Analysis of Florida MSW Landfill Leachate Quality

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ABSTRACT:

Current databases for landfill leachates are not geographically specific; rarely acknowledge the impact of site specific parameters such as age, water balance, type of waste, landfill operation, etc.; and cover such large concentration ranges that they are often of little use. Analysis of data from lined landfills in Florida was needed to provide useful information for the design and management of landfill leachates. The specific objectives of this research, therefore, were to acquire leachate data from Florida municipal solid waste (MSW) lined landfills and analyze these data in an effort to characterize Florida landfill leachate.

Leachate quality data were acquired for Florida MSW lined landfills from Florida Department of Environmental Protection (FDEP) files. Data analysis was performed using the Microsoft Excel Analysis ToolPak, KURV+, and SYSTAT. Various graphical and statistical techniques such as chronological analysis, hypothesis testing, analysis of variance, and cluster analysis were used to characterize leachate from Florida landfills. Analyses were designed to identify trends in the data and to determine the effects of climate, region or location, age of the fill, and waste characteristics on leachate quality.

In general, the Florida climate (e.g. heavy rainfall and warm temperatures) appears to produce dilute leachate, maintaining leachate concentrations at relatively low levels compared to literature values and Browning-Ferris Industries (BFI) landfill data. Leachate from shredded waste fills has significantly higher concentrations of organic pollutants than leachate from unshredded landfills. Also, this research suggested that codisposal of ash with MSW does not appear to adversely impact leachate quality.
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## LIST OF ACRONYMS AND UNITS OF MEASUREMENTS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>BFI</td>
<td>Browning-Ferris Industries</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>FDEP</td>
<td>Florida Department of Environmental Protection</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
</tr>
<tr>
<td>mg/L</td>
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</tr>
<tr>
<td>µg/L</td>
<td>micrograms per liter</td>
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ABSTRACT

Current databases for landfill leachates are not geographically specific; rarely acknowledge the impact of site specific parameters such as age, water balance, type of waste, landfill operation, etc.; and cover such large ranges that they are often of little use. Analysis of data from lined landfills in Florida was needed to provide useful information for the design and management of landfill leachates. The specific objectives of the research, therefore, were to acquire leachate data from Florida municipal solid waste (MSW) lined landfills and analyze these data in an effort to characterize Florida landfill leachate.

Leachate quality data were acquired for Florida MSW lined landfills from Florida Department of Environmental Protection (FDEP) files. Data analysis was performed using the Microsoft Excel Analysis ToolPak, KURV+, and SYSTAT. Various graphical and statistical techniques such as chronological analysis, hypothesis testing, analysis of variance, and cluster analysis were used to characterize leachate from Florida landfills. Analyses were designed to identify trends in the data and to determine the effects of climate, region or location, age of the fill, and waste characteristics on leachate quality.

In general, the Florida climate (e.g. heavy rainfall and warm temperatures) appears to produce dilute leachate, maintaining leachate concentrations at relatively low levels compared to literature values and Browning-Ferris Industries (BFI) landfill data. Leachate from shredded waste fills has significantly higher concentrations of organic pollutants than leachate from unshredded landfills. Also, this research suggested that codisposal of ash with MSW does not appear to adversely impact leachate quality.
EXECUTIVE SUMMARY

INTRODUCTION

Within a landfill, a complex sequence of physically, chemically, and biologically mediated events occurs. As a consequence of these processes, refuse is degraded or transformed. As water percolates through the landfill, contaminants are leached from the solid waste. Mechanisms of contaminant removal include leaching of inherently soluble materials, leaching of soluble biodegradation products of complex organic molecules, leaching of soluble products of chemical reaction, and washout of fines and colloids. The characteristics of the leachate produced are highly variable, depending on the composition of the solid waste, precipitation rate, site hydrology, compaction, cover design, waste age, sampling procedures, interaction of leachate with the environment, and landfill design and operation.

Numerous landfill investigation studies have suggested that the stabilization of waste proceeds in five sequential and distinct phases (Pohland and Harper, 1985). The rate and characteristics of leachate produced and biogas generated from a landfill vary from one phase to another and reflect the microbiologically mediated processes taking place inside the landfill. The progress toward final stabilization of landfill solid waste is subject to the physical, chemical, and biological factors within the landfill environment, the age and characteristics of landfilled waste, the operational and management controls applied, as well as the site-specific external conditions. Movement through the phases is reflected by significant changes in leachate and gas quality. Nonconservative constituents of leachate (primarily organic in nature) tend to decompose and stabilize with time, whereas conservative constituents will remain long after waste stabilization occurs. Conservative constituents include various heavy metals, ammonia, chloride, and sulfide. Metals often are precipitated within the landfill and are infrequently found at high concentrations in leachate, with the exception of iron.

Leachate quality data have been reported in numerous technical reports (Lema et al., 1988; Lu et al., 1985; Pohland and Harper, 1985). In most cases these data are presented as a range. Because of leachate variability, these ranges can cover several orders of magnitude. In addition, landfills characterized prior to the late 1980's are generally unlined. Leachate samples collected from unlined landfills can be erroneously low in concentration due to dilution from groundwater and other sampling errors. These same factors may lead to the variability associated with leachate quality data. With the recent advent of lined landfills, leachate quality data are now more meaningful and useful and perhaps less variable.

Unfortunately, because of the variability in leachate quality, prediction of leachate characteristics as a function of time has been quite difficult. General trends in quality are possible, however these ranges are still large and prediction of the point in time at which each phase begins and ends is not possible as of yet. Current research in landfill management such as the use of leachate recirculation may make it possible to control waste decomposition and consequently make leachate characteristics more predictable.
OBJECTIVES

Current databases for landfill leachates are not geographically specific; rarely acknowledge the impact of site specific parameters such as age, water balance, type of waste, landfill operation, etc.; and cover such large ranges that they are often of little use. Analysis of data from lined landfills in Florida will provide useful information for the design and management of landfill leachates.

The specific objectives of this project, therefore, were to acquire leachate data from Florida MSW lined landfills and analyze these data. The results of this analysis provide insight for the prediction of future trends in leachate quality and the design and operation of leachate management facilities.

METHODOLOGY

As a first step in the investigation, a search of the literature was performed to identify pertinent reports, papers, and studies. The Florida Department of Environmental Protection provided leachate quality data from 55 Class I landfills (i.e. fills receiving MSW only). The landfills that would be included in this study were then determined. Two criteria were used to select the landfills, as follows: each landfill had to be lined and at least one year of data had to be available for each landfill. Only lined landfills were selected for this study because leachate samples collected from unlined landfills can be erroneously low in concentration due to dilution from groundwater and other sampling errors. In addition, trends in leachate quality would be difficult to recognize with less than one year of data. Of the 55 landfills, 39 met the criteria and were included in this study.

Organization of Data

There are many site specific parameters that impact leachate quality such as the composition of the solid waste, interaction of leachate with the environment, waste age, sampling procedures, and landfill design and operation. In order to account for at least one of these factors which cause variations in leachate quality, an attempt was made to separate data for each fill based on the point in time when (and if) each landfill transitioned from the acidogenic phase to the methanogenic phase. Although the stabilization of waste proceeds in five sequential phases, in full-scale landfill operation it is virtually impossible to identify all five stages (Pohland and Harper, 1985). Therefore, only the two most distinct phases were addressed. By identifying the conditions (acidogenic or methanogenic) within the fill at every sampling period, the data for each, landfill could then be categorized by phase.

Chronological Data Analysis

In order to identify trends in BOD and COD levels, a plot of each parameter versus age of the landfill was developed. Every BOD and COD detection for all the landfills were used to create the graphs. Typically, the BOD and COD concentrations will be low initially, and will
increase as waste begins to solubilize. An eventual decline in BOD and COD concentrations is often observed as organic matter is being removed via washout and degradation. This increase and decrease in organic constituents can be modeled by two consecutive first-order processes. The parameters in this equation were estimated using non-linear least squares regression. SYSTAT, a powerful statistical package, was employed to estimate these parameters. This statistical program was used to determine whether the Florida BOD and COD data exhibited a chronological pattern. In addition, KURV+, a software package that fits data to 28 different mathematical linear and non-linear equations, was used in order to identify a function that would accurately describe the BOD and COD concentrations over time. The correlation coefficient of each function was utilized to determine which equation best fit the data. This equation could then be used to predict the concentrations of COD and BOD produced at Florida landfills.

**Toxic and Organic Parameters**

Many toxic and organic constituents have been detected in MSW landfill leachates. In Florida landfills, the concentration of these compounds is usually on the order of micrograms per liter and in many cases the concentrations were below the detection limit. Therefore, when evaluating these types of data, a detection is often more significant than the reported concentration. When analyzing these parameters, not only was the number of detections reported but also the mean, and standard deviation for each phase, and all the data as a group. The concentration of many of these constituents was below the detection limit (i.e. < 5 µg/L). For calculation purposes, these values were replaced with zeros.

**Conventional Parameters**

The conventional parameters that were analyzed in this study are as follows:

- Biological Oxygen Demand (BOD),
- Chemical Oxygen Demand (COD),
- ammonia (NH₃),
- sulfate (SO₄),
- chloride (Cl),
- pH,
- manganese (Mn), and
- zinc (Zn).

These parameters were chosen because sufficient data were available for each one at a majority of the landfill sites. According to Ehrig (1989), BOD, COD, sulfate, pH, manganese, and zinc levels change between the acidogenic and methanogenic phase. The levels of chloride and ammonia show no difference between phases. The number of detections, mean, median, minimum, maximum, and standard deviation were computed for each parameter. Like the toxic and organic parameters, if the concentration of any constituent was listed as non-detected, it was replaced with a zero for calculation purposes.
Also, acidogenic and methanogenic data were combined to create cumulative percentage distributions for each conventional parameter. The distributions presented the data in a compact, yet comprehensible form so that essential characteristics of the data were readily discernable. The advantage of the cumulative percentage distribution is that it readily provides information about the percent of values falling below a given parameter concentration (Ary and Jacobs, 1976).

The landfill data were categorized separately for all the FDEP districts. Dividing the data by districts was a means of regionalizing the landfills throughout the state. Data from the landfills which received more than 50 percent ash, were not included. In order to determine whether the value of each parameter (e.g. BOD, COD, etc.) differed regionally, an analysis of variance (ANOVA) was used. This method was employed because an ANOVA is used to test for differences among the means of two or more populations.

It is possible that the ash data (i.e. data from primarily ash landfills) and the pond data (i.e. data obtained from the analysis of leachate ponds) differ from the general leachate values (i.e. all data excluding pond and ash data). The waste composition at a primarily ash fill can be quite different from a landfill receiving only MSW. Also, the biological and chemical processes occurring within leachate ponds could produce differences in leachate quality as compared to leachate samples from a sump or pipe. A method analogous to proof by contradiction is used in hypothesis testing. The theory to be proven is the alternative hypothesis (H<sub>a</sub>). H<sub>a</sub> was that the means of the parameters for the ash or pond data differ from the means of the general leachate data.

Hypothesis testing was also employed to determine if parameter means for the Florida data differed from the parameter means obtained from Browning-Ferris Industries (BFI) landfill data. This data set represented leachate values nationwide. The null hypothesis stated that the means of each parameter were equal (i.e. μ<sub>1</sub> = μ<sub>2</sub>). For example, the Florida BOD mean is equal to the BFI BOD mean. In addition, the mean values from the acidogenic and methanogenic phase were compared to learn whether the concentrations of each parameter differed between the two phases. The null hypothesis tested was that the mean of the acidogenic data is equal to the mean of the methanogenic data (i.e. μ<sub>1</sub> = μ<sub>2</sub>).

A scoring technique was developed in order to perform a cluster analysis of the data. The cluster analysis grouped all the conventional parameter data from each landfill into a single value or score. However, the data remained separated by phase. Each landfill received a score for each parameter. The individual scores were summed and this value was the total landfill score. Single-factor analysis of variance was used to determine if the scores differed among the regions. The ash data were not included. The null hypothesis tested was that the mean score of each region was equal.

**RESULTS AND CONCLUSIONS**
The purpose of this research was to characterize Florida landfill leachate. MSW lined landfill leachate quality data were acquired from the Florida Department of Environment Protection files. In addition, the study employed national data obtained from Browning-Ferris Industries for comparison with Florida leachate data. Various graphical and statistical techniques such as chronological analysis, hypothesis testing, analysis of variance, and cluster analysis were used to characterize Florida leachates. In general, the Florida climate (e.g. heavy rainfall and warm temperatures) appears to produce dilute leachate, maintaining leachate concentrations at relatively low levels compared to literature values and BFI landfill data. The following results and conclusions were determined from this research:

1. BOD and COD concentrations appear to remain low (less than 1500 mg/L) throughout the life of the landfill, most likely due to dilution and stimulation of methanogenesis. The stimulation of methanogenesis is supported by elevated pH in the acidogenic phase, higher BFI to Florida ratio for BOD relative to the other parameters, low BOD concentrations and significant gas production during the early years of landfill operation. No chronological pattern in BOD and COD concentrations was observed.

2. Leachate from the shredded waste fill has significantly higher concentrations of organic pollutants than leachate from the unshredded waste landfills as evidenced in the high COD and BOD levels from the South Dade Shredded Landfill.

3. A wide variety of toxic and organic compounds can be found in Florida landfill leachate. However, the concentration of these constituents is generally on the order of micrograms per liter.

4. Codisposal of ash with MSW does not appear to adversely impact leachate quality. Concentrations of heavy metals, BOD, COD, and ammonia in leachate from codisposal sites were not statistically higher than values reported for MSW sites. Chloride values were elevated in the ash leachate in the methanogenic phase because of the high chloride content of ash.

5. Florida leachates seem to be dilute compared to national landfill data obtained from BFI.

REFERENCES


KEY WORDS

Leachate

Municipal solid waste leachate

Leachate analysis

Florida landfill leachate

Leachate quality data
SECTION 1
INTRODUCTION

Sanitary landfilling is the preferred method of municipal solid waste (MSW) disposal due to its favorable economics. Within a landfill, a complex sequence of physically, chemically, and biologically mediated events occur. As water percolates through the landfill, contaminants are leached from the solid waste. This water, termed leachate, was generally not a matter of concern prior to 1965 because few cases of groundwater contamination from leachate were noted (Boyle and Ham, 1974). Effective pollution control through the proper design of landfill and leachate management facilities requires an understanding of leachate quality.

Numerous landfill investigation studies have suggested that the stabilization of waste proceeds in five sequential and distinct phases (Pohland and Harper, 1985). The rate and characteristics of leachate produced and biogas generated from a landfill vary from one phase to another and reflect the microbially mediated processes taking place inside the landfill. The progress toward final stabilization of landfill solid waste is subject to the physical, chemical, and biological factors within the landfill environment, the age and characteristics of landfilled waste, the operational and management controls applied, as well as the site-specific external conditions. Movement through the phases is reflected by significant changes in leachate and gas quality. Nonconservative constituents of leachate (primarily organic in nature) tend to decompose and stabilize with time, whereas conservative constituents will remain long after waste stabilization occurs. Conservative constituents include various heavy metals, chloride, and sulfide. Metals often are precipitated within the landfill and are infrequently found at high concentrations in leachate, with the exception of iron.

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Unfortunately, because of the variability in leachate quality, prediction of leachate characteristics as a function of time has been quite difficult. General trends in quality are possible, however these ranges are still large and prediction of the point in time at which each phase begins and ends is not possible as of yet. Research in landfill management, such as the use of leachate recirculation, may make it possible to control waste decomposition and consequently make leachate characteristics more predictable.
Current databases for landfill leachates are not geographically specific; rarely acknowledge the impact of site specific parameters such as age, water balance, type of waste, landfill operation, etc.; and cover such large ranges that they are often of little use. Analysis of data from lined landfills in Florida would provide useful information for the design and operation of leachate management facilities.

The specific objectives of this research, therefore, were to acquire leachate data from Florida MSW lined landfills and analyze these data. The results of this analysis provided important insight for the prediction of future trends in leachate quality, and the design and operation of leachate management facilities. Using statistical and graphical techniques, the effects of climate, region or location, age of the landfill, and waste characteristics on leachate quality were also investigated.
SECTION 2
LITERATURE REVIEW

2.1 INTRODUCTION

Within a landfill, a complex sequence of physically, chemically, and biologically mediated events occurs. As a consequence of these processes, refuse is degraded or transformed. As water percolates through the landfill, contaminants are leached from the solid waste. Mechanisms of contaminant removal include leaching of inherently soluble materials, leaching of soluble biodegradation products of complex organic molecules, leaching of soluble products of chemical reactions, and washout of fines and colloids. The characteristics of the leachate produced are highly variable, depending on the composition of the solid waste, precipitation rates, site hydrology, compaction, cover design, waste age, sampling procedures, interaction of leachate with the environment, and landfill design and operation.

2.2 FACTORS AFFECTING LEACHATE QUALITY

Leachate quality is highly variable. The variation in leachate quality can be attributed to many interacting factors such as the composition and depth of waste, the availability of moisture and oxygen, landfill design and operation, and waste age.

2.2.1 Waste Composition

Municipal waste has great variation in composition and characteristics. The waste composition of refuse determines the extent of biological activity within the landfill (Chen and Bowerman, 1974). Rubbish, food and garden wastes, and crop and animal residues contribute to the organic material in leachate (Pohland and Harper, 1985). Inorganic constituents in leachate are often derived from ash wastes and construction and demolition debris (Pohland and Harper, 1985). Chen and Bowerman (1974) found that increased quantities of paper in solid waste resulted in a decreased rate of waste decomposition. Lignin, the primary component of paper, is resistant to anaerobic decomposition which is the primary means of degradation in landfills. Due to the variability of solid waste, only general assumptions can be made about the relationship between waste composition and leachate quality.

2.2.2 Depth of Waste

Greater concentrations of constituents are found in leachates from deeper landfills under similar conditions of precipitation and percolation (Qasim and Chiang, 1994). Deeper fills require more water to reach saturation, require a longer time for decomposition, and distribute the leached material over a longer period of time (Qasim and Chiang, 1994; Lu et al., 1985). Water entering the fill will travel down through the waste. As the water percolates through the landfill, it contacts the refuse and leaches chemicals from the waste. Deep landfills offer greater contact
time between the liquid and solid phases which increases leachate strength (McBean et al., 1995).

2.2.3 Moisture Availability

Water is the most significant factor influencing waste stabilization and leachate quality. Moisture addition has been demonstrated repeatedly to have a stimulating effect on methanogenesis (Barlaz et al., 1990), although some researchers indicate that it is the movement of moisture through the waste as much as it is water addition that is important (Klink and Ham, 1982). Moisture within the landfill serves as a reactant in the hydrolysis reactions, transports nutrients and enzymes, dissolves metabolites, provides pH buffering, dilutes inhibitory compounds, exposes surface area to microbial attack, and controls microbial cell swelling (Noble and Arnold, 1991). Lu et al. (1985) stated that high moisture flow rates can flush soluble organics and microbial cells out of the landfill and in such cases microbial activity plays a lesser role in determining leachate quality. Also, high moisture application rates can remove the majority of waste contaminants early in the life of the fill. Under low flow rate conditions, anaerobic microbial activity is the significant factor governing leachate organic strength (McBean et al., 1995). The quantity of moisture is important because it directly affects stabilization rates within the landfill. Sulfita et al. (1992) and Miller et al. (1994) both noted the important role of moisture in supporting methanogenic fermentation of solid waste when examining samples removed from operating landfills. Relatively dry landfills (i.e. 20 to 40 percent water) have very slow stabilization rates because there is only a small quantity of moisture to support biological degradation. Recommended moisture content reported in the literature ranges from a minimum of 25 percent (wet basis) to optimum levels of 40 to 70 percent (Barlaz et al., 1990; Chen and Bowerman, 1974).

2.2.4 Available Oxygen

The quantity of free oxygen in a landfill dictates the type of decomposition (i.e. anaerobic or aerobic). Aerobic decomposition occurs during initial placement of waste, while oxygen is available. Aerobic degradation may continue to occur at, and just below, the surface of the fill (McBean et al., 1995). Chemicals released as a result of aerobic decomposition differ greatly from those produced during anaerobic degradation (Bagchi, 1990). During aerobic decomposition, microorganisms degrade organic matter to CO₂, H₂O, and partially degraded residual organics, producing considerable heat. High concentrations of organic acids, ammonia, hydrogen, carbon dioxide, methane, and water are produced during anaerobic degradation (McBean et al., 1995). Phase changes occur in the fill as a result of reductions in the quantity of oxygen in the landfill. For example, a transitional change takes place when oxygen is depleted and an anaerobic environment develops.

2.2.5 Temperature

Landfill temperature, a largely uncontrollable factor influencing leachate quality, has been shown to fluctuate with seasonal ambient temperature variations (Lu et al., 1985). Temperature
affects bacterial growth and chemical reactions within the landfill. Each microorganism possesses an optimum growth temperature, and any deviation from that temperature will decrease growth due to enzyme deactivation and cell wall rupture. Solubility of many salts (e.g., Ca₃(PO₄)₂ and NaCl) increases with temperature. However, a number of compounds in leachate, such as CaCO₃ and CaSO₄, show a decrease in solubility with increasing temperature (Lu et al., 1985).

2.2.6 Codisposal with WWTP Sludge

Codisposal of municipal solid waste and sludge from municipal wastewater treatment plants (WWTP) can have a significant impact on leachate quality. Codisposal can accelerate leachate formation and the rate of biological stabilization through the addition of moisture, microbes, and nutrients provided by the sludge (Lu et al., 1985). With the exception of a more acidic leachate with higher biochemical oxygen demand (BOD) concentrations, the chemical composition of leachate does not appear to change significantly with the codisposal of MSW and WWTP sludge (Qasim and Chiang, 1994; Lu et al., 1985).

2.2.7 Codisposal with MSW Incinerator Ash

Data show that leachate from sites codisposing MSW and ash is similar to leachate from sites accepting domestic waste only (Westlake, 1995). Ash wastes do increase the inorganic content of the refuse (Pohland and Harper, 1985). Codisposal of ash with municipal solid waste may provide a means to attenuate the toxic species within the ash (Westlake, 1995). Poon and Chu (1990) found that leachate from codisposal sites contained more chemical oxygen demand (COD), sulfide, and low molecular weight organic acids (acetate and formate). The greater amounts of acetate and formate generated were expected to depress pH and enhance metal mobility. However, sulfide would tend to immobilize metals due to the low solubility of most metal sulfides. Poon and Chu (1990) also determined that codisposal generated more lead and cadmium in the particulate form.

Roffman and Bradford (1982) conducted a study which characterized leachates from codisposal sites. In general, these researchers found no clear difference between the metal content in leachates from codisposal sites and from municipal sites. This observation suggested that the neutral pH of MSW leachates does not promote leaching of metals from municipal waste combustion ashes. Also, there was no noticeable difference in the number or the detected levels of organic compounds between the leachates collected from the codisposal sites and the municipal disposal sites. Leachates generated by the Toxicity Characteristic Leaching Procedure (TCLP), Extraction Procedure (EP), or Deionized Water Extraction Test Method (SW-924) from ashes collected from codisposal sites did not generate detectable semi-volatile compounds. Table 1 compares the values of several conventional parameters in MSW leachates and in codisposal site leachates (Roffman and Bradford, 1982).
Table 1. Comparison of parameters in MSW and codisposal site leachates

<table>
<thead>
<tr>
<th>Type of Leachate</th>
<th>pH (units)</th>
<th>Ammonia-Nitrogen (mg/L)</th>
<th>Total Organic Carbon (mg/L)</th>
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<td>Codisposal Site Leachates</td>
<td>7.2 - 7.3</td>
<td>160 - 410</td>
<td>436 - 1310</td>
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</tbody>
</table>

A study by Chichester and Landsberger (1996), studied the leaching behavior of 33 elements in municipal solid waste incinerator fly ash. This work showed that most of the potentially toxic elements such as arsenic, barium, and cadmium leached at relatively low concentrations. The one exception was lead. According to the TCLP definition of a hazardous waste, the lead in approximately the first three pore volumes of column leachate was at hazardous levels (Chichester and Landsberger, 1996). The only other elements present above the method detection limit were silver, barium, and chromium. Leachate concentrations of these elements were below legal limits at the start of the experiment (Chichester and Landsberger, 1996).

2.2.8 Processed Waste

Shredding or baling of waste can greatly affect leachate characteristics. Leachate from shredded waste is more highly contaminated during early stages of waste stabilization and less contaminated during later phases than leachate from unshredded waste (Reinhardt and Ham, 1974). Lu et al. (1985) and Qasim and Chiang (1994) also agreed that leachate from shredded fills has significantly higher concentrations of pollutants than leachate from unshredded landfills. This higher strength leachate can be attributed to increased surface area and, consequently, increased rates of biodegradation in shredded waste landfills (Lu et al., 1985). Bookter and Ham (1982) also concluded that shredding increased the rate of decomposition in test cells, as did Otieno (1989). However Tittlebaum (1982) found shredding had no affect on waste degradation in laboratory-scale lysimeters. Attainment of field capacity (i.e. maximum moisture that can be retained without continuous downward percolation by gravity) was delayed for shredded waste landfills, but the rate of pollutant removal, solid waste decomposition, and cumulative mass of pollutants released per unit volume of leachate was significantly increased when compared to unshredded waste fills (Qasim and Chiang, 1994).

Unlike shredding, baling resulted in large volumes of dilute leachate and waste required a longer period to stabilize compared to unbaled wastes (Qasim and Chiang, 1994). Baling can enhance leachate production by decreasing the elapsed time before leaching, reducing the moisture-retention ability of the waste, and by increasing the overall volume of the leachate produced (Lu et al., 1985). However, once the field capacity of the shredded or baled refuse is reached, the cumulative mass of pollutant removal per kg of solid waste will be the same regardless of the type of waste processing (Lu et al., 1985).
2.2.9 Age of Landfill

Leachate quality is greatly influenced by the length of time which has elapsed since waste placement. The quantity of chemicals in the waste is finite and, therefore, leachate quality reaches a peak after approximately two to three years followed by a gradual decline in ensuing years (McBean et al., 1995; Lu et al., 1985). Generally, leachate from new landfills will be high in BOD and COD and will then steadily decline, leveling off after about 10 years (Akyurek, 1995). All contaminants do not peak at the same time. Due to their initially biodegradable nature, organic compounds decrease more rapidly than inorganics with increasing age of the landfill (Chian and DeWalle, 1977). Inorganics are only removed as a result of washout by infiltrating rainwater (Qasim and Chiang, 1994). Organic compounds, however, decrease in concentration through decomposition as well as washout. A decrease in the sulfate to chloride concentration ratio is also observed as shown in Figure 1 due to a rapid decrease in sulfate concentration while the chloride concentration declines more slowly. The rapid decrease in the concentration of sulfate is a result of predominately anaerobic conditions in the landfill under which sulfate is reduced to sulfide (Chian and DeWalle, 1977). Sulfide then precipitates with various metals. Unlike the sulfate concentration, pH increases with time, which reflects the decrease in concentration of the partially ionized free volatile fatty acids (Figure 2) (Chian and DeWalle, 1977). Variations in leachate quality with age should be expected throughout most of the landfill life because organic matter will continue to undergo stabilization (Qasim and Chiang, 1994).

![Figure 1. Changes of SO₄/Cl ratio versus age of the landfill (adapted from Chian and DeWalle, 1977).](image-url)
2.3 LEACHATE COMPOSITION

As a result of the broad spectrum of solid waste characteristics, it follows that leachate composition will vary tremendously. The variation of leachate composition means discussion of this factor must be carried out in terms of ranges and trends rather than mean values which by themselves are not meaningful (Lema et al., 1988). Some of the major factors which directly affect leachate composition include the degree of compaction and composition of the solid waste, climate, site hydrogeology, season, and age of the landfill (Lema et al., 1988). Table 2 shows the wide variation of leachate quality as determined by various researchers.

2.3.1 Phases of Waste Stabilization

Leachate composition is primarily a function of the age of the landfill and the degree of waste stabilization. Numerous landfill investigation studies (Pohland and Harper, 1985) have suggested that the stabilization of waste proceeds in five sequential and distinct phases. The rate and characteristics of waste produced and biogas generated from a landfill vary from one phase to another and reflect the microbially mediated processes taking place inside the landfill. The rate of progress through these stages is dependent on the physical, chemical, and microbiological conditions developed within the landfill with time (Pohland et al., 1985). The phases experienced by degrading wastes are described below.

Figure 3 illustrates the five sequential phases of landfill stabilization. Since landfills have various sections or cells, a landfill is not experiencing a single phase of waste stabilization but rather many phases of stabilization are occurring simultaneously.
Figure 3. Changes in selected indicator parameters during the phases of landfill stabilization. Pohland and Harper (1985).
Table 2. Ranges of various parameters in leachate as determined by different researchers.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>BOD (mg/L)</td>
<td>20 - 40000</td>
<td>80 - 28000</td>
<td>---</td>
<td>4 - 57700</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>500 - 60000</td>
<td>400 - 40000</td>
<td>530 - 3000</td>
<td>31 - 71700</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>3 - 2100</td>
<td>0.6 - 325</td>
<td>1.8 - 22</td>
<td>4 - 2200</td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td>30 - 3000</td>
<td>56 - 482</td>
<td>9.4 - 1340</td>
<td>2 - 1030</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>100 - 5000</td>
<td>70 - 1330</td>
<td>112 - 2360</td>
<td>30 - 5000</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>0.03 - 120</td>
<td>0.1 - 30</td>
<td>---</td>
<td>0.06 - 220</td>
</tr>
<tr>
<td>Total P (mg/L)</td>
<td>0.1 - 30</td>
<td>8 - 35</td>
<td>1.5 - 130</td>
<td>0.2 - 120</td>
</tr>
<tr>
<td>pH (units)</td>
<td>4.5 - 9</td>
<td>5.2 - 6.4</td>
<td>6.1 - 7.5</td>
<td>4.7 - 8.8</td>
</tr>
<tr>
<td>Lead (mg/L)</td>
<td>0.008 - 1.020</td>
<td>0.5 - 1.0</td>
<td>BDL - 0.105</td>
<td>0.001 - 1.44</td>
</tr>
<tr>
<td>Cadmium (mg/L)</td>
<td>&lt; 0.05 - 0.140</td>
<td>&lt; 0.05</td>
<td>BDL - 0.005</td>
<td>70 - 3900</td>
</tr>
</tbody>
</table>

BDL - below detection limits
* - South Florida Water Management District, 1987

2.3.1.1 Phase 1 - Initial Adjustment Phase

This phase is associated with initial placement of solid waste and accumulation of moisture within landfills. An acclimation period (or initial lag time) is observed until sufficient moisture develops and supports an active microbial community. Preliminary changes in environmental components occur in order to create favorable conditions for biochemical decomposition. During this first stage of decomposition, aerobic microorganisms degrade the organic materials to CO₂, H₂O, and partially degraded residual organics; producing considerable heat (McBean et al., 1995). Since only a finite quantity of oxygen is buried within the waste, and there are limitations on air transport into the landfill, aerobic decomposition is responsible for only a small portion of biodegradation within the landfill (Lu et al., 1985; McBean et al., 1995). Any leachate produced during this initial phase is most likely a result of moisture squeezed out of the waste during compaction and cell construction (Lu et al., 1985). Leachate formed during this phase is characterized by the entrainment of particulate matter, dissolution of highly soluble salts initially present in the landfill, and the presence of relatively small amounts of organic species from aerobic degradation (Lu et al., 1985; McBean et al., 1995).
2.3.1.2 Phase II - Transition Phase

In the transition phase, the field capacity is often exceeded, and a transformation from an aerobic to an anaerobic environment occurs, as evidenced by the depletion of oxygen trapped within the landfill media. A trend toward reducing conditions is established in accordance with shifting of electron acceptors from oxygen to nitrates and sulfates, and the displacement of oxygen by carbon dioxide. By the end of this phase, measurable concentrations of COD (480 to 18000 mg/L) and volatile organic acids (VOA) (100 to 3000 mg/L) can be detected in the leachate.

2.3.1.3 Phase III - Acid Formation Phase

The continuous hydrolysis (solvabilization) of solid waste, followed by (or concomitant with) the microbial conversion of biodegradable organic matter results in the production of intermediate VOAs, ammonia, hydrogen, and CO\textsubscript{2} at high concentrations throughout this phase. Acid phase anaerobic biodegradation processes are carried out by a mixed anaerobic population, composed of strict and facultative anaerobes (Lu et al., 1985). Facultative anaerobes aid in the breakdown of materials and reduce the redox potential so that methanogenic bacteria can grow. A decrease in pH values is often observed, and is accompanied by metal species mobilization resulting in a chemically aggressive leachate. Also, a decrease in the sorptive capacity of the refuse is seen during this phase (Lu et al., 1985). The highest concentrations of BOD (1000 to 57700 mg/L), COD (1500 to 71100 mg/L), and specific conductance (1600 to 17100 µhmhos/cm) occur during the acid formation phase (McBean et al., 1995). Viable biomass growth associated with the acid formers (acidogenic bacteria), and rapid consumption of substrate and nutrients are the predominant features of this phase.

2.3.1.4 Phase IV - Methane Fermentation Phase

Transition from the acid formation phase to the methane fermentation phase occurs in the range of 4 to 10 years after waste placement and may continue over a period of several years (Krug and Ham, 1995). During Phase IV, intermediate acids are consumed by methane-forming consortia (methanogenic bacteria) and converted into methane and carbon dioxide. Reducing conditions corresponding to this phase will influence the solubility of inorganics, resulting in precipitation or dissolution of these constituents. For example, sulfate and nitrate are reduced to sulfides and ammonia, respectively. COD and BOD concentrations decline since much of these materials are converted to gas (McBean et al., 1995). A small portion of the original refuse organic content (e.g. lignin-type aromatic compounds) is not degraded to any extent anaerobically and remains in the landfill material. These lignin-type compounds are important factors in adsorption and complexation mechanisms (Lu et al., 1985). The pH level is elevated, being controlled by the bicarbonate buffering system, and consequently supports the growth of methanogenic bacteria. Heavy metals are removed by complexation and precipitation. Methanogens work relatively slowly but efficiently over many years decomposing any remaining degradable organics.
2.3.1.5 Phase V - Maturation Phase

During the final stage of landfill stabilization, nutrients and available substrate become limiting and the biological activity shifts to relative dormancy. Gas production dramatically drops and leachate strength remains steady at much lower concentrations. Oxygen and oxidized species may slowly reappear. However, the slow degradation of resistant organic fractions may continue with the production of humic-like substances.

2.3.2 Organic Compounds

BOD and COD are used to measure the organic content in leachate. Chian and DeWalle (1976) reported COD and BOD values in the range of 31.1 to 71,680 mg/L and 3.9 to 57,000 mg/L, respectively. A BOD range between 20 to 40,000 mg/L was observed by Ehrig (1989). This researcher also reported COD values in the range of 500 to 60,000 mg/L. A decrease in the concentrations of BOD and COD occurs over time. A decline in BOD concentrations can be attributed to a combination of reduction in organic contaminants available for leaching and the increased biodegradation of organic compounds (Krug and Ham, 1995). A constant decrease in COD is also expected as degradation of organic matter continues (Ehrig, 1989). Figure 4 illustrates COD concentrations from some 35 landfills over time. McBean et al. (1995) report COD values ranging from 30,000 to 50,000 mg/L in young leachate. Leachates from old, extensively leached refuse have CODs generally less than 2000 mg/L (McBean et al., 1995).

![COD Versus Age of Landfill](image)

Figure 4. Change in COD concentrations with increasing age of the landfill (adapted from Reinhart, 1996).

Organic contaminants of leachate are primarily soluble refuse components or decomposition products of biodegradable fractions of waste. Organic compounds detected in 19 MSW landfill leachates or contaminated groundwater plumes emanating from landfills included organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, amino-aromatic compounds,
nitro-aromatic compounds, phenols, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls, and organophosphates (Brown and Donnelly, 1988).

The class of organic compounds found at highest concentration in leachates is generally volatile fatty acids (e.g. acetic, propionic, and butyric) produced during the decomposition of lipids, proteins, and carbohydrates (Albaiges et al., 1986; Schultz and Kjeldsen, 1986). Aromatic hydrocarbons, including benzene, various xylenes, and toluene, are also frequently found at lower concentrations (Schultz and Kjeldsen, 1986; Harmsen, 1983). These compounds were considered to be constituents of gasoline and fuel oils. Sawney and Kozloski (1984) reported that the presence of the more soluble, less volatile aromatic components of gasoline suggested that the more volatile components were being stripped by the gas from the landfill. A small complex fraction found in several leachates contained nicotine, caffeine, and phthalate plasticizers (Albaiges et al., 1986). Oman and Hynning (1993) observed that a total of 150 different organic compounds have been identified in multiple studies, however only 29 were identified in more than one. They therefore concluded that leachate composition was quite site specific.

The dominant organic class in leachate shifts as the age of the landfill increases due to the ongoing microbial and physical/chemical processes within the landfill. An investigation of leachates obtained from landfills operated from one to twenty years found that the relative abundance of high molecular weight humic-like substances decreases with age, while intermediate sized fulvic materials (e.g. high density carboxyl and aromatic hydroxyl groups) showed significantly smaller decreases (Chian, 1977). The relative abundance of organic compounds present in leachate was observed to decrease with time in the following order: free volatile fatty acids, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds, and fulvic acids.

2.3.2.1 Organic Indicator Ratios

Chian and DeWalle (1977) found that many ratios of chemical properties, such as COD/TOC, BOD/COD, and VOA/TOC reflect the composition of the organic matter in leachate and are in turn related to the age of the landfill. The parameter found to be most useful in relating to the composition of organic matter was the ratio of COD to TOC (DeWalle and Chian, 1974). It can be seen from Figure 5 that the COD to TOC ratio tends to decrease as the landfill ages. This ratio varied from 3.3 for a relatively young landfill to 1.16 for an old landfill. The maximum possible COD/TOC for several organic compounds is 4.0, and can be as low as 1.3 for organics containing carboxyl groups (Rickert and Hunter, 1971). A decrease in this ratio reflects a more oxidized state of the organic carbon which becomes less readily available as an energy source for microbial growth (Venkataramani et al., 1974; Chain and DeWalle, 1977).
Since the BOD test is predominately a biological test, it generally reflects the biodegradability of the organic matter in leachate. Like the COD/TOC, the BOD to COD ratio, an indicator of the proportion of biologically degradable organic matter to total organic matter, decreases as the landfill ages and more degradation products are leached from deposited residues (Copa et al., 1995; Westlake, 1995). Similar results were obtained in studies conducted by Miller et al. (1974). The calculated ratio of BOD to COD based on Miller's data showed a decrease from 0.47 to 0.07 within a period of 23 years. Chian and DeWalle (1977) found the ratio decreased from 0.49 to 0.05 (See Figure 6).
The ratio of the VOA as a percent of TOC also shows a decrease with the age of the fill from 0.5 to 0 as seen in Figure 7. Since the VOAs are readily biodegradable, a decrease in the ratio of carbon present in free volatile acids to TOC corroborates the decrease in BOD/COD ratio.

2.3.2.2 Microbiology

MSW contains a large microbial population, and may be heavily contaminated with pathogenic microorganisms (Gaby, 1975). MSW landfills often contain pet feces, animal remains, disposable baby diapers, hospital wastes, and sometimes sewage sludges, all of which pose a potentially significant health hazard (Lu et al., 1985).

![Figure 7. Changes of free volatile fatty acids as a percentage of TOC with increasing age of the landfill (adapted from Chian and DeWalle, 1977).](image)

2.3.2.3 Bacteria

Several studies have shown that there can be a significant bacterial population associated with municipal landfill leachates. The actual bacterial content of leachate, particularly the numbers of total coliforms, fecal coliforms, fecal streptococci, and total plate counts, varies dramatically with the age, and thus, chemical properties of the leachate (Senior, 1990). A limited number of bacterial pathogens have been found in leachates from commercial and experimental landfills, and environmental lysimeters (Scarpino and Donnelly, 1979). A comprehensive review of studies on the survival of bacteria in leachates was conducted by Ware (1980) who found increases in bacterial mortality with time of leaching or refuse age due to the bactericidal effects of the leachate and landfill. Relatively high temperatures achieved in the aerobic stage of refuse biodegradation can inhibit bacterial growth and survival (Lu et al., 1985). Also, bacterial inactivation is more rapid at lower pH (Lu et al., 1985). Together, temperature and pH act to accelerate bacterial inactivation (Engelbrecht and Amirhor, 1975).
2.3.2.4 Viruses

Since MSW may contain fecal material from a number of different sources, it is possible that enteric viruses are among the pathogens entering leachate (Lu et al., 1985). In general, enteric viruses are rarely found in municipal landfill leachates (Lu et al., 1985). Engelbrecht et al. (1974) detected no viruses in leachates produced by a large, field-scale MSW lysimeter that had been experimentally contaminated with poliovirus type 1 during the filling operation. Municipal leachate and landfills apparently pose a harsh environment for the survival of viruses, though the mechanisms of viral destruction are unknown (Lu et al., 1985). The rate of viral inactivation in leachates is temperature dependent and proceeds much faster at higher temperatures (20 to 22°C). Therefore, elevated landfill temperature can accelerate the inactivation of viruses (Lu et al., 1985).

2.3.3 Inorganic Compounds

A variety of heavy metals are frequently found in landfill leachates including zinc, copper, cadmium, lead, nickel, chromium, and mercury (Lu, et al, 1985). These metals are either soluble components of the refuse or are products of physical processes such as corrosion and complexation. In several instances, heavy metal concentrations in leachate exceed US Toxicity Characteristic Leaching Procedure standards.

Heavy metal concentrations in leachate do not appear to follow patterns of organic indicators such as COD or BOD, nutrients, or major ions (Lu et al., 1985). Heavy metal release is a function of characteristics of the leachate such as pH, flow rate, and the concentration of complexing agents. Metal solubilities generally decrease with increasing pH. In addition, the hydrogen ion concentration will indirectly influence metal solubility by its impact on such processes as the dissociation of an acid to yield a precipitant anion and reduction-oxidation reactions (Gould et al., 1989). With time, moderate to high molecular weight humic-like substances are formed from waste organic matter in a process similar to soil humification. These substances tend to form strong complexes with heavy metals. The formation of complexes between heavy metals and ligands tends to increase metal solubility although there are conditions under which the opposite may be expected (Gould et al., 1989). Sulfide, however, effectively competes with most complexing agents, and consequently many heavy metals will precipitate as sulfides rather than remain in solution as complexes (Lu et al., 1985). Chian and DeWalle (1976) also reported that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In addition, under neutral or above neutral leachate conditions metal hydroxide precipitation is enhanced. In some instances, a remobilization of metals occurs once the organic content has been stabilized and oxic conditions begin to be reestablished (Pohland et al., 1992). Adsorption is another important mechanism controlling the heavy metal concentration. Under oxidizing conditions, adsorption can regulate the concentration of metals well below the level controlled by precipitation effects (Lu et al., 1985).
Electrochemical processes can influence metal speciation and behavior both directly by modifying the nature of the metal itself and indirectly through conversion by other species in the landfill environment. For example, the toxic non-metal, selenium, can be removed from landfills by reduction to the neutral element or conversion to the selenide ion which will be readily precipitated by ferrous ions (Gould et al., 1989).

Specific conductance is a gross indicator of the total concentration of dissolved inorganic matter or ions present in leachate (Johansen and Carlson, 1976). The primary metal species contributing to specific conductance are calcium, magnesium, sodium, and potassium (Johansen and Carlson, 1976). In general, specific conductance decreases with time as a result of the eventual depletion of soluble inorganic materials within the waste (Krug and Ham, 1995).

2.3.4 Nutrients

Ammonia concentrations between 50 and 200 mg/L have been shown to be beneficial to anaerobic processes. Ammonia concentrations between 200 and 1000 mg/L have been shown to have no adverse effects on anaerobic processes while concentrations ranging from 1500 to 3000 mg/L have been shown to have inhibitory effects at higher pH levels. Concentrations above 3000 mg/L were toxic to microorganisms (Pohland et al., 1992). Ammonia and organic nitrogen produced by decomposition of organics are stable in an anaerobic environment, and therefore represent a high percentage of the soluble nitrogen compounds in leachate (McBean et al., 1995). Leachates of older landfills generally have lower concentrations and percentages of these constituents (Robinson and Maris, 1979). Unlike ammonia concentrations, phosphate levels remain generally low throughout the life of the landfill. During later stages of waste stabilization, phosphorous may be limiting (Pohland and Harper, 1985).

2.3.5 Toxicity

Brown et al. (1991) investigated acute and genetic toxicity of municipal landfill leachate. Results of acute and genetic toxicity bioassays combined with chemical analyses and associated cancer risk assessment clearly showed that leachate from municipal solid waste landfills is just as toxic as leachate from landfills in which residential and hazardous wastes were codisposed. Leachate from MSW landfills even contained many of the same hazardous constituents as found in hazardous waste landfills. In addition, several researchers have found leachate to be quite toxic to rainbow trout and daphnia (Cameron and Koch, 1980; Atwater et al., 1983) and to have some toxicological impact on laboratory mice (Raddi et al., 1987).

2.4 EFFECTS ON LINER SYSTEMS

Due to the chemical composition of leachate, liners can be adversely affected by continued contact with this high strength liquid. Although the high molecular weight of synthetic liners make them highly resistant to biodegradation, organic liquids can cause swelling of the polymers and changes in
properties (Mitchell et al., 1995). In a nine-year study conducted by Emcon Associates (1983), low density polyethylene exposed to full strength leachate appeared unaffected (very little swelling, no punctures, and no leakage). Polyethylene, however, when exposed to chlorinated solvents exhibited high permeation rates (McBean et al., 1995). Chlorinated polyethylene (CPE) liners exposed to full strength leachate showed significant absorption with volume and weight increases of 32 percent, and 28 percent respectively, but no leakage was observed (Farquhar and Parker, 1989). Chlorosulfonated polyethylene (CSPE) in contact with diluted leachate had softened and become swollen. Like CPE, CSPE had increased in volume and weight due to absorption of leachate. There was no evidence of lost permeability in the CSPE, although the seams had blistered and appeared to contain water (Farquhar and Parker, 1989).

Leachate can also affect the integrity of natural liner systems. Quigley and Rowe (1986) presented a report on landfill leachate impacts on barrier systems. The landfill had operated for 15 years prior to the investigation and the barrier consisted of in situ grey clay to a depth of approximately 30 m. Clay samples showed that chloride and sodium had migrated to distances of 1.5 m below the fill, farther than all other contaminants. Concentrations as high as 2000 mg/L and 2890 mg/L were measured for chloride and sodium, respectively. Chloride concentrations in excess of 1000 mg/L are common in MSW leachate but concentrations of sodium greater than 2500 mg/L are not. It is suspected that sodium was released from the clay, exchanged with other cationic species in the leachate (Farquhar and Parker, 1989). Another study at Eau Claire County landfill found some hydraulic conductivities of the clay liner in excess of the general requirement of $10^{-7}$ cm/s (Farquhar and Parker, 1989). Monitoring of the clay barrier began with initial waste placement and continued over a four year period. Mobile chloride moved downward as did divalent metallic ions either from the leachate or as a result of exchange mechanisms within the clay. There was no conclusive evidence that leachate/liner interactions were responsible for the elevated hydraulic conductivities (Farquhar and Parker, 1989).

2.5 Leachate Treatment

The quality of leachate directly affects viable leachate treatment alternatives. Leachate quality is quite variable from site to site and over time as a particular landfill ages. As a result, neither biological treatment nor physical/chemical treatment processes separately are able to achieve high treatment efficiencies (Keenan et al., 1984; Forgie, 1988; Copa et al., 1995). A combination of both types of treatment is the most effective process train for the treatment of leachate (Copa et al., 1995; Forgie, 1988).

The factor that most significantly affects the sequence and effectiveness of leachate treatment processes is the age of the landfill. Leachate from young landfills (first several years of operation) contains high concentrations of readily biodegradable organic matter (e.g. volatile fatty acids) (McBean et al., 1995). This young leachate is derived from complex biodegradation organics and simple dissolved organics. The high organic content of leachate produced at young landfills makes the leachate amenable to biological treatment (Venkataramani et al., 1974; Bagchi, 1990). Physical/chemical
treatment processes used to treat leachate from young fills do not produce the same degree of organic removal that can be accomplished with biological treatment (Qasim and Chiang, 1994). Lema et al. (1988) determined that biological treatment is highly efficient in eliminating compounds with low molecular weight which are primarily found in young leachates. However, the concentration of several parameters contained in young leachate can inhibit biological treatment. To adjust the level of these constituents to an acceptable concentration for biological treatment, physical/chemical pretreatment of the leachate is frequently employed. For example, high concentrations of metals such as copper, zinc, and nickel cause biological inhibition and physical/chemical precipitation can be used to reduce the concentration of these heavy metals (McBean et al., 1995). Also, very high concentrations of ammonia (greater than 1000 mg/L) will inhibit nitrification (McBean et al., 1995). Through the use of physical/chemical methods, the ammonia level can be reduced to a more acceptable concentration prior to biological treatment (McBean et al., 1995).

In addition to their use as a pretreatment technique, physical/chemical processes are effective in the treatment of stabilized leachate from old landfills or leachate which has been stabilized biologically (Qasim and Chiang, 1994). Since old leachate contains refractory organics generally left or formed by bacterial or chemical processes, it is more amenable to treatment using physical/chemical processes rather than biological (Venkataramani et al., 1974). Several constituents found in leachate are not reactive, and therefore are not easily removed. Compounds such as chlorides and sulfates need to be removed using physical/chemical processes because biological treatment is unable to effectively remove these nonreactive constituents (McBean et al., 1995).

It is apparent that neither biological nor physical/chemical treatment processes separately achieve high removal efficiencies because leachate is variable from landfill to landfill, and over time and space in a particular landfill. Physical/chemical processes are needed for the pretreatment of young leachate to make it amenable to biological treatment, and to hydrolyze some organics (refractory organics) found in leachate from older landfills. Biological treatment is primarily used to stabilize degradable organic matter found in young leachates.

2.6 SUMMARY

Leachate quality is highly variable as illustrated in Table 2. Due to the variability of leachate, the ranges in leachate parameters often cover several orders of magnitude. Leachate quality is primarily a function of landfill age and the degree of waste stabilization. However, the characteristics of leachate are also affected by many site specific factors such as waste composition, moisture availability, and climate. Current databases for landfill leachates are not geographically specific; rarely acknowledge the impact of site specific parameters; and cover such large ranges that they are often of little use. Analysis of data from lined landfills in Florida would provide useful information for the design and operation of leachate management facilities.
SECTION 3
METHODOLOGY

3.1 INTRODUCTION

Leachate quality data were acquired from Florida Department of Environmental Protection files (FDEP) for municipal solid waste (MSW) lined landfills. Data analysis was performed with the Microsoft Excel Analysis ToolPak, KURV+, and SYSTAT. In addition, this study employed data obtained from Browning-Ferris Industries (BFI) which are more representative of conditions throughout the country. These data were used for comparison with Florida leachate data.

3.2 ORGANIZATION OF THE DATA

The Florida Department of Environmental Protection provided leachate quality data from 55 Class I landfills (i.e. fills receiving MSW only). The landfills that would be included in this study were then determined. Two criteria were used to select the landfills, as follows: each landfill had to be lined and at least one year of data had to be available for each landfill. Only lined landfills were selected for this study because leachate samples collected from unlined landfills can be erroneously low in concentration due to dilution from groundwater and other sampling errors. In addition, trends in leachate quality would be difficult to recognize with less than one year of data. Of the 55 landfills, 39 met the criteria and were included in this study. Table 3 lists the 39 landfills and provides general information about each one (landfills are grouped by FDEP district).

Information on waste characteristics, the date waste was first placed, and the status of each facility were obtained either from the FDEP or the site operator. This information was used to determine which landfills received a significant quantity (at least 50 percent) of MSW incinerator ash, to identify any fills where leachate samples were collected from leachate storage ponds, and to learn which landfills processed waste prior to placement (i.e. shredding). The presence of primarily ash wastes could produce significant variation in leachate quality compared to what will be called general leachate (i.e. all the data excluding pond and ash data). Similarly, leachate gathered from ponds could differ from general leachate because of the chemical and biological processes taking place within a leachate pond. The addition of domestic sludge may also affect leachate quality due to the addition of moisture, nutrients, and microbes. However, a lack of operational information made it unclear which sites (if any) codisposed MSW and wastewater treatment plant (WWTP) sludge.

There are many site specific parameters that impact leachate quality such as the composition of the solid waste, interaction of leachate with the environment, waste age, sampling procedures, and landfill design and operation. In order to account for at least one of these factors which cause variations in leachate quality, an attempt was made to separate data for each fill
<table>
<thead>
<tr>
<th>Landfills</th>
<th>Opened</th>
<th>Closed</th>
<th>Size, TPD</th>
<th>MSW Inincerator</th>
<th>Leachate Samples</th>
<th>Shredding</th>
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<tr>
<td>Byrd</td>
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<td>May-93</td>
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<td>Closed</td>
<td>Size, TPD</td>
<td>MSW Inincerator Ash Content</td>
<td>Leachate Samples from Ponds</td>
<td>Shredding</td>
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<td>Gulf Coast</td>
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<td>Sep-91</td>
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</table>
based on the point in time when (and if) each landfill transitioned from the acidogenic phase to the methanogenic phase. Although the stabilization of waste proceeds in five sequential phases, in full-scale landfill operation it is virtually impossible to identify all five stages (Pohland and Harper, 1985). Therefore, only the two most distinct phases were addressed. By identifying the conditions (acidogenic or methanogenic) within the fill at every sampling period, the data for each landfill could then be categorized by phase.

The acidogenic phase is the early stage of waste degradation and is generally characterized by a ratio of BOD concentration to COD concentration greater than or equal to 0.1 and sulfate levels between 70 and 1750 mg/L (Ehrig, 1989). Typical characteristics of the later phase of waste decomposition, the methanogenic phase, are BOD/COD less than 0.1 and sulfate values between 10 and 420 mg/L (Ehrig, 1989). The BOD to COD ratio is an indicator of the proportion of biologically degradable organic matter to total organic matter. This value decreases as the landfill ages and more degradation products are leached from deposited residues (Copa et al., 1995; Westlake, 1995). Due to the predominantly anaerobic conditions within the landfill, the sulfate concentration decreases rapidly as sulfate is reduced to sulfide. This tendency increases as the methanogenic phase becomes more established.

As indicators of the conditions within the fill, the BOD to COD ratio and the sulfate concentration were used in this study to separate the data into the acidogenic or methanogenic phase. Florida leachate appears to be weak compared to literature and nationwide leachate values. This is most likely a result of the Florida climate (e.g. heavy rainfall) which produces a dilute leachate. Therefore, the BOD to COD ratio is a more reliable means of separating data than organic parameter concentrations alone.

Limited data were available for each landfill in many cases. Numerous landfills had missing BOD and COD data. If the BOD to COD ratio could not be calculated, the sulfate concentrations were used to identify the conditions within the landfill at each sampling period based on the values reported by Ehrig (1989). Ten landfills had no available BOD, COD, or sulfate data. Rather than discard the remaining pollutant data, the following method was employed to establish when these landfills transitioned from the acidogenic to methanogenic phase. Eleven landfills had sufficient data to determine the age at which each fill entered the methanogenic phase. Using these transition times, an average number of years from the date waste was first placed to the transition to methanogenic conditions was computed. This value is 4.3 years. For each landfill without BOD, COD, or sulfate data, the point at which transition to the methanogenic phase was assumed to occur was approximately 4.3 years after the landfill first received waste.

3.3 CHRONOLOGICAL DATA ANALYSIS

In order to identify trends in BOD and COD levels, a plot of each parameter versus age of the landfill was developed. Every BOD and COD detection for all the landfills was used to create the graphs. The age of the landfill at the time of each BOD and COD detection was determined
based on when waste was first placed in the lined portions of the landfill. The date of initial waste placement was subtracted from each sampling date to determine the time or age of the fill corresponding to the BOD or COD detection. However, landfill age can be somewhat difficult to define. Waste is placed in one cell at a time within a landfill facility until the capacity of the cell is reached. Then a new cell becomes active. Usually a leachate collection system combines the leachate from all the cells. Therefore, it may be misleading to determine a single age for a landfill.

Typically, the BOD and COD concentrations will be low initially, and will increase as waste begins to solubilize (see Figure 3, Chapter 2). An eventual decline in BOD and COD concentrations is often observed as organic matter is being removed via washout and degradation. This increase and decrease in organic constituents can be model by two consecutive first-order processes. Equation 1 describes the sequential first-order reaction.

\[
y = \frac{k_1 C_{\text{init}}}{k_2 - k_1} \left[ \exp(-k_1 t) - \exp(-k_2 t) \right]
\]

where:
- \( y \) = BOD or COD concentration, mg/L
- \( k_1 \) = reaction rate constant of the first sequence, time\(^{-1}\)
- \( k_2 \) = reaction rate constant of the second sequence, time\(^{-1}\)
- \( C_{\text{init}} \) = concentration of the initial reactant, mg/L
- \( t \) = time or age of the landfill, time

The parameters in Equation 1 were estimated using non-linear least squares regression. SYSTAT, a powerful statistical package, was employed to estimate these parameters. This statistical program was used to determine whether the Florida BOD and COD data exhibited a chronological pattern. In addition, KURV+, a software package that fits data to 28 different mathematical linear and non-linear equations, was used in order to identify a function that would accurately describe the BOD and COD concentrations over time. The correlation coefficient of each function was utilized to determine which equation best fit the data. This equation could then be used to predict the concentrations of COD and BOD produced at Florida landfills.

### 3.4 TOXIC AND ORGANIC PARAMETERS

Many toxic and organic constituents have been detected in MSW landfill leachates. In Florida landfills, the concentration of these compounds is usually on the order of micrograms per liter and in many cases the concentrations were below the detection limit. Therefore, when evaluating these types of data, a detection is often more significant than the reported concentration. When analyzing these parameters, not only was the number of detections reported but also the mean and standard deviation for each phase, and all the data as a group. Also, the toxic and organic parameters were separated into four categories: chlorinated compounds,
aromatics, heavy metals, and miscellaneous constituents (parameters that could not be classified into the previous groups). A comparison of the number of detections in each category between the acidogenic and methanogenic phase was performed. The concentration of many of these constituents was below the detection limit (i.e. < 5 µg/L). For calculation purposes, these values were replaced with zeros.

### 3.5 CONVENTIONAL PARAMETERS

The conventional parameters that were analyzed in this study were as follows:

- Biological Oxygen Demand (BOD),
- Chemical Oxygen Demand (COD),
- ammonia (NH₃),
- sulfate (SO₄),
- chloride (Cl),
- pH,
- manganese (Mn), and
- zinc (Zn).

These parameters were chosen because sufficient data were available for each one at a majority of the landfill sites. According to Ehrig (1989), BOD, COD, sulfate, pH, manganese, and zinc levels change between the acidogenic and methanogenic phase. The levels of chloride and ammonia show no difference between phases. The number of detections, mean, median, minimum, maximum, and standard deviation were computed for each parameter. Like the toxic and organic parameters, if the concentration of any constituent was listed as non-detected, it was replaced with a zero for calculation purposes. Below is a list of the various groupings for which these descriptive statistical parameters were computed:

- individual landfill,
- individual FDEP district,
- data obtained from the analysis of leachate ponds (pond),
- data from primarily ash landfills (ash), and
- all data excluding pond and ash data (general leachate data).

Also, acidogenic and methanogenic data were combined to create cumulative percentage distributions for each conventional parameter. The distributions presented the data in a compact, yet comprehensible form so that essential characteristics of the data were readily discernable. The advantage of the cumulative percentage distribution is that it readily provides information about the percent of values falling below a given parameter concentration (Ary and Jacobs, 1976).
3.5.1 Analysis of Variance

The landfill data were categorized separately for all the FDEP districts. Dividing the data by districts was a means of regionalizing the landfills throughout the state. Data from the landfills which received more than 50 percent ash were not included.

In order to determine whether the value of each parameter (e.g. BOD, COD, etc.) differed regionally, a single factor analysis of variance (ANOVA) was used (see Appendix A). This method was employed because an ANOVA is used to test for differences among the means of two or more populations. Single factor means that only one type of grouping is being considered (Chalmer, 1987). In this case, region was the classification considered. The null hypothesis ($H_0$) tested in a single factor ANOVA is that the means of two or more populations are equal (Chalmer, 1987).

\[ H_o: \mu_1 = \mu_2 = \mu_3 = \mu_4 = \mu_5 = \mu_6 \quad (2) \]

where: $\mu$ = sample mean

Therefore, the alternative hypothesis ($H_a$) is that at least one of the means differs from the others.

\[ H_a: \mu_1 - \mu_2 - \mu_3 - \mu_4 - \mu_5 - \mu_6 \quad (3) \]

The single factor ANOVA is inherently a two-tailed test since one is trying to determine if there is a difference, in any direction, among the population means (Chalmer, 1987). A standard level of significance of five percent ($\alpha$ equal to 0.05) was chosen. The decision to reject or accept the null hypothesis is based on the comparison of the computed F statistic to F critical. The F statistic is the ratio of the mean square between groups to the mean square within groups.

\[ MS_w = \frac{SS_w}{N - k} \quad (4) \]

where: $MS_w$ = mean square within groups

$SS_w$ = sum of squares within groups

N = total number data points

k = number of groups

\[ MS_b = \frac{SS_b}{k - l} \quad (5) \]
where: \( MS_b = \) mean square between groups
\( SS_b = \) sum of squares between groups
\( k = \) number of groups

The numerator of the F statistic is thus influenced by the observed differences between the groups, while the denominator represents the error term since it is derived from variation within groups (Ary and Jacobs, 1976). As the difference among the groups increases, the F statistic increases. F critical is a tabulated value and represents the rejection region of the F distribution as specified by the alpha value. If the F statistic does not exceed F critical, the null hypothesis is retained. Conversely, if the F statistic exceeds F critical one would reject the null hypothesis of equal population means. For example, when testing whether the mean of the methanogenic BOD values among the regions are equal, F\(_{\text{stat}} < F_{\text{crit}}\) indicates that the null hypothesis of equal BOD means cannot be rejected. Table 4 lists each parameter for which the ANOVA test was performed. The regions that had missing data for various parameters are indicated. Therefore, these regions could not be included in this test.

Table 4. Regions missing data and were not included in the ANOVA test.

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<tr>
<th>Parameter</th>
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<th>Methanogenic</th>
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<td>Ft Myers</td>
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</tr>
<tr>
<td></td>
<td>Pensacola</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>Orlando</td>
<td>Pensacola</td>
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<td></td>
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3.5.2 Hypothesis Testing

It is possible that the ash and pond data differ from the general leachate values. The waste composition at a primarily ash fill can be quite different from a landfill receiving only MSW. Also, the biological and chemical processes occurring within leachate ponds could produce differences in leachate quality as compared to leachate samples from a sump or pipe. A method analogous to proof by contradiction is used in hypothesis testing. The theory to be proven is the alternative hypothesis. $H_a$ was that the means of the parameters for the ash or pond data differ from the means of the general leachate data.

$$H_a : \mu_1 - \mu_2$$

The null hypothesis was that the mean values of each parameter are equal.

$$H_o : \mu_1 = \mu_2$$

Hypothesis testing computes the likeliness of the results if the null hypothesis were true (Chalmer, 1987). If such results would have been unlikely, it can be concluded that the null hypothesis must not be true, and statistically the alternative has been proven (Chalmer, 1987). Once again a two-tailed test was employed because the researcher was interested in a deviation from the null hypothesis in either direction. An alpha value of 0.05 was used. Appendix A contains an example hypothesis test.

The shape of the population distribution was unknown. However, based on the central limit theorem, the normal distribution is often used to describe uncertainty about sample means when the sample size is large, even though the population distribution may not be normal (Middleton, 1995). A common guideline is that 30 or more data points is considered "large" (Middleton, 1995; Mendenhall and Sincich, 1992). Thus, a normal distribution was used when a parameter had a sample size of 30 or more. A t distribution is often used for testing parameters which have less than 30 data points. The t distribution is used for analyzing small samples, even when the shape of the population distribution is unknown (Middleton, 1995). The test statistic for a normal distribution and a t distribution are the z statistic and t statistic, respectively.

Hypothesis testing uses the same decision approach as the ANOVA test. If the $z_{stat}$ or $t_{stat}$ is less than $z_{crit}$ or $t_{crit}$, the null hypothesis cannot be rejected. Table 5 lists the parameters which did not have any data available and for which no testing was conducted.

Hypothesis testing was also employed to determine if parameter means for the Florida data differed from the parameter means obtained from Browning-Ferris Industries (BFI) landfill data (see Appendix B). The BFI leachate quality data were from approximately sixty landfills across the continental United States. This data set represented leachate values nationwide. The
null hypothesis stated that the means of each parameter were equal (i.e. $\mu_1 = \mu_2$). For example, the Florida BOD mean is equal to the BFI BOD mean. Since, BFI did not report separate methanogenic and acidogenic data, the two phases of Florida data were combined to perform this test. The same testing methods were used as described previously.

In addition, the mean values from the acidogenic and methanogenic phase were compared to learn whether the concentrations of each parameter differed between the two phases. The null hypothesis tested was that the mean of the acidogenic data is equal to the mean of the methanogenic data (i.e. $\mu_1 = \mu_2$).

### 3.5.3 Combined Conventional Parameter Analysis

A scoring technique was developed in order to perform a cluster analysis of the data. The cluster analysis grouped all the conventional parameter data from each landfill into a single value or score. However, the data remained separated by phase. Each landfill received a score for each parameter. The individual scores were summed and this value was the total landfill score.

The following method was used as a means of assigning landfill scores. Five categories were established for each parameter. The data for each parameter were sorted and then divided into five equal groups (i.e. twenty percent of the data fell into each group). These groups were used as the range for each category. Table 6 lists the categories developed for each parameter. Each parameter received a score based on which category its mean fell into. The five categories were assigned the scores one through five. For example, any mean which fell into category one was assigned a score of one, and a score of two was assigned to all values which fell into category two, etc. The scores for each parameter were summed to produce a total score for each landfill. Numerous fills had no data for various parameters. Therefore, the total score was divided by the number of parameters for which there were data to obtain a normalized score.

Single-factor analysis of variance was used to determine if the normalized scores differed among the regions. The ash data were not included. The null hypothesis tested was that the mean score of each region was equal. The same method and level of significance were used as described previously.
Table 6. Categories computed for each parameter

<table>
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<th>Category</th>
<th>BOD$_5$</th>
<th>COD</th>
<th>Ammonia</th>
<th>Sulfate</th>
<th>Chloride</th>
<th>pH</th>
<th>Mn</th>
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<th>Sulfate</th>
<th>Chloride</th>
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<td>&lt; 0.010</td>
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<td>515 – 860</td>
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<td>16 – 43</td>
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<td>7.1 – 7.3</td>
<td>0.18 – 0.31</td>
<td>0.031 – 0.070</td>
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<td>4</td>
<td>72 – 109</td>
<td>861 – 1290</td>
<td>181 – 376</td>
<td>44 – 98</td>
<td>555 – 1070</td>
<td>7.4 – 7.6</td>
<td>0.32 – 0.71</td>
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<tr>
<td>5</td>
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<td>&gt; 1290</td>
<td>&gt; 376</td>
<td>&gt; 98</td>
<td>&gt; 1070</td>
<td>&gt; 7.6</td>
<td>0.71</td>
<td>&gt; 0.15</td>
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CHAPTER 4
RESULTS AND DISCUSSION

4.1 INTRODUCTION

Presented in this chapter are the results of statistical and graphical analyses directed at the characterization of Florida MSW landfill leachate. Tests were designed to identify trends in the data and to determine the effects of climate, region or location, age of the fill, and waste characteristics on leachate quality.

4.2 CHRONOLOGICAL ANALYSIS

BOD and COD are used to measure the organic content in leachate. Typically, the concentration of these constituents will be low initially and will increase as waste begins to solubilize. A decline in BOD and COD concentrations is often observed as organic matter is being removed via washout and degradation.

The Florida leachate data, however, showed no observable increasing and decreasing trend in BOD concentrations (see Figure 8). BOD values ranged from 0.3 to 4800 mg/L. The range in BOD concentrations was an order of magnitude lower than values reported in the literature and obtained from BFI (Ehrig, 1989; Chian and DeWalle, 1977; Pohland and Harper, 1985; Qasim and Chiang, 1994). The magnitude of both the BOD and COD concentrations was low (less than 1500 mg/L). The Florida climate (e.g. heavy rainfall) appears to produce dilute leachate, maintaining BOD concentrations at relatively low levels compared to nationwide (see Table 2, Chapter 2) and BFI BOD values. Slightly higher BOD levels were observed between years 2 and 4, possibly from the opening of new cells. Waste is placed in one cell at a time within a landfill facility until the capacity of the cell is reached, which usually occurs after 2 to 5 years (Reinhart, 1996). Then a new cell becomes active. Usually the leachate collection system combines the leachate from all the cells. As a new cell becomes active, higher BOD concentrations in the leachate are expected due to the addition of solubilized organic matter.

Results of the nonlinear regression analysis found that Equation 1 (Chapter 3) did not accurately describe the BOD data as evidenced by the low R² value (0.005). The KURV+ program was also unable to fit an equation to the data. Therefore, from these results there appears to be no chronological pattern in Florida BOD concentrations. This is likely due to dilution and the difficulty associated with determining the age of each landfill.

COD values ranged from 7 to 50,000 mg/L. The COD concentrations of young leachate were generally less than 1500 mg/L (see Figure 9). Most Florida COD concentrations were an order of magnitude lower than literature and BFI values. As with BOD, efficient waste degradation due to the moist and warm Florida climate can explain the low COD concentrations observed. High gas production during the early years of landfill operation would also suggest effective decomposition of organic matter. Findings by Palumbo (1995) show that gas
Figure 8. BOD data compiled from all the landfills versus time.
Figure 9. COD data compiled from all the landfills versus time.
production early in the life of Florida landfills can be significant indicating that there is an efficient conversion of organic matter to gas within Florida fills. Furthermore, according to Bookter and Ham (1982), waste degradation is considered sufficiently complete when the BOD to COD ratio is less than 0.1. The average BOD to COD ratio for the Florida leachate data was 0.11, another indication that there is efficient degradation of waste in Florida landfills due to the moist warm climate. Therefore, dilution due to heavy rainfall and conversion of organics to gas appear to maintain COD and BOD concentrations at low levels (less than 2000 mg/L).

Figure 10 presents all COD data excluding South Dade Shredded Landfill. Comparison of Figure 9 and 10 shows that a majority of the high (greater than 2000 mg/L) COD detections occurred at South Dade Shredded Landfill. Two of the highest BOD concentrations occurred at this landfill as well. This observation suggests that shredded waste produces a higher strength leachate due to an increase in surface area and, consequently, increased rates of dissolution and biodegradation (Lu et al., 1985). Table 7 shows that the average BOD and COD concentrations are lower when South Dade Shredded Landfill data are excluded from the calculations which further suggests that shredding waste produces higher strength leachate. A hypothesis test was used to determine if the mean BOD and COD values differed statistically with and without the South Dade Shredded Landfill data. The null hypothesis of equal means could not be rejected for BOD. This is probably due to the fact that there were few BOD data available for South Dade Shredded Landfill. However, it was determined that the mean COD values were not equal.

Table 7. Comparison of mean BOD and COD values with and without South Dade Shredded Landfill.

<table>
<thead>
<tr>
<th>Landfill Data</th>
<th>BOD (mg/L)</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>178</td>
<td>1780</td>
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<tr>
<td>Excluding South Dade Shredded Landfill</td>
<td>141</td>
<td>972</td>
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</table>

The nonlinear regression analysis using SYSTAT was unable to converge when estimating the parameters in Equation 1 (Chapter 3) due to the scatter in the data. The KURV+ program was also unable to accurately fit an equation to the COD data as evidenced by correlation coefficients less than 0.037. As with BOD, these findings suggest we were unable to discern a chronological pattern in Florida COD concentrations. Again, this may be attributed to dilution, problems associated with determining the age of each landfill, and difficulty in defining an initial reactant concentration.

**4.3 TOXIC AND ORGANIC PARAMETERS**

Forty-five toxic and organic constituents were consistently detected in the leachate from all the landfills. Tables 8 and 9 list the number of detections, the means, and standard deviations.
Table 8. Comparison of acidogenic and methanogenic statistical results for the toxic and organic compounds

<table>
<thead>
<tr>
<th>Parameter, µg/L</th>
<th>Detects</th>
<th>Mean</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
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<td>Acid</td>
<td>Meth</td>
<td>Acid</td>
</tr>
<tr>
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<td>111</td>
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BDL – below detection limits
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BDL – below detection limits
Table 9. Statistical Results for toxic and organic compounds

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BDL – below detection limits
<table>
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<th>Parameter, µg/L</th>
<th>Detects</th>
<th>Mean</th>
<th>Standard Deviation</th>
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<tr>
<td>Napthalene</td>
<td>64</td>
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</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>117</td>
<td>0.0657</td>
<td>0.459</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>143</td>
<td>5.69</td>
<td>37.5</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>207</td>
<td>4.31</td>
<td>12.1</td>
</tr>
<tr>
<td>Xylene</td>
<td>212</td>
<td>52.5</td>
<td>83.9</td>
</tr>
</tbody>
</table>

BDL – below detection limits
for each parameter for the acidogenic phase, methanogenic phase, and for all the data. When evaluating these data, a detection was often more significant than mean values because the concentration of these parameters was generally on the order of micrograms per liter and many constituents were reported as non-detections. Comparing the number of detections in each phase clearly showed a significantly higher number of detections in the methanogenic phase for every parameter. This same result was observed when the data were separated into four categories: chlorinated compounds, aromatics, heavy metals, and miscellaneous constituents (parameters that could not be classified into the previous groups) (see Table 10). The higher number of detections in the methanogenic phase is most likely because there were more data available in this phase. Only limited data were reported for many landfills. Therefore, when the data were divided into phases, numerous landfills had data available from the methanogenic phase only.

Table 9 shows that the organic compounds with the highest concentrations are the aromatic constituents (e.g. phenol, xylene, toluene, and ethylbenzene). Aromatic hydrocarbons such as xylene, toluene, and ethylbenzene often originate from petroleum products such as gasoline and fuel oils which are common landfill contaminants (Schultz and Kjeldsen, 1986; Harmsen, 1983). The high concentrations of phenol may be attributed to the fact that this compound is a plant derivative. Heavy metal levels remain at low concentrations (less than 1 mg/L) due to direct reduction to the element (for Hg), precipitation by reductively generated sulfide (Cd, Pb, and Ni), and adsorption as observed by Gould et al. (1989). Table 10 indicates that chlorinated compounds are detected more frequently in both phases than heavy metals, aromatics, or the miscellaneous constituents. These chlorinated compounds are either solvents or degradation byproducts of solvents which are widely used.

Table 10. Categorized detections of toxic and organic compounds.

<table>
<thead>
<tr>
<th>Category</th>
<th>Acidogenic</th>
<th>Methanogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metals</td>
<td>423</td>
<td>1480</td>
</tr>
<tr>
<td>Aromatics</td>
<td>292</td>
<td>1277</td>
</tr>
<tr>
<td>Chlorinated compounds</td>
<td>335</td>
<td>2259</td>
</tr>
<tr>
<td>Miscellaneous constituents</td>
<td>20</td>
<td>210</td>
</tr>
</tbody>
</table>

The fate of organic compounds is greatly affected by the extent of interaction with the solid phase. Sorption decreases the mobility of contaminants. Sorption can be defined as the interaction of a contaminant with a solid (Piwoni and Keeley, 1990). The properties of a contaminant have a profound impact on its sorption behavior. The octanol-water partition coefficient ($K_{ow}$) indicates the tendency of a compound to sorb. $K_{ow}$ quantifies the distribution of a chemical between octanol and water in contact with each other under equilibrium conditions (Bedient et al., 1994). In general, $K_{ow}$ is a measure of the hydrophobicity of an organic compound. The more hydrophobic the contaminant is, the more likely it is to partition onto soils or, in this case, the solid waste (Bedient et al., 1994).
Where possible, octanol-water partition coefficients were assigned to organic compounds found at landfills. The twenty-seven compounds for which $K_{ow}$ values could be found are listed in Table 11 (Verschueren, 1983; Nyer, 1993). Eighty-one percent of the compounds had log $K_{ow}$ values less than 3.5 and nineteen percent of the organic constituents had log $K_{ow}$ values greater than 4. The five compounds with log $K_{ow}$ values greater than 4 (extremely hydrophobic compounds) were present at concentrations less than 1 $\mu$g/L or were frequently reported as non-detections. This suggests that mobility of the organic constituents is decreasing with increasing hydrophobicity as measured by $K_{ow}$.

4.4 CONVENTIONAL PARAMETERS

The number of detections, mean, minimum, maximum, and standard deviation were computed for each constituent. These descriptive statistical parameters were calculated for several landfill groupings (i.e. each landfill, each FDEP district, the pond leachate data, the ash landfill leachate data, and the general leachate data). Most of the statistical parameters computed were used to perform the ANOVA and hypothesis tests. The descriptive statistical results are presented in Table 12 and Appendix C. In general, Florida leachates appeared quite dilute compared to the mean values reported in the literature and obtained from BFI.

The cumulative percentage distributions are presented in Appendix D. All the distributions of the conventional parameters with the exception of pH show a rapid increase in the cumulative percentage (i.e. positively skewed distribution). This observation illustrates that a preponderance of the Florida leachate data tend to be at the lower end of the concentration values while the extreme detections are at the high end, again indicating that Florida landfills produce weak leachate. Since a majority of the pH detections were greater than or equal to 7, the distribution was negatively skewed.

4.4.1 Analysis of Variance

Results of the ANOVA test found no differences in the conventional parameters among the regions except for ammonia in the methanogenic phase. This suggests that any variation in climate or waste composition among the regions does not significantly affect leachate quality.

Variations in the regions may exist, however due to the scatter in the data, as evidenced by the high standard deviations (see Table 12), they were not statistically significant. The difference in ammonia may be explained by the fact that much of the ammonia content in leachate is derived from organic material, especially yard waste. A Florida rule enacted on January 1, 1992 banning the disposal of yard waste in lined MSW landfills, could possibly have affected ammonia concentrations. However, it is difficult to predict how the ban on yard waste impacted ammonia levels because of the variations in landfill age within each region.
Table 11. $\text{Log } K_{\text{ow}}$ values of organic compounds found in Florida leachate

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\text{log } K_{\text{ow}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.1</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>6.1</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>6.5</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2.4</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.8</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>1.5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>2.0</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>3.4</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>3.4</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>3.4</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>1.8</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1.5</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>1.8</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>3.1</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>4.4</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>5.2</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>4.6</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>1.3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3.4</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>1.8</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.5</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>2.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.1</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>2.5</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>2.4</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>1.4</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.9</td>
</tr>
<tr>
<td>Type of Data</td>
<td>Acidogenic, mg/L</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td>BOD₅</td>
</tr>
<tr>
<td><strong>Pond</strong></td>
<td></td>
</tr>
<tr>
<td>Detects</td>
<td>0</td>
</tr>
<tr>
<td>Mean</td>
<td>---</td>
</tr>
<tr>
<td>Median</td>
<td>---</td>
</tr>
<tr>
<td>Minimum</td>
<td>---</td>
</tr>
<tr>
<td>Maximum</td>
<td>---</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>---</td>
</tr>
<tr>
<td><strong>Ash</strong></td>
<td></td>
</tr>
<tr>
<td>Detects</td>
<td>1</td>
</tr>
<tr>
<td>Mean</td>
<td>462</td>
</tr>
<tr>
<td>Median</td>
<td>595</td>
</tr>
<tr>
<td>Minimum</td>
<td>595</td>
</tr>
<tr>
<td>Maximum</td>
<td>595</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>---</td>
</tr>
<tr>
<td><strong>General Leachate</strong></td>
<td></td>
</tr>
<tr>
<td>Detects</td>
<td>52</td>
</tr>
<tr>
<td>Mean</td>
<td>462</td>
</tr>
<tr>
<td>Median</td>
<td>595</td>
</tr>
<tr>
<td>Minimum</td>
<td>595</td>
</tr>
<tr>
<td>Maximum</td>
<td>595</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>---</td>
</tr>
</tbody>
</table>

"---" – no data available for this parameter
BDL – below detection limits
4.4.2 Hypothesis Testing

Hypothesis testing was employed to determine whether the means of the ash data differed statistically from the means of the general leachate data (all the data excluding pond and ash data). The results of these tests are shown in Table 13. The null hypothesis was that the mean values for each parameter are equal (i.e. \( \mu_1 = \mu_2 \)). Therefore, a rejection of the null hypothesis would prove that the means of the parameters differed from each other. Table 13 also lists the p-value (probability value) for each test and which type of leachate had the higher mean value for the parameters where \( H_0 \) was rejected. The p-value is another way to summarize the results from a hypothesis test. When calculating the p-value, the assumption is made that the null hypothesis is true and then the sample evidence is considered. If the sample evidence is found to be very

Table 13. Results of hypothesis testing comparing the means of the ash and general data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acidogenic Results (p-value)</th>
<th>Type of Leachate with Higher Mean Value</th>
<th>Methanogenic Results (p-value)</th>
<th>Type of Leachate with Higher Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>No data available</td>
<td>NA</td>
<td>Reject ( H_0 ) (7.48 \times 10^{-14})</td>
<td>General</td>
</tr>
<tr>
<td>COD</td>
<td>Reject ( H_0 ) (0.0032)</td>
<td>General</td>
<td>Reject ( H_0 ) (0.00)</td>
<td>General</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Reject ( H_0 ) (0.00)</td>
<td>General</td>
<td>Reject ( H_0 ) (0.00)</td>
<td>General</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Accept ( H_0 ) (0.254)</td>
<td>NA</td>
<td>Accept ( H_0 ) (0.132)</td>
<td>NA</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Accept ( H_0 ) (0.0598)</td>
<td>NA</td>
<td>Reject ( H_0 ) (0.0146)</td>
<td>Ash</td>
</tr>
<tr>
<td>pH</td>
<td>Reject ( H_0 ) (4.24 \times 10^{-5})</td>
<td>General</td>
<td>Accept ( H_0 ) (0.524)</td>
<td>NA</td>
</tr>
<tr>
<td>Manganese</td>
<td>Reject ( H_0 ) (1.78 \times 10^{-17})</td>
<td>General</td>
<td>Reject ( H_0 ) (3.73 \times 10^{-5})</td>
<td>General</td>
</tr>
<tr>
<td>Zinc</td>
<td>Reject ( H_0 ) (2.22 \times 10^{-12})</td>
<td>General</td>
<td>Reject ( H_0 ) (1.13 \times 10^{-14})</td>
<td>General</td>
</tr>
</tbody>
</table>

\( H_0 \) - null hypothesis which was that the mean values of each parameter are equal, \( \mu_1 = \mu_2 \)
General - all the data excluding pond and ash data
NA - not applicable
\( \alpha = 0.05 \)
improbable based on $H_0$, the null hypothesis is assumed incorrect and is rejected (Ary and Jacobs, 1976). For example, a small p-value is associated with a sample mean that is significantly different from the hypothesized mean (Middleton, 1995).

BOD and COD concentrations are a measure of the organic content in leachate. Ammonia present in leachate often originates from organic matter. Therefore, it is expected that the BOD, COD, and ammonia concentrations would be lower in the leachate from ash fills due to the lack of organic matter in MSW incinerator ash.

Roffman and Bradford (1982) conducted a study which characterized leachates from codisposal sites. This research suggested that the neutral pH of MSW leachates does not promote leaching of metals from municipal waste combustion ashes. This observation could explain the lower levels of manganese and zinc in ash leachates.

Most of the landfills receiving ash were codisposal sites. Results of the hypothesis tests suggest that codisposal of ash with MSW does not adversely affect sulfate concentrations. Hypothesis testing produced different results for chlorides and pH among the two phases. Chloride levels were elevated in the ash leachate in the methanogenic phase because of the high inorganic content of ash. However, no differences in chloride concentrations were detected in the acidogenic phase. The higher level of chlorides in the methanogenic phase for the ash leachate may be due to the fact that MSW has less inorganic (chloride) material to leach and therefore chloride levels decrease as the landfill ages.

Similar tests were conducted to compare leachate obtained from ponds and general leachate (all the data excluding pond and ash data). $H_0$ states that the means of each parameter are equal (i.e. $\mu_1 = \mu_2$). Table 14 summarizes the results. The many differences observed between these two types of leachate are most likely caused by the large variations in leachate quality. However, lower concentrations of ammonia in the pond leachate may suggest that some nitrification is occurring in the leachate ponds. Exposing the leachate to the atmosphere could cause some removal of carbon dioxide from the leachate which tends to raise the pH. Also, the higher mean pH levels of the pond data may be the result of carbon dioxide being utilized by algae.

Hypothesis testing was also employed to determine if the parameter means for the Florida data differed from the BFI landfill data. The null hypothesis was that the means of each parameter were equal (i.e. $\mu_1 = \mu_2$). Since, BFI did not report separate methanogenic and acidogenic data, the two phases of the Florida data were combined to perform this test. Table 15 presents the results of these analyses. A majority of the parameters differed statistically from the BFI data. The mean ammonia and zinc levels in Florida leachate data appeared to be similar to the BFI data. The Florida leachate had significantly lower concentrations of BOD, COD, sulfate, chloride, and manganese compared to the BFI landfill data. This finding further substantiates the theory that Florida leachate is weak compared to nationwide values due to the dilution from heavy rainfall. The BFI to Florida ratio for BOD is significantly higher than all the other parameter ratios.
Table 14. Results of hypothesis testing comparing the means of the pond and general data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acidogenic Results (p-value)</th>
<th>Type of Leachate with Higher Mean Value</th>
<th>Methanogenic Results (p-value)</th>
<th>Type of Leachate with Higher Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>No data available</td>
<td>NA</td>
<td>Accept H₀ (0.893)</td>
<td>NA</td>
</tr>
<tr>
<td>COD</td>
<td>No data available</td>
<td>NA</td>
<td>Accept H₀ (0.151)</td>
<td>NA</td>
</tr>
<tr>
<td>Ammonia</td>
<td>No data available</td>
<td>NA</td>
<td>Reject H₀ (0.00)</td>
<td>General</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Accept H₀ (0.711)</td>
<td>NA</td>
<td>Accept H₀ (0.642)</td>
<td>NA</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Reject H₀ (0.0179)</td>
<td>General</td>
<td>Accept H₀ (0.150)</td>
<td>NA</td>
</tr>
<tr>
<td>pH</td>
<td>Reject H₀ (0.00)</td>
<td>Pond</td>
<td>Reject H₀ (0.00)</td>
<td>Pond</td>
</tr>
<tr>
<td>Manganese</td>
<td>Accept H₀ (0.280)</td>
<td>NA</td>
<td>Accept H₀ (0.298)</td>
<td>NA</td>
</tr>
<tr>
<td>Zinc</td>
<td>Accept H₀ (0.227)</td>
<td>NA</td>
<td>Reject H₀ (1.52 x 10⁻¹²)</td>
<td>General</td>
</tr>
</tbody>
</table>

H₀ - null hypothesis which was that the mean values of each parameter are equal, μ₁ = μ₂
General - all the data excluding pond and ash data
NA - not applicable

α = 0.05

suggesting that waste degradation is more efficient within Florida landfills due to the warm moist climate. Mean pH levels were statistically higher in the Florida data (pH equal to 7.34) compared to the BFI data (pH equal to 6.40). This may be explained by the fact that Florida soils used as daily or intermediate cover have a high limestone content. The carbonate leached from the limestone may act as a buffer and, consequently, pH values are maintained near neutrality.

The mean values from the acidogenic and methanogenic phase were compared to determine whether the concentrations of each parameter differed between the two phases. Again, the H₀ tested was that the mean of the acidogenic data is equal to the mean of the methanogenic data (i.e. μ₁ = μ₂). The findings from these tests are listed in Table 16. The concentration of some parameters differ between phases while the level of other parameters remain relatively constant. The highest concentrations of BOD and COD are expected in the acid formation
Table 15. Results of hypothesis testing comparing the means of the Florida and BFI data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results</th>
<th>Leachate with Higher Mean Value</th>
<th>BFI to Florida Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>Reject $H_0$</td>
<td>BFI</td>
<td>19</td>
</tr>
<tr>
<td>COD</td>
<td>Reject $H_0$</td>
<td>BFI</td>
<td>3.7</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Accept $H_0$</td>
<td>NA</td>
<td>1.0</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Reject $H_0$</td>
<td>BFI</td>
<td>2.6</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Reject $H_0$</td>
<td>BFI</td>
<td>2.7</td>
</tr>
<tr>
<td>pH</td>
<td>Reject $H_0$</td>
<td>Florida</td>
<td>0.87</td>
</tr>
<tr>
<td>Manganese</td>
<td>Reject $H_0$</td>
<td>BFI</td>
<td>2.7</td>
</tr>
<tr>
<td>Zinc</td>
<td>Accept $H_0$</td>
<td>NA</td>
<td>0.85</td>
</tr>
</tbody>
</table>

$H_0$ - null hypothesis which was that the mean values of each parameter are equal, $\mu_1 = \mu_2$

NA - not applicable

$\alpha = 0.05$

The metal content (Mn and Zn) of the leachate did not appear to differ statistically between the phases. Lu et al. (1985) stated that there is an absence of an apparent trend in heavy metal concentrations. Whereas the release of organic indicators is closely tied to the stages of waste stabilization, heavy metals do not show this behavior (Lu et al., 1985). The absence of trends may be attributed to precipitation, dissolution, adsorption, or complexation mechanisms.
Table 16. Results of hypothesis testing comparing the means of the acidogenic and methanogenic phase.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results</th>
<th>Phase with Higher Mean Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>Reject $H_0$</td>
<td>Acidogenic</td>
</tr>
<tr>
<td>COD</td>
<td>Reject $H_0$</td>
<td>Acidogenic</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Reject $H_0$</td>
<td>Acidogenic</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Reject $H_0$</td>
<td>Acidogenic</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Accept $H_0$</td>
<td>NA</td>
</tr>
<tr>
<td>pH</td>
<td>Reject $H_0$</td>
<td>Acidogenic</td>
</tr>
<tr>
<td>Manganese</td>
<td>Accept $H_0$</td>
<td>NA</td>
</tr>
<tr>
<td>Zinc</td>
<td>Accept $H_0$</td>
<td>NA</td>
</tr>
</tbody>
</table>

$H_0$ - null hypothesis which was that the mean values of each parameter are equal, $\mu_1 = \mu_2$

NA - not applicable

$\alpha = 0.05$

which can retain or mobilize metals within the landfill. These mechanisms are often difficult to predict.

4.4.3 Combined Conventional Parameter Analysis

The combined parameter analysis grouped all the conventional parameter data from each landfill into a single value or score. Each landfill received a score for each parameter. The scores were summed and normalized based on the number of parameters for which there were data. Due to the lack of acidogenic data, this phase was not included in the cluster analysis. South Dade Shredded Waste Landfill has the highest score among all the landfills (see Table 17). This again shows that shredded waste produces a higher strength leachate than unshredded waste.

The normalized scores developed from the cluster analysis were used to determine if scores differed among the various regions of the state. Results of the cluster analysis indicated that the mean scores differed among the regions. This contradicts the results of the ANOVA test conducted for each parameter which found no differences in the conventional parameters among the regions except for ammonia in the methanogenic phase. As seen from Table 12, the standard deviations for the parameters are high. This is most likely the reason that the parameter ANOVA tests indicated Florida leachate quality is not affected by geographical location. The cluster analysis is not as sensitive to the scatter in the data, and shows that differences do exist among the
Table 17. Scores for methanogenic phase.

<table>
<thead>
<tr>
<th>Landfill</th>
<th>BOD₅</th>
<th>COD</th>
<th>Ammonia</th>
<th>Sulfate</th>
<th>Chloride</th>
<th>pH</th>
<th>Mn</th>
<th>Zn</th>
<th>Total</th>
<th>Normalized Score</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jacksonville</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Duval</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>---</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>23</td>
<td>3.29</td>
</tr>
<tr>
<td>Putnam Co. Central</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>32</td>
<td>4.00</td>
</tr>
<tr>
<td>Southwest Alachua</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>---</td>
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regions. Therefore, it may be important to use regional data instead of statewide values when designing leachate management facilities.

Figure 11 displays the mean scores of each region throughout the state. Interestingly, the mean scores of the landfills in the eastern portion of the state (Jacksonville and West Palm districts) are higher than the western (Pensacola, Tampa, and Ft Myers districts) with the central area (Orlando district) having the lowest score. It should also be noted that all the scores of the western districts are similar to each other. The mean score of the West Palm region is affected by the very high score for South Dade Shredded Landfill which tends to skew the regional value.

Figure 11. Regional mean scores.

4.5 AFFECTS ON LEACHATE TREATMENT
The quality of leachate directly affects the viable leachate treatment alternatives. When used separately, neither biological treatment nor physical/chemical treatment processes are able to achieve high removal efficiencies (Keenan et al., 1984; Forgie, 1988; Copa et al., 1995). A combination of both types of treatment is the most effective process train for the treatment of leachate (Copa et al., 1995; Forgie, 1988). Florida leachate appears to have low concentrations of organic constituents (e.g. BOD and COD) consequently requiring primarily physical/chemical rather than biological treatment. Physical/chemical processes have been proven effective in the treatment of stabilized leachate (Qasim and Chiang, 1994). Furthermore, Chian and DeWalle (1977) found that biological processes produced poor results in the treatment of leachates with a BOD to COD ratio less than 0.1. However, physical/chemical processes such as reverse osmosis and carbon adsorption are effective in the treatment of leachates with low concentrations of organic matter. The average BOD to COD ratio for Florida leachate was 0.11. The dilute nature of Florida leachate indicates that disposal of leachate at a wastewater treatment plant (WWTP) would not adversely affect plant operations. Therefore, codisposal of Florida leachate and domestic wastewater could provide a viable and cost effective means of leachate treatment.
SECTION 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The purpose of this research was to characterize Florida landfill leachate. MSW lined landfill leachate quality data were acquired from the Florida Department of Environment Protection files. In addition, the study employed national data obtained from Browning-Ferris Industries for comparison with Florida leachate data. Various graphical and statistical techniques such as chronological analysis, hypothesis testing, analysis of variance, and cluster analysis were used to characterize Florida leachates. In general, the Florida climate (e.g. heavy rainfall and warm temperatures) appears to produce dilute leachate, maintaining leachate concentrations at relatively low levels compared to literature values and BFI landfill data. The following conclusions may be drawn from results of this research:

1. BOD and COD concentrations appear to remain low (less than 1500 mg/L) throughout the life of the landfill, most likely due to dilution and stimulation of methanogenesis. The stimulation of methanogenesis is supported by elevated pH in the acidogenic phase, higher BFI to Florida ratio for BOD relative to the other parameters, low BOD concentrations and significant gas production during the early years of landfill operation. No clearly determined chronological pattern in BOD and COD concentrations was observed.

2. Leachate from the shredded waste fill has significantly higher concentrations of organic pollutants than leachate from the unshredded waste landfills as evidenced in the high COD and BOD levels from the South Dade Shredded Landfill.

3. A wide variety of toxic and organic compounds can be found in Florida landfill leachate. However, the concentration of these constituents is generally on the order of micrograms per liter.

4. Codisposal of ash with MSW does not appear to adversely impact leachate quality. Concentrations of heavy metals, BOD, COD, and ammonia in leachate from codisposal sites were not statistically higher than values reported for MSW sites. Chloride values were elevated in the ash leachate in the methanogenic phase because of the high chloride content of ash.

5. Florida leachates seem to be dilute compared to national landfill data obtained from BFI.

5.2 RECOMMENDATIONS
It was difficult compiling and analyzing the data obtained from the FDEP. Values for critical parameters such as BOD and COD were often missing. Also, many landfills only had available data for very limited periods of landfill operation. The limitations of the data could possibly affect the accuracy of the results. It is recommended that the FDEP require landfill sites to submit leachate data on disk in a standard format. This procedure would help reduce the quantity of missing data and would develop a complete database of all Florida leachate quality data. It would be ideal to have leachate data for many landfills from the time waste was first placed in the lined portions of the landfill. Further research of Florida leachate quality data is recommended using a more complete data set in order to develop more detailed time relationships for the organic as well as inorganic parameters. Extensive chronological analysis would aid in the design and operation of landfill systems and leachate treatment facilities. In addition, an improved database of operating parameters such as age of the landfill, waste composition, and depth of waste would be useful in identifying the affects of these site specific parameters on Florida leachate quality.

Florida leachate has low concentrations of organic constituents (e.g. BOD and COD) consequently requiring primarily physical/chemical rather than biological treatment. Because it is dilute codisposal of Florida leachate and domestic wastewater at a WWTP would not adversely effect the WWTP. However, limited treatment of leachate constituents except for ammonia can be expected. Therefore, this method is suggested as a means of leachate treatment.

It is also recommended that an analysis of leachate quantities be conducted. This research could confirm that the nature of leachate produced at Florida landfills is a result of dilution from heavy rainfall, high degradation rates, or both. In addition, development of a more refined cluster analysis technique which incorporates standard deviations and complete data sets is suggested.
SECTION 6
REFERENCES


D.J.L. Forgie, "Selection of the most appropriate leachate treatment methods part 3: A


Appendix A

Examples of Statistical Analyses
Table A.1 ANOVA for acidogenic BOD$_5$ and COD.

**Acidogenic BOD$_5$**

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**ANOVA**  

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<th>P-value</th>
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The computed F statistic does not exceed F critical.  
Therefore, the null hypothesis of equal BOD$_5$ values among the regions cannot be rejected.

**Acidogenic COD**

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**ANOVA**  

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The computed F statistic does not exceed F critical.  
Therefore, the null hypothesis of equal COD values among the regions cannot be rejected.
Table A.2 Hypothesis test for acidogenic COD.

Using t Distribution
H₀: mean non-ash data = mean ash data

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Appendix B

Browning-Ferris Industries Leachate Data
## Table B.1 Browning-Ferris Industries leachate data

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Appendix C

Descriptive Statistics for the Conventional Parameters
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"---" – no data available for this parameter
Appendix D

Cumulative Percentage Distributions
Figure D.2 Cumulative percentage distribution for COD.
Figure D.3: Cumulative percentage distribution for ammonia.
Figure D.4 Cumulative percentage distribution for sulfate.
Figure D.5 Cumulative percentage distribution for chloride.
Figure D.6 Cumulative percentage distribution for pH.
Figure D.7 Cumulative percentage distribution for manganese.
Figure D.8 Cumulative percentage distribution for zinc.