

Characterization of precursors to trihalomethanes formation in Bangkok source water

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Abstract

Resin adsorption techniques using three types of resin (DAX-8, AG-MP-50, and WA-10) were employed to characterize the raw water (RW) from the major 3 million m³/day (793 million gal/day) drinking water treatment plant in Bangkok, Thailand. The dissolved organic carbon (DOC) mass distribution sequences of the six organic fractions in raw water, from high to low, were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid (HPIA), hydrophobic neutral (HPON), hydrophilic base (HPIB), and hydrophobic base (HPOB). HPIN and HPOA were the two main precursors for trihalomethanes formation (THMFP) in this water source following chlorination. The chlorination of HPON and HPIN fractions only led to the formation of mostly chloroform, while other organic fractions formed both chloroform and bromodichloromethane. The linear dependency between each organic fraction concentration and THMFP indicated that the reactions of each organic fraction with chlorine were first-order.

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1. Introduction

Often, surface water is reported to contain organic matter derived both from natural degradation of some organic substances within the ecological systems and from human activities. Organic contaminants in surface water are different from location to location due to the differences in the

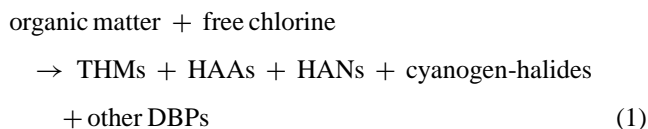
ecosystem and the activities of human beings in each specific location. This organic matter cannot easily be captured using normal water treatment techniques such as coagulation, and therefore it can enter the municipal water treatment system and then distributed through the water supply network. Moreover, during the disinfection process with chlorine, which is a common treatment technique in municipal water supply facilities, the organic matter could potentially be converted to potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). THMs are identified as potential adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the disinfectants/disinfection by-products (D/DBP) rule (with a maximum contaminant level of 0.04 mg/L). THMs are usually measured in terms of the sum of four methane

Abbreviations: RW, raw water; NOM, natural organic matter; DBPs, disinfection by-products; THMs, trihalomethanes; HAAs, haloacetic acids; HAN, haloacetonitrile; THMFP, trihalomethane formation potential; DOC, dissolved organic carbon; TOC, total organic carbon; TOXFP, total organohalide formation potential; HPIA, hydrophilic acid; HPIB, hydrophilic base; HPIN, hydrophilic neutral; HPOA, hydrophobic acid; HPOB, hydrophobic base; HPON, hydrophobic neutral

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derivatives, i.e. chloroform, bromodichloromethane, dibromochloromethane, and bromoform concentrations. The general reaction of organic matter with chlorine can be expressed as follows [1]:



To better understand the formation kinetics of THMs, one can characterize the organic matter. The differentiation between each organic species might not be practical and therefore several past researches focused on grouping the organic matters into several common groups according to the physical/chemical properties of organic species, e.g. size, polarity, molecular weight, etc. Resin adsorption has lately been successfully employed as a successful fractionation technique for organic matter. Generally, DAX-8 resin was used to fractionate dissolved organic matter (DOM) into hydrophobic and hydrophilic fractions [2–5]. With a proper arrangement of a few adsorption resins, Leenheer [6] could separate DOMs into six organic fractions, i.e. hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), and hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). This technique was then employed for the characterization of other water sources [7–9]. The fractionation allowed a thorough investigation of the formation of THMs from the organic matters in water sources. For instance, hydrophobic fraction was often found to have higher THMs reactivity than the hydrophilic [3]. Korshin et al. [7] tested total organo-halide formation potential (TOXFP) of water samples. The hydrophobic acid fraction exhibited the highest level of TOXFP, and TOXFP decreased in the order from HPOA > HPIA > HPIN. Marhaba and Van [8] reported that hydrophobic base fraction was the most reactive in the formation of THMs followed by the hydrophilic acid fraction. Chang et al. [5] demonstrated that 76% of dissolved organic carbon (DOC) was the hydrophilic and hydrophobic acid fractions and it was the hydrophobic acid fraction that exhibited the greatest ability in the formation of THMs.

Lately, Marhaba et al. [10] modified the technique proposed by Leenheer [6] by replacing one of the resins to reduce the contamination from the back elution of the organics. This allowed a more reliable result of the fractionation particularly for the water source that contained low levels of total organic carbon (TOC), less than 5 mg/L.

The main purpose of this paper was to investigate the mass distribution of dissolved organic fraction and their relationship with THMFP using the adsorption technique proposed by Marhaba et al. [10]. The water samples were taken from the Bangkhen Water Treatment Plant (Bangkok, Thailand), which takes raw water (RW) from the Chao Phraya River, the main river in Thailand. This plant is the largest water supply facility (from the total of three water supply facilities) in Bangkok, and produces about 3 million m³/day (793

million gal/day). The characterization of this water source will be useful in the future management of this water treatment facility which services the millions of people living in Bangkok.

2. Methodology

Experimental work herein follows the steps specified in Fig. 1 and is detailed as follows. Note that: Milli-Q water (ELGA, Ultra Analytical) was used for all dilutions, samples and chemicals preparation, and final glassware cleansing in this work.

2.1. Sample collection and preservation

The collection of raw water sample was only performed once, with 400 L of sample being collected on 5 August 2003. This water sample was used for all experiments in this work.

Samples were prepared by filtering through a 0.45 µm membrane and stored in a cold room with a temperature controlled at 4 °C before and after fractionation.

2.2. Fractionation

The resin adsorption procedure as proposed by Marhaba et al. [10] was used to classify DOC into six fractions; HPOA, HPOB, HPON, and HPIA, HPIB, and HPIN by using three types of resin (DAX-8, nonionic resin (Supelco), AG-MP-50, cationic resin (Bio-Rad), and WA-10, weak anionic resin (Supelco)). Only one sample was obtained for each organic fraction, and each sample was then diluted to four concentration levels for the THMFP tests. The fractionation follows the steps below (see also Fig. 2):

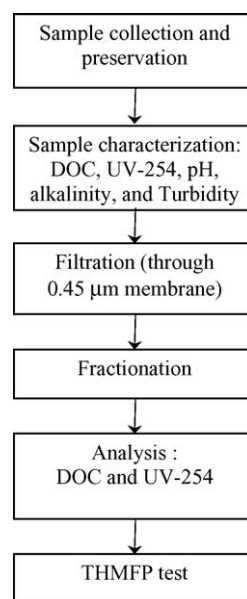


Fig. 1. Experimental procedure.

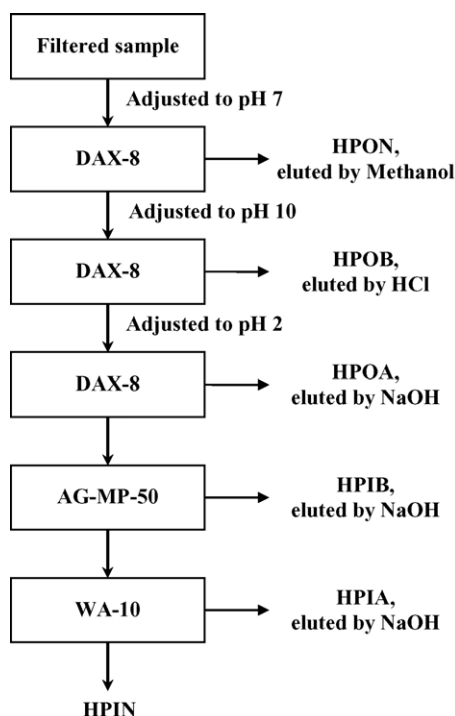


Fig. 2. Fractionation procedure.

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 2 N 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 0.1 N HCl at 0.25 bed volume and 0.01 N HCl at 1.5 bed volumes.
3. The effluent was then acidified to pH 2 with 6 N H₂SO₄ and passed through the last DAX-8 resin packed column. The hydrophobic acid fraction was eluted from resin with 0.1 N NaOH at 0.25 bed volume and 0.01 N 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 1 N 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 0.1 N NaOH at 1.5 bed volumes and 0.01 N NaOH at 1 bed volume.

2.3. Trihalomethane formation potential (THMFP)

As stated in the previous section, each fractionated sample was diluted to four concentration levels prior to the THMFP test. The four concentration levels included the original concentration, and the rests were half, twice, and three times the original. For a quality control of the experimental results,

the THMFP test was triplicate to minimize the error from the experimental procedure. THMFP test were carried out according to the 7-day chlorine test procedure available in the Standard Methods 5710B [11]. The neutralized solutions were buffered by a phosphate solution prior to the incubation at 25 ± 2 °C in amber bottles with PTFE liners. At the end of 7 days reaction period, samples must have a remaining free chlorine residual of between 3 and 5 mg/L. THMs were extracted with pentane according to the procedures mentioned in the Standard Methods 6232B [11]. THMs were then analyzed by the gas chromatography (GC) with electron capture detector (ECD) (series 6890 Agilent with DB 624 column, J&W Science) with the operating conditions as provided in Appendix A.

2.4. Analytical methods

The DOC was measured from the filtered sample using the TOC analyzer (OI Analytical model 1010, 1051) followed the Standard Methods 5310-C [11]. 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 was run every three samples to clean the system.

UV-254 (absorbance of ultraviolet 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 [12]. UV-254 was measured with a Genesys 10 UV thermo-spectronic with a 1 cm quartz cell. All fractionated samples were adjusted to pH 7 by NaOH or H₂SO₄ prior to the measure of DOC and UV-254. Specific ultraviolet absorbent (SUVA) could subsequently be estimated as the ratio between UV-254 and DOC of the same water sample.

In this work, bromide content was measured by using an ion chromatography instrument (DIONEX, ICS-2500).

3. Results and discussion

3.1. Characterization

The results from the analysis of the water samples and from the fractionation are illustrated in Fig. 3. The DOC mass distribution sequences of the six organic fractions in raw water from high to low were HPIN, HPOA, HPIA, HPON, HPIB, and HPOB. It can be seen that the total weight of all organic fractions was about 9% more than the original weight in the water sample. This weight surplus may have come from resin bleeding during the elution process [6]. This level of inaccuracy was considered acceptable as this fractionation technique was often reported to give as much as 10–15% tolerance of DOM recovery [13,14]. Variation from 8 to 12% was also reported by Croue et al. [15].

The results from Fig. 3 revealed that hydrophilic neutral (HPIN) fraction was the major component in the water sample (45%) whilst the hydrophobic acid (HPOA) was the second

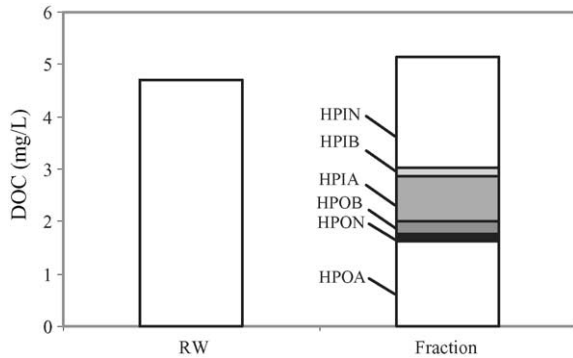


Fig. 3. DOC of raw water (RW) sample and its associated organic fractions.

(34%). These two fractions alone constituted as much as 79% of the total organic content. The remaining of the organic fractions were HPIA (18%) and HPON (6%) whereas the last two fractions (HPIB and HPOB) existed in slight quantity (each at 3%). Comparative evaluation of these results along with the reported data from literature was provided hereafter.

3.2. THMFP

Percentage distribution of THMFP of each organic fraction is shown in Fig. 4. The first two main precursors of THMFP were found to be HPIN and HPOA with 32 and 21% by weight of THMFP obtained from these two fractions, respectively. HPIA, HPOB and HPIB produced the same level of THMFP at around 13–15% by weight, whereas HPON was found to give the smallest quantity of THMFP. The THMFP results of each fraction were evaluated against the other reported data in the following subsections.

Fig. 5 illustrates the comparison between the total THMFP and the specific THMFP from each organic fraction. The total THMFP was defined as the ratio between THMFP from each organic fraction and DOC of the water sample. This was to give an overall picture of how THMs were formed in the water sample. The specific THMFP, on the other hand, was the ratio between THMFP and DOC of each organic fraction. This facilitated the analysis of the reactivity of each organic fraction on the formation of THMs. The total THMFP was derived from each organic fraction with HPIN being the main source whereas HPOA the second. This finding was not

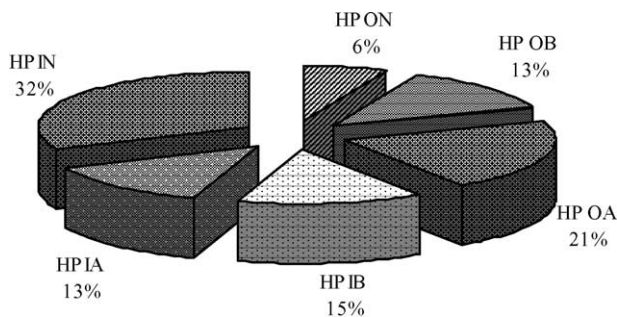


Fig. 4. Percent distribution of THMFP obtained from each organic fraction.

surprising as these two fractions were the two main organic components (79%) in this water source. Other fractions could be ordered according to their capability in forming THMs from high to low as: HPIB, HPOB, HPIA, and HPON, respectively. It should be mentioned, however, that, although organic fractions with larger quantity could potentially lead to more THMs formed during the chlorination, the reactivity of such organic fractions might not follow the same trend. The results from the analysis revealed that the main precursors of THMs in this water source were not observed to be the most active THM precursor, and rather, they were among the most inactive as discussed further below.

3.2.1. HPOA and THMFP

The concentration of HPOA was found to be about 34% (DOC 1.62 mg/L) in raw water and this was capable of producing 21% by weight of THMs (see Figs. 3 and 4). This level was found to be in the reported range of 8–68% in raw waters elsewhere [1,7,13]. In terms of the total THMFP, this fraction was the second most important source and it was the main source of THMFP among the hydrophobic species. However, according to its specific THMFP, this fraction was one of the least active sources (see Fig. 5). This implied that HPOA was the major precursor of THMFP simply because it was presented in large quantity in raw water. This finding was found to be different from other reports. For instance, Chang et al. [5] demonstrated that HPOA fraction was the greatest precursor for disinfection by-products, particularly THMs. This might be due to the differences in the character of the organic species in the water samples.

3.2.2. HPOB and THMFP

This fraction was observed to give the highest specific THMFP at 619 $\mu\text{g}/\text{mg}$. This indicated that HPOB was highly reactive with chlorine in forming THMs. This corresponded well with the report of Marhaba and Van [8]. More importantly, Marhaba and Van [16] reported that this fraction could not be effectively removed by coagulation from the raw water. For this reason, this fraction could be used as one of the

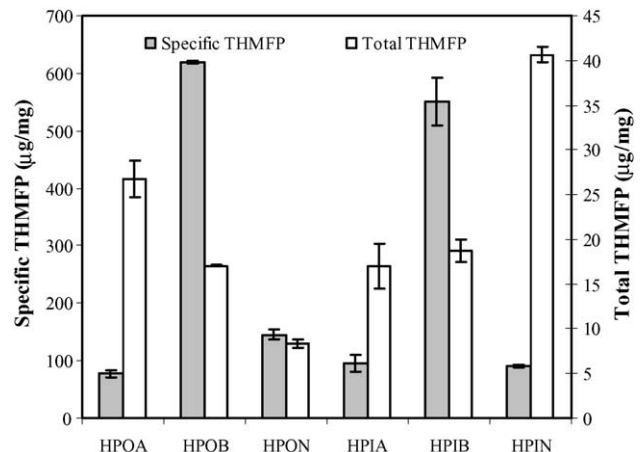


Fig. 5. Specific and total THMFP.

warning signals of THMs in the treatment process. However, in this case, its relatively low total THMFP suggested that this fraction did not exist in large quantity with only 3% by weight of the DOC content in the raw water. This finding was similar to other reports which indicated that the range of HPOB in other water sources was in the range of 0–22% by weight [1,13,7].

3.2.3. HPON and THMFP

HPON was the least problematic precursor to THMs in the water sample as its contribution to the total THMFP was the lowest among the six organic fractions, and it also was relatively inactive to the reaction with chlorine (low specific THMFP). Hence, this fraction was not considered as a problematic precursor for THMs in this water source. In addition, HPON in the water sample existed in a relatively lower quantity (only 6%). The reported data on the quantity of HPON in other water sources were quite variable with the smallest of 0% [7] to the largest of 36% [6]. Other reported data [5,8,16] indicated that this organic fraction did not exhibit high specific THMFP when compared to other organic fractions, which agreed well with the finding in this work.

3.2.4. HPIA and THMFP

Fig. 5 illustrates that HPIA had a rather low specific THMFP compared to other organic constituents in this water sample (in the same level as HPOA and HPIN). This meant that HPIA was quite inactive in forming THMs in the chlorination process. However, the total THMFP from this fraction was quite high. This was because it existed in a large quantity in the water source (18% by weight). This result was quite different from other reports, i.e. Marhaba and Van [8,16] illustrated that HPIA was among the most active organic fraction in the formation of THMs. This was possibly due to the differences in the nature of HPIA from the different water sources. Note, however, that the quantity of HPIA obtained from this work lied within the reported range of 8–53% from other water sources [7,8,13,16]. Nevertheless, the presence of such organic species was rather significant in terms of future management of the treatment plant, as previous investigation [8] revealed that HPIA fraction was one of the most difficult components to be removed by coagulation. Therefore, with its high quantity presented in the water source, this organic species could then be considered a problematic THM precursor.

3.2.5. HPIB and THMFP

Although HPIB was only presented in small quantity in this water source, the results in Fig. 5 demonstrate that the total THMFP from this fraction was relatively high. The same figure shows that HPIB was actually the most active precursor of THMs as its specific THMFP was the second highest among the six organic fractions, and the greatest among the three hydrophilic fractions. It is therefore a major concern for the operation of water treatment plant as an only tiny amount of HPIB could lead to a formation of THMs in large quan-

ty. In addition, the coagulation/sedimentation or filtration was not an effective means in removing this organic fraction [16].

HPIB was also found to be presented in small quantity in the water source reported in [7,8,16]. However, the reactivity of this fraction was only found to be moderate by Marhaba and Van [8]. This meant that HPIB from the two water sources might consist of different organic species.

3.2.6. HPIN and THMFP

Specific THMFP as illustrated in Fig. 5 indicates that HPIN was one of the most inactive organic precursors of THMs. A similar result was reported by Marhaba and Van [8]. This was possible as Bruchet et al. [17] reported that this organic fraction was primarily composed of polysaccharides, which were not quite reactive with chlorine. However, an extremely high total THMFP was obtained from this organic fraction. This was because HPIN was the most dominant constituent among the six organic fractions in this water sample (45% DOC). This was the highest among the reported data which stated that HPIN was in the range from 5 to 19% of the total organic content [6–8,10,16]. Hence, for this particular water source, this fraction should be considered as the major concern in this water treatment facility as the main cause of THMs.

3.2.7. SUVA and THMFP

Table 1 illustrates the level of SUVA obtained from each organic fraction compared with the specific THMFP. The numbers in the table represented the average values of the parameters. The standard deviation was also added to the column to indicate the level of scattering on the experimental results. As can be observed from the previous section, the base fractions, either hydrophobic or hydrophilic properties, seemed to be the most reactive organic species with chlorine. Interestingly, these two base fractions also provided relatively high SUVA values (greater than 2 L/mg m). High SUVA was reported to imply high aromatic character [18,19] and therefore this result implied that the aromatic organic compounds were the active precursors of THMs. The HPON fraction, however, also exhibited high level of SUVA but its specific THMFP was rather low. This meant that only the aromatic content with base property that was active in the chlorination reaction and despite a high content of aromatics, the neutral

Table 1
SUVA and Specific THMFP of organic fractions

Source	SUVA (L/mg m)	Specific THMFP ($\mu\text{g}/\text{mg}$)
Hydrophobic		
Acid	1.67	77.9 \pm 6.5
Base	2.31	619 \pm 2.3
Neutral	2.59	145 \pm 8.6
Hydrophilic		
Acid	0.71	95.6 \pm 15
Base	2.50	551 \pm 41
Neutral	0.94	90.6 \pm 2.8

property of the HPON fraction did not lead to a production of THMs.

3.3. THM species formation potential

THMs evaluated for each sample were the sum of four species, i.e. chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3). The results from the evaluation of THMFP of each water sample revealed that only chloroform and bromodichloromethane were formed during the chlorination of each organic fraction. The two brominated species, i.e. dibromochloromethane and bromoform, were not detected from the method employed in this work.

Fig. 6a displays the specific chloroform formation potential (CHCl_3 -FP) and specific bromodichloromethane formation potential (CHCl_2Br -FP) obtained from each organic fraction. The trend of specific CHCl_3 -FP followed that of specific THMFP quite closely. In other words, specific CHCl_3 -FP was generated mostly from the HPOB fraction followed in order from high to low by HPIB, HPON, HPIN, HPIA, and HPOA. This was because most of the THMFP formed in the water sample was chloroform, and the bromo-species (only bromodichloromethane in this case) was only responsible for as small as 3% of the total THMFP. Fig. 6b illustrates that most

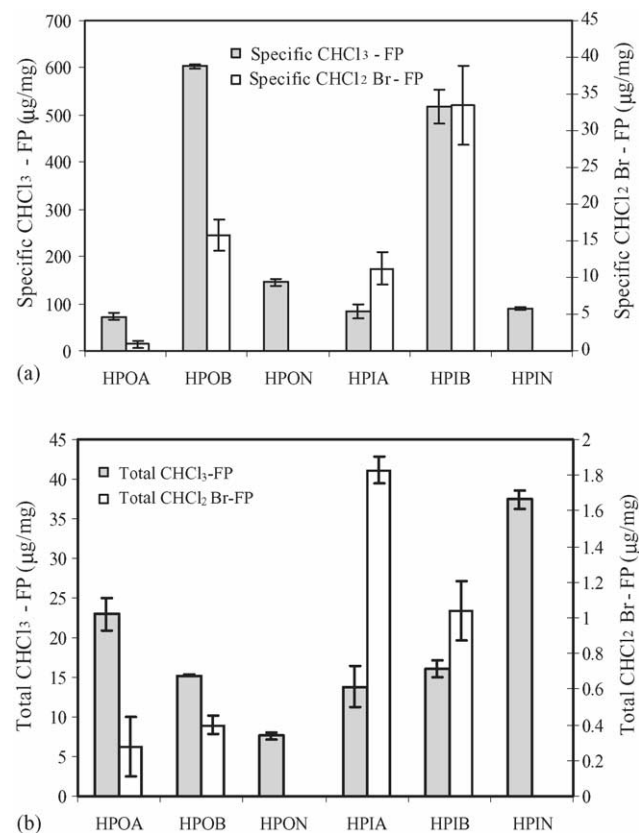


Fig. 6. (a) Specific THM species formation potential from each organic fraction. (b) Total THM species formation potential from each organic fraction.

Table 2
Bromide ion concentration in water samples

Sample	Bromide ion (mg/L)
RW	1.002
HPOA	0.002
HPOB	0.016
HPON	0.007
HPIA	0.069
HPIB	0.004
HPIN	0.000

of the THMs species in the samples was chloroform species where the total CHCl_3 -FP had the same trend as that for total THMFP. In other words, HPIN was the main source of CHCl_3 -FP, and HPOA was the second most important.

The specific CHCl_2Br -FP, however, did not quite follow the trend of the specific THMFP. The most active precursor for this THM species became the HPIB, followed by HPOB, HPIA and HPOA from high to low, respectively. HPON was found not to react with bromide at all. HPIN, however, was not found to give bromodichloromethane but the analysis for the bromide content in this organic fraction revealed an absence of bromide ion (see Table 2). Hence, it could not be concluded that bromide did not involve in the chlorination reaction of HPIN. Fig. 6b shows that the bromo-THM species was only presented in small quantity when compared to that of chloroform. Hence, unlike the case of CHCl_3 -FP, the contribution of CHCl_2Br -FP on the total THMFP was not obvious.

It is interesting to note that each organic fraction contained different amount of bromide ion as indicated in Table 2. This means that the resins used in the fractionation had different capacity in retaining bromide ions and therefore the organic eluants from the back-elution of the organic fractions consisted of bromide ion at different levels. The different bromide ions in each organic fraction might affect the species of the THMs in each fraction of water sample. For instance, HPOA was found not to be active when compared with that of HPIA, but the level of bromide ions presented in HPOA fraction (0.002 mg/L) was also significantly lower than that in HPIA fraction (0.069 mg/L). Hence, it was difficult to conclude that HPIA was more active in forming bromodichloromethane than HPOA. On the other hand, it was clear that HPOB was significantly more active in reacting with bromide ions than other species as there was only a relatively small level of bromide ions in this organic fraction (0.016 mg/L). However, the amount of brominated THM species only accounted for as much as 12% of the total THMs, and our preliminary results (not shown here) also revealed that the influence of bromide concentration (in the range found in the work) on the formation of the various THM species was at most 12%. Hence, the effect of bromide ion concentration was not included in this discussion.

3.4. Relationship between DOC and THMFP

Further investigation was conducted to examine the relationship between the level of organic content and the THMFP

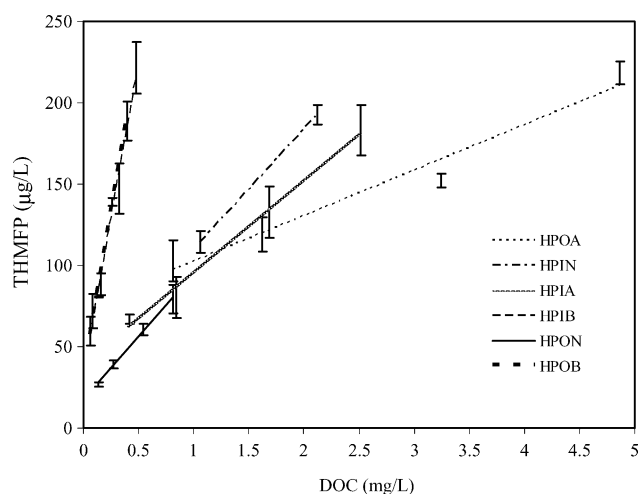


Fig. 7. THMFPP of each organic fraction.

from each organic fraction. Hence, each organic fraction was diluted to four concentration levels, each of which was tested for its THMFPP. The results are displayed in Fig. 7. Linear relationships were found in all cases with the correlations between THMFPP and the DOC of each organic fraction as follows:

$$Y_1 = 27.955X_1 + 74.644(R^2 = 0.966, N = 11) \quad (2)$$

$$Y_2 = 405.85X_2 + 31.363(R^2 = 0.998, N = 12) \quad (3)$$

$$Y_3 = 76.502X_3 + 17.845(R^2 = 0.996, N = 11) \quad (4)$$

$$Y_4 = 56.865X_4 + 38.193(R^2 = 0.993, N = 11) \quad (5)$$

$$Y_5 = 379.04X_5 + 33.665(R^2 = 0.986, N = 12) \quad (6)$$

$$Y_6 = 75.675X_6 + 31.535(N = 7) \quad (7)$$

where Y_{1-6} are the THMFPP of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively ($\mu\text{g/L}$), and X_{1-6} are DOC of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN, respectively (mg/L).

The number of data points used to construct Eqs. (2)–(6) was equal to twelve as there were four concentration levels and the test at each level was triplicate. However, those out-of-range data points were removed in some circumstances and therefore the number of samples was some time reduced to eleven. In addition, the HPIN fraction could not be prepared in a highly concentrated form and therefore there were only two concentration levels available for the construction of such relationship with THMFPP. This made the total sample number of six and with an extra set of experimental data conducted in the formulation of Eq. (7), the total number of samples for this equation became 7. Overall, the linear dependency between the various organic species and THMFPP indicated that the reactions between these organic fractions with chlorine were

first-order, at least for the range of concentrations and source water reported in this work.

4. Conclusion

The investigation illustrated the organic characteristics of the water from the Bangkhen Water Treatment Plant, which is the main water supply facility in Bangkok, Thailand. The dominant organic fractions in this water source were HPIN and HPOA. THMFPP obtained from these two fractions were also found to be in largest quantities when compared to other species. However, the results indicated that the most active precursors for THMFPP were not the species that were present in large quantity, but were HPOB and HPIB. These two species were also found to be quite active in forming chloroform species but the brominated THM species was found to be derived mostly from HPIB and HPOB. The information obtained from this work can be further employed in the design of the control technique and management strategies for the water treatment plant. For example, the choice of coagulant aids might be chosen to ensure the selective removal of the target organic precursors. Finally, it should be mentioned, however, that the conclusion obtained from this work was only based on the quality of the water source during the collection period (August 2003). Future work should therefore be conducted to investigate the effect of seasonal variation on the quality of organic matters and their THM formation potential.

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Appendix A. GC condition for the determination of THMs

Manufacture name/model	Agilent 6890 series
Column	DB 624, J&W Science
Detector	ECD
Injection temperature	225 °C
Initial temperature	75 °C
Temperature program	–15 °C/min to 100 °C holding time 1 min –15 °C/min to 130 °C holding time 1 min –15 °C/min to 180 °C holding time 1 min
Final time duration	11 min

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