CHARACTERIZATION AND TREATMENT OF ORGANIC MATTER, UV QUENCHING SUBSTANCES, AND ORGANIC NITROGEN IN LANDFILL LEACHATES

Natalie Marie Driskill

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John T. Novak, Committee Chair
C. Douglas Goldsmith
Peter J. Vikesland

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ABSTRACT

Landfill leachates are often treated on-site before disposal to municipal wastewater treatment plants, although variations in leachate composition and organic loading continue to have negative impacts on downstream treatment processes. Leachate samples were collected from four landfills both before and after on-site treatment to evaluate the extent of biological treatment. The samples vary in age, location, and on-site treatment processes. Size fractionation utilizing microfiltration (MF) and ultrafiltration (UF) was conducted in conjunction with TOC, nitrogen species, and UV_{254} absorbance analysis to determine the characteristics of organic constituents present in landfill leachate. The size fraction less than 1thousand Daltons (1 kDa) was responsible for a predominant portion of the organic fraction of the landfill leachates studied. Humic substances are refractory components present in landfill leachates that are resistant to biological treatment and responsible for a portion of the UV quenching ability of leachates. Humic substances were also fractionated to humic acid (HA), fulvic acid (FA), and hydrophilic (Hpi) components before being subjected to size fractionation to determine UV_{254} absorbance and organic fractions. Particle size and hydrophobic-hydrophilic fractionation were conducted in series to evaluate the potential for membrane treatment after biological treatment as a cost effective alternative to reverse osmosis processes currently used to decrease the organic fractions present in landfill leachate. The organic nitrogen fraction was predominately in the hydrophilic fraction smaller than 1 kDa.

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1. Introduction

Annual increases in global population are associated with increased waste generation. Additional needs for waste collection and disposal are required for this waste. Municipal solid waste (MSW) is material composed of paper and paper board, food scraps, yard trimmings, plastics, metals, rubber, leather, textiles, wood, and glass. Recycling, composting, incineration, and landfilling are all waste disposal practices used worldwide. Landfilling continues to be the most popular practice for municipal waste management in the United States, with approximately 54.2% of the 250 million tons of the MSW generated in the US in 2010 disposed of in landfills (US EPA, 2011).

Landfilling is an established practice for MSW disposal because it is the cheapest alternative in terms of capital costs and minimizes environmental impacts. Landfills are also beneficial disposal mechanisms for MSW because they operate under engineered conditions to allow wastes to degrade into inert, stabilized solids (Renou et al., 2008). One of the environmental impacts created by decomposition in MSW landfills is landfill leachate. Leachate is generated as rain percolates through the landfill and combines with liquids created through waste decomposition. Leachate is characterized by high organic concentration and inorganic contaminants including ammonia nitrogen, heavy metals, xenobiotics, and inorganic salts (Wiszniowski et al., 2006). Dissolved organic matter, inorganic macro components, heavy metals, and xenobiotic organic compounds are the four major pollutant groups contained in landfill leachate. MSW landfills managers must include practices to collect and treat landfill leachate to prevent negative environmental impacts. Due to the extensive use of landfills for MSW management, there is a large quantity of leachate that needs to be collected and treated before being discharged from the landfill. Liners or leachate collection systems are required in order to prevent leachate from traveling uncontrolled into the environment and potentially polluting groundwater and surface water sources (Kjeldsen et al., 2002).

Landfill leachates are often discharged through municipal sewers or trucks to publicly owned treatment works (POTWs) after biological treatment because it is the most cost effective disposal practice. Contaminants in landfill leachates may have negative effects on downstream treatment processes at municipal wastewater treatment plants (WWTPs); therefore, landfill leachates need to be further evaluated after on-site biological treatment.

Many factors influence leachate quantity and composition. The precipitation and evaporation rates at the landfill associated with the climate have a large influence on volume of liquid leachate generated. Landfill age, seasonal weather variations, and waste types all greatly influence the quality of leachate (Renou et al., 2008). Due to differences between landfills, the quality and quantity of leachate can vary greatly between landfills. The characteristics of specific leachates may dictate the appropriate treatment methods to be used as well as treatment efficiencies.

Conventional treatments can be characterized as leachate transfer, biodegradation, and chemical or physical methods. Leachate transfer includes recycling leachate through the

landfill and combining treatment with domestic sewage, but questions about this method have been raised because inhibitory compounds present in leachate can hinder treatment efficiency. Biological treatment is utilized at many landfills because of its reliability, simplicity, and cost-effectiveness. Microorganisms biodegrade organic material through aerobic treatment and nitrogenous compounds can be treated by combined aerobic and anaerobic treatment of landfill leachates. Chemical and physical treatment methods are used to improve effluent quality, usually after biological treatment. As discharge requirements continue to become more restrictive to prevent additional nutrient loading in downstream systems, chemical and physical treatment methods will become a more prevalent component of landfill leachate treatment (Renou et al., 2008).

The objective of this study is to analyze the potential impacts of leachate disposal to municipal sewers on downstream WWTPs. The third chapter of this study includes analysis of organic matter in terms of TOC, organic nitrogen, and UV_{254} absorbance for four different landfill leachates of varied composition. Analysis was conducted before and after biological treatment in order to analyze the effectiveness of biological treatment and determine the impact of biological treatment on the organic nitrogen fraction. The fourth chapter of this study evaluates the hydrophobicity distribution of humic substances in relation to leachate age and size distribution of the organic constituents. The purpose of this portion of the study was to evaluate the UV quenching ability of individual humic substances in a variety of leachate samples and evaluate the potential downstream effects on UV disinfection processes.

2. Literature Review

2.1 Formation of Leachate

Proper waste management requires handling municipal wastes in a way that protects both the environment and public health. Landfilling is a widely used method of waste management because it is the cheapest form of waste management in terms of capital cost and it is associated with minimized environmental effects. Leachate disposal is a major environmental hazard associated with landfilling practices. Liquids produced from microbial decomposition combined with rain that percolates through landfill waste causes both inorganic and organic contaminants to transfer from the wastes to the liquid, creating the high strength aqueous solution known as landfill leachate (Renou et al., 2008); (Wiszniowski et al., 2006). Biological activity from waste decomposition that contributes to leachate formation may continue for 30-40 years after the landfill is closed; therefore, a large volume of leachate will be produced at each landfill that requires additional treatment before disposal to the environment (Robinson, 2005).

2.2 Leachate Composition

Many factors influence landfill leachate composition. The rate of precipitation and evaporation dictates the volume of leachate production from a landfill; therefore, climate and seasonal weather variations have a large impact on leachate production. The waste type and landfill age also greatly impact leachate composition (Renou et al., 2008). Humic substances are naturally occurring organic polyelectrolytes, and they are responsible for a large portion of organic matter present in landfill leachate. Humic substances are associated with trihalomethane formation during chlorine disinfection and the ability to bind with heavy metals and organic pollutants (Wu et al., 2010). Landfill leachate humic substances are also linked with UV quenching during UV disinfection, which limits the disinfection efficiency of downstream POTWs (Zhao et al., 2012). As landfill leachates age, the biodegradable fraction of organic matter in leachate decreases and recalcitrant humic substances remain (Wu et al., 2010);(Ahn et al., 2002).

Dissolved organic matter, inorganic macro components, heavy metals, and xenobiotic organic compounds are the four major categories of pollutants present in landfill leachate (Kjeldsen et al., 2002); (Wiszniowski et al., 2006). Table 2.1 below reflects typical compositions of both young and mature leachates. This comprehensive analysis of leachate composition includes a broad range of values because many factors influence leachate composition. Total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD) are all parameters used to characterize organic matter in leachates. Other dissolved organic matter includes both volatile acids and refractory humic acids and fulvic acids. Isolation and purification methods are available to further evaluate humic substances present in landfill leachates. Inorganic macro components including calcium, magnesium, iron, manganese, chloride, sodium, and potassium are also present in leachates. Ammonia-nitrogen is present in leachate as a result of decomposition of proteins and remains at high concentrations unless landfill leachate undergoes nitrification-denitrification. Ammonia-nitrogen concentrations in raw landfill

leachates range from 500-2000 mg/L NH3-N (Kjeldsen et al., 2002). Ammonia is considered a primary cause of acute toxicity of landfill leachate; therefore, treatment is required to reduce ammonia-nitrogen concentrations. Heavy metal concentrations differ depending on the landfill and waste composition, but many studies have concluded that heavy metals are not a primary concern for a majority of leachates.

Table 2.1 – Typical Composition of Young and Mature Leachates[a]

	Value, mg/L[b]		
	Young Landfill (less than 2 years)		Mature landfill (greater than 10 years)
Constituent	Range	Typical	
pH	4.5-7.5	6	6.6-7.5
BOD_5 (5-day biochemical oxygen demand)	2,000-30,000	10,000	100-200
TOC (total organic carbon)	1,500-20,000	6,000	80-160
COD (chemical oxygen demand)	3,000-60,000	18,000	100-500
Ammonia nitrogen	10-800	200	20-40
Nitrate	5-40	25	5-10
Organic nitrogen	10-800	200	80-120
Alkalinity as CaCO3	1,000-10,000	3,000	200-1,000
Calcium	200-3,000	1,000	100-400
Magnesium	50-1,500	250	50-200
Potassium	200-1,000	300	50-400
Sodium	200-2,500	500	100-200
Chloride	200-3,000	500	100-400
Sulfate	50-1,000	300	20-50
Total iron	50-1,200	60	20-200

[a] Adapted from (Tchobanoglous et al., 1993)
[b] Except pH, which has no units

Although there are many regulations currently limiting hazardous waste from being disposed of in landfills, some hazardous waste may have entered municipal landfills in the past prior to regulations that exclude these materials. Possible xenobiotic organic compounds present in leachate could be monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and halogenated hydrocarbons (Kjeldsen et al., 2002). The amount of trace xenobiotic organic compound present in landfill leachate depends on the amount of trace compounds present in the gas phase in the landfill that may reach equilibrium with landfill leachate following the fundamentals of Henry's Law. Table 2.2 represents typical concentrations of trace xenobiotic organic compounds in landfill gas from 66 California MSW landfills. The data in Table 2.2 is representative of trace compound concentrations in landfill gas that may transfer to landfill leachate (Tchobanoglous et al., 1993).

Table 2.2 – Typical Concentrations of Trace Compounds Found in Landfill Gas[a]

	Concentration, ppbV[b]		
Compound	Median	Mean	Maximum
Acetone	-	6,838	240,000
Benzene	932	2,057	39,000
1,1 – Dichloroethane	-	2,801	36,000
Ethyl benzene	-	7,334	87,500
Trichloroethylene	-	2,079	32,000
Tetrachloroethylene	260	5,244	180,000
Toluene	8,125	34,907	280,000
Xylenes	-	2,651	38,000

[a] Adapted from (Tchobanoglous et al., 1993)
[b] ppbV = parts per billion by volume

Landfills are known to experience four stages of decomposition: the initial aerobic phase, the anaerobic acid phase, the initial methanogenic phase, and the stable methanogenic phase (Kjeldsen et al., 2002); (Renou et al., 2008). The initial aerobic phase occurs when oxygen is trapped in void space, and it only lasts a few days until oxygen has been consumed through biological activity and converted to carbon dioxide. The anaerobic acid phase occurs after oxygen depletion and results in fermentation processes utilizing organic cellulose and hemicellulose that create methane and carbon dioxide production. This stage is responsible for the highest biological oxygen demand and chemical oxygen demand for landfill leachates as well as acidic pH. Methanogenic bacteria present in the landfill convert acids created during the anaerobic acid phase to carbon dioxide and methane during the initial methanogenic phase. This phase is responsible for increased methane production, COD and BOD decreases, and increased pH. The stable methanogenic phase occurs when methane production reaches a maximum and then decreases depending on hydrolysis reactions dependent on cellulose and hemicellulose present in the waste. The COD present in landfill leachate during this stage is mostly comprised of refractory humic and fulvic acids (Kjeldsen et al., 2002).

2.3 Treatment of Landfill Leachate

Because landfill leachate contains both inorganic and organic contaminants, it requires treatment before disposal to the environment. Variations in leachate composition can cause difficulties during treatment. Anaerobic and/or aerobic biological treatment, chemical oxidation, coagulation-precipitation, activated carbon adsorption, and membrane processes have been applied for treatment of landfill leachates (Tatsi et al., 2003). Landfill leachates can be disposed to sewers, rivers/watercourses, or tankers for alternate treatment, depending on discharge regulations and treatment efficiencies. Sewer disposal to municipal wastewater treatment plants (WWTPs) is a widespread practice because it is the cheapest option, but treatment is required before discharge due to limitations on ammonia and compounds that could harm downstream treatment processes (Robinson, 2005). On-site biological treatment is a common form of treatment for landfill leachates before sewer discharge to WWTPs because it is cost effective (Renou et

al., 2008); (Robinson, 2005). A common treatment for landfill leachate high in COD and ammonia concentrations is the sequencing batch reactor (SBR), which is a form of activated sludge treatment that combines the biological treatment and settling chamber in one unit tank. Microfiltration, ultrafiltration, or reverse osmosis are also membrane applications that have been used to further treat landfill leachate after biological treatment (Robinson, 2005).

The composition of a leachate may dictate the most appropriate and cost-effective treatment technology. Biological treatment is very effective on young leachates because the organics are more readily biodegradable, but the treatment may be less effective as leachates age because refractory humic substances remain present in older more stabilized leachates (Tatsi et al., 2003). Integrated treatment processes utilizing biological, physical, and/or chemical processes may be required to enhance effluent quality of landfill leachate, especially because regulations for discharge standards are becoming more stringent in most countries (Renou et al., 2008). The integrated treatment process of membrane bioreactor activated sludge followed by reverse osmosis is often used to increase treatment efficiency. Nitrification before reverse osmosis has also been shown to increase overall nitrogen removal (Ahn et al., 2002).

Membrane processes are commonly used for treatment of landfill leachates. Microfiltration (MF) is often utilized to remove suspended particles, but it cannot be used alone for removal of organics. Microfiltration is often used as a pre-treatment step for ultrafiltration (UF) or nanofiltration (NF). Ultrafiltration can remove macromolecules and fractionate organic matter based on molecular mass. This process could be used on effluent from biological leachate treatment to remove higher molecular weight organics that could foul reverse osmosis (RO) membranes or interfere with disinfection at downstream WWTPs. Reverse osmosis has proven to be very effective at removing contaminants from landfill leachates after biological treatment. The major disadvantages of RO treatment are membrane fouling and production of concentrate that will need further treatments (Renou et al., 2008).

2.4 Effect of Biological Treatment on Organic Matter of Landfill Leachates

The biodegradability of landfill leachate is influenced by many factors, especially landfill age. The biological treatment efficiencies of organic matter in landfill leachates can be evaluated based on molecular mass distribution. Organics with molecular mass less than 500 Da are often the predominant organic fraction in raw landfill leachates (Ha et al., 2008). Very little organic matter is in the size fraction above 0.45 μm. Organics with molecular weight less than 1,000 Da are the largest size fraction in both raw and treated leachates. The organic fraction tends to decrease as molecular weight increases (Li et al., 2009).

Nitrification and denitrification processes are used to treat landfill leachates to remove nitrogen. The effectiveness of both processes can be hindered by the presence of refractory humic substances or xenobiotic organic compounds. Nitrification converts ammonia to nitrite then nitrate in an aerobic process. Denitrification is an anaerobic

process carried out by heterotrophs that reduces nitrate to create nitrogen gas (Wiszniowski et al., 2006). Either nitrification individually or nitrification-denitrification are processes used to reduce nitrogen concentrations in leachates through biological treatment. Studies have shown that nitrification has a larger effect on organic carbon removal than on the removal of ultraviolet absorbing compounds. Therefore, landfill leachate effluent after nitrification biological treatment often exhibits higher specific ultraviolet absorbance because nonhumic substances are often more biodegradable than refractory humic substances. Biological treatment processes produce effluents comprised of degradation products and soluble microbial products (SMP). Soluble microbial products are organic compounds formed by bacteria during biological treatment from substrate metabolism and biomass decay (Krasner et al., 2009).

Nitrification-denitrification processes are responsible for altering the nitrogen species in landfill leachates. Nitrate and ammonia are the primary forms of nitrogen discharged from wastewater treatment plants (WWTPs). Dissolved organic nitrogen (DON) is another form of nitrogen that remains in WWTP effluent. Dissolved organic nitrogen is typically responsible for less than 10% of nitrogen in wastewater effluent, although advanced nitrogen removal systems can remove dissolved inorganic nitrogen concentrations to the extent that DON becomes the dominant nitrogen species. The bioavailability of nitrogen in a water system may vary depending on the nitrogen species present in the WWTP effluent and bacteria present in downstream watersheds. Dissolved organic nitrogen needs to be studied further to determine the bioavailability within watersheds for a variety of organisms and treatment efficiencies that will decrease the lower molecular weight fraction of dissolved organic nitrogen (Pehlivanoglu & Sedlak, 2004).

Dissolved organic nitrogen is calculated by subtracting the total inorganic nitrogen from the total nitrogen. Inorganic nitrogen is present in much larger proportions than organic nitrogen; therefore, the DON calculations are subject to considerable error in samples with large inorganic nitrogen concentrations (Pehlivanoglu-Mantas & Sedlak, 2008). The lack of analytical methods to calculate DON concentrations is one reason that behavior of DON and effects of biological treatments on DON needs to be further evaluated. Some studies have evaluated DON characterization based on molecular weight distribution and discovered that molecular weight cut-offs below 1800 Da accounts for between 58 – 66 % of DON of wastewater effluents (Keller et al., 1978); (Parkin & McCarty, 1981).

Due to limitations in analytical methods to determine organic nitrogen concentrations, little is known about the organic nitrogen fraction in landfill leachate. The objective of this study is to expand the knowledge about organic nitrogen in landfill leachates through analysis of four landfill leachate samples of varied composition. Analysis was conducted both before and after treatment to determine treatment efficiencies and study the effect of biological treatment on organic nitrogen. Size distribution and hydrophobicity distribution were also conducted for further analysis.

3. Organic Matter in Various Landfill Leachates and the Effectiveness of On-Site Biological Treatment: A Size Distribution Study

Abstract

Landfill leachates are often treated on-site before disposal to publicly owned treatment works (POTWs) to reduce the ammonia and organic load on the downstream system. Leachate samples were collected from four landfills both before and after on-site treatment to evaluate the effectiveness of on-site biological treatment and biodegradation of organic nitrogen. The samples varied in age, location, and on-site treatment processes. Size fractionation utilizing microfiltration (MF) and ultrafiltration (UF) was conducted in conjunction with total organic carbon (TOC), nitrogen species, and UV_{254} absorbance analysis to determine the characteristics of organic constituents present in landfill leachate. The size fraction less than 1thousand Daltons (1 kDa) was responsible for a major portion of the organic matter in terms of TOC for both the untreated and treated landfill leachates. The UV quenching ability of landfill leachates was analyzed because it can interfere with UV disinfection processes. The majority of the UV_{254} absorbance of the leachates before and after biological treatment was also attributed to the size fraction less than 1 kDa. The size distribution of organic nitrogen varied greatly for the leachate samples in this analysis, indicating that the organic nitrogen variation and biodegradation is due to site dependent factors at each landfill.

3.1 Introduction

Waste disposal practices for municipal solid waste (MSW) include recycling, composting, incineration, and landfilling. Landfilling is the most popular practice for MSW management globally due to its low capital cost (Wiszniowski et al., 2006). Approximately 54% of the 250 million tons of MSW generated in the United States in 2010 was landfilled (US EPA, 2011).

Landfills are beneficial because they allow wastes to degrade into inert, stabilized solids under engineered conditions that limit negative environmental impacts. Landfill leachate is a waste stream associated with landfilling practices. Leachate is formed by rain percolation through waste combined with liquids produced by waste decomposition within the landfill (Renou et al., 2008).

Due to the large number of landfills and the biological decomposition that may continue for 30-40 years after landfills are closed, there is a large volume of landfill leachate that needs to be disposed of properly. Liners and leachate collection systems are utilized to prevent leachate from leaving the landfill uncontrolled prior to treatment (Robinson, 2005). Landfill leachates are often collected and disposed of through sewers to publicly owned treatment works (POTWs) after on-site biological treatment because it is the most cost-effective treatment method (Renou et al., 2008). The effluent from on-site biological treatment of leachate may have negative impacts on downstream processes at POTWs; therefore, further evaluation of landfill leachate on-site biological treatment needs to be conducted.

Landfill composition and quality may vary greatly from one landfill to another depending on a variety of factors. Precipitation and evaporation rates, as well as seasonal weather variations affect the volume of leachate produced at a landfill. Landfill age and waste type also influence the composition of leachate (Renou et al., 2008). Due to the large number of aspects that affect leachate composition and quality, the effectiveness of biological treatment for a variety of leachates needs to be evaluated.

The composition of landfill leachate may dictate appropriate treatment. Aerobic biological treatment is utilized to remove organic material, and sequential aerobic and anaerobic treatment removes biodegradable nitrogenous compounds. Discharge regulations are becoming more stringent to prevent further nutrient loading on downstream systems. Therefore, chemical and physical treatments may be used more frequently in the future to improve the effluent quality of landfill leachates after biological treatment.

Nitrification-denitrification processes are becoming more prevalent at POTWs for nitrogen removal. This advanced process of nitrogen removal may result in organic nitrogen concentrations in effluents to be the primary form of nitrogen. Organic nitrogen has been associated with nitrogenous disinfection by-product formation, so the organic nitrogen fraction of landfill leachates before and after treatment needs to be characterized. In addition, regulation in the future may be more restrictive on total nitrogen; therefore, further studies also need to be conducted on the treatability of organic nitrogen.

Landfill leachates are an emerging environmental concern because of varied leachate characteristics and potential impacts on POTWs, including increased organic nitrogen loading. Organic matter in terms of TOC, UV_{254} absorbance, specific UV_{254} absorbance ($SUVA_{254}$), and organic nitrogen were measured in conjunction with size distribution for four landfill leachates with on-site biological treatment for untreated and treated samples. This research specifically focused on:

1) The size distribution of organic matter in terms of TOC for untreated and treated leachates from four different landfills with on-site biological treatment;

2) Comparison of biological treatment effectiveness based on organic matter and UV_{254} absorbance;

3) Evaluation of the distribution of organic nitrogen for untreated and treated leachates between four different landfills.

3.2 Materials and Methods

3.2.1 Leachate Sampling

Leachate samples were collected from four different municipal wastewater treatments both before and after biological treatment in landfill leachate treatment plants from

Kentucky (KY) and Pennsylvania (PA), USA. The Landfill A leachate samples are from Kentucky, while Landfill B, C, and D samples are from Pennsylvania.

All leachate samples were collected as grab samples and placed in polyethylene buckets for transport from the landfill to the lab. Upon arrival, the leachate containers were immediately stored at 4 ^{O}C in the dark to reduce microbial activity.

3.2.2 On-Site Biological Treatment Processes

Landfill A has been open for over 35 years and has a total property of approximately 782 acres. Eight separate cells with varied age and active/inactive status encompass the landfill. Untreated samples were collected from the equalization basin that collects landfill leachates from all cells and combines these for treatment. Two sequencing batch reactors (SBR) are utilized for biological treatment at this landfill.

Landfill B leachate is treated through a sequencing batch reactor (SBR) activated sludge system with a capacity of 113.6 m^3 per day and a HRT of 6-7 days. Both nitrification and denitrification are accomplished in this process. Landfill B opened in 1973 and receives 1500 tons of MSW per day. Treated effluent from SBR treatment is discharged through the municipals sewer system and goes to the downstream POTW.

Landfill C opened in 1993 and receives on average 300 tons per day of MSW and 200-300 tons per day shale cuttings. SBR biological treatment for ammonia and BOD removal also occurs at Landfill C in two 50,000 gallon units that discharge 25,000 gallons per day to a small tributary. An aerated storage lagoon with approximately 1.5 million gallon capacity is used on site.

Landfill D opened in 1987 and received between 500-600 tons of MSW per day. Two aerated 300,000 gallon storage tanks, one 1.5 million gallon storage tank, and MetPro fixed film bioreactors designed for 40,000 GPD for ammonia and BOD removal without denitrification. Secondary clarification occurs on-site with ferric chloride and polymer addition for solids and metals removal. Treated effluent from this landfill is discharged to the local POTW.

3.2.3 Fractionation

Leachate samples were subjected to size fractionation using both microfiltration and ultrafiltration processes. Microfiltration was conducted using a 300 mL filtration cell (GELMAN, Ann Arber, MI), a vacuum pump, and 0.45 μm membrane filters (47 mm, Sartorius Stedim Biotech, Germany). Ultrafiltration was conducted using 200 mL stirred ultrafiltration cells (model 8200, Amicon, Belford, MA) in combination with a nitrogen gas tank (pressure: 120 kPa). Molecular weight (MW) fractionation was conducted using membranes with MW cutoffs of 1 kDa and 3 kDa (PLAC, PLBC, Millipore, Billerica, MA). For microfiltration/ultrafiltration, approximately 200 mL were filtered for each leachate sample, collected in glass bottles, and stored at 4 ^{O}C in the dark for further analysis. The analyses conducted during this study (TOC, nitrogen species,

and UV_{254} absorbance) were conducted on the filtrate from this fractionation process. All leachate containers were shaken before size fractionation and analysis to homogenize settled particles into suspension.

3.2.4 Analysis

All glassware used in the experiments was washed, rinsed with deionized water, and baked for 4 hours at 450 ^{O}C prior to use. All chemicals used were analytical grade. High temperature combustion was used to analyze total organic carbon (TOC) of the leachate samples (Shimadzu TOC-5000A, Japan). The ultraviolet absorbance at 254 nm (UV_{254} absorbance) of each sample was measured using the Beckman DU640 spectrophotometer. Specific UV_{254} absorbance ($SUVA_{254}$) was calculated by dividing UV_{254} absorbance results by TOC data for each respective sample. The leachate samples were diluted during both the TOC and UV_{254} absorbance analysis to ensure that test readings were within the acceptable detection range for each test. Test readings were then multiplied by the dilution factor to give the final test results. Final test results were used for statistical analysis throughout this experiment. The pH of each sample and size fraction was analyzed by a pH meter (Model No. 910, Accumet, Cambridge, MA) with a pH probe (Model No. 13-620-287, Accumet, Petaling Jaya, Malaysia).

Nitrogen species were analyzed during this experiment for each leachate sample and size distribution. Organic nitrogen (ON) was assessed by subtracting the inorganic nitrogen (IN) from the total nitrogen (TN) (Pehlivanoglu-Mantas & Sedlak, 2008); (Zhao et al., 2012). Ammonia, nitrate, and nitrite compose the inorganic nitrogen present in landfill leachate. This calculation for organic nitrogen yields less accurate results if the landfill leachate has a large amount of inorganic nitrogen present in the sample. High inorganic nitrogen values may decrease the accuracy of organic nitrogen calculations. Persulfate digestion was used to analyze total nitrogen for each leachate sample and size fraction (Hach, Loverland, CO). Ammonia concentrations were evaluated for each leachate and size distributions using the salicylate method (Hach, Loverland, CO). Nitrate and nitrite concentrations were evaluated using the dimethylphenol and diazotization methods, respectively (Hach, Loverland, CO). Leachate samples were diluted in order to get test readings within the acceptable detection ranges for each nitrogen species analysis, and then test results were multiplied by the dilution factor in order to get the final test result of each nitrogen species. Statistical analysis was conducted on the final test results. Analysis for organic nitrogen was conducted at least three times for each leachate sample and size distribution.

For treated leachates with high concentrations of inorganic nitrogen, nitrate removal was conducted in order to accurately assess the organic nitrogen present in treated landfill leachate. Nitrate removal was conducted with Dowex 1X8 anion exchange resin (Fluka, Cl^--form, strong basic resin). For this procedure, one gram of resin was packed into a borosilicate glass column (1.0 cm x 10 cm, Thomas Scientific, Swedesboro, NJ) attached to a peristaltic pump using vinyl tubing. The resin was cleaned using 20 bed volumes of 3 N HCl followed by rinsing with 2 bed volumes of HCl acidified deionized water (pH= 2.0) both pumped at a rate of one bed volume per minute. The leachate sample was

acidified to pH of 2.0 with hydrochloric acid before being passed through the column at a rate of one bed volume per minute. The first four bed volumes of the eluted sample were discarded and excluded from analysis (Randall, 2013). The nitrogen species analysis was conducted on the eluted samples. This nitrate removal procedure was conducted on Landfill C and Landfill D treated leachates due to the high concentrations of inorganic nitrogen that interfered with accurate organic nitrogen characterization.

3.2.5 Statistical Analysis

Data was graphed using Microsoft Excel 2010 (Microsoft Corporation, Redmond, CA) and correlation analysis was performed using R language.

3.3 Results

3.3.1 Organic Matter

The organic matter in terms of TOC was analyzed for all leachate samples and size distribution samples. A summary of all test results for both untreated and treated samples is shown in Table 5.1 through Table 5.4. Size distribution values of organic matter are shown before and after treatment for Landfill A and Landfill B leachates in Figure 3.1 (A,B) as well as Landfill C and Landfill D leachates in Figure 3.2 (A,B), respectively. Figure 3.1 (A) shows that the organic fraction less than 1 kDa contributes 76% and 69% of the Landfill A untreated and treated leachates respectively. Landfill B untreated and treated leachate has 68% and 70% of the overall TOC less than 1 kDa as shown in Figure 3.1 (B). Leachates from the Landfill C have 47% and 63% of the organic matter in terms of TOC in the size fraction less than 1 kDa in the untreated and treated samples, respectively in Figure 3.2 (A). Figure 3.2 (B) shows that 51% and 59% of the total Landfill D leachate TOC is less than 1 kDa for the untreated and treated leachate samples. Figures 3.1 and 3.2 both illustrate that the dominant organic matter fraction in terms of TOC is less than 1 kDa molecular weight cut-off (MWCO) and that greater than 90% of organic matter in terms of TOC passed through a 0.45 μm filter. These results are consistent with other studies (Li et al., 2009);(Ha et al., 2008). This study confirms that organic matter with a MWCO less than 1kDa is the dominant organic material in both untreated and treated landfill leachates.

The overall TOC removal efficiency using aerobic treatment was the highest for Landfill A leachate at 54%. In comparison, biological treatment efficiency for the organic matter was 31% for Landfill B leachate, 48% for Landfill C leachate, and 26% for Landfill D leachate. The Landfill A has units with a variety of ages, but a majority of the leachate volume produced was probably from the newer, younger landfill cells since these cells are open to rainfall; therefore, this mix of leachate is probably more characteristic of young leachate. The youngest leachates from Landfill A and Landfill C exhibited the most significant degradation of organic matter, while older leachates from Landfill B and Landfill D experienced less significant degradation due to recalcitrant organic materials.

The size distribution was measured in order to evaluate the effectiveness of biological treatment for specific size fractions. The greatest removal occurred for the Landfill A leachate in the size fraction less than 1 kDa and greater than 0.45 μm, with respective removal efficiencies of 58% and 93%. The intermediate size fractions also decreased, but to a lesser extent after biological treatment. In comparison to Figure 3.1 (A), the Landfill B intermediate size fractions 3 kDa – 0.45 μm and 1 kDa – 3 kDa decreased the most by 49 % and 39% respectively in Figure 3.1 (B). The fraction less than 1 kDa was only 29% removed in terms of TOC by biological treatment. This small removal efficiency for the less than 1 kDa fraction could be due to partial degradation of larger size material, thereby creating smaller organics. It is important to note that the size fraction greater than 0.45 μm increased by 251%. This increase may be due to bio-coagulation and microbial growth resulting from the activated sludge treatment.

The size distribution was also evaluated for Landfill C and Landfill D leachates. The overall organic matter decreased for all size fractions for Landfill C leachate. The greatest removal occurred for the greater than 0.45 μm size fraction at 79% TOC removal. The smallest size fraction, less than 1 kDa, exhibited the smallest organic matter removal efficiency at 30%. This small removal efficiency may be due to partial degradation of organic material from larger size fractions to smaller fractions during biological treatment. For the Landfill D leachate shown in Figure 3.2 (B), the removal efficiency decreased as the size fraction decreased. The TOC size fraction greater than 0.45 μm decreased by 66% in terms of TOC, while the portion less than 1 kDa decreased by only 15%. Because the overall removal efficiency was also low at 26%, results indicate that the organic matter in terms of TOC for Landfill D leachate is primarily biorefractory in nature.

3.3.2 UV_{254} Absorbance and $SUVA_{254}$

UV quenching of landfill leachates due to refractory humic substances is a concern when determining appropriate disposal practices for leachate. Since sewer disposal is a common practice for biologically treated landfill leachates, the UV_{254} absorbance and $SUVA_{254}$ for various leachates was studied to determine possible impacts of leachate disposal on UV disinfection at POTWS.

UV_{254} absorbance and $SUVA_{254}$ were evaluated in this study to assess the effectiveness of biological treatment. Results from UV_{254} absorbance are shown in Figure 3.3 (A, B) for Landfill A and Landfill B leachates and in Figure 3.4 (A, B) for Landfill C and Landfill D leachates, respectively. UV_{254} absorbance decreased for all leachates and all size distributions after treatment. For the unfiltered samples, leachates from Landfill A, Landfill B, and Landfill D achieved 23%, 26%, and 21% removal of UV_{254} absorbance through biological treatment. In comparison, Landfill C unfiltered leachate decreased from 17.3 to 8.1 cm^{-1} after biological treatment, resulting in 55% removal efficiency. This result indicates that the Landfill C leachate treatment performed significantly better than treatment for the other landfills for UV_{254} absorbance removal.

When evaluating the UV_{254} removal absorbance within size fractions before and after treatment, the Landfill A leachate showed increased removal efficiency as the size fraction decreased as shown in Figure 3.3 (A). Figures 3.3 (B) and 3.4 (A) show that largest UV_{254} absorbance removal efficiencies occurred in the > 0.45 μm and < 1 kDa size fractions for the Landfill B and Landfill C leachates, respectively. In contrast, the Landfill D leachate decreased removal efficiencies as size distribution decreased in Figure 3.4 (B).

Size distribution is utilized to evaluate the potential for the use of membrane treatments in conjunction with biological treatment as a form of integrated treatment. The UV_{254} absorbance for treated leachates decreased to 3.0 cm^{-1}, 5.9 cm^{-1}, 4.5 cm^{-1}, and 4.6 cm^{-1} for Landfill A, Landfill B, Landfill C, and Landfill D leachates respectively. This analysis suggests that nanofiltration using a 1 kDa membrane applied to biologically treated leachate samples may be an effective treatment practice to polish leachate samples and decrease complications with UV disinfection before sewer discharge to POTWs.

$SUVA_{254}$ was calculated to determine the relationship between TOC concentration and UV_{254} absorbance before and after treatment. Figure 3.5 (A, B) illustrates the $SUVA_{254}$ results for Landfill A and Landfill B leachate samples. The $SUVA_{254}$ increased after treatment for all size distributions in Figure 3.5, indicating the biorefractory nature for UV_{254} absorbance after treatment for Landfill A and Landfill B leachate samples. The $SUVA_{254}$ analysis for Landfill C and Landfill D leachates is included in Figure 3.6 (A, B). Landfill D leachate samples showed an increased $SUVA_{254}$ after biological treatment in Figure 3.6 (B) similar to results in Figure 3.5, but Landfill C untreated leachates exhibited higher $SUVA_{254}$ results for most size fractions in Figure 3.6 (A). These results imply that the UV_{254} absorbance was less biorefractory for Landfill C leachate than other leachates in this study, and this conclusion is supported by the significant UV_{254} absorbance removal efficiency for Landfill C leachates shown in Figure 3.4 (A).

3.3.3 Organic Nitrogen

The organic nitrogen distribution in all leachate samples was conducted utilizing size distribution analysis in order to analyze membrane treatment alternatives for landfill leachates. Distributive organic nitrogen data for Landfill A and Landfill B leachates is shown in Figure 3.7 (A, B). Figure 3.7 (A) demonstrates the organic nitrogen distribution for Landfill A leachates before and after treatment. Overall, biological treatment removed 44% of the organic nitrogen for Landfill A leachate. The size fraction greater than 0.45 μm decreased by 80% during treatment, but the size fraction between 0.45 μm - 3 kDa increased by 17%. This may indicate partial degradation of larger molecular weight organic nitrogen into the 0.45 μm - 3 kDa size fraction. It is important to note that the size fraction less than 1 kDa decreased by 75%.

Figure 3.7 (B) illustrates that biological treatment removes 23% of organic nitrogen from Landfill B leachate. Biological treatment increased the organic nitrogen concentration greater than 0.45 μm by 10% from 9.6 mg-N/L to 10.6 mg-N/L. This increase after SBR treatment may be due to bio-coagulation during activated sludge treatment or formation

of soluble microbial products (SMP) (Krasner et al., 2009). The size fraction less than 1 kDa increased by 44%, indicating that partial degradation of larger molecular weight organics may have occurred during this treatment. The size fraction 3 kDa – 1 kDa decreased the most at 96% removal of organic nitrogen. This size fraction may have degraded into lower molecular weight compounds during treatment.

Figure 3.8 (A, B) shows organic nitrogen distribution for Landfill C and Landfill D samples respectively. The dominant portion of organic nitrogen in untreated Landfill C leachate in Figure 3.8 (A) is below the 1 kDa molecular weight cut off, comprising 50% of the total organic nitrogen. Biological treatment removed approximately 43% of the total organic nitrogen. It is important to note that the portion of organic nitrogen greater than 0.45 μm increased by 45% after biological treatment, which may be due to bio-coagulation. Removal of approximately 91% for treated samples occurred in the smallest size fraction less than 1 kDa. Dowex 1X8 anion exchange resin (Fluka, Cl^--form, strong basic resin) was used on treated Landfill C leachate as a nitrate removal method due to high concentrations of nitrate that impaired organic nitrogen calculations.

Figure 3.8 (B) demonstrates that biological treatment can remove 68% of organic nitrogen from Landfill D leachate. For untreated Landfill D leachate, 54% of the organic nitrogen is below the 3 kDa molecular weight cut off. Nanofiltration with molecular weight cut off of 1 kDa removed 36% of organic nitrogen from the treated Landfill D leachate. A comparison between organic nitrogen analysis and membrane treatments for this broad range of leachates and treatment practices may indicate that membrane treatments can have a future use with landfill leachates depending on the effectiveness of biological treatment. Dowex 1X8 anion exchange resin was also used on treated Landfill D leachate as a nitrate removal method.

A summary of effluent nitrogen concentrations is included in Figure 3.9 (C). The maximum total organic nitrogen for this analysis was approximately 44 mg/L; therefore, if this landfill leachate was discharged at a rate of 1% total discharge the nitrogen loading for the downstream POTWs could increase as much at 0.44 ppm. This additional nitrogen loading on downstream POTWs may be an issue in the future if total nitrogen regulations are decreased to prevent nutrient loading on downstream receiving waters after wastewater treatment.

3.4 Discussion

Size distribution has been used to analyze the effectiveness of on-site biological treatment and properties of organic matter present in landfill leachate on a molecular mass basis. Previous studies have shown that biological treatment is effective for removal of low molecular weight organic matter and overall organic matter, but some increases have been shown to occur due to biocoagulation of small flocs or partial degradation of larger molecular weight organic matter (Li et al., 2009). Another reason for increases in organic matter may be due to soluble microbial products (SMP), which are organic compounds formed during biological treatment by bacteria as a result of substrate metabolism and biomass decay (Krasner et al., 2009). This research further supports the

prior studies that indicate that organic matter less than 1 kDa molecular weight cut off is the dominant organic matter in terms of TOC (Zhao et al., 2012) for most leachates.

Figure 3.9 (A) indicates that the organic matter in terms of TOC for each treated landfill leachate is primarily in the size fraction less than 1 kDa. The organic matter was approximately 300-400 mg-C/L for all treated leachates except Landfill A, which had a significantly smaller treated effluent concentration. This decreased effluent concentration may be due to the mix of older and younger leachate at Landfill A. The younger Landfill A leachates may have been readily degradable, while the much older leachates had already experienced significant degradation over the past few decades. Analysis shows that microfiltration and ultrafiltration cannot be used alone before direct discharge of landfill leachate because these practices do not provide enough removal of organic matter or UV_{254} absorbance. Microfiltration has been shown to eliminate colloids and suspended matter, while nanofiltration eliminates macromolecules. Microfiltration and nanofiltration are useful pretreatment processes for reverse osmosis (RO) because they remove large molecular weight compounds that could lead to reverse osmosis membrane fouling (Renou et al., 2008). Integrated treatment combining biological treatment before reverse osmosis is a common method for advanced landfill leachate treatment (Ahn et al., 2002).

An important aspect while considering landfill leachate disposal is UV quenching. Landfill leachate is discharged through sewers after pretreatment because of the low operating cost and ease of maintenance, but this disposal method could hinder UV disinfection at downstream wastewater plants. The majority of leachate samples in this analysis did not reflect significant UV absorbance removal as a result of biological treatment, with the exception of Landfill C. The low removal efficiencies for UV_{254} absorbance from biological treatment for Landfill A, Landfill B, and Landfill D leachates indicates that the organic matter responsible for UV quenching was not readily biodegradable in those samples. In addition, the increase in $SUVA_{254}$ for those samples after biological treatment further indicates that the organic matter responsible for UV quenching was resistant to biological treatment. The Landfill C leachate exhibited the most drastic removal efficiencies for UVA_{254}, indicating that the organic matter responsible for UV quenching was removed to a greater extent during biological treatment for Landfill C leachate samples than the other samples in this study. This high degradation of UV_{254} removal may be attributed to the young age of the leachate or the type of waste at Landfill C. Because the $SUVA_{254}$ is strongly correlated to the percentage of aromatic content in the leachate, the decreased $SUVA_{254}$ after biological treatment for Landfill C also indicated that aromatic content was removed through biological treatment. A summary of all treated landfill leachates UV_{254} absorbance size distribution is included in Figure 3.9 (B). All leachates studied had the predominant fraction of UV_{254} absorbance contributed by the size fraction less than 1 kDa, indicating difficulties for membrane application in the future.

This study aimed to further characterize and investigate the occurrence of organic nitrogen in a broader range of landfill leachates before and after biological treatment. The increased use of nitrification-denitrification advanced nitrogen removal methods

causes the organic nitrogen concentration to become predominant because organic nitrogen is not removed during advanced treatment. Organic nitrogen is an emerging issue because of impending regulations that may limit the total nitrogen discharge at POTWs. A summary of the organic nitrogen distribution in all treated leachates is included in Figure 3.9 (C), with effluent organic nitrogen levels ranging from 27- 44 ppm. The organic nitrogen distribution varied greatly for the landfill leachates in this analysis indicating that organic nitrogen may be influenced by many factorings, including municipal waste type and landfill age. Landfill leachate discharge through sewers will increase the total nitrogen loading on downstream municipal wastewater treatment plants due to the increased organic nitrogen.

3.5 Summary and Conclusion

This analysis added to the knowledge of landfill leachates because it utilized size distribution on a wide range of leachate samples to analyze organic matter, organic nitrogen, and UV quenching abilities before and after biological treatment. Sewer disposal of landfill leachates to municipal wastewater treatment plants for further treatment is a common practice because of its cost effectiveness. Landfill leachates can have considerable impacts on downstream wastewater treatment plants due to the additional organic loading and resulting UV quenching ability of the organic matter. The main conclusions from this study are as follows:

1) This study supports prior research concluding that on-site biological treatment is not effective enough to allow landfill leachates to be directly discharged to the environment post treatment.

2) The size fraction less than 1 kDa was predominant for organic matter in terms of TOC for both untreated and treated landfill leachates, indicating difficulties for membrane treatments besides reverse osmosis (RO).

3) Nanofiltration at molecular weight cut offs below 1 kDa can reduce UV quenching of landfill leachates and decrease complications with UV disinfection at downstream POTWs.

4) Organic nitrogen size distribution can vary greatly between various landfills. Factors such as waste type and landfill age may influence this organic nitrogen distribution. Even after biological treatment, landfill leachates discharged through sewers to downstream POTWs at low flows may have substantial impacts on the nitrogen loading of the downstream systems.

5) Although microfiltration and ultrafiltration were able to remove portions of the organic matter in landfill leachates, these processes will most likely need to be used as pre-treatment steps before reverse osmosis (RO) treatment in order to achieve significant organic matter removal and decreased organic loading on downstream systems.

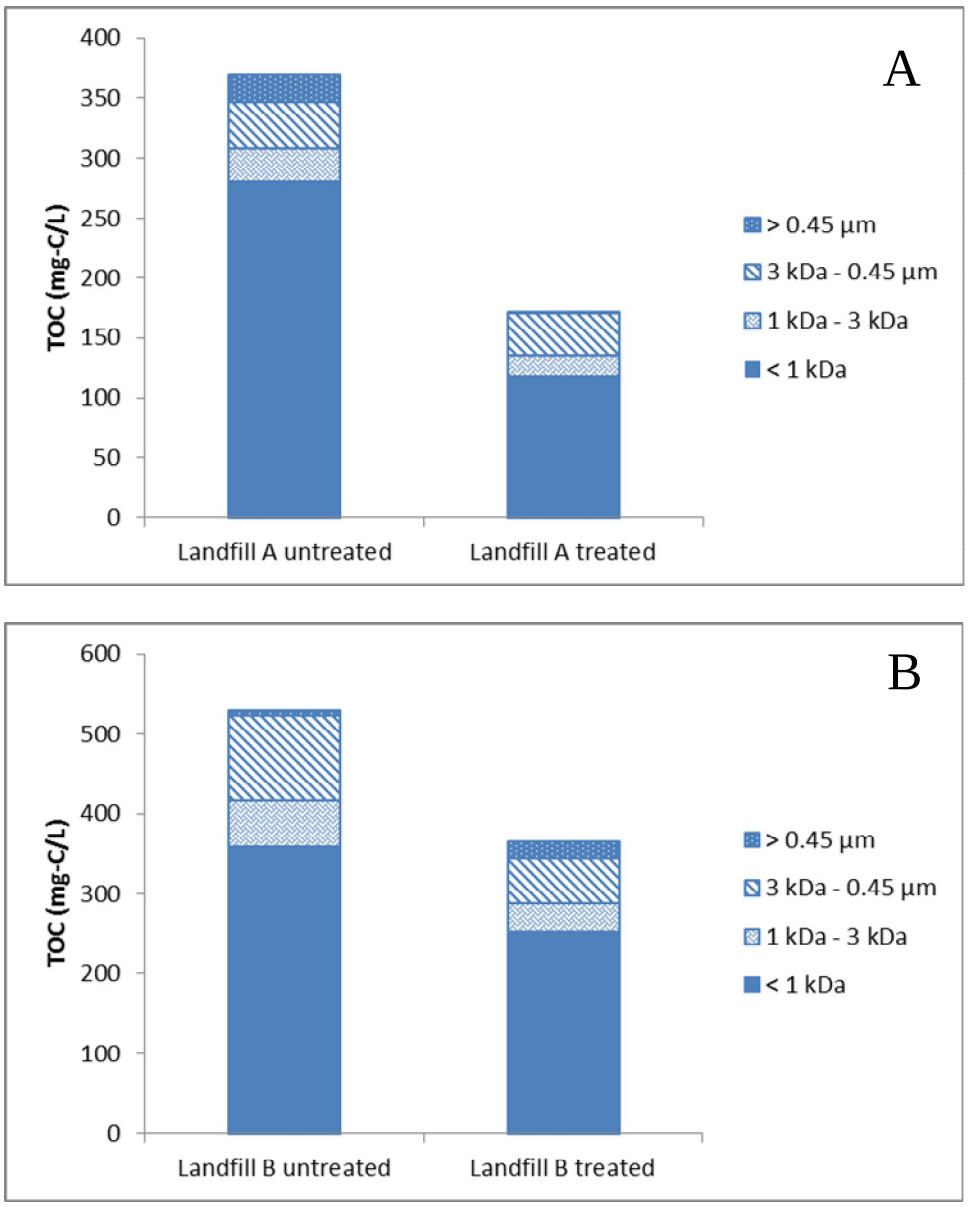
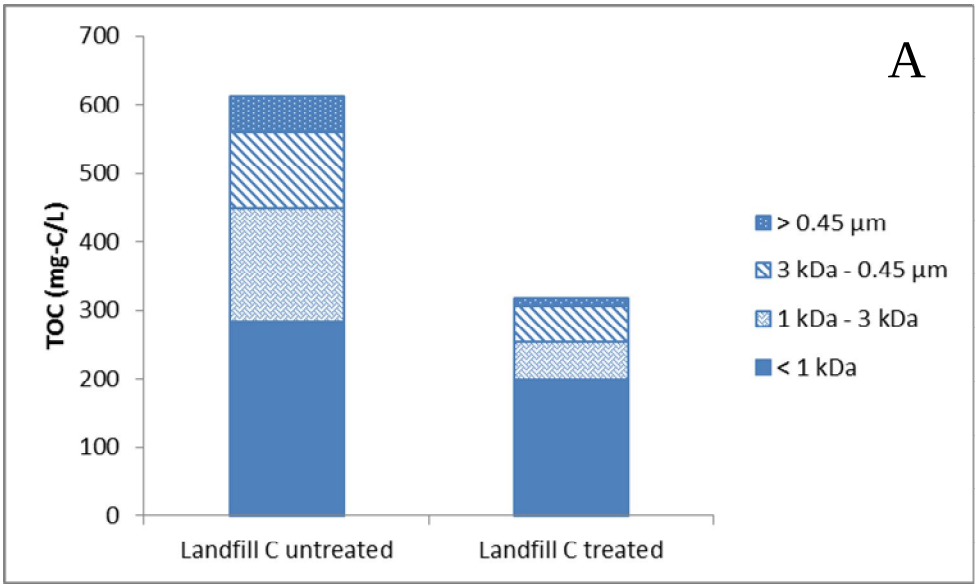


Figure 3.1 – Size distribution of organic matter in terms of TOC shown as (A) distributive data for untreated and treated Landfill A leachates and (B) distributive data for untreated and treated Landfill B leachates. TOC was measured three times for statistical purposes.



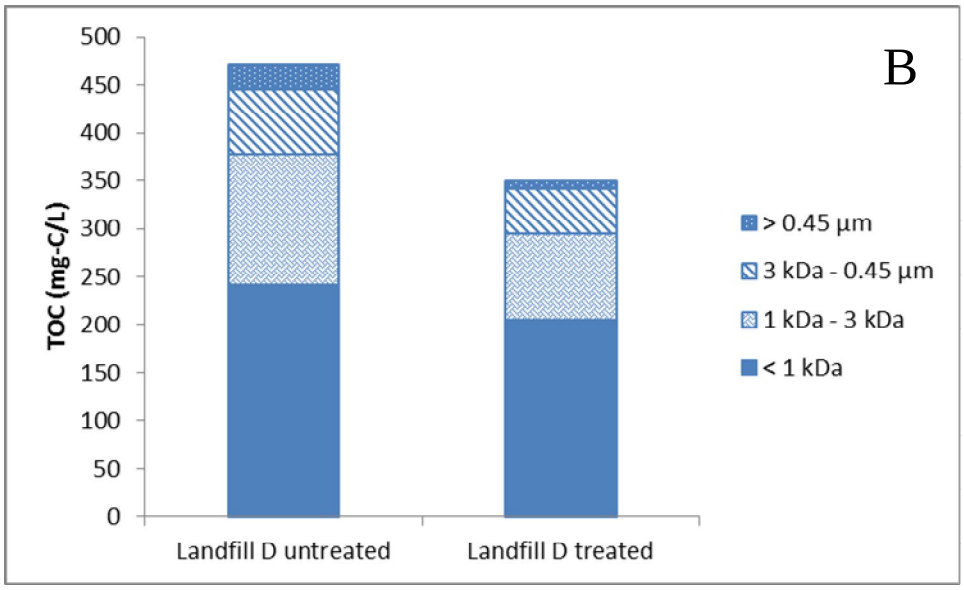


Figure 3.2 – Size distribution of organic matter in terms of TOC shown as (A) distributive data for untreated and treated Landfill C leachates and (B) distributive data for untreated and treated Landfill D leachates. TOC was measured three times for statistical purposes.

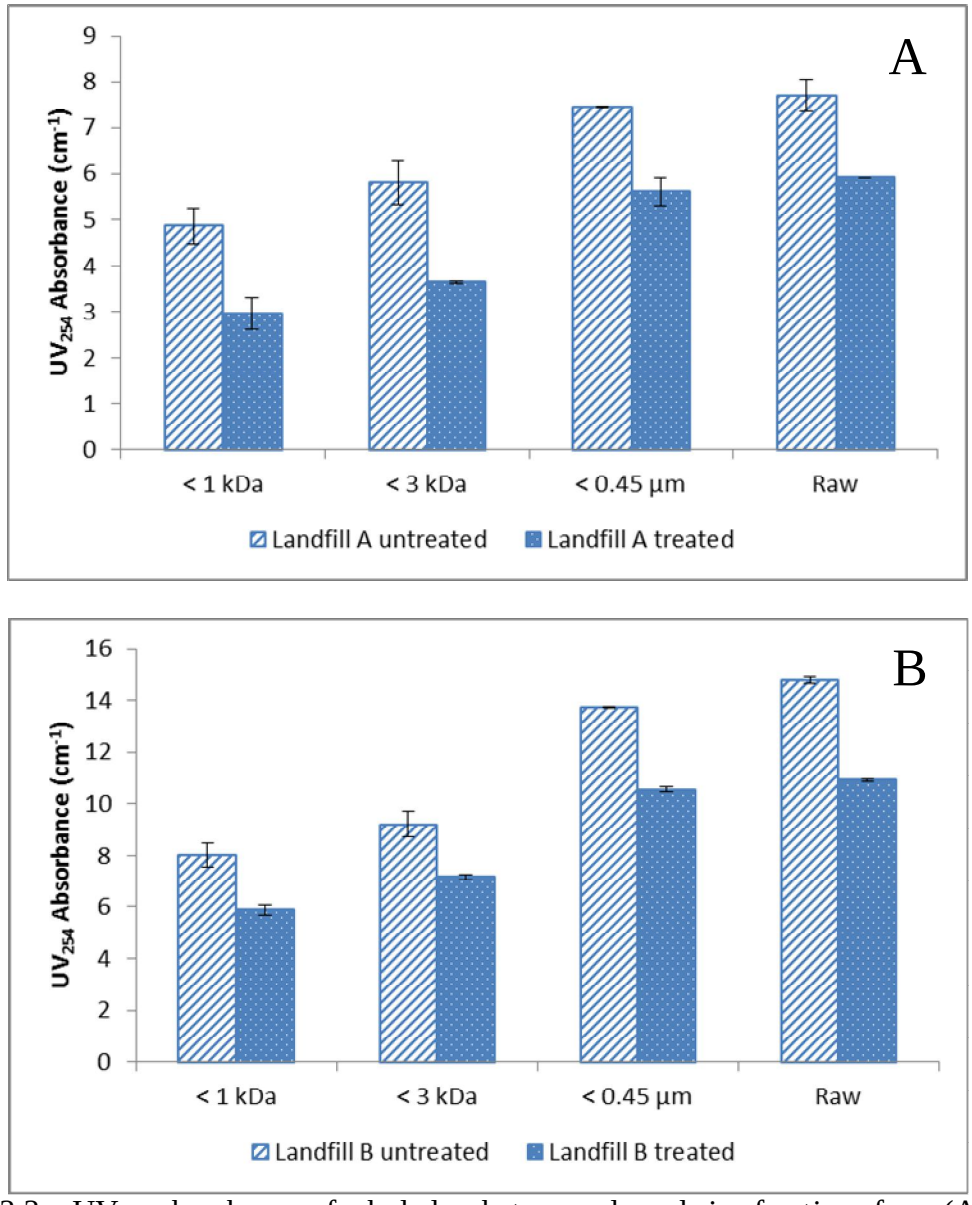


Figure 3.3 – UV_{254} absorbance of whole leachate sample and size fractions from (A) Landfill A and (B) Landfill B. UV_{254} absorbance was measured three times for statistical purposes. (Error bar indicates standard deviation).

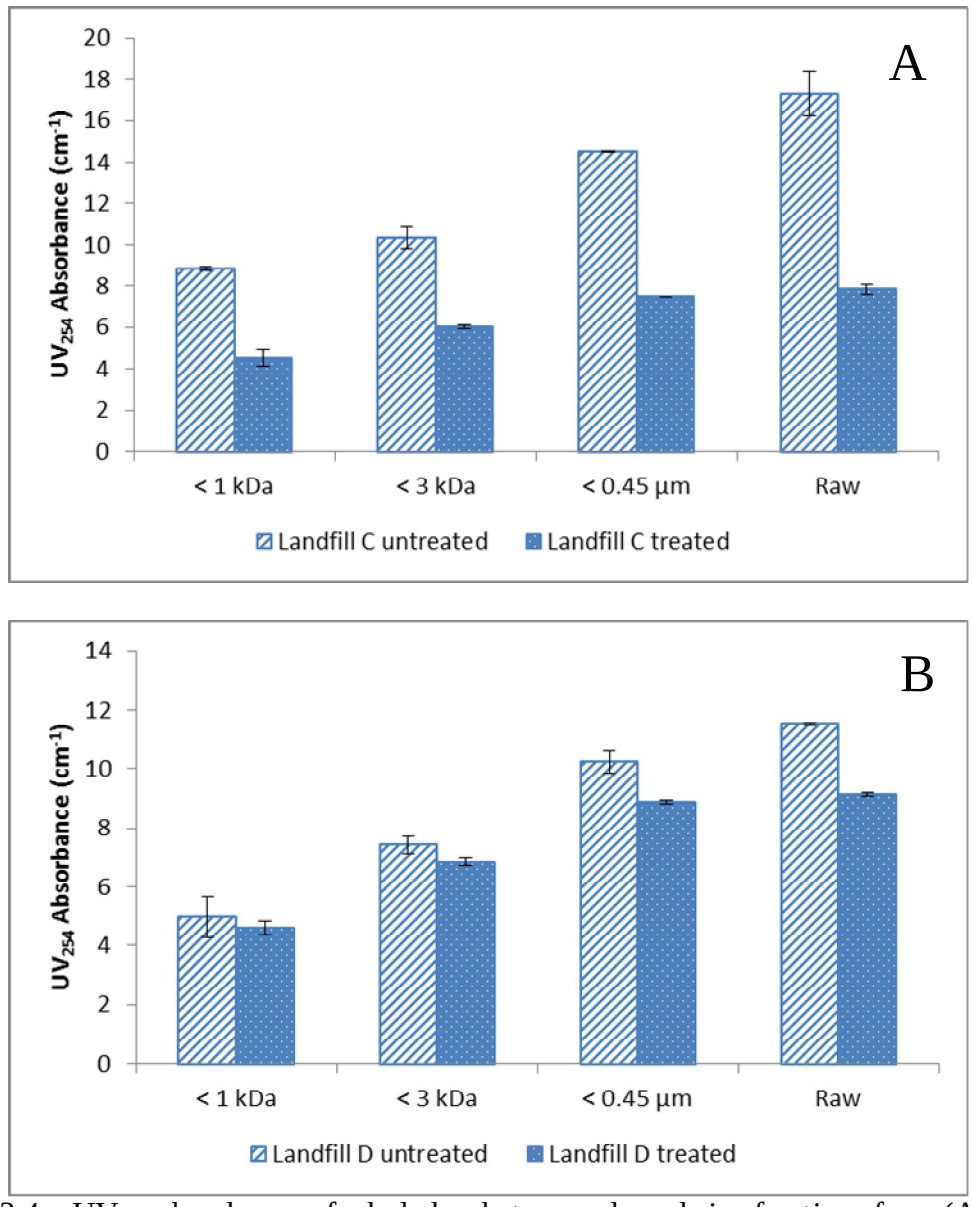
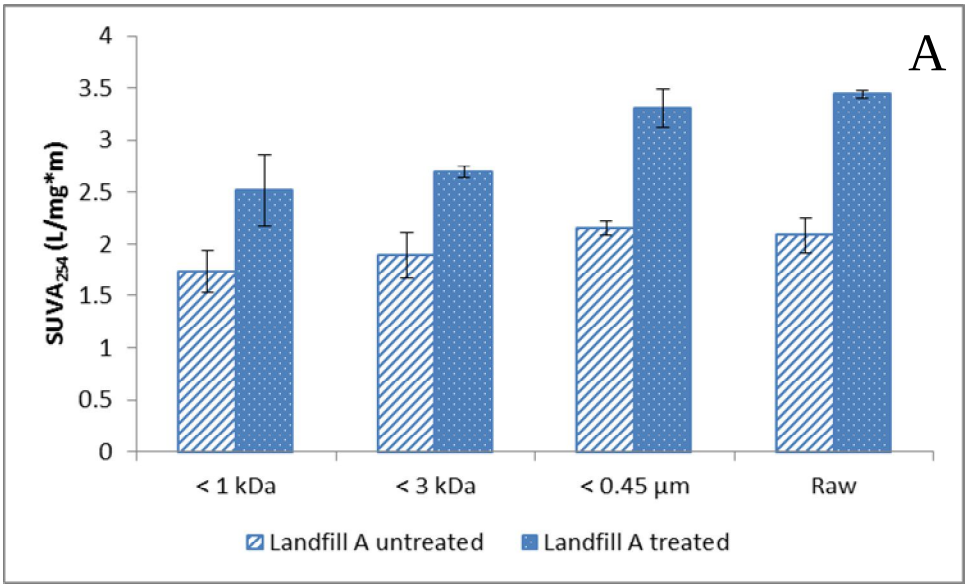


Figure 3.4 – UV_{254} absorbance of whole leachate sample and size fractions from (A) Landfill C and (B) Landfill D. UV_{254} absorbance was measured three times for statistical purposes. (Error bar indicates standard deviation).



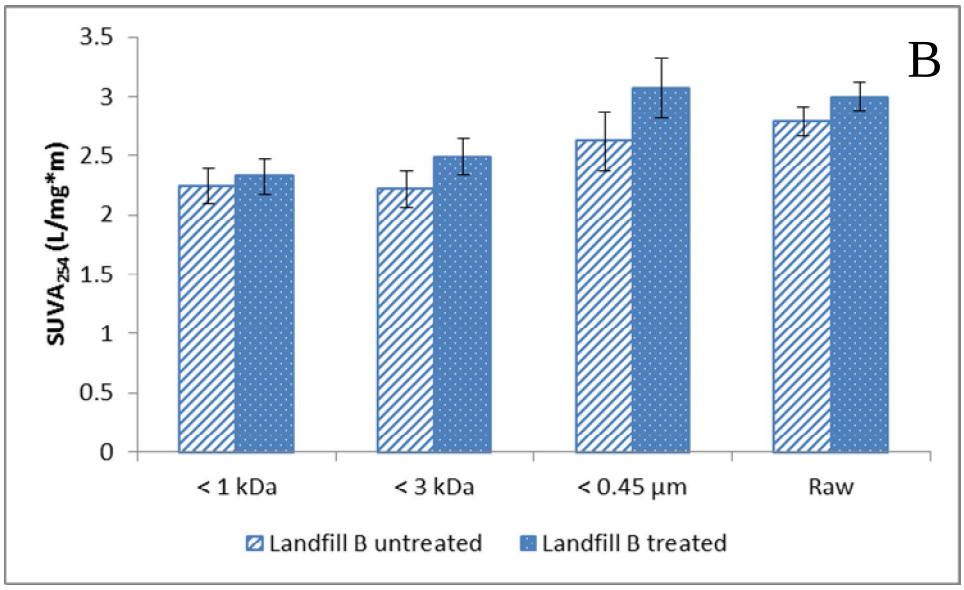


Figure 3.5 –$SUVA_{254}$ absorbance of whole leachate sample and size fractions from (A) Landfill A and (B) Landfill B. (Error bar indicates standard deviation).

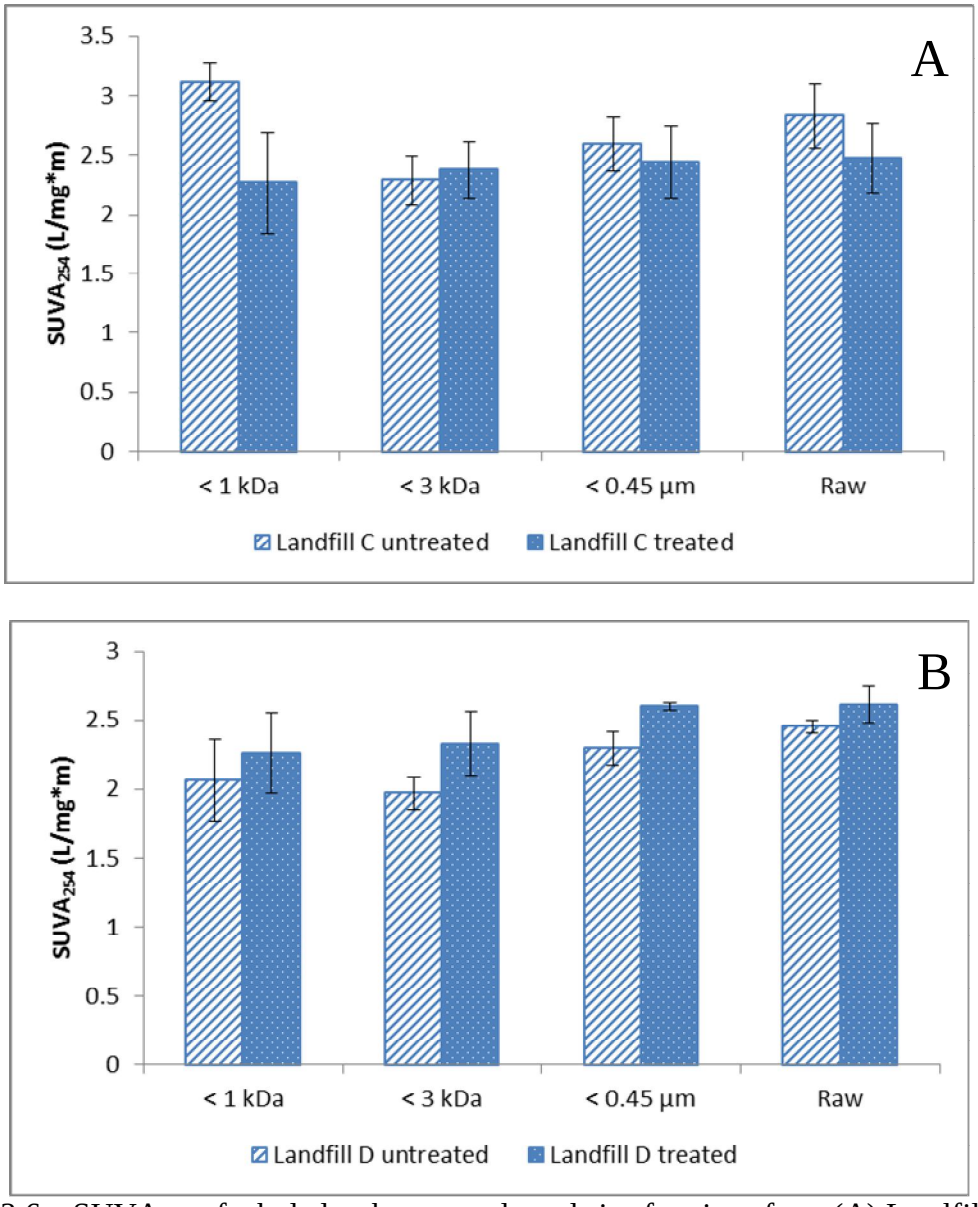


Figure 3.6 – $SUVA_{254}$ of whole leachate sample and size fractions from (A) Landfill C and (B) Landfill D. (Error bar indicates standard deviation).

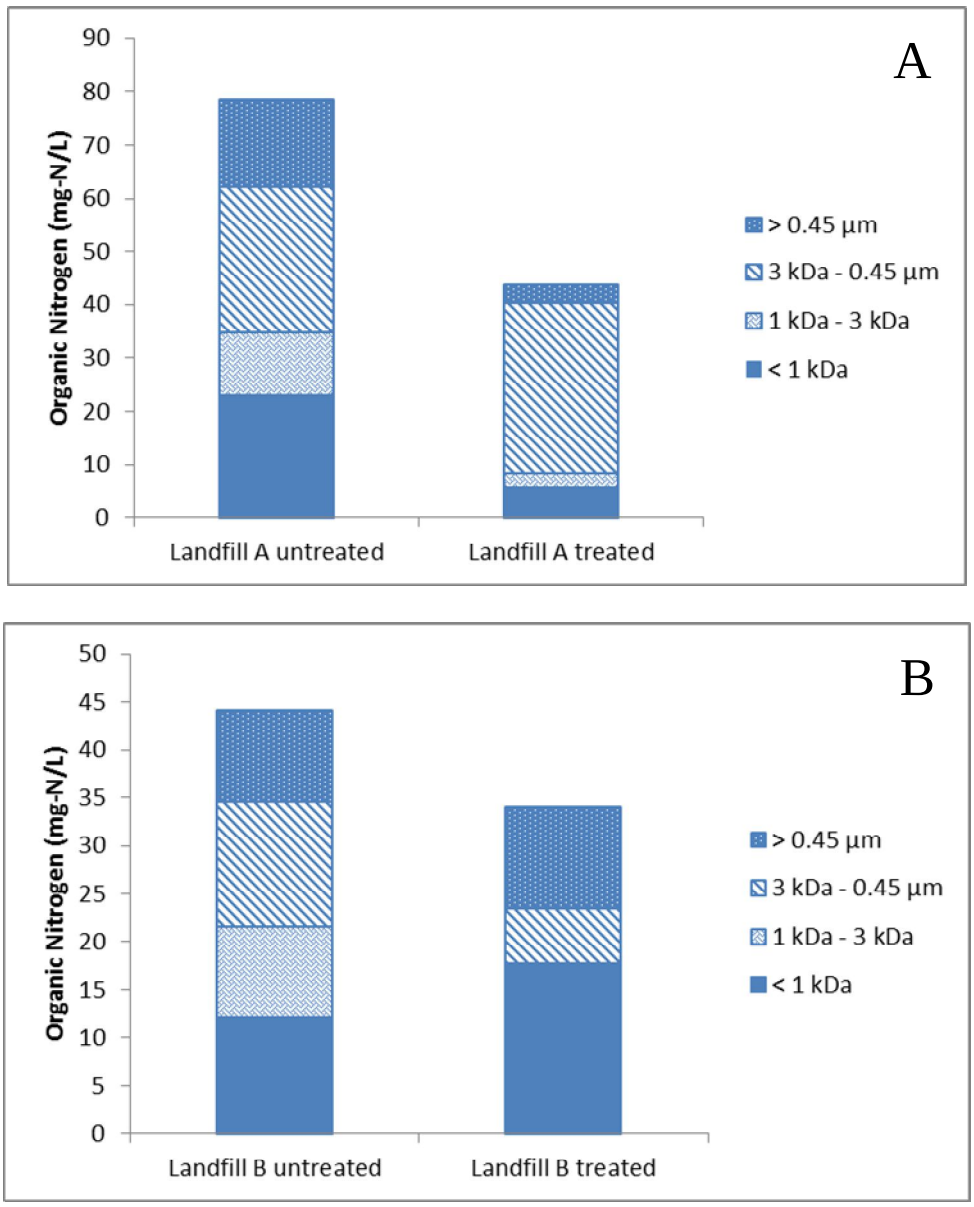
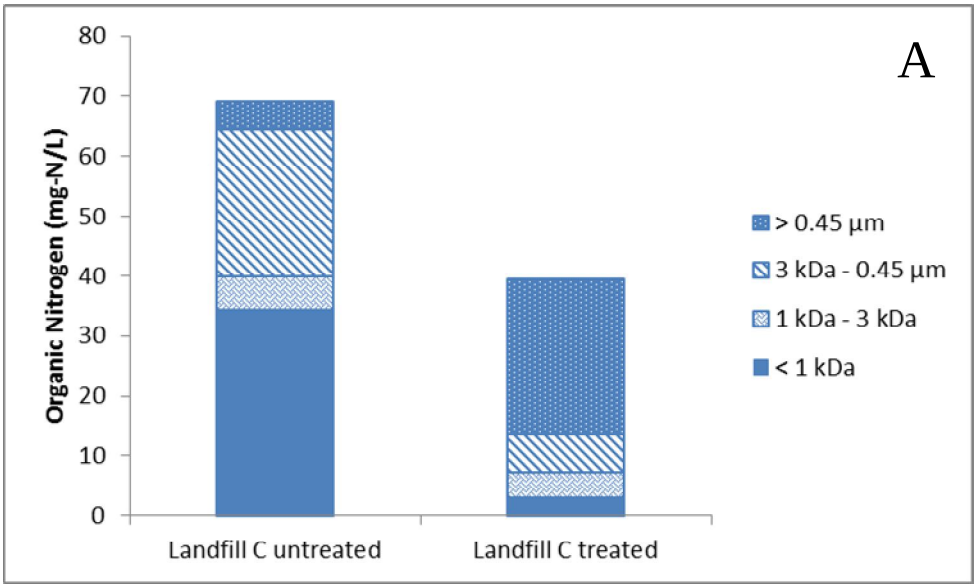


Figure 3.7 – Size distribution of organic nitrogen and untreated and treated leachates shown as distributive data for (A) Landfill A and (B) Landfill B. Organic nitrogen was measured three times for statistical purposes.



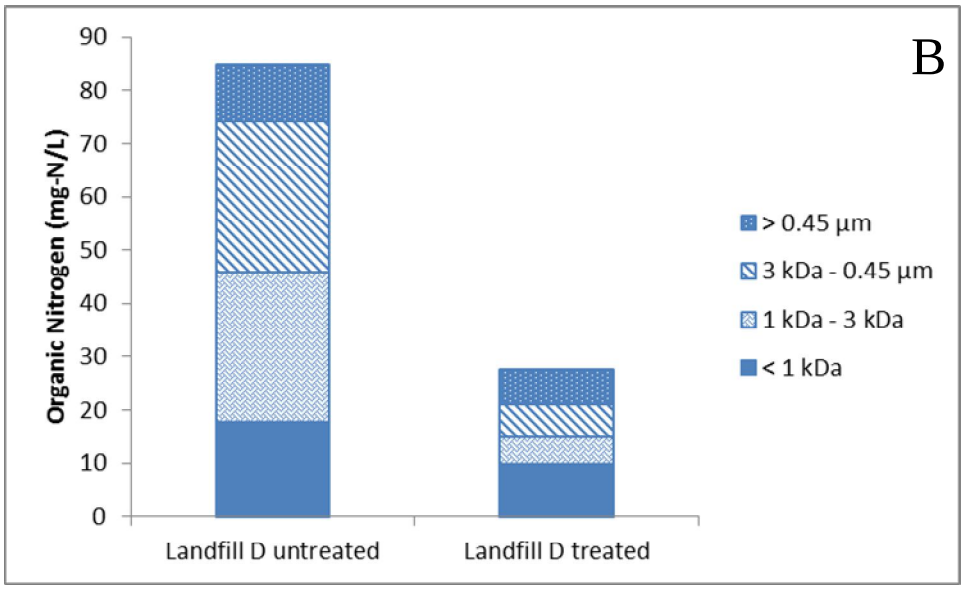


Figure 3.8 – Size distribution of organic nitrogen and untreated and treated leachates shown as distributive data for (A) Landfill C and (B) Landfill D. Organic nitrogen was measured three times for statistical purposes.

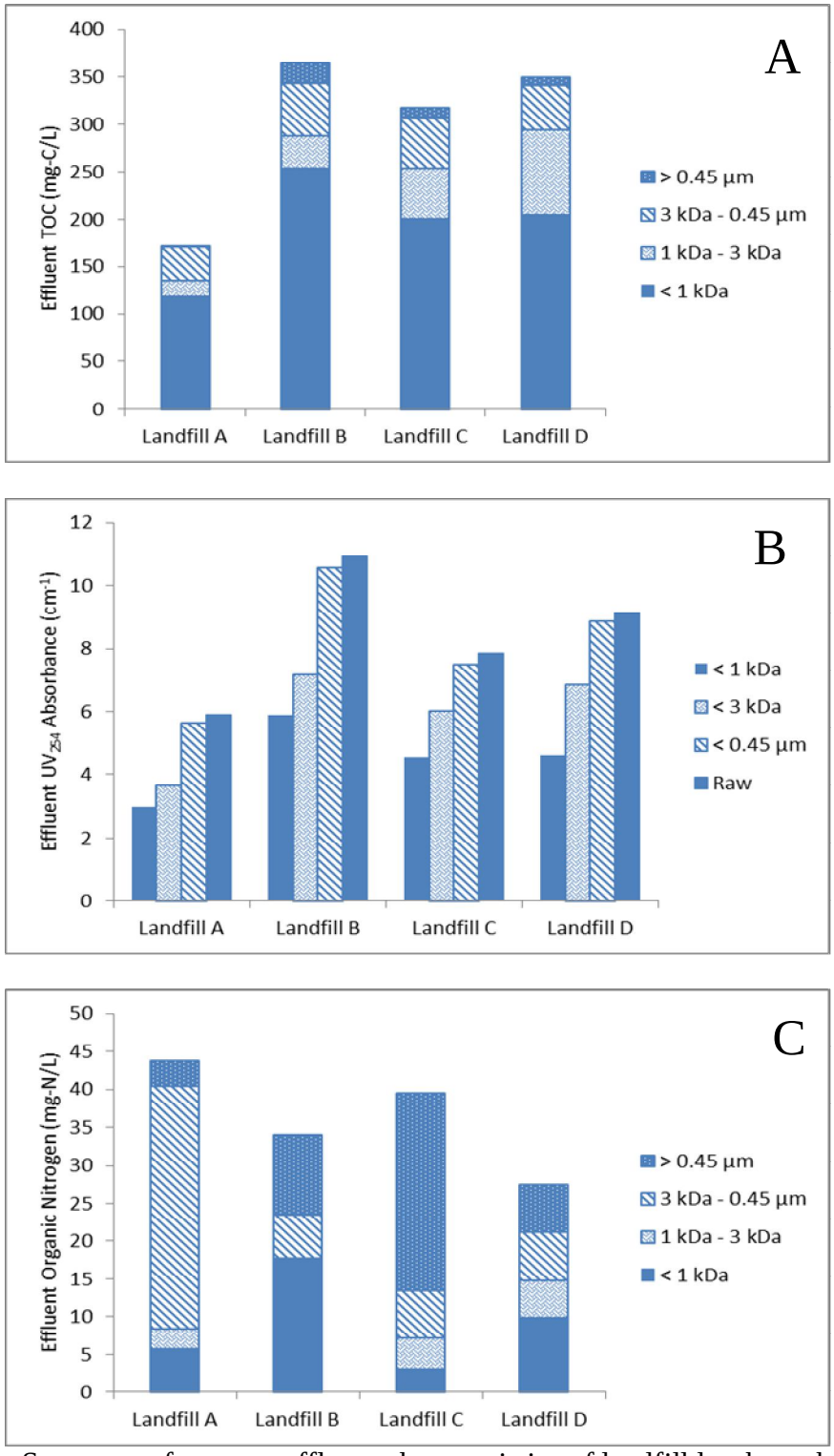


Figure 3.9 – Summary of average effluent characteristics of landfill leachates based on (A) organic matter in terms of TOC, (B) UV_{254} absorbance, and (C) organic nitrogen.

4. Hydrophobicity Distribution of Various Landfill Leachates and Evaluation of Potential Organic Constituents that Influence Publicly Owned Treatment Works (POTWs)

Abstract

Landfill leachates are often discharged through sewers or trucks to publicly owned treatment works (POTWs) after on-site biological treatment. The discharge of landfill leachate is widely accepted because of its cost effectiveness and reliability, but potential impacts of this practice include additional nutrient loading and interference with UV disinfection. Hydrophobicity distribution based on chemical composition and solubility was utilized to fractionate landfill leachate for this analysis into humic acid (HA), fulvic acid (FA), and hydrophilic (Hpi) fractions. The analysis shows that the $SUVA_{254}$ of the humic substances (HA and FA) were significantly higher than for the Hpi fraction. The UV quenching materials were found to be resistant to biological treatment for the majority of leachates. Removal of humic substances was associated with decreased UV quenching and the aromatic content of landfill leachates after biological treatment. Organic nitrogen analysis for size distribution fractions was conducted on the effluent hydrophilic fraction and indicated that the majority of organic nitrogen in landfill leachate is associated with the low-molecular weight (<1 kDa) hydrophilic fraction.

4.1 Introduction

A large quantity of municipal solid waste (MSW) is generated globally and is growing as a result of large population increases. Common practices for waste disposal include recycling, composting, incineration, and landfilling. Landfilling is a common practice throughout the world because of its cost effectiveness and ability to control environmental impacts. In the United States in 2010, approximately 54% of the 250 million tons of MSW generated was landfilled (EPA, 2011).

Landfill leachate is a waste stream associated with the practice of MSW landfilling. Landfill leachate is a contaminated aqueous solution formed by rain percolation through waste combined with liquid by-products of waste decomposition within the landfill (Renou et al., 2008). Microbial decomposition of landfilled waste material can continue for 30-40 years after the landfill is closed (Robinson, 2005) and one ton of MSW can generate up to 0.2 m^3 of landfill leachate (Kurniawan & Lo, 2009). Consequently, a large volume of landfill leachate is generated at each landfill that requires subsequent treatment. Leachates contain high levels of ammonia, organic matter, and humic constituents. Landfill leachates can vary between landfills due to MSW type, age, seasonal precipitation fluctuations, and other parameters. These differences in landfill leachate composition and quantity may cause difficulties for treatment (Renou et al., 2008).

Landfill leachate requires collection on-site through liners and leachate collection systems and treatment is required before discharge to the environment. On-site biological pre-treatment before sewer discharge to POTWs is a common disposal method

for landfill leachate because of its cost effectiveness and reliability. The potential impacts on downstream POTWs associated with sewer discharge of landfill leachate are analyzed in this study.

Possible issues associated with landfill leachate are due to the presence of humic substances. Humic substances are a major constituent of natural organic matter (NOM). They are responsible for the dark brown color of decaying vegetative material. Humic substances are heterogeneous mixtures of polydiversed elements formed by biological and chemical reactions during decomposition of vegetative substances and microbial remains in a process called humification. Humic substances are comprised of humic acids, fulvic acids, and humin. Plant lignin, polysaccharides, proteins, lipids, and nucleic acids are involved with the humification process (International Humic Substances Society, 2008). Vegetation and its by-products account for 48% of the total MSW landfilled in the United States. Paper and paperboard are responsible for 29%, yard trimmings are responsible for 13%, and wood is responsible for 6% (EPA, 2011). This large quantity of vegetative derivatives in landfills supports the humification process and promotes the formation of humic substances in landfill leachates. Humic substances are known to be resistant to biological treatment due to their molecular weight and molecular structure (Krasner et al., 2009).

Disinfection by-products (DBPs) form as a result of chlorination of NOM; therefore, humic substances are also responsible for DBP formation from chlorination of organics. UV disinfection is an alternative to chlorination because it minimizes the potential for DBP formation. Previous studies have concluded that landfill leachates can quench UV light (Zhao et al., 2012); therefore, further studies are needed to evaluate the effects of sewer discharges of landfill leachates on UV disinfection at POTWs.

This study analyzed landfill leachates from four different landfills. Samples were collected before and after on-site biological treatment to evaluate biodegradation, physio-chemical treatability, and UV quenching of each leachate. This research specifically focused on:

1) The UV_{254} absorbance and organic matter in terms of total organic carbon (TOC) for each landfill leachate in order to study the effectiveness of biological treatment at each landfill.
2) Fractionation of dissolved organic matter (DOM) into humic acids (HA), fulvic acids (FA), and hydrophilic (Hpi) fractions for each leachate sample. Further analysis of TOC and UV_{254} absorbance was conducted on each fraction to study the organic matter and UV quenching attributed to each fraction.
3) The organic nitrogen distribution within the hydrophilic (Hpi) fraction, including a size distribution analysis.

4.2 Materials and Methods

4.2.1 Leachate sample locations and processes

In this study, leachates from four municipal solid waste landfills were characterized before and after biological treatment. The Landfill A leachate samples are from Kentucky, while Landfill B, C, and D samples are from Pennsylvania.

Landfill A has been open for over 35 years, with eight separate units ranging in age and levels of activity. Leachate was collected from the equalization basin that collects leachate from all cells of the landfill prior to treatment. Sequencing batch reactor (SBR) biological treatment is utilized at this landfill.

Landfill B leachate is also treated with a SBR activated sludge system that undergoes both nitrification and denitrification, with a capacity of 113.6 m^3 per day and a hydraulic retention time (HRT) of 6-7 days. Landfill B opened in 1973 and receives 1500 tons of MSW daily.

Landfill C is also treated with a SBR activated sludge system for ammonia and BOD removal without denitrification. Two SBR units, each with a capacity of 50,000 gallons, are used to treat 25,000 GPD on average that is discharged to a small tributary. The storage lagoon with aeration is approximately 1.5 million gallons. Landfill C opened in 1993, receiving on average 300 tons of MSW and 200-300 tons shale cuttings per day. The shale cuttings result from the local hydraulic fracturing activity.

Landfill D utilizes two aerated 300,000 gallon storage tanks, one 1.5 million gallon storage tank, and MetPro fixed film bioreactors designed for 40,000 GPD for ammonia and BOD removal without denitrification. Secondary clarification occurs on-site with ferric chloride and polymer addition for solids and metals removal. Treated effluent from this landfill is discharged to local publicly owned treatment works (POTW). Landfill D opened in 1987 and receives between 500-6000 tons of MSW per day.

All leachate samples were collected as grab samples and placed in polyethylene buckets for transport from the landfill to the lab. Upon arrival, the leachate containers were immediately stored at 4 ^{O}C in the dark to reduce microbial activity.

4.2.2 Fractionation

Fractionation of landfill leachate samples into humic acids (HA), fulvic acids (FA), and hydrophilic (Hpi) fractions was conducted based on hydrophobicity characteristics and solubility. Isolation and separation of humic substances was conducted using techniques for aqueous solutions developed by (Thurman & Malcolm, 1981), (Leenheer, 1981), (Christensen et al., 1998), and (Pehlivanoglu-Mantas & Sedlak, 2008). Chemical precipitation was used to remove humic acids by acidifying leachate because humic acids are insoluble below pH 2. The pH of each sample was analyzed by a pH meter (Model No. 910, Accumet, Cambridge, MA) with a pH probe (Model No. 13-620-287, Accumet,

Petaling Jaya, Malaysia). Following humic acid isolation, XAD resin was used to sorb fulvic acids.

Initially, leachate samples were filtered through a 1.5 μm glass fiber filter and acidified to pH 2 with concentrated HCl. Humic acids precipitated at this low pH, and isolation of humic acids was conducted using a 0.45 μm cellulose nitrate membrane (46 mm, Sartorius Stedim Biotech, France). Isolated humic acids were re-dissolved by combining collected humic acids with a 0.1 M NaOH solution including the 0.45 μm membranes to minimize loss of humic acids during transfer. The re-dissolved solution of humic acid was used for analysis.

The supernatant from the 0.45 μm filtration contained both fulvic acid and hydrophilic fractions. This supernatant was passed through approximately 3.5 – 4.5 mL of cleaned XAD-8 resin (Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) packed in a borosilicate glass column (1.0 x 10 cm, Thomas Scientific, Swedesboro, NJ). The method used in this analysis to clean the XAD-8 resin was described by (Leenheer, 1981)**.** The supernatant was passed through the resin column at a flow rate of 10-15 bed volumes per hour. Fulvic acids were retained in the XAD-8 column, while the hydrophilic portion was collected after it passed through the column. Fulvic acids were collected by passing a solution of 0.1 M NaOH through the resin column to elute the fulvic acids sorbed on the resin column.

Ultrafiltration of the hydrophilic portion of the leachate samples was conducted using dead end batch ultrafiltration (Model 8200, Amicon, Belford, MA) and membrane discs with a molecular weight cut off of 1 kDa (PLAC, Millipore, Billerica, MA).

4.2.3 Analysis

All the chemicals used in this analysis were analytical grade. All the glassware was washed, rinsed with deionized water, and baked for four hours at 450 ^{O}C prior to use. Organic matter in terms of total organic carbon (TOC) was analyzed using high temperature combustion method (TOC-5000A, Shimadzu, Japan). Ultraviolet absorbance at 254 nm (UV_{254} absorbance) was analyzed using a spectrophotometer (DU 640, Beckman Coulter, Brea, California). Leachate samples were diluted during both the TOC and UV_{254} absorbance analysis to ensure that readings were within the acceptable detection range for each test. Test readings were then multiplied by the dilution factor to give the final test results used for this analysis. Specific UV_{254} absorbance (SUV_{254}) was calculated by dividing UV_{254} absorbance by TOC.

Organic nitrogen was analyzed through nitrogen species tests for each effluent hydrophilic fraction in order to evaluate potential loading on downstream WWTPs. Organic nitrogen (ON) was evaluated by subtracting the amount of inorganic nitrogen (IN) from the total nitrogen (TN) of each leachate sample (Pehlivanoglu-Mantas & Sedlak, 2008); (Zhao et al., 2012). High concentration of inorganic nitrogen can yield less accurate results with this organic nitrogen calculation. Total nitrogen was measured using the persulfate digestion method (Hach, Loverland, CO). The inorganic nitrogen is

composed of ammonia, nitrate, and nitrite in each landfill leachate. Ammonia was measured using the salicylate method (Hach, Loverland, CO). Nitrate and nitrite concentrations were evaluated using the dimethylphenol and diazotization methods, respectively (Hach, Loverland, CO). Samples were diluted in order to ensure test results within the acceptable limits for nitrogen species analysis, and final results used in this analysis were calculated by multiplying the dilution factors and the test results. Analysis for organic nitrogen was conducted at least three times for each leachate.

4.2.4 Statistics

Statistical analysis was conducted using Microsoft Excel 2010 (Microsoft Corporation, Redmond, WA) and correlation analysis was performed using R language.

4.3 Results

4.3.1 Biodegradation of TOC and UV

Landfill leachates from four different landfills were analyzed with respect to organic matter in terms of TOC and UV_{254} absorbance. An analysis of the biodegradation of TOC and UV_{254} absorbance by on-site biological treatment was conducted in the first stage of this study. Figure 4.1 (A) includes the organic matter concentration in terms of TOC and Figure 4.1 (B) shows total UV_{254} absorbance of each landfill leachate before and after biological treatment. Biological treatment decreased both TOC and UV_{254} absorbance for each leachate.

It can be seen in Figure 4.1 (A) that a large amount of organic matter was removed through biological treatment for each leachate sample. Landfill A and Landfill C experienced the greatest reductions in organic matter. The TOC removal efficiencies for Landfill A, Landfill B, Landfill C, and Landfill D after biological treatment were 54%, 31%, 48%, and 26%, respectively. Landfill A is comprised of eight cells that widely vary in age, but most of the landfill leachate volume was likely contributed by the newer, younger landfill cells because those cells were still open to rainfall. Therefore, the Landfill A leachate mix is probably more characteristic of young leachate. The youngest leachates in this analysis, Landfill A and Landfill C, demonstrated the most significant reductions in organic matter, while the older leachates, Landfill B and Landfill D, exhibited less significant reductions. The less significant reductions appear to be due to recalcitrant organic materials characteristic of older landfill leachates.

Figure 4.1 (B) shows the removal of UV_{254} absorbance after biological treatment for each leachate studied. The removal of UV_{254} absorbance occurred to a much lesser extent than the removal of TOC for the majority leachates in this study. The removal of TOC ranged from 26% - 54%, but UV_{254} removal ranged from 21% - 26% for all leachates except Landfill C. This analysis supports previous studies indicating that the removal of UV quenching substances responsible for UV_{254} absorbance occurs to a lesser extent than the removal of organic matter in terms of TOC after biological treatment (Zhao et al., 2012). The UV_{254} absorbance removal for Landfill C was 55% during this analysis. These data

indicates that the biological treatment at Landfill C was much more effective for UV_{254} absorbance removal than the other biological treatments at the other landfills studied. This high amount of removal may be attributed to a variety of factors, including landfill age and the types of MSW within the landfill.

The specific UV_{254} absorbance ($SUVA_{254}$) was determined in order to study the relationship between TOC and UV_{254} absorbance for each leachate sample. Figure 4.1 (C) reflects the results of the $SUVA_{254}$ calculations. The $SUVA_{254}$ increased for Landfill A, Landfill B, and Landfill D leachates after biological treatment, indicating the biorefractory nature of UV_{254} absorbing organics in these leachates. Landfill C was the only landfill in this study to show a decrease in $SUVA_{254}$ after biological treatment as a result of significant removal of UV_{254} absorbing organics by biological treatment. The decreased $SUVA_{254}$ for the Landfill C further demonstrated that the UV quenching materials in that leachate were less refractory than in the other leachates.

Previous studies have established a strong correlation between $SUVA_{254}$ and the magnitude of aromatic content within various aquatic organic matter samples in the environment through ^{13}C NMR (Weishaar et al., 2003). Increased $SUVA_{254}$ after biological treatment for Landfill A, Landfill B, and Landfill D indicates the biorefractory nature of UV quenching substances, which may be attributed to the biorefractory nature of aromatic compounds. The decreased $SUVA_{254}$ for the Landfill C indicates the significant removal of both organic matter and UV quenching substances. Further analysis was conducted to explore the significant UV_{254} removal efficiency for this landfill leachate by biological treatment.

4.3.2 Hydrophobicity distribution of TOC and UV absorbance and their correlation

The second stage of this study included fractionation of landfill leachates into HA, FA, and Hpi fractions based on chemical composition and hydrophobicity. TOC and UV_{254} absorbance were both measured for each hydrophobic fraction in order to determine the distribution of organic matter in terms of TOC and the UV_{254} absorbance for each landfill leachate. Because HA and FA are humic substances, these fractions were expected to be major contributors to the UV quenching of landfill leachates. Humic substances are expected to have higher aromaticity and UV quenching ability than the hydrophilic fraction due to their chemical structure and lignin and lignin derived composition. The hydrophobicity distribution was included in this study to further analyze the nature of UV_{254} absorbing substances.

Figure 4.2 shows the hydrophobicity distribution for organic matter in terms of TOC for landfill leachates before and after biological treatment. Figure 4.2 (A) shows the distribution of TOC for Landfill A before and after SBR activated sludge treatment. Each fraction decreased after biological treatment. The HA, FA, and Hpi fractions decreased by 68%, 50%, and 43% respectively. Figure 4.2 (B) shows the distribution of TOC for the Landfill B. The HA fraction stayed approximately the same before and after biological treatment, but the FA and Hpi distributions decreased by 50% and 39%, respectively.

Figure 4.3 shows the hydrophobicity distribution for organic matter in terms of TOC for Landfill C and Landfill D. Figure 4.3 (A) shows that all fractions decreased for the Landfill C after biological treatment without a significant change in the hydrophobicity distribution. The HA, FA, and Hpi fractions decreased by 68%, 50%, and 46%, respectively after biological treatment. Figure 4.3 (B) also shows decreases for the Landfill D for each fraction without significant changes in the distribution of organic matter. HA, FA, and Hpi fractions decreased by 52%, 18%, and 23%, respectively. Figures 4.2 and 4.3 both illustrate that biological treatment partially removed a fraction of TOC for the majority of fractions. With the exception of treated Landfill B leachate, the Hpi fraction was larger than either the HA or FA fractions.

The hydrophobicity distribution of landfill leachates with respect to UV_{254} absorbance before and after biological treatment was also included in this study. Figure 4.4 (A) shows the hydrophobicity distribution in terms of UV_{254} absorbance for the Landfill A, while Figure 4.4 (B) shows the distribution for Landfill B leachate. As shown in Figure 4.4 (A), the UV_{254} absorbance was dominated by the FA fraction both before and after biological treatment for the Landfill A leachate. The percent UV_{254} removal was highest for the FA fraction at 35%, while the HA and Hpi fractions decreased to a lesser extent at 19% and 12%, respectively. Figure 4.4 (B) shows that HA and FA fractions dominated the UV_{254} absorbance of Landfill B leachate before biological treatment and the HA fraction dominated after biological treatment. The FA fraction decreased to the greatest extent after biological treatment at 48%, while the HA and Hpi decreased at 22% and 15%, respectively. The small decrease in the HA fraction indicates the biorefractory nature of humic acids in this leachate sample.

The distribution of UV_{254} absorbance for Landfill C and Landfill D leachates before and after on-site biological treatment is presented in Figure 4.5. Figure 4.5 (A) further illustrates significant removal of UV_{254} absorbance as a result of on-site biological treatment at the Landfill C. The HA, FA, and Hpi fractions are relatively equal before biological treatment at 32%, 38%, and 30% of the total UV_{254} absorbance, but the HA fraction decreases to a much greater extent as a result of biological treatment. The HA fraction removal efficiency was 77%, which was the highest removal efficiency for any fraction of landfill leachate in this study. The FA and Hpi fractions also decreased significantly at 32% and 24%, respectively. The large UV_{254} removal efficiencies for each fraction contributed to the large decrease in UV quenching of the Landfill C leachate after biological treatment. Figure 4.5 (B) shows the hydrophobicity distribution of Landfill D leachate in terms of UV_{254} absorbance. The FA and Hpi fractions stayed relatively consistent after biological treatment, but the HA fraction decreased by approximately 44%. The small removal efficiencies for the FA and Hpi fractions contributed to the low removal efficiency of UV_{254} absorbance for Landfill D leachate by on-site biological treatment.

Further analysis on the basis of organic matter in terms of TOC and UV_{254} absorbance was conducted on each fraction of the hydrophobicity distribution through a regression analysis shown in Figure 4.6. This regression analysis was conducted on each individual

fraction in order to characterize the UV_{254} absorbance based on the specific organic matter basis. Statistical analysis supports the hypothesis that UV_{254} absorbance is directly proportional to the magnitude of organic matter in terms of TOC. The p-values for the HA, FA, and Hpi fractions were 4.99e-03, 3.36e-06, and 2.01e-06, respectively. In addition, the R^2 values for HA, FA, and Hpi fractions were 0.87, 0.92, and 0.78, respectively.

Figure 4.6 reflects different slopes for each hydrophobicity fraction. The slopes of the HA and FA fractions were similar, with values of 0.0254 and 0.0251, respectively on the regression curve. The slope of the Hpi fraction was the smallest at 0.009, indicating that the hydrophilic fraction was the weakest UV absorber on an organic matter basis.

Table 4.1 shows the $SUVA_{254}$ data for each fraction of the landfill leachates in this study. Biological treatment resulted in an increased $SUVA_{254}$ for all fractions of Landfill A and Landfill D leachate. For Landfill B and Landfill C leachates, the $SUVA_{254}$ decreased for the HA fraction and increased for the FA and Hpi fractions.

4.3.3 Organic Nitrogen Distribution in the Hydrophilic Fraction

The organic nitrogen distribution was evaluated as part of this study. Previous studies have characterized the total organic nitrogen in biologically treated landfill leachates for this set of landfill leachates. For details, please refer to Chapter 3 of this manuscript. The effluent hydrophilic fraction of each landfill leachate was further evaluated for organic nitrogen because previous studies have shown that a large fraction of organic nitrogen in biologically treated aqueous solutions is comprised of hydrophilic, low-molecular weight compounds less than 1 kDa molecular weight (Pehlivanoglu-Mantas & Sedlak, 2008); therefore, organic nitrogen was also evaluated for the effluent hydrophilic fractions samples at a molecular weight cut off of 1 kDa.

Figure 4.7 shows the effluent organic nitrogen distribution for each landfill leachate in this study. The total effluent organic nitrogen concentrations ranged from 27.5 – 43.7 mg-N/L. The organic nitrogen may become the dominant species of nitrogen for systems with advanced nitrogen removal because organic nitrogen is not oxidized effectively during biological treatment. For the maximum concentration of effluent organic nitrogen of 44 mg-N/L, landfill leachate could increase the organic loading on downstream systems as much as 0.44 ppm at a discharge rate of 1%. This additional nitrogen load could have substantial impacts in the future if total nitrogen regulations are decreased for the systems where landfill leachate is discharged.

The effluent hydrophilic fraction for Landfill A, Landfill B, Landfill C, and Landfill D was responsible for 40%, 79%, 79%, and 91%, respectively of the total organic nitrogen. In addition, the effluent hydrophilic fraction less than 1 kDa contributed 15%, 73%, 61%, and 88% for Landfill A, Landfill B, Landfill C, and Landfill D leachates respectively. These distributions further support previous studies that state a large fraction of the organic nitrogen consists of the hydrophilic fraction, especially the hydrophilic fraction less than 1 kDa molecular weight cut off (Pehlivanoglu-Mantas & Sedlak, 2008).

4.4 Discussion

Landfill leachates are often biologically treated on-site before being discharged to POTWs because this treatment alternative is cost effective and reliable. In this study, four sets of landfill leachates were characterized before and after biological treatment in order to determine the effectiveness of biological treatment. Organic matter in terms of TOC and UV_{254} absorbance was measured in this treatability study to determine the potential impacts on downstream POTWs as a result of sewering landfill leachate.

This study supports previous research that showed that organic matter in terms of TOC degraded to a greater extent than UV_{254} absorbance, indicating the recalcitrant nature of the organics that are responsible for UV quenching in landfill leachate. Humic substances are a major component of landfill leachate due to the humification processes that occur within the landfill as a result of the decomposition of lignin and lignin derivative waste. Humic substances are responsible for UV quenching in landfill leachate and are known to be resistant to biological treatment. A hydrophobicity distribution was included in this analysis in order to determine the fractions of landfill leachate primarily responsible for organic matter in terms of TOC and UV_{254} absorbance.

The hydrophilic fraction dominated the organic matter in terms of TOC for the majority of landfill leachates in this analysis, but the sum of the HA and FA organic matter was greater than the hydrophilic portion. Fulvic acids dominate the UV_{254} absorbance for Landfill A, Landfill C, and Landfill D before and after biological treatment. Both humic and fulvic acids are responsible for the majority of UV_{254} absorbance for Landfill B leachates. These data support previous analysis that humic substances are primarily responsible for the UV quenching associated with landfill leachates. The UV_{254} absorbance was also more resistant to biological treatment than organic matter in terms of TOC, indicating the biorefractory nature of the materials associated with UV quenching.

Landfill C had the most effective treatment in terms of UV_{254} absorbance. After studying the distribution of organic matter in terms of TOC, the low fraction of recalcitrant humic substances in relation to the hydrophilic layer may be responsible for the large removal efficiency of both organic matter and UV_{254} absorbance. Variations between landfills, including waste type and landfill age may also be a factor in the effectiveness of this biological treatment. Landfill C was the only landfill in this study to have a portion of the waste comprised of shale cuttings, and it was the youngest leachate included in this analysis.

The organic nitrogen in each treated leachate was studied to determine potential impacts on downstream POTWs. The largest amount of organic nitrogen was in the hydrophilic fraction for each leachate, indicating fractionation of humic substances decreases the total UV_{254} absorbance of treated leachate but may not decrease the organic loading on downstream systems significantly. In addition, the predominant fraction of the total organic nitrogen in the hydrophilic fraction was less than 1 kDa. This result indicates that organic nitrogen removal may not be achieved by ultrafiltration for landfill leachates.

4.5 Summary and Conclusion

Disposal of landfill leachates to POTWs for further treatment is a common practice because of its cost effectiveness. Landfill leachates can have considerable impacts on downstream wastewater treatment plants due to the additional organic loading, organic nitrogen loading and resulting UV quenching ability of the organic matter.

This analysis adds to the knowledge of landfill leachates because it utilized a hydrophobicity distribution to analyze the specific components responsible for organic matter and UV_{254} absorbance. In addition, organic nitrogen distribution was further studied in conjunction with size distribution for the hydrophilic fraction. The main conclusions from this study are:

1) UV_{254} absorbance was more refractory in nature than organic matter in terms of TOC, indicating the biorefractory nature of UV quenching substances.
2) The $SUVA_{254}$ for the humic substance fraction (HA and FA) was significantly higher than the hydrophilic (Hpi) fraction before and after on site biological treatment.
3) The $SUVA_{254}$ increased as a result of biological treatment for all leachates studied except for the Landfill C landfill leachate. The decrease of $SUVA_{254}$ in Landfill C after biological treatment indicates more significant removal of humic substances, less refractory characteristics of humic substances in this leachate, and decreased aromatic content.
4) The organic nitrogen distribution in landfill leachate was dominated by the hydrophilic fraction, especially the low-molecular weight fraction less than 1 kDa.

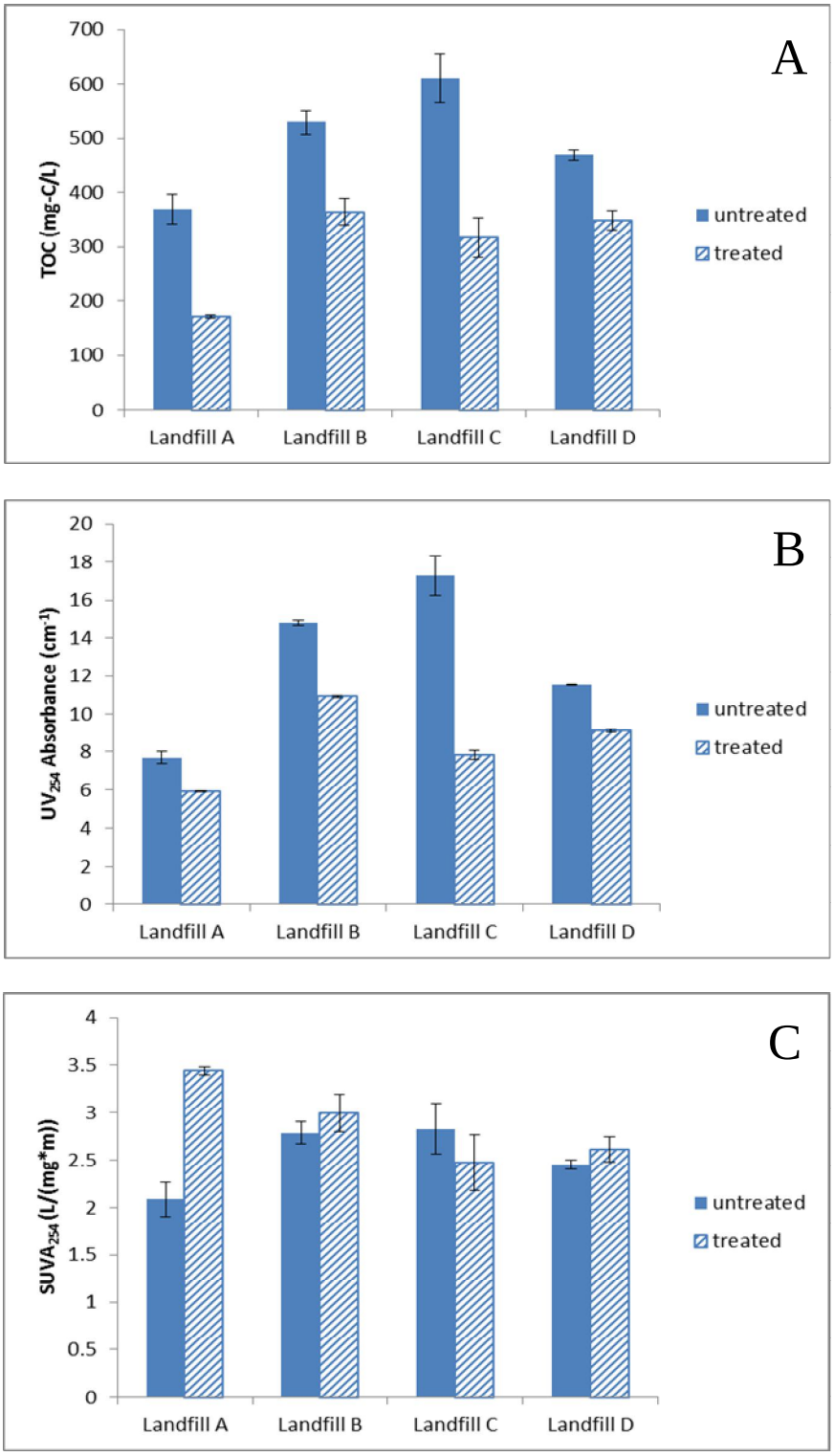


Figure 4.1 - TOC (A), UV_{254} absorbance (B), and $SUVA_{254}$ (C) before and after biological treatment of various landfill leachates.

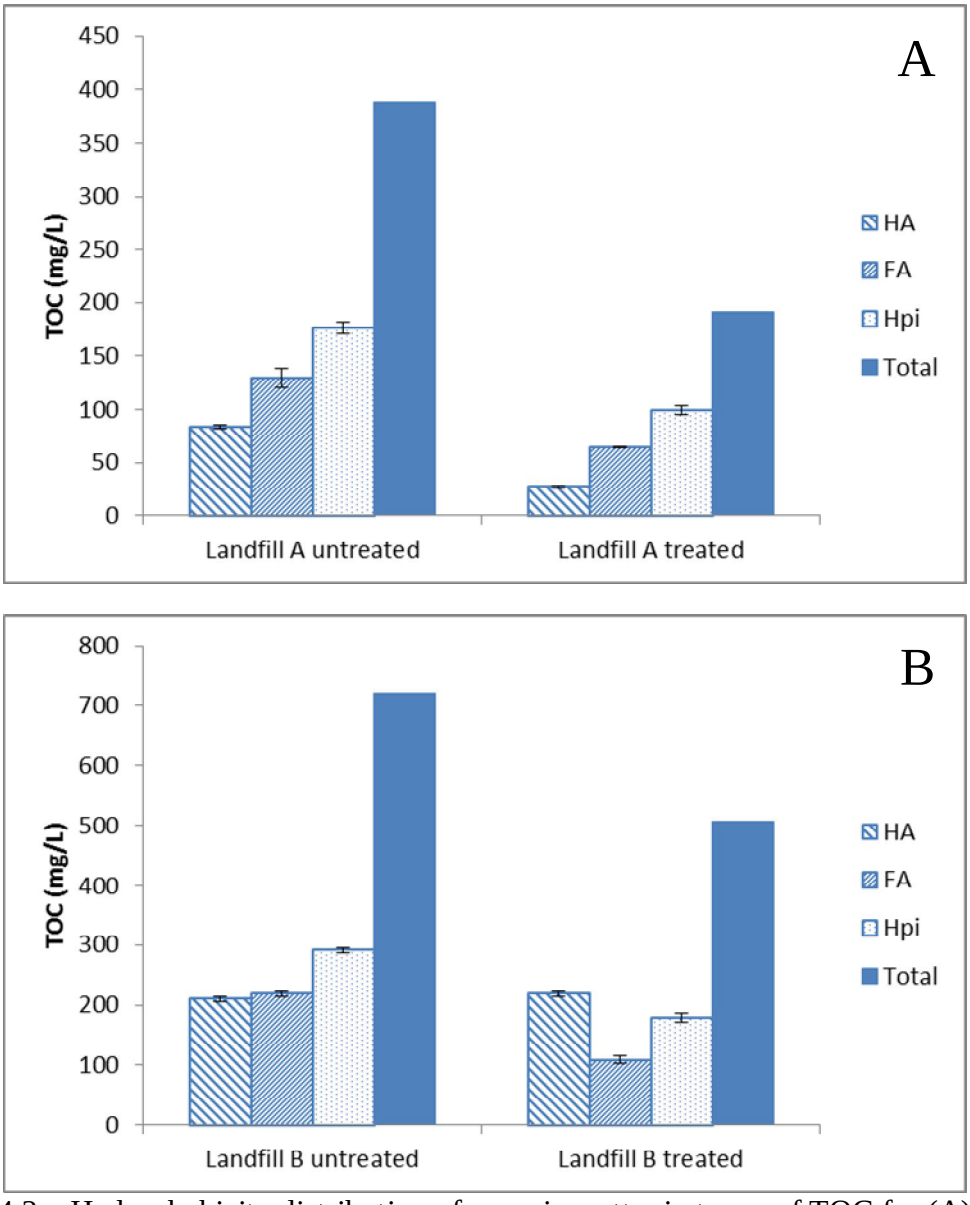


Figure 4.2 – Hydrophobicity distribution of organic matter in terms of TOC for (A) Landfill A and (B) Landfill B. TOC was measured three times for statistical purposes.

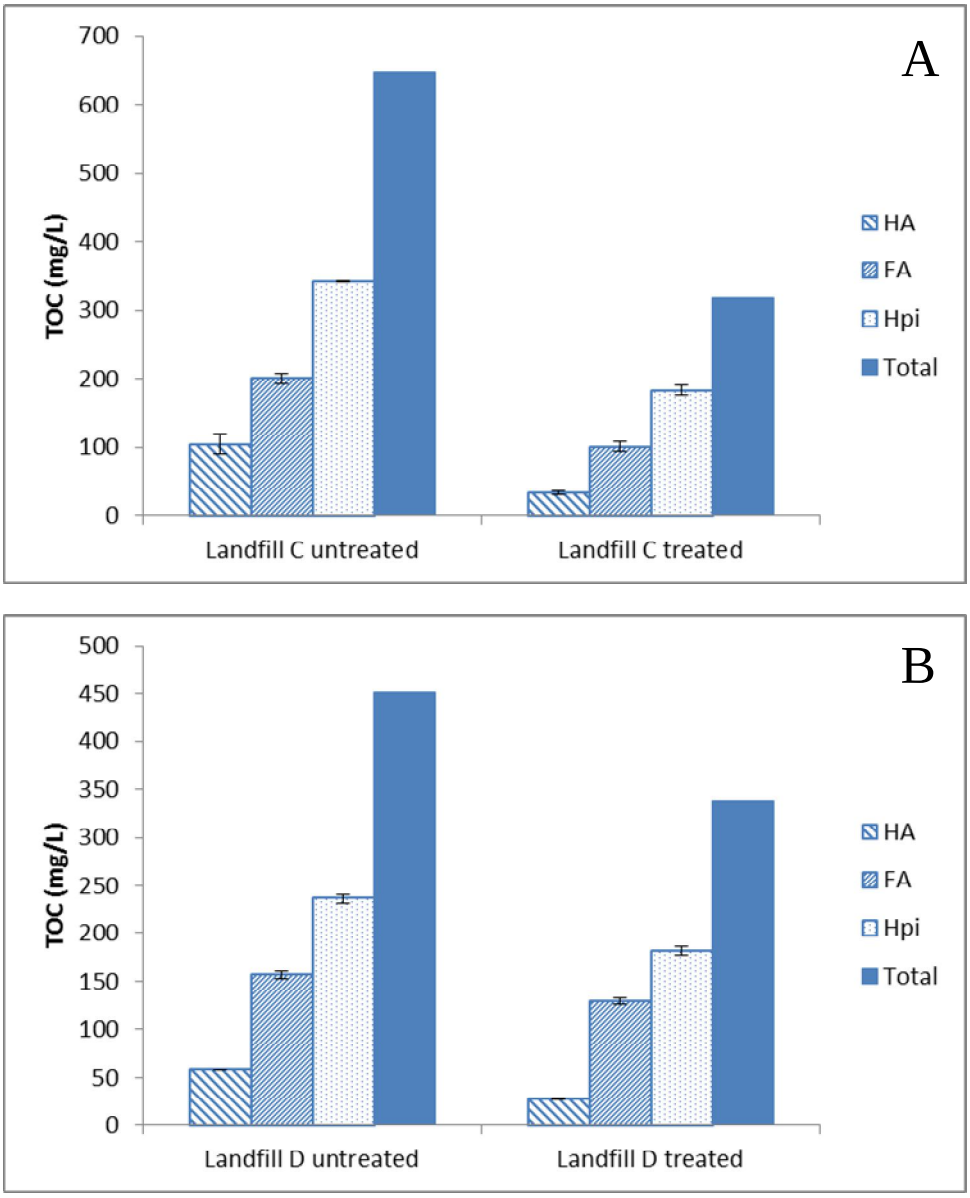


Figure 4.3 - Hydrophobicity distribution of organic matter in terms of TOC for (A) Landfill C and (B) Landfill D. TOC was measured three times for statistical purposes.

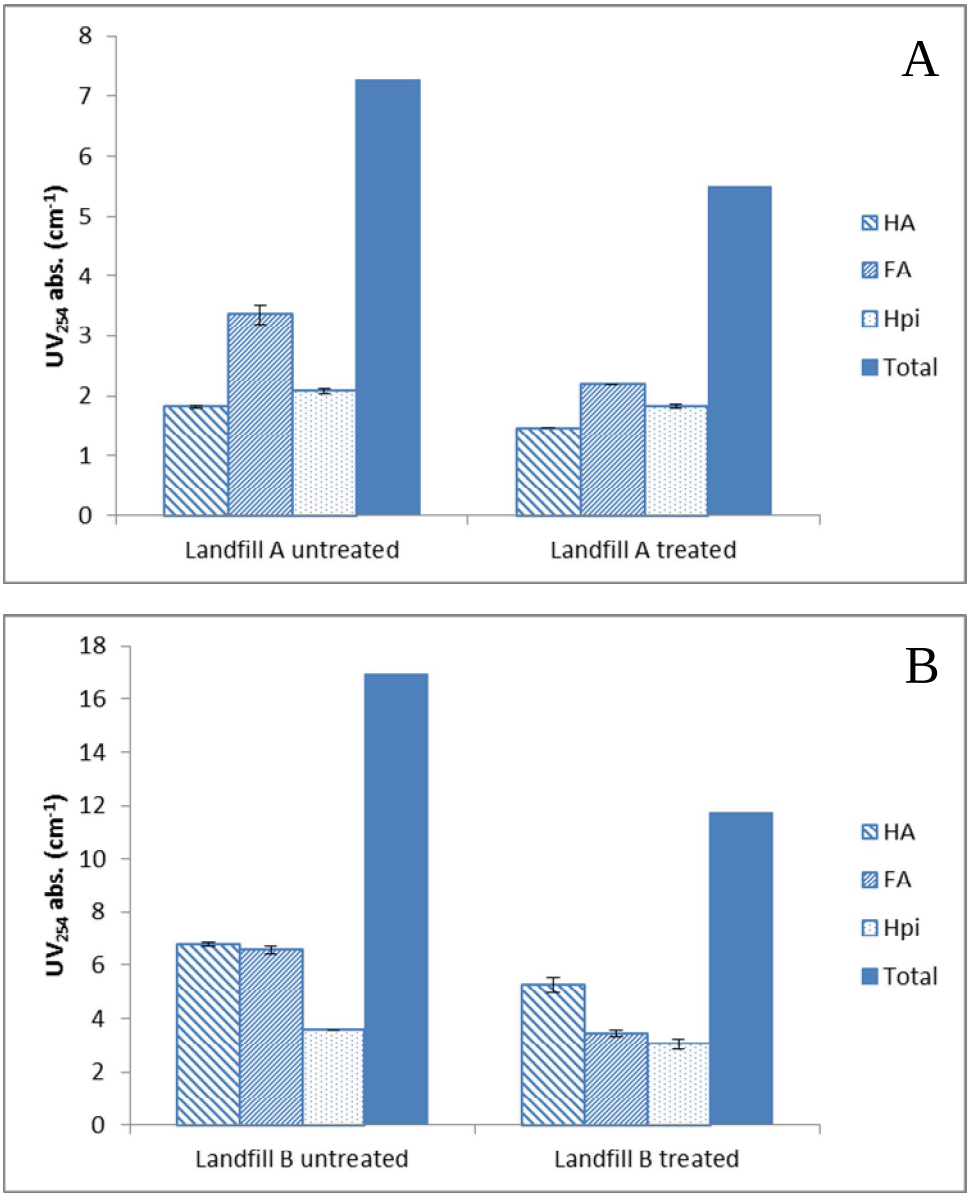


Figure 4.4 - Hydrophobicity distribution in terms of UV_{254} absorbance for (A) Landfill A and (B) Landfill B. UV_{254} absorbance was measured three times for statistical purposes. (Error bar indicates standard deviation).

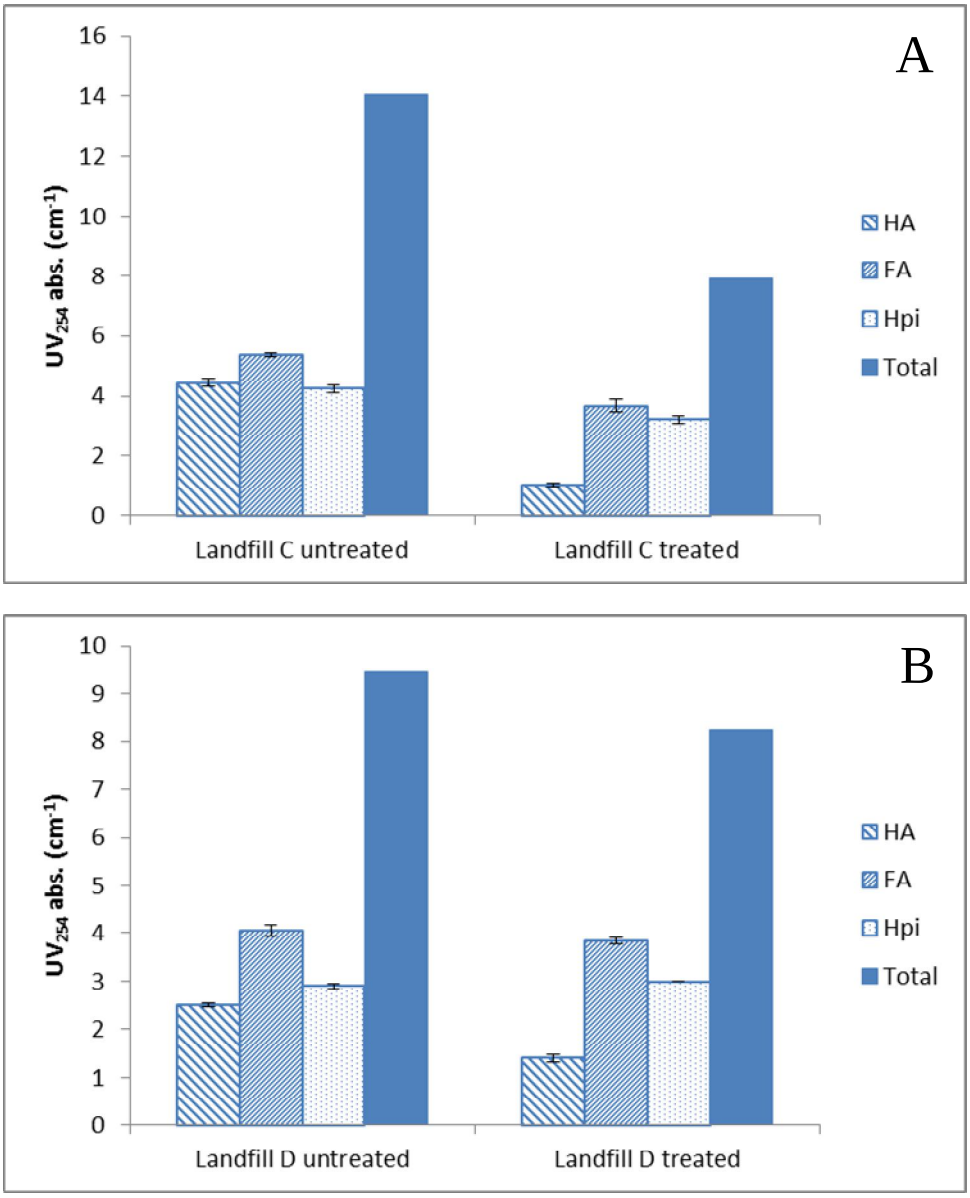


Figure 4.5 - Hydrophobicity distribution in terms of UV_{254} absorbance for (A) Landfill C and (B) Landfill D. UV_{254} absorbance was measured three times for statistical purposes. (Error bar indicates standard deviation).

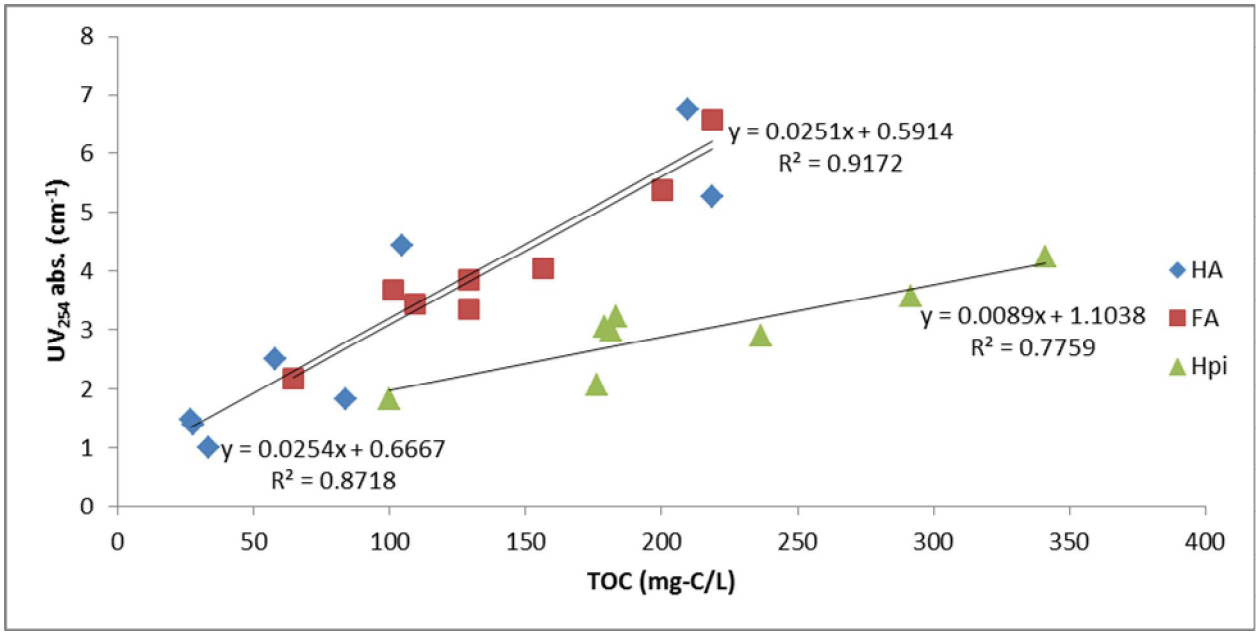


Figure 4.6 – Linear regression analysis of UV_{254} absorbance and organic matter in TOC for humic acids, fulvic acids, and hydrophilic fractions in various landfill leachates.

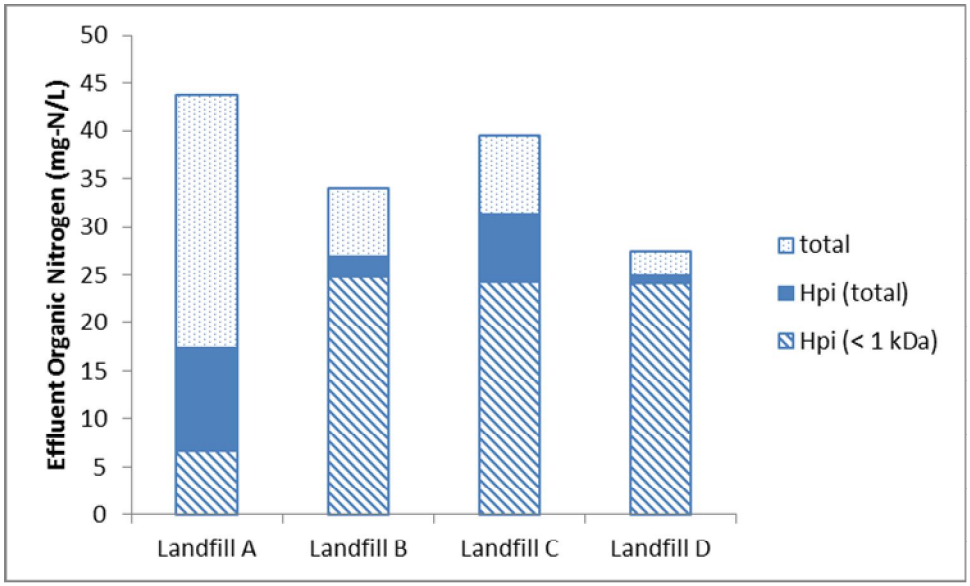


Figure 4.7 – Effluent organic nitrogen distribution for various landfill leachates. Organic nitrogen was measured three times for statistical purposes.

Table 4.1 – $SUVA_{254}$ of hydrophobicity fractions of various landfill leachates.

	$SUVA_{254}$ (L/(mg*m))		
Sample	HA	FA	Hpi
Landfill A Influent	2.18	2.60	1.18
Landfill A Effluent	5.48	3.39	1.84
Landfill B Influent	3.22	3.01	1.23
Landfill B Effluent	2.41	3.15	1.70
Landfill C Influent	4.23	2.69	1.24
Landfill C Effluent	3.03	3.63	1.76
Landfill D Influent	4.35	2.59	1.22
Landfill D Effluent	5.07	2.98	1.65

5. Appendix

Table 5.1 – Characteristics of Landfill A leachates.

		Landfill A Untreated			
Parameter	Unit	Untreated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	369.1 ± 27.0	346.9 ± 10.7	308.4 ± 19.5	280.6 ± 22.7
UV_{254} Abs.	cm^{-1}	7.7 ± 0.3	7.5 ± 0.02	5.8 ± 0.5	4.9 ± 0.4
TN	mg/L	579.3 ± 11.0	558.0 ± 12.2	523.3 ± 15.3	506.7 ± 5.8
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	4.8 ± 0.2	4.6 ± 0.4	3.2 ± 0.2	2.4 ± 0.2
NH_3	mg/L	496.0 ± 7.2	491.3 ± 31.0	485.3 ± 25.5	481.3 ± 9.5
pH	-	7.43	7.67	7.89	7.98
		Landfill A Treated			
Parameter	Unit	Treated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	171.7 ±2.1	170.0 ± 2.1	135.4 ± 2.7	117.6 ± 9.3
UV_{254} Abs.	cm^{-1}	5.91 ± 0.01	5.62 ± 0.3	3.64 ± 0.02	2.96 ± 0.3
TN	mg/L	438.3 ± 7.6	441.7 ± 20.8	411.7 ± 10.4	405.0 ± 10.0
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	394.7 ± 10.3	401.3 ± 11.6	403.3 ± 1.2	399.3 ± 2.3
NH_3	mg/L	n.d.	n.d.	n.d.	n.d.
pH	-	6.31	6.45	6.66	6.72

Table 5.2 – Characteristics of Landfill B leachates.

		Landfill B Untreated			
Parameter	Unit	Untreated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	529.5 ±22.2	523.5 ± 50.6	416.5 ±18.7	358.5 ±11.2
UV_{254} Abs.	cm^{-1}	14.8 ± 0.1	13.7 ± 0.02	9.2 ± 0.5	8.0 ± 0.5
TN	mg/L	813.3 ± 47.3	786.7 ± 37.9	730.0 ± 10.0	720.0 ±10.0
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	8.2 ± 0.4	7.8 ± 0.3	5.1 ± 0.5	3.9 ± 0.8
NH_3	mg/L	761.0 ± 8.5	744.3 ± 4.0	703.3 ± 11.4	704.0 ±21.6
pH	-	7.41	7.71	7.91	7.93
		Landfill B Treated			
Parameter	Unit	Treated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	364.5 ±24.1	343.3 ± 2.0	288.4 ± 3.3	253.3 ± 5.6
UV_{254} Abs.	cm^{-1}	10.9 ± 0.1	10.6 ± 0.1	7.2 ± 0.1	5.9 ± 0.2
TN	mg/L	77.7 ± 8.1	66.7 ± 3.2	57.7 ± 4.9	56.0 ± 2.6
NO_2^-	mg/L	28.3 ± 0.4	28.6 ± 0.8	27.9 ± 0.8	27.7 ± 0.8
NO_3^-	mg/L	13.1 ± 0.4	13.1 ± 1.1	9.9 ± 0.8	9.1 ± 0.7
NH_3	mg/L	2.4 ± 0.5	1.6 ± 0.7	2.1 ± 0.5	1.7 ± 0.01
pH	-	7.72	7.82	7.87	7.99

Table 5.3 – Characteristics of Landfill C leachates.

		Landfill C Untreated			
Parameter	Unit	Untreated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	611.4 ±44.4	559.9 ±49.4	450.3±33.2	284.3 ± 14.5
UV_{254} Abs.	cm^{-1}	17.3 ± 1.1	14.5 ± 0.01	10.3 ± 0.5	8.9 ± 0.1
TN	mg/L	776.7 ± 5.8	756.7 ±25.2	722.0 ± 7.2	708.0 ± 20.3
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	10.1 ± 0.3	10.2 ± 0.1	6.2 ± 0.6	4.4 ± 1.7
NH_3	mg/L	697.3 ± 26.6	682.0 ± 15.1	676.0 ± 15.6	669.3 ± 9.9
pH	-	8.29	8.27	8.39	8.41
		Landfill C Treated			
Parameter	Unit	Treated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	317.4 ±29.5	306.6 ± 30.3	253.5 ± 20.5	200.0 ± 26.8
UV_{254} Abs.	cm^{-1}	7.9 ± 0.2	7.5 ± 0.01	6.0 ± 0.1	4.5 ± 0.3
TN	mg/L	393.3 ± 15.2	375.0 ± 8.7	338.3 ±16.1	336.7 ± 7.6
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	331.3±14.2	340.0 ± 4.0	311.3 ± 8.1	312.7 ± 12.9
NH_3	mg/L	22.5 ± 0.9	21.5 ± 1.2	19.9 ± 0.5	21.0 ± 0.5
pH	-	7.1	7.35	7.62	7.69

Table 5.4 – Characteristics of Landfill D leachates.

		Landfill D Untreated			
Parameter	Unit	Untreated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	470.2 ± 9.5	445.7±15.8	376.6 ± 17.2	241.3 ± 8.3
UV_{254} Abs.	cm^{-1}	11.5 ± 0.04	10.2 ± 0.4	7.4 ± 0.3	5.0 ± 0.7
TN	mg/L	1100.0 ± 20.0	1073.3 ±41.6	1033.3 ± 11.6	1000.0 ± 87.2
NO_2^-	mg/L	2.3 ± 0.2	3.3 ± 0.2	3.2 ± 0.1	3.3 ± 0.2
NO_3^-	mg/L	8.0 ± 3.5	7. 4 ± 0.9	5.0 ± 0.9	3.6 ± 1.5
NH_3	mg/L	1005.0 ± 67.7	988.7 ± 54.4	979.3 ± 29.0	975.3 ± 21.9
pH	-	7.8	7.85	8.11	8.15
		Landfill D Treated			
Parameter	Unit	Treated	0.45 μm	3 kDa	1 kDa
TOC	mg/L	349.5 ±18.1	341.3 ± 3.4	294.4 ± 29.0	204.5 ± 24.1
UV_{254} Abs.	cm^{-1}	9.13 ± 0.1	8.87 ± 0.1	6.86 ± 0.1	4.62 ± 0.2
TN	mg/L	375.0 ± 5.0	370.0 ± 20.0	346.7 ±10.4	356.7 ± 17.6
NO_2^-	mg/L	n.d.	n.d.	n.d.	n.d.
NO_3^-	mg/L	178.9 ± 2.5	182.5 ±2.2	173.5 ±2.3	183.9 ± 6.3
NH_3	mg/L	168.7 ± 6.1	166.3 ±9.3	158.3 ±2.5	163.0 ± 5.3
pH	-	5.3	5.35	5.55	5.59

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