CHAPTER V

CHEMICAL CLASSES OF UNFRACTIONATED AND FRACTIONATED DOM IN INDUSTRIAL ESTATE WASTEWATER TREATED BY STABILIZATION PONDS

5.1 Introduction and Literature Reviews

The major DOM fractions, major THMs precursors and specific THMFPs of DOM fractions were investigated and presented in Chapter 4. Based on specific THMFP of each DOM fractions, HPOB, even when present in low DOC concentration, registered higher specific THMFP values than those of the major DOM fractions and major THMs precursors. This observation may have resulted from the different organic classes in each DOM fraction that led to the difference in the ability of each DOM fraction to form THMs. Clearer information on organic classes in DOM fractions, especially the organic classes that affect THMs, would therefore be useful for improving the removal and control of disinfection by-products (DBPs).

In order to identify the organic classes, a gas chromatography (GC) technique coupled with mass spectrometry (MS) allowed for the identification of the chemical classes of volatile organic compounds (VOCs) in water. However, Dignac *et al.* (2000) proposed that only approximately 45% of the total organic carbon (TOC) of the wastewater and 20% of the TOC of the treated wastewater could be identified by the GC technique. This is because numerous compounds can appear in the refractory, nonchromatographable fraction (Thurman, 1885). In spite of that, using a pyrolyzer coupled with GC/MS could provide a chemical fingerprint (fragment) of both chromatographable and nonchromatographable fractions that could be used to identify the original mixture (polymers) of the DOM in water. Pyrolysis GC/MS, therefore, has been used by many researchers to characterize the chemical classes in river water (Bruchet *et al.* 1990 and White *et al.* 2003), lake water (Biber *et al.* 1996 and White *et al.* 2003), groundwater (White *et al.* 2003), and treated wastewater (Dignac *et al.* 2000 and Sirivedhin and Gray, 2005) and wastewater (Dignac *et al.* 2000). Although, stabilization pond was one of the major wastewater treatment process that was broadly utilized to treat wastewater for many applications, chemical classes of industrial estate wastewater to stabilization pond processes and effluent water from the processes as well as chemical classes of their DOM fractions was not extensively evaluated. This chapter, therefore, focuses on identifying the chemical classes of industrial estate wastewater and treated wastewater as well as the chemical classes of their DOM fractions. In addition, the relationship between the chemical classes of DOM fractions and specific THMFP of DOM fractions is discussed in this chapter.

5.2 Objectives of This Chapter

The main objectives of this chapter were twofold. Firstly, it was to identify the common fragments, prominent major fragments, specific fragments and chemical classes of DOM in influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds and their DOM fractions. Secondly, it was to discuss the relationships between the specific chemical classes/pyrolysis fragments and the formation of THMs.

5.3 Material and Methods

5.3.1 Sample Collection, Sample Preparation and GC/MS Analysis

Influent wastewater and effluent water from the aeration, facultative, oxidation, and detention ponds were collected on February 18, 2005. All water samples were filtered through a pre-combusted (550 °C for 2 h) Whatman GF/F (nominal pore size 0.7 μm) filter. Resin adsorption procedures (Leenheer, 1981 and Marhaba *et al.*, 2003) were used to fractionate fifteen liters of all filtered water samples into six DOM fractions, namely HPON, HPOB, HPOA, HPIB, HPIA and HPIN. The filtered water samples and their six DOM fractions were then analyzed by pyrolysis GC/MS analysis (the details of pyrolysis GC/MS analysis were demonstrated in Chapter 3, Section 3.6). Two replications of the pyrolysis GC/MS measurements of all the water samples were performed and the reproducibility of pyrolysis was confirmed.

5.3.2 Interpretation of Pyrolysis GC/MS Data

Firstly, the peaks composed in a DOM pyrochromatogram of all water samples called fragments (as shown in Appendix B, from Figure B-4 to Figure B-38) matched the mass spectrum libraries of National Institute of Standard and Technology (NIST), USA. Fragments were classified on the basis of their matching percentage into three classes.

When the matching percentage was (i) less than 85%, the fragment was defined as an unknown fragment; (ii) between 85% and 90%, the pyrolysis fragment was defined as an acceptable match fragment; and (iii) more than 90%, the pyrolysis fragment was defined as a satisfactory match fragment, noted by the symbol, "*". An example pyrochromatogram of the influent wastewater is illustrated in Figure 5.1. The pyrochromatograms of all water samples are presented in Appendix B.

When a quantitative analysis of fragments was taken into consideration, Page *et al.* (2002) stated that it was very difficult to quantify the pyrolysis products due to the vast quantity and range of pyrolysis products. In addition, an absolute integration of the peak areas would be unreliable since the weight of the samples and relative amounts of organic material in the samples were different. The relative ratio of the area between fragments and one normalizing fragment was therefore utilized to accomplish a fingerprint of the pyrolysis data as presented in the equation below:

$$\text{Relative ratio} = \frac{\text{Area of pyrolysis fragment}}{\text{Area of a normalizing pyrolysis fragment}} \tag{5.1}$$

With regard to the pyrolysis GC/MS results, toluene was utilized as the normalization fragment because it was present in all water samples and had a high matching percentage (matching percentage $\geq$ 90). The average relative ratios were calculated for the duplicated samples in this study. The average relative ratio of 0.1 was selected as the limit of fragment identification. The fragments with an average relative ratio of less than 0.10 were considerably neglected. In order to define the major fragments in each sample, the average ratio of 0.20 (two times higher than the limit of fragment identification) was selected as the limit of the major fragment. In addition, the major fragments that had average relative ratios of more than 1 (ten times higher than the limit of fragment identification) were defined as prominent major fragments.

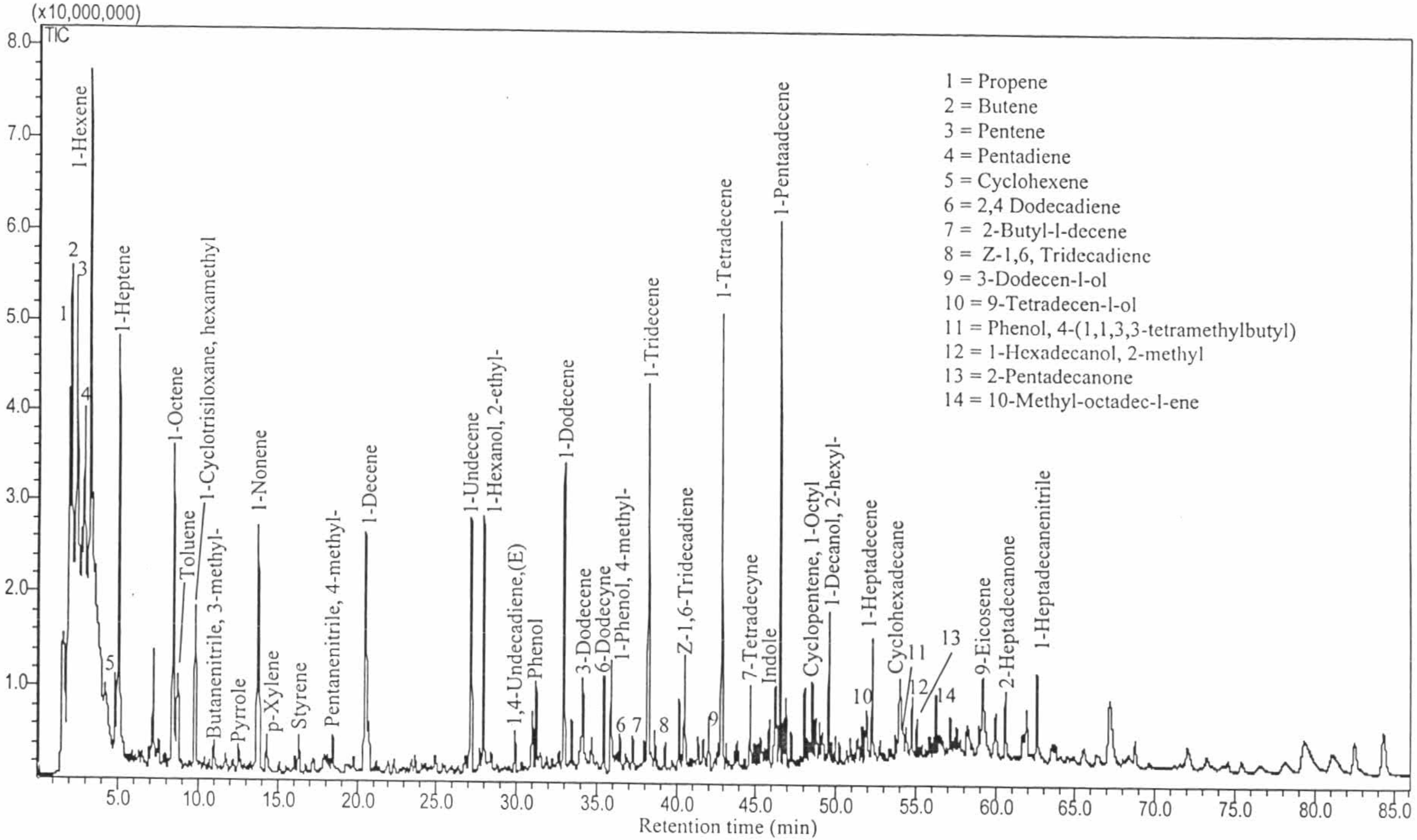

Figure 5.1: Pyrochromatogram of major fragments of influent wastewater

The results from fragment identification are illustrated in Appendix B (from Table B-1 to Table B-7). The lowest summation of average relative ratios of 10.95 was obtained from HPIB of the effluent water from the aerations ponds (Appendix B, Table B-5); whereas the highest summation of average relative ratio of 199.36 was observed from HPIN of the effluent water from the facultative ponds. This meant that the criteria of fragment identification at relative ratio 0.10 could neglect minor fragments whose peak area contributed less than 1% to the total peak area.

When DOM fractions were taken into consideration, the water samples were classified into 6 groups: HPON, HPOB, HPOA, HPIA, HPIB and HPIN. Each group was composed of 5 water samples. The fragments, produced by pyrolysis in each of the 5 water samples in each group, can be recognized as the common fragment in that group. By using the criterion developed by Thaveemaitree (2005) to identify the specific fragments in each group of DOM fractions, the specific fragment in each group of DOM fractions could be classified by using the following equation:

Fragment X is defined as the specific fragment of a group when

$$\left(\frac{\text{Nxg}}{\text{Nsg}} > 0.5\right) \cap \left(\frac{\text{Nxg}}{\text{Nx}} > 0.5\right) \qquad (5.2)$$

Where Nxg = appearing number of fragment X in a group

Nsg = number of samples in a group (5)

Nx = appearing number of fragment X in all the groups

In Equation 5.2, fragment X is defined as the specific fragment of a group when both the appearing number of fragment X in a group divided by the number of samples in a group (equal to 5) and the appearing number of fragment X in a group divided by the appearing number of fragment X in all the groups are more than 0.5 (more than 50%). For example, the appearing number of fluorene and naphthalene fragments in the HPOA group was equal to 4 and 4, respectively ($Nxg_{Fluorene}$ = 4 and $Nxg_{Naphthalene}$ = 4) and appearing number of fluorene and naphthalene fragments in all groups were equal to 4 and 18, respectively ($Nx_{Fluorene}$ = 4 and $Nx_{Naphthalene}$ = 18). Using Equation 5.3 to judge the specificity of the fluorene and naphthalene fragments for the HPOA group could be expressed as follows:

Fluorene fragment: $$\left(\frac{Nxg_{Fluorene}}{Nsg}=\frac{4}{5}=0.80>0.5\right)\cap\left(\frac{Nxg_{Fluorene}}{Nx_{Fluorene}}=\frac{4}{4}=1>0.5\right)$$

Naphthalene fragment: $$\left(\frac{Nxg_{Naphthalene}}{Nsg}=\frac{4}{5}=0.80>0.5\right)\cap\left(\frac{Nxg_{Naphthalene}}{Nx_{Naphthalene}}=\frac{4}{18}=0.22<0.5\right)$$

On this basis, the fluorene fragment was classified as the specific fragment of the HPOA group, because the fluorene fragment appeared in 4 of 5 HPOA samples (80%) and 4 of 4 (100%) of the appeared fluorene fragment in all groups. For the naphthalene fragment, although it appeared in 4 of 5 of the HPOA samples (80%), 4 of 18 (22%) of the appeared naphthalene fragments could be also found in all other groups. The naphthalene fragment, therefore, could not be classified as the specific fragment of the HPOA. The second step was to group the pyrolysis fragments with similar chemical characteristic together (semi-quantitative approach). All chemical fragments of the water samples were taken into consideration and categorized according to their major elements and chemical structures into one of the following classes: aliphatic hydrocarbon (AL), aromatic hydrocarbon (AR), organic nitrogen (ON), phenol (PN), aldehydes (AH) and ketones (KT), others such as alcohol (AC) and carboxylic acids (CA), and unknown (UN).

5.4 Results and Discussions

5.4.1 Chemical Classes in Influent Wastewater and its Treated Effluent

1-octene, 1-nonene, 1-decene, 1-undecene, 1-tretradecene and 1-pentadecene were recognized as the common pyrolysis fragments of the aliphatic hydrocarbon class of unfractionated waters whereas those of the aromatic hydrocarbon class were toluene and styrene as can be seen in Appendix B (Table B-1). Butanenitrile 2-methyl, butanenitrile 3-methyl, heptadecananitrile, and cyclotretrasiloxane octamethyl were classified as the common pyrolysis fragments of organic nitrogen and other compound classes in unfractionated waters, respectively.

Summations of the average relative ratios of the pyrolysis fragments in each chemical class of influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds (Table B-1) were utilized to plot the percent distribution of the chemical classes in the respective waters as shown in Figure 5.2. The aliphatic hydrocarbon class accounted for approximately 70% of the DOM in the influent wastewater. The thirteen prominent major fragments ordered from high to low were as follows: 1-heptene, 1-hexene, 2-butene, 1-pentene, propene, 1-octene, 1-nonene, 1-decene, 1-tridecene, 1-pentadence, 1-tretradecene, 1-undecene and 1-dodecene (Table 5.1). Aromatic hydrocarbon, phenol, organic nitrogen, aldehydes and ketones classes were found at very low percent distributions (more or less 5% of DOM). On this basis, it can be stated that aliphatic hydrocarbons ($C_3 \leq$ prominent major fragments of aliphatic hydrocarbon $\leq C_{15}$) was the major chemical class in the industrial estate wastewater.

In the aeration pond effluent, aliphatic hydrocarbons with about 40% of DOM were the major chemical class. The 12 prominent major fragments from high to low are listed as follows: 1-heptene, 1-hexene, 1-pentene, 1-nonene, 1-octene, 1-pentadence, 1-tretradecene, 1-decene, 1-dodecene, 1-undecene, 2-butene and 1-tridecene. Interestingly, organic nitrogen containing about 25% of DOM was observed in 5 prominent major fragments; ordered from high to low they are as follows: pentadecanenitrile, octadecananitrile, dodecananitrile, heptadecanenitile and tridecananitrile. This indicated that aliphatic organic nitrogen was dominant in the organic nitrogen class. Other chemical classes were obtained in very low percent distributions. However, 1-hexanol, 2-ethyl and 9-tretadecan-1-ol were detected as the prominent major fragments of the alcohol class.

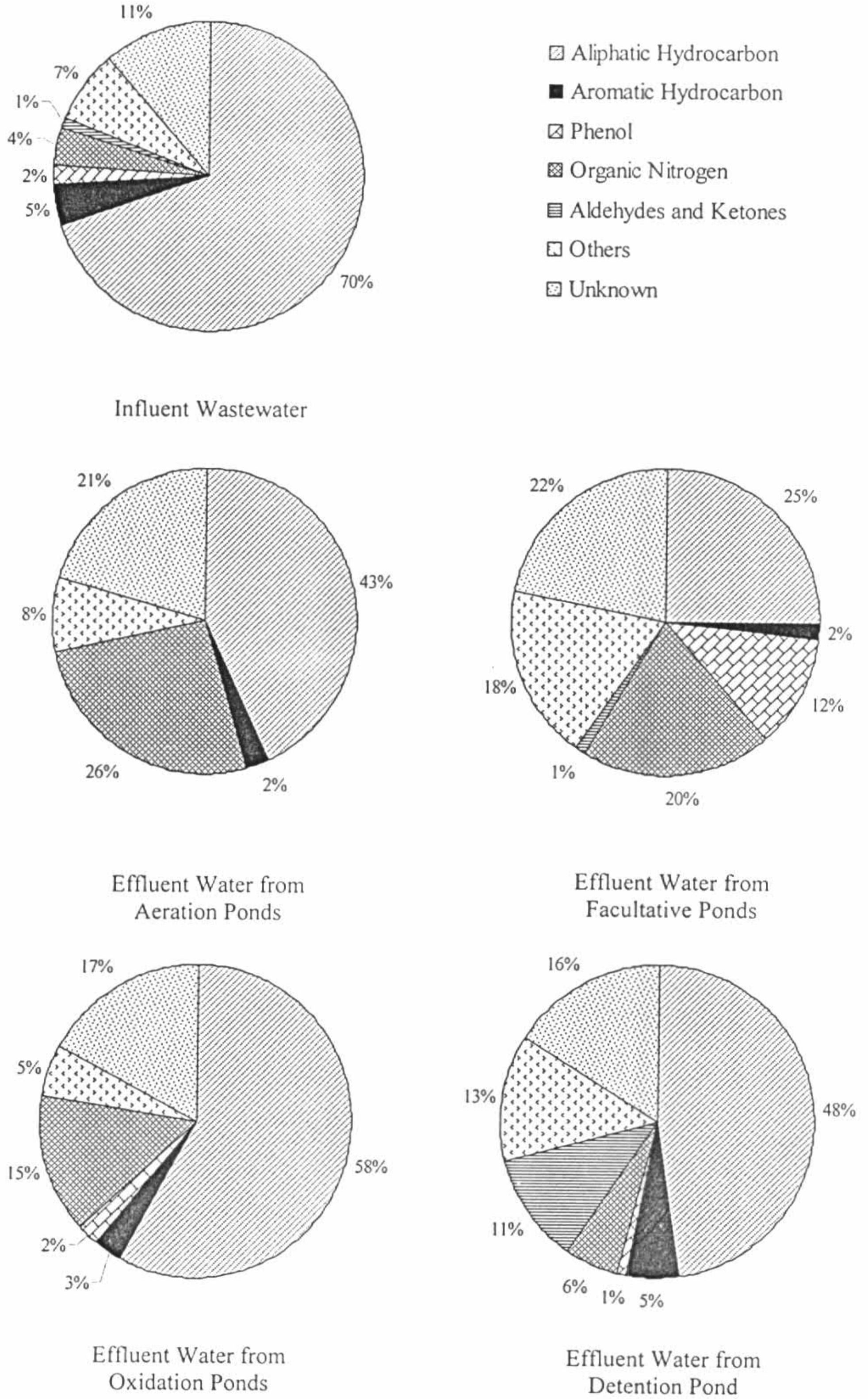

Figure 5.2: Percent distributions of the chemical classes of DOM in the influent wastewater and effluent water of the aeration, facultative, oxidation and detention ponds

Table 5.1: Summary of the prominent major fragments of each chemical class in the unfractionated waters

Chemical class	Prominent major fragments (average relative ratio from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	*1-heptene *1-hexene *2-butene *1-pentene *1-propene ***1-octene*** ***1-nonene*** ***1-decene*** *1-tridecene ***1-pentadecene*** ***1-tetradecene*** ***1-undecene*** *1-dodecene	*1-heptene *1-hexene *1-pentene ***1-nonene*** ***1-octene*** ***1-pentadecene*** ***1-tetradecene*** ***1-decene*** *1-dodecene ***1-undecene*** *1-butene *1-tridecene	*1-heptene *Eicosane, 10-methyl *Nonadecane, 2-methyl ***1-nonene*** *Tricosane ***1-octene*** Octadecane, 2-methyl ***1-decene*** ***1-undecene*** ***1-pentadecene*** ***1-tretradecene***	1-pentene, 4-methyl *Eicosane, 10-methyl *1-heptene ***1-octene*** *Eicosane ***1-nonene*** *1-pentadecene ***1-decene*** ***1-tetradecene*** ***1-undecene*** ***1-tridecene***	2,4-Hexadiyne 1-pentene, 4-methyl *1-pentene ***1-octene*** ***1-pentadecene*** ***1-nonene***
AR[2]	-	-	-	-	-
PN[3]	-	-	*Benzeetanol, alpha.-methyl-3-(1-methyethyl) *.alpha., alpha' Dihydroxy-m-diisopropylben-zene *Phenol	-	-
ON[4]	-	*Pentadecanenitrile Octadecanenitrile *Dodecanenanitrile ***Heptadecananitrile*** *Tridecananitrile	*Acetamide *Benzonitrile *Isobutyronitrile *Hexadecananitrile *Pyrrole ***Heptadecananitrile***	*Hexadecananitrile Ethylamine ***Heptadecananitrile*** *Pentadecanenitrile	-
AH[5] and KT[6]	-	-		-	*Acetaldehydes
OT[7]	*1-Hexanol, 2-ethyl	*1-Hexanol, 2-ethyl *9-Tretradecanol	*Tetradecanoic acid	*1-Hexanol, 2-ethyl	*n-hexadecanoic acid *Acetic acid

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others, Common fragments = Italic letter.

The increase in the percent distribution of the organic nitrogen class may have been due to the fact that firstly, the organic nitrogen in the influent water and the aeration pond effluent may have been equal in concentration. Since the DOC of the influent wastewater (10.3 mg/L) was 50% higher than that of the aeration pond effluent (5.5 mg/L), the percent distribution of organic nitrogen in influent wastewater was significantly low (4%); whereas that of in the aeration pond effluent increased (25%). Another assumption was that the organic nitrogen in the influent wastewater may have occurred in a form that was not detected by the pyrolysis GC/MS technique. After the aeration process, the organic nitrogen may have transformed or combined with other compounds into a form that could be detected by the pyrolysis GC/MS technique. With regard to this obtained result, it can be proposed that after the industrial estate wastewater was treated by the aeration ponds, the major chemical classes were aliphatic hydrocarbons and organic nitrogen. In addition, this implied that the amount of organic nitrogen in the water increased after being treated in the aeration ponds.

After the aeration pond effluent was treated by the facultative ponds, the order of the chemical classes from high to low was as follows: aliphatic hydrocarbon (25 %), organic nitrogen (20%), other compounds (18%), phenol (12%), and aromatic hydrocarbon (2%). The 10 prominent major fragments ordered from high to low in the aliphatic hydrocarbon class were heptene, eicosane, eicosane-10 methyl, nonadecane-2 methyl, 1-nonene, tricosane, 1-octene, octadecane-2 methyl, 1-decene, and 1-undecene. The prominent major fragments ordered from high to low in the organic nitrogen class were acetamide, benzonitrile, isobutyronitile, hexadecananitrile, pyrrole and heptadecananitrile; and for the phenol class, they were benzeneethanol, alpha.-methyl-3-(1-methylethyl), .alpha. alpha.'-dihydroxy-m-diisopropylbezene and phenol. Tretradecanoic acid in the carboxylic acid class was also found to be a prominent major fragment.

The percent distribution of the chemical classes in the effluent wastewater from the facultative ponds was compared with that of effluent water from the aeration ponds. It seems that the percent distribution of the phenol class moderately increased, while the percent distribution figures for the aliphatic hydrocarbon and organic nitrogen classes slightly decreased. Pyrolysis fragments in the phenol class may have mainly occurred after the water was put through the facultative ponds. This may be attributed to the biotransformation process in the facultative ponds, which could have transformed the organic compounds in the other classes into phenol compounds. Another possibility was that phenol compounds may have directly come from algae and some other sources in the facultative ponds.

In the effluent water from the oxidation ponds, aliphatic hydrocarbon of about 58% of the DOM was the major chemical class. The 12 prominent major fragments ordered from high to low are listed as follow: 1-pentene 4 methyl, eicosane-10 methyl, 1-heptene, 1-octene, eicosane, 1-nonene, 1-pentadence, 1-decene, 1-tretradecene, 1-undecene, 1-tridecene and 1-dodecene. Organic nitrogen of about 15% percent was found in 4 prominent major fragments, ordered from high to low, as follows: hexadecananitrile, ethylamine, heptadecanenitile, and pentadecanenitrile. Other chemical classes were obtained in very low percent distribution values. Nevertheless, 1-hexanol 2-ethyl was also detected as the prominent major fragment of the alcohol class.

After the effluent water from the oxidation ponds was treated by the detention pond, the order of the chemical classes from high to low was aliphatic hydrocarbon (48%), other compounds (13%), aldehydes and ketones (11%), organic nitrogen (6%), aromatic hydrocarbon (5%), and phenol (1%). 2,4-hexadiyne, 1-pentene-4 methyl, 1-pentene, 1-octene, 1-pentadecene, 1-nonene and 1-decene were detected as the 7 prominent major fragments from high to low of the aliphatic hydrocarbon class whereas acetaldehyde was the prominent major fragments of aldehydes class. n-hexadecanoic acids and acetic acid were the prominent major fragments of carboxylic acids class. From the obtained results, it can be concluded that the major chemical class in the treated wastewater was the aliphatic hydrocarbon class. This observation was similar to the study of Sirivedkhin and Gray (2005), which demonstrated that treated wastewater from a wastewater treatment plant was found to be more aliphatic and contained a higher organic nitrogen content than the DOM in natural water sources. Debroux (1998), Peschel and Wildt (1998) and Gray *et al.* (2000) showed that treated wastewater was found to be aliphatic-dominated. In other words, Dignac *et.al.* (2000) found treated wastewater to be aromatic-dominated.

Since the major chemical class of both treated wastewater and influent wastewater was aliphatic hydrocarbons, it can be noted that the characteristic of treated wastewater mainly depends upon the nature of the influent wastewater. This observation corresponded well with the study of Dignac *et.al.* (2000). They proposed that the major fragments from the pyrochromatograms of wastewater and treated wastewater from activated sludge treatment processes were not different. In addition, the percent distribution of the organic nitrogen class gradually decreased after treatment in the facultative, oxidation and detention ponds. Interestingly, the percent distributions of the aldehydes and ketone classes considerably increased after the water was put through the detention ponds. This may have been due to the long extension detention times (of about 21 days) of stabilization pond system that could have reduced the organic nitrogen content and transformed other classes of DOM into aldehydes. Another explanation was that aldehydes may have directly discharge into the storm water collection systems and flowed to the detention pond. A comparison of the percent distribution of chemical classes in the unfractionated water samples obtained in this study with that of other water sources is tabulated in Table 5.2 There were significant differences in the chemical characteristics of the wastewater and natural waters. Aliphatic hydrocarbon dominated influent wastewater and its treated effluent, whereas, aromatic, organic nitrogen and aliphatic compounds were predominant in the reported natural waters.

Table 5.2: DOC and percent distribution of chemical classes in unfractionated waters in this study and other water sources from literature data

Water sources	DOC (mg/L)	Percent distribution of chemical classes from high to low (%)
Seine River, Paris, France (Bruchet et al 1990)		
Sampling times: March 1988	2.4	Polysaccharide (44) > Proteins (24) > Losses (12) > Miscellaneous (10) > Amino sugar (4) = Polyhydroxy aromatics (36)
Sampling times: April 1988	3.7	Polysaccharide (40) > Proteins (22) > Polyhydroxy aromatics (14)> Miscellaneous (10) > Amino sugar (10) > Losses (1)
Sampling times: November 1988	2.8	Polyhydroxy aromatics (49) > > Proteins (24) > Amino sugar (10) > Polysaccharide (7) > Miscellaneous (5) = Losses (5)
Sampling times: June 1989	4.4	Polyhydroxy aromatics (36) > Losses (18) > Polysaccharide (17) > Proteins (12) > Miscellaneous (11) > Amino sugar (6)
Seine River, Paris, France (Vilge-Ritter et al 1999)	3.8	Amino sugar (41) > Polysaccharide (21) = Miscellaneous (21) > Polyhydroxy aromatics (14) > Protein (3)
Ohio River, Cincinnati, Ohio, USA (AWWA, 1998)[1]	2.2	Nitrogen containing (35.9) > Aliphatic (34.5) >Aromatic (15.8) >Halogen substituted (13.9)
Mississippi River, Jefferson Parish, La., USA (AWWA, 1998)[1]	5.2	Nitrogen containing (40.7) > Aliphatic (37.7) >Aromatic (13.4) > Unknown (8.3) > Halogen substituted (BDL[2])
Passaic River, N.J., USA (AWWA, 1998)[1]	5.0	Halogen substituted (67.0) > Aliphatic (23.0) >Nitrogen containing (12.0) Aromatic (3.9) > Unknown (4.3)
Lake Gaillard Water, Conn., USA (AWWA, 1998)[1]	2.9	Aromatic (70.0) > Aliphatic (16.3) > Nitrogen containing (7.7) > Unknown (5.8) > Halogen substituted (BDL)
Groundwater, Florida, USA (AWWA, 1998)[1]	13.0	Aromatic (97.0) > Aliphatic (1.4) > Unknown (1.6) >Nitrogen containing (BDL) > Halogen substituted (BDL)
Influent wastewater (this study)	10.3	AL[3] (70) > Unknowns (11) > OT[10] (7) > AR[4] (5) > ON[6] (4) > PN[5] (2) > AH[7] and KT[8] (1)
Effluent water from aeration ponds (this study)	5.6	AL[3] (43) > ON[6] (26) > Unknowns (21) >OT[10] (8) > AR[4] (2)
Effluent water from facultative ponds (this study)	6.0	AL[3] (25) > Unknowns (21) > ON[6] (20) > OT[10] (18) > PN[5] (12) > AR[4] (2) > AH[7] and KT[8] (1)
Effluent water from oxidation ponds (this study)	5.6	AL[3] (58) > Unknowns (17) > ON[6] (15) > OT[10] (5) > AR[4] (3) > PN[5] (2)
Effluent water from detention pond (this study)	6.1	AL[3] (48) > Unknowns (16) > OT[10] (13) > AH[7] and KT[8] (11)> ON[6] (6) > AR[4] (5) > PN[5] (1)

Remark:[1]Percent distribution was based upon peak height, [2]BDL = below detection limit Remark: [3]AL= aliphatic hydrocarbon, [4]AR = aromatic hydrocarbon, [5]PN =phenol, [6]ON = organic nitrogen, [7]AH = aldehydes, [8]KT = ketones, and [10]OT = others.

5.4.2 Chemical Classes of HPON

Propene, 2-butene, 1-octene, 1-nonene, 1-decene, and 1-undecene, as illustrated in Appendix B (Table B-2), were recognized as the common pyrolysis fragments of the aliphatic hydrocarbon class of HPON; whereas toluene, p-xylene, styrene, benzene (1-methylethyl), benzene propyl, .alpha-Methylstryrene, benzene pentyl, naphthalene, benzene (1-pentylheptyl), benzene (1-butyloctyl) and benzene (1-propylnonyl) were identified as the common pyrolysis fragments of the aromatic hydrocarbon class. For the phenol class, the common pyrolysis fragments were phenol, phenol 2-methyl, phenol 4 methyl, phenol 2,4-dimethyl and phenol 4-(1,1,3,3-tretramethylbutyl). Pyrrole was classified as the common pyrolysis fragments of the organic nitrogen class, whereas cyclotretrasiloxane octamethyl was the common pyrolysis fragments of other class.

In Figure 5.3, Table B-2 and Table 5.3, the aromatic hydrocarbon class accounted for approximately 55% of DOM in the HPON fraction of the influent wastewater, in which the 12 prominent major fragments ordered from high to low were benzene (1-butylheptyl), benzene (1-pentylheptyl), benzene (1-propyloctyl), benzene 1-butyloctyl), benzene (pentylhextyl), benzene (1-butylhextyl), benzene, (1-ethylnonyl), benzene (1-propylheptyl), benzene (1-propylnonyl), benzene, (1-pentyloctyl), benzene (1-ethyloctyl), and benzene hexyl. Aliphatic hydrocarbon at about 10% of DOM in the HPON fraction of the influent wastewater was determined in which 1-heptene and 1-propene were two of the prominent major fragments. Phenol, organic nitrogen, aldehydes and ketone, and the other compounds classes were detected in very low percent distributions (approximately 5%), in which phenol, 4-(1,1,3,3-tetramethylbutyl), phenol, 4-(1-methyl-1-phenylethyl) and dodecanamide were found as the prominent major fragments.

In the case of effluent water from the aeration ponds, interestingly, ester and carboxylic acids classes were also found in the high percent distribution range (of about 28 percent) where 2-propenoic acid, 2-methyl-, methyl ester, 2-propenoic acid, 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl) oxy]methyl]-1-3-propanediyl ester, 2-propenoic acid, 2methyl-, oxiranylmethyl ester, pentadecanoic acid, tetradecanoic acid and 2-propenoic acid, 2 methyl were the prominent major fragments ordered from high to low.

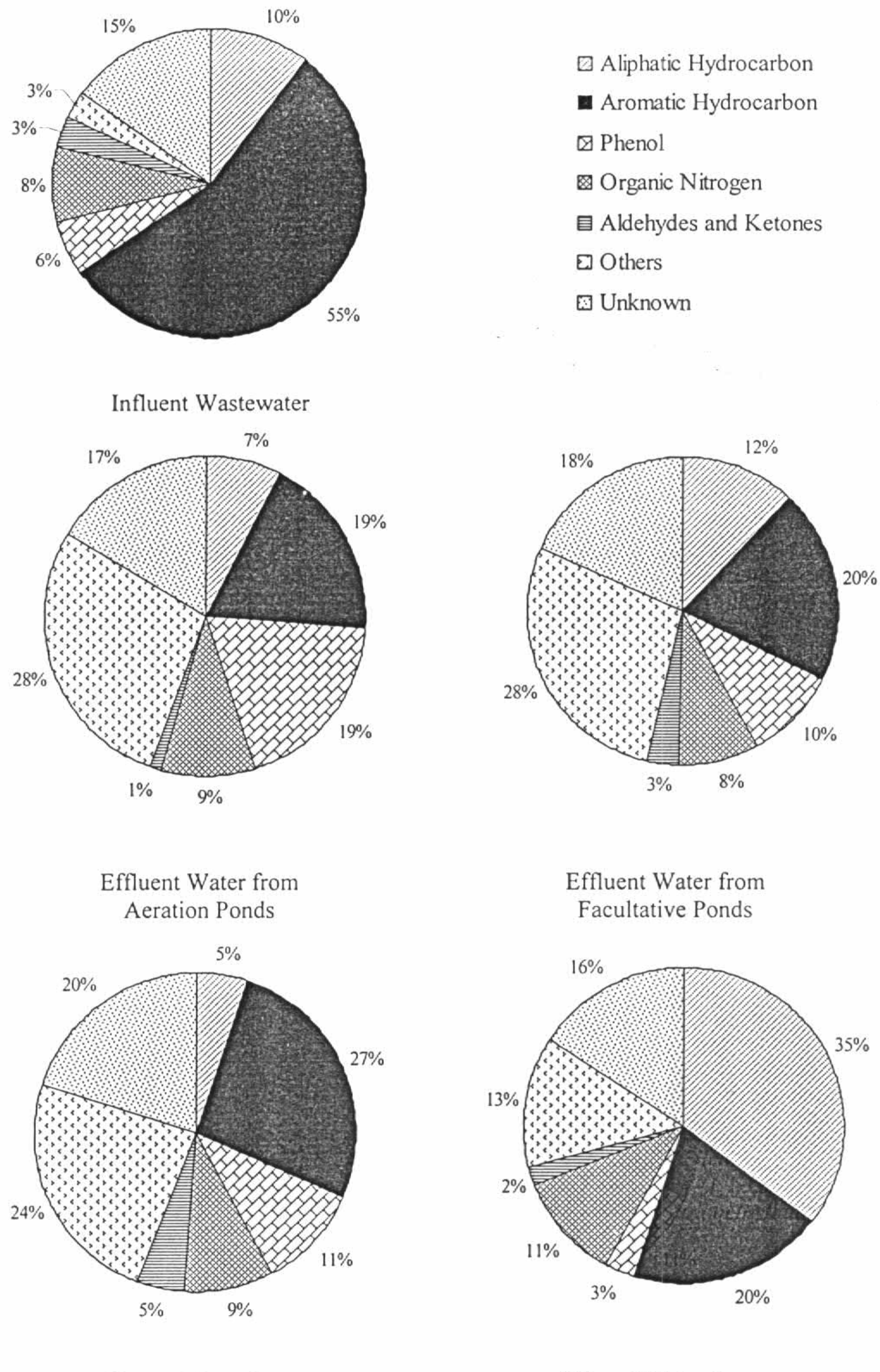

Figure 5.3: Percent distribution of chemical classes of DOM in HPON of influent wastewater and effluent water from aeration, facultative, oxidation and detention ponds

Table 5.3: Summary of the prominent major fragments of each chemical class in HPON

Chemical class	Prominent major fragments (average relative ratios from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	*1-heptene ****1-propene***	****1-propene*** 2,4 Hexadiyne ****2-butene***	1-pentene, 4- methyl	-	****1-nonene*** *1-hexene ****1-octene*** ****1- decene***
AR[2]	Benzene, (1-butylheptyl) ****Benzene, (1-pentylheptyl)*** *Benzene, (1-propyloctyl) ****Benzene, (1-butyloctyl)*** *Benzene, (1-pentylhextyl) *Benzene, (1-butylhextyl) *Benzene, (1-ethylnonyl) ****Benzene, (1-propylheptyl)*** *Benzene, (1-propylnonyl) Benzene, (1-pentyloctyl) *Benzene, (1-ethyloctyl) *Benzene, (hexyl)	Benzene, (1-methyldecyl) *Benzene, (1-pentyloctyl) *Benzene, (1-ethylnonyl) ****Benzene, (1-propylnonyl)*** ****Benzene, (1-pentylheptyl)*** ****Benzene, (1-butyloctyl)***	*Benzene	-	*Benzene
PN[3]	*Phenol , (4-(1-methyl-phenylethyl) ****Phenol, 4-(1,1,3,3-tramethylbuthyl)***	****Phenol, 4-(1,1,3,3-tamethylbuthyl)*** *Phenol , (4-(1-methyl-phenylethyl) p-Isopropenyl – phenol *Phenol , (4-(1-methylethyl) ****Phenol***	-	-	-

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes, [6]KT = ketones, and [7]OT = others. Common fragments = Italic bold letter.

Table 5.3: Summary of the prominent major fragment of each chemical class in HPON *(continues)*

Chemical Classes	Prominent major fragments (average relative ratio from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
ON[4]	*Dodecanamide	*1H-benzotriazole 1-methyl *Dodecanamide	*Aniline *1H-benzotriazole 1-methyl	*1H-benzotriazole 1-methyl	-
AH[5] and KT[6]	-	*2-Pentanal	-	-	-
OT[7]	-	*2-propenoic acid, 2-methyl-, methyl ester *2-propenoic acid, 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl) oxy]methyl]-1-3-propanediyl ester 2-propenoic acid, 2methyl-, oxiranylmethyl ester *Pentadecanoic acid *Tetradecanoic acid 2-propenoic acid, 2 methyl	*2-propenoic acid, 2-methyl-, methyl ester *2-propenoic acid, 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl) oxy]methyl]-1-3-propanediyl ester	*2-propenoic acid, 2-methyl-, methyl ester *2-propenoic acid, 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl) oxy]methyl]-1-3-propanediyl ester	*2-propenoic acid, 2-methyl-, methyl ester *1-Hexanol, 2-ethyl

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes, [6]KT = ketones, and [7]OT = others. Common fragments = Italic bold letter.

Aromatic hydrocarbons containing about 19% of DOM were detected, of which the 6 prominent major fragments from high to low were benzene (1-methyldecyl), benzene (1-pentyloctyl), benzene (1-ethylnonyl), benzene (1-propylnonyl), benzene, (1-pentylheptyl), and benzene (1-butyloctyl). The phenol class with approximately 19% of DOM in HPON were found in which phenol, 4-(1,1,3,3- tramethylbuthyl), phenol (4-(1-methyl-phenylethyl), p-Isopropenylphenol, phenol (4-(1- methylethyl) and phenol, ordered from high to low, were the 5 prominent major fragments. As mentioned earlier, the pyrolysis fragment in the phenol class was not detected in the effluent water of the aerations ponds. On this basis, the pyrolysis fragments of the DOM fractions could be different from those of their unfractionated waters. Organic nitrogen with about 9% of

DOM was determined. The prominent major fragments of this chemical class were 1H-benzotriazole 1-methyl and dodecanamide. The rest of the chemical classes were obtained at very low percent distributions. However, the prominent major fragments of the aliphatic hydrocarbon class was 1-propene, 2,4 hexadiyne and 2-butene; whereas, 2-pentanal was found as the prominent major fragments of the aldehydes class.

Other compounds (28%), aromatic hydrocarbons (20%), aliphatic hydrocarbons (12%), phenol (10%), organic nitrogen (8%) and aldehydes and ketones (3%) were determined as the chemical classes of HPON in effluent water from the facultative ponds. Other compound (ester) and aromatic hydrocarbon classes were dominant in the HPON fraction of this water sample. 1-methyl, 2-propenoic acid, 2-methyl-, methyl ester and 2-propenoic acid; and 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl)oxy]methyl]-1-3-propanediyl ester were the prominent major fragments of other class. Benzene was detected as the prominent major fragment of the aromatic hydrocarbon class. 1-pentene 4-methyl was the prominent major fragment of the aliphatic hydrocarbon class, whereas aniline and 1H-benzotriazole were the prominent major fragments of the organic nitrogen class.

In the case of HPON in oxidation pond effluent, the order of the chemical classes of HPON from high to low was aromatic hydrocarbon (27%), other compounds (24%), phenol (11%), organic nitrogen (9%), aliphatic hydrocarbon (5%) aldehydes and ketones (5%). The prominent major fragments of the aromatic hydrocarbon, phenol, aliphatic hydrocarbon, and aldehydes and ketones classes were not detected. 1H-benzotriazole 1-methyl was the prominent major fragment of the organic nitrogen class. 2-propenoic acid, 2-methyl-, methyl ester and 2-propenoic acid, 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl)oxy]methyl]-1-3-propanediyl ester were the prominent major fragments of other compound classes.

The chemical classes of the HPON in the detention pond effluent ordered from high to low were aliphatic hydrocarbon (35%) aromatic hydrocarbon (20%), other compounds (13%), organic nitrogen (11%), phenol (3%), and aldehydes and ketones

(2%). 1-nonene, 1-hexene, 1-octene and 1-decene were the 4 prominent major fragments of the aliphatic hydrocarbon class. Benzene was the prominent major fragment of aromatic hydrocarbon class, where as 2-propenoic acid, 2-methyl, methyl ester, and 1-hexanol 2 ethyl were the prominent major fragments of other compound and alcohol classes, respectively. The prominent major fragments of the phenol, organic nitrogen and aldehydes and ketones classes were not detected.

The obtained results in this part indicated that aromatic hydrocarbon was the first major chemical class in HPON, followed by other chemical class, which was mainly composed of ester, and the phenol class. In the detention pond effluent, unlike the other effluent, the aliphatic hydrocarbon and aromatic hydrocarbon classes were the first and second major chemical class in HPON.

5.4.3 Chemical Classes of HPOB

There were no common pyrolysis fragments of aliphatic hydrocarbon class in HPOB as seen in Appendix B (Table B-3). Toluene, p-xylene, styrene, and naphthalene were the common pyrolysis fragments of the aromatic hydrocarbon class. The common pyrolysis fragment of the phenol class was phenol. Furfural was the common pyrolysis fragments of the aldehydes class, whereas cyclopentanone was identified as the common pyrolysis fragments of the ketone class. Cyclotretrasiloxane octamethyl was identified as the common pyrolysis fragments of other compound class.

Figure 5.4 and Tables B-3 (Appendix B) and 5.4 provided data that showed that the aliphatic hydrocarbon class accounted for approximately 36% of the DOM in the influent wastewater's HPOB concentration. 2, 4 hexadiyne was the only prominent major fragment of the aliphatic hydrocarbon class. The order of other chemical classes from high to low was organic nitrogen (19%), aldehydes and ketones (13%), other compounds (12%), aromatic hydrocarbon (8%) and phenol (6%). There was no prominent major fragment observed for all the mentioned chemical classes. On this basis, it can be proposed that aliphatic hydrocarbon was the major chemical class of the HPOB fraction in the influent wastewater.

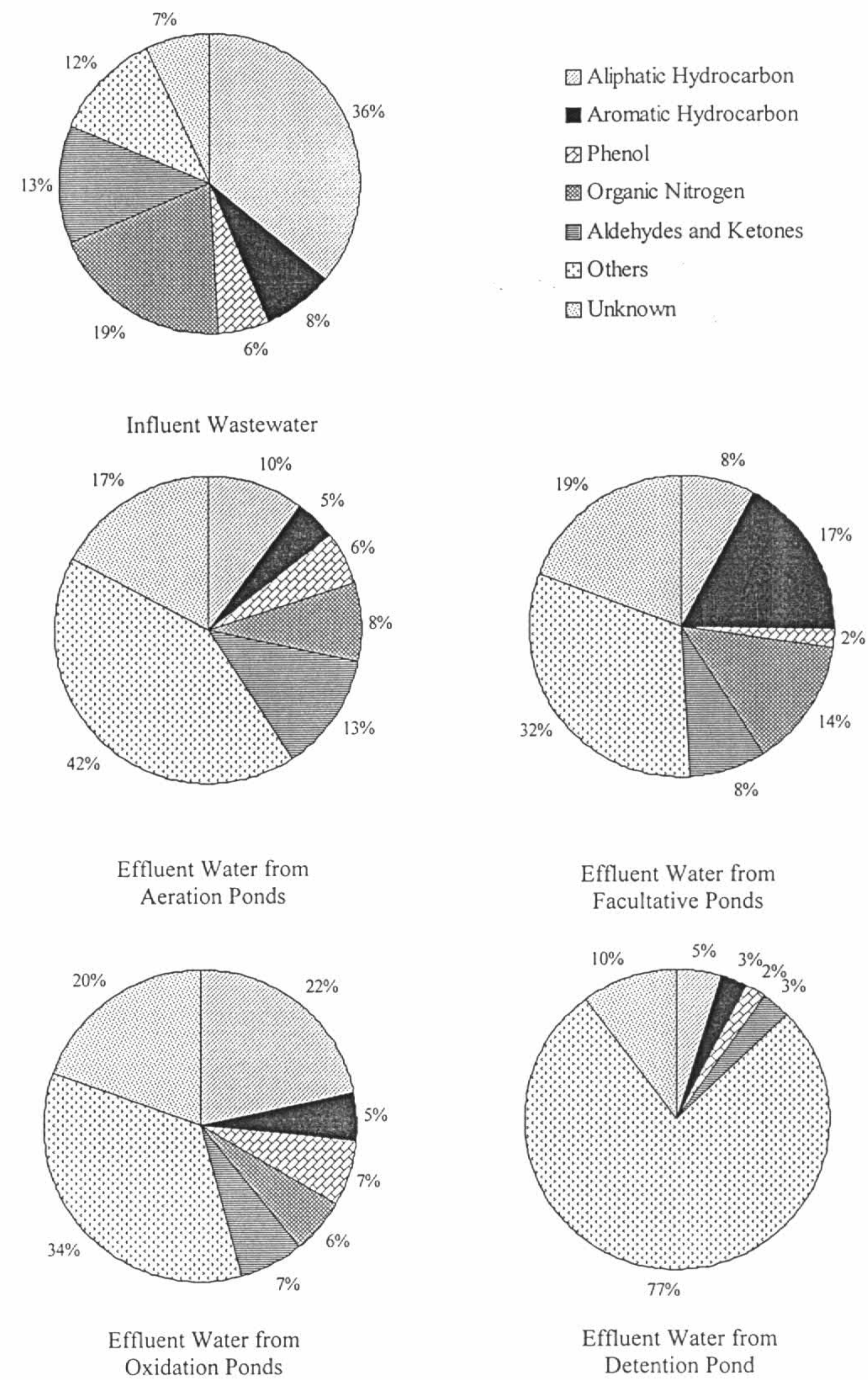

Figure 5.4: Percent distribution of the chemical classes of DOM in HPOB of the influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

Table 5.4: Summary of the prominent major fragment of each chemical class in HPOB

Chemical class	Prominent major fragments (average relative ratio from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	2,4-hexadiyne	2,4-hexadiyne *Eicosane	1-pentene, 4-methyl	2,4-hexadiyne *1-decene	-
AR[2]	-	-	*Benzene ****Styrene***	-	-
PN[3]	-	****Phenol***	-	****Phenol***	-
ON[4]	-	*1-benzotriazole	Ethylamine *Acetronitrile *1H-Pyrrole, 1-methyl	*1-benzotriazole	-
AH[5] and KT[6]	-	*2-Furancarboxal - dehyde , 5-methyl ****Furfural***	*2,3-butanedione	-	-
OT[7]	-	*n-hexadecanoic acid *Acetic acid *Tetradecanoic acid	*n-hexadecanoic acid *Tetradecanoic acid *Pentadecanoic acid	*n-hexadecanoic acid *Tetradecanoic acid *Acetic acid	Heptadecanoic acid *n-hexadecanoic acid *Tetradecanoic acid *Pentadecanoic acid *Acetic acid

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others. Common fragments = Italic bold letter

In the aeration pond effluent, the other compound class accounted for 42% of the HPOB fraction. n-hexadecanoic, acetic acid and tetradecanoic acid ordered from high to low were the 3 prominent major fragments. The order of the other chemical classes from high to low is listed as follows: aldehydes and ketones (13%), aliphatic hydrocarbon (10%), organic nitrogen (8%), phenol (6%), and aromatic hydrocarbon (5%). 2,4 hexadiyne and eicosane were the prominent major fragments of the aliphatic hydrocarbon class. 1-benzotriazole and phenol were classified as the prominent major fragments of phenol class, whereas 2-furancarboxaldehyde 5-methyl and furfural were the prominent major fragments aldehydes class. After aeration pond effluent was treated by the facultative ponds, the other compound class made up about 32% of the HPOB fraction. n-hexadecanoic, tetradecanoic acid, and pentadecanoic acid, ordered from high to low, were the 3 prominent major fragments. The order of the rest of the chemical classes of HPOB from high to low was aromatic hydrocarbon (17%), organic nitrogen (14%), aldehydes and ketones (8%), aliphatic hydrocarbon (8%) and phenol (2%). Benzene and styrene were identified as the prominent major fragments of aromatic hydrocarbon class, where as ethylamine, and 1H-pyrrole 1-methyl were the prominent major fragments of organic nitrogen class. 2,3-butanedione was the prominent major fragments of ketone class. The prominent major fragment of the aliphatic hydrocarbon class was 1-pentene 4-methyl.

The other compound class accounted for 34% of the HPOB fraction in the effluent water after being put through the oxidation ponds. n-hexadecanoic, tetradecanoic acid and acetic acid, ordered from high to low, were the 3 prominent major fragments. The 22% of aliphatic hydrocarbon class was observed where 2,4 hexadiyne and 1-decene were the 2 prominent major fragments. The rest of the chemical classes were obtained at very low percent distribution levels (approximately 5%). When the HPOB fraction of the wastewater treated by the detention pond was taken into consideration, the other compound that was mainly composed of carboxylic acids, accounted for 77% of the HPOB content where heptadecanoic acid, n-hexadecanoic, tetradecanoic acid, pentadecanoic acid and acetic acid were the 5 prominent major fragments. The rest of the chemical classes were obtained at very low percent distribution levels (approximately 5%).

From the obtained results, it can be concluded that aliphatic hydrocarbon and organic nitrogen were major chemical classes of HPOB in influent wastewater, while carboxylic acids was the major chemical class in the effluent from the aeration, facultative, oxidation and detention ponds.

5.4.4 Chemical Classes of HPOA

Based on the results expressed in Chapter 4, HPOA was the major DOM fraction and major THM precursor in all the water samples. The characteristics of HPOA, therefore, were overwhelmingly important. From Appendix B (Table B-4), propene, 2-butene, 1,3-cyclopentadiene, and 1,3-cyclohexadiene were the common pyrolysis fragments of the aliphatic hydrocarbon class in HPOA; whereas benzene, toluene, and indene were the common pyrolysis fragments of the aromatic hydrocarbon class in HPOA. The common pyrolysis fragments of organic nitrogen class were butanenitrile 3-methyl, pyrrole and indole. Methyl isobutyl ketone and cyclopentanone 2,4,4-trimethyl, were identified as the common pyrolysis fragments of ketone class.

According to Tables B-4 (Appendix B) and 5.5 and Figure 5.5, the order of the chemical classes of HPOA in the influent wastewater from high to low was aliphatic hydrocarbon (42%), aromatic hydrocarbon (31%), organic nitrogen (8%), aldehydes and ketones (8%) phenol (2%) and other compounds (2%). 1,3-cyclopentadiene was the only prominent major fragment of the aliphatic hydrocarbon class, whereas benzene was detected as the prominent major fragment of the aromatic hydrocarbon class. The major fragments of the rest of the chemical classes were not observed. After the industrial estate wastewater was treated by the aeration ponds, the aromatic hydrocarbon class accounted for more than 40% of HPOA. The rest of the chemical classes ordered from high to low was aliphatic hydrocarbon (17%), organic nitrogen (12%), aldehydes and ketones (12%), phenol (9%) and other compounds (1%). Benzene was the only prominent major fragment that was observed in the aromatic hydrocarbon class, and no prominent major fragments were detected for the rest of the chemical classes.

Table 5.5: Summary of prominent major fragment of each chemical class in HPOA

Chemical class	Prominent major fragments (average relative ratio from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	****1,3cyclopentadine***	-	****1,3cyclopentadine***	-	****1,3cyclopentadine***
AR[2]	****Benzene***	****Benzene***	****Benzene***	****Benzene***	****Benzene***
PN[3]	-	-	-	-	-
ON[4]	-	-	-	-	-
AH[5] and KT[6]	-	-	-	-	-
OT[7]	-	-	-	1-decanol, 2-methyl	-

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others. Common fragments = Italic bold letter.

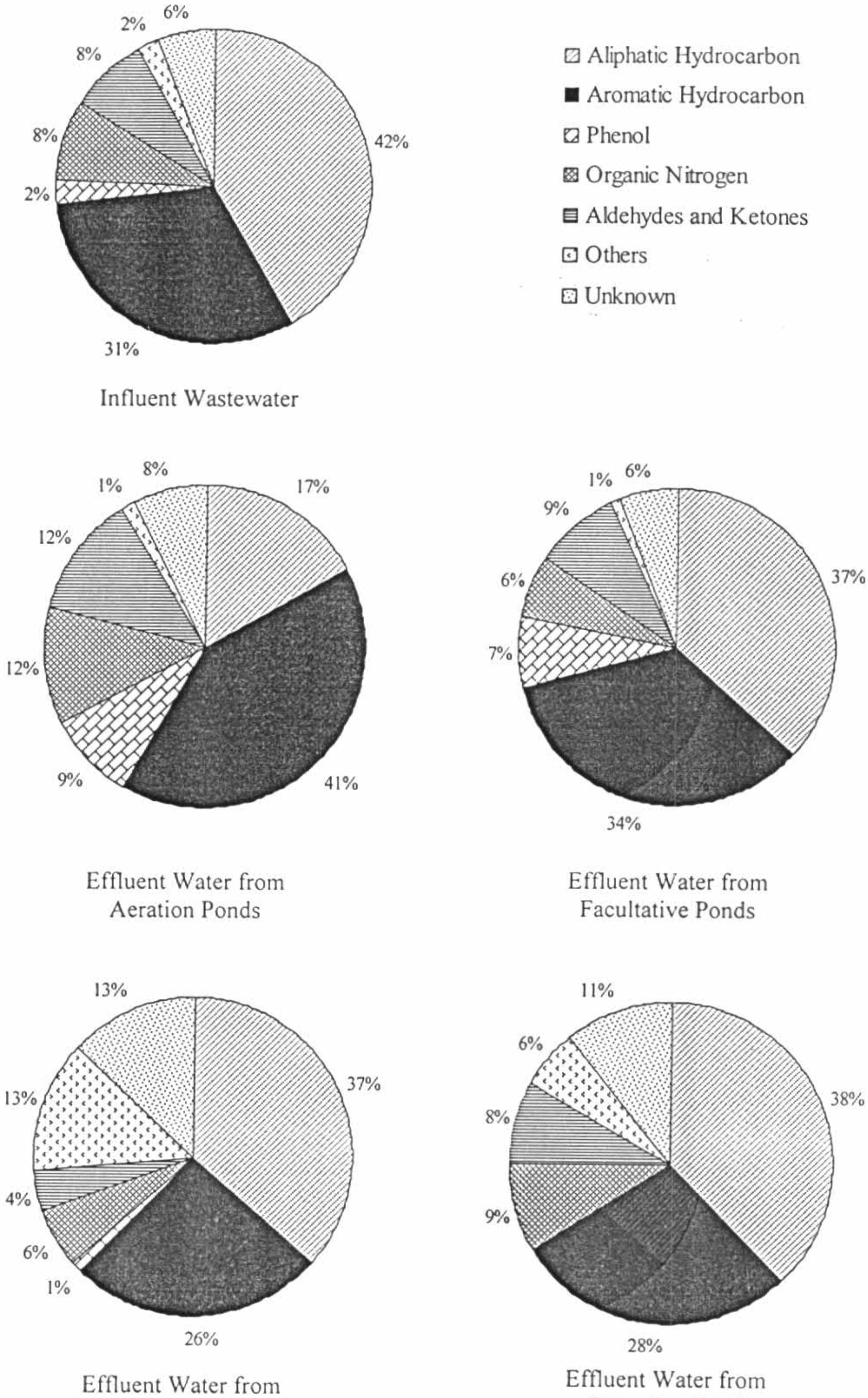

Figure 5.5: Percent distribution of chemical classes of DOM in HPOA of influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

For the facultative ponds, the order of the chemical classes of HPOA in the influent wastewater from high to low was as follows: aliphatic hydrocarbon (37%), aromatic hydrocarbon (34%), aldehydes and ketones (9%) phenol (7%), organic nitrogen (6%), and other compounds (2%). 1,3-cyclopentadiene was only prominent major fragment of the aliphatic hydrocarbon class, while benzene was detected as the only prominent major fragment of the aromatic hydrocarbon class. Major fragments for the rest of the chemical classes were not observed.

The observed presence of the chemical classes of the effluent water treated by the oxidation ponds from high to low was as follows: aliphatic hydrocarbon (37%), aromatic hydrocarbon (26%), other compounds (13%), organic nitrogen (6%), and aldehydes and ketones (4%). Benzene was detected as the only prominent major fragment of the aromatic hydrocarbon class; whereas, 1-decanol 2 methyl was the prominent major fragment of the alcohol classes. Major fragments of the rest of the chemical classes were not found. After the effluent water of the oxidation ponds was treated by the detention pond, the HPOA fraction of the treated wastewater was composed from high to low of aliphatic hydrocarbon (38%), aromatic hydrocarbon (28%), organic nitrogen (9%), aldehydes and ketones (8%) and other compounds (6%). 1,3-cyclopentadiene was the only prominent major fragment of the aliphatic hydrocarbon class. Benzene was detected as the only prominent major fragment of the aromatic hydrocarbon class. Major fragments of the other chemical classes were not observed.

From the obtained results, it can be deduced that aliphatic and aromatic hydrocarbons were the major chemical classes in HPOA. Organic nitrogen and aldehydes and ketones were found to be in the minority. The prominent fragments that should receive more considered in HPOA are 1,3-cyclopentadiene and benzene.

5.4.5 Chemical Classes of HPIB

1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecence were identified as the common fragments of the aliphatic hydrocarbon class in HPIB as can be seen in Appendix B (Table B-5); whereas those of the aromatic hydrocarbon and organic nitrogen classes were toluene and styrene, and pyrrole and butanenitrile 3 methyl, respectively.

Based on the results in Tables B-5 (Appendix B) and 5.6 and Figure 5.6, the chemical classes of HPIB in the influent wastewater were aliphatic hydrocarbon (49%), organic nitrogen (36%), aromatic hydrocarbon (6%), and phenol (1%). 2,4-hexadiyne and 1,3-clyopentadine were the two prominent major fragments of the aliphatic hydrocarbon class, whereas acetronotrile and 2-propenenitrile were identified as two prominent major fragments of organic nitrogen. Major fragments for the other chemical classes were not observed. It can be noticed that aliphatic hydrocarbon and organic nitrogen classes were dominant in the HPIB fraction of the influent wastewater.

After the industrial estate wastewater was treated by the aeration ponds, the aliphatic hydrocarbon class accounted for more than 50% of HPIB. The other chemical classes ordered from high to low were aromatic hydrocarbon (12%), aldehydes and ketones (6%), other compounds (6%), organic nitrogen (6%). and phenol (5%). 2,4-hexadiyne was the only prominent major fragment observed in the aliphatic hydrocarbon class, while no prominent major fragments were found for rest of the chemical classes.

In the case of effluent water after being put through the facultative ponds, the order of the chemical classes of HPIB from high to low was aliphatic hydrocarbon (68%), aromatic hydrocarbon (7%), aldehydes and ketones (7%) and organic nitrogen (7%). 2,4-hexadiyne, pentadecene, 1-nonene, and 1-octene were the 4 prominent major fragments of the aliphatic hydrocarbon class. Acetaldehyde was the prominent major fragments of the aldehydes class. Major fragments for the rest of the chemical classes were not observed.

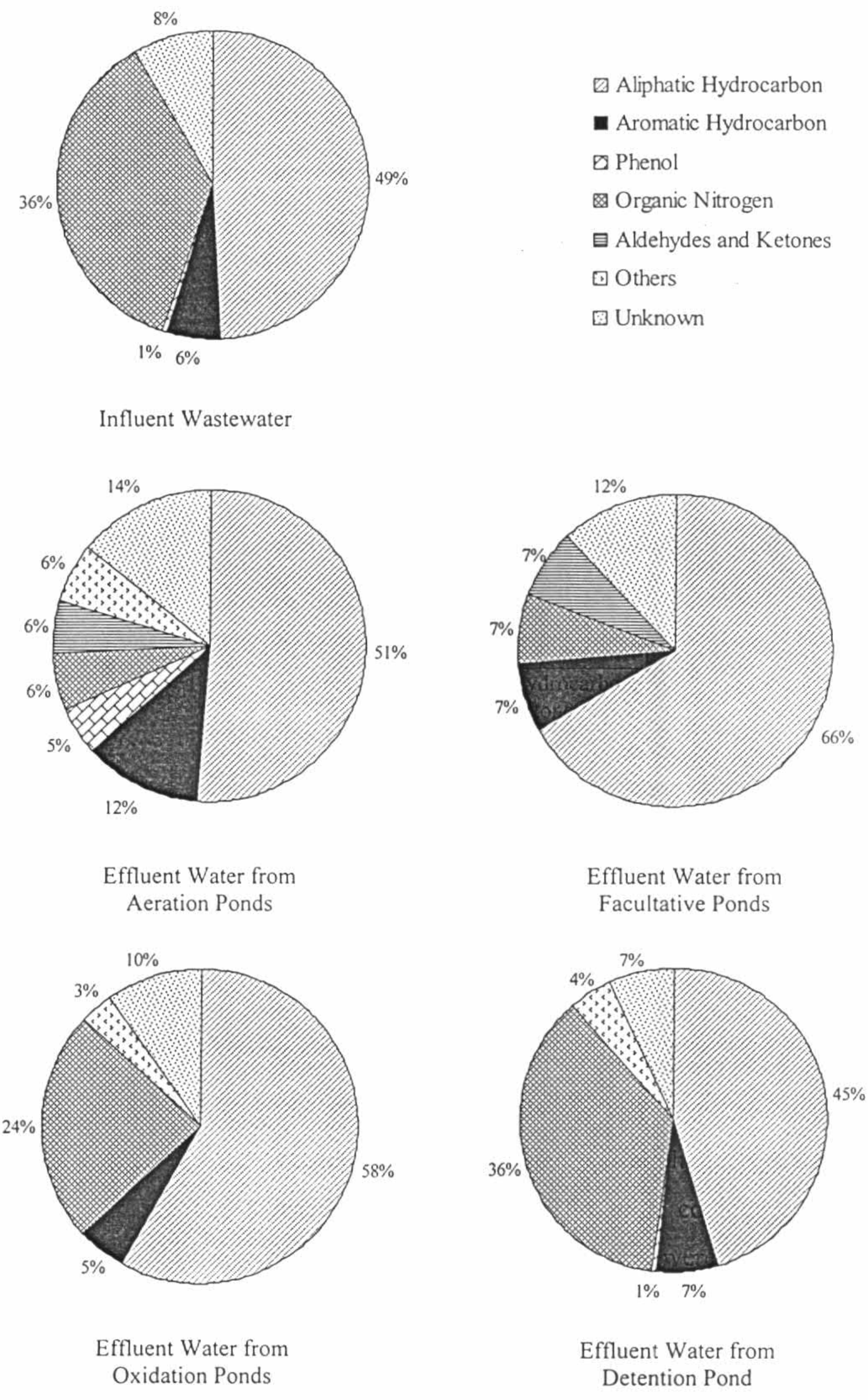

Figure 5.6: Percent distribution of chemical classes of DOM in HPIB of influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

Table 5.6: Summary of the prominent major fragments of each chemical class in HPIB

Chemical class	Prominent major fragments (average relative ratios from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	2,4-hexadiyne *1,3cyclopentadine	2,4-hexadiyne	2,4-hexadiyne *1-pentadecene ****1-nonene*** ****1-octene***	2,4-hexadiyne ****1-octene*** ****1-nonene*** ****1-decene*** *1-undecene	2,4-hexadiyne *1-hexene *1-pentene *1-propene
AR[2]	-	-		*Benzene	*Benzene
PN[3]	-	-	-	-	-
ON[4]	*Acetronitrile *2-propenenitrile	-	-	1, 2-propanediamine	*Acetronitrile *Butanenitrile, 3-methyl *Isobutyronitrile
AH[5] and KT[6]	-	-	*Acetaldehyde	-	-
OT[7]	-	-	-		-

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others, Common fragment = Italic bold letter

By considering the chemical classes of the effluent water treated by the oxidation ponds, it was found that the order of chemical classes of HPIB from high to low was aliphatic hydrocarbon (58%), organic nitrogen (24%), aromatic hydrocarbon (5%), and other compounds (3%). The prominent major fragments from high to low of aliphatic hydrocarbon were 2,4-hexadiyne, 1-octene, 1-nonene, and 1-decene. 1,2-propanediamine was the prominent major fragment of the organic nitrogen classes. Major fragments for the other chemical classes were not observed. With regard to HPIB in the treated wastewater, it consisted of aliphatic hydrocarbon (45%), organic nitrogen (36%), aromatic hydrocarbon (7%), other compounds (7%) and phenol (1%). 2,4-hexadiyne, 1-hexene, 1-pentene and 1-propene were the prominent major fragments ordered from high to low of the aliphatic hydrocarbon class. Benzene was the only prominent major fragment of the aromatic hydrocarbon class; whereas acetronitrile, butanenitrile 3 methyl, and isobutyronitrile were classified as the prominent major fragments of organic nitrogen. Major fragments for the other chemical classes were not observed.

The obtained results clearly demonstrated that aliphatic hydrocarbons (C_3<aliphatic hydrocarbon fragments< C_{19}) was the domimant chemical class in HPIB. The aliphatic organic nitrogen and aromatic hydrocarbon classes were found to be in the minority.

5.4.6 Chemical Classes of HPIA

Based on the results in Chapter 4, HPIA was the second major DOM fraction and the major THM precursor in effluent water treated by the facultative, oxidation and detention ponds. The characteristics of HPIA were considerably important. The common pyrolysis fragments of the aliphatic hydrocarbon class in HPIA were 1-octene, 1-nonene, 1-decene, 1-undecene, 1-tridecene, 1-tetradecene and 1-pentadecene as tabulated in Appendix B (Table B-6). The common pyrolysis fragments of the aromatic hydrocarbon class included toluene and styrene. Common pyrolysis fragments for the other chemical classes were not found.

As can be seen from the results in Tables B-6 (Appendix B) and 5.7 and Figure 5.7, the aliphatic hydrocarbon class accounted for more than 60% of HPIA in the influent wastewater. Other chemical classes were found at very low percent distributions (approximately 5%). 1-heptene, 1-hexene, 1-octene, eicosane, 1-propene, 1-nonene, 1-pentene, nonadecane 2-methyl, eicosane 10-methyl, 1-decene and 1-undecene were the 11 prominent major fragments ordered from high to low of the aliphatic hydrocarbon class. 1-hexanol 2 ethyl was the only prominent major fragment of the alcohol class. Major prominent fragments for the rest of the chemical classes were not detected.

After the industrial estate wastewater was treated by the aeration ponds, the percent distributions of the chemical classes in HPIA was significantly similar to those of the influent wastewater, where aliphatic hydrocarbon of about 66% of HPIA was the major chemical class and 2,4-hexadiyne, 1-hexene, 1-pentene, 1-propene, 2-butene 1-octene, 1-nonene and 1-pentadecene were classified as the prominent major fragments. Prominent major fragments for the rest of the chemical classes were not observed for HPIA in the aeration pond effluent.

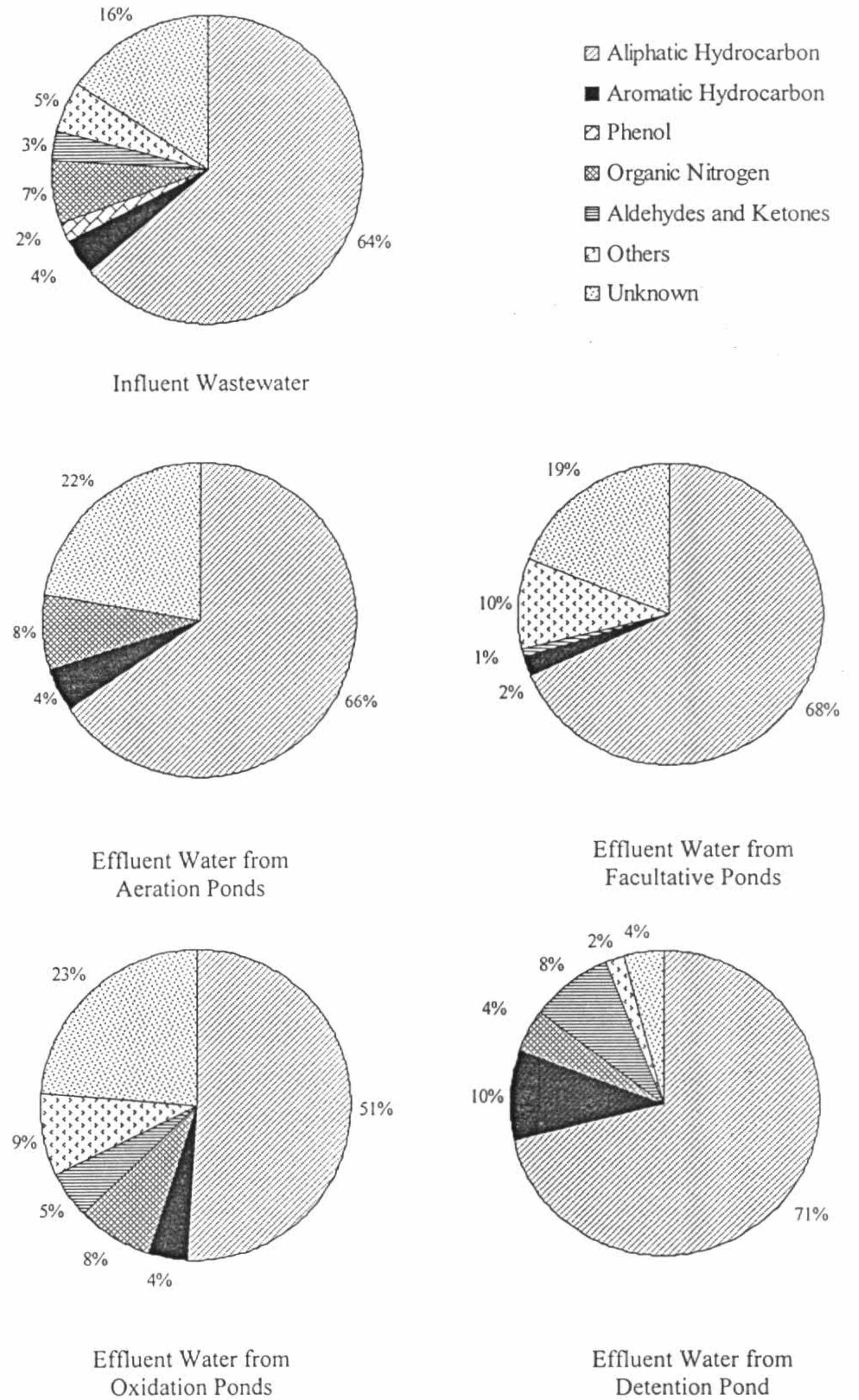

Figure 5.7: Percent distribution of chemical classes of DOM in HPIA of influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

Table 5.7: Summary of the prominent major fragments of each chemical class in HPIA

Chemical class	Prominent major fragments (average relative ratio from high to low)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	*1-heptene *1-hexene ***1-octene*** *Eicosane *1-propene ***1-nonene*** *1-pentene *Nonadecane, 2-methyl *Eicosane, 10-methyl ***1-decene*** ***1-undecene***	2,4-hexadiyne *1-hexene *1-pentene *1-propene *2-butene ***1-octene*** ***1-nonene*** ***1-pentadecene***	****Tridecane*** ****Pentadecene*** Tetradecane, 2-methyl 2,4-hexadiyne Undecane, 2,10-dimethyl *1-Heptadecene ***1-decene*** ***1-undecene*** *Dodecane, 2,6,11-trimethyl *1-dodecene Cyclopetene ***1-nonene*** Tridecane, 3-methyl ***1-octene*** ***1-tetradecene*** Cyclopentene, 1--octyl	*1-heptene ***1-octene*** ***1-nonene*** ***1-decene*** ***1-undecene***	*1-heptene *1-hexene ***1-octene*** *1-propene ***1-nonene*** ***1-decene***
AR[2]	-	-	*Benzene, nonyl *Styrene	-	*Styrene
PN[3]	-	-	-	1,2-propanediamine	-
ON[4]	-	-	-	-	-
AH[5] and KT[6]	-	-	-	-	*Acetaldehyde
OT[7]	*1-hexanol, 2-ethyl-	-	*1-octanol, 2-butyl *Tetradecen-1ol *2-ethyl-1-dodecanol *1-hexanol, 2-ethyl	*1-hexanol, 2-ethyl	-

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others. Common fragment = Italic bold letter

In the facultative, oxidation, and detention pond effluent, aliphatic hydrocarbon of about 68, 51 and 71% of HPIA in respective water samples were determined. Tridecane, pentadecene, tetradecane 2-methyl, 2,4-hexadiyne, undecane 2,10-dimethyl, 1-heptadecene, 1-decene, 1-undecene, dodecane 2,6,11-trimethyl, 1-dodecene, cyclopetene, 1-nonene, tridecane 3-methyl, 1-octene, 1-tetradecene, and cyclopentene 1-octyl, ordered from high to low, were the prominent major fragments of the aliphatic hydrocarbon class in the facultative pond effluent. The prominent major fragments of the aliphatic hydrocarbon class the in the oxidation pond effluent were 1-heptene, 1-octene, 1-nonene, 1-decene and 1-undecene. And the prominent major fragments of aliphatic hydrocarbon in the detention pond effluent were 1-heptene, 1-hexene, 1-octene, 1-propene, 1-nonene and 1-decene.

Benzene nonyl and styrene were classified as the prominent major fragments of aromatic hydrocarbon class. 1-octanol 2 butyl, tretradecan-1-ol, 2-ethyl-1-dodecanol and 1-hexanol 2-ethyl were the prominent major fragments of the alcohol class in HPIA of the facultative ponds effluent. 1, 2-propanediamine and 1-hexanol 2 ethyl were the major prominent fragments of the organic nitrogen and alcohol classes in the effluent water after treatment in the oxidation ponds. The prominent major fragments of the aromatic hydrocarbon and aldehydes classes in the treated wastewater were styrene and acetaldehyde, respectively.

From the percent distribution of HPIA, it was very clear that aliphatic hydrocarbon (C_3 <aliphatic hydrocarbon <C_{23}) was the major chemical class in HPIA of the industrial estate wastewater and its treated effluent.

5.4.7 Chemical Classes of HPIN

As reported in Chapter 4, HPIN was the second major DOM fraction in the influent wastewater and effluent from the aeration ponds. Therefore, understanding the characteristics of HPIN was crucial. The common pyrolysis fragments of the aliphatic hydrocarbon class in HPIN were 1-octene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene and 1-tetradecene (Appendix B, Table B-7). The common pyrolysis fragments of the aromatic hydrocarbon class in HPIN were toluene, p-xylene and styrene; and the common pyrolysis fragment of the organic nitrogen class in HPIN was pyrrole. Common pyrolysis fragments for the other chemical classes were not detected.

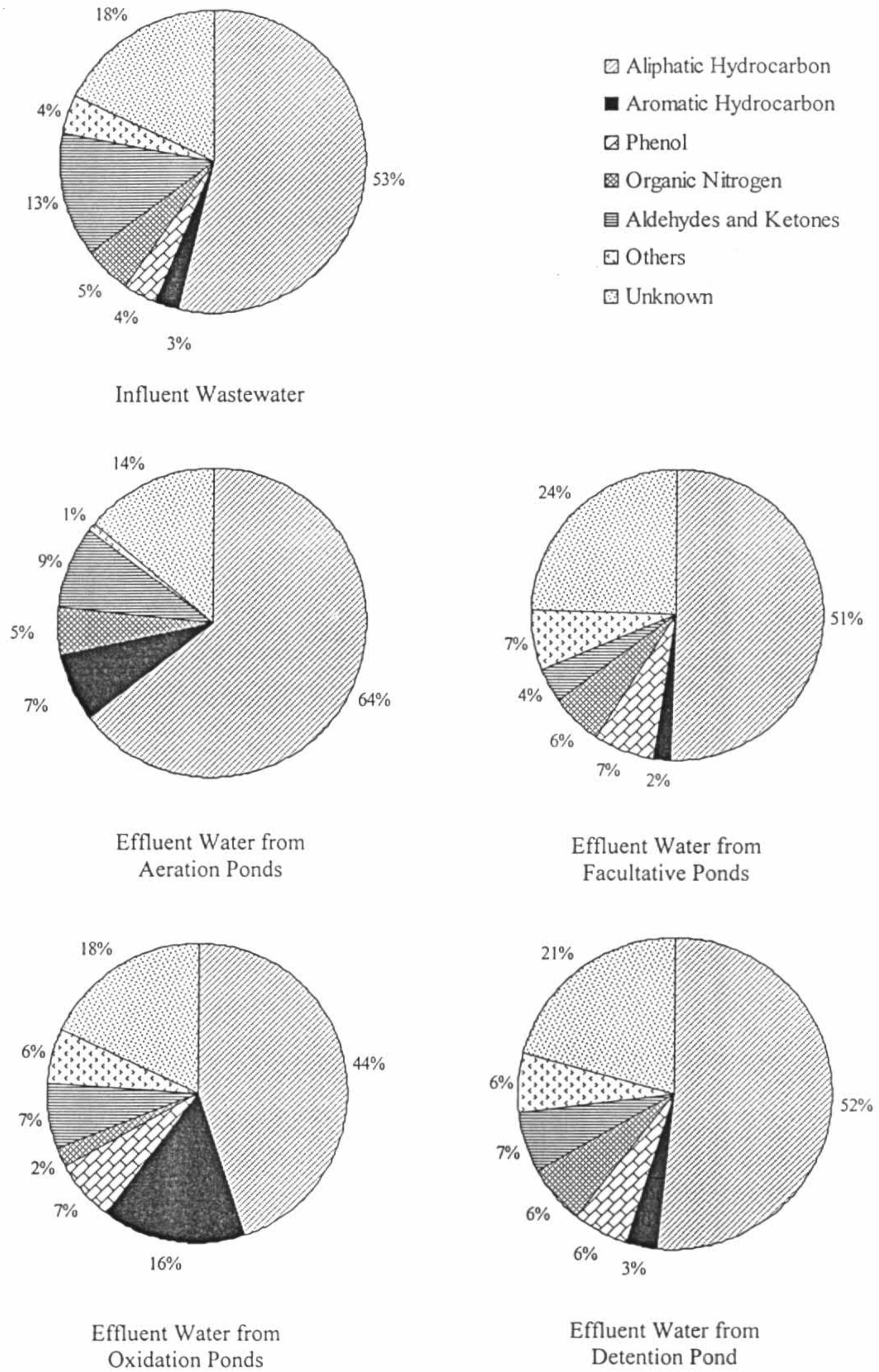

Figure 5.8: Percent distribution of the chemical classes of DOM in the HPIN fraction of the influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

Table 5.8: Summary of the prominent major fragments of each chemical class in HPIN

Chemical class	Prominent major fragments (from high to low average relative ratio)				
	Influent wastewater	Effluent water from aeration ponds	Effluent water from facultative ponds	Effluent water from oxidation ponds	Effluent water from detention pond
AL[1]	*1-heptene *Eicosane Heneicosane *1-hexene *2-butene *Nonadecane, 2-methyl *Tricosane *1-propene *1-pentene *1-nonene ***1-octene*** ***1-decene*** ***1-undecene*** Nonadecane	*Eicosane, 2-methyl *Nonadecane, 9-methyl Eicosane, 10-methyl 2,4-hexadiyne *9-Eicosene	*Eicosane Heneicosane *Nonadecane, 2-methyl Nonadecane, *1-butene *1-heptadecene 2,4-hexadiyne ***1-tridecene*** ***1-tetradecene*** ***1-dodecene*** *1-nonene ***1-decene*** ***1-undecene*** ***1-octene***	Eicosane, 10-methyl *Eicosane, 2-methyl *Tetracosane *Eicosane	Heniecosane *Eicosane *Tricosane *1-Heptene *1-Hexene *Nonadecane, 2-methyl *1-butene *1-pentadecene Octadecane, 2-methyl *1-nonene ***1-decene*** ***1-tridecene*** *1-pentene
AR[2]	-	-	-	Benzene	***Styrene***
PN[3]	*Phenol	-	*Phenol,4-(1,1,3,3-tramethylbuthyl *Phenol *Phenol, m-tert-butyl		*Phenol *Phenol,4-(1,1,3,3-tramethylbuthy
ON[4]	-	-	Caprolactam *Acetamide *Acetronitrile *Pyrrole		Caprolactam
AH[5] and KT[6]	*2-butanone *2-cyclopente-1-one *2-cyclopente-1-one, 2-methyl	*Acetone	*2-cyclopente-1-one, 2-methyl		
OT[7]	*1-hexanol, 2-ethyl-	-	*1-octanol, 2-butyl *1-hexanol, 2-ethyl		*2-propanol, 4-methyl

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes,[6]KT = ketones, and [7]OT = others. Common fragments = Italic bold letter

Based on the results shown in Tables B-7 (Appendix B) and 5.8 and Figure 5.8, the chemical classes of HPIN in the influent wastewater were aliphatic hydrocarbon (53%), aldehydes and ketones (13%), organic nitrogen (5%), phenol (4%), other compounds (4%) and aromatic hydrocarbon (3%). 1-heptene, eicosane, heneicosane, 1-hexene, 2-butene, nonadecane 2-methyl, tricosane, 1-propene, 1-pentene, 1-nonene, 1-octene, 1-decene, 1-undecene and nonadecane were the 14 prominent major fragments ordered from high to low of the aliphatic hydrocarbon class. Phenol was identified as the prominent major fragment of the phenol class. The major prominent fragment of the ketone class was 2-butanone, 2-cyclopente-1-one, 2-cyclopente-1-one 2-methyl. 1-hexanol, 2-ethyl was found as the prominent major fragments of the alcohol class. The aliphatic hydrocarbon and ketones classes, therefore, were dominant in the HPIN fraction of the influent wastewater.

After the industrial estate wastewater was treated by the aeration ponds, the aliphatic hydrocarbon class accounted for more than 64% of HPIN; the other chemical classes ordered from high to low were aldehydes and ketones (9%), aromatic hydrocarbon (7%), organic nitrogen (5%) and other compounds (1%). In the case of the prominent major fragments of HPIN in the effluent water treated by the aeration ponds, eicosane 2-methyl, nonadecane 9-methyl, eicosane 10-methyl, 2,4-hexadiyne, 9-eicosene and 2,4-hexadiyn were the prominent major fragments of the aliphatic hydrocarbon class ordered from high to low. Acetone was classified as the prominent major fragment of the ketone class, whereas for the rest of the chemical classes, no prominent major fragments were found.

After the effluent water from the aeration ponds was treated by the facultative ponds, the order of the chemical classes of HPIN from high to low was aliphatic hydrocarbon (51%), phenol (7%), other compounds (7%), organic nitrogen (6%), aldehydes and ketones (4%), and aromatic hydrocarbon (2%). Eicosane, heneicosane, nonadecane 2-methyl, nonadecane, 1-butene, 1-heptadecene, 2,4-hexadiyne, 1-tridecene, 1-tetradecene, 1-dodecene, 1-nonene, 1-decene, 1-undecene, and 1-octene, ordered from high to low, were detected as the prominent major fragments of the aliphatic hydrocarbon class. Phenol 4-(1,1,3,3-tramethylbuthyl), phenol, phenol m-tert-butyl, and caprolactam, were the prominent major fragments of the phenol class of HPIN in the facultative pond effluent; whereas those of the organic nitrogen class were acetamide, acetronitrile and pyrrole. 2-cyclopente-1-one, 2-methyl, was the prominent major fragment of the ketone class. 1-octanol 2-butyl and 1-hexanol 2-ethyl were the prominent major fragments of the alcohol class of HPIN in the facultative ponds effluent,

After the industrial estate wastewater was treated by the oxidation ponds, the aliphatic hydrocarbon class accounted for more than 40% of HPIB; while the other chemical classes ordered from high to low were aromatic hydrocarbon (16%), aldehydes and ketones (7%), phenol (7%), other compounds (6%), and organic nitrogen (2%). Eicosane, 10-methyl, eicosane 2-methyl, tetracosane and eicosane were the prominent major fragments of the aliphatic hydrocarbon class; whereas benzene was the only prominent major fragment of the aromatic hydrocarbon class. Prominent major fragments for the rest of the chemical classes were not observed

In the case of detention pond effluent, the order of chemical classes of HPIN from high to low was as follows: aliphatic hydrocarbon (52%), aldehydes and ketones (7%), phenol (6%), organic nitrogen (6%), other compounds (6%), and aromatic hydrocarbon (3%). Heniecosane, eicosane, tricosane, 1-heptene, 1-hexene, nonadecane, 2-methyl, 1-butene, 1-pentadecene, 1-nonene, 1-decene, 1-tridecene and 1-pentene, ordered from high to low, were the 12 prominent major fragments of the aliphatic hydrocarbon class. Styrene was the prominent major fragments of the aromatic hydrocarbon class whereas phenol and phenol,4-(1,1,3,3- tramethylbuthy) were the prominent major fragment of the phenol class. Caprolactam was identified as the prominent major fragments of the organic nitrogen whereas 2-propanol 4-methyl was the prominent major fragment of the alcohol class.

From the percent distribution of HPIN, it was clear that aliphatic hydrocarbon, especially high molecular weight aliphatic hydrocarbon fragments, was the major chemical class of the HPIN fraction in the industrial estate wastewater and treated effluent. The aldehydes and ketone classes were found to be in the minority.

5.4.7 Specific Pyrolysis Fragments of DOM Fractions

The specific pyrolysis fragments of DOM fractions were determined by using Equation 5.2, illustrated in Section 5.3. A specific pyrolysis fragment could be used as a representative of each of the DOM fractions. As can be seen from Table 5.9, specific pyrolysis fragments of HPON could be determined in all the chemical classes (with the exception of the aliphatic hydrocarbon class). In spite of that, a large number of specific pyrolysis fragments of the aromatic hydrocarbon class (the major chemical class) was determined. With regard to HPOB, 5 specific pyrolysis fragments were observed in the carboxylic acid (the major chemical class) and aldehydes chemical classes. Acetic acid, benzoic acid, dodecanoic acid, pentadecanoic acid and n-hexadecanoic acid was classified as the specific pyrolysis fragments of the carboxylic acid class. Furfural and octanal were the specific pyrolysis fragment in aldehydes chemical class.

When investigating the major DOM fractions in all the samples, HPOA, 1,3,5-hexatriene, cyclohexadiene, cyclopentene 3-ethenyl, 1,3-cyclopentadiene, and 5,5-dimethyl were identified as the specific pyrolysis fragments in the aliphatic hydrocarbon class (the major chemical class). Indene and fluorine were the specific pyrolysis fragment in the aromatic hydrocarbon class (the major chemical class). Isobutyronitrile, and methyl isobutyl ketone and cyclopentanone 2,4,4-trimethyl were classified as specific pyrolysis fragment of organic nitrogen and ketone classes, respectively.

In the case of HPIB, 2,4 hexadiyne was found as the only specific pyrolysis fragment of aliphatic hydrocarbons (the major chemical class) among all the chemical classes. For HPIA, there was no specific pyrolysis fragment. This could have been due to aliphatic hydrocarbons (approximately more than 50% of HPIA) being the dominant chemical class in all HPIA. However, aliphatic hydrocarbons were also part of the composition of all the fractions; therefore, it was difficult to find the specific pyrolysis fragments of HPIA. For HPIN, 1,3,5-hexatriene and nonadecane 2-methyl were classified as its specific fragments in the aliphatic hydrocarbon class (the major chemical classes). 2-cyclopenten-1-one, cyclopentanone 2,5-dimethyl and butyrolactone were classified as the specific fragments of HPIN in the ketones class.

Table 5.9: Specific fragments of the six DOM fractions

Chemical class	Specific pyrolysis fragment					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
AL[1]	-	-	*1,3,5-hexatriene *Cyclohexadiene *Cyclopentene, 3ethenyl *1,3-cyclopentadiene, 5,5-dimethyl	2,4-hexadiyne	-	*Nonadecane, 2-methyl
AR[2]	*Benzene, (1-methylethyl) *Benzene, propyl *.alpha.-Methylstyrene *Benzene, pentyl *Benzene, (1-pentylhexyl) Benzene, (1-butylheptyl) *Benzene, (1-propyloctyl) *Benzene, (1-ethylnonyl) *Benzene, (1-methyldecyl) *Benzene, (1-pentylheptyl) *Benzene, (1-butyloctyl) *Benzene, (1-propylnonyl) Benzene, (1-pentyloctyl)	-	*Indene Fluorene	-	-	-

Table 5.9: Specific pyrolysis fragment of six DOM fractions *(Continues)*

Chemical class	Specific pyrolysis fragment					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
AR[2]	Benzene, (1-butylnonyl) Benzene, (1-propyldecyl)	-		-	-	-
PN[3]	*Phenol, 2,4-dimethyl *Phenol, 4-ethyl *Phenol, 4-(1-methylethyl) *Phenol, 4-(1-methylpropyl) *Phenol, 4-(1,1,3,3-tetramethylbutyl) *Phenol, 4-(1-methyl-1-phenylethyl)	-	-	-	-	-
ON[4]	1H-Pyrazole, 3-methyl *Aniline *1H-Benzotriazole, 1-methyl	-	Isobutyronitrile	-	-	-
AH[5] and KT[6]	2-pentenal 2,6,6-Trimethyl-2-cyclohexene-1,4-dione	*Furfural *Octanal	*Methyl Isobutyl Ketone *Cyclopentanone, 2,4,4-trimethyl-	-	-	*2-cyclopenten-1-one *Cyclopentanone, 2,5-dimethyl *Butyrolactone
OT[7]	*Methane, chloro Silane, tetramethyl	*Acetic acid *Benzoic acid Dodecanoic acid *Pentadecanoic acid *n-hexadecanoic acid		-	-	-

Remark: [1]AL= aliphatic hydrocarbon, [2]AR = aromatic hydrocarbon, [3]PN =phenol, [4]ON = organic nitrogen, [5]AH = aldehydes, [6]KT = ketones, and [7]OT = others.

5.4.8 Summary of the Prominent Pyrolysis Fragments and Specific Fragments in DOM fractions

In the last section, the specific fragment was used as a representative of each DOM fraction. As mentioned earlier, the prominent major fragments of the chemical classes were also very important due to their presence in very high average relative ratios. In this section, a summary of the specific fragments and prominent major fragments of each of the DOM fractions is presented. The DOM fractions were classified into 6 groups: HPON, HPOB, HPOA, HPIA, HPIB and HPIN. Each group was composed of 5 water samples. The criterion for selecting the prominent major fragments as representative fragments of each DOM fraction was defined by equation below.

The prominent pyrolysis fragment X was selected as the "representative prominent major fragment" of each DOM fraction when

$$\left(\frac{Nx}{Ns} > 0.5\right) \tag{5.4}$$

Where Nx = appearing number of prominent pyrolysis fragment X in a group

Ns = appearing number of water samples that the chemical class of prominent pyrolysis fragment X was observed in group. In the case of Ns < 3, the prominent pyrolysis fragment X was not considered as the representative prominent major fragment.

In Equation 5.3, fragment X is selected as the representative prominent major fragment of a group when the appearing number of fragment X in a group divided by appearing number of water sample that chemical class of prominent pyrolysis fragment X was found in the group, was more than 0.5. For example, the appearing number of benzene and 1-propene fragments as the prominent major fragments in the HPON group was 4 and 2, respectively ($Nx_{Benzene} = 4$ and $Nx_{1\text{-}propene} = 2$) and appearing number of water sample that chemical classes of prominent pyrolysis benzene and 1-propene (aromatic hydrocarbon and aliphatic hydrocarbon class, respectively) were observed in

HPON group, was equaled to 4 and 4, respectively ($Ns_{Benzene}$ = 4 and $Ns_{1\text{-propene}}$ = 4). To judge the specificity of benzene and 1-propene as prominent major fragments for the HPON group, equations could be written up as follows:

$$\text{Benzene fragment:} \quad \left(\frac{Nx_{Benzene}}{Ns} = \frac{4}{4} = 1 > 0.5\right)$$

$$\text{1-propene fragment:} \quad \left(\frac{Nx_{1\text{-propene}}}{Ns} = \frac{2}{4} = 0.5 = 0.5\right)$$

On this basis, the benzene fragment was selected as the representative prominent major fragment of the HPON group; whereas, the 1-propene fragment was not defined as the representative prominent major fragment of the HPON group. Table 5.10 provides a summary of the chemical classes of HPON, HPOA, HPOB, HPIA, HPIB and HPIN, which included their specific fragments and representative prominent major fragments obtained in this study and from literature data.

Table 5.10: Organic compound classes of the DOM fractions obtained in this study and from literature data

Fractions	Chemical classes : specific and representative prominent major fragments	Dissolved organic compound class
HPON	***Aromatic hydrocarbon:*** benzene, benzene,(1-methylethyl), benzene, propyl .alpha. Methylstyrene, benzene pentyl, benzene (1-pentylhexyl), benzene, (1-butylheptyl), benzene (1-propyloctyl), benzene (1-ethylnonyl), benzene (1-methyldecyl), benzene (1-pentylheptyl), benzene (1-butyloctyl), benzene (1-propylnonyl), benzene (1-pentyloctyl), *Phenol:* phenol, phenol, 4-ethyl phenol 2,4-dimethyl, phenol, 4-(1,1,3,3-tetramethylbutyl), phenol 4-(1-methylethyl), phenol 4-(1-methylpropyl) and phenol, 4-(1-methyl-1-phenylethyl), *Organic nitrogen*:1H-benzotriazole 1-methyl, aniline, 1H-pyrazole 3-methyl, *Aldehydes and ketones*: 2-pentanal and 2,6,6-trimethyl - 2 cyclohexene-1, 4-dione, and *Ester:* 2-propenoic acid 2-methyl ester2-propenoic acid, and 2methyl-, 2 ethyl-2-[[(2-methyl-1-oxo-2-propenyl) oxy]methyl]-1-3-propanediyl ester *Other compounds*: Methane chloro, silane, tetramethyl	Hydrocarbons; > C_5 aliphatic alcohol, amides, esters, ketones, and aldehydes; > C_9 aliphatic carboxylic acids and amines; > 3-ring aromatic carboxylic acids and amines; chlorophyll and related pigments; linear alkyl benzene sulfonate (LAS) and optical brighteners (Barber *et al.* 2001); Hydrocarbons, pesticides, carbonyl compound and LAS.(Imai *et al.* 2001); Hydrocarbon/tannins (Leenheer and Croue, 2003)
HPOB	***Carboxylic acids;*** acetic acids, n-hexadecanoic acids, tetradecanoic acid, pentadecanoic acids, dodecanoic acid and benzoic acid, *Aliphatic hydrocarbon;* 2,4 hexadiyne, *Organic nitrogen*: 1-benzotriazole, *Phenol*: phenol, and *Aldehydes*; furfural and octanal	1-and 2-ring aromatic amines except pyridine; proteinaceous substances; cationic surfactants (Barber *et al.* 2001); aromatic amines. (Leenheer and Croue, 2003)
HPOA	***Aromatic hydrocarbon***: benzene, indene, fluorene, ***Aliphatic hydrocarbon***: 1,3 cyclopentadiene, 1,3,5-hexatrene, clyclopentene 3ethenyl, 1,3-cyclopentadiene 5,5-dimethyl, *Organic nitrogen:* isobutyronitrile and *Ketones*: methyl isobutyl ketone and cyclopentanone, 2,4,4-trimethyl	C_5-C_9 aliphatic carboxylic acids; 1-and 2-ring aromatic carboxylic acids1-and 2-ring phenol; fulvic acid; LAS, LAS degradation products. (Barber *et al* 2001); Aquatic humic substances (humic and fulvic acids) (Imai *et al* 2001) Fulvic acids (Leenheer and Croue, 2003)
HPIB	***Aliphatic hydrocarbon***: 2,4-hexadiyne, *Aromatic hydrocarbon*: benzene, *Organic nitrogen*: acetronitrile	< C_9 aliphatic amines; pyridine; amino acids. (Barber *et al.* 2001). Peptide/amino acids (Leenheer and Croue, 2003)
HPIA	***Aliphatic hydrocarbon:*** 1-propene, 1-heptene, 1-hexene, 1-octene, 1-nonene, 1-decene and 1-undecene, *Aromatic hydrocarbon*; styrene, *Alcohol*: 1-hexanol 2ethyl.	< C_5 alphatic carboxylic acids; polyfunctional carboxylic acids;LAS degradation products (Barber *et al.* 2001); Sugar acids, fatty acids, hydroxyl acids (Imai *et al* 2001). Polyuronic acids (Leenheer and Croue, 2003)
HPIN	***Aliphatic hydrocarbon***: 1-butene, 1-nonene, 1-decene, eicosane, heneicosane, nonadecane 2 methyl, *Phenol*: phenol and phenol, 4-(1,1,3,3-tetramethylbutyl), *Organic nitrogen*: caprolactam, *Ketones*: 2-cyclopenten-1-one, cyclopentanone 2,5-dimethyl and butyrolactone and *Alcohol:* 1-hexanol 2-ethyl.	< C_5 aliphatic amide, alcohols, aldehydes, esters and ketones; polyfuctional alcohol; carbohydrates; cyclic amides (Barber *et al.* 2001); Oligosaccharides, polysaccharides. (Imai *et al* 2001). Sugar (Leenheer and Croue, 2003)

*The major chemical class = Italic bold letter, chemical classes = Italic letter

5.4.9 Relationship between Specific THMFP and Chemical Classes

In order to discuss the relationship between specific THMFP and the chemical classes of the DOM fractions, the DOC (with standard deviation ranges), percent distributions of chemical classes, and specific THMFP (with standard deviation ranges) of each DOM fraction of the influent wastewater and effluent from the aeration, facultative, oxidation and detention ponds were plotted as shown in Figure 5.9.

The DOC of HPON was moderately low, while the specific THMFP of HPON was moderately high. Aromatic hydrocarbons, phenol and ester classes in HPON, therefore, could possibly react with chlorine and form THMs. Interestingly, HPOB, which was observed at very low DOC concentrations, had moderately high specific THMFP values. THMs could have easily been associated with the carboxylic acid class. In the case of HPOA (the major DOM fraction in all the samples), moderately high specific THMFPs were found. The aromatic and aliphatic hydrocarbons classes in HPOA could actively react with chlorine. On this basis, it can be summarized that THMs could be easily associated with hydrophobic organic fractions that are composed mainly of aromatic hydrocarbons, carboxylic acids, phenol and ester classes.

In hydrophilic organic fractions, HPIB was found at a low amounts of DOC and contained a moderately low specific THMFP. The aliphatic hydrocarbon and organic nitrogen classes (mainly composed of aliphatic organic nitrogen fragments) in HPIB, therefore, may be inactive with chlorine when it comes to forming THMs. The lowest specific THMFP of the DOM fraction was determined from the specific THMFP of HPIN, which contained slightly high concentrations of DOC. The aliphatic hydrocarbon and ketone classes in HPIN may also be inactive with chlorine. With regard to HPIA, its DOC content was moderately high (major DOM fractions), and its specific THMFP was also moderately high. Aliphatic hydrocarbon classes in HPIA, therefore, could possibly react with chlorine to form THMs.

From this obtained results, it was found that organic fragments in the aliphatic hydrocarbon classes differed in their ability for creating THMs. High molecular weight fragments of the aliphatic hydrocarbon class were dominant in HPIN ($C_{18} \leq$ aliphatic hydrocarbon fragments $\leq C_{24}$), and low and medium molecular weight fragments of the aliphatic hydrocarbon class ($C_5 \leq$ aliphatic hydrocarbon fragments $\leq C_{11}$) were dominant in HPIB and HPIA. It can be deduced that THMs could be easily associated with the aliphatic hydrocarbon class, which creates low and medium molecular weight aliphatic hydrocarbon fragments after pyrolysis. On the other hand, the aliphatic hydrocarbon class, which creates high molecular weight aliphatic hydrocarbon fragments after pyrolysis, and the organic nitrogen class when combined with chlorine could be inactive and fail to form THMs.

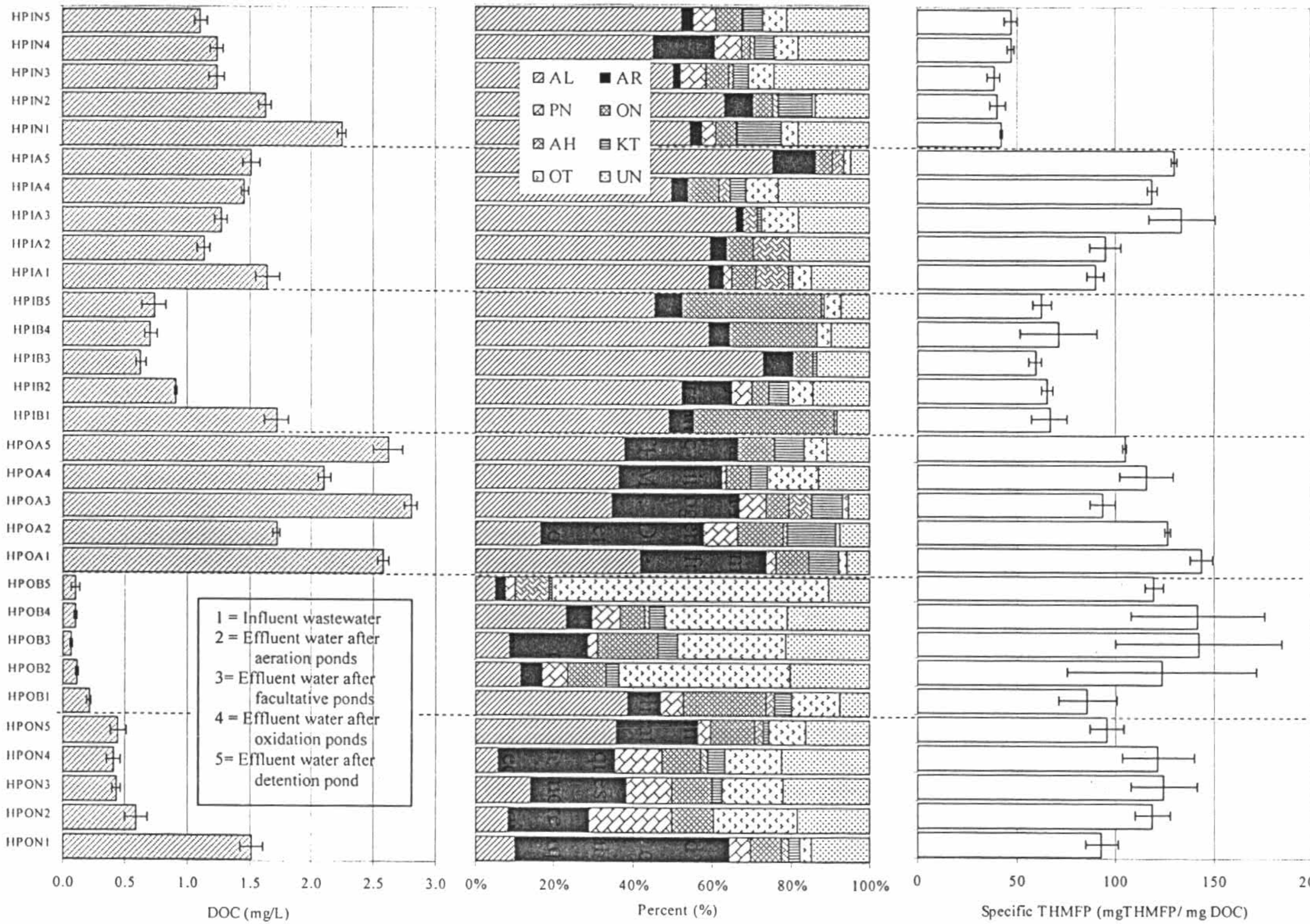

Figure 5.9: DOC, percent distribution of chemical classes, and specific THMFP of DOM fractions

5.5 Concluding Remarks

The major objectives of this chapter were to identify the chemical classes of the DOM and DOM fractions in the influent wastewater and effluent water of the aeration, facultative, oxidation and detention ponds. The results showed that aliphatic hydrocarbon was dominant in the influent wastewater and in the treated effluent. After the fractionation processes, aromatic hydrocarbon was the major chemical class of HPON; whereas carboxylic acids was the major chemical class of HPOB. Aliphatic and aromatic hydrocarbons were classified as the major chemical classes of HPOA (the major DOM fractions). When considering the chemical classes of the hydrophilic organic fractions, the aliphatic hydrocarbon class was identified as the major chemical class in HPIB, HPIA, and HPIN. With regard to THM formation, THMs could be easily associated with hydrophobic organic fractions that are mainly composed of the aromatic hydrocarbon, carboxylic acids, phenol, and ester classes, along with the aliphatic hydrocarbon class ($C_5 \leq$ aliphatic hydrocarbon fragments $\leq C_{11}$). The aliphatic hydrocarbon ($C_{18} \leq$ aliphatic hydrocarbon fragments $\leq C_{24}$) and organic nitrogen classes (mainly composed of aliphatic organic nitrogen fragments), when combined with chlorine, could be inactive and fail to form THMs. Due to the complicated nature of the pyrolysis GC/MS procedure, it would be useful to employ other techniques that could rapidly identify DOM. The rapid identification of DOM could be more quickly obtained using three-dimensional fluorescence spectroscopy. This technique, therefore, could be helpful as another supportive method for characterizing the DOM in wastewater and treated wastewater. The next chapter will present the use of three-dimensional fluorescence spectroscopy in measuring influent wastewater, treated wastewater and their DOM fractions.