ORIGINAL ARTICLE

Trihalomethane formation potential of shrimp farm effluents in Chachoengsao Province, Thailand

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Abstract

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Shrimp farm effluents along Bangpakong River in Chachoengsao Province, Thailand, were evaluated for their trihalomethane formation potential (THMFP), which were shown to be in the range of 810-3,100 µg/L. Samples from river locations, both upstream and downstream from these selected farms, were also tested for their existing THMFP. These river samples were illustrated to have notably lower level of THMFP

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than the shrimp farm effluents. The downstream concentration was, however, found to be significantly higher than the upstream (as much as 5 times). This indicated that the contamination of shrimp farm effluents could have increased the formation potential of THMs in the natural water source. The experimental results showed a positive correlation between salinity and THMFP. The formation of various THM species depended significantly on the level of salinity in the water sample. Low salinity (0-5 ppt) often led to a high formation of chloroform and bromodichloromethane while high salinity (5-15 ppt) resulted in a great quantity of dibromochloromethane and bromoform. FTIR spectra of the samples before and after chlorination suggested that the functional groups involved in the reaction were hydroxyl group, amines group, aromatic ring, aliphatic chloro compounds and aliphatic bromo compounds, whereas C-O was the product from the reaction.

Key words : THMFP, disinfection by-products, salinity, DOC, FTIR

บทคัดย่อ

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การก่อตัวของสารไตรฮาโลมีเทนในน้ำทิ้งจากบ่อเลี้ยงกุ้งในบริเวณจังหวัดฉะเชิงเทรา ประเทศไทย

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งานวิจัยนี้ศึกษาความสามารถในการก่อตัวของสารไตรฮาโลมีเทนในน้ำทิ้งจากบ่อเลี้ยงกุ้งบริเวณแม่น้ำบางปะกง จังหวัดฉะเชิงเทรา ประเทศไทย ซึ่งมีค่าอยู่ในช่วง 810- 3,100 ไมโครกรัม/ลิตร และรวมถึงการศึกษาผลกระทบของน้ำทิ้งจากนากุ้งต่อความสามารถในการก่อตัวของสารไตรฮาโลมีเทนในแม่น้ำบางปะกง เมื่อเปรียบเทียบค่าความสามารถในการก่อสารไตรฮาโลมีเทนช่วงต้นน้ำหรือบริเวณที่มีพื้นที่นากุ้งเบาบาง และช่วงท้ายน้ำหรือหลังผ่านบริเวณที่มีการทำนากุ้งหนาแน่น พบว่าตัวอย่างน้ำในช่วงท้ายน้ำที่ผ่านนากุ้งมาแล้วมีค่าความสามารถในการก่อตัวของสารสูงกว่าตัวอย่างน้ำจากบริเวณก่อนถึงช่วงการทำนากุ้ง (ประมาณ 5 เท่า) ดังนั้นน้ำทิ้งจากนากุ้งอาจมีผลต่อความสามารถในการก่อตัวของสารไตรฮาโลมีเทนในแหล่งน้ำได้ ผลการศึกษาแสดงให้เห็นว่าความสามารถในการก่อตัวของสารไตรฮาโลมีเทนแปรผันตรงกับค่าความเค็มของน้ำโดยความเค็มที่สูงขึ้นจะช่วยส่งผลให้ค่าความสามารถในการก่อตัวของสารนี้สูงขึ้น โดยน้ำทิ้งที่มีค่าความเค็มต่ำ (0-5 ppt) จะมีความสามารถในการก่อตัวของสารประเภทคลอโรฟอร์มและโบรโมไดคลอโรมีเทนค่อนข้างมาก ในขณะที่น้ำทิ้งที่มีค่าความเค็มสูง (5-15 ppt) จะมีความสามารถในการก่อตัวของสารไดโบรโมคลอโรมีเทนและโบรโมฟอร์มค่อนข้างสูง ผลจากตรวจสอบกลุ่มฟังก์ชันของตัวอย่างก่อนและหลังการเติมคลอรีนโดยใช้เครื่อง FTIR แสดงให้เห็นว่ากลุ่มฟังก์ชันที่น่าจะเกี่ยวข้องกับปฏิกิริยาคลอริเนชั่นประกอบไปด้วยกลุ่มไฮดรอกซิล กลุ่มเอมีน กลุ่มเบนซีน กลุ่มสารอินทรีย์สายโซ่ยาวที่มีองค์ประกอบของคลอรีน และกลุ่มสารอินทรีย์สายโซ่ยาวที่มีองค์ประกอบของโบรมีน ในขณะที่กลุ่ม C-O น่าจะเป็นผลิตภัณฑ์ที่ได้จากปฏิกิริยานี้

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Low salinity culturing method for black tiger prawn (*penaeus monodon*) has been developed and conducted in freshwater area in Thailand since 1998. In 1999 alone, as much as 40% of Thailand's cultured shrimp production was obtained from 22,455 hectare (ha) of inland shrimp farms (see Table 1) (Szuster and Flaherty, 2000). Chachoengsao Province is among the largest areas of inland shrimp farming covering about 8,400 ha and contains approximately 5,000 farms (Braaten and Flaherty, 2000). Despite the success in shrimp culture, unplanned and uncontrolled shrimp culture expansion raises water quality problems. Chemicals used in shrimp farming such as fertilizers, pesticide and disinfectants, etc (Graslund and Bengtsson, 2001) often find their ways to leave the culture pond and enter the environment, usually together with shrimp farm effluents. The high nutrient content in the effluent could deteriorate the quality of both surface and ground water. In the case where this water is reused, a water treatment facility must be employed to adjust the quality of the water. One of the treatment techniques is disinfection, often with chlorinated compounds such as chlorine, sodium hypochlorite, etc. During this process, organic constituents in the culture effluent could undergo chemical reactions with disinfecting agents and form potentially carcinogenic compounds. The increasing levels of disinfection by-products from the reaction of organic constituents with disinfecting agents can then be expected in the treated water, which might enter domestic use (Graslund and Bengtsson, 2001).

Trihalomethanes (THMs) belong to a group of organic chemicals formed in water when chlorine reacts with natural organic matters. The mechanism of trihalomethanes formation can be expressed as (Symons *et al*., 1981):

$$\text{Free chlorine (or bromine)} + \text{Precursors (Humic substances)} \rightarrow \text{THMs} + \text{Other by-products} \quad (1)$$

Although THMs include other halogenated species such as iodide and fluoride, the most commonly found species are only chlorinated and brominated species as these species are obtained from the chlorination reaction where iodine and fluorine do not usually exist. Bromide species, on the other hand, could be found if the water source contains bromide ion as this ion is active and involves in the reaction with organic precursors. Hence, in this work, the total trihalomethanes (THMs) is considered as a sum of the four chlorinated methane species, i.e. chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$) and dibromochloromethane ($CHClBr_2$). The formation of THMs depends on several factors such as precursor concentration, contact time, chlorine dose, bromide concentration, pH, and

Table 1. Inland shrimp farms in the central region of Thailand

Province	Area (hectare)
Chachoengsao	8375
Prachinburi	4577
Nakhon Pathom	2204
Nakhon Nayok	1752
Chon Buri	1631
Suphanburi	1359
Samut Prakan	518
Phra Nakhon Si Ayutthaya	451
Ratchaburi	350
Phetchaburi	322
Pathum Thani	244
Samut Sakhon	206
Ang Thong	193
Khrung Thep	51
Lop Buri	48
Chai Nat	46
Nakhon Sawan	44
Nonthaburi	22
Kanchanaburi	19
Saraburi	16
Sing Buri	12
Uthai Thani	10
Samut Songkhram	5
Total	**22,455**

Source: Szuster and Flaherty (2000)

temperature (Marhaba and Hochar, 2000). THMs are known to cause serious health problems, e.g. an increasing risk of cancers, a risk of bladder cancer and colorectal cancer, heart, lung, kidney, liver, and central nervous system damage, and also reproductive problems including miscarriage (Amy *et al.*, 1985). This problem has been realized by several authorities worldwide. For instance, the United State Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) of 100 μg/L for THMs and imposed a new MCL of 80 μg/L in the stage 1 of the disinfection by-product rule (D/DBP Rule) where the stage 2 of the D/DBP Rule may see lower MCLs for THMs by as much as 50% or 40 μg/L (Shorney and Freeman, 1998).

This work focused at the investigation of the impact of shrimp farm effluents on water sources in terms of THM formation potential (THMFP). Moreover, it also examined factors influencing the formation of THMs. The results from this study will be useful for: (i) increasing awareness of the long term problems from the shrimp farm effluent discharge containing large quantity of organic substance to natural water source; and (ii) better understanding of the relationship between THMFP and the various environmental parameters in the shrimp farms or other aquaculture areas. This will finally lead to the development of proper strategies for reducing the problems of the increasing risk of THMFP in natural water when contaminated with shrimp farm effluents.

Experimental procedures

Sample collection

All experiments were conducted on inland shrimp farms located in the Bangpakong watershed, Chachoengsao Province, Thailand (between points number 4 and 5 in Figure 1), from May to November 2003. Sixteen shrimp farms were chosen at their harvest days, when the entire volume of the effluent was discharged. Samples were collected at the effluent points in the amber glass bottles with TFE-lined screw caps (10-15 liters per farm). River water samples were also collected upstream and downstream along the river from the shrimp farm area (a total of 6 sampling points as indicated in Figure 1). Salinity, conductivity and turbidity of the samples were measured on-site before the transportation of the samples back to the laboratory. The transportation was performed by preserving the samples at 4^{o}C to prevent any possible reactions that might have occurred in the sample. Samples were stored in the refrigerator at 4^{o}C before the analysis. Milli-Q water was used for all dilutions, solution preparation, and final glassware washing.

Organic carbon analysis

THM precursors were analyzed in terms of organic carbon using the TOC analyzer (O.I. analytical college station Texas model 1010). The analytical method followed the standard method 5310-D, wet oxidation (APHA, AWWA and WEF, 1995). All samples were filtered through a 0.45μm cellulose nitrate filter to remove suspended particles prior to analysis. The analyzer was regularly calibrated with 1,000 ppm potassium biphthalate (KHP) standard. The analyzer was programmed accordingly with the proper amount of 5%v/v orthophosphoric acid, 100 g/L sodium persulfate, and reaction time, as recommended by the manufacturer.

THMs formation potential analysis

The tests of the THM formation potential or THMFP was devised in accordance with the Standard Method 5710-B (APHA, AWWA and WEF, 1995). The formation potential was determined by exposing filtrated water samples (250 mL) in an excess of oxidizing disinfectant, calcium hypochlorite solution, for 7 days at 25^{o}C. Before their incubation for 7 days, the pH of sample was adjusted to 6-7 by 0.1N H_2SO_4 and 0.1N NaOH. Phosphate buffer was added to control the pH during the experiment. Chlorine residual was measured at the end of the 7 days incubation time. Only the samples with a residual chlorine concentration of 3-5 mg/L were selected where 0.1mL of

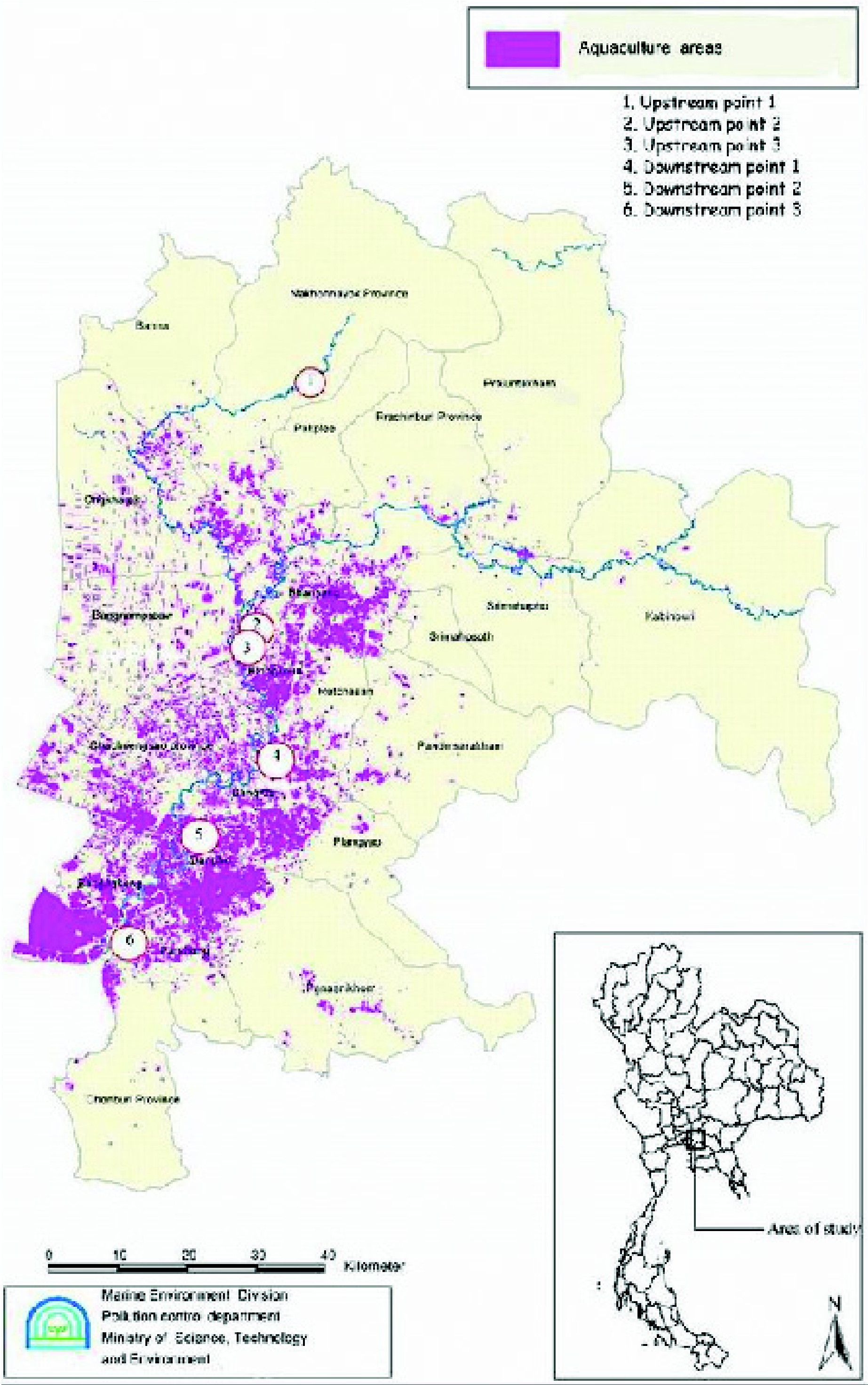

Figure 1. Study area and sampling points of Bangpakong River

100g/L sodium sulfite (Na_2SO_3) was added to the samples to de-chlorinate all the residual chlorine. The change in their THM concentration relative to time zero was the THMFP. THMs were analyzed in accordance with the EPA method 551.1 by using gas chromatography equipped with HP-1 column (L 30 m ID 0.32 mm film 0.25 µm), micro electron capture detector (see Appendix A for analysis conditions). THM mixed standard containing four species: chloroform, bromodichloromethane, dibromochloromethane, bromoform concentrations of 200 and 2,000 mg/mL were used during all experiments. Pentane was used as the only extraction solvent for THM species. Bromofluorobenzene and decafluorobiphenyl were internal and surrogate standards, respectively. GC signals were interpreted by using the ChemStation program, Agilent.

Fourier transform infrared spectrometry (FTIR)

Samples were freeze-dried before and after chlorination for FTIR analysis. The functional groups of the organic fractions were detected by using Fourier transform infrared spectrometry (FTIR) Perkin Elmer 1760X. Infrared spectra were obtained using 0.2 mg of filtrated sampling isolates in 150 mg of potassium bromide pellets (Kelly *et al*., 2002). FTIR was set to scan from 4,000 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.

Results and Discussion

Physical-chemical characteristics of river water and shrimp farm effluents

The characteristics of all shrimp farm effluent samples along with samples from the river are summarized in Tables 2 and 3. Salinity in river water varied from near zero at upstream locations to 5.8 ppt downstream location. Downstream samples tended to have higher salinity level than those of upstream. Sea water intrusion with high salinity level (20-30 ppt) could well be the main cause for this difference in salinity. The release of shrimp farm effluents to the river might also have

Table 2. Physical-chemical parameters of shrimp farm effluents.

Shrimp farm number	Culture days (days)	Salinity (ppt)	Conductivity (µs/cm)	Turbidity (NTU)	DOC (mg/L)
No 1	105	0.4	860	47.1	12.7
No 2	100	0.5	947	86.4	13.6
No 3	95	1.4	2660	27.1	12.6
No 4	96	6.4	11250	41.9	3.7
No 5	75	14.0	31700	49.2	3.9
No 6	75	14.5	24100	20.0	4.2
No 7	100	0.3	680	64.4	10.4
No 8	90	1.0	1954	21.7	13.9
No 9	85	0.7	1385	15.7	13.3
No 10	120	0.6	1278	163.3	13.3
No 11	125	0.7	1433	150.3	12.3
No 12	135	1.8	3400	102.0	15.5
No 13	98	6.9	12080	58.2	8.9
No 14	135	11.8	19870	111.8	4.4
No 15	93	4.7	8450	33.5	10.2
No 16	109	0.5	1086	49.0	8.3

Table 3. Physical-chemical parameters of samples from Bangpakong River

Source water	Salinity ppt	Conductivity (µs/cm)	Turbidity (NTU)	DOC (mg/L)
Upstream 1 (No.1)	0	50	12.3	2.4
Upstream 2 (No.2)	0.1	150	228.2	5.5
Upstream 3 (No.3)	0.1	183	286.4	5.6
Downstream 1 (No.4)	0.1	233	106.4	4.5
Downstream 2 (No.5)	0.1	245	66.2	7.7
Downstream 3 (No.6)	5.8	10380	52.6	2.3

contributed to the high salinity downstream as the salinity of shrimp farm effluents (0.4-14.5 ppt) was significantly higher than that of the river (0-5.8 ppt) and there were an enormous number of shrimp farms in this area.

Turbidity varied from 15-160 NTU for shrimp farm effluents and 12-286 NTU for the river samples. Turbidity possibly resulted from the erosion of the land surface, type of pond (clay or concreted pond), feeds, algae, and microorganisms etc. in the shrimp farms. Conductivity of river samples at upstream locations was lower than that of downstream. The higher conductivity in downstream river was due to: (1) sea water intrusion; (2) contamination from several substances released from the shrimp farms, e.g. inorganic dissolved solids from additive substances such as chloride, nitrate, sulfate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations (Graslund and Bengtsson, 2001); (3) clay soil run offs both from clay ponds and terrain. Clay soil could significantly influence conductivity because it could be ionized when washed into water.

Conductivity of shrimp farm effluents ranged between 680 and 31,700 µs/cm. This was in a much higher scale than the conductivity of upstream river (50–183 µs/cm). In addition, Figure 2 indicates that there was an almost linear relationship between conductivity and salinity in all samples collected from shrimp farm effluents. Water samples with higher level of salinity contained more highly electrically conductive potential substances, e.g. Br and Cl ions, Mg, Ca, Na, etc. and this resulted in an apparently high level of conductivity (Rosenmeier, 2004). The following section illustrates that samples with low salinity would potentially carry a higher level of DOC. The low conductivity in these low salinity samples may also be due to the presence of high level of compounds with low conductivity electrical potential such as organic compounds like oil, phenol, alcohol, and sugar.

DOC of river samples ranged from 2 to 8 mg/L. Upstream samples tended to have lower levels of DOC than downstream, except for the last point of downstream river. At that point, the downstream river sample was supposed to have even higher amount of DOC, but an opposite result was observed. The intrusion of low DOC content sea water might explain this finding. This last point of sample collection location was nearest to the sea and there was an intrusion of low DOC sea water.

DOC of shrimp farm effluents ranged from 3 to 15 mg/L and experimental results revealed clearly that there was a well defined relationship between salinity and DOC in these shrimp farm samples (see Figure 2). Accordingly, DOC was found to decrease with an increase in salinity. This agreed with the finding from Kavanaugh (1978) who reported that DOC in sea water samples was often lower than DOC in the fresh water samples. Figure 3 indicates that there was no relationship between DOC and turbidity in all samples collected from shrimp farm effluents.

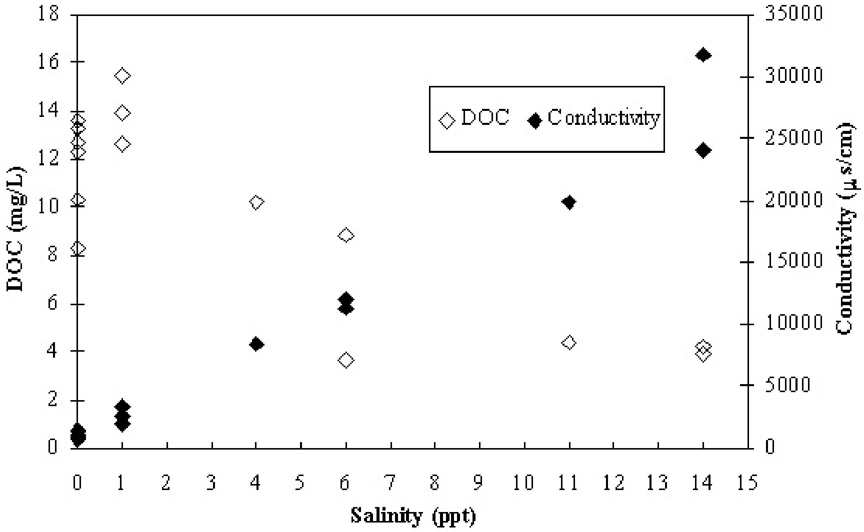

Figure 2. Relationships between salinity, DOC, and conductivity in the shrimp farm effluent samples

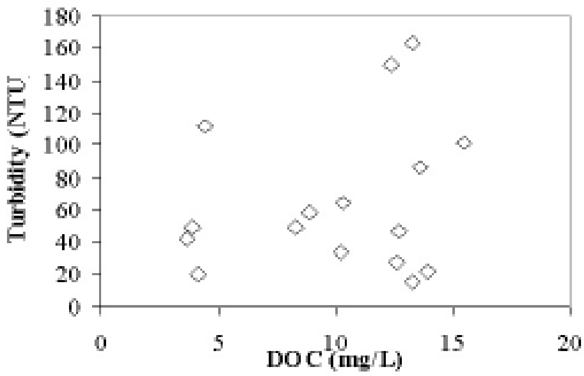

Figure 3. Relationship between Turbidity and DOC

Trihalomethane formation potential

Both river water and shrimp farm effluents were analyzed for their THMFP (Tables 4 and 5). In this section, THMFP is reported as a standardized THMFP (THMFP/DOC) which is equivalent to the ratio between the quantity of THMs formed and the DOC in the sample or can be expressed as:

$$THMFP/DOC = THMFP / DOC \qquad (2)$$

Figure 4 illustrates the relationship between THMFP/DOC and salinity of samples both from river and from shrimp farm. The increase in the salinity was found to have a positive effect on the formation of THMs and an almost linear dependency between these two parameters could be observed with Pearson's correlation coefficient of more than 0.9 at 99% confidential level which means that these two parameters have strong linear dependency. Additionally, the 2-tail significance levels (assuming normal distribution of data set) were both higher than 95% which emphasized the accuracy of these linear relationships.

Figure 5 illustrates the relationships between the salinity level and the formation of each species of THMs. At low salinity, species with chlorine components seemed to be the main disinfection by-products. On the other hand, high salinity samples often led to a formation of bromide-products (bromoform and dibromochloroform). This was not a surprising finding as the presence of bromide ion could interfere with the THM forming reaction and the bromo-associated species were obtained. It should be noted that bromide ion was often reported to be reactive in the formation of brominated THMs (Rook *et al.*, 1978; Oliver, 1980; Amy *et al.*, 1985).

Turbidity is representative of how the water sample was contaminated with visible impurities. Figure 6 illustrates that this was not the case for

Table 4. THMFP and its components in the selected shrimp farms

Farm No.	THMFP (µg/L)	$CHCl_3$ FP (µg/L)	$CHCl_2Br$ FP (µg/L)	$CHClBr_2$ FP (µg/L)	$CHBr_3$ FP (µg/L)
1	1357	1293	64	0	0
2	893	844	50	0	0
3	993	180	628	186	0
4	2027	19	151	506	1351
5	2093	0	40	306	1747
6	2067	0	34	285	1748
7	1309	903	319	78	0
8	1325	355	530	353	87
9	1253	633	1253	633	1253
10	812	412	296	104	0
11	1544	434	661	402	47
12	1686	409	700	474	102
13	2476	42	145	525	1765
14	3105	29	70	445	2561
15	2228	87	245	613	1283
16	1103	296	473	249	86

Table 5. THMFP and its components in river samples

Sampling point	THMFP (µg/L)	$CHCl_3$ FP (µg/L)	$CHCl_2Br$ FP (µg/L)	$CHClBr_2$ FP (µg/L)	$CHBr_3$ FP (µg/L)
Upstream 1	30	30	0	0	0
Upstream 2	69	69	0	0	0
Upstream 3	279	279	0	0	0
Downstream 1	583	486	72	14	11
Downstream 2	1007	858	136	0	0
Downstream 3	1103	0	54	309	740

either of the samples examined here (from the river or from the shrimp farms). No trends could be noticed between turbidity and THMFP/DOC which demonstrated that the amount of impurities in water samples did not directly represent the quantity of organic matters. However, high turbidity seemed to result in low THMFP/DOC. This might be due to the interference of turbidity on the interaction between chlorine and organic substances during the chlorination process.

The influence of shrimp farms on THMFP could be observed by comparing THMFP from the river samples upstream and downstream. The upstream sample had THMFP at around 30-280 µg/L whereas the downstream value was at 580-1,100 µg/L. This indicated that with the contamination from shrimp farm effluent, THMFP of the water source (Bangpakong River in this case) could be significantly enhanced. However, further work regarding this finding should be conducted to investigate the effect of THMFP in shrimp farm effluents on the THMFP in the river.

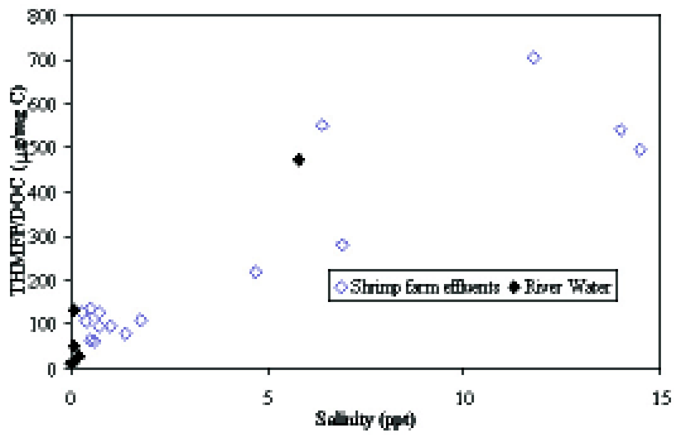

Figure 4. Relationship between THMFP/DOC and salinity

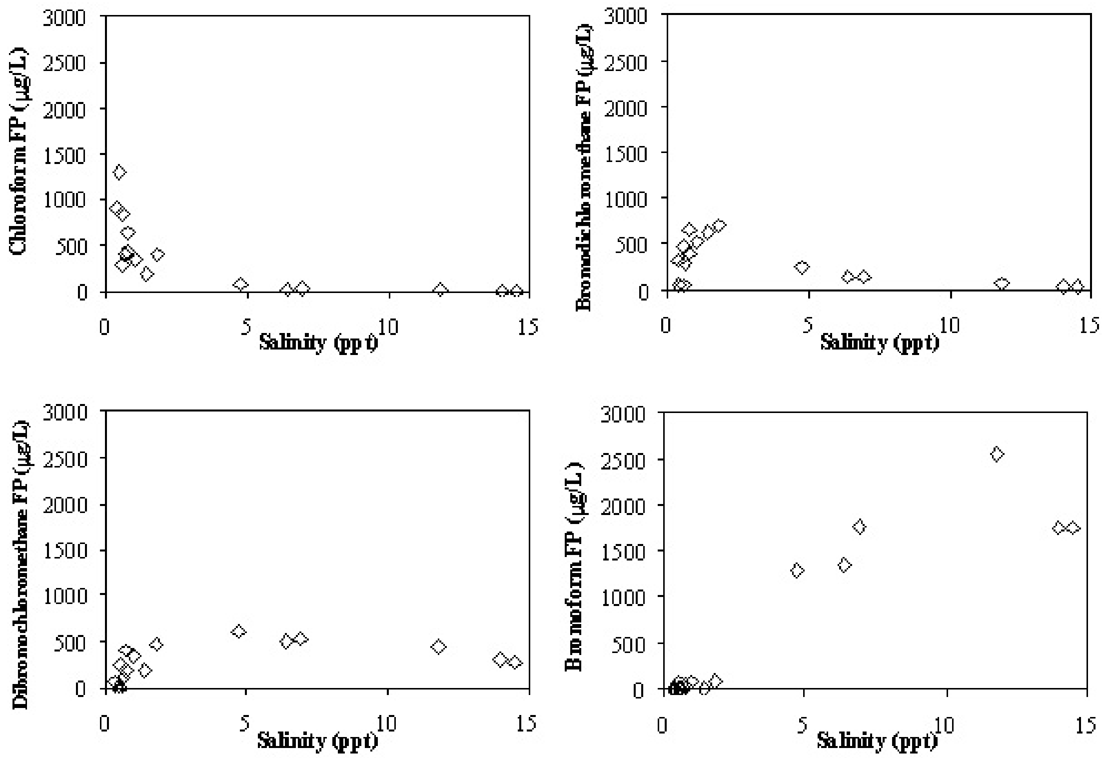

Figure 5. Relationship between salinity and each species of trihalomethanes

Evaluation for functional groups

FTIR results revealed that there were a total of six major functional groups in all of the samples examined here, i.e. (i) hydroxyl group (phenolic compound), (ii) N-H (amines group), (iii) C=C (aromatic ring), (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, the comparison between the

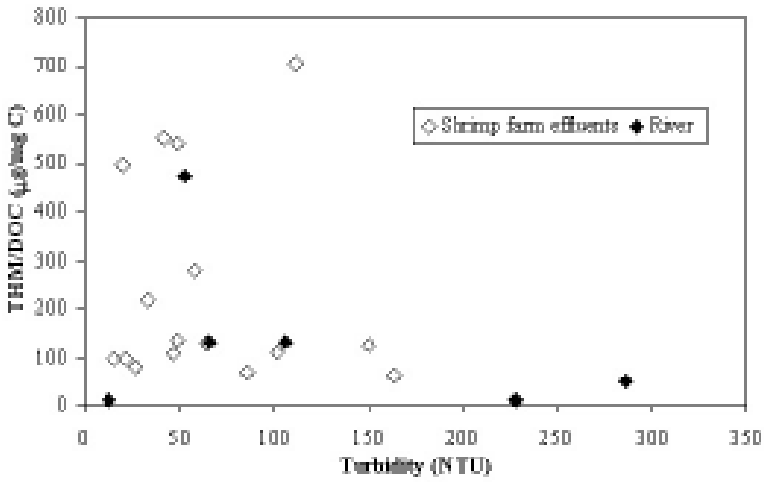

Figure 6. Relationship between THMFP/DOC and turbidity

Table 6. FTIR results of shrimp farm effluents

Wave number (cm^{-1})	Functional group	Change in absorption spectrum	Typical compounds
3600-3300	O-H	Decrease	Carbohydrates, humic and fulvic acid
Near 3500	N-H	Decrease	Protein
Near 1650	C=C	Decrease	Aromatic hydrocarbon
1300-1000	C-O	Increase	Carbohydrates
800-600	C-Cl	Decrease	Aliphatic chloro compounds
600-500	C-Br	Decrease	Aliphatic bromo compounds

results from the same sample before and after the reaction (for THMFP measurement) could lead to some approximate quantitative analysis of the possible associated functional groups as identified by the method. For instance, Figure 7 provides the FTIR absorption spectra before and after the reactions with NaOCl (chlorination) of the samples No.4, 5, 6, 13, and 14. A difference between the areas under each curve could be well observed (visually) which indicated whether there were changes in the quantity of the corresponding function groups.

Table 6 summarizes the quantitative and qualitative analyses of FTIR spectra obtained from all samples. O-H (phenolic compound), N-H (amines group), C=C (aromatic ring), C-Cl (aliphatic chloro-compounds), and C-Br (aliphatic bromo-compounds) were found to decrease after the THMFP measurement. It was possible that OCl^- reacted with these groups during the THM formation reaction which resulted in a decrease in their concentrations. C-O was observed to increase in concentration which led to the conclusion that this functional group was obtained as a product from the chlorination reaction.

Conclusion

This work demonstrated the influence of the presence of shrimp farms on the formation potential of THMs. Bangpakong River at Chacheongsao Province was selected as a studied

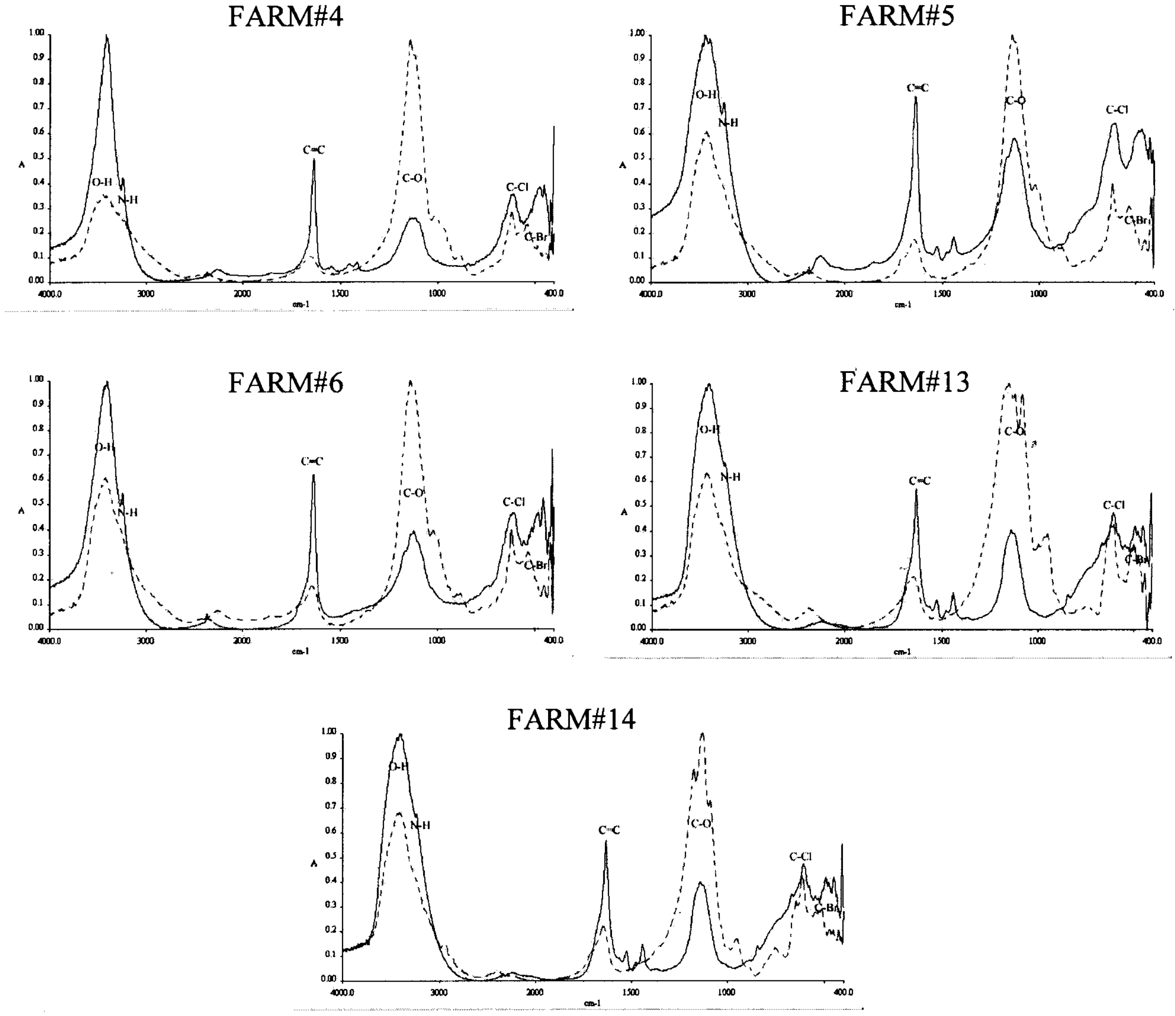

Figure 7. FTIR spectra before and after chlorination (day 0 and day 7)
——— Before chlorination (day 0)
-------- After chlorination (day 7)

location as there was intensive practice of inland shrimp farming in this area. THMFP of the river downstream was found to be much higher than that upstream. The characterization of the shrimp farm effluents indicated that a notably high level of THMFP (810-3,100 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. Salinity was also shown to have strong influence in the formation of THMFP. The chloro-species were found to occur in large quantity for the water with low salinity whereas the bromo-species occurred more significantly at high salinity. Therefore, the high THMFP in the downstream location of Bangpakong River might also be the result from the salinity imposed by the sea water intrusion.

The potential functional groups that took part in the chlorination reaction were also identified. This included hydroxyl group (phenolic compound), N-H group (amine group), C=C (aromatic ring), C-Cl (aliphatic chloro-compounds) and C-

Br (aliphatic bromo-compounds). The information from this work can be further employed for the management of the shrimp farm effluent as it provides detailed information on the kinetics of the disinfection reaction which will facilitate in the future development of safer purification technique.

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Appendix A:
GC conditions for analyzing THMs

A.1 Inlet condition
Mode: split
Initial temp: 225(C
Pressure: 12.38 psi
Split ratio: 10:1 split flow 30 mL/min
Gas Type: helium
Total flow: 35.9 mL/min.

A.2 Oven condition

Ramp	Rate (°C/min)	Final temperature (°C)	Holding time of final temperature (minute)	Remark
1	10	40	1.00	Initial temp.: 35°C, Initial temp. Holding Time 1.00 min
2	15	130	1.00	-
3	30	180	1.00	-

A.3 Detector condition
Temperature: 250°C
Mode: constant make up flow
Makeup flow: 60 mL/min
Makeup gas type: nitrogen