Trihalomethanes formation potential of shrimp farm effluents

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Abstract

Shrimp farm effluents along the Bangpakong River in the Chachoengsao Province of Thailand were evaluated for their trihalomethane formation potential (THMFP) and related parameters. The dissolved organic carbon (DOC), salinity and bromide ion concentrations of shrimp farm effluents were in the ranges of 12–14 mg/L, 0.1–14.5 ppt, and 0–14 mg/L, respectively. The dissolved organic matter was fractionated into hydrophobic and hydrophilic fractions having a range concentration of 3–5 and 8–10 mg/L, respectively. The THMFP for all shrimp farm effluents analyzed was in the range of 810–3100 µg/L. The hydrophilic organic fraction was found to be a more active precursor of trihalomethanes (THMs) with 700–966 µg/L THMFP obtained from this fraction, while only 111–363 µg/L THMFP was derived from the hydrophobic fraction. The experimental results showed that salinity and bromide played crucial roles in the formation of THMs. At low salinity and bromide levels, chloroform was the dominant THM species, whereas at high salinity and bromide levels, bromoform became the dominant species. A Fourier Transform Infrared (FTIR) spectrum analysis of the samples before and after chlorination illustrated that the functional groups involved in the THM formation reaction were phenolic compounds, amines, aromatic hydrocarbons, aliphatic bromo-compounds, and aliphatic chloro-compounds.
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1. Introduction

Low-salinity shrimp farming is one of the most commonly applied shrimp culture techniques in Thailand [1–3]. Approximately, 40% of Thailand's cultured shrimp production came from 22,455 ha of inland shrimp farms [4,2]. Despite the success of shrimp culture, the unplanned and uncontrolled expansion of shrimp farming into inland-freshwater areas has raised several environmental issues, such as the contamination of surface and ground water by organic matter and chemicals used in shrimp culturing (a rough estimate of the water consumption of shrimp farms per 1 ha per one crop is 9000–33,000 m³/ha, [2,5]). Another hidden problem, but significant in terms of public health, is the increasing risk of having potentially carcinogenic contaminants, such as trihalomethanes (THMs), in the potable water due to the release of potential THM precursors from shrimp farm effluents into source waters.

Past research works indicated that the chlorination of natural water containing organic matters could lead to the formation of harmful disinfection by-products such as THMs [6–9] and haloacetic acids (HAAs) [10–12]. THMs, in particular, are known to have the potential to cause cancer, harmful reproductive effects, and kidney, liver, and mental disorders [13–18]. For this reason, several researchers have investigated the potential of the formation of such compounds. THMs formed during the chlorination process not only quantitatively but also qualitatively depend on the characteristics of the water source, particularly the type of organic/inorganic components. Often natural water sources rich in organic carbon were found to have a higher potential to form THMs [19]. Some specific organic species such as 3,5-dihydroxybenzoic acid, resorcinol, orcinol, and 1,3-dihydroxybenzenes were reported to result in high levels of THMs [20–23]. Inorganic species, such as the bromide ion, were also reported to have a significant effect on the formation of

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brominated THM species [24]. In general, the three conditions most suitable for the formation of THMs were reported to be: (i) high pH, (ii) high chlorine dosage, and (iii) a long period of chlorine contact time [25–28].

THM formation potential (THMFP) is often the term employed to indicate the amount of THMs that could be produced during the chlorination process. The tests for THMFP can be quite tedious and time-consuming [29]. For this reason, attempts have been made to examine the relationships between various potential surrogates and THMFP. THMFP was found to be influenced mainly by the types of organic matters in the water sample. Generally the type of organic matters is identified by several parameters such as dissolved organic carbon (DOC), ultraviolet absorption at a wavelength of 254 nm ($UV_{254\,nm}$), and specific ultraviolet absorbance (SUVA), which is the ratio between UV_{254} and DOC [30–39]. However, the relationship between each surrogate and THMFP was often specific to each particular water source, i.e. the relationship at one water source might not be suitable for the others.

Shrimp farms are contaminated with organic constituents from the feeds and shrimp excretion. The release of shrimp farm effluent into the Bangpakong River therefore increases the risk of exposure to the potential carcinogenic compounds since there are 8375 ha of shrimp farming area in Chachoengsao Province [40,5]. Hence, there is a clear need for the investigation of this issue which became the main purpose of this work. The three specific objectives of this research were as follows: (i) to measure the THMFP of shrimp farm effluents collected from different shrimp farms located along the Bangpakong River, Chachoengsao Province, (ii) to examine the parameters which have an influence on THMFP, with a special focus on the effects of organic matter, salinity, and bromide ions and to find the correlation between those parameters and THMFP, and (iii) to identify the functional groups that could be involved in the formation of THMs.

2. Experimental and analytical methods

2.1. Sample collection

All samples were collected from inland shrimp farms located in the Bangpakong Watershed of Chachoengsao Province (Fig. 1), from May 2003 to November 2003. About 10–15 L samples were collected at the effluent points (grab sampling) in amber glass bottles with TFE-lined screw caps on a harvest day when the entire volume of the pond was discharged. Note that the culture period, which is the length of time period for farmers before the harvest, ranged from 90 to 140 days as indicated in Table 1. Samples were immediately analyzed for the various parameters required in the study. Milli-Q water was used for dilution, solution preparation, and final glassware washing.

The samples from the Bangpakong River were also collected (via grab sampling). The sampling points were distributed along the length of the river in the vicinity of the shrimp farm area as shown in Fig. 1. This was to evaluate the differences in the THMFP in the river from the upstream to the downstream.

2.2. Isolation and fractionation

The fractionation method employed here followed the procedure proposed by [41]. Each sample was filtrated through 0.45 μm cellulose nitrate filter paper to remove all suspended solids. The filtrated water was then fractionated into two fractions, hydrophobic and hydrophilic, using XAD-8 resin (a macroporous methylmethacrylate copolymer). The resin was prepared for use by immersing it in 0.1N NaOH for 24 h during which time, the floating resin was decanted off. This resin was then rinsed with Milli-Q water to remove all NaOH. Prior to fractionation, the resin was further purified in the soxhlet set with acetone and hexane for 24 h, respectively. Subsequently, the resin was rinsed with methanol and packed into the column. About 0.1N NaOH, 0.1N HCl, and Milli-Q were consequently passed through the column. The resin was ready for use only when the DOC and conductivity of the effluent from the column at this stage were less than 0.2 mg/L and 10 μs cm^{-1}, respectively. Filtered water was acidified to pH 2 with 0.1N H_2SO_4 and pumped through the column at 30 bed volume/h. XAD-8 retained the hydrophobic fraction, allowing the hydrophilic to pass through. The hydrophobic fraction was then back eluted with 0.1N NaOH (1.5 bed volume) and 0.01N NaOH (one bed volume). All fractions were preserved at 4 °C.

2.3. Organic carbon analysis and ultraviolet absorbance

THM precursors were analyzed in terms of their organic carbon content by using the TOC analyzer (O.I. analytical college station Texas model 1010). The analytical method followed standard method 5310-C, wet oxidation [28]. Potassium biphathalate (KHP) at 2.5, 5, 10, and 15 mg/L were used for preparing the calibration curve. The two reagents, 5% (v/v) phosphoric acid and 100 g/L sodium persulfate, were re-prepared every 2 weeks. The TOC analyzer was set in accordance with the suggestions from the manufacturer, i.e. 10 min reaction time with 1000 μL of sodium persulfate and 200 μL of phosphoric acid. The measurements for $UV_{254\,nm}$ (cm^{-1}) absorption were performed using a UV spectrophotometer (Helios Alpha Thermo Electron Corporation).

2.4. Bromide ion

The analysis of bromide ions was performed in accordance with EPA method 300.0A, before and after the THMFP tests, using the Dionex ICS-2500 Reagent-Free Modular IC System connected with an EG 50 Eluent Generator (with ASI-100 autosampler). KOH at 100 mM was used as the eluent. The bromide standard curve was prepared from the standard NaBr solution at 1000 mg/L.

2.5. Functional groups

The functional groups of the organic fractions were detected by using Fourier transform infrared spectrometry (FTIR-Perkin-Elmer 1760X). The samples were freeze-dried and mixed with
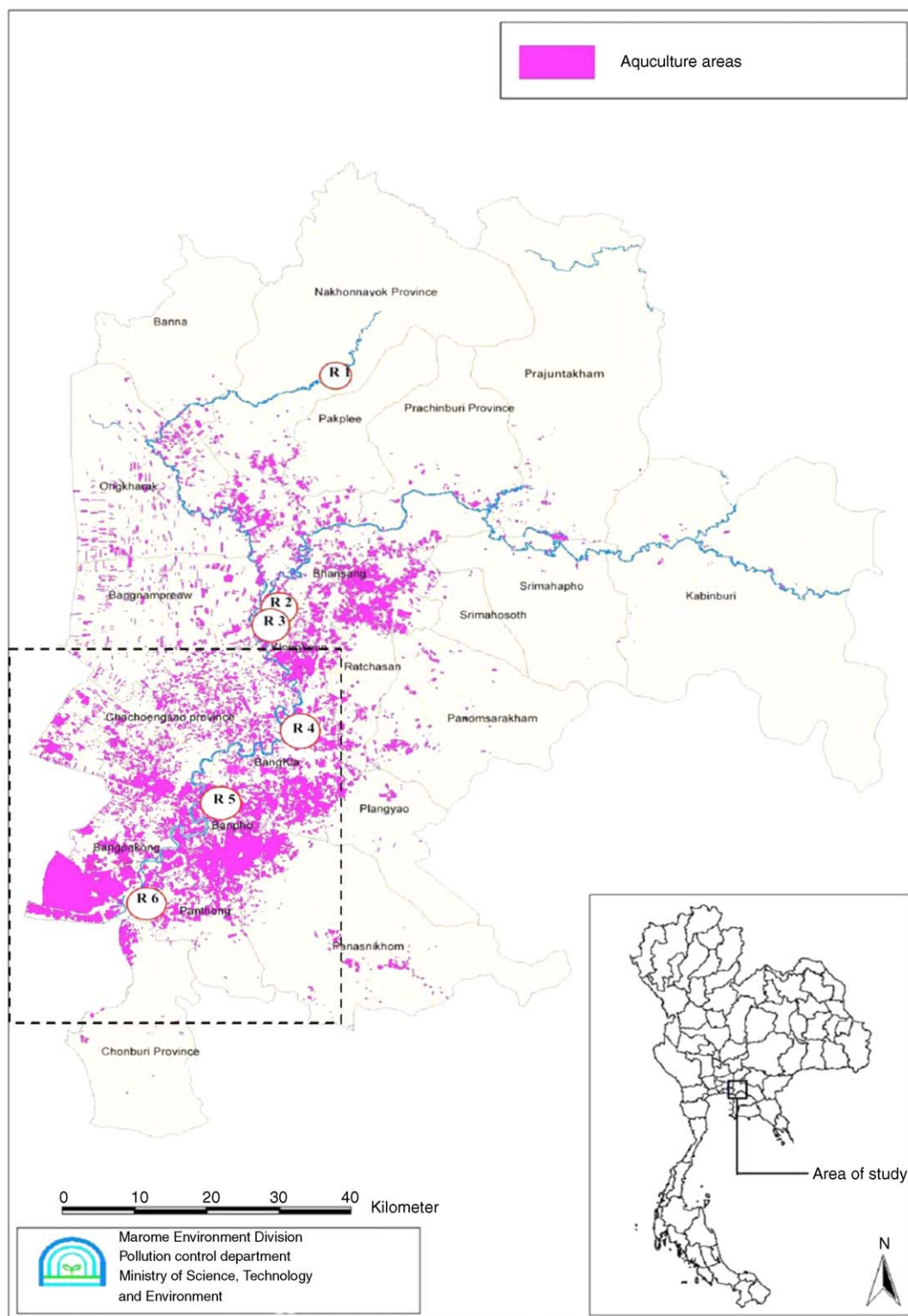
Fig. 1. Locations of the study area and six sampling points along the Bangpakong River.

potassium bromide pellets. FTIR was set to scan from 4000 to $400\,cm^{-1}$, averaging 8 scans at $1.0\,cm^{-1}$ intervals with a resolution of $8\,cm^{-1}$. All spectra were normalized after acquisition to a maximum absorbance of 1.0 for comparative purposes.

2.6. Trihalomethane formation potential (THMFP)

THMFP tests were performed in accordance with standard methods 5710-B [28]. The formation potential was determined by exposing 250 mL samples (filtrated water, hydropho-

bic, and hydrophilic fractions) to an excess of oxidizing disinfectant, 12.5% (w/v) sodium hypochlorite solution, for 7 days at 25 °C. Before the incubation, samples were adjusted to pH 7. Five milliliters of phosphate buffer (a mixture of 68.1 g KH_2PO_4 potassium dihydrogen phosphate-anhydrous and 11.7 g NaOH in 1 L water) was added to the sample. Residual chlorine was measured at the end of the 7-day holding time. Only the samples with a residual chlorine concentration of 3–5 mg/L were selected for further analysis. The selected samples' residual chlorine was then removed by the addition of 0.1 mL of 100 g/L sodium sulfite. The change in the THM concentration relative to the initial concentration was determined as the THMFP. THMs were analyzed according to EPA method 551.1 by using gas chromatography equipped with an HP-1 column, micro electron capture detector. The THM mixed standard was used: a mixture of the four THM species, chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$), each at 200 and 2000 mg/mL. Pentane was used as the only extraction solvent in this method. Bromofluorobenzene and decafluorobiphenyl were employed as internal and surrogate standards, respectively. GC signals were interpreted by using the ChemStation program (Agilent Inc., USA).

2.7. Statistical analysis

2.7.1. Pearson correlation

The Pearson correlation was used to illustrate the relationship of two parameters without controlling the other parameters (zero-order correlation). The values of the correlation coefficient range from −1 to 1. The sign of the correlation coefficient indicates the direction of the relationship (positive or negative). The absolute value of the correlation coefficient indicates the strength, with larger absolute values indicating stronger relationships. The significance level (sig. or *p*-value) is the probability of obtaining results as extreme as the one observed. If the significance level is very small (less than 0.05) then the correlation is significant and the two variables are linearly related. If the significance level is relatively large (for example, 0.50) the correlation is not significant and the two variables are not linearly related.

3. Results and discussion

3.1. Water characteristics

The characteristics of the samples from the shrimp farm effluents (S1–S16) and the river (R1–R6) including dissolved organic carbon (DOC), UV, and SUVA, are summarized in Tables 1 and 2. Fig. 2 illustrates that DOC in the shrimp farm effluents was linearly related to salinity (Pearson's correlation = −0.847 and *p*-value = 0.000). The negative Pearson's correlation demonstrated that DOC decreased with an increase in salinity. This agreed well with the findings of [42] who reported that DOC in the seawater sample was often lower than that of the freshwater samples. A similar trend was also found between DOC and SUVA with a Pearson's correlation of −0.905 and *p*-value of 0.000 (Fig. 3).

Salinity of shrimp farm effluents varied from 0.1 to 14.5 ppt and bromide concentrations in shrimp farm effluents (at day 0, i.e. before THMFP test chlorination) ranged from 0 to 14 mg/L (Table 3). Salinity represents the conductivity of several ions in seawater, which farmers generally adjust to suit their needs in their culture. For this reason, a linear relationship between

Table 1

Characteristics of water samples from shrimp farm effluents (S1–S16) and the Bangpakong River (R1–R6)

Source water	Temperature (°C)	Culture period (days)	pH	Salinity (ppt)	Conductivity ($\mu s\,cm^{-1}$)	Turbidity (NTU)	Alkalinity (mg/L as $CaCO_3$)
S1 (28 May 2003)	29.8	100	8.7	0.3	680	64	75
S2 (20 June 2003)	26.1	90	7.2	1.0	1954	22	93
S3 (5 June 2003)	32.3	85	8.8	0.7	1385	16	40
S4 (10 June 2003)	33.7	120	7.6	0.6	1278	163	93
S5 (19 June 2003)	30.7	125	7.5	0.7	1433	150	65
S6 (28 June 2003)	30.2	135	8.5	1.8	3400	102	130
S7 (3 July 2003)	30.6	98	8.2	6.9	12080	58	180
S8 (12 July 2003)	32.2	135	7.4	11.8	19870	112	120
S9 (22 July 2003)	30.7	93	8.7	4.7	8450	34	65
S10 (29 July 2003)	32.3	109	9.9	0.5	1086	49	90
S11 (6 August 2003)	30.2	105	7.9	0.4	860	47	83
S12 (20 August 2003)	27.6	100	8.1	0.5	947	86	110
S13 (10 September 2003)	27.5	95	7.9	1.4	2660	27	135
S14 (26 September 2003)	29.0	96	8.2	6.4	11250	42	105
S15 (17 October 2003)	23.2	75	7.9	14.0	31700	49	55
S16 (28 October 2003)	32.3	75	6.8	14.5	24100	20	40
R1 (1 November 2003)	27.3	–	6.5	0.0	50	12	28
R2 (1 November 2003)	30.1	–	6.1	0.1	150	228	40
R3 (1 November 2003)	29.2	–	6.7	0.1	184	286	55
R4 (1 November 2003)	27.1	–	7.0	0.1	233	106	40
R5 (1 November 2003)	31.4	–	7.0	0.1	245	66	50
R6 (1 November 2003)	30.0	–	6.9	5.8	10380	53	78

Table 2
Organic carbon, UV, and SUVA of shrimp farm effluents and the Bangpakong River

Sample code[a]	Water Sources	Organic carbon (mg/L)	UV (1 cm^{-1})	SUVA (L/mg m)
S1	Filtered	10.35	0.17	1.660
	Hydrophobic	2.98	0.053	1.762
	Hydrophilic	7.15	0.083	1.160
S2	Filtered	13.95	0.189	1.358
	Hydrophobic	3.01	0.050	1.665
	Hydrophilic	10.05	0.108	1.078
S3	Filtered	13.28	0.222	1.673
	Hydrophobic	4.63	0.082	1.778
	Hydrophilic	8.50	0.091	1.066
S4	Filtered	13.26	0.267	2.015
	Hydrophobic	3.71	0.084	2.259
	Hydrophilic	8.89	0.117	1.314
S5	Filtered	12.34	0.183	1.483
	Hydrophobic	3.06	0.071	2.327
	Hydrophilic	8.43	0.096	1.142
S6	Filtered	15.46	0.282	1.824
	Hydrophobic	4.96	0.142	2.866
	Hydrophilic	9.89	0.121	1.220
S7	Filtered	8.87	0.293	3.303
	Hydrophobic	3.77	0.158	4.187
	Hydrophilic	7.24	0.175	2.417
S8	Filtered	4.41	0.244	5.533
	Hydrophobic	2.65	0.265	10.015
	Hydrophilic	3.43	0.131	3.823
S9	Filtered	10.24	0.195	1.905
	Hydrophobic	3.23	0.071	2.200
	Hydrophilic	7.89	0.101	1.281
S10	Filtered	8.30	0.146	1.759
	Hydrophobic	2.77	0.067	2.416
	Hydrophilic	5.13	0.061	1.190
S11	Filtered	12.69	0.242	1.906
S12	Filtered	13.62	0.264	1.939
S13	Filtered	12.64	0.235	1.859
S14	Filtered	3.68	0.184	5.005
S15	Filtered	3.88	0.218	5.613
S16	Filtered	4.18	0.217	5.194
R1	Filtered	2.35	0.057	2.403
R2	Filtered	5.46	0.149	2.718
R3	Filtered	5.58	0.177	3.174
R4	Filtered	4.47	0.158	3.532
R5	Filtered	7.70	0.192	2.495
R6	Filtered	2.33	0.121	5.193

[a] S: sample from shrimp farm and R: sample from the river.

salinity and bromide ion was expected since bromide is one of the abundant ionic constituents in seawater. However, the results indicated that this was not the case and such relationship was not quite strong with a Pearson's correlation of only 0.537. The possible explanation was that the composition of seawater depended significantly on the source location. Different shrimp farms might have used seawater from different sources and therefore the relationship between bromide and salinity could not be established with a high level of confidence. It should be noted that the concentration of bromide ions in the samples from the Bangpakong River were relatively low (at day 0, before chlorination in the THMFP tests) compared to the bromide ion concentration in seawater (approx. 67.3 mg/L at 35 ppt salinity; [43]).
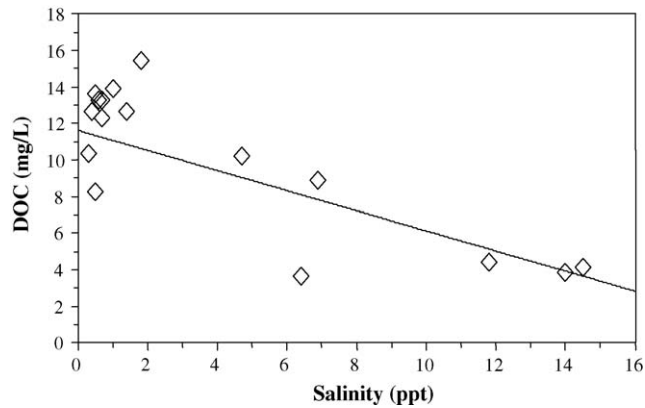
Fig. 2. Relationship between salinity and DOC of shrimp farm effluents.
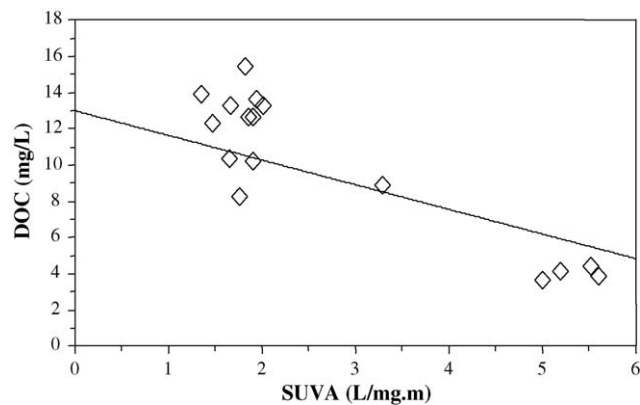

Fig. 3. Relationship between the DOC and SUVA of shrimp farm effluents.

Table 3
Bromide ion content in shrimp farm effluents and the Bangpakong River

Sample code	Bromide ion (mg/L)	
	Day 0 (before THMFP test chlorination)	Day 7 (after TFMFP test chlorination)
S1	ND	ND
S2	ND	ND
S3	ND	ND
S4	ND	ND
S5	ND	ND
S6	2.38	44.53
S7	3.52	18.02
S8	6.56	22.13
S9	2.12	23.34
S10	0.03	3.07
S11	0.27	30.58
S12	0.32	31.91
S13	1.83	41.15
S14	13.74	116.02
S15	7.81	38.56
S16	3.02	9.41
R1	0.02	0.56
R2	0.07	11.19
R3	0.67	11.17
R4	0.05	11.16
R5	0.08	19.56
R6	0.14	33.66

ND: no data.
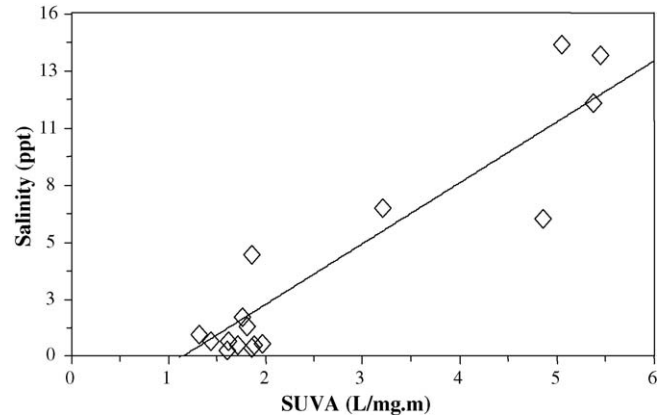
Fig. 4. Relationship between the SUVA and salinity of shrimp farm effluents.

3.2. Fractionation

It is generally accepted that the SUVA corresponds to the nature of organic matter in the water source. Samples with an SUVA ≥ 4 L/mg m have a relatively high content of hydrophobic organic compounds, while samples with an SUVA ≤ 3 L/mg m are largely hydrophilic [35,39]. According to Table 2, the SUVA of most samples was lower than 3 L/mg m, which may have led to the preliminary conclusion that hydrophilic was the main fraction in the samples. Moreover, a linear relationship between SUVA and salinity was obvious (Fig. 4) and this suggested that samples with high salinity (S7–S9, S14–S16) also contained a relatively larger quantity of hydrophobic organic matter than low salinity samples. To evaluate whether this conclusion was applicable to the samples from the shrimp farms, shrimp farm effluent no. S1–S10 were fractionated into hydrophobic and hydrophilic fractions. The results summarized in Table 4 illustrate that the hydrophilic fractions were always the dominant species in shrimp farm effluents (56–77%). This corresponds well with the preliminary conclusion mentioned earlier. Hence, two conclusions can be drawn from the experiments in this part. Firstly, the shrimp farm effluents were more abundant with hydrophilic organic compounds than hydrophobic. Secondly, high SUVA could be employed as a surrogate for the hydrophobic fraction in shrimp farm effluents.

It is worth noting that hydrophilic fractions mainly consist of carboxylic acids, carbohydrates, amino acids, amino sugars, and proteins as reported by [44]. The abundance of this hydrophilic fraction perhaps came from the additives used during shrimp cultivation such as feed and could also be from shrimp excretion. Hydrophobic fractions, on the other hand, usually contain acidic products which come naturally from the degradation of lignin, more aromatic moieties and low in organically bound nutrients such as phosphorous, nitrogen, sulfer [44].

The mass balance of each fraction was calculated in terms of percentage surplus to evaluate the effectiveness of the fractionation procedure (Table 4). The loss of DOC was found to be from 1 to 7% whereas the excess of DOC ranged from 8 to 38%. The possible reasons for the unbalance of DOC in the process of fractionation are discussed below.

Table 4
Mass balance of fractions

Sample code	DOC (mg/L)	Mass (mg)				
		DOC	Sum of fractions	Hydrophobic	Hydrophilic	Percentage of surplus
S1	10.35	31.06	30.37	8.94 (29%)	21.44 (71%)	−2.22
S2	13.95	41.84	39.18	9.03 (23%)	30.16 (77%)	−6.36
S3	13.28	39.83	39.39	13.89 (35%)	25.51 (65%)	−1.11
S4	13.26	35.81	34.64	10.20 (29.5%)	24.43 (70.5%)	−3.28
S5	12.34	24.68	22.98	6.12 (27%)	16.86 (73%)	−6.90
S6	15.46	30.92	29.68	9.91 (33%)	19.77 (67%)	−4.02
S7	8.87	17.74	22.03	7.55 (34%)	14.48 (66%)	24.15
S8	4.41	8.82	12.15	5.29 (44%)	6.85 (56%)	37.71
S9	10.24	20.47	22.23	6.45 (29%)	15.77 (71%)	8.58
S10	8.30	16.60	15.80	5.55 (35%)	10.25 (65%)	−4.84

The loss of DOC (in samples S1–S6 and S10) could be from the limitation of the fractionation procedure as small humic acid molecules could not be completely desorbed from the resin [45]. In addition, hydrophobic neutral fractions were not easily desorbed by NaOH [41], a single eluent in this work. Hence, there was always a loss of some organics during the fractionation. On the other hand, it is also possible to have an excess of DOC as observed from the results of sample S9 (samples S7 and S8 with a very DOC high surplus are discussed later). This surplus could be due to the inorganic material, acids (H_2SO_4 and HCl) and base (NaOH), added to adjust the pH and back elution [46]. This could have resulted in an elution of the resin itself into the solution and led to a weight surplus.

Moreover, for those cases with a very low accuracy on mass balance of the DOC (24 and 38% surplus in samples S7 and S8, respectively), it was observed that these cases were always found in the samples with high salinity. The error was thought to be due to a limitation on the usage of XAD-8 adsorption resin on high salinity samples. Firstly, XAD-8 could not adsorb large humic molecules (MW > 30,000) [45]. It was evident that seawater was dominated by polymeric high molecular weight compounds which had a range of molecular weights of 2000–300,000 [47]. Hence, these organic constituents might not have been well adsorbed by this resin. Secondly, chloride and bromide ions in high salinity water might interfere with the sorption of hydrophobic substances on a column [48].

3.3. Trihalomethane formation potential

The shrimp farm effluents were analyzed for their THM content and it was found that THMs could not be detected in these samples (THM_0 < detection limit). An addition of chlorine in the samples (7 days incubation period) resulted in the formation of THMs (THM_7) in the range from 810 to 3100 μg/L. The difference between THM_7 and THM_0 in a sample is considered its trihalomethane formation potential or (THMFP), and in this case, THMFP was equal to THM_7 (Fig. 5). This range of THMFP was considered a very high figure as the maximum contaminant level (MCL) for THMs in drinking water was set at as low as 80 μg/L [49]. The possible effect of a direct discharge of shrimp farm effluents could be illustrated by revealing the variation in the level of THMFP along the Bangpakong River. The THMFP
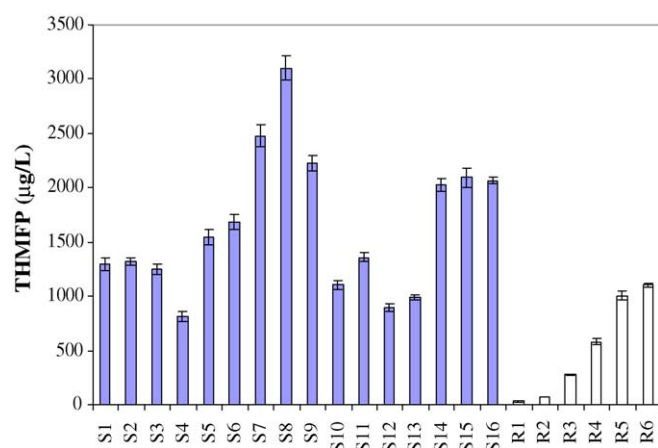

Fig. 5. THMFP of shrimp farm effluents and the Bangpakong River.

of the upstream river (R1–R3), scattered by a small number of shrimp farms, ranged from 30 to 280 μg/L whereas the THMFP values in the downstream portion of the river (R4–R6), clustered by shrimp farms, ranged from 580 to 1100 μg/L. It was clear that the downstream river samples possessed higher THMFP than those from upstream. This could well be due to the increasing number of shrimp farms from upstream to downstream. In other words, the river which acted as a reservoir for shrimp farm effluents for it was more contaminated at the downstream locations,
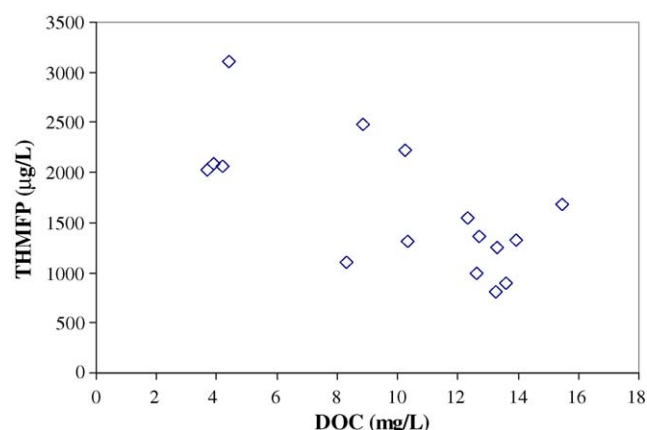

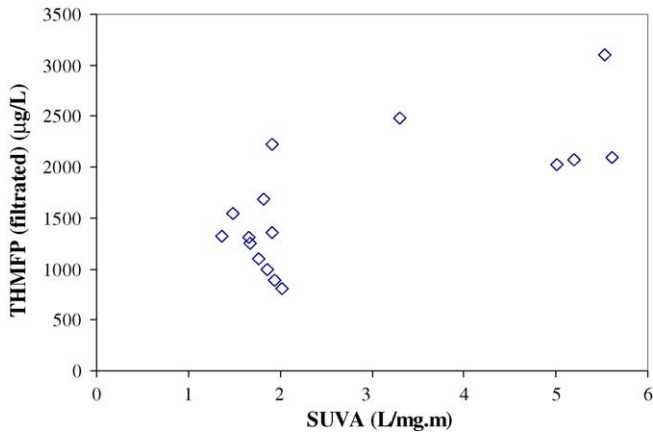Fig. 6. Relationship between the THMFP and DOC of shrimp farm effluents.

Fig. 7. Relationship between the THMFP and SUVA of shrimp farm effluents.

in the various shrimp farms might not have the same form since a higher level of DOC should have led to higher THMFP. The difference in the characteristics of DOC in each shrimp farm effluent prevented the use of organic carbon as a good indicator of THMFP.

The SUVA is often taken as a parameter that indicates the level of aromatic organic in the water. Hence, a higher SUVA should raise the level of THMFP. Fig. 7 demonstrates that this was the case, but with a relatively low level of confidence, i.e. SUVA followed the variation of THMFP with a Pearson's correlation of 0.724 and p-value of 0.002. Similarly, this indicated that the SUVA did not represent the same set of organic substances in the shrimp farm effluents.

which received a larger quantity of discharges from the shrimp farms.

3.4. Surrogate parameters for THMFP

It was not uncommon to have a direct relationship between THMFP and DOC as DOC is the main reactant for THMs. However, an analysis indicated that THMFP was negatively correlated to organic carbon with a Pearson's correlation of -0.676 and p-value of 0.004 (Fig. 6). This meant that the organic species
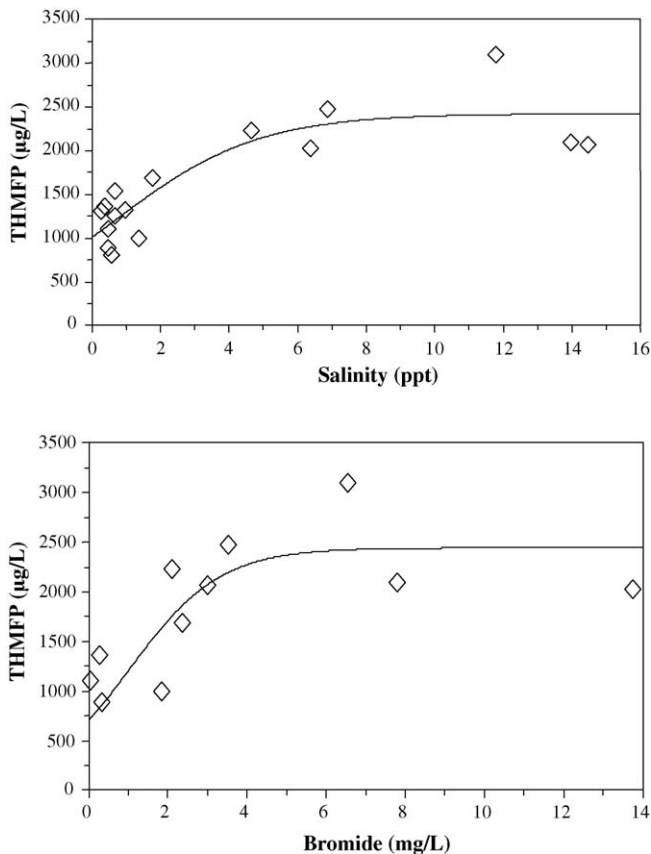

Fig. 8. Relationship between the THMFP, bromide levels, and salinity of shrimp farm effluents.
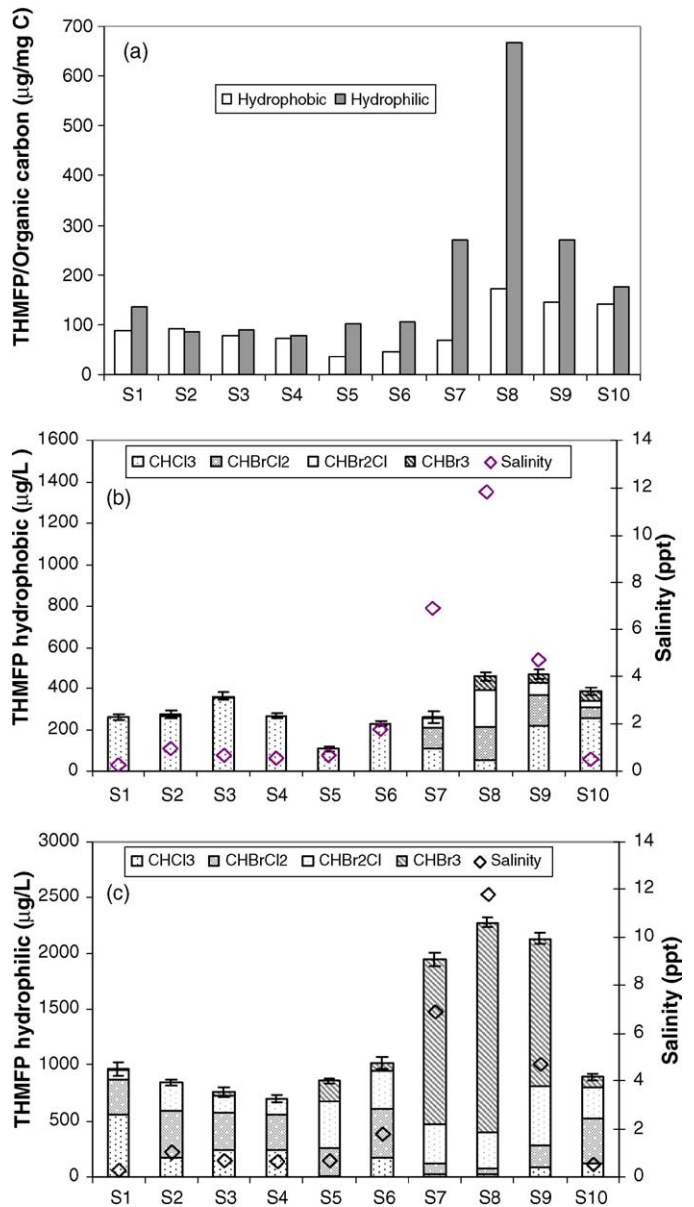

Fig. 9. Effects of the types of organic substances on THMFP: (a) specific THMFP, (b) THMFP from hydrophobic fraction, and (c) THMFP from hydrophilic fraction.

In this study DOC and SUVA were found not to be good surrogate parameters for monitoring THMFP. The differences in the sample quality may be due to the differences of additives, feeds, fertilizers, and seawater source locations. Fig. 8, on the other hand, illustrates an interesting finding as THMFP was actually found to follow the level of salinity and bromide in the water samples (not a linear dependency). This indicated that salinity and bromide might well be employed as surrogate parameters for THMFP in the shrimp farm effluents. The effect of salinity and bromide on the formation of THMs is discussed in the next section.

3.5. The formation of THMs

Fig. 9(a) shows that the specific THMFP (THMFP per unit weight of organic species) for the hydrophilic species was usually higher than that of hydrophobic species. This indicated that the hydrophilic fraction was a more reactive precursor for THMs than the hydrophobic fraction. This result might not agree with the findings of some previous studies. For example [50] summarized that the hydrophobic fraction was a major precursor of disinfection by-products (DBPs). The difference between the previous data and these experimental results might be due to the nature of the water sources. In this work, samples were obtained from shrimp farms, which were contaminated with chemicals, such as fertilizers or palletized feed, liming material, and oxidant. On the other hand, most reported data were for natural water sources usually enriched with hydrophobic than hydrophilic fractions.

Fig. 9(b) illustrates, for low salinity samples, that hydrophobic organic species always were converted to $CHCl_3$. Other THM species such as $CHBrCl_2$ and $CHBr_2Cl$ were only formed when there was an adequate level of salinity. Interestingly, most brominated THM species were converted from hydrophilic organic fractions (see Fig. 9(c)). At a high level of salinity in particular, the hydrophilic organics seemed to be very reactive with bromide ions and a large quantity of THM species with the highest proportion of bromide ions, i.e. $CHBr_3$, could be observed. It was possible that bromide ions were more reactive with aliphatic precursors, which mainly existed in the hydrophilic fractions, than with the aromatic precursors or hydrophobic fractions.

3.6. Effect of salinity and bromide ions

To illustrate the influence of salinity and bromide ions on the formation of THMs in the shrimp farm effluents, the quantity of each species of THMs formed during the disinfection process was plotted against the level of salinity (Fig. 10) and bromide ions (Fig. 11). Fig. 10 demonstrates that species with a high dose of chlorine components (chloroform and bromodichloromethane) seemed to be the main disinfection by-products. On the other hand, high salinity samples often led to a formation of brominated THMs (bromoform and dibromochloromethane). The same trend was observed with the plot between THM species and bromide ions in Fig. 11. As the quantity of bromide ions varied according to the salinity level (despite a nonlinear relationship as indicated earlier), this similarity was not unexpected. Consequently, it was clear that bromide ions
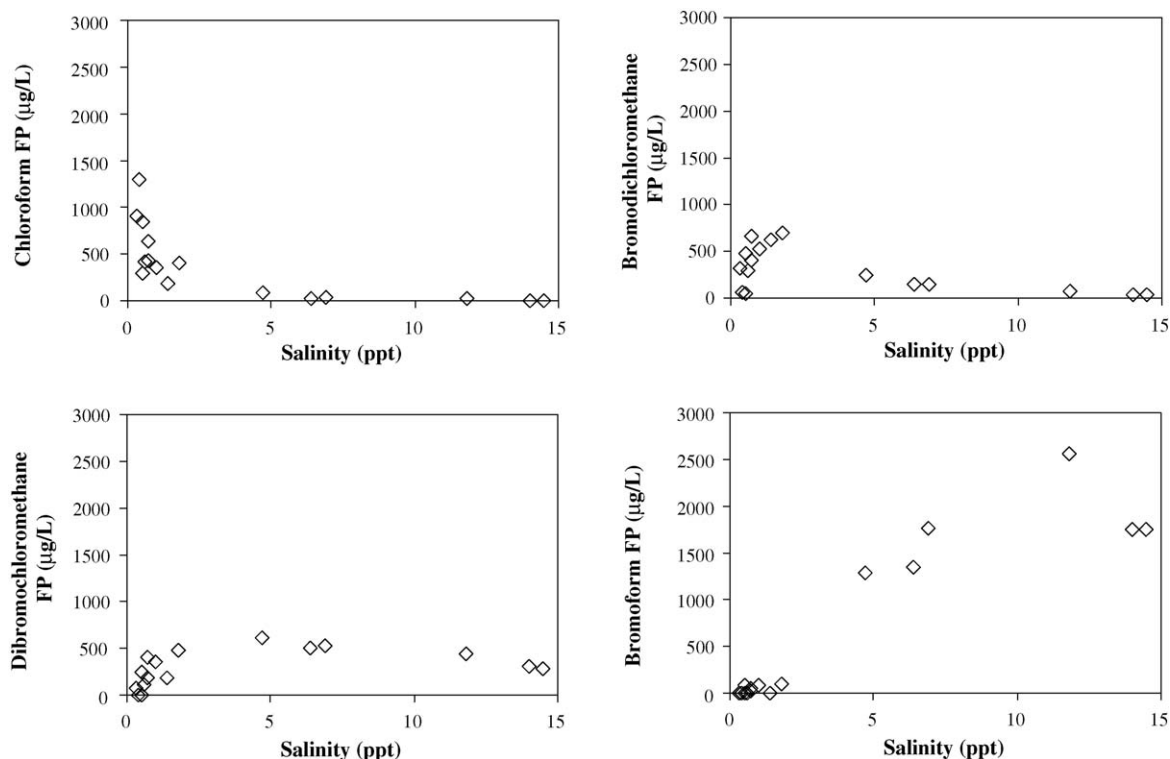

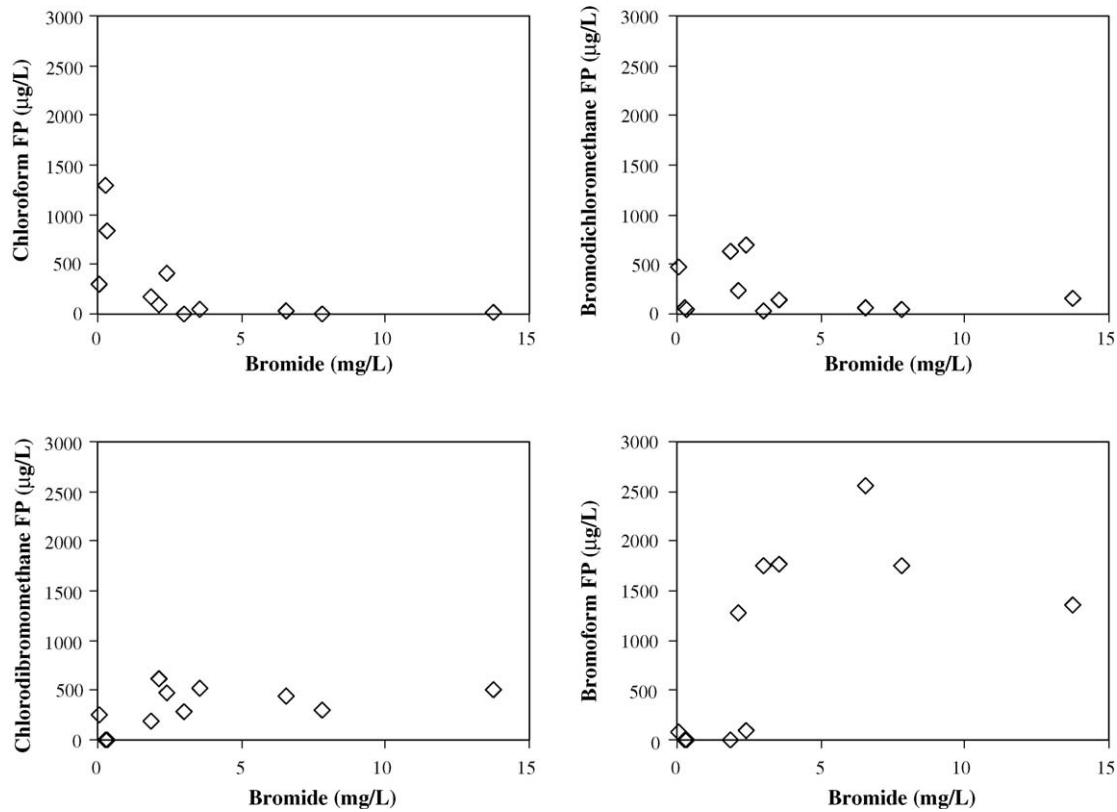Fig. 10. Relationship between salinity and each of the THM species.

Fig. 11. Relationship between bromide concentrations and each of the THM species.

played a very significant role in the formation of THMs in the shrimp farm effluent samples. This finding was in good agreement with data presented in the literature as elucidated further below.

Past work demonstrated that bromide ions were more reactive to form THMs than other related ions such as the chloride ion. This was because chlorine (NaOCl), which was added during day 7 of the THMFP tests, oxidized all of the dissolved bromide ions in the water and formed the reactive species, hypobromous acid, while free chlorine from NaOCl was almost completely hydrolyzed to hypochlorous acid [51]. Hypobromous acid reacts relatively faster with DOC to form THMs than hypochlorous acid [52–55]; thus the rate of formation of brominated THMs was often found to be greater than the formation rate of $CHCl_3$.

In addition, it was observed that bromide ion concentrations of day 7 THMFP tests were higher than that of day 0 (Table 3). This phenomenon can be explained by the reaction between NaOCl used in THMFP test and unsaturated aliphatic bromocompounds in the water sample, which finally released bromide ions into the water according to the following equation:

$$4H^+ + 4ClO^- + BrHC{=}CHBr \ \rightarrow \ C_2H_2Cl_4 + 2Br^- + 4OH^-$$

(1)
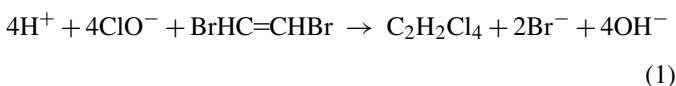
3.7. Evaluation for functional groups

FTIR results revealed that there were a total of six major functional groups in all of the samples examined here; e.g.
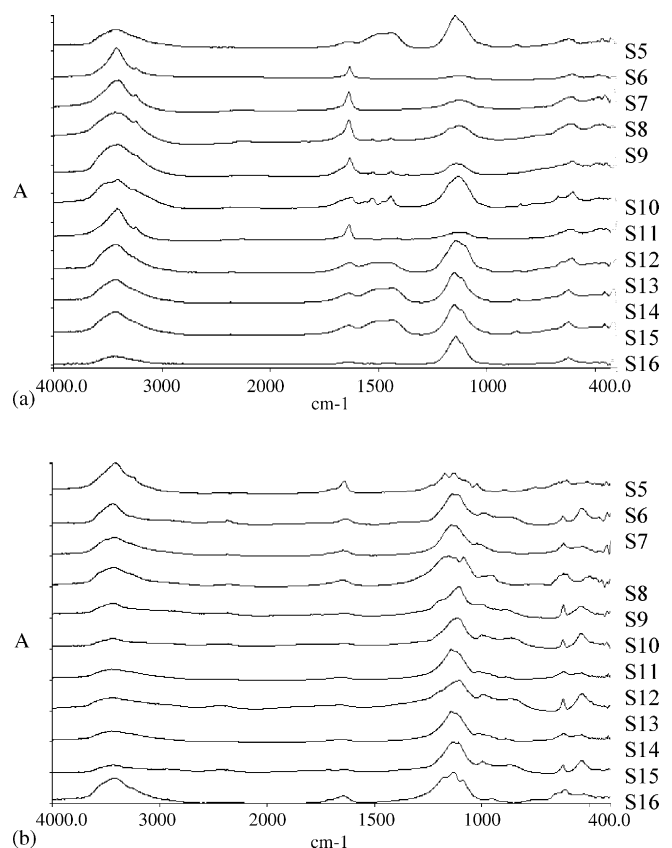

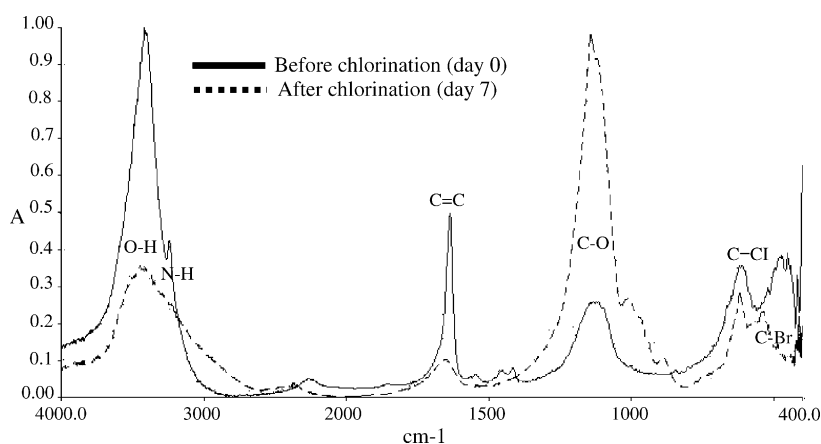Fig. 12. IR spectra of shrimp farm effluents: (a) before chlorination (day 0) and (b) after chlorination (day 7).

Fig. 13. IR spectra of shrimp farm effluents before and after chlorination (days 0 and 7).

Table 5
Summarized IR results of shrimp farm effluents

Wave number (cm^{-1})	Functional group	Changing	Typical compounds
3600–3300	O—H	Decrease	Carbohydrates, humic and fulvic acid
Near 3500	N—H	Decrease	Protein
Near 1650	C=C	Decrease	Humics, lignins
1300–1000	C—O	Increase	Carbohydrates, humic and fulvic acid
800–600	C—Cl	Decrease	Aliphatic chloro-compounds
600–500	C—Br	Decrease	Aliphatic bromo-compounds

(i) O—H (hydroxyl groups), (ii) N—H (amines groups), (iii) C=C (aromatic hydrocarbons), (iv) C—Cl (aliphatic chloro-compounds), (v) C—Br (aliphatic bromo-compounds), and (vi) C—O. Although FTIR results could not be accurately used to determine the quantity of each functional group, a comparison between the results from the same sample before and after the reaction (THMFP test) could lead to some approximated quantitative analysis of the possible associated functional groups as identified by the method. Fig. 12 (a) and (b) illustrate the absorbance of the IR spectra at days 0 and 7 of THMFP tests, while Fig. 13 provides larger scales of IR spectra at day 0 (solid line) and day 7 (dashed line). It was obvious that, at day 0, O—H presented a broad peak near 3600–3300 cm^{-1} and C—O near 1300–1000 cm^{-1}. This suggested that phenolic compounds are available in these samples. N—H was found to have a medium absorption range near 3500 cm^{-1}. It was not quite clear whether this broad region overlapped with that of O—H but it was possible that N—H was available in shrimp farm effluents as it constituted amino compounds, a major component of humic substances. A strong absorption band was found at 1650 cm^{-1}, which could imply the presence of C=C. Additionally, a medium absorption appearing on the IR spectrum at 800–600 cm^{-1} implied that C—Cl was one of the significant groups in the samples; this group is generally found in marine water. The last, a weak absorption, which appeared at 600–500 cm^{-1} could be classified as C—Br.

After the THMFP tests (dashed line), O—H, N—H, C=C, C—Cl, and C—Br were found to decrease. [56] reported that O—H is one of the main target functional groups for NaOCl in the formation mechanism of THMs. Similarly, C=C, e.g. 1,3-dihydroxybenzene, 3,5-dihydroxytoluene, and

1,3-dihydroxynaphthalene was also reported as an active functional group that could form THMs [23]. The reduction of N—H showed a good agreement with the study of [9], who revealed that the H—N bonds in the aromatic hydrocarbons were activated in aromatic hydrocarbons containing O—H constituents, and created reactive sites for chlorine and subsequent haloform formation. Moreover, the reaction between NaOCl and C—Br led to the reduction in the concentration of C—Br and resulted in the release of Br$^-$ ions into the sample solution. This corresponded well with the increase in the bromide ion concentration of the water samples at day 7 as reported in Table 3. On the contrary, C—O was observed to increase in concentration and this functional group might have occurred as a by-product from the chlorination reaction. The quantitative and qualitative analyses of FTIR spectra obtained from all samples are summarized in Table 5.

4. Conclusion

This work demonstrated the influence of the presence of shrimp farms on the formation potential of THMs. The Bangpakong River at the Chachoengsao Province (Thailand) was selected as a study location as there was intensive practice of inland shrimp farming in this area. The THMFP of the river downstream was found to be much higher than that of the upstream. The characterization of the shrimp farm effluents indicated that a notably high level of THMFP (810–3100 µg/L) could be easily obtained. Hence, the contamination of shrimp farm effluents to the river could well be the cause of high THMFP in the river downstream. Hydrophilic fractions were the domi-

nant species in shrimp farm effluents with 56–77% by weight of the total organic content. The unbalance of the DOC in the fractionation process might result in an error in the reported weight fraction as presented above. During the fractionation process, the loss of DOC was found to be from 1 to 7% while the excess of DOC was 8–38%. The excess of DOC could be a result of organic leaching from the resins especially at high salinity. Additionally, the hydrophilic fractions were the effective fraction in the formation of THMs. Salinity and bromide ions were also shown to have strong influences on the formation of THMs. Chloro-species were found to occur in large quantities in the water with low salinity and a low concentration of bromide ions, whereas the bromo-species occurred more significantly at high salinity and bromide levels.

The potential functional groups that took part in the chlorination reaction were also identified. This included phenolic compounds, N−H (amines groups), C=C (aromatic hydrocarbons), C−Cl (aliphatic chloro-compounds), and C−Br (aliphatic bromo-compounds). The information from this work can be further employed in the management of shrimp farm effluents, as it provides information on the kinetics of the disinfection reactions, which can facilitate in the future development of safer purification techniques.

Acknowledgement

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