Desalination and Water Treatment

51 (2013) 6288–6298 September



www.deswater.com

doi: 10.1080/19443994.2013.780812

### Analysis on the Natural Organic Matter and Disinfection By-Products in Full-scale Advanced Water Treatment Plant and Conventional Water Treatment Plant

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Received 13 November 2012; Accepted 13 January 2013

#### ABSTRACT

This study aimed to compare the removal efficiencies of natural organic matter (NOM) and disinfection by-products (DBPs) in Koyang Advanced Water Treatment Plant or KAWTP, Ilsan Conventional Water Treatment Plant or ICWTP, and a mixed-water point in the distribution system. Aside from doing conventional water treatment, KAWTP also carries out postozonation and granular activated carbon adsorption followed by chlorination. NOM removal efficiencies of advanced treated water, conventional finished water, and blended water were 74, 22, and 31%, respectively. Biodegradable dissolved organic carbon (BDOC) removal efficiencies of advanced treated water, conventional finished water, and blended water were 78, 66, and 52%, respectively. The removal efficiencies of DBPs in comparison with conventional finished water were also analyzed. Trihalomethans, chloral hydrate, and haloacetic acids in the advanced treated water had removal efficiencies of 88, 97, and 98%, respectively. It was concluded that DBPs are efficiently controlled by advanced water treatment process. Blending can be applied to other distribution systems to which water is supplied from both conventional treatment plants and advanced treatment plants

Keywords: Ozone; NOM; BDOC; DBPs; Blending

#### 1. Introduction

For the sake of meeting consumer desires for good quality tap water and thereby remove consumer

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complaints about tap water, an advanced water treatment process has been introduced in South Korea since 1994. The existing conventional treatment had failed to remove persistent microorganic pollutants (e.g., endocrine disruptors, pharmaceuticals, and

Presented at The Fifth Desalination Workshop (IDW 2012), October 28-31, 2012, Jeju, Korea

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personal care products), as well as some recalcitrant the taste and odor of tap water (2-MIB, Geosmin). In particular, the Koyang regional water purification center under the Han River, which supplies water to more than 25,000,000 out of the total 50,000,000 Korean population, has introduced advanced water treatment facilities that consist of ozonation and granular activated carbon (GAC) in order to address recurring problems in the taste and odor of the tap water coming from its source, Lake Paldang. Koyang advanced water treatment plant (KAWTP), which introduced an advanced water treatment process for the first time in the Han river, is the subject of this study. Since it opened in July 2009 until at present, its daily capacity of water supply amounts to  $120,000 \text{ m}^3/\text{day}$ , using the following processes: prechlorination-mixer-flocculation/sedimentation basinrapid filtration-ozonation-GAC-post chlorination. Ilsan conventional water treatment plant (ICWTP), which was chosen for comparison in this study, is located not more than 1km away from Koyang Advanced Water Treatment Plant (KAWTP). Since 1995, ICWTP supplies 120,000 m<sup>3</sup>/day of water daily to the same region using the following conventional water treatment processes: prechlorination-mixer-flocculation/ sedimentation basin-rapid filtration-postchlorination. It is noteworthy that advanced treated water was supposed to be supplied only to certain distribution area, which resulted in different drinking water quality in a same city. Accordingly, to address such issues, water from KAWTP and from ICWTP were mixed in the ratio of 1-5 and supplied to distributing water reservoirs where previously only ICWTP supplied treated water to minimize the difference in tap water quality. Lake Paldang is the water source of both water treatment plants. Through a 45-km-long pipeline, it first supplies water to ICWTP and then to KAWTP through a less than 2-km pipeline from the 45-kmlong pipeline as shown in Fig. 1.

Natural organic matter (NOM) leads to the production of hazardous materials by reacting with chlorine during the purification process [1]. As far as the removal of biodegradable dissolved organic carbon (BDOC) among NOM by ozone and GAC advanced water treatment is concerned, rapid filtration using a sand filter effectively removes dissolved organic carbon (DOC) but has little effect on removing BDOC. Moreover, it appeared that there was an increase in BDOC from the ozone process and a decrease in both DOC and BDOC from the GAC process [2]. However, little research has been performed based on the blending effect of advanced treated water and conventional treated water in the distribution system. Another research suggests that removing BDOC can reduce the formation potential of chlorination disinfection by-products (DBPs) [3]. High hydrophilic fraction in DOC enhances the production of trihalomethans (THMs) formation potential (THMFP) and haloacetic acids formation potential (HAAFP), which contribute to the production of DBPs in the chlorination [4]. THMs and HAAs among DBPs were proved to be effectively removed using both the ozone and biological activated carbon processes [5].



(a) Satellite photo of water treatment plant

(b) Water supply region by water treatment plant

Fig. 1. Location of water treatment plant and water supply region.

This study investigated and evaluated the removal efficiency of NOM and DBPs using an advanced water treatment process that consist of the ozone and GAC processes. This study compared the advanced water treatment process with conventional water treatment that uses the same source water. Furthermore, the study examined the effect of blending water of the advanced water treatment and conventional water treatment in terms of removing NOM and DBPs in water distribution system.

#### 2. Materials and methods

#### 2.1. LC-OCD analysis

To analyze NOM, the liquid chromatographyorganic carbon detection (LC-OCD) system was used. This system manufactured by DOC-LABOR DR HUBER in Germany and model serial number is 13. The system consists of an autoinjector, size exclusion chromatography-based column, and thin film reactor (TFR) that oxidizes components divided from the column into CO<sub>2</sub> and UV254 detector, non-dispersive infrared (NDIR) detector. To draw the calibration curve for the organic carbon concentration of LC-OCD, potassium hydrogen phthalate, which was manufactured by Fluka, was dissolved in distilled water for the measurement. To manufacture the acid solution for the removal of inorganic carbon, potassium peroxo disulfate was dissolved in distilled water, after which phosphoric acid (H<sub>3</sub>PO<sub>4</sub> 85%) was added to it. A phosphate buffer was used as the mobile phase solvent after  $KH_2PO_4$  and  $Na_2HPO_4 \times 2H_2O$  were dissolved in deionized-distilled water. To draw the UVD254 calibration curve of LC-OCD, suwanee river humic acid std II (2S101H) and suwanee river fulvic acid std I (1S101F), which were manufactured by IHSS were dissolved with deionized distilled water for the measurement. In the meantime, the principle divided according to its molecular weight should be applied to high performance size exclusion chromatography, since a high-molecular-weight substance cannot deeply penetrate the pore of the column fillers and passes through it fast, and a low-molecular-weight substance takes much time to penetrate the pore and pass out. A 0.028 mol/L phosphate buffer was used as the mobile phase solvent. The compounds that were separated through the column were first measured with a UV254 detector, then combined with phosphate, and finally, transferred to TFR. Phosphate was used to remove the inorganic carbon. Among the samples that were transferred to the TFR, the inorganic carbon was removed through the top of the reactor by stripping the high-purity nitrogen gas that was injected into the reactor. In the case of the organic carbon, it is transferred to the lower part by nitrogen gas, oxidized into CO<sub>2</sub> with a UV lamp that had a wavelength of 185 nm, and detected with an NDIR detector in real time. The detected signal was converted into organic substance concentrations through a quantitative analysis program and had a detection limit of  $5-50 \,\mu\text{g/L}$  by molecular size. The NOM chromatogram measured by LC-OCD represents characteristics of samples. The first peak, which is separated about 20 to 40 min after the injection, involves a series of biopolymer peak with organic colloid and protein, consisting of more than 20,000 g/mol of molecular weight. The second and third peaks represent humic materials and building blocks (polycarboxylic acid), which show a range of molecular weight from  $\sim 1,000 \text{ g/mol}$  to 350-500 g/mol, respectively. The fourth peak has organic acid of low molecular weight as its main component. The fifth also has low molecular weight of neutrals and amphiphilic species (amino acid, alcohol, aldehyde, ketone, and others) with less than 350 g/mol as the main components.

LC-OCD measures the mass of carbon (OC) which is in organic combination. Apart from this, absorbance at 254 nm is measured. Analysis results are automatically classified into Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Particular Organic Carbon, Hydrophobic Organic Carbon and Hydrophilic DOC. Among these, Hydrophilic DOC (or chromatographic dissolved organic carbon) is analyzed with its subdivisions such as biopolymers, humic substance, building blocks, neutrals and acids. BDOC is generally interpreted as biodegradable DOC substance that is could be related with the regrowth of microorganisms in the pipeline [6,7]. Polysaccharides, low-molecular-weight organic acids and low-molecular-weight neutrals are reported to be included in this category. For the BDOC measurement, a 1 ml source waster was added to the sample for seeding of the microorganisms, and it was incubated at approximately 25°C in the dark for 13 days. Afterwards, it was filtered with a 0.45-µm membrane filter, and then, the variation of the measured NOM concentration and the initial NOM concentration were obtained.

#### 2.2. *DBPs*

Among disinfection by-products, as for THMFP, THMs, 5 mL of specimen was analyzed using gas chromatography-flame ionization detector (Varian CP-3800) following the purge and trap (Teledyne Tekmar) pretreatment process. As for HAAFP, HAAs, they were analyzed using gas chromatography-electron capture detector (GC-ECD) (Varian CP-3800) following

derivatization after a liquid-liquid extraction of 4 mL MTBE (Tert-butylmethylether) in acidic pH from a 40 mL specimen. On the other hand, CHFP and chloral hydrate (CH) were analyzed using GC-ECD (Varian CP-3800) through a liquid-liquid extraction of 3 mL MTBE (Tert-butylmethylether) after melting by adding 10g of NaCl into 40 mL specimen. DBPFP including THMs, CH, and HAAs formation potential was measured after a 3-day incubation period. The samples were individually chlorinated with 0.1% sodium hypochlorite (NaOCl) and incubated at 20°C. The input concentration of sodium hypochlorite (NaO-Cl) in the sample was 10%. After 3 days incubation, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to the vial to quench the residual chlorine. TOC was analyzed using Sievers 5310 C Laboratory TOC Analyzer. GC analysis conditions used in this research are shown in Table 1.

#### 2.3. Sampling points and analysis chemicals

To evaluate the efficiency of the advanced water treatment process, source water, filtered water, ozone treated water, GAC treated water, finished water, distribution station and tap water (Tap A) coming from KAWTP were analyzed. To compare advanced water treatment efficiency with conventional water treatment efficiency, finished ICWTP water was also analyzed. In order to evaluate efficiency when advanced treatment water and conventional treatment water were blended in the distribution systems, tap water (Tap B) was analyzed. Taps A and B were selected due to the high possibility of changes in the quality of their water, since they were located in the longest part of the distribution networks (the length of the pipeline from the water treatment plant to the water pipe, in the case of Tap A, about 19.4 km, and Tap B, about 10 km). In this research, each sample was analyzed once to twice monthly to measure NOM, BDOC, TOC,

GC analysis con	ditions		
Item	THMFP/THMs	HAAFP/HAAs	CHFP/CH
Detector	FID	ECD	ECD
Carrier gas	N <sub>2</sub>	N <sub>2</sub>	$N_2$
Column	CP-select 624 CB	Rtx-1701	Rtx-5
Detector temp.	250°C	250°C	280°C
Injector temp.	250°C	220°C	250°C
Injector mode	Split 7:1	Split 10:1	Split 20:1
Oven temp.	30℃, hold 7 min	$50^{\circ}$ C, hold 3 min	35℃, hold 7 min
	To 200℃ 8℃/min, hold 1 min	To 230℃ 15℃/min, hold 16 min	To 47°C 1.5°C/min, hold 15 min To 100°C 6.1°C/min, hold 2 min To 180°C 12°C/min, hold 3 min

Table 1 GC analysis conditions UV254, THMs, THMFP, HAAs, HAAFP, CH, and CHFP. The analytical research was carried out from August 2009 to July 2010, and the research period was divided into the blending period and the nonblending period by stopping the blending from 27 October 2009 to 31 April 2010 for the analysis of the results.

#### 3. Results and discussion

#### 3.1. NOM

OC analysis data were presented in Table 2. Also, as shown in Fig. 2, analysis data show reveal that NOM showed 28% average removal efficiency compared with the source water after rapid filtration in KAWTP and 22% in finished water of ICWTP. On the other hand, removal efficiency compared with the source water of GAC treated water for NOM accounted for 74% in KAWTP. Thus, a large amount of NOM is removed through the GAC process. After GAC adsorption, there was a gradual increase of NOM through postchlorination, and KAWTP finished water showed 64% average removal efficiency compared with the source water. An average NOM concentration around Tap A amounted to 521 µg/L for the advanced water treatment, and Tap A showed 66% average removal efficiency compared with the source water. As for Tap B, the average removal efficiency compared with the source water was 29% in the case with blending, and 22% in the case without blending, which leads to the conclusion that the increase in the removal efficiency compared with the source water of Tap B was due to the dilution effect of the blending.

As shown in Fig. 3, BDOC showed a partial increase after the ozonation. It is attributed to the decomposition of the macromolecule organics into the low molecular organics by the ozone, and which led to an increase in the organic bioavailability. This was

Item		KAWTP								Blended water	
		Raw water	Filtered	Ozonated	GAC	Finished water	Distribution sta. A	Tap A	Finished water	Distribution sta. B	Tap B
NOM	Average (µg/L)	1,548	1,109	1,023	395	561	580	521	1,202	1,119	1,092
	Removal efficiency (%)		28	47	74	64		66	22		29
BDOC	Average (μg/L)	221	79	121	49	79	13	43	74	30	80
	Removal efficiency (%)		64	45	78	64		80	66		64
TOC	Average (µg/L)	1955	1,322	1,169	573	612	784	652	1,355	1,343	1,247
	Removal efficiency (%)		32	40	71	69		67	31		36

Table 2Analysis result of the mass of organic carbon

Note: All removal efficiency compared with the source water.

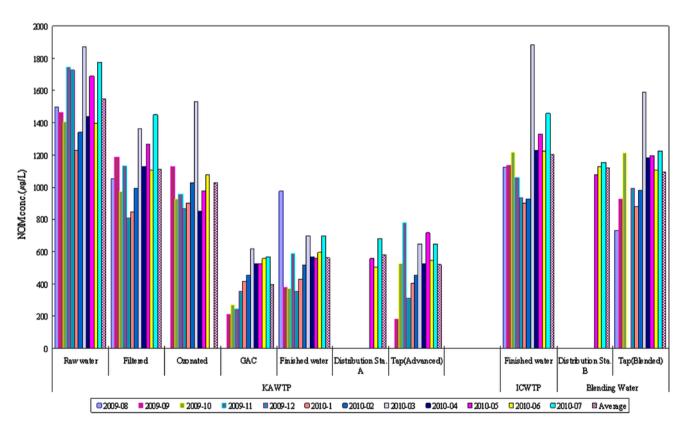


Fig. 2. Characteristics comparison of NOM variation in water using advanced treatment and conventional treatment.

in agreement with the results from previous studies [8,9]. Through the GAC process, the removal efficiency compared with the source water was 78%, which is similar to that for NOM. This suggests similar removal efficiency of NOM and BDOC using the

advanced water treatment process. With the finished water, the average concentration KAWTP was  $79 \,\mu g/L$  and ICWTP  $74 \,\mu g/L$ . Concentration was an almost same from each other. It passed through the distribution system, Tap A amounted to  $43 \,\mu g/L$  showing a

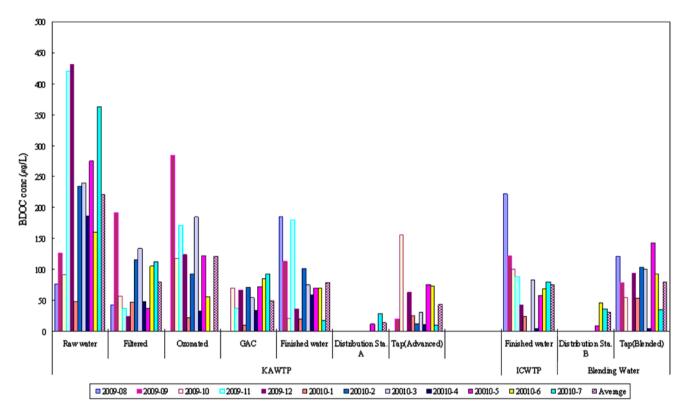


Fig. 3. Characteristics comparison of BDOC variation in water using advanced treatment and conventional treatment.

decrease in the distribution system. In the case of Tap B, the average concentration of finished water from ICWTP was  $109 \,\mu\text{g/L}$  during the blending period, and the average concentration at Tap B was  $87 \mu g/L$ , which indicates that the concentration decreased through the distribution system and the blending, as it did at Tap A. Moreover, during the non-blending period, the average concentration of finished water of ICWTP was  $31 \,\mu g/L$ , and the average concentration at Tap B was  $71 \,\mu g/L$ , which indicates that the concentration increased through the distribution system. In other words, the BDOC of the advanced treated water and of the water that was mixed with the advanced treated water was consumed or diluted through the distribution system, and that of the conventional treated water increased through the distribution system. Thus, it was confirmed that as known in several literature that were referred to, the BDOC of the advanced treated water was consumed through the distribution system, since ozonation increases the biodegradability of organic [6,7].

TOC had an average concentration of  $1,955 \,\mu g/L$  ( $1,500-2,840 \,\mu g/L$ ) in the source water. As shown in Fig. 4, the TOC removal efficiencies from the KAWTP filtered water and the ICWTP finished water were 32 and 31%, respectively, which indicate that the TOC removal efficiency of the conventional water treatment

process was about 30%, which is the same as the average removal efficiency of the conventional water treatment process through mixer-flocculation/sedimentation basin-rapid filtration, as reported in the existing literature [10]. In the advanced treatment process, an average removal efficiency of 40% after the ozonation and an average removal efficiency of 71% after the GAC process were found compared with the source water. It was found that there was an additional 38% of TOC removal compared with the source water through the ozone and GAC process. While the water passed through the distribution system, at Tap A, it changed little compared with the finished water; and at Tap B, the average TOC concentration was  $1,294 \,\mu g/L$ , lower than the average TOC concentration of the finished water of  $1,514 \mu g/L$ , due to the blending effect during the blending period, whereas there was little change during the nonblending period compared with the finished water, as at Tap A.

#### 3.2. DBPs

#### 3.2.1. THMs

The DBPs analysis data are presented in Table 3. It was observed that in the initial period of the operation, THMs was mostly removed as it passed through the GAC process in the advanced water treatment. As

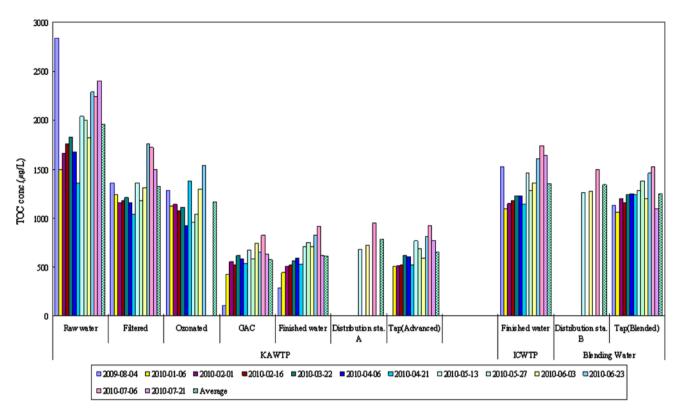


Fig. 4. Characteristics comparison of TOC variation in water using advanced treatment and conventional treatment.

#### Table 3 Analysis result of DBPs

		KAWTP							ICWTP	Blended water	
		Raw water	Filtered	Ozonated	GAC	Finished water	Distribution sta. A	Tap A	Finished water	Distribution sta. B	Тар В
THMs	Average (mg/L)	0.0911	0.0156	0.0126	0.0106	0.0113	0.0132	0.0154	0.021	0.0242	0.0246
	Removal efficiency (%)		83	86	88	88		83	77		73
СН	Average (mg/L)	0.0162	0.0028	0.0013	0.0005	0.0007	0.0009	0.0012	0.0036	0.0033	0.0042
	Removal efficiency (%)		83	92	97	96		92	78		74
HAAs	Average (mg/L)	0.1007	0.0094	0.0089	0.0021	0.0025	0.0031	0.0039	0.0129	0.0152	0.0161
	Removal efficiency (%)		91	91	98	98		96	87		84

Notes: All removal efficiency compared with the source water.

Result of raw water means a formation potential.

shown in Fig. 5, however, the removal efficiency decreased as the GAC bed volume increased and became similar to that for the conventional treated

water after a year, which indicates that the THMs adsorption removal mechanism has already reached a breakthrough point. In the KAWTP finished water, the

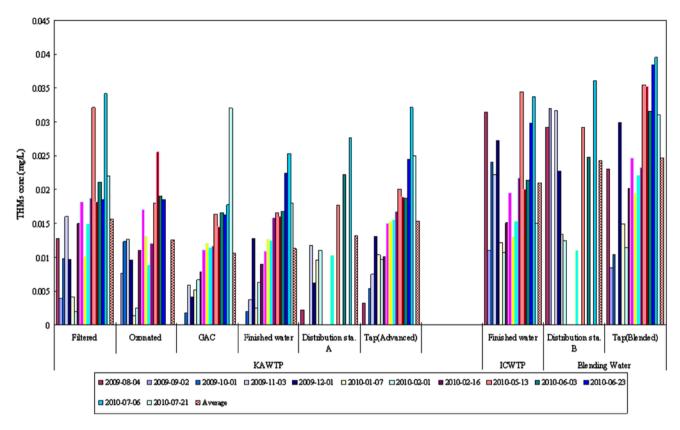


Fig. 5. Characteristics comparison of THMs variation in water using advanced treatment and conventional treatment.

average removal efficiency compared with the source water FP was 83%; and in the ICWTP finished water, the average removal efficiency compared with the source water FP was 77%, which shows that an additional 6% of THMs was removed in the advanced treatment process. This result reflects high removal efficiency in the initial period of the operation, however, so it is considered that additional THMs removal will not occur at the breakthrough point in the advanced treatment process as the operation progresses. In addition, while passing through the distribution system, the THMs concentration in the KAWTP, ICWTP and blended water all increased at almost the same rate, which indicates that there was little difference in the change in the THMs concentration depending on the distribution system of the advanced treatment and the conventional treatment.

#### 3.2.2. Chloral hydrates (CH)

CH was not detected in the GAC treated water during the research period, except in March and July as shown in Fig. 6. The removal efficiency compared with the source water FP for the KAWTP finished water was 96%, which is higher than that of the ICWTP finished water of 78%. The concentration in the KAWTP, ICWTP and blended water increased as the water passed through the distribution system, but by 4% in the advanced treated water and the blended water, and by 7% in the ICWTP, which indicates that the CH removal efficiency of the conventional treatment process was low. In addition, it turned out that the rate of increase in the CH in the water as it passed through the distribution system was high, since at Tap A, the average concentration at the end of the pipeline was 0.0012 mg/L, and at Tap B, 0.0042 mg/L, which shows that the increase rate in the conventional treated water at the end of the pipeline was 3.5 times higher than that in the advanced treated water at the end of the pipeline.

#### 3.2.3. Halo acetic acids (HAAs)

As shown in Fig. 7, HAAs was hardly removed during the ozonation process. However, it was almost removed by the GAC process with an average concentration of 0.0021 mg/L at KAWTP finished water, which is a very low level. As it went through the distribution system, it slightly increased with the average concentration of 0.0039 mg/L at Tap A. The average concentration of ICWTP finished water was 0.0129 mg/L, which was 5.2 times higher than that in the advanced water treatment. The average

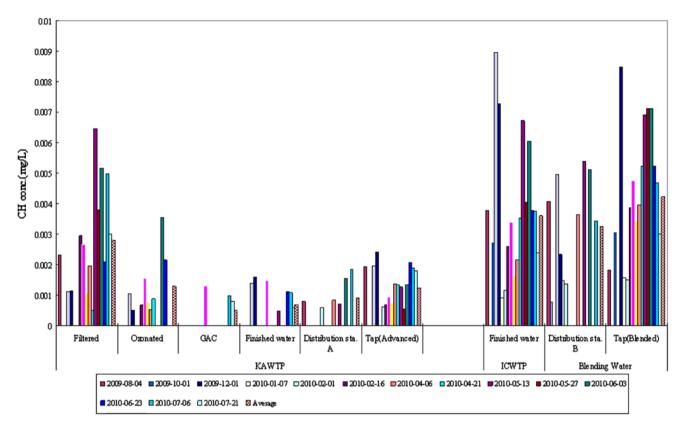


Fig. 6. Characteristics comparison of CH variation in water using advanced treatment and conventional treatment.

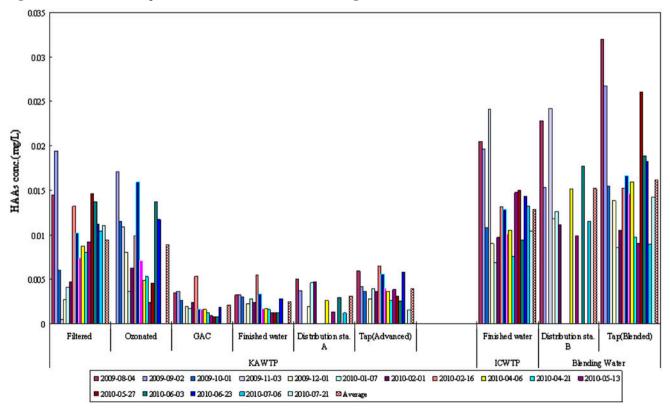


Fig. 7. Characteristics comparison of HAAs variation in water using advanced treatment and conventional treatment.

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Item		KAWTP (%)				ICWTP (%)		
		Ozone	GAC	Finish water	Tap A	Finish water	Тар В	
THMs	Removal efficiency II	86	88	88	83	77	Blended	72
							Non blended	74
	Removal efficiency II	19	16	-6	-36	-	Blended	-15
							Non blended	-23
CH	Removal efficiency I	92	97	96	92	78	Blended	73
							Non blended	75
	Removal efficiency II	54	60	-37	-75		Blended	-17
							Non blended	-45
HAAs	Removal efficiency I	91	98	98	96	87	Blended	83
							Non blended	86
	Removal efficiency II	6	76	-18	-60		Blended	-32
							Non blended	-32

Removal efficiency of disinfection by-products compared with formation potential of DBPs and previous treatment step

Notes: Removal efficiency I: Total average removal efficiency compared with the source water.

Removal efficiency II: Average removal efficiency compared with the previous treatment step.

concentration at Tap B also increased regardless of the blending. As for the removal efficiency compared with the source water FP, the rate of increase was 4% during the blending period and 3% during the nonblending period.

Table 4

## 3.2.4. Comparison of DBPs removal efficiency by unit process

Table 4 shows the removal efficiency of disinfection by products per unit process. As shown in Table 4, CH and HAAs were mostly removed in the advanced water treatment process. No breakthrough in the GAC process was observed during the one-year operation period, except with respect to the THMs. In particular, it turned out that removal by ozonation rarely occurred since the HAAs removal efficiency of the ozone process compared with the rapid filtration process was very low (6%). More than 76% of the HAAs were removed, however, compared with in the ozone process via the GAC process. Three disinfection by-products showed removal efficiency of more than 88% increase by the advanced water treatment process. Despite a partial increase in the finished water after the postchlorination process, it was found that more than 88% of the DBPs had been removed. This accounts for higher removal efficiency than the 77-87% removal efficiency of the conventional water treatment process. Moreover, as the water passed through the distribution system, all the DBPs items increased, and the rate of increase compared with the finished water at Tap A through the advanced

treatment was 36-75%, which is higher than the rate of increase of 15-32% in the conventional treated water after blending at Tap B and of 23-45% after nonblending. Unlike the removal efficiency, the final concentrations of the THMs, CH, and HAAs were 0.0154, 0.0012, and 0.0039 mg/L, respectively, at Tap A, which are lower than the final concentrations (0.0207, 0.0041, and 0.0131 mg/L) at Tap B without blending, and still lower than the final concentrations (0.0281, 0.0043, and 0.0188 mg/L) with blending. Accordingly, it turned out that the DBPs concentration in the final consumption stage was much lower in the advanced treated water than that in the conventional treated water even if the DBPs increase rate due to the increase in the water retention time within the pipeline was higher in the advanced treated water.

#### 4. Conclusion

This study compared the removal efficiency of NOM and DBPs in the advanced water treatment process to conventional water treatment process based on a full-scale plant operation. Moreover, it also compared the tap water quality of blended water with the tap water that went through the advanced water treatment. Conclusion was drawn as follows;

• The average removal efficiency of NOM in advanced water treatment was 74%, compared with that of source water, and the average removal efficiency of the conventional treatment process was 22%. While the water passed through the

distribution system, the average concentration compared with that in the finished water at Taps A and B, slightly decreased, but it is considered that the removal efficiency increased due to the dilution effect, since in the decrease rate of the concentration at Tap B during the blending period, the removal efficiency compared with the source water at Tap B increased to 31% from 19% compared with the source water of the ICWTP finished water.

- As reported in other studies, the BDOC partially increased in the ozonation process. Moreover, the BDOC appeared to have decreased, compared with in the finished water, while the water passed through the distribution system at Tap A and after the blending at Tap B. At Tap B during the nonperiod, the BDOC blending concentration increased, compared with that in the ICWTP finished water. That is, the conventional treated water was not consumed as it passed through the distribution system, which verifies that the BDOC content of the advanced treated water had higher chemical reactivity and bioavailability than that of the conventional treated water.
- TOC appeared to have about 30% removal efficiency using conventional water treatment. The additional TOC removal efficiency in the ozone and GAC processes was 38% compared with the source water. Except for the dilution effect of blending, specific concentration changes were not observed while the water passed through the distribution system.
- The removal efficiency of THMs, CH, and HAAs in advanced water treatment was 88, 97, and 98%, respectively. With conventional water treatment, the removal efficiency of THMs, CH, and HAAs were 77, 78, and 87%, respectively, compared with formation potential of disinfection by products.
- The DBPs during the distribution process increased regardless of blending. The DBPs concentration was lower at Tap A which was supplied with advanced treated water than at Tap B, but the rate of increase compared with the finished water was

higher at Tap A than at Tap B, which shows the characteristic of a much higher DBPs increase rate in the advanced treated water while it passed through the distribution system.

In the future, factors affecting removal efficiency of organic compounds such as temperature, turbidity and algae will be further studied as well as seasonal changes to establish the optimal treatment.

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