

CHARACTERIZATION OF RECALCITRANT DISSOLVED ORGANIC MATTER IN LAKE AND INFLOW RIVER WATERS

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Abstract : The hydrophilic or hydrophobic characteristics of dissolved organic matter (DOM) from different origins in lake and river waters were investigated using spectrometric and chromatographic analyses of water samples. DOM in a deep, mesotrophic lake (Lake Unmun) was fractionated using three types of ion exchange resins and classified into aquatic humic substances (AHS), hydrophobic neutrals (HoN), hydrophilic acids (HiA), hydrophilic neutrals (HiN), and bases (BaS). The DOM fractionation provided insight into the understanding of the nature of heterogeneous DOM molecules present in different water sources. The UV/DOC ratios were determined for samples from the influent river and lake waters during DOM fractionation and incubation. AHS prevailed over DOM in the lake and river waters. After biodegradation, the relative contribution of AHS in the total DOM became more significant. It indicates that the AHS fraction would increase while water stay long time in the lake.

Key Words : Lake Unmun, Aquatic humic substances, Fractionation of DOM, Biodegradability, Molecular weight

INTRODUCTION

There is a growing interest in the contribution of dissolved organic matter (DOM) such as humic substances to biological, physical, and geochemical processes in natural water systems. Many studies have been done to quantify the distribution and characteristics of DOM in surface water.¹⁻²⁾ Nevertheless, DOM in natural waters still remains poorly characterized due to its complex nature, and thereby its physio-chemical characteristics are not well understood.³⁾ DOM is an important constituent of surface water, soil pore water, and

shallow ground water in terms of concentration and reactivity.⁴⁾ From a limited number of studies we know that the molecular weight of DOM present in streams and rivers varies substantially.⁵⁻⁶⁾ It is also known that humic substances dominate the DOM pool in stream water⁷⁾ and play an important role in ecosystem metabolism.⁸⁾ The majority of DOM in lakes and rivers is comprised of different organic acids, i.e., hydrophobic and hydrophilic acids. The hydrophobic- hydrophilic nature could be related to the chemical structure of DOM, some recalcitrant portion of which can be accumulating in the lake water.⁹⁻¹⁰⁾

The accumulation of DOM in lake water certainly imposes some problems on the management of lakes as well as the quality of drinking water sources. Several recent studies reported that

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chlorine consumption and disinfection by-products (DBPs) formation were directly proportional to the content of DOM and thus a lot of efforts have been made to remove DOM prior to chlorination.¹¹⁻¹²⁾ Recalcitrant DOM usually becomes a dominant precursor of carcinogenic trihalomethanes and haloacetic acids being produced during chlorination in water treatment. On the other hand, DOM in soil interstitial waters can exert a profound influence upon nutrient availability, cation leaching processes, trace metal toxicity, microbial community dynamics, mineral weathering, and acid-base chemistry in forest soils. Thus, there is a need for improved understanding of the chemistry of DOM molecules and the factors controlling their release and transport in water and soil environment. In this geochemical investigation, some studies were conducted to examine the chemistry and leaching patterns of DOM and associated organic solutes in forest soils and lake-watershed ecosystems.³⁾ Thus, the characteristics of DOM in natural water and the interaction with soils should be evaluated via the physico-chemical properties of DOM.

An approach to characterize DOM is to classify DOM based on size distribution and physico-chemical characteristics. It was found that in some natural waters, fulvic acids are the major fraction (20-80%) of DOM, while in other cases humic acids are the major fraction accounting for 30-80 % of DOC.¹³⁾ DOM fractionation methods based on the polarity and acidity, namely hydrophobic-hydrophilic and acid-base functionalities, appear to be reasonable for evaluating the characteristics of DOM in waters. Thus, the ion exchange resin method are being used most frequently for the isolation of DOM in natural water.¹⁴⁾

Therefore, in this study, we tried to fractionate DOM using three types of resins into five portions with different hydrophobicity and acidity. Particularly, the characteristics of DOM in two river and its receiving lake waters was evaluated and compared with water samples taken at different sites and depth with respect to carbon concentration level, ultraviolet absorbance, size distribution, and biodegradability.

MATERIALS AND METHODS

Site Description of Lake Unmun and Sampling

Lake Unmun is one of the deepest and cleanest lakes in Korea, which is located in the eastern part of the Gyeongbuk province 30km southeast of Daegu metropolitan city (35° 44' N, 128° 80' E ; 155 m above elevation level). The lake receives water from the two rivers the Dongchang (D-River) and Unmoon (U-River) rivers (Table 1 and Figure 1), which are adjacent to the Nakdong River.

Table 1. Hydrological characteristics and utilization of drainage basin of Lake Unmun (Yearly average records from 2003-2004)

Function	water supply in dry season flood control hydroelectric power generation
Shape	dendritic lake
Trophic state	oligo-mesotrophic
Circulation type	warm monomimetic
Drainage area	301.34 km ²
Dam height	55 m
Dam length	407 m
Water capacity	135,300,000 m ³
Surface area	7.8 km ²
Mean depth	17 m
Maximum depth	30 m
Hydraulic residence time	0.41 yr
Yearly average inflow	37,754 m ³ /month
Yearly average outflow	39,049 m ³ /month

The lake and rivers are linked to a few small towns and domestic sewage discharge as well as runoff. More than 7,000 people live in the lake's watershed (301.34 km²). Specific land usage of the overall watershed area for forest, paddy field, and residential purposes is 88%, 8%, and 3%, respectively. The shape of the Lake Unmun basin is smooth and narrow with a surface area of 7.83 km² and a mean depth of 17.0 m (additionally, the deepest water level is approximately 30 m below the surface).

Water samples were collected in a one-liter glass bottle with a van dorn sampler in the lake every month from September 2003 to May 2004. The concentrations of chlorophyll-*a* (chl.-*a*), total

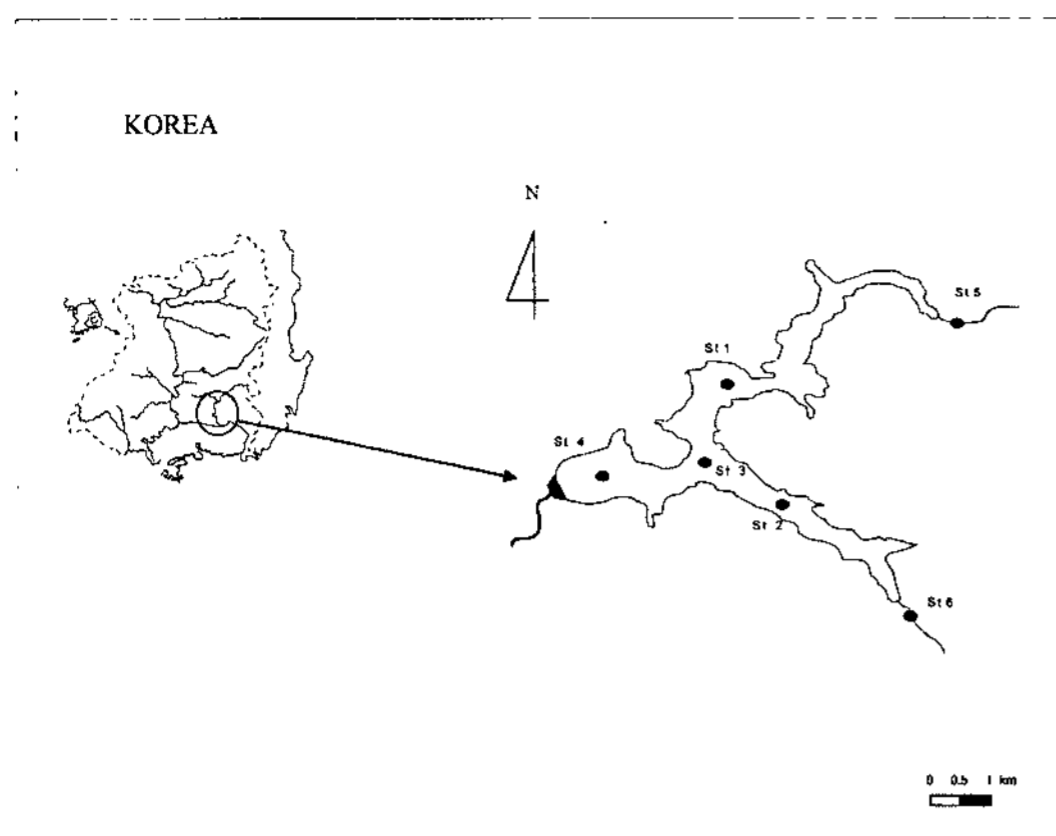


Figure 1. Location of the sampling sites in Lake Unmun. St.1 : Dongchang Points ; St.2 : Unmoon Points ; St.3 : Dongchang and Unmoon river combined water ; St.4 : Dam Center; St.5 : Influent river, the Dongchang River, into Lake Unmun ; St.6 : Influent river, the Unmoon River, into Lake Unmun.

phosphorus (TP), and total nitrogen (TN) in the water sample taken at the center of the lake was $6.1 \mu\text{g L}^{-1}$, $10 \mu\text{g L}^{-1}$ and 1.37mg L^{-1} , respectively. The water samples taken were immediately stored in an ice cooler and shipped to the laboratory. Raw water was filtered through a precombusted (combustion temperature and duration: 450°C ; 4 h) Whatman GF/F filter with a nominal pore size of $0.7 \mu\text{m}$. The filtrate was kept at 3°C in a clean glass bottle before analysis.

Water samples from the inflow rivers were also collected on monthly basis in dry seasons, but frequent sampling such as three or four times per day were suggested in rainy seasons. This was because water quality varied a lot with the change of water flow rates at that moment. The samples from the river water were managed in the same manner as described above.

Fractionation of DOM

DOM in lake and river waters was fractionated through a series of macroporous resin adsorbents into 5 fractions such as hydrophobic acids (equivalent to aquatic humic substances ; AHS), hydrophobic neutrals (HoN), hydrophilic acids (HiA), Bases (BaS), and hydrophilic neutrals (HiN).¹⁵⁾

Hydrophobic neutrals (HoN) was negligible, so the analysis of that portion was omitted. Hereafter hydrophobic acids are referred to as AHS. Three different ion exchange resins were used for fractionation, such as Nonionic Amberlite XAD-8 resin (Rohm and Hass, 20-60 mesh), strong cation exchange resin (Bio-Rad AG-MP-50, 50-100 mesh) and strong anion exchange resin (Bio-Rad AG-MP-1, 50-100 mesh). The column capacity factor was 50 for the separation of hydrophobic acids using the XAD-8 resin column. For the DOM fractionation, hydrophobic solutes are defined as those solutes that are retained on XAD-8, while hydrophilic solutes are defined as those solutes that are eluted the XAD-8 column.¹⁶⁾ XAD-8 resin was cleaned up and conditioned according to the procedure performed by Thurman and Malcolm.¹⁷⁾ Three milliliters (on wet volume basis) of the XAD-8 resin were packed in a glass column and then were rinsed 3 times, alternating 0.1M NaOH and 0.1M HCl before the application of the samples. A blank sample was collected in the final stage of rinsing with 0.1M HCl (B1). Both AG-MP-50 (hydrogen-form) and AG-MP-1 (chloride-form) resins were Soxhlet- extracted for 24 hr with methanol. The AG-MP-1 resin was then converted into the free-base form with 1M NaOH and rinsed with distilled pure water. Two glass columns containing 6mL (wet volume) of the cation exchange resin and 12mL (wet volume) of the anion resin were operated in series and conditioned by pumping approximately 1-liter distilled pure water. Other blank samples (B2 and B3) were collected from each column during filtration of distilled pure water after the conditioning step. The detailed DOM fractionation procedure is summarized as follows (Figure 2).

Step 1: acidify the $0.7\text{-}\mu\text{m}$ GF/F filtrate (DOM1) to pH 2.0 using 6M HCl , pass the filtrate (200mL) through the XAD-8 column using a peristaltic pump with tygon tubing at a flow rate of approximately 1mL min^{-1} , and rinse the column with three bed volumes of 0.1M HCl .

Step 2: Elute the column in the reverse direction with more than 3 bed volumes of 0.1M NaOH at a flow rate not exceeding 0.5mL min^{-1} (DOM2).

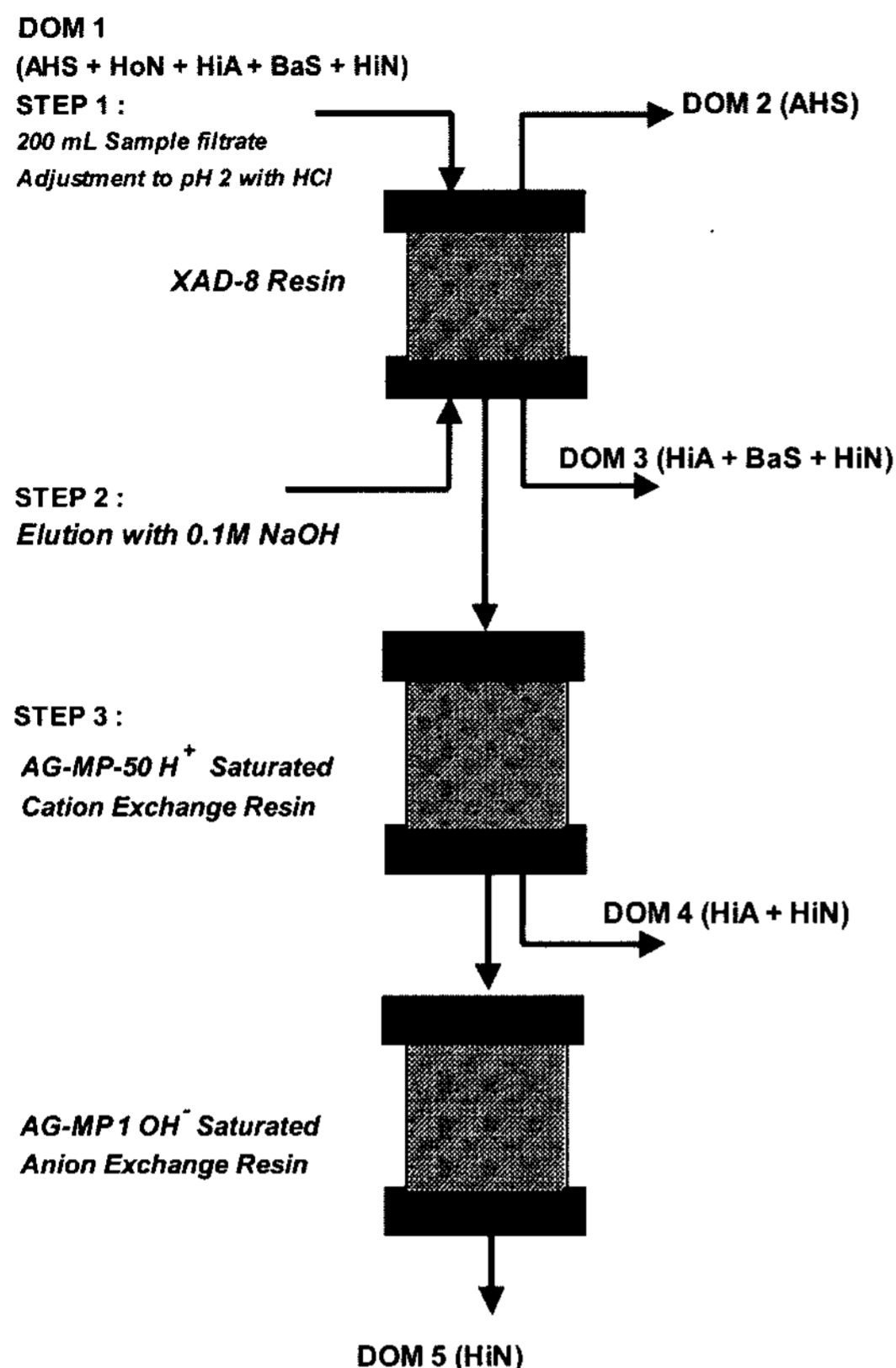


Figure 2. Experimental procedure for dissolved organic matter fractionation. DOM fractions are AHS, aquatic humic substances ; HoN, hydrophobic neutrals ; HiA, hydrophilic acids ; BaS, bases ; HiN, hydrophilic neutrals.

Step 3: Pump the sample obtained from Step 2 (DOM3) through a series of the cation-anion resin columns at a flow rate of approximately 1 mL min⁻¹. After pumping 1-2 bed volumes of the sample, collect eluant samples from the anion resin column (DOM5) and then from the cation resin column (DOM4).

DOM fractionation was done two times for each sample. After the fractionation, the DOM concentration and ultraviolet absorbance were determined for each fraction and the blank samples. The average carbon content of B1, B2 and B3 was 0.57±0.34 mg C L (n=72), 0.63±0.37 mg C L (n=72) and 0.61±0.38 mg C L (n=72), respectively. The background contamination was negligible. The blank DOC from the XAD-8 resin column during 0.1 M NaOH elution was also neglected

since its concentration was found considerably low as compared with the DOC concentration of the DOM 2 fraction. When Milli-Q water was adjusted to pH 2 with HCl and passed through the XAD-8 resin column and then the cation-anion resin columns, the DOC concentration in B2 was no more than that in B1. Thus, the DOC blank contribution from the XAD-8 resin column to DOM4 and DOM5 was considered negligible.¹⁸⁾

Biodegradability Experiments

Filtrate that had passed through a precombusted Whatman GF/F filter was incubated in a sterile 500 mL glass bottle at 20°C in the dark without shaking. We took some samples of approximately 10 mL at incubation times of 15, 30, 60, and 100 days for the determination of DOC concentration.¹⁹⁻²⁰⁾

Determination of DOM Molecular Weight Distributions

The apparent molecular weight distribution of lake water and fractionated samples was characterized using a high-pressure size exclusion chromatograph²¹⁻²³⁾ (HPSEC) equipped with a Rheodyne 7125 sample injector, a Hitachi L-6200 pump, a Hitachi L-4200-UV detector, and a Hitachi data integrator. A Waters Protein-Pak 125 column containing a glycol-functionalized silicagel with a rated molecular weight range of 100 micron was used. The carrier solution was a 0.004 M phosphate buffer (which contained 0.1 M NaCl, 0.002 M KH₂PO₄, and 0.002 M Na₂HPO₄) and it was adjusted to pH 6.8. A flow rate of 0.5 or 1.0 mL/min was applied. The HPSEC system was calibrated with a set of standard polystyrene sulfonates (PSS) with molecular weights ranging from 1800 to 35000 Dalton (Da) (Polyscience, Inc., PA) along with acetone (58 Da, HPLC grade, Aldrich).¹⁾ A linear calibration equation in the form of log (molecular weight) = a-b(t) was obtained: t is the peak retention time, and a and b are the constants. In the calibration, R² = 0.99.

Analytical Methods

The dissolved organic carbon (DOC) was de-

terminated using a Sievers 820 total organic carbon analyzer equipped with a membrane conductivity detector. Triplicate measurements were made for each sample, and the analytical precision was within $\pm 1\%$. Potassium hydrogen phthalate was used as a DOC standard. The ultraviolet (UV) absorbance was measured with a Shimadzu UV-2101 UV/VIS spectrophotometer at 260 nm using a quartz cell with a path length of 1cm. All the samples were adjusted to pH 2 with HCl before measurement. Distilled pure water was used as blank.

The absorbance spectra of the samples exhibited a monotonous decrease showing no characteristic maximum as the wavelength was increased from 200 nm to 500 nm. The decrease in absorbance along with wavelength was not sample-specific. In this study, the wavelength of 260 nm was selected for UV absorbance analysis.²⁴⁾ This is because (1) the maximum UV absorbance of phenolic, benzene carboxylic and polycyclic aromatic groups (π - π^* transition) in DOM is observed at a wavelength of 200-290 nm and (2) the presence of nitrate and borate does not affect the measurement of UV absorbance at that wavelength.²⁵⁾ Other physico-chemical methods were adopted from Standard Methods for determining biochemical oxygen demand (BOD), chlorophyll-a (Chl.-a), total nitrogen (TN), ammonia nitrogen (NH₃-N), nitrate nitrogen (NO₃-N), total phosphorus (TP), and orthophosphate phosphorus (PO₄-P).²⁶⁾

RESULTS AND DISCUSSION

Characteristics of Lake Unmun and Inflow Rivers

The qualities of water samples from different sites are shown in Table 2. It was clear that the Dongchang river was relatively highly contaminated compared to the Unmoon river (refer to St. 6). Water quality from St. 3 through St. 5 became better almost in all of the parameters with the exception of COD and DOC levels, whereas the water quality trend from St. 3 through St. 6 was nearly opposite to the Dongchang river(St.5) side. The water quality in the St.1, 2 worse than other station because transport of contaminants from St.5, St.6. After the two water streams met together, the water quality appeared to be more dilution stabilized as observed at St. 4.

The concentration level of BOD, COD, and Chl.-a in the lake water was the highest at the St.1, St.5 and decreased at the St.2, St.5. The range of concentrations with COD was smaller than that observed in the year 1999,¹⁸⁾ while the concentration of Chl.-a in the epilimnion was the highest during the late summer bloom and decreased in winter. The suspended solids (SS) concentration was mostly below 5.9 mg L⁻¹, but it increased up to 24.4 mg L⁻¹, when all the turbid water was discharged during the effect of rainfall. This increase in surface SS concentration may result in an unexpected large flux from the watershed. In the deep reservoirs of Korea, storm runoff usually flows into the metalimnion because inflowing streams at high flow rate have a lower temperature than that on lake surfaces, and form

Table 2. Seasonal variations of water quality parameters in Lake Unmun from September 2003 to May 2004

Sample Station	Items	SS (mgL ⁻¹)	BOD (mgL ⁻¹)	COD (mgL ⁻¹)	D-COD (mgL ⁻¹)	DOC (mgL ⁻¹)	Chl.-a (mgM ⁻³)	T-N (mgL ⁻¹)	NH ₃ -N (mgL ⁻¹)	NO ₃ -N (mgL ⁻¹)	T-P (mgL ⁻¹)	PO ₄ -P (mgL ⁻¹)
St.1		8.21	2.03	3.46	2.98	1.31	3.56	1.26	0.31	0.84	0.021	0.012
St.2		5.28	1.13	2.97	2.95	1.30	2.09	1.15	0.23	0.82	0.014	0.004
St.3		7.25	1.45	3.62	3.03	1.49	2.43	1.07	0.35	0.71	0.019	0.012
St.4		6.56	1.62	2.82	2.16	1.52	2.34	1.46	0.14	0.59	0.012	0.005
St.5		8.74	2.35	1.76	1.20	0.57	4.34	1.89	0.69	1.04	0.033	0.016
St.6		4.22	1.20	1.64	1.04	0.45	1.97	0.79	0.28	0.55	0.005	0.002

Note; precisions are less than $\pm 2\%$ -17% for BOD, 1%-2.9% for D-COD, less than $\pm 1\%$ for DOC. $\pm 0.5\%$ -2.5% for T-N, $\pm 0.5\%$ -25% for NH₃-N, $\pm 0.5\%$ -3.4% for NO₃-N, $\pm 1.0\%$ -43% for T-P, and $\pm 1.5\%$ -47% for PO₄-P, St.3 and St.4 samples consist of Epilimnion, Metalimnion, Hypolimnion samples.

turbid intermediate layers that remain several months in the reservoirs. This phenomenon is apparently a typical feature in deep reservoirs of monsoon regions, which has a great impact on their aquatic ecosystems.¹⁹⁾

The DOC level of Lake Unmun water ranged from 1.30 to 1.52 mg L⁻¹ (averaging out 1.41 mg L⁻¹) during a period from Sep. 2003 to May 2004 (Figure 3). The lake DOC exhibited a tendency of increasing slightly from fall to winter and then declining gradually thereafter. Overall, however, except for the data between Oct. and Nov. 2003, the DOC remained relatively constant. The DOC concentrations in two rivers (Dongchang and Unmoon rivers) flowing into Lake Unmun were in the range of 0.45 - 0.57 mg L⁻¹ with an average value of 0.51 mg L⁻¹ during the time period investigated. Presumably, the higher DOC concentration in the lake water results from the carbon release from the bottom zone of the lake, where suspended or coagulated organics was accumulated since the lake was built.

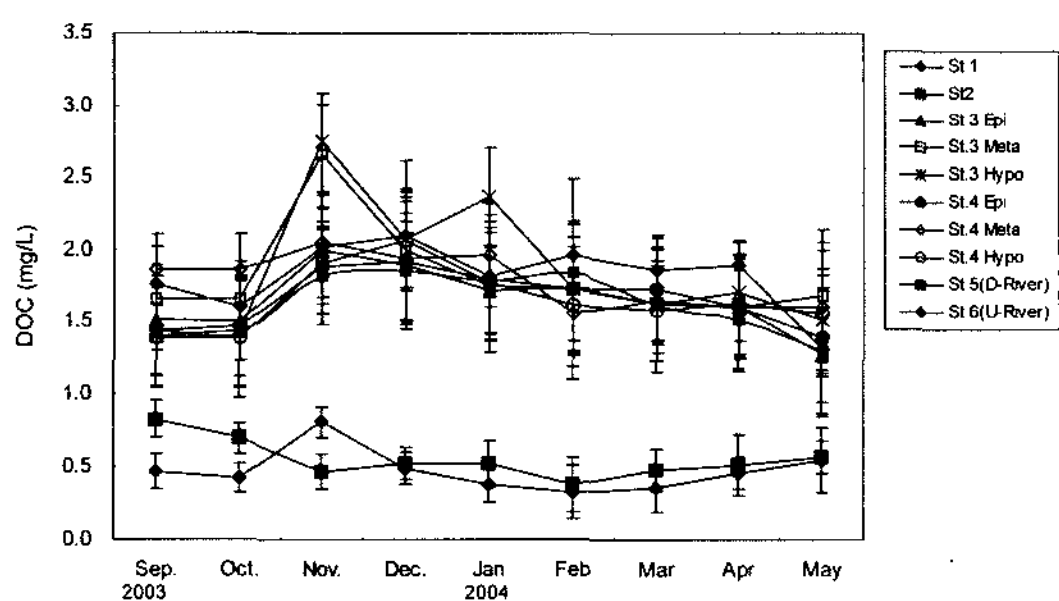


Figure 3. Seasonal variations of dissolved organic carbon (DOC) in Lake Unmun water and rivers inflowing to Lake Unmun from September 2003 to May 2004.

DOM Fractionation of the Lake and River Waters

Figure 3 shows that in Lake Unmun and river waters, the AHS fraction was predominant in the overall DOM (Figure 4). The AHS accounted for approximately 50-60% of the total DOM, except for the DOM in the lake sediment (18%). HiA varied from 2~27% (corresponding to 0.54~0.90 mg C L⁻¹ in concentration) depending on the locations of water samples taken, whereas the

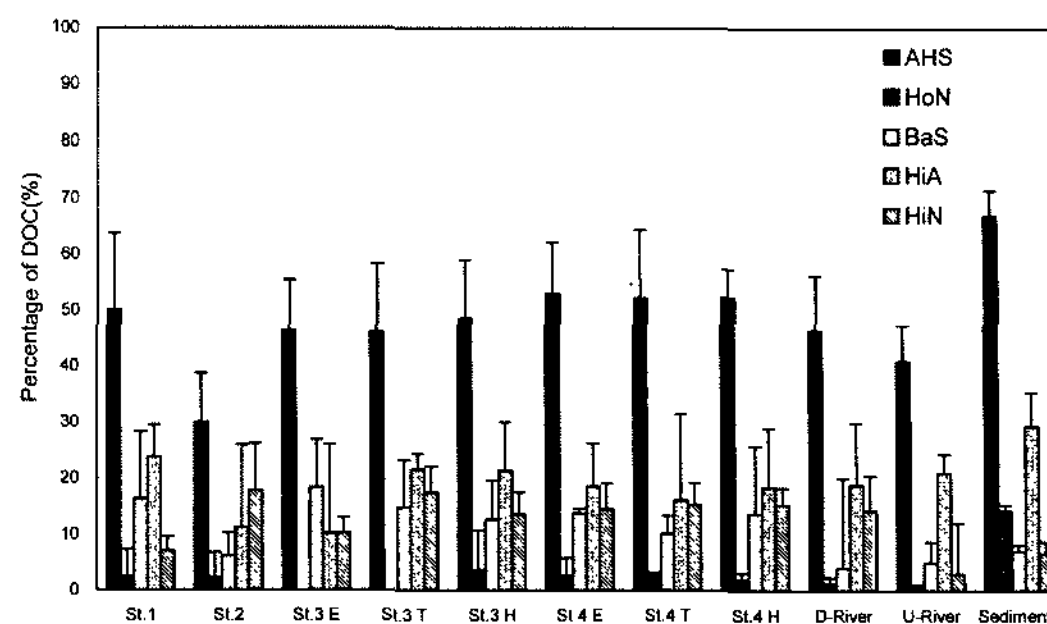


Figure 4. DOM fraction distributions in Lake Unmun. DOM fractions are AHS, aquatic humic substances ; HoN, hydrophobic neutrals ; BaS, bases ; HiA, hydrophilic acids ; HiN, hydrophilic neutral. Error bars represent \pm 1 standard deviation. St.1 : Epilimnion (1 m), St.2: Epilimnion (1 m), St.3 : Epilimnion (1 m), Metalimnion (12 m), Hypolimnion (25 m), St.4 : Epilimnion (1 m), Metalimnion (15 m), Hypolimnion (30 m), St.5 : Influent river, the Dongchang River (D-River), into Lake Unmun, St.6 : Influent river, the Unmoon River (U-River), into Lake Unmun, Sediments : Dam center sediment samples.

BaS portion was relatively high in the U-River water. The HoN fraction was around 0~8% (corresponding to 0.0~0.13 mg C L⁻¹), indicating that the organics such as hydrocarbon, pesticides, carbonyl compounds, and LAS did not contribute significantly to the lake DOM. The average percentage fraction of HiN was in the range of 8~21% of the total DOM. Protein or carbohydrate-like DOMs may not be present in a significant quantity in lake water.

The observed characteristics of the Unmun lake DOM were found different from the previous observation, that is, in 1998, AHS and HiA existed almost at the same level of 52% and 9%. In this study, AHS appears to be a more dominant constituent in lake water as compared with river water. The HoN, BaS and HiN fractions accounted for 17%, 13% and 12%, respectively. The lake and river DOM contain more hydrophobic fraction than the hydrophilic one. These results suggest that the lake and river waters are basically rich in AHS but poor in HiA because their major DOM is allochthonous, but lake waters contain

more AHS and HiA as the autochthonous DOM sources outweigh the allochthonous one in this study. It appears that in Lake Unmun the DOM may become more algal-derived and be originated from influent rivers. On the other hand, its inflowing rivers may have less allochthonous or pedogenic DOM sources. The DOM distributions for different water sources also showed an interesting feature that organic acids, AHS, and HiA dominated the DOM pool of all the samples (Figure 4).

However, the DOM fraction showed different patterns depending on the origin of samples. The river water had a DOM fraction distribution distinctively different from the lake water. The high HoN content in the lake sediments may be due to the presence of hydrocarbons, carbonyl compounds and linear alkylbenzene sulfonate like DOM, do not contribute significantly to DOM in the lake. The DOM is mostly of microbial origin and may be refractory to bacterial degradation because it is the remainder after extensive biodegradation.²⁰⁾ This suggests that both AHS and HiA may accumulate as recalcitrant DOM in the water when external organics is discharged into the lake.

UV Absorbance to DOC Ratio in Lake and River Waters

The UV absorbance to DOC (UV/DOC) ratio for each fraction exhibited a distinctive pattern depending on the lake and river water samples (Figure 5). The UV/DOC ratio of the lake water increased in the order of Lake-DOM, AHS and HiA (corresponding to 26, 21, and 16 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$, respectively). The UV/DOC ratio for the D-River and U-River waters showed a similar trend but lower values as compared with that of the lake water (DOM, HiA and AHS : 18, 10 and 8 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$, respectively).

Allochthonous or pedogenic DOM is essentially aromatic whereas autochthonous or aquagenic DOM is mainly aliphatic.²⁷⁾ Accordingly, allochthonous DOM is greater in the UV/DOC ratio than autochthonous DOM. It was reported that the UV/DOC ratio of the pedogenic DOM was in the

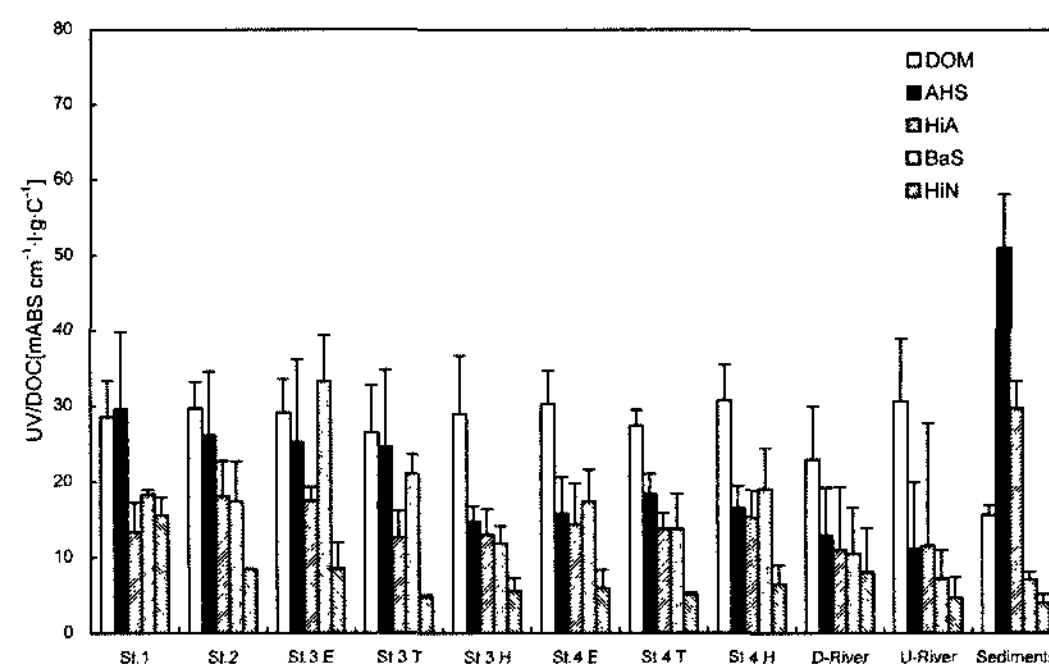


Figure 5. The ratio of ultraviolet absorbance over dissolved organic carbon (UV/DOC) in Lake Unmun and its inflowing river waters. DOM fractions are DOM, dissolved organic matter (Lake DOM, River DOM) ; AHS, aquatic humic substances ; HiA, hydrophilic acids. Error bars represent ± 1 standard deviation. St.1 : Epilimnion (1 m), St.2: Epilimnion (1 m), St.3 : Epilimnion (1 m), Metalimnion (12 m), Hypolimnion (25 m), St.4 : Epilimnion (1 m), Metalimnion (15 m), Hypolimnion (30 m), St.5 : Influent river, the Dongchang River (D-River), into Lake Unmun, St.6 : Influent river, the Unmoon River (U-River), into Lake Unmun, Sediments : Dam center sediment samples.

range of 23-58 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$, while that of aquagenic DOM was about 12 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$ ²⁸⁾. The higher ratio of the AHS in Lake Unmun than that in its inflowing rivers indicates that a significant portion of the lake AHS is pedogenic-derived allochthonous AHS. Thus it was reasonable that the ratio of the lake water DOM was greater than that in river DOM. The UV/DOC ratio of AHS in D-River water was approximately 17 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$, while the HoA in U-River DOM had a UV/DOC ratio of 19 $\text{mAbs cm}^{-1} \text{Lg C}^{-1}$. It was even less than the values of river DOM. Thus it is interesting to note that the UV/DOC ratio of AHS in U-River water and lake water was significantly higher than that of the D-River water. The high UV/DOC ratio of AHS fraction from the lake DOM may be originated from the lake sediment. The highest UV/DOC ratio of AHS and BaS showed large variations in both lake water and river water, which may result from the sediment or inflowing domestic sewage.

When AHS is further degraded with time, it produces molecular which have low UV absorbance, even though AHS is a bit recalcitrant. The UV/DOC ratio reflected the characteristics of organics in each fraction. The DOM fractionation with subsequent measurement of UV/DOC ratio can be a useful tool for evaluating the characteristics of DOM as well as the origin of DOM in lake and river waters.

Biodegradation Test of Lake and River Waters

In Lake Unmun and River waters, the AHS fraction was still predominate in DOM pool after 100-day biodegradation (Figure 6). AHS and HiA collectively accounted for more than 70% of the DOM after degradation test. AHS and HiA represented 28~43% ($0.5\sim0.9\text{ mgC L}^{-1}$) and 1~41% ($0.01\sim0.66\text{ mgC L}^{-1}$) in the St.1 epilimnion, respectively, whereas BaS were dominant in the lake water. The HoN fraction was nearly negligible (which was 0~4% corresponding to $0\sim0.2\text{ mgC L}^{-1}$). The average percentage fraction of HiN was 9~28% of the DOM, respectively. Protein and carbohydrate-like DOMs may not be present in a significant quantity in lake water.

However, different from the river dissolved organic matter, AHS and HiA existed at almost the same average level of 44% and 16%, respectively. AHS was still a dominant constituent in river water as compared with lake water. The HoN, HiB and HiN fractions accounted for 0%, 20% and 21%, respectively. The lake and river DOM may become more hydrophobic, so the DOM in Lake Unmun may be more algal-derived and originated from release of sediment. The inflowing rivers may be less allochthonous or pedogenic.

This is the same as the distributions in the river and lake DOMs. However, their DOM fraction resulted in more widely different patterns depending on the origin of sample. However, it had a DOM fraction distribution different from the lake water. The DOM is mostly of microbial origin and may be refractory to bacterial degradation because most of DOM remained after extensive biodegradation.

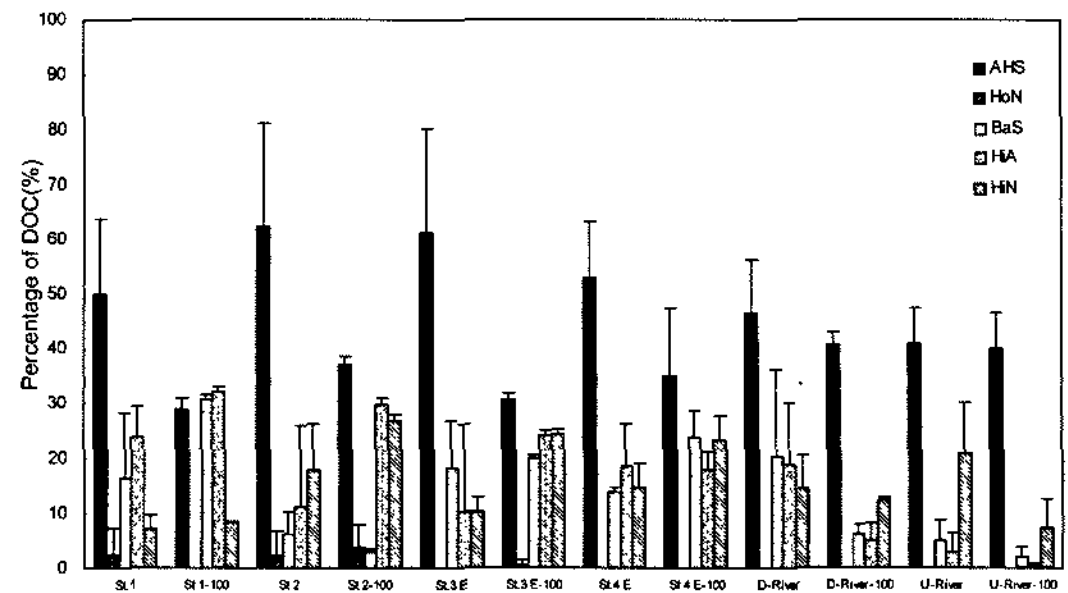


Figure 6. DOM fraction distributions in Lake Unmun. DOM fractions are AHS, aquatic humic substances ; HoN, hydrophobic neutrals ; BaS, bases ; HiA, hydrophilic acids ; HiN, hydrophilic neutral. Error bars represent ± 1 standard deviation. St.1 : Epilimnion (1 m), St.2: Epilimnion (1 m), St.3 : Epilimnion (1 m), St.4 : Epilimnion (1 m), St.5 : Influent river, the Dongchang River (D-River), into Lake Unmun, St.6 : Influent river, the Unmoon River (U-River), into Lake Unmun, Sediments : Dam center sediment samples, -100: Biodegradation test of 100 days.

So AHS and HiA can accumulate as recalcitrant DOM in the lake. In this study, considering the retention time of water in Lake Unmun and the low degradability of DOM, we could assume that the DOM (88~89% of the total) which remained after 100 days of incubation is refractory. The labile DOM portion was estimated to be 11~12%. The percent of DOM that is labile in Lake Unmun was somewhat smaller than that observed in one mesotrophic lake(30~50%)²⁹⁾ but higher than that observed in St.5 and St.6 of river water (refractory, 68~77%; labile, 23~33%).

UV Absorbance to DOC Ratio of Biodegradation Test

The UV/DOC ratio of each water fraction after incubation exhibited a distinctive pattern depending on the lake and river water samples (Figure 7). The UV/DOC ratio of the lake water increased in the order of lake total DOM, AHS, and HiA (corresponding to 25.2, 17.2 and $12.2\text{ mAbscm}^{-1}\text{ LgC}^{-1}$, respectively). The UV/DOC ratio for the D-River and U-River waters showed a similar trend but greater value as compared with that of the lake water (D-River DOM, AHS and HiA :

10.1, 15.6 and 5.7 mAbs cm⁻¹LgC⁻¹, U-River DOM, AHS and HiA : 17.2, 4.6 and 2.9 mAbs cm⁻¹LgC⁻¹, respectively).

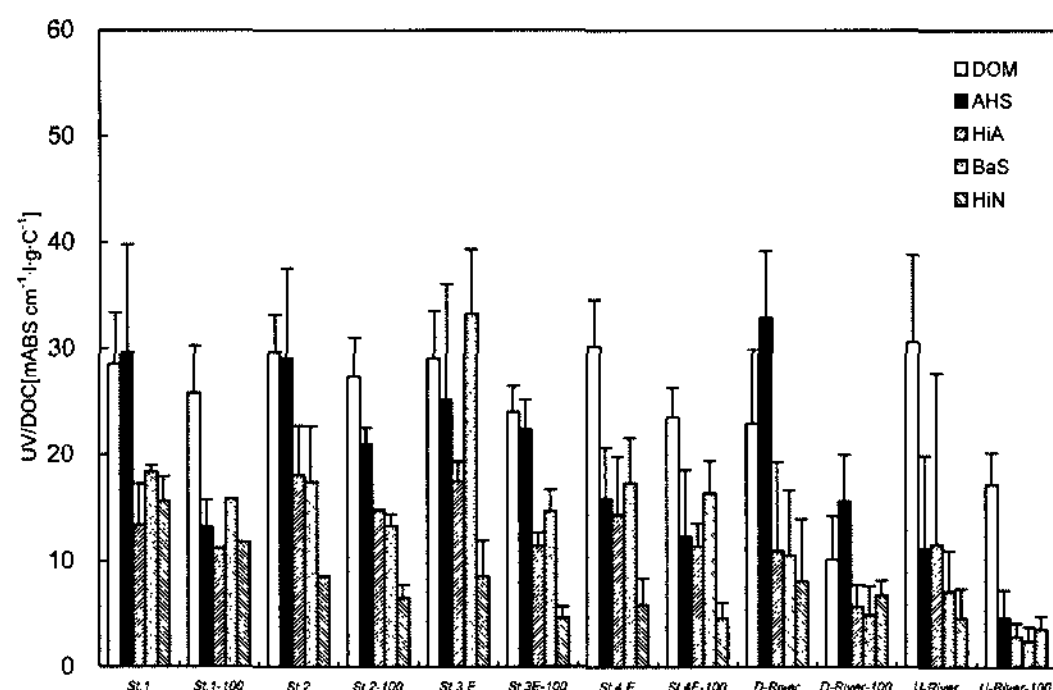


Figure 7. The ratio of ultraviolet absorbance over dissolved organic carbon (UV/DOC) in Lake Unmun and its inflowing river waters. DOM fractions are DOM, dissolved organic matter (Lake DOM, River DOM) ; AHS, aquatic humic substances ; HiA, hydrophilic acids. Error bars represent ± 1 standard deviation. St.1 : Epilimnion (1 m), St.2: Epilimnion (1 m), St.3 : Epilimnion (1 m), St.4 : Epilimnion (1 m), St.5 : Influent river, the Dongchang River (D-River), into Lake Unmun, St.6 : Influent river, the Unmoon River (U-River), into Lake Unmun, Sediments : Dam center sediment samples, -100: Biodegradation test of 100 days.

Aquagenic DOM was approximately 25 mAb cm⁻¹LgC⁻¹ after degradation. The higher ratio of the AHS in Lake Unmun that in its inflowing rivers indicates that a significant portion of the lake AHS is pedogenic-derived autochthonous AHS. The UV/DOC ratio of AHS in D-River water was extremely high, about 33 mAbs cm⁻¹LgC⁻¹; on the other hand, the AHS in U-River DOM had a UV/DOC ratio of 4.6 mAbs cm⁻¹LgC⁻¹. The UV/DOC ratio of AHS in D-River water and lake waters was significantly higher than that of the U-River water. The high UV/DOC ratio of AHS fraction from lake DOM may be due to the input of allochthonous DOM. Since AHS is considered recalcitrant, the AHS in lake and river waters may be present in a state where it is associated with partially degraded carbohydrates and protein which are easily-biodegradable and

have a low UV absorptivity. Both DOM distribution and UV/DOC ratio varied a lot depending on the origin of samples. The UV/DOC ratio also reflected the characteristics of DOM, AHS and HiA in lakes and river waters.

The large increase in the UV/DOC ratio of the lake water during the long-term incubation can be explained by a gradual rise in the portion of pedogenic constituents (St.1 before: 13 \pm 4, after: ; $p < 0.0001$; St.2 before: 12 \pm 2, after: ; $p < 0.0001$; St.3 before: 14 \pm 4, after: ; $p < 0.0001$; St.4 before: 14 \pm 3, after: ; $p < 0.0001$ by paired t-test).

Distribution of Molecular Weight by HPSEC

A comparison of molecular weight distributions (MWD) of DOM was made using the following parameters: number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), polydispersivity (M_w/M_n), and molecular weight range (80% confidence limits). The M_w/M_n ratio can provide useful and reliable molecular weight distributions of DOM in drinking water supplies.^{22,30,31)}

The results for M_n and M_w are listed in Table 3. The M_w of lake and river water samples measured by HPSEC is high, and the M_w of the biodegradation samples is low after biodegradation test. Though the apparent molecular weight increases for both M_n and M_w , the magnitude of the increases is greater for M_w than for M_n . If the M_w for the lake and river water is correct, then in general, the HPSEC results for the AHS fractions are higher than the HiF(HiA+BaS+HiN) fraction results, whereas the biodegradation test results are lower. The HPSEC chromatograms of DOM from Lake Unmun water showed a polydispersity of less than 2 in almost all cases, indicating that the DOM molecules occupy a relatively narrow size fraction. The weight-averaged molecular weight of the DOM was ranging from 810 to 1180 Dalton, while its weight-averaged molecular weight after biodegradation was ranging from 630 to 1053 Dalton. The HPSEC chromatograms of the lake DOM samples were quite

Table 3. Weight-averaged molecular weight, number-averaged molecular weight and polydispersity of dissolved organic matter in Lake Unmun

Sampling Station (Aquatic Humic Substance)	HPSEC (Detector Wavelength : 260 nm)					
	Number-averaged molecular weight (Mn)		Weight-averaged molecular weight (Mw)		Polydispersity (Mw / Mn)	
	DOM	After Bio-degradation	DOM	After Bio-degradation	DOM	After Bio-degradation
St.1	566	566	810	810	1.43	1.43
St.2	711	448	839	630	1.18	1.41
St.3	615	581	850	803	1.38	1.38
St.4	1025	912	1181	1053	1.16	1.19
St.5	827	772	1041	983	1.26	1.27
St.6	603	415	826	689	1.37	1.66

similar, exhibiting three distinctive peaks at 6.18, 10.02, 11.78, and 14.29 min, which correspond to 52,920, 1,160, 200, and 17 Dalton, respectively. AHS fractions were: 6.21 min (51,360 Dalton); 10.18 min (990 Dalton); 12.8 min (70 Dalton); and 14.34 min (15 Dalton) Hydrophilic fractions were: 6.24 min (49,860 Dalton); 10.32 min (860 Dalton); 12.77 min (70 Dalton); and 14.4 min (15 Dalton).

The molecular weight of AHS in the lake water contain both high and low molecular weight. The molecular weight of DOM is bigger than that of hydrophilic fraction samples (Figure 8). The HPSEC chromatograms of lake water samples were different from the type of lake water. The molecular weight values for DOM determined in this study were greater than the molecular weight

of AHS. Since the DOM contains AHS as well as the other fractions such as HiA, HoN, BaS, and HiN, the molecular weight of DOM may be different from that of AHS unless AHS is the most predominant in DOM.

CONCLUSIONS

Dissolved organic carbon in Lake Unmun, and its inflowing rivers DOM sources to the lake in its catchment area was fractionated using three different resin adsorbents into the major five classes : AHS, HoN, HiA and HiN. The aquatic humic acid fraction of dissolved organic matter dominated in lake water. AHS significantly dominated lake and inflowing river waters. The UV/DOC ratio could be useful for reflecting the characteristics of DOM, AHS and HiA in lake and river water samples. The UV/DOC ratio in both lake and river waters increased in the order of DOM, AHS, and HiA. The river water exhibited the lower UV/DOC lower ratios for them than the lake waters. Autochthonous DOM and AHS, which have been reported to have a higher UV/DOC ratio, may be contributing significantly in the lake. For the river water, the UV/DOC ratios of DOM, AHS, and HiA were the lowest among the samples. Its HiA showed a UV/DOC ratio even less than AHS in all the other samples. The percentage of DOM that is refractory in lake water samples during biodegradable testing corresponded to 88-89%, which

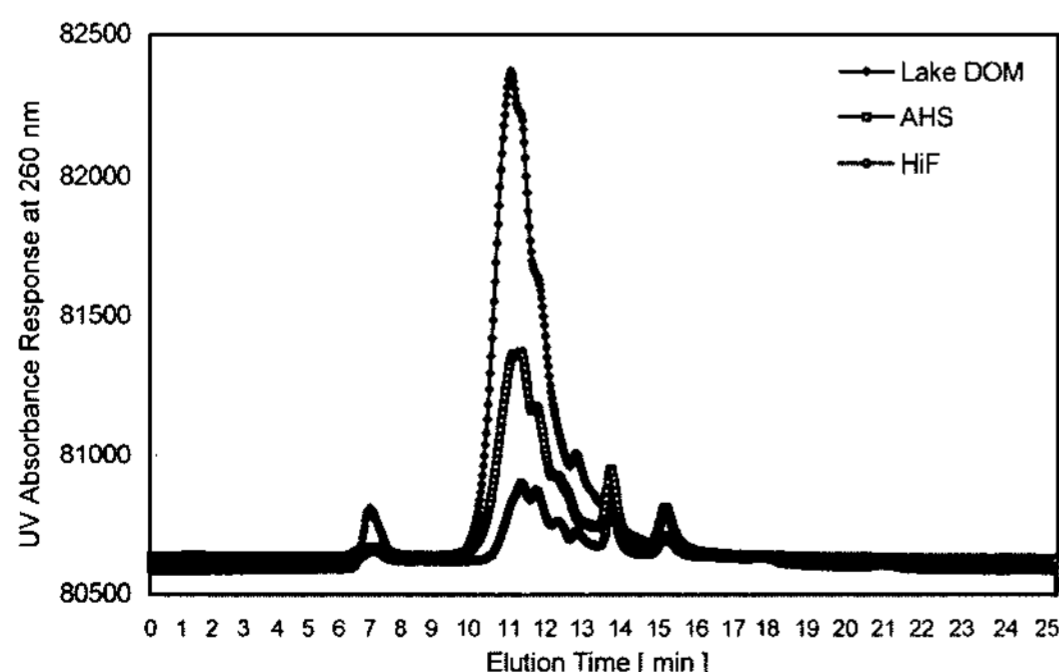


Figure 8. HPSEC chromatograms of the averaged lake DOM, AHS, and hydrophilic in Lake Unmun, lake DOM, AHS; aquatic humic substances, HiF; hydrophilic fraction (HiA+BaS+HoN).

implies that the ratio of recalcitrant dissolved organic matter to DOM increased. It was also found that the UV/DOC ratio of AHS fraction showed 26-36 mAbscm⁻¹LgC⁻¹ after biodegradation. Although biodegradation reduced the labile portion of DOM, the decomposed fraction had a high UV/DOC ratio with AHS and HiA. Biodegradation tests and chromatographic separation of DOM helped understand the origin, characteristics of DOM in each fraction. Besides, It is presumed that AHS material occupied higher portion in the lake DOM according to the result of SEC Chromatography in the lake. And, also it is estimated lake is becoming to be lake which is influenced by load from interior lake sediment than load from outside since influence level of DOM in the lake sediment is high.

ACKNOWLEDGEMENTS

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (R08-2003-000-10065-0). We would like to thank Dr. Kwang-Ho Choo, KyungPook National University, for his helpful review and TOC measurements on the manuscript. The authors also sincerely thanks to Dr. Akio Imai, National Institute for Environmental Studies (NIES), for their help during the postdoctoral STA fellowship program, Japan.

NOMENCLATURE

DOM	Dissolved organic matter
AHS	Aquatic humic substances
HoN	Hydrophobic neutrals
HiA	Hydrophilic acids
HiN	Hydrophilic neutrals
BaS	Bases
UV/DOC	Ultraviolet absorbance over dissolved organic carbon
DBPs	Disinfection by-products
HPSEC	High-pressure size exclusion chromatography
PSS	Polystyrene sulfonates
MWD	Molecular weight distributions

Da	Dalton
Mn	Number-averaged molecular weight
Mw	Weight-averaged molecular weight

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