

# Change of Molecular Weight of Organic Matters through Unit Water Treatment Process and Associated Chlorination Byproducts Formation

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## Abstract

The objectives of this study were to evaluate the change of molecular weight (MW) profiles in natural organic matter (NOM) through various treatment processes (coagulation, granular activated carbon (GAC), and ozonation) using high performance size exclusion chromatography based on ultraviolet absorbance and dissolved organic detection (HPSEC-UVA-DOC). In addition, relationships between MW profiles and disinfection by-product (DBP) formation were evaluated. Each treatment process results in significant different effects on NOM profiles. Coagulation is effective to remove high molecular weight NOM, while GAC is effective to remove low molecular weight NOM. Ozonation removes only a small portion of NOM, while it induces a significant reduction of UV absorbance due to breakdown of the aromatic groups. All treated waters are chlorinated, and chlorination DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) are measured under formation potential conditions. Both THM and HAA formation potentials were significantly reduced through the coagulation process. GAC was more effective to reduce THM formation compared to HAA formation reduction, while ozonation showed significant HAA reduction compared to THM reduction.

*Keywords:* NOM, HPLC, SEC, THM, HAA

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## 1. Introduction

Natural organic matter (NOM) is composed of various types of organic compounds; humic acids, fulvic acids, low molecular weight organic acids, carbohydrates, proteins and other compound classes. The quantity of NOM is commonly represented by the amount of dissolved organic carbon (DOC). Humic substances are the major constituents of NOM: Approximately 50% of the DOC is accounted for by humic substances, while approximately 30% of the DOC is comprised of hydrophilic acids.<sup>1)</sup> The remaining 20% of the DOC is carbohydrates (including polysaccharides), carboxylic acids, proteins, and amino acids.

The major issue associated with drinking waters is that NOM is the precursor of disinfection by-products (DBPs) when chlorine is applied.<sup>2,3)</sup> In addition, it exerts a demand for chlorine and other oxidants (e.g., ozone). One of the most effective strategies to reduce the formation of chlorination DBPs is to reduce the amount of NOM prior to chlorination. Various treatment processes, used by water treatment utilities not only reduce the

amount of NOM, but also induce changes in NOM characteristics, and accordingly result in changes of DBP reactivity. The majority of research has focused on removal efficiencies of NOM through treatment process.<sup>3-8)</sup> However, these studies have provided the limited explanations of NOM profiles and DBP formation through treatment processes.

Various methods have been developed for understanding NOM characterization. These methods include spectroscopy using ultraviolet (UV), infrared, fluorescence, water affinity (hydrophilicity and hydrophobicity) using XAD resin, and molecular weight (MW) distribution using gel permeation chromatography and ultrafiltration. Even though the traditional methods are significant to understand the NOM characteristics, these methods usually require the greater effort for detailed structural analysis or represent higher or lower values with regards to chromophoric (light absorbing) and fluorophoric (light emitting) moieties.

Chin et al. (1994) used high performance size exclusion chromatography (HPSEC) and determine number and weight average molecular weight; this paper concluded that there was good agreement between HPSEC and other techniques to measure molecular weight for a large and diverse number of NOM samples. While HPSEC with UVA detector shows great potential in determining the molecular weight of humic substances, size

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exclusion chromatography SEC values are slightly higher than those measured by other methods.<sup>9)</sup> SEC based on UVA and DOC detection is a recently emphasized technique employed in NOM profiling.<sup>10-13)</sup> The use of HPSEC with sequential UVA and DOC detectors overcomes the limitations of UVA because the DOC analyzer detects virtually all of the organic carbon in the sample. Thus, this method is able to provide further identifying to molecular weight distribution of NOM.

Chlorination DBP formation is affected by many variables including pH, temperature, and reaction time. Even under the same chlorination conditions, the diversity of the characteristics of NOM (organic precursor) and Br- (inorganic precursor) concentration results in the different DBP formation, as well as the different distribution of the DBP species. While trihalomethanes (THMs) are readily formed from the reaction of chlorine with non-polar, larger MW NOM, lesser amounts of THMs can be formed from polar and smaller MW NOM.<sup>14,15)</sup> Both aromatic (resorcinol) and aliphatic (pyruvic acid) compounds in NOM appear to react with chlorine and form haloacetic acids (HAAs).<sup>16)</sup> Larger molecular weight fractions of NOM readily form HAAs.<sup>15)</sup> However, both humic and non-humic fractions are significant to form HAAs.

Unit treatment processes differently remove NOM portions. For instance, coagulation preferentially removes non-polar (hydrophobic) and larger MW NOM over polar (hydrophilic) and smaller MW NOM. The implication is that each treatment process affects the NOM characteristics and the reactivity of DBP formation differently.

The objectives of this research were i) to evaluate the changes of MW profiles in NOM from unit water treatment process including coagulation, GAC, and ozonation using HPSEC with UVA and DOC detectors, and ii) to investigate the relationship between MW profiles and DBP formation.

## 2. Materials and Methods

### 2.1. HPSEC-UVA-DOC

Figure 1 illustrates the schematic of HPSEC-UVA-DOC system. The system is composed with a high performance liquid chromatography (HPLC, LC-20A, Shimadzu) with UVA (SPD-20AD, Shimadzu) and DOC detectors (modified Sievers total organic carbon analyzer 820 turbo). The DOC detector is connected directly to the UVA detector waste line. The DOC detector analyzes DOC every four seconds. A DOC analyzer detects dissolved organic matter through UV/persulfate oxidation. A conductivity detector is utilized to measure CO<sub>2</sub> gas generated. The UVA detector is a sensitive photometer, which is operated over wide wavelength ranges. The UVA wavelength applied in this experiment was based on 254 nm.

The SEC column separates compounds due to hydrodynamic molecular size. The retention time depends on the effective molecular size. Molecules that are larger than the pore size of the packing material are excluded and elute first. Smaller molecules can penetrate throughout the porous infrastructure and are attenuated. Therefore, smaller molecules have long retention

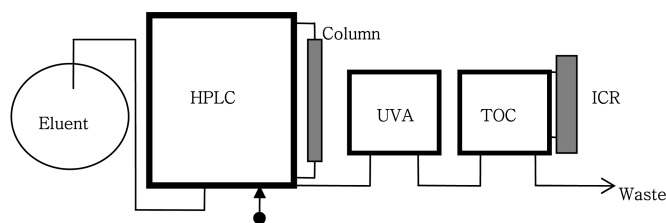


Fig. 1. Schematic of HPLC-UVA-DOC system.

time while larger molecules have short retention time. The column employed in the study was a HW-50S (Grom) column, which has a high cross sectional area (2 cm radius, 25 cm long). Large volume of sample (2 mL) was injected in order to obtain high resolution and low backpressure.

Eluent composition significantly affects separation of components by HPSEC. A 0.025 M Na<sub>2</sub>SO<sub>4</sub> eluent solution with a phosphate buffer solution (0.0024 M NaH<sub>2</sub>PO<sub>4</sub> + 0.0016 M Na<sub>2</sub>HPO<sub>4</sub>) was employed in the experiment. Eluent produces an ionic strength of 0.1 M. Standard solutions for the MW calibration curve were made with polyethylene glycol (MW = 200, 600, 2K, and 12K daltons). Details on all these analyses are described separately.<sup>11,12)</sup>

### 2.2. THMs and HAAs Analysis

Samples were chlorinated with sodium NaOCl and analyzed for THMs and HAAs under formation potential conditions (FP: pH = 7, temperature = 20°C, Cl<sub>2</sub>/DOC ratio = 3 mg/mg, contact time = 7 days). Four species of THMs and nine species of HAAs were measured by gas chromatography (GC) after liquid-liquid extraction with methyl-tert butyl ether. A GC (Simadzu GC-2010) equipped with an electron capture detector and a DB-1 GC column were used to analyze THMs and HAAs according to EPA method 551. Calibration curves were made with commercial standard solutions (Supelco).

### 2.3. Descriptions of Treatment Processes and Samples

A surface water was collected from Han River located in Gyeonggi-Do province, Korea. The Han river raw water sample (HG-Raw) was subsequently treated with several lab scale treatment processes including alum coagulation (HG-A1), iron coagulation (HG-Fe), granular activated carbon (HG-GAC), and ozonation (HG-O3). NOM MW profiles were evaluated with treatment processes. A summary of the lab scale experimental conditions is presented in Table 1. Table 2 shows a summary water quality of raw and treated waters.

## 3. Results and Discussion

### 3.1. MW Distribution

Figure 2 shows MW distributions using SEC for the raw water measured with UVA and DOC detectors. MW greater than 10,000 daltons was not included in the analysis since the HS-50K column covers up to 10,000 dalton range. There was somewhat

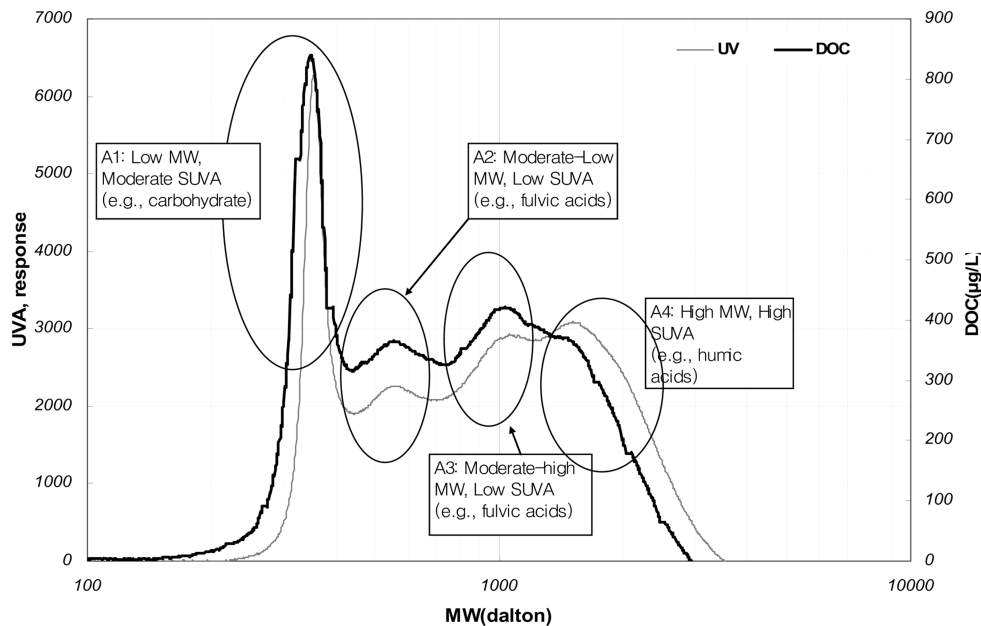


Fig. 2. Comparison of MW distribution with UVA and DOC detectors (HG-Raw).

difference between MW distribution measured with the DOC detector and the UVA detector. Both high UV absorbance and high DOC response were observed between 100 and 430 daltons. A relatively low UVA response was observed over the range of 430 - 1,200 daltons compared to the DOC response. However, a relatively high UV absorbance was observed between 1,200 and 3,500 daltons. From these results, potential components of NOM would be: i) carbohydrates or amino acids in a range of 100 to 430 daltons (A1 in Figure 2), ii) fulvic-like substance in a range of 430 to 1,200 daltons (A2 and A3, respectively), and iii) humic-like substance in a range of 1,200 to 3,500 daltons (A4).<sup>11,12)</sup> The previous study where fluorescence was employed partially supports these results although the MW ranges are somewhat different from these results.<sup>12)</sup>

Figure 3 shows the changes of MW distribution with several treatment processes including coagulation, GAC and ozonation. Larger MW NOM (> 1,000 daltons) was preferentially removed by coagulation, while smaller MW NOM (< 450 daltons) was not effectively removed based on DOC detector (Figure 3). This

result suggests that coagulation is more effective to remove larger MW NOM than the other processes (i.e., ozonation and GAC). The sharp peak at the lower MW range (approximately 300 daltons) is expected to be salt boundary fraction. In addition, this would be influenced by nitrate and other inorganic solutes in the sample waters. Separate studies reported that coagulation is not effective to remove small MW components, while large MW components of NOM are efficiently removed.<sup>17,18)</sup>

GAC removed small and medium MW NOM (< 1,500 daltons), while larger MW NOM (> 1,500 daltons) was not removed significantly with both UVA and DOC detectors. Unlike coagulation and GAC, ozonation resulted in significant MW changes. Ozonation is effective to reduce NOM size through the entire MW ranges based on UVA detector, while small NOM reduction was observed in a range of greater than 800 daltons (A3 and A4 in Figure 2). In addition, the increase in DOC was observed in a lower MW range (A1 and A2 in Figure 2). Relatively low removal of DOC occurs during ozonation<sup>19,20)</sup>, while UVA removals of greater than 70% are observed at the high

Table 1. Summary of experimental conditions

Coagulation		GAC	Ozone
Alum ( $\text{Al}_2(\text{SO}_4)_3$ )	Ferric chloride ( $\text{FeCl}_3$ )	Calgon F-400	4.6 mg/L
Dose: 30 mg/L	Dose: 40 mg/L	EBCT: 15 min	Contact time: 10 min

Table 2. A summary of water quality of raw and treated waters

	Sample code	TOC (mg/L)	UV <sub>254</sub> ( $\text{cm}^{-1}$ )	SUVA (L/mg-m)	NH <sub>3</sub> -N (mg/L)	Note
Raw water	HG-Raw	1.90	0.032	1.68	0.21	Han River
Treated water	HG-Al	1.04	0.015	1.44	NA	Alum coagulated
	HG-Fe	0.82	0.013	1.58	NA	Iron coagulated
	HG-GAC	1.25	0.018	1.44	NA	GAC treated
	HG-O3	1.70	0.012	0.71	NA	Ozone treated

NA = not available

$O_3$ /DOC ratios.<sup>21)</sup> The result indicates that some of large MW NOM (800 daltons) is transferred to small MW NOM due to breakdown.

As a result, coagulation appears to be effective to remove humic-like substance (A4 in Figure 2), while ozonation is effective on small MW NOM removal (A1 and A2 in Figure 2). However, GAC effectively removes small and medium MW NOM, while larger MW NOM (> 1,500 daltons) was virtually not affected.

### 3.2. MW Fractions

Based on the DOC chromatograms, four different molecular size fractions were identified for the samples. As described previously, fraction 1 (A1) had relatively small MW and moderate SUVA values in a range of 100 to 430 daltons (carbohydrate-like substance), while fraction 2 (A2) had moderate-low MW and low SUVA values in a range of 430 to 700 daltons (fulvic-like substance). In addition, fraction 3 (A3) had moderate-high MW values in a range of 700 to 1,200 daltons (fulvic-like substance), while fraction 4 (A4) had relatively large MW and high SUVA values in a range of 1,200 to 3,500 daltons (humic-like

substance). In order to quantify MW distribution, four sections were divided, and the areas of chromatogram for each section were calculated. Table 3 shows the area of each section for four MW fractions.

Figure 4 shows a radial shape graph of fraction areas and fraction area percentage, respectively. Figure 4 illustrates that ozonation process has an insignificant effect on the reduction of NOM based on DOC detector, even though UVA detector shows significant reduction through the entire MW ranges. It is also noted that small MW fractions (A1 and A2) were slightly increased through ozonation process. Coagulation shifts large MW distribution to small MW distribution and reduces SUVA values, resulting in less aromatic NOM characteristics. GAC slightly increases large MW and high SUVA portions, while ozonation increases small MW proportions.

### 3.3. DBP Formation and Reactivity

Figures 5 and 6 show THM/HAA formation and THM/HAA reduction under formation potential conditions. Both THM/HAA formation potentials were significantly reduced through the coagulation process. Coagulation was more effective in HAA re-

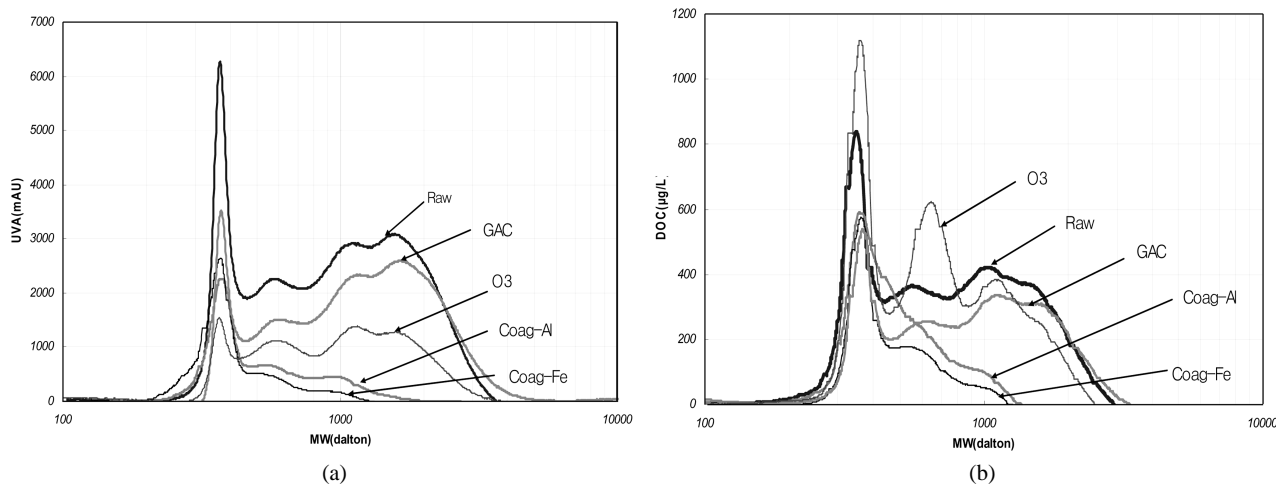


Fig. 3. Changed of MW distribution through various treatment processes (coagulation, GAC, and ozonation) with (a) UVA detector and (b) DOC detector.

Table 3. A summary of area for each fraction based on UVA and DOC chromatograms

Area	DOC					UVA				
	Total	A1	A2	A3	A4	Total	A1	A2	A3	A4
HG-Raw	701763	79096	93004	191549	338114	5956140	412548	572697	1306477	3664418
	(100)	(11.3)	(13.3)	(27.3)	(48.2)	(100)	(6.9)	(9.6)	(21.9)	(61.5)
HG-Al	186391	63804	71054	50369	1164	580132	203967	165676	202168	8321
	(100)	(34.2)	(38.1)	(27.0)	(0.6)	(100)	(35.2)	(28.6)	(34.8)	(1.2)
HG-Fe	120225	48512	43809	27891	13	446571	250711	118716	76828	316
	(100)	(40.4)	(36.4)	(23.2)	(0.0)	(100)	(56.1)	(26.6)	(17.2)	(0.1)
HG-GAC	591526	45974	63307	143600	338645	5646920	194119	370905	953701	4128196
	(100)	(7.8)	(10.7)	(24.3)	(57.2)	(100)	(3.4)	(6.6)	(16.9)	(73.1)
HG-O3	616878	95022	124792	183234	213829	2428488	113892	272534	550066	1491997
	(100)	(15.4)	(20.2)	(29.7)	(34.7)	(100)	(4.7)	(11.2)	(22.7)	(61.4)

A1, 100 to 430 daltons; A2, 430 to 700 daltons; A3, 700 to 1,200 daltons; A4, 1,200 to 3,500 daltons. Parenthesis ( ) denotes percentage of each fraction area

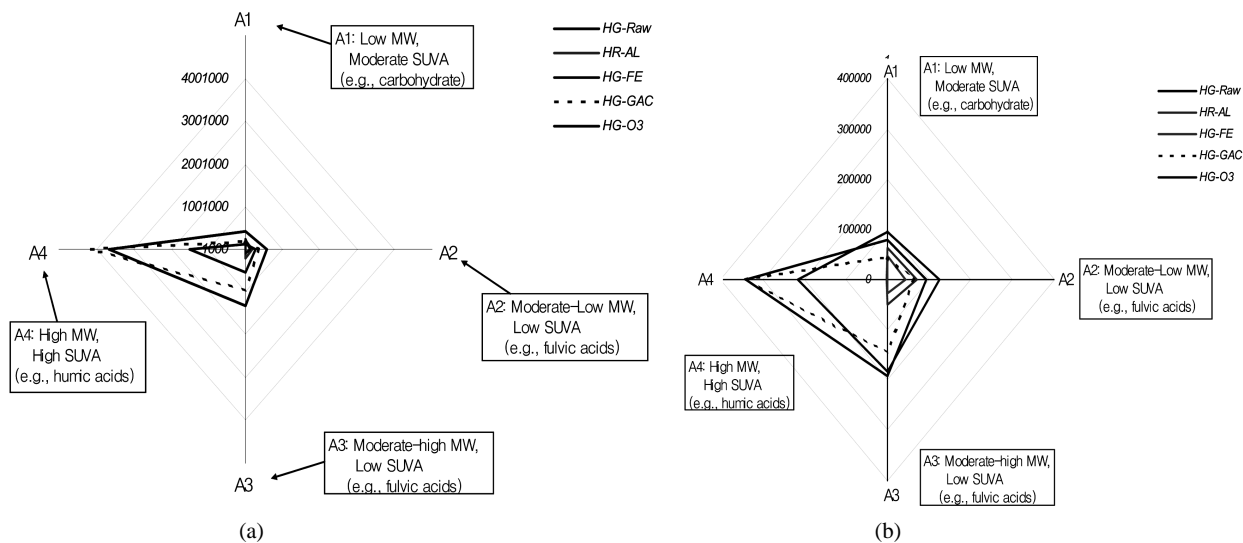


Fig. 4. A radial shape graph of fraction areas with (a) UV detector and (b) DOC detector.

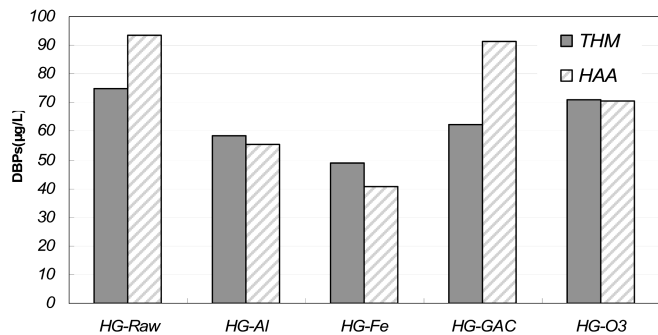


Fig. 5. THM and HAA formation with treatment processes under FP conditions.

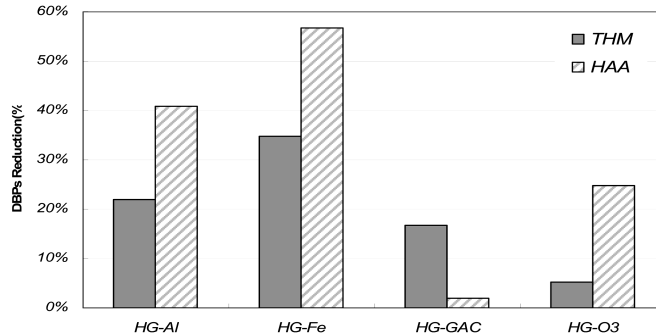


Fig. 6. THM and HAA reduction with treatment processes.

duction than THM reduction. GAC was more effective to reduce THM formation compared to HAA formation reduction, while ozonation showed significant HAA reduction compared to THM reduction.

Both MW and NOM compositions are important in THM and HAA formation. Aromatic components containing phenolic groups in NOM are considered as reactive sites of THM, while both aromatic and aliphatic components in NOM appear to be reactive to HAAs.<sup>3,16</sup> Larger MW fractions of NOM readily form HAAs.<sup>15</sup> In addition, both humic and non-humic fractions are significant to form HAAs. Ozonation significantly reduced specific UVA (SUVA, UVA divided by DOC) levels, indicating that ozone selectively attacks aromatic components in NOM. In addition to SUVA reduction, ozonation also makes higher MW to smaller MW (see Figure 3(b)). The results exhibited that GAC effectively reduce THM formation, and ozonation preferential reduce HAA formation. Possible explanations are that MW distribution affects significantly in the formation of THM and HAA, and larger MW is more reactive in HAA formation. Further research is needed to verify this result.

Figure 7 shows changes in both THM and HAA reactivities (i.e., DBP normalized to DOC) with each treatment process. It is noted that the THM and HAA reactivities varied depending

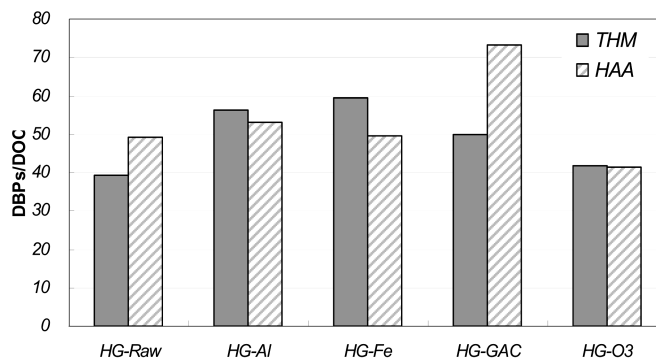


Fig. 7. THM and HAA reactivity with treatment processes.

on the treatment processes; coagulation and GAC tended to increase DBP reactivity, while ozonation tended to decrease reactivity. This result implies that GAC are not effective in removing DBP reactive NOM especially in HAA reactivity (e.g., relatively large MW fractions of NOM).

### 3.4. Correlation Between MW and DBP Formation

Table 4 represents a correlation coefficient matrix describing relationships among MW area and DBP formation. The correla-

Table 4. Correlation coefficient matrix for MW area versus DBP formation

r2	DOC					UVA				
	A1	A2	A3	A4	TOT	A1	A2	A3	A4	TOT
THM	0.77	0.84	<b>0.94</b>	0.77	<b>0.91</b>	0.24	<b>0.82</b>	0.80	0.64	0.70
HAA	0.23	0.41	0.86	<b>0.97</b>	<b>0.92</b>	0.32	<b>0.92</b>	<b>0.96</b>	<b>0.96</b>	<b>0.98</b>

tion coefficient ( $r$ ) is used to determine the extent to which values of the two variables are proportional to each other. The correlation coefficient represents the linear relationship between two variables. Strong correlations between MW area and DBP formation were observed. It should be noted that A3 (medium-high MW, low SUVA) based on DOC detector exhibited a strong correlation with both THM and HAA formation. A4 (high MW, high SUVA) based on both the DOC and UVA detectors exhibited a strong correlation with HAA formation, while A3 based on the DOC detector showed a strong correlation with THM formation. This result indicates that HAA formation has a stronger relationship with MW distribution (large MW showing a strong correlation with HAA formation) than THM formation (overall MW related to THM formation).

#### 4. Conclusions

HPSEC with UVA and DOC detectors is able to identify the molecular weight distribution of NOM present in source water, and NOM removal with various treatment processes including coagulation, GAC, and ozonation. Coagulation preferentially removed larger MW NOM, while ozonation significantly shifted NOM to smaller MW. The result also indicates that HAA formation is more related with MW distribution (large MW has a strong correlation with HAA formation) than THM formation (overall MW relates to THM formation). This study can provide water utilities with valuable information of selective NOM removal efficiencies and DBP reduction with different treatment processes.

#### Acknowledgement

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