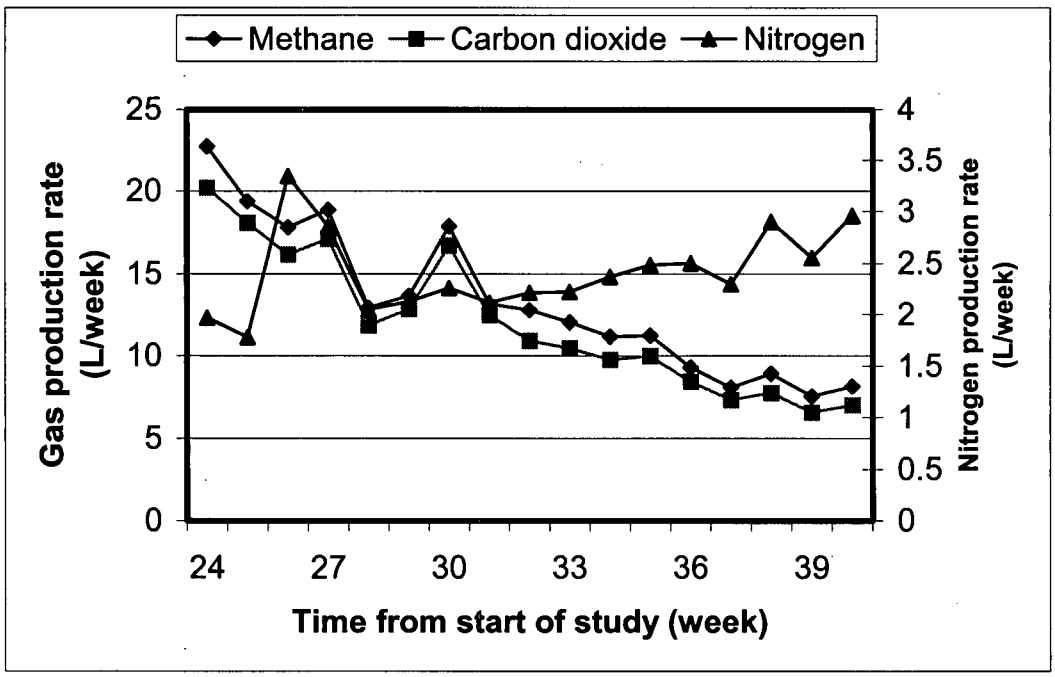

Figure 58 The weekly gas production rate from lysimeter 3 (medium carbon content) during phase 1.4

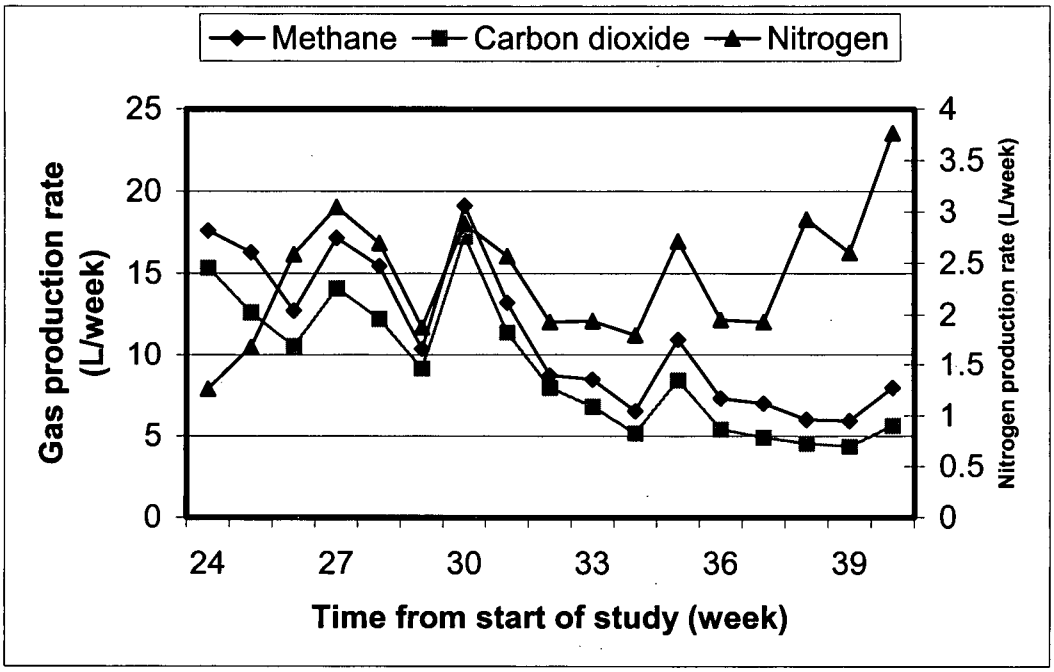

Figure 59 The weekly gas production rate from lysimeter 8 (high carbon content) during phase 1.4

The data also show that the production rate of nitrogen gas was stable and that neither the denitrification efficiency nor the carbon content of the lysimeter can be correlated with it. This indicates that there was a certain capacity for complete denitrification and that this capacity was exceeded, regardless of the total carbon content of the lysimeter. To better understand these results, the physical movements of the denitrification zone and the intermediate products have to be considered.

Denitrification in the lysimeters takes place in a zone with a limited depth. The depth of that zone may vary, based on waste characteristics and their effects on the kinetics of the process. Initially, this zone starts at the first layer of the waste. While the feed passes through the active zone of the lysimeter, the NO_x^- concentration will be reduced to its minimum value and no further reduction will occur within the lysimeter below the active zone. As time passes, denitrification consumes the carbon of that zone and moves downward, leaving the upper layer carbon deprived (Figure 60). As such, the upper layer will no longer be used for denitrification.

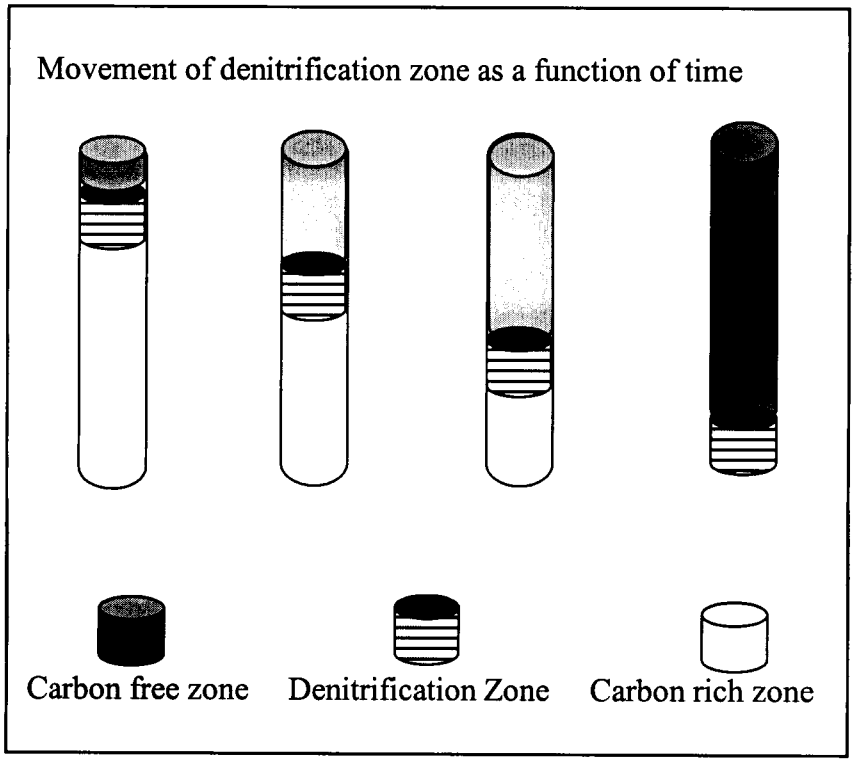

Figure 60 The hypothesized movement of the denitrification zone in an anoxic landfill bioreactor

In the first step of denitrification, nitrite is produced and appears in the leachate. In the following step, the nitrite is reduced to nitric oxide in the gaseous state. Then, the NO_x^- free leachate continues its path to the lower layers of the waste where it is collected and analyzed for NO_x^-.

Many factors govern the gas movement through the waste. These factors include molecular diffusion, waste porosity, saturated vapor concentration, gas density, and the depth (Tchobanoglous *et al.* 1993). Difficulties associated with predicting the path of nitric oxide are attributed to the number of factors affecting the gas movement, in addition to the fact that some of these factors are a function of time and the level of microbial activity. Further reduction of nitric oxide to nitrous oxide depends on its solubility, pH (Hanaki *et al.*, 1992), availability of carbon in its path, and its flux. Although nitrous oxide is similar to nitric oxide; it has a couple of advantages over nitric oxide. Nitrous oxide has a higher density and solubility (Windholz 1983). Hence, there is

a higher possibility for further reduction of nitrous oxide to nitrogen gas (Figure 61). Nitrous oxide is about 1.5 times as dense as air and 2.8 times as dense as methane (Windholz 1983) As a result, nitrous oxide has a tendency to migrate downward with a greater chance for further reduction due to carbon availability. Therefore, the reduction of nitric oxide could be a bottleneck in the denitrification at a landfill bioreactor.

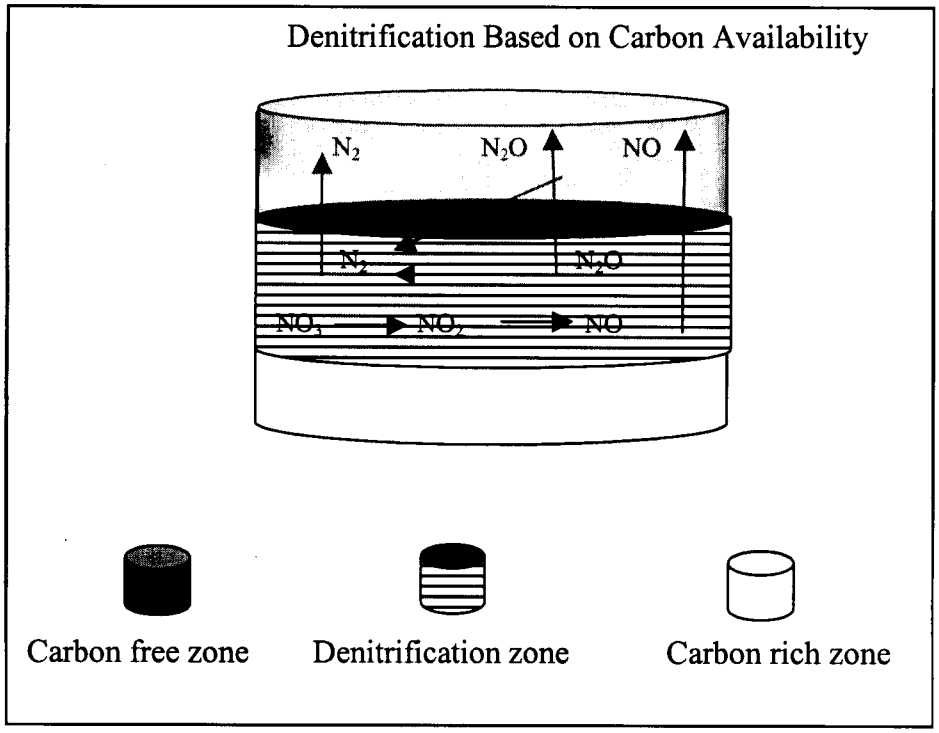

Figure 61 The hypothesized movement of the denitrification intermediate by-products in an anoxic landfill bioreactor

The high efficiency of denitrification (Figure 50) contradicts the low volume of nitrogen gas produced from the lysimeters (Figure 57, Figure 58, and Figure 59). The missing link is that the efficiency of denitrification was calculated based on the effluent NO_x^- concentration, and not on nitrogen gas. This means that it considers only the first two steps in which nitrate is converted to nitrite and then to the gaseous nitric oxide. As the nitrogen moves from the soluble phase to the gaseous phase, it passes through the upper layers of waste, which lack the carbon needed for complete denitrification. This hypothesis can explain the stable level of nitrogen gas production and its independence of the nitrate concentration or the carbon content of the lysimeter.

To support the hypothesis of incomplete denitrification, gas samples were analyzed by others for nitrogen oxides gases. Results of these samples were positive, and confirmed the presence of nitrogen oxides in the gas stream of all the denitrifying lysimeters.

6.1.5.4 Overview –Phase 1.4

The carbon content of the lysimeter is an important parameter that affects the efficiency of denitrification. As a lysimeter ages, its carbon content decreases, hence, reduces the efficiency of denitrification.

The mass balance on nitrogen showed a significant error in the nitrogen output: input ratio (55%). This can be explained by the hypothesis that denitrification through a landfill may suffer from incomplete denitrification, producing nitric and nitrous oxides instead of nitrogen gas. Moreover, the nitrogen gas production rate was not affected by the carbon content and/or the denitrification efficiency. The limited carbon availability –in the nitrogen oxides path- may be the cause of the incomplete denitrification through a landfill bioreactor.

6.1.6 Experiment (1) –Phase 1.5

The objective of this phase (1.5) was to investigate the potential for methane to serve as a carbon source and/or ED for denitrification. To acheive this goal, two lysimeters (3 and 8) were prepared. Preparations included adapting the denitrifying bacteria to a high nitrate concentration and reducing the internal available carbon source, so that the system was carbon-deprived. The thermodynamics of denitrification reactions favor VFAs over methane for denitrification; hence for methane to be used, VFAs concentration must be insufficient to support the process. Therefore, controlling carbon availability is important when targeting methane utilization.

During this phase, the influent nitrate concentration was 1500 mg-N /L with a flow rate of 400 mL/ d. After two weeks, the nitrate started to break through in the leachate, with the tendency for its concentration to increase with time (Figure 62). The effluent nitrate concentration was more than 10% of the feed nitrate concentration. On the other hand, the leachate BOD and TOC concentrations were decreasing (from the previous phase (1.4), indicating that the organic carbon availability was limited. Thus, carbon concentration in the leachate was not sufficient to support the process of denitrification. The characteristics of leachate and gas for lysimeters 3 and 8 on day 14 of phase 1.5 are shown in Table 35. The data in Table 35 demonstrate that the lysimeters were ready to start the experiment (leachate was low in carbon and relatively high in nitrate). Since the methane production rate was low during this phase of landfill stabilization, pure methane gas was introduced to lysimeter 8 on day 15 at a rate of 24 L/d, to insure that the quantity of methane was sufficient for complete denitrification.

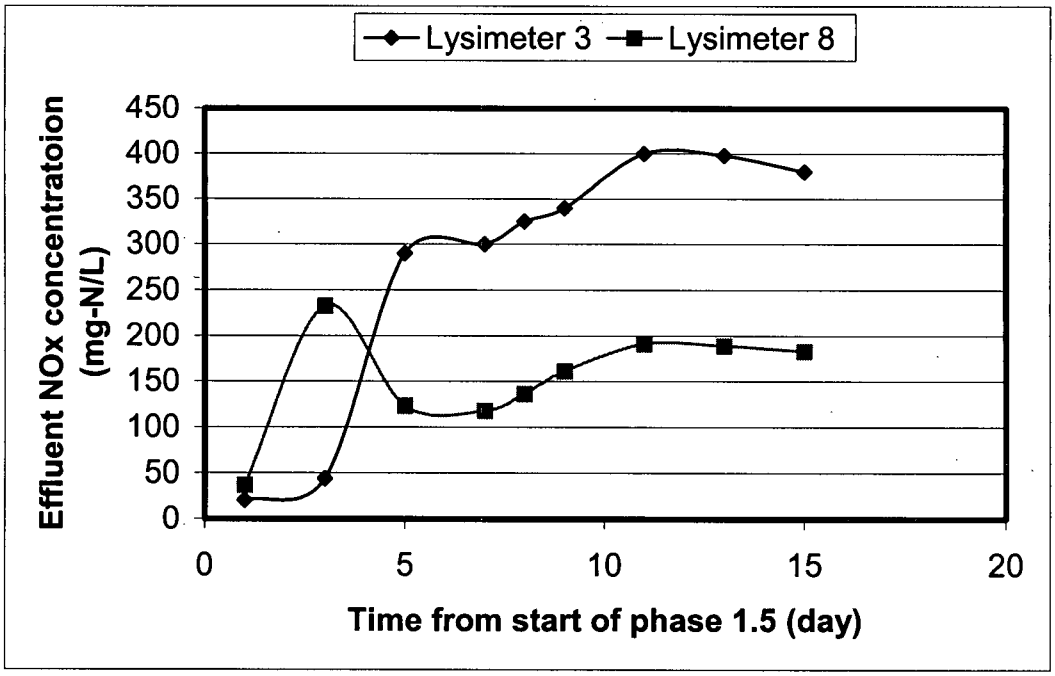

Figure 62 The effluent NO_x concentration for lysimeters 3 and 8 during the first two weeks of phase 1.5

Table 35 Characteristics for leachate and gas from lysimeters 3 and 8 on day 14 of phase 1.5

Characteristic	Lysimeter 3	Lysimeter 8
BOD (mg/L)	100	20
NOx (mg-N/L)	290	233
Efficiency of denitrification %	80%	82%
pH	7.0	7.8
TOC (mg-C/L)	67	52
Methane production rate (L/week)	8.1	8.0
Carbon dioxide production rate (L/week)	7.0	5.6
Nitrogen gas production rate (L/week)	2.9	3.7

6.1.6.1 Denitrification efficiency

The efficiency of denitrification is shown in Figure 63. The data show that the efficiency of denitrification for lysimeter 3 was decreasing for 10 days to reach the minimum of 73%. Then the efficiency increased to 80% and remained in this range for a month. Starting from the 50th day, the efficiency started to decrease again, reaching 60% at the end of the experiment. Lysimeter 8 shared the decreasing behavior at the beginning. However, the behavior completely changed as methane was introduced to the lysimeter on day 15. After that day, the efficiency started to increase, reaching its maximum in less than three weeks. The high efficiency continued even after methane was stopped. After three weeks, the efficiency started to decrease again to reach its minimum of 82% by the end of the experiment. Methane addition was stopped on the 37th day to confirm that it was the cause for this reduction in the effluent nitrate concentration. However, it took the nitrate 23 more days to start to show up in the effluent leachate.

Even though autotrophic denitrification (using reduced-sulfur compounds) was not responsible for the high denitrification efficiency, to eliminate any uncertainty, with respect to autotrophic denitrification, the analysis of sulfate would be desirable. The data obtained in this experiment show that the availability of methane increases the denitrification efficiency in an anoxic environment. The possible explanation for this behavior is that methane may be used directly or indirectly as a carbon and/or ED source for denitrification. This result is of great importance since a high efficiency was achieved using methane with a relatively high concentration of nitrate (more than 250 mg-N/L). To

help explain these results, the leachate and gas characteristics were also studied in the following sections.

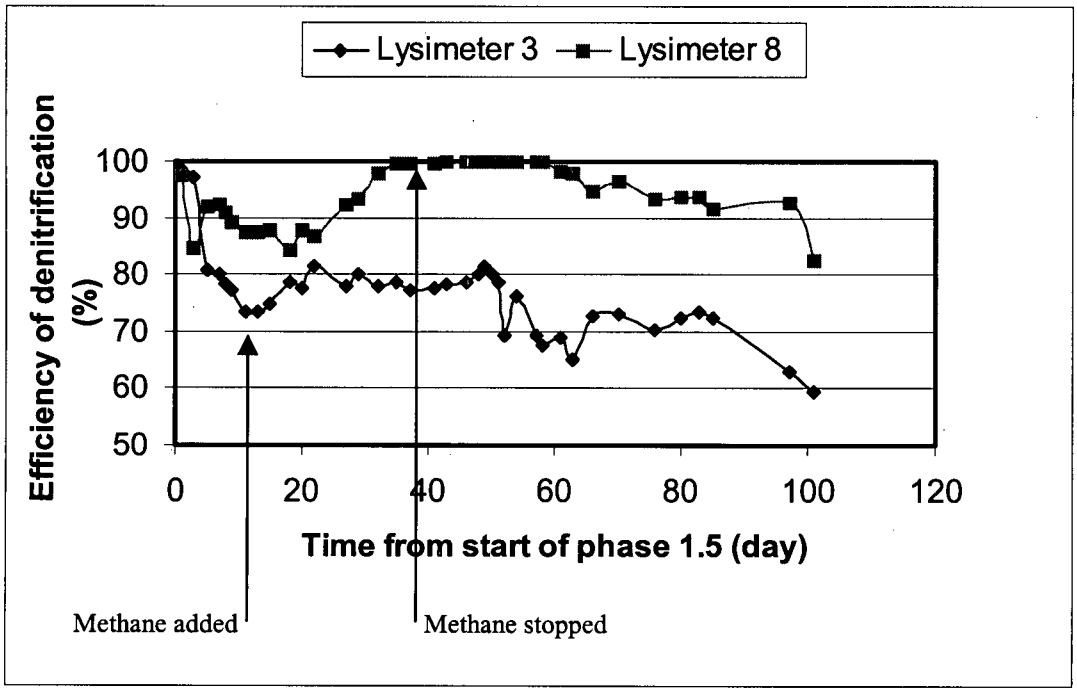

Figure 63 The efficiency of denitrification for lysimeters 3 (as a control) and 8 (where methane was added to be used as a source of carbon) during phase 1.5[20]

6.1.6.2 Basic Leachate Characteristics

The leachates were analyzed for TOC and VFA during this phase of the study. The results of the TOC analyses are shown in Figure 64, while the results for VFAs are shown in Figure 65. The carbon measured by the TOC test does not include methane, because the carbon analyzer purges the sample before testing it. The data show that the TOC for lysimeter 3 was stable throughout the test. It also shows that the TOC of lysimeter 8 started below 100 mg-C /L, and increased after the methane addition started. The TOC

[20] The addition of methane started on day 15 and stopped on day 37

continued to increase, reaching high levels of carbon (about 500 mg-C /L) even after methane addition was stopped. However, shortly after the methane addition stopped, the TOC declined sharply (to 120 mg-C /L) signifying that the TOC source had diminished. At the end of this test, the TOC of lysimeter 8 was below 100 mg-C /L. These results suggest that methane supplies the carbon to the lysimeter. However, this carbon (in methane) is converted to another source of carbon, which is detected as dissolved organic carbon in the leachate.

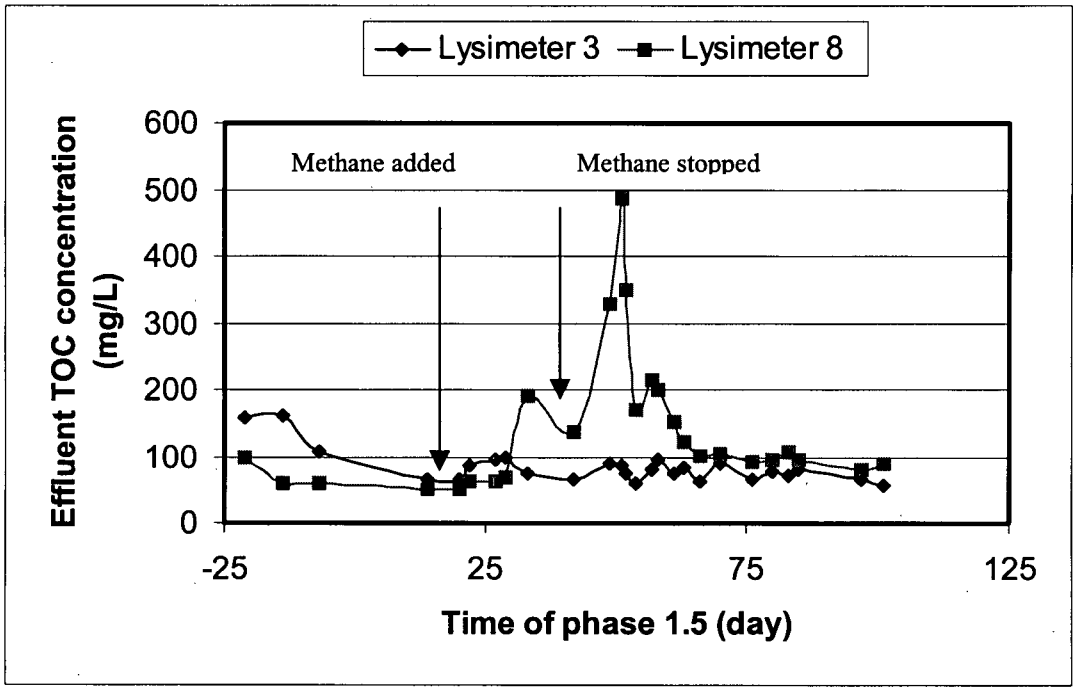

Figure 64 Comparison of the effluent TOC concentration for lysimeters 3 (control) and 8 during phase 1.5

The VFAs of both lysimeters were studied to obtain a better understanding of this conversion (Figure 65). The data of lysimeter 8 show that prior to methane addition, VFAs concentration was below 5 mg/L, and the VFAs concentration increased after the addition of methane. On the other hand, Figure 66 shows that acetic acid was the major component of the VFAs. It also shows that acetic acid concentration increased dramatically after methane introduction, and decreased after methane addition was stopped. This behavior shows that there is a strong link between methane, and acetic acid, and that the availability of methane increases the concentration of acetic acid. This phenomenon can be explained by two hypotheses. First, that methane enhances the

production of acetic acid from another source of carbon, and second that methane is converted directly or indirectly to acetic acid.

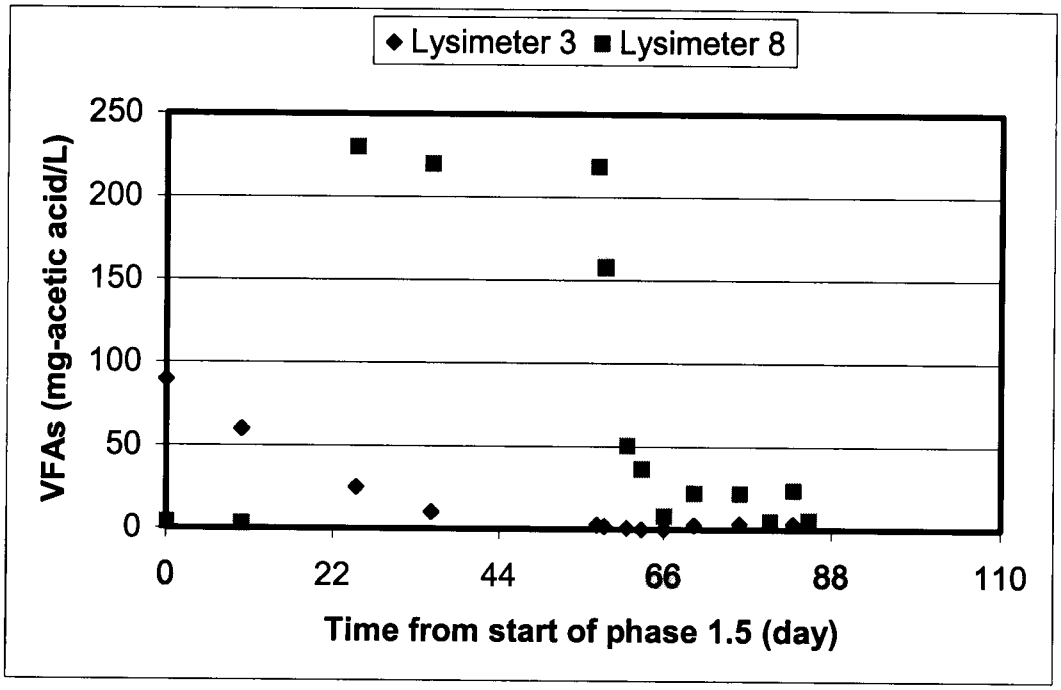

Figure 65 The effluent leachate total VFAs concentration for lysimeters 3 (control) and 8 (methane added) during phase 1.5

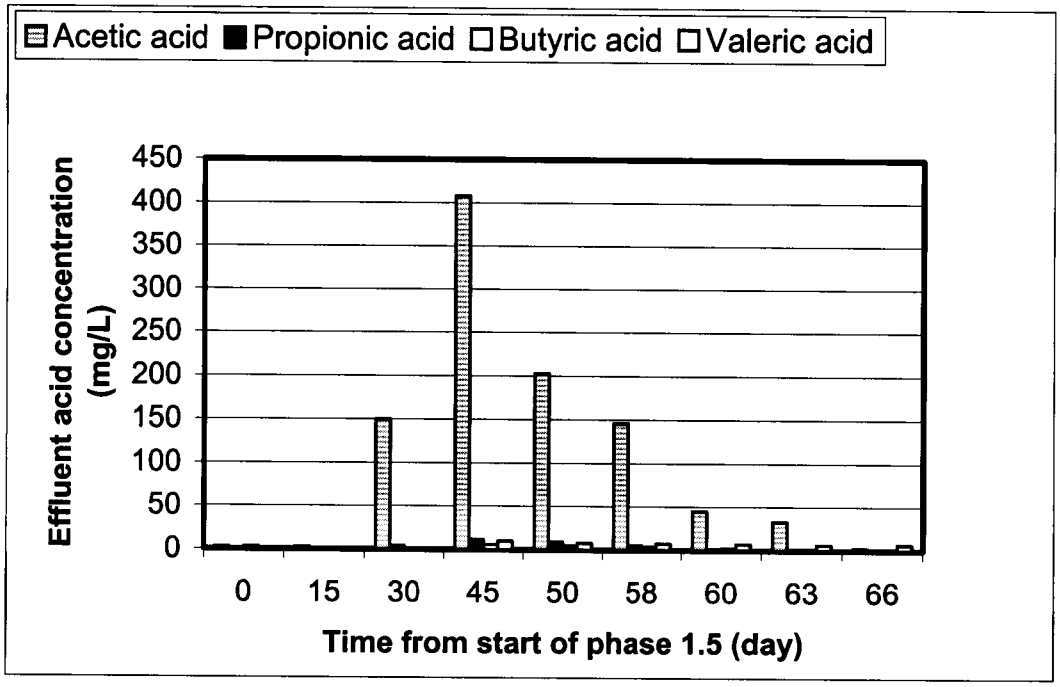

Figure 66 The effluent leachate VFAs concentrations for lysimeter 8 (methane added) during phase 1.5

In the first explanation, methane movement through the lysimeter may have helped in flushing the toxins (such as nitric and nitrous oxides), and enhancing waste degradation, producing a higher concentration of acetic acid. However, this flushing is unlikely to have happened, because the lysimeter was in the maturation phase. This means that carbon availability was limited. Moreover, a recent study by Costa *et al.* (2000) found that oxidizing methane produced acetate. Their finding supports the second assumption.

The general belief has been that methane could only be oxidized to methanol under a certain level of oxygen[21] (Rajapakse and Scutt 1999, Thalasso *et al.* 1997, and Werner and Kayser 1991). This belief was held until Costa and others (2000) showed that in oxygen-limited environments (1.5 to 9 mM), methane could be oxidized to acetate. They demonstrated this conversion using ^{13}C labeled methane.

In the current study, the lysimeters were airtight, i.e. oxygen was not available. Assuming that methane was oxidized to acetate, another source of oxygen must have been used. Thermodynamically, it is possible to oxidize methane anaerobically with an alternative electron acceptor (Table 36). However, bacteria that perform this process have never been isolated (Eisentraeger *et al.* 2001). Possible sources of electron acceptors that are available in landfills include: nitrate, sulphate, and iron oxides. These electron acceptors may be used individually or as a mixture, according to their availability, environmental factors, and thermodynamics. This modeling is potentially very complicated because of the various possible influencing factors. The heterogeneity of the lysimeter makes this process even more complicated. In addition, the literature is limited, and does not provide useful information on anoxic oxidation of methane to acetic acid. Complete methane oxidation is recognized using sulfate (Zehnder and Brock 1980, Hansen *et al.* 1998, see section 6.2.1.3.1 for further details), while very little is known about other electron acceptors. At this point, there is strong evidence that methane is converted to acetic acid, yet the mechanism for the process is still unclear.

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[21] The dissolved oxygen concentration was not less than 5 mg/L for denitrification to occur.

Table 36 Gibbs free energy for methane as electron donor and various inorganic electron acceptors at pH 7 and 25°C

Electron acceptor	Gibbs free energy (kcal/e$^-$)
CO_2	0
SO_4^{2-}	-0.67
FeOOH(s)	-5.4
MnO_2(s)	-19.46
NO_3^-	-22.77
O_2	-24.6

Adapted from Zehnder and Brock 1980

The leachate color, from lysimeter 3, did not vary (light brown) during the test, while the leachate color of lysimeter 8 changed. The color of lysimeter 8 leachate started with a light brown, and after methane addition started, the leachate color started to darken. With time (about 10 days after methane introduction), the leachate color was solid black.

The pH of a leachate sample, taken from lysimeter 8, was reduced to pH 2 by adding drops of hydrochloric acid. As the pH of the leachate sample decreased, the color diminished. This phenomena suggests that the leachate dark color may be due to the presence of sulfides (which is produced from sulfate reduction), or colored humic-like substances (Frankowsky 2000). Moreover, a sulfurous odor became present as the pH of the sample was reduced. Although hydrogen sulfide is a colorless gas, the mineral sulfides could contribute color to the leachate. This behavior suggests that methane introduction enriched the leachate with hydrogen sulfide. Sulfate is one of the biodegradation by-products. Under anoxic conditions, a consortium of bacteria and archaea are capable of oxidizing methane to carbon dioxide, producing hydrogen sulfide. This process has been well documented. The exact mechanism for this reaction and specifically the microorganisms involved are, however, not yet known in detail.

The data from section 6.1.6.1 show that methane addition enhanced the efficiency of denitrification, and the data in this section proves that methane addition increases the leachate carbon by increasing the acetic acid concentration. Thus, methane availability enhances the efficiency of denitrification, apparently by providing the carbon needed for this process. However, the path and mechanisms for this phenomenon are not well

understood. Further investigation was conducted on the gas stream to enhance the understanding of this process.

6.1.6.3 Gas Characteristics

To evaluate the effect of methane addition on gas characteristics, the gas composition and production rates of lysimeters 3 and 8 were compared at three points: before methane addition was started, 10 days after methane addition was stopped, and two months after methane addition was stopped. The results for these three times are shown in Figure 67 and Figure 68. The results for lysimeter 3, which was used as a control with no added methane, show that the gas production rate decreased with time. Methane, carbon dioxide and nitrogen production rates were reduced by 60%, 54% and 40% respectively. Alternatively, the gas production rates of lysimeter 8 followed a different trend. For example, 10 days after methane addition was stopped, methane was still being emitted at a high rate. The carbon dioxide decreased after methane introduction and kept decreasing to reach a low value of 0.8 L-CO_2/week (this is discussed later in this section). In contrast, the nitrogen gas production rate increased as a result of methane introduction, but its value was lower after 2 months with no methane addition.

The carbon dioxide concentration from lysimeter 8 decreased with time, and the pH of the leachate of this lysimeter was stable (around 8). At this high pH, and with the production of alkalinity due to the process of denitrification, the carbon dioxide dissolved in the leachate. The leachate from lysimeter 8 contained a relatively high alkalinity (4.2 g/L as $CaCO_3$), which supports the hypothesis that carbon dioxide was going to the leachate instead of the gas stream.

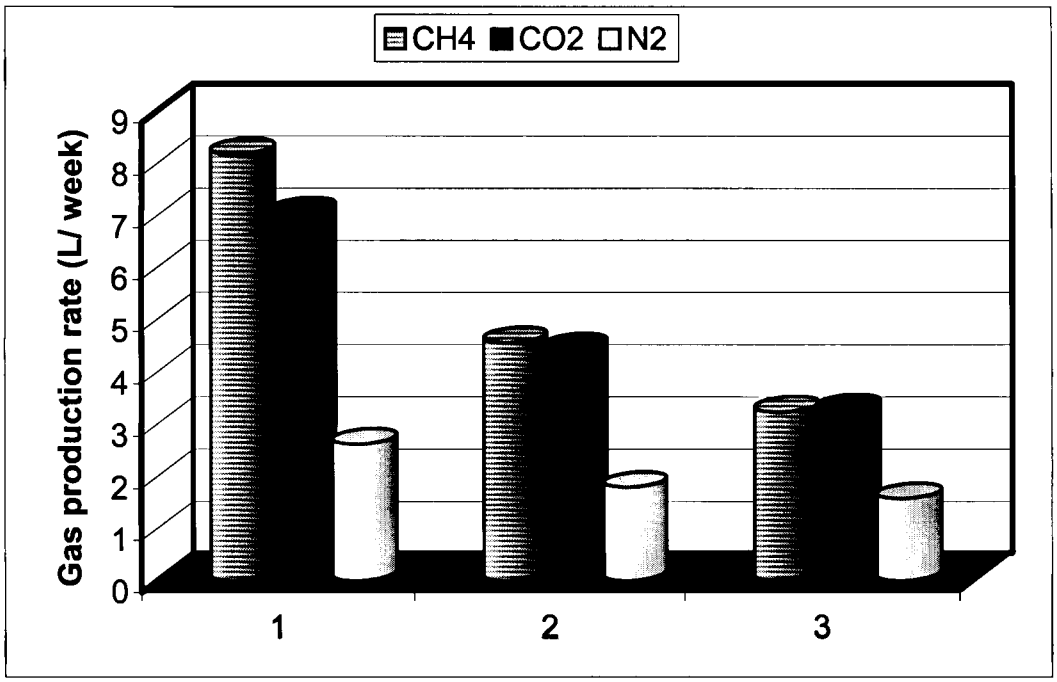

Figure 67 Gas production for lysimeter 3 (control) at three points (1: before methane addition, 2: 10 days after methane addition stopped, and 3: 2 months after methane addition stopped) during phase 1.5

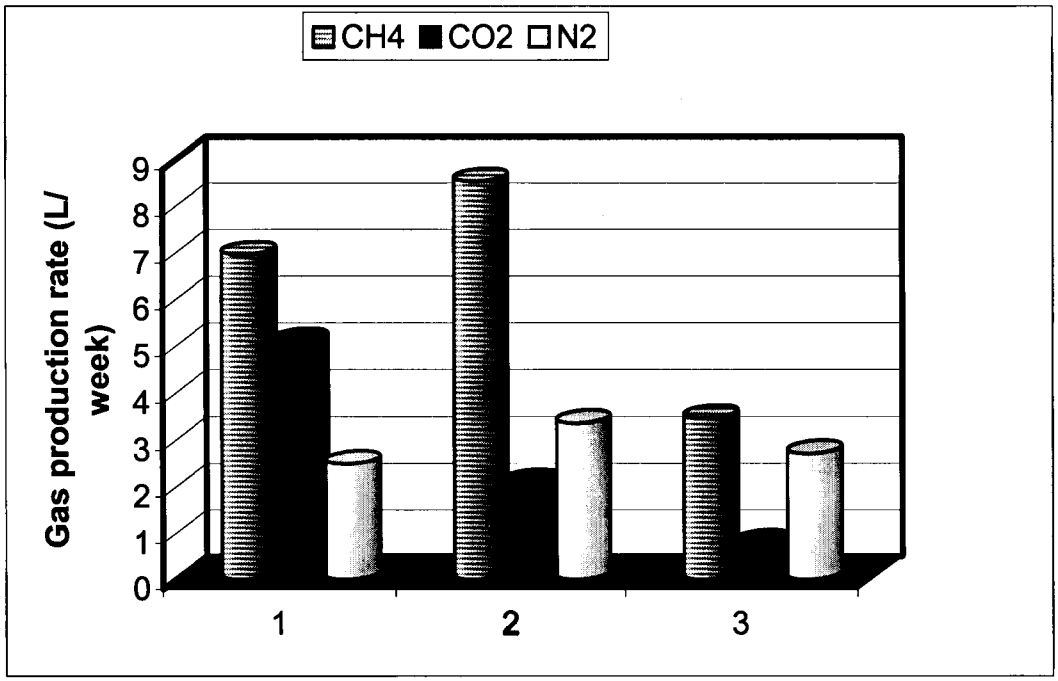

Figure 68 Gas production for lysimeter 8 (methane added) at three points (1: before methane addition, 2: 10 days after methane addition stopped, and 3: 2 months after methane addition stopped) during phase 1.5

The amount of carbon dioxide, which was dissolved in leachate, was estimated based on alkalinity to be 7.3 and 6.8 L $-CO_2$/week for lysimeters 3 and 8 respectively (Eaton *et al.* 1995). Figure 69 and Figure 70 show the production rates of the gas components of each lysimeter two months after methane addition stopped (including the dissolved carbon dioxide), and compare these results to the previous ones (without the dissolved carbon dioxide). The difference between the amount of carbon dioxide and methane produced was high. Carbon dioxide was about twice the amount of methane in both cases. This outcome does not compare with the results reported in the literature, which indicates that both gases should be produced in comparable quantities by methanogens producing methane from acetate (Table 6 and Figure 1). The data presented in Figure 69 and Figure 70, support the previous findings that methane enhanced the process of denitrification.

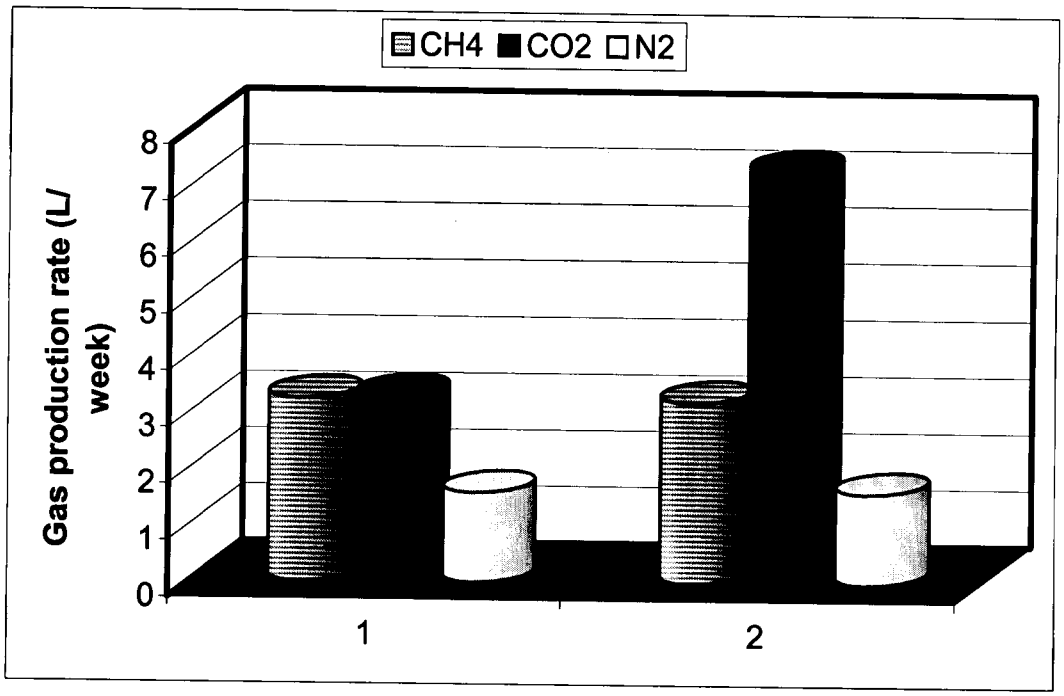

Figure 69 Gas production with dissolved CO_2 for lysimeter 3 (control) at two points (1: 10 days after methane addition stopped and 2: 2 months after methane addition stopped) during phase 1.5

In the first phase (1.1), the possibility of utilizing methane for denitrification was eliminated. This was due to the availability of carbon and the similar production rate of methane and carbon dioxide. In this phase (1.5), the preceding factors were absent: carbon availability was restricted to methane and its products, and the production rate of

carbon dioxide was a lot higher than the emission rate of methane. In lysimeter 3, all sources of carbon were eliminated except methane. In both lysimeters there was evidence that methane may be the source of carbon for denitrifiers[22].

The amount of nitrogen gas produced by lysimeter 8 reached its maximum during this phase (1.5). A mass balance was done on nitrogen and the results are shown in Table 37 and Table 38. A sample of the calculation is shown in Appendix 3 (section 9.3.5).

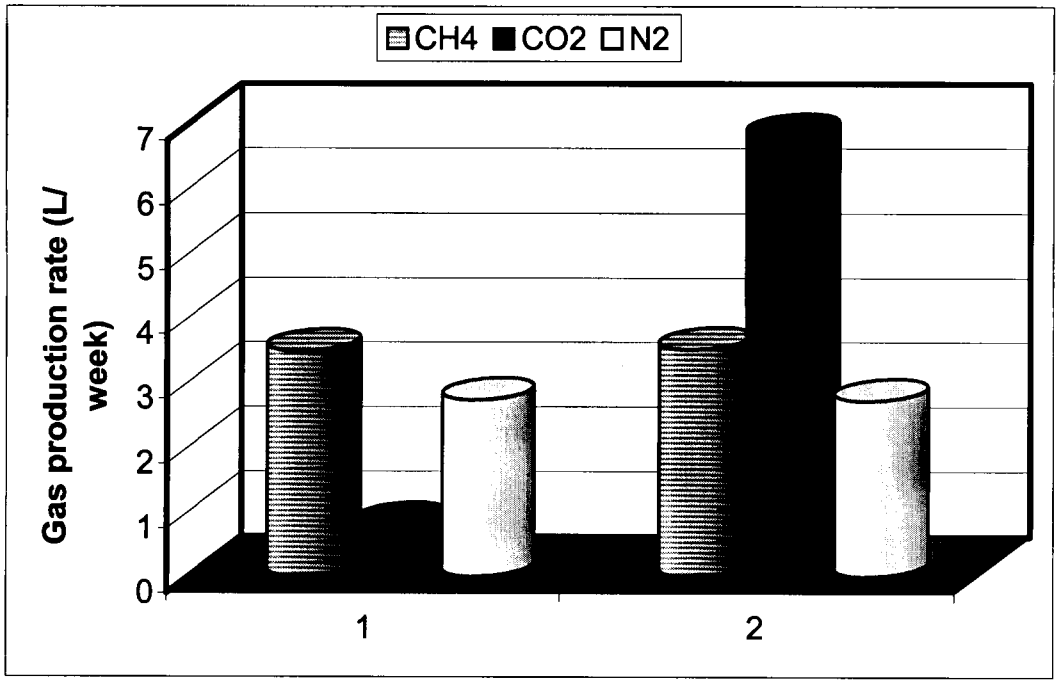

Figure 70 Gas production with dissolved CO_2 for lysimeter 8 (methane added) at two points (1: 10 days after methane addition stopped and 2: 2 months after methane addition stopped) during phase 1.5

Table 37 Mass balance on nitrogen at lysimeter 3 (no methane added)

	Nitrogen (mg-N /week)			
Sampling time	N-Feed	N-Leachate	N-Gas	% Error
Before methane introduction started	4200	1114	2937	3.5
10 days after methane stopped	4200	840	2016	32
2 months after methane stopped	4200	1700	1773	17

[22] Other sources of organic carbon dissolved in leachate have low concentration as shown in Table 35.

Table 38 Mass balance on nitrogen at lysimeter 8 (methane added)

	Nitrogen (mg-N /week)			
Sampling time	N-Feed	N-Leachate	N-Gas	% Error
Before methane	4200	529	2794	21
10 days after methane stopped	4200	4.5	3763	10.3
2 months after methane stopped	4200	739	3060	8.4

The data presented in Table 37 and Table 38 show that methane not only enhanced the efficiency of denitrification, but it also produced more nitrogen gas, and hence, reduced the possibility of incomplete denitrification. Therefore, it is expected that with methane addition, smaller amounts of nitric and nitrous oxides are produced.

The results of the previous phase (1.4) suggest that incomplete denitrification was associated with using a landfill bioreactor (section 6.1.5.3). In addition, it was shown that the nitrogen gas production rate was stable, and not affected by the carbon content of the lysimeter or the efficiency of denitrification. This was explained by the hypothesis of the downward movement of the active denitrification zone and the upward movement of the nitrogen gases produced (nitric and nitrous oxides) as shown in Figure 60. In this phase (1.5), the methane gas was moving upwards, making carbon available at all levels. Under such conditions, nitrogen oxides have a better opportunity to be further reduced to nitrogen gas. Therefore, the production rate of the nitrogen gas reached its maximum during this phase. Interestingly, this production rate was maintained throughout phase 1.5.

6.1.6.4 Overview –Phase 1.5

In this phase (1.5), the ability of methane to serve as the carbon source for denitrification through a landfill bioreactor was investigated. At a methane addition rate of 24 L/d, it was found that carbon deficiency declined, and consequently, denitrification efficiency was enhanced. These results were the first to confirm that methane can support denitrification in the absence of oxygen.

As a result of methane addition, the concentration of acetic acid, and hence, TOC, was dramatically elevated, and leachate rich in hydrogen sulfide was produced. This suggests that methane was oxidized to acetic acid; however the electron acceptor and the

mechanisms are unknown. It also suggests that acetic acid was used as the direct carbon source for denitrification, and methane was the indirect source of carbon for denitrification.

The nitrogen gas production rate increased and the carbon dioxide production rate was twice the production rate of methane. The results of this phase (1.5), also support the previous hypothesis, which stated that incomplete denitrification was due to the absence of a carbon source that allowed nitrogen oxides to accumulate.

6.1.7 Overview – Landfill Bioreactor Denitrification Experiment

This experiment proved that the use of the landfill by-products as carbon sources for denitrification in a landfill bioreactor is feasible. The results show that the process of denitrification in a bioreactor was associated with lower rates of gas production, hence, lower levels of waste degradation, at high influent nitrate concentration (800 mg-N/L). Moreover, at high influent nitrate concentrations (1500 to 2000 mg-N/L), the efficiency of denitrification was dependent on the assumed carbon content of the lysimeter (the higher the lysimeter carbon content, the higher the denitrification efficiency). At low influent nitrate concentration (less than 100 mg-N/L), high efficiency was achieved during all of the landfill stabilizing phases. In addition, the effect of denitrification on waste degradation was minimal.

This experiment also showed that the effect of denitrification at high influent nitrate concentration (800 mg-N/L) was substantial during the initial phases of landfill stabilization. Once methanogens were well established, the effect of denitrification on waste degradation was minor at nitrate concentrations as high as (1500 mg-N/L).

Denitrification in a landfill bioreactor was successful in removing the nitrate and nitrite from leachate; however, the nitrogen mass balance could not be closed. The error was due to the low production rate of nitrogen gas. The error in the nitrogen mass balance increased (at high influent nitrate concentrations) as the landfill aged and the carbon availability became limited, suggesting that incomplete denitrification was taking place.

In a mature landfill, where leachate carbon availability was not adequate to provide complete denitrification, methane at a sufficient level was shown to enhance the denitrification efficiency substantially. Moreover, a high concentration of acetic acid was found in the leachate after the addition of methane. The concentration of acetic acid was dependent on methane availability, indicating that methane was the source of acetic acid. However, the mechanism of the oxidation of methane is unknown. The results suggest that acetic acid was the carbon source for denitrification, which was able to overcome the lack of carbon and support denitrification. Therefore, methane availability provided a higher level of denitrification and produced nitrogen gas. Yet, direct methane oxidation was not confirmed.

6.2 The Denitrification Batch Test Experiment

The results of the previous experiment (Landfill Bioreactor Denitrification), showed that denitrification in a landfill bioreactor was feasible using the landfill leachate and –with some uncertainty- gas. More work was needed to investigate the process more closely and to confirm the ability of methane to serve as a carbon and/or energy source for this process. This experiment was designed to achieve these goals.

6.2.1 Experiment (2) Phase 2.1

Four batch tests were conducted for denitrification with nitrate concentrations ranging between 10 and 400 mg-N /L. Each test used a different carbon source, such as methanol, leachate and methane. The first two tests were performed to assess the quality of the results of the following tests. In the third and fourth tests, leachate and methane were tested thoroughly. The results of these kinetic studies are illustrated and discussed in the following sections.

6.2.1.1 Preliminary Test

The objective of this test was to determine the procedure for tests that would follow. This test evaluated the efficiency of the seed, buffer, vitamin solutions and the adequacy of the HRT and the reactor volume. To achieve this goal, eight batch reactors (400 mL) were

setup with different seed concentrations and carbon: nitrate ratios. In addition, this test was carried out to prove that vitamin E solution is a carbon source which affects the results of denitrification.

The results of the eight batches used in this test are shown in Figure 71. The results show that all batches were able to denitrify. It also shows that there was a lag phase of about 15 hours before active denitrification started. Regardless of the carbon content (see Table 19), nitrate was consumed completely in all seeded batches (batches 3 to 8), reaching high removal efficiency. The time needed to remove all of the nitrate ranged between 29 and 34 hours, including the lag phase. After the lag phase, the average denitrification rate (for batches 5 to 8), was calculated to be 6.65 mg-N/L/hr.

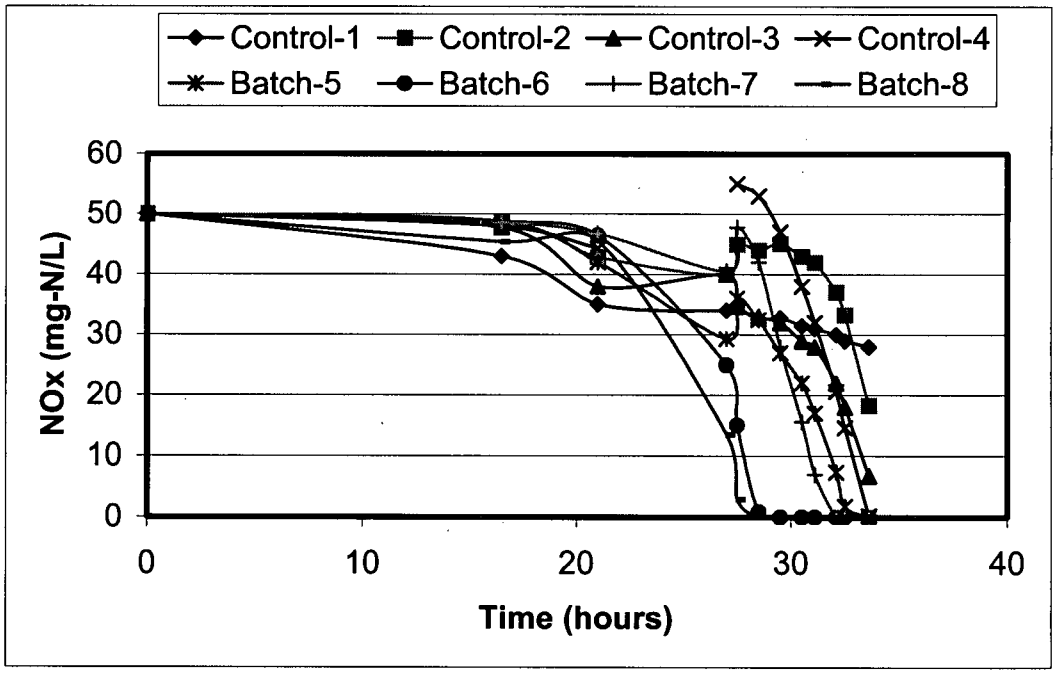

Figure 71 Denitrification as a preliminary test using vitamin E

The other important observation made was that the control batches (3 and 4), which were not provided with methanol as the only carbon source, consumed 100% of the nitrate. These batches were used as controls for carbon, and were designed to be carbon-free; hence, no denitrification was expected. The effect of the seed as a carbon source was negligible because it was low in carbon. Further investigation was needed to identify the carbon source used in this preliminary test.

A TOC test was conducted on each solution used to make these batches, to confirm that vitamin E was the source of the carbon. The results were positive for vitamin E solution (as expected), and negative for the other solutions. Due to the high concentration of carbon found in vitamin E (ethanol) solution, this solution was eliminated in all of the following tests.

6.2.1.2 Methanol

In this test, methanol was used as the only source of carbon. The objective of this test was to provide criteria, so that the performance of denitrification supported by leachate or methane could be compared with the performance of denitrification supported by methanol. The test was conducted five times (see Table 20), with three replicates in each series (run).

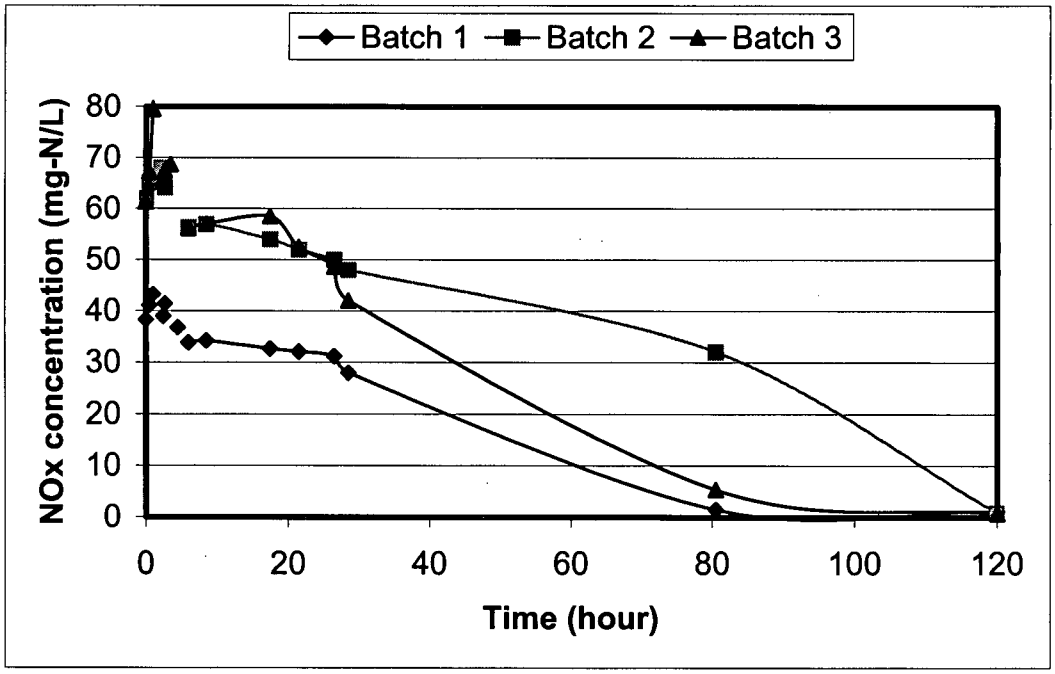

Figure 72 First test for denitrification with methanol (three replicate batches)

The results of the first run are shown in Figure 72. In this run, the lag period was found to be less than 40 hours, and the carbon-nitrogen consumption ratio was found to be 4 g-C/g NO_3-N. Since the purpose of this run was to activate the system and to avoid a lag phase

in the following tests, the results of this test are not included in the calculation of a final consumption rate of nitrate.

After the first run, three other runs were conducted. The results of these runs are shown in Figure 73 and Table 39. The results show consistency in the nitrate removal rate with respect to time, while the reduction rates of nitrate with respect to TOC were not consistent. The TOC was not an accurate method to measure the consumption of methanol. When growing on methanol, bacteria use the carbon in methanol and convert it into cell mass, carbon dioxide and produce soluble by-products. Therefore, the reduction measured in TOC only accounts for the release of carbon dioxide.

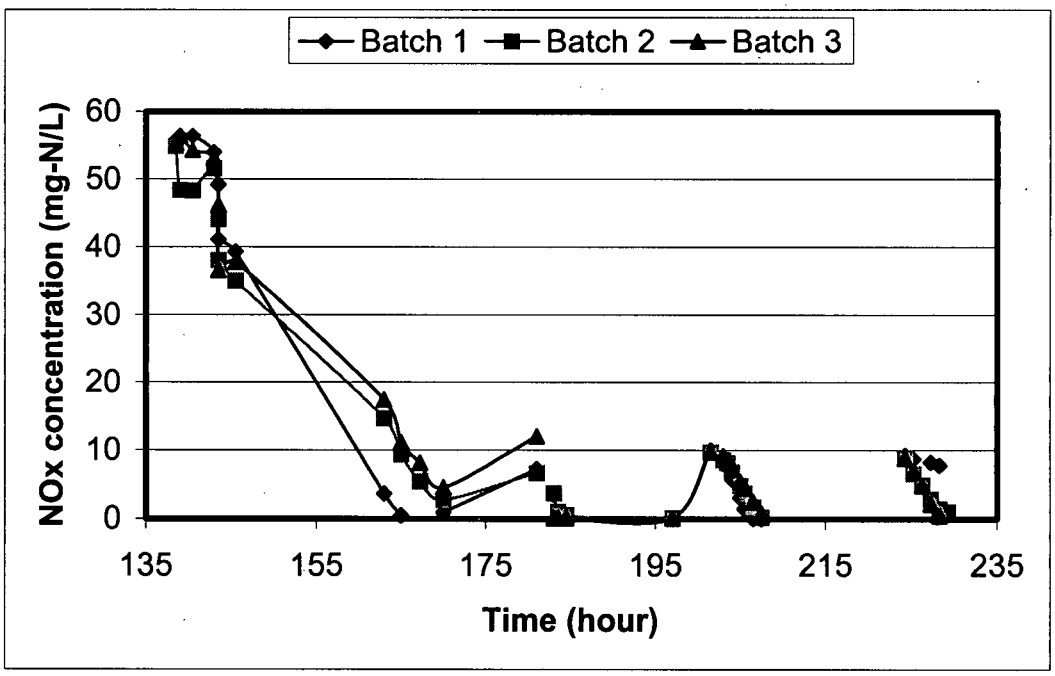

Figure 73 Denitrification with methanol

Table 39 Summary of methanol test

	Second run	Third run	Fourth run
ΔNitrate (mg/L-N)	52.6	6.9	9.5
ΔCarbon (mg/L)	150	82.5	45.7
ΔTime (hr)	31.5	3.5	6
ΔC/ΔNitrate	2.86	NA	4.87
Efficiency (%)	95.1	100	96.6
ΔNitrate/ΔTime (mg-N/L· hr)	1.67	1.97	1.58
R^2	0.96	0.92	0.96

Comparing the results of the methanol test to the results of the preliminary test (see section 6.2.1.1 for details), denitrification with vitamin E was found to be 3.7 times faster than that of denitrification with methanol. The large difference in the denitrification rate is probably due to vitamin E availability (vitamin E solution contains ethanol). McCarty *et al.* (1969) found that denitrification with ethanol was about two times faster than that with methanol, which supports the previous result. According to the same authors, both carbon sources have similar denitrification rates, but methanol required a longer adaptation time. Therefore, the overall denitrification rate for methanol was slower. In the present test, the bacteria were adapted to methanol in the first run, and the denitrification rate was calculated based on three runs with no lag phases, yet the denitrification rate with methanol was slower than that for ethanol. On the other hand, Blaszczyk (1983) showed that denitrification with methanol was three times faster than ethanol.

6.2.1.3 Methane

The results of experiment 1 phase 1.5 showed that methane was able to support denitrification in a bioreactor landfill. However, the process involved accumulation of acetic acid (by an unknown mechanism). There was a need for further investigation to confirm and clarify the process of denitrification with methane as the source of carbon. The next test was designed to help understand that process.

Three batches were set to evaluate the kinetics of denitrification with methane. One reactor was used as a control with no methane, and the other two were considered the methane reactors. The test was run five times and with different nitrate concentrations (5 to 50 mg-N/L). Since this test was started in parallel with the preliminary tests, i.e. received vitamin E, the results of this run were eliminated. After that run, more nitrate was added to consume any residual carbon. Methane was not considered to be the only source of carbon until a substantial change in the denitrification rate was observed.

Denitrification with methane passed through three major stages (Figure 74). Initially and for the first day, a rapid rate of denitrification was observed in all of the batches (including the control batch). However, the rate of denitrification decreased with time as Figure 75 illustrates. As the nitrate concentration stabilized and the rate of denitrification

reached its minimum values, a new stage started. In this stage, a lag period of about six days was found in all of the reactors before the last stage started. In the last stage, denitrification started again only in the reactors that received methane. The denitrification rate of the last stage was found to be slow compared to the results of the preliminary test and the methanol test.

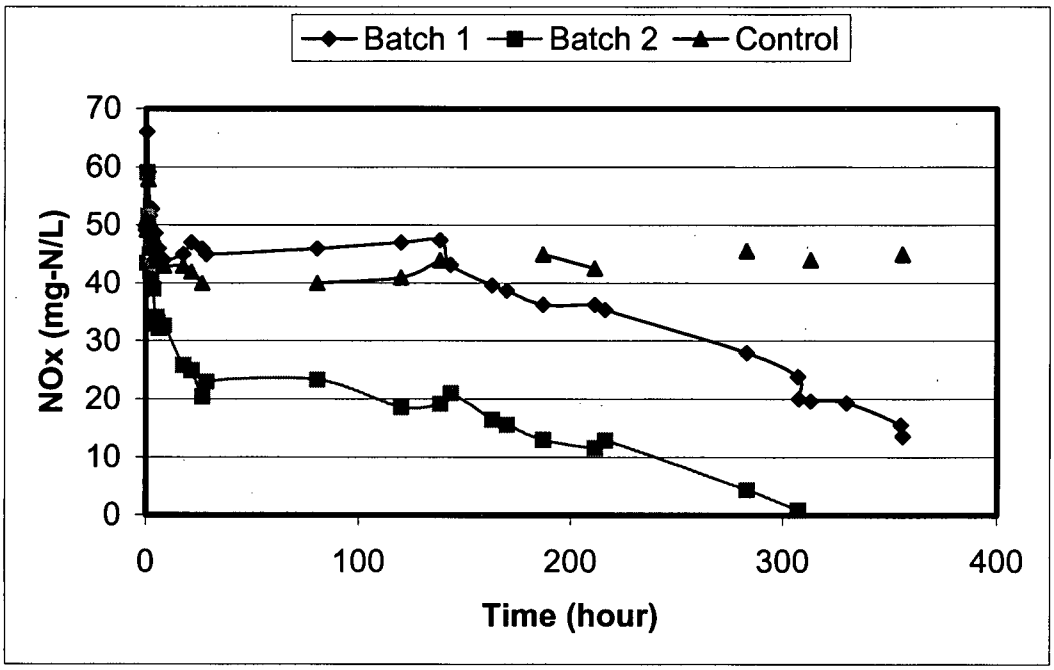

Figure 74 Nitrate concentration during denitrification batch test with methane as a carbon source

The total organic carbon (methane was not included) was measured during this run and the results are shown in Figure 76. The TOC also passed through three stages (batch 1 and 2). In the first two stages, the TOC behavior was similar to that of the nitrate. It decreased at a high rate during the first 27 hours, then stabilized for another seven days. In the last stage, the TOC followed an increasing trend, whereas the nitrate was decreasing. Also, parallel to the nitrate results, the increasing TOC was observed only in reactors that received methane (batch 1 and 2).

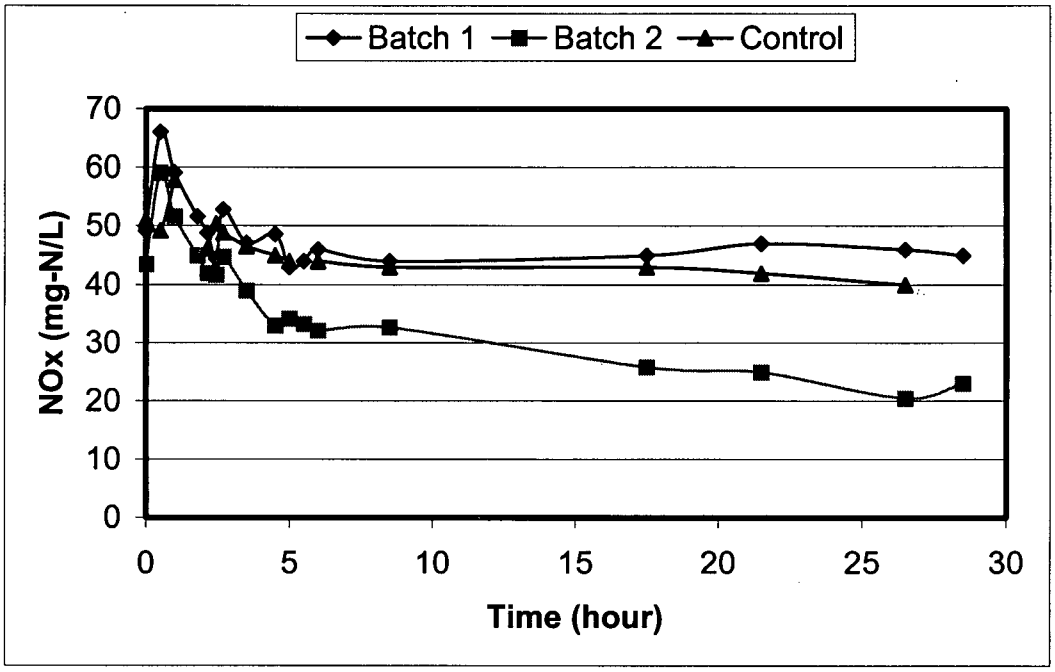

Figure 75 Nitrate concentration during the initial phase of denitrification batch test with methane (in the presence of vitamin E)

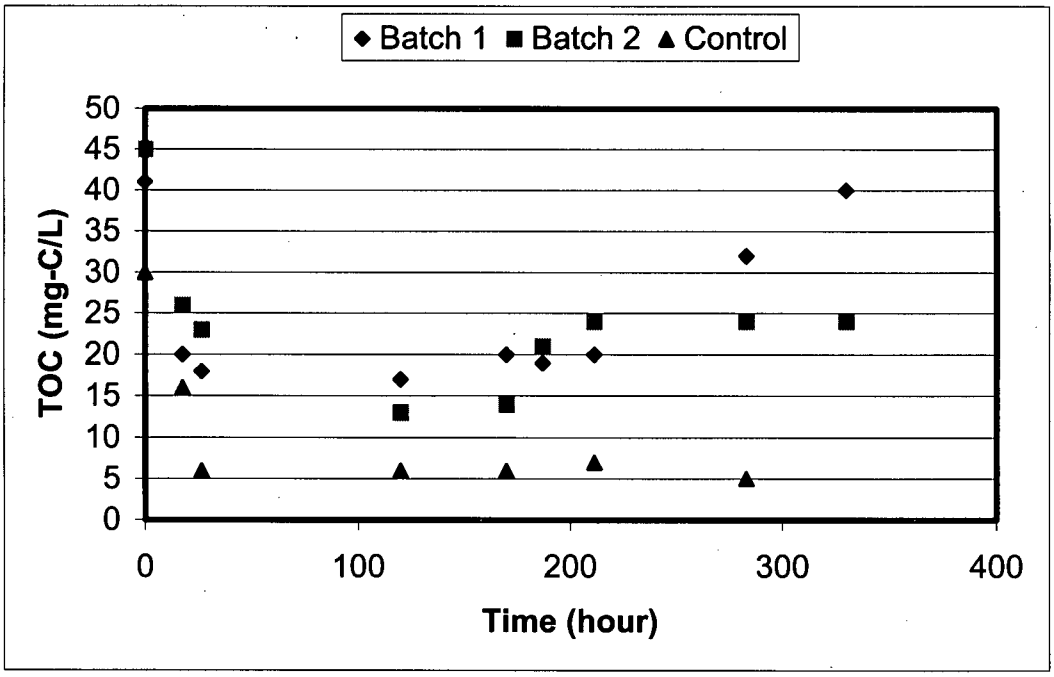

Figure 76 The concentration of the TOC during denitrification with methane

On the first day, while the carbon was decreasing sharply, the nitrate was also decreasing at a high rate. This behavior was observed in the three batches, which suggests that there

was a source of carbon other than methane that was responsible for this high rate of nitrate removal. The second stage started as this external carbon vanished. In this stage, the denitrification suffered from a carbon deficit, and hence, no further denitrification was observed for about six days. During this time, denitrifiers were adapting to the new source of carbon (methane) and started using it to denitrify. The third stage started by establishing the denitrification environment. As the nitrate decreased, more carbon was observed in the samples.

Further investigation was conducted to identify this carbon. The first assumption was that the carbon was present due to an accumulation of bacterial mass. This assumption was based on the fact that the denitrification rate was slow, and that, therefore, this carbon was probably not an attractive source for denitrifying bacteria. Samples were filtered before measuring the TOC, yet the filtered TOC increased, following the same trend that the unfiltered TOC had.

In the presence of oxygen, methane may be oxidized to methanol (Thalasso, *et al.* 1997, Werner and Kayser 1991, and Houbron *et al.* 1999), which can be used as the ultimate source of carbon and energy for denitrification. Thus, other samples were analyzed for methanol, but all of the results turned out to be negative.

Costa and others (2000) conducted a study that traced methane in the presence of oxygen using C^{13} methane. They found that methane was oxidized to $HC^{13}O_3^-$ and $C^{13}O_2$ at a high oxygen concentration and to $CH_3C^{13}OO^-$, $HC^{13}O_3^-$, $C^{13}O_2$, and $C^{13}H_3COO^-$ at a low oxygen concentration. Based on these results, samples were analyzed for acetate and acetic acid but the results showed that none was present. These two tests support the assumption that the reactors were completely sealed against air and that oxygen was not available. Further samples were tested for VFAs and methane. The VFAs results were negative, and only methane was found in low and steady concentrations (around 7 mg/L).

The possible explanation for this TOC content is that it may be soluble by-products that result from the microbial activities taking place in the reactor. These by-products are not easily degraded, and therefore TOC continued to accumulate. The fact that the TOC

concentration increased as the denitrification process continued and stabilized as denitrification stopped, adds strength to this explanation.

To insure that the methane was the only source of carbon for denitrification, the gas addition was stopped for two days in batch 1. During these days, the nitrate concentration did not change (Figure 77). This result demonstrated that methane was indeed, the source of carbon for denitrification.

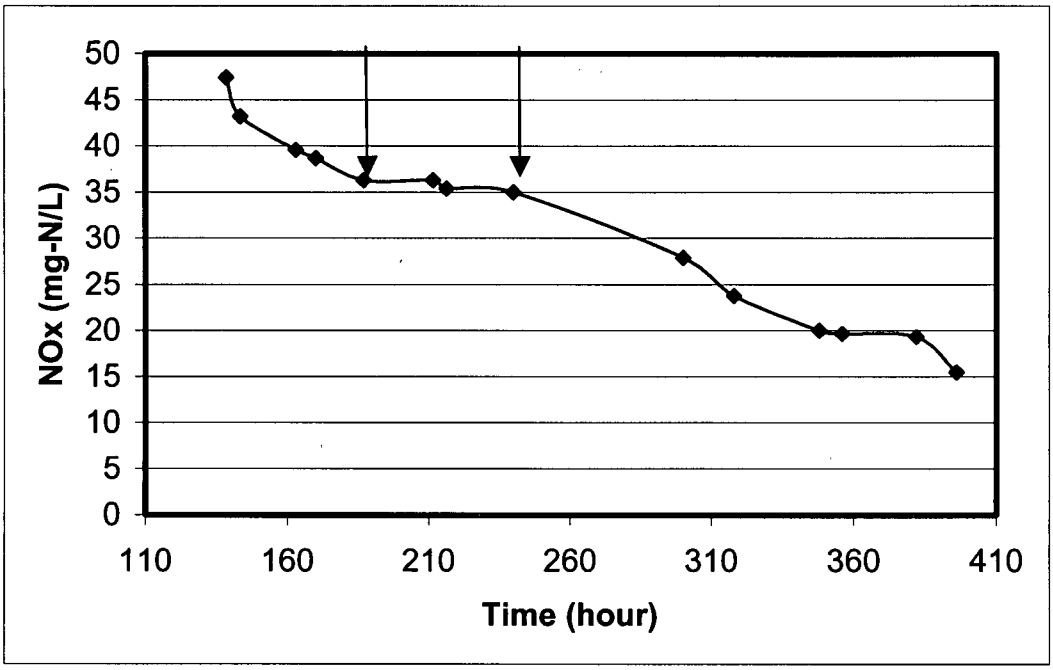

Figure 77 The nitrate concentration in the denitrification test with methane and no methane[23] for 48 hours

In the second run, the methane flow rate was increased from 30 mL/min to 300 mL/min (Figure 78). The results of these changes were negligible. These results suggest that methane flow rate was not the limiting factor. Due to the low solubility of methane, the solution may be saturated; hence, excess flow was wasted. Parameters that enhance methane solubility may also result in an increased denitrification rate, due to carbon availability.

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[23] The arrows refer to the time methane was off.

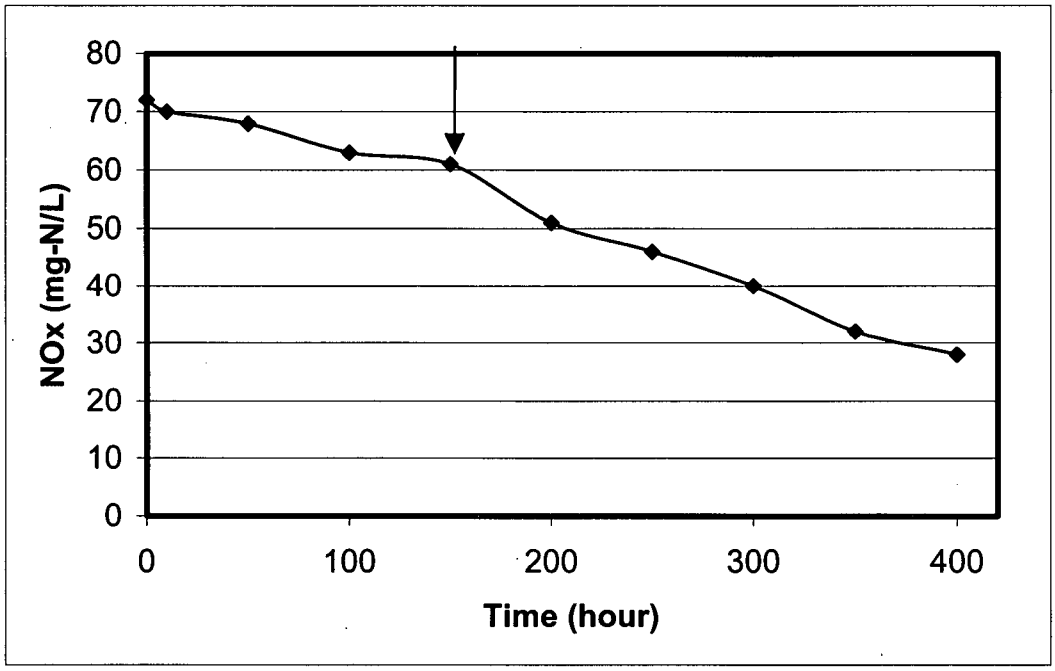

Figure 78 Effect of increasing methane flow rate on nitrate removal [24]

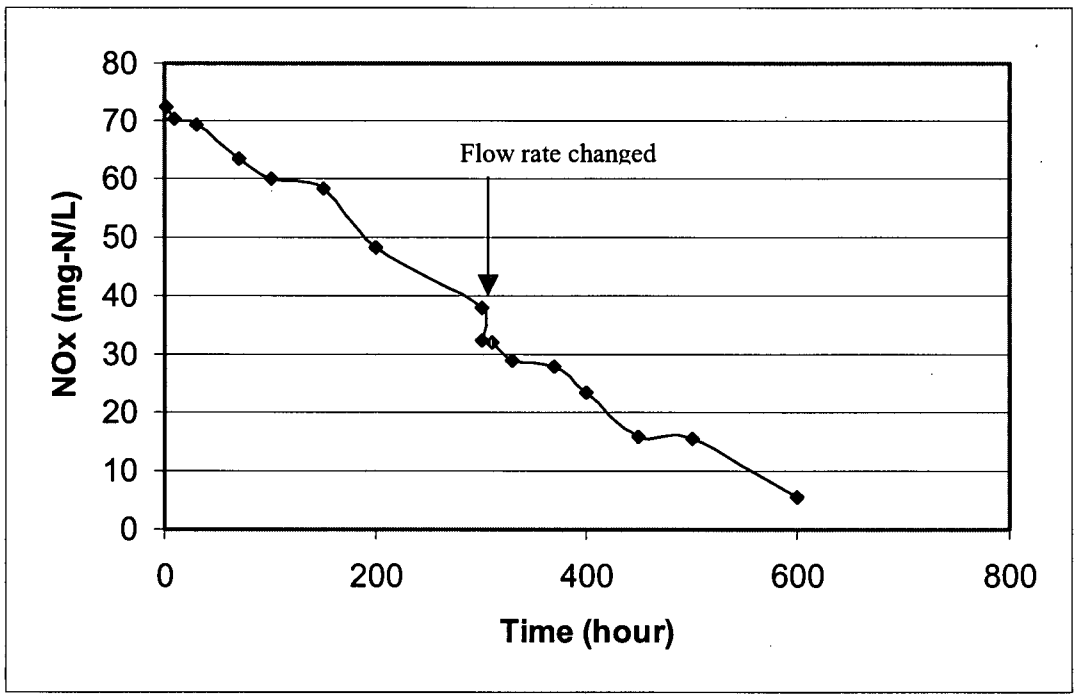

Figure 79 Denitrification with pure methane (started at time = 300 hour)

[24] The arrow refers to the point at which the flow rate of methane was increased from 30 to 300 mL/min.

Since natural gas contains trace amounts of other carbon compounds, pure methane was tested instead of natural gas to evaluate the effect of these trace gases. The results of this run are shown in Figure 79. The same rate of nitrate utilization was observed with pure methane as with natural gas. In addition, no lag phase was observed after the switch to pure methane.

In the last two runs, two types of fixed film medium (plastic tubes and synthetic sponges) were added as described in section 4.3.1.3.3. The purpose of adding medium was to investigate its effect on the nitrate utilization rate. The results of this test (shown in Figure 80) were collected two weeks after the addition of media, to avoid the effect of carbon residual leaching from the media. Media improved the rate of denitrification. In contrast with the results from the previous runs, the addition of media doubled the denitrification rate from 0.1 mg /L· hr to 0.2 mg-N /L· hr. Yet, the rate of nitrate utilization was still low compared to the same rate with methanol as the carbon source.

Denitrification supported by methane was found to be feasible, but slow. The addition of media (about 20% of reactor volume) enhanced the rate; nevertheless the rate was low. Moreover, oxidation of methane to acetic acid was not detected. The results of this test (denitrification batch test with methane) were quite different from the results of the previous experiment phase 1.5; this may be due to the effect of the mixed culture and/or the materials available in the lysimeter as explained in the following section.

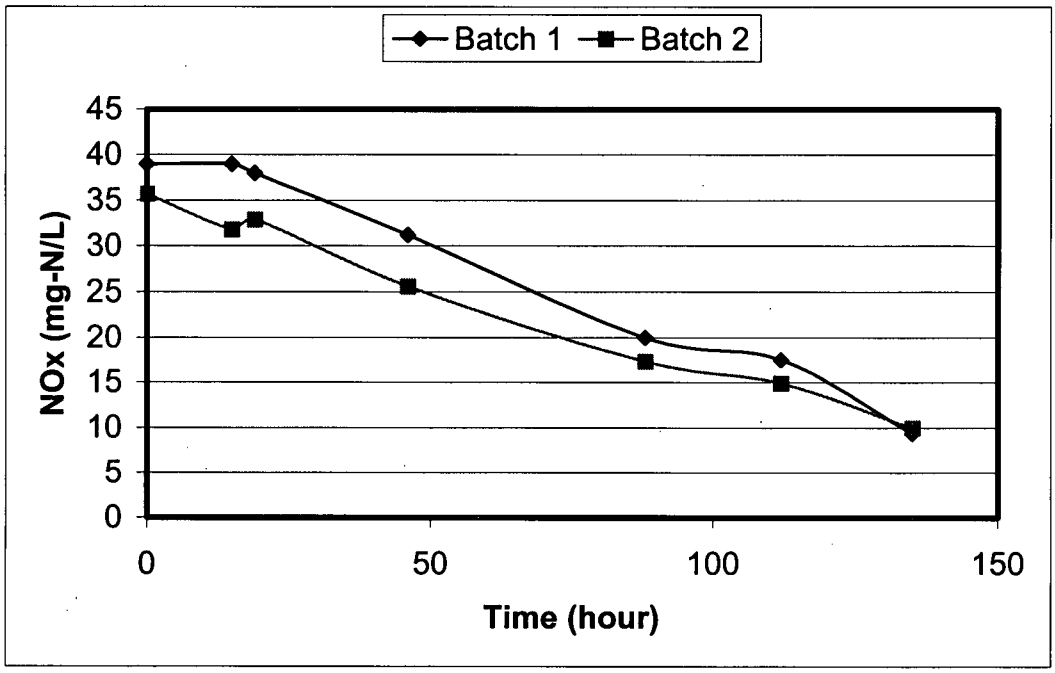

Figure 80 Denitrification with media (1:plastic tubing, 2:synthetic sponge)

6.2.1.3.1 Overview of Anoxic Methane Oxidation

It was deemed possible for anoxic methane oxidation to occur (section 6.1.6, Experiment (1) –Phase 1.5). High nitrate concentrations were completely reduced using methane. However, in this test, the rate of denitrification was very low and no other sources of carbon i.e. acetic acid, were accumulated. A better understanding of the process may be gained by comparing these results with the process of anoxic oxidation of methane using sulfate.

The process of anoxic methane oxidation was observed first in the late 1970's (Martens and Barner 1977, Panganiban 1979), nevertheless, it is still surrounded with uncertainties (Zehnder and Brock 1980, Niewoehner *et al.* 1998, Segers 1998). Although the process of sulfate-methane oxidation is well documented, all attempts to isolate a pure culture, of sulfate reducers by methane, have failed (Eisntrager *et al.* 2001). The researchers stress that this process had to occur in an environment that contained a consortium of bacteria and in some cases even archaea. Methanogens and sulfate-reducing bacteria are the most probable members of this consortium.

Two main hypotheses were suggested to explain this process. In the first one, a direct oxidation of methane was proposed as (Hansen *et al.* 1998, and Martens and Barner 1977):

Equation 17 Anoxic methane oxidation

$$CH_4 + SO_4^{2-} + 2H^+ \rightarrow CO_2 + H_2S + 2H_2O \ (\Delta G° = -25.1 \text{ kJ})$$

The hypothesis of a direct or indirect pairing between methane oxidation and sulfate reduction was further strengthened by observations of a corresponding maximum rate of methane oxidation and sulfate reduction in a narrow transition zone between sulfate and methane (Hansen *et al.* 1998). However, no *in situ* observations have confirmed a direct coupling between methane oxidation and sulfate-reducing bacteria. The second hypothesis proposed that anoxic methane oxidation occurred in two steps (Hoeler *et al.* 1994). In the first step, "reverse methanogenesis" produces carbon dioxide and hydrogen by the following equation:

Equation 18 Anoxic methane oxidation (half reaction)

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

In the second step, the oxidation of hydrogen by sulfate-reducing bacteria takes place according to the following equation:

Equation 19 Sulfate reduction

$$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$$

Thus, the overall reaction does not differ from the reaction proposed under the first hypothesis, yet the microorganisms and mechanism differ. The author concluded that this two step reaction is only possible at H_2 concentrations < 0.29 nM, and in the presence of active sulfate-reducing bacteria. Hansen *et al.* (1998) proved the ability of methanogens and sulfate-reducers to oxidize methane to carbon dioxide under anoxic conditions. Their belief was that methanogens were "the real methane oxidizers".

Since the issue of anoxic methane oxidation has been studied for more than three decades with many unanswered questions, this research was not expected to provide a full

understanding of methane oxidation with nitrate. The fact that more than one species of bacteria may be involved might affect the results of the denitrification batch test. Yet, the area of potential anoxic methane oxidation is wide open for further studies to solve this mystery.

6.2.1.4 Leachate

The results of the first experiment discussed in section 6.1.2 through section 6.1.5, show that landfill leachate is a good source of carbon and energy for the process of denitrification as long as the leachate contains VFAs. The purpose of this test was to confirm the previous finding, and to determine the kinetics of the reaction. The carbon sources used in this test were acetic acid, propionic acid, a mixture of propionic acid and acetic acid and the same mixture, but with leachate as the background to the matrix.

The results (Figure 81 and Table 40) show that the denitrification rates were in the range of 3.2 to 5.2 mg-N /L· hr, with correlation coefficients ranging between 0.9799 and 0.9939. Leachate was not expected to perform as well as other carbon sources such as methanol, because it is potentially rich in toxins. However, results showed otherwise. Comparing these results (3.2 to 5.2 mg-N /L· hr) with the results of the methanol test (1.7 to 1.95 mg-N /L· hr), leachate was found to be more efficient in reducing nitrate. However, comparing the denitrification rate supported by leachate (3.5 mg-N /L· hr) to the denitrification rate supported by the mixture of acetic acid and propionic acid (4 mg-N /L· hr), show that the presence of leachate (25% by volume) reduced the denitrification rate by 12 to 13%, on average.

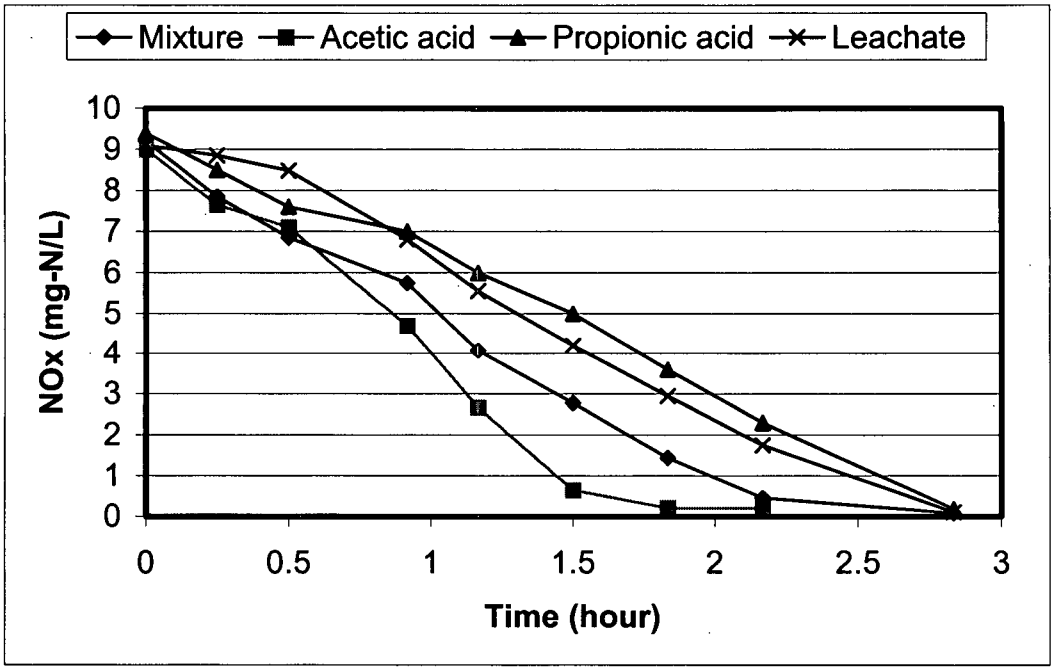

Figure 81 Nitrate concentration for denitrification with different carbon sources in the leachate batch test

Table 40 Rate of denitrification with acetic acid, propionic acid, a mixture of acetic acid and propionic acid, and leachate spiked with VFAs

Carbon Source	Acetic acid	Propionic acid	Acetic and propionic acids.	Leachate spiked with VFAs
Nitrate/ Time (mg-N/L/hr)	5.2	3.2	4	3.5
R^2	0.980	0.992	0.994	0.987

Leachate appears to be as good as other carbon sources used for denitrification, even better than methanol, as long as it is rich in VFAs. However, the effect of leachate on the process requires further investigation, in order to achieve a better understanding of the high rate of denitrification observed with leachate. This subject is discussed in the following section.

6.2.2 Over-view Phase 2.1

In this phase, denitrification with leachate was found to be faster (3.7 times) than denitrification with methanol. Thus, the results show that leachate can be used as a source of carbon as long as it has VFAs. In addition, denitrification with methane was found to be feasible but slow. Fixed film media have enhanced the rate of denitrification on

methane; yet, it was slower than denitrification with leachate and methanol. The results of this phase (2.1) have also proved that the use of vitamin E as a nutrient solution for testing the feasibility of methane to support denitrification provides misleading results. This is most likely due to the high concentration of ethanol in the vitamin E solution.

6.2.3 Experiment (2) –Phase 2.2

In the previous phase (2.1, see section 6.2.1.4 for details), the leachate denitrification rate was surprisingly good (3.5 mg-N/L· hr). This denitrification rate was higher than the denitrification rate when using methanol (1.8 mg-N/L· hr) as the carbon source. The effect of the leachate (25% by volume) matrix on the kinetics of the microorganisms was minor. Thus, more investigations were needed to evaluate the effect of increasing the leachate strength on the kinetics of denitrification. To accomplish, three leachate strengths were tested according to section 4.3.2.3. The results of these tests are illustrated and discussed in this section.

Data were analyzed for both nitrate and nitrite, and the results are shown in Figure 82 through Figure 84. Leachate at the three different strengths was able to serve as a carbon source for denitrification. Complete denitrification was achieved (for the three strengths) in less than four hours. At the weakest strength of 25%, complete denitrification was achieved with no nitrite accumulation. Since the nitrite concentration was low during the test, the rate of NO_x^- utilization was equal to the rate of NO_3^- utilization. The 20 mg-N/L of nitrate was utilized in 2.4 hours, and this utilization can be represented as a straight-line function.

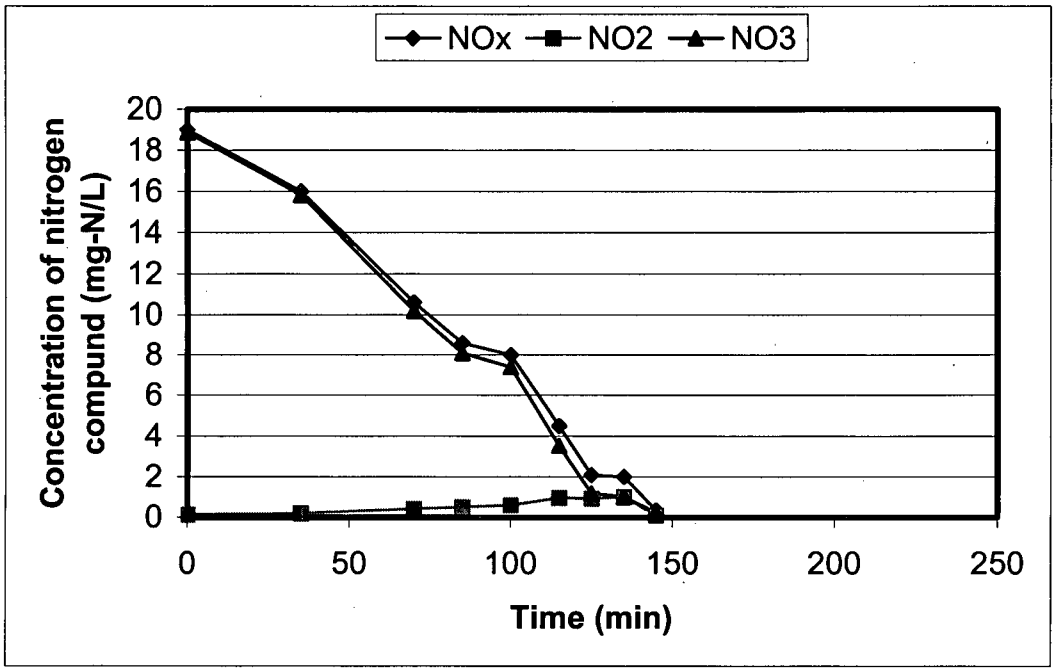

Figure 82 Denitrification with 25% leachate strength

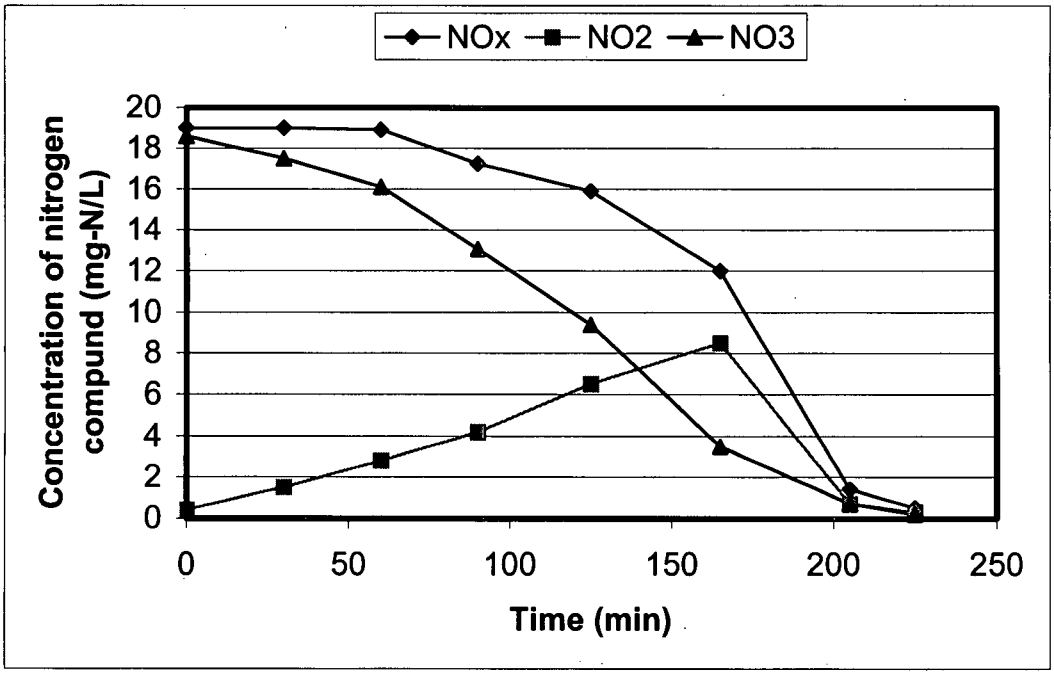

Figure 83 Denitrification with 50% leachate strength

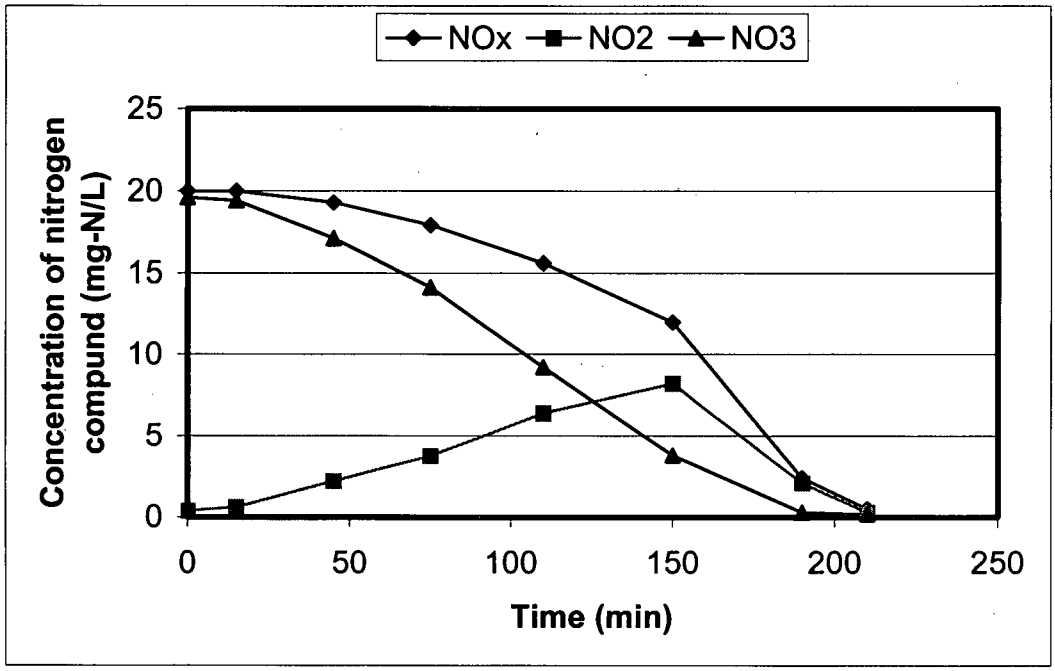

Figure 84 Denitrification with 100% leachate strength

Figure 83 shows that longer time was needed to consume the 20 mg-N/L of nitrate (3.75 hours) when the leachate strength was increased from 25% to 50%. It also shows that the NO_x^- utilization line passed through two phases. The first phase lasted for 2.75 hours and had a low utilization rate (Table 41). Although the nitrate utilization rate was three times faster than the overall NO_x^- utilization rate, nitrite was accumulating and caused the overall rate to be reduced. In the second phase, however, the nitrite concentration began to decrease instead of increase and boosted the overall reduction rate to be an order of magnitude faster than that of the first phase. Comparing the 50% leachate strength results to those at 25% showed that the increase in the leachate strength had little influence over the nitrate utilization rate. In contrast, it did have an influence over the nitrite reduction rate, which caused the overall reduction rate to be slower.

Table 41 Utilization rates for 50% leachate strength

Removal rate of compound (mg-N/L· min)	NO_x^-	NO_3^-	NO_2^-	Duration
Phase 1	-0.04	-0.09	+0.05	165 min
Phase 2	-0.20	-0.06	-0.14	60 min

Figure 84 shows that the test with 100% leachate strength followed the same trend as that test with the 50% leachate strength. Not only did it follow the trend, but similar values

were achieved, with the 100% leachate strength being slightly higher (Table 41 and Table 42). It was expected that the 100% leachate strength would be slower than the 50% leachate strength and even more so than the 25% leachate strength; however, the results show that the increase in the strength from 50% to 100% did not further hinder the process of denitrification.

Table 42 Utilization rates for 100% leachate strength

Removal rate of compound (mg-N/L· hr)	NO_x	NO_3	NO_2	Duration
Phase 1	-0.05	-0.11	+0.06	150 min
Phase 2	-0.20	-0.06	-0.14	60 min

All batches were spiked with the same amount of VFAs and nitrate before the first test; hence, differences in the results (VFAs consumption) were expected to be minimal. The results of VFA measurements (Figure 85) show that only acetic and propionic acids were present in the leachate during the second test. It appears that the butyric and valeric acids were consumed in the activation of the first test. Moreover, the results of the VFAs showed that the 50% leachate strength had the lowest VFAs concentration.

Denitrification with either the 50% or 100% leachate strength was associated with nitrite accumulation, whereas no nitrite accumulation was observed at the 25% leachate strength. Several studies have confirmed this behavior (nitrite accumulation) with different sources of carbon (such as acetate, methanol, ethanol, glucose, acetone) (McCarty 1969, Blaszczyk 1983, Paul and Beauchamp 1989, Fass et al. 1994).

The TOC results are shown in Figure 86. The 100% leachate strength started with a higher TOC, although its VFAs were comparable to that of the 25% leachate strength. This suggests that the difference in TOC was due to the high percentage of leachate. The amounts of carbon consumed during this test were 3.7, 2.8 and 10 mg-C /mg-N for the 25%, 50% and 100% leachate strengths respectively. Comparing these numbers shows that the difference between the 25% and the 50% leachate strengths were minor while the 100% leachate carbon consumption rate was more than triple that of the 50% leachate carbon consumption rate. This high a carbon consumption rate appeared only at the start of the run; otherwise, the carbon utilization rate was comparable to those at the other leachate strengths.

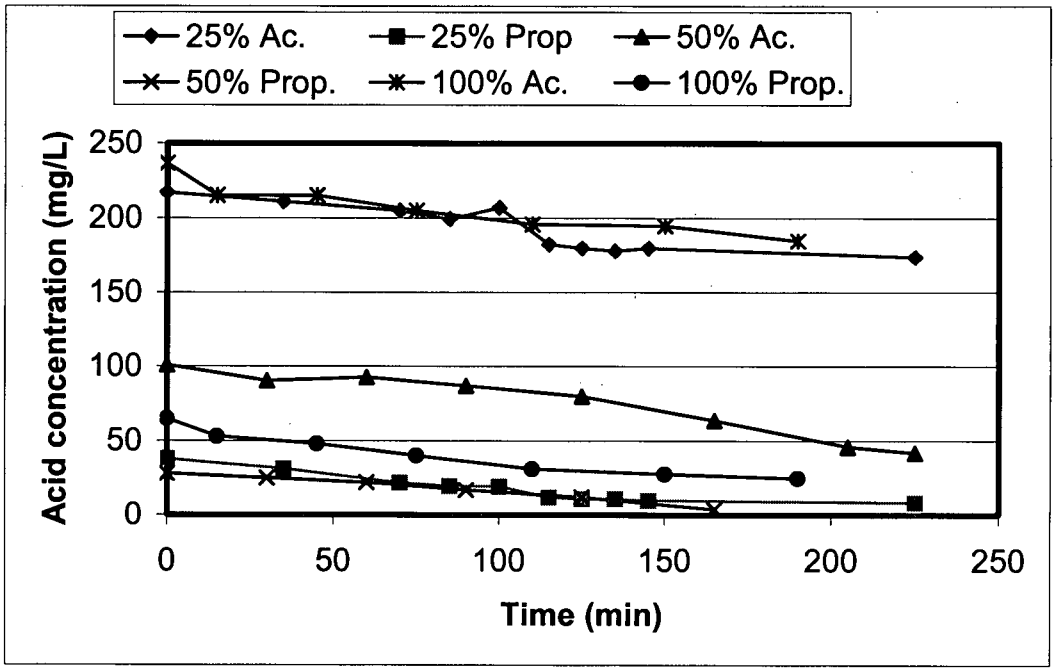

Figure 85 VFA for different leachate strengths for the second test

The final component that was investigated in this test was the concentrations of the mixed liquor volatile suspended solids (MLVSS), which were expected to indicate the growth rate of the bacterial mass during this test. The results of the MLVSS concentrations were expected to increase with the activity level, and stop after nitrate depletion. Nevertheless, this behavior was not clear (Figure 87). The nature of the leachate, which is characterized by its high suspended solids content, may have prevented the bacterial growth from displaying a more accurate picture of bacterial behavior.

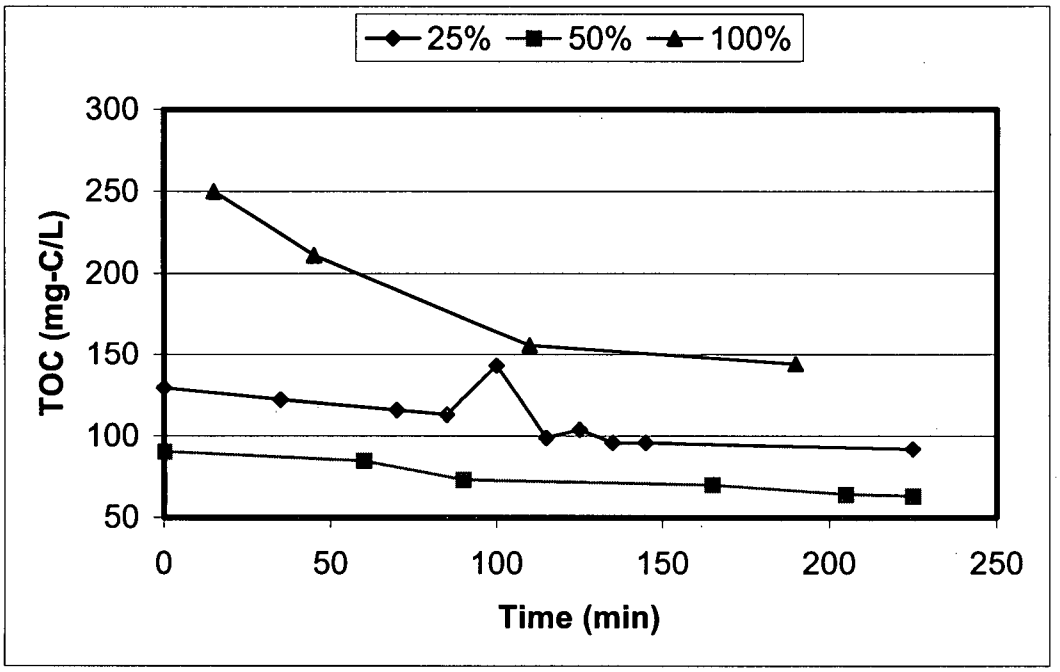

Figure 86 TOC for the different leachate strengths

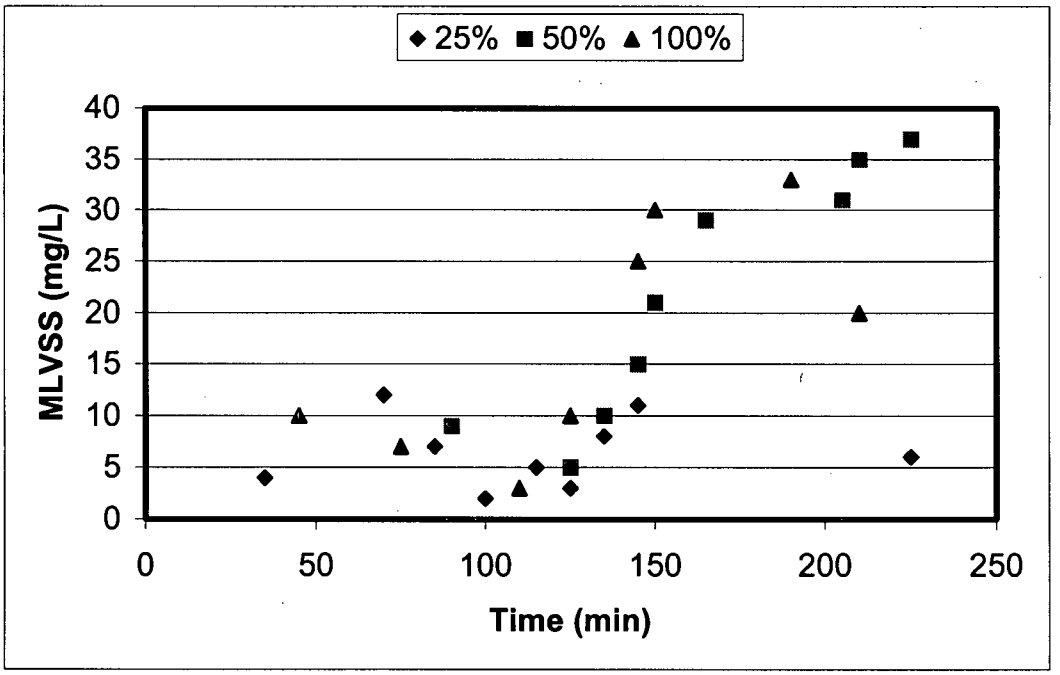

Figure 87 MLVSS for different leachate strengths

6.2.3.1 Overview –Leachate Test

The leachate was found to be a good source of carbon for denitrification and its presence did not appear to hinder the denitrification process. High denitrification rates were

achieved with leachate. As the leachate strength increased, the denitrification rate slightly decreased. However, as long as the leachate contained a sufficient amount of VFAs for complete denitrification, leachate denitrification rates were higher than those with methanol.

6.3 Potential Application

In this research, the feasibility of using a landfill bioreactor for denitrification was confirmed, but with a few limitations.

- Denitrification may suffer from carbon deficiency, thus incomplete denitrification may be the result. At low carbon to nitrate ratios, the production of nitrogen oxides is expected. If emitted to the atmosphere, these nitrogen oxides have an extremely high potential for global warming (more than 10 times the methane potential). In a landfill bioreactor, this problem may dominate if the site is not managed properly.

- Denitrification has been shown to pose a threat to the process of waste degradation at high nitrate concentration. This effect is considered to be high during the initial phases of landfill stabilization and minimal in the following phases. The results of this work suggest that denitrification reduces the activity of all of the degradation phases, starting from the hydrolysis and ending with the methanogenesis.

To reduce the effect of denitrification on waste degradation, nitrate has to be applied to a landfill cell that has reached the methanogenesis phase. In doing so, the effect of denitrification on the major steps of waste degradation is reduced. To minimize this effect, the nitrate must be gradually introduced to activate the denitrifiers and avoid a shock of denitrification. In addition, the maximum concentration of nitrate has to be limited, based on its effect on the bacterial activities.

Since the mechanism of the effect of denitrification on waste degradation is still not clear, it is important to operate the denitrification process within a designated zone in which

denitrification is completed. The leachate has to be free of denitrification by-products as it passes to the anaerobic zone. The border line/zone between the denitrification zone and the anaerobic zone has to be designed so that no toxic denitrification by-products can pass through it to the anaerobic zone. This border line/zone must be maintained as long as denitrification is practiced.

The depth of the denitrification zone is the most critical parameter in the design. It has to be deep enough to ensure complete denitrification, yet shallow enough to ensure sufficient methane production and enhanced waste degradation in the anaerobic zone. The depth of this zone is site-specific and mainly depends on the nitrate concentration and the carbon availability. Lysimeter (8) was used as a denitrification bioreactor to treat high nitrate concentrations during all the phases of the first experiment. This lysimeter, with a volume of 28 L, was able to denitrify 121 g of nitrate-N during the period of experiment 1 (Table 43). However, the capacity of a certain volume also depends on its age and the level of methanogenic activity.

Table 43 Capacity for denitrification

	Nitrate concentration (mg-N/L)	Duration (weeks)	Treated nitrate g-N
Phase1.1	800	15	33.6
Phase 1.2	600	7	11.8
Phase 1.4	2000	3	16.8
Phase 1.4	1500	14	58.8

A thin zone of denitrification is recommended to reduce the effect of denitrification on methanogens and the other bacterial species. Therefore, a leachate with a high nitrate concentration has to be managed before entering the anoxic zone, to avoid the consequences of increasing the depth of that zone. Once the depth of the denitrification zone increases, the expected outcomes are as follows: reduced methane production, reduced denitrification efficiency and less waste degradation.

To avoid the consequences of incomplete denitrification, the ratio between the depth of the denitrification zone and the depth of the anaerobic zone has to be selected so that the anaerobic zone produces methane in a sufficient quantity; this has the potential to solve the problem of incomplete denitrification.

Denitrification in a landfill bioreactor is recommended at deep landfills where the anoxic and the anaerobic zones can co-exist without the interfering outcome. The depth of a landfill cell can help in providing the sufficient volume needed to treat the nitrate and to produce methane at the same time. In shallow landfills, denitrification is applicable only at low nitrate concentrations. At high concentrations, the depth of the landfill may not provide adequate volume for methanogens, and hence, less methane production is expected. At low gas production rates, incomplete denitrification may occur.

In addition to the depth of the landfill cell, its age is another important factor in determining the feasibility of applying this process. At new landfills, denitrification may hinder the process of waste degradation. Moreover, nitrogen oxides may be produced due to the lack of carbon. Recycling leachate may help in providing the carbon needed for complete denitrification. Denitrification at new landfills may be achieved but it is not recommended before methanogens are well established.

At old landfills (in the final maturation phase), in which most of the waste has been degraded and methane production is not significant, denitrification is also not recommended. The absence of methane reduces the availability of carbon in the denitrification zone. Therefore, incomplete denitrification is expected. One way to solve the problem of incomplete denitrification is to introduce leachate from a new landfill cell. New leachate is rich in carbon and is able to solve the problem of incomplete denitrification.

Leachate may be considered as an attractive source of carbon/ED for denitrification at wastewater treatment plants (WWTP). The use of the leachate at a WWTP depends on its reliability (i.e. its consistency in production rate and carbon content), the effect it may have on the existing systems, and the cost associated with adopting this method.

7 Conclusions and Recommendations

7.1 Conclusions

In response to the objectives outlined in Chapter 3, the following conclusions, can be made.

1. Landfill bioreactors were capable of providing nitrate removal without the need for an external carbon source (self-sufficient).

2. Denitrification in a landfill bioreactor reduces the production of landfill gas and the overall process of waste degradation. As the nitrate concentration increases, the effect on landfill gas increases. This effect is significant during the initial phases of landfill stabilization and is minimal after methanogenic activities are well established.

3. Methane can be used as a source of carbon for denitrification at a landfill bioreactor.

4. Methane addition to an anoxic landfill bioreactor boosts the efficiency of denitrification and increases the nitrogen gas production rate. These results suggest that methane addition reduces the possibility of incomplete denitrification by providing carbon at higher levels in the bioreactor. The results also show that acetic acid is produced due to methane addition in the lysimeter.

5. An anoxic landfill bioreactor system (treating nitrate) failed to provide a solution for the release of methane as a GHG. In fact, it was hypothesized that this system, if not managed properly, has a potential to produce nitric and nitrous oxides, both of which impact the environment.

6. A landfill bioreactor treating nitrate at low concentration (< 100 mg-N/L) was able to produce NO_x-free leachate during all of the landfill stabilization phases. However, at high nitrate concentrations (up to 2000 mg-N /L), the landfill carbon

content (i.e. its age) was found to affect the NO_x concentration of the effluent leachate. As the landfill ages, the carbon content decreases and, hence, the NO_x concentration in the leachate increases.

7. High removal efficiencies (up to 99 %) for nitrate concentrations up to 2000 mg-N/L at landfill bioreactors are possible regardless of the age of the landfill. However, such high efficiencies depend on carbon availability, which is manageable (even in matured landfills).

8. In a batch test, the ability of leachate (spiked with sufficient amount of VFAs) was confirmed to support high denitrification rates. The effect of leachate strength (percentage wise) on the rate of denitrification was minimal.

9. Denitrification, using methane as a carbon source in batch tests, was found to be feasible, but slow. The rate of denitrification can be enhanced by the addition of fixed media into the reactor.

7.2 Recommendations

The results of this study have answered some of the initial questions; however there are several issues that have to be explored.

1. Since the main objective was to manage nitrogen, there is a need to explore the complete process including nitrification and denitrification.

2. In this work, denitrification in a landfill bioreactor was investigated without using LR. Therefore, there is a need to explore this process using nitrate-rich leachate.

3. There is also a need to investigate the kinetics of this process and to study the effect of landfill aging, carbon availability, and carbon source on the kinetics.

4. Denitrification in a landfill bioreactor was found to be associated with reduced waste degradation. To overcome this difficulty, the effect of denitrification on waste degradation must first be investigated. The literature has mentioned only the effect of denitrification on methanogens and has neglected the other processes.

The effect on each process that contributes to the degradation chain has to be investigated.

5. The results of this work suggest that carbon availability in the pathway of nitrogen oxide gases (carbon deprived zones) can support complete denitrification and increase the production of the nitrogen gas. However, the amount of methane needed to treat a certain concentration of nitrate has not been specified. Therefore, there is a need to develop a model to help in determining the optimum design. The depth of the denitrification zone is the most critical parameter. Another important parameter is the ratio between the depth of the anoxic zone and that of the anaerobic zone. This ratio has to be designed so that a sufficient amount of gas can be produced to insure complete denitrification.

6. The effect of denitrification on waste degradation may be neglected in deep cells. The effect of the depth of the landfill cell on waste degradation has to be explored to optimize the waste degradation and the nitrate concentration.

7. This work has also shown that the process of anoxic methane oxidation is possible, but the mechanism is unknown. The source/s of electron acceptor is/are undetermined. More research is needed to investigate the mechanism of this process.

8. This work suggests that methane can be oxidized to acetate in the absence of oxygen. However, more research is required to investigate the electron acceptor of this oxidation, the carbon pathway and the reaction mechanism.

9. The process of methane oxidation was possible in a lysimeter, but not in a batch test. There is a need to evaluate the two environments and investigate the causes of these results.

10. The efficiency of denitrification, calculated on the basis of leachate NO_x concentration, may be misleading. A proper mass balance on nitrogen (that accounts for nitrogen oxide gases) can better represent the efficiency.

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9 Appendices

9.1 Appendix 1 Data for: "Denitrification Landfill Bioreactor" Experiment

NOx **mg/L**

Week	Lysimeter Number							
	1	2	3	4	5	6	7	8
1	0.11	0.107	0.18	0.18	0.09	0.08	0.18	0.18
2	0.09	0.11	0.18	0.17	0.15	0.19	0.17	0.96
3	0.46	0.28	0.28	0.28	0.28	0.3	0.28	0.33
4	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.9
5	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.22
6	5.96	2.04	2.4	2.7	2.2	1.7	3.82	6.98
7	0.5	1.5	0.1	1.2	0.5	0.1	2	1.7
8	0.5	0.4	0.4	1.4	0.41	0.44	2.3	2.93
9	0.5	0.46	1	0.89	0.45	0.48	6.4	9.25
10	0.43	0.47	0.55	1.1	0.5	0.48	9	2.3
11	0.9	0.58	1.5	1.24	0.4	1.32	3.1	7.5
12	0.636	0.436	2.533	0.757	0.46	0.474	5.361	7.05
13	0.596	0.453	3.9	1.89	0.45	0.4	5.26	2.56
14	0.677	0.65	8.8	0.57	0.62	0.64	23.1	12.5
15	1.57	0.9	4.5	0.32	0.86	0.9	3.4	2.5
16	1	1.7	0.8	0.2	0.8	0.9	10.5	6
17	1.7	1.9	6.9	1.3	1.67	3.96	4.1	6.7
18	1.6	1.7	2.3	1.1	3	2	2.1	1.9
19	0.53	0.56	3.03	0.52	0.85	1.16	5.86	5.6
20	0.343	0.52	0.63	0.193	0.522	1.08	0.447	1.03
21	0.161	0.085	0.058	0.217	0.082	0.064	0.068	0.056
22	0.212	0.086	0.091	0.152	0.162	0.089	0.194	0.368
23	0.185	0.151	11.225	0.786	0.176	0.128	0.16	0.11
24	0.184	0.144	1.98	0.408	0.182	0.149	0.175	0.156
25	0.777	1.467	0.712	140	2.3	1.17	0.947	0.813
26	0.763	0.851	36.97	207	3.6	1.65	0.98	0.827
27	0.1	0.1	69	180	1.2	0.24	0.1	13
28	0.5	0.5	15.6	170	0.4	0.5	0.6	2.1
29	0.1	0.1	119	278	0.1	0.1	0.1	0.1
30	0.1	0.1	11.01	164	1.6	0.03	0.1	0.1
31	0.026	0.035	106	251	0.016	0.01	0.013	0.083
32	0.3	0.4	174	342	0.4	0.7	0.8	0.95
33	2.65	2.68	281	442	0.4	0.4	0.4	0.3
34	0.4	0.4	38	344	0.5	0.4	0.4	0.3
35	0.4	0.4	4.8	399	0.7	0.5	0.4	0.2
36	0.4	0.5	242	228	1.7	3.3	0.5	16.94
37	0.84	0.61	224	409	0.58	0.55	0.6	12
38	0.6	0.6	5.8	449	0.56	0.6	0.7	19.6
39	0.6	0.6	50	460	0.6	1	1	86
40	0.2	0.2	0.56	508	0.4	0.2	0.2	78.6
41	0.37	0.48	234	523	0.6	0.6	0.4	86

COD (g/L)

Week Lysimeter Number

week	1	2	3	4	5	6	7	8
1	16.4	30.8	21.4	27	32.6	26.9	24.3	22.1
2	24.3	36.7	28.3	27.9	38	37.8	31.6	25.3
3	30.1	36.2	31.8	39.5	36.5	41.3	31	27
4	26.7	30.1	40.8	33.2	35.1	35.26	35	32.5
5	32.8	31.2	32.3	34.3	31.8	42.5	32.6	27.6
6	28.1	25.9	32.4	30	23.5	33.4	26.8	20.2
7	30	27.9	31	26	26.2	39	26	33
8	28.7	25.3	30.5	25.7	24	32.4	26.7	20.6
9	23.4	23	24.1	18.2	20.5	28.2	23.6	18.5
10	19.3	19.6	21.3	12.6	18.6	24.4	21.6	17.2
11	16.9	16.8	17.3	11.3	14.6	19.8	20	17
12	15.4	16.9	18	8.8	14.4	18.6	20.2	17.4
13	13.5	14.3	15.5	5.4	12.6	18.2	17.4	16.9
14	10.6	8.07	13.52	3.1	10	11.9	15.4	13.26
15	7.56	6.67	11.74	1.6	10	7.3	14.8	11.5
16	6.67	11.1	6.3	0.96	6	8	13	11.74
17	3.6	3.4	8.3	0.5	4.7	4.5	12.6	7.5
18	2.1	2.86	7.94	0.58	4.5	5.9	9.8	8.19
19	1.3	2.88	7.75	0.8	2.8	3.48	10.26	8.77
20	0.85	1.87	6.97	0.6	1.49	4.28	8.42	6.5
21	0.33	1.15	5.04	0.53	1.11	5	6.25	5.87
22	0.59	1.34	11.27	0.74	0.97	6.32	7.37	6.44
23	0.68	1.17	8.79	0.65	1.15	3.04	7.88	6.23
24	0.52	0.89	7.43	3.46	0.78	1.53	5.74	7.52
25	0.52	0.15	1.2	0.99	0.78	1.3	4	6.93
26	0.336	0.146	0.465	0.262	0.410	0.550	1.689	4.860
27	0.326	0.349	0.628	0.448	0.400	0.330	1.560	3.693
28	0.275	0.215	0.800	0.463	0.280	0.250	0.424	2.856
29	0.283	0.255	1.295	0.450	0.250	0.180	0.666	2.634
30	0.202	0.141	1.080	0.486	0.220	0.150	0.632	1.965
31	0.170	0.160	0.613	0.365	0.207	0.160	0.559	0.943
32	0.158	0.160	0.584	0.384	0.192	0.216	0.282	1.031
33	0.190	0.202	0.516	0.241	0.151	0.267	0.355	0.681
34	0.204	0.129	0.588	0.287	0.212	0.216	0.421	0.982
35	0.214	0.139	0.849	0.309	0.190	0.170	0.319	0.618
36	0.195	0.143	0.598	0.299	0.158	0.143	0.292	0.435
37	0.165	0.129	0.523	0.236	0.163	0.143	0.323	0.481
38	0.199	0.153	1.160	0.272	0.195	0.175	0.272	0.647
39	0.229	0.229	1.138	0.292	0.292	0.163	0.382	0.299
40	0.160	0.097	1.070	0.212	0.146	0.109	0.190	0.270
41	0.165	0.063	1.167	0.255	0.165	0.146	0.243	0.277

BOD mg/L

Week Lysimeter Number

	1	2	3	4	5	6	7	8
1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6	6300-12150	3300-12900	9300-17400	10800-16650	(4200-12900)	3300-18900	300-9900	(2700-7650)
7	12300-9150	3300-9150	12150-15300	12150-24300	12150-18300	15150-27300	13650-19800	6300-9150
8	14250-17625	9750-12375	8625-11250	9750-13125	9750-11625	15750-16875	9000-12375	6750-10875
9	10000	10000	12000	7000	6900	13700	9500	7500
10	11500	11800	17100	7000	20000	21000	13700	9600
11	10600	11000	11700	7000	10200	12300	12100	10500
12	13500	12100	19000	7000	12500	14700	16500	11600
13	12000	10000	12300	7500	6500	11200	20000	18000
14	13500	9300	11000	12000	14000	20000	12000	17000
15	13500	10000	24000	10000	23000	25000	25000	18000
16	5800	12000	4500	1800	6000	5400	12000	7000
17	1600	3500	6400	500	4500	4500	9400	6000
18	500	2400	3900	800	1800	6300	9200	6300
19	1000	1900	4500	300	1000	3400	6600	5500
20	400	1300	3800	360	900	2600	3400	4900
21	350	600	2500	1100	380	1000	2600	2200
22	250	700	400	40	200	800	3000	1000
23	30	250	2000	100	200	400	1500	1500
24	50	200	2000	130	200	400	1700	1600
25	45	115	300	15	110	300	850	1800
26	24	20	265	20	75	210	1000	1600
27	20	80	20	25	75	25	420	1150
28	51	56	1100	40	80	48	350	1000
29	35	30	350	20	42	40	300	870
30	10	12	100	12	35	37	260	700
31	15	20	600	10	16	24	80	220
32	20	20	400	2	24	50	90	300
33	20	23	150	6	13	37	67	118
34	23	12	100	9	23	38	41	270
35	27	19	111	22	29	30	44	170
36	30	18	235	75	52	35	48	95
37	20	20	200	15	30	30	40	66
38	20	20	130	10	20	20	25	85
39	16	20	110	12	22	18	45	40
40	8	5	100	20	19	16	25	20

pH

week	1	2	3	4	5	6	7	8
1	5.27	5.45	5.09	5.51	5.36	5.15	5.12	5.09
2	5.17	5.1	4.87	5.2	5.2	4.88	4.83	4.88
3	5.13	5.2	4.99	5.28	5.29	4.94	4.94	4.96
4	5.08	5.16	4.97	5.28	5.2	4.91	4.92	4.93
6	5.25	5.3	5.25	5.56	5.32	5.2	5.2	5.15
7	5.12	5.15	5.17	5.57	5.17	5.1	5.1	5.07
8	5.22	5.21	5.18	6	5.16	5.17	5.17	5.13
9	5.23	5.18	5.16	6.03	5.09	5.07	5.25	5.22
10	5.28	5.05	5.04	6.36	5	4.97	5.17	5.19
11	5.63	5.14	5.14	6.48	5.15	5.08	5.27	5.26
12	5.74	5.12	5.14	6.63	5.02	5.08	5.36	5.42
13	5.75	5.11	5.14	6.61	5	5.13	5.32	5.31
14	5.6	5.21	5.08	7.4	4.91	5.1	5.44	5.38
15	5.91	5.73	5.21	7.42	5.14	5.42	5.47	5.59
16	6.05	6.04	5.34	6.85	5.36	5.66	5.79	5.67
17	6.18	6.12	5.5	6.83	5.47	5.78	5.84	5.97
18	6.31	6.2	5.75	6.91	5.76	5.85	6.1	6.28
19	6.32	6.24	5.66	6.84	5.91	5.95	6.04	6.28
20	6.26	6.4	5.71	6.91	6.24	6.06	6.27	6.36
21	6.37	6.3	6.14	6.97	6.31	6.23	6.42	6.53
22	6.32	6.45	5.82	6.9	6.43	6.43	6.55	6.47
23	6.29	6.4	6.3	6.93	6.4	6.44	6.63	6.57
24	6.25	6.36	6.46	6.95	6.32	6.44	6.73	6.67
25	6.66	6.6	7.4	7.28	6.76	6.79	7	6.91
26	6.06	6.21	7.29	7.19	6.41	6.53	6.81	6.83
27	5.96	6.05	7.33	7.29	6.33	6.41	7.02	6.89
28	6.07	6.32	7.09	7.23	6.17	6.4	6.75	6.98
29	6	6.32	7.21	7.49	6.18	6.37	6.76	7.03
30	6.02	6.15	7.34	7.14	6.17	6.3	6.7	7.09
31	6.05	6.34	7.6	7.2	6.18	6.4	6.87	7.08
32	5.98	6.16	7.74	7.3	6.16	6.41	6.7	7.23
33	5.96	6.02	8	7.4	6.2	6.4	6.8	7.55
34	6.1	6.5	8.2	8.23	6.34	6.38	6.74	7.64
35	5.83	6.06	8.08	7.84	6.25	6.37	6.63	7.9
36	5.8	6	7.6	7.2	6	6.2	6.4	7.5
37	5.88	6	8	7.4	6.3	6.3	6.5	8
38	5.8	6	7.9	7.8	6.2	6.3	6.45	7.8
39	5.76	5.97	7.85	7.25	6.13	6.31	6.38	7.66
40	6.4		7.9	7.72	6.5	6.37	6.44	7.81

Phosphate (mg/L)

Week	Lysimeter Number							
week	1	2	3	4	5	6	7	8
1	11.2	10.7	5.1	16.9	1.4	14	14.5	26.4
2	16.6	26.2	13.4	30	2	17.5	31	28.3
3	11.1	13.7	11.2	34.3	1.6	8.8	25.8	17.3
4	14.6	16.8	22.3	24.8	1.8	13.2	19.7	18.3
5	12.3	13.7	22.3	11.3	0.092	12.68	20.2	15.6
6	13	10.5	19	6.6	1.3	11.9	16.98	14.96
7	8.3	5.4	7.9	4.9	1.4	8.1	10.3	12.1
8	3	2.6	5.6	1.6	0.88	5.1	4.9	3.6
9	5.4	4	7.4	0.01	1	3.6	6.7	4.6
10	3.2	3.7	7	1.1	1	6	3.1	4.26
11	2.24	2.3	2.7	0.8	0.6	4	3.38	3
12	0.369	1.675	2.47	0.311	0.78	1.16	2	1.36
13	1.08	1.93	2.6	0.36	1.2	3.16	2.35	3.4
14	0.822	0.847	0.955	0.866	0.9	0.895	0.906	0.872
15	0.3	0.3	0.9	0.36	0.422	0.4	0.5	0.4
16	0.29	0.2	0.26	0.32	0.37	0.3	0.3	0.38
17	1	1.16	1.4	0.88	1.6	1.3	1.6	1.37
18	1.1	1	1.2	0.9	1.2	1.1	2	2
19	1.3	0.9	1.04	1	0.89	0.822	2.5	2.5
20	0.457	0.25	1.17	0.4	0.35	0.87	1	0.76
21	0.491	0.733	0.87	1.183	0.452	1.039	1.93	1.882
22	0.871	0.85	1.3	0.8	0.36	0.33	1.4	1
23	0.85	0.84	1	1.2	0.5	1	0.5	1.3
24	1.2	1.2	0.7	1.4	0.45	1.2	1.5	1.2
25	1.3	1.1	0.97	0.9	0.94	0.95	1.4	1.25
26	1.3	0.9	1.2	1	1	1.5	1.6	1.4
27	1.1	1.2	0.7	0.45	0.5	0.9	1.7	0.44
28	1.3	1	1.7	1.5	0.7	1	1.76	1.2
29	1	0.8	0.75	0.5	0.5	0.75	1.5	0.9
30	1	0.87	1.7	1.25	0.6	0.8	1.8	1.5
31	1.069	0.928	0.551	0.533	0.357	0.958	1.9	2.03
32	3.6	0.4	0.8	0.6	0.5	0.5	0.7	1.5
33	6.5	6	0.8	0.5	0.5	1	1.5	2
34	1.1	0.6	0.7	0.5	0.5	0.9	1.4	1.6
35	1	0.7	1.2	0.6	0.5	0.8	1.3	1.2
36	1	1	0.6	0.4	0.6	0.7	1.4	0.8
37	1.2	1.5	1.7	1	0.9	1.1	1.6	1.8
38	1.6	1.8	3.2	1.7	1.7	1.6	1.9	2.2
39	2	2	2.6	1.8	1.8	1.9	2.3	1.8
40	0.42	0.26	3	1.5	0.3	0.5	0.8	1.5

TOC (g/L)

Week	Lysimeter Number							
	1	2	3	4	5	6	7	8
1	4.920	9.240	6.420	8.100	9.780	8.070	7.290	6.630
2	7.290	11.010	8.490	8.370	11.400	11.340	9.480	7.590
3	9.030	10.860	9.540	11.850	10.950	12.390	9.300	8.100
4	8.010	9.030	12.240	9.960	10.530	10.578	10.500	9.750
5	9.840	9.360	9.690	10.290	9.540	12.750	9.780	8.280
6	8.430	7.770	9.720	9.000	7.050	10.020	8.040	6.060
7	9.000	8.370	9.300	7.800	7.860	11.700	7.800	9.900
8	8.610	7.590	9.150	7.710	7.200	9.720	8.010	6.180
9	7.020	6.900	7.230	5.460	6.150	8.460	7.080	5.550
10	5.790	5.880	6.390	3.780	5.580	7.320	6.480	5.160
11	5.070	5.040	5.190	3.390	4.380	5.940	6.000	5.100
12	4.620	5.070	5.400	2.640	4.320	5.580	6.060	5.220
13	4.050	4.290	4.650	1.620	3.780	5.460	5.220	5.070
14	3.180	2.421	4.056	0.930	3.000	3.570	4.620	3.978
15	2.268	2.001	3.522	0.480	3.000	2.190	4.440	3.450
16	1.334	2.775	1.260	0.240	1.200	2.400	3.900	3.522
17	0.720	0.850	1.660	0.125	0.940	1.350	3.780	2.250
18	0.420	0.715	1.588	0.145	0.900	1.770	2.940	2.457
19	0.260	0.720	1.550	0.200	0.560	1.044	3.078	2.631
20	0.170	0.468	1.394	0.150	0.298	1.284	2.526	1.950
21	0.066	0.288	1.008	0.133	0.222	1.500	1.875	1.761
22	0.118	0.335	2.254	0.185	0.194	1.896	2.211	1.932
23	0.156	0.293	1.758	0.163	0.288	0.760	2.364	2.056
24	0.120	0.223	1.486	0.865	0.195	0.383	1.722	2.482
25	0.120	0.038	0.240	0.248	0.195	0.325	1.200	2.287
26	0.077	0.037	0.093	0.065	0.103	0.138	0.507	1.604
27	0.075	0.087	0.126	0.112	0.100	0.083	0.468	1.219
28	0.063	0.054	0.160	0.116	0.070	0.063	0.127	0.942
29	0.065	0.064	0.259	0.113	0.063	0.045	0.200	0.869
30	0.046	0.035	0.216	0.122	0.055	0.038	0.190	0.648
31	0.039	0.040	0.123	0.091	0.052	0.040	0.168	0.311
32	0.036	0.040	0.117	0.096	0.048	0.054	0.085	0.340
33	0.274	0.050	0.103	0.060	0.038	0.067	0.107	0.225
34	0.047	0.032	0.118	0.072	0.053	0.054	0.126	0.324
35	0.049	0.035	0.170	0.077	0.047	0.043	0.096	0.204
36	0.045	0.036	0.120	0.075	0.040	0.036	0.088	0.144
37	0.038	0.032	0.105	0.059	0.041	0.036	0.097	0.159
38	0.046	0.038	0.232	0.068	0.049	0.044	0.082	0.213
39	0.053	0.057	0.228	0.073	0.073	0.041	0.115	0.099
40	0.037	0.024	0.214	0.053	0.036	0.027	0.057	0.089
41	0.038	0.016	0.233	0.064	0.041	0.036	0.073	0.091

VFA

	Lysimeter Number				Lysimeter Number			
g/L	1	1	1	1	2	2	2	2
week #	acedic	propionic	butyric	valaric	acedic	propionic	butyric	valaric
1	5	1.25	5		7.3	1.375	7.28	
2	5.75	1.65	5.95		9.95	1.9	8.3	
3	7.65	3.05	7.8		8.6	2.4	7	
4	6.5	3.025	6.65		9	3.85	6.2	
5	6.95	3.7	6.6		8.25	4.75	4.25	
6	6.45	3.55	5.05		7.9	5.1	3.35	
7	6.8	4.05	4.45		7.05	5.2	2.65	
8	7.335	4.3	4.9		7.1	5.25	2.8	
9	4.25	4.725	2.85		4.65	6.15	1.5	
10	2.005	3.95	1.9	1.58	3.7	5.58	1	1.05
11	1.25	5.15	1.65	1.72	3.38	6.15	0.8	0.985
12	1.8	5.5	1.9	1.86	2.97	6.335	0.6	0.92
13	1.1	5.8	1.4	2	2.25	6.558	0.32	0.855
14	0.6	6.4	0.9	2.14	1.53	6.781	0.03	0.79
15	0.4	6.5	0.4	2.28	0.8	7.004	0.01	0.725
16	0.7	6.8	0	2.42	0.07	7.227	0.006	0.66
mg/L	alkalinity increased and the samples were not preserved properly w25-w29							
20	3	2	1.5	0.6	9	20	1	
25	1	0.8	3	0.1	15.7	12.4		
29	5.2	1.1	0.01	0.5	7	4.5	0.4	0.7
32	9.5	8			15	11	1	
33								
33	21.8	16.7			8	3.4		
34	2				6.2	1.3		
37	4.7	1.04			7.4	2.7	0.53	
38	5.94	0.93	0.4	0.04	6.1	1.1	0.5	
39	1.8	0.16			8.4	1.8		
40	1.8	0.15			2.3	0.8		
41	1.8				2.7	0.8		
42	1.8				2.7			

Lysimeter Number				Lysimeter Number			
3	3	3	3	4	4	4	4
acedic	propionic	butyric	valaric	acedic	propionic	butyric	valaric
5.35	0.85	6.25		8.05	0.9	12.35	
6.85	1.2	7.8		7.85	1.55	9.25	
6.45	1.45	7.95		7.35	2.65	9.15	
6.35	2.3	8.65		6.15	3.2	7.1	0.04
6.4	3.15	8.05		6.05	4.25	6.25	
6.1	3.4	6.25		4.9	4.4	4.15	
7	4.45	5.6		4.55	4.95	4.15	
6.35	3.95	5.2		4.35	4.7	4.15	0.985
5.725	4.68	2.45		2.56	4.25	2.05	
4.85	4.4	1.78	0.95	1.6	3.85		0.795
4.7	4.1	1.4	0.95	1.55	4.1	1.05	0.7
3.95	5.5	1.2	0.9	0.8	5	0.7	
3.3675	6	1.6	0.86	0.09	5.3	0.08	0.2
2.785	6.7	0.9	0.8	0.075	5.54	0.065	0.35
2.2025	6.3	1.1	0.9	0.035	5.77	0.04	0.09
1.62	6.9	0.86	0.75	0.02	6	0.038	0.06

15	10	3		6	2
10.8	7.8	1	1	2.4	
115	140	7	12	5	3
5	2			3	0.7
3.9	2.5			2.5	0.6
3.5	0.4			2.7	
210	78.1	7.5	7.6	6.7	1.6
202	78	7	7.8	5.6	1.4
15.6	3.7	2.8		2.1	
15.6	3.7	2.7		0	
84	9	4	4.4		
77	8.9	3.7	4.8		

Lysimeter Number				Lysimeter Number			
5	5	5	5	6	6	6	6
acedic	propionic	butyric	valaric	acedic	propionic	butyric	valaric
7.45	0.85	11.4		4.6	0.6	10.35	
8.15	0.975	13.4		4.5	0.8	14.05	
8	1.15	12.6		4.3	1.3	15.7	
7.05	1.4	9.25		5.4	2.4	14.3	
7	2.2	7.05		5.85	2.55	11.3	
6.9	3.55	4.6		5.9	2.55	9.35	
6.15	3.95	3.25		5.6	2.65	7	
6.35	4.05	3.45		5.745	2.8	7.15	
5.2	4.07	2.3		4.5	2.935	5.05	
4.25	4.15	1.35	0.95	3.5	2.75	3.5	0.95
3.6	4.4	1	0.95	3	3.05	3.1	1.05
3.2	4.5	0.95	0.65	4.2	3.6	2.7	1.15
2.86	4.6	0.86	0.62	4.1	3.9	2.3	1.25
1.5	4.8	0.62	0.39	4	4	1.9	1.35
1.1	4.68	0.2	0.08	3.9	4.3	1.5	1.45
0.87	5	0.06	0.068	3.8	4.4	1.1	1.55
25	12			29	45	2	0.6
17.6	9			23	30	1.4	2
14	3.2			8		7.5	
2				2			
1		1.4			1.3		
2.7				2.8			
3.3	0.6	0.9		3.3	0.6	1.2	
3	0.5	0.7		3	0.6	0.9	
9.7	1.5	1.1		6.8		1.2	
9.6	1.4	1.1		6.8		1.1	
1.3				0.9			
1.2				1.4			

Lysimeter Number				Lysimeter Number			
7	7	7	7	8	8	8	8
acedic	propionic	butyric	valaric	acedic	propionic	butyric	valaric
5.15	0.55	6.25		5.6	0.8	6.1	
7.5	1.05	7.9		6	1.15	6.35	
8.25	1.7	9.6		6.6	1.6	7.15	
6.95	2.35	7.85		6.15	2.25	6.75	
7.75	3.65	7.5		6.4	2.75	5.25	
6	3.35	4.6		5.7	3.05	3.6	
6.3	3.85	3.65		5.5	3.2	2.85	
6.65	4.1	4.05		5.595	3.25	3.025	
5.95	4.15	2.4		5.3	3.25	2.1	
5.6	4.1	1.95	0.7	4.8	3.035	1.735	0.6
5.55	4	1.75	0.8	5.15	3.15	1.83	0.65
5.72	5.2	0.9	0.9	5	4	0.714	0.69
5.6	5.6	0.65	1	4.8	3.89	0.8	0.75
5.4	6	0.09	1.1	4.3	4.1	0.2	0.82
5.3	6.3	0.06	0.8	3.9	4.6	0.06	0.85
5.1	6.7	0.02	0.6	3.8	4.2	0.025	0.6
120	68	1.5	6	86	168	23	18
36.8	43.5	2.5	4.4	67	109	10	16
114.7	92	2	2	471	584	36	53
2.2				1.4			
				15.6	27.3	2(iso)	
7.1	3			7	3.5		
7.2				3.1		0.8	1
7.9	1.1	0.6	2	80	23.3	2.3	
7.9	1.2	1.9		75	23.5	2	
5.68	1.6			19	10.9	3	
5.5	1.7			18	10	3	
7.2	1.6	3.1		3.2	0.4	0.7	
7.3	1.6	2.9		3.2	0.4		

Ammonia mg/L

Week	Lysimeter Number							
	1	2	3	4	5	6	7	8
1	169	470	269	465	111	200	270	200
2	310	715	385	745	200	237	384	298
3	455	826	510	902	256	292	512	360
4	593	840	680	769	305	326	629	395
5	648	696	847	534	248	300	376	225
6	724	690	875	602	324	429	733	386
7	500	545	850	630	224	300	810	350
8	590	392	725	727	236	392	775	288
9	533	403	575	466	185	341	660	302
10	355	263	387	355	162	198	318	268
11	399	271	349	349	126	264	594	265
12	362	219	305	291	104	245	570	194
13	356	205	249	240	90	256	505	259
14	338	120	233	246	86	243	445	246
14	301.95	140	235	235	81	238.5	454	216
15	267	130	190	200	75	203.8	432.5	203.8
16	196.8	161.35	106.6	131.3	61.1	184.65	365	182.5
17	155.95	103.75	156	167	73.4	185.7	350	179.3
18	132.2	90.8	139	139	51.1	196.75	331.5	177.95
19	92.4	80.2	153.9	119.7	39.9	163.9	351.7	170.9
20	89	69	120	118	27.6	157	283	144
21	60	49.5	89.5	104.5	22	120	250	108.75
22	42.3	42.4	88.7	102.4	18.2	101.4	181.1	97.8
23	40	43.4	87.8	109	20	110	146	89.5
24	32	38	72	88	15	103	126	83
25	25.8	29.6	68	85	12	91	124	94
26	19	17	52	98	9	100	112	91
27	24	29	80	129	12	95	104	98
28	23	32	63	142	10	75	92	99
29	21	33	65	122	9	62	76	90
30	17	27	41	134	8	49	50	104
31	18.6	35.4	57.5	105.8	9.3	63.7	59.6	98.5
32	17	31	47	115	8	62	50	100
33	10.4	23	32	47	6.7	24	18	45
34	6.1	11	22.7	43	4.8	33	16.7	33.7
35	11.5	17.2	48.2	118	7.87	57.1	21.4	93.4
36	7.7	17.7	49.1	94.1	5.9	61.3	16.1	82.8
37	6.7	15	23.6	20	4	29.5	8.6	79
38	0	22.3	48.7	106.5	9	56	17	76.1
39	0	26.2	49.3	108	10.9	45	18.5	70.2
40	11	11	60	112.5	10	58	14	81
41	10.5	18.5	47	94	10.3	44	11.2	74.6

Ammonia mg/L

Week	Lysimeter Number							
	1	2	3	4	5	6	7	8
1	169	470	269	465	111	200	270	200
2	310	715	385	745	200	237	384	298
3	455	826	510	902	256	292	512	360
4	593	840	680	769	305	326	629	395
5	648	696	847	534	248	300	376	225
6	724	690	875	602	324	429	733	386
7	500	545	850	630	224	300	810	350
8	590	392	725	727	236	392	775	288
9	533	403	575	466	185	341	660	302
10	355	263	387	355	162	198	318	268
11	399	271	349	349	126	264	594	265
12	362	219	305	291	104	245	570	194
13	356	205	249	240	90	256	505	259
14	338	120	233	246	86	243	445	246
14	301.95	140	235	235	81	238.5	454	216
15	267	130	190	200	75	203.8	432.5	203.8
16	196.8	161.35	106.6	131.3	61.1	184.65	365	182.5
17	155.95	103.75	156	167	73.4	185.7	350	179.3
18	132.2	90.8	139	139	51.1	196.75	331.5	177.95
19	92.4	80.2	153.9	119.7	39.9	163.9	351.7	170.9
20	89	69	120	118	27.6	157	283	144
21	60	49.5	89.5	104.5	22	120	250	108.75
22	42.3	42.4	88.7	102.4	18.2	101.4	181.1	97.8
23	40	43.4	87.8	109	20	110	146	89.5
24	32	38	72	88	15	103	126	83
25	25.8	29.6	68	85	12	91	124	94
26	19	17	52	98	9	100	112	91
27	24	29	80	129	12	95	104	98
28	23	32	63	142	10	75	92	99
29	21	33	65	122	9	62	76	90
30	17	27	41	134	8	49	50	104
31	18.6	35.4	57.5	105.8	9.3	63.7	59.6	98.5
32	17	31	47	115	8	62	50	100
33	10.4	23	32	47	6.7	24	18	45
34	6.1	11	22.7	43	4.8	33	16.7	33.7
35	11.5	17.2	48.2	118	7.87	57.1	21.4	93.4
36	7.7	17.7	49.1	94.1	5.9	61.3	16.1	82.8
37	6.7	15	23.6	20	4	29.5	8.6	79
38	0	22.3	48.7	106.5	9	56	17	76.1
39	0	26.2	49.3	108	10.9	45	18.5	70.2
40	11	11	60	112.5	10	58	14	81
41	10.5	18.5	47	94	10.3	44	11.2	74.6

Weekly Gas Production Rate L

Lysimeter Number

week	1	2	3	4	5	6	7	8
1	32.96	17.55	9.63	34.82	36.65	10.00	15.30	21.44
2	34.52	22.19	11.81	36.77	37.63	12.00	16.56	21.80
3	36.08	26.82	13.99	38.72	38.62	15.00	17.82	22.17
4	37.64	31.46	16.17	40.68	39.60	20.00	19.08	22.53
5	39.20	36.10	18.35	42.63	40.58	22.00	20.34	22.89
6	40.76	40.74	20.54	44.58	41.57	30.00	21.60	23.25
7	42.32	45.38	22.72	46.53	42.55	32.00	22.86	23.61
8	43.88	50.01	24.90	48.48	43.53	37.00	24.12	23.97
9	45.44	54.65	27.08	50.43	44.52	40.00	25.38	24.34
10	47.34	44.46	27.70	44.78	45.86	42.00	23.32	25.00
11	47.34	44.46	27.70	44.78	45.86	42.00	23.32	25.00
12	55.01	75.82	27.40	51.67	46.68	37.89	31.24	23.40
13	50.59	99.31	44.40	71.70	40.22	38.56	35.08	28.30
14	51.27	95.63	43.40	74.57	52.14	42.00	35.08	24.50
15	50.28	92.80	43.20	72.38	60.61	51.77	35.08	27.00
16	56.91	78.31	44.00	66.66	56.15	69.67	35.08	28.20
17	60.17	88.14	43.60	60.63	48.78	89.17	36.40	27.20
18	60.23	81.66	40.50	54.50	48.59	73.60	30.48	26.70
19	56.15	77.09	42.50	48.98	48.41	65.71	26.64	27.20
20	51.72	71.76	41.60	47.22	51.60	63.92	22.40	25.00
21	54.17	69.60	43.45	46.90	53.55	61.29	23.12	23.00
22	47.17	54.23	41.20	44.30	49.69	52.55	24.56	28.70
23	47.24	59.06	42.90	45.97	53.60	51.51	21.76	31.10
24	48.31	59.94	44.90	41.91	20.66	45.87	23.04	34.50
25	40.74	42.04	39.20	39.10	17.11	39.67	16.72	30.60
26	39.80	47.37	37.30	34.94	41.31	35.81	17.12	25.90
27	40.13	48.77	38.80	35.98	47.05	36.00	16.72	34.30
28	28.14	36.58	26.80	26.83	34.22	28.11	12.88	30.40
29	23.85	34.93	28.60	17.99	31.76	28.58	6.72	21.40
30	36.05	39.50	36.80	28.39	38.95	34.59	23.84	39.80
31	25.93	22.61	28.00	20.07	28.12	23.78	25.28	27.50
32	21.91	20.96	25.90	16.12	25.57	17.01	16.40	18.60
33	20.17	17.53	24.70	14.66	23.11	14.10	7.36	17.20
34	19.23	13.34	23.30	14.25	25.30	13.72	2.24	13.50
35	17.76	13.08	23.70	12.06	23.30	17.01	1.52	22.10
36	16.42	12.19	20.30	10.82	22.84	18.24	1.36	14.70
37	15.68	10.03	17.60	10.61	25.03	18.71	1.60	14.00
38	13.67	3.05	19.60	8.53	20.48	16.36	1.12	13.50
39	15.21	2.03	16.40	8.22	20.75	17.30	0.08	13.20
40	11.79	1.40	17.70	5.93	19.47	13.25	0.00	17.70

Production of Methane (L/week)

Lysimeter Number

week	1	2	3	4	5	6	7	8
1	8.83	6.53	4.00	9.33	11.18	4.05	5.89	4.61
2	9.60	7.57	4.19	11.40	12.13	4.74	6.05	5.34
3	10.64	10.33	5.57	17.97	14.64	5.69	6.63	6.05
4	15.66	12.55	6.94	20.22	15.44	8.34	6.97	7.10
5	17.64	15.45	8.44	22.46	18.55	10.03	7.69	6.29
6	17.83	16.62	9.18	23.58	20.16	14.25	8.96	7.79
7	20.48	20.65	10.84	24.43	20.76	15.65	8.92	8.83
8	18.39	23.91	11.80	25.28	21.98	19.24	9.89	9.21
9	23.49	29.57	13.24	26.30	22.48	21.04	10.91	9.83
10	23.36	23.36	12.50	23.80	23.20	21.50	9.87	9.04
11	24.12	23.08	13.57	23.14	22.85	21.04	10.13	10.90
12	29.65	39.34	13.04	26.80	23.92	18.87	13.32	9.30
13	26.53	50.33	21.49	38.15	20.09	19.61	15.82	11.81
14	26.22	49.60	20.21	38.24	25.63	21.10	14.71	10.23
15	26.48	48.52	21.90	38.09	30.78	28.20	16.37	12.36
16	31.07	41.97	21.07	35.10	27.74	37.96	16.25	13.05
17	32.92	49.22	22.52	32.58	24.60	48.72	17.62	12.78
18	33.22	46.23	19.07	28.43	24.44	39.59	14.28	13.16
19	30.02	44.64	21.18	26.68	24.71	36.56	12.66	13.00
20	28.51	39.63	20.19	24.51	25.79	35.27	11.28	12.96
21	29.24	38.41	21.65	24.33	27.07	34.00	12.09	12.14
22	25.88	31.34	20.46	23.71	25.56	29.69	13.16	15.38
23	25.07	33.72	21.74	23.74	27.11	29.42	12.13	15.99
24	26.29	34.17	22.73	22.01	10.51	25.59	13.16	17.61
25	22.27	23.67	19.36	19.61	8.63	22.48	9.57	16.27
26	21.85	27.75	17.79	17.66	21.25	21.34	9.28	12.75
27	22.02	26.97	18.84	18.08	23.82	21.28	9.35	17.16
28	15.02	21.39	12.93	13.42	16.47	16.82	7.09	15.44
29	12.57	20.04	13.64	8.87	15.78	16.68	3.85	10.37
30	18.64	23.08	17.84	13.99	21.57	20.23	13.53	19.11
31	14.11	12.92	13.15	10.30	14.14	13.59	14.39	13.24
32	11.61	11.99	12.77	7.82	12.71	9.97	9.38	8.72
33	11.01	9.93	12.02	7.28	11.57	8.22	4.23	8.47
34	10.29	7.52	11.16	6.85	12.78	8.10	1.31	6.52
35	9.49	7.55	11.22	5.92	11.82	10.20	0.90	10.96
36	8.95	7.13	9.31	5.29	11.74	10.84	0.81	7.32
37	8.62	5.92	8.10	5.20	12.51	11.22	0.96	7.00
38	7.58	1.86	8.93	4.15	10.43	9.89	0.67	6.03
39	8.36	1.24	7.54	4.03	10.58	10.38	0.05	5.94
40	6.49	0.85	8.14	2.90	9.93	7.95	0.00	7.97

Production of CO2 (L/week)

Lysimeter Number

week	1	2	3	4	5	6	7	8
1	23.73	10.70	5.49	24.72	24.92	5.70	8.42	15.01
2	24.51	14.20	7.44	24.64	25.21	7.08	9.77	14.61
3	24.90	15.83	8.25	20.14	23.56	9.15	9.98	14.41
4	21.46	18.25	9.06	19.93	23.76	11.40	10.69	13.52
5	21.17	19.85	9.73	19.61	21.91	11.88	10.98	15.34
6	22.83	23.22	11.09	20.51	21.20	15.60	11.23	13.49
7	21.58	24.05	11.59	21.40	21.70	16.00	12.12	12.75
8	25.01	25.51	12.70	21.94	21.55	17.76	12.30	12.71
9	21.22	23.88	13.24	22.82	22.04	18.96	12.44	12.31
10	20.03	18.56	13.20	19.41	22.67	19.19	10.62	11.70
11	23.22	19.93	13.39	21.64	23.02	19.98	11.65	12.74
12	25.35	34.52	13.39	22.43	22.75	17.56	15.29	12.55
13	24.06	43.88	21.93	33.55	20.12	18.95	17.52	15.08
14	25.05	40.40	21.83	33.09	25.65	20.23	17.82	11.85
15	22.43	38.96	20.53	30.70	29.82	23.57	17.26	13.35
16	25.84	36.34	22.04	30.76	27.22	31.72	17.47	13.55
17	27.24	38.92	19.61	27.23	24.18	40.45	17.12	12.55
18	27.02	35.43	17.68	25.07	24.15	34.01	14.19	11.77
19	26.13	32.44	20.34	21.59	23.70	29.15	11.62	11.97
20	23.22	32.12	18.76	21.11	24.90	28.65	10.15	11.11
21	24.93	31.18	20.64	21.30	26.12	26.82	10.42	10.15
22	21.29	22.89	19.58	19.55	24.07	22.85	10.60	12.30
23	22.16	25.33	20.00	21.80	26.49	22.09	9.40	14.29
24	21.24	25.77	20.21	18.42	10.15	19.00	9.88	15.34
25	17.99	18.18	18.06	17.41	8.28	16.51	7.15	12.65
26	17.95	19.62	16.17	14.66	20.07	14.22	7.17	10.57
27	18.12	20.84	17.10	15.19	22.96	14.49	7.10	14.09
28	12.22	15.19	11.82	11.27	16.46	10.80	5.25	12.26
29	11.29	14.89	12.83	7.56	15.62	11.39	2.79	9.15
30	17.41	16.09	16.70	12.41	17.11	14.06	10.17	17.25
31	11.82	9.38	12.46	7.89	13.77	9.50	10.13	11.41
32	10.21	8.82	10.91	6.05	12.72	6.35	6.90	7.95
33	9.16	6.93	10.46	5.49	11.33	5.36	2.80	6.80
34	8.51	5.65	9.77	5.20	12.08	5.10	0.86	5.18
35	8.07	5.43	9.99	4.30	11.17	6.39	0.58	8.43
36	7.46	4.97	8.45	3.60	10.81	6.83	0.52	5.43
37	7.06	3.91	7.33	3.50	11.66	7.01	0.59	4.94
38	6.09	1.16	7.77	2.72	9.88	6.21	0.41	4.55
39	6.82	0.78	6.57	2.51	9.76	6.51	0.03	4.36
40	5.28	0.53	7.02	1.74	9.12	4.99	0.00	5.64

Production of Nitrogen (L/week)

Lysimeter Number

week	1	2	3	4	5	6	7	8
1	0.40	0.32	0.14	0.77	0.55	0.25	0.99	1.82
2	0.41	0.42	0.18	0.74	0.29	0.18	0.75	1.85
3	0.54	0.67	0.17	0.62	0.42	0.17	1.21	1.71
4	0.53	0.66	0.18	0.53	0.40	0.26	1.43	1.91
5	0.39	0.79	0.18	0.55	0.12	0.09	1.67	1.26
6	0.10	0.90	0.27	0.49	0.21	0.15	1.40	1.98
7	0.25	0.68	0.30	0.70	0.09	0.35	1.83	2.03
8	0.48	0.60	0.40	1.26	0.00	0.00	1.93	2.06
9	0.73	1.20	0.60	1.31	0.00	0.00	2.03	2.19
10	3.12	2.04	1.73	1.58	0.67	1.01	2.53	3.60
11	0.00	1.14	0.74	0.00	0.63	0.68	1.54	1.36
12	0.00	1.55	0.87	2.03	0.59	1.15	2.41	1.46
13	0.00	4.12	0.98	0.00	0.54	0.00	1.75	1.41
14	0.00	5.63	1.36	2.63	0.87	0.50	2.26	2.16
15	1.04	4.16	0.76	2.91	0.00	0.00	1.45	1.29
16	0.00	0.00	0.89	0.80	0.91	0.00	1.35	1.53
17	0.00	0.00	1.36	0.82	0.00	0.00	1.57	1.69
18	0.00	0.00	3.18	0.99	0.00	0.00	1.76	1.57
19	0.00	0.00	0.98	0.72	0.00	0.00	2.05	1.93
20	0.00	0.00	2.32	1.44	0.75	0.00	0.91	0.92
21	0.00	0.00	1.16	1.27	0.36	0.47	0.60	0.71
22	0.00	0.00	1.16	1.04	0.05	0.00	0.80	1.02
23	0.00	0.00	1.16	0.43	0.00	0.00	0.24	0.83
24	0.64	0.00	1.97	1.48	0.00	0.00	0.00	1.26
25	0.38	0.19	1.78	1.82	0.02	0.24	0.00	1.68
26	0.00	0.00	3.35	2.63	0.00	0.26	0.67	2.59
27	0.00	0.71	2.85	2.72	0.27	0.23	0.09	3.05
28	0.71	0.00	2.05	2.13	0.36	0.28	0.05	2.70
29	0.00	0.00	2.13	1.56	0.36	0.29	0.08	1.88
30	0.00	0.21	2.26	1.98	0.27	0.30	0.14	2.89
31	0.00	0.24	2.12	1.79	0.22	0.20	0.24	2.57
32	0.09	0.14	2.21	2.25	0.14	0.69	0.12	1.93
33	0.00	0.00	2.22	1.89	0.22	0.48	0.26	1.94
34	0.00	0.00	2.37	2.20	0.44	0.52	0.07	1.80
35	0.00	0.00	2.48	1.85	0.30	0.43	0.04	2.71
36	0.00	0.00	2.50	1.93	0.29	0.51	0.03	1.95
37	0.00	0.00	2.30	2.02	0.36	0.44	0.03	1.93
38	0.00	0.00	2.90	1.67	0.17	0.26	0.04	2.93
39	0.00	0.00	2.56	1.75	0.23	0.25	0.00	2.60
40	0.00	0.00	2.96	1.34	0.21	0.14	0.00	3.77

ORP

Week	Lysimeter Number							
	1	2	3	4	5	6	7	8
4	-39.3	-62.5	-34.4	-80.3	-55.9	-31.7	-28.4	-12.3
6	2.2	-34	-35.6	-58	-23	-10.5	-1.1	3.5
7	22	-0.9	-9.1	-41.1	-5.5	2	8.2	18
8	44	11.1	15	-124	-4	8	12.6	18.4
9	72	87	76	-57	55	42	40	42
10	33	60.5	57	-58	59.7	55	40	41.6
11	76.2	105.8	110	-34.5	75	77	54	52
12	30	76		-80	80	72	56	50
13	59	111	95	-89	74.5	54	11	19
14	12	80	80.7	-103	59.6	40	9.6	-12
15	18.2	33	74	-106	50.6	13.6	31.6	9.5
16	-10.8	-7.5	42	-107	46.6	-21	4	-15
17	-40	-46.5	18	-115	25	-35	-33.8	-70
18	8.8	-16.8	27.5	-83.5	33.9	-1	-26	-70
19	21	-5.3	42.8	-60.5	28.7	-20	-0.4	-12.5
20	-28	-2.4	52	-48	37	-3.3	-8.1	-26.5
21	-47	-44	-24	-61	-31	-47	-44	-52

9.2 Appendix 2: Data For "Denitrification Batch Test" Experiment

Prelimenery test
start on wednesday 21/2/2001 at about 4.30

	Nitrate and nitrite in mg/L							
Time (hr)	control-1	control-2	control-3	control-4	5	6	7	8
0	50	50	50	50	50	50	50	50
16.5	43	48.6	47.8	48	48.8	48.8	48.6	45.4
21	35	42.9	38	44.3	42	46.5	46.8	45.56
27	34	40	40		29.3	25	40.5	13.5
27.5	34.6	45	34.7	55	36	15	47.8	3
28.5	32.6	44	33	53	32.5	0.9	42	0
29.5	32.8	45.1	32	47	27	0	28	0
30.5	31.5	43	29	38	22	0	15.6	0
32.1	30	37	22	20.6	7.4	0	0	0
32.5	29	33.3	18	14.6	1.8	0	0	0
33.6	28	18.32	6.8	0.28	0	0	0	0

Methanol Test

		Nitrate Concentration			Total Organic Carbon		
		mg-N/L			mg-C/L		
	Time hr	1	2	3	1	2	3
First run	0	38.31	62.01	61.29	242	276	288
	0.5	41.1	65.1	67.2			
	1	43.2	82.5	79.5			
	1.8						
	2.15		68.1				
	2.45	38.97	65.28	65.82			
	2.7	41.4	64.2	67.5			
	3.5			68.7			
	4.5	36.81					
	5						
	5.5						
	6	33.81	56.37	56.19			
	8.5	34.2	57	57			
	17.5	32.67	54	58.5			
	21.5	32.1	52	52.5			
	26.5	31.2	50	48.6			
	28.5	28	48	42			
	35	29.5	48	47			
	40	25	42	46			
	45	12	35	44			
	60	5	30	38			
	70	2	22	32			
	75	1.8	18	24			
	78	1.5	5	12			
	80.5	1.5	2.2	8			
	120	1.2	0.87	0.66			
	80.5	1.5	32.1	5.4			
	120	1.2	0.87	0.66	10	27	66

Methanol Test

		Nitrate Concentration			Total Organic Carbon		
		mg-N/L			mg-C/L		
	Time hr	1	2	3	1	2	3
second run	138.5	55.8	54.9	55.2	274	298	378
	139	56.4	48.42	56.37			
	140.5	56.4	48.3	54.3			
	143	54	51.6	53.1			
	143.5	49.2	44.1	46.2			
	143.5	41.1	38.1	36.6			
	145.5	39.3	35.1	37.8			
7/3/01	163	3.6	14.7	17.4			
	165	0.45	9.33	11.1			
	167.25		5.4	8.1			
	170	0.9	2.7	4.5	147	155	206
third run	171	7.2	6.6	12	150	177	206
	171.5						
	173	3.5	3.7	0.1			
	173.5	0.8	1	0.16			
	174.5	0.1	0.5	0.1			
	187	0.1	0.1	0.1	63	77	100
fourth run	191.5	10	9.7	9.7	63.8	77.4	93.6
	74.2	8.7	8.6	9.2	58.5	74.2	88.2
	78.6	7.5	8.1	8.6	60.4	78.6	90.6
	78	5.7	6.8	7.2	64	78	97
	71	3	4.8	5.4	59	71	86
	74	1.4	3.7	4.5	58	74	88
	67	0.06	1.7	2.5	57	67	82
	63	0	0.24	0.8	59	63	80
	211.5				25	33	40
fifth run	214.25	9.24	8.9	8.76			
	215.25	8.7	6.5	6.8			
	216.25		4.9	4.8			
	217.25	8.22	2.8	2.1			
	218.25	7.75	1.4	0.4			
	219.25	7.4	0.98				
	283	7.4	0.2	0	7	11	8

Denitrification with methane

Nitrate (mg/L)				TOC (mg/L)		
Time hr	1	2	control	1	2	control
0	49.14	43.5	51	41	45	11
0.5	66	59.1	49.2			
1	59.1	51.6	57.9			
1.8	51.6	45				
2.15	48.81	42	46.2			
2.45	44.4	41.7	50.4			
2.7	52.8	44.7	48.9			
3.5	47.1	39	46.5			
4.5	48.6	33	45			
5	43	34.2	44			
5.5	44	33.3				
6	46	32.1	44			
8.5	44	32.7	43			
17.5	45	25.8	43	20	26	6
21.5	47	24.9	42			
26.5	46	20.4	40	18	23	6
28.5	45	23				
80.5	46	23.3	40			
120	47	18.6	41	17	13	6
138.5	47.4	19.2	44			
143.5	43.2	21				
163	39.6	16.5				
170	38.7	15.6		20	14	6
187	36.3	13.05	45	19	21	
211.5	36.3	11.64	42.6	20	24	7
216.25	35.4	12.9				
283	27.9	4.4	45.6	32	24	5
307	23.8	0.9				
307.5	20					
313	19.67		44			
329.75	19.3			40	24	
355	15.5					
356	13.6		45			

Denitrification with no methane		
Time (hr)	Nitrate mg/L	
138.5	47.4	
143.5	43.2	
163	39.6	
170	38.7	
187	36.3	Mtehane stopped
211.5	36.3	
216.25	35.4	
240	35	
300	27.9	
318	23.8	Methane back
348	20	
356	19.67	
382	19.3	
396	15.5	

Flow rate change		
Time (hr)	Nitrate mg/L	
0	72	
10	70	
50	68	
100	63	
150	61	flow rate change
200	51	
250	46	
300	40	
350	32	
400	28	

Pure Methane		
Time (hr)	nitrate	
1	72.3	
10	70.3	
30	69.3	
70	63.3	
100	59.9	
150	58.3	
200	48.3	
300	38	pure methane
301	32.3	
310	32	
330	29	
370	28	
400	23.4	
450	16	
500	15.4	
600	5.4	

Leachate 1

Time hr	Nitrate Concentration 1	2	4	3	5	6
Test 1						
0	9.1	9.5	9.5	8.6	10.2	8.7
1.5	5.89	7.11	9.29	7.73	8.01	8.53
15.8	0	0	0	6.69	0	0
16.3	8.66	8.88	16.5	15.5	9	9.15
16.6	0.24	0.16	0.12	15	2.1	0.4
18.6				13.5		
22.1				10		

	Total Organic Carbon					
Time	1	2	4	3	5	6
283	8	10	18	7	11	8
314	208	192	284	272	218	206
330	131	123	242	248	136	139

Test 2

0	9	9.4	9	9.4	8.9	9.3
0.25	7.6	8.1	7.65	8.5	9.2	8.5
0.5	6.6	7.1	7.1	7.6	8.26	8.7
0.92	5.2	6.3	4.7	7	6.6	7
1.17	3.5	4.65	2.67	6	5.3	5.8
1.5	2.25	3.3	0.64	5	3.8	4.6
1.83	0.88	2	0.2	3.6	2.7	3.2
2.17	0.1	0.8	0.2	2.3	1.5	2
2.83		0.15		0.18	0.1	0.1

Batch #	Carbon Source
1	Propionic acid and acetic acid
2	Propionic acid and acetic acid
3	Acetic acid
4	Propionic acid
5	Leachate
6	Leachate

Leachate Test 2
Kinetics

25% leachate			
Time	NOx	NO2	NO3
0	19	0.12	18.9
35	16	0.18	15.8
70	10.6	0.4	10.2
85	8.6	0.5	8.1
100	8	0.6	7.4
115	4.5	0.96	3.54
125	2.1	0.93	1.17
135	2	1	1
145	0.34	0.1	0.24

50% leachc			
Time	NOx	NO2	NO3
0	19	0.4	18.6
30	19	1.5	17.5
60	18.9	2.8	16.1
90	17.3	4.2	13.05
125	15.9	6.5	9.4
165	12	8.5	3.5
205	1.4	0.7	0.7
225	0.5	0.3	0.2

100% leachc			
Time	NOx	NO2	NO3
0	20	0.4	19.6
15	20	0.6	19.4
45	19.3	2.2	17.1
75	17.9	3.76	14.1
110	15.6	6.4	9.2
150	12	8.2	3.8
190	2.4	2.1	0.3
210	0.5	0.3	0.2

All concentratio
are in mg/L

Time is in minut

Time	mg/L MLVSS		
	25	50	100
15			
30			
35	4		
45			10
60			
70	12		
75			7
85	7		
90		9	
100	2		
110			3
115	5		
125	3	5	10
135	8	10	
145	11	15	25
150		21	30
165		29	
190			33
205		31	
210		35	20
225	6	37	

TOC mg/L			
Time	25%	50%	100%
0	129		
35	122		
70	116		
85	113		
100	143		
115	99		
125	104		
135	96		
145	96		
225	92		
0		90.5	
60		84.8	
90		73.1	
165		70	
205		64	
225		63	
15			250
45			211
110			156
190			144
dtC/d	3.7	2.75	10

VFA's mg/L						
	25%		50%		100%	
Time	acetic	prop	acetic	prop	acetic	prop
0	217	38				
35	211	31.3				
70	205	21.8				
85	200	19.7				
100	207	19.2				
115	183	12				
125	180	11				
135	178	11				
145	180	9.9				
225	174	8.3				
0			101	28		
30			90.5	25		
60			92.7	22		
90			86.9	17		
125			80	12		
165			63.7	3.7		
205			46			
225			42			
0					236.6	65
15					215	53
45					215	48
75					205	40
110					196	31
150					195	27.6
190					184.9	24.9

9.3 Appendix 3: Sample Calculation

9.3.1 Sample Calculation For Nitrogen in Gas

Equation 20 Gas concentrations

P V = n R T

Where;

P = Atmospheric pressure (1 atm) (This was multiplied by the weekly partial pressure (concentration) of the nitrogen gas)

V = Volume of gas (L)

n = number of moles in that volume (mole)

R = constant (0.082 L atm / mole K)

T = Temperature at Kelvin degrees (°K = 304)

n/V = P/RT

= 1/(0.082· 304)

= $4 \cdot 10^{-2}$ mole / L

Equation 21 Nitrogen Concentration in Gas

N-concentration = P/RT (mole /L) · Weight of Nitrogen / Mole (g-N_2/mole)

= $4 \cdot 10^{-2}$ mole / L · 28 g-N_2/mole

= 1.12 g –N_2 /L

Sample Calculation for Nitrogen Mass Balance During Phase 1.1

A mass balance for nitrogen from the lysimeters which receive the high nitrate feed.

Mass of nitrogen in nitrate feed = daily flow rate · nitrogen concentration · 7 days

= 0.4 L/d · 800 mg-N/L · 7 days/week

= 2240 mg/week

Mass of nitrogen out (leachate) = daily flow rate · nitrogen concentration · 7 days

= 0.4 L/d · 5.6 mg-N/L · 7 days/week

= 15.7 mg/week

Mass of nitrogen out (gas) = weekly flow rate · nitrogen concentration

= 1.7 L-N_2/week · 1.12 g-N/L

= 1.904 g-N/L

Mass balance:

Mass in = Mass out

2240 mg-N/week = 15.7 mg-N/week + 1904 mg-N/L + Error

Error = 2240 mg-N/week – (15.7 + 1904) mg-N/L

Error = 320.3 mg-N/week

Error % = Error / mass in

= 320 mg-N/week / 2240 mg-N/week · 100%

= 14.3%

Mass out / Mass in = 100 – 14.3

= 85.7%

9.3.2 Calculation of carbon mass in VFAs

Equation 22 Total leachate carbon based on VFAs

Total Leachate Carbon = carbon in acetic acid g/L + carbon in propionic acid g/L + carbon in butyric acid g/L + carbon in valeric acid g/L

Where carbon in each acid = Concentration of the acid (g/L) · (Carbon weight (number of moles of carbon per mole of acid · weight of carbon mole (12 g/ mole) / weight of one mole of the acid)

Equation 23 Carbon in acetic acid

Carbon in acetic acid = Acetic acid concentration (g/L)· ((12· 2)/60)

Equation 24 Carbon in propionic acid

Carbon in propionic acid = Propionic acid concentration (g/L)· ((12· 3)/74)

Equation 25 Carbon in butyric acid

Carbon in butyric acid = Butyric acid concentration (g/L)· ((12· 4)/88)

Equation 26 Carbon in valeric acid

Carbon in valeric acid = Valeric acid concentration (g/L)· ((12· 5)/102)

9.3.3 Calculation for carbon in the gas stream

The calculation of the carbon is based on Equation 20 and the following equations:

Equation 27 Carbon concentration in gas

Carbon-concentration (g-C/L) = P/RT (mole /L) · Weight of Carbon / Mole (g-C/mole)

= 4 · 10^{-2} mole / L · 12 g-C/mole

= 0.48 g -C /L

Equation 28 Carbon from carbon dioxide

Carbon from CO_2 (g-C) = 0.48 g-C/L · Total volume of gas (L) · % of CO_2

Equation 29 Carbon from methane

Carbon from CH_4 (g-C) = 0.48 g-C/L · Total volume of gas (L) · % of CH_4

Equation 30 Total carbon in gas

Total carbon in gas (g-C) = [C –CO_2 + C –CH_4]

9.3.4 Theoretical Oxygen Demand for VFAs

Equation 31 Oxygen demand for acetic acid

$CH_3COOH + 2O_2 \rightarrow 2CO_2 + H_2O$

(2 moles-O_2 · 32 g-O_2/ mole-O_2)/(1 mole-CH_3COOH · 60 g-CH_3COOH / mole-CH_3COOH) = 1.0 g-O_2 / g- CH_3COOH

The THOD for 1 g of acetic acid is 1.0 g.

Equation 32 Oxygen demand for propionic acid

$CH_3CH_2COOH + 3.5O_2 \rightarrow 3CO_2 + 3H_2O$

The THOD for 1 g of propionic acid is 1.5 g.

Equation 33 Oxygen demand for butyric acid

$CH_3(CH_2)_2COOH + 5O_2 \rightarrow 4CO_2 + 4H_2O$

The THOD of 1 g of butyric acid is 1.8 g.

Equation 34 Oxygen demand for valeric acid

$CH_3(CH_2)_3COOH + 6.5O_2 \rightarrow 5CO_2 + 5H_2O$

The THOD of 1 g of valeric acid is 2.0 g.

9.3.5 Nitrogen Mass Balance During Phase 1.5

The nitrogen concentration in gas was calculated using Equation 20 and Equation 21. The mass of nitrogen gas produced per week was calculated based on Equation 35. In calculating the mass balance of nitrogen, leachate ammonia was not included. The sample of the calculation is shown below (based on 2 months after methane addition was stopped).

N-concentration in gas = 1.12 g $-N_2$ /L (see Equation 21)

Equation 35 Nitrogen gas production rate

N (g / week) = **N- concentration (g-N_2/L) · Volume N_2 (L/week)**

= 1.12 g $-N_2$ /L · 2.7 L/ week

= 3.06 g-N_2/week

Mass of nitrogen in nitrate feed = daily flow rate · nitrogen concentration · 7 days

= 0.4 L/d · 1500 mg-N/L · 7 days/week

= 4200 mg/week

Mass of nitrogen out (leachate) = daily flow rate · nitrogen concentration · 7 days

= 0.4 L/d · 264 mg-N/L · 7 days/week

= 739 mg/week

Mass of nitrogen out (gas) = 3.06 g-N/L (see Equation 35)

Mass balance:

Mass in = Mass out

4200 mg-N/week = 739 mg-N/week + 3060 mg-N/L + Error

Error = 4200 mg-N/week – (739 + 3060) mg-N/L

Error = 401 mg-N/week

Error % = Error / mass in

= 401 mg-N/week / 4200 mg-N/week · 100%

= 8.4%