CHAPTER 4

RESULTS AND DISCUSSIONS

The results of the experiments are presented here in the following four sections. Section 4-1 contains the results of the physical and chemical characteristics of shrimp farm effluents. Section 4-2 contains THMFP results in shrimp farm effluents and the Bangpakong River, Section 4.3 is the influences of various factors on THM formation. Section 4.4 the suggested models for the estimate of THMFP and other THM species from surrogate parameters whereas Section 4-5 is the results of potential functional groups reactive to chlorine in forming trihalomethanes.

4.1 Physical and chemical characteristics of shrimp farm effluents and Bangpakong River

The important characteristics of the selected 16 shrimp farm effluents in Amphor Bangkla and Banphoe, all of which are located between downstream points 1 and 2 (Figure 3.2) investigated between May and November 2003, are summarized in Table 4.1 and those of the Bangpakong River samples are in Table 4.2.

Temperature and pH will not be discussed in this work since during the collection, these two parameters were manipulated according to the collection procedure to ensure there were no further changes in the water sample.

In this section, Pearson's correlation analysis was used as a tool for determining the relationship between the two parameters from the 16 different shrimp farms. The Pearson Product Moment Correlation (called Pearson's correlation, r, for short) is a correlation between two variables reflecting the degree to which the variables are related. In fact, Pearson's correlation reflects the degree of linear relationship between two variables. This correlation ranges from -1 to +1, where a correlation of +1 means that there is a perfect positive linear relationship between variables, and a correlation of –1 means that there is a perfect negative linear relationship between variables. A correlation of zero means there is no linear relationship between the two variables. Pearson's correlation analysis also provides the significant level of the statistical results, in terms of "p". A high level of "p" means that the results are of low significant level and should not be trusted whereas a small "p". indicates high level of significance.

4.1.1 Conductivity

From Table 4.1, the conductivity of shrimp farm effluents were in the range of 680 – 31,700 µs/cm. This was relatively high when compared with upstream and downstream samples from the Bangpakong River which ranged from 50 – 10,380 µs/cm. The variation in the conductivity of the Bangpakong River was a result of the tidal effect of saline water as the Bangpakong River is located near the Gulf of Thailand. Table 4.2 illustrates that there is a relationship between conductivity and the distance between the sampling point and the Bangpakong estuary. Those points near the estuary exhibited higher conductivity than those of the upstream samples, which clearly demonstrated that there was the influence of sea water intrusion.

Conductivity was also found to be linearly dependent on chloride and bromide concentrations. These are illustrated in Figure 4.1. The Pearson correlation was found to be 0.546 for conductivity and chloride, and 0.548 for conductivity and bromide. A high level of accuracy was also obtained from the statistical analysis for the linear relationship between these parameters. It can then be concluded that bromide and chloride ions increased with an increase in conductivity.

4.1.2 Turbidity

Turbidity was often a result from the erosion of colloidal materials such as clay, silt, rock fragments, and metal oxides from the soil. Vegetable fibers and microorganisms in shrimp ponds may also contribute to turbidity. From Table 4.1, the range of turbidity of shrimp farm effluents was 20-163.3 NTU. This was not in a similar range in comparison to the river where turbidity was between 12.3-286.4 NTU. The turbidity at the upstream and downstream locations of the Bangpakong River was slightly higher as there were more turbulence in the river than in the farm. The highest turbidity result of the Bangpakong River was at upstream point # 3, as this sampling point was located near the meeting point between the Nakhonnayok and Prachinburi Rivers where the effects of turbulent current were most severe.

4.1.3 Salinity

Salinity is a measure of the amount of salts in the water. Because dissolved ions increase salinity as well as conductivity, the two measurements are related. Table 4.1 shows that the salinity of shrimp farm effluents varied from 0.3 to 14.5 ppt. The source of salinity in shrimp farm effluents came from the saline water used for the dilution of low salinity shrimp cultures. A well positive with strong relationship (r = 0.984) was obtained between salinity and conductivity. This is also reflected in Figure 4.2, and it can be concluded that conductivity increased with an increase in the salinity. The salinity of upstream and downstream samples of the Bangpakong River was in the range of 0 –5.8 ppt (Table 4.2). This was quite low when compared with that of shrimp farm effluents.

4.1.4 TOC and DOC

The shrimp farm practice usually resulted in a large quantity of dissolved organic matters being released to the environment and therefore the high formation of TTHMs found from these samples was not unexpected. The organic carbon in the shrimp farm effluents and the Bangpakong River was analyzed by a TOC analyzer before and after the evaluation for their THMFP. The raw water samples were also filtrated to determine the TOC of the filtrate, which was considered here as a dissolved fraction or dissolved organic carbon (DOC).

From Table 4.3, TOC concentrations of 16 shrimp farm effluents ranged from 3.190 to 18.267 mg C l^{-1}, with an average of 10.811 mg C l^{-1} during the sampling period. The maximum concentration was observed at shrimp farm No. 10 at 18.267 mg C l^{-1}.

The same table illustrates that the DOC of shrimp farm effluents ranged from 3.680 to 15.461 C l^{-1}. In some cases, the TOC was found to be lower than the DOC of the same sample. This strange result might be the reason of the settling of the unfiltrated particulates in raw water during the injection of the TOC needle. Therefore, the results from the TOC analyzer did not include the organic fraction from the settled fraction resulting in a low organic content.

However, Figure 4.3 illustrates that there was a strong relationship between TOC and DOC with a Pearson correlation of 0.941, and a significant value of $p<0.0001$.

For the river samples, Table 4.4 illustrates that the TOC upstream of the Bangpakong River ranged from 2.007 to 4.969 mg/L, while the downstream ranged from 1.936 to 5.150 mg/L. TOC of downstream sample point # 1 was found to be the highest. This was not surprising as this location was the point where the Nakhonnayok River combines with the Prachinburi River. The turbulence from this combination must have led to the high distribution of sediment and resulted in a high TOC level.

The DOC of the Bangpakong river ranged from 2.330 to 7.696 mg/L. Most of the TOC and DOC values upstream were lower than those of downstream, except the last downstream river point, which was located nearest to the Gulf of Thailand where TOC and DOC were found to be lower than the estimated values. The influence from salinity and tidal effects from the Gulf of Thailand might play a significant role in this phenomenon.

4.1.5 Bromide and chloride concentrations

Table 4.5 shows that chloride and bromide concentrations in shrimp farm effluents ranged from 93.428 to 3927.308 mg/L and 0.03 to 13.739 mg/L, respectively. The average bromide and chloride concentrations in the 16 selected shrimp farm effluents were between 2.9218 and 1169.734 mg/L, respectively. Both of the highest bromide and chloride concentrations were found in shrimp farm No. 4. These results seem to be quite close to the salinity trend mentioned earlier. This supported the conclusion that chloride and bromide concentration increased with an increase in salinity.

The concentrations of bromide and chloride in the Bangpakong River ranged from 0.017 to 0.673 mg/L and 3.936 to 124.03 mg/L, respectively (Table 4.6). The lowest bromide and chloride concentrations were obtained from upstream point # 1. As this point was very far from the gulf of Thailand, and there seemed to be no shrimp farms located nearby this sampling point, the low bromide and chloride concentration were therefore not unexpected.

Comparing the results of the 16 shrimp farm effluents with the Bangpakong River, it appeared that the bromide and chloride concentrations of shrimp farm effluents were relatively higher than those in the Bangpakong River. This was because most of shrimp farmers use saline water, which contains high doses of Cl^- and Br^- for shrimp culturing.

4.2 Trihalomethanes formation potential (THMFP)

Prior to do the THMFP, it necessary to determine the chlorine demand of the sample for estimating the range of chlorine used for 7 days as described in Section 3.4.5. The approximate chlorine demand for the shrimp farm effluent samples are given in Table 4.7.

In shrimp farm effluents, THMFP in raw water ranged from 864.28 up to 3345.71 μg/L (Table 4.8) and THMFP in filtrated water ranged from 811.83 to 3105.01 μg/L. The majority of THMFP species in shrimp farm effluents was chloroform when salinity values were in the ranges of 0.3 - 1.8 ppt., whereas bromoform became a more important species with higher levels of salinity (in the range of 4.7 – 14.5 ppt.).

On the other hand, THMFP in raw water from the Bangpakong River was only 128.13 – 1091.45 μg/L (Table 4.9) and 29.52 – 1103.15 μg/L for the filtrated samples. The majority of THMFP in Bangpakong River samples was found to be the chloroform species, except at downstream point # 3 which was located near the Gulf of Thailand and had a higher bromoform than other species. Interestingly, only the chloroform species was found in all upstream samples.

Furthermore, THMFP in the Bangpakong River was found to be influenced by the tidal effect from the Gulf of Thailand. From Table 4.9, it can be observed that those sampling points near the Gulf of Thailand exhibited a high level of THMFP due to the intrusion of sea water, and consequently, higher levels of THMFP was detected.

When comparing the THMFP in shrimp farm effluents with that of the Bangpakong River, it can be observed that the upstream sample from point # 1 in Nakhonnayok province, with no shrimp farms located in the nearby vicinity, had the lowest THMFP or that of about 26 times lower than the highest THMFP values found in shrimp farm effluents (see also Tables 4.8 and 4.9).

4.3 Factors influencing THMFP

4.3.1 Conductivity

To normalize the effect of each parameter on THMFP, the THMFP was divided by TOC. This was done to consider the level of THMFP for each unit of TOC. The relationship between conductivity and THMFP /TOC is illustrated in Figure 4.4. A linear relationship was found between these two quantities with a strong positive Pearson coefficient ($r = 0.820$). It can be concluded that THMFP/TOC increased when conductivity increased.

4.3.2 Turbidity

Again, THMFP was divided by TOC to normalize this parameter with one unit of organic substance in the water samples. A plot of turbidity against THMFP/TOC was shown in Figure 4.5. No statistically significant linear relationship between turbidity and THMFP/TOC was exhibited as indicated by a weak Pearson's correlation coefficient of $r_p = -0.178$). It was therefore concluded that turbidity could not be used for estimating the THMFP of the water samples from the shrimp farms in this area. It was possible that the majority of THMFP was derived from the Dissolved Organic Compound (DOC) fraction and not the suspended fraction as implied in turbidity.

4.3.3 Salinity

Figure 4.6 showed the effects of salinity on THMFP/TOC in shrimp farm effluents. A statistically significant relationship between salinity and THMFP/TOC was established with a Pearson's correlation coefficient of 0.896, $p<0.0001$. This meant that there was a well defined trend between THMFP/TOC and salinity, i.e. THMFP increased with an increase in salinity. Bromide and chloride are naturally present in the raw water of coastal cities like those located in Chachoengsao province and hence, salinity is the parameter indicating the main quantity of chloride and bromide ions in water samples. Since THMFP were the product between the reaction of organic constituents with either Br or Cl, or both ions, the coexistence of the organic matters and Br and Cl ions in the water samples led to a high possibility of THMFP being produced.

Figure 4.7 illustrates the relationships between the salinity level and the formation of chloroform. The results exhibited a statistically significant relationship between salinity and $CHCl_3$/TOC with a Pearson's correlation coefficient of -0.834. This indicated that chloroform species had a strong negative linear relationship with salinity.

Figure 4.8 illustrates the relationships between the salinity level and the formation of bromodichloromethane species. The results, on the other hand, did not exhibit a statistically significant relationship between salinity and $CHCl_2Br$/TOC (too low Pearson's correlation coefficient). It was therefore concluded that bromodichloromethane was not affected by salinity.

Figure 4.9 demonstrates the relationships between the salinity level and the formation of each species of THMFP. A strong positive relationship between $CHClBr_2$/TOC and salinity could be established with a pearson's correlation of 0.704.

Figure 4.10 illustrates that there was a strong positive relationship between the salinity level and the formation of bromoform. This was reflected in the high positive Pearson correlation of 0.932.

In conclusion, at low salinity, chloroform seemed to be the main disinfection by-products. On the other hand, high salinity samples often led to the formation of bromide-products (bromoform and dibromochloroform). It is possible that chlorine reacted with organic matters in the water samples more rapidly at low salinity level resulting in a high chloro-species whereas, at high salinity levels, bromide ions because significantly involved in the formation of THMs species.

4.3.4 Bromide

Since the determination of Br^- required that the raw water be filtrated, the standardization for THMFP was performed by DOC instead of TOC. DOC was used to quantify the amount of dissolved organic matter in the filtrated samples.

Most of the samples contained bromide ions at concentrations lower than 6.555 mg/L, except for farms No.4 and 5 which contained bromide ions at concentrations higher than 7.807 mg/L. The highest bromide concentration of 13.739 mg/L was found in farm No. 4. Figure 4.11 demonstrates the relationship between bromide and salinity. As expected, bromide concentrations increased with an increase in salinity. However, the relationship was not quite strong with a Pearson correlation of only 0.537.

Turning now to the effect of the bromide ion on the THMFP, Figure 4.12 illustrates that there was a strong linear relationship between the two parameters (Pearson 's correlation = 0.774, $p < 0.005$). It was concluded that THMFP increased with an increase in bromide. This result was in good agreement with that of Symons et al. (1996), who reported that bromide was oxidized by chlorine to a hypobromous acid, which contributed to the formation of bromo-THMs.

Figure 4.13, on the other hand, shows that there was no relationship between bromide and bromodichloromethane concentrations ($r_p = 0.05$, $p < 0.8855$). Figures 4.14 and 4.15 demonstrate that dibromochloroform and bromoform were linearly dependent on bromide concentrations with high positive Pearson's correlations.

Past research demonstrated that the bromide ion was more reactive and correlative than the chloride ion and formed brominated THMs. This was because chlorine (NaOCl), which was added during the 7-d THMFP method oxidized all of the dissolved bromide in the water and formed the reactive species hypobromous acid, while free chlorine from NaOCl was almost completely hydrolyzed to hypochlorous acid (Larson and Weber, 1994). The bromide oxidation reaction was very rapid and scavenged bromide out of the water, converting it to hypobromous acid (Morris, 1978; Rook et al., 1978). Hypobromous acid reacts much faster with DOC to form THMs than does hypochlorous acid (Rook et al., 1978; Oliver, 1980; Amy et al., 1985; Symons et al., 1993); thus the rate of formation of brominated THMs was often found to be greater than the rate of formation of $CHCl_3$.

4.4 Suggested multi-variable models for estimating THMFP and other THM species

To ensure that the influences of various parameters were taken into account, the multi-variable regression models were established for the prediction of THMFP and its various species. Table 4.10 summarizes the results from the regression. The primary variables in the development of the model are bromide, TOC, DOC, conductivity, and salinity. Each model was aimed for the prediction of the various species of THMFPs. Specifically, Model number 1 was designed for the prediction of THMFP whilst Models

2, 3, and 4 were for the estimations of Bromoform FP, Dibromochloromethane FP, and Chloroform FP, respectively. These models were established according to the statistical relations between these parameters without taking into account the actual interaction between them.

4.5 Functional groups which are reactive to chlorine in the formation of trihalomethanes

Filtrated shrimp farm effluents No. 1, 2, 3, 4, 5, 6, 12, 13, 14,15, and 16 were freezed dried both prior to and after chlorination at day zero and day seven for the evaluation of FTIR. Several IR spectrum bands are observed from shrimp farm effluents, and although some of these were sharp, they overlapped with features from other matrix components in the samples.

Figures 4.16 to 4.26 illustrate changes in the absorbance of IR spectrums at day zero and day seven of shrimp farms No. 1, 2, 3, 4, 5, 6, 12, 13, 14, 15, and 16, respectively. It was obvious that at day zero (Blue line), the hydroxyl group (O-H) presented a broad peak near 3600-3300 cm^{-1} and C-O near 1300 – 1000 cm^{-1}. This suggested that phenol groups were available in these samples. Furthermore, according to Ertel et al.(1984)'s studies, aquatic humic substances derived from lignin, for instance, were found to have relatively large amounts of aromatic carbon, and they were high in phenolic content. It was concluded with some confidence that phenolic compounds appeared in shrimp farm effluents.

Amines (N-H stretch) 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 the hydroxyl group (O-H). It was possible that Amines (N-H stretch) were available in shrimp farm effluents as it constituted amino compounds, a major components of humic and fulvic acids in humic substances.

A strong absorption band was found at 1650 cm^{-1}, which could imply that an aromatic ring was one of the major functional groups in humic substances present in the samples. A medium absorption appeared on IR spectrum at 800-600 cm^{-1} which suggested that aliphatic chlorides (C-Cl) was also one of the groups in the sample. This was likely to be case as this group was naturally present in marine water that the farmer used for dilution in this shrimp cultures. The last, a weak absorption appeared at 600-500 cm^{-1}, and it could be classified as aliphatic bromo compound (C-Br).

Next, the FTIR spectrum after the seventh day of chlorination (in THMFP method) is seen as a red line in Figures 4.16 to 4.26. A broad peak of the OH group decreased from the day zero absorbance values. O-H was the main target for Cl_2 in the formation of THMs. Rockwell and Larson (1978) reported that the presence of phenolic-OH could lead to THM production because O-H, an electron-donating substituent, activated the ring that favored the reaction with chlorine resulting in the formation of THM and other chlorinated by-products. Hence, the results strongly recommended that there was a reduction in the O-H available in the shrimp farm effluent samples.

The reduction in the absorption intensity near 3500 cm^{-1} could also be associated with the presence of the amines (N-H) group. Although this could not be distinguished clearly from the O-H band, it was a possibility, as Morris and Bauem (1978) revealed that pyrrole rings (or other aromatic structures with nitrogen in the ring) could become carbonion, a reactive site for chlorine attack. The hydrogen-nitrogen bonds in this ring were activated like those in aromatic rings containing O-H substituents, and created reactive sites for chlorine and subsequent haloform formation.

A significant decrease in absorption occurred at the region 1650 cm^{-1} which implied the presence of aromatic rings. Hence, aromatic rings could be one of the functional groups that might lead to the formation of trihalomethanes. Literature reports that there were many aromatic rings which could form THMs, e.g. 1,2-dihydroxybenzene (Catechol), 1,3-dihydroxybenzene (Resorcinol), 3,5-dihydroxytoluene (Orcinol), and 1,3-dihydroxynaphthalene (Naphthoresorcinol) (Boyce and Hornig, 1983). Figures 4.29 and 4.30 show some possible reaction pathways for the conversion of 1,3-dihydroxyaromatic substrates to chloroform ($CHCl_3$) (Boyce and Hornig, 1983) and the halogenation of resorcinol in saline solution (Howard et al., 1984).

Figures 4.16 to 4.26 illustrate that there was a clear decrease in the absorption band at 800 - 600 cm^{-1} which is the typical spectra of aliphatic chloride (C-Cl). This disappearance of aliphatic chlorides (C-Cl) may be due to the chlorination of aliphatic chloride into one of the trihalomethanes species.

In addition, the decrease of FTIR spectra of the shrimp farm was found at ~ 500 cm^{-1}. This band was usually assigned to aliphatic bromides (C-Br). This peak was not clearly observed because it was located near the peak of aliphatic chlorides (C-Cl) and there was also noises from the end of the scanned wavelength.

In conclusion, IR results revealed that there were a total of five major functional groups in all of the samples examined in the work. They are (i) phenols (O-H), (ii) amines (N-H), (iii) aromatic compounds (C=C), (iv) Aliphatic bromo compounds (C-Br), and (v) Aliphatic chloro compounds (C-Cl). Although IR results could not be accurately used in determining the quantity of each functional group, the comparison between the results from the same sample before and after the reaction (for THMFP measurement) could lead to some approximate quantitative analysis of the functional groups identified by the method.

Table 4.11 summarizes the quantitative and qualitative analysis of the changes in FTIR spectrums obtained from all samples. Specifically speaking, O-H (phenol group), N-H (amine group), aromatic compounds (C=C), aliphatic chloro compounds (C-Cl), and C-Br (Aliphatic bromo compounds) were found to decrease after the THMFP measurement.

Table 4.1 Physical and chemical parameters of shrimp farm effluents

Source number*	Salinity (ppt)	Conductivity (µS/cm)	Turbidity (NTU)
No 1	0.4	860	47.1
No 2	0.5	947	86.4
No 3	1.4	2660	27.1
No 4	6.4	11250	41.9
No 5	14.0	31700	49.2
No 6	14.5	24100	20.0
No 7	0.3	680	64.4
No 8	1.0	1954	21.7
No 9	0.7	1385	15.7
No 10	0.6	1278	163.3
No 11	0.7	1433	150.3
No 12	1.8	3400	102.0
No 13	6.9	12080	58.2
No 14	11.8	19870	111.8
No 15	4.7	8450	33.5
No 16	0.5	1086	49.0
Average	4.1	7695.8	65.1
Minimum	0.3	680	15.7
Maximum	14.5	31700	163.3

* All sources are located between downstream point number 1 and 2 (Figure 3.2)

Table 4.2 Physical and chemical parameters of Bangpakong River water samples.

Source water (see Figure 3-3)	Salinity (ppt)	Conductivity (µs/cm)	Turbidity (NTU)
Upstream 1	0	50.2	12.3
Upstream 2	0.1	150.3	228.2
Upstream 3	0.1	183.7	286.4
Downstream 1	0.1	233.0	106.4
Downstream 2	0.1	245	66.21
Downstream 3	5.8	10380	52.58
Average	0.9	1654.4	112.16
Minimum	0	50.2	12.3
Maximum	5.8	10380	286.4

Table 4.3 Total organic carbon and dissolved organic carbon in selected shrimp farm

Farm No.	Raw water [TOC (mg/L)]	Filtrated water [DOC(mg/L)]
1	13.459	12.694
2	14.397	13.616
3	12.800	12.642
4	3.190	3.680
5	4.318	3.884
6	3.880	4.180
7	14.811	10.354
8	15.034	13.948
9	13.782	13.278
10	18.267	13.263
11	14.209	12.340
12	15.783	15.461
13	8.026	8.871
14	6.742	5.410
15	8.491	10.236
16	7.787	8.300
Average	10.811	10.072
Minimum	3.190	3.680
Maximum	18.267	15.461

Table 4.4 Total organic carbon (TOC) and dissolved organic carbon (DOC) in Bangpakong River

Sampling point	Raw water [TOC (mg/L)]	Filtrated water [DOC(mg/L)]
Upstream 1	2.007	2.351
Upstream 2	4.498	5.464
Upstream 3	4.969	5.576
Downstream 1	5.150	4.470
Downstream 2	4.574	7.696
Downstream 3	1.936	2.330
Average	3.856	5.486
Minimum	2.007	2.330
Maximum	5.150	7.696

Table 4.5 Concentration of bromide and chloride of shrimp farm effluents

Farm No.	Chloride concentration(mg/L)		Bromide concentration (mg/L)	
	Day 0	Day 7	Day 0	Day 7
1	182.227	296.812	0.271	30.576
2	206.198	334.372	0.316	31.912
3	354.696	627.585	1.831	41.15
4	3927.308	3960.550	13.739	116.019
5	2297.878	2438.327	7.807	38.561
6	963.486	1030.437	3.024	9.407
7	-	-	-	-
8	-	-	-	-
9	-	-	-	-
10	-	-	-	-
11	-	-	-	-
12	880.278	1052.52	2.384	44.527
13	1088.791	1176.559	3.520	18.018
14	1895.248	2015.424	6.555	22.130
15	704.650	752.011	2.120	23.338
16	93.428	97.934	0.030	3.074
Average	1169.734	1018.89	2.9218	22.2174
Minimum	93.428	97.934	0.03	3.074
Maximum	3927.308	3960.55	13.739	116.019

Table 4.6 Concentrations of bromide and chloride of upstream and downstream of Bangpakong River

Sampling Point	Chloride concentration(mg/L)		Bromide concentration (mg/L)	
	Day 0	Day 7	Day 0	Day 7
Upstream 1	3.936	4.256	0.017	0.555
Upstream 2	24.860	69.910	0.069	11.19
Upstream 3	25.390	71.830	0.067	11.171
Downstream 1	39.318	82.850	0.052	11.16
Downstream 2	51.780	92.460	0.084	19.56
Downstream 3	124.030	963.673	0.141	33.658
Average	44.885	214.163	0.173	14.549
Minimum	3.936	4.256	0.017	0.555
Maximum	124.03	963.673	0.673	33.658

Table 4.7 Approximate chlorine demand of shrimp farm effluents

Farm No.	**Chlorine demand (mg/L)**	
	Raw water	**Filtrated water**
No.1	56	34
No.2	52	27
No.3	48	29
No.4	45	24
No.5	49	27
No.6	45	18
No.7	36	26
No.8	86	45
No.9	79	39
No.10	91	29
No.11	71	48
No.12	75	60
No.13	98	95
No.14	97	93
No.15	101	100
No.16	91	86
Average	70	49
Minimum	36	18
Maximum	101	100

Table 4.8 THMFP and its components in the selected shrimp farms.

Farm No.	Water Type	THMFP (µg/L)	$CHCl_3$ FP (µg/L)	$CHCl_2Br$ FP (µg/L)	$CHClBr_2$ FP (µg/L)	$CHBr_3$ FP (µg/L)
1	Raw	1223.12	1223.12	0	0	0
	Filtrated	1357.13	1293.31	63.81	0	0
2	Raw	864.28	692.58	133.32	26.89	11.49
	Filtrated	893.30	843.66	49.63	0	0
3	Raw	902.25	411.95	427.62	62.68	0
	Filtrated	992.70	180.01	627.64	186.05	0
4	Raw	1337.59	16.40	128.51	370.73	822.15
	Filtrated	2027.04	19.31	150.91	506.06	1350.76
5	Raw	1432.49	0	43.17	259.33	1129.99
	Filtrated	2093.00	0	40.02	305.71	1747.27
6	Raw	2201.50	0	34.27	301.15	1866.08
	Filtrated	2066.90	0	33.88	284.66	1748.36
7	Raw	1475.80	1119.62	259.43	63.52	0
	Filtrated	1308.80	902.87	318.54	78.42	0
8	Raw	1964.92	1122.85	595.13	226.70	20.24
	Filtrated	1325.33	355.18	530.25	353.06	86.83
9	Raw	1399.43	900.77	1399.43	900.77	1399.43
	Filtrated	1252.79	632.95	1252.79	632.95	1252.79
10	Raw	1683.05	1308.11	354.10	20.84	0
	Filtrated	811.83	411.82	295.88	104.14	0
11	Raw	1134.69	625.49	384.72	124.49	0
	Filtrated	1543.61	434.32	660.62	401.60	47.07
12	Raw	1102.94	658.36	432.31	0	12.27
	Filtrated	1685.70	408.82	700.32	474.11	102.44
13	Raw	3345.71	75.36	309.17	872.15	2089.03
	Filtrated	2475.99	41.61	144.68	524.61	1765.08
14	Raw	2814.43	39.15	136.07	551.78	2087.43
	Filtrated	3105.01	28.51	70.32	445.49	2560.70
15	Raw	2467.32	131.98	401.34	775.44	1160.06
	Filtrated	2228.22	87.30	244.60	613.30	1283.01
16	Raw	1130.40	568.91	344.65	155.94	60.91
	Filtrated	1103.24	296.03	472.57	249.04	85.60
Average	Raw	1654.99	555.90	336.45	294.53	666.19
	Filtrated	1641.91	370.98	353.47	322.45	751.87
Minimum	Raw	864.28	0	0	0	0
	Filtrated	811.83	0	33.88	0	0
Maximum	Raw	3345.71	1308.11	1399.43	900.77	2089.03
	Filtrated	3105.01	1293.31	1252.79	632.95	2560.70

Table 4.9 Concentration of THMFP in each species of Bangpakong River samples

Sampling point	Water Type	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	Raw	128.13	128.13	0	0	0
	Filtrated	29.52	29.52	0	0	0
Upstream 2	Raw	258.50	258.50	0	0	0
	Filtrated	69.41	69.41	0	0	0
Upstream 3	Raw	282.63	282.63	0	0	0
	Filtrated	278.59	278.59	0	0	0
Downstream 1	Raw	329.00	257.98	47.43	12.79	10.81
	Filtrated	582.91	485.63	72.31	14.14	10.83
Downstream 2	Raw	517.22	404.47	96.14	0	0
	Filtrated	1007.07	858.35	135.81	0	0
Downstream 3	Raw	1091.45	0	65.29	317.40	708.77
	Filtrated	1103.15	0	53.79	309.27	740.09
Average	Raw	434.49	221.95	34.81	55.03	119.93
	Filtrated	511.77	286.92	43.65	20.57	125.15
Minimum	Raw	128.13	128.13	0	0	0
	Filtrated	29.52	29.52	0	0	0
Maximum	Raw	1091.45	404.47	47.43	317.40	708.77
	Filtrated	1103.15	858.35	135.81	309.27	740.09

Table 4.10 Summarized multi-variable regression models of shrimp farm effluents for predict THMFP and each THM species.

Model	Equation	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	$THMFP = TOC\{100.323 Salinity - [(3.62 \times 10^{-2}) Conductivity] + 85.944\}$	0.958	0.917	0.904	57.63997
2	$Bromoform\ FP = DOC(37.811\ Bromide + 53.116)$	0.712	0.506	0.452	162.52803
3	$Dibromochloromethane\ FP = DOC\ (9.469 Bromide + 16.900)$	0.909	0.825	0.806	18.95991
4	$Chloroform\ FP = TOC(-5.148\ Salinity + 62.265)$	0.834	0.695	0.673	18.00595

Table 4.11 Summarized IR results of shrimp farm effluents

Wavenumber (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	Aromatic ring (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

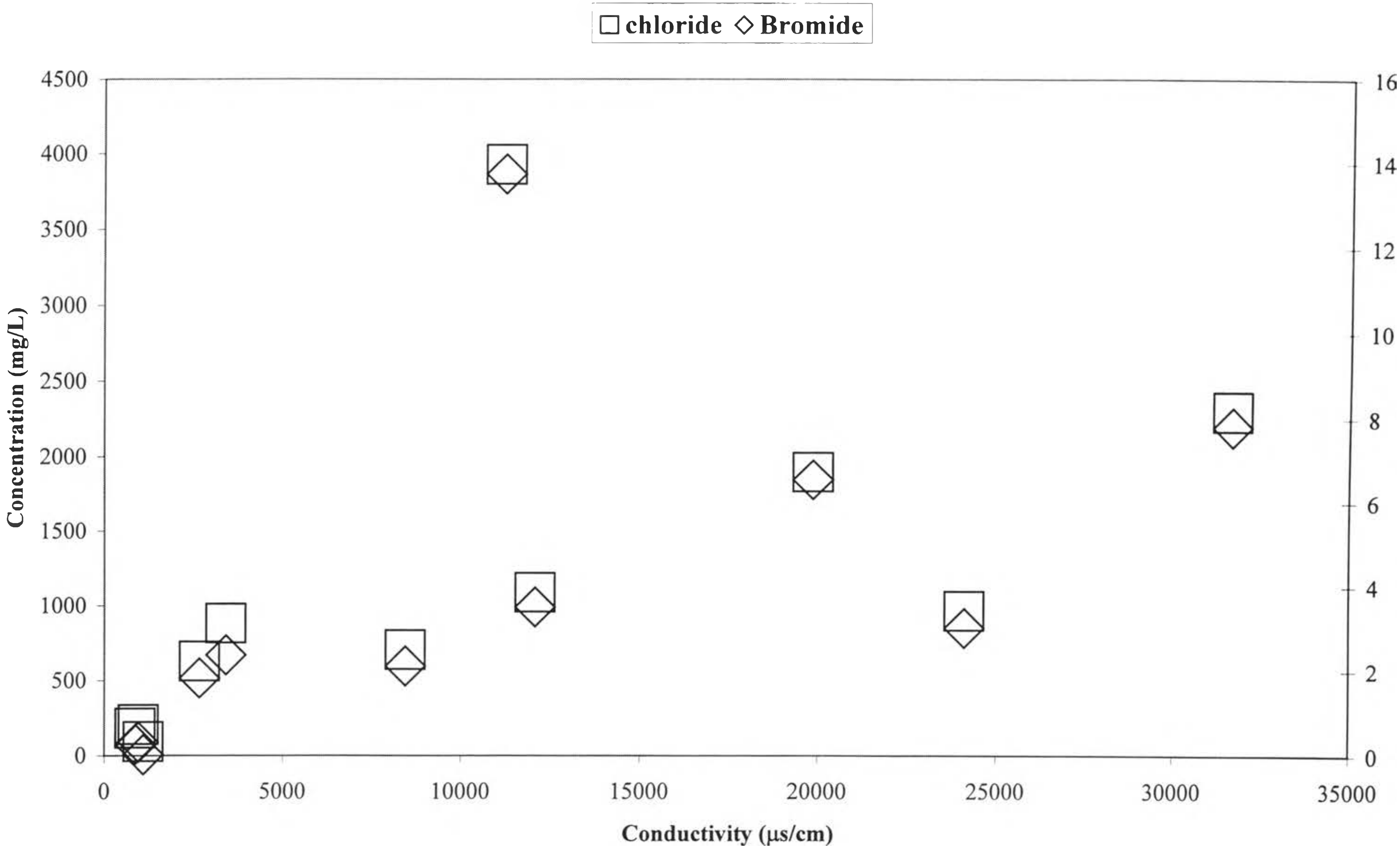

Figure 4.1 Relationship between bromide, chloride and conductivity in shrimp farm effluents

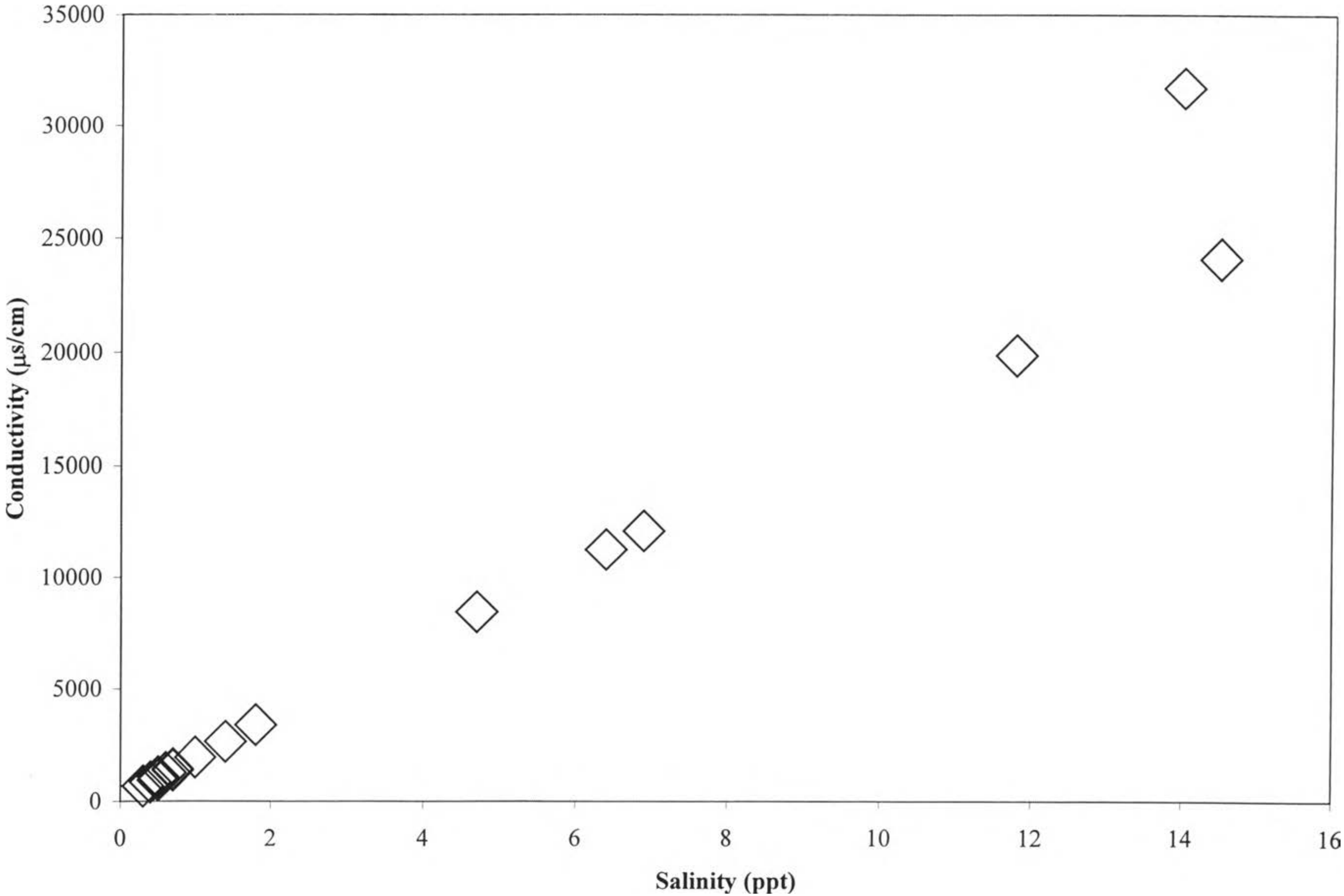

Figure 4.2 Relationship between salinity and conductivity in shrimp farm effluents

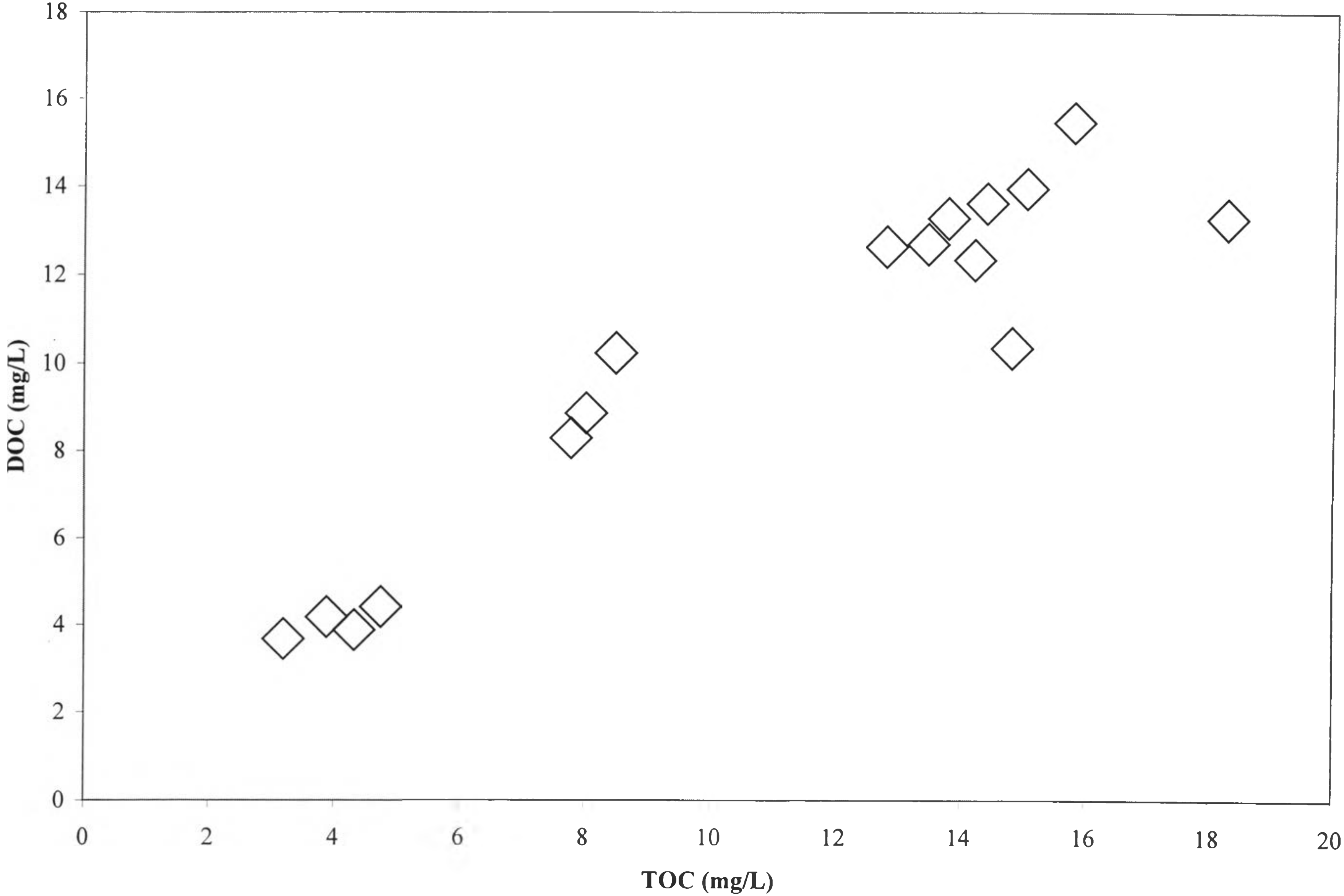

Figure 4.3 Relationship between TOC and DOC in shrimp farm effluents

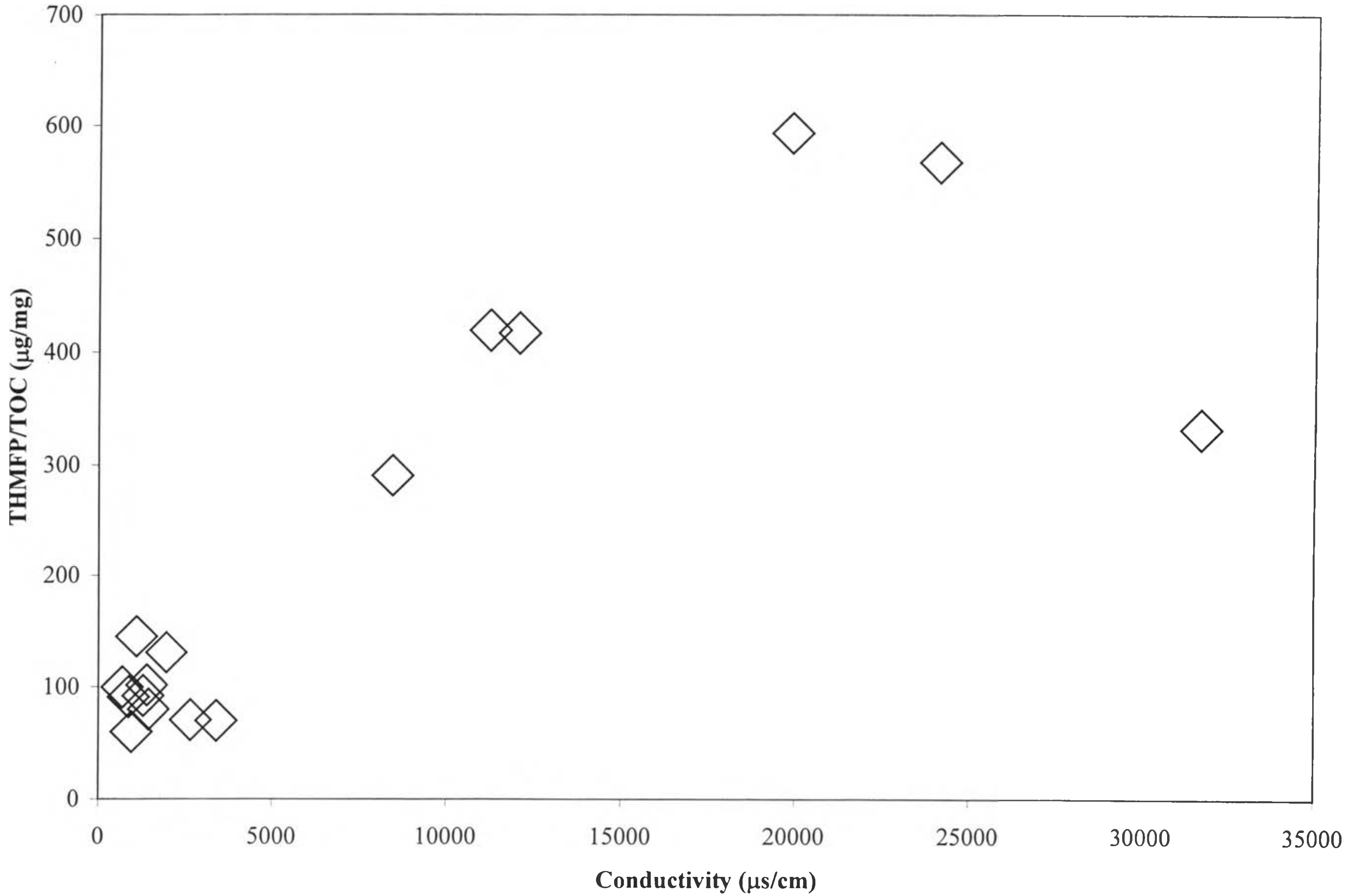

Figure 4.4 Relationship between conductivity and THMFP/TOC in shrimp farm effluents (raw water)

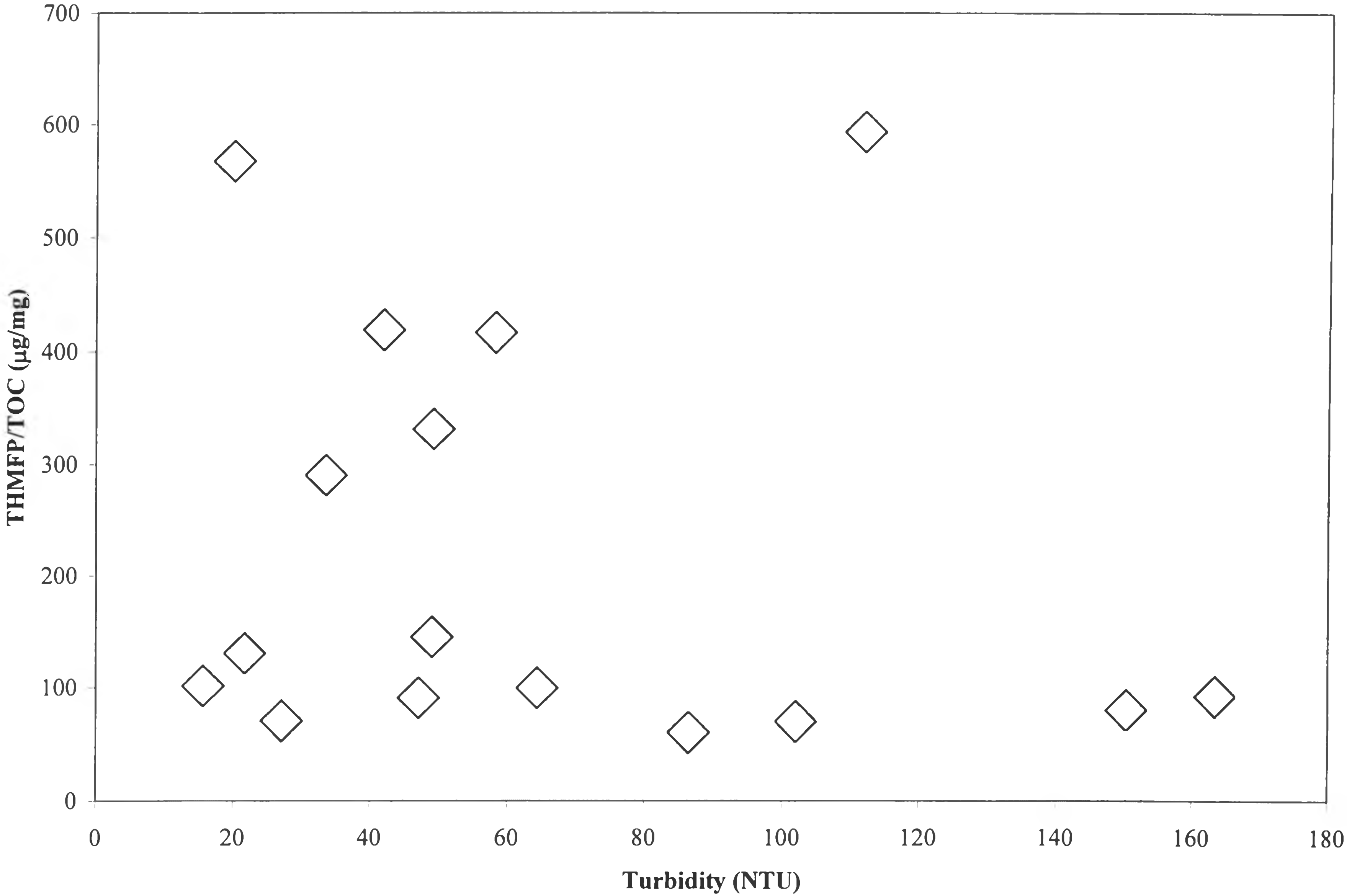

Figure 4.5 Relationship between turbidity and THMFP/TOC in shrimp farm effluents (raw water)

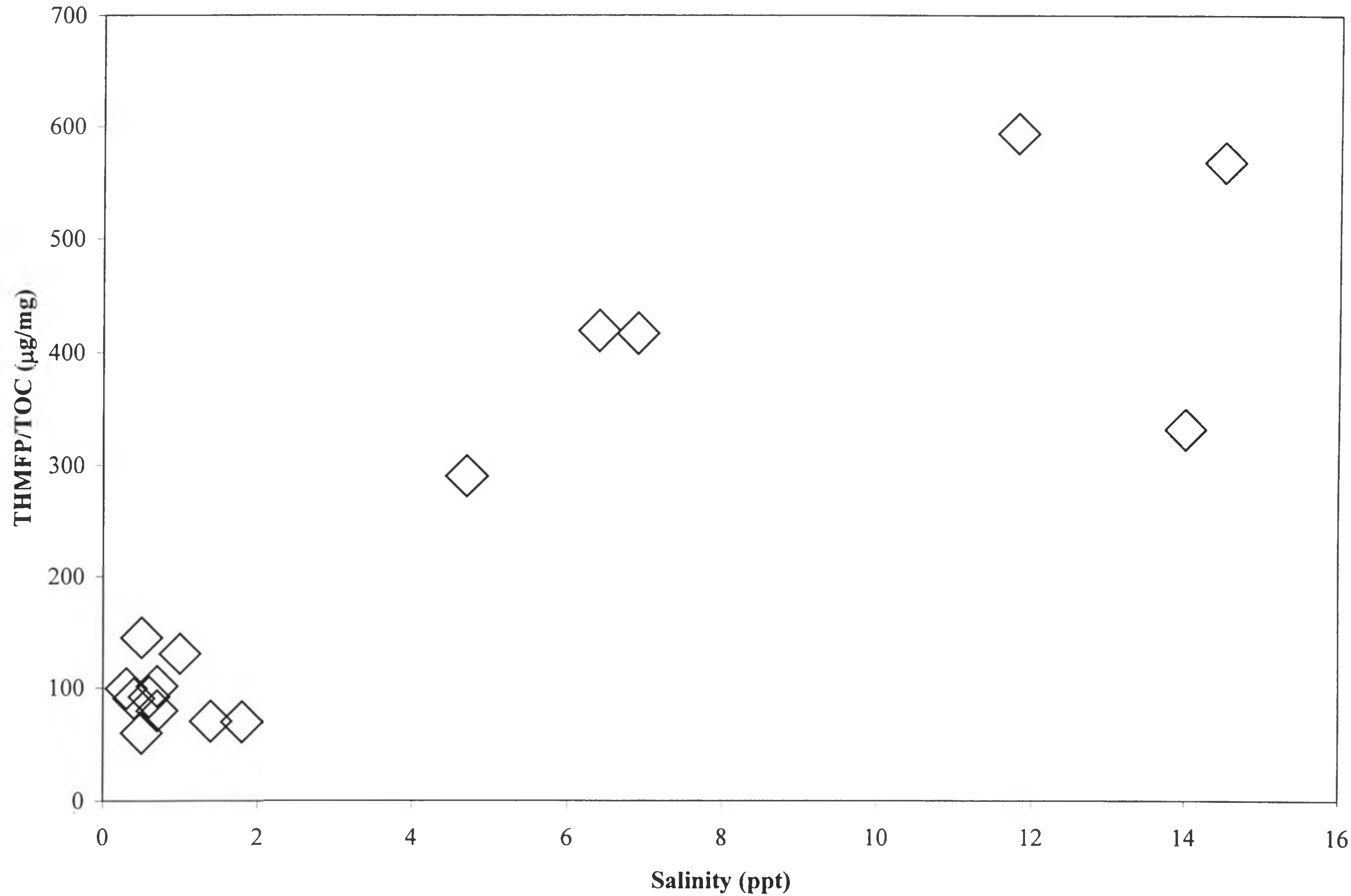

Figure 4.6 Relationship between salinity and THMFP/TOC in shrimp farm effluents (raw water)

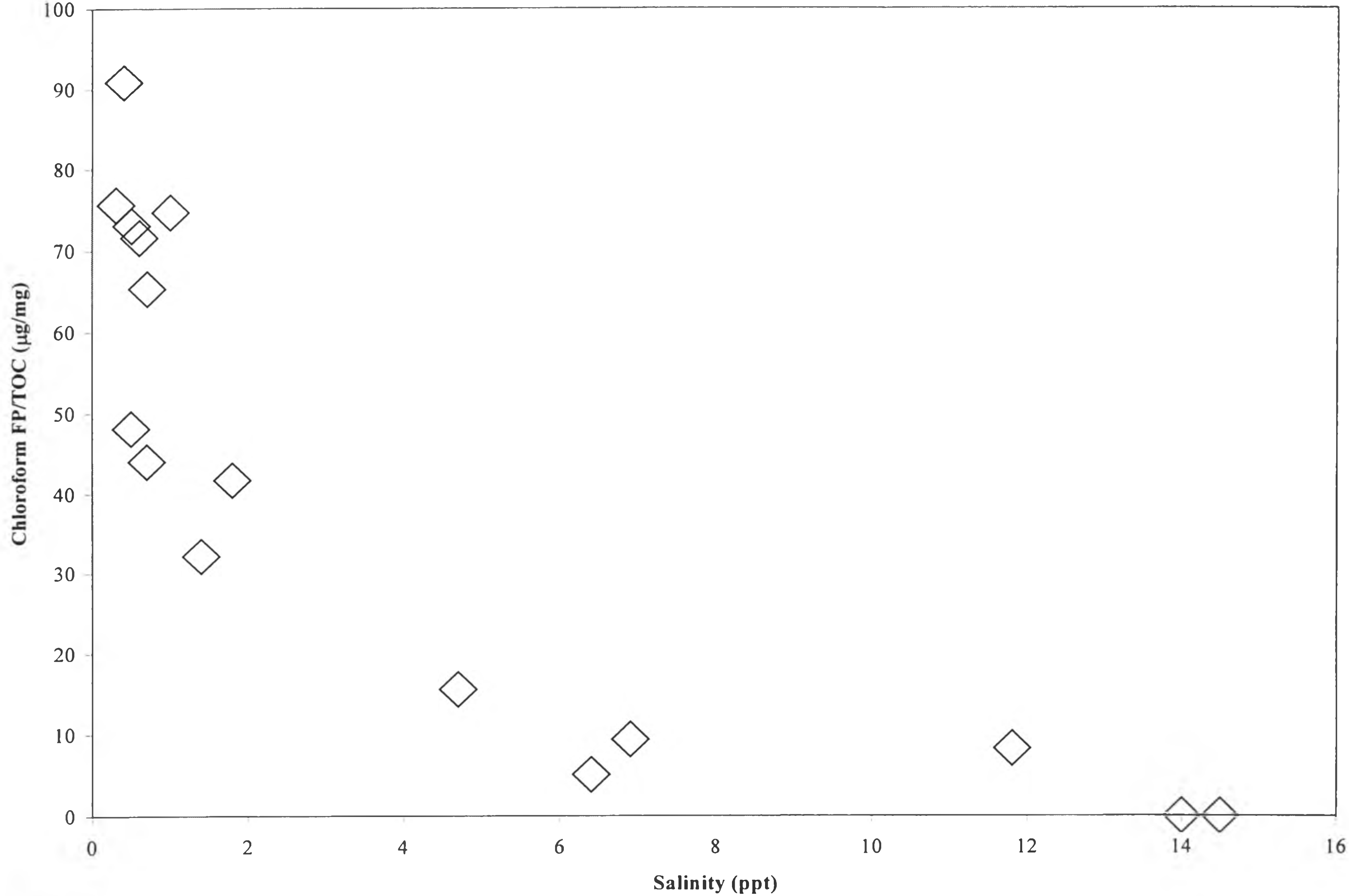

Figure 4.7 Relationship between salinity and chloroform formation potential/TOC in shrimp farm effluents (raw water)

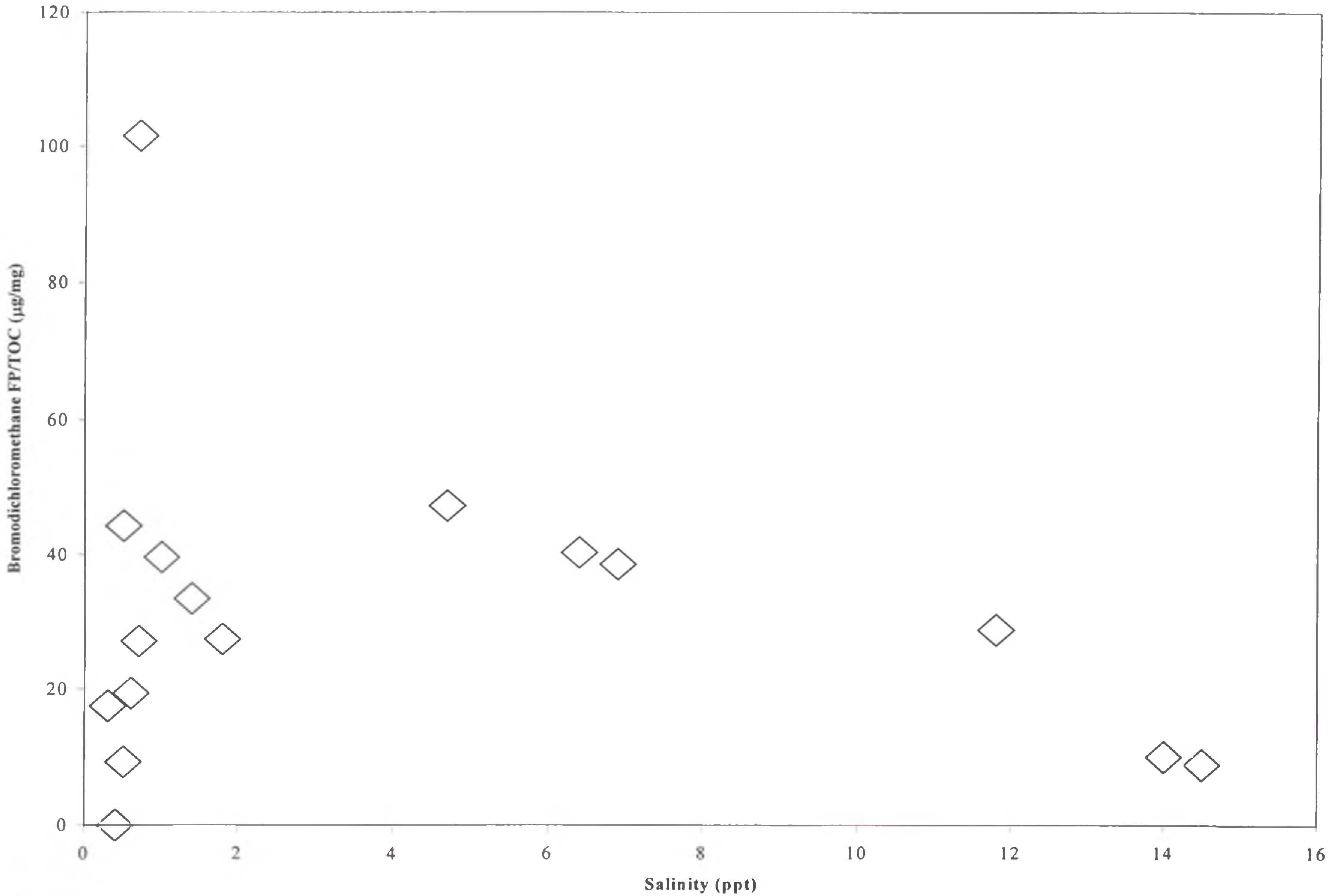

Figure 4.8 Relationship between salinity and bromodichloromethane formation potential/TOC in shrimp farm effluents (raw water)

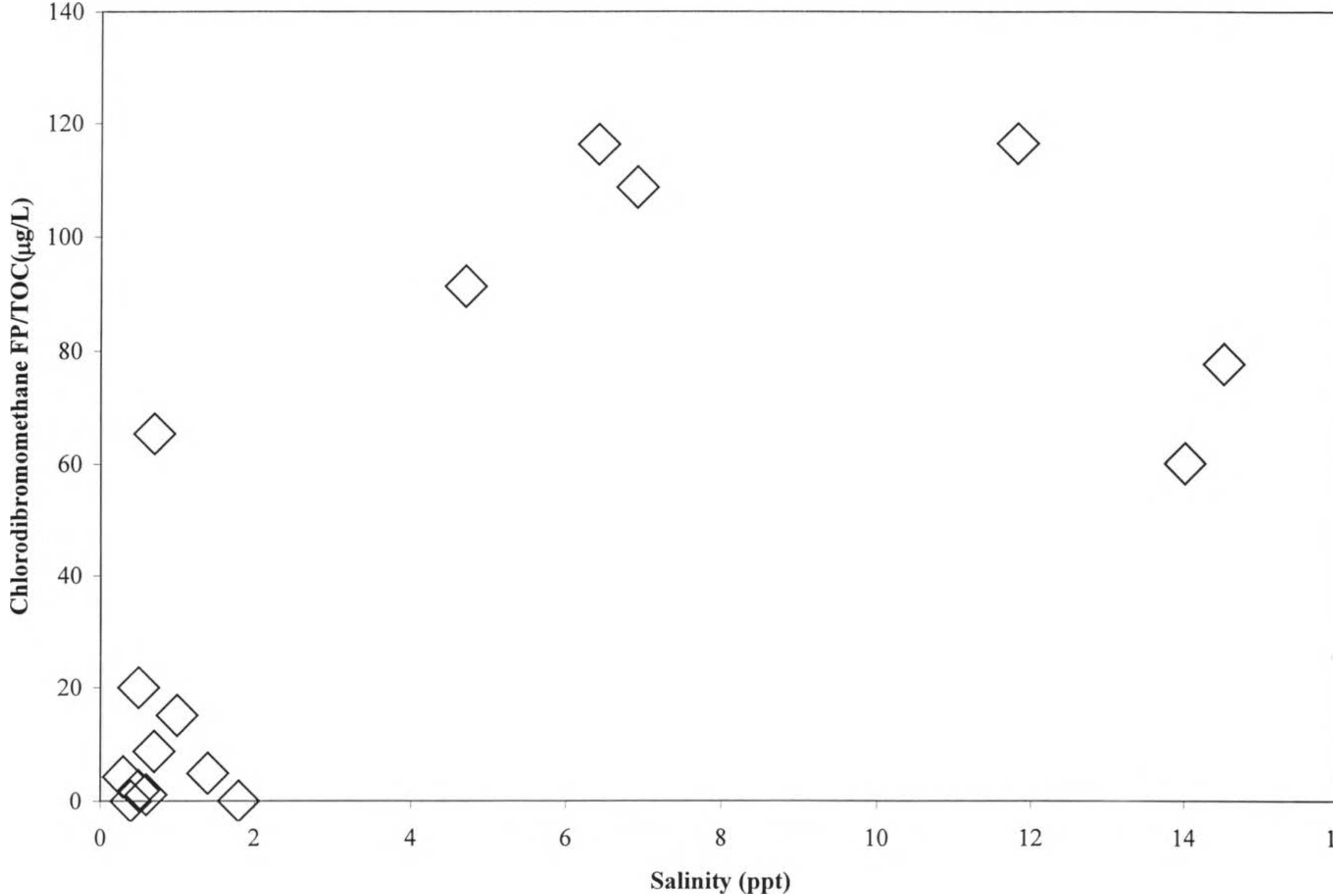

Figure 4.9 Relationship between salinity and chlorodibromomethane formation potential/TOC in shrimp farm effluents (raw water)

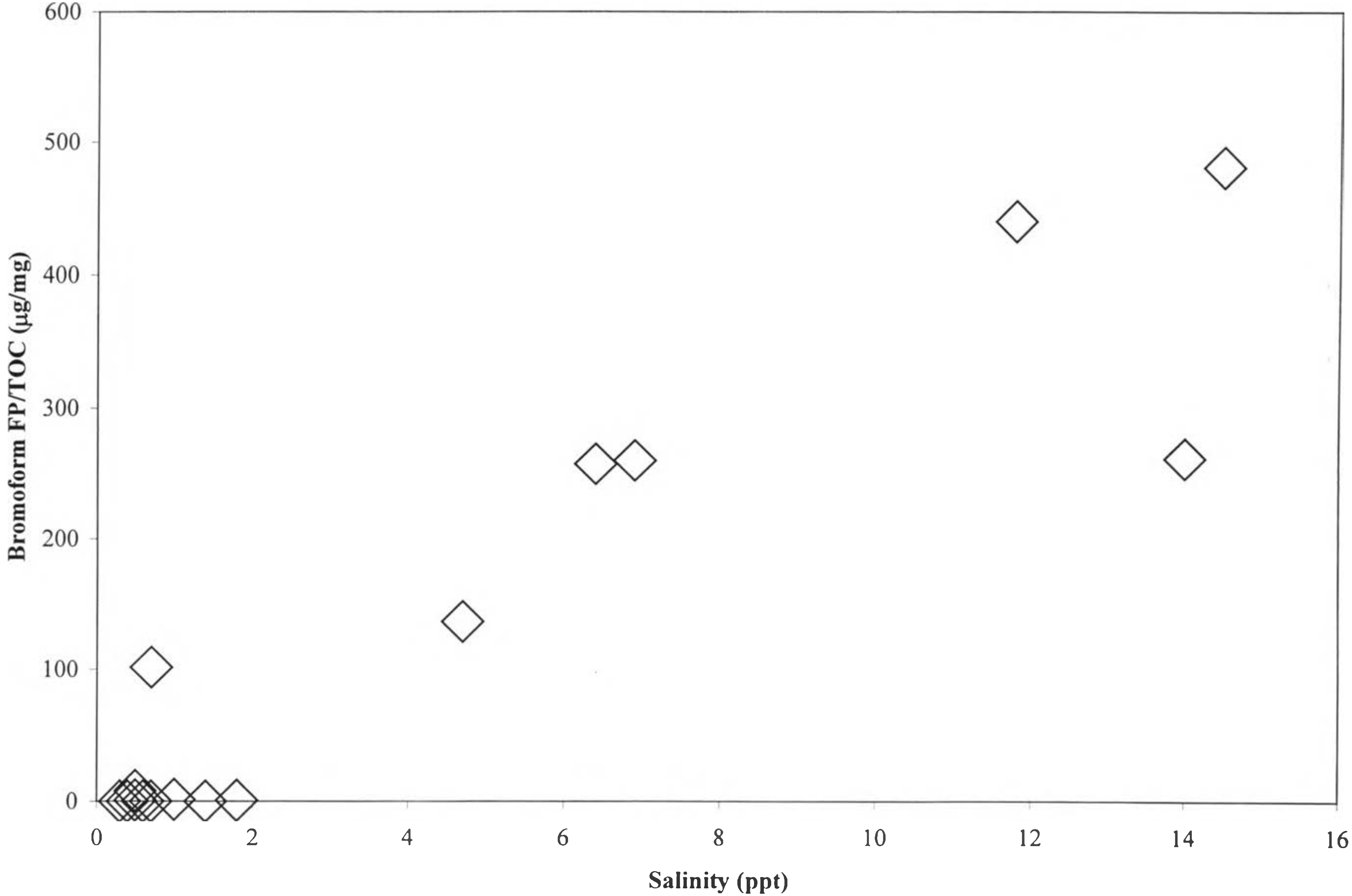

Figure 4.10 Relationship between salinity and bromoform formation potential/TOC in shrimp farm effluents (raw water)

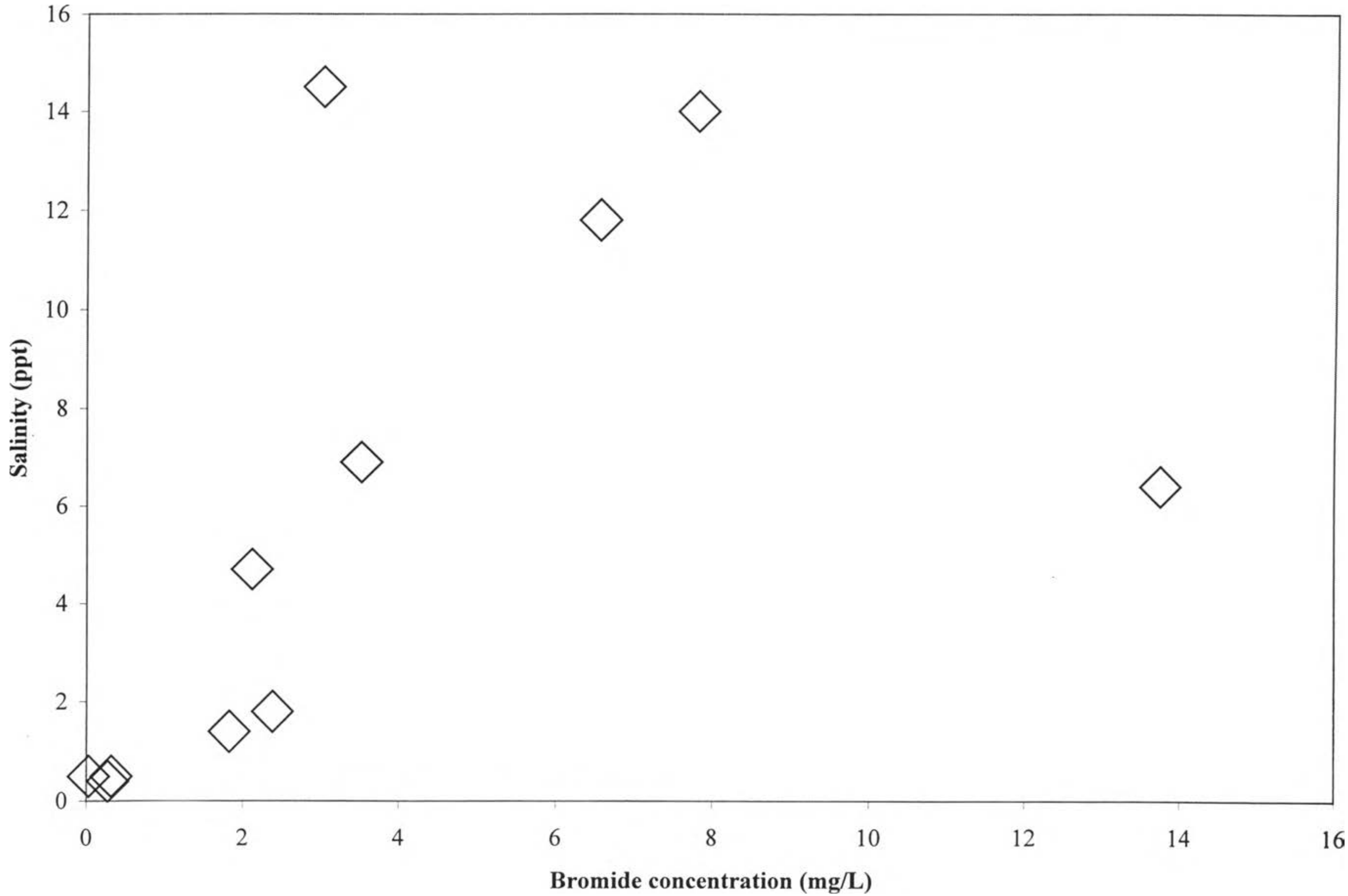

Figure 4.11 Relationship between bromide concentration and salinity in shrimp farm effluents

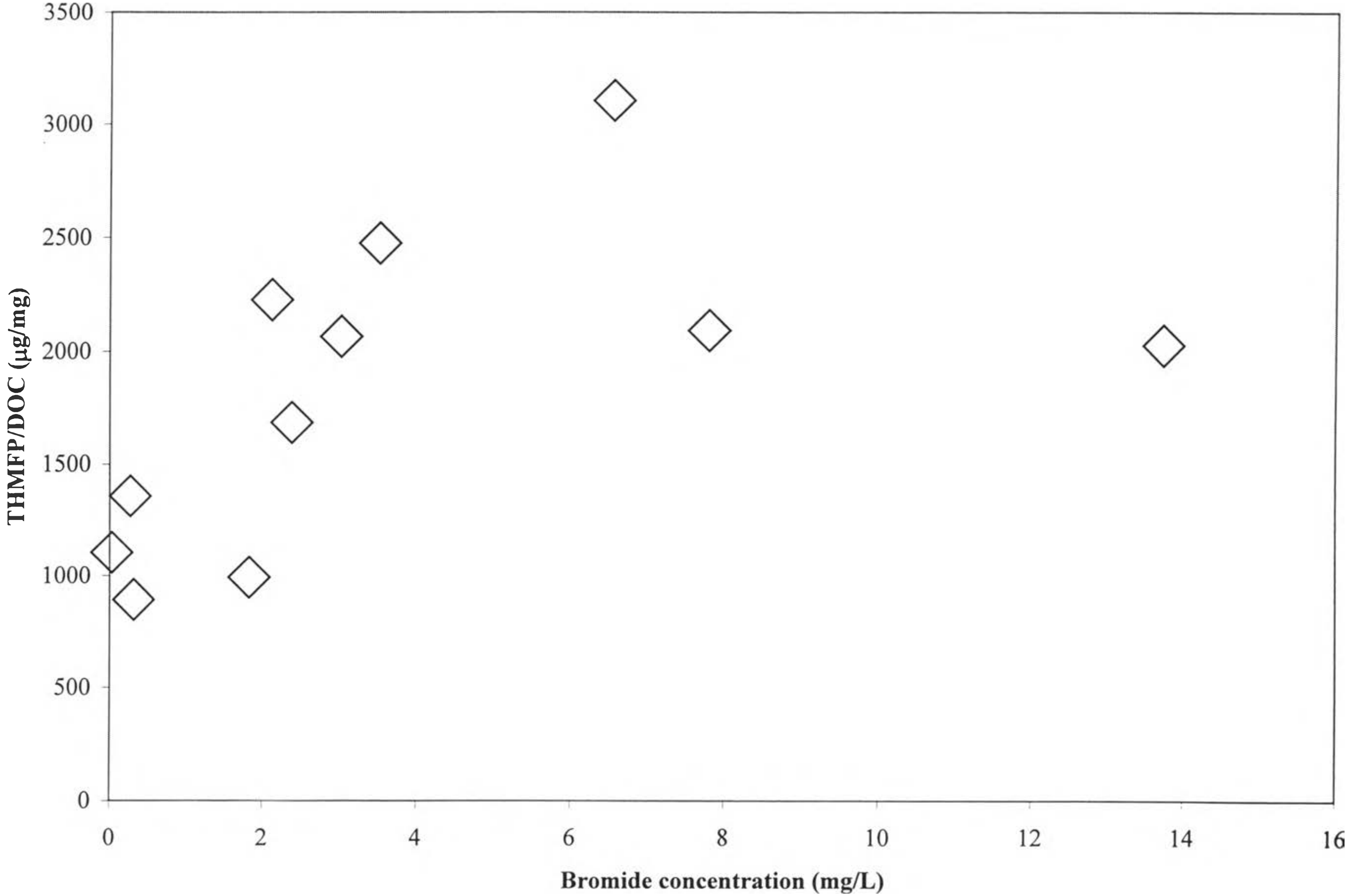

Figure 4.12 Relationship between bromide concentration and THMFP/DOC in shrimp farm effluents (filtrated water)

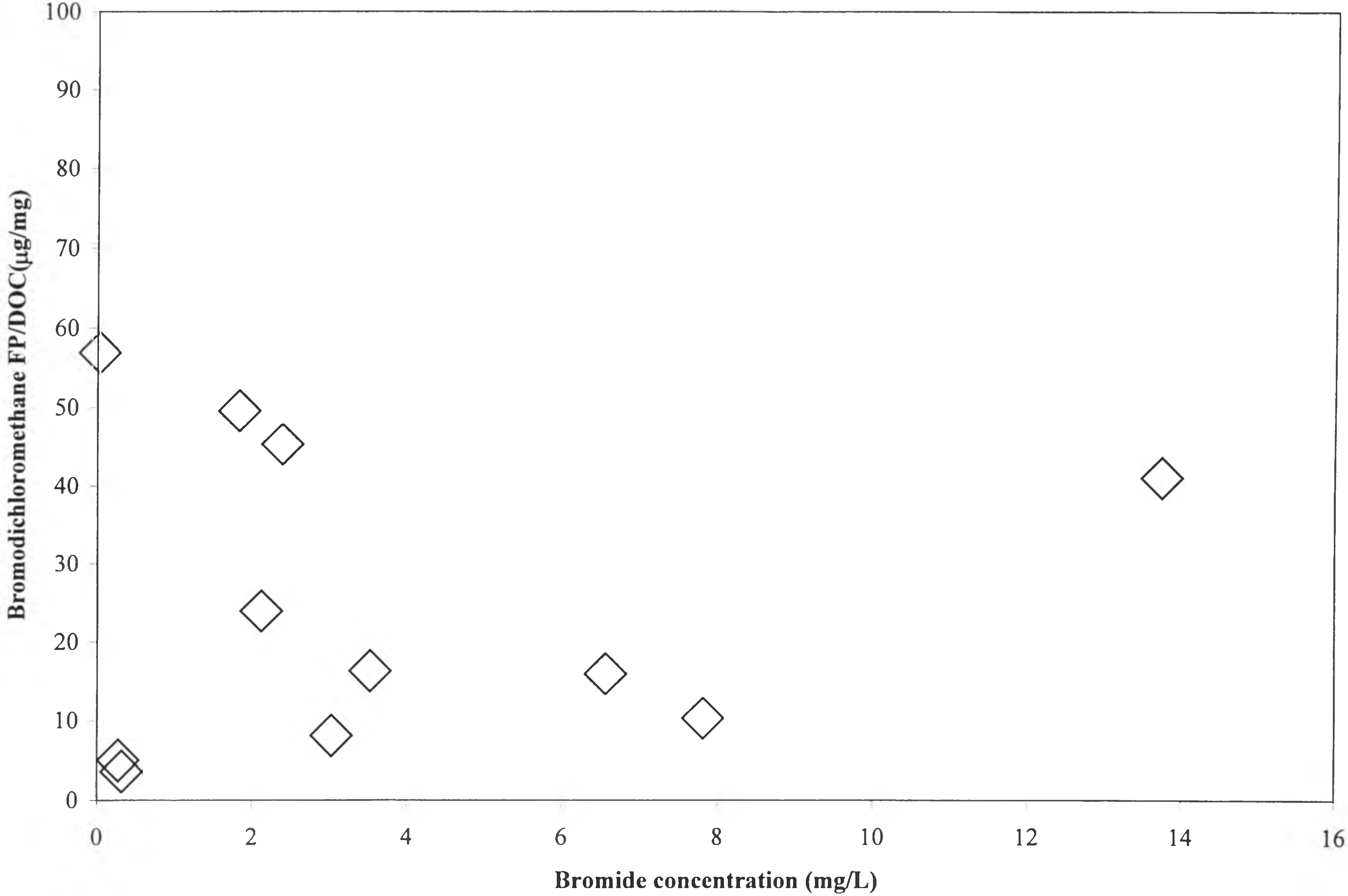

Figure 4.13 Relationship between bromide concentration and bromodichloromethane formation potential/DOC in shrimp farm effluents (filtrated water)

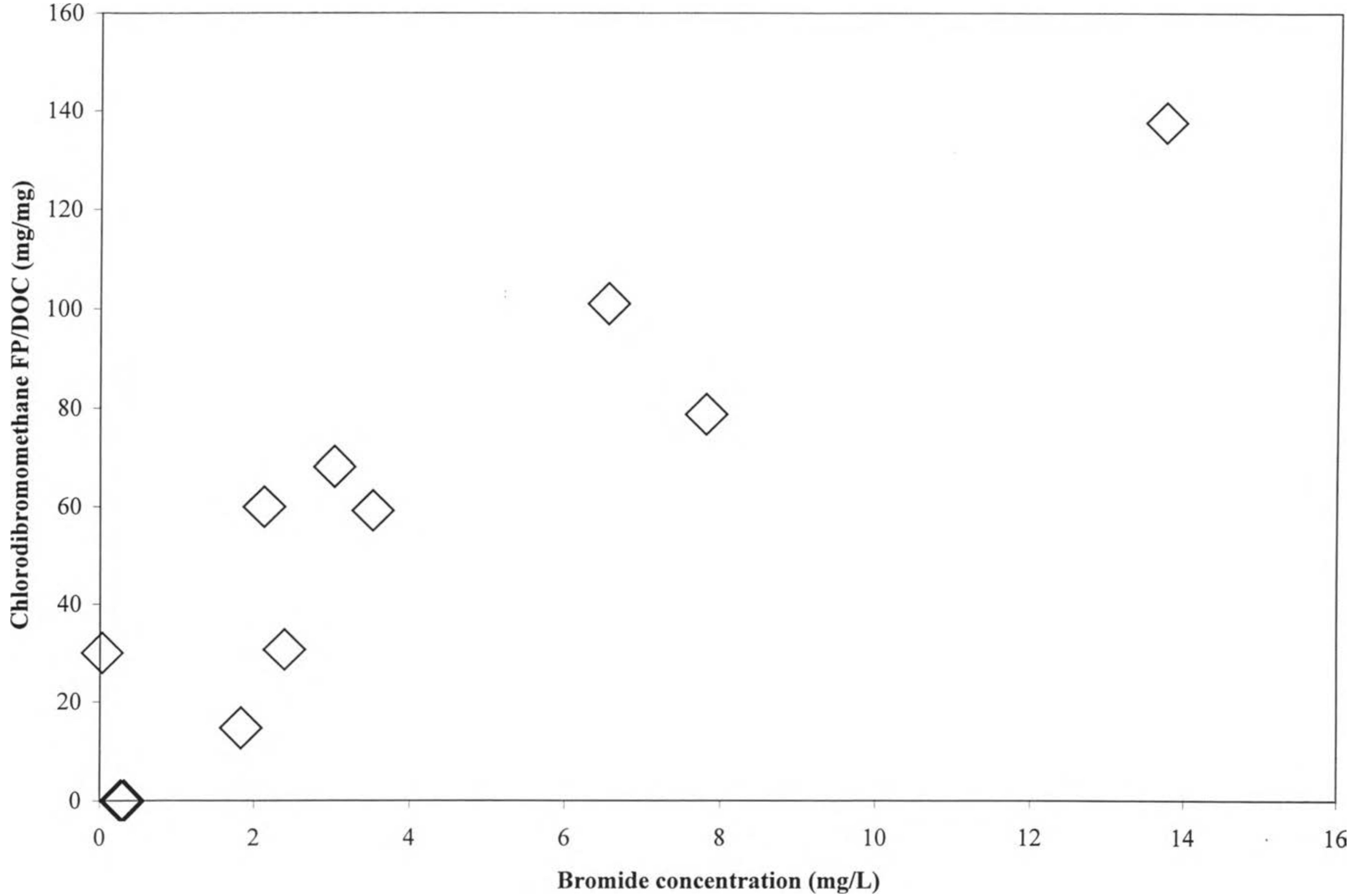

Figure 4.14 Relationship between bromide concentration and chlorodibromomethane formation potential/DOC in shrimp farm effluents (filtrated water)

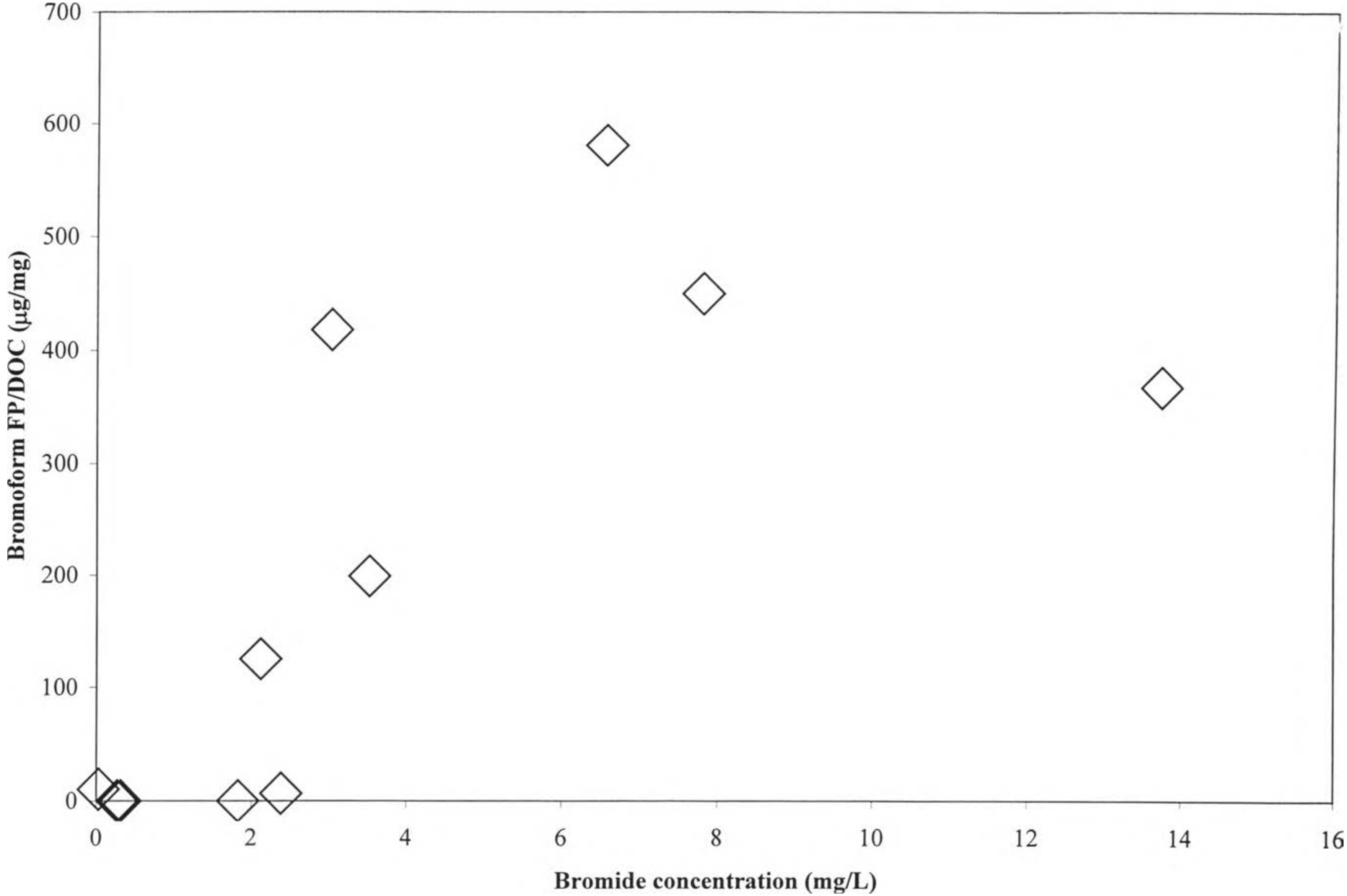

Figure 4.15 Relationship between bromide concentration and bromoform formation potential/DOC in shrimp farm effluents (filtrated water)

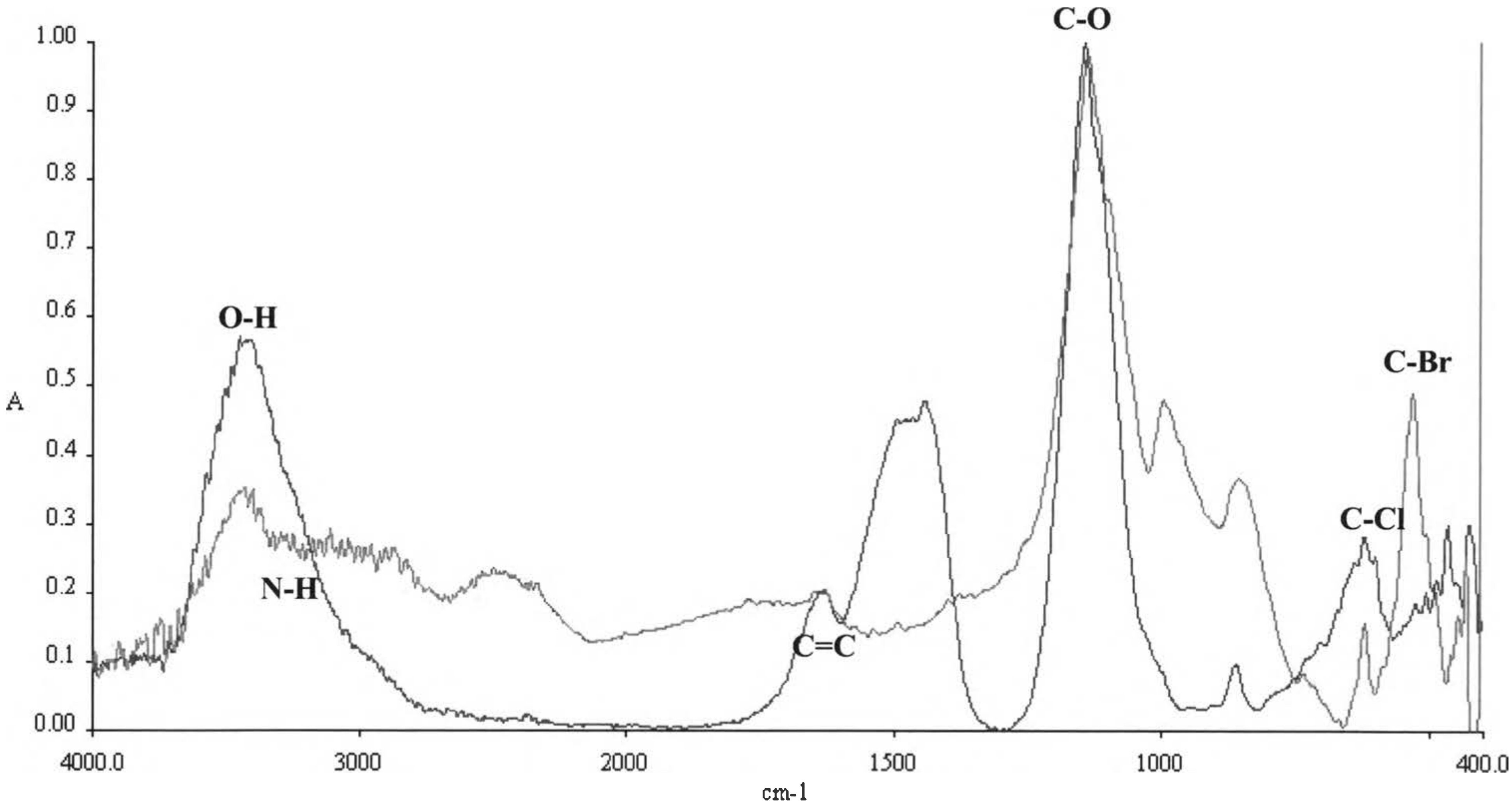

Figure 4.16 IR spectrum of shrimp farm effluent No. 1 before and after chlorination (day 0 and 7)
Before chlorination(day 0)
After chlorination(day 7)

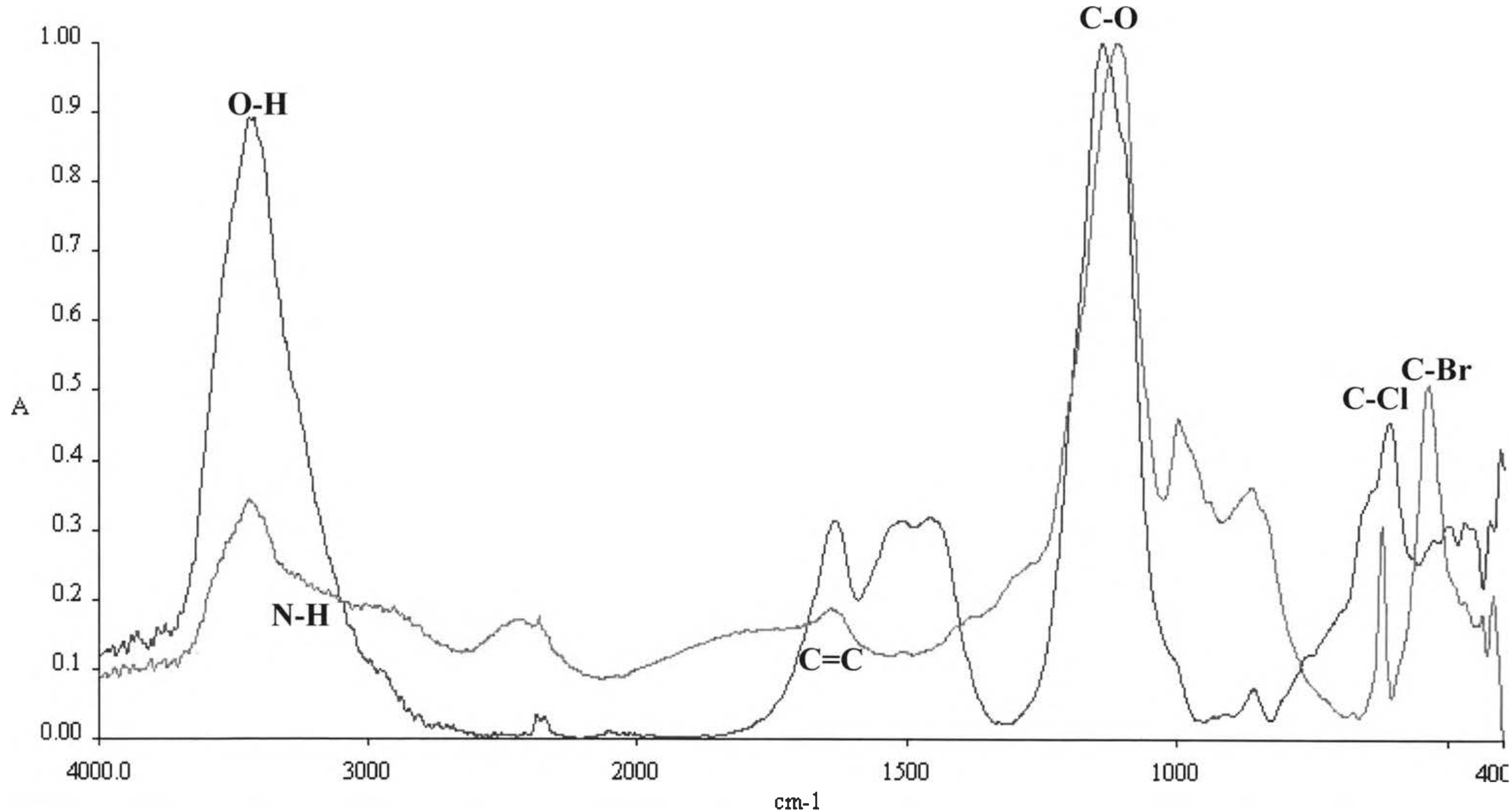

Figure 4.17 IR spectrum of shrimp farm effluent No. 2 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

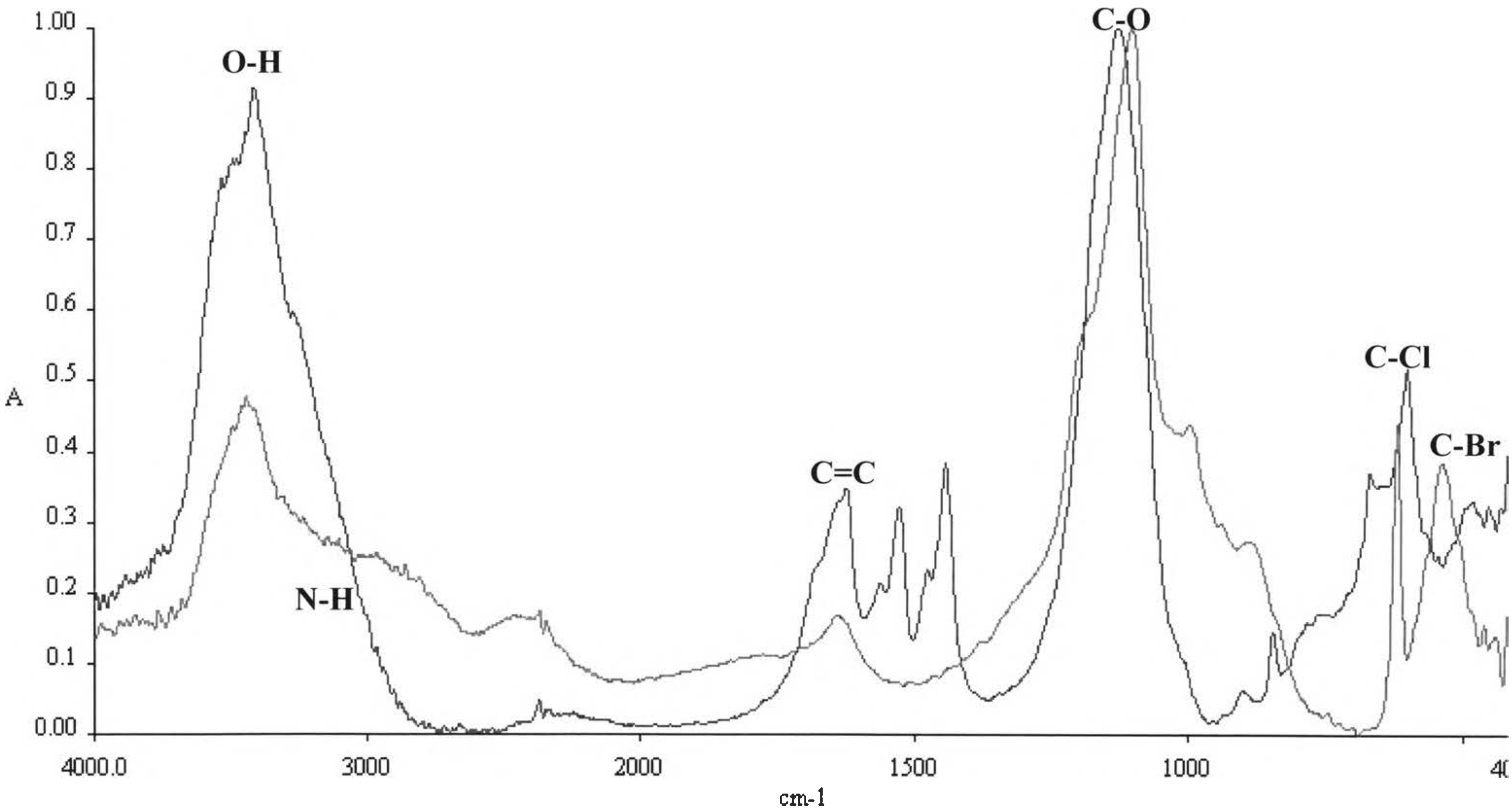

Figure 4.18 IR spectrum of shrimp farm effluent No. 3 before and after chlorination (day 0 and 7)
Before chlorination(day 0)
After chlorination(day 7)

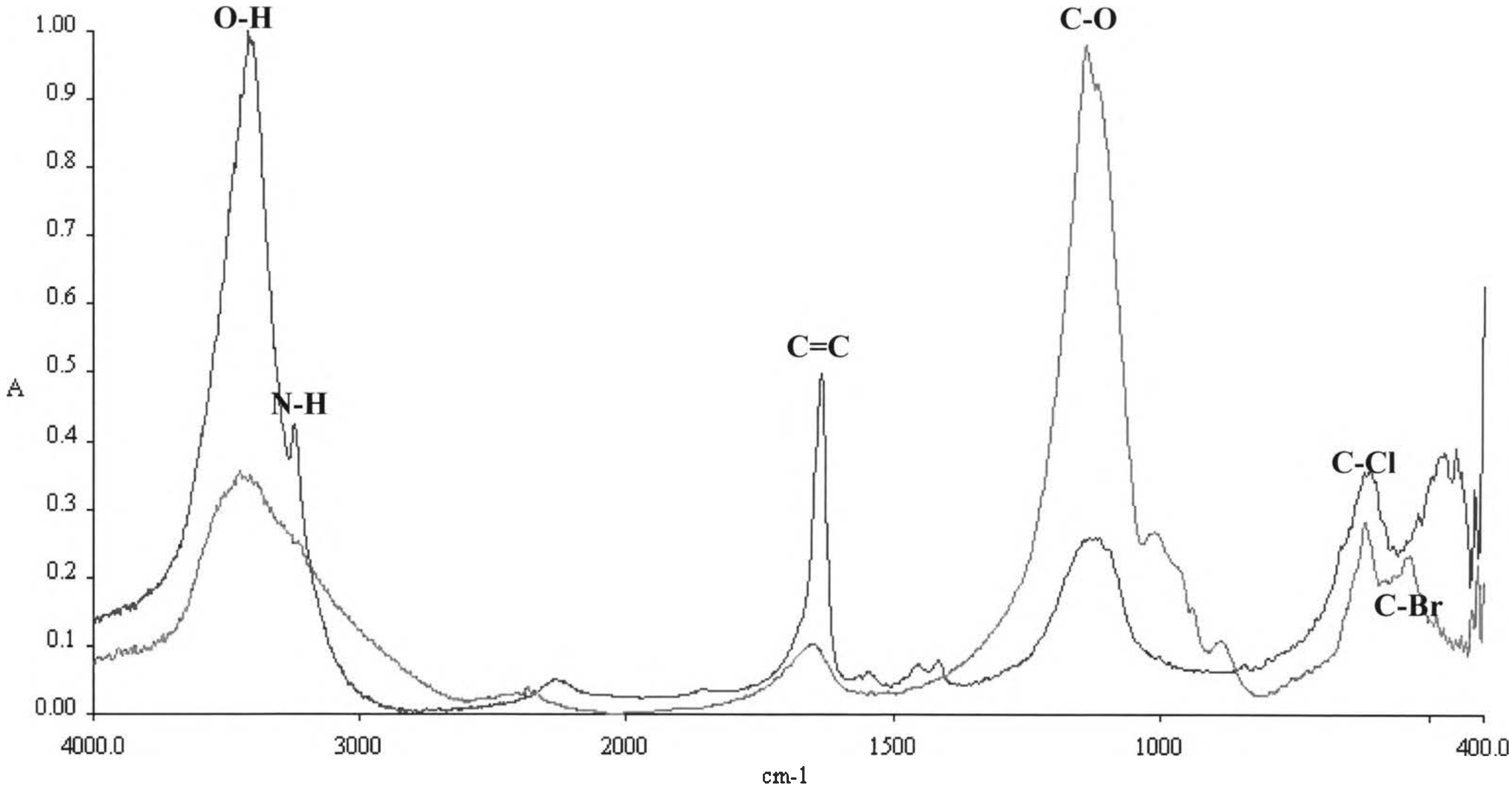

Figure 4.19 IR spectrum of shrimp farm effluent No. 4 before and after chlorination (day 0 and 7)
Before chlorination(day 0)
After chlorination(day 7)

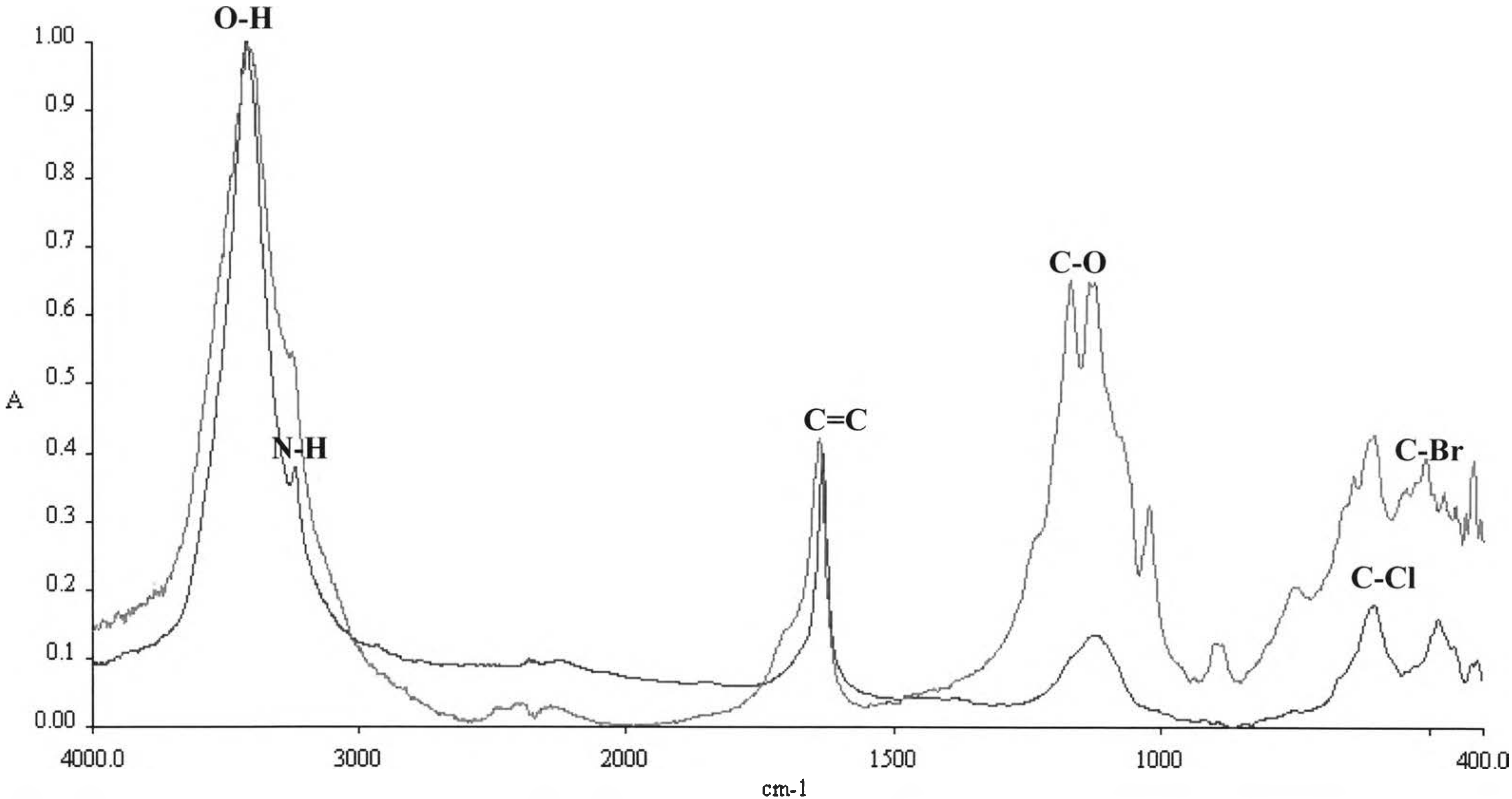

Figure 4.20 IR spectrum of shrimp farm effluent No. 5 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

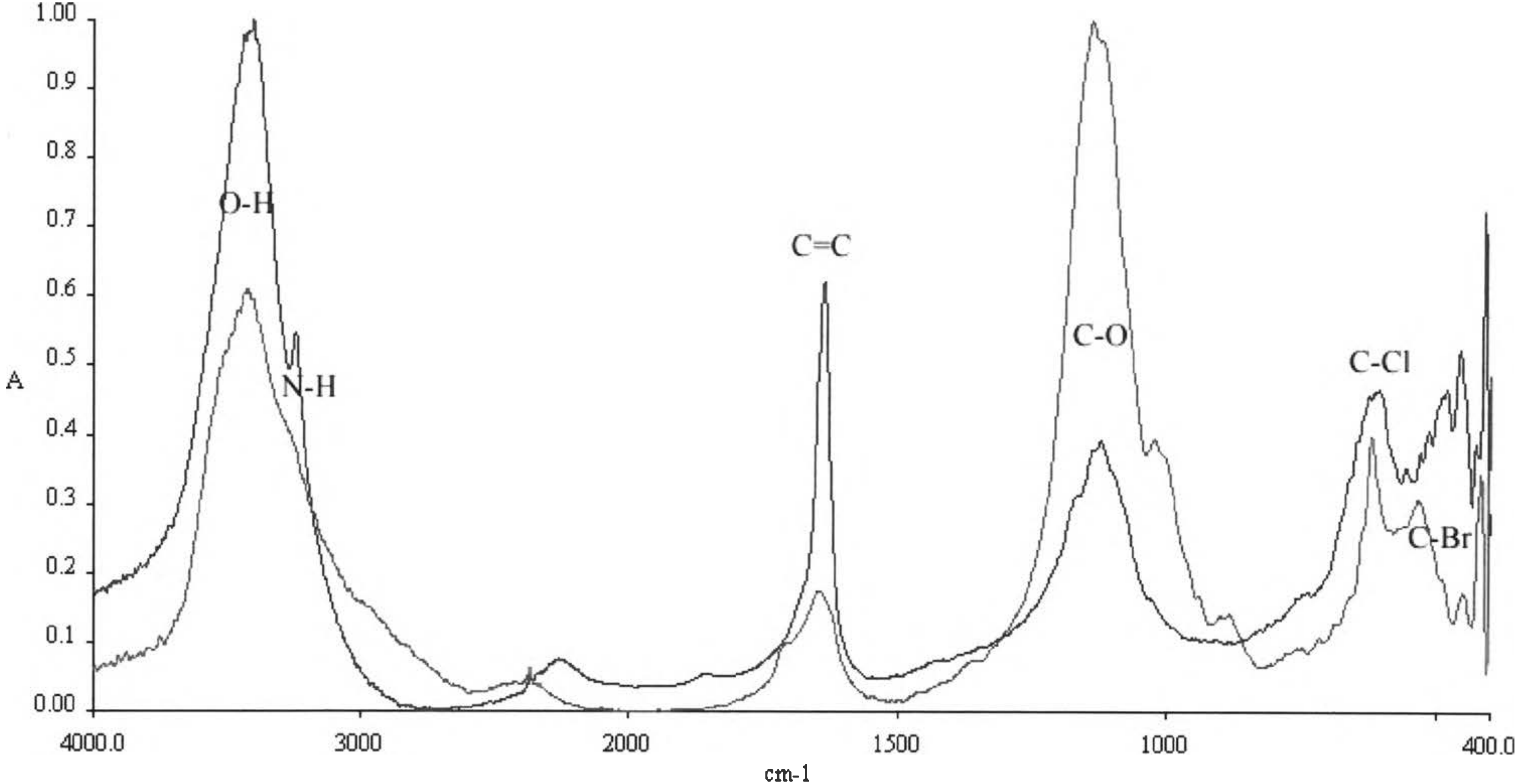

Figure 4.21 IR spectrum of shrimp farm effluent No. 6 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

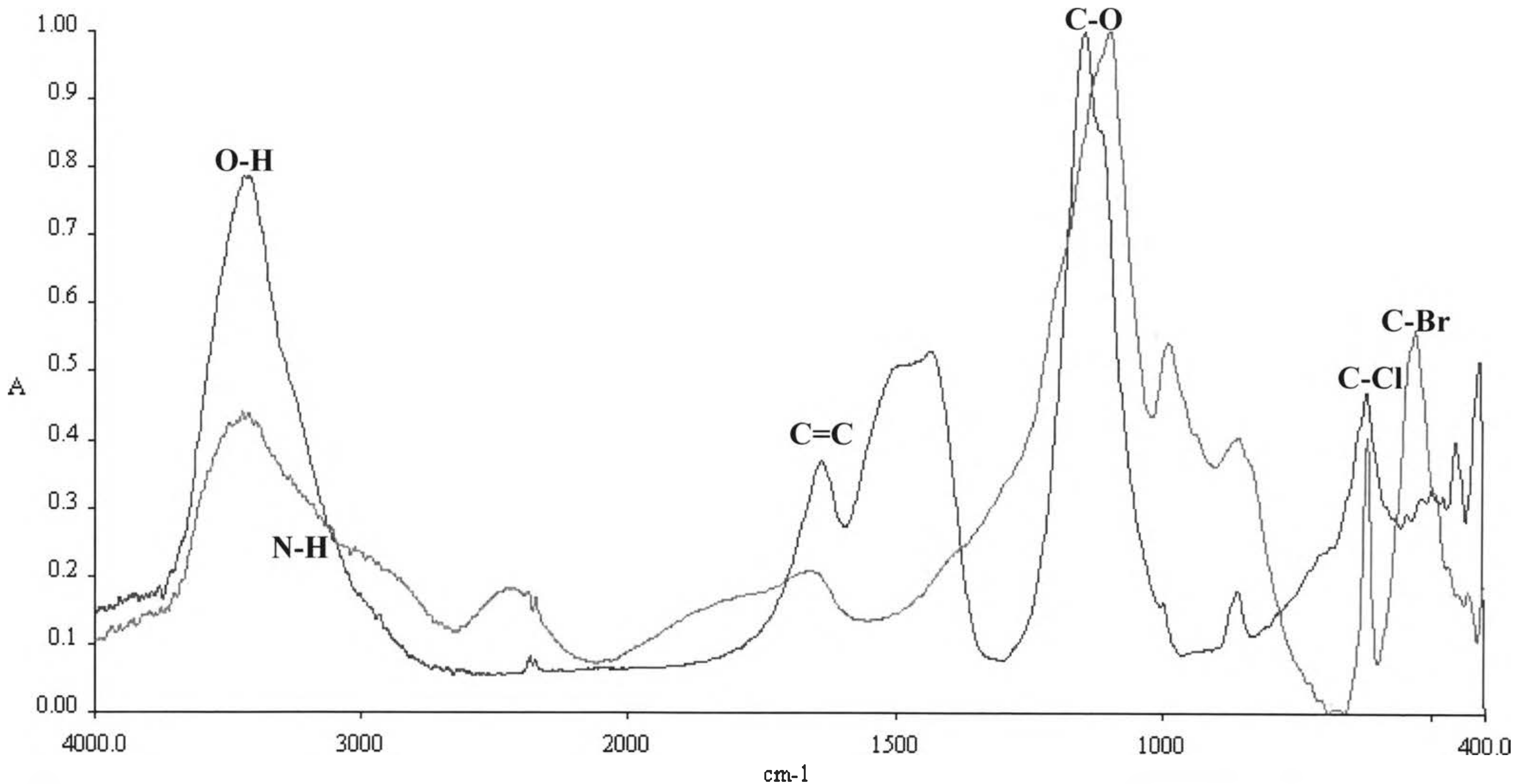

Figure 4.22 IR spectrum of shrimp farm effluent No. 12 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

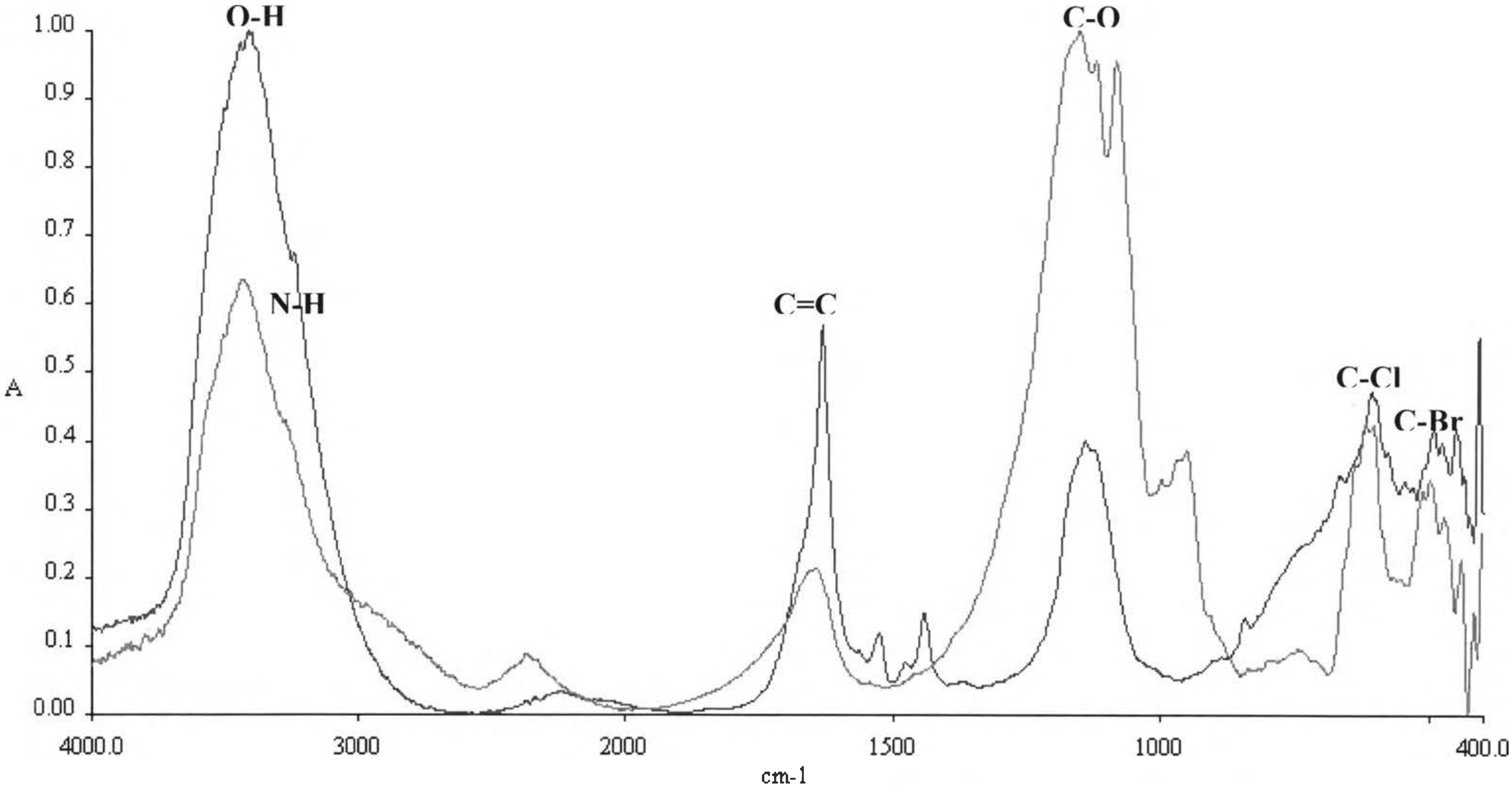

Figure 4.23 IR spectrum of shrimp farm effluent No. 13 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

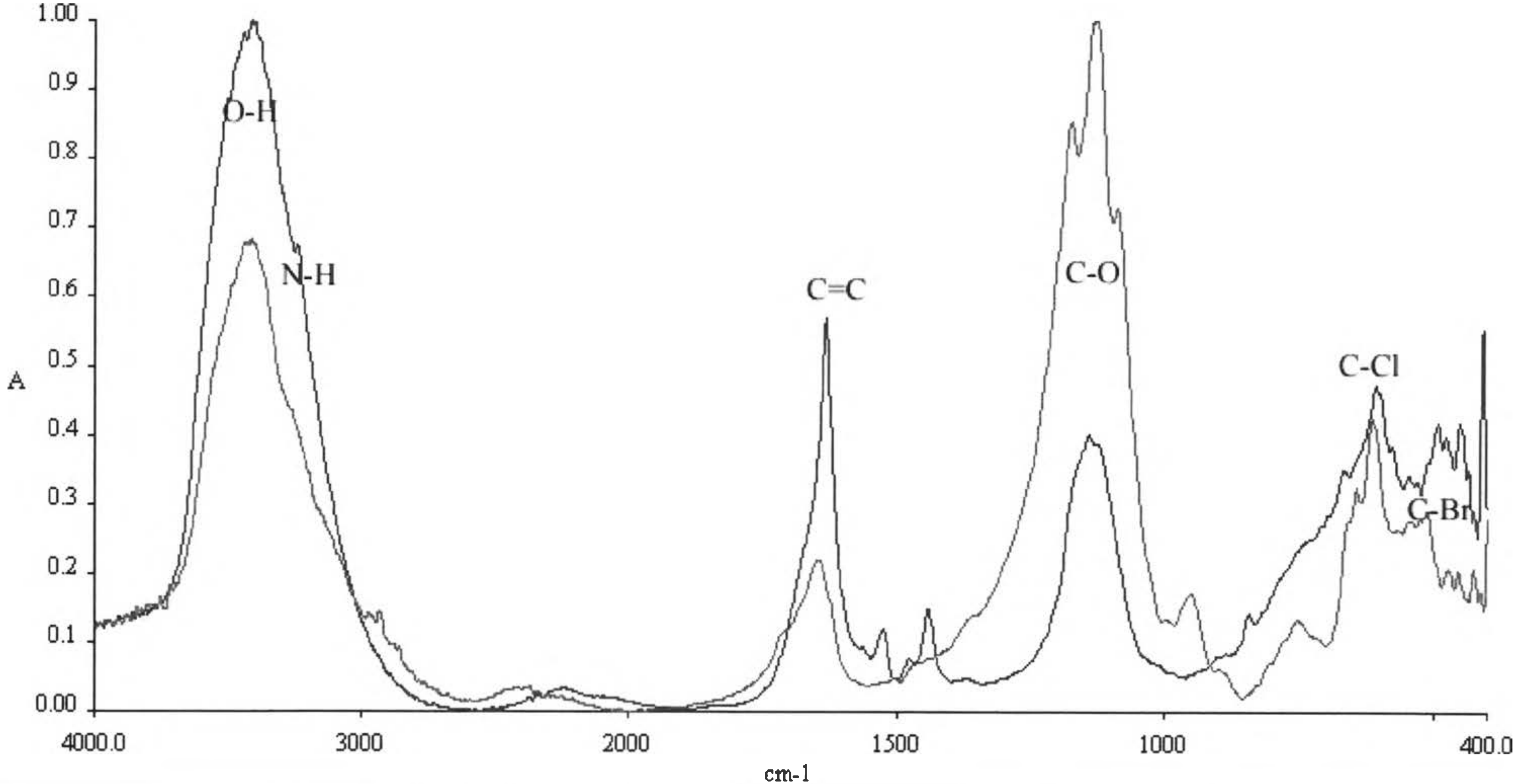

Figure 4.24 IR spectrum of shrimp farm effluent No. 14 before and after chlorination (day 0 and 7)
Before chlorination(day 0)
After chlorination(day 7)

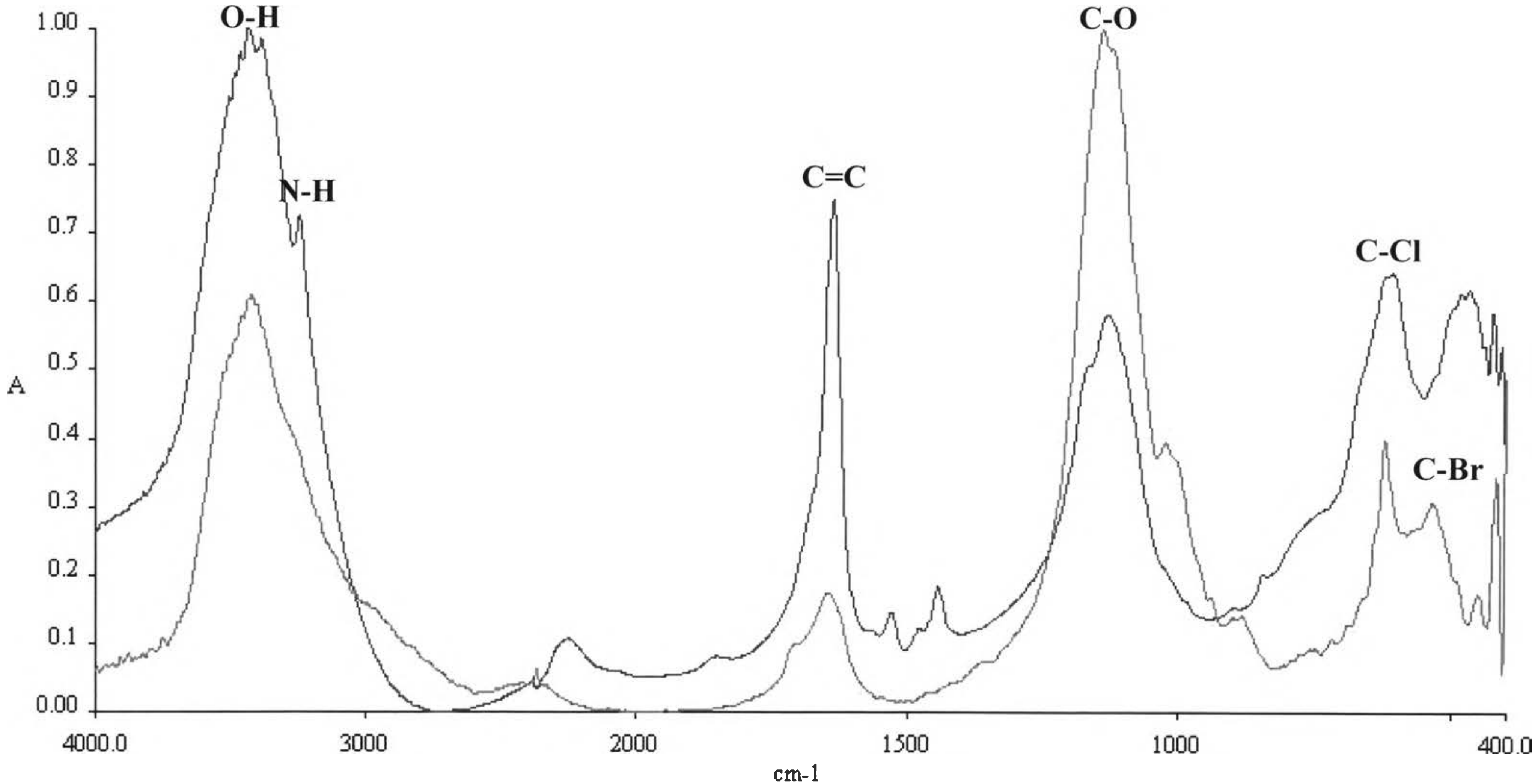

Figure 4.25 IR spectrum of shrimp farm effluent No. 15 before and after chlorination (day 0 and 7)

Before chlorination(day 0)

After chlorination(day 7)

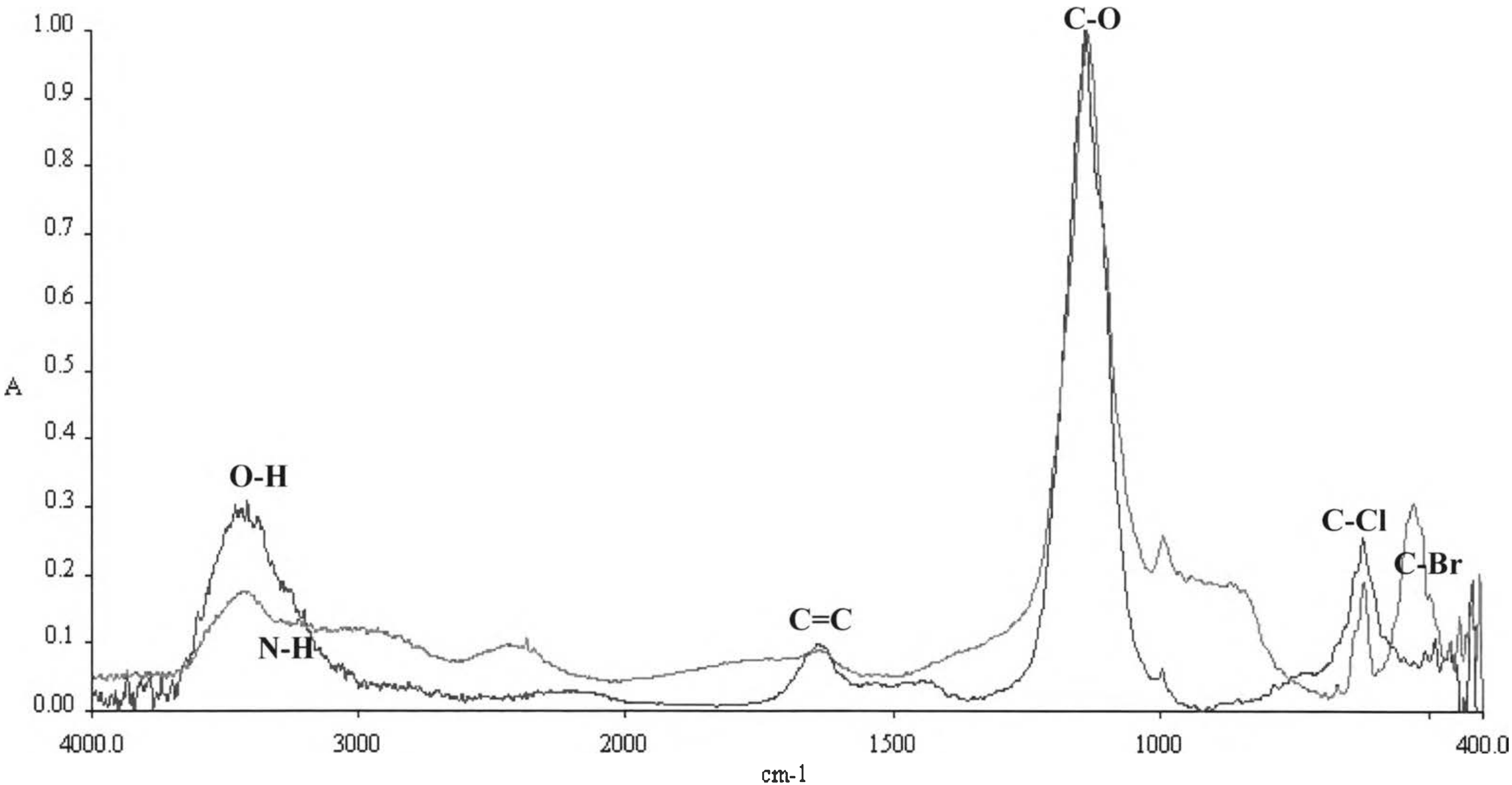

Figure 4.26 IR spectrum of shrimp farm effluent No. 16 before and after chlorination (day 0 and 7)
Before chlorination(day 0)
After chlorination(day 7)

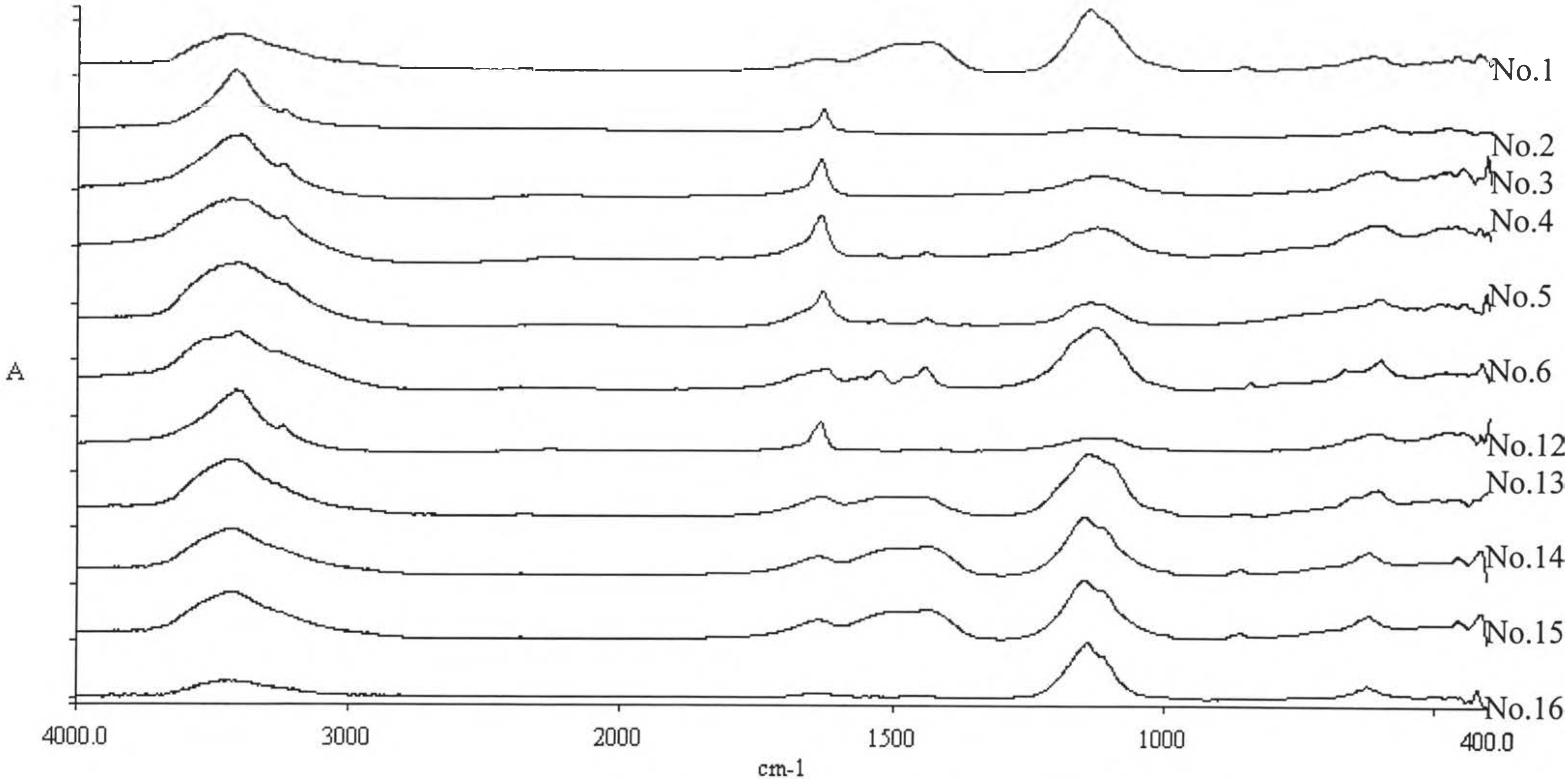

Figure 4.27 IR spectrum of shrimp farm effluent No. 1,2,3,4,5,6,11,12,13,14,15, and 16 before chlorination (day 0)

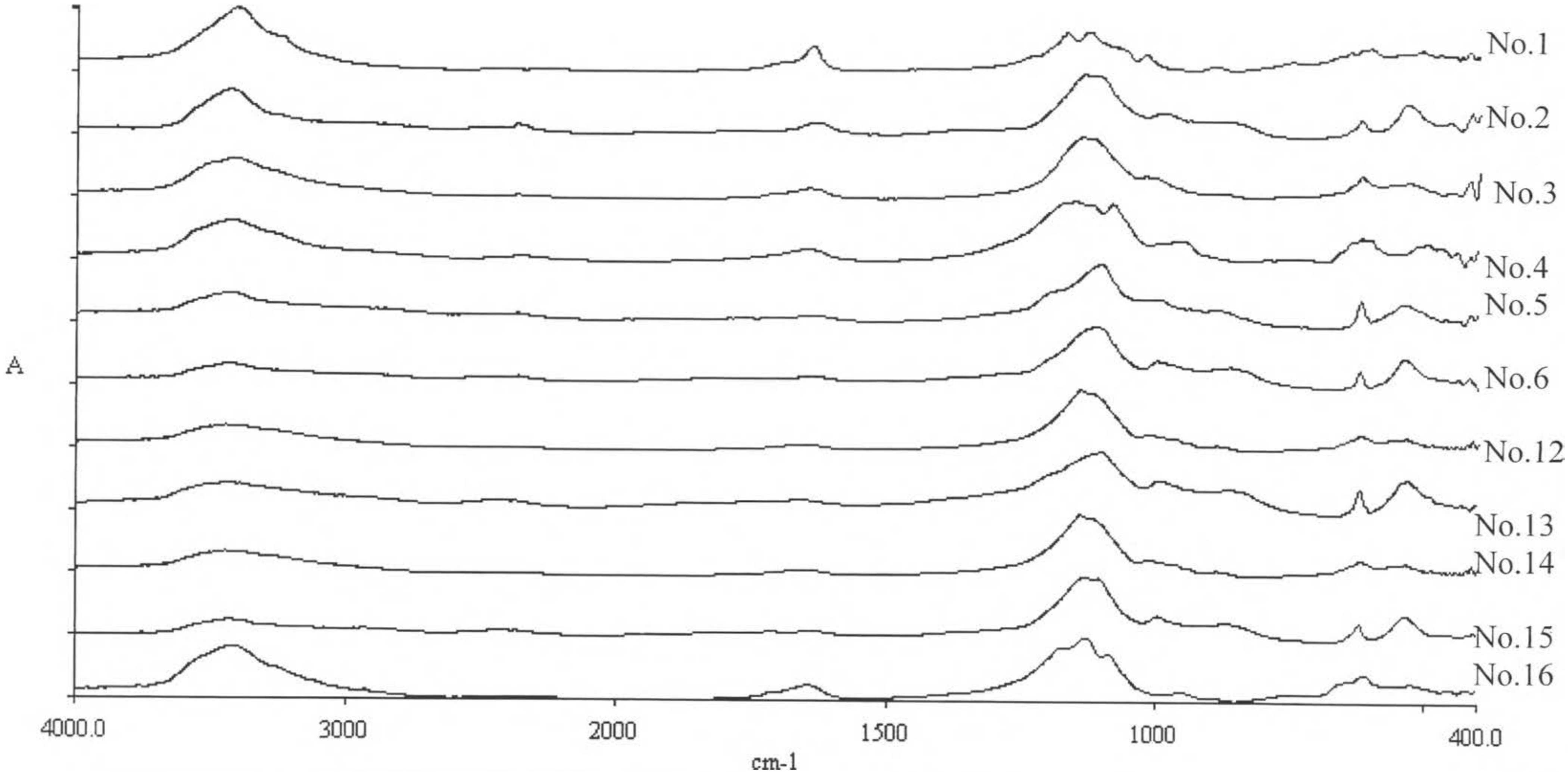

Figure 4.28 IR spectrum of shrimp farm effluent No. 1,2,3,4,5,6,11,12,13,14,15, and 16 before chlorination (day 7)

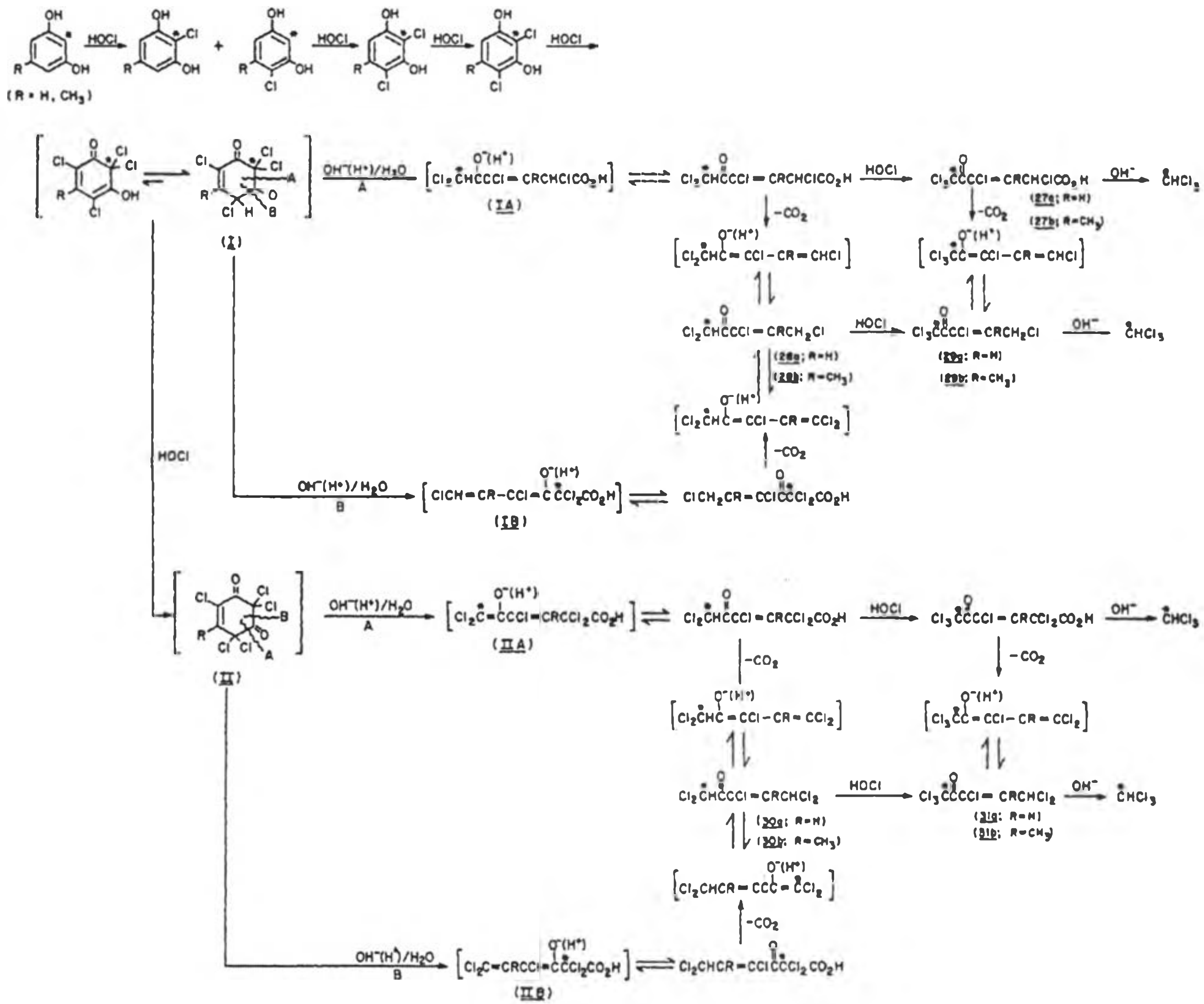

Figure 4.29 Reaction pathways for the conversion of 1,3-dihydroxyaromatic substrates to $CHCl_3$

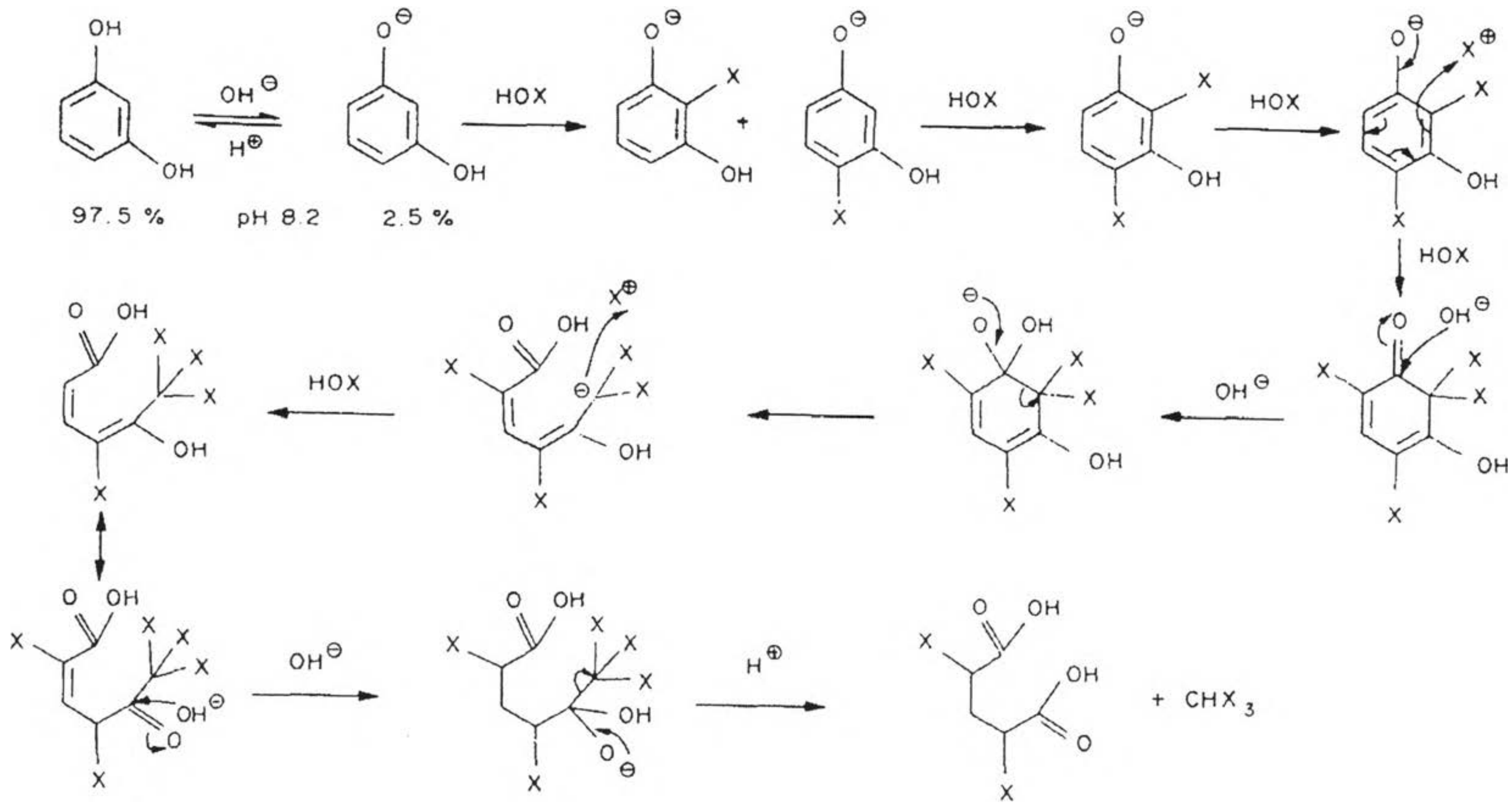

Figure 4.30 Proposed mechanism for the halogenation of resorcinol in saline solution