

Characterization and isolation of natural organic matter from a eutrophic reservoir

Cheng-Nan Chang, Ying-Shih Ma, Guor-Cheng Fang and Fang-Fong Zing

ABSTRACT

Isolation of natural organic matter (NOM) into various organic fractions has proved that it is possible to investigate the characteristics of water samples and by-products formation during chlorination. In this study, three types of resin were used to study water samples collected from a eutrophic reservoir. Seven types of organic fractions such as hydrophobic bases, hydrophobic neutrals, humic acids, fulvic acids, hydrophilic bases, hydrophilic neutrals and hydrophilic acids were isolated; sodium hypochlorite (NaOCl) was used as the oxidant to test the reactivity of each fraction. Experimental results indicated that the distribution of hydrophilic and hydrophobic fractions was similar; also, hydrophilic neutrals were the main constituent of the NOM. When the NaOCl reacted with each organic fraction, fulvic acids generated the highest potential of disinfection by-products such as trihalomethanes and adsorbed organic halides. With respect to the THMFP (trihalomethane formation potential) and AOXFP (adsorbed organic halide formation potential), it was found that a satisfactory relationship could be observed between SUVA (specific ultra-violet light adsorbance) and THMFP or AOXFP. In conclusion, the fulvic acids that can be isolated from a eutrophic reservoir play an important role in both the purification and disinfection steps.

Key words | adsorbed organic halide formation potential, disinfection by-products, eutrophic reservoir, natural organic matters, organic fraction, trihalomethane formation potential

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INTRODUCTION

In Taiwan, the Te-Chi Reservoir is used as a drinking water source to serve the municipal water demand of the population of central Taiwan. Hence, the authors have focused on studying the characteristics of Te-Chi Reservoir water, which has been polluted by pesticides and fertilizers, from August 1994 to March 1999. The presence of natural organic matter (NOM) in drinking water sources leads to several problems such as taste, odor and color; it also leads to difficulties in water treatment due to the consumption of chlorine, formation of disinfection by-products (DBPs) and regrowth of bacteria. In fact, NOM in a water supply significantly influences many aspects of water treatment, including the performance of unit processes (i.e., oxidation, coagulation and adsorption), application of disinfectants and biological stability. Considering the above problems, the formation of DBPs

such as trihalomethanes (THMs) and haloacetic acids (HAAs) are the main concern because they have been proven to be animal carcinogens and possible human carcinogens (Craun *et al.* 1994; Symons *et al.* 1994). New and pending regulations in the field of drinking water treatment require researchers to investigate the characteristics of NOM, based on isolation procedures, to find out the importance of NOM distribution and its by-products during chlorination. As part of this effort, it is useful to understand the fundamental characteristics of NOM for a drinking water resource, especially for a eutrophic reservoir located in Taiwan.

Sources of NOM in water can be divided into three parts. First, when animals or plants die and are decomposed by microorganisms, NOM is produced and carried by run-off of ground water and solubilization of soil into

the rivers or reservoirs (Galapate *et al.* 1997). The NOM produced from decomposed plants contains a large amount of polyhydroxy aromatics; these compounds have high reactivity with chlorine and are not easily decomposed by microorganisms. Humic substances mainly constitute this part of NOM. Secondly, metabolization and decomposition of algae lead to the presence of extracellular products (ECPs). ECPs are one type of NOM, which is constituted by polysaccharides, proteins and amino sugar (Fogg 1996). Also, Fogg (1996) proposed that the ECPs contribute 7 to 50% of dissolved organic carbon (DOC) in water. The third part of NOM such as fats, fatty acids, carbohydrates, proteins and amino acids comes from manmade pollution (Boller 1993).

With the characteristics of NOM described above, Leenheer (1984) and Thurman (1985) defined the soluble NOM as hydrophobic/hydrophilic and acidic/basic portions using the resins of Amberlite XAD-8, Bio-Rad AG-MP-50 and Amberlite IRA-93. It is well known that the NOM can be divided into seven types, including hydrophobic bases, hydrophobic acids, hydrophobic neutrals, hydrophilic bases, hydrophilic neutrals, humic acids and fulvic acids. Earlier studies have shown that the nature and extent of the interaction between NOM and chlorine depends on numerous factors such as pH value, chlorine dose, contact time and temperature (Pourmoghaddas *et al.* 1993; Hellerr-Grossman *et al.* 1993; Harrington *et al.* 1996). If bromide or iodide is present, chlorine can oxidize them as reactive halogen species that are analogous to chlorine. Activated aromatic rings, aliphatic β -dicarbonyls and amino nitrogen are examples of electron-rich organic structures that react strongly with chlorine. Owing to this fact, the composition and distribution of NOM in water is an important factor in determining the reactivity with chlorine and formation of DBPs within disinfection procedures.

Since the early 1980s, researchers have developed methods such as the pyrolysis-GC/MS and ^{13}C NMR for evaluating the structural characteristics of NOM. Göbbels & Püttmann (1997) isolated the humic substances from a sewage wastewater treatment plant and analyzed the functional groups surrounding the humic substances using a pyrolysis-GC/MS. It was implied that more than 36 types of functional groups such as benzene, toluene, phenol and

pentadecanoic acid were observed when the pyrolysis temperature was set to 770°C. Harrington *et al.* (1996) studied the characteristics of several water samples collected from France and analyzed them by means of a pyrolysis-GC/MS. The total organic carbon concentration (TOC) of these water samples ranged from 3.1–17.4 mg/L; hydrophobic compounds isolated by the resin XAD-8 contributed 16–71% of TOC. It was found that the phenolic structure amounted to 28.7–50.7% of the functional groups and was followed by toluene and acetic acid. Hence, the objectives of this work are to isolate the NOM from a eutrophic reservoir, study the composition and characteristics of the NOM and investigate its reactivity with chlorine.

MATERIALS AND METHODS

Sample

The water sample used in this study is collected from the Te-Chi Reservoir, which has been polluted by pesticides and fertilizers used in agriculture, and is located in central Taiwan. Table 1 summarizes the general characteristics of water samples in recent years (from August 1994 to March 1999). An average pH value is 8.6 ± 0.8 , which is slightly basic; this phenomenon indicates that the profile of the pH value over these years is insignificant. Considering the water parameters of dissolved oxygen (DO), nitrate, ammonia nitrogen and total phosphate (TP), it is clear that the Te-Chi Reservoir sample could be identified as a eutrophic water source, due to a very high concentration of DO which was observed; in addition, maximum TP concentration determined in this sample was 0.05 mg/L, which is remarkably higher than the level cited by USEPA (0.02 mg/L). Prior to isolation steps, the water sample was filtered through a continuous-flow filter equipped with glass fibers (Whatman GF-C, porosity 1.0 μm and 0.45 μm).

Isolation and fractionation

The procedures described by Leenheer (1984) and Thurman (1985) were used for the isolation of the water sample. In this study seven types of organic fractions,

Table 1 | Characteristics of water samples collected from the Te-Chi reservoir located in central Taiwan

Item	1994/08	1995/11	1997/03	1997/05	1997/08	1997/10	1998/02	1998/05	1998/09	1998/12	1999/03	Range
pH	7.9	8.9	9.4	9.1	9.6	9.6	8.1	8.0	8.3	8.2	7.3	8.6 ± 0.8
DO (mg/L)	6.1	9.6	13.2	9.9	11.1	11.3	9.2	9.0	7.4	8.4	5.5	9.2 ± 2.6
Temp. (°C)	23.8	15.8	17.4	19.8	25.6	21.4	14	21.6	23.8	15.3	16.5	20.0 ± 3.7
Conductivity (µs/cm)	530	181	130	266	191	211	214	268	241	204	273	251 ± 103
TDS (mg/L)	280	247	187	323	166	183	130	238	129	156	121	201 ± 66
SS (mg/L)	28.5	21.7	24.3	19.2	40.7	38.3	7.5	18.7	22.5	34.0	77.0	30.2 ± 17.4
Alkalinity ^a	120	182	190	200	160	170	180	200	190	160	230	180 ± 26
Hardness ^a	— ^b	147	118	133	116	129	108	140	127	100	118	124 ± 14
DOC (mg/L)	—	6.4	3.5	4.1	—	—	3.2	3.8	3.6	3.8	3.5	5.1 ± 3.3
A ₂₅₄ (abs)	—	0.014	0.011	0.012	—	—	0.014	0.011	0.010	0.012	0.010	0.011 ± 0.004
Nitrate (mg/L)	2.3	0.9	2.2	1.3	1.4	1.1	1.4	2.6	2.6	1.9	2.5	1.8 ± 0.6
Br ⁻ (mg/L)	—	0.345	0.210	0.173	—	—	0.183	0.201	0.187	0.195	0.152	0.206 ± 0.068
TP (mg/L)	—	0.035	0.010	0.030	0.050	0.042	0.038	0.028	0.021	0.018	0.015	0.029 ± 0.012
NH ₃ -N (mg/L)	—	0.14	0.02	0.06	0.08	0.10	0.06	0.10	0.23	0.27	0.19	0.13 ± 0.07

^amg as CaCO₃/L.^bNot determined.

described above, were recovered. The macroreticular resin used in this study was Amberlite XAD-8 (Sigma, USA), the cation-exchange resin was Bio-Rad AG-MP-50 (Bio-Rad, Dowex, USA) and the anion-exchange resin was Amberlite IRA-93 (Sigma, USA). The column (Pyrex glass columns, 5 cm ID × 60 cm) preparation procedures can be found elsewhere (Leenheer 1984).

The procedures for cleaning the Amberlite XAD-8 resin were as follows. XAD-8 was introduced into the NaOH solution of 0.1 N for 3 days then it was eluted with distilled and deionized water. After this, XAD-8 was cleaned with methanol in a Soxhlet extractor for 24 hours followed by hexane and acetonitrile, individually. The resin was then rinsed several times with distilled and

deionized water and loaded into the Pyrex-glass column to a height of 40 cm. Before using the resin for isolating NOM, 0.1 N NaOH and HCl and distilled and deionized water of a volume of 1-L was introduced into the column every day until the concentration of DOC in the effluent was lower than 0.02 mg/L.

To remove the impurities from AG-MP 50 resin, the resin and methanol were introduced into the column of the Soxhlet extractor together for 48 hours, then the resin was cleansed with distilled and deionized water. The height of the AG-MP 50 resin in the isolation column was also 40 cm. Before using the AG-MP 50 resin, 3 N NH₄OH was introduced into the column at a flow rate of 25 mL/min followed by 2 N HCl and distilled and

deionized water until the concentration of DOC in the effluent was lower than 0.02 mg/L.

Procedures for cleaning the IRA-93 resin were similar to the above procedures for AG-MP 50 resin, but the methanol was replaced by acetone. The resin was then rinsed with 1 N HCl at a flow rate of 25 mL/min. After this, 3 N NH₄OH solution was introduced into the column until the color of the IRA-93 resin changed from brown to yellow, then the resin was rinsed with distilled and deionized water.

Prior to isolation, the water sample was passed through the filters to remove suspended solids and was adjusted to pH 7 by HCl or NaOH. Then the water sample was passed through three types of resin. The compounds adsorbed by XAD-8 resin were eluted using 0.1 N HCl; this part was named as hydrophobic bases. The effluent from the XAD-8 resin was adjusted to pH 2 with 2 N HCl then re-introduced into the column string (XAD-8, AG-MP 50 and IRA 93). After this, 0.1 N NaOH was used to elute the organic matter adsorbed by XAD-8 resin, then the brown solution of humic substances was obtained. This brown solution was adjusted by 0.1 N HCl to pH 1 and passed through a filter equipped with a 0.45 μm membrane. The residual on the membrane was humic acids; the filtered solution was defined as fulvic acids. The XAD-8 resin was then dried at 60°C and the residue was washed out by methanol; a vacuum concentrated instrument combined with high purity nitrogen gas (99.99%) was used to concentrate this solution. The concentrated residual was dissolved in distilled and deionized water, and defined as hydrophobic neutrals. To obtain the hydrophilic bases, 1 N NH₄OH solution was used to elute the organic matter adsorbed by AG-MP 50 resin. Similarly, 3 N NH₄OH solution was used to elute the organic matter adsorbed by IRA 93 resin, which included hydrophilic acids and inorganic anions. To remove the inorganic anions, 0.1 N HCl and NaOH and XAD-8 resin were applied. The final solution, which had been passed through three types of resins, was the hydrophilic neutrals.

Formation potential studies

Studies on the formation potential (FP) of seven types of organic fraction and sodium hypochlorite (NaOCl) were

conducted in a 40-mL batch Pyrex-glass vial and incubated at 25°C for 7 days. The initial ratio of NaOCl to DOC for each sample was adjusted to 3. The pH value was not pre-adjusted before chlorination; two kinds of solutions such as KH₂PO₄ and NaOH were used as the buffer solutions to maintain the pH value as constant. Before analysis, Na₂SO₃ was dosed into the vial to remove residual chlorine.

Pretreatment for chlorinated compounds analysis

The pretreatment procedures for trihalomethane formation potential (THMFP) and adsorbed organic halide formation potential (AOXFP) were performed according to the USEPA method 524.2 and the 19th edition of *Standard Methods for Examination of Water and Wastewater* (APHA *et al.* 1992). For analyzing THMFP, the samples were taken and injected into a Purge & Trap instrument (Tekmar LSC 2000, Cincinnati, USA). High purity (99.999%) nitrogen gas purged the sample for 11 min with a flow rate of 40 mL/min. Then the sample was cooled down to a temperature of –150°C immediately followed by a preheat (175°C) and desorb step (180°C for 4 min). After this, the sample was automatically injected into the gas chromatography/electron capture detector (GC/ECD) (GC-14B, Shimadzu Co., Kyoto, Japan) equipped with a recorder (SIC Chromatocorder 12, Alphatech Corp., Tokyo, Japan). Prior to the analysis of AOXFP, 50 mL of sample were taken and introduced into a column (0.3 cm ID × 2 cm) containing activated carbon (Lot No TX070, M.C.O., Japan) so that the organic halides could be adsorbed on the activated carbon. Potassium nitrate solution of 0.08 N was used to remove the inorganic halides with a flow rate of 5 mL/min. Then the activated carbon was taken from the column and oxidized at 850°C; in this step the carbon content in the sample was oxidized as CO₂ and halides were oxidized as HCl or HBr, which could be quantified by a silver-titration procedure. The instrument for analyzing AOXFP was a TOX-10Σ (Mitsubishi, Japan).

Instrumental analysis

Analyses of THMFP were performed by GC/ECD with a 50 m × 0.22 mm ID SGE BP-5 capillary column. Helium

Table 2 | Determination of method detection limits for the analyses of THMFP

Species	Calibration Equation	R ²	Range (µg/L)	Recovery (%)	MDL ^a (µg/L)
Trichloromethane	$Y = 162847 X - 405865$	0.999	2.5–500	94.3 ± 2.3	1.03
Dichlorobromomethane	$Y = 425950 X + 1000000$	0.998	2.5–500	95.2 ± 1.8	1.68
Dibromochloromethane	$Y = 310789 X - 752084$	0.999	2.5–500	93.4 ± 3.2	1.79
Tribromomethane	$Y = 102680 X - 552717$	0.997	2.5–500	92.3 ± 1.9	1.18

^aMDL: method detection limits.

(10 mL/min) was used as the carrier gas. The column was heated from 50°C (holding time 3 min) to 200°C (holding time 3 min) at a ramp of 5°C/min. The temperatures of the injector and detector were 200°C and 260°C, respectively. Determination of method detection limits and recovery for the analyses of THMFP are listed in Table 2. DOC concentration of the sample was determined using a TOC analyzer (Model TOC-5000, Shimadzu Co., Kyoto, Japan). Ammonia nitrogen (NH₃-N) was determined by the titrimetric method; total Kjeldahl nitrogen (TKN) was determined by the semi-micro-Kjeldahl method. UV absorbance was measured at 254 nm (A₂₅₄) by a spectrophotometer (UV 1201, Shimadzu, Japan). Concentration of bromide was determined by ion chromatography using an Ion Pac, AS9-HC column (Dionex Corp., Sunnyvale, USA).

RESULTS AND DISCUSSION

Table 1 summarizes recent general characteristics of water collected from the Te-Chi Reservoir. Based on the results shown in this table, insignificant changes in water parameters are obtained. There are two important water parameters, DOC and Br⁻ concentration, to focus on. The concentration of DOC is in a range of 3.2 to 6.4 mg/L; the average is 5.1 ± 3.3 mg/L. In our earlier study, Chang *et al.* (1995) proposed that the formation of THMs by each mg of DOC was 30 µg when the chlorination of commercial humic acids was taking place. Koshin *et al.* (1997) collected the sample from Judy Reservoir; the DOC

concentration was 5 mg/L. When the water sample reacted with chlorine, the authors proposed that the formation of trichloromethane was ranging from 250–700 µg/L at various pH levels. Therefore, if the DOC concentration of the water sample is 5.1 mg/L, it is estimated that the formation of THMs could exceed 150 µg/L, which is higher than the maximum contaminant level (MCL) cited by USEPA (AWWA 1999). Another important water parameter is the presence of bromide. It is well known that the presence of bromide leads to the formation of brominated THMs and HAAs. Therefore, in this study, formation of brominated THMs is investigated to understand the contribution of bromide in the chlorination step.

Distribution of NOM

As the water sample was isolated by three types of resin, it was found (Figure 1) that the hydrophilic neutrals were the major constituent, contributing 27.8% of the total NOM. Considering the contribution of hydrophilic and hydrophobic compounds, the result was similar (hydrophilic and hydrophobic compounds were 45.8% and 46.1% of the NOM, respectively). In fact, 8.1% of the NOM could not be clearly isolated and identified. Agbekodo *et al.* (1996) also proposed a comparable result; when the water sample was isolated, it was found that 8% of the NOM could not be identified. This gives us important information, that is, even though three types of resin combined with HCl, NaOH and NH₄OH solutions were used to isolate the NOM, a small portion of the NOM still

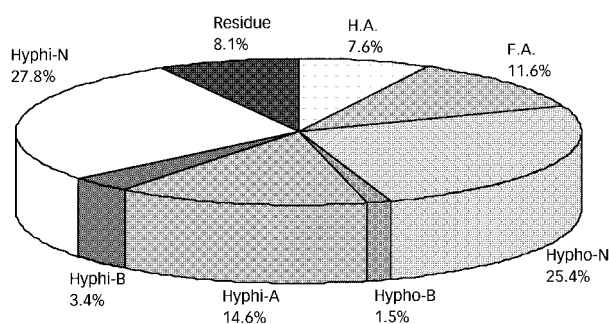


Figure 1 | Distribution of various compounds isolated from Te-Chi Reservoir.

could not be readily identified. Hence the researchers should give further attention to improving the isolation procedures.

Table 3 summarizes the results of NOM isolation from different kinds of water samples in the literature and this study. Malcolm & MacCarthy (1992) studied the characteristics of water samples collected from the Charente Reservoir. Hydrophobic and hydrophilic compounds constituted 50% of total NOM, individually. For a detailed consideration, Table 3 shows that fulvic acids are the major component in the hydrophobic part of NOM. Reckhow *et al.* (1996) proposed that the concentration of fulvic acids was 25 times that of humic acids; Krasner *et al.* (1996) proposed that fulvic acids concentration was 14 times that of humic acids. Several researchers (Agbekodo *et al.* 1996; Xu *et al.* 1997) found that the ratio of fulvic acids to humic acids was in a range of 1.9 to 6. In this study, 7.6 and 11.6% of NOM represented by the DOC concentration in the water sample was constituted by humic acids and fulvic acids, respectively; that is, the concentration of fulvic acids was 1.5 times that of humic acids. Even though the ratio of fulvic acids to humic acids shown in this study is lower than other studies, it was still found that fulvic acids are the larger constituent of the hydrophobic part of NOM.

Formation of THMFP

As we know the composition of NOM as represented by seven kinds of organic fraction in a water sample, it is

interesting to investigate the formation of THM and AOX when the water sample is chlorinated with sodium hypochlorite. Figure 2 shows the THMFP concentration of seven kinds of organic fraction and a chlorinated raw water sample. In fact, trichloromethane was determined in the water sample only; the concentrations of three other types of brominated THMs were lower than their MDLs. It is obvious that the concentration of THMFP was more than 70 $\mu\text{g/L}$ as the incubation with sodium hypochlorite for 7 days; also, humic acids, fulvic acids, hydrophobic neutrals and hydrophilic neutrals show greater reactivity with sodium hypochlorite than other components. However, summarizing the concentration of THMFP for various organic fractions only leads to 57% of the THMFP concentration produced by the reaction between the raw water sample and sodium hypochlorite. This phenomenon could be explained by the reaction mechanisms between each organic fraction with sodium hypochlorite, which were different from the raw water sample with sodium hypochlorite.

To understand the effect of the characteristics of each organic fraction on the formation of THMs, Figure 3 shows the result of THMFP/DOC for various organic fractions. In this figure it is apparent that fulvic acids generated the highest formation potential for THMs, as for each mg of DOC consumed, 47.1 μg of THMs were produced. Humic acids are another component which has high formation potential for THMs. Each mg of DOC consumption led to the formation of 24.7 μg THMs. The five other kinds of organic fraction play minor roles in the formation of THMs. Agbekodo *et al.* (1996) also found a comparable result. The authors isolated the chlorine-free pulping process mill effluents into seven kinds of organic fraction such as humic acids, fulvic acids, hydrophobic neutrals, miscellaneous, hydrophilic acids, hydrophilic neutrals and amino compounds. They proposed that humic acids and fulvic acids mainly contributed to the formation of DBPs. As each mg of humic acids and fulvic acids was consumed by chlorination, 42.6 and 21.8 μg of THMs were produced, respectively. Krasner *et al.* (1996) isolated the water sample collected from Apremont Reservoir into four kinds of organic fraction such as humic acids, fulvic acids, hydrophilic acids and hydrophobic neutrals. As the organic fractions were chlorinated, humic

Table 3 | Isolation and characterisation of organic fractions in water samples cited in literature and this study

Author Year	Malcolm & MacCarthy 1992	Yeh & Huang 1993	Reckhow <i>et al.</i> 1996	Krasner <i>et al.</i> 1996	Agbekodo <i>et al.</i> 1996	Xu <i>et al.</i> 1997	This study 1999
Water source	Charente Reservoir	Feng-San water treatment plant	Lake Gaillard water treatment plant	Apremont Reservoir	Biotreated CTMP effluent	Taihu Lake water	Te-Chi Reservoir
Hydrophobic	Hypho substances = 50%	HA = 4.2% FA = 16% Hypho-B = 2.4% Hypho-N = 19.4%	HA = 1.1% FA = 28.1% Hypho-B = 0.6% Hypho-N = 3.1%	HA = 3% FA = 43% Hypho-N = 5%	HA = 18% FA = 35% Hypho-N = 1%	HA = 6% FA = 36% Hypho-N = 18% Hypho-B = 10%	HA = 7.6% FA = 11.6% Hypho-B = 1.5% Hypho-N = 25.4%
Summary	50%	42%	32.9%	51%	54%	70%	46.1%
Hydrophilic	Hyphi-A = 16%	Hyphi-A = 6.3% Hyphi-B = 7.3% Hyphi-N = 44.4%	Hyphi-A = 36.5% Hyphi-B = 4% Hyphi-N = 25%	Hyphi-A = 18%	Hyphi-A = 6% Hyphi-N = 0.6%	Hyphi-A = 16% Hyphi-B = 13% Hyphi-N = 1%	Hyphi-A = 14.6% Hyphi-B = 3.4% Hyphi-N = 27.8%
Summary	16%	58%	65.3%	18%	6.6%	30%	45.8%
Others	Non-acid Hydrophilics = 34%			Non-adsorbed Hydrophilic = 25%	Miscellaneous = 28% Amino compound = 3% Non-adsorbed = 8%		Residue = 8.1%
Summary	34%	—	—	25%	39%	—	8.1%

Hypho-A: hydrophobic acids; Hypho-B: hydrophobic bases; Hypho-N: hydrophobic neutrals; HA: humic acids; FA: fulvic acids.
Hyphi-A: hydrophilic acids; Hyphi-B: hydrophilic bases; Hyphi-N: hydrophilic neutrals.

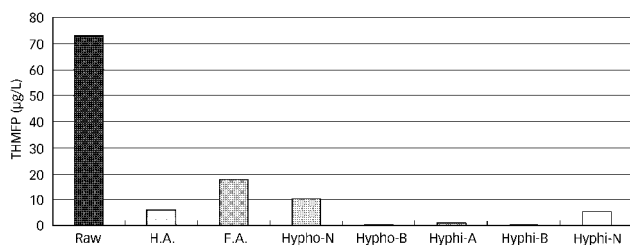


Figure 2 | Distribution of THMFP for various organic fractions.

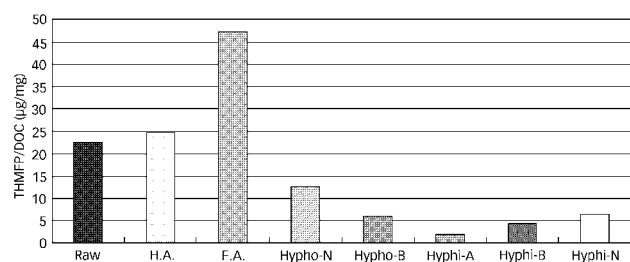


Figure 3 | Distribution of THMFP/DOC for various organic fractions.

acids was the major one to induce the formation of THMs. In this study, the authors also found that the organic fraction of hydrophobic acids such as humic and fulvic acids mainly led to the formation of THMs. Amy *et al.* (1987) proposed that the ratio of THMFP/DOC of fulvic acids was 63.7 µg/mg DOC, which is 1.5 times the result shown in this study. This fact could be explained by the source of fulvic acids. In Amy's study, the fulvic acids were isolated from peat. It is well known that fulvic acids isolated from soil or peat have stronger reactivity with chlorine leading to a higher production of THMs than the fulvic acids isolated from a reservoir water sample.

Formation of AOX

Considering the formation of AOX, it is interesting to discuss the characteristics of NOM and its reactivity with chlorine. Figure 4 shows the result of AOXFP concentration produced by the reaction between various organic fractions and sodium hypochlorite. It is obvious that hydrophobic neutrals and hydrophilic neutrals play an important role in the formation of AOX. This phenomenon is in contrast to Figure 2. It is illustrated that humic

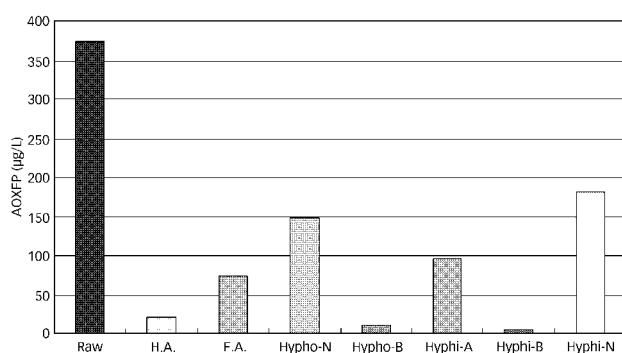


Figure 4 | Distribution of AOXFP for various organic fractions.

acids and fulvic acids have higher reactivity with chlorine to generate disinfection by-products with lower molecular weights, due to several well known functional groups such as ketone, aldehyde and carboxyl surrounding the surface of humic and fulvic acids (Rook 1977; Gulyas *et al.* 1994; Chang & Ma 1995). The functional groups surrounding the surface of hydrophobic and hydrophilic neutrals have not been clearly identified until now. However, based on the results shown in Figure 4, it is estimated that there are long-chain functional groups surrounding the surface of hydrophobic and hydrophilic neutrals, due to the high concentration of AOXFP observed in Figure 4. In fact, when the NaOCl reacted with these long-chain functional groups, it was not strong enough to break the long-chain structure and lead to the production of THMs, hence a low concentration of THMFP is observed in Figure 2.

To study the contribution of each mg of DOC consumption for various organic fractions on the formation of AOX, the results are shown in Figure 5. It is understood that the hydrophilic bases play a minor role in the formation of AOX. In addition, the potential of fulvic acids, hydrophobic neutrals and bases and hydrophilic acids and neutrals for the formation of AOX are similar. Based on the results shown in Figures 3 and 5, it is found that the hydrophobic fractions (including bases, acids and neutrals) generate a higher output in the formation of THM by DOC consumption, which is 7 times that of the hydrophilic fractions. Considering the AOX formation by DOC consumption, the results for hydrophilic and hydrophobic fractions are comparable. Therefore, if the

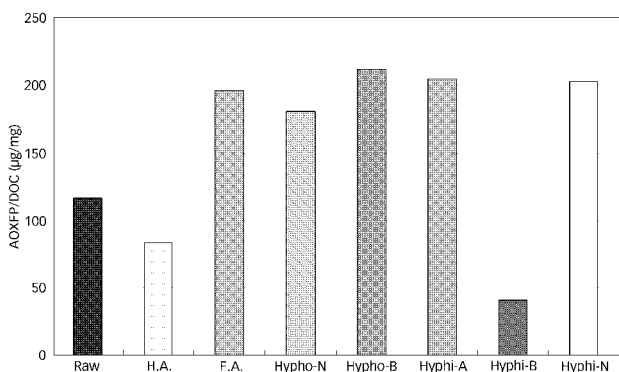


Figure 5 | Distribution of AOXFP/DOC for various organic fractions.

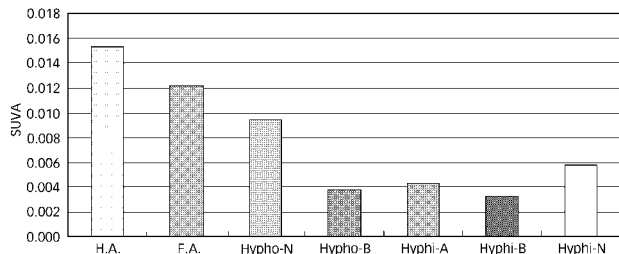


Figure 6 | Comparison of SUVA values for various organic fractions.

formation of THMs only in the drinking water purification steps is considered, the composition and distribution of NOM, especially the fraction of hydrophobic acids in the water sample, need to be focused on. In other words, if the formation of total halides is the major point we consider, the effect of hydrophilic fractions on the formation of DBPs should not be ignored.

Relationship between SUVA and DBPFP

Figure 6 shows the results of A_{254} by unit DOC (defined as SUVA – specific ultraviolet light adsorbance), for various organic fractions. It is apparent that the SUVA values of humic and fulvic acids are significantly higher than the other five organic fractions. Goel *et al.* (1995) demonstrated that the higher the A_{254} , the higher the unsaturated bonds (such as C = C double bond) or aromatic structures contained in organic compounds. Hence these compounds have a higher reactivity with oxidants including ozone, chlorine and hydrogen peroxide. Also, the ratio of

SUVA could be used as a surrogate parameter to investigate the formation of DBPs (Amy *et al.* 1998). Generally speaking, the hydrophobic organic fraction has a greater SUVA value due to its aromatic composition. Comparing the results shown in Figures 3 and 6, it is clear that the formation of THM by unit of DOC is closely linked to the value of SUVA. To further study the relationship between SUVA and THMFP and AOXFP, several researchers' results are summarized in Table 4. Many researchers (Croue *et al.* 1993; Agbekodo *et al.* 1996; Krasner *et al.* 1996) proposed similar results, that is, the ratio of THMFP/DOC or AOXFP/DOC increased with the increase of SUVA. Even though the water samples presented in previous studies were collected from different sites, it is interesting to draw a figure to clearly indicate the relationship between SUVA and THMFP/DOC or AOXFP/DOC. The results are compared and illustrated as Figures 7 and 8.

Even though the isolation procedures used in previous studies (Croue *et al.* 1993; Agbekodo *et al.* 1996; Krasner *et al.* 1996) are different from this study, and the NOM is divided into different kinds of organic fractions, it is still found that there is a satisfactory linear relationship between SUVA and THMFP/DOC as shown in Figure 7; i.e. formation of THM by mg of DOC consumption is in a linear relationship with SUVA values. In Figure 8, a linear relationship between SUVA and AOXFP/DOC is also found, although the organic fractions such as hydrophobic neutrals and bases and three types of hydrophilic fractions show a very low SUVA but a relatively high AOXFP/DOC value. This result verifies the phenomenon proposed by Amy *et al.* (1998).

CONCLUSIONS

Three types of resin such as XAD-8, IRA-93 and AG-MP 50 were used to isolate the water sample into various organic fractions. Experimental results revealed that the summation of hydrophobic and hydrophilic neutrals constituted 53.2% of the total NOM. Hydrophobic acids, such as fulvic and humic acids, mainly led to the formation of THM; for each mg of DOC consumed, 24.7 and 47.1 µg of

Table 4 | Comparison of parameters such as SUVA (UV₂₅₄/DOC), THMFP/DOC and AOXFP/DOC for water samples cited in literature and this study

Reference Water source	Krasner <i>et al.</i> (1996) Apremont Reservoir		Agbekodo <i>et al.</i> (1996) Chlorine-free pulping process mill effluents		Croue <i>et al.</i> (1993) Apremont Reservoir		This study (1999) Te-Chi Reservoir									
	Fraction	Value	Fraction	Value	Fraction	Value	Fraction	Value								
SUVA	Hydrophilic part	0.020	Hydrophobic part	0.020–0.046	Hydrophilic part	0.01–0.059	Hydrophobic part	0.015	Hydrophilic part	0.004–0.015	Hydrophobic part	0.003–0.006				
THMFP/DOC (µg/mg)		21		12–51		11.8–42.6		13.1		27–46		27		5.9–47.1		1.9–6.3
AOXFP/DOC (µg/mg)		101		40–277		— ^a		— ^a		144–307		117		83.3–210.6		40.8–203.5

^aNot analyzed.

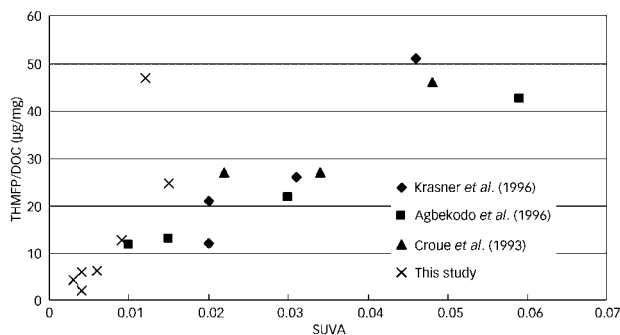


Figure 7 | Relationship between SUVA and THMFP/DOC cited in various studies.

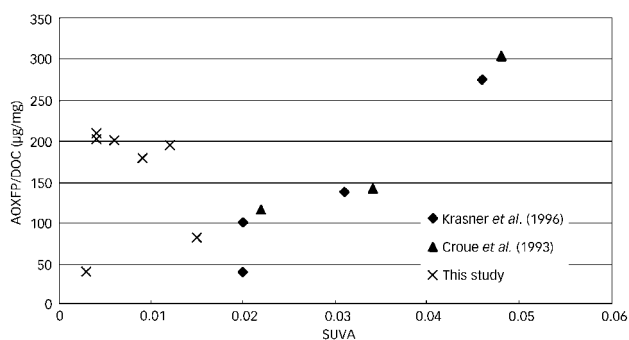


Figure 8 | Relationship between SUVA and AOXFP/DOC cited in various studies.

THM were produced by humic and fulvic acids, respectively. For AOXFP, hydrophobic bases, hydrophilic acids and neutrals play an important role in the reaction with NaOCl. Therefore, since the formation of THMs was investigated, it was concluded that the distribution of hydrophobic acids in NOM should be noticed; otherwise, distribution of hydrophilic fractions in NOM should be focused on. SUVA is an available parameter to investigate THMFP and AOXFP.

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NOMENCLATURE

A_{254} : adsorbance of UV light with a wave length of 254 nm

AOX: adsorbed organic halides

AOXFP: adsorbed organic halides formation potential

DBPs: disinfection by-products

DO: dissolved oxygen

DOC: dissolved organic carbon

ECP: extracellular products

GC/ECD: gas chromatography/electron capture detector

GC/MS: gas chromatography/mass spectrometry

HAAs: haloacetic acids

NOM: natural organic matter

SUVA: specific ultra-violet light adsorbance

THMFP: trihalomethanes formation potential

THM: trihalomethanes

TKN: total Kjeldahl nitrogen

TP: total phosphate

UV: ultra violet

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