The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water

Chul-Woo Jung*,† and Hee-Jong Son**

**Ulsan Regional Innovation Agency, Ulsan Industry Promotion Techno Park,
758-2, Yeonamdong, Buggu, Ulsan 638-804, Korea
**Water Quality Research Institute, Busan Water Authority, Gimhae, Gyeongnam 621-813, Korea*

Abstract−The influence of the characteristics of natural organic matter (NOM) on disinfection by-product formation was investigated for Maeri raw water, located in downstream of Nakdong river and Hoedong reservoir at Busan in Korea. The NOM was chlorinated and analyzed for trihalomethanes (THMs), 5 haloacetic acids (HAA-5) and total organic halide (TOX). Aromatic contents determined by specific UV absorbance at 254 nm (SUVA) correlated well with THMs, HAA-5 and TOX formation for the NOM in the Maeri raw water and Hoedong reservoir. Especially, THMFP/ DOC showed better correlation with SUVA than HAAFP-5/DOC and TOXFP/DOC with SUVA. Chloroform formation showed good correlation with SUVA for Maeri raw water, but poor correlation with SUVA for the Hoedong raw water. In addition, TCAA formation potential showed good correlation with SUVA for both raw waters. In contrast, a lack of correlation was observed for DCAA formation for both raw waters. THM formation per unit DOC concentration was 70.2-81.1% and 18.9-29.8% for hydrophobic and hydrophilic organic matter in the Maeri raw water, respectively, in which the hydrophobic organic matter had much higher THM formation. In contrast, HAA-5 formation per unit DOC concentration varied seasonally for Maeri raw water. THM formation in the Maeri raw water had a good correlations with SUVA regardless of the ratio of hydrophobic and hydrophilic fraction, and THM formation per unit DOC concentration was higher for the order of humic acid>fulvic acid>hydrophilic organic matter. HAA-5 formation per unit DOC concentration for the hydrophilic organic matter was about 30 μg per mg DOC regardless of SUVA values, but HAA-5 formation per unit DOC concentration for the hydrophobic organic matter was proportionally increased with increasing SUVA values. However, the HAA-5 formation per mg DOC was the highest for the hydrophilic organic matter.

Key words: NOM, SUVA, Hydrophilic/Hydrophobic, DBPs, THMs, HAAs, TOX

INTRODUCTION

Raw water quality has significant influence on the design and operation of the water treatment process as well as the application of new treatment technologies. In general, raw water contains organic matter of different characteristics depending upon geological conditions and the surrounding watershed. The organic matter gives taste, odor, and color in water and increase coagulant and disinfectant demand in the water treatment process. Organic matter also consumes residual chlorine in the distribution system and contribute to microbial regrowth by providing heterotrophic bacteria with carbon sources [1-3]. Above all, natural organic matter (NOM) existing in raw water reacts with chlorine or other disinfectants, and then generates halogenated disinfection by-products (DBPs) which are known to have adverse health effects [4-6]. The principal DBPs in drinking water usually include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, haloketones, chloral hydrate, and chloropicrin, and their number is on the increase with advancing analytical technologies [7]. A survey of the water treatment facilities located along the four major rivers in South Korea found that THMs and HAAs accounted for as high as 69-79% of DBPs [8]. Major factors affecting the generation of DBPs include the concen-

tration and characteristics of NOM, the type and concentration of disinfectants, pH, temperature, and the concentration of bromide ion. Among them, the concentration and characteristics of NOM were reported to have the most significant influence on the generation of DBPs [9-11]. NOM in raw water consists of hydrophobic fractions like humic acid and fulvic acid, and hydrophilic fractions [12] and they are comprised of organic molecules of various sizes ranging from 300 to 30,000 dalton [13,14]. Other researchers reported that the hydrophobic fractions accounted for more than 50% of DOC in natural waters [15,16] and the composition varies to a great extent depending on seasons [17]. In addition, an investigation about formation potentials of DBPs for hydrophobic and hydrophilic fractions found that hydrophobic fractions showed much higher THM formation potential (THMFP) [18] and, of hydrophobic fractions, the THMFP of humic acid was higher than the one of fulvic acid [19]. However, Owen et al. [15] reported that in the case of the Colorado River, hydrophilic fractions accounted for 65% of the total NOM, and produced higher THMFP [15]. From research on NOM in raw water of the downstream of the Nakdong River in South Korea, Son et al. [20] found that the composition of hydrophobic fractions was almost the same as the hydrophilic fractions, and that fulvic acid consisted of 78% of the total hydrophobic fractions [20]. They also reported that the hydrophobic fraction yielded twice as much THMs as hydrophilic fractions. NOM characteristics also vary seasonally in the raw water. This is because it is greatly influenced by

sewage treatment plant effluent and the natural decomposition of algae, and other organisms present in the water body. Thus, NOM characteristics in water vary greatly according to the characteristics of water systems [21,22]. Accordingly, we examined the characteristics of formation of DBPs depending on the characteristics NOM in raw water of the Maeri area in the downstream of the Nakdong River and the Hoedong reservoir that are used as a raw water for the drinking water supplied to the Busan city in Korea. In addition, we investigated the characteristics of changes in NOM and DBPs formation during different seasons.

EXPERIMENTAL

1. Characterization of NOM in Raw Waters

Raw water samples used in this study were collected from the Maeri area in the downstream of the Nakdong River (MR) and the Hoedong reservoir (HD) located in Busan city from June 2002 to October 2003. This study examined the formation potentials of DBPs depending on the changes in properties of NOM in raw water. Characteristics of MR and HD waters used in this experiment are listed in Table 1. UV254 and DOC were measured for the measurement of dissolved organic matter in raw water. In addition, SUVA (specific ultraviolet absorbance at 254 nm) was calculated as a ratio of UV254 value to DOC and used as an indicator of the aromaticity of NOM. The classification of hydrophobic and hydrophilic fractions was done by using XAD-8 resin (Supelco, U.S.A.) according to the procedure proposed by Thurman and Malcolm [23]. With the sample water set at below pH 2, the water that flowed out from the column in which the XAD-8 resin had been put was classified

as hydrophilic fraction and the matter that was detached from the XAD-8 resin with 0.1 N-NaOH were classified as hydrophobic fraction. The detached hydrophobic fractions were adjusted at below pH 1 and placed in a 20 °C thermo-hygrostat for 3 hours before being filtered through a 0.2 μm membrane filter. The sample that passed through the filter was classified as fulvic acid and the deposits that settled on the filter paper were classified as humic acid.

2. Chlorination of Samples and Analysis of DBP

For analysis of DBPs including THMFP, HAAFP-5 and TOXFP, the sample did not undergo the filtering process.

The chlorination conditions selected for the test are as follows: incubation time=24 h, incubation temperature=20 °C in darkness for 24 hours, incubation pH=8, free chlorine residual after 24 hr=1.5± 0.2 mg/L and the samples were quenched and buffered with Na_2SO_4 and H_3PO_4 (1+10). THMFP was analyzed by using GC/ECD with a headspace auto sampler; HAAFP-5 was analyzed with GC/ECD in accordance with USEPA Method 552.2 [24]; and TOXFP was analyzed by using an organic halide analyzer in accordance with the adsorption pyrolysis amperometric titration method [25]. Pretreatment was conducted by using HNO_3 and Na_2SO_4 to curb additional formation of TOX by remaining chlorine.

RESULTS AND DISCUSSION

1. Relationship between NOM Properties and DBPs Formation Potential

The chemical composition of NOM is known to have significant influence on the formation of DBPs. Goel et al. (1995) reported that as the unsaturated bonds like the carbon double bond in water and

Table 1. Water quality characteristics of samples used in this study

		Nakdong River (Maeri)			Hoedong Reservoir		
		Min.	Max.	Mean	Min.	Max.	Mean
DOC	(mg/L)	1.93	3.94	2.86	1.79	3.61	2.58
UV-254	(cm^{-1})	0.04988	0.09971	0.06352	0.02833	0.05344	0.03906
SUVA	(m^{-1}·L/mg)	1.33	3.92	2.16	1.06	2.39	1.74
Turbidity	(NTU)	3.5	745.0	54.6	1.7	27.7	10.4
Alkalinity	(mg/L CaCO$_3$)	22	63	44	15	25	21
pH	(-)	6.4	8.6	7.4	6.9	7.9	7.2

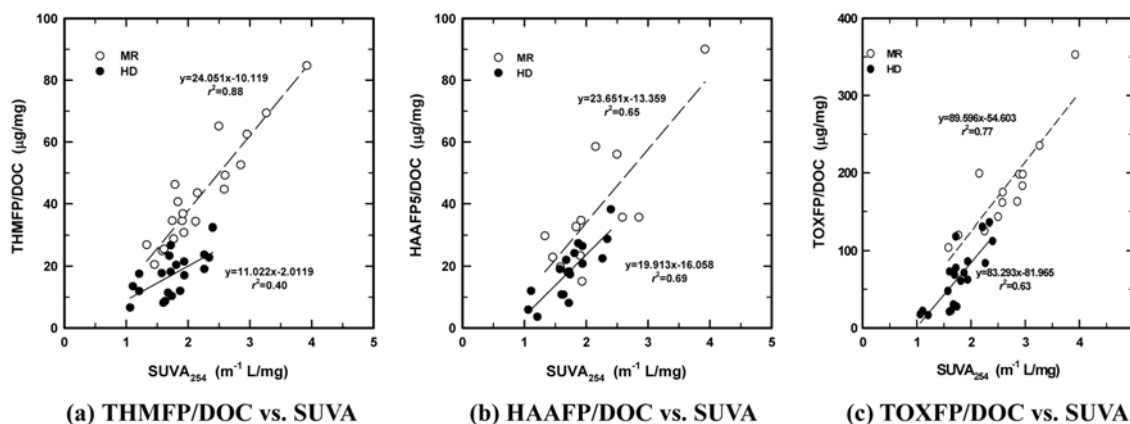(a) THMFP/DOC vs. SUVA   (b) HAAFP/DOC vs. SUVA   (c) TOXFP/DOC vs. SUVA

Fig. 1. Disinfection by-product formation potentials as a function of SUVA for the Nakdong water water and Hoedong reservoir water.

the content of aromatic substances increase, the UV254 values also increase, and that these substances show high reactivity with oxidizing agents like ozone and chlorine. Besides, SUVA, which represents the aromaticity of organic matter in water, can be used as an index to indirectly evaluate the formation potentials of DBPs [9,26, 27]. Fig. 1 shows the relationship between aromaticity of NOM, or SUVA, and DBPFP for MR and HD waters. As shown in Fig. 1(a), indicating relationship between SUVA and THMFP/DOC, the MR water with a relatively high level of aromaticity shows the correlation coefficient of 0.88, indicating a much stronger correlation than HD water with a correlation coefficient of 0.40. As a function of SUVA for THMFP/DOC, the slope value for the MR water is 24, which is more than double the value of the HD water, 11, implying that the increase of THMFP with increasing SUVA of MR water is more than double that of HD water. In Fig. 1(b), indicating HAAFP/ DOC as a function of SUVA, the correlation coefficient for MR water is 0.65, a lower correlation coefficient than the one shown in THMFP shown in Fig. 1(a); but the correlation coefficient for HD water is 0.69, a higher correlation coefficient than THMFP shown in Fig. 1(a). The slope values for MR and HD waters are 23 and 19, respectively, showing a smaller difference between the slope values than THMFP. As shown in Fig. 1(c), indicating TOXFP/DOC as a function of SUVA, the slope values are 89 and 83 for MR and HD waters, respectively. This suggests that, in the case of these raw waters, TOXFP/DOC increases almost similarly with increasing SUVA values, even though showing different TOXFP from the same SUVA values for the two waters. Chang et al. [33] found that the SUVA values of hydrophobic organic matter like humic acid, fulvic acid and hydrophobic neutral were more than two times higher than

those of hydrophilic organic matter and that the THMFP/DOC showed high correlations with the SUVA values. They also found that, despite low SUVA values, the TOXFP was high, and thus no tendency was shown toward any differences in TOXFP depending on the ratios of hydrophobic to hydrophilic fractions of the organic matter. According to them, however, when the SUVA values were compared with TOXFP/DOC, TOX formation potentials decreased as the SUVA values increased. But other studies [19,31,35] reported that the reactivity of THM and TOX with the organic matter in water was highly correlated with the SUVA values, indicating that the formation of DBPs can differ depending on the characteristics of raw water. In the case of MR and HD waters, investigated in this study, the assessment of DBPFP per DOC depending on the aromaticity of NOM showed that the formation potentials of THM, HAA-5, and TOX all increased as SUVA values increased, and THMFP in particular was very sensitive to the level of aromaticity.

Among the formation potential of THM and HAA-5 for MR and HD waters, Fig. 2 shows the formation potential of chloroform (chloroformFP), trichloroacetic acid (TCAAFP), and dichloroacetic acid (DCAAFP) as a function of SUVA not by bromination reaction but by the reaction of chlorine with NOM. As shown in Fig. 2(a), indicating the correlation between the chloroformFP/ DOC and SUVA, the chloroformFP for MR water shows a similar tendency to the THMFP, even though the correlation of chloroformFP with SUVA was a little stronger than that with THMFP. However, for the HD water, the correlation between the chloroformFP and the THMFP and SUVA was much poorer than MR water, indicating a strong contrast between the two raw waters. In turn, the HD water, which has a relatively lower level of aromaticity than MR water, shows
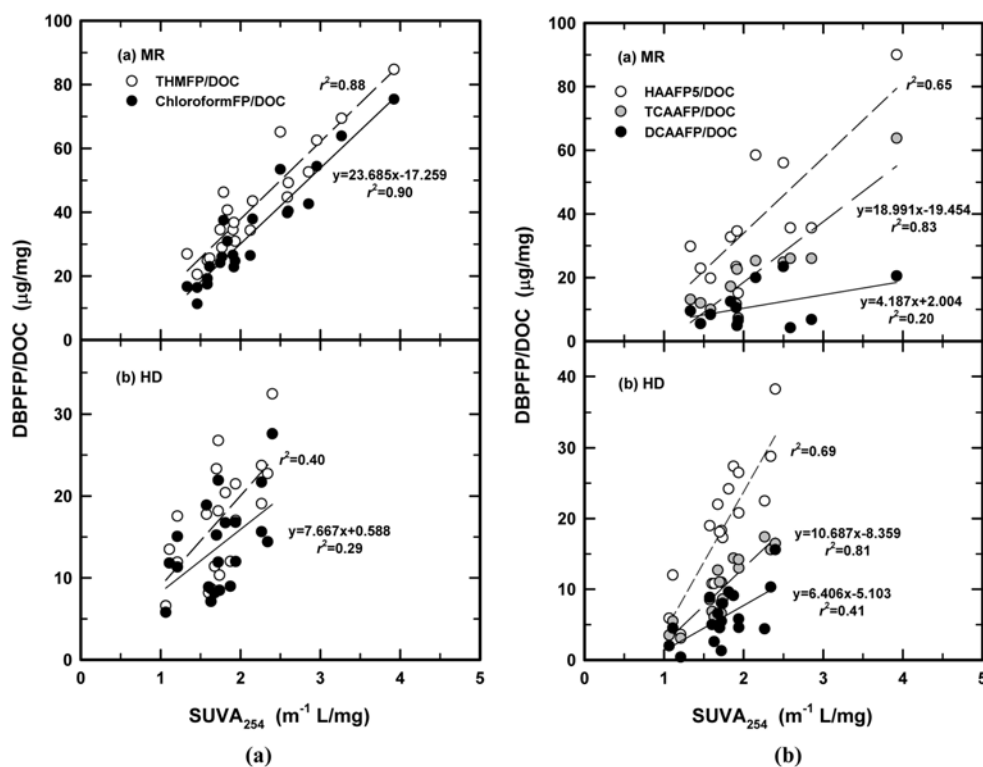

Fig. 2. Disinfection by-product formation potentials as a function of SUVA for the Nakdong river and Hoedong reservoir water (when Br-effect is insignificant).

very poor correlations between chloroformFP/DOC and SUVA. Fig. 2(b) shows that the correlation coefficients of TCAAFP and DCAAFP with SUVA for MR water are 0.83 and 0.20, respectively. It indicates that TCAAFP has much stronger correlation with SUVA than DCAAFP. Besides, the slopes for TCAAFP DCAAFP show that TCAA formation is much more favored in the presence of UV absorbing NOM for both MR and HD waters, although there is a little difference between these two waters. Using raw waters with high and low aromaticity, Croué et al. [26] compared the DBPFP with the changes in SUVA and reported that the TCAAFP showed a very high correlation with SUVA, but the DCAAFP showed a very low correlation with SUVA irrespective of the level of aromaticity [26]. In addition, Reckhow et al. [27] studied the relations between NOM and DBPFP, and reported that the formation potentials of THM, TOX, and TCAA showed high correlations with SUVA and thus the aromatic substances are considered to be important in the formation of DBPs by chlorine treatment [27]. However, they reported that the DCAAFP showed low correlations with SUVA values and thus organic matter structures other than aromatic organic matter structures seemed to engage in the formation of DCAA in chlorine treatment, which demonstrated similar findings to the result observed in this study. In the case of MR water with high aromaticity, the chloroformFP showed a high correlation with SUVA, but HD water with low aromaticity showed a low correlation. In the case of TCAA formation potential, both MR and HD waters showed
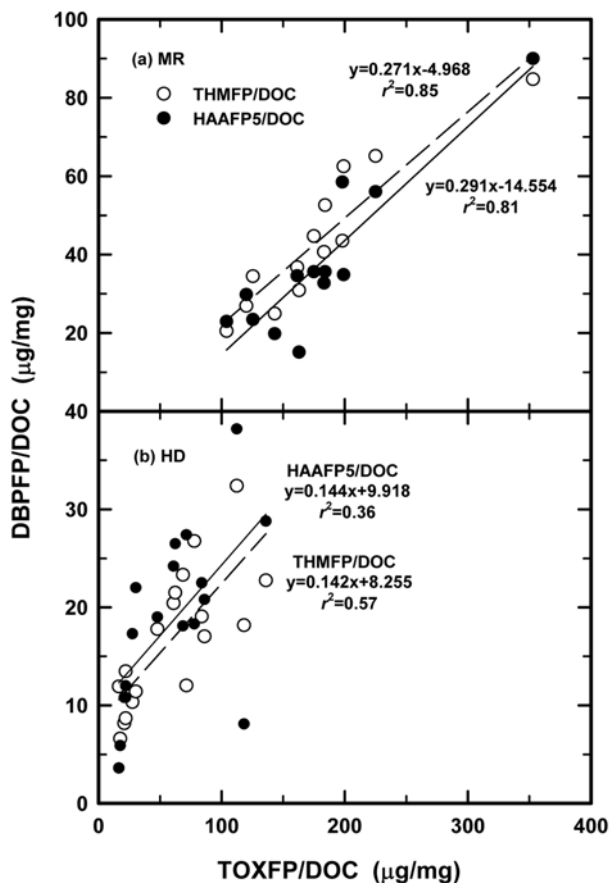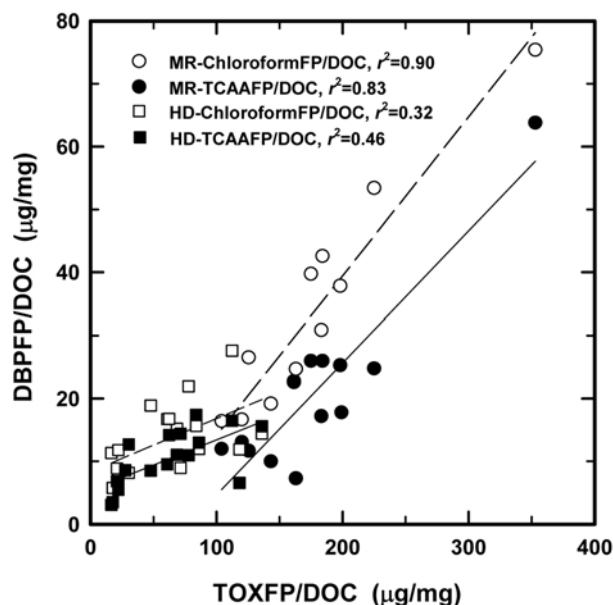

Fig. 4. **Correlations between TOXFP and chloroformFP and TCAAFP for the Nakdong river and Hoedong reservoir water.**

high correlations of above 0.80 with SUVA but DCAA showed low correlations with SUVA.

Fig. 3 shows the relationship of TOX/DOC with THM/DOC and HAA5/DOC for MR and HD waters. This result indicates the distribution of TOX into THM and HAA5. THM accounts for higher fraction of TOX for MR water, whereas HAA5 accounts for higher fraction of TOX for HD water. Furthermore, the increasing tendency of THM and HAA5 relative to TOXFP is almost similar between the MR water and the HD water, In other words, the proportion of these substances consisting of TOX formed was almost similar.

Fig. 4 shows relationships between TOX formed per DOC and chloroform and TCAA formed per DOC for MR and HD waters. As shown in Fig. 4, MR water represents much stronger correlation of chloroform and TCAA with TOX than HD water. In the case of MR water, the chloroformFP/DOC is higher than TCAAFP/DOC, accounting for a higher proportion of the TOXFP/DOC. However, in the case of HD water, of the substances comprising TOX/DOC, HAA5 was higher than THM in Fig. 3. But in Fig. 4, when only chloroform and TCAA among the substances comprising TOX/DOC are compared, chloroform accounts for a greater proportion of TOX than TCAA.

2. Seasonal Variation of the Characteristics of NOM in MR Water

In an effort to understand the reactions between chlorine and NOM fractions on a more fundamental level, the correlation between observed DBPs yields and seasonal characteristics of NOM fractions was studied. Table 2 shows the concentration variation of hydrophobic and hydrophilic organic matter in the MR water throughout the year investigated. The concentration of the hydrophilic organic matter throughout the year ranged from 0.96 to 1.87 mg/L, which was 41-50% of DOC, while the one of the hydrophobic organic matter ranged from 1.38 to 1.92 mg/L, which was 50-59% of DOC,

Fig. 3. **Correlations between TOXFP and HAA-5FP and THMFP for the Nakdong river and Hoedong reservoir water.**

Table 2. Seasonal variation of SUVA values and DOC concentration of Nakdong River (Maeri) according to the characteristics of NOM

	June 2002		November 2002		March 2003		October 2003	
	SUVA (m^{-1}L/mg)	DOC (mg/L)	SUVA (m^{-1}L/mg)	DOC (mg/L)	SUVA (m^{-1}L/mg)	DOC (mg/L)	SUVA (m^{-1}L/mg)	DOC (mg/L)
Hydrophilic	1.26	1.87 (50)	2.16	1.64 (46)	2.24	1.28 (46)	2.21	0.96 (41)
Hydrophobic								
Humic acid	2.92	0.41 (11)	3.12	0.81 (23)	3.52	0.51 (18)	3.07	0.58 (25)
Fulvic acid	2.44	1.46 (39)	3.45	1.11 (31)	2,87	1.01 (36)	2.96	0.80 (34)

-Parentheses show % of DOC.

Table 3. Isolation and characterization of organic fractions in water samples cited in literature and this study [19,28-33]

|	Malcolm and MacCarthy [28]	Yeh and Huang [29]	Reckhow et al. [30]	Krasner et al. [19]	Agbekodo et al. [31]	Xu et al. [32]	Chang et al. [33]	This study (2002-2003)
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	Nadong River (Maeri)
Hydrophobic	50%	42%	32.9%	51%	54%	70%	46.1%	50-59%
HA : FA	-	1 : 3.8	1 : 25.5	1 : 14.3	1 : 1.9	1 : 6	1 : 1.5	1 : 1.4-1 : 3.6
Hydrophilic	50%	58%	65.3%	43%	46%	30%	45.8%	41-50%

-HA: Humic acid, FA: Fulvic acid.

thus indicating that the variation in the composition ratios of hydrophobic and hydrophilic organic matter is relatively small throughout the year. In addition, humic acid consisted of 22-42% and fulvic acid 58-78% in the hydrophobic organic matter, indicating higher content of fulvic acid than humic acid.

Table 3 compares the characteristics of NOMs contained in the MR water to other water samples from references, in which the composition ratios of hydrophobic and hydrophilic fractions vary to a great extent depending on water samples. With respect to the ratios of humic acid to fulvic acid, the content of fulvic acid was 1.5-25.5

times higher than that of humic acid in most of the raw waters listed in Table 3. Thus, the content of fulvic acid is usually higher than that of humic acid.

Fig. 5 shows the distribution of THMFP/DOC and the HAA5FP/DOC for hydrophobic and hydrophilic organic fractions in the MR water throughout the year investigated. As shown in Fig. 5, the THMFP/DOC for the hydrophobic substances ranged from 70.2 to 81.1%, indicating much higher THM fraction compared to the hydrophilic substances (18.9-29.8). In addition, as shown in Fig. 5, the hydrophilic fractions formed 57.5% of HAAFP/DOC in June 2002, but 36.6% in November 2002, showing seasonally varied formation of HAA. However, In March 2003, the HAAFP/DOC for hydrophilic fractions and hydrophobic fractions was 50.6% and 49.7%, respectively, whereas 46.7% and 53.3%, respectively, in October 2003, showing relatively similar formation of HAA seasonally. In other words, the HAAFP/DOC for hydrophobic and hydrophilic fractions varied to a certain extent depending on the seasonal characteristics of raw water.

Fig. 6 shows the relation between DBPFP/DOC and SUVA for NOM fractions in the MR water. The THMFP/DOC linearly increases with increasing SUVA for both hydrophilic and hydrophobic fractions. Although not shown in the graphs, the r2 values for humic acid and fulvic acid were 0.90 and 0.77, respectively, and the hydrophilic fraction is 0.40, indicating a stronger correlation between SUVA and the THMFP/DOC for hydrophobic fractions than for hydrophilic fractions. In proportion to SUVA, the greatest THM was formed with humic acid followed by fulvic acid and hydrophilic fractions. With respect to HAAFP, hydrophilic fractions formed about 30 µg of HAA5/DOC irrespective of SUVA value, but HAAFP/DOC for hydrophobic fractions increased linearly with increasing SUVA value, indicating that HAA formation is not correlated with aromaticity of the NOM studied. However, hydrophobic fractions showed strong correlations between HAAFP and SUVA value, and the hydrophilic fractions formed the greatest HAAFP/DOC.
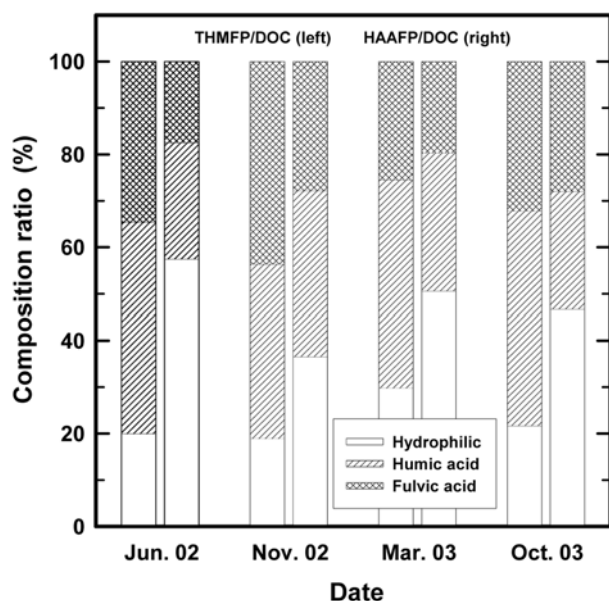
Fig. 5. Distribution of THMFP/DOC and HAA-5FP/DOC of Nakdong river water (Maeri) fractions during June 2002-October 2003.

(a) THMFP/DOC vs SUVA   (b) HAA-5FP/DOC vs SUVA   (c) THMFP/DOC vs HAA-5FP
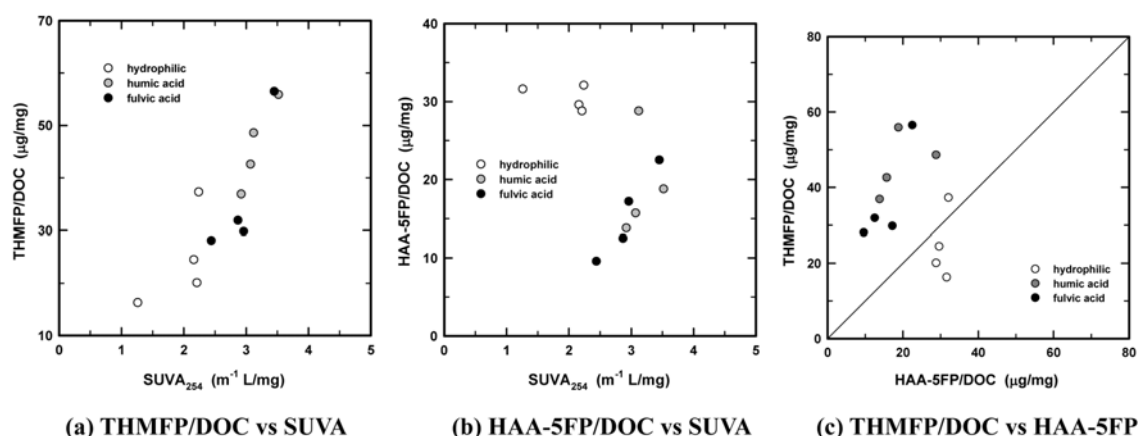
Fig. 6. Chlorination of hydrophobic and hydrophilic fractions of NOM: relationship between THMFP/DOC (a), HAA-5FP/DOC (b) and SUVA, and between THMFP/DOC and HAA-5FP/DOC (c).

Table 4. Comparison of parameters, such as SUVA, THMFP/DOC and TOXFP/DOC, for water samples cited in literature and this study [17,19,31,33,35]

Water source	Krasner et al. [19] Apremont reservoir		Agbekodo et al. [31] Chlorine-free pulping process mill effluents		Crou et al. [35] Apremont reservoir		Chang et al. [33] Te-Chi reservoir		Goslan et al. [17] Albert WTP influents		This study (2002-2003)	
	HPI	HPO	HPI	HPO	HPI	HPO	HPI	HPO	HPI	HPO	HPI	HPO
SUVA	2.0	2.0	1.5	1.0	2.2	3.4	0.3	0.4	0.6	3.9	1.26	2.44
(m^{-1} L/mg)		-4.6		-5.9		-4.8	-0.6	-1.5	-3.7	-6.1	-2.24	-3.52
THMFP/DOC	21	12	13.1	11.8	27	27	1.9	5.9	26.5	73.2	16.3	28.1
(μg/mg)		-51		-42.6		-46	-6.3	-47.1	-256.7	-305.4	-37.3	-56.5
TOXFP/DOC	101	40	-	-	117	144	40.8	83.3	-	-	45.6	162.3
(μg/mg)		-277					-203.5	-210.6				

-HPI: hydrophilic, HPO: hydrophobic.

Fig. 6(c) shows the relationship between THMFP/DOC and HAAFP/DOC for NOM fractions. HAAFP/DOC for humic acid and fulvic acid ranged from 10 to 30 μg/mg, which is much lower than the THMFP/DOC (30-60 μg/mg) for humic and fulvic acid. Thus, the hydrophobic fraction has a stronger reactivity with THM formation than with HAA formation. However, the hydrophilic fraction has a rather higher HAA formation than THM formation.

Table 4 compares DBPFP for NOM indicated in references to DBPFP for the MR water. Overall, THMFP and TOXFP per DOC are higher with hydrophobic fractions than with hydrophilic fractions. In addition, the THMFP and TOXFP per DOC vary to a great extent depending on the characteristics of water samples. Weishaar et al. [34] also studied the reactivity of SUVA values and DOC with chlorine by utilizing 13 different types of NOM, and they reported that SUVA values showed close correlations with the aromatic elements of NOM regardless of the types of NOM, but they did not show any consistent correlation with the reactivity of DOC with chlorine [34].

CONCLUSIONS

This study examined DBP formation characteristics depending on the characteristics of dissolved organic matter contained in raw water samples collected from the Hoedong reservoir and the Maeri

area in the downstream of the Nakdong River whose water is used for the sources of the tap water supplied to the Busan area. In addition, the study classified the seasonal characteristics of dissolved organic matter and investigated the characteristics of seasonal changes and the formation characteristics of DBPs. The findings of the study can be summarized as follows:

1. In the case of Maeri and Hoedong raw water, the assessment of DBP formation potentials per DOC depending on the aromaticity of dissolved organic matter found that all of the THM, HAA-5, and TOX formation potentials showed high correlations with SUVA and the THM formation potential in particular was more sensitive to the magnitude of aromaticity than the HAA-5 and TOX formation potentials.

2. The chloroform formation potentials of Maeri raw water with high aromaticity showed high correlations with SUVA but Hoedong raw water with low aromaticity showed low correlations with SUVA. The TCAA formation potentials showed high correlations with SUVA in both Maeri and Hoedong, but DCAA showed low correlations with SUVA.

3. In Maeri raw water, the ratios of hydrophilic and hydrophobic organic matter were 41-50 percent and 50-59 percent, respectively, throughout the year, indicating that the composition ratios do not vary so greatly. Fulvic acid accounted for 58-78 percent of the hydrophobic fractions, showing that the content of fulvic acid is higher

than that of humic acid.

4. In Maeri raw water, the THM formation ratios per DOC of hydrophobic fractions were 70.2-81.1 percent, showing much higher ratios than hydrophilic fractions (18.9-29.8%). The variation of the HAA-5 formation potentials per DOC showed seasonal differences depending on the characteristics of raw water.

5. In Maeri raw water, the THM portion of dissolved organic matter showed high correlations with SUVA irrespective of hydrophobic or hydrophilic. In proportion to SUVA, the greatest formation amount per DOC was found in humic acid followed by fulvic acid and hydrophilic fractions. With respect to the HAA-5 formation potentials per DOC, about 30 μg of HAA-5 was formed per DOC in hydrophilic fractions irrespective of the increase or decrease in SUVA; but the HAA-5 formation potentials per DOC increased in proportion to the increase in SUVA in hydrophobic fractions. The greatest formation amount per DOC was found in hydrophilic fractions.

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