

# Characterization of natural organic matter and assimilable organic carbon from an advanced full-scale drinking water treatment plant to tap

Ji Won Park<sup>a</sup>, Woo-hyeun Joe<sup>b</sup>, Sung Kyu Maeng<sup>a,\*</sup>

<sup>a</sup>Department of Civil and Environmental Engineering, Sejong University, 209 Nengdong-ro, Gwangjin-gu, Seoul 05006, Korea, Tel. +822-3408-3858; Fax: +822-3408-4332; email: smaeng@sejong.ac.kr (S.K. Maeng) <sup>b</sup>Division of Water Treatment, Seoul Water Institute, Seoul Metropolitan Government, 716-10, Cheohho-daero, Gwangjin-gu, Seoul 04981, Korea

Received 1 July 2019; Accepted 18 November 2019

#### ABSTRACT

Natural organic matter (NOM) is not only a precursor of disinfection by-products but also the source of carbon for microbial growth. The effects of the characteristics of NOM on the biological stability of water are not well defined. NOM comprises a complex mixture of recalcitrant and biologically labile organic carbon. In this study, the changes in NOM and assimilable organic carbon (AOC) in water from the source to the customers' taps were investigated through both conventional and advanced drinking water treatment processes. Conventional water treatment exhibited a considerable removal of high molecular weight NOM via coagulation–sedimentation, which resulted in 39% removal of AOC. Therefore, conventional treatment units are important for biostable drinking water supply. Rapid sand filtration and ultrafiltration membrane processes showed no significant differences in terms of the removal of NOM and AOC (p > 0.05). AOC was significantly increased at the consumer tap (150–230 µg L<sup>-1</sup>) possibly because of the interaction between aged pipes, biofilms, residual chlorine, and NOM.

Keywords: Assimilable organic carbon (AOC); Biostability; Natural organic matter (NOM); Tap water

# 1. Introduction

Access to safe drinking water is the most critical for public health [1–3]. Tap water consumption may vary because of numerous reasons such as housing conditions, age, personal income, education, and taste [3,4]. Tap water is recommended to drink because it is relatively convenient and safe. However, only developed countries including Australia, Japan, Western Europe, and Northern America guarantee the safety of drinking water from the tap, according to the traveler's guidance report of United States Centers for Disease Control and Prevention (CDC) [5].

Moreover, residual chlorine is one of the factors because of which people avoid drinking tap water because of disadvantages such as the aesthetically unfavorable taste and odor of chlorine. Because many Koreans do not drink tap water (less than 10%) [6], public water utilities for tap water quality have been improved by enhancing and renovating water treatment processes. In Korea, the production of drinking water from advanced water treatment processes (e.g., granular activated carbon filtration (GAC) and/or ozone) has been increased by two-fold from 4,895,000 to 10,819,000 m<sup>3</sup> per day (2007–2017) [7]. Especially, tap water in Seoul in The Republic of Korea is produced via advanced water treatment processes since 2015. To reduce customer complaints, Seoul metropolitan waterworks has reduced the chlorine dosage to minimize the odor, taste, and disinfection by-products (DBPs). However, the lowered residual chlorine may increase microbial growth in the water at the point of consumption (i.e., household and building taps).

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986 © 2020</sup> Desalination Publications. All rights reserved.

Microbial growth during water distribution may impact tap water quality by causing the occurrence of opportunistic pathogens, increasing invertebrate abundance, causing pipe corrosion, and deteriorating the color, taste, and odor [8-12]. To control microbial growth in tap water with less chlorine, it is necessary to enhance the biological stability of drinking water. Biological stability is often attained by controlling nutrients (N and P), carbon sources (assimilable organic carbon (AOC) and biodegradable dissolved organic carbon), and biomass formation (adenosine triphosphate, total cell count (TCC), heterotrophic plate count, and other health-relevant microorganisms) [1,8,12-15]. According to Smeets et al. [16], chlorine is necessarily avoided to produce biologically stable water. They also stated that the choice of biologically stable groundwater is the best option for safe water production. However, this is a considerable challenge for countries that use surface water as their drinking water sources and introduce chlorine like in old distribution systems. Moreover, previous studies have evaluated the biological stability during surface water treatment processes (Table 1), but meeting the guidance levels of AOC for the nonchlorinated drinking water system was a challenging task (e.g., less than 10 µg-AOC L<sup>-1</sup>) [17].

Natural organic matter (NOM) is not only a precursor of DBPs but also a microbial carbon source. However, the impact of NOM compositions on the biological stability of water has not been understood. NOM comprises a complex mixture of recalcitrant and biologically labile organic carbon. AOC is known as readily biodegradable organic matter in bulk water and is one of the most critical parameters responsible for bacterial growth and biofilm formation in distribution systems [8,11,18]. Recently, the removal of high molar or particulate organic matter in drinking water treatment plant (DWTP) has gained attention because the removal of macromolecule organic matter reduces the occurrences of biofilm and the presence of Aeromonas, invertebrates, and other microbes [12,19]. Notably, several studies have demonstrated that coagulation, sedimentation, and low-pressure membrane techniques are effective for reducing the macromolecular biodegradable NOM in untreated water [19-21]. Previous studies were not performed in the same water treatment system, but in our study, both conventional and advanced processes (including membrane filtration) were performed in one treatment plant.

Maintaining water quality from the treatment plant until the customers' taps is also essential for aesthetic and hygienic requirements for customers. Therefore, understanding the controlling factors in the main and household plumbing systems has recently gained attention (Fig. 1). The water distribution system, which acts as a complex living interface for microbes, is known to be affected by microorganisms in bulk water, biofilm formation, suspended particles, loose

Table 1

The range of total, dissolved, and assimilable organic carbon (TOC, DOC and AOC, respectively) in surface water treatment systems

Source water				Reference		
TOC, mg L <sup>-1</sup>	DOC, mg L <sup>-1</sup>	AOC, μg L <sup>-1</sup>	TOC, mg L <sup>-1</sup>	DOC, mg L <sup>-1</sup>	AOC, µg L <sup>-1</sup>	[15,17,36–38]
			0.6-4.3*		17–118	Polanska et al. [17]
	1.2-20.9	56–395		0.7-7.0	37–75	Vital et al. [15]
2.0*		33-148		0.8-1.1	53–151	Ohkouchi et al. [37]
0.6-1.1*		118-159		n.a.	27	Yang et al. [36]
	1.5	63		0.7	36	Choi et al. [38]



Fig. 1. Factors influencing the biological stability of drinking water from the treatment plant to tap [8,9,11–14,16,18,22–29].

deposits, hydraulic shear stress, and pipe material [22,23]. At the household level, the biological stability of tap water can vary because of water consumption, stagnation time, elevated temperatures, residual disinfectants, plumbing material, and diameter and length of pipes [11,24–26]. Thus, it is challenging to maintain water quality from the treatment plant until the customers' taps.

However, limited studies have evaluated the change in biological stability from the treatment plant until the consumers' taps [24,27,28]. In our study, the fate of NOM and AOC from the source to the customer's tap was evaluated. Moreover, the change in NOM and AOC levels was investigated through both conventional and advanced drinking water treatment processes (e.g., coagulation, sedimentation, rapid sand filtration (RSF), membrane filtration, ozonation, and GAC filtration).

#### 2. Materials and methods

# 2.1. Sampling location

# 2.1.1. Full-scale advanced treatment plant

We monitored a water treatment train in the DWTP 'A' over three months. We collected source water (SW) once every two weeks, as well as effluents from coagulation/sedimentation (CS), RSF, ultrafiltration (UF), ozonation (Ozo), GAC, and disinfection (Dis) (n = 5).

In this study, the surface water (Seoul, Korea) was chlorinated (1-2 mg L<sup>-1</sup>, chlorine) and used as a source for the following water treatment system. The capacity of the treatment train was 250,000 m3 d-1. The conventional water treatment processes in DWTP 'A' involved coagulation, sedimentation, and RSF. The advanced water treatment process included UF, ozonation, and GAC filtration. RSF and UF were individually performed using the CS treatment effluent (Fig. 2). Note that the CS processes before RSF and UF were different; that is, three- and two-stage coagulant addition, respectively, was performed (coagulant dosage ratio = 3:2). Polyaluminium chloride was added as the coagulant. A detailed operational dosage is not available in this study. A horizontal sedimentation basin (L 59 m × W 16 m × H 4.5 m) was used to settle and remove flocs. The rate of RSF, which consisted of two layers including 0.3 m sand and 1.0 m anthracite, was 194 m<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>. The UF process comprised

six trains of pressurized membrane units (0.05  $\mu$ m pore size, polyvinylidene fluoride (PVDF), hollow-fiber type, 1.5 m<sup>3</sup> m<sup>-2</sup> d<sup>-1</sup>). Note that treated effluents from both RSF (200,000 m<sup>3</sup> d<sup>-1</sup>) and UF (50,000 m<sup>3</sup> d<sup>-1</sup>) were blended prior to ozonation. The ozone dosage was up to 2.0 mg L<sup>-1</sup>, and the contact time was 20 min. Next, GAC filters were filled with coal-based activated carbon media, and the empty bed contact time was 15.6 min. The treated effluents from the advanced treatment processes were finally disinfected with chlorine (0.65 mg L<sup>-1</sup>, 1 h contact time), and then, the water produced was supplied to three districts of Seoul.

## 2.1.2. Treatment plant to tap

In addition to an effluent sample from each treatment step, tap water was collected during the sampling campaign. To investigate changes in NOM and AOC levels in treated water through the distribution pipes, we first collected treated water from the storage tanks in the treatment plant, and then, we collected tap water from the customers' locations. The sampling location of the tap water was a type of office building located in Seoul (37°31'10.4"N 126°52'11.2"E). The traveling distance of water from the DWTP 'A' to the customer tap was roughly 4 km. All samples were taken to the laboratory and analyzed within 4 h.

We also collected additional drinking water samples produced from another treatment plant and tap. During the sampling campaign for DWTP 'B' and 'C', samples from the finished water storage tank were collected and then from the taps of customers of DWTP 'B' and 'C' systems. The treatment schemes of both DWTP 'B' and 'C' were similar to that of DWTP 'A', except for UF (detailed information is provided in Table 2). The traveling distances of drinking water from DWTP 'B' and 'C' to the consumers' taps were 6 and 10 km, respectively. All tap water samples were chlorinated via the disinfection process at each DWTP. We quenched the residual chlorine using a sodium thiosulfate solution to perform further analysis. Because of limited access to DWTPs and the building tap, few grab samples from treatment steps to the tap were obtained during the sampling campaign. Although the detailed chemical and microbial qualities of the produced drinking water may have differed between the treatment plants, all water treatment plants in the present study were supplied with the same SW.



Fig. 2. Layout of the sampling location (DWTP 'A' and tap). (CS, coagulation/sedimentation; RSF, rapid sand filtration; UF, ultrafiltration; Ozo, ozonation; GAC, granular activated carbon filtration; Dis, disinfection).

DWTP	А	В	С
Pretreatment	<2.0 mg L <sup>-1</sup> , Chlorine	<1.5 mg L <sup>-1</sup> , Chlorine	n.a., Chlorine
Coagulation	Polyaluminium chloride	Polyaluminium chloride	Polyaluminium chloride
Sedimentation	1.3 h, RT,	3 h, RT,	3 h, RT
Rapid sand filter	0.3 m, sand, 1.0 m, anthracite,	1.2 m, sand, 36 beds,	0.6 m, sand, 0.4 m,
	16 beds, 194 m d <sup>-1</sup>	149 m d <sup>-1</sup>	gravel, 12 beds, 200 m d <sup>-1</sup>
Ultrafiltration	0.05 μm pore, PVDF, hollow-	None	None
(DWTP A)	fiber, 1.5 m d <sup>-1</sup>		
Ozonation	$<2.0 \text{ mg } \text{L}^{-1}$	<1.5 mg L <sup>-1</sup>	<1.5 mg L <sup>-1</sup>
Granular activated	15.6 min, EBCT	n.a.	n.a.
carbon filter			
Disinfection	0.65 mg L <sup>-1</sup> , Chlorine	n.a., Chlorine	n.a., Chlorine

Table 2 Comparison of drinking water treatment plants 'A', 'B', and 'C'

n.a.: non applicable; RT: retention time; EBCT: empty bed contact time)

#### 2.2. Natural organic matter characterization

# 2.2.1. Liquid chromatography–organic carbon detection (LC-OCD)

The molecular weight (MW) distribution of the dissolved organic carbon (DOC) was investigated to understand the relation between NOM composition and AOC. Although real-time NOM characterization techniques cannot predict the results of the culture-dependent method (i.e., AOC assay), it is still important for identifying the relations between NOM removal and bacterial growth potential. AOC has been generally regarded as low MW organic matters (e.g., acetate and oxalate) which are readily utilizable by conventional inoculum strains such as Spirillum sp. NOX and Pseudomonas fluorescens P-17. In contrast, recent studies have revealed that indigenous bacteria and Flavobacterium utilize high MW NOM such as proteins and polysaccharides [12,20,30]. Thus, understanding the changes in the MW distribution of NOM per treatment method is required to provide better performance of water treatment for the production of biostable water.

MW distribution and sub-fractions of NOM were determined using liquid chromatography–organic carbon detector (LC-OCD) (Model 8 system, DOC-Labor, Germany) equipped with a cation exchange chromatographic column. DOC concentrations of each sub-fraction were calculated based on the chromatogram peaks and using the software, ChromCALC (DOC-Labor, Germany). The sub-fractions were biopolymers (>20 kDa), humic substances (1–20 kDa), building blocks (300–500 Da), low MW acids, and neutrals (<300 Da) [31]. Biopolymers contain proteins and polysaccharides. Building blocks are known as breakdown products of humic substances. Low MW acids and neutrals were distinguished based on the ionic strength.

# 2.2.2. Excitation emission matrix (EEM)

The three-dimensional (3d) excitation-emission matrix (EEM) technique was used to characterize the changes in fluorescent moieties of NOM during the water treatment processes. The arbitrary intensities of four components including tryptophan- (T1 and T2), fulvic- (A), and humic-like (C) were recorded using an RF-5301PC fluorescence spectrophotometer (Shimadzu, Japan) equipped with a 150 W Xenon lamp. Before EEM analysis, all samples were filtered with a 0.45  $\mu$ m syringe filter. Each 3 mL filtered sample was poured into a quartz cuvette, and then, the fluorescence spectra were obtained. No dilution was needed for water samples in this study. The emission (em) spectra were read at wavelengths from 280 to 600 nm with 1 nm intervals. The wavelengths of excitation sources ranged between 220 and 400 nm with 10 nm intervals. The ex–em wavelengths of the components were as follows: T1 (ex: 220–240 nm; em: 330–360 nm), T2 (ex: 270–280 nm; em: 330–360 nm), A (ex: 230–260 nm; em: 400–450 nm), and C (ex: 300–340 nm; em: 400–450 nm) [20].

# 2.3. Assimilable organic carbon

#### 2.3.1. Bioassay

An AOC assay was performed using the indigenous bacteria in the GAC effluent of the DWTP. A 100 mL aliquot of the GAC effluent sample was filtered with a 0.1 µm prewashed filter (Sartorius, Germany) and re-inoculated with the unfiltered GAC effluent. After 10 d of incubation, the TCC in the sample reached the stationary phase and served as the inoculum for the following AOC measurement. Before performing the bioassay, carbon-free glassware was prepared in a 550°C muffle furnace to remove all residual organic carbon. The pretreated borosilicate glass vial, 50 mL, was used for the following microbial pasteurization, inoculation, and incubation. Residual chlorine was quenched with sodium thiosulfate. For the pasteurization process, water samples were heated at 70°C for at least 30 min and then cooled to room temperature. The chilled water samples were filtered using a 0.1 µm filter (Sartorius) to remove the bacterial cells and debris. A 20 mL aliquot of each filtrate was used to perform inoculation and incubation for the determination of the AOC. For carbon-limited conditions, the mineral supplement for the AOC assay was prepared based on a previous study by Wen et al. [26]. The mineral solution, 660 µL, was added to 20 mL of each prepared filtrate (i.e., pasteurized

and filtered water samples). Finally, the prepared inoculum was added to meet the initial cell count  $(1.0 \pm 0.3 \times 10^4 \text{ cell})$  in the water samples. The inoculated samples were stored and incubated in a 35°C water bath for 5 d or more. The grown cells generally entered the stationary phase within 5 d.

#### 2.3.2. Flow cytometry analysis

Flow cytometric cell counts were carried out to obtain the densities of cells grown in the resultant AOC incubation samples. SYBR Green I working solution (×100) was prepared by diluting SYBR Green I nucleic acid gel stain concentrate (×10,000) (Invitrogen, USA) with filtered dimethyl sulfoxide. The stored working solution was thawed and warmed at 35°C in a water bath for 30 min before the use. A 1 mL aliquot of the incubated AOC sample was transferred into an autoclaved amber microtube (1.5 mL), and 10 µL of Sybr Green I working solution was added. The microtubes were incubated at 35°C for 10 min. The stained samples were diluted with ultrapure water, and then, they were analyzed using a flow cytometer (488 nm laser light source) (Cube 6, Partec, Germany). TCC was determined based on the green fluorescence intensity (520 nm) and electronic gating utilizing the software, FCS Express 4 (De Novo Software, USA). The recorded cell count was converted into AOC concentrations. The growth yield,  $1 \times 10^7$  cell  $\mu g^{-1}$  acetate eq., was adopted from Hammes and Egli [32] (see function 1).

$$AOC(\mu g L^{-1}) = \frac{1,000 \times (TCC_f - TCC_i)}{\gamma}$$
(1)

 $\text{TCC}_{i}$  (cell mL<sup>-1</sup>) is the final cell count in the incubated samples in which bacteria entered the stationary phase.  $\text{TCC}_{i}$  (cell mL<sup>-1</sup>) is the initial cell count in the sample before incubation. *Y* is the growth yield based on the bacterial growth potential equivalent to the assimilated acetate-C concentration.

#### 2.4. Statistical analysis

# 2.4.1. Mean comparison

Statistical analysis was performed using PASW statistics 18 software (IBM, USA). Mean comparison and post-hoc test (Tukey method) were performed to analyze the significant changes between the water treatment processes. Based on the analysis of variance (ANOVA), an asterisk (\* or \*\*) illustrates a significance level of 0.05 or 0.01, respectively, of the difference between the analyte values in this study.

## 3. Results and discussions

#### 3.1. NOM characteristics in the water treatment plant

The SW type (e.g., groundwater, lake, and river) and seasonal impact (e.g., algal bloom, water temperature, rainfall, and snow melting) influenced the characteristics of organic matter in the SW [14,33-38]. Previous studies have demonstrated that NOM characteristics influence the biological stability of treated water [20,30,33]. In this study, DOC in SW ranged from 1.37 to 2.85 mg  $L^{-1}$  (2.12 ± 0.57 mg  $L^{-1}$ ). Biopolymers, humic substances, building blocks, low MW acids, and neutrals were  $0.13 \pm 0.08$ ,  $0.82 \pm 0.23$ ,  $0.35 \pm 0.04$ ,  $0.17 \pm 0.05$ , and  $0.65 \pm 0.31$  mg L<sup>-1</sup>, respectively (Fig. 3). Note that the DOC was similar to that of upstream where we investigated previously (2.25  $\pm$  0.40 mg L<sup>-1</sup>, DOC in prechlorination effluent) [20]. Even though the intake station of DWTP 'A' was in urban downstream, we did not observe the dramatic difference in NOM characteristics vs. Paldang Lake, upstream water protection zone for Seoul and Gyeonggi-do province [20].

In the DWTP, CS decreased DOC by 18%. Notably, high MW NOMs (i.e., biopolymers and humic substances) were effectively removed via CS (p < 0.01) (Fig. 3). Consistent with the LC-OCD results, EEM analysis showed a significant decrease in fulvic- and humic-like components (A and C peak, respectively) between SW and CS (p < 0.01). However, a discrepancy was observed between biopolymers



Fig. 3. DOC changes from the treatment plant to tap. Dissolved organic matter fractions determined by LC-OCD (a) and normalized concentration by source water (b).

and tryptophan-like components; hence, biopolymers were likely to consist of polysaccharides. Although biopolymers (i.e., polysaccharides and proteins) are less abundant compared to humic substances, we should carefully monitor the removal of polysaccharides and proteins in terms of microbial utilization in oligotrophic drinking water [30]. Humic substances are often regarded as naturally stable; however, chlorination may alter humic substances to form more biologically utilizable versions in drinking water systems [39]. In Korea, the prechlorination step in water treatment plants has been widely applied to reduce ammonia, manganese, algae, and bacterial activity. Therefore, the humic substances after the prechlorination step, as potential AOC precursors, had needed to be effectively removed by CS. In contrast, no changes in building blocks, low MW acids, and neutrals were found via CS. Small-sized organic matter cannot be easily removed by coagulation, flocculation, and sedimentation [31].

RSF and low-pressure membrane filtration have been suggested to remove particles, turbidity, and some microorganisms, and the UF membrane was reported to be less effective in the removal of NOM [21,40]. However, RSF and UF did not show significant differences with respect to NOM removal, according to ANOVA. Only the removal of building blocks and low MW acids was slightly better via RSF compared with that via UF. In this study, there was no difference in the removal of NOM between the RSF and the UF systems.

Ozonation has been known to generate small-sized products such as organic acids, ketones, and aldehydes, which are utilizable by bacteria [34]. However, no significant change in the MW distribution of NOM was observed, and changes in NOM characteristics via ozone could be due to factors including ozone contact time, ozone dosage, and NOM characteristics. Negligible changes in NOM MW via intermediate-ozonation were consistent with our previous findings [20]. Meanwhile, 28%–32% of selected EEM components were effectively decreased via ozonation. Notably, NOM was not transformed into a smaller size but changed into an aliphatic or hydrophilic structure.

NOM adsorption by the GAC filter was responsible for the removal of biopolymers (33%), building blocks (25%), and low MW acids (30%). However, it was not effective for low MW neutrals. All EEM components (i.e., T1, T2, A, and C) were effectively reduced by 44%–46% after GAC filtration. The reduced fluorescent NOM molecules possibly contained biopolymers (e.g., protein-like substances), building blocks, and low MW acids. As shown in Fig. 3, biopolymers were dramatically increased through the water distribution network, and no difference was found in EEM components (Fig. 4), which was probably due to the aliphatic structure of polysaccharides.

In summary, LC-OCD results showed that high MW NOMs, that is, humic substances and biopolymers, were significantly decreased via CS. However, it was less effective in the removal of NOM at the following treatment train, except for GAC filtration (e.g., building blocks and low MW acids). EEM results demonstrated that fluorescent moieties of NOM were gradually decreased by the water treatment train (namely, CS, Ozo, and GAC), and NOM characteristics were altered to form hydrophilic or aliphatic structures. Notably, aliphatic NOMs are commonly known to be relatively biode-gradable compared with aromatic or double-bonded NOM structures. Therefore, the removal of hydrophilic organic portions in drinking water should be further improved to supply biologically safe water to customers.

#### 3.2. Changes in the AOC concentration in water treatment plants

Controlling AOC levels in SW is also a challenging task because AOC dramatically changes because of water type, temperature, rainfall, algal bloom, and other environmental conditions [8,33,35,38]. In Seoul, brown algae (diatom) bloom during winter (January–March) is the primary precursor for AOC formation in perchlorinated water [38], but note that we conducted the present study during summer (June–September).

AOC levels in the SW ranged from 148 to 270 (217  $\pm$  54)  $\mu$ g L<sup>-1</sup> and were higher than that observed Choi et al. [38]



Fig. 4. Changes in the fluorescence intensities of tryptophan-, fulvic-, and humic-like EEM components (T1, T2, A, and C) (a) and normalized intensities by source water (b).

(24–272  $\mu$ g L<sup>-1</sup>), likely due to the differences of bioassay inoculum (P17+NOX vs. indigenous bacteria) and sampling date. Interestingly, the AOC was dramatically decreased by 39% (from 217 to 133  $\mu$ g L<sup>-1</sup>) via the CS process. Note that CS removed relatively high MW NOM sub-fractions (i.e., biopolymers and humic substances). Therefore, the removal of high or intermediate MW organic matter influenced the removal of AOC, which is known to mainly consist of low MW or small organic molecules. This explains that the SW contained various MW ranges of AOC. This result was consistent with the findings from recent studies [12,19-20] that have highlighted the importance of removal of macromolecular NOM. These findings are related to the improvement of the AOC bioassay using Flavobacterium and a mixture of indigenous bacteria from drinking water systems. New methods have revealed that these inoculums could utilize proteins, polysaccharides, and other high MW organics.

Although NOM characteristics were not significantly different between the effluents from RSF and UF, the AOC in the RSF effluent ( $86 \pm 50 \ \mu g \ L^{-1}$ ) was slightly lower than that in the UF effluent ( $106 \pm 48 \ \mu g \ L^{-1}$ ). 'CS + RSF' or 'CS + UF' processes were effective in the attenuation of AOC in the SW (see post-hoc test in Fig. 5b). Previous studies suggest that RSF can be biologically active; thus, 9%–87% of AOC was removed via biofiltration in full-scale water treatment plants [15,37,38] possibly due to the preoxidation step (e.g., prechlorination or preozonation). Therefore, biological stability can also be improved by RSF; however, it is not effective during the winter season [37,38].

Considering the treatment volume of RSF and UF, the AOC concentration in the feed water for ozonation was assumed to be  $88 \ \mu g \ L^{-1}$ , and we confirmed a 1.2-fold increase of AOC by ozonation (107 ± 50  $\ \mu g \ L^{-1}$ ). Ozonation has been reported to generate AOC in comparison with conventional treatment (3–180% increase), but the AOC levels highly fluctuated because of seasons and operational conditions [13,15,37,38]. AOC decreased by 14% via GAC filtration, but it was not significantly less compared to that in previous studies (58%–86% removal) [13,15,20]. During the courses of sampling, water utility periodically backwashed the GAC

filters using chlorinated water. Hence, the use of chlorine may influence the performance of GAC filters by decreasing the microbial activity of biomass associated with GAC.

The disinfection process increased AOC content from  $92 \pm 43$  to  $121 \pm 16 \ \mu g \ L^{-1}$  because of the reaction between residual chlorine and residual NOM. In addition, AOC in the tap water increased from  $121 \pm 16$  to  $150 \pm 23 \ \mu g \ L^{-1}$  during distribution. Based on NOM characteristics, this change was probably related to the increase of biopolymers and low MW neutrals through the network system (Fig. 3). The interaction between residual chlorine, NOM in bulk water, and biofilm on the pipe surface may induce an increase in AOC.

The comparison between AOC and NOM demonstrates that AOC removal via conventional treatment was possible by removing high MW NOM sub-fractions. Although the multi-barrier water treatment processes were not designed to supply biostable drinking water, previous studies have shown the importance of monitoring biological stability parameters along with NOM composition, seasonal impact, and operational conditions of medium filters [20,36,37,41]. In our study, AOC in treated water always remained above 100  $\mu$ g L<sup>-1</sup> (i.e., guidance level in chlorinated drinking water system) maybe because of the low MW, hydrophilic, or aliphatic residual NOM. Hence, further optimization of the biofiltration and other post-treatment are required to supply biologically stable drinking water [19].

#### 3.3. Treatment plant to tap; DWTP A, B, and C

We investigated the change in NOM and AOC from the three different DWTPs. The three DWTPs use the same river for SW. Changes in DOC in the finished water through the distribution networks were observed in all tap water samples. DOC concentrations in the treated water from the treatment plant and tap water were in the range of 1.05–1.52 and 1.09–1.72 mg L<sup>-1</sup>, respectively. DOC in tap water was increased by 4%–53%, but the DOC composition was not similar in the pretreated water samples (Table 3) maybe because of the differences in the performance of the three water treatment plants. All tap water samples contained 25%–130% higher



Fig. 5. From treatment plant to tap; AOC (a) and heatmap based on the significant differences between the water samples using posthoc test (b).

DWTP	A ( <i>n</i> = 2)		B ( <i>n</i> = 1)		C ( <i>n</i> = 1)	
	Treated	Тар	Treated	Тар	Treated	Тар
DOC (mg L <sup>-1</sup> )	1.52	1.72	0.73	1.12	1.05	1.09
Biopolymers	0.02	0.06	0.02	0.03	0.01	0.01
Humic substances	0.41	0.43	0.10	0.27	0.30	0.27
Building blocks	0.26	0.29	0.07	0.20	0.23	0.20
Low MW acids	0.13	0.15	0.07	0.11	0.11	0.11
Low MW neutrals	0.70	0.59	0.47	0.51	0.40	0.50
AOC (mg L <sup>-1</sup> )	0.12	0.15	0.10	0.23	0.15	0.22
Distance (km)	_	4	_	6	_	10

Tuble 5	
Changes in DOC and AOC levels from	n the treatment plant to the tap

AOC than samples collected from selected DWTPs. In DWTP 'A' and 'B', the increase in various NOM sub-fractions was responsible for the higher AOC detected (Table 3). In contrast, only low MW neutrals likely affected the AOC content in the DWTP 'C' system.

The interaction between residual chlorine, NOM in bulk water, biofilms, sediments, pipe materials, pipe age, and other factors may underlie the changes in biological stability [11,22]. However, their interactions are likely site-specific and cause differences in tap water quality (Table 3). Therefore, understanding the monitoring sites and distribution systems is essential to manage the biological stability of tap water.

For tap water management, we should pay more attention to secure the water quality at the household or building plumbing levels [24-26,29]. Although AOC, pH, temperature, and inorganic nutrients play as an important role in determining the biological instability of tap water [11,13,17,41], AOC assay is a culture-dependent and time-consuming method. Thus, it is important to develop tools that can determine biostability more quickly for water utilities. Despite the challenges in real-time analysis, the measurement of biological stability parameters along with NOM characterization tools will be informative and should be further investigated at the point of consumption.

# 4. Conclusions

Table 3

The main findings of this study are as follows:

- Relatively high MW NOM (>1 kDa) and AOC levels were effectively decreased by CS; thus, conventional treatment units are important for biostable drinking water supply.
- RSF and UF processes showed no significant differences in terms of the removal of NOM and AOC (p > 0.05); however, RSF showed slightly better removal of AOC.
- AOC was significantly increased at the consumer tap (150-230 µg L-1) possibly because of the interaction between factors such as aged pipes, biofilms, residual chlorine, and NOM.
- For enhancing the biological stability of tap water, tap water should be further analyzed considering the point of consumption.

### Acknowledgment

This research was supported by the Korea Ministry of Environment "Global Top Project (2016002110002)". Additional support was provided by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2019R1A2C1087828).

# References

- [1] A.M. Gall, B.J. Marinas, Y. Lu, J.L. Shisler, Waterborne viruses: a
- barrier to safe drinking water, PLoS Pathog., 11 (2015) e1004867. C.L. Abberton, L. Bereschenko, P.W. van der Wielen, C.J. Smith, Survival, biofilm formation, and growth potential [2] of environmental and enteric Escherichia coli strains in drinking water microcosms, Appl. Environ. Microbiol., 82 (2016) 5320-5331.
- H.Y. Chen, Y.Y. Zhang, L.L. Ma, F.M. Liu, W.W. Zheng, Q.F. Shen, H.M. Zhang, X. Wei, D.J. Tian, G.S. He, W.D. Qu, [3] Change of water consumption and its potential influential factors in Shanghai: a cross-sectional study, BMC Public Health, 12 (2012) 450, doi: 10.1186/1471-2458-12-450.
- L. Wang, L. Zhang, J. Lv, Y. Zhang, B. Ye, Public awareness [4] of drinking water safety and contamination accidents: a case study in Hainan Province, China, Water, 10 (2018) 446.
- [5] United States Centers for Disease Control and Prevention (CDC), Traveler's Health, 2019, Available at: https://wwwnc.
- (cdc.gov/travel/destinations/list (Accessed in September 2019). Korea-Herald, Drink Tap Water? 'No Way,' Say Koreans, 2015. Available at: http://www.koreaherald.com/view.php? [6] ud=20150526000906 (Accessed in September 2019)
- [7] Korean Statistical Information Service, Drinking Water Treatment Facility Status, 2017. Available at: http://kosis.kr/statHtml/ statHtml.do?orgId=106&tblId=DT\_106N\_06\_0100055&vw\_cd= MT\_ZTITLE&list\_id=106\_005&seqNo=&lang\_mode=ko& language=kor&obj\_var\_id=&itm\_id=&conn\_path=MT\_ZTITLE (Accessed in September 2019).
- C.J. Volk, M.W. LeChevallier, Assessing biodegradable organic [8] matter, J. AWWA, 92 (2000) 64-76.
- C.C. Chien, C.M. Kao, C.D. Dong, T.Y. Chen, J.Y. Chen, [9] Effectiveness of AOC removal by advanced water treatment systems: a case study, Desalination, 202 (2007) 318–325.
- [10] J.H.M. van Lieverloo, W. Hoogenboezem, G. Veenendaal, D. van der Kooij, Variability of invertebrate abundance in drinking water distribution systems in the Netherlands in relation to biostability and sediment volumes, Water Res., 46 (2012) 4918-4932.
- [11] E.I. Prest, F. Hammes, M.C.M. van Loosdrecht, J.S. Vrouwenvelder, Biological stability of drinking water: controlling factors, methods, and challenges, Front. Microbiol., 7 (2016), doi: 10.3389/fmicb.2016.00045.
- [12] W.A.M. Hijnen, R. Schurer, J.A. Bahlman, H.A.M. Ketelaars, R. Italiaander, A. van der Wal, P. van der Wielen, Slowly

biodegradable organic compounds impact the biostability of non-chlorinated drinking water produced from surface water, Water Res., 129 (2018) 240–251.

- [13] M.J. Lehtola, I.T. Miettinen, T. Vartiainen, P.J. Martikainen, Changes in content of microbially available phosphorus, assimilable organic carbon and microbial growth potential during drinking water treatment processes, Water Res., 36 (2002) 3681–3690.
- [14] I.C. Escobar, A.A. Randall, Assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC): complementary measurements, Water Res., 35 (2001) 4444–4454.
- [15] M. Vital, D. Stucki, T. Egli, F. Hammes, Evaluating the growth potential of pathogenic bacteria in water, Appl. Environ. Microbiol., 76 (2010) 6477–6484.
- [16] P.W.M.H. Smeets, G.J. Medema, J.C. van Dijk, The Dutch secret: how to provide safe drinking water without chlorine in the Netherlands, Drink. Water Eng. Sci., 2 (2009) 1–14.
- [17] M. Polanska, K. Huysman, C. van Keer, Investigation of assimilable organic carbon (AOC) in flemish drinking water, Water Res., 39 (2005) 2259–2266.
- [18] D. van der Kooij, G.L. Bakker, R. Italiaander, H.R. Veenendaal, B.A. Wullings, Biofilm composition and threshold concentration for growth of *Legionella pneumophila* on surfaces exposed to flowing warm tap water without disinfectant, Appl. Environ. Microbiol., 83 (2017), doi: 10.1128/AEM.02737-16.
- [19] R. Schurer, J.C. Schippers, M.D. Kennedy, E.R. Cornelissen, S.G. Salinas-Rodriguez, W.A.M. Hijnen, A. van der Wal, Enhancing biological stability of disinfectant-free drinking water by reducing high molecular weight organic compounds with ultrafiltration posttreatment, Water Res., 164 (2019) 114927.
- [20] J.W. Park, H.C. Kim, A.S. Meyer, S. Kim, S.K. Maeng, Influences of NOM composition and bacteriological characteristics on biological stability in a full-scale drinking water treatment plant, Chemosphere, 160 (2016) 189–198.
- [21] J.W. Park, Y.J. Lee, A.S. Meyer, I. Douterelo, S.K. Maeng, Bacterial growth through microfiltration membranes and NOM characteristics in an MF-RO integrated membrane system: lab-scale and full-scale studies, Water Res., 144 (2018) 36–45.
- [22] G. Liu, Y. Zhang, W.J. Knibbe, C.J. Feng, W.S. Liu, G. Medema, W. van der Meer, Potential impacts of changing supply-water quality on drinking water distribution: a review, Water Res., 116 (2017) 135–148.
- [23] I. Douterelo, R.L. Sharpe, J.B. Boxall, Influence of hydraulic regimes on bacterial community structure and composition in an experimental drinking water distribution system, Water Res., 47 (2013) 503–516.
- [24] K. Lautenschlager, N. Boon, Y. Wang, T. Egli, F. Hammes, Overnight stagnation of drinking water in household taps induces microbial growth and changes in community composition, Water Res., 44 (2010) 4868–4877.
- [25] L. Zlatanovic, A. Knezev, J.P. van der Hoek, J.H.G. Vreeburg, Influence of an extended domestic drinking water system on the drinking water quality, Water, 10 (2018), doi: 10.3390/ w10050582.
- [26] G. Wen, S. Kotzsch, M. Vital, T. Egli, J. Ma, BioMig-a method to evaluate the potential release of compounds from and the formation of biofilms on polymeric materials in contact with drinking water, Environ. Sci. Technol., 49 (2015) 11659–11669.

- [27] W. Liu, H. Wu, Z. Wang, S.L. Ong, J.Y. Hu, W.J. Ng, Investigation of assimilable organic carbon (AOC) and bacterial regrowth in drinking water distribution system, Water Res., 36 (2002) 891–898.
- [28] W.Y. Li, J.P. Zhang, F. Wang, L. Qian, Y.Y. Zhou, W.Q. Qi, J.P. Chen, Effect of disinfectant residual on the interaction between bacterial growth and assimilable organic carbon in a drinking water distribution system, Chemosphere, 202 (2018) 586–597.
- [29] J.W. Park, K.Y. Park, Y. Na, S. Park, S. Kim, J.H. Kweon, S.K. Maeng, Evaluation of organic migration and biomass formation on polymeric components in a point-of-use water dispenser, Water Res., 165 (2019) 115025.
- [30] E.L. Sack, P.W. van der Wielen, D. van der Kooij, Polysaccharides and proteins added to flowing drinking water at microgramper-liter levels promote the formation of biofilms predominated by bacteroidetes and proteobacteria, Appl. Environ. Microbiol., 80 (2014) 2360–2371.
- [31] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND), Water Res., 45 (2011) 879–885.
- [32] F.A. Hammes, T. Egli, New method for assimilable organic carbon determination using flow-cytometric enumeration and a natural microbial consortium as inoculum, Environ. Sci. Technol., 39 (2005) 3289–3294.
- [33] I.T. Miettinen, T. Vartiainen, P.J. Martikainen, Determination of assimilable organic carbon in humus-rich drinking waters, Water Res., 33 (1999) 2277–2282.
- [34] C.J. Volk, M.W. Lechevallier, Effects of conventional treatment on AOC and BDOC levels, J. AWWA, 94 (2002) 112–123.
- [35] F. Hammes, S. Meylan, E. Salhi, O. Koster, T. Egli, U. von Gunten, Formation of assimilable organic carbon (AOC) and specific natural organic matter (NOM) fractions during ozonation of phytoplankton, Water Res., 41 (2007) 1447–1454.
  [36] B.M. Yang, J.K. Liu, C.C. Chien, R.Y. Surampalli, C.M. Kao,
- [36] B.M. Yang, J.K. Liu, C.C. Chien, R.Y. Surampalli, C.M. Kao, Variations in AOC and microbial diversity in an advanced water treatment plant, J. Hydrol., 409 (2011) 225–235.
- [37] Y. Ohkouchi, B.T. Ly, S. Ishikawa, Y. Aoki, S. Echigo, S. Itoh, A survey on levels and seasonal changes of assimilable organic carbon (AOC) and its precursors in drinking water, Environ. Technol., 32 (2011) 1605–1613.
- [38] Y. Choi, H. Park, M. Lee, G.-S. Lee, Y.-j. Choi, Seasonal variation of assimilable organic carbon and its impact to the biostability of drinking water, Environ. Eng. Res., 24 (2019) 501–512.
- [39] A.K. Camper, Involvement of humic substances in regrowth, Int. J. Food Microbiol., 92 (2004) 355–364.
- [40] K.Y. Choi, B.A. Dempsey, In-line coagulation with low-pressure membrane filtration, Water Res., 38 (2004) 4271–4281.
- [41] A. Nescerecka, T. Juhna, F. Hammes, Identifying the underlying causes of biological instability in a full-scale drinking water supply system, Water Res., 135 (2018) 11–21.