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Estimation of Dissolved Organics Characteristics and THM Formation from Different Organics Sources Based on Molecular Weight Distribution

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요 약

본 연구는 근원에 따른 용존 유기물의 특성을 평가하기 위해 하천수, 호소수, 하수 2차 처리 유출수의 자연수 및 Aldrich, Wako 사에서 공급된 휴믹산을 대상으로 분자량 분포에 따른 물리 화학적인 수질 특성, 생분해도, 소독부산물의 생성 등을 고찰하였다. SUVA를 이용해서 자연수의 생분해 가능성을 평가한 결과 호소수, 하수, 하천수 순으로 예측되었으며 이는 실제 생분해도 실험 결과와 유사하였다. 생분해 반응 중 저분자 영역대의 용존 유기물은 점차 감소하였고 반면에 고분자 영역대의 용존 유기물은 증가하였다. SMP는 전체 용존 유기물의 0.7-5.5% 정도 관찰되었으며 고분자 물질을 많이 함유한 시료에서 높게 나타났다. THM 생성은 대체로 고분자 물질이 높을수록 증가하였으며 THMFP도 Wako 휴믹산을 제외한 샘플에서 이와 유사한 경향을 나타냈다.

Keywords: THM (trihalomethane), SUVA (specific ultraviolet light absorbance), DOC (dissolved organic carbon), AMWD (apparent molecular weight distribution)

I. Introduction

The purpose of potable water treatment is to produce safe and sanitary tap water. The formation of by-products is directly related to organic characteristics and passing through treatment processes. The systematical water managements from the acquirement of raw water to the selection of a suitable treatment are needed to get the superior tap water quality. Even if chlorine disinfection was performed, it causes bacterial growth on a water distribution system because it is difficult to remove fine particles and dissolved organics in water using conventional treatments such as coagulation, sedimentation, filtration, and disinfection.[1-6]

The major sources of organic matter in natural water supplies may be synthetic organic matter, natural organic matter and by-product from water treatment.[7] Natural organic matter can be classified as fulvic acid, humic acid, weak hydrophobic acids, hydrophilic acids, hydrophobic neutrals, hydrophilic neutrals, hydrophobic bases and hydrophilic bases.[8] In other hands, synthetic organic matters consist of supremely diverse group of compounds. It reported some synthetic organic matter, being lower molecular weight, more hydrophilic with lower specific ultraviolet light absorbance (SUVA) values, is more difficult to be eliminated in water purification.[9]

The properties of organics generally considered in water treatment are biodegradability, molecular weight distribution, degree of aromaticity, and saturation of organics. Several researchers reported that disinfection by-products were related to the characteristics of organics.[10-12]

The coagulation and sedimentation processes have been used to remove suspended particles. Most materials eliminated in coagulation are

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colloidal inorganic materials. Kim *et al.* reported the removal efficiency was shown 50-75% for the organics over molecular weigh (MW) 11,000 daltons when Nakdong River water was used as a water treatment sample for coagulation and sedimentation with 8-12 mg/*l* ferric chloride dosage.[13] Veenstra *et al.* (1984) found that most materials over 50,000 MW were removed by adding alum and polymer to direct filtration.[10] Organics between 500 and 1,000 MW were effectively removed by granular activated carbon (GAC), while high molecular weigh organics were not eliminated because there were limitations to diffusion due to size.[14-17]

Disinfection is the process of inactivating pathogens and microorganisms that have potential risk. Trihalomethanes (THMs) are the major components of disinfection by-products (DBPs) which are formed by the disinfection of drinking water. But it had not been noticed until Rook in the Netherlands announced the fact in 1970 that THMs could be produced by reaction of chlorine with organic materials dissolved in water.[18,19]

This research was performed to address organic characteristics from different origins based on apparent molecular weight distribution, organic behavior due to biodegradation, and the formation of disinfection by-products.

II. Materials and Method

1. Sample Preparation

The samples for these experiments were selected as follows; Ilkam Lake as lake water, secondary effluent from the Gwacheon sewage treatment plant as sewage treatment effluent, Surface water (Han river water) were taken from under the Chamshil bridge, and the sources of humic acid were commercial products supplied by Aldrich chemical (USA) and Wako chemical (Japan), respectively. The samples were used to observe organic characteristics representing individual water origins. Table 1 shows the water parameters characterizing the samples. All samples were collected by grap sampling. The items of pH, dissolved organic carbon (DOC), and heterotrophic plate counts (HPC) were analyzed immediately after sampling, and the remaining samples were preserved in a refrigerator under 4°C. The humic acid stock solution was prepared using the following method; 1 g of humic acid was dissolved with NaOH, and then ultra-pure distillation water was added to the solution and stirred for 24 hr at room temperature.

2. Analytical Method

Items for temperature, pH, HPC were measured without filtration and DOC, biodegradable organic carbon (BDOC), UV_{254}, and apparent molecular weight distribution (AMWD) were performed after filtration through a 0.45 μm membrane filter. HPC was inoculated by spreading a plate on an R_2A medium, incubated for 7 days at 20 ± 1°C, and expressed as colony forming unit (CFU)/m*l*.

DOC was analyzed by a TOC 5000 analyzer (Shimadzu) as an NPOC mode. The value of BDOC was calculated by estimating the difference between initial DOC and minimum DOC after cultivation. UV_{254} was measured using a UV visible spectrophotometer (UV 1601, Shimadzu) with a 10 mm cell at 254 nm.

Trihalomethanes (THM) and trihalomethane formation potential (THMFP) were measured with an EPA 551-1. A sample was prepared in a vial and then the same volume of pentane was injected into the sample, shaken for 20 sec and extracted after 30 min of stationing. The extracted sample was analyzed with a GC/ECD (HP5890 series II,

Table 1. Characteristics of water samples

Sample	pH	DO (mg/*l*)	DOC (mg/*l*)	UV254 (m^{-1})	SUVA (L/m·mg)	HPC (CFU/m*l*)	NH_3-N (mg/*l*)
River	8.15	9.9	1.95	3.87	2.03	5×10^4	0.10
Lake	8.87	7.7	8.15	6.40	0.76	1.5×10^4	0.85
Sewage	7.27	4.4	6.54	1.04	1.54	7×10^5	22.7
Aldrich HA	8.10	8.4	3.62	59.0	16.3	-	0.33
Wako HA	6.59	7.6	3.41	41.9	12.2	-	0.84

Hewlett Packard).

Molecular weight distribution was classified by ultra-filtration equipment which consisted of 20 m*l* volumes of UF cells and clamps. Samples were then put inside cells with 55 psi of pure nitrogen. Samples were stirred by a magnetic stirrer to reduce intensity polarization. After filtration through membranes, samples were collected inside vials were treated to acid and heat. The initial 10 m*l* of the samples was discarded by membrane washing to reduce differences and the last 90% of the samples was used to measure DOC and UV_{254}. It transcribed as low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW) for the molecular weight ranges <1,000, 1,000-10,000, >10,000 dalton for convenience in this study.

III. Results and Discussion

1. DOC Physiochemical Characteristics

Fig. 1 illustrates the variation in molecular distribution for all DOC samples. The LMW materials to total DOC for surface water and secondary effluent were 77% and 65%, respectively which was considered very high. However, HMW was less than 10%. LMW, MMW, and HMW were 37%, 25%, and 38% for lake water and were distributed uniformly through all molecular weight areas. HMW occupied 66% to 81% for Aldrich HA, and Wako HA and LMW were less than 10%, respectively. It was thought that organics in lake water might convert to high molecular materials under the influence of algae and vegetable plankton.

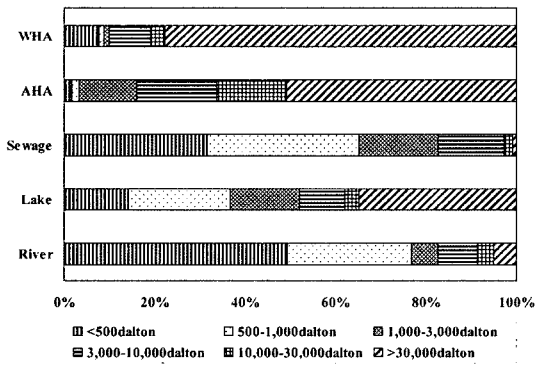

Fig. 1. Molecular weight distribution of DOC.

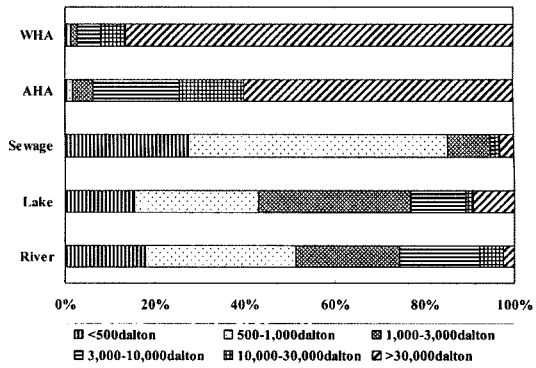

Fig. 2. Molecular weight distribution of UV absorbance.

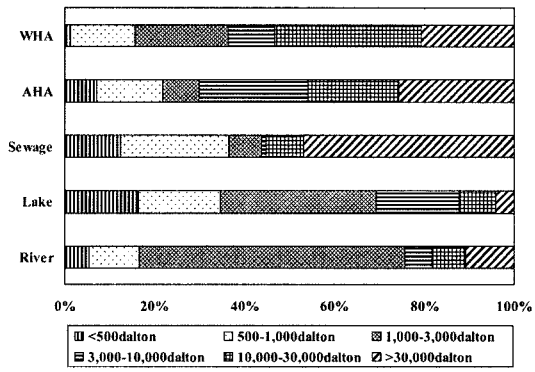

Fig. 3. Molecular weight distribution of SUVA.

The UV absorbance of molecular weight distribution showed low values for surface river water, lake water, and secondary effluent for HMW. Humic acid of Aldrich HA and Wako HA also exhibited high values for HMW (Fig. 2). The value for SUVA was high for MMW of surface river water, lake water, while secondary effluent and two types of humic acid showed high values for HMW (Fig. 3). A higher order of potential biodegradability by SUVA appeared in lake and sewage water, surface river water, Wako HA, and Aldrich HA.

2. The Biodegradability Assessment of DOC

This experiment was performed by examining the consistency between BDOC and SUVA as a biodegradation index. Fig. 4 shows biodegradability by BDOC of surface river water, lake water, secondary treated sewage effluent, Aldrich humic acid, and Wako humic acid. It took 3 days for the lowest value of DOC and the lowest reaching point of

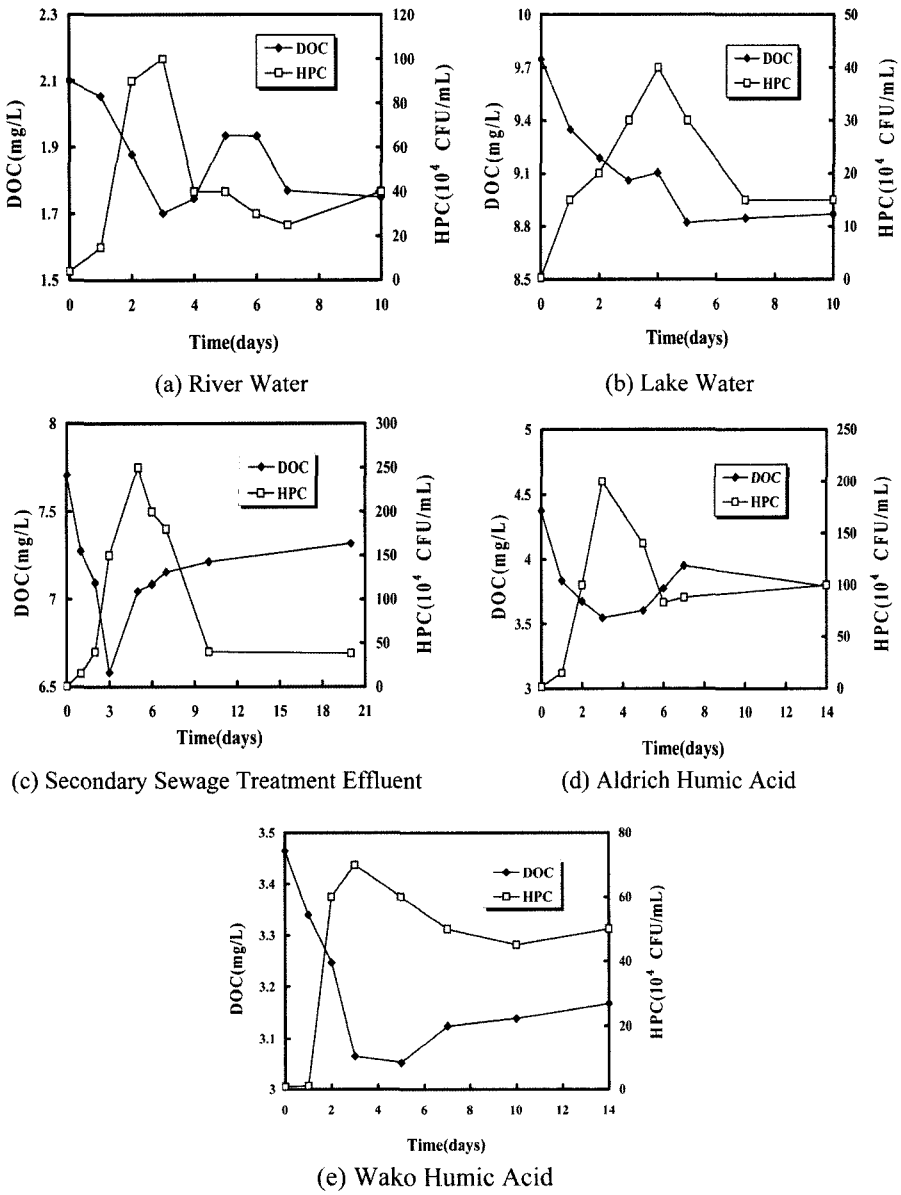

Fig. 4. Biodegradation according to organic sources.

substrate to be consistent with the highest value for biomass in surface river water. The percentage of BDOC to total DOC for surface river water was approximately 19%. It took 5 days to reach the lowest DOC levels, which was longer than surface river water in lake water, and the proportion of BDOC was 9.5% in lake water, which indicated that it was difficult to biodegradable. It took 3 days to reach the lowest DOC value for relatively rapid degradation by microorganisms for secondary sewage effluent. The ratio of BDOC to DOC was 14%, the behavior of DOC and microorganisms was stable, and values scarcely changed after 10 days in secondary sewage effluent. An increase of DOC was observed after 3 days which was anticipated SMP.

The ratio BDOC to DOC was 18.9% in Aldrich HA. Degradation was considered rapid and reached the lowest point after 3 days. After that, it increased slowly and then registered another decrease after 7 days. Wako HA reached the lowest point after 5 days, which was different from Aldrich HA. In addition, the ratio of BDOC to DOC was 11.9%, which was lower than Aldrich HA. SMP were observed after 5 days and the value of DOC continuously increased for Wake HA.

The highest value of HPC for sewage water was 2.5×10^6 CFU/m*l* and increased 285 times compared to the initial value, which it was the highest multiplication. On the other hand, Wako HA increased approximately 87.5 times compared to the initial value, which was the lowest multiplication value. The HPC for lake water and Aldrich HA showed that a low DOC value and high UV absorbance

Table 2. Molecular weight distribution of DOC during biodegradation (Unit: %)

Sample	Time	<500 dalton	500-1,000 dalton	1,000-3,000 dalton	3,000-10,000 dalton	10,000-30,000 dalton	>30,000 dalton
River	0 hour	30.7	27.9	8.9	12.0	2.0	18.4
	72 hours	30.7	29.7	14.8	13.4	11.0	0.4
	240 hours	40.1	18.6	24.1	3.1	13.6	0.5
Lake	0 hour	22.7	9.1	16.6	6.9	1.7	43.0
	120 hours	28.0	16.7	7.7	11.3	0.3	36.1
	240 hours	29.0	16.8	35.9	1.5	10.8	6.1
Sewage	0 hour	29.8	33.5	15.8	12.7	6.9	1.4
	72 hours	15.4	14.3	21.3	21.3	7.2	20.4
	240 hours	13.3	33.1	21.3	4.5	7.6	20.2
Aldrich HA	0 hour	1.4	1.6	12.8	15.9	13.8	54.5
	72 hours	6.7	2.6	5.7	25.7	20.8	38.5
	336 hours	4.6	1.8	2.6	4.2	27.0	59.8
Wako HA	0 hour	8.1	1.0	1.4	9.0	3.5	77.0
	120 hours	2.7	0.8	8.7	4.0	12.7	71.0
	336 hours	3.7	10.3	4.8	8.7	3.4	69.1

Table 3. Molecular weigh distribution of UV254 during biodegradation (Unit: %)

Sample	Time	<500 dalton	500-1,000 dalton	1,000-3,000 dalton	3,000-10,000 dalton	10,000-30,000 dalton	>30,000 dalton
River	0 hour	17.9	33.3	23.1	17.9	5.1	2.6
	72 hours	18.4	26.3	31.6	15.8	5.3	2.6
	240 hours	15.0	20.0	32.5	17.5	5.0	10.0
Lake	0 hour	16.4	22.4	38.8	7.5	1.5	13.4
	120 hours	26.9	28.4	6.0	13.4	7.5	17.9
	240 hours	13.1	24.6	39.3	1.6	6.6	14.8
Sewage	0 hour	25.0	50.0	13.8	5.2	3.4	2.6
	72 hours	21.9	20.2	33.3	4.4	6.1	14.0
	240 hours	15.7	37.0	13.9	20.4	0.9	12.0
Aldrich HA	0 hour	0.5	1.3	5.0	19.5	15.6	58.1
	72 hours	1.1	2.3	2.3	23.1	16.5	54.7
	336 hours	0.5	2.4	3.5	0.4	38.6	54.6
Wako HA	0 hour	0.5	0.7	1.7	5.7	6.2	85.1
	120 hours	0.7	0.2	2.7	3.0	14.5	78.8
	336 hours	0.7	0.2	2.7	3.0	14.5	78.8

Table 4. Molecular weight distribution of SUVA during biodegradation (Unit: %)

Sample	Time	< 500 dalton	500-1,000 dalton	1,000-3,000 dalton	3,000-10,000 dalton	10,000-30,000 dalton	>30,000 dalton
River	0 hour	5.3	10.7	23.3	23.3	13.6	23.8
	72 hours	5.0	7.7	18.4	10.0	4.2	54.8
	240 hours	1.3	3.6	4.4	18.5	1.1	71.1
Lake	0 hour	9.4	32.1	30.2	13.2	11.3	3.8
	120 hours	3.5	6.3	8.4	76.9	1.4	3.5
	240 hours	6.4	21.3	14.9	14.9	8.5	34.0
Sewage	0 hour	14.4	24.4	14.4	6.7	8.9	31.1
	72 hours	23.1	23.1	25.0	3.7	13.9	11.1
	240 hours	14.4	13.6	8.0	55.2	1.6	7.2
Aldrich HA	0 hour	7.9	15.7	7.9	24.5	22.6	21.4
	72 hours	3.6	19.4	8.9	19.8	17.3	31.1
	336 hours	2.3	25.8	25.6	1.7	27.3	17.4
Wako HA	0 hour	1.1	14.0	22.0	11.4	31.8	19.7
	120 hours	7.0	7.7	8.1	19.0	29.6	28.6
	336 hours	3.6	6.5	37.5	11.3	11.3	29.8

were approximately 117 to 143 times greater than that of initial value. It was speculated that BDOC was directly related to SUVA in selected natural water samples and so potential biodegradability could be estimated by SUVA when the measurement of BDOC was difficult.

The molecular distribution of DOC, UV_{254}, and SUVA during biodegradation for surface river water, lake, sewage secondary water, Aldrich HA, and Wako HA are presented in Table 2-4. The value of DOC reached the lowest and then it increased again by SMP in Fig. 4. These two points were selected in Table 2-4 for evaluating the distribution of MW for DOC, UV254 and SUVA during biodegradation.

DOC registered the lowest values for surface river water after 3 days. Approximately 19% of DOC was eliminated compared to the initial concentration and BDOC was 0.4 mg/*l*. It was eliminated in the area of HMW and it was converted to MMW. After 10 days, DOC increased an additional 2.9% compared to DOC at 3 days. For the initial 3 days, UV absorbance material in the LMW area slightly decreased and then increased 4 times in HMW after 10 days under the influence of SMP. SUVA at the area of HMW to total SUVA was shown 59% at 3 days for surface water and then it increased to 72% at 10 days.

The variation of DOC, UV245, and SUVA for lake water is as follows; the lowest DOC value was appeared after 5 days and BDOC occupied 7.2% of total DOC. DOC were removed in the area of MMW mostly in lake water and converted to LMW materials. However, DOC in the area of HMW decreased but significantly increased in MMW after 10 days. UV absorbance material showed similar tendencies with DOC variation. Materials in MMW converted to LMW and increased the area of MMW and HMW within the initial 5 days.

The variation of organics for secondary effluent sewage water is as follows; Initial DOC distribution was 63.3%, 28.4%, and 8.3% for the LMW, MMW, and HMW areas in secondary effluent sewage. The proportion of LMW was high and HMW was low. The most variable part was in the LMW and should be characterized DOC removal by biodegradation and humification. DOC increased rapidly after 3 days of incubation and continuously decreased. The variation in UV absorbance was similar to DOC. However, the change in SUVA differed in various aspects from DOC and UV absorbance. It explained degradation in the area of HMW and conversion of portions of LMW to MMW.

The initial molecular distribution of Aldrich HA was 3%, 28.8%, and 68.3% for LMW, MMW, and HMW, which were in reverse order for sewage

water. Material in MMW converted to HMW. The variation of UV absorbance showed the conversion of MMW to HMW which was same tendency with DOC. SUVA showed very high values in Aldrich HA and high molecular materials converted to low molecular materials.

The lowest DOC in Wako HA was shown after 5 days of incubation. Most DOC was eliminated in the LMW and MMW areas while the HMM portion increased within 5 days. A decrease in HMW was registered and a continuous increase in LMW and MMW was registered in 14 days. The HMW portion was 80% of total DOC, which was higher than other samples. LMW and MMW portions were relatively low. MMW materials converted HMW materials and materials over 30,000 dalton converted that between 10,000 and 30,000 dalton after 5 days for UV254. However, there was no noticeable change in the distribution of molecular weight for 14 days.

4. Characteristics of DOC and Formation of THM

Fig. 5 illustrates the formation of THM according to origin. DBP formation was influenced by organic characteristics. The more HMW and UV absorbance materials present in a sample, the greater concentration of THM. However, a high concentration of THM formed despite containing large amounts of low molecular materials and a small quantity of UV absorbance materials for surface river water. The ratio of THM to THMFP was 4 times, which was the highest value for the Aldrich HA sample, whose organics appeared to degrade slowly to the

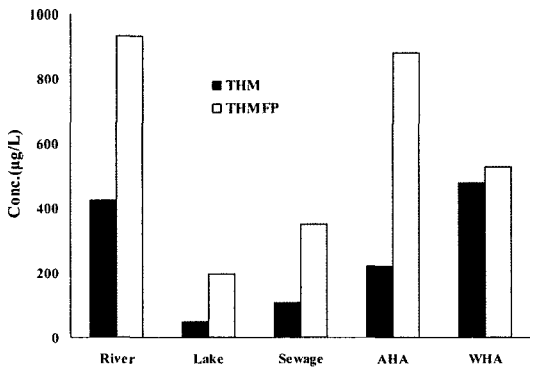

Fig. 5. THM formation according to organic sources.

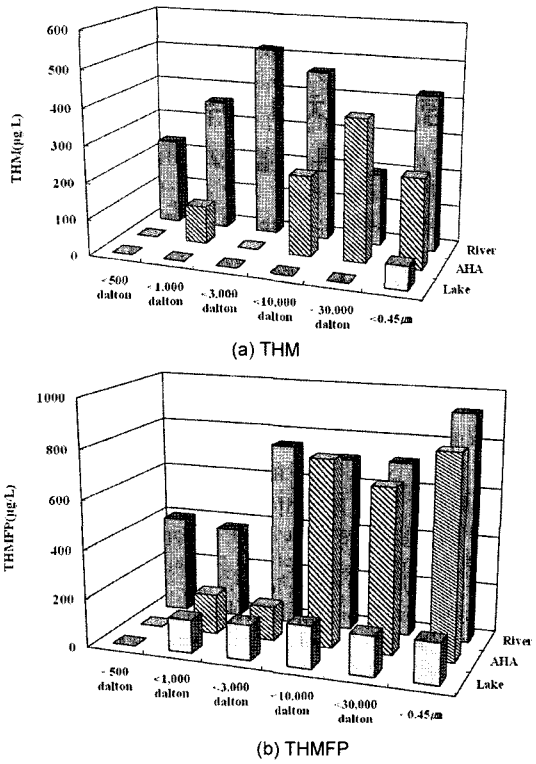

Fig. 6. THM formation based on molecular weight distribution.

HMW range. The lowest ratio of THM to THMFP was 1.1 at the Wako HA, which maintained a HMW ratio.

Fig. 6 presents DBP formation of molecular weight distribution. The formation of THM and THMFP increased as molecular weight increased. However, THM formation in surface river water was very high at the range of MMW and low at the range of LMW and HMW. The formation of THM was insignificant at MW under 0.5K and showed a 3 to 4 times increase in THM and THMFP over 0.5 K. According to these results, it was thought that THM formation was higher when the content of UV absorbance and molecular weight increased.

IV. Conclusion

This research aimed to evaluate characteristics on the origin of organics. It examined physico-chemical characteristics of dissolved organics, biodegradation, and THMs formation on the distribu-

tion of molecular weight for surface river water, lake water, sewage secondary effluent, Aldrich humic acid, and Wako humic acid.

Organics occupied 77% and 64% of the LMW area for surface and sewage water and 66% and 81% of the LMW area for Aldrich and Wako humic acid. Biodegradation tests for surface water showed the lowest DOC values after 3 days for HMW and 4 days for MMW and HMW. It took 5 days for lake water through all MW. The LMW organics decreased and HMW increased during biodegradation. The formation of SMP was 0.7%-5.5% of total DOC and showed a tendency for a high value of SMP when a significant amount of HMW matter was present in the samples.

The higher order for potential biodegradation was lake water, sewage secondary effluent, surface water estimated by SUVA. The results according to SUVA were consistent with real biodegradation tests for natural water samples. THM formation was higher for the sample in a significant amount of HMW materials.

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