

## CHAPTER VII

### REDUCTION OF DISSOLVED ORGANIC MATTER AND FRACTIONATED DISSOLVED ORGANIC MATTER IN INDUSTRIAL ESTATE WASTEWATER TREATED BY STABILIZATION PONDS

#### 7.1 Introduction and Literature Reviews

The previous chapters presented and discusses data related to dissolved organic carbon (DOC) mass distributions, trihalomethane formation potential (THMFP), specific THMFP, chemical classes, fluorescent excitation-emission matrix (FEEM) of unfractionated water and fractionated dissolved organic matter (DOM). These obtained results were utilized to evaluate the reduction of DOM by stabilization ponds.

A stabilization pond is a water treatment process that is commonly used for domestic and industrial applications in Thailand and other countries. However, information on performance capability of stabilization pond processes for reducing DOM and fractionated DOM remains to be evaluated. This type of information could be used to gain a better understanding on the fate transformation of DOM in stabilization pond processes. Conclusive results from past research have shown that the major surrogate parameters for representing the level of DOM in water and wastewater are DOC, ultraviolet light absorbance at 254 nm (UV-254), specific ultraviolet absorption (SUVA), and THMFP. These mentioned parameters, therefore, were utilized to measure the reductions of DOM and DOM fractions by stabilization ponds, the results of which are expressed in this chapter. The pyrolysis gas chromatography mass spectrometer (GC/MS) procedure in Chapter V is recognized as the semi-quantitative approach; therefore, it was not used to determine the reductions of DOM. As mentioned in Chapter VI, fluorescent excitation-emission matrix (FEEM) could be used to classify the complex composition of fluorescent organic matter in water and it has the advantage of its simplicity due to its minimal sample amount, pretreatment and analysis time requirements. Therefore, it must be useful to evaluate the reduction of fluorescent DOM by stabilization pond processes using FEEM.

## 7.2 Objectives of This Chapter

Firstly, the aim was to evaluate the reduction of DOM in terms of DOC, UV-254, SUVA and THMFP, and the reduction of the six DOM fractions in terms of DOC and THMFP by stabilization pond process. Next, the objective was to utilize FEEM analysis to evaluate the reduction of fluorescent organic matter by the stabilization ponds.

## 7.3 Material and Methods

### 7.3.1 Sample Collection

There were four collection times, during which influent wastewater and effluent water from the aeration, facultative and oxidation ponds were collected: September 16 2004, October 22, 2004, February 18, 2005, and July 27, 2005. The treatment system was designed so that most of the rainwater is directed towards the final detention pond; therefore, each of the prior treatment ponds only receives the rain that falls directly onto its surface. This amount of rainwater was estimated to be less than 5% of the total water in each pond; therefore, the effect of dilution was considered to be minimal. Since the final detention pond was affected by the larger amount of rainwater, it was excluded from this investigation. The effluent from the oxidation ponds was deliberately classified as the treated wastewater from the stabilization ponds. All water samples were filtered through a pre-combusted (550 °C for 2 h) Whatman GF/F (nominal pore size 0.7 µm) filter. The filtered waters were kept at 4 °C until analysis.

### 7.3.2 Experimental Procedure

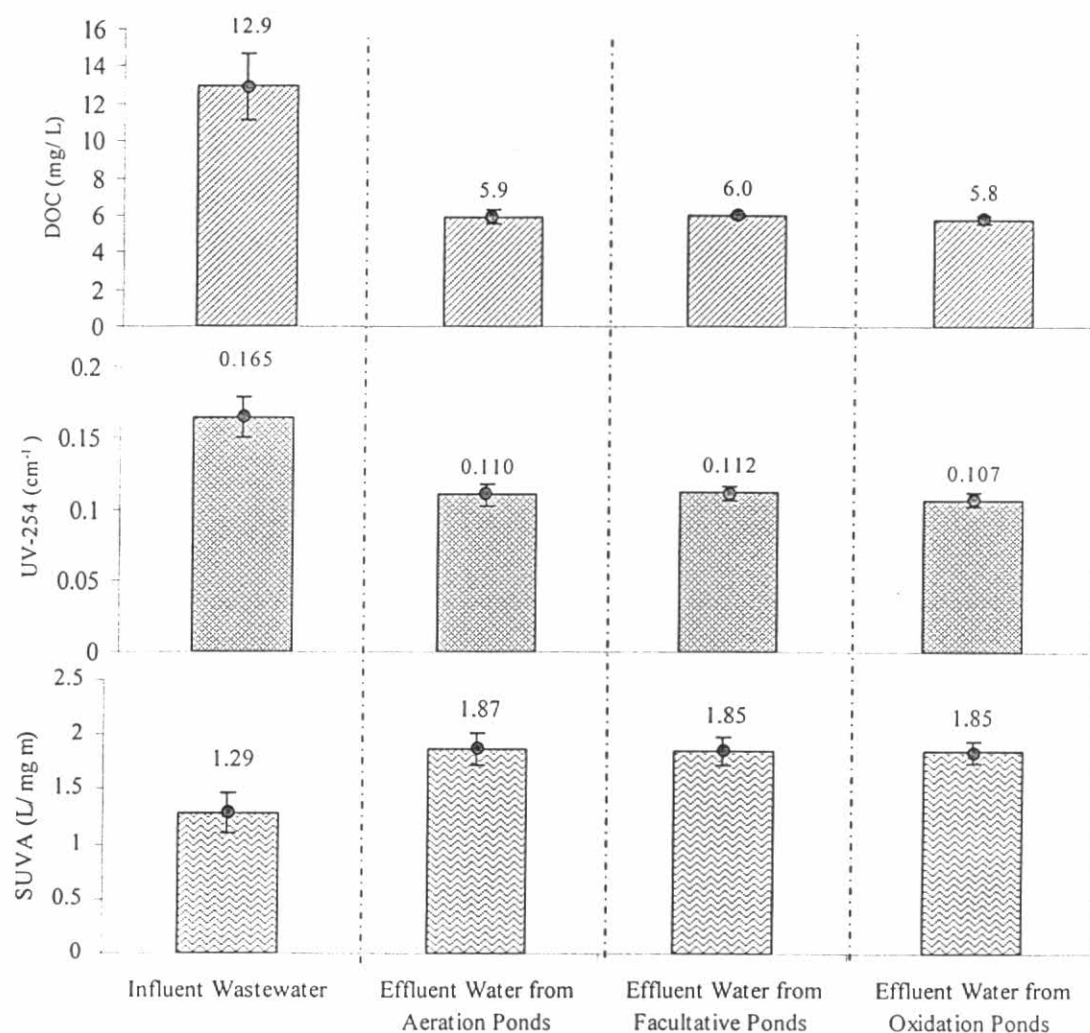
All water samples collected in September 2004, October 2004 and July 2005 were measured for UV-254, DOC, SUVA, THMFP and FEEM.

Influent wastewater and effluent water from the aeration, facultative and oxidation ponds collected in February 2005 were analyzed for UV-254, DOC, SUVA, THMFP and FEEM. Subsequently, the resin adsorption procedure was used to fractionate fifteen liters of the mentioned water samples into six DOM fractions, namely HPON, HPOB, HPOA, HPIB, HPIA and HPIN. The six DOM fractions of each water sample were analyzed for UV-254, SUVA, DOC, THMFP and FEEM.

## 7.4 Results and Discussion

### 7.4.1 Reduction of DOC, UV-254 and SUVA

DOC and UV-254 are commonly utilized as surrogate parameters for DOM in water and wastewater. These parameters are capable of providing significantly different information on DOM properties. DOC could be used to represent the level of organic carbon in water, whereas UV-254 represents the aromatic character of humic and fulvic acids. Figure 7.1 illustrates the average values of DOC, UV-254 and SUVA (with standard deviation ranges) in the influent and effluent samples of the aeration, facultative, and oxidation ponds. The samples were collected in September 2004, October 2004, February 2005 and July 2005.



**Figure 7.1:** Average values of DOC, UV-254 and SUVA (with standard deviation ranges) of the influent and effluent of the aeration, facultative, and oxidation ponds

**Table 7.1:** Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on DOC, UV-254 and SUVA

Parameters	Reduction efficiency <sup>1</sup>			Accumulated reduction efficiency <sup>2</sup>		
	Aeration ponds	Facultative ponds	Oxidation ponds	Aeration ponds	Facultative ponds	Oxidation ponds
DOC	54	(-2)	3	54	53	55
UV-254	33	(-2)	4	33	32	33
SUVA	(-45)	1	0	(-45)	(-43)	(-43)

Remark: <sup>1</sup>DOC reduction efficiency

$$= \left[ \frac{\text{Average DOC}_{\text{influent water to pond}} - \text{Average DOC}_{\text{effluent water from pond}}}{\text{Average DOC}_{\text{influent water to pond}}} \right] \times 100$$

<sup>2</sup>Accumulated DOC reduction efficiency

$$= \left[ \frac{\text{Average DOC}_{\text{influent wastewater}} - \text{Average DOC}_{\text{effluent water from pond}}}{\text{Average DOC}_{\text{influent wastewater}}} \right] \times 100$$

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on UV-254 and SUVA were calculated using the mentioned equations.

The average value of DOC observed in the influent wastewater was 12.9 mg L<sup>-1</sup>. Table 7.1 depicts the reduction efficiency of each pond on DOC, UV-254 and SUVA and the accumulated reduction efficiency of the ponds based on these parameters. It was found that the aeration ponds could remove DOC by 54%, and the average value of DOC in the aeration pond effluent was 5.9 mg L<sup>-1</sup>. The facultative ponds did not seem to further treat DOC. The average concentration of DOC in the facultative pond effluent of 6.0 mg L<sup>-1</sup> was slightly higher than the average DOC concentration in the influent. This small increase of DOC in the effluent from the facultative ponds may have been due to the effect of algae growth (or the growth of other microorganisms) within the ponds. The oxidation ponds did not further enhance DOC removal. The average DOC concentration in the oxidation pond effluent was 5.8 mg L<sup>-1</sup>. The difference between the DOC observed in the facultative pond effluent and in the oxidation pond effluent was due to the inadvertent analytical deviation.

The average value of UV-254 in the influent wastewater was 0.165 cm<sup>-1</sup>. The aeration ponds reduced UV-254 by 33%. The average value of UV-254 in the aeration pond effluent was 0.110 cm<sup>-1</sup>. However, UV-254 could not be reduced by the facultative ponds and oxidation ponds. An average UV-254 value of 0.112 cm<sup>-1</sup> was observed in the effluent water from the facultative ponds; the average UV-254 value of the oxidation pond effluent was similar.

Tambo (1989) classified organic substances in DOCs on the basis of their ability to adsorb light in the UV range. He divided them into two fractions: UV-sensitive and UV-insensitive. McKnight *et al.* (1994) proposed that the UV-sensitive fraction was mostly hydrophobic or aromatic in nature. According to the UV-254 reduction results in Table 7.1, the stabilization ponds had moderate difficulty in removing UV-sensitive organic fractions with aromatic characteristics when compared with the overall reduction of DOC.

In general, SUVA could be utilized to provide a relative index of the humic content of the DOC in water (AWWA, 1993). An average SUVA value of 1.29 L mg<sup>-1</sup> m<sup>-1</sup> was observed in the influent wastewater. The SUVA value in the aeration pond effluent increased moderately to 1.87 L mg<sup>-1</sup> m<sup>-1</sup>. It was suspected that the biological process in the aeration ponds easily removed the UV-insensitive fraction from the influent wastewater; therefore, the remaining dissolved organic matter in the treated wastewater was mainly composed of more UV-sensitive fractions that provided a high relative index of DOC humic content. Fukushima *et al.* (1996) reported that the SUVA of total DOM increased as the lake water, influenced by pedogenic DOC, was allowed to further stabilize through biodegradation over a long period of time. Imai *et al.* (2002) reported that since a biological treatment had been employed in the sewage treatment plants, the SUVA value for its effluent should have been higher than that of its influent. It was noted that further treatment in the facultative ponds did not reduce SUVA. The SUVA of the effluent was observed to be 1.85 L mg<sup>-1</sup> m<sup>-1</sup>, which was close to the value measured from samples at the inlet level. Similarly, no further SUVA reduction was achieved by the oxidation ponds.

Based on the DOC and UV-254 reduction results, it can be stated that the aeration pond was the main course of action that reduced DOC and UV-254. The reduction of dissolved organic matter at the central wastewater treatment plant relied primarily on the efficiency of the aeration ponds. In terms of the overall efficiency of the system, the stabilization ponds were able to reduce DOC and UV-254 by 55 and 33%, respectively; however, they did not reduce SUVA.

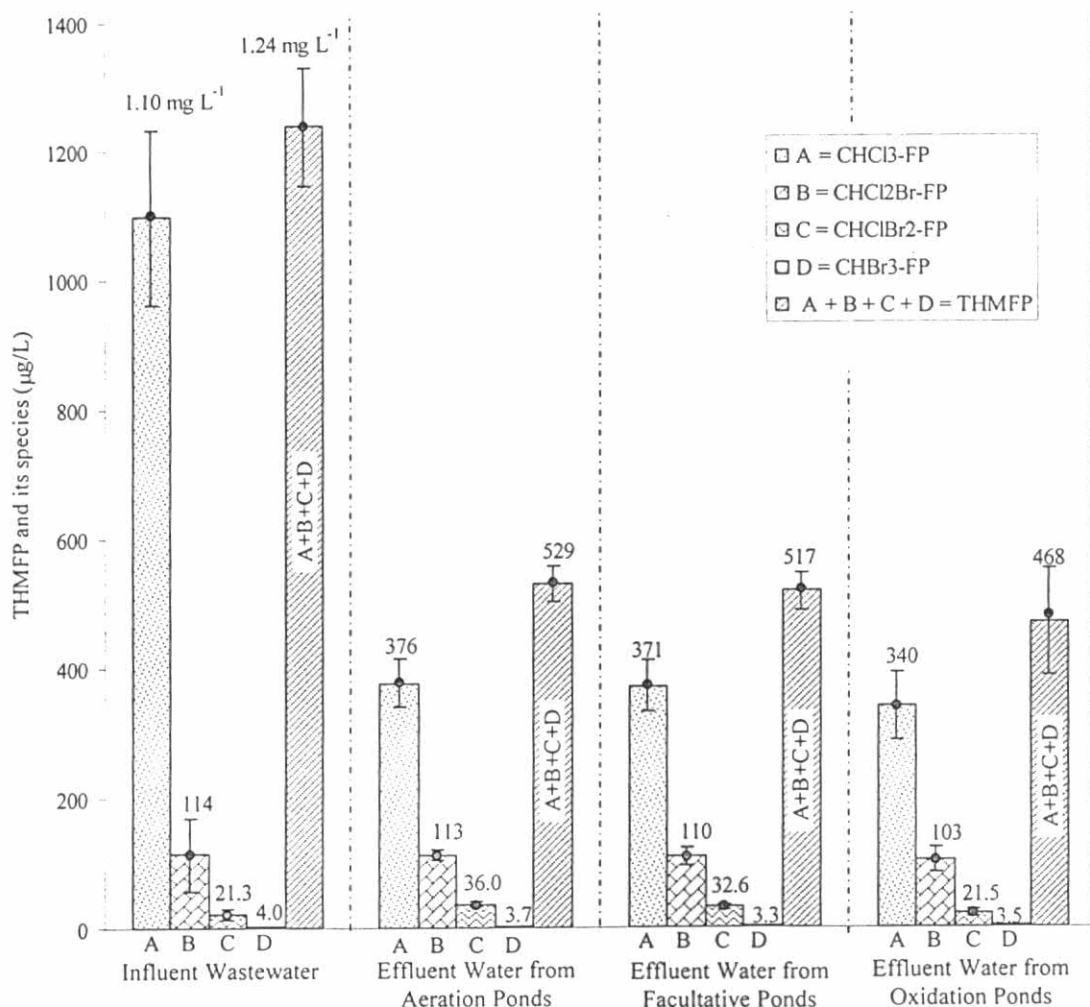
#### 7.4.2 Reduction of THMFP and its THMs Species

In general, the THM value refers to the concentration of THMs measured in the water at the time of the sampling. This value represents the amount of THMs that could adversely affect the consumers who utilize the water. THMs have recently been put under regulation in the USEPA Disinfectant/Disinfection By-Products (D/DBPs) Rule (United States Environmental Protection Agency or USEPA, 1998). The current drinking water maximum contaminant level covers four THMs, namely chloroform ( $\text{CHCl}_3$ ), dichlorobromoform ( $\text{CHCl}_2\text{Br}$ ), dibromochloroform ( $\text{CHClBr}_2$ ) and bromoform ( $\text{CHBr}_3$ ), is set at  $40 \mu\text{g L}^{-1}$ . The World Health Organization (WHO, 1996) has set the health related guideline values (GV) of 200, 60, 100 and  $100 \mu\text{g L}^{-1}$  for  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$ , respectively.

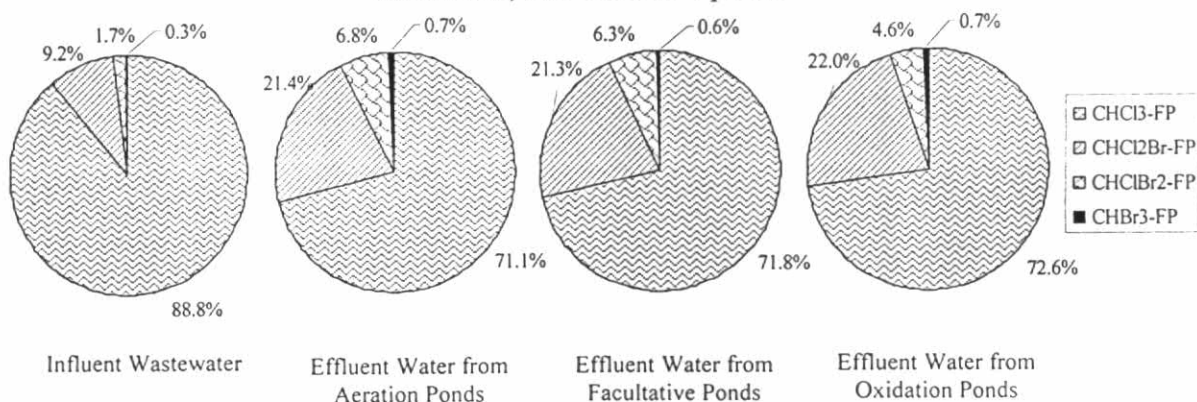
In order to gain a better understanding of THM formation due to the reaction of DOM in water sources with chlorine, the THMFP has been commonly utilized to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. Water with a high THMFP value could potentially form a high level of THMs. In addition, the reduction of the THMFP by water treatment processes can be used to represent the reduction of DOM, which has an active ability of forming THMs. THMFP, therefore, was deemed to be an appropriate indicator and was utilized to monitor the highest possible concentrations of THMs in the water. The THMFP was determined from the summation of the chloroform formation potential ( $\text{CHCl}_3\text{-FP}$ ), dichlorobromoform formation potential ( $\text{CHCl}_2\text{Br-FP}$ ), dibromochloroform formation potential ( $\text{CHClBr}_2\text{-FP}$ ), and bromoform formation potential ( $\text{CHBr}_3\text{-FP}$ ).

The average THMFP and THM species values (with standard deviation ranges) for the influent and effluent samples taken from the aeration, facultative, and oxidation ponds in September 2004, October 2004, February 2005 and July 2005 are illustrated in Figure 7.2. Percent distributions of  $\text{CHCl}_3\text{-FP}$ ,  $\text{CHCl}_2\text{Br-FP}$ ,  $\text{CHClBr}_2\text{-FP}$  and  $\text{CHBr}_3\text{-FP}$  in the influent wastewater and effluent water from the ponds are depicted in Figure 7.3. An average THMFP value of  $1.24 \text{ mg L}^{-1}$  was observed in the influent wastewater. This value came from the summation of the  $\text{CHCl}_3\text{-FP}$  at  $1.10 \text{ mg L}^{-1}$ ,  $\text{CHCl}_2\text{Br-FP}$  at  $114 \mu\text{g L}^{-1}$ ,  $\text{CHClBr}_2\text{-FP}$  at  $21.3 \mu\text{g L}^{-1}$  and  $\text{CHBr}_3\text{-FP}$  at  $4.0 \mu\text{g L}^{-1}$ .  $\text{CHCl}_3$ , therefore, was the major THMs species in the influent wastewater and made up about 88.8% of the total

THMFP. The percentages of  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  were 9.2, 1.7 and 0.3%, respectively.



**Figure 7.2** Average values (with standard deviation ranges) of THMFP,  $\text{CHCl}_3$ -FP,  $\text{CHCl}_2\text{Br}$ -FP,  $\text{CHClBr}_2$ -FP and  $\text{CHBr}_3$ -FP in the influent and effluent of the aeration, facultative, and oxidation ponds



**Figure 7.3:** Percent distributions of  $\text{CHCl}_3$ -FP,  $\text{CHCl}_2\text{Br}$ -FP,  $\text{CHClBr}_2$ -FP and  $\text{CHBr}_3$ -FP in the influent and effluent of the aeration, facultative, and oxidation ponds

**Table 7.2:** Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on THMFP,  $\text{CHCl}_3$ -FP,  $\text{CHCl}_2\text{Br}$ -FP,  $\text{CHClBr}_2$ -FP and  $\text{CHBr}_3$ -FP

Parameters	Reduction efficiency <sup>1</sup>			Accumulated reduction efficiency <sup>2</sup>		
	Aeration ponds	Facultative ponds	Oxidation ponds	Aeration ponds	Facultative ponds	Oxidation ponds
THMFP	57	2	9	57	58	62
$\text{CHCl}_3$ -FP	66	1	8	66	66	69
$\text{CHCl}_2\text{Br}$ -FP	1	3	6	1	4	10
$\text{CHClBr}_2$ -FP	(-69)	9	34	(-69)	(-53)	(-1)
$\text{CHBr}_3$ -FP	8	11	(-6)	8	18	13

Remark: <sup>1</sup>THMFP Reduction efficiency

$$= \left[ \frac{\text{Average THMFP}_{\text{influent water to pond}} - \text{Average THMFP}_{\text{effluent water from pond}}}{\text{Average THMFP}_{\text{influent wastewater}}} \right] \times 100$$

<sup>2</sup>Accumulated THMFP reduction efficiency

$$= \left[ \frac{\text{Average THMFP}_{\text{influent wastewater}} - \text{Average THMFP}_{\text{effluent water from pond}}}{\text{Average THMFP}_{\text{influent wastewater}}} \right] \times 100$$

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the THMs species were calculated using the mentioned equations.

As can be seen from Table 7.2, there was as much as a 57% THMFP reduction due to the aeration pond. At a 66% reduction,  $\text{CHCl}_3$  was the major THM species reduced in the aeration ponds. On the other hand,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  were not reduced by the aeration ponds. The average THMFP value of the aeration pond effluent was  $529 \mu\text{g L}^{-1}$ . This value came from the summation of the  $\text{CHCl}_3$ -FP of  $376 \mu\text{g L}^{-1}$ ,  $\text{CHCl}_2\text{Br}$ -FP of  $113 \mu\text{g L}^{-1}$ ,  $\text{CHClBr}_2$ -FP of  $36.0 \mu\text{g L}^{-1}$  and  $\text{CHBr}_3$ -FP of  $3.7 \mu\text{g L}^{-1}$ . The facultative ponds did not reduce the THMFP; similarly, they did not remove THM species. The average THMFP value of the facultative pond effluent was  $517 \mu\text{g L}^{-1}$  ( $\text{CHCl}_3$ -FP of  $371 \mu\text{g L}^{-1}$ ,  $\text{CHCl}_2\text{Br}$ -FP of  $110 \mu\text{g L}^{-1}$ ,  $\text{CHClBr}_2$ -FP of  $32.6 \mu\text{g L}^{-1}$ , and  $\text{CHBr}_3$ -FP of  $3.3 \mu\text{g L}^{-1}$ ). The oxidation ponds neither reduced the THMFP nor removed THM species. An average THMFP value of  $468 \mu\text{g L}^{-1}$  in the oxidation pond effluent was observed ( $\text{CHCl}_3$ -FP of  $340 \mu\text{g L}^{-1}$ ,  $\text{CHCl}_2\text{Br}$ -FP of  $103 \mu\text{g L}^{-1}$ ,  $\text{CHClBr}_2$ -FP of  $21.5 \mu\text{g L}^{-1}$  and  $\text{CHBr}_3$ -FP of  $3.5 \mu\text{g L}^{-1}$ ).  $\text{CHCl}_3$ , therefore, was the major THMs species in the oxidation pond effluent, as it accounted for about 72.6% of total THMFP. The percentages of  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  were approximately 22.0, 4.6 and 0.7%, respectively. The difference between the THMFP and THMs species observed in the facultative pond effluent and that of in the oxidation pond effluent was entirely due to the inevitable analytical deviation. The THMFP of the treated wastewater obtained in this study was compared with other raw water supply sources in Thailand (as shown in Table 7.3). It was found that the THMFP values of the treated wastewater in this study were considerably higher than those of other raw water supply sources in Thailand, e.g. the



Chao Phraya River, Bangkok; Aung-Keaw Reservoir, Chiang Mai; Mae-Kuang Reservoir, Chiang Mai; and Bhumibol Dam Reservoir, Tak. Based on this finding, the DOM in the treated effluent must be more effectively removed by the reclamation process prior to the reuse of such water in the water supply plant.

**Table 7.3:** THMFP and THMs species in the treated effluent of this study compared with the values from other raw water supply sources in Thailand

Water Source	Sampling Times	THMFP ( $\mu\text{g L}^{-1}$ )	CHCl <sub>3</sub> -FP ( $\mu\text{g L}^{-1}$ )	CHCl <sub>3</sub> -FP ( $\mu\text{g L}^{-1}$ )	CHCl <sub>3</sub> -FP ( $\mu\text{g L}^{-1}$ )	CHCl <sub>3</sub> -FP ( $\mu\text{g L}^{-1}$ )
The Chao Phraya River Bangkok, Thailand (Panyapinyopol <i>et al.</i> , 2005)	August 2003	313	262 (84%) <sup>1</sup>	43.8 (14%)	6.9 (2%)	ND <sup>2</sup>
Aung-Keaw Reservoir, Chiang Mai, Thailand (Homklin, 2004)	November 2004	403	372 (92%)	20.3 (5%)	11.1 (3%)	ND
Mae-Kuang Reservoir, Chiang Mai, Thailand (Homklin, 2004)	December 2004	236	214 (90%)	15.4 (7%)	6.9 (3%)	ND
Mae-Sa River, Chiang Mai, Thailand (Homklin, 2004)	February 2005	113	94 (83%)	11.7 (10%)	7.0 (7%)	ND
Bhumibol Dam Reservoir, Tak, Thailand (Panyapinyopol <i>et al.</i> , 2005)	April 2005	318	292 (92%)	25.6 (8%)	ND	ND
Treated effluent from this study	-	468	340	103	21.5	3.5

Remark: <sup>1</sup>( ) = percent distribution and <sup>2</sup>ND = Not detected

When considering the presence of THM species, it was found that CHCl<sub>3</sub> was the major THM species in the treated effluent of the treatment plant in this study and in all other water supply sources in Thailand. This observation also corresponded well with the results of previous research. Rodriguez *et al.* (2003) found that, at about 80%, CHCl<sub>3</sub> was the predominant THM compound in treated water from the two major drinking water utilities of the greater area of Qu bec City, Canada. In addition, CHCl<sub>3</sub> levels of approximately 90% were found in treated water from three other major drinking water utilities of the greater area of Qu bec City. Thacker *et al.* (2002) reported that CHCl<sub>3</sub> was the major THMFP species found in the treated water of the Panjrapur, Bhanup, Tulsi and Vehar treatment plants in India.

Based on the obtained results, the aeration ponds were the main process capable of reducing THMFP and THM species. Therefore, this plant relied on the efficiency of its aeration ponds for reducing the THMFP in the water. In terms of overall efficiency, the stabilization ponds could reduce the THMFP by 62%.  $\text{CHCl}_3$ , which was reduced by 69%, was the major THM species that was reduced.

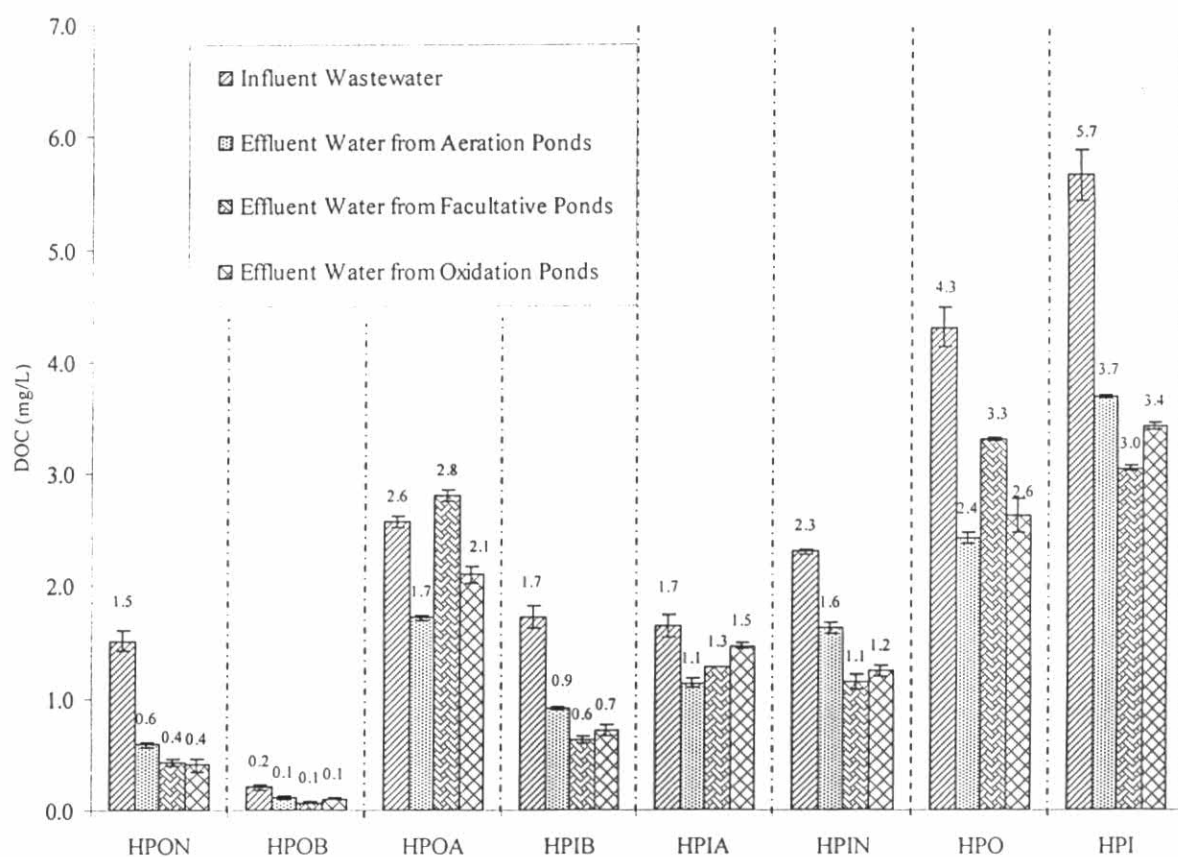
The THMFP of  $468 \mu\text{g L}^{-1}$  of the oxidation pond effluent was extremely high when compared with the maximum contamination level of  $40 \mu\text{g L}^{-1}$  for drinking water (US.EPA, 1998). According to the report of the WHO (1994), the maximum acceptable levels for  $\text{CHCl}_3$  and  $\text{CHCl}_2\text{Br}$  are 200 and  $60 \mu\text{g L}^{-1}$ , respectively. In terms of toxicity,  $\text{CHCl}_2\text{Br}$ , is therefore more hazardous than  $\text{CHCl}_3$ . However,  $\text{CHCl}_3$  was present at much higher concentrations than the other THM species, and therefore it was considered to carry a higher level of human-health concern. In this study,  $340 \mu\text{g L}^{-1}$  of  $\text{CHCl}_3$  and  $103 \mu\text{g L}^{-1}$  of  $\text{CHCl}_2\text{Br}$  were found in the oxidation pond effluent. It can be stated that the DOM in the treated wastewater has a high potential for forming THMs at levels that exceed the maximum acceptable level recommended by the WHO.

#### 7.4.3 Reduction of DOC and THMFP of DOM Fractions

The DOC measurements (with standard deviation ranges) of the six DOM fractions of influent and effluent of the aeration, facultative, and oxidation ponds collected in February 2005 (as reported in Chapter 4) were utilized to plot the bar graph seen in Figure 7.4. The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the DOC concentrations of HPON, HPOB, HPOA, HPIB, HPIA and HPIA are tabulated in Table 7.4.

The levels of DOC in three hydrophobic organic (HPO) fractions, HPON, HPOB, HPOA, of about 1.5, 0.2 and 2.6 mg/L, respectively, were determined in the influent wastewater. A DOC reduction in HPOB could not be determined since the DOC concentration was very low; the difference between the DOC observed in the influent water and in the effluent water from each pond, therefore, was completely due to the inadvertent analytical deviation. The aeration ponds could remove HPON and HPOA by 61 and 33%, respectively. The DOC concentrations of HPON, HPOB and HPOA in effluent water from the aeration ponds were 0.6, 0.1, and 1.7 mg/L, respectively. The

facultative ponds could remove HPON by 27%. However, it did not remove HPOA as seen by the DOC of HPOA of 2.8 mg/L that was observed after the treatment. The oxidation ponds could remove HPOA, but did not remove HPON. Interestingly, with regard to the DOC reduction of the unfractionated water, the facultative ponds and oxidation ponds did not reduce DOC. However, in the case of DOM fractions, HPON was reduced by the facultative ponds, whereas HPOA was reduced by the oxidation ponds. This may have been due to the fact that the HPON in the facultative ponds and the HPOA in the oxidation ponds may have transformed by a biological process into other DOM fractions. The stabilization pond system (i.e., the aeration, facultative and oxidation ponds) was able to reduce HPON and HPOA by 73, and 18%, respectively.



**Figure 7.4:** DOC concentrations (with standard deviation ranges) of HPON, HPOB, HPOA, HPIB, HPIA and HPIN in influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds collected on February 18, 2005

**Table 7.4:** Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the DOC concentrations of HPON, HPOB, HPOA, HPIB, HPIA, and HPIN

Parameters	Reduction efficiency <sup>1</sup>			Accumulated reduction efficiency <sup>2</sup>		
	Aeration ponds	Facultative ponds	Oxidation ponds	Aeration ponds	Facultative ponds	Oxidation ponds
HPON	61	27	5	61	72	73
HPOB	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>
HPOA	33	(-63)	25	33	(-9)	18
HPIB	47	31	(-13)	47	63	60
HPIA	31	(-12)	(-15)	31	23	11
HPIN	29	30	(-9)	29	50	46
HPO	44	(-36)	21	44	23	39
HPI	35	17	(-12)	35	46	40

Remark: <sup>1</sup> Reduction efficiency

$$= \left[ \frac{(\text{DOC of DOM fraction}_{\text{influent water to pond}} - \text{DOC of DOM fraction}_{\text{effluent water from pond}})}{(\text{DOC of DOM fraction}_{\text{influent water to pond}})} \right] \times 100$$

<sup>2</sup> Accumulated THMFP reduction efficiency

$$= \left[ \frac{(\text{DOC of DOM fraction}_{\text{influent wastewater}} - \text{DOC of DOM fraction}_{\text{effluent water from pond}})}{(\text{DOC of DOM fraction}_{\text{influent wastewater}})} \right] \times 100$$

<sup>3</sup>NA = not available. (DOC of HPOB was very low; therefore, the difference between the DOC observed in the influent water and in the effluent water was utterly due to the inadvertent analytical deviation)

As mentioned earlier, the summation of HPON, HPOB and HPOA could be used to represent the level of HPO in water, The DOC concentration of HPO in the influent wastewater was 4.3 mg/L (Figure 7.4). The aeration ponds could remove HPO by 44% (Table 7.4). The DOC concentration of HPO of 2.4 mg/L was detected in the water after it was treated by the aeration ponds. The facultative ponds did not remove HPO as seen by the observed DOC in HPO of 3.3 mg/L. The oxidation ponds could remove HPO by 21%. The stabilization pond system reduced HPO by 39%.

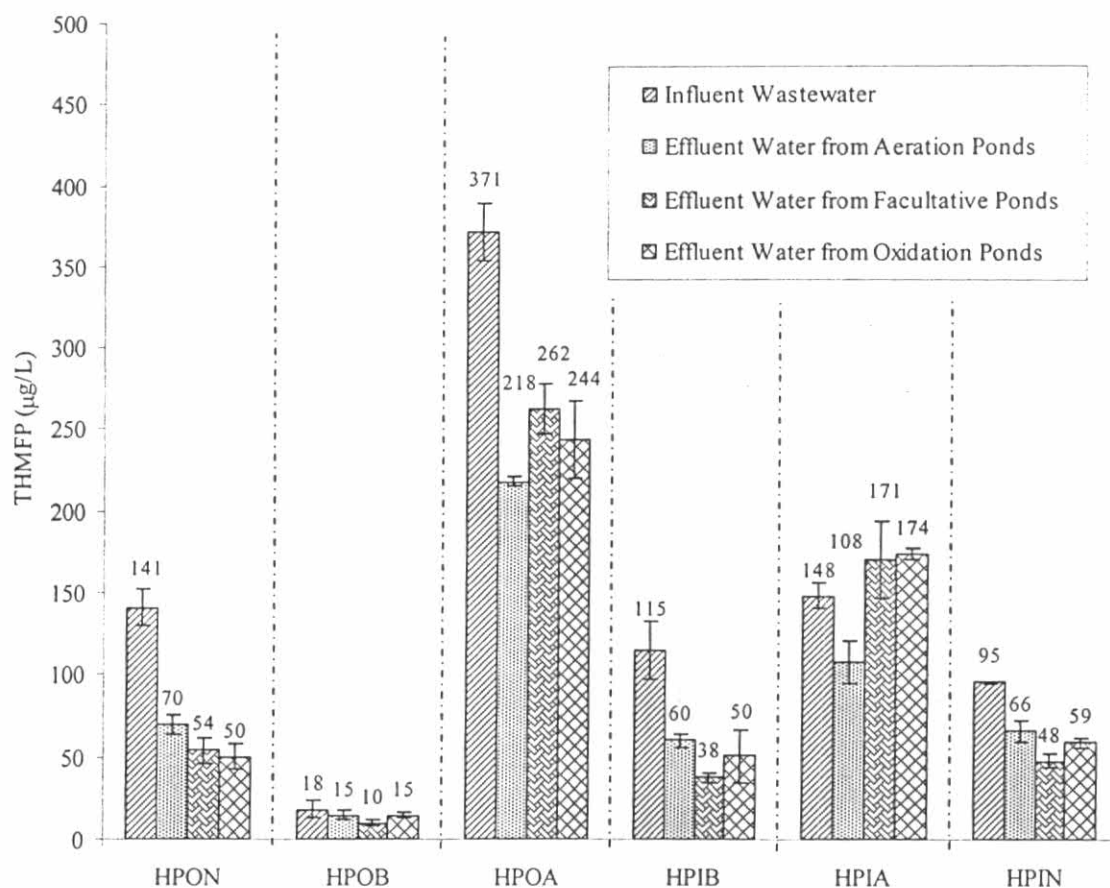
The DOC concentrations of the three hydrophilic organic fractions, HPIB, HPIA and HPIN, of 1.7, 1.7 and 2.3 mg/L were found in the influent wastewater. After influent wastewater was treated by aeration ponds, the DOC values of HPIB, HPIA and HPIN were reduced by 47, 31 and 29%, respectively. The DOC values of the respective DOM fraction after the aeration ponds were 0.9, 1.1 and, 1.6 mg/L. The facultative ponds could remove HPIB and HPIN by 31 and 30%, respectively. These results may have been due to biological transformations in these ponds. However, HPIA removal did not occur as seen by the DOC of 1.3 mg/L of HPIA that was observed after treatment. The oxidation ponds did not remove these three hydrophilic organic fractions. It must be noted that the

DOC levels of HPIA gradually increased after the facultative and oxidation ponds. The biological transformation in these respective ponds may have transformed HPON, HPOB, HPIB and HPIN into the HPIA fraction. With regard to total percent reduction, the stabilization pond system, consisting of aeration, facultative, and oxidation ponds, could reduce HPIN, HPIB, and HPIA by 46%, 60%, 11%, respectively.

As mentioned earlier, the summation of HPIB, HPIA and HPIN could be used to represent the level of HPI in water. The DOC concentration of HPI in the influent wastewater was 5.7 mg/L. The aeration ponds could remove HPI by 35%. A DOC concentration of HPI of 3.7 mg/L was detected after aeration pond treatment. The facultative ponds removed HPI by 17% as seen by the DOC of HPI of 3.0 mg/L that was observed after treatment. The oxidation ponds did not remove HPI. The system was able to reduce HPI by 40%.

From this observation, it can be concluded that the aeration and facultative ponds were the main processes that reduced HPON, HPIN, and HPIB. In the case of HPOA and HPIA (organic acids), the aeration ponds were the main process that reduced these organic acids since HPOA and HPIA values gradually increased after treatment in the facultative ponds. After the oxidation ponds, HPIA increased while HPOA slightly decreased. With more detailed consideration on total percent reduction, HPON, HPIB and HPIN were removed earlier by stabilization pond processes [aeration + facultative + oxidation ponds], while HPOA and HPIA were hardly removed. This information could be used to support the previously obtained results that HPOA and HPIA were the major DOM fractions in the facultative and oxidation pond effluent.

The THMFPs (with standard deviation ranges) of the six DOM fractions in the influent and effluent of the aeration, facultative, and oxidation ponds collected in February 2005, as reported in Chapter 4, were utilized to plot a bar graph shown in Figure 7.5. The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the THMFPs of HPON, HPOB, HPOA, HPIB, HPIA and HPIA are tabulated in Table 7.5.



**Figure 7.5:** THMFP of HPON, HPOB, HPOA, HPIB, HPIA and HPIN in influent wastewater and effluent water from the aeration, facultative, oxidation and detention ponds

**Table 7.5:** Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the THMFPs of HPON, HPOB, HPOA, HPIB, HPIA, and HPIN

Parameters	Reduction efficiency <sup>1</sup>			Accumulated reduction efficiency <sup>2</sup>		
	Aeration ponds	Facultative ponds	Oxidation ponds	Aeration ponds	Facultative ponds	Oxidation ponds
HPON	50	23	7	50	62	64
HPOB	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>	NA <sup>3</sup>
HPOA	41	(-20)	7	41	30	34
HPIB	48	37	(-34)	48	67	60
HPIA	27	(-58)	(-2)	27	(-15)	(-18)
HPIN	31	27	(-22)	31	50	39

Remark: <sup>1</sup>Reduction efficiency

$$= \left[ \frac{(\text{THMFP of DOM fraction}_{\text{influent water to pond}} - \text{THMFP of DOM fraction}_{\text{effluent water from pond}})}{(\text{THMFP of DOM fraction}_{\text{influent water to pond}})} \right] \times 100$$

<sup>2</sup>Accumulated THMFP reduction efficiency

$$= \left[ \frac{(\text{THMFP of DOM fraction}_{\text{influent wastewater}} - \text{THMFP of DOM fraction}_{\text{effluent water from pond}})}{(\text{THMFP of DOM fraction}_{\text{influent wastewater}})} \right] \times 100$$

<sup>3</sup>NA = not available. (THMFP of HPOB was very low; therefore, the difference between the THMFP observed in the influent water and in the effluent water was due to the inadvertent analytical deviation)

The THMFP of three hydrophobic organic (HPO) fractions, THMFP<sub>HPON</sub>, THMFP<sub>HPOB</sub>, and THMFP<sub>HPOA</sub>, were observed to be 141, 18 and 371 µg/L, respectively in the influent wastewater. The reduction of THMFP in HPOB could not be determined since the THMFP of HPOB was very low. The difference between the THMFP observed in the influent water and in the effluent water from each pond, therefore, was due to the inadvertent analytical deviation. The aeration ponds could reduce the THMFP<sub>HPON</sub> and THMFP<sub>HPOA</sub> by 50 and 41%, respectively. The THMFP<sub>HPON</sub>, THMFP<sub>HPOB</sub>, and THMFP<sub>HPOA</sub> in effluent water of the aeration ponds were approximately 70, 15, and 218 µg/L, respectively. The facultative ponds could reduce THMFP<sub>HPON</sub> by 23%. However, it did not reduce the THMFP<sub>HPOA</sub> as seen by the THMFP<sub>HPOA</sub> of about 262 µg/L that was observed after treatment. The increase in THMFP<sub>HPOA</sub> may have been due to the increase of DOC in HPOA after facultative pond treatment. The oxidation ponds considerably did not reduce THMFP<sub>HPON</sub> and THMFP<sub>HPOA</sub>. The difference between the THMFP observed in the influent water and in the effluent water of the oxidation ponds was entirely due to the inadvertent analytical deviation. In terms of the overall efficiency of the system, it was found that the three types of ponds could reduce THMFP<sub>HPON</sub> and THMFP<sub>HPOA</sub> by 64 and 34%, respectively.

When the THMFP of three hydrophilic organic fractions were taken into consideration, THMFP<sub>HPIB</sub>, THMFP<sub>HPIA</sub> and THMFP<sub>HPIN</sub> registered as 115, 148 and 95 µg/L, respectively in the influent wastewater. After treatment by the aeration ponds, the THMFP<sub>HPIB</sub>, THMFP<sub>HPIA</sub> and THMFP<sub>HPIN</sub> were reduced by 48, 27 and 31%, respectively. The THMFP of HPIB, HPIA, and HPIN in effluent water from the aeration ponds were approximately 60, 108 and, 66 µg/L, respectively. The facultative ponds could reduce HPIB and HPIN by 37 and 27%, respectively. However, it did not remove HPIA as seen by the THMFP<sub>HPIA</sub> of about 171 µg/L that was observed after treatment. The oxidation ponds did not reduce the THMFP of these three hydrophilic organic fractions. It must be noted that the THMFP<sub>HPIA</sub> gradually increased after the facultative and oxidation ponds. This may have been due to the gradually increase of DOC after treatment by the facultative and oxidation ponds as mentioned previously. In terms of the overall efficiency of the system, the three ponds reduced the THMFP<sub>HPIB</sub> and THMFP<sub>HPIN</sub> by 56%, and 39%, respectively. The stabilization ponds did not reduce the THMFP<sub>HPIA</sub>.

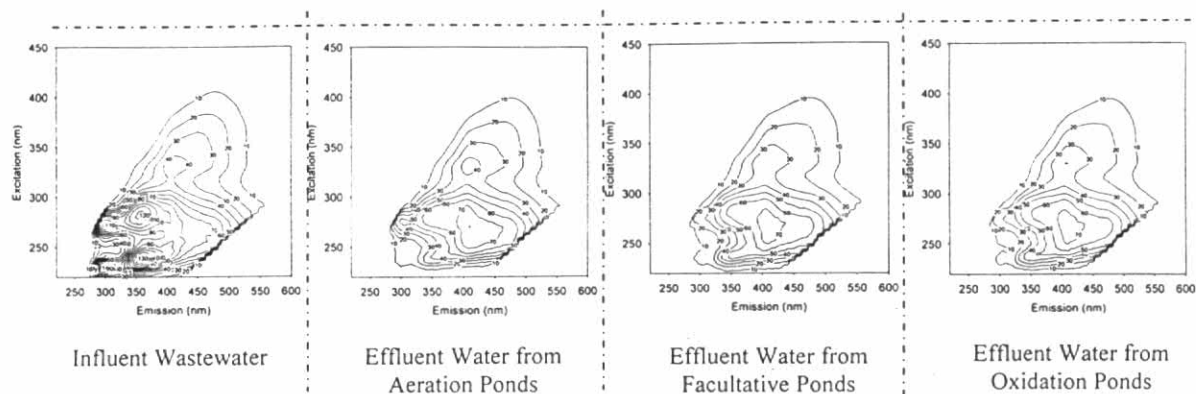
#### 7.4.4 Reduction of Fluorescent Organic Matter Evaluated by using FEEM

As mentioned earlier in Chapter 6, the location of fluorescent peaks in a FEEM analysis can provide information on the putative origin of fluorescent organic matter. Based on what was gained from the literature data from numerous researchers (Smart *et al.* 1976; Welfbeis, 1985; Coble 1996; Baker and Genty, 1999; Baker, 2001; Her *et al.* 2001; McKnight *et al.* 2001; Chen *et al.*, 2003; Leenheer and Croué, 2003; Nakajima *et al.* 2002; Yamashita and Tanoue, 2003; Goslan *et al.* 2004; Sierra *et al.*, 2005), the putative fluorescent organic matter in this study was classified into three substance groups: tyrosine-like, tryptophan-like, and humic and fulvic acid-like.

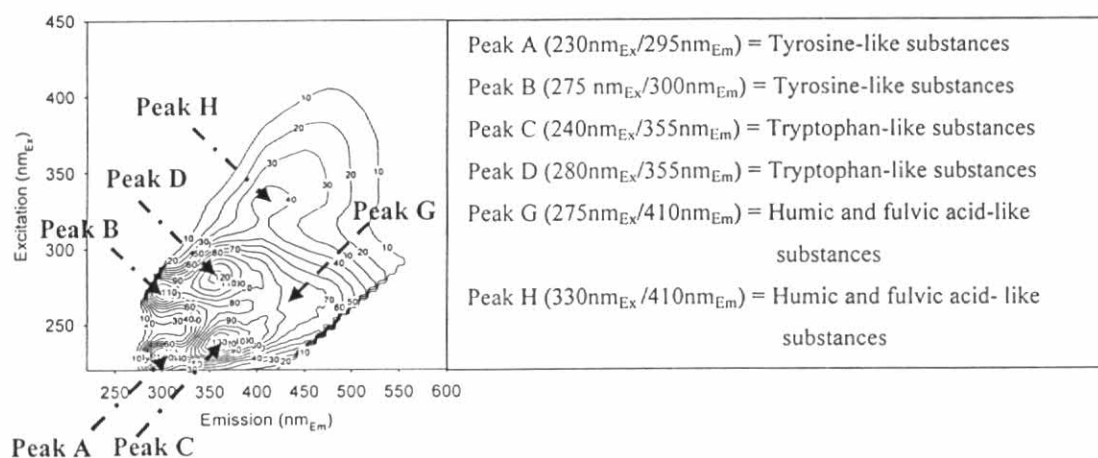
With more detailed consideration, the fluorescent intensities at each of the fluorescent peaks could be utilized for determining the quantity of each fluorescent organic matter in water. A summation of the fluorescent intensities of all outstanding fluorescent peaks in a FEEM has been proposed to determine the quantity of the total fluorescent organic matter in water (in QSU). In addition, the reduction of each fluorescent organic matter was also evaluated by the reduction of the fluorescent intensity of each peak. The reduction of the total fluorescent organic matter by stabilization ponds was evaluated by the reduction of the summation of the fluorescent intensities of overall outstanding peaks. The results of these analyses were compared with the DOC results in order to assess the usefulness of the FEEM technique for determining fluorescent organic matter and the reduction of fluorescent organic matter by stabilization ponds.

Four out of a total of sixteen FEEMs with contour intervals of 10 QSU are presented in Figure 7.6. As described by the FEEM analysis in Chapter 6, the fluorescent excitation-emission wavelengths ( $E_x/E_m$ ), which exhibited outstanding fluorescent emission intensities, were classified as the fluorescent peaks shown in Figure 7.7. In this study, six major peaks at  $230nm_{E_x}/295nm_{E_m}$  (peak A),  $275nm_{E_x}/300nm_{E_m}$  (peak B),  $240nm_{E_x}/355nm_{E_m}$  (peak C),  $280nm_{E_x}/355nm_{E_m}$  (peak D),  $275nm_{E_x}/410nm_{E_m}$  (peak G), and  $330nm_{E_x}/410nm_{E_m}$  (peak H) were observed in the FEEMs.



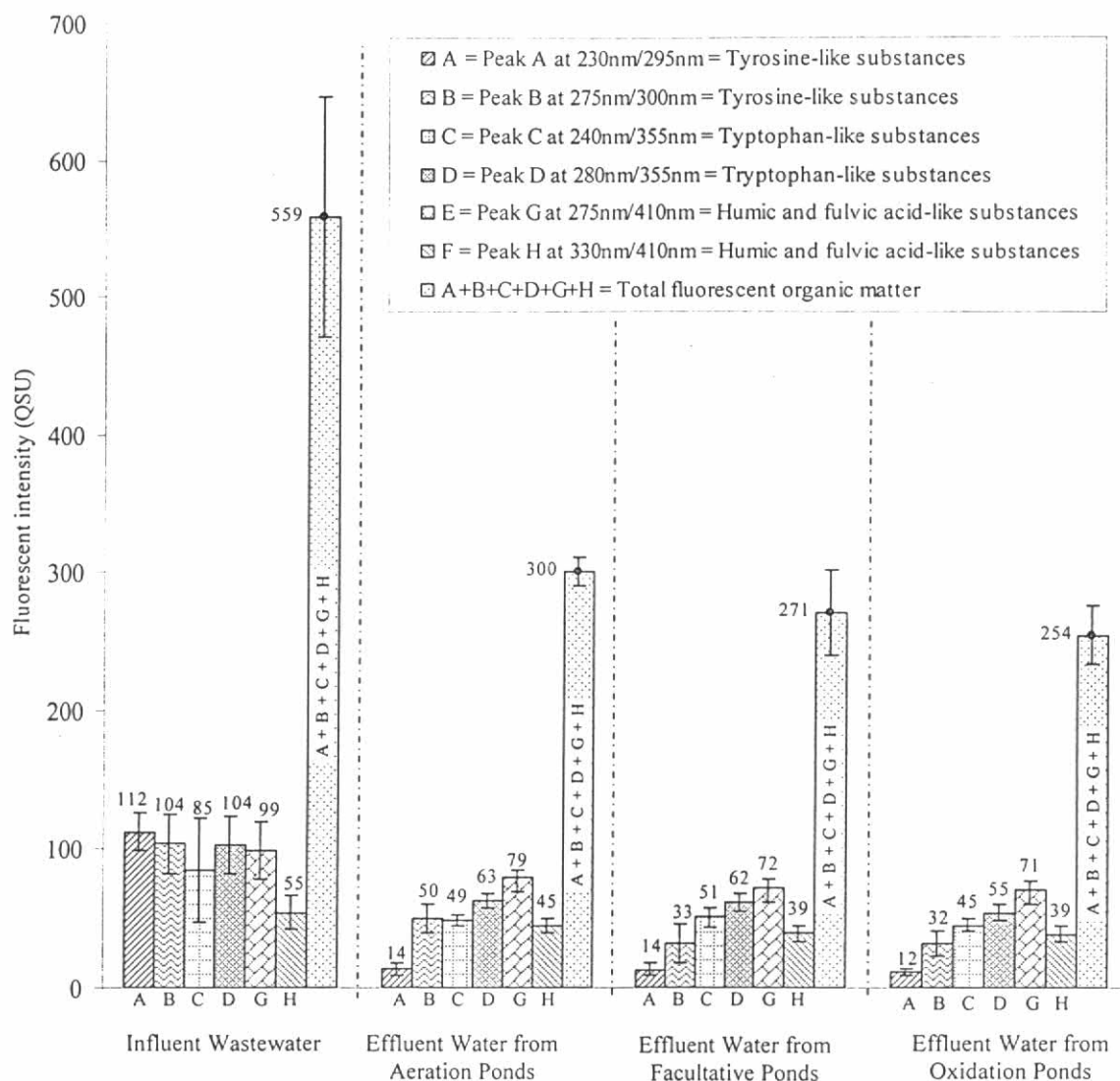


**Figure 7.6:** Samples of the patterns of FEEMs (contour interval of 10 QSU) of influent wastewater and effluent water from the aeration, facultative and oxidation ponds in October 2004



**Figure 7.7:** A demonstration of peak positions A, B, C, D, G and H in a FEEM of the influent wastewater in October 2004

The putative fluorescent organic matter of each FEEM peak could be defined as follows: peaks A and B are tyrosine-like substances, peaks C and D are tryptophan-like substances and peaks G and H are humic and fulvic acid-like substances. Average values of the fluorescent intensities at each of the fluorescent peaks and average values of the summation of the fluorescent intensities of the six outstanding peaks in the FEEMs of influent wastewater and effluent water after treatment by the aeration, facultative and oxidation ponds are illustrated in Figure 7.8.



**Figure 7.8:** Average fluorescent intensities at peaks A, B, C, D, G and H, and summations of the fluorescent intensities of peaks A, B, C, D, G and H of influent wastewater and effluent water from the aeration, facultative and oxidation ponds

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the fluorescent intensity of each peak and overall peaks by using the values of fluorescent intensities in Figure 7.8 could be deduced and are depicted in Table 7.6. The result shows that after the wastewater was put through the aeration ponds, the tyrosine-like substances at peaks A and B were reduced by 88 and 52%, respectively. The facultative ponds could reduce tyrosine-like substances at peak B by 34%, however, these ponds could not reduce the tyrosine-like substances at peak A. The oxidation ponds could only slightly reduce the tyrosine-like substances at peaks A and B by 14 and 3%, respectively.

**Table 7.6:** Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the fluorescent intensity of each peak and overall peaks

Putative origins of FEEM peaks	Reduction efficiency <sup>1</sup>			Accumulated reduction efficiency <sup>2</sup>		
	Aeration ponds	Facultative ponds	Oxidation ponds	Aeration ponds	Facultative ponds	Oxidation ponds
Tyrosine-like substances at peak A	88	0	14	88	88	89
Tyrosine-like substances at peak B	52	34	3	52	68	69
Tryptophan-like substances at peak C	42	(-4)	12	42	40	47
Tryptophan-like substance at peak D	39	2	11	39	40	47
Humic and fulvic acid-like substances at peak G	20	9	1	20	27	28
Humic and fulvic acid-like substances at peak H	18	13	0	18	29	29
Summation of all tyrosine-like, tryptophan-like and, humic and fulvic acid-like substances (total fluorescent organic matter of peaks A+B+C+D+G+H)	46	10	6	46(54) <sup>3</sup>	51(53) <sup>3</sup>	54(55) <sup>3</sup>

Remark:

<sup>1</sup>Tyrosine-like substances at peak A reduction efficiency

$$= \left[ \frac{\text{Average fluorescent intensity at peak A}_{\text{influent water to pond}} - \text{Average fluorescent intensity at peak A}_{\text{effluent water from pond}}}{\text{Average fluorescent intensity at peak A}_{\text{influent water to pond}}} \right] \times 100$$

<sup>2</sup>Accumulated DOC reduction efficiency

$$= \left[ \frac{\text{Average fluorescent intensity at peak A}_{\text{influent wastewater}} - \text{Average fluorescent intensity at peak A}_{\text{effluent water from pond}}}{\text{Average fluorescent intensity at peak A}_{\text{influent wastewater}}} \right] \times 100$$

<sup>3</sup>( ) = Total percent reduction of DOM in term of DOC as shown in Figure 7.1.

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on other fluorescent organic matters were calculated using the mentioned equations.

In the case of the reduction of tryptophan-like substances by the aeration ponds, the tryptophan-like substances at peaks C and D were reduced by 43 and 39%, respectively. Facultative ponds slightly reduced the tryptophan-like substances at peak D, but did not affect the tryptophan-like substances at peak C. Oxidation ponds reduced the tryptophan-like substances at peaks C and D by 12 and 11%, respectively. In the case of the reduction of humic and fulvic acid-like substances, the humic and fulvic acid-like substances at peaks, G and H were slightly reduced by 20 and 18%, respectively, after aeration pond treatment. The facultative ponds reduced the humic and fulvic acid-like substances at peaks G and H by 9 and 13%, respectively. After the oxidation ponds, the humic and fulvic acid-like substances at peak G were only slightly reduced, while at peak H they could not be reduced. In terms of the overall efficiency as seen by the total percent

reduction of fluorescent intensity after aeration, facultative, and oxidation ponds, the tyrosine-like substances at peaks A and B, tryptophan-like substances at peaks C and D, and humic and fulvic acids-like substances at peaks G and H were reduced by 89 and 69%, 47 and 47%, and 28 and 29%, respectively.

Based on the FEEM results, it can be stated that the stabilization ponds could remove protein and amino acids (i.e., tyrosine-like and tryptophan-like substances) more easily than humic and fulvic acid-like substances. This observation corresponded well with the study of Lee and Ahn (2004), which reported that the fluorescent intensities of protein-like fluorescent peaks were significantly reduced by a biological treatment plant, while the fluorescent intensities of humic-like fluorescent peaks did not decrease after being treated by a biological treatment plant. In addition, DOM could be classified as either humic substances (humic and fulvic acids) or nonhumic substances (hydrophilic acids, proteins, amino acids and carbohydrates; Collins *et al.* 1986). As can be seen in Table 7.6, it was found that the stabilization pond process removed non-humic substances as opposed to humic substances. The remaining organic substances in the treated wastewater could become more humic and fulvic acid-like. The summation of fluorescent intensities of peaks A, B, C, D, G and H was utilized to represent the total fluorescent organic matter in the water which was mainly composed of tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances. After the aeration ponds, total fluorescent organic matter was reduced by 46%. The facultative ponds could reduce total fluorescent organic matter by 10%, while the oxidation ponds could reduce the total fluorescent organic matter by 6%.

In the case of overall efficiency of ponds for reducing total fluorescent organic matter, it was found that aeration ponds; the aeration + facultative ponds; and the aeration + facultative + oxidation ponds could reduce total fluorescent organic matter by 46, 51 and 54%, respectively. These values were notably similar to the overall efficiency of the DOC reduction by the respective processes at 54, 53, and 55%, respectively. It could be established that FEEM analysis can be used to evaluate the reduction of single organic substances in stabilization ponds through the reduction of the fluorescent intensity at a certain peak. It could also be used to evaluate the reduction of total fluorescent organic

matter by using the summation of the fluorescent intensities of the outstanding peaks. In addition, the FEEM results showed that the aeration pond was the main reducer of tyrosine, tryptophan, and humic and fulvic acid-like fluorescent organic matter since these organic matter decreased only slightly after being put through the facultative and oxidation ponds.

## 7.6 Concluding Remarks

The aims of this chapter were to evaluate the reduction of DOM in terms of DOC, UV-254, SUVA and THMFP and the reduction of the six DOM fractions in terms of DOC and THMFP by the stabilization pond process of the studied industrial estate through the use of FEEMs. The aeration pond was the main process capable of reducing DOC, UV-254 and THMFP. However, the SUVA value showed a moderate increase in the aeration pond effluent. The facultative ponds and oxidation ponds did not reduce the DOC, UV-254, SUVA and THMFP in the water. The average THMFP values of the treated effluent were considerably high in comparison to the THMFP values of raw water for other raw water supply sources in Thailand. In addition,  $\text{CHCl}_3$  and  $\text{CHCl}_2\text{Br}$  in the treated effluent were found at levels that exceeded the maximum acceptable level recommended by the WHO. In the case of DOM fraction reductions and their THMFPs, the aeration and facultative ponds were the main processes capable of reducing HPON, HPIN, and HPIB and their THMFPs. Only the aeration ponds could moderately reduce HPOA and HPIA and their THMFP. For the overall efficiency of ponds for reducing DOCs of DOM fraction, the aeration + facultative + oxidation ponds could reduce HPON, HPIN, HPIB, HPOA, and HPIA by 73%, 46%, 60%, 18%, and 11%, respectively. With regard to the overall efficiency of the stabilization ponds on the THMFP of the DOM fraction reductions, the aeration + facultative + oxidation ponds could reduce the  $\text{THMFP}_{\text{HPON}}$  and  $\text{THMFP}_{\text{HPIN}}$ ,  $\text{THMFP}_{\text{HPIB}}$ , and  $\text{THMFP}_{\text{HPOA}}$  by 64%, 39%, 60%, and 34%, respectively. The  $\text{THMFP}_{\text{HPIA}}$  could not be reduced by the stabilization pond process. When the FEEM was used to evaluate the reduction of fluorescent organic matter, the aeration pond was identified as the main process for reducing tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances. In terms of overall efficiency, the stabilization ponds reduced tyrosine-like substances most efficiently followed by tryptophan-like substances. Humic and fulvic acid-like substances were barely removed by the stabilization ponds. The overall percent reduction of total fluorescent organic matter from aeration ponds,

facultative ponds, and oxidation ponds were 46, 51 and 54%, respectively. These values were significantly similar to the total percent reduction of DOC by the respective processes at 54, 53, and 55%, respectively. Based on these results, it can be stated that the FEEM could be utilized to evaluate the removal of different types of organic matter and bulk organic matter in a stabilization pond system.