CHAPTER VI

INTERACTION BETWEEN ORGANIC SPECIES IN THE FORMATION OF HALOACETIC ACIDS DURING DISINFECTION

6.1 Theoretical backgrounds

HAAs are divided into nine species. Only three species of HAAs were found in this experiment, monochloroacetic acids (MCAA), dichloroacetic acids (DCAA), and trichloroacetic acids (TCAA). The detailed descriptions of these three HAA species are:

(i) Monochloroacetic acids (MCAA): Wilson and Mabury (2000) indicated that one source of MCAA was a photodegradation product of herbicide metolachlor. MCAA was considered degradable in water in the presence of microorganism and slowly destroyed by photolysis (Mangiapan *et al.*, 1997).

(ii) Dichloroacetic acids (DCAA): DCAA, non-volatile disinfection by-product, is a product of anaerobic microbial degradation of TCAA in the digestive tracts of mammals (Moghaddam *et al.*, 1996). DCAA differently affects the replication rates of normal hepatocytes and has effects on male reproduction. The formation of DCAA was shown to be not affected by pH (Steven *et al.*, 1989). World Health Organization (WHO) has concluded that the induction of mutations by DCAA is very improbable at the low doses that would be encountered in chlorinated drinking water. DCAA has been used as a pharmacological agent investigating metabolic pathways for many years (Stacpoole, 1989). It has been reported to be slowly degradable in both aerobic and anaerobic conditions (Moghaddam *et al.*, 1996). Nonetheless, Rodriguez *et al.* (2004) mentioned that DCAA concentrations declined with increasing residence time in the distribution system in particular at high water temperature.

(iii) Trichloroacetic acids (TCAA): One source of TCAA into environment maybe through the volatilization of short chain chlorocarbons from kraft pulp mills that use ClO_2 as a bleaching agent (Juuti *et al.*, 1995). TCAA formation in chlorinated water was reported to be higher at lower pH (Steven *et al.*, 1989). Data from Bowmer (1987) suggested that TCAA, non-volatile disinfection by-products, presented only slight carcinogenic hazard to humans at the low concentrations found in drinking water. TCAA has been used as herbicide to control the growth of aquatic plants in irrigation canals. Although TCAA was considered more refractory for biological degradation, Dojlido *et al.* (1999) illustrated that TCAA could be destroyed during boiling (more than 70%). TCAA could also be converted to DCAA under anaerobic conditions (Moghaddam *et al.*, 1996).

Literature mainly focused on sources and the influences of environmental parameters on the formation of HAA species, and some worked on the removal of such compounds. To date, there is no thorough investigation on the HAA formation potential from organic fractions which could provide useful information regarding the elimination of these disinfection by-products. Our preliminary results indicated that each organic fraction exhibited different reactivity when mixed with chlorine, and that the resulting HAA species were significantly different from each other. In addition, the reaction of a mixture of organic fractions with chlorine led to the results that could not be predicted by the plain combinational effect from individual organic species. This chapter intended to scrutinize this aspect by providing the experimental findings on the formation potential from the single-component and multi-component mixtures of the six organic fractions. Specific emphasizes would be on the information of speciation of HAAs formation. Moreover, empirical correlations relating HAAFP from each individual organic fraction were presented.

6.2 Objective of this chapter

The objective of this chapter was to evaluate HAA species formation potential of organic fractions.

6.3 Materials and methods

The tests for haloacetic acids formation potential (HAAFP) were performed according to the procedure stated in Section 3.7 for a subset of a full matrix combination of six organic fractions which includes:

- One organic fraction: the HAAFP tests were performed at four different concentrations of each individual organic fraction. For brevity in writing, the following abbreviations are used hereafter in this chapter: ON for HPON, OB for HPOB, OA for HPOA, IB for HPIB, IA for HPIA, and IN for HPIN.

- Combined two fractions: the HAAFP tests were performed with the mixture of two organic fractions with the following combination:

ON + OB	OB + OA	OA + IB	IB + IA
ON + OA	OB + IB	OA + IA	IB + IN
ON + IB	OB + IA	OA + IN	IA + IN
ON + IA	OB + IN		
ON + IN			

Note: The concentration of each fraction was fixed at the original level (the same as those found in the raw water).

- Combined three fractions: the following combinations of three organic species were investigated for their HAAFP:

ON + OB + OA	ON + IB + IA	OB + IB + IN
ON + OB + IB	ON + IB + IN	OB + IA + IN
ON + OB + IA	ON + IA + IN	OA + IB + IA
ON + OB + IN	ON + OA+ IB	OA + IB + IN
ON + OA + IB	ON + OA+ IA	OA + IA + IN
ON + OA + IA	ON + OA+ IN	OA + IA + IN
ON + OA + IN	ON + IB + IA	

Note: The concentration of each fraction was fixed at the original level (the same as those found in the raw water).

- Combined four fractions: the following combinations of four organic species were investigated for their HAAFP:

ON + OB + OA + IB	ON + OA + IA + IN
ON + OB + OA + IA	ON + IB + IA + IN
ON + OB + OA + IN	OB + OA + IB + IA
ON + OB + IB + IA	OB + OA + IB + IN
ON + OB + IB + IN	OB + OA + IA + IN
ON + OB + IA + IN	OB + IB + IA + IN
ON + OA + IB + IA	OA + IB + IA + IN
ON + OA + IB + IN	

Note: The concentration of each fraction was fixed at the original level (the same as those found in the raw water).

- Combined five fractions: the following combinations of five organic species were investigated for their HAAFP:

ON + OB + OA + IB + IA
ON + OB + OA + IA + IN
ON + OB + OA + IA + IN
ON + OB + IB + IA + IN
ON + OA + IB + IA + IN
OB + OA + IB + IA + IN

Note: The concentration of each fraction was fixed at the original level (the same as those found in the raw water).

- Combined six fractions: only one combination was available for the six organic fractions. The concentration of each fraction was fixed at the original level (the same as those found in the raw water).

ON + OB + OA + IB + IA + IN

6.4 Results and discussion

In the following discussion, unless specified otherwise, HAAFP represents the specific HAAFP which is equal to the ratio between the actual HAAFP and DOC from each fraction. The specific HAAFP indicates the reactivity of organic fraction in the formation of HAAs.

6.4.1   HAAFP from individual organic fraction

6.4.1.1 Dependencies of HAAFP with various surrogates

It was often reported that an increase in HAA formation was obtained with increasing DOC, SUVA, and chlorine demand content in natural waters. Experimental results obtained from this work also emphasized this finding. For instance, Figure 6-1 displays the relationship between the HAAFP and the DOC of each organic fraction. It can be seen that the HAAFP depended linearly on the concentration of each organic fraction. A simple linear regression analysis shows that "R^2" for these relationships were more than 0.96 which emphasized the applicability of the linear correlations in the description of such dependencies, at least for the range of concentration studied in this work. The relationships could be summarized in the following mathematical form:

$$HAAFP_i = k_{i,1} \, [\alpha_i] + k_{i,2} \qquad (6.1)$$

where $k_{i,1}$ or the slope of the curve is the potential for the organic fraction i to form HAA, $k_{i,2}$ is a constant, and α_i is the DOC of each fraction. The application of this equation should only be limited to a small range of DOC as indicated in Table 6-1. In this case, the fraction with the highest potential to form HAAs was HPOB (with $k_{i,1}$ of 2140.5) and the lowest was HPOA and HPIN (with $k_{i,1}$ of 29.26 and 26.48, respectively).

In fact, Chapter 4 already mentioned that HPOB fraction was the most active organic species when considered the reactivity with chlorine during the disinfection reaction. This finding agreed well with the report by Gjessing *et al.*

(1998) and Croue *et al.* (2000) who indicated that specified sites such as amino acids structures in HPOB could potentially lead to the formation DCAA. FTIR analysis in Chapter 5 further emphasized this finding as HPOB in the water sample from Bangkhen water treatment facility was found to have amino acid structure.

Turning now to the least active species, the low specific HAAFP for HPOA species as reported in Chapter 4 already demonstrated that this organic fraction was not quite reactive with chlorine. In addition, FTIR (Chapter 5) illustrates that HPOA contained the carboxylic acid group which was reported not to be active in forming HAA (Duarte *et al.*, 2003). The results from this chapter, therefore, just confirmed previous findings by showing that the reactivity of such organic fraction was relatively low at all range of DOC concentration.

Note that HPIN was the last organic fraction obtained from the fractionation method. Unlike all other fractions, this organic constituent was not obtained in a concentrated form as the volume of the last fraction was almost equal to the original. Hence, the analysis as shown in Figure 6-1 only could evaluate the reactivity of such fraction at original organic concentration ($\alpha_l = 1$) or lower ($\alpha_l < 1$), and within this work, the examination was performed for only two concentration points.

This empirical model was finally validated for its precision by comparing the estimate with the measure of the sample collected approx. 1 year later, on Sep 1, 2004, and the results are illustrated in Table 6-2. It can be seen clearly that, for most organic species, the model could well predict the HAAFP with the error of approximately 7 - 17 %. The estimate was particularly bad for HPIN with the error of as high as 36 %. However, with HPIN as a relatively inactive species, the error from the prediction of this fraction could only slightly contribute to the total HAAFP. This finding led to an important conclusion that the quality of the water source for this WTP remained relatively unaltered with time, and therefore the ability in the estimate of HAAFP of the model in Eq. (6.1) was satisfactorily.

Note that, when HAAFP was plotted against the other two surrogates, i.e. SUVA and chlorine demand, no direct relationships between these quantities could be found, and it is difficult to formulate a simple mathematical formula to predict HAAFP from these two quantities.

6.4.1.2 Types of HAA species

The evaluation for HAAs is generally based on the total amount of various different types of HAAs. With the detection limit of the methods employed in this work, only three species were detected, i.e. monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) (as stated earlier in this chapter). The other two species: monobromoacetic and dibromoacetic acids, were also found, but in a tiny amount. Specifically, the bromoform species were non-detectable for over 95% of the samples and for those with brominated species, these two components only contributed to less than 5% of the total HAAs (results are not shown here). This indicates that the water source selected for this work did not contain high level of bromide. Low brominated species might be attributed to two possible reasons: (i) not adequate amount of bromide in the water sample, and (ii) slower reaction rate of organic compounds and bromide compared with chlorine. For the later, Dalvi *et al.* (2000) stated that chlorine could react first with organics in the water sample and form chloro-derivatives by substitution reaction. Subsequently excess chlorine oxidized bromide to OBr^- which could form bromo-derivatives. Therefore, water samples with low organic contents such as those encountered in this work might not contain adequate quantity of organics for the formation of brominated species. Thus, the work hereafter would only discuss the formation mechanism of the three chloro-derivatives.

6.4.1.3 Formation potential of HAA species

Figure 6-2 illustrates that all three HAA products, i.e. MCAA, DCAA, and TCAA, increased with an increase in the concentration of each individual organic fraction. Quantitatively, DCAA was often found to be the predominant HAA species followed by MCAA and TCAA, respectively, although there was an exception for the case of HPON organic fraction, where the major HAA species was found to be

MCAA, followed by DCAA and TCAA, respectively. The plot in Figure 6-2 also demonstrates a linear relationship between the concentration of organic fraction and the resulting specific HAAFP. This was consistent with the previous discussion of the overall HAAFP where HAAFP was proportional to the quantity of organic reactants. The following section provides a detailed discussion regarding these findings.

MCAA:

In all cases, MCAA was not formed (up to the detection limit) at low organic concentration. At adequately high organic content, the quantity of MCAA being generated from the chlorination varied linearly with DOC. MCAA was often found to be the second most abundant HAA species (provided that it was generated at all) except for the HPON fraction where MCAA was the major HAA component. The following subsection describes potential reaction mechanism for the formation of MCAA.

Possible formation mechanism for MCAA:

MCAA is likely to occur when the carbon–carbon bond is attacked by chlorine during the chlorination reaction. During the chlorination process, chlorine which is a strong oxidizing agent breaks the single bond of aliphatic organic structure, and subsequently substitutes the hydrogen atom to form MCAA. This mechanism was best elucidated by examining the results from the chlorination of HPON organic fraction. MCAA was found to be the dominant HAA species for this organic fraction, and from the FTIR spectrum (presented in the previous chapter), HPON was shown to be the only organic species that consisted of aliphatic alcohol band which could well be the main reactant for MCAA.

In fact, the carbon-carbon bond is least reactive in the chlorination or other oxidation reactions compared with carbon-carbon double and triple bonds as there are no free electrons available for the oxidants. This explained why MCAA was only formed in the case where the concentration of organics was not too low.

DCAA:

According to the results obtained in this work, DCAA was often the predominant HAA species among the three chloro-derivatives formed. This finding was consistent with past observations of Krasner *et al.* (1996), Dojlido *et al.* (1999), Hwang *et al.* (2000), and Chellam and Krasner (2001). In particular, Hwang *et al.* (2000) and Krasner *et al.* (1996) suggested that DCAA species were formed to a similar degree from both hydrophobic and hydrophilic fractions, and in the same study, they stated that DCAA species was predominant not only for hydrophobic but also for hydrophilic fractions.

Possible formation mechanism for DCAA:

One potential mechanism for the formation of DCAA is the chlorination of the alicyclic compounds and of the aliphatic that contains double bonds as the chlorine can attach itself to the broken bonds of carbon (oxidation reaction). Single bond aliphatic organics should also play a role in generating DCAA via the breakage of the two single bonds, but as this single bond was not quite reactive with chlorine, DCAA formation from this reaction should not be of great quantity.

It should be noted that the carbon-carbon triple bond is most reactive with chlorine and the chlorination of such triple bond should lead to the formation of TCAA. However, in most cases, the dominant HAA species was DCAA, this indicated perhaps that the water sample contained a larger amount of organic matters in alicyclic structures or compounds with carbon-carbon double bonds should be presented, rather than other organic species.

TCAA:

TCAA species was found to occur in the smallest quantity compared to the above two HAA species. This might be due to the suggestion from Croue *et al.* (2000) that non-aromatic character was a poor precursor for TCAA. To further illustrate this, the report of SUVA in Table 4-6 was re-considered along with Figure 6-3. SUVA often is used to represent the aromatic characteristics of the water sample which meant that samples with high SUVA would contain higher aromatic organic compounds than those with low SUVA. Figure 6-3 shows that this explanation was most applicable to the water samples examined here. For instance,

HPIA exhibited the lowest SUVA, and hence, the quantity of TCAA obtained from this fraction was also the smallest, whereas HPON with the highest level of SUVA gave the highest level of TCAA among the six organic fractions.

Possible formation mechanism for TCAA:

TCAA should be the product from the chlorination of the precursors with triple bonds and aromatic structure. In fact, the reaction with saturated aliphatic might also lead to the formation of TCAA but this meant that chlorine had to attack at least three carbon bonds. Normally, triple bond or aromatic structures are most reactive with chlorine or other strong oxidizing agents. However, the amounts of triple bond and aromatic compounds should be lower than other potential reactive structures as TCAA was always found to be the lowest among the three HAA species.

6.4.2 HAAFP from mixture of organic fraction
6.4.2.1 HAAFP

The aforementioned discussion illustrates that each individual organic fraction had different characters in forming HAAs during the chlorination. Nonetheless, a diversity of organic normally presented in the source water may inhibit or support the others in generating HAAs during the chlorination. To figure out the effectiveness of each precursor, the HAA formation tests were conducted with combining samples of two, three, four, five, and six of fixed concentrations of the six organic fractions.

Figure 6-4a illustrates HAAFP from the combination of HPON with the other organic fraction(s) selected from the remaining five fractions. Note that all fractions were selected with their original concentrations. Typically, HPON alone did not exhibit high potential in forming HAAs. However, when this fraction was combined with HPOB or HPIB, a relatively high HAAs became obvious. Similar results were also obtained with the combination of three organic compounds containing HPON, HPOB and HPIB. This could be perhaps explained using the results on specific HAAFP in Chapter 4 where HPOB and HPIB were found to have the highest potential among the six organic fractions in forming HAAs. In this case, these two components behaved like a reaction supporter for HPON and helped

improved the reaction of chlorine with HPON. However, in the combination of four, five, and six fractions, both HPOB and HPIB could not exhibit beneficial effect to the HAA formation reaction. This meant that the competition of multi-component matrix organic fractions might play more important role in inhibiting HAAFP formation than the potential of both HPOB and HPIB fractions. This phenomenon occurred in the same fashion for the combining mixtures of HPOB and HPIB fractions with other five fractions as demonstrated in Figure 6-4b and 6-4d, respectively.

Figures 6-4c and 6-4e illustrate the HAAFP from the combinations of HPOA and HPIA fractions with other fractions, respectively. The average concentrations of HAAFP from these two mixed fractions were not significantly different from each other in all multi-component fraction sets. Even with the mixture between these fractions with the HAA forming potential promoters like HPOB and HPIB, HPOA and HPIA still could not produce, under chlorination reaction, high level of HAAs. As stated in Chapter 5, acid fractions (HPOA and HPIA) which contain carboxylic acids were the least effective precursor to HAA formation, and the combination with these two acid fractions could exhibit inhibitory effects which lowered down the formation of HAAs.

The HAAFP from the combination of HPIN fraction set is displayed in Figure 6-4f. Similar to the acid fractions, all of the mixtures containing HPIN did not lead to the changes in the HAAFP. Nevertheless, the multi-component HPIN mixtures had slightly higher HAAFP value than those of acid mixture fraction sets. This result emphasized the observation that neutral fractions played more important role than acid fractions in generating HAAs during the chlorination.

6.4.2.2 Formation of various HAA species

Figure 6-4a to 6-4f also illustrate the concentrations of three chloro-derivative species. Surprisingly, MCAA species which was found to occur in smallest quantity in the raw water was formed in a much greater extent than DCAA and TCAA. Consequently, the increasing MCAA species decreased both the formations of DCAA and TCAA species. This could well be due to the fact that multi-component mixtures had higher DOC concentration than the single-component

fractions. As MCAA was formed better at high DOC level, higher MCAA in the combined fractions were expected and proven by the experimental results shown in these figures.

6.5 Concluding remarks

This chapter thoroughly investigated the formation of three HAA species from the chlorination of an individual and the mixtures of six organic fractions. An excellent linear correlation relationships obtained at all DOC concentration ranges suggested that the reactions between the organic fractions and chlorine were first order. It was also illustrated that DCAA was the predominant species in most of the chlorinated fractions followed by MCAA and TCAA, respectively. However, MCAA was only found in the fraction with a relatively high organic concentration.

In the examination of the HAA formation from the multi-component mixtures of six organic fractions revealed that HPOB and HPIB fractions played an important role in supporting the formation of HAAs whereas HPOA and HPIA fractions had an inhibiting effect when they presented in mixture components. Experimental results obtained from this study could be analyzed in the formation of a regression model capable of estimating the specific HAAFP from organic matter presented in this particular water source. This model could be used with moderate accuracy as a predictive tool to help assess HAAs risk prevention, regulatory compliance, and control strategies.

Table 6-1 Coefficients for a relationship of organic fraction and HAAFP

Organic fraction	k_1	k_2	R^2	Application organic concentration range (mg/L)
Hydrophobic neutral	279.48	- 0.06	0.9768	0.136 – 0.816
Hydrophobic base	2140.5	- 69.7	0.9999	0.065 – 0.390
Hydrophobic acid	29.26	- 0.55	0.9981	0.811 – 4.869
Hydrophilic base	685.58	25.04	0.9964	0.082 – 0.492
Hydrophilic acid	63.81	- 17.73	0.9636	0.421 – 2.526
Hydrophilic neutral	26.48	7.31	1.000	1.060 – 2.120

Table 6-2 Comparison between the model prediction and the measurement of HAAFP from the raw water of Bangkhen Water Treatment Facility

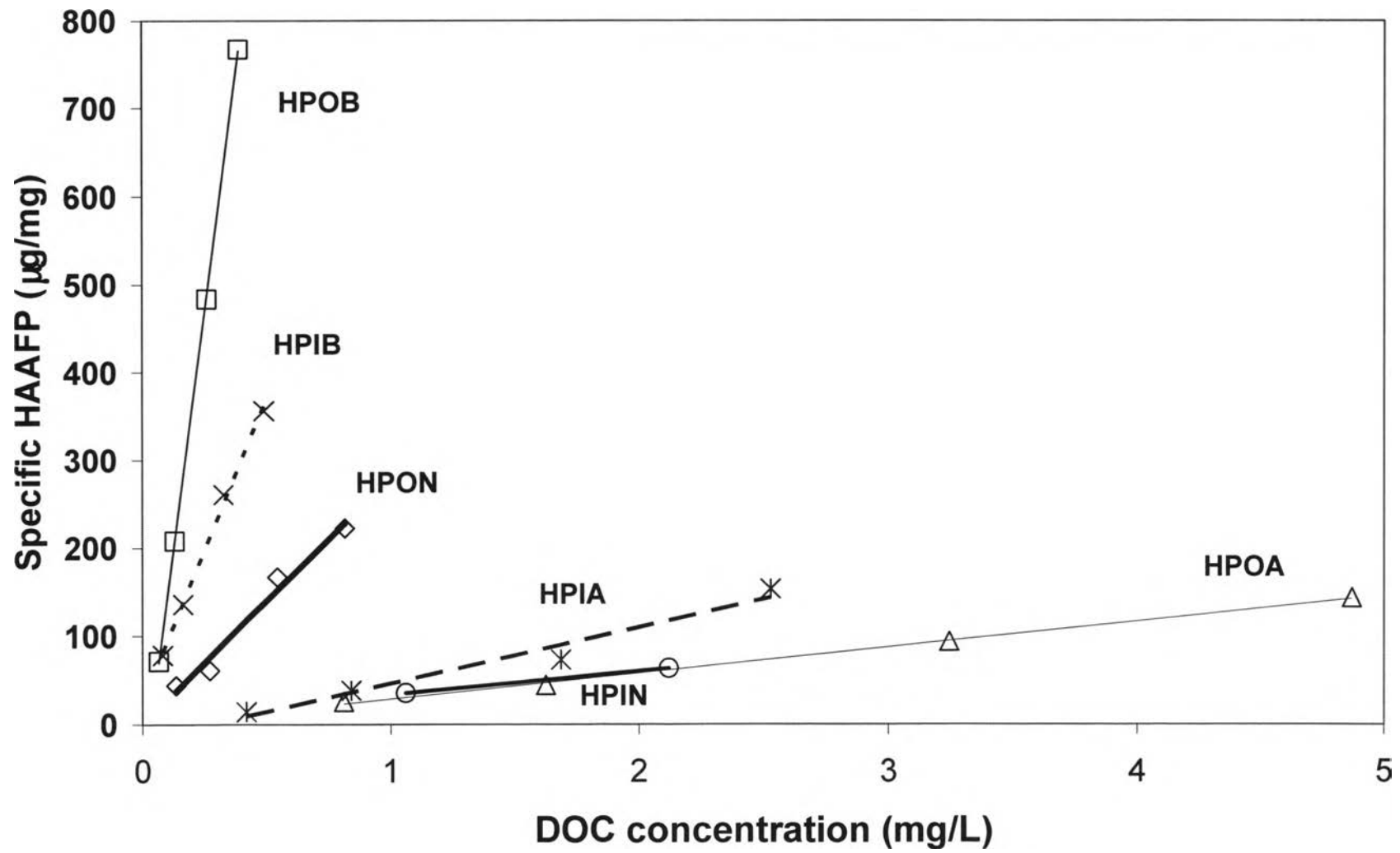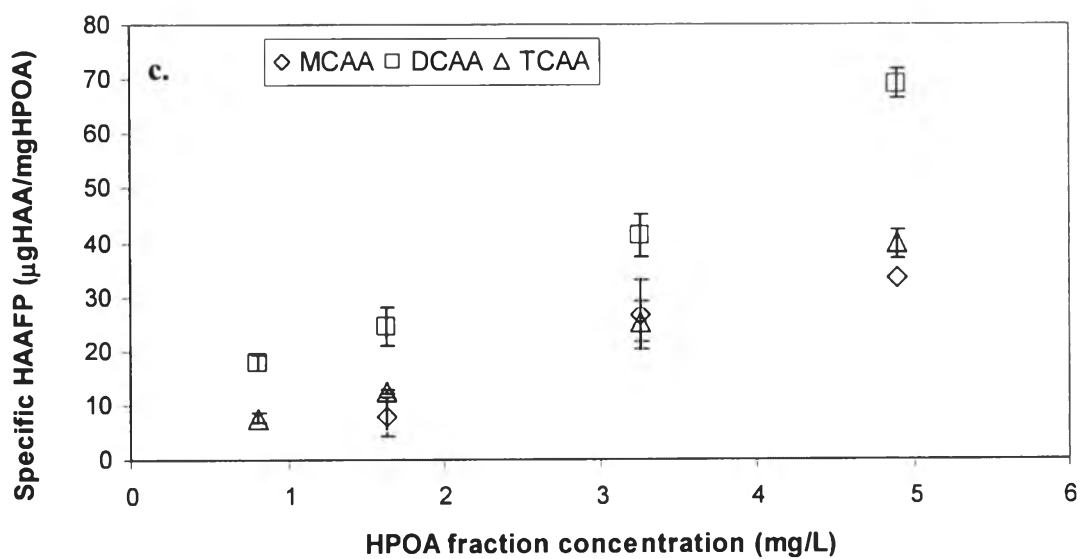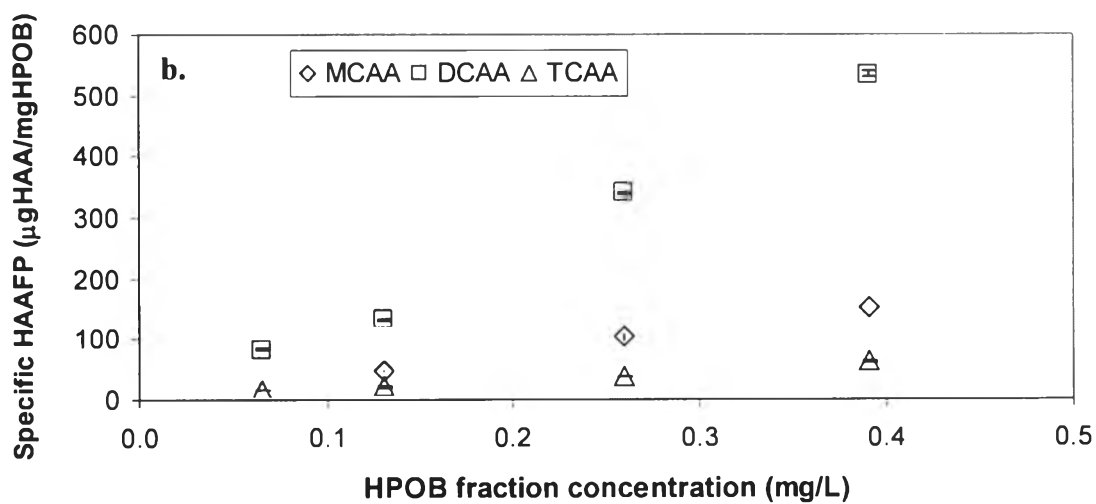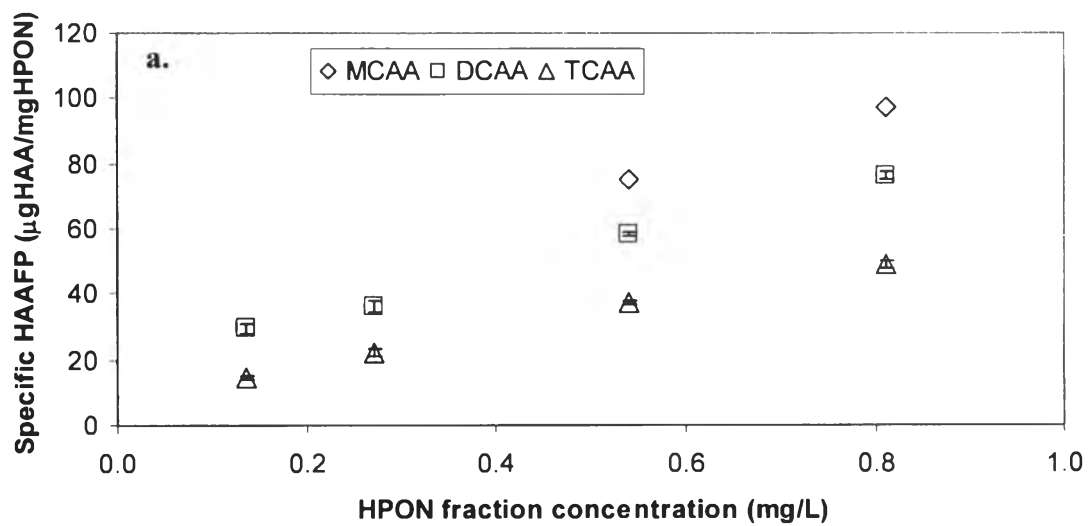| Organic fraction	Measured HAAFP ($\mu g/mg$)	Estimate HAAFP ($\mu g/mg$)	Percent error
Hydrophobic neutral	81.2	94.96	-16.95
Hydrophobic base	148.9	122.95	17.43
Hydrophobic acid	45.5	50.95	-11.98
Hydrophilic base	119.4	134.73	-12.84
Hydrophilic acid	64.5	60.12	6.79
Hydrophilic neutral	63.1	40.15	36.37

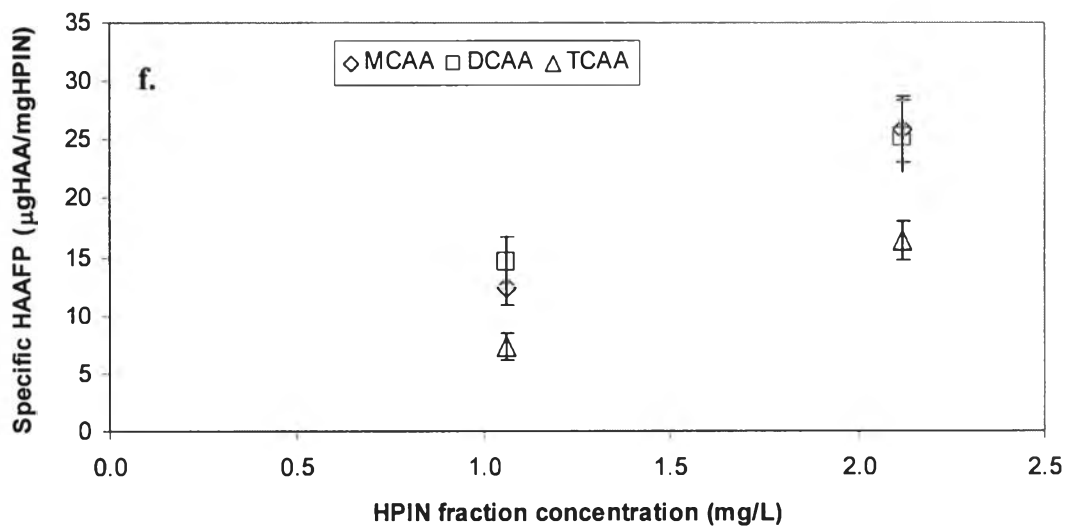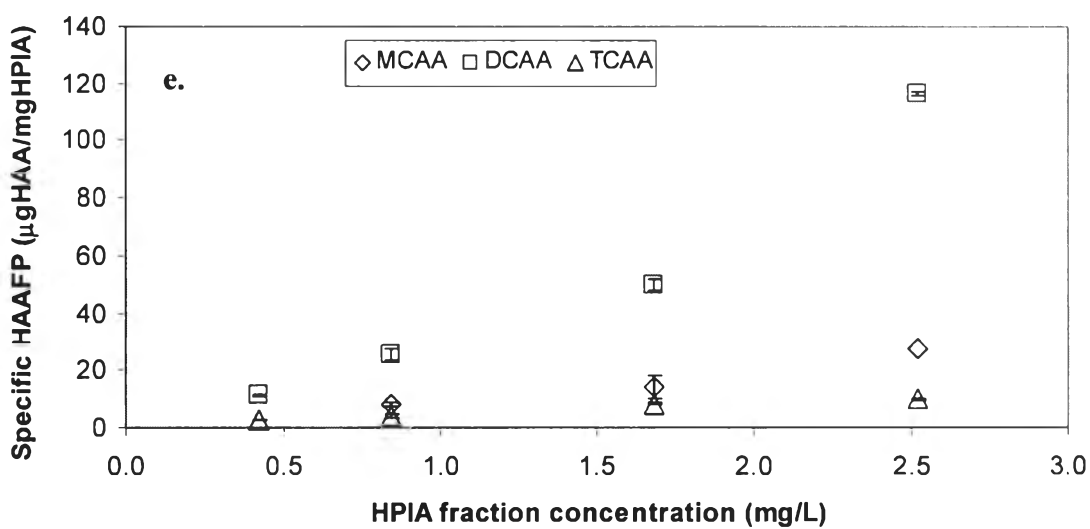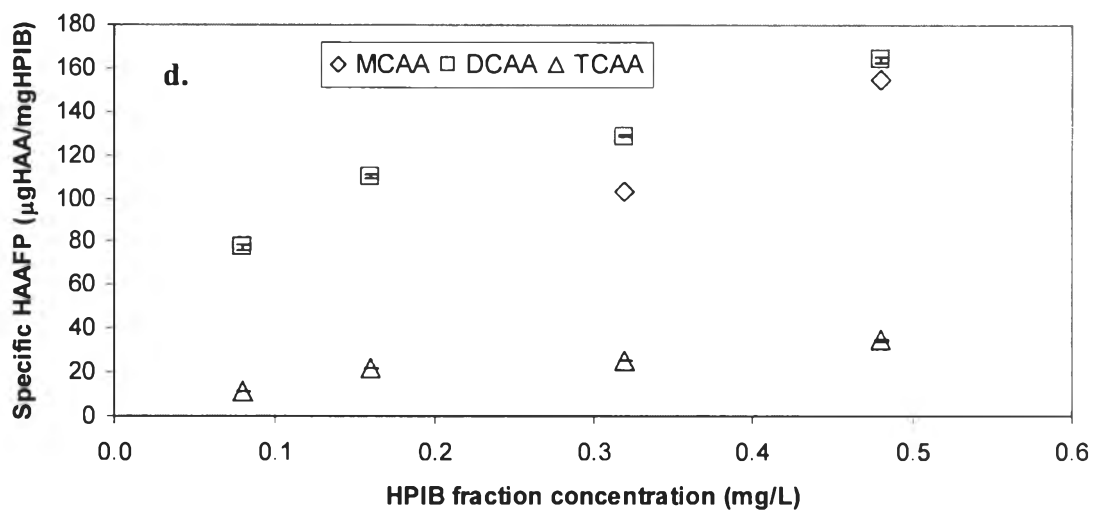**Figure 6-1** HAAFP varied with DOC concentration

88

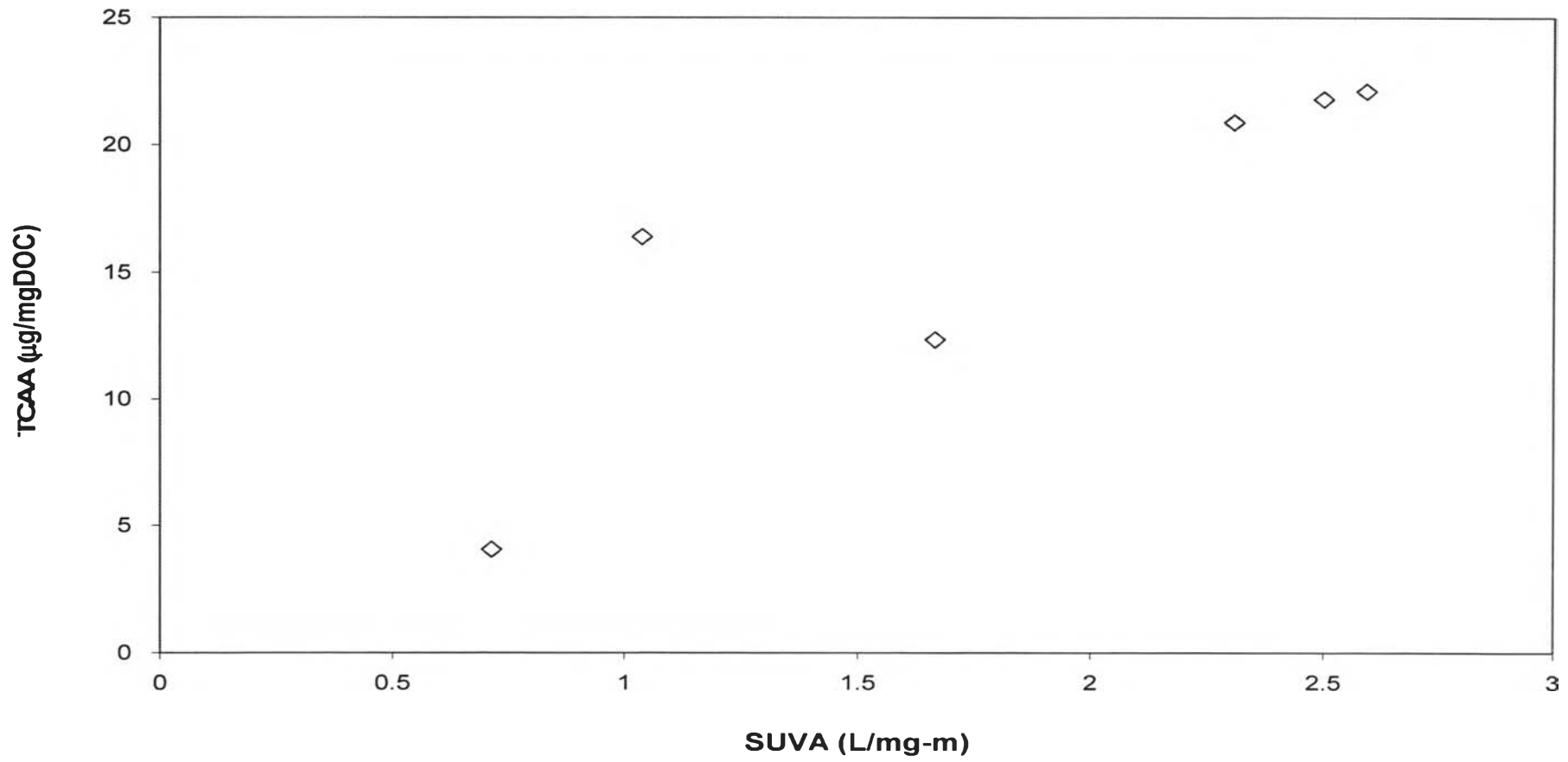**Figure 6-2** Influence of organic concentration on the formation of HAA species

Figure 6-3 Relationship between SUVA and TCAA

b.

Specific HAAFP (µgHAA/mgDOC)

■ MCAA ▦ DCAA □ TCAA

200

150

100

50

0

	IA	IN	IN	IN	IN
IB	IB	IB	IA	IA	IA
OA	OA	OA	OA	IB	IB
ON	ON	ON	ON	ON	OA
OB	OB	OB	OB	OB	OB

																IB	IA	IN	IA	IN	IN	IA	IN	IN	IN	
					OA	IB	IA	IN	IB	IA	IN	IA	IN		OA	OA	OA	IB	IB	IA	IB	IB	IA	IA	
	ON	OA	IB	IA		ON	ON	ON	ON	OA	OA	OA	IB	IB	IA	ON	ON	ON	ON	ON	ON	OA	OA	OA	IB	
OB	OB	OB	OB	OB	IN OB	OB	OB	OB	OB	OB	OB	OB	OB	OB	IN OB	OB	OB	OB	OB	OB	OB	OB	OB	OB	IN OB	

94

Figure 6-4 HAAFP from multi-component fractions