CHARACTERIZATION OF DISSOLVED ORGANIC MATTER IN A SHALLOW EUTROPHIC LAKE AND INFLOWING WATERS

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Abstract: The seasonal patterns of dissolved organic matter (DOM) in Lake Kasumigaura, a shallow, eutrophic lake, and several DOM sources in its catchment area were investigated. DOM was fractionated using three resin adsorbents into classes: aquatic humic substances (AHS=humic acid+fulvic acid), hydrophobic neutrals (HoN), hydrophilic acids (HiA), bases (BaS) and hydrophilic neutrals (HiN). The DOM produced significantly different fraction distributions depending on the origin of sample. AHS and HiA prevailed over AHS in the lake while AHS and HiA existed at almost the same concentration levels in the rivers. AHS seems to be a more dominant component in river water than lake water. The dominance of organic acids was also observed in the DOM sources: forest stream (FS), plowed field percolate (PFP), domestic sewage (DS) and sewage treatment plant effluent (STPE).

Key Words: aquatic humic substances, DOM fractionation, hydrophilic acid, hydrophobic acid

INTRODUCTION

The quality of drinking water in freshwaters is greatly affected by the amount of dissolved organic matter (DOM) because of its adverse health effects as well as unpleasant taste and odor caused by chlorination. At the same time, DOM can function as a source of carbon and energy for both heterotrophic microorganisms and higher trophic levels in freshwater ecosystems.

Generally, the majority of DOM in lakes and rivers is comprised of organic acids; hydrophobic acids and hydrophilic acids. The hydrophobic

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hydrophilic breaks may be related to the aromaticity of DOM. The hydrophobic acids consist mainly of humic substances, which are colored, polyelectrolytic, and relatively large molecular weight acids. Aquatic humic substances (AHS) are of largest fraction of dissolved organic carbon in natural water due to their refractory characteristics by aquatic microflora.

Thus, some recalcitrant dissolved organic matter may have been accumulating in the lake water.¹ The accumulation of dissolved organic matter in lake water certainly imposes a serious challenge for lake environment as well as drinking water management.

DOM, a representative index for dissolved organic matter, is regarded basically as a source of organic pollution, and also as an
energy source for microbially-based aquatic food webs, as a factor in the cycling of trace elements and as an influence on the biological activity of phytoplankton and bacteria. The increases in DOM may also cause a serious problem to the quality of drinking water.

Recalcitrant DOM can be a dominant precursor of carcinogenic trihalomethanes produced during chlorination in water treatment when lake water is utilized as a source of drinking water.

Understanding the mechanism by which recalcitrant DOM gradually increases in lake water is thus urgently needed. Despite several decades of research, however DOM continues to be the least understood reservoir of reduced carbon. DOM in natural waters is a complicated and heterogeneous mixture of organic compounds. Its physico-chemical characteristics have not been clearly understood. Thus, the first step toward the understanding should be the evaluation of the characteristics of DOM in natural waters. An appropriate approach is to separate DOM into well-defined macro-fractions and examine their distribution and physico-chemical characteristics.

Aquatic humic substances are typical naturally occurring recalcitrant dissolved organic matter, constitute 30 to 80% of DOM, and are the largest fraction of natural organic matter in water. They are polar, straw-colored, hydrophobic organic acids that are derived from soil humus, terrestrial and aquatic plants, and plankton. AHS is comprised of humic acids (high-molecular weight fraction) and fulvic acids (low-molecular weight fraction). Fractionation methods of DOM based on the separation of AHS, namely hydrophobic-hydrophilic and acid-based breaks, seem to be reasonable for our purpose in evaluating the characteristics of DOM in waters.

There are two major DOM sources to lake: autochthonous DOM, that is photosynthetic inputs of the littoral and pelagic flora through secretions and autolysis of cellular contents, and allochthonous DOM, composed largely of terrestrial humic substances refractory to rapid bacterial degradation. Therefore, the separation and quantification of AHS in lake waters are likely to lead to valuable information on the origin of the DOM, whether autochthonous or allochthonous.

In this study, authors modified the method of DOM fractionation developed by Leeheer. DOM was fractionated using three kinds of resin adsorbents into five classes: hydrophobic acids (equivalent to AHS), hydrophobic neutrals, hydrophilic acids, hydrophilic neutrals and bases (hydrophobic+hydrophilic bases).

The objectives of this study are to apply the DOM fractionation method to the waters of a shallow eutrophic lake and its inflowing rivers as well as several DOM sources in its watershed such as forest stream, domestic sewage, sewage treatment plant effluent, plowed field percolate and then to evaluate the characteristics of the DOM by comparing their DOM fraction distributions and ultraviolet absorption properties.

**MATERIALS AND METHODS**

**Sampling Stations in Lake Kasumigaura**

Lake Kasumigaura, the second largest lake in Japan, is located in the eastern part of the Kanto Plain, 50 km northeast of Tokyo. The lake has two large bays Takahamairi and Tsuchiurairi (Figure 1).

More than 600,000 people live in the lake’s watershed (1,577 km²). Land use in the watershed is 30% forest, 25% paddy field, 25% plowed field, 10% residential, and 10% others. The lake watershed is smooth and shallow, with a surface area of 171 km², a mean depth of 4.0 m, and a maximum depth of 7.3 m. Because of extremely high loads of organic matter and nutrients, this lake is well known for eutrophic state, with mean concentrations of chlorophyll-α, phosphorus, and nitrogen of 65 μg/L, 95 μg/L and 1.15 mg/L, respectively at the center of the lake.

Water samples were collected in one-liter glass bottle with a 2 m column sampler at the
center of lake monthly from May 1994 to February 1996. The samples were immediately cooled in an ice cooler and brought back to laboratory. The water was then filtered through a precombusted (450°C for 4 h) Whatman GF/F filter (nominal pore size 0.7 μm). The filtrates were kept at 3°C in a precombusted glass bottle until analysis.

In May, Aug., and Nov. 1995 and Feb. 1996, water samples were also obtained at downstream stations of 10 influent rivers that collectively account for 86% of the total discharge into Lake Kasumigaura (Figure 1). The samples of the lake water were collected at the center of lake. And, the samples of river water were collected in an acid washed polycarbonate container and treated in the same manner as the lake samples.

**DOM Fractionation**

The sample filtrate was fractionated into hydrophobic acids (equivalent to AHS), hydrophobic neutrals (HoN), hydrophilic acids (HiA), bases (BaS) and hydrophilic neutrals (HiN) fractions through their adsorption on a series of macroporous resin adsorbents. Non-ionic 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) were used.

The column capacity factor k' for separating hydrophobic acids using the XAD-8 resin column was 50. This separation condition was identical to the one where AHS was isolated with XAD-8 resin. From now on, hydrophobic acids will be referred to as AHS. Appropriate classification of organic compounds according to the DOM fractionation is listed in Table 1.

XAD-8 resin was cleaned-up and conditioned according to Thurman and Malcolm. 3 mL (wet volume) of the XAD-8 resin was packed.
Table 1. Average concentrations of dissolved organic carbon (DOC) in Lake Kasumigaura, its inflowing rivers and other DOM sources

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sampling period</th>
<th>DOC (mg C/L)</th>
<th>SD*</th>
<th>n**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake water</td>
<td>May-94 to Feb-96</td>
<td>3.88</td>
<td>0.63</td>
<td>22</td>
</tr>
<tr>
<td>River water</td>
<td>May-94 to Feb-95</td>
<td>3.08</td>
<td>0.90</td>
<td>16</td>
</tr>
<tr>
<td>Forest stream (FS)</td>
<td>May-95 to Feb-96</td>
<td>0.47</td>
<td>0.07</td>
<td>4</td>
</tr>
<tr>
<td>Plowed field percolate (PFP)</td>
<td>May-95 to Aug-96</td>
<td>0.28</td>
<td>0.07</td>
<td>4</td>
</tr>
<tr>
<td>Domestic sewage (DS)</td>
<td>May-95 to Aug-96</td>
<td>16.62</td>
<td>5.53</td>
<td>4</td>
</tr>
<tr>
<td>Sewage treatment plant effluent (STPE)</td>
<td>May-95 to Aug-96</td>
<td>4.93</td>
<td>0.85</td>
<td>4</td>
</tr>
</tbody>
</table>

* SD: standard deviation, ** n: sample number

into a glass column and was rinsed 3 times, alternating from 0.1 M NaOH to 0.1 M HCl just before application of sample. A blank sample was collected in the final rinse with 0.1 M HCl (B1). Both AG-MP-50 (hydrogen-form) and AG-MP-1 (chloride-form) resins were Soxhlet-extracted for 24 h with methanol. AG-MP-1 was then converted into free-base-form with 1 M NaOH and rinsed with Milli-Q water (Milli-Q SP.TOC, Millipore). Glass columns containing 6 mL (wet volume) of the cation resin and 12 mL (wet volume) of the anion resin were connected in series and conditioned by pumping about 1 L Milli-Q water. Blank samples (B2 and B3) were collected from the Milli-Q water and each column after the conditioning. The procedure of the DOC fractionation is given in Figure 2. Step 1: acidify the filtrate (DOM 1) to pH 2.0 with 6 M HCl; pass 200 mL of the filtrate through the XAD-8 column by a peristaltic pump with Tygon tubing at a flow rate of about 1 mL/min, and rinse the column with bed volumes of 0.1 M HCl. Step 2: elute the column in the reverse direction with more than 3 bed volumes of 0.1 M NaOH at a flow rate not exceeding 0.5 mL/min (DOM 2); and measure the eluant volume. Step 3: pump the sample effluent from the XAD-8 column (DOM 3) through a series of the cation-anion resin columns at a flow rate of about 1 mL/min and after pumping 1~2 bed volumes of the sample, collect eluant samples (DOM 4 and DOM 5) from the anion resin column and then from the cation resin column.

Figure 2. Schematic diagram of procedure for DOM fractionation. DOM fractions are AHS, aquatic humic substances: HoN, hydrophobic neutrals: HiA, hydrophilic acids: Bas, bases: HiN, hydrophilic neutrals.

DOM fractionation was conducted twice for one sample. After the fractionation, DOM and ultraviolet absorbance were measured for each DOM fraction and the blank samples. The average values of B1, B2 and B3 were 0.43 ± 0.24 (SD) mg C/L (n=111), 0.43 ± 0.26 (SD) mg C/L (n=194) and 0.51 ± 0.28 (SD) mg C/L (n=199), respectively. These DOM concentrations were less than half of the blank values reported by Leenheer.6) The background
RESULTS AND DISCUSSION

DOC Concentrations in the Waters of Lake, River and DOM Sources

DOM at the center of Lake Kasumigaura ranged from 2.97 to 4.80 mg C/L and averaged 3.88 mg C/L during a period from May 1994 to February 1996 (Table 1). The lake DOC exhibited a tendency of increasing from spring to fall and then declining gradually thereafter (Figure 3). However, excluded the data in Jan. ~ Dec. 1996, the DOC appeared to remain relatively constant.

DOC concentrations in 10 rivers inflowing to Lake Kasumigaura varied from 1.49 to 6.45 mg C/L with an average value of 3.08 mg C/L during May 1995 to February 1996 (Table 1). Contrary to the lake DOC, in most of the rivers, the DOC had greater values in May and August than those in November and February. And the flowrate-weighted DOC concentration in the river waters was significantly lower than the lake DOC in November and February (Figure 3). Since the 10 rivers accounted for 86% of the total riverine discharge into Lake Kasumigaura, it is suggested that the river DOC do not contribute dominantly to the lake DOC. The waters of the DOM sources showed a characteristic difference in DOC concentration. As expected, DS had the greatest DOC concentration. FS and PFP were the lowest. STPE had a concentration of DOC similar to the lake.

DOM Fractionation of the Water in Lake, River and DOM Sources

In Lake Kasumigaura, the AHS and HiA were dominated fractions of DOC (Figure 4). AHS and HiA collectively accounted for more than 70% of the DOC. The lake DOM is predominantly acidic. HiA was found dominant over AHS, amounting to 43% of the DOC against AHS being 32%. The HoN fraction was around 9%, indicating that hydrocarbon, pesticides, carbonyl compounds and LAS may not contribute significantly to the lake DOC. The
average percentage fraction of BaS and HiN was 10 and 4% of the DOC, respectively. Protein-like and carbohydrate-like DOM may not be present in a significant quantity in lake water.

The DOM fraction distribution of river waters exhibited a significantly different pattern as compared with that of the lake water (Figure 4). Like the lake DOM, the AHS and HiA fractions dominated in the riverine DOM, accounting for more than 70%. The riverine DOM is also rich in organic acids. However, different from the lake DOM, AHS and HiA existed at almost the same level, 35 and 36%. AHS appears to be a more important constituent in river water as compared with lake water. The HoN, BaS and HiN fractions accounted for 12, 10 and 6%, respectively. The river DOM contained more AHS, HoN and HiN and less HiA as compared with the lake DOM. The river DOM may be more hydrophobic than the lake DOM. Thurman\(^4\) reported that generally, AHS and HiA account for 40 and 41% of DOC in lakes, respectively. He also stated that AHS is the major component of DOC in rivers, accounting for about 50% of the DOC with HiA being about 25%. McKnight et al.\(^5\) found in studying lakes where DOC is mostly derived from phytoplankton that AHS accounted for 13–20% of the DOM. These suggest that river waters are basically rich in AHS but poor in HiA because their major DOM is allochthonous and that lake waters contain more HiA over AHS as the autochthonous DOM sources outweigh the allochthonous ones in lakes. Our results for the waters of Lake Kasumigaura and its inflowing rivers are consistent with these reported findings. It appears that in Lake Kasumigaura the DOM seems to come from the decay of phytoplankton. On the other hand, its inflowing rivers may have less allochthonous or pedogenic DOM sources. DOM fraction distributions for the waters of DOM sources also showed an interesting feature. Organic acids, AHS and HiA dominated all the samples (Figure 5).

This is the same as the distributions in the river and lake DOM. However, their DOM fraction resulted in more widely different patterns depending on the origin of sample. FS and PFP were dominated by AHS, which accounted for more than 60 and 70%, respectively. Both FS and PFP have only allochthonous DOM source; thus, such high percentages in AHS are expected. The muddy sediment may diffuse the DOM containing much more HiA than AHS. DS includes a significantly greater amount of HiA than AHS water. However, it possessed a DOM fraction distribution distinctively different from the lake water. The HoN fraction was the greatest
among the samples studied, accounting for 25% of the DOM. The sample was foamy indicating that DS contained a great amount of synthetic detergent such as LAS, which is categorized as HoN. The high HoN in the DS may be due to the presence of LAS-like DOM. The STPE also contained more HiA (45%) than AHS (27%), being the greatest HiA percentage fraction among the samples studied. The DOM in STPE is mostly of microbial origin and may be refractory to bacterial degradation because it is the remaining after extensive biodegradation. This suggests that AHS and HiA may accumulate as a recalcitrant DOM in the water when STPE is discharged into the lake.

**UV Absorbance to DOC Ratio of the Waters in Lake, River and DOM Sources**

The ratios of UV absorbance to DOC (UV/DOC) based on the sample DOM, AHS and HiA exhibited a distinctive pattern depending on the origin of sample. The ratios of UV to DOC the lake water was found to increase in the order of HiA, lake-water DOC and AHS (12.0, 16.1 and 22.4 [(ABS/cm)/(DOC/mg/L)]) (Figure 6). The ratio of the AHS was 85% greater than that of HiA. The ratios of UV to DOC in the river waters showed a similar trend but were greater than that of the lake water (HiA, DOM) and AHS: 14.7, 21.1 and 28.1 [(ABS/cm)/(DOC/mg/L)], respectively). The ratios of UV to DOC was 31, 26 and 22% greater in DOM, AHS and HiA, respectively.

Allochthonous or pedogenic DOM is essentially aromatic and autochthonous or aquagenic DOM is mainly aliphatic. Accordingly, allochthonous DOM is greater in the ratios of UV to DOC than autochthonous DOM. The ratios of UV to DOC the pedogenic DOM was reported to be 23~58 [(ABS/cm)/(DOC/mg/L)], while that of aquagenic DOM was about 12 [(ABS/cm)/(DOC/mg/L)]. Thus it is reasonable that the ratio of the river DOC was greater than that in Lake Kasumigaura. This relationship is also true of AHS. McKnight et al. reported that AHS in a river where soil-derived DOM is dominant exhibited a UV to DOC ratio of 40 [(ABS/cm)/(DOC/mg/L)] and that AHS in a lake where algal-derived DOM dominates did 16~17 [(ABS/cm)/(DOC/mg/L)].

The lower ratio of the AHS in Lake Kasumigaura over that in its inflowing rivers indicates that a significant portion of the lake AHS is algae-derived autochthonous AHS.

DS and STPE showed the same order in the
ratios of UV to DOC as the lake and river waters did, namely, AHS > lake and river DOM > HiA. The UV to DOC ratio of AHS in PFP was extremely low, about 12 [(ABS/m/cm)/ (DOCmg/L)]. For the FS sample, the UV to DOC ratio decreased in the order of the total DOC, AHS and HiA. PFP exhibited a different pattern regarding the UV to DOC ratio. For the FS sample, the ratios of UV to DOC decreased in the order than DOC and HiA. PFP may contain dissolved organic matter having a high UV to DOC ratio other than AHS and HiA. It is interesting to note that the ratios of UV to DOC AHS in both FS and PFP were significantly lower than that of the rivers. The low UV to DOC ratio of AHS from PFP may be due to specific removal of AHS possessing high UV to DOC ratio during percolation through soil layers.

The UV to DOC ratios in DS resulted in quite different values. Its ratios of UV to DOC the total-DOC, AHS and HiA were the lowest among the samples studied. Surprisingly, the AHS had an UV to DOC ratio of 9.4 [(ABS/m/cm)/(DOCmg/L)], even less than the values of HiA in all the other samples. STPE has a similar distribution pattern in DOM fractions to the lake lower. Consider that the sewage treatment plant increased considerable the ratio of AHS. Since AHS is considered recalcitrant, the AHS in DS may be present in a state where it is associated with partially degraded carbohydrates and protein which are easily-biodegradable and significantly low UV absorptivity.

Both DOM fraction distribution and UV to DOC ratio were found to exhibit distinct variations depending on the sample of origin. The UV to DOC ratio also reflected the characteristics of total-DOC, AHS and HiA. The DOM fractionation with subsequent measurement of UV to DOC ratio can be a useful tool for evaluating the characteristics of DOM as well as the origin of DOM in lakes.

CONCLUSIONS

Dissolved organic matter (DOM) in Lake Kasumigaura, its inflowing rivers and several DOM sources to the lake in its catchment area was fractionated using three resin adsorbents into five classes: AHS, HoN, HiA, BaS and HiN.

AHS was the most abundant fraction in FS and PFP. HiA abounded in DS and STPE. Only DS contained a significant amount of HoN, which may be due to the presence of LAS-like DOM. The ultraviolet absorbance to DOC (UV/DOC) ratio was found to be a useful indicator for reflecting the characteristics of DOM, AHS and HiA and the origin of sample. The ratios of UV to DOC in both lake and river waters was in the order of AHS, DOM, HiA. The lake water exhibited the lower ratios in DOM, AHS and HiA than the river waters did. Autochthonous DOM and AHS, which have been reported to have a lower UV to DOC ratio, may contribute significantly those in the lake. For the AHS dominated FS and PFP, the ratio was in the order of DOM, AHS, HiA and DOM, HiA, AHS, respectively. For DS, the UV to DOC ratios of DOM, AHS and HiA were the lowest among the samples. Its AHS showed an UV to DOC ratio even less than those of HiA in all the other samples.

REFERENCES

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