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Kinetics of Trihalomethane Formation From Organic Contaminants in Raw Water From the Bangkhen Water Treatment Plant*

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The fractionation of raw water from Bangkhen water treatment plant, Bangkok, Thailand revealed that the mass distribution sequence of the six organic fractions from high to low was hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid, hydrophobic neutral, hydrophilic base, and hydrophobic base. The main organic matter components in raw water were HPIN and HPOA, which were also the two most important contributors of trihalomethane formation potential (THMFP). Linear dependencies between the level of each organic fraction and the formation potential of THM species were observed, which suggested the reactions between the organic fraction and chlorine during the chlorination were first order. The fractionation led to a deviation of bromide concentration in each organic fraction from the original concentration, and this affected the formation of brominated THM species. However, this effect was demonstrated to be

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within an acceptable range. The chlorination of an individual organic fraction resulted in a higher level of THMFP than that of the raw water and mixed fractions, indicating an inhibitory effect between the organic species.

Key Words: Chlorination; Disinfection by-products; Hydrophilic; Hydrophobic.

INTRODUCTION

Chlorination is one of the most widely used disinfection processes in water treatment plants. The remnant of dissolved organic carbon (DOC) can therefore undergo chlorination and results in the formation of chlorination by-products, such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetoni-triles (HANs). THMs are proven to have adverse effects on human beings. They consist of several methane derivative compounds. The species of most concern include chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHBr_2Cl), and bromoform (CHBr_3). Brominated species were suspected to be much stronger carcinogens and mutagens than their chloride-containing analogues.^[1] Therefore, brominated THM species are considered more toxic than nonbrominated species. Fortunately, brominated THM species were commonly found to account for only about 20–25% of the total THMs value.^[2]

Several environmental factors such as DOC, pH, temperature, bromide concentrations, and operational factors (for chlorination) like chlorine dose and contact time were reported to significantly affect the formation of THMs.^[3–5] Among these factors, DOC is the most important in the formation of THMs. The U.S. Environmental Protection Agency proposed this parameter as an indirect measure of disinfection by-product (DBPs) precursors.^[6] The general reaction for the formation of DBPs from DOC and chlorine can be simplified as follows^[7]:



The variety in the nature of organic compounds in different watercourses usually affected the formation of THMs. This is obvious as the relationship between the level of DOC in the water samples and THM formation potential (THMFP) varied from one source to another.^[8–10] Therefore, it might be reasonable to conclude that DOC alone does not always represent reactive precursors that form DBP.

To better understand the formation kinetics of THMs during chlorination, DOCs should be further categorized into smaller groups according to their chemical properties. This could be achieved by using the resin adsorption method as proposed by Leenheer^[11] where DOC was fractionated into six organic fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). Recently, Marhaba et al.^[12] modified this technique

by changing one of the resins from Duolite A7 to WA-10, the resin for which they claimed to reduce the contamination from the back elution of the organics. Past research indicated that each organic fraction possessed different reactivities in the formation of THMs. For instance, Marhaba and Van^[2] reported that hydrophobic base fraction was the most reactive in forming THMs followed by the HPIA fraction. Chang et al.^[13] demonstrated that 76% of DOC was the HPIA and HPOA fractions but the HPOA exhibited the greatest ability in the formation of THMs. The difference in the reported active species from one source to another suggested that although DOC was further categorized into various organic fractions, the THM formation mechanism still could not be generalized. Hence, it is important that THM formation characteristics be examined for each water source, particularly those with significant municipal impact.

The aim of this article was to investigate the formation kinetics of various THMs species during the chlorination of raw water from the Bangkok water treatment plant, which is among the three largest main water treatment plants in Bangkok, Thailand. The dissolved organic matters were categorized into several organic fractions to investigate the effect of each organic type on the formation of THM species. The effect of organic fractionation method on the formation of THMs was also examined.

MATERIALS AND METHODS

Sample Collection and Preservation

Approximately 200 L of water sample was collected from the intake of the Bangkok water treatment plant, Bangkok, Thailand. Samples were prepared by filtering through a 0.45- μm membrane and were stored in a cold room that use temperature controlled at 4°C before and after fractionation.

Fractionation

The resin adsorption procedure as proposed by Marhaba et al.^[12] was used to categorize the dissolved organic components in the water samples into six fractions, HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, by using three types of resins (DAX-8, AG-MP-50, and WA-10). The fractionation follows the steps below (see also Figure 1). 1. The filtered sample was adjusted to pH 7 and passed through the packed column with DAX-8 resin. The hydrophobic neutral fraction was retained in the resin and was extracted out by CH₃OH (analytical grade). 2. The sample effluent was then adjusted to pH 10 by using 2N NaOH and passed to the second DAX-8 resin packed column. This time, the hydrophobic base fraction was retained and eluted from the resin with 0.1N HCl at 0.25 bed volume and 0.01N HCl at 1.5 bed volumes. 3. The effluent was then acidified

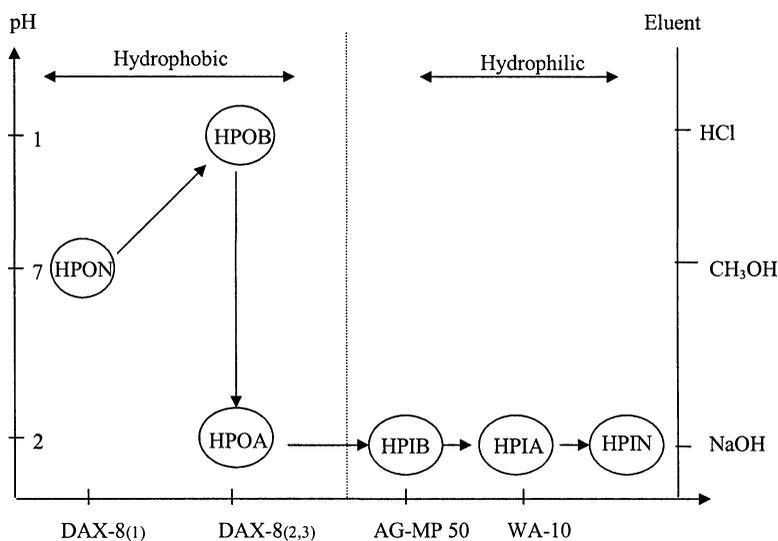


Figure 1: Fractionation procedure.^[12]

to pH 2 with 6N H_2SO_4 and passed through the last DAX-8 resin packed column. The hydrophobic acid fraction was eluted from resin with 0.1N NaOH at 0.25 bed volume and 0.01N NaOH at 1.25 bed volumes. 4. The effluent, free of hydrophobic fractions, was passed through AG-MP-50 resin. The hydrophilic base fraction was eluted from the resin with 1N NaOH at 1 bed volume. 5. The effluent was then passed through the WA-10 resin packed column. The effluent contained hydrophilic neutral and the adsorbate, hydrophilic acid was eluted with 0.1N NaOH at 1.5 bed volumes and 0.01N NaOH at 1 bed volume.

Trihalomethane Formation Potential

THMFP tests for all samples were carried out according to the 7-day chlorine test procedure available in the Standard Methods 5710B.^[14] The neutralized solutions were buffered by a phosphate solution before the incubation at $25 \pm 2^\circ\text{C}$ in amber bottles with PTFE liners. At the end of the 7-day reaction period, samples should have a remaining free chlorine residual of between 3 and 5 mg L^{-1} . THMs were extracted with pentane according to the procedures mentioned in the Standard Methods 6232B.^[14] THMs were then analyzed by the gas chromatography (GC) with electron capture detector (ECD) (Agilent technologies Inc., Wilmington, DE).

Analytical Methods

The DOC was measured from the filtered sample using the TOC analyzer (OI Analytical, College Station, TX) followed the Standard Methods 5310C.^[14]

At least three replications of each measurement were carried out, and more replications were executed in the cases where the variation between each measurement exceeded 5%. Milli-Q water (ELGA, Lane End, HW) was run at every three samples to clean the system.

UV-254 (or the UV absorbance at a wavelength of 254 nm) was reported to represent the aromatic character of organic matters as they imparted an ability to absorb light in the UV range.^[15] UV-254 was measured in compliance with the Standard Methods 5910B using Genesys 10 UV (Thermoelectron Corp., Madison, WI) with a thermospectronic with a 1-cm quartz cell. All fractionated samples were adjusted to pH 7 by NaOH or H₂SO₄ before the measurements of DOC and UV-254.

Residual chlorine was measured according to the procedures mentioned in the Standard Method 4500-Cl G,^[14] that is, *N,N*-dethyl-p-phenylenediamine colorimetric method. The level of chlorine was then represented by the light absorbance at 515 nm (using Genesys 10 UV thermospectronic). Bromide content was measured by using an ion chromatography instrument (Dionex Corp., Sunnyvale, CA).

Note that Milli-Q water (ELGA, Lane End, HW) was used for all dilutions, sample and chemical preparation, and final glassware cleansing in this work.

RESULTS AND DISCUSSION

Organic Content in Raw Water from Bangkhen Water Treatment Plant

The results from the analysis (DOC and UV) and the fractionation of raw water from the Bangkhen water treatment plant are illustrated in Table 1. A 9% weight surplus of the organic constituents in the six organic fractions from the original organic content in the water sample was observed. This weight surplus may have come from resin bleeding during the elution process.^[11] This fractionation technique was often reported to give as much as 8–15% tolerance

Table 1: Characteristics of organic fraction and raw water

	TOC (mg L ⁻¹)	UV (cm ⁻¹)
RW	4.72	0.122
HPOA	1.62	0.027
HPOB	0.13	0.003
HPON	0.27	0.007
HPIA	0.84	0.006
HPIB	0.16	0.004
HPIN	2.12	0.020
Total	5.14	

DOC: Dissolved organic carbon.

of DOM recovery,^[16,17] and therefore this level of inaccuracy was considered acceptable. HPIN was found to be the major organic component in this water source, whereas the rest of organic components were ordered according to their quantities from large to small as HPOA, HPIA, HPON, HPIB, and HPOB, respectively.

THM Species Formation Potential

Four THM species, including CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 , were considered in this work. Table 2 shows that only chloroform and bromodichloromethane were generated from the chlorination of each organic fraction, and the different organic fractions were observed to have different influence on the formation of these two THM species. Most chloroform (~33% of the total chloroform) was found to occur as a result of the chlorination of HPIN species, whereas chloroform from HPOA was responsible for another 20%. HPIB, HPOB, and HPIA resulted in a similar range of chloroform formation (12–14%), whereas HPON was least significant in forming chloroform (7%). For bromodichloromethane, HPIA was observed to be the most important reactant for this water source where as much as 52% of bromodichloromethane was obtained from the chlorination of this fraction alone. The rest could be ordered from the most significant to the least as follows: HPIB, HPOB, and HPOA. Interestingly, bromodichloromethane was not detected from the chlorinated HPIN and HPON samples.

To examine the reaction kinetics of THM species, each organic fraction was adjusted to various concentration levels and tested for its THMFP. The results displayed in Figure 2 suggest that linear relationships could be established in all cases. Note that dibromochloromethane was detected from the HPIA sample when the concentration of HPIA was increased above twice as much as the raw water concentration. It was possible that dibromochloromethane was also formed at low HPIA concentration but with the quantity below the detection limit of the measuring method used in this

Table 2: THMFP from each organic fraction.

	CHCl_3 ($\mu\text{g L}^{-1}$)	CHBrCl_2 ($\mu\text{g L}^{-1}$)	CHBr_2Cl ($\mu\text{g L}^{-1}$)	CHBr_3 ($\mu\text{g L}^{-1}$)	Total THMs ($\mu\text{g L}^{-1}$)	Chlorine demand (mg L^{-1})
HPOA	118	1.42	ND	ND	120	1.3
HPOB	78	2.06	ND	ND	80	0.2
HPON	39	ND	ND	ND	39	0.6
HPIA	71	9.4	ND	ND	80	0.4
HPIB	83	5.35	ND	ND	88	1.3
HPIN	193	ND	ND	ND	193	3.5
Total of each THM species (ΣFP)	582	18.23	ND	ND	600	7.3

ND, not detected.

work. Similarly, bromodichloromethane was not found from the HPON fraction at original organic concentration. However, at elevated level of HPON bromodichloromethane was observed, which could be a result of the detection limit or it might be that the original HPON concentration was far too low for the generation of bromodichloromethane. Results in Figure 2 could be used to

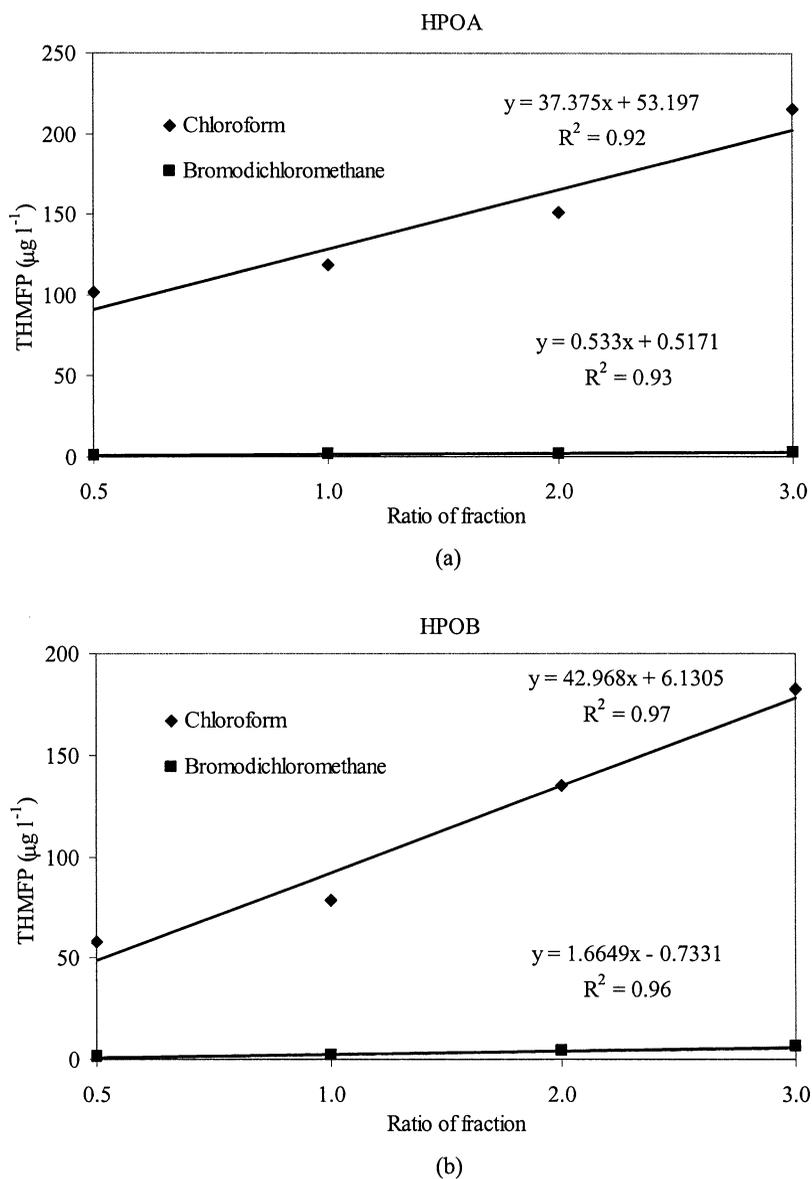
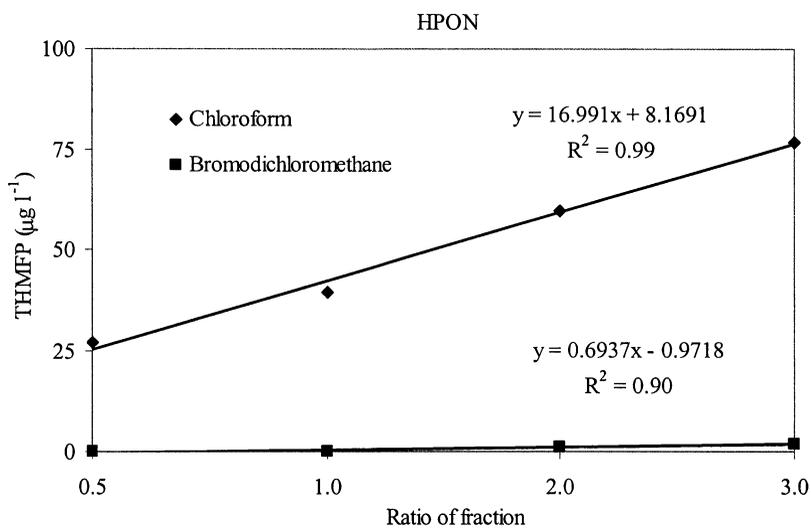
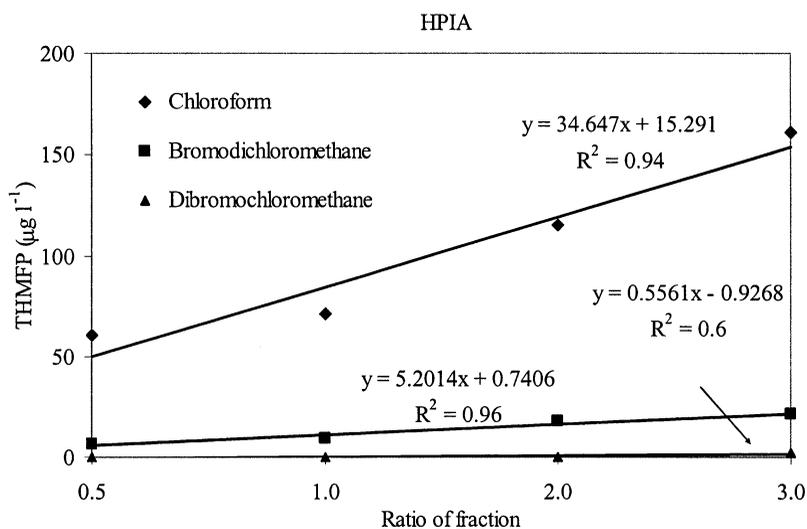


Figure 2: THM species formation potential from each organic fraction: (a) hydrophobic acid, (b) hydrophobic base, (c) hydrophobic neutral, (d) hydrophilic acid, (e) hydrophilic base, (f) hydrophilic neutral. (Continued)



(c)



(d)

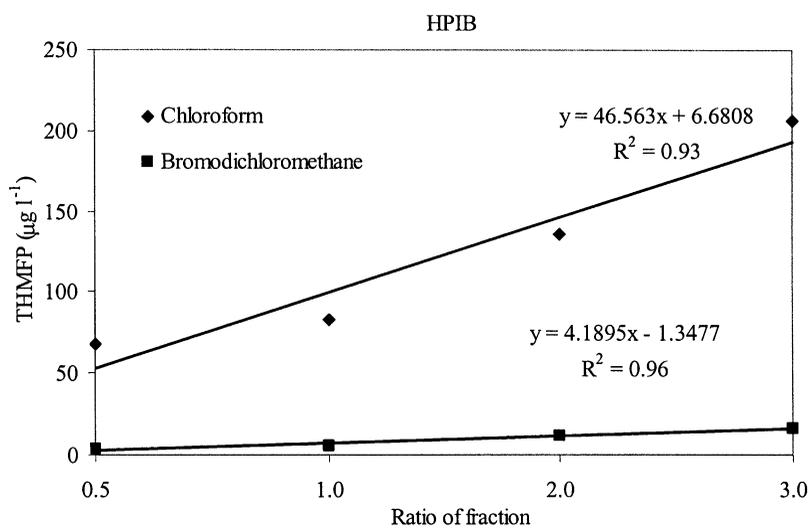
Figure 2: (Continued)

formulate the equations that described the formation of each THM species as follows:

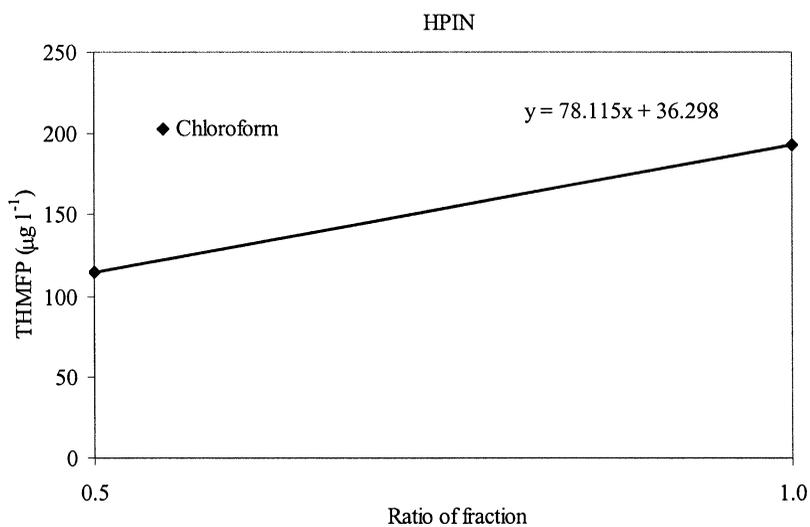
For HPOA fraction:

$$\text{Chloroform} = 37.37 \text{ DOC} + 53.197 \quad (2)$$

$$\text{Bromodichloromethane} = 0.533 \text{ DOC} + 0.517 \quad (3)$$



(e)



(f)

Figure 2: (Continued)

For HPOB fraction:

$$\text{Chloroform} = 42.968 \text{ DOC} + 6.131 \quad (4)$$

$$\text{Bromodichloromethane} = 1.665 \text{ DOC} - 0.733 \quad (5)$$

For HPON fraction:

$$\text{Chloroform} = 16.991 \text{ DOC} + 8.169 \quad (6)$$

$$\text{Bromodichloromethane} = 0.694 \text{ DOC} - 0.972 \quad (7)$$

For HPIA fraction:

$$\text{Chloroform} = 34.647 \text{ DOC} + 15.291 \quad (8)$$

$$\text{Bromodichloromethane} = 5.201 \text{ DOC} + 0.741 \quad (9)$$

$$\text{Dibromochloromethane} = 0.556 \text{ DOC} - 0.927 \quad (10)$$

For HPIB fraction:

$$\text{Chloroform} = 46.563 \text{ DOC} + 6.681 \quad (11)$$

$$\text{Bromodichloromethane} = 4.189 \text{ DOC} - 1.348 \quad (12)$$

For HPIN fraction:

$$\text{Chloroform} = 78.115 \text{ DOC} + 36.298 \quad (13)$$

Effect of Fractionation Method on THMFP

Table 3 demonstrates interesting results on the THMFP of the various water samples from the same source. The first row reports the THM species obtained from the chlorination test of the raw water without passing through the fractionation resins. This sample is called the “raw water sample” or “RW” hereafter. The second row shows the result from the mixed sample where the six organic fractions were mixed together before the THMFP test (this is called the “mixed sample” or “MS”). The last row shows the summation of the test results from each organic fraction and is called “fractionated samples” or “FS.”

Let us first focus on the brominated species. Table 3 clearly states that more brominated species were formed in the RW than in the MS and FS. Specifically, the total brominated species in the RW was $50.74 \mu\text{g L}^{-1}$ ($43.76 \mu\text{g L}^{-1}$ of bromodichloromethane and $6.98 \mu\text{g L}^{-1}$ of dibromochloromethane), whereas 14.01

Table 3: THMFP from raw water and mixed fraction.

	CHCl ₃ ($\mu\text{g L}^{-1}$)	CHBrCl ₂ ($\mu\text{g L}^{-1}$)	CHBr ₂ Cl ($\mu\text{g L}^{-1}$)	CHBr ₃ ($\mu\text{g L}^{-1}$)	Total ($\mu\text{g L}^{-1}$)	Chlorine demand (mg L^{-1})
Raw water	262	43.76	6.98	ND	313	9
Mixed fractions ^a	291	14.01	ND	ND	319	6
ΣFP^b	582	18.23	ND	ND	600	7.3

^aMixed fractions = THMFP from the mixed organic fractions (fractionated sample).

^b ΣFP = sum of the THMFP from the chlorination of each organic fraction (mixed sample).
ND, not detected.

Table 4: Bromide concentration in each water sample.

	Bromide (mg L ⁻¹)
RW	0.891
HPOA	0.029
HPOB	0.004
HPON	0.004
HPIA	1.393
HPIB	0.014
HPIN	0.000

and 18.23 $\mu\text{g L}^{-1}$ were found in the MS and FS, respectively. To understand this variation in the formation of brominated species in these various samples, it is useful to look at the bromide concentration in the samples demonstrated in Table 4. The raw water from the Bangkhen water treatment plant was found to contain a rather high level of bromide (0.891 mg L⁻¹). This bromide, however, was neither adsorbed by the DAX-8 (non-ionic) nor AG-MP-50 (cationic) resins, and this resulted in a low bromide level in each organic fraction eluted from these resins. There was an exception for HPIA where bromide concentration was found to be extremely high, even higher than in the raw water.

The reason for a high bromide concentration in this fraction still could not be concluded at the time of this work, but it could be that some bromide ion was released from the molecular structure of the various organic compounds during the harsh fractionation conditions. In addition, the resulting high bromide level in this fraction might be because the anionic WA-10 resin had very high adsorption capacity for bromide. This adsorbed bromide was then eluted together with HPIA fraction and this led to a high bromide level only in this organic fraction. Therefore, during the THMFP test, most organic fractions were subject to an extremely "low" bromide concentration (much lower than the raw water concentration). This led to an absence of brominated species in these fractions as observed from the results in Table 2. It is worth noting here that HPIA must not be active for the formation of dibromochloromethane. This was obvious from the results where a very high bromide level in HPIA was observed without generating dibromochloromethane at its original organic concentration. This dibrominated species could only be seen in the case where the concentration of HPIA was increased by three times (see the previous section).

Although there seemed to be a limitation on the use of the resin adsorption technique on the samples that contained high level of bromide, the error obtained from the absent brominated species only accounted for approximately 10–12% when compared with the total THMFP obtained from the raw water sample. This level of inaccuracy should be tolerable compared with the errors associated with the fractionation procedure or THMFP test.

A more significant deviation of THMFP results was observed in the test for the THMFP for each organic fraction. Table 3 indicates that THMFP of

the RW was far lower (almost 100% lower) than that of the FS. The results demonstrated clearly that this deficiency was due to the chloroform species as the chloroform generated from the FS was as great as $582 \mu\text{g L}^{-1}$, whereas that of RW was only $262 \mu\text{g L}^{-1}$. By adding the six fractions together, the chloroform formation was reduced greatly from 582 to $291 \mu\text{g L}^{-1}$ (as obtained from the MS sample). The level obtained from the MS sample was in the same level as that of RW. This demonstrated that there must exist some inhibition effect on the formation of THMs when the six organic fractions were present together in the same sample during the chlorination process.

CONCLUSIONS

Water samples from the Bangkhen water treatment plant were analyzed to examine the potential that THMs were formed during the chlorination process. This work revealed that HPIN and HPOA, were the main precursors for THMs, although they might not be the most active. The key THM component obtained from these organic fractions was chloroform, which accounted for as much as 52 wt% of the total THMs. On the other hand, most brominated species were found to occur from the chlorination of other organic components. Interestingly, experiment results indicated that bromide levels in the fractionated samples were not the same as that of the original water source as the different resins possessed different affinity for bromide. It was the last resin in the procedure (WA-10) that was observed to have great affinity for bromide, and therefore a very high bromide level was detected in the HPIA fraction eluted from this resin. It was demonstrated that although the different bromide adsorption capacities from each resin could lead to some confusion in the interpretation of the results, its associated error was shown not to be significant. A more important finding regarding the fractionation method was on the kinetics of the formation of THMs. The results clearly illustrate that an individual organic fraction had greater capability in forming THMs from the reaction with chlorine than the mixed samples.

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