5-2015

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Alicja Trzopek
Montclair State University

Recommended Citation

Trzopek, Alicja, "Characterization of UV-Quenching Dissolved Organic Matter in Landfill Leachate" (2015). *Theses, Dissertations and Culminating Projects*. 648.
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MONTCLAIR STATE UNIVERSITY

CHARACTERIZATION OF UV-QUENCHING DISSOLVED ORGANIC MATTER IN LANDFILL LEACHATE

by Alicja Trzopek

A Master's Thesis Submitted to the Faculty of
Montclair State University
In Partial Fulfillment of the Requirements
For the Degree of
Master of Science in Geoscience

May 2015

College of Science and Mathematics

Department of Earth and Environmental Studies

Thesis Committee:

[redacted]

Thesis sponsor: Dr. Yang Deng

[redacted]

Committee Member: Dr. Ranzun Zhao

[redacted]

Committee Member: Dr. Huan Feng

ABSTRACT

Discharge of landfill leachate to publicly owned treatment works (POTWs) is a common and preferred practice in the United States. Namely, the leachate is mixed with municipal wastewater prior to traditional secondary wastewater treatment, including physical screening, primary settling, aerobic biological degradation, secondary settling and disinfection. Recently, ultraviolet (UV) light has been increasingly applied as a disinfection method at POTWs as an alternative for traditional chlorination, because the latter can produce unwanted disinfection byproducts. However, high strength dissolved organic matter (DOM) in leachate significantly increase the UV absorbing properties of the mixed wastewater at POTWs and decrease the disinfection efficiency of UV irradiation. Unfortunately, the origin and nature of the unique leachate-induced compounds are poorly understood. The objective of this study was to investigate UV-quenching characteristics of landfill leachate. Typical leachate samples were collected from two landfills in Pennsylvania (PA) and North Carolina (NC). Column isolation tests were first used to fractionate DOM into humic acids (HA), fulvic acids (FA) and hydrophilic fractions (Hpi) in terms of their polarity. Subsequently, these groups were further separated using ultrafiltration techniques into different molecular weight (MW) groups (i.e. >100 kDa, 10-100 kDa, 1-10 kDa, and <1 kDa). In both of the samples, results showed that the HA, FA, and Hpi all significantly contributed to the UV_{254} absorbance with the following order in terms of their significance: FA > Hpi > HA. However, HA had the highest specific UV absorbance at 254 nm (SUVA, defined as UV_{254}/DOC) and UV_{254}/COD, followed by FA and Hpi. The UV absorbance properties are most likely associated with aromatic degrees in molecular structures. In both samples, low MW leachate DOM (<1 kDa) contributed to the most UV_{254} absorbance in all the fractions (HA, FA and Hpi) but the UV_{254} absorbance due to FA was the highest. In both samples, FA <1 kDa MW fraction was the most abundant in terms of DOC and COD. A positive correlation between SUVA and COD/DOC was observed in the PA leachate, but not in the NC leachate. These findings provide a better understanding of UV-quenching DOM in landfill leachate.

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A THESIS

Submitted in partial fulfillment of the requirements
For the Degree of Master of Science

By:

ALICJA TRZOPEK

Montclair State University

Montclair, NJ

May, 2015

Acknowledgements

My sincere appreciation goes to Dr. Yang Deng (PE, Associate Professor at MSU), my thesis advisor, who provided invaluable support, knowledge and dedication through this entire research process. Also, I would like to thank Dr. Renzun Zhao (PE, Senior Engineer at Entex Technologies, Inc.), my thesis committee member, who has shared with me his expertise in the subject and delivered valuable feedback. Furthermore, I would like to express gratitude to Dr. Huan Feng (Professor, Graduate Program Coordinator at MSU), my thesis committee member, who provided helpful comments and assisted me in the thesis writing process. I would like to thank Nanzhu Li (Ph.D. candidate at MSU) and Dr. Chanil Jung (Postdoctoral Research Associate at MSU) for enormous help in the laboratory, priceless reviews, evaluations and knowledge.

I could not forget my family and friends for supporting me during this journey and believing in me. Moreover, I would like to recognize all the friends and colleagues from Mallory Hall 358S and 358N for friendship and good words.

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1. INTRODUCTION

1.1 Waste management in the United States

Disposal of municipal solid waste (MSW) to landfills is the most common waste management practice in United States. In 2012, this country generated approximately 251 million tons (U.S. short tons) of MSW from residential, commercial and institutional areas, of which 53.8% (i.e., 135 million tons) was discarded to landfills (US EPA 2014). The largest component of MSW is organic waste such as paper/paperboard, yard cuttings, food and wood (US EPA 2014). After recycling and composting, the aforementioned waste made up 52.8% of discarded MSW. The remaining MSW primarily includes plastics, rubber, leather, textiles, metals, glass and other waste. Of note, MSW does not contain industrial, hazardous, or construction waste (US EPA 2014).

1.2 MSW decomposition in landfills

MSW decomposes within landfills through a series of chemical and biochemical processes. Four landfill stabilization phases have been observed during landfilling, sequentially including aerobic phase, anaerobic acid phase, initial methanogenic phase, and stable methanogenic phase. Other four succeeding phases, including methane oxidation, air intrusion, carbon dioxide and soil air, are postulated to occur after the stable methanogenic phase (Kjeldsen, et al. 2002). During the initial aerobic phase that only lasts a few days, oxygen present in the void spaces between buried MSW is rapidly aerobically utilized to produce carbon dioxide (CO_2). The depletion of oxygen produces

Table 1. Nomenclature

Nomenclature:			
BOD	Biological oxygen demand	MSW	Municipal solid waste
COD	Chemical oxygen demand	MW	Molecular weight
Da	Dalton	NC	North Carolina
DBP	Disinfection byproducts	PA	Pennsylvania
DI	Deionized	POTW	Publicly owned treatment works
DOC	Dissolved organic carbon	SPE	Solid phase extraction
DOM	Dissolved organic matter	SUVA	Specific ultraviolet absorbance
FA	Fulvic acid	THM	Trihalomethanes
HA	Humic acid	TOC	Total organic carbon
HAA	Haloacetic acids	UV	Ultraviolet
Hpi	Hydrophilic	UVA	Ultraviolet absorbance
ICP-OES	Inductively coupled plasma - optical emission spectrometry	UVT	Ultraviolet transmittance

anaerobic conditions under which several types of bacteria begin to break down cellulose and hemicellulose. In the subsequent anaerobic phase, high concentrations of chemical oxygen demand (COD) and biological oxygen demand (BOD) are reported. Acids accumulated during the fermenting processes, thereby leading to pH decrease, increase the solubility of compounds. These acids are converted to methane (CH_4) and CO_2 during the methanogenic phase. Accompanied with the acid consumption, COD and BOD decrease, and pH increases. During the stable methanogenic phase, CH_4 release peaks, and its production rate depends heavily on the hydrolysis rate of cellulose and hemicellulose. With the further organic degradation, remaining organic matter becomes more refractory (e.g. humic and fulvic acids). Moisture significantly influences the MSW degradation rate. Refuse buried in arid regions decomposes less rapidly than those in the regions receiving more than 50-100 mm of rainfall annually (Kjeldsen, et al. 2002).

1.3 Characteristics of landfill leachate characteristics

As a result of oversaturation within a landfill, primarily due to precipitation, a highly contaminated wastewater, also known as leachate, is produced. Four types of major pollutants in landfill leachate have been categorized, including dissolved organic matter (DOM), inorganic macro components, heavy metals and xenobiotic organic compounds (Kjeldsen, et al. 2002). These constituents change throughout the lifecycle of a landfill. Young leachate, produced from landfills younger than five years old, is formed during the acid phase of landfill biodegradation. Therefore, it is primarily composed of highly biodegradable organic acids. In contrast, old leachate, produced from landfills older than five years old, is formed during the methanogenic phase, and principally contains recalcitrant organic compounds (Kjeldsen, et al. 2002) (Renou, et al. 2008). Average chemical compositions for young and mature leachates are shown in Table 2. It has been estimated that, on the average, 1 ton of landfilled MSW produces 0.2 m^3 of leachate (Kurniawan and Lo 2009).

1.4 Treatment and management of landfill leachate

Once released into the environment, leachate can severely pollute groundwater and surface water, as it contains toxic and carcinogenic substances. Modern landfills are required by law to be designed with geomembranes and clay soil liners that prevent the leachate leaching, and leachate collection systems that can transfer leachate outside landfills, thereby protecting the underlying groundwater and soil from leachate pollutions. In addition, to comply with federal regulations, landfills have to be situated away from environmentally sensitive areas and within geologically suitable areas.

Table 2. Average chemical compositions for young and old leachates (Kjeldsen, et al., 2002)

Indicators	Landfill Leachate	
	Young	Old
pH	6.1	8.0
BOD_5 (mg/L)	13,000	180
COD (mg/L)	22,000	3,000
BOD_5 /COD	0.58	0.06
SO_4^{2-} (mg/L)	500	80
Ca^{2+} (mg/L)	1,200	60
Mg^{2+} (mg/L)	470	180
Fe (mg/L)	780	15
Mn (mg/L)	25	0.7
NH_3-N (mg/L)	740	
Cl^- (mg/L)	2,120	
K^+ (mg/L)	1,085	
Na^+ (mg/L)	1,340	
Total P (mg/L)	6	
Cd^{2+} (mg/L)	0.005	
Cr (mg/L)	0.28	
Co^{2+} (mg/L)	0.05	
Cu^{2+} (mg/L)	0.065	
Pb (mg/L)	0.09	
Ni^{2+} (mg/L)	0.17	
Zn^{2+} (mg/L)	5	0.6

Meanwhile, on-site environmental monitoring systems ought to be regularly performed (US EPA 2012). Discharge of leachate to publicly owned treatment works (POTWs), where it is combined with domestic wastewater, is a common and preferred leachate management practice in the United States due to low operating cost and low management complexity (Renou, et al. 2008). Depending on local regulations, leachate might be pretreated on site using biological treatment before discharge into POTWs, or directly transported to POTWs without any pretreatment. Within POTWs, most of the leachate BOD in young leachate can be biologically degraded. However, the process is not effective for DOM in mature leachates due to the presence of refractory organic compounds (Renou, et al. 2008).

1.5 Organic matters in landfill leachate

Although discharge of landfill leachate to POTWs is a common practice in the United States, bio-recalcitrant organic matter (Renou, et al. 2008) presents significant complications at POTWs (Zhao, et al. 2013). The low biodegradability of leachate, particularly mature leachate, is primarily attributed to humic substances (humic acids and fulvic acids) (Han, et al. 2009) (Zhao, et al. 2013). Humic substances are dark-colored, heterogeneous and complex products of humification, a process of various biochemical and chemical reactions during plant and microbial decay. Major components of humification are plant lignin, polysaccharides, proteins and lipids which are mainly derived from paper, yard trimmings, wood and vegetative foods (Zhao, et al. 2013). Recalcitrant leachate DOM cannot be largely and truly degraded at POTWs at which they are only diluted by sewage. Increasing number of POTWs are complaining about the treatment process because the DOM may significantly increase the UV quenching properties of the mixed wastewater and thus reduce the efficiency of UV disinfection, which is increasingly applied at POTWs for inactivation of pathogenic microbes.

1.6 UV disinfection and UV absorbance

Chlorination is a traditional disinfection process applied at drinking water plants and POTWs. However, cancerogenous chlorination disinfection byproducts (DBPs) (Zhang, et al. 2005) (Nikolaou, et al. 2004) can be produced during chlorination. DBPs, primarily including trihalomethanes (THMs) and haloacetic acids (HAAs), are formed when chlorine reacts with certain organic matter, such as humic and fulvic substances (Nikolaou, et al. 2004) (Hua, et al. 2009). As a result, federal regulations concerning DBPs in drinking water have been increasingly more stringent in terms of allowable DBP levels with the same disinfection results (US EPA 2006). The growth of UV disinfection technology has been limited due to the low cost of chlorine and many operational problems with early UV disinfection equipment. However; UV disinfection has been increasingly used in water and wastewater industries over the last decades as a result of improved UV disinfection technologies and elimination of unwanted DBP (US EPA 2006). During UV disinfection, electromagnetic energy is transferred from a mercury arc lamp to a pathogen's genetic material, rendering it unable to reproduce. The most effective germicidal wavelength range is between 250 and 279 nanometers (nm) (US EPA 1999), while the most readily generated UV light by mercury lamps is at 254 nm wavelength (i.e. UV_{254}) (Zhao, et al. 2013).

Humic substances found in surface waters (Alkan, et al. 2007) and in landfill leachate (Zhao, et al. 2012) (Zhao, et al., 2013) have been reported to negatively affect the UV disinfection by absorbing the UV light. UV absorbance depends primarily on the electronic structure of a molecule. Humic acids are aromatic; their molecules contain conjugated systems of π electrons, in which the maximum stabilization of the molecule comes from the ability of hybridized sp^2 orbitals to delocalize around the molecule. Aromatic conjugated systems exhibit highest UV absorbance between 200 and 380 nm wavelengths in the UV spectra (Weishaar, et al. 2003).

1.7 Previous studies

Although reduction of leachate DOM has been studied since 1970s, very few efforts focused on the UV quenching DOM in leachate. Zhao et al. (2012) (2013) investigated sources and treatability of UV absorbing DOM in leachate, and found that hydrophobic DOM (humic and fulvic acids) showed higher specific UV_{254} absorbance (SUVA = UV_{254}/DOC) than hydrophilic DOM. However, the overall UV absorbance of the hydrophilic fraction was higher than that of hydrophobic fractions due to the high concentration of hydrophilic substances. Zhao et al. (2012) (2013) also reported that activated carbon adsorption removed UV_{254} by 54.3% (Zhao, et al. 2012), whereas aerobic biological treatment failed to reduce UV_{254} (Zhao, et al. 2013). Other treatment methods were attempted. Fenton's reagents achieved up to 95% UV_{254} reduction (Gupta, et al. 2014), and up to 94% UV_{254} reduction was accomplished when various ion exchange resins were used (Pathak 2013). However, the mechanisms behind these observations are poorly understood. Overall, the knowledge on the origin and nature of UV-quenching DOM in landfill leachate is still extremely limited, and the technologies for the UV reduction are not well tested, optimized, and developed.

2. HYPOTHESIS AND OBJECTIVE

The long-term goal of this study is to develop successful strategies to address the UV absorbance issues for solid waste and wastewater treatment industries. Previous studies show that landfill leachate-induced UV absorbance can be significantly reduced after an effective removal of leachate DOM, suggesting that the UV transmittance problem is principally caused by DOM. The central hypothesis is that leachate UV quenching property is primarily caused by certain dissolved organic matter, and is thus correlated with certain DOM characteristic parameters. The overarching objective of this thesis study is to categorize UV-quenching DOM in landfill leachate in terms of polarity and molecular weight, and understand the correlation of UV_{254} absorbance with DOC, COD and SUVA in different groups. To achieve the goal of this thesis, the following three specific tasks were pursued:

- To sequentially fractionate landfill leachate DOM into different groups based on their hydrophobicity and molecular weight.
- To quantify UV_{254} absorbance, COD, DOC and SUVA in different groups.
- To examine correlation between UV_{254} and these aggregate organic content parameters.

3. METHODOLOGY

3.1 Materials

Two landfill leachate samples investigated in this research were collected from a Pennsylvania (PA) landfill and a North Carolina (NC) landfill, respectively (Figure 1). The samples were collected prior to on-site treatment. Once collected, the samples were shipped to the environmental chemistry laboratory at Montclair State University, and stored in 20-liter containers at a room temperature. Prior to analyses, the samples were filtered through 0.45 μm Durapore® membrane filters to remove large, suspended particles. All the chemicals used were of analytical grade, except as noted. Deionized (DI) water was obtained from a Milli-Q® ultrapure water filtration system (> 18.0 MΩ.cm).

3.2 Fractionation

Leachate samples were sequentially fractionated based on polarity and molecular weight (MW) of the DOM. Hydrophobic substances (non-polar) including humic acids (HA) and fulvic acids (FA), and hydrophilic substances (Hpi) (polar) were first fractionated using chromatography-based solid phase extraction (SPE) with Visiprep™ SPE vacuum manifold. This method was modified based on the classical methodology from Thurman and Malcolm (1981) and Christensen et al. (1998), as follows. The leachate sample was acidified to pH 2.0 using 5 M hydrochloric acid (HCl). A 24 hour sedimentation allowed all the HA to form precipitates that were subsequently removed with 0.45 μm membrane filtration. The HA was collected and then rinsed with 0.1 M sodium hydroxide (NaOH) until all the solid HA re-dissolved. Appropriate amount of DI water was added so that the volume of HA solution was back to that in which the HA was originally present. Thereafter, the solution pH was re-adjusted to a neutral condition with 5 M HCl for further analyses. The HA-free filtrate was pumped to go through Supelite™ DAX-8 resin beads packed in 6 mL plastic filtration tubes (Supelco™) at a flow rate of 1 mL/min. Prior to the SPE separation, the resin beads were rinsed with DI water for approximately 10 hours until the effluent DOC was 1.0 mg/L or below (Leenheer 1981).

Figure 1. Two leachate samples (right: from PA; left: from NC)

FA was adsorbed on the resins, while Hpi was present in the effluent. The pH of Hpi solution was re-adjusted to a neutral condition with NaOH for further analyses. To desorp FA on the resins, 0.1 M NaOH was pumped to pass through the columns at a flow rate of 1 mL/min. The eluate containing FA was collected and the solution pH was re-adjusted to a neutral condition with HCl for further analyses.

Following the SPE fractionation, DOM in the HA, FA and Hpi fractions were further separated based on their MW using a Millipore stirred ultrafiltration cell, separately. The equipment is composed of a stirring table that is magnetically attached to a stirring bar, which ensures a completely mixed state of a solution and prevents undesirable particle buildup on the membranes. Pressurized nitrogen (N_2) gas was used to drive the liquids through Millipore ultrafiltration membranes on the cell. Pore sizes used in this study were 100 kilo Dalton (kDa), 10 kDa and 1 kDa. After the MW fraction was completed, the samples were immediately collected in glass bottles for further analyses.

3.3 Chemical analyses and data process

Before use, all glassware was soaked in 10% nitric acid (HNO_3), washed with warm, soapy water, and then rinsed with DI water. If needed, prior to analyses the samples were appropriately diluted with DI water to meet the detection limit of UV_{254} absorbance, DOC or COD measurements. UV_{254}, COD and ammonical-nitrogen (NH_3-N) were analyzed with a HACH DR 5000 UV-Vis spectrophotometer, using different HACH test kits (COD – Reactor Digestion Method, NH_3-N – Salicylate Method). DOC was measured with a Shimadzu Total Organic Carbon-LCPH (TOC-L) analyzer using 680°C combustion catalytic oxidation. Solution pH was measured using a Thermo Scientific pH meter. Metal analyses (Na, Ca, Mg and Cu) were conducted using HORIBA Scientific

Ultima C inductively coupled plasma – optical emission spectrometry (ICP-OES). ICP-OES was calibrated with standard solutions. Microsoft Office Excel was used to record and plot the data. Ratios of COD and DOC (COD/DOC), UV_{254} and COD (UV_{254}/COD), and UV_{254} and DOC (UV_{254}/DOC or SUVA) were computed, separately. In addition, UV transmittance (UVT) was calculated. UVT is described as the ability of a fluid to transmit ultraviolet light. Wastewater treatment industry typically uses 65% as a minimum UVT to ensure a sufficient disinfection (National Water Research Institute 2012). UVT can be calculated from its UVA as follows.

$$\text{UVT}\ (\%) = 10^{-\text{UVA}} \times 100 \quad (1)$$

4. RESULTS AND DISCUSSIONS

4.1 Raw Leachate Characterization

Basic water quality parameters of the two landfill leachates are shown in Table 3. As seen, both of the leachates had alkaline pH values and relatively low COD, indicating that they were both mature and the landfills were most likely in a methanogenic phase of decomposition (Kjeldsen, et al. 2002). Between the two leachates, the PA sample (823.98 mg/L DOC and 3,672 mg/L COD) showed a higher organic strength than the NC sample (439.08 mg/L DOC and 2,855 mg/L COD). Moreover, PA leachate also had a greater UV_{254} absorbance (22.84 cm^{-1}) than NC leachate (14.35 cm^{-1}). However, SUVA of PA leachate was less than that of NC leachate (2.77 L/mg·m vs. 3.27 L/mg·m, respectively). SUVA is defined as the ratio of UV_{254} to DOC, and quantifies the contribution of UV_{254} from a unit mass of DOC. Also, UV/COD was used to determine the UV_{254} absorbance due to a unit mass of COD. Results showed similar UV/COD ratios in both leachates (0.62 L/mg·m and 0.50 L/mg·m for PA and NC leachates, respectively). Moreover, PA leachate showed a lower COD/DOC ratio than NC leachate (4.46 vs. 6.50). COD/DOC indicates the oxidation state of organic carbon in DOM, and a lower COD/DOC suggested a more highly oxidized state of organic carbon that is less readily available for microbial growth (Deng 2007). As seen, the PA leachate is more oxidized and less microbiologically available than the NC leachate. UVT of the PA and NC leachates were both 0.00%; significantly less than 65% (the minimum UVT level for satisfactory UV disinfection) as recommended by National Water Research Institute (2012). Table 3 also shows the concentrations of other major leachate constituents, including ammonical nitrogen (PA leachate: 1,235 mg/L vs. NC leachate: 31 mg/L) and metals.

Table 3. Basic water quality parameters of PA and NC leachates

	PA leachate	NC leachate
pH	8.76	7.90
DOC (mg/L)	823.98 ±72	439.08 ±16
COD (mg/L)	3,672.00 ±157	2,855.00 ±283
UV_{254} (cm^{-1})	22.84 ±2	14.35 ±0.3
SUVA (L/mg·m)	2.77	3.27
UV/COD (L/mg·m)	0.62	0.50
COD/DOC	4.46	6.50
UVT (%)	0.00	0.00
NH_3-N (mg/L)	1,235.33 ±22	31.00 ±1
Na^+ (mg/L)	4,258.98	5,033.32
Ca^{2+} (mg/L)	18.17	334.29
Mg^{2+} (mg/L)	250.03	168.78
Cu^{2+} (mg/L)	0.00	0.00

4.2 Characterization of landfill leachate DOM in the hydrophobic/hydrophilic groups

Two leachate samples were separated into HA, FA and Hpi fractions using the chromatography-based SPE technique. UV_{254}, COD and DOC were analyzed for each fraction. Figures 2-A and 2-B show the UV_{254} distribution of HA, FA and Hpi fractions in PA and NC leachates, respectively. As seen in Figures 2-A and 2-B, the three groups all contributed to the significant UV_{254} absorbance in both leachates, and followed the same order in terms of UV_{254} absorbance contribution: FA > Hpi > HA. Between the PA and NC leachates, the UV_{254} absorbance was more evenly distributed among the PA leachate fractions; in contrast, the UV_{254} absorbance due to FA was greater than the sum of UV_{254} absorbance due to HA and Hpi in the NC sample. Figures 3-A and 3-B show the DOC distribution of HA, FA and Hpi fractions in PA and NC leachates, respectively. As shown, the DOC distribution patterns were similar to the UV_{254} patterns for the different fractions in both leachates, except that the DOC levels of the FA and Hpi fractions in the PA sample were almost equal. Figures 4-A and 4-B show the COD distribution of the HA, FA and Hpi fractions in PA and NC leachates, respectively. The COD distribution also exhibited similar patterns to the UV_{254} absorbance distribution as shown in Figures 2-A and 2-B. The recovery rates of the fractionation procedures for all fractions and parameters are listed in Table 4.

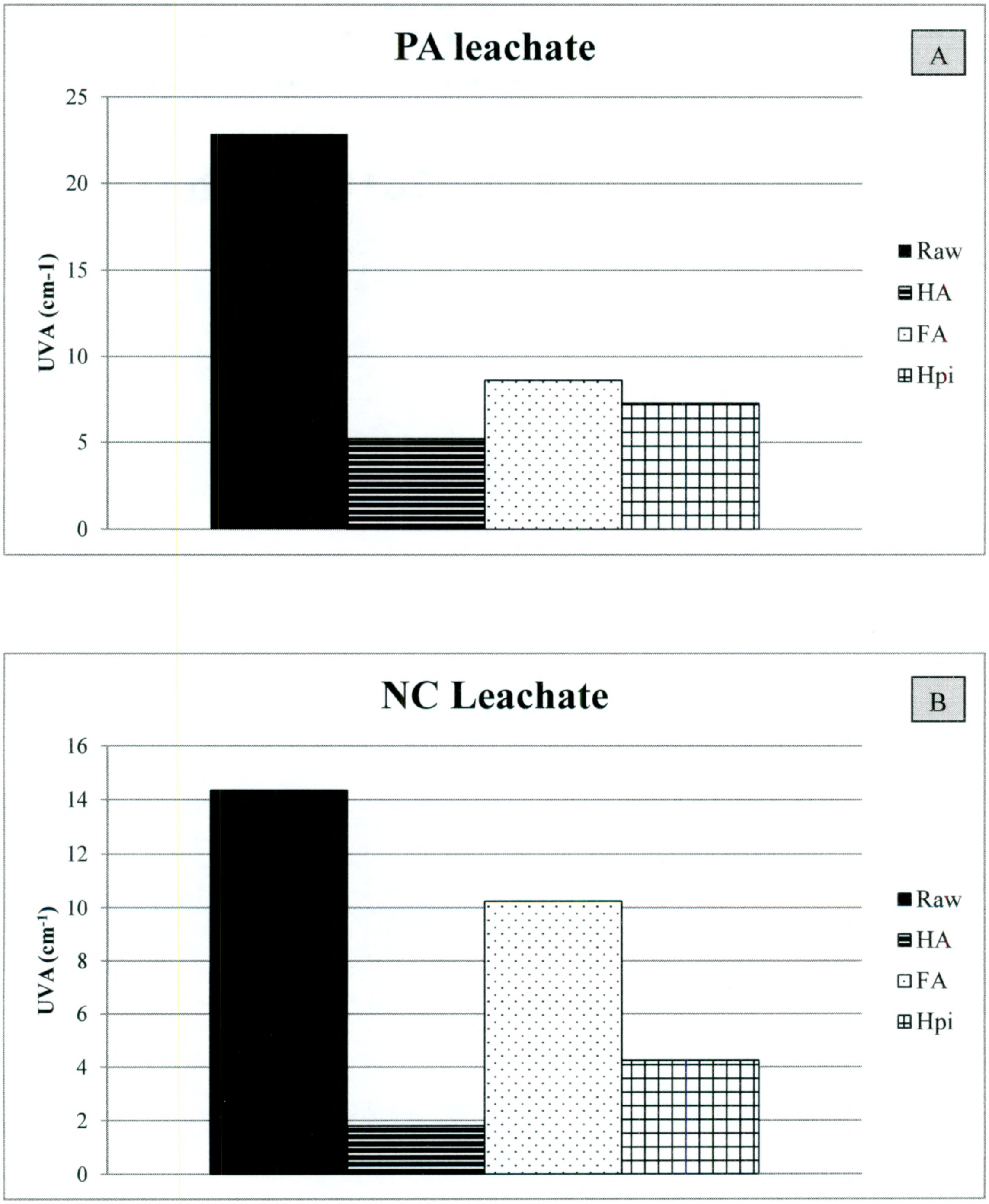


Figure 2. UVA distribution of Raw, and HA, FA, Hpi fractions in PA (A) and NC (B) leachates

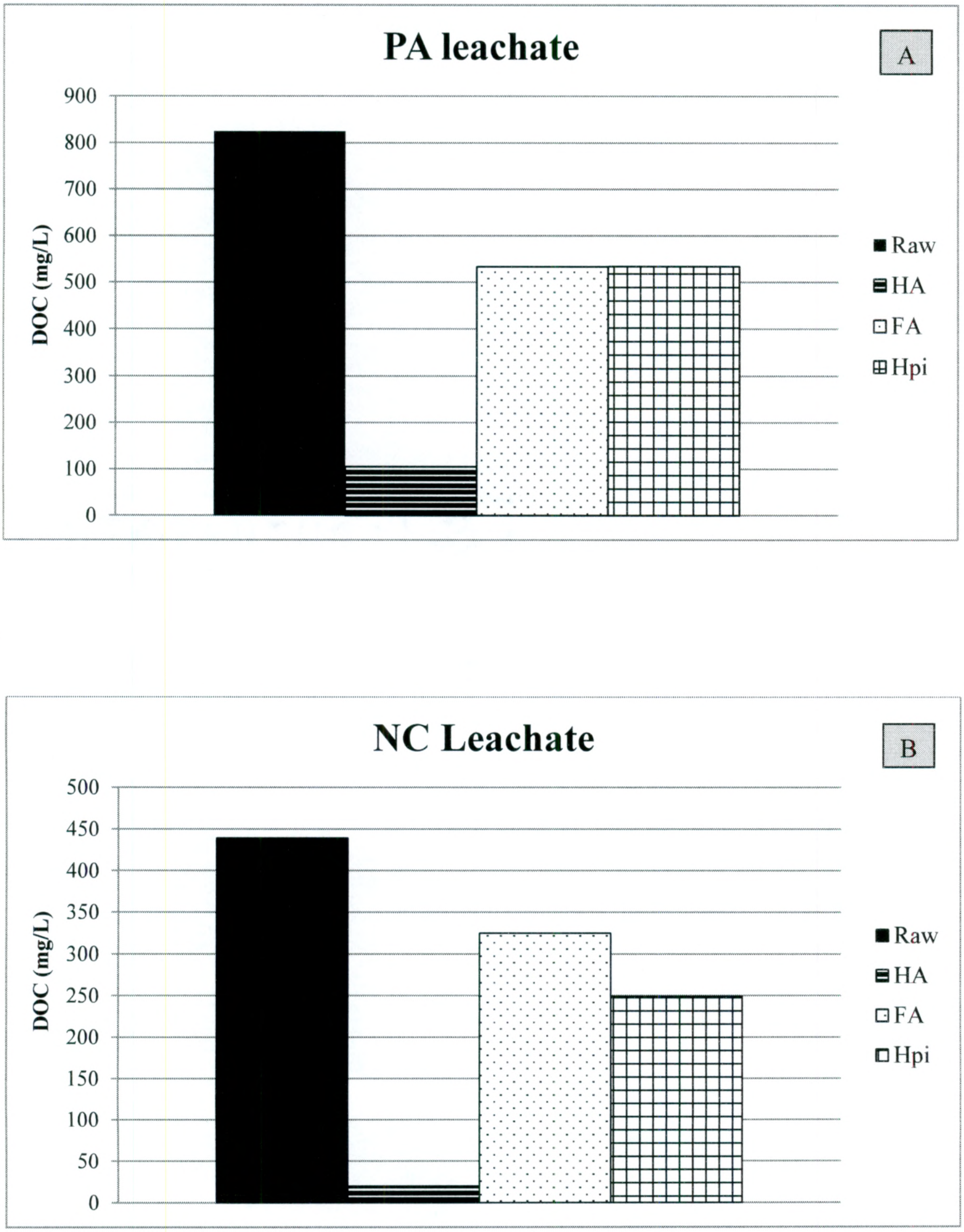
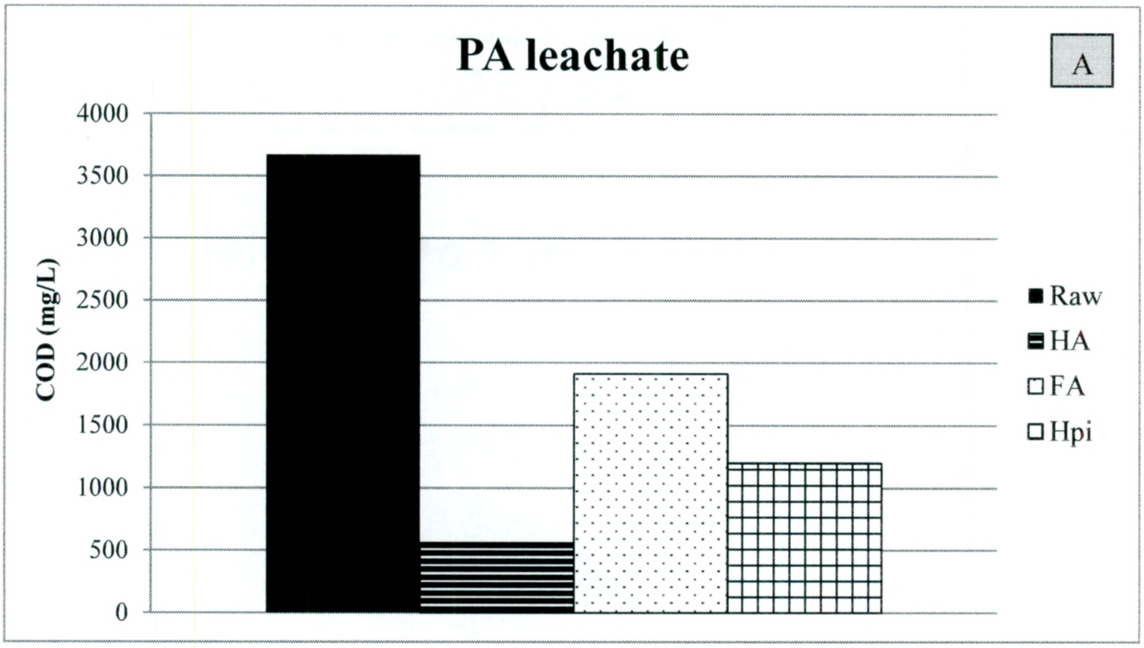


Figure 3. DOC distribution of Raw and HA, FA, Hpi fractions in PA (A) and NC (B) leachates



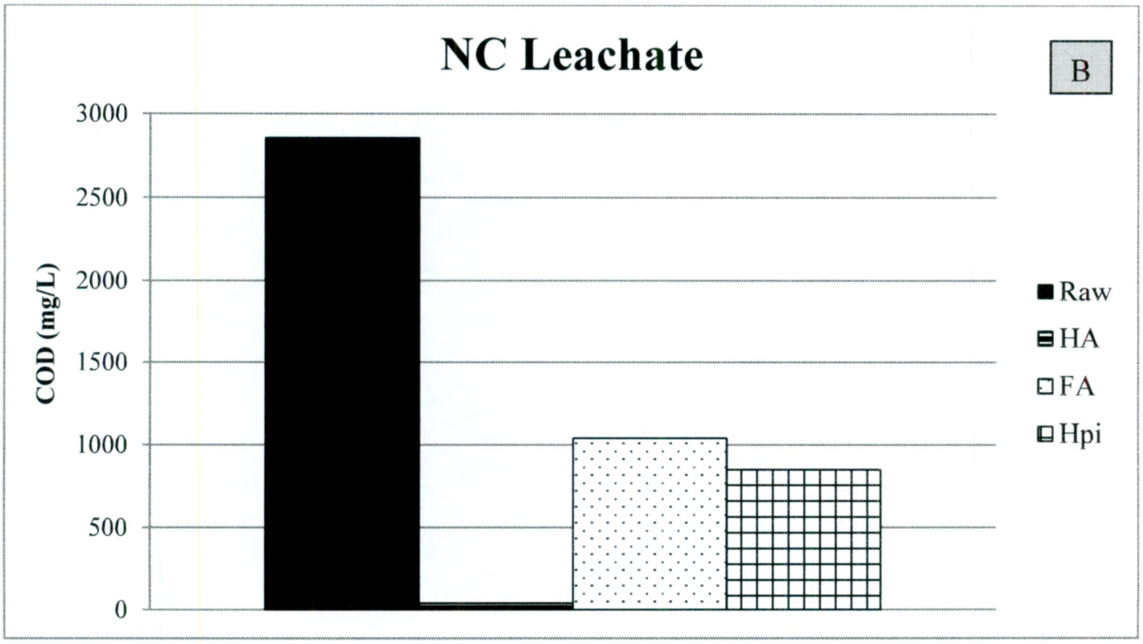


Figure 4. COD distribution of Raw and HA, FA, Hpi fractions in PA (A) and NC (B) leachates

Table 4. Recovery Rates

	PA leachate					NC leachate				
	Raw	HA	FA	Hpi	HA+FA+Hpi	Raw	HA	FA	Hpi	HA+FA+Hpi
UVA (cm^{-1})	22.84	5.20	8.60	7.25	21.05	14.35	1.80	10.25	4.25	16.30
UVA (%)	100.00	22.77	37.65	31.74	92.16	100	12.54	71.43	29.62	113.59
DOC (mg/L)	823.98	104.6	533.35	533.8	1171.75	439.08	19.70	325	249.10	593.80
DOC (%)	100	12.69	64.73	64.78	142.21	100	4.49	74.02	56.73	135.24
COD (mg/L)	3672	560	1912	1200	3672	2855	39	1040	850	1929.00
COD (%)	100	15.25	52.07	32.68	100	100	1.37	36.43	29.77	67.57

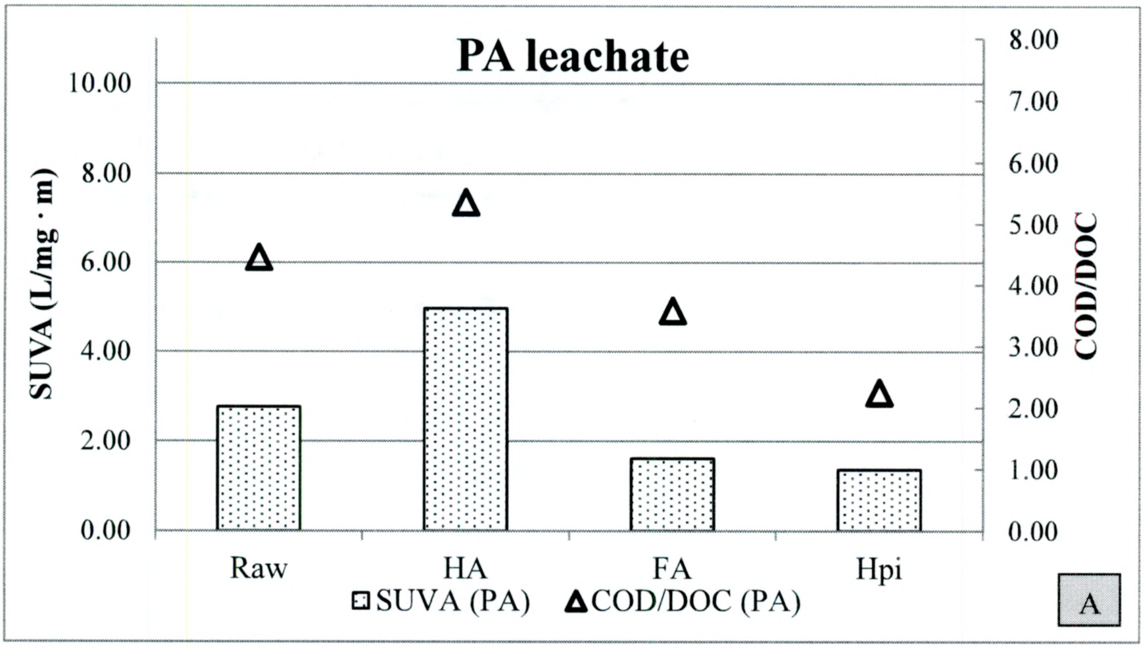
Figures 5-A and 5-B show SUVA and COD/DOC relationships in different hydrophobic and hydrophilic groups in PA and NC leachates, respectively. Figures 6-A and 6-B show UV/COD and COD/DOC relationships in different hydrophobic and hydrophilic groups in PA and NC leachates, respectively. The data is summarized in Table 5. For either leachate, HA exhibited the highest SUVA (4.97 L/mg · m in PA leachate, and 9.15 L/mg · m in NC leachate) and the highest UV/COD (0.93 L/mg · m in PA leachate, and 4.62 L/mg · m in NC leachate) among all the fractions. These findings are to be expected, since HA possesses abundant aromatic ring structures that have a high UV absorbance capacity. In contrast, FA and Hpi showed lower SUVA values, which were also comparable (FA: 1.61 L/mg · m for PA, 3.15 L/mg · m for NC; Hpi: 1.36 L/mg · m for PA, 1.70 L/mg · m for NC). FA and Hpi also showed lower UV/COD (FA: 0.45 L/mg · m for PA, 0.99 L/mg · m for NC; Hpi: 1.60 L/mg · m for PA, 0.50 L/mg · m for NC). Of note, the SUVA levels of different hydrophobic/hydrophilic groups are approximately in agreement with the typical ranges of HA (> 4 L/mg · m), FA (2-4 L/mg · m), and Hpi (< 2 L/mg · m) (Edzward and Malley 2011). The overall SUVA of unfractionated PA and NC leachates were 2.77 L/mg · m and 3.27 L/mg · m.

COD/DOC indicates an oxidation state of leachate DOM. In the PA leachate, the COD/DOC followed an order of HA (5.36) > FA (3.58) > Hpi (2.25). It should be noted that the COD/DOC order mirrored the SUVA order as mentioned above, suggesting a positive correlation between COD/DOC and SUVA. However, such a finding was not observed in the NC leachate. The COD/DOC in NC leachate followed an order of Hpi (3.41) > FA (3.20) > HA (1.98). The overall COD/DOC of unfractionated PA and NC leachates were 4.46 L/mg · m and 6.50 L/mg · m, respectively.

Both, the SUVA and COD/DOC, seemed to be acceptable parameters to indicate UV_{254} absorbance from a unit mass of leachate DOM in different fractions, since majority of UV_{254} absorbance is due to the presence of aromatic ring structures. Meanwhile, COD/DOC showed a correlation with SUVA in the PA leachate, but not in the NC leachate. Additional investigation is needed to further study whether COD/DOC may be used as an indicator to estimate the UV_{254} absorption property.

Table 5. Parameter calculations for PA & NC leachate fractions

	SUVA (L/mg·m)			UV/COD (L/mg·m)			COD/DOC		
	HA	FA	Hpi	HA	FA	Hpi	HA	FA	Hpi
PA leachate	4.97	1.61	1.36	0.93	0.45	0.60	5.36	3.58	2.25
NC leachate	9.15	3.15	1.70	4.62	0.99	0.50	1.98	3.20	3.41



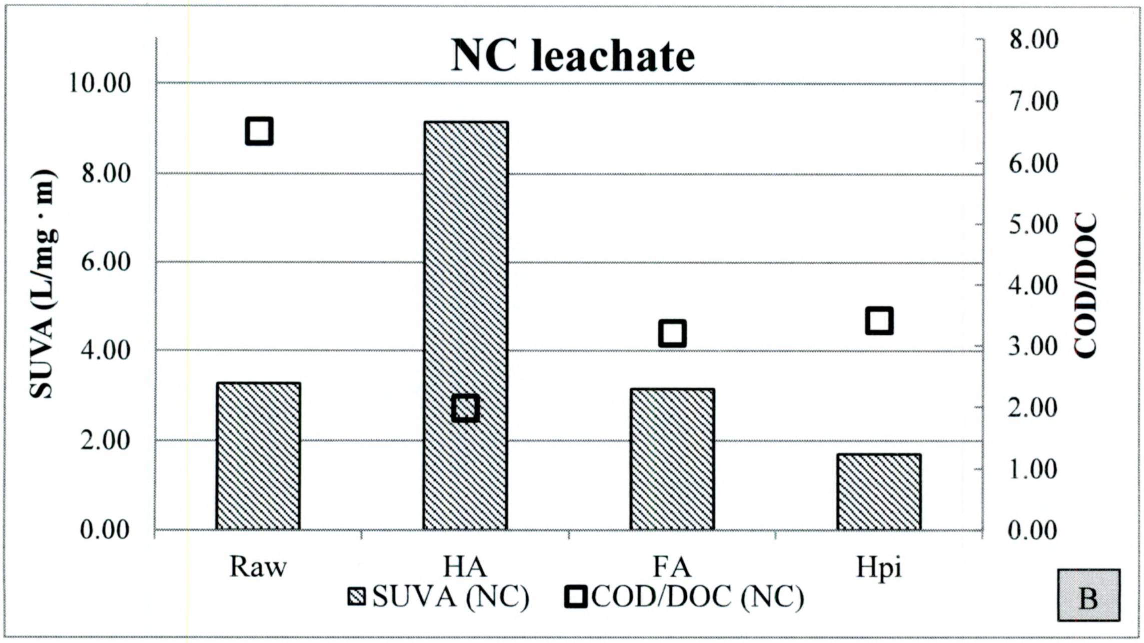
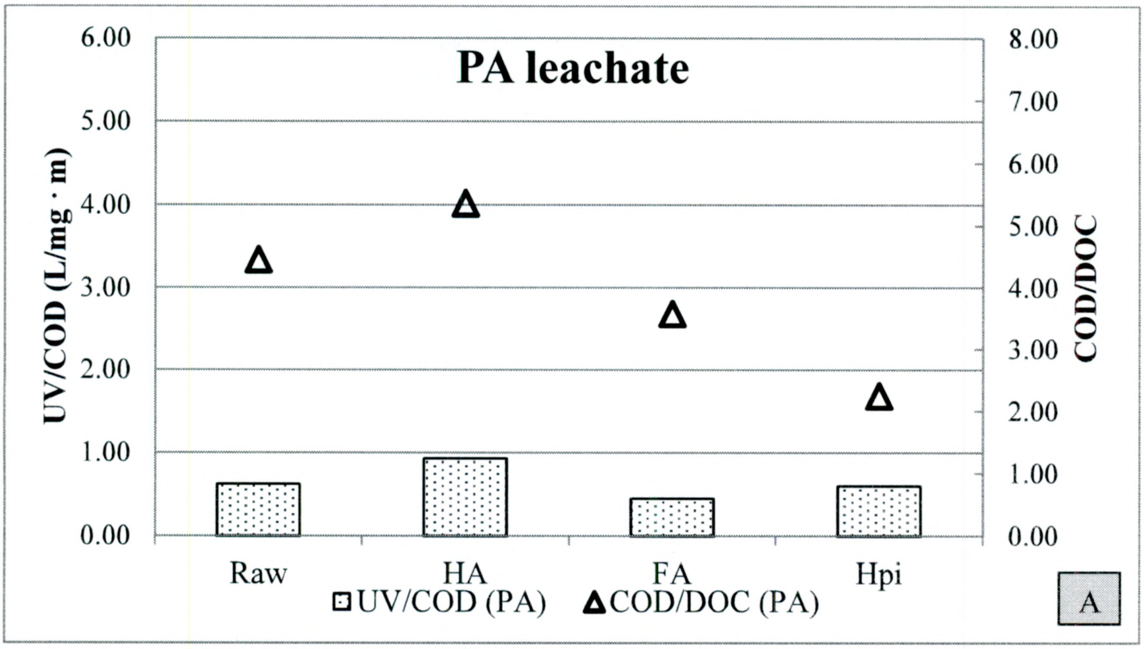


Figure 5. SUVA and COD/DOC relationship in different hydrophobic/hydrophilic groups for PA leachate (A) and NC leachate (B)



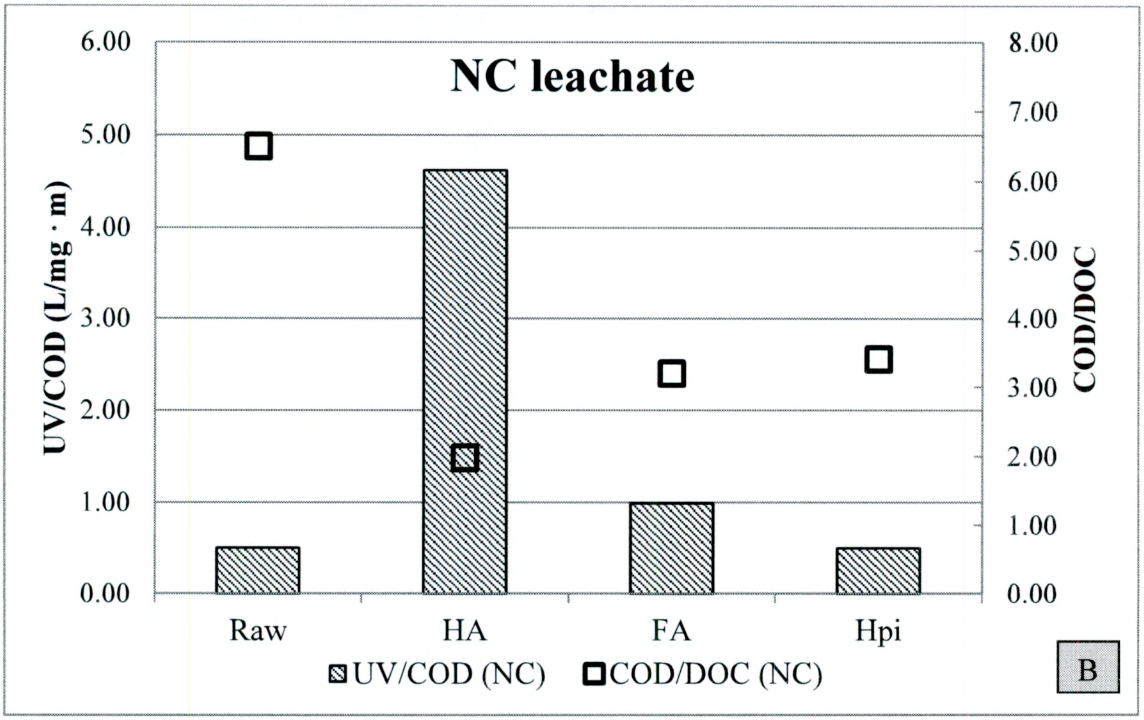


Figure 6. UV/COD and COD/DOC relationship in different hydrophobic/hydrophilic groups for PA leachate (A) and NC leachate (B)

4.3 Characterization of landfill leachate DOM in the different hydrophobic/hydrophilic and MW groups

The leachate DOM fractionated in terms of polarity were further separated into four groups based on MW: >100 kDa, 10-100 kDa, 1-10 kDa and <1 kDa. For each subgroup, UV_{254}, DOC and COD were analyzed. The UV_{254}, DOC and COD distributions in different MW groups for PA and NC leachates are shown in Figures 7 (A-B), 8 (A-B), and 9 (A-B), respectively. The data are summarized in Table 5.

As seen, for either leachate, the majority of organic fraction was composed of small organic compounds with MW <1 kDa (639 mg/L DOC and 2,360 mg/L COD for PA, and 372 mg/L DOC and 1,284 mg/L COD for NC) that contributed to the most UV_{254} absorbance among the different MW groups (10.45 cm^{-1} and 14.08 cm^{-1} for PA and NC, respectively). Specifically, the <1 kDa organic compounds in the HA, FA, and Hpi contributed to 14.3%, 21.1%, and 14.3% of the overall UV_{254} absorbance in the PA leachate, respectively, and 9.5%, 54.9%, and 21.9% of the overall UV_{254} absorbance in the NC leachate, respectively. That is, the small MW organic molecules accounted for 49.7% and 86.3% of the overall UV absorbance for the PA and NC leachates, respectively. Of note, the FA fraction accounted for the most UV absorbance in the <1 kDa DOM in both leachates (21.1% for PA leachate, and 54.9% for NC leachate). DOM sized 1-10 kDa was the number two MW fraction contributing to UV_{254} absorbance in the PA and NC leachates (34.4 % and 9.3% of the overall UV_{254} for PA and NC, respectively). Similarly, FA accounted for the largest fraction in 1-10 kDa MW group in both samples. Hpi was primarily observed in <1 kDa, 1-10 kDa and >100 kDa MW fractions in the PA leachate, while it was most abundant in <1 kDa and 1-10 kDa MW fractions in the NC leachate. Very similar DOC and COD patterns were found in the different MW groups. The DOC and COD fractions due to HA were much less than the UV_{254} absorbance fractions due to HA in the <1 kDa and 1-10 kDa MW groups in both samples. Because HA had the highest SUVA and UV/COD a low concentration of HA sufficiently yielded a high UV absorbance.

For both leachates, the <1 kDa MW group was the most abundant in terms of COD and DOC, and also contributed to the most of UV_{254} absorbance among all the fractions. However, the <1 kDa MW group was not evenly distributed in the different fractions of both leachates. As seen in Table 5, it can be concluded that the DOC and COD fractions of the <1 kDa MW group in the NC leachate followed the order of HA> Hpi > FA, suggesting that the percentage of >1 kDa portion in HA fractions, is larger than that of Hpi fractions, while the percentage of >1 kDa portion in Hpi fractions is larger than that of FA fractions. These results suggest that microfiltration with membranes less than or equal to 1 kDa pore sizes could sufficiently remove HA but might allow the Hpi and FA fractions to pass through since these are mostly composed of <1 kDa fractions. In contrast, the PA leachate exhibited a different DOC distribution pattern: Hpi> HA>FA. These results imply that microfiltration with membranes less than or equal to 1 kDa pore sizes could sufficiently remove HA and Hpi, but allow the FA fractions to pass through due to smaller sizes of FA fractions. Moreover, the COD distributions of the <1 kDa MW group in PA leachate followed the order of FA>HA>Hpi. The COD size distribution of the PA leachate suggests that the membrane filtration with 1 kDa pore sizes would remove FA and HA fractions, and let the Hpi fractions through

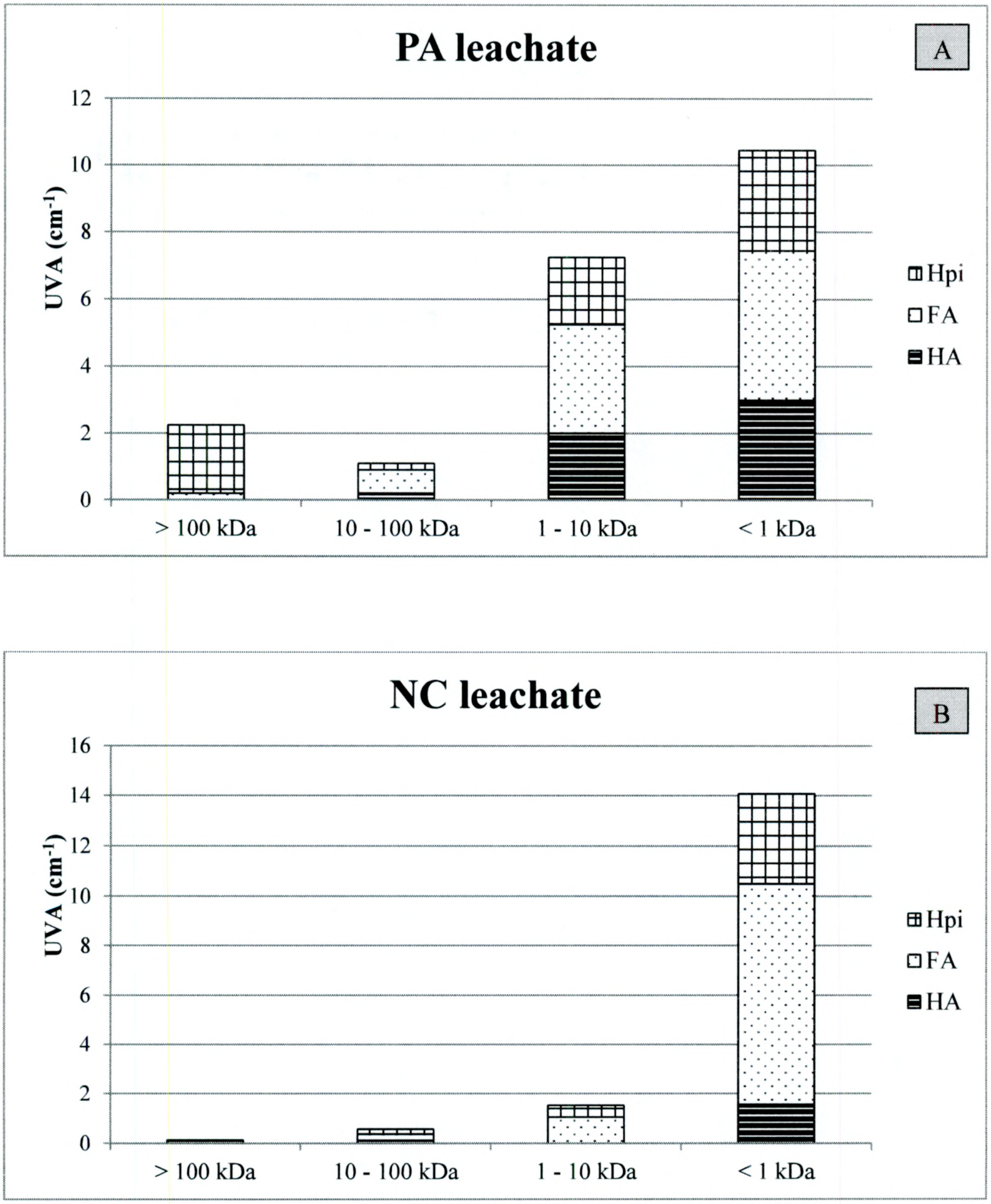


Figure 7. UVA distribution among various MW fractions for HA, FA and Hpi fractions in PA (A) and NC (B) leachates

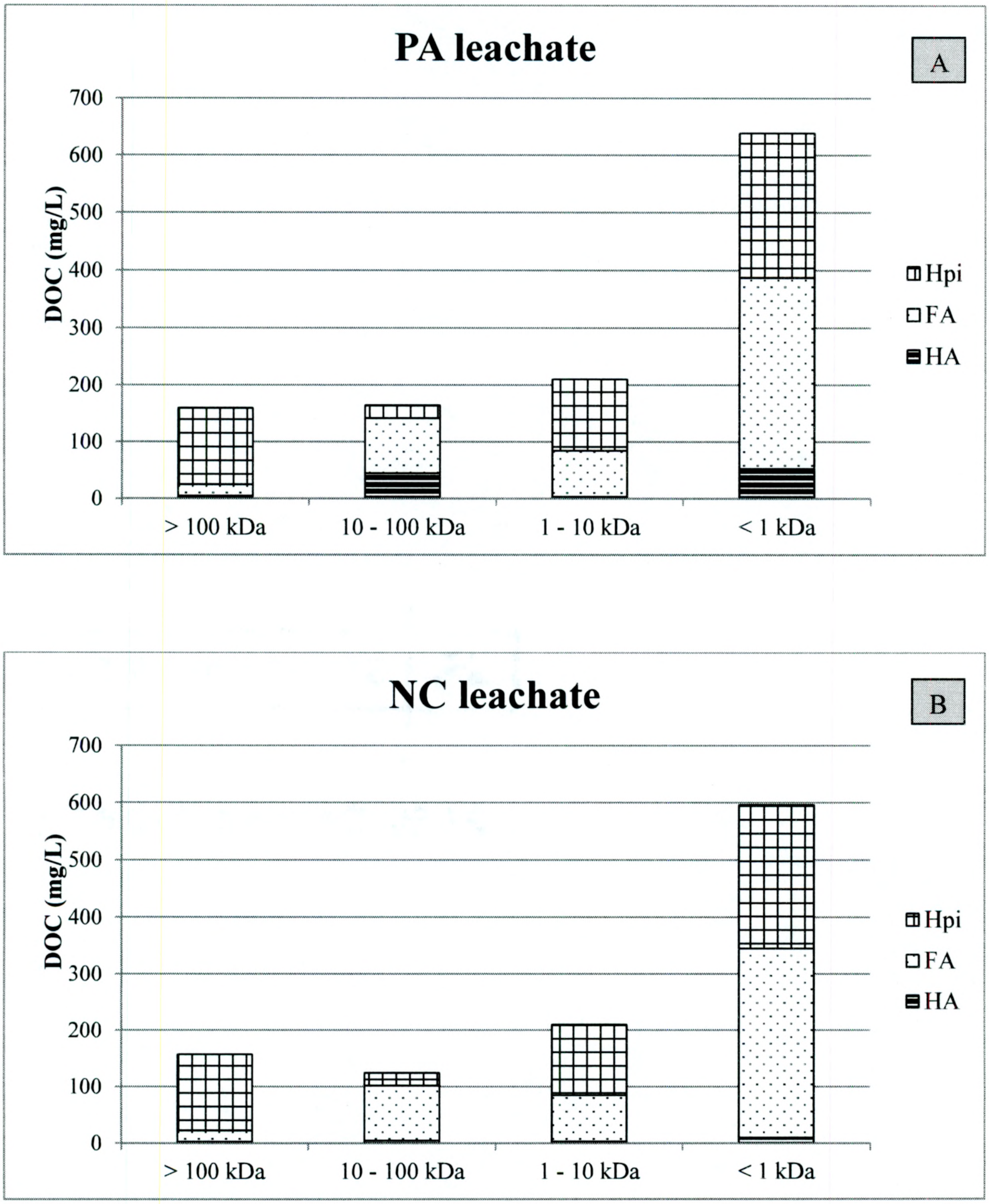


Figure 8. DOC distribution among various MW fractions for HA, FA and Hpi fractions in PA (A) and NC (B) leachates

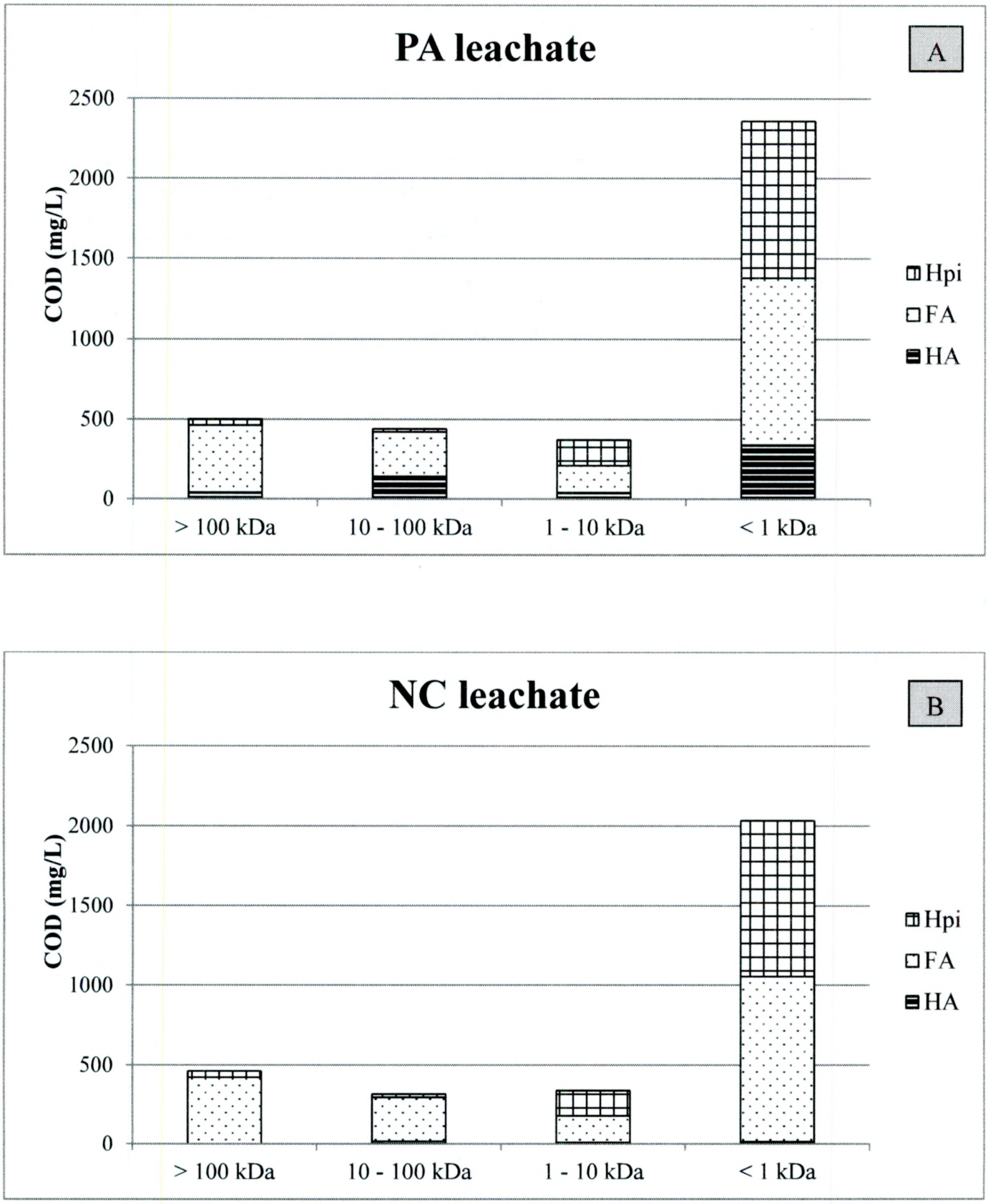


Figure 9. COD distribution among various MW fractions for HA, FA and Hpi fractions in PA (A) and NC (B) leachates

Table 6. MW distribution data for HA, FA and Hpi fractions in PA (A) and NC (B) leachates

	UVA (cm^{-1}) (for each fraction, the first data column is UV absorbance, cm^{-1}; the second data is the UV distribution in different MW groups)											
	PA leachate						**NC leachate**					
	HA		**FA**		**Hpi**		**HA**		**FA**		**Hpi**	
>100 kDa	0.00	0.0%	0.20	1.0%	2.05	9.7%	0.13	0.8%	0.00	0.0%	0.00	0.0%
10-100 kDa	0.20	1.0%	0.70	3.3%	0.20	1.0%	0.12	0.7%	0.25	1.5%	0.20	1.2%
1-10 kDa	2.00	9.5%	3.25	15.4%	2.00	9.5%	0.00	0.0%	1.05	6.4%	0.48	2.9%
<1 kDa	3.00	14.3%	4.45	21.1%	3.00	14.3%	1.55	9.5%	8.95	54.9%	3.58	21.9%
	DOC (mg/L) (for each fraction, the first data is DOC, mg/L; the second data is the DOC distribution in different MW groups)											
>100 kDa	4.73	0.4%	19.85	1.7%	134.45	11.5%	2.35	0.4%	13.35	2.2%	7.47	1.3%
10-100 kDa	44.51	3.8%	97.00	8.3%	22.65	1.9%	4.63	0.8%	0.00	0.0%	64.05	10.8%
1-10 kDa	3.04	0.3%	81.25	6.9%	125.55	10.7%	3.18	0.5%	92.66	15.6%	34.15	5.8%
<1 kDa	52.28	4.5%	335.25	28.6%	251.15	21.4%	9.53	1.6%	218.98	36.9%	143.4	24.2%
	COD (mg/L) (for each fraction, the first data is COD, mg/L; the second data is the COD distribution in different MW groups)											
>100 kDa	40.00	1.1%	422.00	11.5%	40.00	1.1%	0.00	0.0%	0.00	0.0%	0.00	0.0%
10-100 kDa	140.00	3.8%	280.00	7.6%	20.00	0.5%	16.00	0.8%	110.00	5.7%	260.00	13.5%
1-10 kDa	40.00	1.1%	170.00	4.6%	160.00	4.4%	9.00	0.5%	220.00	11.4%	30.00	1.6%
<1 kDa	340.00	9.3%	1,040.00	28.3%	980.00	26.7%	14.00	0.7%	710.00	36.8%	560.00	29.0%

5. SUMMARY AND CONCLUSIONS

Landfill leachate, a highly contaminated wastewater, is commonly treated at POTWs in the United States. However, it can significantly reduce UV disinfection efficiency due to the UV-absorbing properties of leachate DOM (Zhao et. al, 2012). In this study, DOM of two mature landfill leachates were sequentially fractionated in terms of their hydrophobicity/hydrophilicity and molecular weight, and analyzed for UV_{254} absorbance, COD and DOC. Correlations and relationships between these parameters were sought in attempt to characterize the complex DOM. The major findings are summarized below.

1) UV_{254} absorbance of the two mature leachates was extremely high, making UVT close to 0%, suggesting that leachate DOM exhibited a high UV absorbance property;
2) For the two leachates tested, FA, Hpi and HA all significantly contributed to UV_{254}, and followed the order in terms of their corresponding UV_{254} fractions in the overall UV_{254}: FA > Hpi > HA;
3) For the two leachates tested, HA exhibited the highest SUVA and UV/COD among the different hydrophobic/hydrophilic fractions, though it had the lowest fractions in the organic content expressed as DOC and COD. These findings are likely due to abundance of aromatic molecules in HA;
4) A positive correlation between SUVA and COD/DOC was observed for the PA leachate, but not for the NC leachate. Further investigation is needed;

5) For the two leachates tested, low MW leachate DOM (<1 kDa) contributed to the most UV_{254} absorbance. In the <1 kDa DOM, HA, FA, and Hpi all contributed to UV_{254}, and the UV_{254} due to FA was the highest;

6) For the two leachates tested, the low MW DOM (1-10 kDa) were the second most significant fraction contributing to UV_{254};

7) Overall, the PA leachate showed more heterogeneity in terms of DOM particle size, while particles <1 kDa were still the most abundant. Overall, the NC leachate showed more homogeneity in terms of DOM particle size with particles <1 kDa in largest quantities. This suggests that leachate DOM composition is highly variable;

8) In both leachates SUVA follows: HA>FA>Hpi, with highest SUVA in 1-10 kDa and <1 kDa HA DOM fractions, suggesting that pressure-driven membrane technologies with a pore size <1 kDa are able to sufficiently remove the UV-quenching particles;

9) NC leachate particle size distribution follows HA>Hpi>FA in terms of DOC and COD, while PA leachate particle size distribution follows Hpi>HA>FA in terms of DOC and FA>HA>Hpi in terms of COD.

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